DETERMINATION OF TOTAL ARSENIC AND THE RELATIONSHIP BETWEEN THE ARSENIC LEVELS AND OTHER DETERMINED PHYSICOCHEMICAL PROPERTIES OF SOME BIOLOGICAL AND ENVIRONMENTAL SAMPLES FROM SELECTED TOWNS IN THE AMANSIE WEST DISTRICT OF THE ASHANTI REGION

By

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A Thesis submitted to the Department of Chemistry, College of Science, Kwame Nkrumah University of Science and Technology, Kumasi in partial fulfilment of the requirements for the award of degree of MASTER OF PHILOSOPHY (Analytical Chemistry)

OCTOBER 2013

DECLARATION

I declare that I personally, under supervision, undertook this research and this report contains to the best of my knowledge no material previously published by another person except where due reference has been made.

……..... ……

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I declare that I supervised this student in undertaking this study. I hereby confirm that the student had my permission to present this thesis for assessment.

…… ……..……

Dr. Sylvester K. Twumasi Date

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…… ……

Dr. Ray Bright Voegborlo Date

(Head of Department)

DEDICATION

This work is dedicated to my parents, Mr. Mante Samuel and Miss Comfort Owusu who have enormously supported me in my academic pursuit.

ACKNOWLEDGEMENT

Glory be to the most high God for granting me the grace and strength to go through this project successfully.

My profound gratitude goes to Dr. Sylvester K. Twumasi, my supervisor for spending time off his busy schedule to attend to my project and smoothening all rough edges. My warmest gratitude goes to Dr Anthony K. Gershon, a medical doctor at St Martins Catholic Hospital at Agoroyesum who took me through the history of Buruli ulcer in the district (hospital data) as well as facts concerning the disease.

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ABSTRACT

Amansie West District of the Ashanti region is rich in gold deposits so surface mining is the most important economic activity in the District. The mining causes weathering of rocks and increases arsenic levels in foods, water and soils. Total arsenic concentrations of soil, water and cassava from the district were analysed (with hydride generation AAS) as well as the relationship between the arsenic levels and other physicochemical parameters of the samples. The pH, conductivity and surrounding temperature were determined with probes. TDS, TSS and TS were gravimetrically determined. The research was conducted between October 2011 and May 2012.

The ranges for all the water samples were: pH 5.05 to 7.98, conductivity 29.33 to 429.07 µS/cm, TDS 22 to 275 mg/L, TSS 189 to 892 mg/L and TS from 226 to 1045 mg/L.

For soil samples, the ranges were: pH from 4.18 to 6.50, conductivity from 189.38 to 598.49 µS/cm and moisture content, from 6.54 to 33.06%.

The pH range for the cassava samples was 4.99 to 6.83 and the peel was 4.03 to 6.68. The conductivity for the cassava ranged from 59.12 to 78.07 µS/cm whiles the peel was 60.11 to 77.89 µS/cm. The moisture content of the cassava and peel were respectively 11.07 to 22.98% and 38.97 to 50.65%.

The range of arsenic levels in the samples were: water below 1 ppb (below detection) to 14 ppb, soil 3.12 to 8.48 mg/kg, cassava 0.08 to 1.20 mg/kg and peel from 0.22 to 1.20 mg/kg.

There was an irregular trend or no specific pattern (scattered diagrams) between arsenic levels, sample properties and towns. This means the factors affecting arsenic levels differ from town to town.

TABLE OF COMMONLY USED ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
A.P.H.A.	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
AWD	Amansie West District
BU	Buruli Ulcer
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
HCL	Hollow Cathode Lamp
HGAAS	Hydride Generation Atomic Absorption Spectroscopy
MoH	Ministry of Health
PMT	Photomultiplier Tube
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
TS	Total Solid
UNICEF	United Nations International Children Emergency Fund
WHO	World Health Organization
WML	World Health Organization Maximum Limit

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CHAPTER ONE

1.0 INTRODUCTION

Arsenic is a naturally occurring mineral found in soils and bedrock so its existence in the environment is inevitable. It is the 20th commonest element in the Earth's crust and 12th commonest in the human body (Alice *et al*, 2008). It can also be introduced in the environment through the use of inorganic arsenic pesticides and fertilizers.

It is highly destructive. The acute toxicity of arsenic at high concentrations has been known for centuries (UNICEF, 2006; 1ARC, 2004). Some of its major effects include skin and liver cancer, high blood pressure, stomach upset, gastrointestinal irritations, cardiovascular and nervous breakdown. Chronic arsenic poisoning can lead to arsenicosis which can make one bed-ridden. Notwithstanding these effects, it has uses which are worthy of note. Some of these uses include electronic components, wood preservatives and parasitic drugs (Edward and Marcel, 2005).

Mines produce tailings with residual Arsenic content due to the presence of arsenopyrite (FeAsS) in the ore (Lide, 1992). Food and water are of particular interest due to accumulation and risk from human consumption. Bioaccumulation is the increase in a chemicals concentration in an organism over time, compared with the chemicals concentration in the environment. Though biological samples are of major interest, environmental samples like soil accumulate significant arsenic levels.

Arsenic exposure is mainly through inhalation and ingestion. High incidence of Buruli ulcer in aquatic mining areas has been linked to arsenic presence (Buckle *et al*, 1948).

Elevated concentrations of arsenic can be found in both surface and ground water due to mine run-off, treated and untreated discharges (Ministry of Health, 1999).

1.1 Statement of Problem

This project has therefore been necessitated by high incidence of Buruli ulcer, acute and chronic diseases, environmental and biological toxics at the Amansie West District of the Ashanti region which has been partly attributed to arsenic by Duker *et al*, 2005.

In 1989, Van der Werf *et al* described 96 Buruli ulcer cases in the Asante Akim North District of Ashanti Region. This report was followed by the description of a major endemic focus in Amansie West District in the same region. Amansie West had the highest prevalent rate (150.8 per 100,000), followed by Asante Akim North (131.5 per 100,000) and Upper Denkyira (114.7 per 100,000) – Ministry of Health Report, 1999.

Arsenic dissolves in water and it is suspected to enhance the growth of *Mycobacterium ulcerans*, the aquatic bacteria which causes Buruli ulcer (Bentley, 2002). Upon contact with wounds, it is believed to catalyse the toxin called mycolactone which causes damage to the soft tissues and skin and hinders the body's immunological response (Gebel, 2002).

There are suspicions of linkage between arsenic and Buruli ulcer since high arsenic levels have been detected in some areas of the district like Kumpese where Buruli ulcer is high (Amofah, 1993). Aquatic-arsenic medium such as ponds, swamps, sluggish flowing water which is believed to be breeding grounds for *mycobactrium ulcerans* is abundant in the district.

Although pentavalent arsenic is considered a low risk, bacterial activity can readily convert them back into inorganic arsenic (iii) which is more mobile and more toxic (Harkins, 1910). This toxic form is believed to have a hand in Buruli ulcer situation at the district (Amofah, 1993).

Surface, drinking and groundwater passing through soils with geologically high concentrations of arsenic can become contaminated and contamination promotes Buruli ulcer (Clancey, 1964) and there are numerous surface and ground water in this district.

Inorganic arsenic can be methylated in the environment forming monomethylarsonic or dimethylarsonic acid (M/DMA) and thus enter the food chain in different forms (Mac Callum *et al*, 1948). This makes arsenic ingestion extremely dangerous.

Unlike organic pollutants, arsenic cannot be transformed into a non-toxic material; it can only be transformed into a form that is less toxic to organisms in the environment (Hughes, 2002).

Arsenic trioxide, an amphoteric substance, is very dangerous (Sabina, 2005). Biochemically, arsenic (iii) oxides have high affinity for thiols which are found at the active site of enzymes (Norman, 1998). It is readily absorbed by the digestive system but has no known physiological function.

Mine waste tailings are dumped in water bodies and they drain into larger water bodies. These tailings contain significant levels of arsenic. This depicts direct discharge of arsenic into the environment and this may be the situation in this district due to vigorous mining.

1.2 Objectives

1. To determine total arsenic levels in some soils, water and cassava from Amansie West District.
2. To compare arsenic levels in samples with set limits and make recommendations.
3. To determine pH, conductivity and solid matter content of the water samples and find the relationship between these properties and the arsenic levels.
4. To determine pH, conductivity and moisture content of the soil samples, cassava samples and cassava peels and find the relationship between these properties and the arsenic levels.
5. Compare arsenic levels in surface and ground water.
6. To compare arsenic levels in cassava (edible part) and its peels.
7. To determine the relationship between soil profile and arsenic levels.
8. To know the distribution of arsenic in the district.
9. To determine the relationship between arsenic levels in soil, water and cassava.

1.3 Justification of Objectives

Recent study (Duker *et al*, 2005) in parts of Amansie West District showed Buruli ulcer prevalence in settlements along arsenic-enriched drainage channels and farmlands.

Arsenic is toxic irrespective of the source or dosage (Norman, 1998). Arsenic is present in natural waters, marine, environmental and biological samples (Cullen *et al*, 1989) and its determination is key for water quality analysis.

High arsenic content of foods and water in Amansie West District is a major factor responsible for Buruli ulcer in that district (Amofah and Moses, 1993).

Arsenic in soils cannot be washed away by running water because its compounds bind to soils and only move short distances when water percolates down the soil (Kitchin, 2001). Its presence in water may be transferred to plants, invertebrates, fishes and bioaccumulate through the food chain. Toxicity affects livestock, agricultural products, mother to baby transfer in mother's milk.

CHAPTER TWO

2.0 LITERATURE REVIEW

This literature review gives the theoretical background of the chemistry, biochemical processes of arsenic, occurrence, sources and recommended levels of arsenic in water, soil and cassava. It also covers the uses, toxicological effects, relationship between mining, arsenic and Buruli ulcer as well as methods of determining arsenic.

2.1 The Element Arsenic (As)

Arsenic (specific gravity of 5.4 - 5.9) is a naturally occurring mineral found in soils and bedrock. It behaves like a metal, has atomic number 33 and relative atomic mass 74.92. It is regarded as a hazardous heavy metal though it is actually a semi-metal (Brooks, 1972).

Arsenic is found in the ore, arsenopyrite (FeAsS). Arsenopyrite is a common impurity in gold- and copper-containing ores and liberates arsenic trioxide upon heating in air. This ore is structurally related to iron pyrite. Arsenic is also found in arsenolite (As_2O_3), olivenite (Cu_2OHAsO_4), mimetite ($Pb_5Cl(AsO_4)_3$ and cobaltite (CoAsS). Minerals with the formula MAsS and MAs_2 (M = Fe, Ni, Co) are the dominant commercial sources of arsenic, together with realgar (an arsenic sulphide mineral, As_2S_2). Arsenic also occurs in various organic forms in the environment. It is also found in other sulphides and sulfosalts like orpiment (As_2S_3), lollingite and tennantite. These ores are usually not mined as such but recovered as a by-product from the smelting of copper, lead, zinc and other ores.

In its pure form, it is a silver-gray or a white brittle metal. Arsenic is odourless, water soluble and almost tasteless. It is ubiquitous because of its redox conversion between trivalent and pentavalent states. The interaction of arsenicals with bacteria is thought to account for changes in oxidation state and chemical form of arsenic in organic substances (Henders, 2000).

The most common oxidation states for arsenic are: −3 in the arsenides, such as alloy-like intermetallic compounds; +3 in the arsenites and most organoarsenic compounds and +5 (pentavalent). It typically occurs in the +3 and +5 states, illustrated by the halides AsX_3 (X = F, Cl, Br, I) and AsF_5.

The formation of the element of arsenic can be achieved by smelting loellingnite ($FeAs_2$) at 675°C in the absence of air and condensing the sublimed element.

$$FeAs_2(s) \xrightarrow{(675^\circ C)} Fe + 2As(g) \xrightarrow{(Condensing)} As(s)$$

Arsenic will not react with water without air (Jerome, 1994).

Heating arsenic in the air will produce a blue flame and give off a garlic-like odour. The reaction is shown below:

$$4As(s) + 3O_2(g) \longrightarrow 2As_2O_3(s)$$

Arsenic makes arsenic acid with concentrated nitric acid, arsenious acid with dilute nitric acid, and arsenic trioxide with concentrated sulphuric acid (William *et al*, 2001).

Arsenic forms colourless, odourless, crystalline oxides As_2O_3 ("white arsenic") and As_2O_5, which are hygroscopic and readily soluble in water to form acidic solutions. It is reported that the predominant oxidation state of inorganic arsenic in sea water is the

pentavalent arsenate (Buchanan, 1962) but methylated forms have also been reported by Braman and Forebac (1973).

In the weathering of sulphides, arsenic can be oxidised to arsenite and arsenate. Arsenic oxide is also formed as a by-product of copper, lead and nickel smelting.

Arsenic is found in a wide array of chemical species that vary in toxicity and mobility. These species can readily be transformed by biological activity, redox potential or pH changes. This creates the possibility of a wide variety of unstable arsenic species in the environment.

2.1.1 Sources and Estimated Levels of Arsenic in Some Samples

The exact levels of arsenic in biological and environmental samples are subject of debates; values from literature are estimates.

2.1.1.1 Natural Sources

About one third of atmospheric arsenic comes from natural sources, such as volcanoes, and the rest come from man-made sources. It is naturally present in the environment, usually as a component of inorganic compounds. For example, the terrestrial crust contains 3 mg/kg arsenic usually in the form of arsenopyrite (FeAsS).

Arsenic in ground water results primarily from natural geochemical interactions between water and arsenic-containing rocks and minerals (Welch *et al*, 2000). These minerals are usually metal oxides (aluminium and iron) and the natural phenomena are usually weathering and volcanic eruptions. In sea water, arsenic is naturally occurring.

Leaching of arsenic from soil, landfills, or slag deposits is a source of arsenic in groundwater.

Although industrial, agricultural and mining wastes are potential sources of arsenic contamination in groundwater, the primary source of arsenic in groundwater is naturally-occurring arsenic (Welch et al., 2000). Arsenic is commonly concentrated in sulphide minerals and hydrous iron oxides (Nordstrom, 2002), which may be present in aquifer sediments.

Marine organisms can contain hundreds of mg/kg of arsenic, accumulated from their surrounding water, sediments and food sources, especially in organisms which feed on the ocean floor. Also, seafood, which is the main source of total arsenic in the human diet, contains mainly organic arsenic species. Arsenic is also found in seawater at concentrations of 2-5 µg/L (Johnson, 1972).

Environmental levels of arsenic vary. In air, levels are lowest in remote and rural areas, higher in urban areas, and highest close to industrial sources. In water, levels of arsenic are lowest in seawater, higher in rivers and lakes and highest in water from underground areas containing volcanic rock or arsenic-rich mineral deposits.

Soils averagely contain 0.05–0.2 mg/kg but agricultural activities have produced a concentration of approximately 10 mg/kg (William and Frakenberger, 2001). However, WHO has set 20 mg/kg as the maximum limit for arsenic in soils for agricultural fields (Duker *et al*, 2004). Soils in some parts of Cornwall (extreme southWest of England) have the world's highest concentration of arsenic, up to 2500 ppm. The presence of

arsenic in soil is such a universal occurrence that scientist have noted that even virgin soils contain 4 ppm of arsenic.

Marine sediments can accumulate up to 40 mg/kg (William and Frakenberger, 2001). In seas and oceans, arsenic is present at a uniform concentration of 2 µg/kg, usually as inorganic arsenic with low concentrations of monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA).

Microbes in soil and sediment also release substances containing arsenic into the atmosphere. Erosion of natural deposits is a source of arsenic.

Arsenic is generally present in sea-living animals at higher levels than in freshwater animals, or plants and animals that live on land (WHO, 2001). Plants on land can accumulate arsenic compounds via uptake from soil and/or deposition from air onto leaves.

2.1.1.2 Anthropogenic/Man Made Introduction of Arsenic

Anthropogenic influence depends on intensity of human activity, distance from pollution sources and pollutant dispersion pattern (Cheng, 1985, 1992). It is estimated that the amount of arsenic released as a result of human activities is about twice that from weathering (Ferguson & Gavis, 1972). Arsenic trisulphide has been reported from coal combustion, organic arsines from oil combustion, and arsenic trichloride from refuse incineration (Scolari, 1999).

Anthropogenic sources of arsenic release to water include mining, nonferrous metals, copper smelting, waste water, dumping of sewage sludge, coal burning power plants, urban runoff, atmospheric deposition and poultry farms. Significant amounts of arsenic

are released in liquid effluents from gold-milling operations using cyanide (Hochella, 2000).

Arsenic may also enter the environment as inorganic arsenic from pesticides and fertilizers and also from industrial processes such as the production of alloys, electronics and glass.

Arsenic concentrations in US surface soils are in the range of 0.1 to 97.0 mg/g with the major source being a result of human activities (Benson, 1983).

Nriagu (1994) estimated global anthropogenic inputs of arsenic into rivers, lakes and oceans for 1983. The annual estimated inputs ranged from 11,600 to 70,300 metric tons with a median value of 41,800 metric tons.

2.1.2 Route of Exposure to Arsenic

It is known that trace metal elements are distributed in the environment via primary dispersion (ingenuous activity) and secondary dispersion (weathering). A third process (tertiary dispersion) results from human activities (Brooks, 1972). The major routes of exposure are discussed below.

2.1.2.1 Occupational Exposure

Exposure to arsenic in the workplace can be quite high, but the amounts present in the air in the workplace are controlled in many countries. Occupational exposure to arsenic may occur with copper or lead smelting and wood treatment, among workers involved in the production or application of pesticides containing organic arsenicals.

2.1.2.2 Breathing

Arsenic in food or water does not evaporate into the air. However, burning arsenic-containing materials such as treated lumber will put arsenic fumes into the air. Tobacco smoke contains traces of arsenic. The quantities of arsenic breathed in by non-smokers are very small, except in industrially polluted areas.

2.1.2.3 Food/Water

Food is usually the largest source except in areas where drinking water is naturally contaminated with arsenic. Humans are exposed to arsenic through drinking water and food (meat, fish and poultry). Poultry is usually the largest source of food-based arsenic ingestion due to usage of certain antibiotics in chicken feed (Ferreira, 2004). Arsenic was also found in wine if arsenic pesticides are used in the vineyard. Organic arsenic exposure can occur by eating sea foods.

2.1.3 Arsenic Toxicity

Arsenic has notoriety for being a toxic element but it is established that its toxicity critically depends on the chemical form in which it is found (Smith *et al*, 1992). Health risk depends on the amount exposed, the number of years exposed, period of exposure, individual sensitivity (bioavailability) and route of exposure. The age of persons can also influence toxicity. For example, young children are more susceptible to the effects of exposure because they absorb several times the percent ingested compared with adults and because their brains are more plastic and even brief exposures influence developmental processes (Griffis *et al*, 2002).

Toxicity is a function of solubility. Insoluble compounds as well as the metallic forms often exhibit negligible toxicity.

In general, trivalent forms (reduced forms) are more toxic than pentavalent forms, and inorganic forms are more toxic than organic forms. Arsenic trioxide (inorganic) is 500 times more toxic than pure arsenic.

High levels of arsenic in natural waters may be transferred to plants (e.g., rice), invertebrates and, finally, fish through the food chain. Arsenic toxicity affects livestock, agricultural products and can be transferred from mother to baby through breast feeding (Bentley *et al*, 2002).

Long-term exposure to toxic forms of arsenic may cause digestive problems, vomiting, abdominal pains, diarrhoea often accompanied by bleeding, convulsions, kidney inflammation, abnormalities in the coagulation of the blood, skin cancer, high blood pressure, stomach upset, gastrointestinal irritations, cardiovascular collapse nervous system breakdown (Gebel, 2002). It also causes low intelligent quotient (IQ) if it affects developing foetus and young children (Goldfrank, 2006). Arsenic is related to stroke (cerebrovascular diseases), chronic lower respiratory diseases and diabetes. The final result of arsenic poisoning is coma which may eventually lead to death.

Long term exposure to arsenic is related to vitamin A deficiency which results in heart diseases and night blindness (Hammond, 2000). Acute minimal lethal dose of arsenic in adults is estimated to be 70 to 200 mg or 1 mg/kg/day.

In general organoarsenic compounds are less toxic than their corresponding oxyacids. Organoarsenic compounds are usually found in lower concentrations, however, under

the right conditions, they can be found in very high concentrations. For example, in freshwater lakes, methylated arsenic can make up to 60% of the total arsenic.

Arsenic also occurs in various organic forms in the environment. Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation.

According to the International Agency for Research on Cancer (IARC) 1990 report, there is enough evidence to conclude that "arsenic and arsenic compounds" can cause cancer in humans.

WHO recommends a limit of 0.01 mg/L (10 ppb) of arsenic in drinking water. However, recent findings show that consumption of water with levels as low as 0.00017 mg/L (0.17 ppb) over long periods of time can lead to arsenicosis.

Toxicity in foods is dangerous because arsenic in foods do not evaporate into the air. Averagely, a person's average intake is about 10–50 µg/day. Values about 1000 µg are not unusual following consumption of fish or mushrooms and this makes all and sundry susceptible to arsenic toxicity.

The recommended limit of arsenic in foods is 1 mg/kg (WHO, 2001).

Although arsenic is toxic, the human body has ability to eliminate it. Organic arsenic as arsenates (+5 form of arsenic) and elemental arsenic are handled fairly easily by the body and eliminated by the kidneys through urine and faeces. The liver converts absorbed arsenic to less hazardous forms and the kidneys then remove it in the urine (Abernathy *et al*, 1999). Most of the arsenic is gone several days after exposure. Most arsenic leaves the body within a few days though traces in hair and nails may be

detected after death. When extremely exposed arsenic may be detected in hair or fingernails after six to twelve months (ATSDR, 2007).

2.1.3.1 Biochemical Basis of Arsenic Toxicity

The high affinity of arsenic (III) oxides for thiols is usually assigned as the cause of the high toxicity. Thiols, in the form of cysteine residues, are situated at the active sites of many important enzymes. These enzymes are destroyed by arsenic (Mohapatra *et al*, 2007).

Arsenic and many of its compounds are potential poisons. Arsenic disrupts ATP production through several mechanisms. At the level of the citric acid cycle, arsenic inhibits pyruvate dehydrogenase and by competing with phosphate, it uncouples oxidative phosphorylation, thus inhibiting energy-linked reduction of NAD+, mitochondrial respiration, and ATP synthesis (Alloway, 1990). Hydrogen peroxide production is also increased, which might form reactive oxygen species and oxidative stress. These metabolic interferences lead to death from multi-system organ failure probably from necrotic cell death.

2.1.3.2 Arsenic in the Body

When arsenic is inhaled due to its presence in airborne particles, the amount absorbed into the blood stream depends on two things – how soluble the particular form of arsenic is and how small the particles are. In the gut, soluble arsenic compounds present in food are rapidly absorbed into the blood stream (Murphy and Guo, 2003).

Many arsenic compounds are quickly transformed and eliminated from the body via the urine. However, there are individual differences in the ability to get rid of arsenic compounds.

The amount of arsenic in the body can be estimated by determining arsenic in the blood, urine, hair or nails. Arsenic disappears rapidly from blood, so measurements in blood only tell you about recent high exposures, such as poisonings, or long-term exposures if they are repeated and high. Levels in urine are the best measure of recent exposure, whereas levels in hair and nails can tell you about past exposure.

2.2 Mining

Mining is the extraction of valuable minerals or other geological materials from the earth, from an ore body, vein or (coal) seam. Mining techniques can be divided into two common excavation types: surface mining and sub-surface (underground) mining. Surface mining is much more common, and produces, for example, 85% of minerals (excluding petroleum and natural gas) in the United States, including 98% of metallic ores. Targets are divided into two general categories of materials: *placer deposits*, consisting of valuable minerals contained within river gravels, beach sands, and other unconsolidated materials; and *lode deposits*, where valuable minerals are found in veins, in layers, or in mineral grains generally distributed throughout a mass of actual rock. Both placer and lode ore deposits are mined by both surface and underground methods.

Processing of placer ore material consists of gravity-dependent methods of separation, such as sluice boxes. Only minor shaking or washing may be necessary to disaggregate (unclump) the sands or gravels before processing. Processing of ore from a lode mine,

whether it is a surface or subsurface mine, requires that the rock ore be crushed and pulverized before extraction of the valuable minerals begins. After lode ore is crushed, recovery of the valuable minerals is done by one, or a combination of several, mechanical and chemical techniques.

Surface mining is done by removing (stripping) surface vegetation, dirt, and if necessary, layers of bedrock in order to reach buried ore deposits. Techniques of surface mining include; Open-pit mining which consists of recovery of materials from an open pit in the ground, quarrying or gathering building materials from an open pit mine, strip mining which consists of stripping surface layers off to reveal ore/seams underneath, and mountaintop removal, commonly associated with coal mining, which involves taking the top of a mountain off to reach ore deposits at depth. Most (but not all) placer deposits, because of their shallowly buried nature, are mined by surface methods. Landfill mining, finally, involves sites where landfills are excavated and processed.

Sub-surface mining consists of digging tunnels or shafts into the earth to reach buried ore deposits. Ore, for processing, and waste rock, for disposal, are brought to the surface through the tunnels and shafts. Sub-surface mining can be classified by the type of access shafts used, the extraction method or the technique used to reach the mineral deposit. Drift mining utilizes horizontal access tunnels, slope mining uses diagonally sloping access shafts and shaft mining consists of vertical access shafts.

Additional sub-surface mining methods include hard rock mining, bore hole mining, drift and fill mining, long hole slope mining, sub level caving and block caving.

Heavy machinery is needed in mining for exploration and development, to remove and stockpile overburden, to break and remove rocks of various hardness and toughness, to process the ore and for reclamation efforts after the mine is closed. Bulldozers, drills, explosives and trucks are all necessary for excavating the land. In the case of placer mining, unconsolidated gravel, or alluvium, is fed into machinery consisting of a hopper and a shaking screen or trommel which frees the desired minerals from the waste gravel. The minerals are then concentrated.

Mining and processing operations include crude methods in digging, tunneling, timbering as well as in the use of the toxic chemical mercury in the extraction of gold from the ore.

2.2.1 Mining and Arsenic

Mines produce tailings with residual arsenic content due to the presence of arsenopyrite (FeAsS) in the ore (Lide, 1992). Arsenic is a natural component of the bedrock and mining results in weathering resulting in increases levels of arsenic in the environment.

2.3 Buruli ulcer

Buruli ulcer frequently occurs near water bodies – slow flowing rivers, ponds, swamps and lakes (Muelder, 1992). Activities that take place near water bodies, such as farming is a risk factors. *Mycobacterium ulcerans* (M. *ulcerans*) is a pathogen which infects the upper layers of the skin in humans. A toxic substance released called mycolactone suppresses the immune system and causes the healthy body cells to undergo

programmed death or apoptosis. It is a treatable disease but very little is known about this ailment.

The reasons for the growing spread of the disease remain unclear. All ages and sexes are affected, but most patients are among children under 15 years (Barker, 1973). In general, there is no difference in the infection rate among males and females. The disease can affect any part of the body, but in about 90% of cases the lesions are on the limbs, with nearly 60% of all lesions on the lower limbs.

Symptoms

Buruli ulcer often starts as a painless, hard, abnormal mobile swelling in the skin called nodule. Others include skin pimples, infection on the face or abdomen in children, fever, physical trauma and gross bone deformities. Permanent disabilities are seen in 25% of patients (Bayley, 1971).

Infection often leads to extensive destruction of skin and soft tissue with the formation of large ulcers usually on the legs or arms. Delayed treatment may cause irreversible deformity, long-term functional disability such as restriction of joint movement and extensive skin lesions.

Transmission

The exact mode of transmission is still under investigation.

2.3.1 Buruli ulcer and Arsenic

Arsenic is environmentally permanent. It is water soluble and suspected to stimulate the growth of *Mycobacterium ulcerans*, the aquatic bacteria which causes Buruli ulcer (Bentley, 2002). Arsenic trioxide is amphoteric and upon contact with wounds, catalyses the toxin called mycolactone which causes damage to the soft tissues and skin. This adverse effect is believed to prepare the grounds for Buruli ulcer. .

Mycobacteruim ulcerans is an environmental mycobacterium. The bacteria can be cultured provided the incubation temperature is kept between 29–33 °C (MacCallum *et al*, 1948).

Arsenic compounds being water soluble, amphoteric, ability to be methylated and ability to undergo redox may have a hand in polymer chain reaction (Clancey, 1964).

Gyasi *et al*, (2012) conducted a study to determine the arsenic levels in streams and soil around Buruli ulcer (BU) endemic and non endemic communities in the Amansie West District of the Ashanti Region of Ghana over a period of 12 months. When the levels of arsenic during the study were analysed based on endemicity, it was revealed that arsenic concentration for streams and sediments in BU endemic communities were higher (0.8720 ± 0.4235 mg/L) compared to their non-endemic counterparts (0.739 ± 0.4188 mg/L). Mean levels of arsenic in the soil when stratified based on endemicity revealed that, endemic levels (1.820 mg/kg) were higher than that of the non-endemic (1.108 mg/kg) areas. It is an undeniable fact that long-term exposures to arsenic via drinking water are known to cause a number of arsenic related diseases including cancer of the skin. In the absence of clear cut pathogenesis to *M. ulcerans* infections, these elevated arsenic levels in Buruli ulcer endemic community cannot be ignored.

Gyasi *et al* (2012) again conducted a study to determine the effect of arsenic on mice with a possible linkage to Buruli ulcer. Six-week old Imprinting Control Region (ICR) mice bred in the animal facility of the Department of Pharmacology, KNUST, Ghana, were used for the study. ICR mice were introduced to 0.8 to 4.8 mg/L arsenic, synonymous to arsenic detected from streams and soils in Buruli ulcer endemic communities of the Amansie West District of the Ashanti Region of Ghana, via their drinking water. For three weeks, there was no effect. However, after thirty-one days, mice with arsenic exposure of 4.0 to 4.8 mg/L developed inflammation, loss of hair, tail deformities, erythema and open ulcers on skin (with scab formation). Histopathological studies revealed liver and spleen damage. There was hepatic cell swelling with the loosening of cell wall and degenerative change with cells showing cytoplasmic vacoulation with nuclear blebbing and gradual cell loss. The spleen developed a lymphoid background with multinucleate cells formation. Hematological examination revealed significant dose-dependent decrements in white blood cells indicating a detrimental effect on the body's immune system, a situation which makes the body susceptible to infections including M. *ulcerans*.

In a work published in 2004 using spatial dependency, samples of water from arsenic enriched domains and farmlands in the Amansie West district (part of which has a high prevalence of BU) was carried out and it was hypothesized that arsenic in drinking water indirectly may contributes to Buruli ulcer infection (Duker *et al*., 2004).

Asiedu *et al*, 2000 had arsenic levels in stream sediments in Buruli ulcer endemic regions above 15 ppm in the Amansie west District.

2.3.2 Buruli ulcer Occurrence in Ghana

The first probable case of Buruli ulcer in Ghana was reported in the Greater Accra Region in 1971. Numerous Buruli ulcer cases have since been reported in Ghana.

Table 2.1 below shows the prevalence rates of Buruli ulcer in 10 districts in Ghana with the highest caseloads.

Table 2.1 Prevalence Rates of Buruli ulcer in Ten Most Endemic Districts in Ghana (Ministry of Health, 1999)

District	Region	No. of Cases	No. of Active and Healed Lesions	Prevalence Rate(Per 100,000)
Ga	Greater Accra	467	1113	87.7
Amansie West	Ashanti	159	474	150.8
Assin	Central	159	173	83.7
Gomoa	Central	158	161	81.9
Asante Akim North	Ashanti	138	265	131.5
Wassa Amenfi	Western	136	167	61.1
Kwahu South	Eastern	122	132	57.0
Upper Denkyira	Central	121	306	114.7
Afigya Sekyere	Ashanti	118	149	107.1
North Tongu	Volta	107	129	85.7

2.4 Water

The chemistry of water parameters in relation to arsenic content of the water has been given prominence by many authors some of which are reviewed below.

The depth at which the water is sampled makes the water surface or ground as shown in fig 2.1.

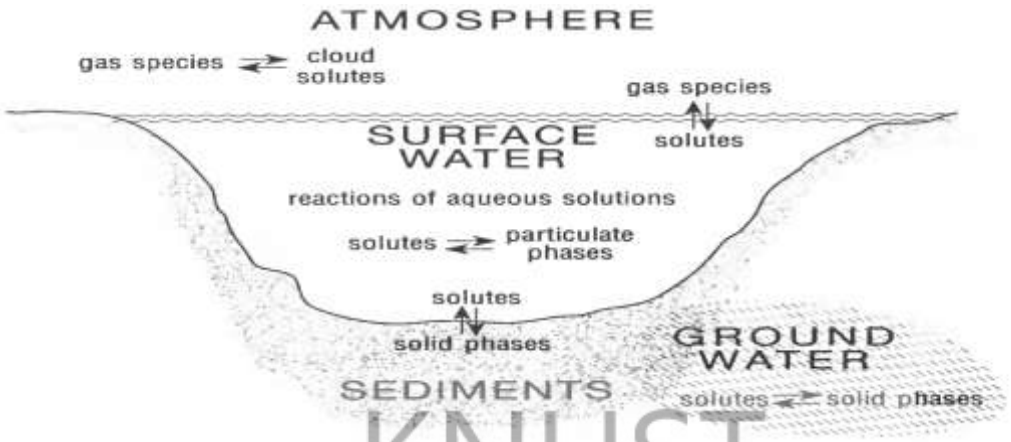


Fig 2.1 The depth of the water makes the water surface/ground water (Johnsons, 1972)

2.4.1 The chemistry of Arsenic in Water

In aquatic systems, inorganic arsenic occurs primarily in two oxidation states, As (V) and As (III). Both forms generally co-exist, although As (V) predominates under oxidizing conditions (such as in surface water) and As (III) predominates under reducing conditions (ground water containing high levels of arsenic).

Arsenic in water can undergo a complex series of transformations, including redox (an arsenic atom taking or losing electrons to another atom), ligand exchange (electron exchanges involving other atoms which are combined with a central arsenic atom), biotransformation (chemical changes to arsenic atoms within the body of a living thing) and precipitation (Hochella and White, 2000). Rate constants for these various reactions are not readily available, but the factors most strongly influencing fate processes in water are redox potential, pH, metal sulphide and sulphide ion concentrations, iron concentrations, temperature, salinity, distribution and composition of the biota, season,

nature and concentration of natural organic matter (Moore and Ficklin, 1988). Based on these interactions, many arsenic compounds can dissolve in water.

In the pH range of natural-waters, the predominant aqueous inorganic As (V) species are $H_2AsO_4^-$ and $HAsO_4^{2-}$; the main inorganic As(III) species is $As(OH)_3$ (Asante and Ntow, 2007).

Inorganic arsenic is generated when arsenic binds with elements such as oxygen, chlorine and sulphur (Asante *et al*, 2007). Arsenic in plants and animals binds with carbon and hydrogen, forming organic arsenic. Inorganic species of arsenic are predominant in aquatic environments. The main organic species in fresh water are monomethylarsonates (MMA) and dimethylarsonates (DMA); however, these species are usually present at lower concentrations (Smedley, 1996). The main organoarsenic species in ground water are: monomethylarsenic acid, dimethylarsenic acid, trimethylarsine oxide and trimethyl arsine. Aquatic microorganisms may reduce the arsenate to arsenite, as well as methylate arsenate to its mono- or dimethylated forms (Smedley *et al*, 1996; Amasa, 1975; Amoah, 2006). Methylated species are also produced by the biogenic reduction of complex organoarsenic compounds like arsenocholine or arsenobetaine. Reduction and methylation of As (V) may lead to increased mobilization of arsenic.

Comparison of arsenate and arsenite was done experimentally by Allison *et al* (1991). They deduced the following: generally, leaching of arsenate is slow because of binding to hydrous iron and aluminium oxides. Metal arsenites are much more soluble than the corresponding metal arsenates, and arsenites are adsorbed less by solid phases. The

concentration of As (III) decreases overtime as it oxidizes to As (V). Either arsenate [As (V)] or arsenite [As (III)] can be the dominant inorganic form in ground water. Arsenate ($H_nAsO_4^{n-3}$) generally is the dominant form in oxic waters whiles arsenite ($H_nAsO_3^{n-3}$) dominates in sulphidic and methanic waters (Benner *et al*, 1995), including deeply circulating geothermal water (Aggett and Kriegman, 1987).

Table 2.2 below gives the principal reactions affecting inorganic arsenic concentrations in ground water and the conditions favouring the reactions.

Table 2.2 Main Reactions Affecting Inorganic Arsenic Concentrations in Ground water and Prevailing Conditions for the Reactions (Moore *et al*, 1988)

Redox Condition	Important Phases	Important Reactions	Conditions That Arsenic Mobility
Oxic (DO present)	Fe-oxides	Adsorption/desorption and precipitation	pH, presence of competing adsorbent; oxygen and Fe^{3+} concentration
Oxic (DO present)	Sulphide minerals	Sulphide oxidation	pH and microbial activity; oxygen and NO_3 transport
Post-oxic (DO and sulphide absent)	Fe-oxides	Adsorption/desorption and precipitation	pH, presence of competing adsorbent; oxygen and Fe^{3+} concentration, Oxidation state of arsenic
Post-oxic (DO and sulphide absent)	Fe-oxides	Adsorption/desorption	pH
Post-oxic (DO and sulphide absent)	Fe-oxides	Dissolution	Presence of organic carbon
Sulphidic (sulphide present)	Sulphide minerals	Precipitation	Sulphide, arsenic and iron concentration

2.4.2 pH of Water and Its Effects on Arsenic

The pH of water affects the solubility of arsenic in water (Amasa, 1975). At pHs that dissolves the mineral phase, anything bound to the compound will be released. At high pH, arsenic may be released from surface binding sites that lose their positive charge (Amoah *et al*, 2006). Hence, as the pH rises, the arsenic concentration rises though the correlation is not always perfect. Arsenic, at pH 8 and above, is readily soluble and thus transported easily through ground water. Smedley (1996) deduced that dissolved total arsenic levels are higher in deeper ground waters (at Obuasi) under conditions of lower electrode potential and higher pH (greater than 6). The increased solubility and concentration of arsenic at alkaline pH may also be due to increased hydrophilic characters at these pH values (Amonoo-Neizer and Amekor, 1993). Also the pH of the groundwater may be high due to the dry, arid conditions. Water evaporates under these conditions, raising the concentration of everything (including arsenic) dissolved in it.

Based on experimental findings, Stute and van (2006) recommended that arsenic removal from alkaline ground water should be carried out by first lowering the pH.

Arsenic mobility in water is influenced by pH of the water. Wilkie and Hering (1996) examined the effects of high pH on arsenic mobility in a sandy aquifer in Washington and concluded that high pH of ground water enhanced arsenic mobility. It is established (Smedley, 1996) that higher pHs favour arsenic solubility in ground water. By extension, the greater the solubility, the greater the mobility. At neutral pH values, As (III) is more mobile than As (V) because it is less strongly adsorbed on most mineral surfaces.

The pH of water has a bearing on the ability and extent of arsenic adsorption onto substrates. In acidic and near neutral waters, As (V) is extensively adsorbed, while As (III) is relatively weakly adsorbed onto iron oxides, suspended solids and sediments in water column (Dzombak and Morel, 1990). The adsorption of As (V) at higher pH is because $H_2AsO_4^-$ carries a single negative charge at or below pH 7, but it loses a proton at higher pH, resulting in a doubly charged anion, $HAsO_4^{2-}$. The singly charged anion is adsorbed more effectively from solution than the doubly charged species. However, at high water pHs (greater than 9), As (V) desorption is favoured and sediment-bound arsenic may be released back into the water by chemical or biological interconversions of arsenic species (Anawar and Akai, 2004). The desorption is because as the pH is raised, the charge on the arsenic compounds becomes more negative and they should be better at binding to positively charged sites on the soil surface (Dzombak and Morel, 1990). This is however not the case because the soil binding sites are also affected by the pH. As the pH goes up and the water becomes more basic, OH^- groups from the water also associate with the adsorption or ion exchange sites on the soil, neutralizing them. Once they have been neutralized, they are not attractive to the arsenic compounds. The higher pH in borehole water is attributed to buffering from dolomite that is exposed in the borehole and remains saturated under non-pumping conditions (Allison *et al*, 1991).

The form of arsenic that will be in solution is affected by the water pH. Up to pH of 7, all trivalent arsenic species in water exist as H_3AsO_3 (arsenous acid). For pH 7 and 8, it exists as H_3AsO_3 and $H_2AsO_3^-$ though most exist (over 80%) as H_3AsO_3. At pH of 9,

equilibrium is reached and there is an equal fraction of H_3AsO_3 and $H_2AsO_3^-$. From pH 9 to12, most trivalent arsenic is present as $H_2AsO_3^-$ though fractions of H_3AsO_3 are present. Beyond pH 12, all arsenic (iii) species in solution exist is as $H_2AsO_3^-$ (Benner *et al*, 1995). Most pH range of ground water is 6.5 to 8.5 and $H_2AsO_3^-$ is the predominant form of trivalent arsenic.

This is vividly illustrated in figure 2.2 below.

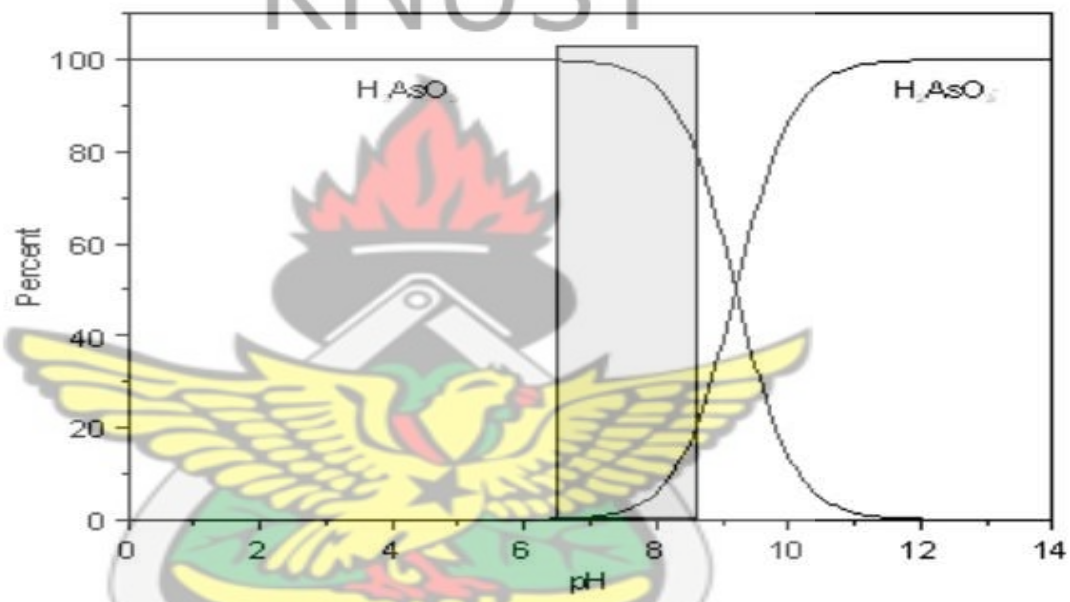


Fig 2.2 Concentrations of the As (III) species: H_3AsO_3 and $H_2AsO_3^-$ at different pH values. The shaded area is the pH range of most ground waters (Benner *et al*, 1995)

For pentavalent arsenic, at pH less than 2, it exists as H_3AsO_4 though $H_2AsO_4^-$ is also present (Benner *et al*, 1995). H_3AsO_4 and $H_2AsO_4^-$ are in equilibrium at pH of 2. Between pH 2 and 6.5, $H_2AsO_4^-$ dominates. $HAsO_4^{2-}$ dominates at pH range of 6.5 to 10.5. From pH of 10.5 to 14, pentavalent arsenic is predominantly AsO_4^{3-}. The

commonest range of pH of ground water is 6.5 to 8.5 and in this range, arsenic (v) exists as $HAsO_4^{2-}$.

The As (V) variation based on pH is shown in fig 2.3

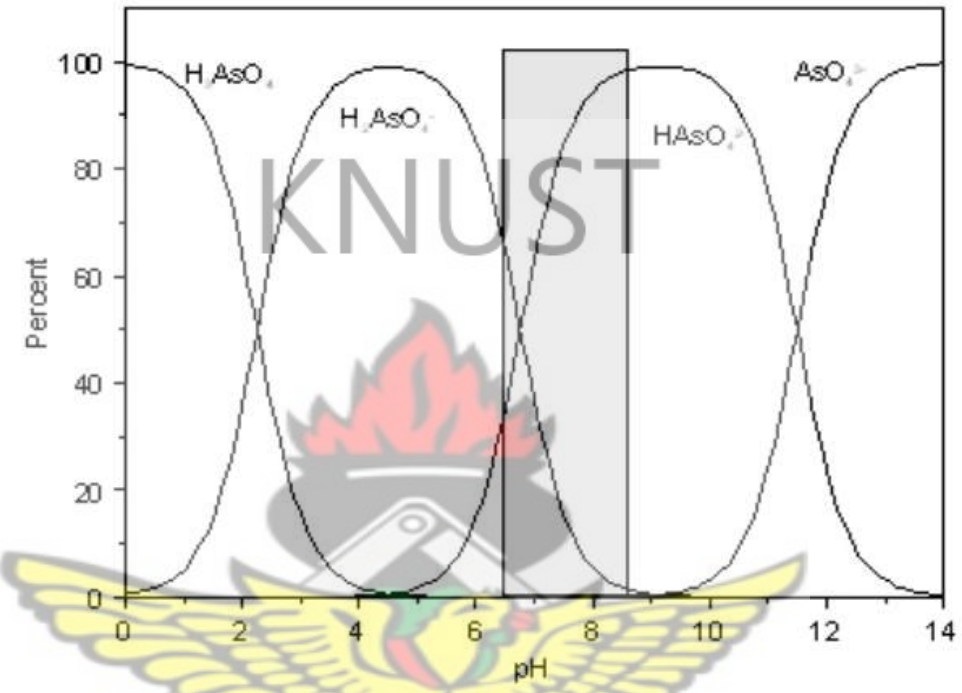


Fig 2.3 Concentrations of the As (V) species: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} at different pH values. The shaded area is the pH range of most ground waters ((Benner *et al*, 1995)

2.4.3 Conductivity of Water and Its Relationship with Arsenic

Conductivity is a measure of the salts dissolved in a sample. It measures how well water sample conducts an electrical current, a property that is proportional to the concentration of ions in solution and their mobility. It is an indirect measure of the presence of inorganic dissolved solids, such as chlorides, nitrate, sulphates, phosphates, sodium, magnesium, ammonium, potassium, bicarbonate, calcium and iron. These substances

conduct electricity because they are charged in aqueous medium. Sources of these ions include- calcium (gypsum), calcium and magnesium (clay minerals), sulphate (oxidation of sulphide ores, gypsum), chloride (igneous and sedimentary rocks), bicarbonate/carbonate (limestone).

Conductivity is also affected by human influences, for example, agricultural runoffs can raise conductivity because of the presence of phosphates and nitrates. Generally, conductivity values below 3500 µS/cm are acceptable for drinking water (Faulkner *et al*, 1989).

We reference all electrical conductivity (EC) readings at 25°C to eliminate temperature differences associated with seasons and depths (Campbell, 1990).

All other things being equal, water conductivity rises as arsenic levels rise (Acharyya *et al*, 2000). Experiment by Mahimairaja *et al* (2005) led to the conclusion that water conductivity has poor correlation with arsenic content. They attributed it to the fact that arsenic is generally not a major ion in water so any rise or fall in conductivity value is not likely to be caused by arsenic.

2.4.4 Factors That Influence Arsenic Solubility and Mobility in Water

The solubility of arsenic species depends on a number of factors including pH, cations present (iron, manganese and their respective oxides) and adsorbing surfaces (Appelo *et al*, 2002). Higher pH favours arsenic solubility (as explained under pH).

Sulphate-reducing conditions reduce the solubility of arsenic by promoting the precipitation of arsenic-containing sulphide solid phases (Bagga and Peterson, 2001).

Although the redox state of a system is important, arsenic solubility and transport is dominated by adsorption reactions that occur at the surface of reactive iron and aluminum oxide minerals. As (V) is the form that is more readily co-precipitated with or absorbed on metal oxides and this limits the solubility of pentavalent arsenic species relative to trivalent ones. Therefore, immobilization of arsenic in the environment occurs through precipitation of low-soluble salts and adsorption onto soils and sediments.

Recent evidence suggests that natural organic matter (NOM) can complex arsenic to form stable solution complexes (Redman *et al*, 2002). The arsenic solubility increases due to the presence of such stable arsenic-NOM complexes. However, details of these interactions are limited.

Arsenic sulphides are less soluble arsenic-containing solid phases but they become very soluble due to the oxidation of sulphide that occurs at very low redox potentials and the consequent generation of acid drainage.

Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility (Wilkie and Hering, 1996). Arsenic mobilization is high in reducing conditions (Stute and Geen, 2006) though not all reducing water contains arsenic.

From above, there are two independent factors that are likely to increase the mobility of arsenic under reducing conditions which are: the reduction of As (V) to As (III), which is more mobile and the reduction of binding sites that releases bound arsenic.

Water bacteria can catalyse the reduction of As (V) to As (III). That reaction would increase the mobility of arsenic in water. Bacteria does this by reducing the arsenic

(directly) or indirectly (by reducing the binding site). These activities in groundwater are usually limited by the amount of food available to the bacteria. Therefore, bacteria influence increase arsenic mobility.

Organic carbon (from sedimentary-organic matter and anthropogenic organic compounds) in water also increase arsenic mobility (Akai *et al*, 2004). The carbon acts as a reductant by reducing the redox potential and fueling the reduction of As (V) to As (III) and Fe (III) to Fe (II).

In a nutshell, two categories of processes largely control arsenic mobility in aquifers: (1) adsorption and desorption reactions and (2) solid-phase precipitation and dissolution reactions.

The use of phosphates fertilizers stimulate arsenate release through competition for binding site and increase arsenic mobility (Dowdle *et al*, 1996).

Vameralı *et al* (2009) suggested that the elevated concentrations of dissolved arsenic in Mexican waters may be due to the presence of calcium carbonate (limestone) that buffers acidity and introduces alkalinity. Arsenic is more soluble and more mobile in basic medium.

2.4.5 Solid Matter Content of Water

Soil matter content of water refers to total, dissolved and suspended solids. These solids can be determined by gravimetry or estimated from the conductivity value. In gravimetry, the substance being determined is converted into an insoluble precipitate which is collected and weighed (Hem, 1970).

TS (total solids) refers to all matter in a water or wastewater sample that is not water and may be differentiated according to size into TDS (total dissolved solids) and TSS (total suspended solids). All solids passing through filter paper of a 2 µm pore size are called dissolved, and those retained are termed suspended. Therefore, the overall definition of total dissolved solids is: all matter that is not retained by a filter, and is not lost by evaporation and drying to constant weight.

TDS is a measure of the amount of material dissolved in water including carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions.

If TDS concentrations are too high or too low, the growth of many aquatic lives can be limited, and death may occur. Similar to TSS, high concentrations of TDS may also reduce water clarity, contribute to a decrease in photosynthesis, combine with toxic compounds and heavy metals, and lead to an increase in water temperature.

TDS is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and/or high water hardness, and could result in a laxative effect.

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contaminants and point source water pollution discharge from industrial sewage.

Some rocks and soils release ions very easily when water flows over them; for example, if acidic water flows over rocks containing calcite ($CaCO_3$), the ions will dissolve into the water. Therefore, TDS will increase. However, some rocks, such as quartz-rich

granite, are very resistant to dissolution, and don't dissolve easily when water flows over them.

As plants and animals decay, dissolved organic particles are released and can contribute to the TDS concentration.

In theory, TSS could be used for assessing particle removals during water treatment. Volatile solids determinations are rarely made on potable water samples since far more accurate and precise information on organic content can be obtained by TOC (Total Organic Carbon) analysis. Typical Solid Concentrations in Water are shown in table 2.3 below.

Table 2.3 Some Typical Solid Concentrations in Water (Connell *et al*, 1984)

Source		**Concentration (mg/L)**		
		Low	Average	High
Natural Waters				
Fresh	TDS	20	120	1,000
Brines	TDS	5,000		300,000
Domestic Waste Water				
Raw	TDS	350	600	900
	VDS	165	285	600
	TSS	100	200	350
	VSS	75	135	215
Secondary Effluent	TSS	10	30	60
Activated Sludge Mixed Liquor (conventional)	TSS	1,500		3,000
Activated Sludge Mixed Liquor (extended aeration)	TSS	3,000		6,000
Primary Sludge	TSS	20,000		70,000
Secondary Sludge	TSS	5,000		12,000
STORM WATER	TSS	5	300	3,000

VDS-Volatile Dissolved Solids

The classification of water based on the TDS levels and the source of the water is shown in fig 2.4 below.

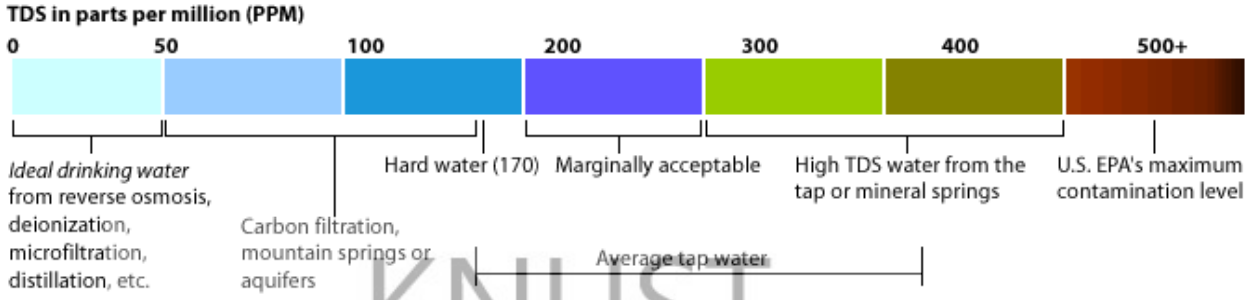


Fig 2.4 Classification of Water Based on TDS Levels and the Source of the Water (Ohio EPA, 2000)

2.4.6 Effect of Organic Matter on Arsenic Concentration in Water

Organic matter (a component of total solid in water) increases arsenic concentration and mobility in aquifer systems. It does this by influencing arsenic sorption onto HFO (Hydrous ferric oxide). Organic matter reduces the sorption and releases bound arsenic into water (Redman *et al*, 2002).

The adsorption of arsenate and arsenite to mineral surfaces is reduced in the presence of natural organic matter (NOM) (Grafe *et al*, 2001; Grafe *et al*, 2002; Redman *et al*, 2002). NOM consists of a heterogeneous mixture of polyfunctional molecules of varying size and reactivity. The effects of NOM on arsenic adsorption differ depending upon the NOM source, as well as the charging characteristics and surface area of the adsorbent mineral (Grafe *et al*, 2001; Grafe *et al*, 2002). Like sulphate and phosphate, the reduction in arsenic adsorption is presumed to result from competition between arsenic and NOM for surface sites (Grafe *et al*, 2001; Grafe *et al*, 2002). Redman *et al* (2002), however, present evidence that supports the formation of stable arsenic-NOM

solution complexes, which could be the reason for the reduced arsenic adsorption. The complexation of arsenic by NOM depended upon the NOM source and increased with NOM-bound cationic metals, particularly Fe (Redman *et al*, 2002).

Contrary to Redmans report, Manning and Goldberg (1996) stated that turbidity of water (associated with organic matter /colour/TS of the water) has no or low effect on arsenic levels in water. This may be due to the fact that arsenic is colourless. Manning and Goldberg concluded that if water turbidity is the main factor determining arsenic levels in water, then simple filtration will remove arsenic in water but this is not the case. The removal of arsenic in water requires extensive reverse osmosis. Hence, the exact relationship between solid matter and arsenic levels in water is not known but it is established that in many instances water turbidity may not correlate with arsenic concentration. What has been established beyond doubt is that, it is easier to remove arsenic from less turbid water than water with high turbidity using reverse osmosis.

2.4.7 Factors Leading to Low Arsenic Concentration in Water

Generally, low arsenic levels in shallow aquifer water could be due to in-situ iron mineralization forming siderite that significantly reduces the ability of arsenic to be in solution (Moore, 1988).

According to Fujii (1995), arsenic is also lost/removed via absorption onto the surface of ferric hydroxides (rust) or by integrating locally available iron nails with a bio-sand filter. As water enters diffuser basin, it oxidizes the iron nails from Fe(0) to Fe(II). Dissolved oxygen in the water further oxidizes Fe(II) into Fe(III) which

complexes as ferric hydroxide, $Fe(OH)_3$, more commonly known as rust. These dissolved ferric hydroxide particles then bind to the arsenic in the water creating an iron arsenic complex. By this mechanism, the arsenic will not be free to be in solution.

The low level of arsenic in most of the deep wells of the Kathmandu Valley (Nepal) could be due to the incomplete reduction of iron oxy-hydroxides (Acharyya *et al*, 2000). Complete reduction would lead to a high release of arsenic from the iron oxy-hydroxide. The oxidation state of the arsenic in water can lead to a decline in the arsenic levels in the water. Arsenate is removed more easily from water onto positive sites of sediments than arsenite, because of its greater ionic charge. This makes removal/loss of As (V) in water easier with time. Therefore, if arsenic levels in water is due to As (V), then the concentration of the arsenic will decrease with time.

The absence of phosphates and silicate lead to low arsenic levels in water. Phosphates and silicates compete with arsenic for adsorptions sites on the surface of iron oxides. When these competitors are absent, the arsenic is adsorbed onto iron oxide sediments and the arsenic will not be available in solution.

According to Bhumbla (1994), the following explanations may be attributed to the low arsenic content of dug well water:

- The oxidation of dug well water due to its exposure to open air and agitation during water withdrawal can cause precipitation of dissolved arsenic and iron.
- Dug wells accumulate groundwater from top layer of a water table. This water table is replenished each year by arsenic-free rain and surface waters by

percolation through aerated zone of the soil. The fresh recharges have diluting effects on contaminated groundwater.

- The presence of air and aerated water in well can oxidize the soils around dug wells. This infiltration of water into wells through this oxidized soil can significantly reduce the concentration of arsenic in well water.

2.4.8 Reasons for High Arsenic Concentration in Some Water Bodies

Although arsenic in water bodies comes from run-offs, certain factors lead to its high concentration including climate and geology.

Arsenic release from iron oxide (desorption) appears to be the most common cause of widespread arsenic concentrations exceeding 10 µg/L in ground water (Gosselin *et al*, 1984.). This can occur in response to different geochemical conditions, including release of arsenic to ground water through reaction of iron oxide with either natural or anthropogenic organic carbon.

Guo (2003) found that significant levels of iron oxides present in the natural aquifer material caused some retention of arsenic in a heavily mined area which led to high arsenic concentration.

Evaporation of water leads to increased arsenic levels. In Southwestern United States, ground water is highly alkaline due to the dry, arid conditions (Acharyya *et al*, 2000). Water evaporates under these conditions, raising the concentration of everything (including arsenic) dissolved in it.

When organic carbon is present in water, it can feed bacteria. The Bacteria have a hand in high concentration levels of arsenic in water. They can reduce Fe (III) on soil surfaces

to Fe (II), which is released into the water. Any arsenic that was attached to the Fe (III) binding site on the soil particle would also be released into the groundwater. The bacteria can increase the arsenic concentration by directly reducing As (V) to As (III), which is more soluble (Appelo *et al*, 2002). Arsenic trapped in sulphide minerals can be released when the minerals are exposed to oxygen. This can happen when the water level drops and the minerals are exposed to air (Stefanakis and Kontopoulos, 1988). Arsenic polluted water can be attributed to organic-rich sediments. This is the case in Bangladesh and Eastern India (Bagga and Peterson, 2001).

Ahmed (2002) showed that arsenic concentrations in shallow aquifers of Kathmandu (Nepal) increase roughly linearly with the age of the groundwater at a rate of approximately 20 ug/L yr^{-1}. This is due to long time accumulation of arsenic in older water bodies. Hence, the age of the water may have a relationship with its arsenic content.

The type of water has effect on the arsenic level in the water. Geothermal waters (e.g., "hot springs") release arsenic into groundwater, particularly in the Western United States. Therefore, areas of geothermal activity have higher tendency to accumulate arsenic. Arsenic concentrations in geothermal water are generally above those in non-thermal water (DeVitre *et al*, 1981). Based on water type, arsenic contamination is higher in ground than surface water due to the use of deep tube wells for water supply. Arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater, owing to the anoxic conditions of the subsurface.

In oxic water (oxygenated water), dissolution of sulphide minerals, most notably pyrite and arsenopyrite, contributes arsenic to ground and surface water in many parts of the United States.

The presence of competitive ions like phosphate leads to high arsenic content of water. Phosphate competes with arsenic for binding sites on sediments and weakens the adsorption of arsenic on the soil or in some cases, causes arsenic to desorb from the sediments. When the arsenic is desorbed, it enters the water making the water more arsenic-containing.

On the whole, three general geochemical processes govern the release of arsenic to groundwater: oxidation of arsenic-bearing sulphide minerals (by dissolved oxygen and other oxidants); desorption of arsenic ions sorbed to aquifer sediments by competitive ions, such as phosphate or bicarbonate; or reductive dissolution of arsenic-bearing mineral oxides. These reactions may be reversible, in chemical disequilibrium, and may be abiotic or microbially mediated.

2.5 Soil

The arsenic cycle in soils is complex, with many biotic and abiotic processes controlling its overall fate and environmental impact (Panno, 1994).

2.5.1 The Chemistry of Arsenic in Soil

Arsenic in soil exists in various oxidation states and chemical species, depending upon soil pH and redox potential. Under most environmental conditions and at pH 5 to 7, inorganic As (V) will exist as a mixture of arsenate anions, $H_2AsO_4^-$ and $HAsO_4^{2-}$, and

inorganic As (III) will exist as H_3AsO_3 (Parkhurst, 1995). The arsenate and arsenite oxyanions have various degrees of protonation depending upon pH. As (V) predominates in aerobic soils, and As (III) predominates in slightly reduced soils (e.g., temporarily flooded) or sediments (Oscarson *et al*, 1980).

As (V) has relatively low solubility and mobility.

In a typical surface soil, the most important inorganic forms of arsenic are arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}). It is unusual to find arsenic sulphides in soils, even under waterlogged conditions, because any sulphide mineralisation will have been converted to sulphate and leached out during weathering process (O'Neill, 1995).

Arsenic species vary with pH and redox potential (Norvell, 1995). Under oxidizing conditions at pH 6.9, $H_2AsO_4^-$ is the major species, and at higher pH, $HAsO_4^{2-}$, becomes dominant.

Peters *et al* (1999) reported that microorganisms found in natural marine sediments and sediments contaminated with mine-tailings are also capable of methylating arsenic under aerobic and anaerobic conditions.

The behaviour of arsenic distinctly differs under flooded (anaerobic) and non-flooded (aerobic) soil conditions, with flooded conditions being likely the most hazardous in terms of uptake by plants (Raven *et al*, 1998).

Mono and dimethylarsenic acid (M/DMA) are the most common organic species in the soil, but their natural presence is low compared to inorganic arsenic (Robertson, 1989).

Trivalent and pentavalent arsenic have different affinity for soils. Hydrous aluminium oxides and clay minerals have lower affinity for As (III) adsorption than amorphous and

crystalline hydrous iron oxides (Schlottmann and Breit, 1992). As (V) adsorbs less extensively on kaolinite, illite and other clay minerals than onto hydrous iron or aluminium oxides at equal site concentrations.

In a nutshell, arsenate is the most common pentavalent form of arsenic found in soil except when the soils are extremely wet and the redox potential is very low.

Although a major portion of inorganic arsenic in soil is adsorbed and rendered immobile by organic matter, the ultimate fate of arsenic in soil depends on several other factors as well. Arsenic in soils can microbially be decomposed to yield arsine gases (Wood, 1996). The production of arsine gases from inorganic arsenic occurs as a result of fungal and bacterial methylation processes. Arsenate can be reduced and methylated in soil to organoarsenicals and the production of arsine gases are the predominate reactions of arsenic in soil (Ziegler, 1993).

Fig 2.5 below shows the transformation pathways of arsenic in the environment

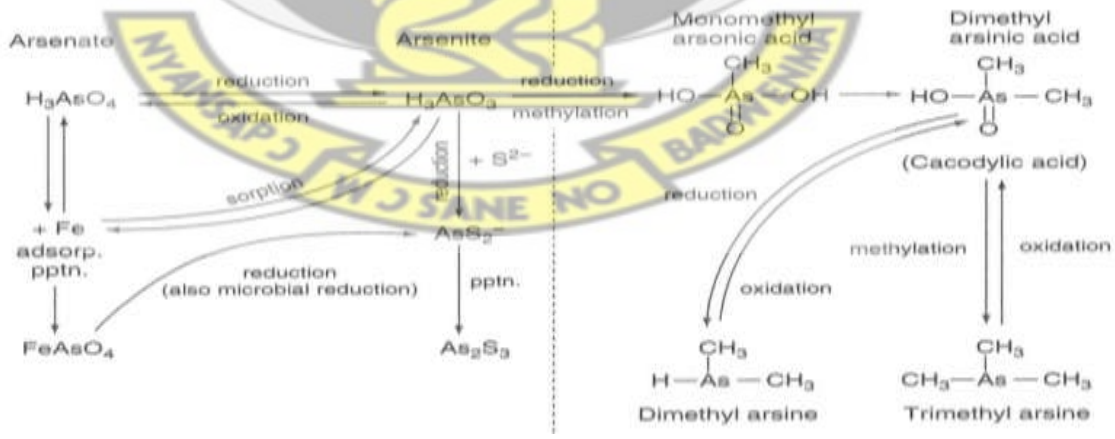


Fig 2.5 Simplified Transformation Pathways of Arsenic in the Environment (Azcue and Nraigu, 1994)

2.5.2 Factors Leading to Arsenic Depletion in Soils

Arsenic found in soils either naturally occurring or from anthropogenic releases, forms insoluble complexes with iron, aluminum, and magnesium oxides found in soil surfaces; and in this form, arsenic is relatively immobile. However, under reducing conditions (in sediments and floods), arsenic can be released from the solid phase, resulting in soluble mobile forms of arsenic, which may potentially leach into groundwater or result in runoff of arsenic into surface waters (Abernathy, 1983). This leads to a depletion of arsenic in the original source.

Arsenic in soil may be transported by wind leading to a shortfall in arsenic concentration (Ahmann *et al*, 1997).

The presence of competing ions like phosphates leads to a decline in arsenic levels in soils. The chemistry of arsenic is similar to phosphate and they compete for binding site on soils. This reduces the adsorption efficiency of the arsenic leading to a decline in arsenic levels in soils. Organic matter, phosphates, sulphates and molybdenum oxides affect arsenic adsorption by competing for sites (Nagorski and Moore, 1999).

Arsenicals applied to soils may be methylated by microorganisms to arsines (gaseous arsenic-AsH_3), which are lost through volatilization (Nesbitt *et al*, 1998).

Under anaerobic conditions, hydrous iron hydroxides (FeOOH) bound to arsenic readily dissolves and arsenic is released into the soil solution leading to loss of arsenic in the soil (Newman, 1997).

In general, Oxidation of organic matter leads to the breakdown of ferric hydrides and release of trace amounts of arsenic that are bound to it (Swartz, 1995).

Experimental data shows that arsenic availability decreases with application of iron and zinc. The decrease in arsenic may be due to formation of unavailable iron or zinc-arsenate as well as adsorption of soluble arsenic on hydrous ferric oxides (Swartz *et al*, 1996).

Fulvic or humic acids form stable complexes with mineral surfaces effectively blocking arsenic from adsorption on iron oxides, alumina, quartz or kaolinite (Nicholson, 1994).

Organic anions deplete arsenic content in soils by enhancing arsenic leaching.

Soil arsenic concentrations typically decrease with increasing distance from the source.

2.5.3 Factors Leading to High Arsenic Concentration in Soils

Although soil arsenic generally emanate from natural and anthropogenic sources (weathering, mining, volcanic eruption), certain factors help accumulate it in the soil.

The presence of iron hydroxides and clay minerals lead to accumulation of arsenic because these hydroxides adsorb onto arsenic (Von *et al*, 1968).

Both aerobic and anaerobic conditions favour arsenic accumulation. Arsenate is sorbed under aerobic conditions whiles arsenite is adsorbed in anaerobic medium. This dual phenomenon is believed to be responsible for high arsenic levels in soils (Hopenhayn-Rich, 2000).

Geological processes that may lead to high arsenic concentrations in rocks and subsequently the surrounding soil are hydrothermic activity and pegmatite formation (Caldwell *et al*, 2003). In the first case, thermal activity results in the dissolution and transport of metals, including the metalloid arsenic, which are precipitated in fractures in

rocks. In the second process, cooling magmas may concentrate metals that are injected into rocks, crystallizing as pegmatites.

Organic matter in the soil increases the adsorptive capacity for metals and other solutes (Chen and Ahsan, 2004). Furthermore, organic matter enhances the soil structure, which increases the water holding capacity of the soil. The higher the moisture content, the higher the ability of the soil to accumulate arsenic because leaching of arsenic in polluted wetland soil is low.

The low volatility of arsenic combined with the very low solubility of arsenic-soil cation complexes means that arsenic has a low potential for leaching and can be very persistent in soils so can easily accumulate (Smedley, 1996).

2.5.4 Relationship between Moisture Content of Soils and Arsenic Levels

Under equal parameters, there is a direct relationship between soil moisture and arsenic levels. Experimental work by Belzile and Tessier (1990) revealed that an increase of moisture from 20 to 40% increased arsenic holding capacity of soils by 5.78 to 8.44 mg/kg.

2.5.5 Soil pH and Its Effects on Arsenic

Under many conditions, soils tend to become far more acidic than alkaline over time if steps are not taken to maintain a balance (Connell *et al*, 1984).

The most common classes of soil pH are presented in table 2.4 below

Table 2.4 Common Classes of Soil pH (Chappell, 2009)

Soil pH	Classification	Soil pH	Classification
3.5-4.4	Extremely acidic	6.6-7.3	Neutral
4.5-5.0	Very strongly acidic	7.4-7.8	Slightly alkaline
5.1-5.5	Strongly acidic	7.9-8.4	Moderately alkaline
5.6-6.0	Moderately acidic	8.5-9.0	Strongly alkaline
6.1-6.5	Slightly acidic	Above 9	Very strongly alkaline

Soil pH influences the extent of arsenic adsorption onto soils and by extension, arsenic concentration in soils (Abedin *et al*, 2002). Greater the arsenic adsorption onto soil particles increases arsenic concentration in the soil. Arsenate sorption to iron oxides peaks around pH 5 to 7 and is less pronounced in more basic solutions. The decrease of As (V) adsorption at higher pH is due to the increasing negative surface potential and increasing concentration of negatively charged As (V) species in solution which leads to repulsion. At oxidizing conditions, Fe (III)-arsenate compounds are stable. Under reducing conditions, Fe (III) is converted to Fe (II) and arsenate to arsenite, significantly increasing arsenic solubility at that pH (Meharg *et al*, 2004).

Generally, sorption of arsenic onto soils and sediments is strongest below neutral pH. This means arsenic concentrations in soils are higher in the acidic region. For instance, Arsenate adsorption on kaolinite and montmorillonite were high at low pH, peaked between pH 4 to 6, and decreased at pH greater than 6 (Norra *et al*, 2005).

To sum up, both arsenite, As (III) and arsenate, As (V) have strong affinities for iron complexes however they behave oppositely with respect to pH. In general in the pH range 3–10, adsorption of arsenate decreases with increasing pH while the adsorption of arsenite increases.

The soil pH has a bearing on the strength of competing ions. Rahman *et al* (2008) studied the effect of competing anions on the adsorption of arsenite and arsenate on ferrihydrite. They realized that, the effect of phosphate on arsenate adsorption was greater at higher pH than at low pH and the opposite trend was observed for arsenite.

In soils with low concentrations of oxidic minerals, increasing pH had little effect on the amount of As (V) sorbed while in highly oxidic soils, sorption of As (V) decreased with increasing pH (Taylor and McLennan, 1985). This decrease was attributed to the increasing negative surface potential on the plane of As (V) sorption and increasing amount of negatively charged arsenic species in soil solution. In contrast to As (V), sorption of As (III) increased with increasing pH.

Soil pH or soil reaction may affect the degree of arsenic toxicity. Under acidic conditions, iron and aluminium are present. These may tie up the arsenate into relatively insoluble compounds and reduce its effectiveness or toxicity (Johnson and Wurzel, 2001).

2.5.6 Arsenic Solubility and Mobility in Soils

Soil electrical conductivity (EC) is the ability of soil to conduct electrical current. It is influenced by soil physical properties such as water content and salinity.

Sand, silt and clay have low, medium and high conductivities respectively. Dry soil is much lower in conductivity than moist soil.

Increasing concentration of electrolytes (salts) in soil water will dramatically increase soil EC. Generally, soils saturated with water have high arsenic solubility (Nicholson, 1994).

In soil, arsenic is found as a complex mixture of mineral phases, such as co-precipitated and sorbed species, as well as dissolved species (Swartz, 1995, 1996). The degree of arsenic solubility in soil depends on the amount of arsenic distributed between these different mineral phases. The distribution between these phases may reflect the arsenic source (e.g., pesticide application or mining operations), and may change with weathering and associations with iron and manganese oxides and phosphate minerals in the soil (Van *et al*, 1989).

The form and behaviour of arsenic vary greatly between flooded soils and non-flooded soils. The most important arsenic species are arsenate (As V) under non-flooded conditions and arsenite (As III) under flooded conditions. As III has a higher solubility than As (V), resulting in a higher mobility of arsenic in flooded soils. Under more reducing conditions, As III becomes more and more predominant and the solubility of arsenic increases sharply (Rhoades, 1989).

Mixing high rates of monoammonium phosphate (MAP) or monocalcium phosphate fertilizers with soil may increase arsenic solubility in soils because of competitive PO_4-AsO_4 exchange. This process also enhances arsenic mobility.

Arsenic forms insoluble precipitates in soils such as $Ca_3(AsO_4)_2$, $Mn_3(AsO_4)_2$, $AlAsO_4$ and $FeAsO_4$ (Fuoss, 1957) and reduces the arsenic solubility.

The solubility of arsenic depends on its oxidation state of the arsenic and solution pH. For example, the solubility of Fe-As (V) decreases with a decrease in pH, whereas the solubility of Fe-As (III) decreases as the pH increases (Voelker, 1986). As (III) commonly partitions to the aqueous phase in anoxic environments, and would be more

mobile. As (V) usually remains bound to minerals, such as ferrihydrite and alumina, limiting its mobility and bioavailability (Vroblesky, 1989).

Arsenite is moderately unstable in the presence of oxygen; however, it can be found under aerobic conditions as well (Brannon and Patrick, 1987). Arsenate is rapidly desorbed as the system becomes anaerobic. Once it is desorbed, arsenate can be reduced to arsenite, which exhibits greater mobility in soils (Andreae, 1980, 1983).

Arsenic is nearly immobile in top soils. Soil conductivity increases with depth of soil. Dissolved organic carbon in soil and water are able to increase the mobility of arsenic through redox reactions and soluble complex formation. The availability of organic carbon as electron donor is important for microbially mediated processes which can also affect arsenic mobility.

As (III) commonly partitions to the aqueous phase in anoxic environments, and would be more mobile. As (V) usually remains bound to minerals, such as ferrihydrite and alumina, limiting its mobility and bioavailability (Angino *et al*, 1970).

Under reducing conditions, the most stable soluble form of inorganic arsenic is as arsenious acid (As (III)). Under oxidizing conditions, most of the arsenic will be in the more stable As (V) form, arsenic acid. Arsenic mobility depends on its charge, so at neutral pH, arsenious acid is more mobile than the dissociated forms of arsenic acid. That means arsenic will be more mobile under reducing conditions because more of the arsenic will be present as arsenious acid.

Soil phosphorous content can also affect the mobility of inorganic arsenic. Phosphate and arsenic ions compete for binding sites. In this case, arsenic may display slightly greater mobility and less stability in soil (Ashley, 1997).

The major cations and anions making up salinity of soils are: sodium, calcium, magnesium, potassium, bicarbonate, sulphate, zinc, lead, cadmium, copper, chromium, nickel, chloride and nitrate. Sources of these ions include- calcium (gypsum), calcium and magnesium (clay minerals), sulphate (oxidation of sulphide ores, gypsum), chloride (igneous and sedimentary rocks), bicarbonate/carbonate (limestone).

2.5.7 Relationship between Soil Type and Arsenic Levels

Generally, arsenic levels increase or remains about the same with increasing soil depth (Sorg, 1978) and the migration is greater in sand than clay (Kabatas and Pendias, 1984). Hence, down the soil profile, arsenic levels increase for sandy soils than the increase for clay soils.

Total arsenic is significantly related to soil texture. Soils with high clay content adsorb more arsenic than sandy soils with low clay content because high clay soils have pronounced metal binding properties (Sorg, 1978, 1993). Sand has large pores, least water content and least arsenic due to easy leaching (Faulkner, Patrick and Grambrell, 1989).

Clay retains more water because it leaches with difficulty. Its arsenic holding capacity is above that of silt (Ponnamperuma, 1972). Hydrous iron hydroxides (FeOOH) which have high tendency to adsorb arsenic are mainly present in the clay size soil fraction.

Hence, clayey soils generally have higher arsenic content compared to more sandy soils (Griffin and Shimp, 1978).

In terms of housing arsenic, clay is above silt which in turn is above sand when all other things are equal. Higher arsenic concentrations are found in alluvial soils and soils with high organic content (Bhumbla and Keefer, 1994).

At equal soil concentration, clayey soils are less toxic compared to sandy soils because arsenic is more strongly bound in the clayey soils and not readily available in solutions to cause any harm.

In calcareous soils, adsorption of As (V) and As (III) occurs strongly also on carbonate minerals (Merry *et al*, 1983). Therefore calcareous soils have more arsenic than non-calcareous ones.

Mohapatra *et al*, (2007) explained that the presence of calcium in matrices (soils, water and food) lead to high concentration of total dissolved arsenate because calcium and arsenic form concentrated mineral complexes including- weilite ($CaHAsO_4$), pharmacolite ($CaHAsO_4 \cdot 2H_2O$), haidingerite ($CaHAsO_4 \cdot H_2O$), and phaunouxite [$Ca_3(AsO_4)_2 \cdot 11H_2O$]. Therefore, soils with high calcium content will have higher levels of arsenic.

According to Preyea and Creger (1994), arsenic tends to be adsorbed by inorganic constituents found in soil matter by forming insoluble salts with soil cations (i.e. iron, aluminiumand calcium) which immobilize the arsenic in the soil matrix (Quaghebeur *et al*, 2005).The immobilization process is more likely to occur in clay soils and in soils with high matter content.

2.5.8 Factors Influencing Arsenic Uptake by Plants

Organic matter and soil moisture increase the availability of arsenic to crop plants while application of iron, zinc minimize the availability of arsenic in soil and its uptake by plants.

In general, clay and silt accumulate higher levels of arsenic than sandy soils (Jahiruddin *et al*, 2000). However, Al Rmalli *et al* (2005) discovered lower levels of arsenic in plants grown on clays and silts than in plants grown in lighter soils (sands and sandy-loam). This behaviour reflects the fact that the amount of an element in a plant depends on the root system and the ability of the plant to absorb the element. Deep-rooted crops like cassava accumulate much arsenic than shallow-rooted ones (Al Rmalli *et al*, 2005). Roots of plants grown in sandy soils penetrate the soil with ease and can adsorb much arsenic.

The adsorption of metals from the liquid phase to the solid phase controls the concentrations of metal ions and complexes in the soil solution and thus exerts a major influence on their uptake by plant roots (Alloway, 1995). Reports indicate that inorganic arsenic absorbed by plants may be converted to organic arsenic compounds (Smith, 2009) so it is unclear whether organic arsenic in plants is taken up from the soil or is formed naturally by the plants (Gao *et al*, 2006; Redman, 2002).

Even when crops are cultivated on highly polluted arsenic soils, the arsenic level taken up by the plants is comparatively low (Smith, 2009). According to Cobb *et al* (2000), flooded conditions (anaerobic) are more hazardous than non-flooded (aerobic) soil conditions in terms of arsenic uptake by plants.

Generally soil pH range of 4.5 to 5.5 favours arsenic sorption onto cassava and the arsenic accumulation increases in more acidic soils (Audu, 1982).

The presence of phosphates affects arsenic accumulation by cassava from soils. Phosphate ions compete for uptake by plants and reduce arsenic accumulation by cassava in aerobic soils where arsenate dominates (Bauer and Blodau, 2006; Bhumbla and Keefler, 1994).

It is not yet possible to predict arsenic uptake and/or toxicity in plants from soil parameters because arsenic accumulation in plants depends on the plant species, soil composition, planting season, geographical location, growing method and other unknown factors. Generally, crops cultivated in the rainy season have higher levels of arsenic accumulation than those cultivated in the dry season due to large amount of slightly acidic rainwater during the rainy season which promotes the release of adsorbed arsenic from the soil (Reilly *et al*, 2001).

Intensive use of highly arsenic contaminated water to irrigate crops elevates the arsenic content of the crops (Yang and Donahoe, 2007).

Of all factors, phosphorous content and pH of soils are the most important ones influencing arsenic uptake by plants (Yan-Chu, 1994).

Soil conductivity of 650 μS/cm is acceptable for most crops and 1300 μS/cm is the upper limit for moderately tolerant crops (F.A.O., 1990). Common ions in cassava include cadmium (ii) and zinc (ii) with arsenic ions generally present in negligible amounts (F.A.O., 1990).

2.6 Methods of Determining Arsenic

Colorimetry and atomic absorption spectroscopy are the common methods of arsenic determination. These methods are discussed below

2.6.1 Colorimetric Methods (UV-Visible Spectrophotometry)

Colorimetry based on the development of arsenic-molybdate blue complex can be employed. The blue colour is stable for a day and its intensity depends on arsenic concentration.

This method can be used for arsenic determination though it has a very low detection limit and a lot of inherent challenges. According to Snell (1948), for an ideal colorimetric method-

1. It is desirable that the colour developed from a small amount of the test substance be intense to give maximum sensitivity.
2. The colour developed should be stable so that the determination needs not be completed rapidly, and so that natural standards will be reasonably permanent. Causes of instability are often air-oxidation or photoelectric effect but when recognized can be controlled.
3. Colour is desirable but little affected by pH changes. If so affected, the pH should be controllable by adding a simple buffer or colorimetric indicator.
4. When a reagent can be used that is not itself coloured, the complications of excess reagent are lessened but by no means avoided. If the reagent is coloured, the total visual effect is the sum of that due to the test substance, and the excess reagent.

5. It is advantageous if colour formation proceeds at room temperature and that variation in temperature has slight effect. Variation from this makes the procedure more complex.
6. In the ideal case, approached but never realized, the reagent would react solely with the test substance and not give colour with any interfering substance.
7. The colour developed should be independent of excess reagent meaning, a large excess reagent should give a constant effect.
8. The nature of the reaction should be known to permit better control of conditions. Conventionally, it is by redox, complex ion formation or coupling with a large molecule.
9. The test substance and reagent are should be in the same solvent so that excess reagent will neither precipitate nor cause precipitation of other substances.
10. For simplicity, the coloured solution should require no special treatment, such as extraction with an organic solvent and the order of mixing should not be critical.

2.6.1.1 Chemistry of Molybdenum Blue Method Reactions

Salts of molybdic acid, H_2MoO_4, are known as molybdates. The acid polymerises with reaction of water molecules. The commercial ammonium molybdate is $(Mo_7O_{24})^{6-}$. Arsenate combines with ammonium molybdate to give a heteropoly molybdi-arsenate blue complex.

$$As^{5+} + (Mo_7O_{24})^{6-} \rightarrow (AsMo_7O_{24})^{-}$$

Blue complex

The Mo (vi) is reduced by hydrazine sulphate to Mo (v).

Mo (vi) $\xrightarrow{N_2H_4.H_2SO_4}$ Mo (v)

The blue complex results due to charge transfer between Mo (v) and Mo (vi). The blue colour is stable for 24 hrs and its intensity depends on the concentration of arsenic.

Phosphates if present interfere with the determination. It is prevented by precipitating out the phosphate in the form of zirconyl phosphate. To achieve this, zirconium nitrate is added to an acidified solution of the sample and the precipitate is filtered out.

$HPO_4^{2-} + ZrO^{2+} \rightarrow ZrO(HPO_4)$

2.6.2 Atomic Absorption Spectroscopy (AAS)

Generally, metals are determined by AAS and ICP-AES (inductively coupled plasma atomic emission spectroscopy). AAS is an instrumental technique used to determine the amount of trace metals dissolved in a solution (Haswall *et al*, 1988). It is used in modern analysis because of the high sensitivity, selectivity, broad scope and reliability (Welz, 1999).

In their elemental forms, metals will absorb UV light when they are thermally excited. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and onto a detector.

2.6.2.1 Flame Atomic Absorption Spectroscopy

In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers.

In flame AAS, flame is used to generate the atoms. The oldest and most commonly used atomizers in AAS are flames, principally the air-acetylene flame with a temperature of about 2300 °C and the nitrous oxide (N_2O)-acetylene flame with a temperature of about 2700 °C.

The processes in the flame include the following stages:

- Desolvation (drying) – the solvent is evaporated and the dry sample nano-particles remain;
- Vaporization (transfer to the gaseous phase) – the solid particles are converted into gaseous molecules;
- Atomization – the molecules are dissociated into free atoms;
- Ionization – depending on the ionization potential of the analyte atoms and the energy available in a particular flame, atoms might be in part converted to gaseous ions.

Ionization is generally undesirable, as it reduces the number of atoms that is available for measurement, i.e., the sensitivity.

The flame AAS can be used for arsenic analysis but it has challenges ranging from its low detection limit to other inherent interference problems.

2.6.2.1a Processes and Principles Underlying Flame AAS by Walsh, 1995

The capillary of the AAS is put into the sample solution which is then sucked and aspirated into a flame. The meatal sample (arsenic) is then converted to atomic vapour. Some of the atoms are thermally excited by the flame but most remain in the ground state. The ground state atoms can absorb radiation given off by the special source made

from the metal hollow cathode lamp. The wavelength of the radiation given off by the source is the same as those absorbed by the atoms in the flame. The absorption follows the Beers law. That is, the absorption is directly proportional to the path length in the flame and the concentration of atomic vapour in the flame. Both of these variables are difficult to determine but the path length can be held constant and the concentration of atomic vapour is directly proportional to the concentration of analyte in the aspirated solution.

2.6.2.1b Problems Associated With Flame AAS

In flame AAS, the type and temperature of the flame used is critical. With improper conditions, chemical and ionization interferences can occur.

Background or non-specific absorption can occur from particles produced in the flame that can scatter the flame and produce apparent absorption signal (Broekaert, 1998). Light scattering may be encountered when solutions of high salt contents are being analysed. They are more severe when measurements are being made at shorter wavelengths (for example, below 250nm). Spectral interferences result when an atom different from the one being measured absorb a portion of the radiation. Hence, the use of a multi-element HCL is discouraged.

Ionization interference occurs when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and the presence of other easily ionized atoms. Sodium or potassium is frequently used as ionization suppressant.

Fig 2.6 below gives a block representation of flame AAS.

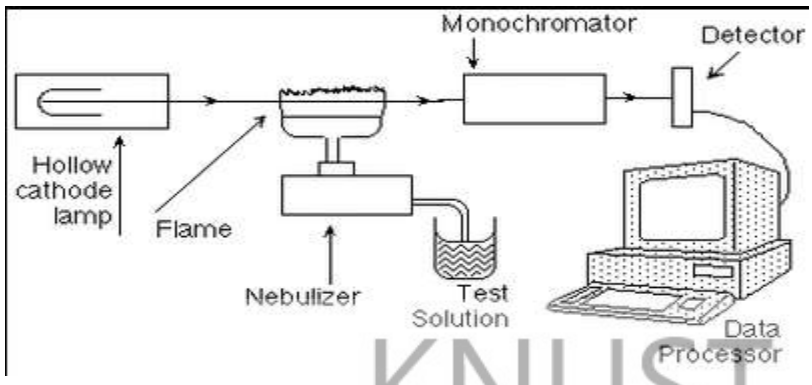


Fig 2.6 Flame AAS in Block Representation (Welch and Stollenwerk, 2003)

2.6.2.2 Hydride Generation Atomic Absorption Spectroscopy (HGAAS).

AAS is one of the commonest instrumental methods for analyzing metals and some metalloids (Sandberg and Allen, 1975). Because of interferences, poor reproducibility and poor detection limits, an alternative method (HGAAS) for some elements, mostly metalloids, has been developed. It "only" requires the hydride generation module (Bermejo, 1998).

AAS enables hydride generation which permits the isolation of the element of interest from the matrix. Formation of covalent volatile hydrides of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by reaction with sodium tetrahydroborate provides an excellent automated method for the separation of these elements as gases from a wide range of matrices.

2.6.2.2a The Chemistry behind HGAAS

The technique comprises many distinct processes, namely hydride generation, hydride collection (optional) and atomization. Variations exist and have been the subject of several reviews.

2.6.2.2b Reagents

Hydride generation is accomplished by the reducing agent, sodium tetrahydroborate (iii) or sodium borohydride. A freshly prepared solution of sodium tetrahydroborate (iii) is more efficient, especially for continuous flow systems. This reductant concentration must be optimised for the particular analyte element and for the equipment concerned. A variety of concentrations are recommended usually 5 to 50 g/L aqueous solution made alkaline with potassium or sodium hydroxide. After filtration, this reductant is sufficiently stable for three weeks.

The rapid reaction between sodium tetrahydroborate (iii) and hydrochloric acid may generate troublesome foam particularly when undigested biological fluids such as urine and blood plasma are analysed.

The purity of all reagents is important and all new reagents should be checked in blank determinations. Also, regular checks for contamination and for loss of sensitivity must be included in each series of determinations. Where possible, acids used in trace analysis should be purified by sub-boiling point distillation. The concentration of acid (usually hydrochloric) has a considerable effect on the yield of hydride but the optimum concentration for a particular element and matrix is best established in trials (Haswall *et al*, 1988).

2.6.2.2c Equipment

Many of the main parts of the HGAAS system are identical to that of AAS: a HCL, air/acetylene flame, and optical system but include (in most systems) an optical cell and the relatively complex hydride generation system. The nebulizer required in AAS is not used in HGAAS. The system described here is a continuous flow system, but batch flow systems have been used in the past.

One of the attractions of the original hydride generation method was the simplicity of the equipment which allowed the method to be used with a conventional AAS. Subsequent developments, some arising from a desire to automate the system and others to help overcome interferences or enable the ultimate in trace analysis to be accomplished, have led to a wide variety of equipment now being used. In its simplest form, the generated hydride and hydrogen are transported immediately to the atomizer, normally in a carrier gas.

The hydride generation in the reaction vessel is delayed for a few seconds to allow the generation reaction to proceed to completion but the inherent instability of the hydride must be taken into consideration when this technique is contemplated (Welz, 1999). Others use a low temperature trapping device to concentrate the hydride so that it may be transported to the atomiser without dilution with the large volume of generated hydrogen.

Continuous flow equipment, with peristaltic pumps for sample and reagent as in the autoanalyser systems, has been used for hydride generation both with and without air segmentation and the hydride has been separated with conventional gas-liquid separators or by membrane separation. These systems have the advantage of intimate

mixing of reagents with better pH control and also they appear to be much more tolerant of elements which normally interfere in the hydride generation. However they usually have a lower detection limit compared to batch systems. Sturman designed a special gas liquid separator for his system in which sample, acid and sodium tetrahydroborate (iii) are mixed continually using a peristaltic pump. This method has been shown to tolerate nitric acid in the sample digest when applied to the determination of arsenic in a variety of matrices and to give good analyte recoveries in the presence of many of the metals which normally interfere in hydride generation.

A continuous reagent flow system combined with continuous sample flow has the advantage that it provides a constant output signal as soon as equilibrium is reached. With this system, the carrier gas (argon) is introduced into the reaction mixture of sample and reagents before separation in a PTFE (polytetrafluoroethylene) microporous membrane tube separator. Here, a short reaction time before separation of the hydride favours better tolerance to interfering elements such as copper (ii) and nickel (ii).

2.6.2.2d Carrier Gas

Both argon and nitrogen (less frequently) are now used as the carrier gas and under most circumstances either may be used without loss of sensitivity. However to avoid condensation of liquid argon, helium or nitrogen is the preferred carrier gas when using a liquid nitrogen trap particularly if the trap is of the U- tube type. A mixture of 1% $^{V}/_{V}$ oxygen in argon is reported to give enhanced optical absorbance compared to nitrogen. A trace of oxygen increases the efficiency of atomisation.

2.6.2.2e Desiccants

The hydride generation takes place with considerable effervescence and it is easy to get a carryover of reagent mist into the atomiser particularly when using the batch type equipment with an immediate transfer of generated hydride to the atomiser. Condensation of water vapour and/or reagent mist on the transfer lines must be avoided because this moisture can trap the hydride and release it slowly in the gas stream giving low results and high blank values. McDaniel *et al* used ^{75}Se as a radiotracer to show that anhydrous calcium chloride is effective as a desiccant and reports hydride losses no more than 4%.

2.6.2.2f Overcoming Interferences

Increasing sodium tetrahydroborate (iii) concentration appears to enhance the capture of a matrix containing transition metal ions. Hydride generation in 6M HCl is much more tolerant to interfering elements than solutions of lower acid concentrations. Also the extra reaction time afforded in equipment of the stopped flow type appears to favour good yields of hydride.

Pierce and Brown report much less interference from oxidising anions including nitric acid when the sample solution is acidified before the addition of sodium tetrahydroborate (iii).

2.6.2.2g Hydride Atomisation

The useful resonance lines for arsenic are below 200 nm in a region where interferences from flame radical absorption is very damaging. The heated quartz tube avoids many of the disadvantages of the flames and gives considerable signal enhancement. However

studies of heated quartz tube atomisation show that there are many problems associated its usage particularly when dealing with solutions containing more than one hydride forming element.

It was initially believed that atomisation arose from thermal decomposition of the hydride but this is extremely unlikely at temperatures around 800-1000 ^{0}C which are normally attained in the quartz tube. Those who use carbon furnace atomisation recommend a temperature of about 2000°C for the decomposition of hydrides.

Low carrier gas flow rates might be expected to give enhanced sensitivity but this is not always the case. The heated quartz tubes currently in use vary in design from a simple quartz T-cell to quite complex designs. Sturman found that a 7 mm internal diameter tube gave good sensitivity. The quartz tube is heated either electrically or in a fixed position over a conventional laminar flow air-acetylene burner. Increased signal stability and less memory effect was observed with the shorter nitrous oxide-acetylene burner head but using air-acetylene fuel.

2.6.2.2h Disadvantages

It requires complete decomposition and dissolution of sample prior to analysis which increases analysis time, risk of contamination and losses of analyte. In addition, the problem with using large amounts of reagents during treatment leads to increased blank values.

The presence of particulate matter in samples can plug up the aspiration line or the burner so filtration before analysis is inevitable.

The functions of each component of the HGAAS have been summarized in table 2.5

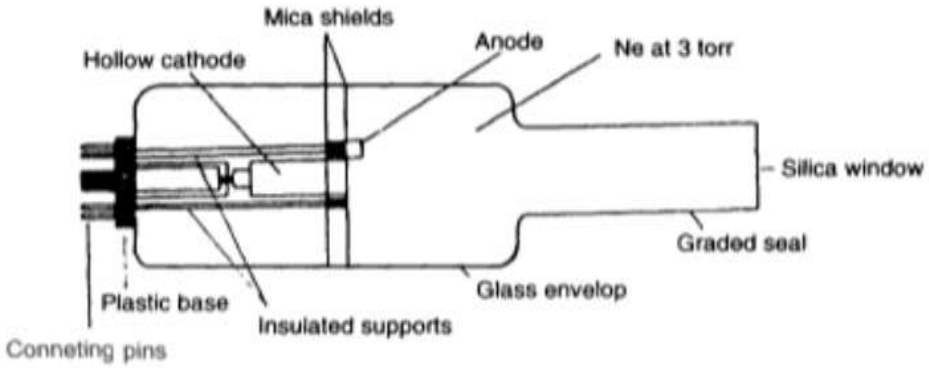
below.

Table 2.5 Functions of Each Component of the HGAAS (Welz, 1999)

PART	FUNCTIONS
Hollow cathode lamp	Provides the analytical light line for the element of interest. It also provides a constant, yet intense beam of that analytical line.
Hydride generation system	Sucks up (aspirate) liquid sample at a controlled rate and mixes it with sodium borohydride and HCl. It also creates a volatile hydride of the analyte metalloid from that reaction. In addition, it flows that gaseous hydride into the optical cell
Optical cell and flame	Decompose the hydride form of the metalloid from the hydride generation module and thereby create atoms (the elemental form) of the element of interest namely Se0, Sb0, Te0, etc.
Monochromator	Isolate analytical lines' photons passing through the optical cell. Removes scattered light of other wavelengths from the optical cell and in doing this, only a narrow spectral line impinges on the PMT.
Photomultiplier tube (PMT)	As the detector, the PMT determines the intensity of photons of the analytical line exiting the monochromator.

The Hollow Cathode Lamp (HCL)

It uses a cathode made of the element of interest with a low internal pressure of an inert gas. A low electrical current (approximately 10 mA) is imposed in such a way that the metal is excited and emits a few spectral lines characteristic of that element. The light is emitted directionally through the lamp's glass transparent window.



The Optical Cell and Flame

The optical cell is fused silica glass tube (transparent in the visible and UV wavelengths and thermally stable at high temperatures) through which the HCL's beam passes on the way to the monochromator and PMT. The gaseous, metalloidal hydride flows into the optical cell from the hydride generation module pushes by an inert purge gas. In the optical cell, it decomposes into the elemental form which can absorb the HCL's beam.

The Monochromator and PMT

Tuned to a specific wavelength and with a specified slit width chosen, the monochromator isolates the HCL's analytical line. Since the basis for the HGAAS process, like AAS, is atomic absorption, the monochromator seeks to only allow the light not absorbed by the analyte atoms in the optical cell to reach the PMT. That is, before an analyte is aspirated, a measured signal is generated by the PMT as light from the HCL passes through the optical cell. When analyte atoms are present in the cell from hydride decomposition—while the sample is aspirated, some of that light is

absorbed by those atoms (only volatile hydride gets to the optical cell and then only decomposed hydride produces the elemental form). This causes a decrease in PMT signal that is proportional to the amount of analyte (Welz, 1995).

The signal is therefore a decrease in light intensity.

Double Beam Instruments

The light from the HCL is split into two paths using a rotating mirror: one pathway passes through the optical cell and another around. Both beams are recombined in space so they both hit the PMT but separated in time. The beams alternate quickly back and forth along the two paths: one instant the PMT beam is split by the rotating mirror and the sample beam passes through the cell and hits the PMT. The next instance, the HCL beam passes through a hole in the mirror and passes directly to the PMT without passing through the optical cell. The difference between these beams is the amount of light absorbed by atoms in the optical cell.

The double beam instrument is to help compensate for drift of the output of the hollow cathode lamp or PMT. If the HCL output drifts slowly the subtraction process described immediately above will correct for this because both beams will drift equally on the time scale of the analysis.

Likewise if the PMT response changes the double beam arrangement take this into account.

Ignition, Flame conditions, and Shut Down

Lighting the AAS flame involves first putting the optical cell in place and connecting

the hydride gas transfer line. Next the fuel and the oxidant are turned on and then the flame is lit with the instrument's auto ignition system (a small flame or red-hot glow plug). After only a few minutes the flame is stable. Deionized water or a dilute acid solution can be aspirated between samples (but experimentation is required to ascertain what produces the best reproducibility). An aqueous solution with the correct amount of acid and no analyte is often used as the blank. To stabilize the HGAAS system the acidic blank is often flowed through the sample inlet tube for 5 or 10 minutes; although the longer this goes on, the more acidic waste is produced.

Careful control of the fuel/air mixture is important because each element's response depends on successful decomposition of the volatile hydride in the heated optical cell. The flame's heat must break down the hydride and reproducibly create the elemental form of the analyte atom. Optimization is accomplished by aspirating a solution containing the element and then adjusting the fuel/oxidant mix until the maximum light absorbance is achieved. Also the position of the burned head, optical cell, and sample uptake rate are similarly "tuned." Most computer controlled systems can save variable settings so that methods for different elements can be easily saved and reloaded.

Shut down involves aspirating deionized water through all three inlet tubes (borohydride, acid, and sample inlets) for a short period and then closing off the fuel. Most modern instruments control the ignition and shutdown procedures automatically.

Nebulizer, Oxidants, Burner Heads and Waste: The nebulizer chamber thoroughly mixes acetylene (the fuel) and oxidant (air or nitrous oxide), and by doing so, creates

a negative pressure at the end of the small diameter, plastic nebulizer tube. This negative pressure acts to sucks or aspirates the liquid sample up the tube into the nebulizer chamber. A small glass impact bead and/or a fixed impeller inside the chamber create a heterogeneous mixture of gases (fuel + oxidant) and suspended aerosol. This mixture flows immediately into the burner head where it burns as a smooth, laminar flame evenly distributed along a narrow slot in the well-machined metal burner head.

Liquid sample not flowing into the flame collects on the bottom of the nebulizer chamber and flows by gravity through a waste tube to a glass waste container (this is still highly acidic). For some elements that form refractory oxides (molecules hard to break down in the flame) nitrous oxide (N_2O) needs to be used instead of air (78% N_2 + 21% O_2) for the oxidant. In that case, a slightly different burner head with a shorter burner slot length is used.

A diagrammatic representation of the Hydride Generator is shown in fig 2.7

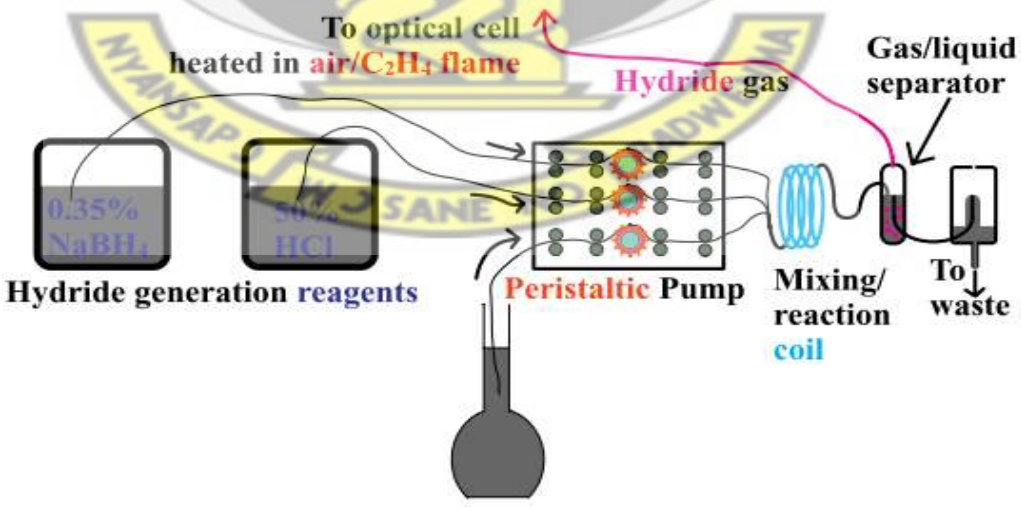


Fig 2.7 Diagram of the Hydride Generator (Welz, 1999).

Acidic Content and Oxidation State of Samples and Standards

The samples and standards are often prepared with duplicate acid concentrations to replicate the analyte's chemical matrix as closely as possible. In HGAAS, acid contents of samples and standards of 10% to 50% are common; this is much much higher than in normal AAS. The oxidation state of the analyte metalloid is important in HGAAS. For instance, HGAAS analysis of selenium requires the Se (iv) oxidation state (selenite).

Also important is the concentration of $NaBH_4$ and HCl reagents fed into the hydride generation reaction vessel: optimization of this is important and may be different for different elements. Common concentrations are 0.35% $NaBH_4$ and 50% HCl. This acid content is not necessarily identical with the acid content of the samples and standards themselves.

The reagent acid's content is aimed at producing a reproducible amount of hydride in the module.

The general optimum parameters for Arsenic determination are shown in table 2.6 below.

Table 2.6 General Optimum Parameters for Arsenic Determination (Welz, 1999)

Parameters	**Varian (Model Spectra AA-20)**
Lamp Current	10mA (hollow cathode)
Wavelength	193.7 nm
Slit	0.5 nm
HCl flow rate	1 ml min^{-1}
HCl concentration	5M
$NaBH_4$ flow rate	1.5 ml min^{-1}
$NaBH_4$ concentration	1.5% (w/v) in 0.5% (w/v) NaOH solution
Carrier gas	Nitrogen
Carrier gas flow rate	50 ml min^{-1}
Flame	Air-Acetylene

CHAPTER THREE

3.0 MATERIALS AND METHODS

The description of sampling site, samples and sampling procedures, materials and equipment used for the analyses, procedures for determining the physicochemical parameters, the arsenic concentrations in soil, water and cassava samples are covered in the following subsections.

3.1 Materials Used For the Analysis

The materials include the glass wares and equipment, the chemical reagents, water, soil and cassava samples.

3.1.1 Glassware and Equipment

The glass wares used for the chemical analyses are as follows:

- beaker (50 ml, 100 ml)
- conical flasks (50-250 ml)
- digestion and filter flasks
- measuring cylinder (50 ml)
- pipette (5 ml, 10 ml)
- volumetric flask (50 ml, 250 ml)

The equipment used in the analyses were as follows:

- Analytical balance
- Hot plate (burner) and oven

- United States Orion 5 star thermo scientific meter (measures pH, conductivity and surrounding temperature)
- Varian AA 240 FS hydride generation AAS (from Australia).

3.1.1.1 Cleaning of Glass ware

Glass wares were first washed under running tap water and soaked in detergent solution overnight. They were then washed and dried. Glass wares that were extremely dirty were soaked in 10% HNO_3 overnight, rinsed with 1 litre distilled water and dried.

3.1.2 Chemical Reagents

All reagents were of analytical grade (BDH chemical limited, Poole, England) unless otherwise stated. Distilled water was used for preparation of all solutions. The reagents were:

- 95 % ammonium oxalate (analar from Aldrich Chemicals, England)
- 37% hydrochloric acid (6 M, 12.08 M)
- 63% nitric acid (15.6 M)
- 60% perchloric acid (9.2 M)
- 96% potassium iodide (analar from Philips reagent, England)
- 98% sodium arsenate and arsenite (standards)
- 99% sodium borohydride (0.6% concentration)
- 96% sodium hydroxide (0.5% in concentration)
- 98% sulphuric acid (13.39 M)
- Orion Thermo scientific standard buffer solutions of pH 4.01, 7 and 10.01

3.1.3 Water, Soil and Cassava Samples

The water samples were from boreholes, open wells, ponds, swamps, rivers, streams and pipe borne water. The soils were also picked. The cassava samples were unpeeled tubers from local farms. These samples were picked from selected towns in the Amansie West District.

3.1.3.1 Study Area

Sampling was done in selected towns in Amansie West District (AWR) which covers an area of about 1,141 km^2 (fig 3.1 and 3.2). The district capital, Manso Nkwanta, is about 40 km south of Kumasi. The entire AWR is rich in gold deposits; with mining emerging as the most important economic activity. The district has about 310 settlements (though not all these settlements are mapped) with a population of 108,726 as at 2000. The water sources are rivers, streams, hand dug wells, boreholes and pipe borne water. The pipe borne water serves only two towns namely, Atwere and Esaase.

Swamps exist in every town visited in the district. There are two rainy seasons with the maximum in June/July and the least in October. Besides mining, the majority of the people are farmers and fisher folks.

The sampling towns were- Akwasiso, Asamang, Atwere, Ayerebikrom, Bonsaso, Dadiase, Datano, Edubia, Esaase, Kensere Nkwanta, Konianse-nkran, Kumpese, Manso Nkwanta, Nkuntin, Nyankumasi, Takorase, Tontokrom and Yawkrom,.

Fig 3.1 below shows the map of Ghana highlighting the Amansie West District.

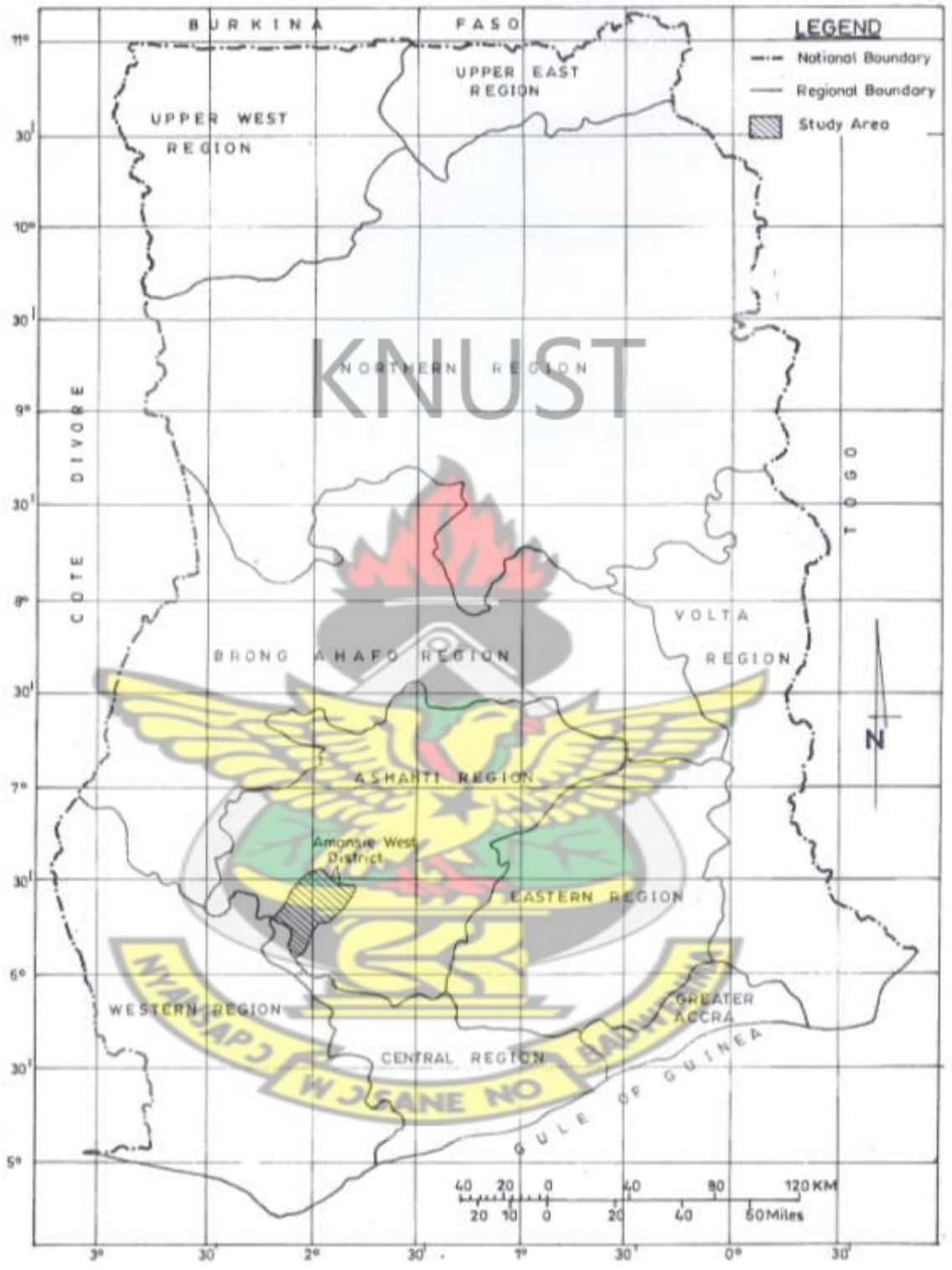


Fig 3.1 Map of Ghana Showing Amansie West District (Survey Dept of Ghana, 1994)

Fig 3.2 shows a map of Amansie West District highlighting some of the sampling towns.

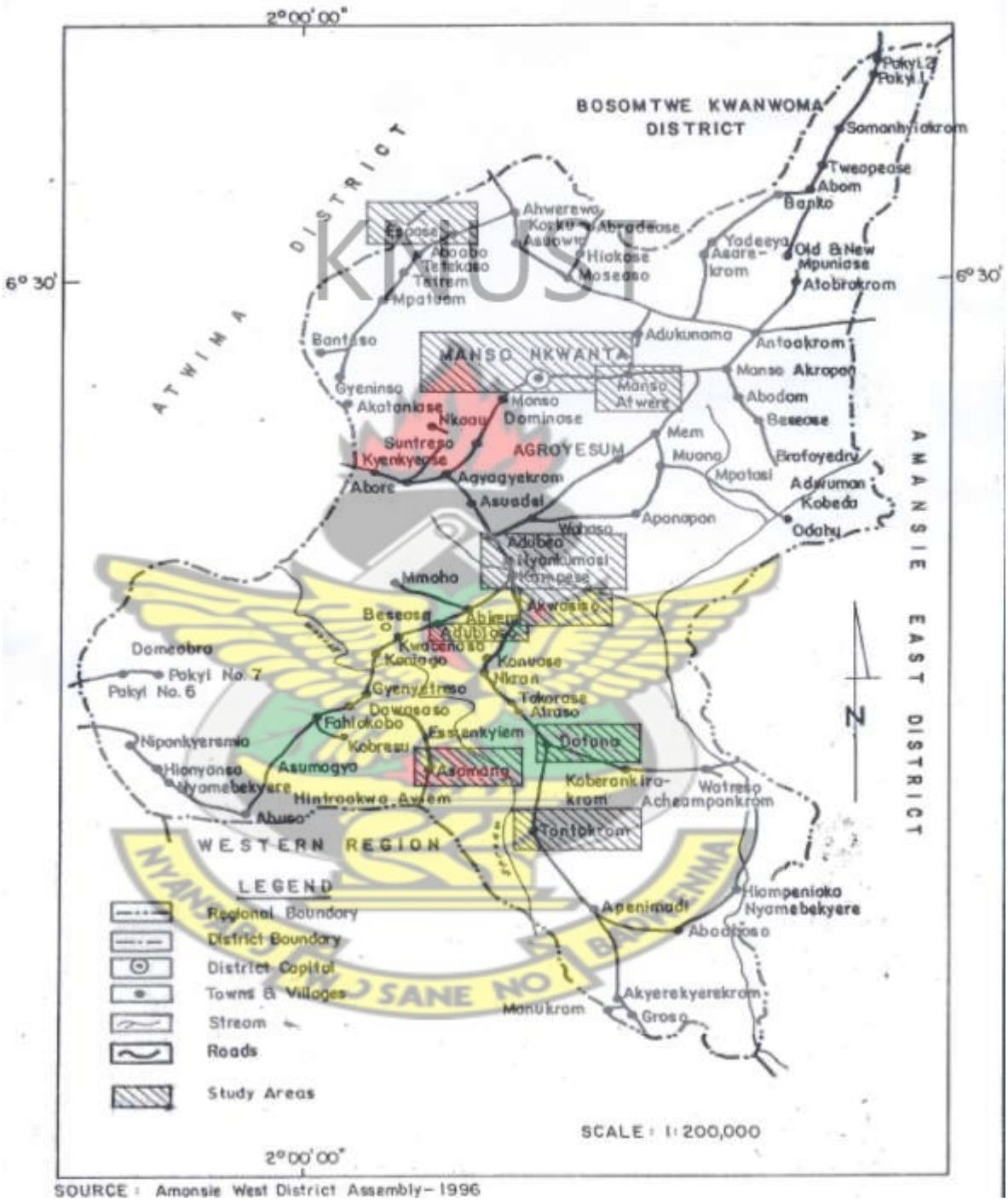


Fig 3.2 Map of Amansie West District (Amansie West District Asembly, 1996).

3.1.3.2 Sampling

The water, soil and cassava samples were picked on 17th November, 2011 from 8am to 5pm to span active day time when majority of environmental and economic activities take place. The containers for sampling were identical and treated in the same way to create an even platform for comparison. Each sample was placed in a well washed plastic container and properly labeled.

3.1.3.2a Water Sampling

Plastic containers were used to sample approximately 1000 mL of forty five (45) different ground water (mechanized bore-holes and open wells) and surface water (streams, ponds and swamps) together with two pipe-borne water. The boreholes were sixteen (16) whiles the open wells totalled ten (10). The number of streams, ponds and swamps were seven, five and seven respectively. Out of the sixteen boreholes, six were sampled close to the mining site (less than 5 m). The borehole water were obtained from deep wells by manual pumping into the sampling container while open wells were also from deep wells (just like borehole) but water was drawn out by fetching directly with sampling container tied to a rope (no pumping involved).

The pipe-borne water was fetched by placing the sampling container under opened tap. Swamp, pond and stream water were fetched by putting the container directly into the water.

Samples were taken upstream and downstream at points where inhabitants take water for domestic consumptions. These are the same water used for irrigation.

Immediately after sampling, they were shaken and field measurements (pH, conductivity, surrounding temperature) were taken with calibrated probes. Concentrated nitric acid was added to the water samples to preserve them. The samples were covered with air-tight lids and labeled indicating the town, water type and distance to mining site where applicable.

The rest were stored in cold ice chest and transported to the project lab of KNUST for further analysis.

3.1.3.2b Soil Sampling

Twenty four (24) soil samples, each weighing about 100 g were collected at intervals of 10 m from eight different mining sites in the following towns Atwere, Ayerebikrom, Bonsaso, Dadiase, Kumpese, Manso Nkwanta, Kensere Nkwanta and Tontokrom. These samples were fetched directly from the ground (with the hand) into polythene bags. Gloves were worn during the sampling and after each sampling, the gloves were changed to avoid cross contamination.

Twenty four extra samples (100 g each) were taken from flood-prone areas within the same mining towns. At each sample point, three samples (0-15 cm), (15-30 cm), 30-45 cm depth were taken with shovel into polythene bags. Tape measure was used for depth measurements. For the flood-prone soils, some were picked under trees (farm lands), on the street, from rock tailings and the rest were sampled near water bodies.

Immediately after sampling, field measurements (pH, conductivity and surrounding temperature) were taken with calibrated probes. The samples were labeled indicating the town, soil depth and distance to mining site where applicable.

3.1.3.2c Cassava Sampling

A total of thirty (30) selected cassava tubers (unpeeled) were dug and uprooted from local farms into black polythene bags. Ten samples were chosen from flood prone areas and another ten were selected between 2 and 5 meters from mining site. Ten extra samples were randomly selected neither from flood-prone areas nor close to the mining site. The top soil was first scraped off with a cutlass before the cassava was uprooted with the hand. The root tubers were collected by cutting them with a stainless steel knife from the stem. All foreign matter especially adhering soils were thoroughly removed from the cassava (*Manihot esculentus*) from the farms using distilled water.

On the average, each cassava tubers weighed between 300 and 400 g.

Immediately after sampling, field measurements (pH, conductivity and surrounding temperature) were taken. The samples were labeled indicating the town and exact spot of collection.

3.2 Methods

This covers preparation of solutions, sample treatment and determinations. The determinations include recovery rate, pH, conductivity, surrounding temperature, moisture content, solid matter content as well as arsenic.

3.2.1 Preparation of Solutions

Stock Arsenic Standard Solution (1000 ppm) – 0.05 g of sodium arsenate ($Na_2HAsO_4.7H_2O$) standard was weighed into 50 ml digestion flask and made to volume.

From the above arsenic stock solution, 5 ppm, 10 ppm, 15 ppm and 20 ppm solutions were prepared by diluting 0.5 ml, 1.0 ml, 1.5 ml and 2.0 ml each to 100 ml with distilled water for the recovery analysis.

Aqua-Regia of HCl and HNO_3 (3:1) – 600 ml concentrated HCl (12.08 M) and 200 ml HNO_3 (15.6 M) were transferred into 1L conical flask. The mixture was shaken, allowed to cool and stored until needed.

Ammonium Oxalate Solution – 25 g of ammonium oxalate solid was dissolved in 175 ml distilled water. Cautiously, 280 ml concentrated sulphuric acid was added and allowed to settle. 400 ml distilled water was then added. The solution was allowed to cool and diluted to 1litre.

Sodium Borohydride Solution (0.6%) – 6 g of sodium borohydride solid was transferred into 1 L conical flask. 500 ml distilled water was added to dissolve the solid. It was then made to volume with the distilled water.

Sodium Hydroxide Solution (0.5%) – 5 g of sodium hydroxide pellet was transferred into 1 L conical flask. 500 ml distilled water was added to dissolve the solid. It was then made to volume with the distilled water.

Hydrochloric Acid (6 M) – 500 ml of the stock hydrochloric acid (12.08 M) was measured and diluted with distilled water to 1 litre. It was then stored until needed for hydride generation.

3.2.2 Sample Treatment

Samples were mainly treated by wet ashing (heating with concentrated acids).

3.2.2.1 Water Samples

50 mL of the water samples was filtered through a 2 μm membrane filter and pipetted into 100 mL pyrex volumetric flask. 20 mL concentrated HNO_3 was added and shaken. The content was heated for about 10 minutes or till about 15 mL of the content was left. The solution was cooled, filtered into a 50 mL volumetric flask and topped up to the mark with distilled water and analysed spectrophotometrically. Blanks were prepared with the same procedure, except that the sample was absent.

3.2.2.2 Soil Samples

Detergents were added to caked soil, dried and ground.

About 1.0 g of oven-dried lump-free soil (passed a 2 mm sieve) was weighed and quantitatively transferred into a 10 mLl test-tube. It was wet ashed with 3 mL aqua-regia and placed on a hot plate 95^{o}C to heat for an hour or until all brown fumes cease. The solution was cooled, filtered and topped to the 10 mL mark with deionised water. It was then sent for hydride generation AAS analyses.

Blanks were prepared with the same procedure, except that the sample was absent. In this case, instead of the sample, 50 mL distilled water was used.

3.2.2.3a Cassava (Edible Part)

All foreign matter especially adhering soils or sand were thoroughly removed from the cassava (*manihot esculentus*) from the farms using distilled water.

50 g of coarsely ground material (ground with mortar and pestle) was placed in 1 L conical flask. The following reagents were added, heated and cooled – 10 mL water, 40

mL HNO_3 and 20 mL of H_2SO_4. 75 mL water and 25 mL ammonium oxalate were added and re-heated to evolve sulfur trioxide vapour.

Heating was done cautiously to avoid excess foam. HNO_3 was added to destroy organic matter and a clear solution with copious vapour of sulfur trioxide resulted. It was then cooled, transferred into a 250 ml volumetric flask and diluted to volume with water.

Blanks were prepared with the same procedure, except that the sample was absent. In this case, instead of the sample, 50 ml distilled water was used.

3.2.2.3b Cassava Peels

Cassava was peeled with stainless steel knife. They were water washed, oven-dried at 100^oC for 4 days and pulverized.1 g of each peel was wet-ashed with 10 mL mixture of concentrated HNO_3 and H_2SO_4 (1:1) for an hour.

After each treatment above, the solution was cooled, filtered and made to the 10mL mark with distilled water and sent for arsenic analyses.

Blanks were prepared with the same procedure, except that the sample was absent. In this case, instead of the sample, 50 ml distilled water was used.

3.2.3 Calibration of Probes

The pH and conductivity probes were calibrated with standards at 25^oC. The procedure for calibration is described below.

3.2.3.1 pH probe Calibration

It was calibrated with Orion Thermo scientific standard buffer solutions of pH 4.01 (made of deionized water, potassium hydrogen phthalate and amaranth dye), pH 7 (made of deionized water, Na_2HPO_4, KH_2PO_4, Na_2CrO_4, $K_2Cr_2O_7$) and pH 10.01 (deionized water, $NaHCO_3$, Na_2CO_3, methyl paraben).

The pH probe was immersed into the lowest pH solution (4.01) and the pH reading was allowed to stabilize. The control knob was adjusted until the expected pH (4.01) was read.

The probe was rinsed in distilled water, immersed in the other solutions (of pH 7 and 10.01) and the knob was adjusted to read the expected values.

3.2.3.2 Conductivity Probe Calibration

The Conductivity probe was calibrated by immersing its electrode which had been washed with distilled water into 25 ml standard 0.01 N KCl solution. The conductivity meter was adjusted to read 1413 µS/m for the KCl solution and the value saved on the meter. The electrode was then removed, washed with distilled water and then immersed again into the KCl solution to confirm the conductivity [APHA, 1998].

3.2.4 Water Sample Analysis

The pH, conductivity and solid matter content of the water samples were determined. The pH and conductivity of the distilled water used for preparation of solutions and digestion were also determined.

3.2.4.1 pH and Conductivity of Water Sample

20 mL of water sample transferred in 50 mL beaker. It was shaken and the calibrated pH and conductivity probes were inserted into the partly settled water suspension. The readings were allowed to stabilize and the pH and conductivity recorded. The surrounding temperature (temperature at which the pH and conductivities were determined) was recorded.

The pH and conductivity of the distilled water were determined likewise.

3.2.4.2 Determination of Total Solids (TS) of Water Sample

The sample was vigorously shaken and 100 ml of sample was rapidly transferred into the dish using 100 ml graduated cylinder. The sample was evaporated on a water bath and the evaporated sample was dried for an hour at 105^{o}C in an oven.

The increase in weight over that of the empty dish represents the total solids.

Calculations-

Total solids (mg/L) = (A-B/C) X 10^{6}

Where, A = weight of the dried residue and dish (g)

B = Weight of dish alone (g)

C = volume of sample (ml)

3.2.4.3 Determination of Total Suspended Solids (TSS)

TSS are portions of total solids that are trapped (residue) by a standard filter paper of 2 µm (or smaller) nominal pore size.

100 ml sample was filtered (with 2 µm pore size) and the residue was evaporated on a water bath. The obtained sample after evaporation was dried to constant weight in an oven at 105^{o}C.

The increase in weight over that of the empty dish is the weight of the total suspended solids.

3.2.4.4 Determination of Total Dissolved Solids (TDS)

TDS are portions of total solids that pass through a standard filter paper of 2 µm (or smaller) nominal pore size. Mathematically, the difference between TS and TSS gives the TDS.

TDS was determined independently (without subtracting TSS from TS) by the procedure below.

200 ml sample was vigorously shaken and filtered through filter paper. 100 ml sample of the filtrate was pipetted into an already weighed evaporating dish and evaporated to dryness on a water bath. The evaporated sample was dried to constant weight in an oven at 105^{o}C.

The increase in weight over that of the empty dish is the weight of the total dissolved solids. This weight includes liquids, solids and materials that have passed through the chosen filter media that are not volatized during the drying process.

Calculations-

Total dissolved solids (mg/L) = (A-B/C) $\times 10^{6}$

Where, A = weight of the dried residue and dish (g)

B = Weight of dish (g)

C = Sample volume (ml)

3.2.5 Soil Sample Analysis

The pH, conductivity and moisture content of the soil samples were determined as described in the following subsections.

3.2.5.1 pH and Conductivity of Soil Sample

About 20 g of soil (passed a 2 mm sieve) was weighed into a 50 ml beaker. 20 ml distilled water was added and allowed to stand for about 30 minutes. The calibrated pH and conductivity probes were inserted into the partly settled suspension. The pH and conductivity were recorded when the values were steady. The surrounding temperature was recorded.

3.2.5.2 Moisture Content of Soil Samples

An empty crucible was weighed and the weight was recorded. 1 g of soil was weighed into the crucible. The soil in the crucible was oven-dried at 105 ^{o}C to constant weight. The samples were taken from the oven and cooled to room temperature. The dried soil was weighed.

The moisture content is calculated as follows-

$$M\ (\%) = \frac{A-B}{A-D} \times 100$$

Where

M (%) = Percentage moisture content

A = Weight of original soil sample (wet) + crucible

B = Weight of ashed soil (dried) + crucible

D = Weight of crucible

3.2.6 Cassava Sample Analysis

The pH, conductivity, and moisture content of the cassava samples were determined.

3.2.6.1 pH and Conductivity of Cassava Sample

About 2 g of cassava was ground. Distilled water was added. The suspension was allowed to partly settle and the calibrated pH and conductivity probes were inserted. The pH, conductivity and surrounding temperature were recorded simultaneously.

3.2.6.2 Moisture Content of Cassava Sample

An empty crucible was weighed and the weight was recorded. About 20 g of the cassava was weighed into the crucible and oven-dried to constant weight. The samples were taken from the oven and cooled to room temperature. The dried cassava was weighed.

The % Moisture $= (\frac{A-B}{A}) \times 100$

Where A = Weight of Wet Cassava (g)

B = Weight of Dried cassava (g)

3.2.7 Cassava Peel Analysis

The pH, conductivity and moisture content of the cassava peels were determined.

3.2.7.1 pH and Conductivity of Cassava Peels

A small peeled part of the cassava was ground. Distilled water was added and solution was solution was swirled to muddy it. The suspension was allowed to partly settle. The calibrated pH and conductivity probes were inserted and the reading was allowed to settle. The pH and conductivity were recorded together with the temperature at which the readings were done (surrounding temperature).

3.2.7.2 Moisture Content of Cassava Peels

An empty crucible was weighed and the weight was recorded. About 3 g of the cassava peel was weighed into the crucible and oven-dried to constant weight. The samples were taken from the oven and cooled to room temperature. The dried cassava was weighed.

The % Moisture $=(\frac{A-B}{A}) \times 100$

Where A = Initial weight of the cassava peel (g)

B = Final weight of cassava peel (g)

3.2.8 Instrumentation

Australian Varian AA 240 Fast sequential Hydride generation AAS (at Ghana Atomic Energy Commission) was used for all arsenic determinations.

The instrument was set up according to manufacturer's specification. It has been equipped with argon to drive the hydride system. The HCl (6 M) and $NaBH_4$ (0.6%) generate the hydride.

The manufacturers specifications were as follows:

PARAMETER	VARIAN AA 240FS
Lamp Current	10 mA (Arsenic hollow cathode)
Wavelength	193.7 nm
Slit	0.5 nm
HCl	6 M at 1 ml/min flow rate
NaOH	0.5%
Detection limit	0.001 mg/L
$NaBH_4$	0.6% at 1.5 ml/min
Fuel	Acetylene
Support	Air

Before any measurement, potassium iodide was added to all digested samples to liberate any iodine.

When the set-up conditions above were met:

1. The instrument was switched on.
2. The HCL was allowed to warm for about 15 minutes.
3. Three different capillaries were inserted into the digested solution, the HCl (6 M) and $NaBH_4$ (0.6%) simultaneously.
4. The hydride generation system sucked up (aspirated) the standards, sodium borohydride and HCl and mixed them up.
5. A volatile hydride of the analyte (arsenic) was created from the reaction.
6. The Gas-liquid separator separated the gas (hydride) and any liquid present.

7. The liquid drained down and collected with a container (waste) but the hydride flowed to the optical cell.
8. The hydride form of the metalloid was decomposed and created atoms of the element of interest.
9. The monochromator removed scattered lines of other wavelengths and by so doing, only a narrow spectral line or band reached the photomultiplier tube (PMT).
10. The PMT as the detector determined the intensity of photons of the analytical line and the results (concentration in mg/L) was displayed.

Steps 4 to 10 are in-built processes.

The blanks and samples were taken through the same process.

During the arsenic determinations, the results of arsenic concentration were subtracted from blank readings and after five sample read ups, standards were run to make sure that the obtained results were correct. Duplicate analyses were done to ensure consistency (precision) and the mean arsenic concentration as well as the standard deviation was reported for each sample.

Treated distilled water (blank) was aspirated between each sample to avoid cross contamination. Every sample was tested in parallel with a blank.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The results obtained for distilled water analysis, physicochemical parameters determined in water, soil and cassava samples and their arsenic concentrations together with the recovery are reported in this chapter. The findings are also discussed.

4.1 Water Samples

Results obtained after analyses of the water samples are presented and discussed in this section

Table 4.1 Results obtained for the pH, conductivity, surrounding temperature and arsenic levels of the distilled water used for solution preparation and digestion (blank)

pH	Conductivity, µS/cm	Temp, ^{o}C	Arsenic Conc, mg/L
6.39	5.02	25.1	0.001
6.40	5.04	25.2	0.000
6.38	5.00	25.1	0.001

Table 4.2 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in the borehole water samples.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Akwasiso	7.72	366.41	26.5	75	579	650	0.010±0.001	10
Asamang	6.98	312.11	23.9	61	459	515	0.006±0.003	6
Atwere	7.57	309.02	26.4	65	493	553	0.008±0.003	8
Bonsaso	6.01	119.27	26.6	50	400	536	0.005±0.001	5
Datano	7.98	392.38	24.8	74	600	671	0.011±0.001	11
Manso Nkwanta	6.76	286.93	25.4	53	413	460	0.005±0.003	5
Nkuntin	7.60	298.10	21.1	62	512	572	0.010±0.003	10
Nyankumasi	7.33	372.15	27.8	69	540	602	0.008±0.001	8
Tontokrom	7.12	357.64	25.2	64	529	589	0.007±0.002	7
Yawkrom	7.58	304.69	27.9	65	498	561	0.009±0.001	9

Table 4.3 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in open well water samples.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Akwasiso	5.96	239.12	26.1	63	486	589	0.005±0.001	5
Asamang	7.21	180.29	25.2	83	592	666	0.010±0.002	10
Atwere	5.94	108.19	26.1	59	479	565	0.004±0.003	4
Bonsaso	6.89	250.85	26.0	67	500	533	0.008±0.003	8
Dadiase	7.37	312.06	24.1	82	586	668	0.011±0.001	11
Datano	7.10	300.90	25.8	86	515	597	0.008±0.002	8
Kumpese	6.72	210.19	24.6	73	534	605	0.007±0.001	7
Nyankumasi	7.03	273.11	27.4	79	528	604	0.008±0.001	8
Takorase	6.62	245.07	25.2	69	491	557	0.006±0.002	6
Yawkrom	6.93	112.17	26.0	72	519	542	0.007±0.003	7

Table 4.4 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in pond water samples.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Akwasiso	6.81	384.02	24.4	245	791	1030	0.014±0.001	14
Bonsaso	6.99	429.09	25.1	275	892	1172	0.015±0.003	15
Tontokrom	5.84	198.19	26.9	124	693	811	0.012±0.002	12
Dadiase	6.75	315.97	25.9	202	750	949	0.010±0.001	10
Konianse-nkran	5.92	215.15	26.5	138	724	826	0.014±0.001	14

Table 4.5 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in swamp water samples.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Dadiase	5.98	130.13	25.8	100	613	711	0.008±0.001	8
Kensere Nkwanta	6.01	189.42	26.1	135	649	780	0.009±0.001	9
Kumpese	6.09	268.17	24.4	171	700	869	0.011±0.001	11
Manso Nkwanta	6.13	192.07	25.1	213	744	952	0.011±0.003	11
Takorase	6.20	363.85	26.9	250	800	1045	0.012±0.002	12
Tontokrom	6.08	214.91	25.9	158	712	861	0.012±0.001	12
Yawkrom	6.19	361.47	26.5	180	729	904	0.014±0.001	14

Table 4.6 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in streams.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Dadiase	5.17	148.19	25.4	88	587	684	0.006±0.001	6
Kensere Nkwanta	5.92	213.61	26.0	124	591	759	0.009±0.002	9
Kumpese	6.04	274.97	24.2	167	649	814	0.007±0.001	7
Manso Nkwanta	6.38	216.20	25.3	199	723	936	0.010±0.003	10
Takorase	5.05	372.07	26.5	243	792	1012	0.010±0.002	10
Tontokrom	6.09	236.51	25.6	147	684	762	0.010±0.001	10
Yawkrom	6.11	312.18	26.2	164	697	894	0.012±0.002	12

Table 4.7 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in pipe-borne water.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Atwere	6.18	43.09	25.5	37	189	226	0.001±0.001	1
Esaase	6.02	29.33	26.9	22	249	271	Below Detection	<1

Table 4.8 Results obtained for the pH, conductivity, surrounding temperature, TDS, TSS, TS and arsenic levels in borehole water samples picked close to mining site.

Town	pH	Conductivity, µS/cm	Temp, ^{o}C	TDS, mg/L	TSS, mg/L	TS, mg/L	Arsenic Conc, mg/L	Average Arsenic Conc, ppb
Akwasiso	6.23	384.22	30.5	153	618	800	0.013±0.001	13
Asamang	5.38	379.08	28.9	126	592	715	0.012±0.003	12
Atwere	6.52	332.18	31.4	145	600	739	0.011±0.003	11
Bonsaso	5.86	135.88	28.6	123	486	601	0.009±0.001	9
Datano	6.93	418.90	27.8	109	712	809	0.011±0.001	11
Manso Nkwanta	6.14	312.99	27.4	89	534	621	0.008±0.003	8

From Table 4.1, the distilled water used for solution preparation and digestions had pH range of 6.38 to 6.40. It had conductivity range of 5.00 to 5.04 µS/cm. Distilled water is produced by distillation and has an electrical conductivity and TDS less than 10 µS/cm and 10 mg/L respectively (APHA, 1992). This range (5 to 5.04 µS/cm) makes the water suitable. Triplicate analysis of arsenic content of the distilled water (blank) gave 0.001 mg/L (1 ppb), below detection limit (0.000 mg/L) and 0.001 mg/L. Based on these readings, the arsenic content was picked as 0.001 mg/L which was subtracted from the sample readings. The 1 ppb is insignificant compared to the WHO threshold of 10 ppb. Arsenic in the distilled water may be due to the fact that arsenic is environmentally permanent and water soluble. A deduction from table 4.1 is that, the conductivity recorded could be due to the presence of the arsenic and other ions.

From table 4.2 (boreholes), the pH of the water ranged from 6.01 to 7.98. pH values outside the standard range of 6.5 to 8.3 indicate poor water quality. All the water samples were within the standard range with the exception of Bonsaso which recorded

6.01. Hence, using pH values alone, one can endorse the entire water sample for usage except Bonsaso. According to Allison *et al* (1990), the high pH of borehole water is due to buffering from dolomite (a sedimentary rock of calcium and magnesium) and other alkaline mineral deposits. The conductivity ranged from 119.27 to 392.38 µS/cm. The high conductivity may be due to the presence of ions like calcium, magnesium and carbonates (from limestone). The ranges for the solid matter content were 50 to 75 mg/L, 400 to 600 mg/L and 460 to 671 mg/L for TDS, TSS and TS respectively. The arsenic content ranged from 5 to 11 ppb. With the exception of Datano which recorded 11 ppb, no sample was above the WHO threshold of 10 ppb. A graph of the arsenic concentrations against their respective towns is shown in Appendix 1A, page 143**.** This graph also includes the WHO limit of 10 ppb for comparison.

From table 4.3 (open wells), the pH ranged from 5.94 to 7.37. With the exception of Akwasiso and Atwere, pH 5.96 and 5.94 respectively, all the wells were within the standard range of 6.5 to 8.3. The open wells were more acidic than the boreholes (closed underground water) due to the dissolution of atmospheric carbon dioxide or acid rain that may enter the open well. The conductivity ranged from 108.19 to 312.06 µS/cm. The TDS, TSS, TS and arsenic levels ranged from 59 to 86 mg/L, 479 to 592 mg/L, 553 to 668 mg/L and 4 to 11 ppb respectively. With the exception of Dadiase (11 ppb), no other sample was above the WHO limit of 10 ppb.

A graph of the arsenic concentrations in these open wells samples against their respective towns is shown in Appendix 2A, page 143**.** Graph 2A also includes the WHO limit for comparison.

Conductivity values below 3500 µS/cm are acceptable for drinking (Faulkner *et al*, 1989). Hence, based on conductivity alone, all the groundwater (borehole and open well) are potable.

According to Ohio EPA water standards of 2000 (fig 2.4, page 36), TDS levels below 50 mg/L are most ideal for drinking. Levels between 50 and 170 mg/L are hard water but acceptable. All the ground water had TDS far below 170 mg/L and hence potable. Borehole water from Bonsaso recorded 50 mg/L which meets the most ideal condition for water use.

Arsenic in ground water comes from natural interaction between water and arsenic-containing rocks and minerals (Welch *et al*, 2000). This could be the source of arsenic in the ground water.

A plot of the arsenic levels of borehole water samples and their pHs in the various towns yields a scattered chart (Appendix 10A, page 147) indicating that there is no specific pattern among the three variables. However, a line of best fit gives a direct relationship between pH and arsenic levels. This general trend of rising arsenic concentration with rising pH is consistent with literature. According to Smedley (1996), all other things being equal, arsenic concentration and solubility in water increases with increasing pH (especially pHs greater than 6). Amonoo-Neizer and Amekor (1993) attribute the high pH associated with high arsenic levels to increasing hydrophilic character of arsenic at these pH values.

The conductivity of the borehole water samples and their arsenic levels in the various towns studied were subjected to graphical analysis (Appendix 11A, page 148). A scatter

diagram results indicating a poor correlation and by extension, one cannot use the conductivities of the samples to predict the trend of the arsenic levels. All other things being equal, water conductivity rises as arsenic levels rise (Acharyya *et al*, 2000). The non-conformity could be due to the differences in the types and/or concentrations of other ions. The major water ions are calcium, potassium, sodium, chlorides, carbonates, phosphates, sulphates, nitrates and iron (Mahimairaja *et al*, 2005).

From literature (Redman *et al*, 2002), under equal parameters, arsenic content rises as TS and TSS rises because solid matter forms stable arsenic-solid matter complex in water. However, a scattered diagram results for a plot of arsenic levels against TS for open wells in the studied towns (Appendix 12A, page 148). Similarly, a scattered diagram results for a plot of arsenic levels and TSS of borehole water samples (Appendix 13A, page 142). The scatter leads to the conclusion that there are different factors (eg. soil texture, surrounding temperature, water pH) affecting arsenic levels in different towns, not solid matter content alone. This irregular trend (scatter diagram) was explained in 2001 and 2002 by Grafe et al. The effects of solid matter on arsenic adsorption onto hydrous iron oxides differ depending upon the source and surface area of the adsorbent mineral. Based on this, it is possible that a particular sample may have little TS but the source of that solid and the surface area of the adsorbent material will make it compete very well with arsenic for adsorption onto the site and in the end, displace the arsenic from the binding site into the water, increasing the arsenic content of the water. Manning and Goldberg (1996) further confirms the independence between solid matter and arsenic levels in water by stating that, turbidity of water (associated with solid matter content of the water) has no or low effect on arsenic levels in water.

This may be due to the fact that arsenic is colourless. Manning and Goldberg concluded that if water turbidity is the main factor determining arsenic levels in water, then simple filtration will remove arsenic in water but this is not the case. The removal of arsenic in water requires extensive reverse osmosis.

From table 4.4 (pond water which is surface water), the ranges were: pH 5.84 to 6.99, conductivity 198.19 to 429.07 µS/cm and TDS 124 to 275 mg/L. The TSS and TS ranged from 693 to 892 mg/L and 811 to 1030 mg/L respectively. The arsenic levels ranged from 10 to 15 ppb with 80% above the 10 ppb limit. A graph of the arsenic concentrations in the ponds against their towns is shown in Appendix 3A, page 144**.** This graph also includes the WHO limit.

From table 4.5 (swamp which is a surface water), the pH ranged from 5.98 to 6.20. The conductivity ranged from 130.13 to 363.85 µS/cm. The TDS ranged from 100 to 250 mg/L. The TSS and TS ranged respectively from 613 to 800 mg/L and 711 to 1045 mg/L. The arsenic levels ranged from 8 to 14 ppb. A graph of the arsenic concentrations in swamps against their respective towns is shown in Appendix 4A, page 144**.** This graph also includes the WHO limit.

From table 4.6 (stream which is a surface water), the ranges were: pH 5.05 to 6.38, conductivity 148.19 to 372.07 µS/cm, TDS 88 to 243 mg/L, TSS 587 to 792 mg/L, TS 684 to 1012 mg/L and arsenic level from 6 to 12 ppb. A graph of the arsenic levels in streams against their towns is shown in Appendix 5A, page 145**.** This graph also includes the WHO limit.

In general, the surface water was more acidic than the ground water. The general acidic nature of the surface water is attributable to the high acidic nature of the soils (from tables 4.9 and 4.10). Acid rain which gets easy access to these surface water and dissolution of atmospheric CO_2 can also account for the low pHs of the surface water.

Vigorous agricultural and mining activities in the district may be responsible for the high conducting nature of some of the surface water through release of ions. In general, a higher conductivity indicates more dissolved materials and more contaminants. It is therefore not surprising that the ponds which had the highest conductivities also had the highest TDS/TSS/TS.

The high arsenic levels in the surface water can be due to agrochemicals deposits, leaching of arsenic-containing soils and probable use of phosphate fertilizers. Phosphates compete with arsenate for binding site on soils. By this processes, arsenate is dislodged from the soil site into the water leading to high arsenic concentration in the water.

The ponds had the highest arsenic content due to natural organic matter (NOM) in these ponds. NOM can complex arsenic to form stable solution complexes. The arsenic solubility, mobility and concentration increases due to such stable arsenic-NOM complexes.

The low levels of arsenic in some of the surface water (streams) can be due to low levels of arsenic in some of the soil samples.

A plot of the arsenic levels of ponds against their pHs in the various towns studied (Appendix 14A, pg 149) yields a scattered chart. This means the factors affecting

arsenic levels and pH differ from town to town and a perfect correlation can be ruled out. At high pH, arsenic may be released from surface binding sites that lose their positive charge (Amoah *et al*, 2006). This could explain the pH increase with increase in arsenic levels though the correlation is not perfect.

A scattered diagram resulted for a plot of conductivity of swamps against their arsenic levels in the studied towns (Appendix 15A, page 150). A swamp may have a high conductivity but low arsenic level because of temperature, concentration and mobility differences of other ions like iron, magnesium, calcium among others (major water ions) and not necessarily arsenic. In all, a line of best fit shows a direct proportionality. This indicates that under equal parameters, arsenic levels increase with increasing conductivity.

A plot of arsenic concentrations against their TS in streams in the studied towns gave a scattered diagram (Appendix 16A, page 150) signaling that arsenic levels in the surface water, total solid matter and their towns are independent.

From table 4.7 (pipe borne water), the pHs were 6.18 and 6.02. The conductivities were 43.09 µS/cm and 29.33 µS/cm. The TDS, TSS and TS for Atwere were respectively 37 mg/L, 189 mg/L and 226 mg/L whiles TDS, TSS and TS for Esaase were 22 mg/L, 149 mg/L respectively. The arsenic content of Atwere pipe borne water was 1 ppb whiles that for Esaase was below detection. Therefore Esaase pipe water had arsenic level below 0.001 mg/L or 1 ppb.

The pipe-water met the Ohio EPA standard (Fig 2.4, page 36) of less than 50 mg/L TDS to make them most potable. They also had conductivity less than 5 µS/cm making them ideal for use according to APHA 1992 water standard criteria. They had arsenic level far below the 10 ppb limit.

A graph of the arsenic concentrations of the pipe-borne water against their respective towns including the WHO limit is shown in Appendix 6A, page 145.

From table 4.8 (boreholes close to mines), the pH ranged from 5.86 to 6.93 and conductivity from 135.88 to 418.90 µS/cm. The TDS, TSS, TS and arsenic levels ranged respectively from 89 to 145 mg/L, 486 to 712 mg/L, 601 to 809 mg/L and 8 to 13 ppb. They had higher TDS, TSS and TS than their non-mine counterparts meaning mining introduces solids into water bodies.

Arsenic levels in borehole samples close to the mines against their towns and also WHO limit is shown graphically at Appendix 7A, pg 146.

Comparison of the arsenic levels in borehole water from mines and that from the non-mine is represented by a bar chart in Appendix 8A, page 146. Mine water is more acidic due to the oxidation of sulphide minerals (Alpers and Blowes, 1994). Mine water was more arsenic containing due to leaching of arsenic from soils, mining effluents and erosion of mine soils into these water bodies.

On the whole, arsenic levels in ground water ranged from 4 to 11 ppb whiles surface water ranged from 6 to 14 ppb. Though the general trend is that surface water is more contaminated, two deviations exist. Dadiase well had 11 ppb whiles the stream recorded 6 ppb. Similarly, Kumpese open well recorded 7 ppb, the stream also recorded 7 ppb

and the swamp recorded 11 ppb. The fact that the well (ground water) recorded same level as the stream (surface) diffuses the general statement that ground water is less contaminated. These deviations may be due to the peculiar nature of the water in these towns.

This relationship between surface and ground water with respect to arsenic levels is graphically shown in Appendix 9A, page 147. From above, using water type (surface or ground) to predict arsenic levels is not ideal. Determination of arsenic levels in water samples requires experiment not parametric prediction (prediction based on a known parameter).

4.2 Soil Samples

Results obtained after analyses of the soil samples (flood-prone and mining site) are presented and discussed in this section

Table 4.9 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in soils from flood-prone areas

Town	Soil Depth/cm	pH	Conductivity, µS/cm	Temp, ^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Atwere	0-15	6.50	319.92	25.2	6.54	0.312±0.015	3.12
Atwere	15-30	6.46	285.75	25.2	8.06	0.454±0.034	4.54
Atwere	30-45	6.42	319.02	25.2	9.11	0.583±0.053	5.83
Ayerebikrom	0-15	6.37	278.79	25.5	9.19	0.411±0.072	4.11
Ayerebikrom	15-30	6.29	291.11	25.5	10.70	0.509±0.091	5.09
Ayerebikrom	30-45	6.18	250.18	25.5	12.59	0.622±0.020	6.22
Bonsaso	0-15	6.41	279.15	25.1	19.09	0.329±0.041	3.29
Bonsaso	15-30	6.34	326.19	25.1	21.69	0.478±0.062	4.78
Bonsaso	30-45	6.32	294.04	25.1	24.01	0.599±0.063	5.99
Dadiase	0-15	6.31	264.95	25.9	23.18	0.336±0.094	3.36
Dadiase	15-30	6.28	269.02	25.9	25.13	0.412±0.085	4.12
Dadiase	30-45	6.17	324.09	25.9	27.95	0.604±0.076	6.04
Kumpese	0-15	5.96	270.08	26.4	21.58	0.511±0.009	5.11
Kumpese	15-30	5.91	281.12	26.4	24.70	0.548±0.021	5.48
Kumpese	30-45	5.89	310.19	26.4	28.61	0.569±0.042	5.69
Kensere Nkwanta	0-15	6.05	189.38	25.8	23.05	0.498±0.063	4.98
Kensere Nkwanta	15-30	6.01	216.23	25.8	25.47	0.521±0.084	5.21
Kensere Nkwanta	30-45	5.88	240.06	25.8	27.26	0.532±0.015	5.32
Manso Nkwanta	0-15	5.55	450.13	27.7	27.45	0.628±0.016	6.28
Manso Nkwanta	15-30	5.48	502.25	27.7	24.09	0.639±0.037	6.39
Manso Nkwanta	30-45	5.41	534.86	27.7	25.59	0.692±0.058	6.92
Tontokrom	0-15	5.62	480.80	28.2	27.79	0.742±0.079	7.42
Tontokrom	15-30	5.52	521.57	28.2	29.95	0.769±0.091	7.69
Tontokrom	30-45	5.46	539.49	28.2	31.58	0.778±0.010	7.78

Table 4.10 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in soils close to mining sites.

Town	Distance (m)	pH	Conductivity, µS/cm	Temp, ^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Atwere	10	6.19	307.45	32.1	12.02	0.706±0.041	7.06
Atwere	20	6.24	326.05	32.1	11.34	0.691±0.062	6.91
Atwere	30	6.29	312.98	31.9	9.26	0.604±0.063	6.04
Ayerebikrom	10	6.04	326.47	30.2	14.91	0.693±0.094	6.93
Ayerebikrom	20	6.11	314.01	29.9	13.06	0.612±0.085	6.12
Ayerebikrom	30	6.27	338.20	29.9	11.92	0.591±0.076	5.91
Bonsaso	10	6.02	348.26	29.9	26.22	0.613±0.050	6.13
Bonsaso	20	6.11	339.81	29.9	25.09	0.604±0.042	6.04
Bonsaso	30	6.23	321.50	29.4	24.33	0.595±0.030	5.95
Dadiase	10	5.92	394.97	30.1	29.77	0.583±0.021	5.83
Dadiase	20	6.03	362.18	30.1	28.90	0.579±0.010	5.79
Dadiase	30	6.19	329.30	30.0	27.92	0.524±0.010	5.24
Kumpese	10	5.19	237.11	29.1	31.96	0.782±0.009	7.82
Kumpese	20	5.23	309.23	29.1	31.03	0.719±0.081	7.19
Kumpese	30	5.27	286.09	28.7	29.48	0.673±0.039	6.73
Kensere Nkwanta	10	5.19	259.48	27.9	29.02	0.559±0.011	5.59
Kensere Nkwanta	20	5.23	242.21	27.9	28.11	0.543±0.036	5.43
Kensere Nkwanta	30	5.27	325.27	27.9	27.03	0.532±0.018	5.32
Manso Nkwanta	10	4.18	598.49	32.8	33.06	0.780±0.011	7.80
Manso Nkwanta	20	4.24	546.58	32.4	31.98	0.771±0.010	7.71
Manso Nkwanta	30	4.63	532.51	32.3	31.96	0.745±0.013	7.45
Tontokrom	10	4.08	568.81	32.6	29.56	0.848±0.016	8.48
Tontokrom	20	4.59	549.24	32.6	28.97	0.812±0.019	8.12
Tontokrom	30	4.79	511.36	32.2	27.86	0.787±0.061	7.87

From table 4.9 (flood prone soils), the ranges were: pH 5.41 to 6.50, conductivity 189.38 to 539.49 µS/cm, moisture content 6.54 to 31.58% and arsenic level from 3.12 to 7.78 mg/kg. Soil conductivity increased down the soil profile because ion-containing runoffs settle down the soil. The high conductivities can be due to fertilizers used for cultivation.

Soils averagely contain 0.05–0.2 mg/kg (without external influence) but agricultural activities have produced a concentration of approximately 10 mg/kg (William and Frakenberger, 2001). All the soils had arsenic level above the natural composition of 0.05-0.2 mg/kg but less than the 10 mg/kg approximation that results from external influence. All the soil samples had levels less than the WHO threshold of 20 mg/kg.

Soils with low arsenic are attributable to arsenic leaching and erosion since flood-prone soils are easily leached and eroded. Methylation also reduce arsenic content. Arsenic can be methylated by microbes to form arsine (gaseous AsH_3) which is lost by volatilization (Nesbitt *et al*, 1998). Humic acids deplete arsenic in soils by forming stable complexes with soil mineral surfaces and blocks arsenic adsorption onto soil sediments and iron oxides in the soil (Nicholson, 1994). The differences in arsenic levels can be due to differences in soil properties in terms of soil texture and soil composition.

A graph of the arsenic concentration of flood-prone soils against their respective towns in shown in Appendix 1B, page 152. This graph also shows the variation of arsenic levels with soil depth and also compares the arsenic levels with the William and Frakenberger approximation and WHO limit of 10 and 20 mg/kg respectively.

Comparison of results (irrespective of soil depth) with William and Frakenberger gives a clue to the extent of agriculturaltural and economic influence on arsenic levels.

Generally as the soil depth increased, arsenic levels increased (bar chart, Appendix 1B, page 152) which can be due to arsenic-containing substances that drain down the soil. This observation is consistent with literature which states that, arsenic levels increase or remains about the same with increasing soil profile (Kumi, 2007). The increasing arsenic levels with soil depth is a source of worry because it is the depth at which plants obtain their nutrients.

When the arsenic levels in flood-prone soils were plotted against their pHs in the various towns, there was a scattered diagram indicating that the three parameters are independent (Appendix 4B, page 154). However, a line of best fit gives an inverse relationship between pH and arsenic levels. This is consistent with literature. From literature, generally as soil pH decreases, arsenic level increases but will deviate if the strength of other factors like temperature, phosphate interference in arsenate adsorption onto soils exceed the influence of soil pH. Therefore, the strength of these factors differs from town to town.

A plot of arsenic levels against conductivities of flood prone soils in the studied towns gave a scattered diagram (Appendix 5B, page 154). This means the factors affecting conductivity and arsenic levels in these towns are independent. A particular town may have higher soil conductivity but lower arsenic concentration due to the difference in temperature, concentration and mobility of other ions.

On the whole, soil conductivity and arsenic levels are independent.

From table 4.10 (soils from mines), the ranges were: pH 4.18 to 6.29, conductivity 237.11 to 598.49 µS/cm, moisture content 9.26 to 33.06% and arsenic level from 5.24 to 8.48 mg/kg.

On the whole, all soils were acidic. This confirms literature that under many conditions soils tends to be far more acidic than alkaline (Connell *et al*, 1984). Organic matter (plant litter, compost and manure) decrease soil pH by decomposition. The arsenic contents of the soils were all above the natural composition of 0.05-0.2 mg/kg but below the both William and Frakenberger approximation and WHO limit of 10 and 20 mg/kg respectively. High arsenic levels in the soil is due to the dual nature of arsenic in soils. Both aerobic and non-aerobic conditions favour arsenic accumulation in the soil. Arsenate is strongly adsorbed by soil under aerobic conditions and arsenite, under anaerobic conditions (Hopenhayn-Rich, 2000). Geothermal activities like mining generally increase arsenic levels because these activities result in the dissolution and transport of metalloids like arsenic.

Wet soils had the highest arsenic level because they leach with difficulty.

The mines soils had higher arsenic levels than the flood-prone soils. This is graphically shown with a bar chart (Appendix 2B, page 153). This graph also compares arsenic levels in mine soils with the WHO limit and William and Frakenberger approximation.

Graphical representation of arsenic levels with moisture levels for mine soils in the selected towns yielded a scatter diagram (Appendix 6B, page 155) indicating that these three parameters do not correlate. This may be because the strength of other factors like phosphate interference, methylation by microorganisms which can influence arsenic

content in soils outweighs the influence of soil moisture. However, a line of best fit gives a direct relationship. The good correlation was because wet soils leach with difficulty so wet soils have more arsenic than dry soils when all other parameters are equal.

Arsenic levels increased with closeness to the mining site (bar chart, Appendix 3B, page 153).

4.3 Cassava Samples

Results obtained after analyses of the cassava samples are presented and discussed in this section

Table 4.11 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in the randomly selected cassava samples

Town	pH	Conductivity, µS/cm	Temp ,^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	6.76	64.11	26.8	14.18	0.031±0.003	0.62
Bonsaso	6.55	61.43	26.5	12.92	0.006±0.008	0.12
Edubia	6.09	69.75	26.3	13.63	0.033±0.003	0.66
Esaase	6.41	67.97	26.5	11.07	0.039±0.001	0.78
Kumpese	6.83	70.09	26.8	14.90	0.045±0.002	0.90
Kensere Nkwanta	6.36	64.82	26.7	12.22	0.041±0.004	0.82
Manso Nkwanta	5.52	68.24	26.1	13.43	0.042±0.005	0.84
Nyankumasi	4.99	68.36	26.2	13.46	0.033±0.009	0.66
Tontokrom	5.85	72.60	26.3	12.81	0.034±0.003	0.68
Yawkrom	6.34	65.58	26.4	14.63	0.031±0.004	0.62

Table 4.12 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in cassava samples from flood prone areas

Town	pH	Conductivity, µS/cm	Temp,^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	6.92	60.21	25.6	17.21	0.027±0.006	0.54
Bonsaso	6.67	59.12	25.6	15.44	0.004±0.001	0.08
Edubia	6.21	67.90	25.8	17.65	0.028±0.003	0.56
Esaase	6.49	66.41	25.8	14.43	0.035±0.004	0.70
Kumpese	6.93	68.95	25.9	18.26	0.040±0.005	0.80
Kensere Nkwanta	6.53	61.25	25.7	17.01	0.036±0.006	0.72
Manso Nkwanta	5.64	66.91	25.9	16.98	0.039±0.008	0.78
Nyankumasi	5.03	66.42	25.7	17.35	0.030±0.003	0.60
Tontokrom	5.99	70.10	25.8	15.07	0.029±0.003	0.58
Yawkrom	6.48	62.95	25.7	19.89	0.027±0.001	0.54

Table 4.13 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in the cassava samples from mining site.

Town	pH	Conductivity, µS/cm	Temp ,^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	5.13	73.80	26.8	19.20	0.043±0.004	0.86
Bonsaso	5.10	67.25	26.5	18.05	0.019±0.007	0.38
Edubia	6.00	74.51	26.3	20.19	0.041±0.004	0.82
Esaase	5.50	73.89	26.5	18.47	0.048±0.002	0.96
Kumpese	5.11	77.98	26.8	18.25	0.060±0.003	1.20
Kensere Nkwanta	5.09	68.15	26.7	14.06	0.050±0.005	1.00
Manso Nkwanta	5.77	71.61	26.1	24.19	0.055±0.004	1.10
Nyankumasi	4.92	78.07	26.2	22.85	0.056±0.008	1.12
Tontokrom	5.89	74.50	26.3	22.98	0.044±0.002	0.88
Yawkrom	5.78	63.27	26.4	19.90	0.042±0.001	0.84

From table 4.11 (randomly selected cassava), the pH ranged from 4.99 to 6.83, conductivity 61.43 to 72.60 µS/cm, moisture content 11.07 to 14.90% and arsenic levels 0.12 to 0.9 mg/kg. All samples had arsenic levels less than the WHO limit of 1 mg/kg for arsenic levels in foods.

From table 4.12 (cassava samples from flood-prone areas), the pH ranged from 5.03 to 6.93, conductivity from 59.12 to 70.10 µS/cm, moisture content from 14.43 to 19.89%, the arsenic levels from 0.08 to 0.80 mg/kg. All the samples had arsenic concentration less than 1 mg/kg.

From table 4.13 (cassava samples close to mining site), the pH ranged from 4.92 to 6.00, conductivity from 63.27 to 78.07 µS/cm, moisture level from 14.06 to 22.98%, the arsenic levels ranged from 0.38 mg/kg to 1.20 mg/kg. Kumpese, Manso Nkwanta and Nyankumasi recorded 1.20 mg/kg, 1.10 mg/kg and 1.12 mg/kg respectively which is above the 1 mg/kg limit.

The pH of the cassava samples, like most foods, are in the acidic region. Cassava samples close to the mines had the highest arsenic levels. This variation in arsenic levels with the source is represented by a bar chart in Appendix 1C, page 157. This graph also compares the arsenic levels in all the cassava (random, flood-prone and close to the mine) with the WHO of 1 mg/kg arsenic in foods.

The high arsenic levels in some of the cassava is due to high arsenic levels in the soil. Cassava is a deep rooted crop and has high tendency to accumulate arsenic from arsenic-polluted soils (Al Rmalli, 2005). The use of arsenic-contaminated water for irrigation and soil pH have a hand in the high arsenic content of some of the cassava. Generally,

soil pH range of 4.5 to 5.5 favours arsenic sorption from soils onto cassava and some of the soils were in this range.

The low level of arsenic in the flood-prone cassava may be due to leaching or the high tendency for the arsenic to be washed away. Also phosphates when present in the soils will compete with arsenic for attachment onto the cassava. This results in weak adsorption of the arsenic onto the cassava and eventually lead to low arsenic levels in the cassava.

A scattered diagram results for a plot of arsenic levels in randomly selected, flood-prone and mining site cassava samples against their pH, conductivity and percentage moisture respectively (Appendices 4C, 5C and 6C; pages 158, 159 and 159 respectively). These graphs also include their respective towns.

The scatter means different factors affect arsenic levels in different towns.

4.4 Cassava Peels

Results obtained after analyses of the cassava peels are reported and discussed in this section.

Table 4.14 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in the cassava peels from randomly selected cassava samples

Town	pH	Conductivity, µS/cm	Temp,°C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	6.13	60.11	26.8	38.97	0.090±0.003	0.90
Bonsaso	6.14	68.72	26.5	50.65	0.042±0.008	0.42
Edubia	5.86	74.04	26.3	44.75	0.096±0.003	0.96
Esaase	6.06	72.71	26.5	43.12	0.106±0.001	1.06
Kumpese	6.28	75.19	26.8	42.33	0.120±0.002	1.20
Kensere Nkwanta	6.07	72.95	26.7	44.55	0.114±0.004	1.14
Manso Nkwanta	5.35	71.89	26.1	44.74	0.112±0.005	1.12
Nyankumasi	4.51	73.50	26.2	45.96	0.096±0.009	0.96
Tontokrom	5.36	75.92	26.3	44.08	0.094±.003	0.94
Yawkrom	6.02	70.16	26.4	44.29	0.090±0.004	0.90

Table 4.15 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in cassava peels from flood prone areas

Town	pH	Conductivity, µS/cm	Temp,^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	6.68	65.07	25.6	43.43	0.064±0.001	0.64
Bonsaso	6.25	65.76	25.6	44.62	0.022±0.002	0.22
Edubia	5.91	74.27	25.8	46.81	0.074±0.003	0.74
Esaase	6.03	73.64	25.8	45.10	0.080±0.004	0.80
Kumpese	6.56	74.18	25.9	44.12	0.094±0.005	0.94
Kensere Nkwanta	6.18	68.54	25.7	39.23	0.090±0.006	0.90
Manso Nkwanta	5.17	72.77	25.9	42.48	0.088±0.002	0.88
Nyankumasi	4.89	71.39	25.7	43.90	0.074±0.003	0.74
Tontokrom	5.74	77.80	25.8	40.14	0.076±0.001	0.76
Yawkrom	6.30	68.26	25.7	44.65	0.068±0.001	0.68

Table 4.16 Results obtained for the pH, conductivity, surrounding temperature, % moisture content and arsenic levels in the cassava peels from mining site.

Town	pH	Conductivity, µS/cm	Temp ,^{o}C	% Moisture	Arsenic Conc, mg/L	Average Arsenic Conc, mg/kg
Ayerebikrom	5.06	70.71	26.8	39.67	0.086±0.002	0.86
Bonsaso	5.96	68.16	26.5	45.93	0.038±0.005	0.38
Edubia	5.02	77.01	26.3	45.01	0.082±0.002	0.82
Esaase	5.93	75.51	26.5	42.35	0.096±0.001	0.96
Kumpese	5.56	77.89	26.8	46.50	0.120±0.001	1.20
Kensere Nkwanta	5.18	72.99	26.7	41.32	0.100±0.002	1.00
Manso Nkwanta	4.03	72.00	26.1	46.05	0.110±0.001	1.10
Nyankumasi	4.20	68.36	26.2	46.87	0.112±0.003	1.12
Tontokrom	4.91	76.75	26.3	49.07	0.088±0.002	0.88
Yawkrom	5.19	69.19	26.4	48.14	0.084±0.001	0.84

4.5 Recovery (Determining Efficiency of Instrument/Treatment Process)

To ascertain the reliability of the instrument, standard arsenic solutions of concentrations 5, 10, 15 and 20 ppm were taken through the treatment processes and analysed for their arsenic content using HGAAS. For each of the standards run after every five determinations, the average concentration and the recovery rate are tabulated below.

Arsenic Standard Conc/ppm	Mean Concentration Recovered /ppm	% Recovery
5	4.927	98.54
10	9.891	98.91
15	14.859	99.06
20	20.002	100.02

Recovery range = 98.54-100.02%

From table 4.14 (cassava peels of randomly selected cassava samples), the pH ranged from 4.51 to 6.28 and conductivity ranged from 60.11 to 75.92 µS/cm. Moisture content ranged from 39.97 to 50.65% whiles arsenic levels ranged from 0.42 mg/kg to 1.14 mg/kg.

From table 4.15 (cassava peels from flood-prone cassava samples), the pH ranged from 4.89-6.68 and conductivity from 65.07 to 77.80 µS/cm. Moisture content ranged from 39.23 to 46.81% whiles the arsenic concentration ranged from 0.22 mg/kg to 0.94 mg/kg.

From table 4.16 (cassava peels from cassava samples close to mining site), the pH ranged from 4.03 to 5.96 and conductivity from 68.16 µS/cm to 77.89 µS/cm. Whiles

the moisture content ranged from 39.67% to 49.07%, the arsenic levels ranged from 0.38 to 1.20 mg/kg.

A comparison of arsenic content of cassava and its peel reveals that, the cassava peel had more arsenic than the edible part of the cassava. This is because the peel is in direct contact with the soil so has higher tendency to be affected by the high arsenic level of the soils. It was also observed that as the arsenic levels in the cassava increased, that in the peel also increased. These two observations are graphically shown in Appendix 2C, page 157.

Towns like Bonsaso, Kumpese, Kensere Nkwanta, Manso Nkwanta, and Tontokrom where all sample types (water, soil and cassavas) were used as a yardstick to determine whether or not there existed a relationship between the arsenic levels in the samples. It was observed that there is an irregular trend between the arsenic levels in the three samples. For instance, Bonsaso had 9.25 ppb as the average arsenic level in the water, 5.36 mg/kg for soil and 0.27 mg/kg for cassava. Meanwhile, Kumpese water averagely recorded 8.33 ppb, 6.34 mg/kg for soil and 1.04 mg/kg for cassava. Whiles Bonsaso had more arsenic in the water than Kumpese, Kumpese also had higher levels in the soil and cassava than Bonsaso. Similarly, Kensere Nkwanta had 9 ppb as the average arsenic level in the water, 5.31 mg/kg as the average arsenic level in the soil and 0.93 mg/kg as the average level in the cassava. By comparison, Kensere Nkwanta had more arsenic in cassava than Bonsaso but Bonsaso had more arsenic in its water and soil.

This means different towns have different arsenic content in different samples. This irregular variation is shown with a bar chart in Appendix 3C, page 158.

The distribution of arsenic in the district was determined by plotting the the average arsenic contents of each sample (water, soil and cassava) against their respective towns. The graphs also include the WHO limits. The distribution of arsenic in the water samples in the selected towns in the district is shown in Appendix 1D, page 160 and the distribution of arsenic in the soil samples in the selected towns in the district is shown in Appendix 2D, page 161. The distribution of arsenic in the cassava samples in the selected towns in the district is shown in Appendix 3D, page 161.

For the relationship between arsenic levels detected and Buruli ulcer, it is quite difficult to establish. The difficulty in linking or disconnecting the arsenic levels detected in this work and Buruli ulcer is because only chemical analysis was done (no biological study). Secondly, BU is believed to develop over time. Meanwhile, most arsenic is eliminated by the kidneys through urine and faeces within few days unless the exposure is high (Miessler and Tarr, 1991). The levels detected in this work are not high to delay elimination. Therefore, the arsenic may not last long in the body to cause BU.

Upon the above shortcomings, the arsenic levels may have a link with BU. This is because Asiedu *et al* (2000) had arsenic levels in stream sediments in Buruli ulcer endemic regions above 15 ppm in the Amansie west District. Asiedu *et al* had high arsenic levels at a time when the BU was high. This work recorded low values for arsenic (0 to 0.015 mg/L) at a time when the BU levels have declined according to Ministry of Health report (2011). This shows a direct proportionality between arsenic levels and BU in the district. Also, arsenic levels detected were low but may bioaccumulate in the body with time and promote the growth of Buruli ulcer.

With the possible linkage between arsenic and BU, the BU may be due to the ponds since the ponds recorded levels from 10 to 15 ppb.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

This chapter presents the summary of major findings of the study, conclusions and recommendations.

5.1 Summary of results

The pH of all the water samples ranged from 5.05 to 7.98. However, most were acidic. The conductivity of all water samples ranged from 29.33 to 429.07 µS/cm. The TDS, TSS and TS ranges were 22 to 275 mg/L, 189 to 892 mg/L and 226 to 1045 mg/L respectively. The arsenic concentration ranges for all the water samples were from below 1 ppb (below detection) to 14 ppb.

For borehole water, only Datano and for open wells, only Dadiase exceeded 10 ppb. All the ponds had their arsenic level above 10 ppb except Dadiase. All swamps had levels above 10 ppb except Dadiase and Kensere Nkwanta. None of the streams had levels above 10 ppb limit. Esaase pipe-borne water had the least arsenic level which is below 1 ppb (below detection). Mining site boreholes had levels above those far from the mining site.

The soils ranged from a pH of 4.18 to 6.50 and conductivity from 189.38 µS/cm to 598.49 µS/cm. The soils were generally more acidic and more conducting than the water. The moisture content of the soils ranged from 6.54 to 33.06%. The arsenic levels

in the soils ranged from 3.12 to 8.48 mg/kg. All soils had arsenic levels above the minimum 0.05-0.2 mg/kg but were less than the WHO limit and William and Frakenberger approximation of 20 and 10 mg/kg respectively.

The pH for all cassava and their peels were in the acidic region but the peels were more acidic and more arsenic containing. The cassava and their peels ranged from a pH of 4.99 to 6.83 and 4.03 to 6.68 respectively. The conductivity of the cassava and their peels ranged from 59.12 to 78.07 µS/cm and 60.11 to 77.89 µS/cm respectively. The moisture content of cassava and their peels ranged from 11.07 to 22.98% and 38.97 to 50.65% respectively. The arsenic level in the cassava and their peels ranged respectively from 0.08 to 1.20 mg/kg and 0.22 to 1.20 mg/kg. The cassava had arsenic level below the 1mg/kg WHO limit except Kumpese, Manso Nkwanta and Nyankumasi cassava close to the mines. The arsenic levels in the cassava just like their peels were highest for samples picked close to the mining site.

There was an irregular trend between the arsenic levels in the samples, their properties and corresponding towns.

5.2 Conclusion

The research gave the general distribution of arsenic in water, soil and cassava from selected towns in the Amansie West District. It is conclusive that mining sites have higher arsenic levels which can be attributed to the surface mining activities.

The soils were more contaminated than the cassava. Generally, surface water was more contaminated than ground water.

From my interaction with residents and Dr Anthony at St Martins hospital, I can conclude that poor sanitary conditions may also have a hand in BU in the district.

5.3 Recommendations

1. Future works should look at arsenic variation with soil types as different soil types (like clay, loam, etc) have different affinity for arsenic leading to different arsenic levels in the soil.
2. More work should be done to ascertain how arsenic causes BU. This is because arsenic levels were generally low but fresh BU cases as well as re-occurrence of the disease still exist in the district according to Dr Anthony Kobla Gershon of St. Martins Hospital, Agroyesum in AWD.
3. Findings of this research should be accessible to ministry of health and other establishments working on arsenic and BU.
4. Pond water should not be used for drinking since 80% of ponds investigated had arsenic levels above the WHO limit.
5. There are non-mining towns in the district like Antoakrom where BU exists. This calls for work to determine whether the arsenic truly comes from the mines and whether the arsenic has a role in BU.
6. Though the general trend is that surface water is more contaminated than ground water, Dadiase and Kumpese wells which are ground water had arsenic levels (11 and 7 ppb respectively) equal or above their corresponding surface water. This calls for work to ascertain the cause of the deviation.

7. Work should be done to compare the solid matter content as well as arsenic levels in Amansie West District with forest areas where there is no mining or fertilizer application.
8. Work should be done to ascertain the form in which the arsenic exists (organic or inorganic) as well as the arsenic speciation (oxidation state).

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APPENDICES

ABBREVIATIONS FOR CHARTS- WATER (APPENDIX A)

GRAPHS 1A-7A, 10A-16A

AK	Akwasiso	**KU**	Kumpese
AS	Asamang	**MNK**	Manso Nkwanta
AT	Atwere	**NK**	Nkuntin
BO	Bonsaso	**NY**	Nyankumasi
DA	Dadiase	**TA**	Takorase
DT	Datano	**TTK**	Tontokrom
ES	Esaase	**YK**	Yawkrom
KN	Konianse-nkran	**WHO**	WHO maximum Limit
KNT	Kensere Nkwanta		

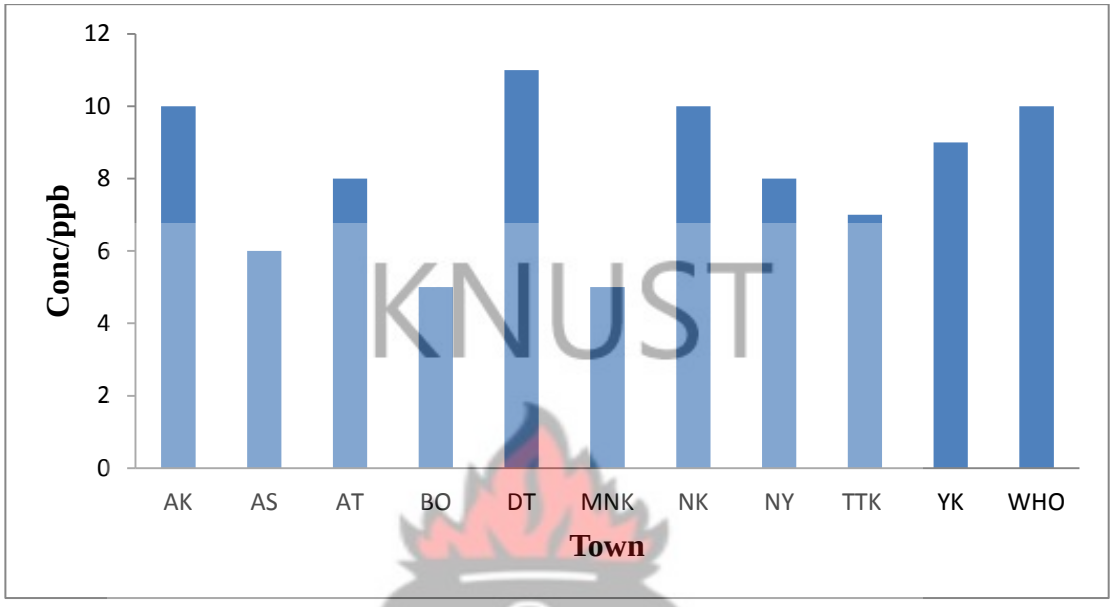
GRAPH 8A

AKM	Akwasiso Mine	**BOM**	Bonsaso Mine
AKW	Akwasiso Non Mine	**BON**	Bonsaso Non Mine
ASM	Asamang Mine	**DAM**	Datano Mine
ASN	Asamang Non Mine	**DAN**	Datano Non Mine
ATM	Atwere Mine	**MNKM**	Manso Nkwanta Mine
ATN	Atwere Non Mine	**MNKN**	Manso Nkwanta Non Mine

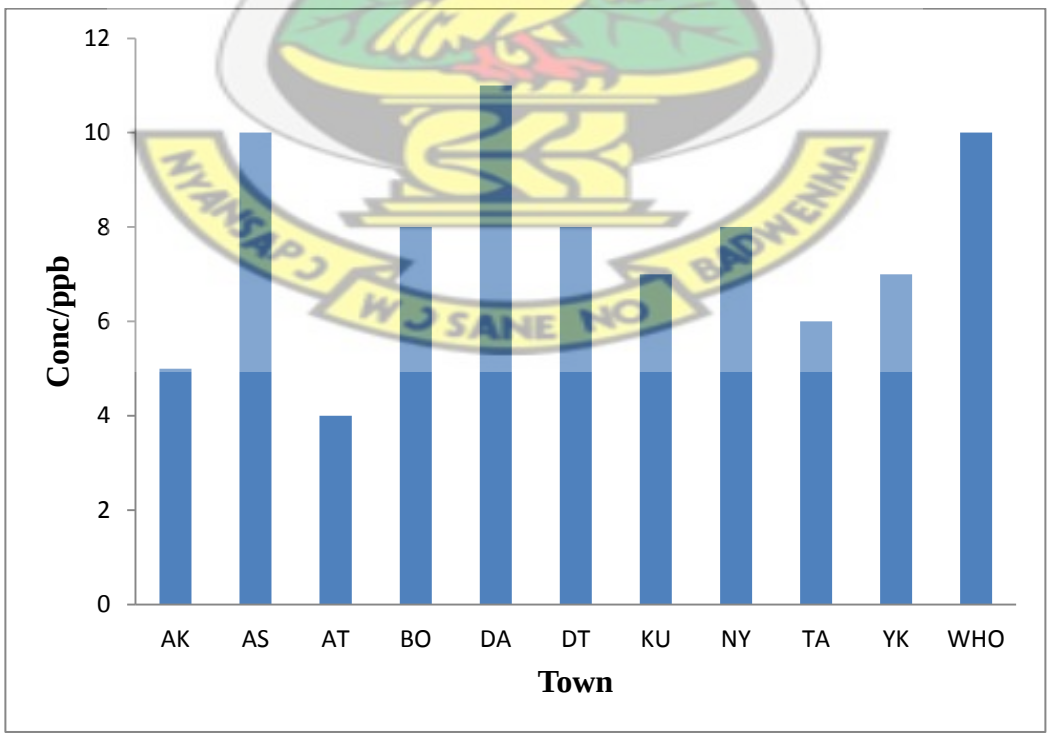
GRAPH 9A

AKB	Akwasiso borehole	**TTKP**	Tontokrom pond	**KUST**	Kumpese stream
AKOW	Akwasiso open well	**TTKSW**	Tontokrom swamp	**KUSW**	Kumpese swamp
AKP	Akwasiso pond	**YKB**	Yawkrom borehole	**DAOW**	Dadiase opem well
BOB	Bonsaso borehole	**YKOW**	Yawkrom open well	**DAP**	Dadiase pond
BOW	Bonsaso open well	**YKST**	Yawkrom stream	**DASW**	Dadiase swamp
BOP	Bonsaso pond	**YKSW**	Yawkrom Swamp	**DAST**	Dadiase stream
TTKB	Tontokrom borehole	**KUOW**	Kumpese open well		

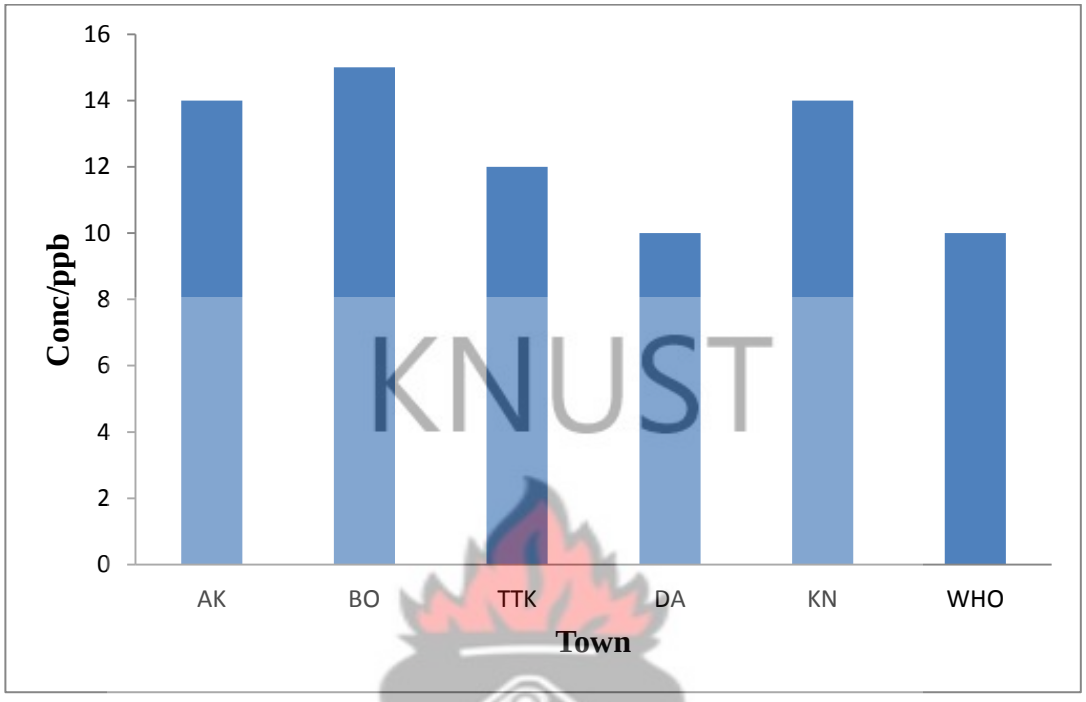
1A Graph of Arsenic Concentration (ppb) in Boreholes against their Respective Towns



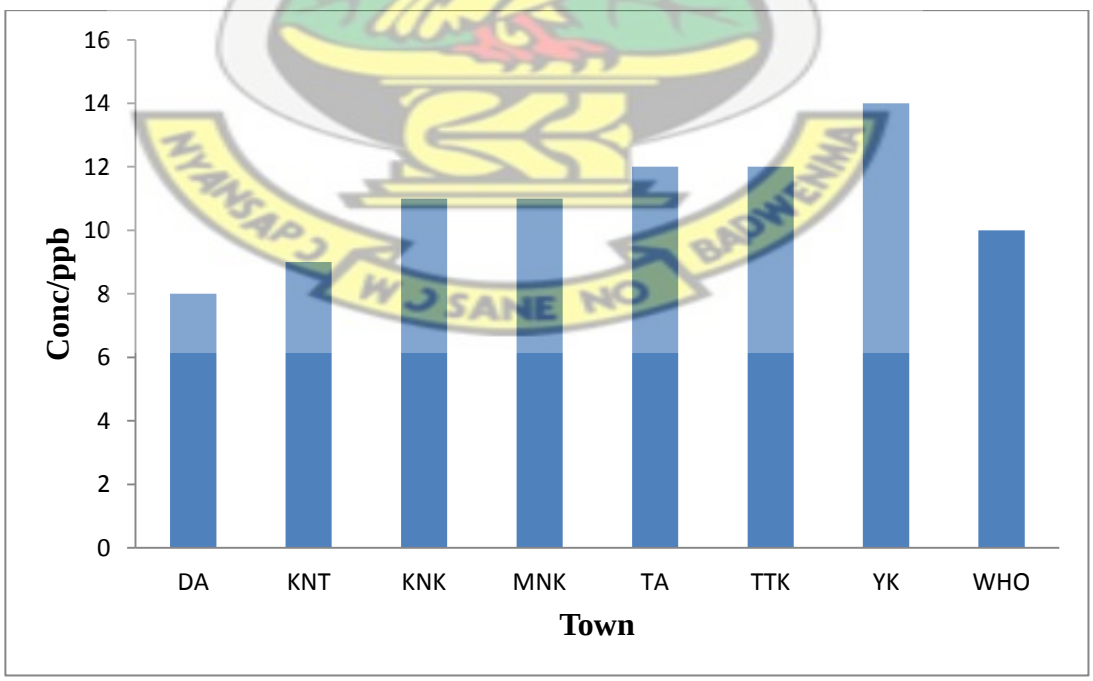
2A Graph of Arsenic Concentration (ppb) in Open wells against their Towns (Table 4.3)



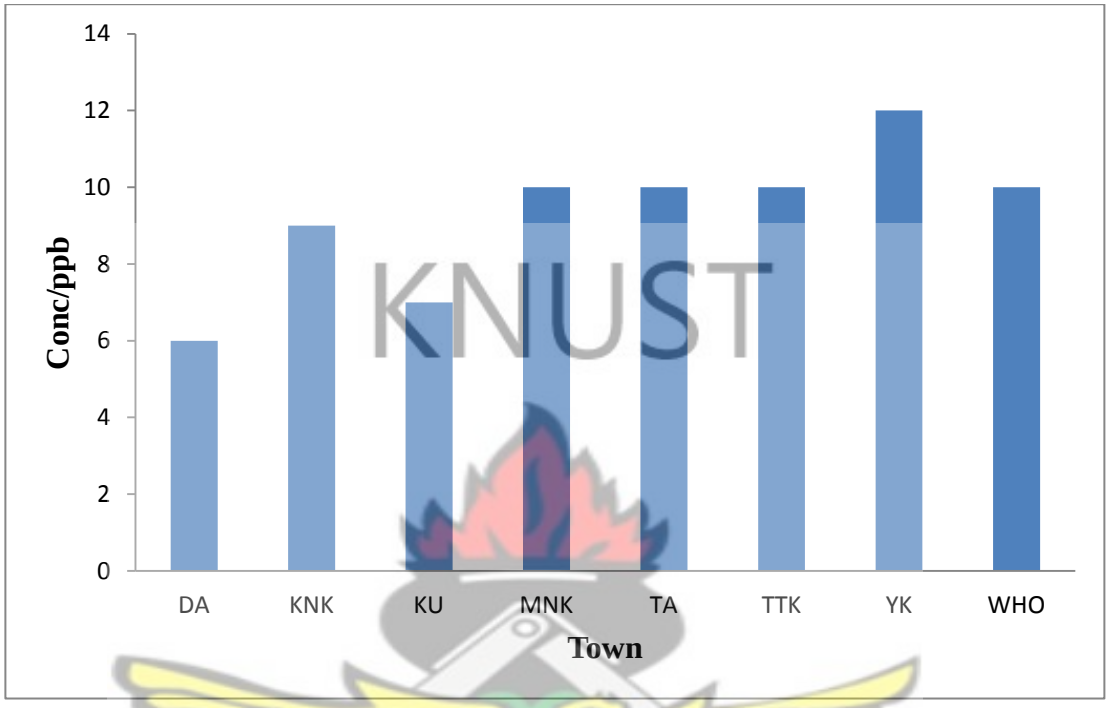
3A Graph of Arsenic Concentration (ppb) in Ponds against their Towns (Table 4.4)



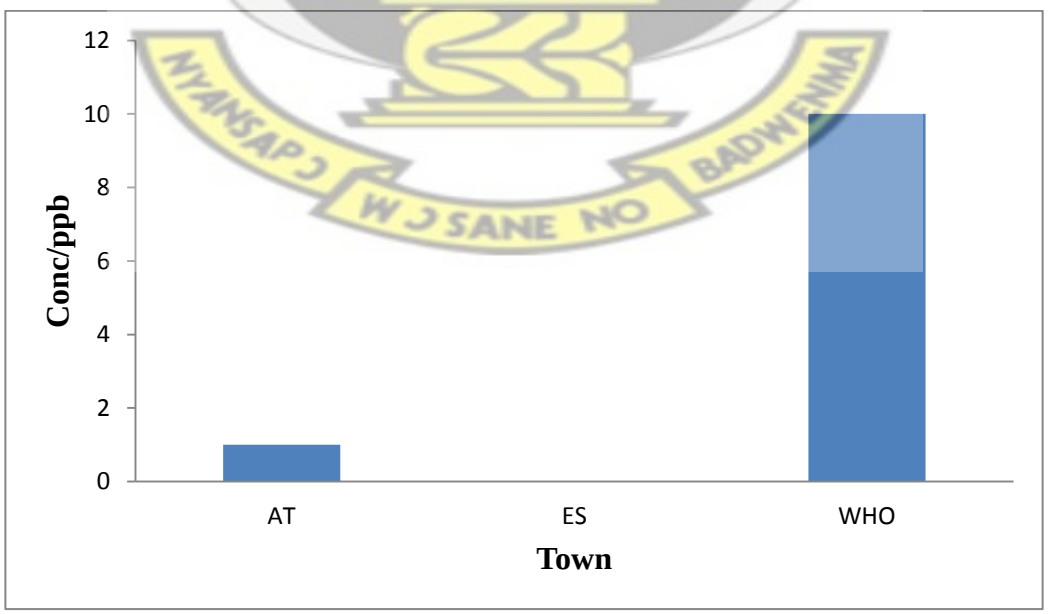
4A Graph of Arsenic Concentration (ppb) in Swamps against their Towns (Table 4.5)



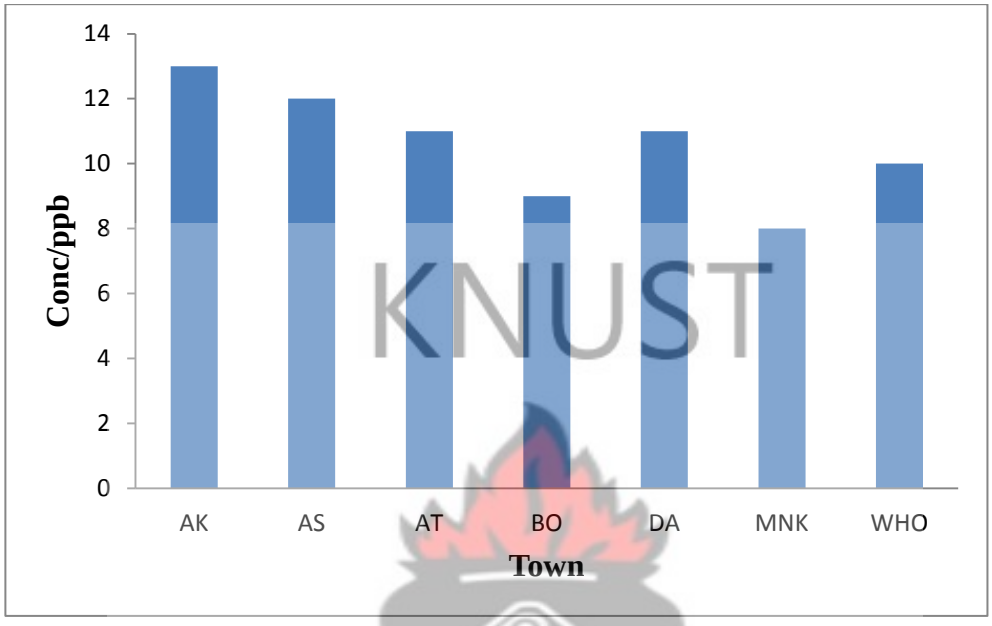
5A Graph of Arsenic Concentration (ppb) in Streams against their Towns (Table 4.6)



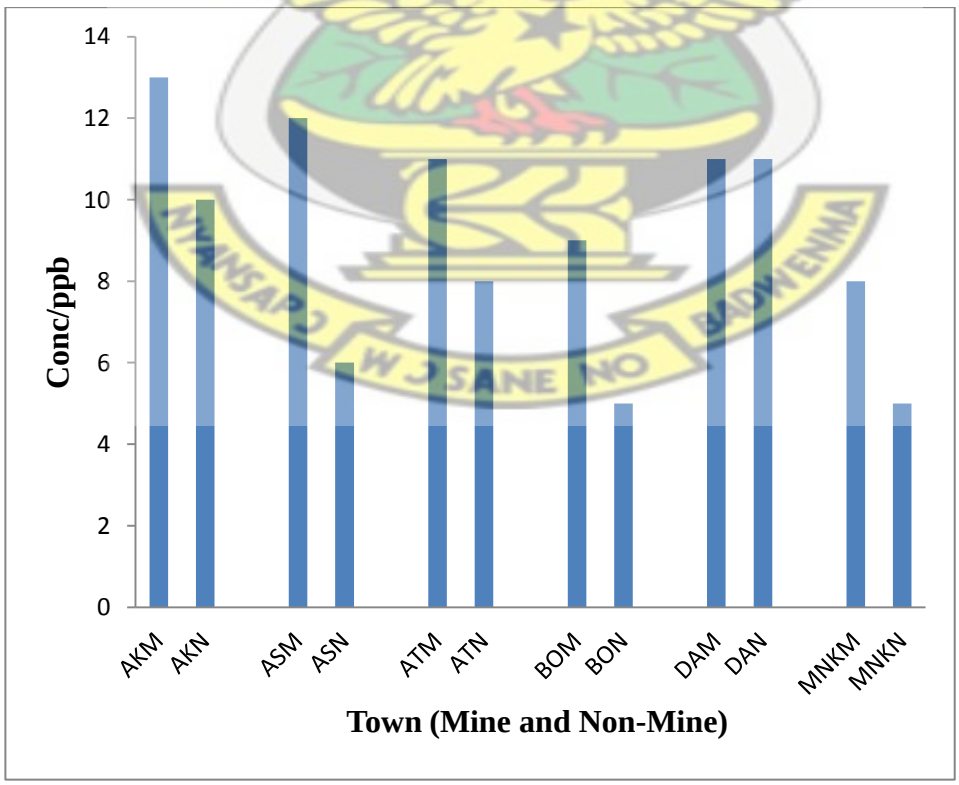
6A Graph of Arsenic Concentration (ppb) in Pipe Water against their Towns (Table 4.7)



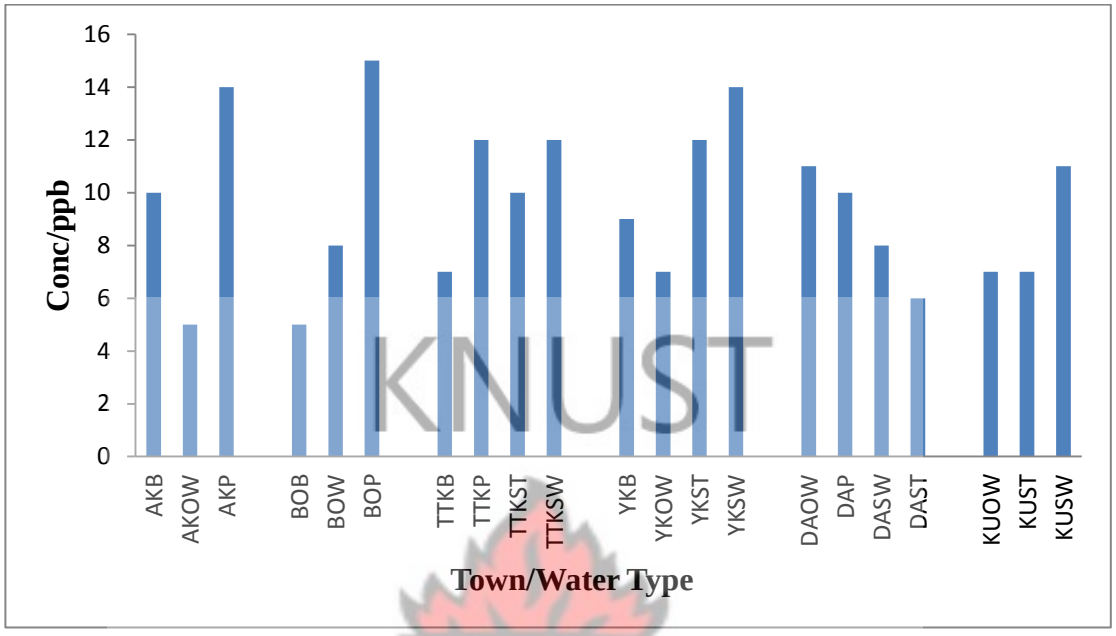
7A Graph of Arsenic Conc in Boreholes Close to Mines against their Towns (Table 4.8)



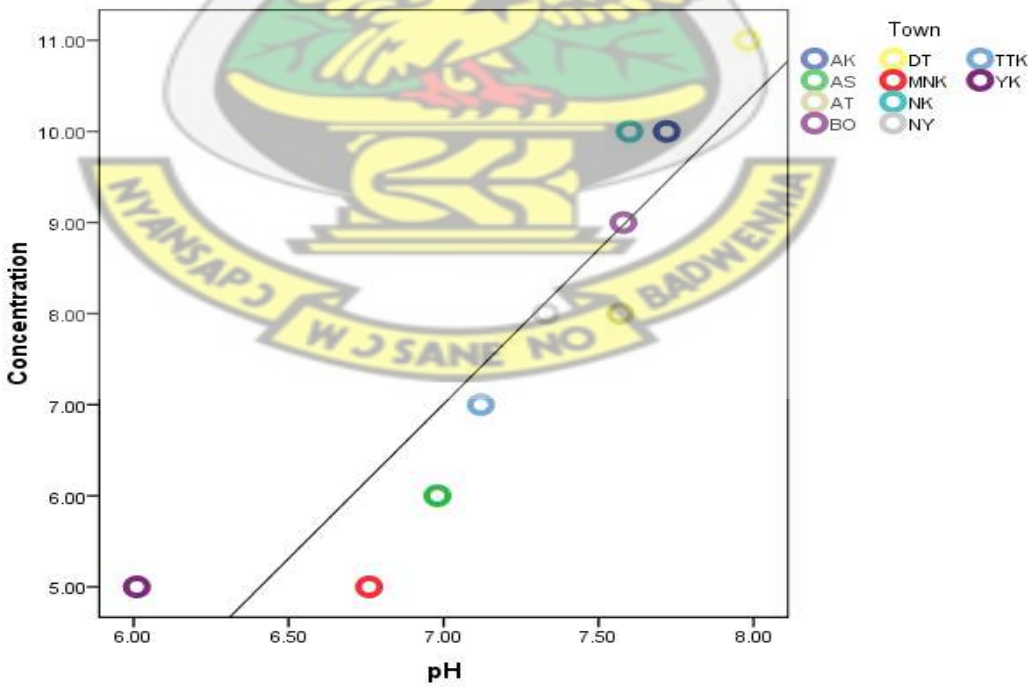
8A Comparison of Mine Borehole Water with Non-Mine (Tables 4.2 and 4.8)



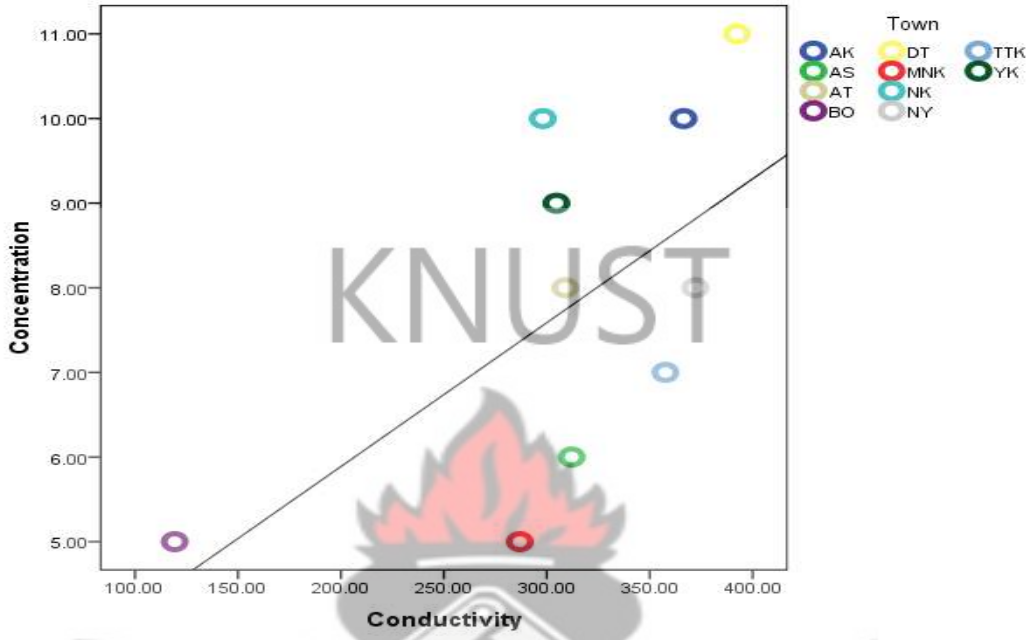
9A Comparison of Surface and Ground Water (Tables 4.2-6)



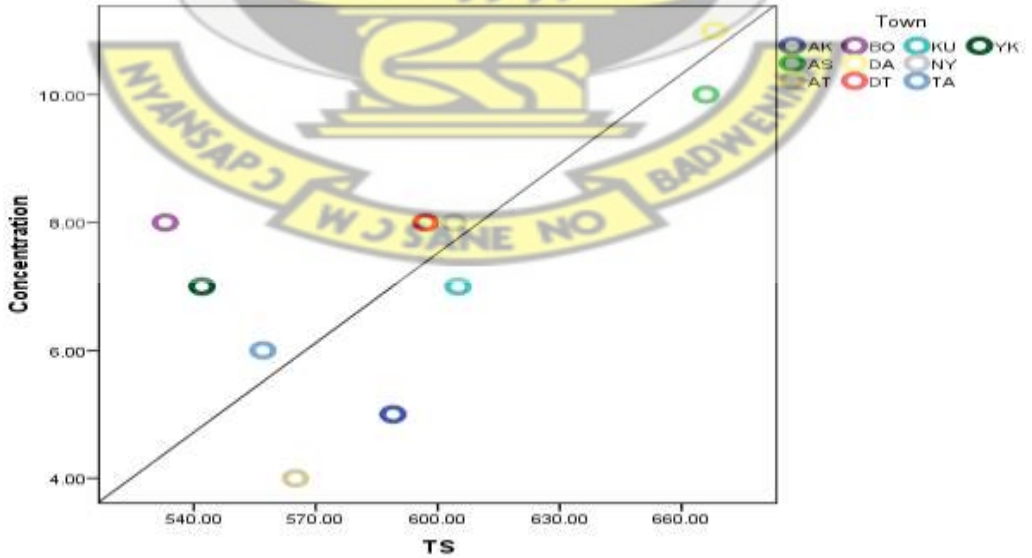
10A Graph of Borehole Arsenic Conc (ppb) against their pHs in the Invistigated Towns



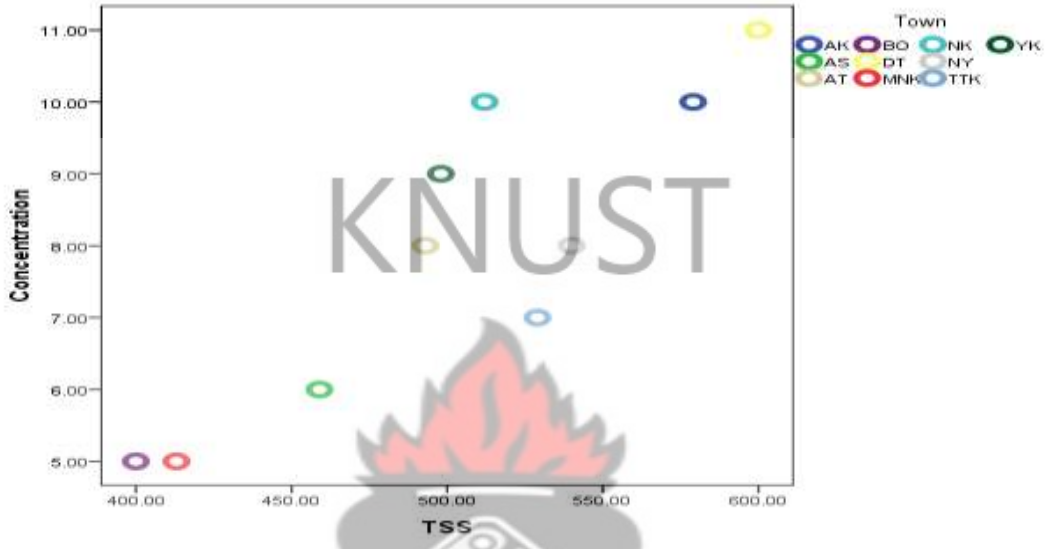
11A Graph of Arsenic Concentration (ppb) of Boreholes against their Conductivities (µS/cm) in the Studied Towns (Table 4.2)



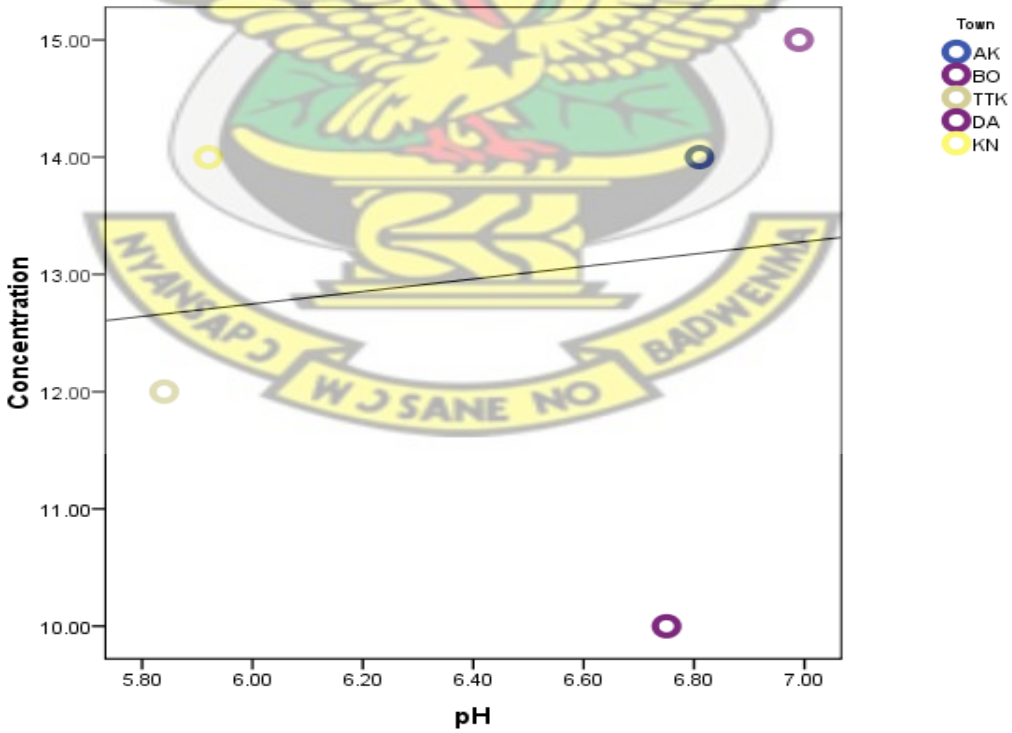
12A Graph of Arsenic Conc (ppb) of Open wells against their Total Solids (mg/L) in the Invistigated Towns (Table 4.3)



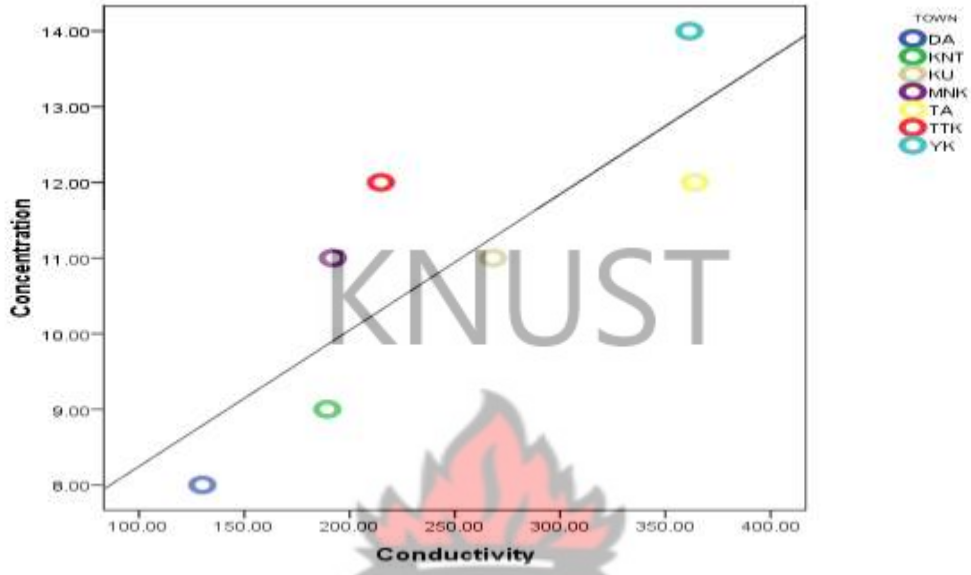
13A Graph of Arsenic Conc (ppb) of Boreholes against TSS (mg/L) in the Studied Towns



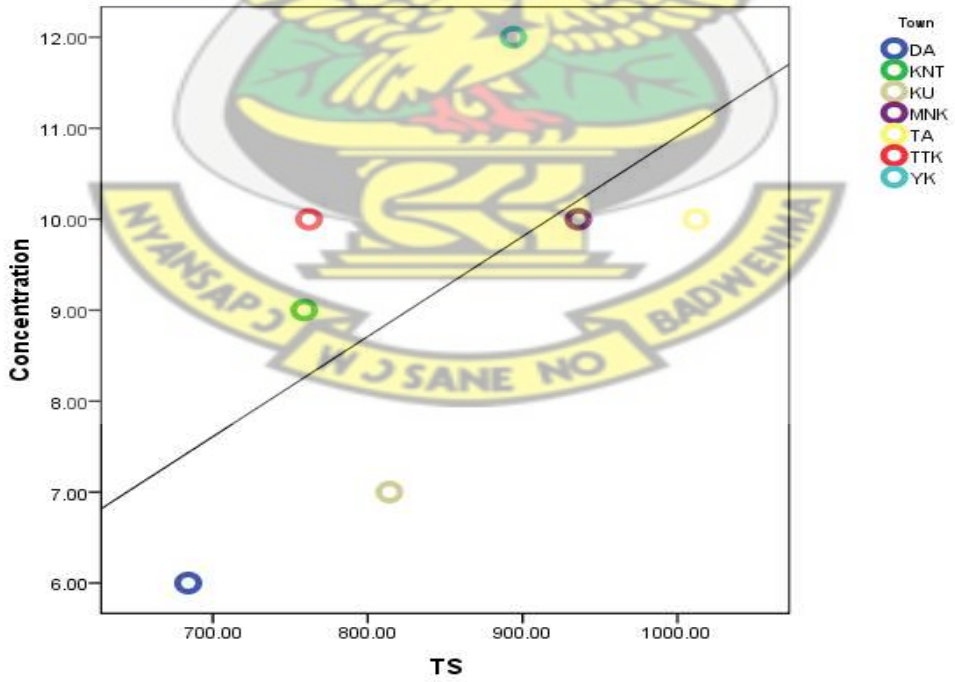
14A Graph of Arsenic Conc (ppb) of Ponds against their pHs in the Selected Towns



15A Graph of Arsenic Concentration (ppb) of Swamps against their Conductivities (µS/cm) in the Invistigated Towns (Table 4.5)



16A Graph of Arsenic Concentration (ppb) of Streams against their Total Solids (mg/L) in the Studied Towns (Table 4.6)



ABBREVIATIONS FOR CHARTS- SOIL (APPENDIX B)

WFA= William and Frakenberger Approximation WHO= WHO limit

GRAPH 1B

AT1	Atwere, 0-15 cm soil depth	**KU1**	Kumpese, 0-15cm soil depth
AT2	Atwere, 15-30 cm soil depth	**KU2**	Kumpese, 15-30 cm soil depth
AT3	Atwere, 30-45 cm soil depth	**KU3**	Kumpese, 30-45 cm soil depth
AYI	Ayerebikrom, 0-15 cm soil depth	**KNK1**	Kensere Nkwanta, 0-15 cm soil depth
AY2	Ayerebikrom,15-30 cm soil depth	**KNK2**	Kensere Nkwanta, 15-30 cm soil depth
AY3	Ayerebikrom, 30-45 cm soil depth	**KNK3**	Kensere Nkwanta, 30-45 cm soil depth
BO1	Bonsaso, 0-15 cm soil depth	**MNK1**	Manso Nkwanta, 0-15 cm soil depth
BO2	Bonsaso, 15-30 cm soil depth	**MNK2**	Manso Nkwanta, 15-30 cm soil depth
BO3	Bonsaso, 30-45 cm soil depth	**MNK3**	Manso Nkwanta, 30-45 cm soil depth
DA1	Dadiase, 0-15 cm soil depth	**TTK1**	Tontokrom, 0-15 cm soil depth
DA2	Dadiase, 15-30 cm soil depth	**TTK2**	Tontokrom,15-30 cm soil depth
DA3	Dadiase, 30-45 cm soil depth	**TTK3**	Tontokrom, 30-45 cm soil depth

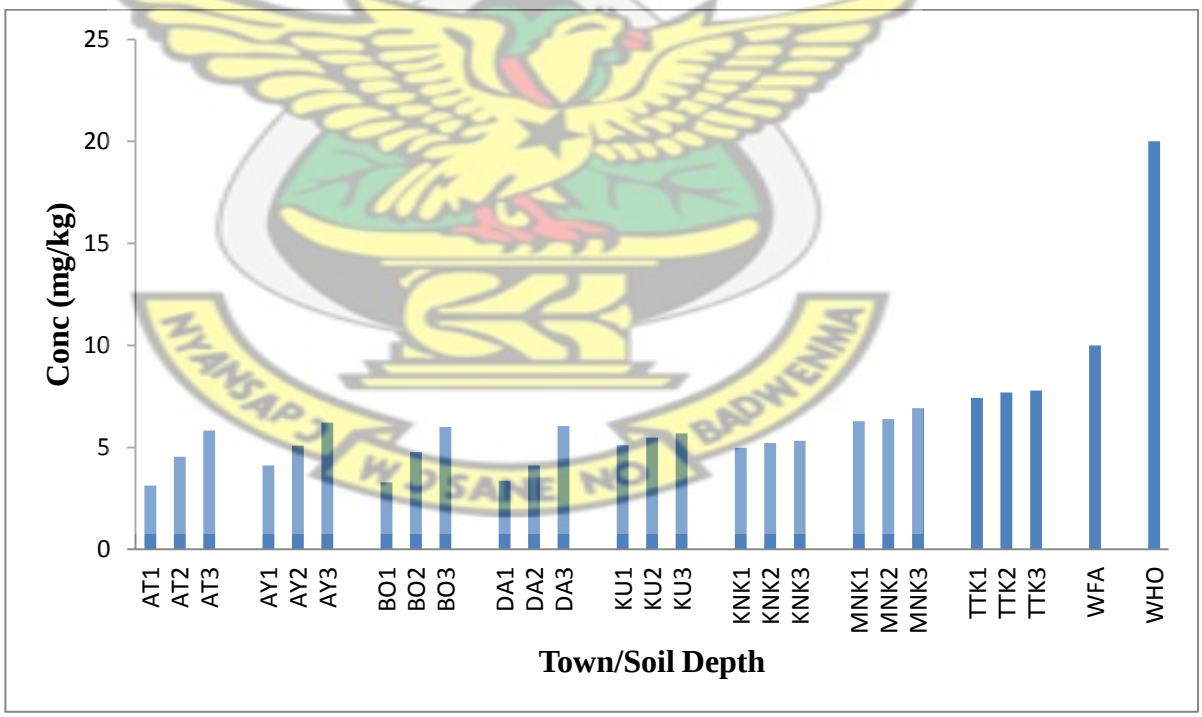
GRAPH 2B

ATF	Atwere soil from flood prone area	**KUF**	Kumpese flood prone soil
ATM	Atwere soil close to mine	**KUM**	Kumpese soil close to mine
AYF	Ayerebikrom flood prone soil	**KNKF**	Kensere Nkwanta flood soil
AYM	Ayerebikrom soil close to mine	**KNKM**	Kensere Nkwanta mine soil
BOF	Bonsaso soil from flood prone area	**MNKF**	Manso Nkwanta flood prone soil
BOM	Bonsaso soil close to mine	**MNKM**	Manso Nkwanta mine soil
DAF	Dadiase soil from flood prone area	**TTKF**	Tontokrom flood prone soil
DAM	Dadiase soil close to mine	**TTKM**	Tontokrom soil close to mine

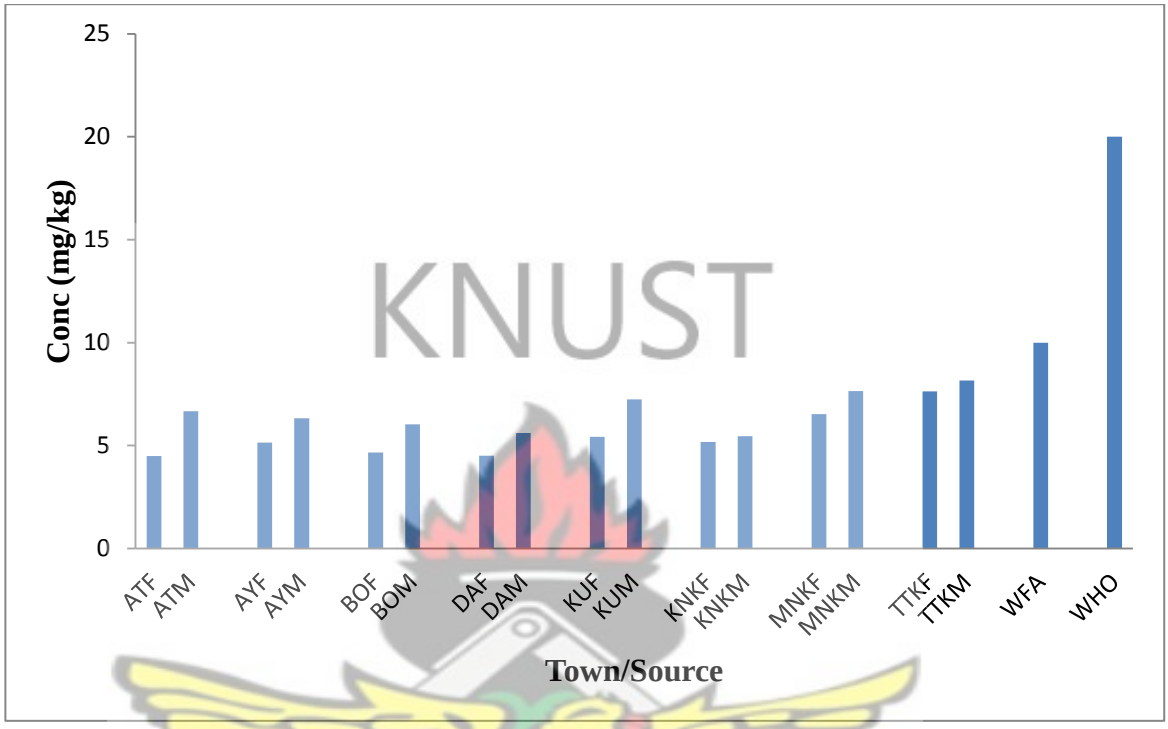
GRAPH 3B

AT10	Atwere soil, 10 m from mines	**KU10**	Kumpese soil, 10 m from mines
AT20	Atwere soil, 20 m from mines	**KU20**	Kumpese soil, 20 m from mines
AT30	Atwere soil, 30 m from mines	**KU30**	Kumpese soil, 30 m from mines
AY10	Ayerebikrom, 10 m from mines	**KNK10**	Kensere Nkwanta soil, 10 m from mines
AY20	Ayerebikrom, 20 m from mines	**KNK20**	Kensere Nkwanta soil, 20 m from mines
AY30	Ayerebikrom, 30 m from mines	**KNK30**	Kensere Nkwanta soil, 30 m from mines
BO10	Bonsaso soil, 10 m from mines	**MNK10**	Manso Nkwanta soil, 10 m from mines
BO20	Bonsaso soil, 20 m from mines	**MNK20**	Manso Nkwanta soil, 20 m from mines
BO30	Bonsaso soil, 30 m from mines	**MNK30**	Manso Nkwanta soil, 30 m from mines
DA10	Datano soil, 10 m from mines	**TTK10**	Tontokrom soil,10 m from mines
DA20	Datano soil, 20 m loam mines	**TTK20**	Tontokrom soil, 20 m from mines
DA30	Datano soil, 30 m from mines	**TTK30**	Tontokrom soil, 30 m from mines

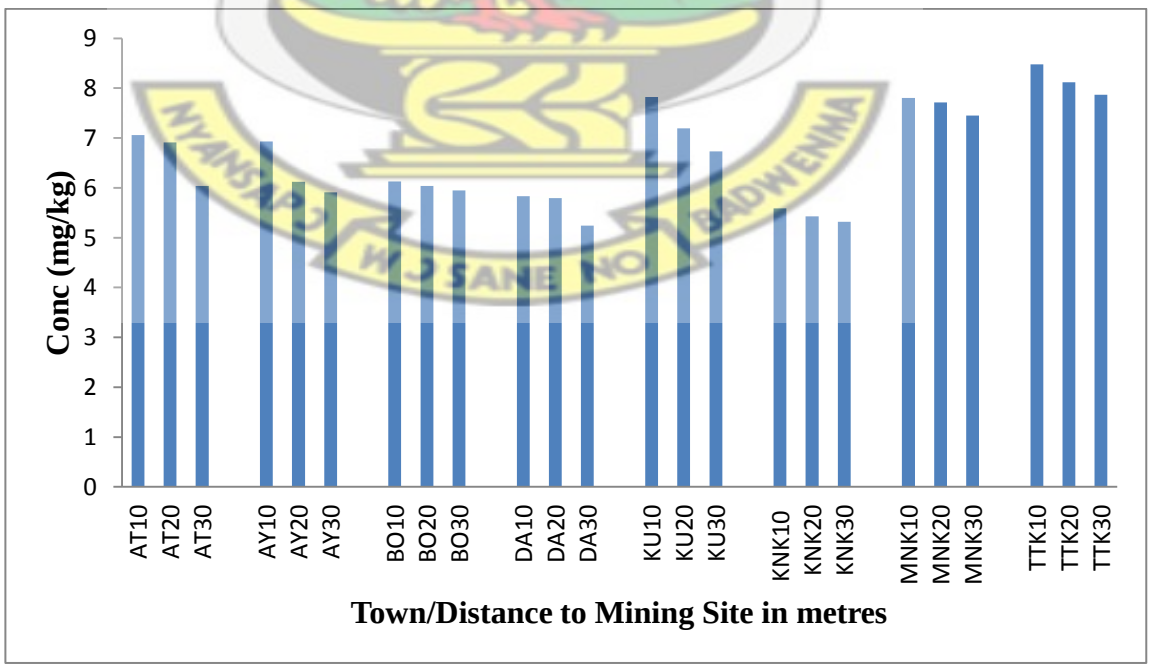
1B Variation of Arsenic Level (mg/kg) with Soil Depth (Flood-Prone Soils) – Table 4.9



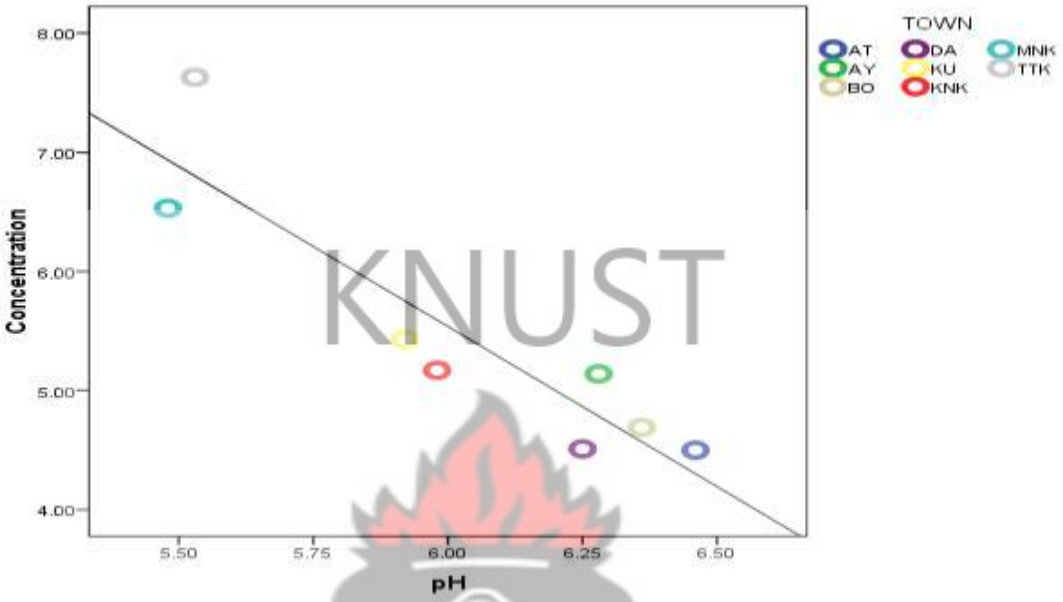
2B Comparison of Arsenic Levels (mg/kg) in Flood-Prone and Mine Soils (Tables 4.9/10)



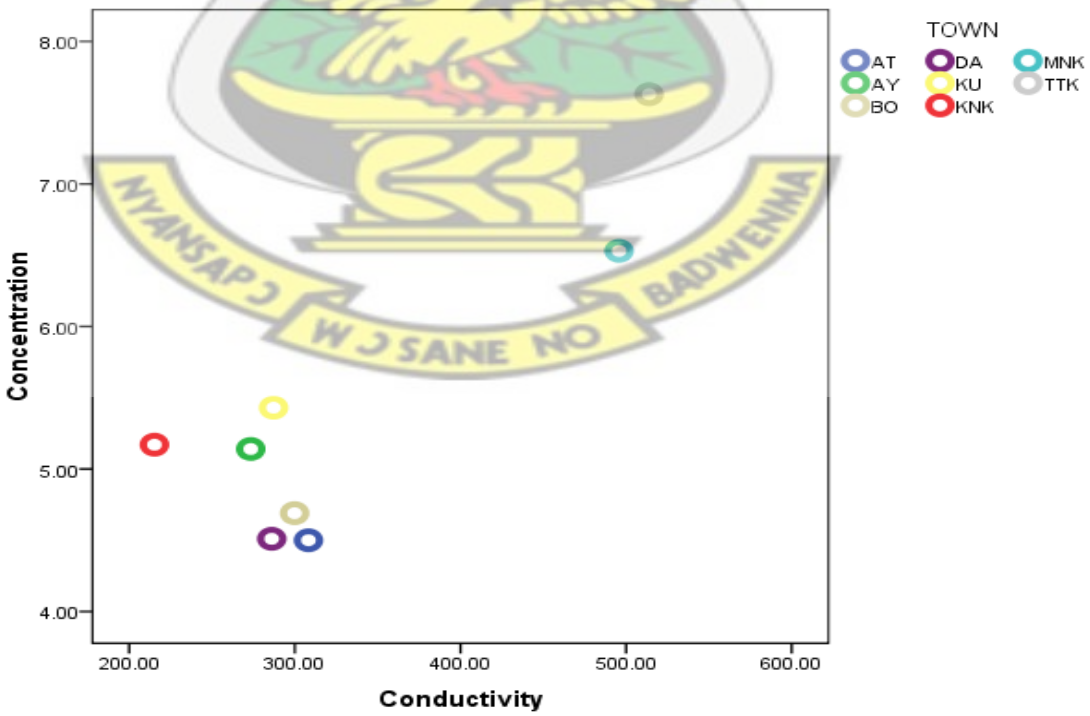
3B Variation of Arsenic Level (mg/kg) of Soils with Distance to Mining Site (Table 4.10)



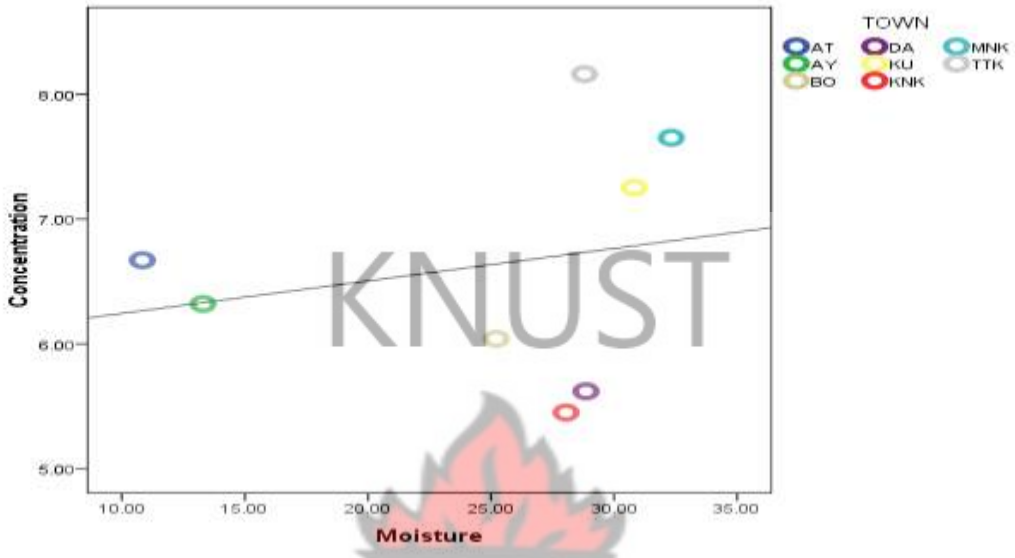
4B Graph of Arsenic Conc (mg/kg) of Flood-Prone Soils against their pHs in Selected Towns (Table 4.9)



5B Graph of Arsenic Conc (mg/kg) of Flood-prone Soils against Conductivities (µS/cm) in the Invistigated Towns (Table 4.9)



6B Graph of Arsenic Concentration (mg/kg) of Mine Soils against Moisture Content (%) in the Studied Towns (Table 4.10)



ABBREVIATIONS FOR CHARTS- CASSAVA AND CASSAVA PEEL (APPENDIX C)

GRAPH 1C - CASSAVA

AYR	Ayerebikrom, randomly picked	**TTKM**	Tontokrom, close to mines
AYF	Ayerebikrom, flood prone area	**YKR**	Yawkrom, randomly picked
AYM	Ayerebikrom, close to mines	**YKF**	Yawkrom, flood prone area
EDR	Edubia, randomly picked	**YKM**	Yawkrom, close to mines
EDF	Edubia, flood prone area	**KUR**	Kumpese, randomly picked
EDM	Edubia, close to the mine	**KUF**	Kumpese, flood prone area
ESR	Esaase, randomly picked	**KUM**	Kumpese, close to mines
ESF	Esaase, flood prone area	**NYR**	Nyankumasi, randomly selected
ESM	Esaase, close to mine	**NYF**	Nyankumasi, flood prone area
TTKR	Tontokrom, randomly picked	**NYM**	Nyankumasi, close to mines
TTKF	Tontokrom, flood prone area	**WHO**	WHO maximum limit

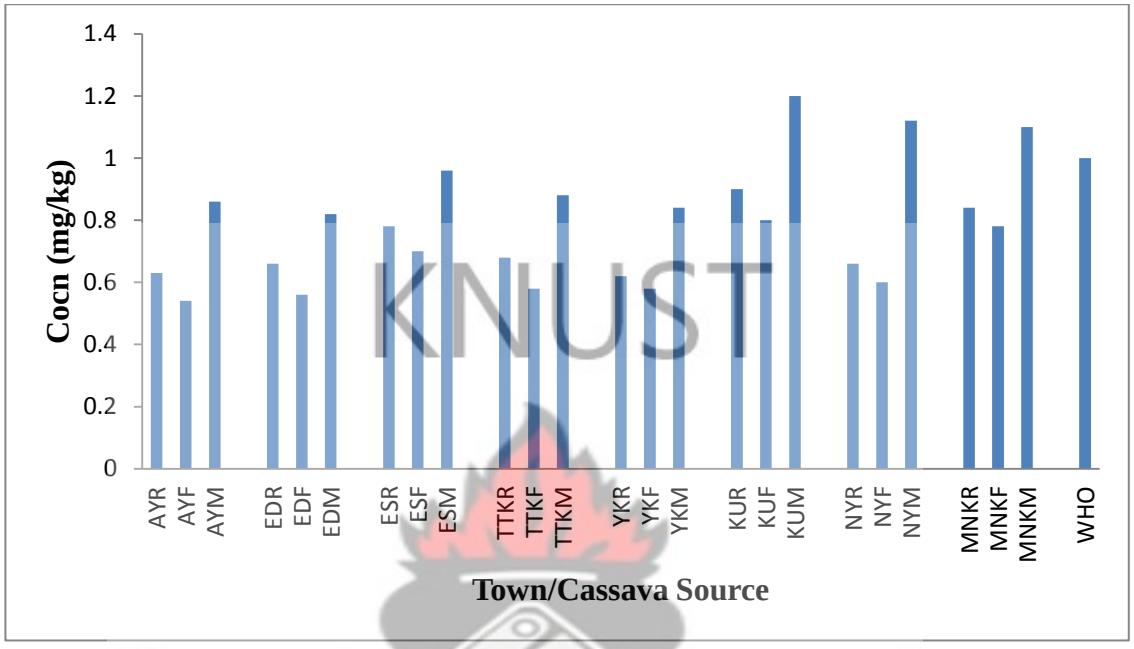
GRAPH 2C

AYCE	Ayerebikrom, edible cassava	**KUCP**	Kumpese, cassava peel
AYCP	Ayerebikrom, cassava peel	**KNKCE**	Kensere Nkwanta, edible cassava
BOCE	Bonsaso, edible cassava	**KNKCP**	Kensere Nkwanta, cassava peel
BOCP	Bonsaso, cassava peel	**MNKCE**	Manso Nkwanta, edible cassava
EDCE	Edubia, edible cassava	**MNKCP**	Manso Nkwanta, cassava peel
EDCP	Edubia, cassava peel	**NYCE**	Nyankumasi, edible cassava
ESCE	Esaase, edible cassava	**NYCP**	Nyankumasi, cassava peel
ESCP	Esaase, cassava peel	**TTKCE**	Tontokrom, edible cassava
KUCE	Kumpese, edible cassava	**YKCE**	Tontokrom, cassava peel

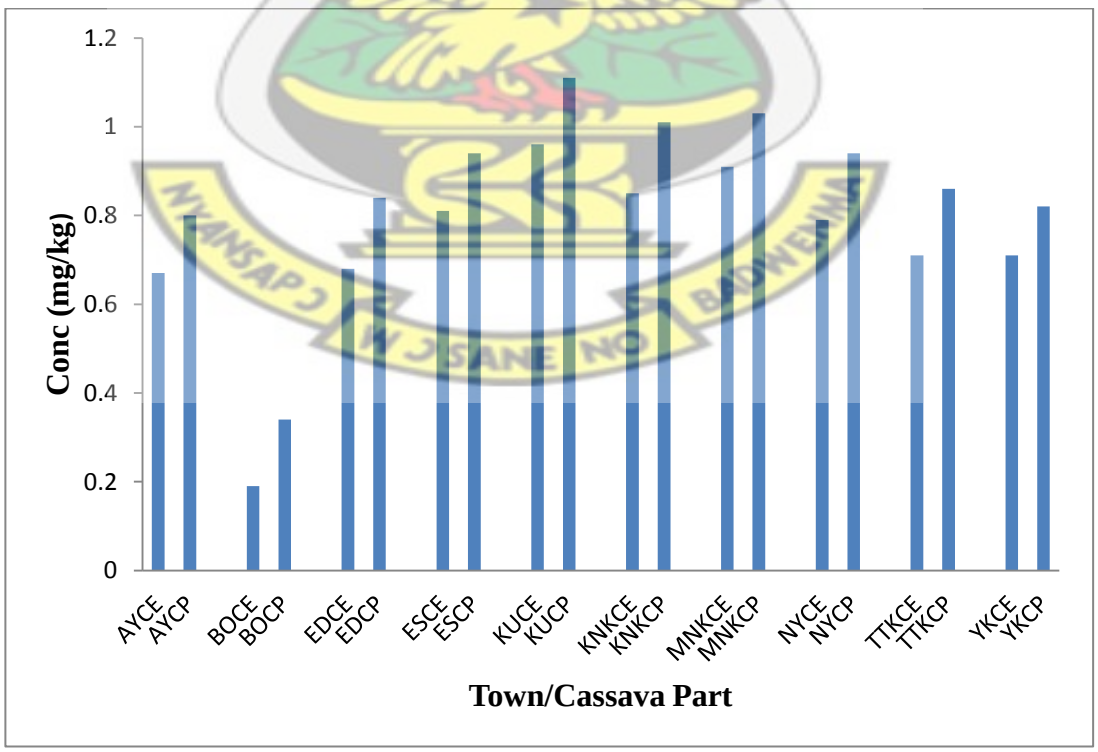
GRAPH 3C

BOW	Bonsaso water	**KNKC**	Kensere Nkwanta cassava
BOS	Bonsaso soil	**MNKW**	Bonsaso water
BOC	Bonsaso cassava	**MNKS**	Bonsaso soil
KUW	Kumpese water	**MNKC**	Bonsaso cassava
KUS	Kumpese soil	**TTKW**	Bonsaso water
KUC	Kumpese cassava	**TTKS**	Bonsaso soil
KNKW	Kensere Nkwanta water	**TTKC**	Bonsaso cassava
KNKS	Kensere Nkwanta soil		

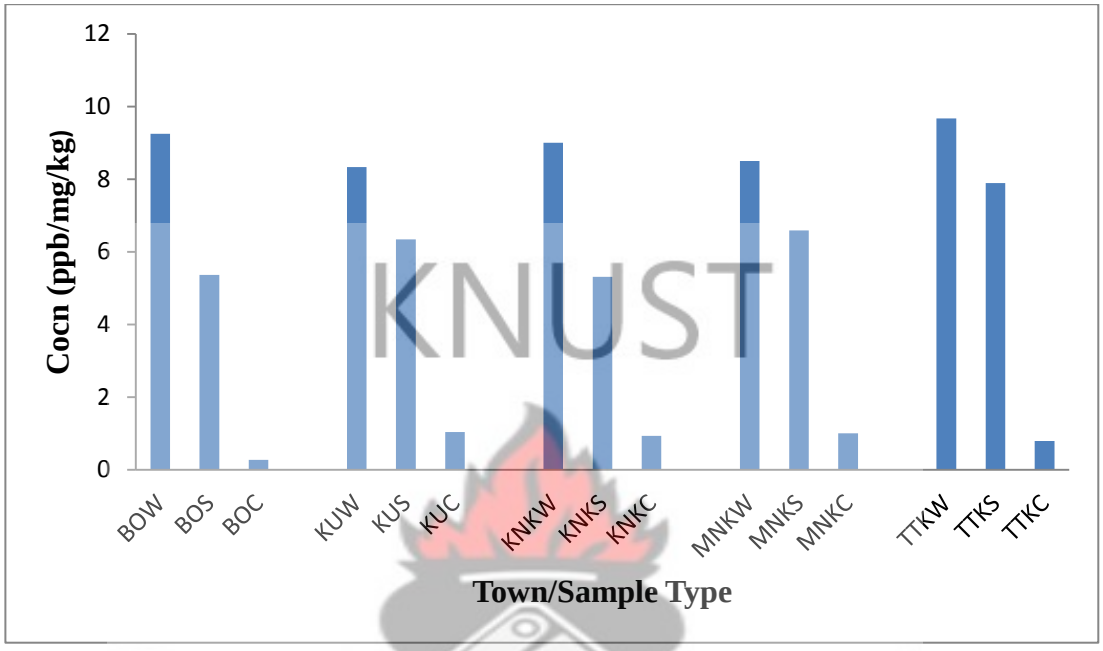
1C Comparison of Arsenic Levels (mg/kg) in Randomly Selected, Flood-Prone and Mining Site Cassava Samples (Tables 4.11, 12 and 13).



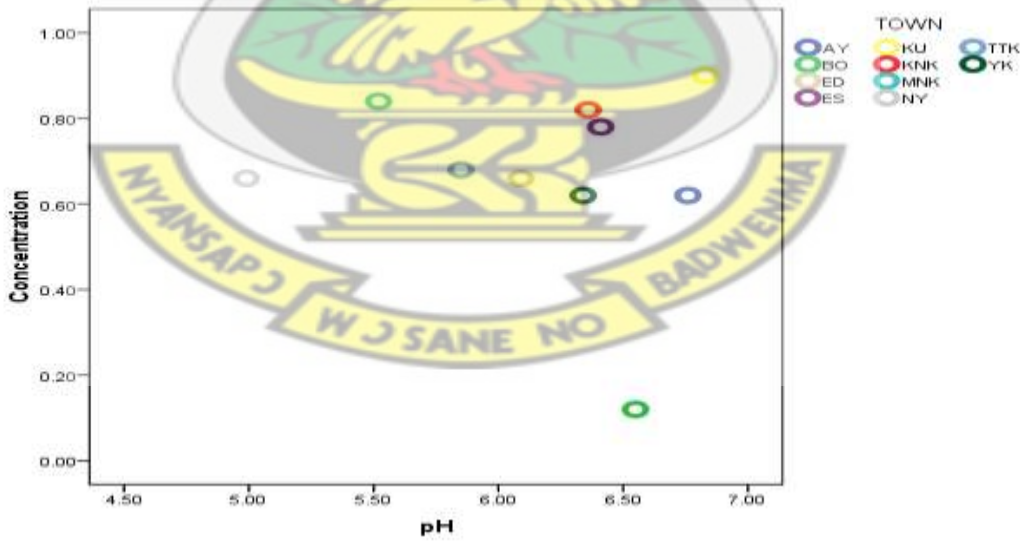
2C Comparison of Average Arsenic Levels (mg/kg) in Cassava (Edible Part) and Peels.



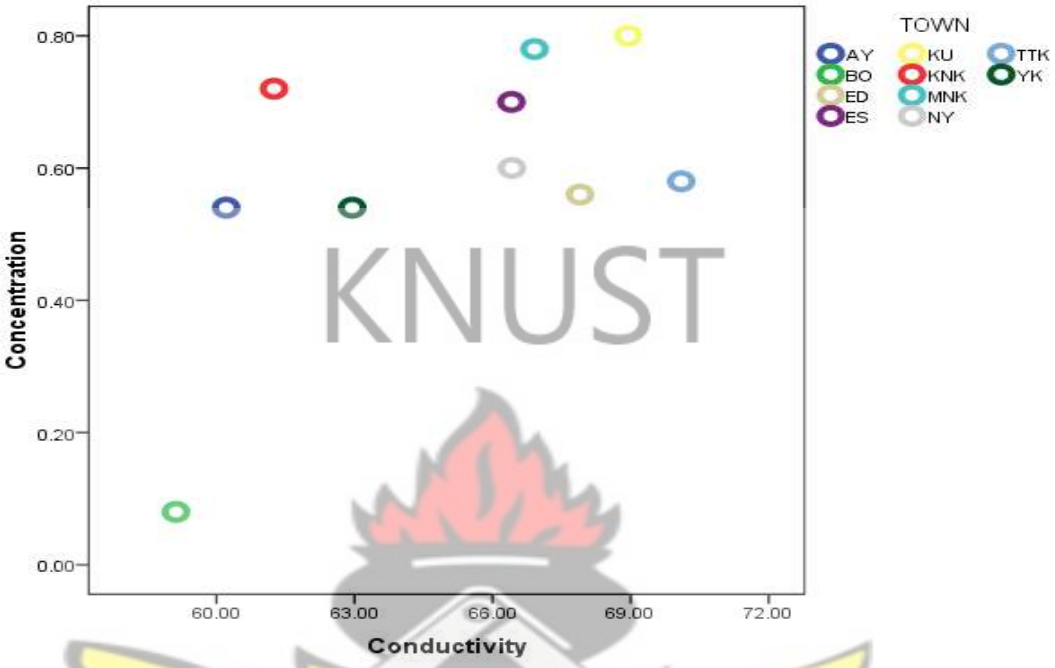
3C Relationship between Arsenic Levels in Water (ppb), Soils (mg/kg) and Cassava (mg/kg)



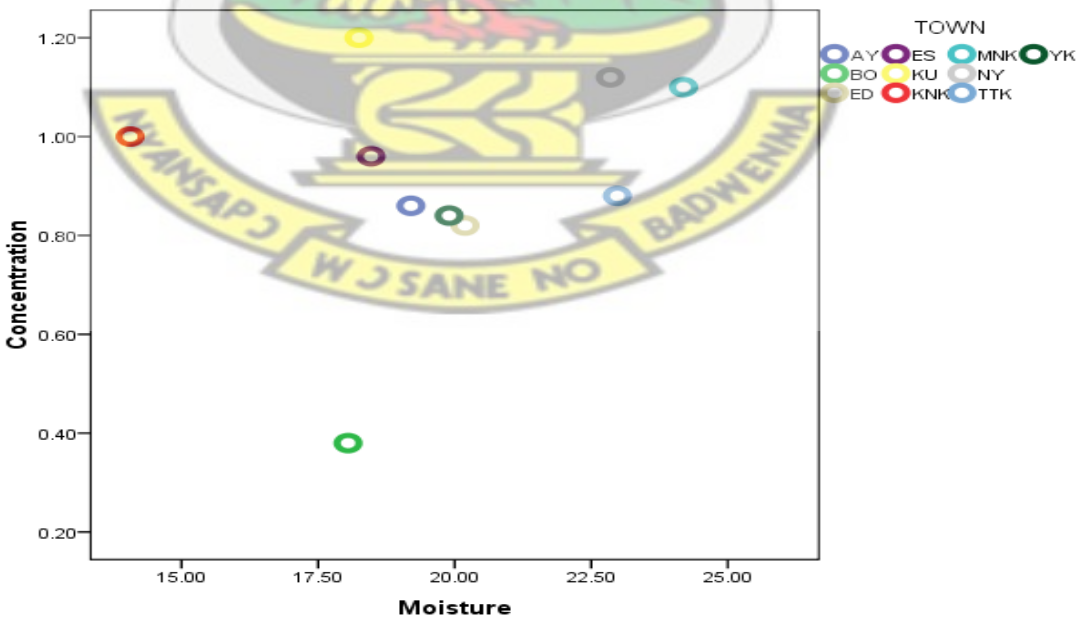
4C Graph of Arsenic Levels (mg/kg) in Randomly Selected Cassava against their pHs in the Studied Towns (Table 4.11)



5C Graph of Arsenic Levels (mg/kg) in Flood-Prone Cassava against their Conductivities (µS/cm) in the Selecetd Towns (Table 4.12)



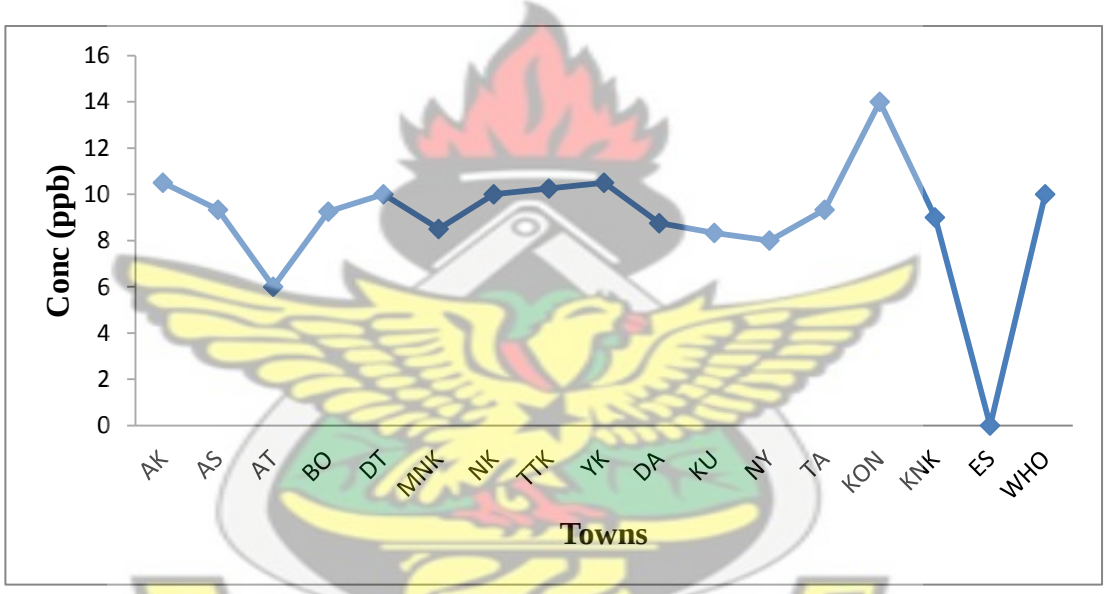
6C Graph of Arsenic Levels (mg/kg) in Mining Site Cassava against their Moisture Content (%) in the Studied Towns (Table 4.13)



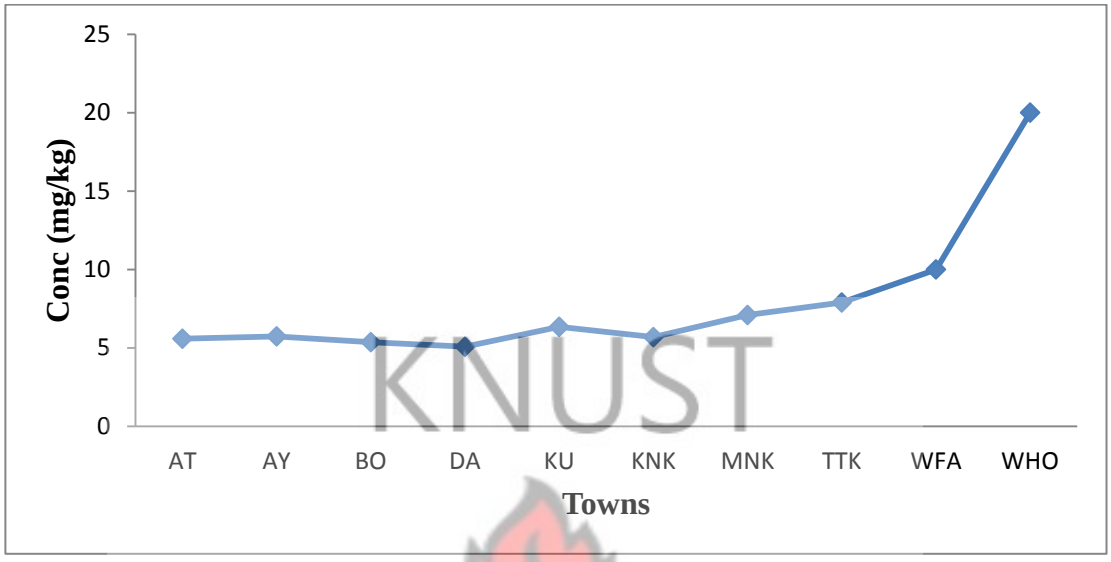
ABBREVIATIONS FOR GRAPHS 1D-3D

AK	Akwasiso	**ED**	Edubia	**NY**	Nyankumasi
AS	Asamang	**ES**	Esaase	**TA**	Takorase
AT	Atwere	**KNK**	Kensere Nkwanta	**TTK**	Tontokrom
AY	Ayerebikrom	**KON**	Konianse-nkran	**WHO**	WHO Limit
BO	Bonsaso	**KU**	Kumpese	**YK**	Yawkrom
DA	Dadiase	**MNK**	Manso Nkwanta		
DT	Datano	**NK**	Nkuntin		

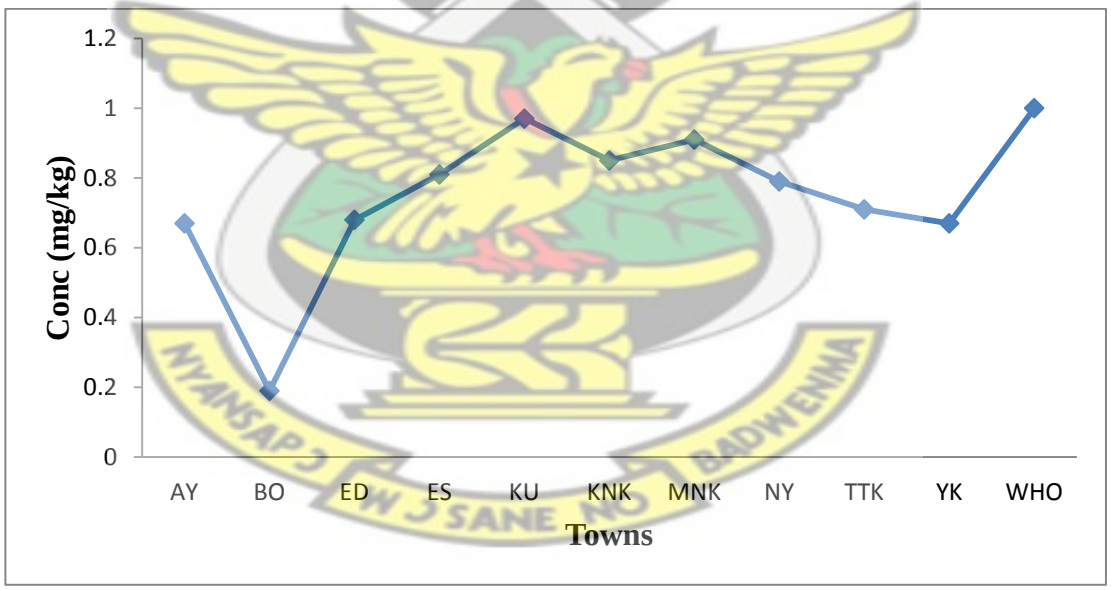
1D Distribution of Arsenic (ppb) in the District with Respect to Water



2D Distribution of Arsenic (mg/kg) in the District with respect to Soil



3D Distribution of Arsenic (mg/kg) with Respect to Cassava



Concentration of Stock Arsenic Standard Solution- Sodium arsenate ($Na_2HAsO_4.7H_2O$)

Concentration = $\frac{m}{MV} = \frac{0.05}{312 \times 0.05}$ = 0.003205 mol/L

Mass concentration = $0.003205 \times 312 = 1\ g/L$ =1000 mg/L =1000 ppm

Table 4.1.2 Arsenic level in borehole

For Akwasiso, arsenic level = 0.010±0.001 mg/L. The average is then 0.010 mg/L or 0.009 ppm

Converting 0.010 mg/L = $\left(\frac{0.009 \times 1000 \mu g}{1\ litre}\right) = 10\ \mu g/L$ or 10 ppb.

Table 4.2.1 Arsenic level in Atwere soil from 0-15 cm soil depth

Arsenic level = 0.312±0.015 mg/L. The average is then 0.312 mg/L or 0.009 ppm

Volume of Digested Solution = 10ml = 0.01 L

Mass of sample= 1g = 0.001 Kg

Converting, $\left(\frac{\frac{0.312mg}{L} \times 0.01L}{0.001kg}\right) = 3.12$ mg/kg.

Table 4.3.1 Arsenic level in Ayerebikrom Randomly Selected Cassava

Arsenic level = 0.031±0.003 mg/L. The average is then 0.031 mg/L

Volume of Digested Solution = 1 L

Mass of Digested Sample = 50g = 0.05 Kg

Converting, $\left(\frac{\frac{0.031mg}{L} \times 1L}{0.05kg}\right) = 0.62$ mg/kg.

Table 4.4.1 Cassava Peels

Bonsaso randomly selected = 0.042±0.008 mg/L. The average concentration will be 0.042 mg/L

Volume of Digested Solution = 10 ml = 0.01 L

Mass of Digested Sample = 1 g = 0.001 Kg

Converting, $\left(\frac{\frac{0.042mg}{L}\times 0.01L}{0.001kg}\right)$ = 0.42 mg/kg.