DETERMINATION OF TOTAL ARSENIC IN STREAMS AND SEDIMENTS FROM OBUASI GOLD MINES

BY

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DETERMINATION OF TOTAL ARSENIC IN STREAMS AND SEDIMENTS FROM OBUASI GOLDMINES

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DEDICATION

To my Dad, Mr. Pek Bamoah-Asomaning.

DECLARATION

It is hereby declared that the following is the result of the research project undertaken by the author under supervision, and that it has neither wholly nor partly been presented for another degree elsewhere.

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ABSTRACT

In this work streams and sediments of Obuasi, a major gold mining town in Ghana were analysed. In addition to the total arsenic the parameters determined included the levels of Fe, Al, Mn and Au, and nutrients. Leaching of arsenic from the sediment was also carried out to ascertain the rate at which As will be removed from the sediment to acceptable levels.

Results indicate that in spite of the newly installed Arsenic Recovery Plant (ARP) which is able to remove about 90% of the arsenic dusts, the streams in the area remain heavily polluted with arsenic. In the water Total Arsenic values range between 0.13 - 20.00ppm. The sediments are also polluted to a depth of at least 30cm with values ranging from 15.38 - 50.00ppm.

Contrary to expectations, the gold concentration in both the water and sediment are too low and may not be suitable for exploration.

The leaching results show that very little amount of arsenic was leached from the sediments. Even after 20 weeks of continuous leaching less than 1% of As had been leached. This was attributed to the ability of arsenic to form sparingly soluble compounds with Fe, Al, Mn etc in the sediment environment.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The exploration of natural resources is a means of enhancing man's standard of living from primitive life to a more advanced and enjoyable life. However, technological processes sometimes lead to adverse effects on the environment and human health.

In the extraction of gold from its ore, as is done at Obuasi goldmines, the roasting process results in the expulsion of poisonous smoke of arsenic (III) oxide and sulfur oxides into the atmosphere. This has lead to serious defoliation of the vegetation within about five miles from the stack. Inhabitants in and around the area are reported to have developed chronic eye inflammation[1]. Also some of the effects of this poisonous smoke are inflammation and itching of the skin, stomach upset, diarrhoea, nausea and loss of blood. The long term effects include dermatitis, skin and lung cancer and loss of hair[2].

Studies to assess the impact of arsenic pollution not only in Obuasi but also in Prestea, Konongo, Bibiani, and Tarkwa have been carried out. Amasa[1], formerly of the University of Science and Technology, Kumasi, Manful and

Verloo[3] of the University of Gent, Belgium, analysed hair and nails of mine workers and citizens of Obuasi and concluded that the levels of arsenic found in the hair and the nails are abnormal and attributed this to excessive exposure. Vegetation, foodstuffs and water in the immediate periphery (about 1 mile to the north) of the stack have been shown by Amasa[1] and Amekor[4] to be polluted with arsenic. Amonoo-Neizer and Busari[5] also analysed soils from both mining and non-mining areas of Ghana. They concluded that the level of arsenic in the mining areas were much higher than those of the non-mining areas, and they attributed this to arsenic fallout to the environment from the mines.

All these and other studies have neglected the sediments of the streams and rivers in these areas. But the sediments are important habitat of aquatic organisms, many of which serve as a source of food for man. Through natural and anthropogenic events, metals accummulate to high levels and may be incorporated in the biota. The sediment may also influence the flux of metals into aquatic food chain. An understanding of the nature of the sediment, the distribution and geochemical behaviour of metals is critical to an understanding of the biological availability of metals in sedimentary environment.

1.2 PURPOSE AND SCOPE OF STUDY

In this work streams and sediments of Obuasi, a major gold mining town in Ghana, will be analysed to ascertain the

extent of arsenic pollution. Since the distribution of elements in sediments depends on such physico-chemical variables as the nature and concentration of ligands and heavy metals in the (Fe^{3+}, Mn^{2+}, Al^{3+} etc and humic acid), the nature and concentration of solid substrate (eg. Al_2O_3, Fe_2O_3, clay particles, organic matter, etc), nutrients (K, Na, P), pH and redox potentials[6], the levels of arsenic should be seen in direct relationship to these parameters.

In addition, leaching tests will be conducted to ascertain how long it will take for the sediments to redeem itself, if the environment was left on its own.

This study, it is hoped, will be useful in evaluating the health hazards and environmental contamination and give a better understanding and pictorial relationship between the emitted pollutants and their impact on the streams and their sediments so that control strategies can be promulgated to mitigate and protect the environment.

CHAPTER 2

CHEMISTRY OF ARSENIC

2.1 GENERAL CHARACTERISTICS

Arsenic, atomic number 33, atomic mass 74.9216, is a metalloid belonging to the group of V(A) elements (N, P, As, Sb and Bi). In nature, it normally exists in these possible oxidation states: the metalloid (As^0), the trivalent states (As^{3+} and As^{3-}) and the pentavalent state (As^{5+}). Arsenic binds covalently with non-metals and metals and forms stable organic compounds in both trivalent and pentavalent states[7]. Arsenic closely resembles phosphorous analogs for chemical binding sites. The behaviour of arsenate (AsO_4^{3-}) therefore resembles that of phosphates and vanadates.

Arsenic has achieved great noteriety because of the toxic properties of a number of its compounds. Fortunately there are great differences in the toxicity of these different compounds. The species that are commonly found in soils are not the most toxic[8]. The organo-As coumpounds are less toxic than inorganic As compounds[8]. The order of toxicity of Arsenicals is[7]:

arsenites (inorganic trivalent compounds) > arsenoxides (organic trivalent compounds) > arsenates (inorganic pentavalent compounds) > arsonium compounds > metallic arsenic.

Some workers have focused attention on the differential toxicity of arsenic in its various forms. Inorganic arsenic

(III) and arsenic (V) compounds are generally observed to be of higher toxicity to mammals than the various oxidation forms[8]. Some of the common chemical compounds of arsenic are listed below:

NAME	FORMULA(E)
Arsenous oxide	As_2O_3 (or As_4O_6)
Arsenite	$H2AsO3^-$, $HAsO3^{2-}$, $AsO3^{3-}$
Arsenate	$H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}
Methylarsonic acid (MMA)	$CH_3AsO(OH)_2$
Dimethylarsinic acid (DMA)	$(CH_3)_2AsO(OH)$
Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$
Arsenocholine	$(CH_3)3As^+CH_2CH_2OHX^-$
Dimethylarsinoylathanol	$O=As(CH_3)_2CH_2CH_2OH$
Trimethylarsine	$(CH_3)_3As$
Trimethylarsine oxide	$(CH_3)_3As=O$

2.2 OCCURENCE OF ARSENIC

Arsenic is ubiquitous in the environment, ranking 20th among the elements in relative abundance in the crust of the earth[9]. The element is present in low but detectable concentrations in soils, atmospheric dust, waters, plants and animals[10]. It may exist in compartments as arsenic trioxide, arsenite, arsenate, other inorganic and organic forms. The presence of As in the environment may be due to both natural and anthropogenic activities.

2.2.1 NATURAL SOURCES

Over 200 As containing minerals have been identified with approximately 60% being arsenates, 20% sulphides and sulpho-salts and the remaining 20% including arsenides, arsenites, oxides and elemental As[11]. The most common of the As is found associated with many types of mineral deposites, especially including sulphide mineralisation[12]. The arsenic content of these minerals varies usually between 0.02 to 0.5%. The pyrite minerals can sometimes contain as much as 5% arsenic. These arsenic-sulfides readily oxidize when exposed to air yielding inorganic arsenic salts which are usually water soluble[13]. The arsenic content of igneous rocks varies considerably (up to 100mg/kg), but averages 2 to 3mg/kg. Sedimentary rocks also vary in the arsenic content, from small amounts in limestone and sandstone up to 1,500mg/kg in some manganese ores[14].

Arsenic is present in all soils and exists there as an unweathered mineral, an inorganic ion bound to soil cationsor it may be bound to organic matter. Soils contain from 0.1 to 40mg/kg elemental As naturally[15]. Soils overlying sulfides ore deposits commonly contain arsenic at concentrations of several hundred mg/kg[15]. The As contents of metamorphic rocks reflect those of the original igenous or sedimentary rocks.

Arsenic is naturally present in all waters and has a mean concentration ranging from 1 to 2µg/l[11]. Trace levels

of arsenic may be present in the air at concentrations approaching 0,01µg As per meter^3 [16], and are usually the result of natural weathering processes and biological reduction of arsenicals by microbiota and other organisms, particularly in soil. Volcanic activity, if present, contributes substantially to levels of arsenic in the air[17]. Arsenic is also present in both the animal and plant kingdoms. The arsenic content of plants varies between 0.01 and 5mg As per kilogram (dry weight)[18]. Differences in arsenic content reflect species differences in plants and environmental and edaphic factors in a particular geographic region. All living organisms contain As, with crustaceans generally having higher levels than fishes. Man usually contain arsenic within the range of 0.1 to 1.0mg/kg (dry weight)[18]. Some tissues, such as hair and nails, may however, concentrate arsenic at much higher levels. This is usually indicative of increased exposure.

2.2.2 ANTHROPOGENIC SOURCES

These exceed natural sources in the environment by a ratio of 3:1[17]. Man in his utilization of natural resources releases arsenic into the air, water and soil. These emissions can ultimately affect residual levels in plants and animals. The metal industry and pesticides usage (agricultural) are the main sources of anthropogenic arsenic. Arsenic compounds have been widely used as pesticides for over hundred years, but their use is now declining, having

probably halved in the decade from 1970 to 1980[8]. There has been a shift from the inorganic insecticides (lead and calcium arsenate, copper acetoarsenite) to arsenic herbicides (arsenic acids, sodium arsenite, methane arsonic acid and its salts, and cacodylic acids and its salts). Their major uses are as desiccants and defoliant in the cotton industry and for general weed control. Several organic arsenicals (arsanilic acid, 3-nitro-4-hydroxy-phenylarsonic acid etc.) continue to be used as growth promoters for poultry and swine. The use of arsenic as a wood preservative is increasing; ammonical copper arsenate and chromated copper arsenate are the most common formulations used for this purpose. The cotton and wood-preservative industries represent approximately 90% of the arsenic pesticide market[13].

Arsenic is naturally present in all lead, copper and gold ores and during the smelting of these metals arsenic becomes available as either a gaseous emission or solid waste product[19]. These gaseous and solid waste emissions represent between 50 and 60% of the total global emission. This source of arsenic generally tends to be geographically confined and as such, considerably affects arsenic residues within the localized community. The smelters at Obuasi in Ghana, Tacoma in Washington State of the U.S.A. and Yellowknife in Canada are prime examples of this. In Obuasi the concentration of arsenic in the ambient air ranged from 2.94 to 126$\mu g/m^3$ [20]. In Tacoma, air levels ranged from 0.5 to

2.5µg/m^3 at the smelter property line and decrease to between 0.02 and 0.13µg As per $meter^3$ 8 miles away[21].

Mining operations are a source of arsenic to the environment. Globally, this source is minor. However, in a regional setting, this source can be very major. Mining operations, whether they are above or underground, produce large quantities of usuable tailings [22,23] that are often rich in arsenic. These tailings are often left behind as large heaps, and the waste mineral is exposed to weathering process. This source of arsenic tends to be geographically confined unless the tailings are transported elsewhere for land filling[24]. Also the tailings are transported into rivers and streams when it rains.

2.3 EARLY USES OF ARSENIC

Arsenic has been used as a medicine and a poison since man first became interested in chemistry. Its medicinal properties were known to the ancient Greek physicians. Its use as an agricultural insecticide, herbicide and fungicide however, followed the development of the industrial revolution as the consequence of being an inexpensive by-product of the smelting of copper, iron, silver, cobalt, nickel, lead, gold, zinc, manganese and tin. Since then the hydrocarbon insecticides have progessively and largely replaced it. In the first half of the 19^{th} century, arsenic along with opium shared first place as a cause of fatal poisoning in England, Wales and France[25]. Its popularity as poison

declined in the latter half of the 19th century. However, due to the advent of reliable tests for measuring small amounts in body fluid, it is now rarely used as a homicidal or a suicidal agent.

Flower's solution (1% potassium arsenite) was used for many years as a tonic and treatment for psoriasis and asthma. Prolonged use of this medication produces chronic arsenic poisoning, and it was withdrawn from use in the 1950's. However, cases of poisoning are occasionally encountered[26]. Arsenic is still widely used in medications in the Far east[27]. The mechanism of its action as a tonic is not known, but the enthusiasm with which it was used for many years probably speaks for its effectiveness. Possibly related was its use for many years as a growth stimulant for farm animals prior to the widespread use of antibiotics for this purpose.

Major accidental poisonings occur from time to time. Some 6,000 people were poisoned by arsenic in the Manchester area of England around the year 1900 and at least 80 died. The source of arsenic was found to be beer; sugar used in the production was prepared by hydrolysing starch with sulphuric acid which was contaminated with arsenic. Iron pyrites is normally used as a catalyst in sulphuric acid production and in this case the pyrites contained arsenic[28]. In 1955 12,131 Japanese infants were poisoned by dried milk contaminated with arsenic and 130 died. Sodium

phosphate contaminated with arsenic had been used as a stabilizer[29]. Again in 1956, more than 400 people in Japan were poisoned by soy sauce accidentally contaminated with inorganic arsenic[30].

The phytotoxic effects of As compounds made them attractive as herbicides and as desiccants to allow cotton to be easily harvested after defoliation. However, there have been concerns about the build-up of As residues in soils and lake sediments which has occurred after the use of large quantities of inorganic As compounds[8]. World wide usage has been recently estimated to be 8,000 tons As/yr as herbicide, 12,000 tons As/yr as cotton desiccant and 16,000 tons As/yr as preservatives[31].

2.4 CURRENT USES OF ARSENIC

The 1970's saw a major decline in the usage of inorganic arsenicals in agriculture, but small amounts are still used for this purpose[32]. Other uses of arsenic are in the glass industry where it is used as a clarifier. Traditionally, arsenic trioxide was used for this purpose, but has been replaced with arsenic acid because of the carcinogenic risk of the former[33]. In electronic industry, gallium arsenide and its alloys are used to make semi-conductors for constructing lasers, solar cells, micro-wave devices, photoemissive surfaces and light-emitting diodes. Arsenic is prepared by distillation prior to the production of various alloys[34]. Organic arsenicals are still used as food addi-

tives to promote growth in farm animals[35].

Some authors have claimed that arsenic is an essential trace element for some species[36]. Schwarz[37], fed rats on a synthetic diet with an arsenic content of less than 0.05 ppm and demonstrated a significantly lower growth rate than in animals fed on the same diet with arsenic supplementation. The authors estimated the arsenic requirement for optimal growth to be between 0.25ppm and 0.5ppm in the diet. Jacobson-Kram et al[16] reminded us that one of the criteria for accepting a compound as an essential dietary component is the demonstration in the animal under study of a unique physiological (metabolic) role for the compound in question. Such a role has not been demonstrated for arsenic and, until it has, great care must be taken about accepting it as an essential nutrient. Large amounts of arsenicals are used as wood preservatives[38]. Poisoning has recently been reported from burning this wood in a stove[39].

2.5 TOXICOLOGICAL EFFECTS OF ARSENIC IN MAN

The clinical effect of acute arsenic poisoning have been well studied by Lander et al[40]. Symptoms are those of acute gastrointestinal irritation. The patient suffers from severe vomitting and diarrhea which may be blood stained accompanied by abdominal colic that may proceed to peripheral circulatory collapse and death. The fatal dose is probably between 100mg and 200mg of arsenic trioxide although

people have survived larger doses[25]. Neuropathy may follow non-fatal acute poisoning.

The most toxic arsenic compound is the arsine[7]. Arsine is formed when nascent hydrogen is formed in the presence of arsenic. Thus it can be formed by the action of acids or even water on metal arsenides. Accidental poisoning occurs occasionally in the steel, gold, tin and zinc idustries from this cause[41]. Arsine is used in the transistor industry to stabilize selenium and poisoning can occur from leackage of the cylinders in which it is stored[42]. The main feature of its toxicity is the devastating haemolysis.

The general features of chronic arsenic poisoning are chronic weakness, general debility and lassitude, loss of appetite and energy, loss of hair, hoarseness of the voice, loss of weight and variable degree of dementia. Anemia, apparently due to bone marrow suppression (normochromic and normocytic), is common and leukopenia may also occur. Basophilic strippling of the erythrocytes may be present[43]. It has been reported in one of the several poisoned patients in a studies conducted in 1977[44]. Megaloblastic champs have been reported[45] as have been disorders of haem synthesis[46]. Urine porphyrins, aminolevulinic acid and porphobilinogen levels were however normal in several poisoned patients[44]. Chronic renal and liver damage may be a feature of chronic arsenic poisoning. Many studies have been associated with liver cirrhosis with arsenic exposure, but

in many reports excess alcohol consumption may have been at least partly responsible. Presinusoidal portal hypertension without cirrhosis apparently due to portal tract fibrosis appears to be associated, but is a rare complication of arsenic exposure[26]. More specific features of chronic arsenic poisoning include dermatologic, cardiovascular and neurological changes[26].

The Fourth Annual Report on Carcinogens of the U.S. Health and Human Services reports that there is sufficient evidence that skin cancer in humans is causally associated with the exposure of inorganic arsenic compounds in drugs, drinking water and the occupational environment. The risk of lung cancer was increased 4 to 12 times in certain smelter workers who inhaled high levels of arsenic trioxide[47].

2.6 TOXICOLOGICAL EFFECTS OF ARSENIC ON PLANTS

The physiological effect of arsenic on plants is usually closely related but variables such as the type of arsenic compound, plant species, geographic location, soil type and climate can strongly modify the response. For example, most vegetables do not develop significant arsenic content when grown on soil having high concentration of applied As_2O_3 but it is the opposite when lead arsenate is applied to the soil[4]. Usually, fibrous plants taking arsenic from the top soil tend to develop high arsenic content in contrast to the tap-rooted plants which get access to only the leached arsenic. The effect of arsenic contamination in plants

ranges from decrease in yields, withering to death. It has been found that the application of small quantities of arsenic to light soil decreases the yields of cotton and cowpeas[5]. Some investigators also found that increased concentration of arsenic in the soil resulted in increased accumulation of the element in plants[48]. Arsenic toxicity in plants results in plasmolysis and leaf wilting followed by root discolouration and necrosis of leaf tips and margins. Furthermore, these symptoms indicated that water movement into the plant was limited and this may eventually lead to death. The concentration of soluble arsenic in soils high enough to cause injuries varied from 1ppm for cowpeas (*Vigna senensis* Endl.) to 7ppm for rice (Epps and Sturgis, 1930)[5].

2.7 REGULATIONS FOR ARSENIC

Environmental Protection Agency (EPA), Food and Drug Administatrion (FDA) and Occupational Saftey and Health Administartion (OSHA) all of U.S. have regulated the use of arsenic and its compounds [47].

EPA limits arsenic in drinking water to a maximum level of 0.05mg/l and have established effluent guidlines controlling the environmental releases of such compounds for certain industrial categories. FDA enforces tolerance levels for residues of arsenic containing pesticides in fruits and vegetables (0.35 to 7.0mg/kg), fruit crops and cotton (0.7 to 2.8 mg/kg) and livestock (cattle and horses, 0.7 to

2.7mk/kg).

OSHA promulgated a final standard in 1978 limiting occupational exposure level of inorganic arsenic compounds to 10μg/m^3. The permissible exposure level of 0.5mg/m^3 for organic arsenic as an 8-hour time weighted average was adopted by OSHA in 1971. Additionally this standard required personal protective equipment, training, medical surveillance, signs, labels and engineering controls[47].

2.8 CONTROL MECHANISMS FOR ARSENIC IN THE ENVIRONMENT

There are many mechanisms that influence where arsenic may be found in the environment, the major ones include methylation and volatilization, adsorption, complexation, precipitation, oxidation and reduction.

2.8.1 METHYLATION AND VOLATILIZATION

Biological methylation was first reported in 1815 when Gmelin[49] reported that a mold growing on the arsenical pigments of damp wall paper emitted a volatile arsenical that caused the death of a number of people. Some fungi and bacteria are able to methylate and demethylate inorganic arsenic. The mechanism is thought to be initial reduction to arsenite with subsequent methylation. A model for the transformation of arsenite-arsenate to methyl arsines in aquatic sediment was first proposed by Wood[50].

Arsenic is known to be methylated by a number of dif-

ferent organisms found throughout the environment, particularly in soil and water that are rich in biota. The methylation can occur under either aerobic or anaerobic conditions. Brinkman et al[51] have shown that a mixed bacterial fungal population cultured from fresh pond sediments can release trimethylarsine under both aerobic and anaerobic conditions. Figure 1 shows a simplified schematic representation of a methylation cycle for arsenic in the environment.

Although the cycle is incomplete and simplified, it illustrates how arsenic can by biological means change form and as a result relocate within the environment. Andreae[52] suggests that biological methylation is the dominant process responsible for the regeneration of inorganic arsenic from methylated arsenicals.

2.8.2 ADSORPTION, COMPLEXATION AND PRECIPITATION

Adsorption and co-precipitation onto clay particles and co-precipitation into metal-ion precipitates are important mechanisms for arsenic removal from air and water and are also important mechanisms for arsenic stabilization in soil and sediments.

Arsenic forms insoluble precipitates with calcium, sulphur, iron, aluminium and barium compounds in natural water, although some of these reactions are slow[53,54]. Also various arsenate compounds are formed by complexation

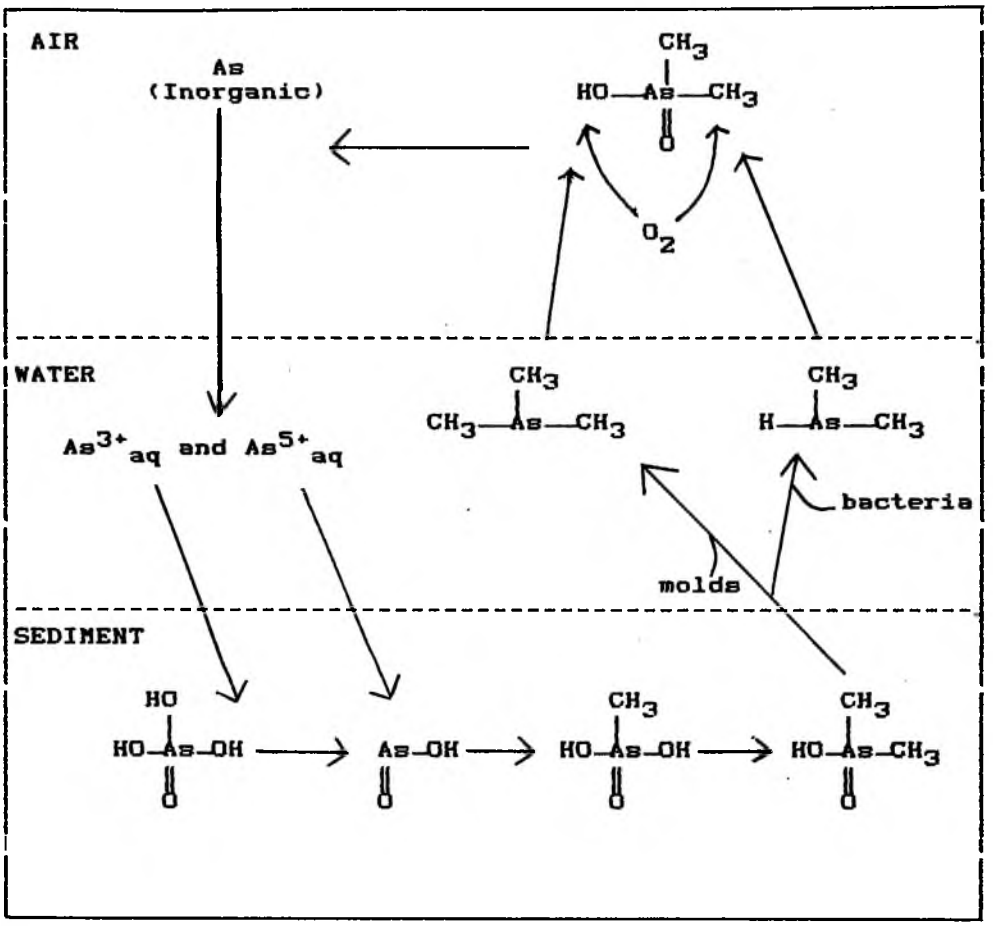


Fig. 1: Modified schematic representation of the biological cycle proposed by Wood[19]. The cycle illustrates inorganic and organic transformations that occur among air, water and sediment compartments.

processes with manganese (Mn) and lead(Pb). The species of

arsenate in solution for each of the compounds could be predicted as follows[55]: $AlAsO_4.2H_2O$, $FeAsO_4.2H_2O$ or $Fe(OH)_3$, $Ca_3(AsO_4)_2.14H_2O$; $Pb_3(AsO_4).4H_2O$ and $Mn_3(AsO_4)_2$.

Due to the slow reaction rates, any soluble arsenic species is most likely to be adsorbed on the surface of inorganic or organic substrates[56]. Holm et al[57] carried out a study of the sorptive characteristics of arsenate, arsenite, monomethyl-arsonic acid and cacodylic acid. In studies carried out in the Menominee river sediments, the four oxygenated arsenic species were present together and competing among themselves and with phosphate for the same sorptive sites. They found that phosphate was adsorbed onto the sediment to a greater extent than arsenate, monomethy-larsonic acid, arsenite and cacodylic acid respectively. They showed that adsorption was the only process occuring. Wauchope and Yamamoto[58] showed a similar pattern of adsorption of arsenic in aerobic alluvial soils.

2.8.3 OXIDATION AND REDUCTION

Oxidation and reduction of arsenicals can occur by either chemical or biological reactions or by a combination of both processes. Inorganic arsenicals can participate in either reaction while organic arsenicals are transformed mostly through biochemical reactions[56]. Organic arsenicals will either be oxidized or reduced depending upon the pH and pE (oxidation - reduction potential) of the environmental compartment. Bacteria[56] and phytoplankton can reduce

arsenate to arsenite and the oxidation of arsenate is known to be catalysed by a number of bacteria(52).

Other processes such as dissolution, hydration, hydrolysis, carbonation and leaching may also affect the fate of arsenicals in the environment.

2.9 THE ARSENIC CYCLE

The cycling of arsenic through the environment is accomplished by a number of different mechanisms that are occuring simultaneously and continuously. The residence times of arsenic in the various environmental compartments have been tabulated in Table 1 using data reported by MacKenzie et al[60]. The residence times vary from 9 days in the air to 99.8 million years in sediments.

Table 1 Residence Times of Arsenic

COMPARTMENT	RESIDENCE TIME (YEARS)
Sediments	99,800,000
Ocean (dissolved)	9,400
Land	2,400
Terrestical biota	17
Oceanic biota	0.07
Air	0.03

The cycle includes the major natural and arthropogenic sources along with the major mechanisms responsible for the transport and distribution within the various compartments. A discussion of the various compartments follows.

2.9.1 SOIL COMPARTMENT

Arsenic is present naturally in all soils with an average concentration of between 5 and 6mg/kg. Soils overlying sulfide ore deposits may have concentrations as high as 8,000mg/kg[18]. Soils may also be contaminated with sources such as atmospheric fallout or slag disposal from smelting operations, fallout from burning fuel and fly ash or residues resulting from pesticides application. For example, soils from land repeatedly treated with inorganic arsenicals often contain levels of arsenic 10 to 100-fold greater than those of untreated areas[61].

These arsenicals form very insoluble and stable complexes in soil systems which contribute to their long residence time (99.8 million years). Organic and inorganic arsenicals in the soil behave similarly. Another complicating factor may be the presence of clay minerals, Fe and Al oxides and organic matter (organic C and N) which can influence solubility and rate of oxidation. The equilibria for arsenous acid (As(III)) and arsenic acid (As(V)) in aqueous solutions are given below. The pka values indicate that the species that should be thermodynamically most stable over the normal soil pH ranges of 4 - 8 will be[8]:

i) H_3AsO_3 (up to about pH 9);

ii) $H_2AsO_4^-$ (approximately pH 2 - 7);

iii) $HAsO_4^{2-}$ (pH above 7).

Arsenic acid:

$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+$ pka 2.20

$H_2AsO_4^- + H_2O \rightleftharpoons HAsO_4^{2-} + H_3O^+$ pka 6.97

$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+$ pka 11.53

Arsenous acid:

$H_3AsO_3 + H_2O \rightleftharpoons H_2AsO_3^- + H_3O^+$ pka 9.22

$H_3AsO_3^- + H_2O \rightleftharpoons HAsO_3^{2-} + H_3O^+$ pka 12.13

$HAsO_3^{2-} + H_2O \rightleftharpoons AsO_3^{3-} + H_3O^+$ pka 13.40

The adsorption is a function of arsenic concentration as well as the sorptivity of soil components - chiefly iron and manganese[62]. As might be expected, sandy or low clayey soils have less affinity for arsenic and under these circumstances, arsenic becomes more mobile, especially at higher levels of pH[63].

Phosphate fertilizers tend to mobilize arsenic because of competition for the same sorptive sites. Generally, because of the strong adsorptive capability of soil for arsenic and its low leacheability, the threat of groundwater contamination by arsenic is reduced. Stevens et al[64] were unable to detect arsenic in soil 23cm below the surface following the application of 180kg As per hectare to a sandy soil. Similarly, other investigators found arsenic to have a slow downward mobility[65]. However, Comanor et al[66] were able to detect arsenic in soil 60cm beneath a tailings pile from a gold mine known to be rich in arsenic.

Oxidation/reduction interconversions of the various

arsenicals in the soil occur concurrently and the reactions are both chemically and biologically mediated. The thermodynamic reactions in soil are believed to be governed primarily by its pH and iron content. Normally the pH of soils and sediments determined in distilled water does not give the true picture of the H^+ concentration in solutions. The limitation here is that measurements done in distilled water give only approximate values since some H^+ ions are absorbed onto the surfaces of the negatively charged sites on the colloid soil particles. The use of 0.01M $CaCl_2$ has been recommended by Schofield and Taylor[48] and is supposed to more effectively displace H^+. However, 0.01M KCl is routinely used as the solution for measuring soil pH, since it more effectively masks differences in salt concentration and also displaces a higher percentage of exchangeable H^+ and Al^{3+}. The pH value obtained in distilled water extract is about 1.0 to 1.5 units higher than that of the soil solution near to the solid surfaces where reactions take place[8]. This dilution effect is usually overcome by measuring the pH in a suspension of soil in a solution of neutral salts such as KCl. It is usually assumed that the pH value quoted for soils and sediments is for distilled water unless otherwise stated.

Iron dominates the redox potential (Eh) of the soil compartment[67]; high iron levels favour high Eh levels which in turn favour arsenate formation. Redox potential

(Eh) is a quantitative measure of the tendency of a given system to oxidize or reduce susceptible substances. Eh is positive and high in strongly oxidizing systems; it is negative and low in strongly reducing systems[68]. Published values for potentials of reduced groundwater, the interstitials solutions of reduced ocean muds, reduced lake waters and the solutions of reduced soils usually range from 0.02 to 0.00V and rarely drop below -0.05 V. By contrast, reduced soils and lake and ocean muds give potentials to values as low as -0.40 V[68].

When the Eh value drops below about + 300 mV at pH 4 and - 100 mV at pH 8, H_3AsO_3 becomes the thermodynamically stable As species[68] in the absence of complexing species and methylating organisms. Hindmarsh[19] noted that arsenate is predominant arsenic in soil unless the soil has a low pH. Conditions in which an Eh of less than 300mV may occur, for example, during flooding, favour the reduction of arsenate, in which case arsenite content begins to become significant[19]. Usually under these circumstances, soil micro-organisms aid in the reoxidation to arsenate. Also the rate of change in oxidation state with a change in Eh or pH conditions does not always appear to be very rapid in aqueous systems. Therefore the proportion of the various arsenic species present in soil porewaters may not correspond to the expected distribution[8].

2.9.2 AIR COMPARTMENT

The relatively high volatility of a number of As compounds means that geochemical cycle of As contains significant fluxes passing through the atmosphere. However, the vapour phase has been estimated to make up only about 7% of the atmospheric burden, with the remaining As associated with the particulate phase[8].

Arsenic is naturally present in all air with levels in the vicinity of 0.002µg As per meter^3 [26]. In a non-industrial setting where contribution of coal is the major source of arsenic in this compartment levels of arsenic is approximately 0.02µg As per meter^3 [26]. The residence time of arsenic in air is the shortest of all the compartments (9 days). Johnson and Braman[69] indicate that methylated arsenic has been found in air samples, but attributed its presence to the biotic activity or the use of methylated arsenic herbicides. Andreae[70] suggests that these methylated forms are due primarily to anthropogenic rather than natural sources. Regardless of their origin, the methylated forms of arsenic are rapidly oxidized in air to inorganic forms (arsenate/arsenite)[70]. The resultant arsenic combine with other particles and settle out or are washed from the atmosphere by rain and re-enter the other compartments.

2.9.3 WATER COMPARTMENT

Arsenic is found naturally in all waters with an average concentration approaching 1 to 2µg/l. It is naturally

introduced into surface waters mainly as a result of erosion and weathering of rocks, soils and minerals. Anthropogenic sources can add substantially to the arsenic content of surface water. Groundwaters are indirectly influenced by anthropogenic sources, but the weathering of arsenic bearing minerals is believed to be a major source of arsenic in this compartment.

The arsenic released into surface waters enter into a number of reactions which include oxidation/reduction, precipitation and methylation. Most surface water supplies have Eh and pH levels which favour arsenate predominance and stability. Thermodynamic calculations predict a 10:1[35] of arsenate to arsenite in oxygenated water with a pH of 8.16[60]. The presence of any other form suggests insufficient time for the oxidation process to occur, a reducing or lower Eh than usual; and biological activity causing reduction of arsenate to arsenite.

Water has a self-cleansing action for arsenic and a number of other metals. Arsenite and arsenate form insoluble salts with cations (usually iron) that are dissolved or suspended in the water and these particles generally settle out in the sediment. Cercelius et al[71] reported that river particulates (> 0.45µm size) carry 33 to 67% of the total arsenic load of a river and that all arsenic in the river sediment originally comes from the river particulates. The arsenic concentration in Lake Michigan is reported to range from 0.5 to 2.4 ppb, whereas the sediment has a range of

7,000 to 29,000 ppb[72]. This example is typical of many surface waters and illustrates the self cleansing ability of such waters. This removal process prevails provided there is a constant supply of the cleansing agent; otherwise the arsenic concentration can increase in the water.

Methylation processes keep the cycle dynamic. Phytoplankton and other biological activities in the photic zone transform arsenic into various methylated forms. Little methylation, if any, occurs below the thermocline[73]. The evidence for biomethylation of arsenic in the sediment is inconclusive. It is reported that methylation in sulfur-rich sediments is unlikely due to the reaction of sulfides with reducing arsenic to form arsenic sulfides which are apparently incapable of being biomethylated[73]. Woolson[13], Wood[50] and others suggest otherwise. The methylated by-products in surface water become available for oxidation/reduction, adsorption/precipitation and/or methylation.

2.9.4 PLANT AND ANIMAL COMPARTMENTS

Arsenic uptake into plants occur either via root or by foliar uptake[17]. Arsenic levels from root uptake are generally low due to the stability of most soil arsenic complexes. Residue levels in plants generally follow levels found in soil[17]. Soil levels in excess of 200 to 300mg/kg are necessary for plants to absorb sufficient arsenic to reach edible plant levels of 1mg As per kilogram fresh

weight(13). However, there are exceptions, egg plant and beet roots were found to contain approximately 20mg As per kilogram of dry weight (1 to 2mg As per kilogram of fresh weight) when grown on soil containing 40 to 116mg As per kilogram[74]. Evidence for increased plant residues from atmospheric arsenic fallout exists[75].

Arsenic, because of its ubiquity, is ingested by all animals. Abnormally large intakes may be derived from eating plants or drinking water contaminated with arsenic, from breathing arsenic-containing dusts, or by ingesting arsenic as a medicine or poison. Fish and fish products contain the highest concentrations of arsenic in animal kingdom, concentrations in marine bottom-feeding fish (cod, flounder) have contents ranging from 2.5 to 4.9mg/kg; in crustaceans (clams, lobsters and shrimp) range from 1.2 to 10.9mg/kg, while in non-bottom feeding fish (tuna, herring) range from 0.2 to 0.8mg/kg[76]. The overall effect of plant and animal kingdom on the total global arsenic emission is approximately 1%.

The arsenic cycle is complex and dynamic. Man influences it to a major extent by causing considerable local confined cycling. Man's influence on global arsenic cycling is small.

CHAPTER 3

REVIEW OF ANALYTICAL METHODS FOR THE DETERMINATION OF TOTAL ARSENIC IN ENVIRONMENTAL SAMPLES

3.1 SAMPLING AND SAMPLE TREATMENT

Sampling is defined as the operation of securing portions of a system under investigation for subsequent laboratory testing and analysis. The most important step in the analysis of environmental samples is the acquisition of adequate and representative sample; that is the properties of the collected sample must be reasonably close to those of the system under study. Besides obtaining a representative sample, the sampling process should not alter the sample in any way. Any loss or contamination of the sample is unacceptable. Utilization of the most sophisticated analytical tools and expertise may even lead to inaccurate and invalid conclusion if improper sampling procedures are used.

Arsenic poses some special problems in sampling not experienced in the determination of other trace metals. Water, urine and biologically active samples should either be analysed within a few hours or frozen and stored[77]. This is because low concentrations of arsenic compounds found in natural waters for example decrease with time, unless stabilized in some way to prevent losses due to adsorption to the walls of the container. Also the biomethy-

lation of inorganic arsenic in a biologically active sample can cause a change in its composition.

In trace element analysis, sample treatment more often than not involves some type of preconcentration prior to analysis. This is to increase the concentration of the analyte and sometimes reduce or remove completely the matrix thereby lowering the error involved in the measurement. Typical of preconcentration methods that have been successfully applied to the analysis of arsenic are: conversion of arsenic to arsine, co-precipitation with iron(III) hydroxide, distillation as arsenic(III) chloride and extraction. If the preconcentration step or the final step in the analytical method requires conversion of organo-arsenic compounds to an inorganic form, oxidative procedures (such as acid-persulphate or acid-permanganate) may be necessary. However sea and fresh natural waters are generally analysed without oxidative treatment prior to a preconcentration step, when molecular forms of arsenic are to be analysed. Arsine generation followed by cold trapping in liquid nitrogen, volatilization as trichloride or tribromide as well as co-precipitation with hydroxide are techniques commonly employed in preconcentrating arsenic in sea and natural fresh waters before analysis.

3.1.1 DIGESTION TECHNIQUES FOR SEDIMENT/SOILS

Procedures for the determination of trace metal in sediment / soil usually require three distinct steps:

1) Sample preparation

2) Dissolution or extraction

3) Final measurement by AAS or other suitable techniques.

Steps 1 and 2 are equally important in determining the final outcome of the analysis. In the determination of the total or near-total metal content of a sediment, the first step usually involves drying the sample, grinding to ensure subsample representativity and facilitate decomposition and sieving to a selected size fraction.

Dissolution which usually involves decomposition techniques for sediment can be classified as:

Total - capable of releasing all the metals from all phases,

Strong - capable of releasing a large portion of metals associated with the lattice of the minerals.

Partial - the partial dissolutions are intended only to extract metals from organic and non-detrital components and can further be divided into those that are selective for a particular phase and those that are non-selective in their action. Dilute HCl and strong acid either alone or coupled with a reducing agent have been used to liberate 'readily extractable' or 'non-detrital' metals with minimum degradation of silicates. The use of HCl alone is the most simple and effective method of removing non-detrital components

with least damage to silicates[6]. Similar results can be obtained with citrate-dithionite extraction but contamination of this reagent makes it inconvenient for routine use. Acetic acid gave poor recoveries[6].

The reagents widely used for decomposition or as extractants for trace metals from sediments/soils are summarized in Table 2.

Table 2: Decomposition and extraction techniques for determination of trace metals in sediments

DECOMPOSITION/ EXTRACTION	REAGENTS COMMMONLY USED
Total Decomposition	HF + HNO_3/$HClO_4$/HCl, alkali fusion or analysis by XRF, NAA, etc.
Strong Decomposition	hot concentrated mineral acids without HF e.g. $HClO_4$ + HNO_3 or HNO3 + HCl, H_2SO_4 + HNO3 + HClO4
Partial Decompositions	
Non-selective	0.1 - 1.0M HCl
Selective	
Exchangeable	Ammonium acetate; $MgCl_2$; $BaCl_2$
Organic matter	H_2O_2; NaOCl
Fe/Mn oxides	Hydroxylamine hydrochloride, Acid ammonium oxalate, Sodium dithionite, Hydrazine

The best wet digestion method for total arsenic involves the use of a mixture of H_2SO_4, HNO_3 and $HClO_4$[78]. Perchloric acid is used to speed up the digestion and hence reduce the volume of nitric acid used and shorten the time taken to complete the destruction of all organic matter. There is considerable risk that in the absence of sulphuric acid the

digest boils to dryness, thus increasing the possibility of hazards due to explosion.

Digestion procedures are sometimes followed by extraction methods. Sequential extractions, (i.e. extracting the sample sequentially with different reagents) despite their lack of specificity are capable of providing information on partitioning of metals between operationally useful sinks in sediments. No single standard sequential scheme can be recommended, nevertheless the following simplified scheme might be a useful tool for many purposes including exchangeable pore water (i.e. water found in soil pores) and resistate minerals (minerals strongly bound to soil particles).

Table 3: Simplified sequential schemes for the extraction of metals from sediments.

OPERATIONAL DEFINITION	PHASES MOST AFFECTED	REAGENTS
Readily leachable	Carbonate + Exchangeable pore water	CH_3COONa/CH_3COOH pH 5
Oxidizable	Organic + Sulfides	H_2O_2 - HNO_3 or NaOCl
Reducible	Mn/Fe oxides armophous or poorly crystallized	$NH_2OH.HCl$ + either CH_3COOH or Na-citrate
Residual	Resistate minerals	HF - HNO_3

Once the extraction is completed, the supernatant liquid must be separated from the insoluble residue as soon as

possible to minimize any losses of metals by re-adsorption. This can be done by centrifugation or filtration.

3.2 ANALYTICAL METHODS FOR THE DETERMINATION OF ARSENIC

The numerous procedures available for the determination of arsenic can be grouped into two, namely chemical and instrumental methods.

3.2.1 CHEMICAL METHODS

In these methods arsenic is converted chemically into forms for quantitative determination. The chemical methods include: the Gutzeit method[79], the Molybdenum blue method[79] and the silver diethyldithiocarbamate method (SDDC)[79].

The Gutzeit method is one of the very early common methods employed for the determination of total arsenic. In this method, essentially nascent hydrogen (generated fron Zn and HCl) is used to convert all arsenic(III) in solution to arsine, which is determined colorimetrically.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$H_3AsO_3 + 3H_2 \longrightarrow AsH_3 + 3H_2O$$

The method has the disadvantage of too much dependence on the the rate of evolution of arsine, which is not necessarily the same as the rate of evolution of hydrogen and it is doubtful, whether the accuracy exceeds 10% of the true

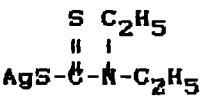
value.

The main feature of the molybdenum blue method is the conversion of all the arsenic in a sample solution to a coloured blue complex. The As(V) in arsenate, for example, is converted to the arseno-molybdenum complex by the reaction:

$$AsO_4^{3-} + 12MoO_4^{2-} + 3NH_4^+ + 24H^+ \longrightarrow (NH_4)_3AsMo_{12}O_{40} + 12H_2O$$

The complex actually contains the trimolybdate ion $Mo_3O_{10}^{2-}$ in which molybdenum is in the oxidation state of +6. Hence its composition should be written as $(NH_4)_3As(Mo_3O_{10})_4$. This method has the chemical problem of the conversion of all the arsenic in the sample into the coloured blue complex. With very small amounts of arsenic the conversion may not be rapid or stoichiometric. Interference from other substances present in the sample e.g. phosphate, which also forms blue complex with the molybdenum has to be considered.

In the SDDC method, arsenic in the sample is distilled as arsine and this is made to react with a solution of silver diethyldithiocarbamate



in pyridine to form a soluble red complex with maximum absorption at 540nm. As a colorimetric method, it also has problem of not rapidly or stoichiometrically converting all the arsenic in the sample into the coloured state. Heat is

at times used to reduce the time required for the development of maximum colour. Interference from antimony which also forms stibine, SbH_3, a red coloured compound with maximum absorption at 510nm has to be considered.

3.2.2 INSTRUMENTAL METHODS

A variety of instrumental methods have successfully been employed for the determination of trace amounts of arsenic in all sorts of matrices. The most important of all has been the atomic absorption spectrometry.

3.2.2.1 ATOMIC ABSORPTION SPECTROPHOTOMETRIC (AAS) METHOD

Atomic Absorption Spectrometry (A.A.S.) has now been used for 30 years[80]. The technique is well established and current publications reveal mostly subtle though important improvements. The A.A.S has various techniques involving flame atomic absorption (F.A.A.), graphite furnance atomic absorption (G.F.A.A.), hydride generation atomic absorption (H.G.A.A.). Chemical analysis with the AAS technique involves converting the sample, at least partially into an atomic vapour and measuring the absorbance of this vapour at a selected wavelength which is characteristic for each indiviual element (193.7nm for As). The measured absorbance is proportional to the concentration of the analyte of interest and analyses are usually made by comparing the absorbance with that given by reference samples of known

composition and concentration under the same experimental conditions.

Fig. 2: Schematic diagram of the instrumentation of an Atomic Absorption Spectrometer

Samples analysed by AAS usually are made into a solution and sprayed into the flame as such or after appropriate dilution. For most accurate results, those metals to be determined should produce absorption between 20% and 80% (i.e. absorbance between 0.10 and 0.70). Latest trends in research are directed towards the analysis of solid samples[81]. Electrothermal Atomic Absorption Spectrometry (EAAS) with use of Solid Sampling technique is one of the most attractive methods for determining trace elements in solid biological samples. There can be advantages in introducing the sample into the furnace as a powder rather than in the form of a solution. It eliminates many steps for sample pre-treatment such as dissolution and dilution or enrichment which increases risks of contamination and loss of analyte. Although many works have been carried out to analyse various solid samples directly with EAAS one problem yet to be solved is the preparation of standards for cali-

bration. Headridge et al[82] employed the use of a metal powder and an aqueous solution as standards for pre-analysis of alloys, while Atsuya, I. et al[83] also investigated the suitability of the direct calibration procedure using simple reference solutions for the determination of trace elements in biological samples. Results obtained for the analysis of Cu, Cr and Mn gave lower values than the certified values.

The method of standard addition has been employed for the analysis of solutions, especially of biological samples[83]. However, it is often difficult to verify whether a substance used for standard addition behaves the same way as an analyte in an unknown sample. Many Standard Reference Materials (S.R.M.) are commercially available. They are prepared from various naturally occurring materials, however, for concentrations less than several mg/g there is a scarcity of SRMs that could be applied for the calibration.

Trace element standards must have small sampling error (in the mg and sub-mg range) and thus must be homogenous at these levels. Synthetic Reference Materials (S.R.M.) such as phenolformaldehyde resin, silica, gelatin ion exchange beads and copolymerisate of acrylamide have been reported[84] but there are few S.R.M.s for multi-element analysis of biological materials by EAAS with solid sampling technique. Akatsuka and Atsuya[81] have proposed a powder S.R.M. prepared by coprecipitation with magnesium(II)-8-hydroxyquinolinate for

solid sampling EAAS analysis of biological samples. The powder S.R.M is stable and suitable for use at sub-mg and mg weights and is highly accurate for the determination of trace elements in different kinds of solid biological samples. The limits of detection for Al, Cd, Co, Cu, Mn, Ni, Pb and Zn in solids were found to be 0.087, 0.008, 0.012, 0.05, 0.003, 0.043, 0.14 and 0.013µg/g respectively.

3.2.2.1.1 INTERFERENCES IN AAS

The techniques of AAS are subject to various interferences. When concomitant elements affect an alternation in those physical or chemical properties or processes that control the final population of neutral groundstate atoms of the sample in the absorption cell interference with the analytical signal results. This interference is of various kinds viz spectral, flame emission, chemical, matrix, scattering and ionization processes. The majority of difficulties arise from the last four mentioned interferences.

Spectral and Flame Emission Interferences

These are instrument related interferences and with the continuous improvement on the make, model and function of instruments, these interferences have virtually been eliminated. Flame emission interference, for example, which is caused by emission of elements at the same wavelength at which absorption occurs is corrected by increasing source current or by closing down the slit, that is implying an

increase in signal-to-noise ratio (S.N.R.). There is no simple way to greatly reduce analyte flame emission noise short of replacing the hollow cathode lamp with an electrodeless discharge lamp, which will increase interferences. O'Haver et al[85] revealed that the radiance of a prefocussed Xe arc continuum lamp source, measured over the spectral width of a corresponding hollow cathode lamp, was significantly greater than every cathode lamp tested. The ratio (continuum/line source) varied from 2.5 for As at 193.696nm to 107 for Ca at 422.673nm. Therefore a continuum-source based Flame Atomic Absorption Spectrometry (F.A.A.S.) system such as the wavelength-modulated spectrometer with Cermax Xe arc continuum source system should possess a SNR advantage over convectional line source atomic absorption instrumentation for FAAS measurements of high concetrations of emissive elements in high temperature atomizers. This hypothesis was tested and verified for Ca in a study by Messman and O'Haver[86]. Ca was selected as test analyte because of (i) its low excitation potential, (ii) high FAAS snsitivity and (iii) presence as a major constituent in many sample types. The measurment precision obtained using wavelength-modulated continuum source was found to be superior to that obtained with an instrument using a hollow cathode lamp line source when Ca concentration exceeds 5ng/l.

Chemical Interferences:

Chemical interference occurs when the analyte is contained in a chemical compound that is not broken down by the flame or furnance. This results in a lower concentration of 'free' ground state analyte atoms than would occur in the absence of the interferent. Atomic absorption, can only occur by free atoms. An example of chemical effect in analytical flame spectroscopy is the depression of calcium atomic concentration in the presence of phosphate. Sulphuric acid also has a similar effect on the determination of calcium.

Calcium combines with phosphate to form calcium phosphate. This compound, when heated, is converted to calcium pyrophosphate, which is relatively stable at the temperature of air-acetylene flame. This chemical reaction reduces the free calcium atom population in flame compared to that obtained for similar calcium solutions without phosphate.

In work with flames, chemical interferences can be minimized by using a higher-temperature flame or by the addition of a releasing agent. In some instances releasing agents preferentially combine with the interfering ion, thus releasing the analyte atom. In other cases, combustible releasing agents such as ethylene-diamine tetraacetic acid (EDTA) combined preferentially with the analyte atom and then burn in the flame, releasing analyte atoms. Magnesium has been successfully utilized as a releasing agent to suppress the interference of phosphate, sulphate, aluminium and

silicate in the determination of calcium in plant materials by AAS. Also the interference of silica in the AAS determination of iron and manganese was reduced by the addition of calcium as releasing agent[87]. EDTA is used to complex cations such as Co, Fe, Ni, Zn, etc. preventing their association with anion, also lanthanum chloride solution is added to calcium solution containing phosphate to release Ca due to the preferential formation of lanthanum phosphate.

In a study by Boampong et al[88] Fe(II) was used as a releasing agent for As and Se determination. It behaves as an oxidizing agent and the reduction of Fe(III) to Fe(II) is kinetically favoured over the reduction of Ni(II) to Ni(O). Thus the formation of As hydride is essentially complete before the strongly interfering, low oxidation-state Ni has had a chance to form and interact with arsine. L-cysteine was chosen as a reagent that might have an effect on the interference from transition metals. It is cheap and readily available and gives a low blank for As and has much lower toxicity than, for example urea.

Although higher temperature flames do successfully overcome some chemical interferences they do not alleviate all such problems. Van Loon[89] found that the depressive effect of Zirconium on Yttrium absorbance could not be fully overcome in the nitrous oxide-acetylene flame even, in the presence of a releasing agent. The method of standard additions is useful for overcoming chemical interference partic-

ularly in electrothermal work. This technique is, however, time consuming compared to the above approach.

Ionization Interference:

Atoms of elements possessing very low ionization potentials can become ionized at flame and furnance temperatures i.e. excitation of ground state atoms to such an extent that one or more electrons are lost and ionization occurs. This interference, also known as vapour phase interference, reduces the free-atom population. Elements that commonly present such a problem are cesium, rubidium, potassium and sodium. At nitrous oxide-acetylene flame temperature, calcium, rare earths, strontium and barium are also ionized to an appreciable extent. This problem is usually overcome by the selection and optimization of furnance operating conditions.

Non-Specific Absorption Interferences:

One of the most important interferences being encountered using electrothermal atomizers results from signals due to light scattering or molecular absorption. This results in the enhancement of analytical results at ppm or ppb levels due to the solution containing high concentration of dissolved salts. This problem is most severe at ultraviolet wavelength and also in the visible region of the spectrum. It can be corrected by solvent extraction to remove the element from the interfering matrix, repeating the determination at a nearly non-absorbing line or using a deuterium backgrounds corrector.

Matrix Interference:

Includes enhancement or depression of analytical sensitivity due to the presence of other components apart form the analyte atoms. This interference can be corrected by:

1) The method of standard additions.
2) Matching the matrix of the standard with that of the sample.
3) Relating the erroneous value obtained to an accurate value by using a factor determined by other means.
4) Removal of the cations to be determined from the interfering matrix by processes such as solvent extraction, Chromatography, but especially for arsenic the hydride generation technique.

3.2.2.1.2 HYDRIDE GENERATION METHOD

This method is applicable to the analysis of elements which form volatile hydrides - Hg, As, Se, Sb, Sn etc[90]. Through this process an analyte is simultaneously concentrated as its hydride and separated from the sample matrix. Reduction of As to AsH_3 with subsequent release from solution and transport to the flame leaves behind behind many potential interferents and substantially increases the sensitivity.

The basic chemical principle involves the use of sodium

borohydride, $NaBH_4$, (or tin(II) chloride) as a reducing agent (reductant). $NaBH_4$ liberates hydrogen on contact with acids. The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. The following equations represent simplifications of the reduction process for mercury and arsenic respectively:

$$Hg^{2+} + 2BH_4^- \longrightarrow Hg + H_2 + B_2H_6$$

$$2As^{3+} + 6BH_4^- \longrightarrow 2AsH_3 + 2H_2 + 3B_2H_6$$

$$AsH_3 \longrightarrow As.$$

Sensitivity and detection limit are improved and spectral interference is reduced. Briddle and Xiao-Chun Le[9] found that if the hydride is introduced to the DC-plasma while a solution of easily ionized element (EIE) such as KCl or CsCl with constant concentration, is separately nebulised and transported to the plasma jet, it is possible to obtain an improved signal-to-noise ratio which is beneficial to trace analysis. Hydride generation is an ideal situation where interference by EIEs could become an advantage increasing the sensitivities and improving the detection limits of the hydride-forming element. The replacement of distilled water by solutions of EIEs allows the signal enhancement effect EIEs to be put to advantage. Boampong et al[88] have determined Sb, As, Ge, Pb and Sn by hydride generation coupled with DC-plasma in Atomic Emission Spec-

trophotometer (AES).

Hydrides may be decomposed by atomization technique other than the flame such as He or Ar plasmas, tube furnaces (electrically heated with or without use of H_2 diffusion flame, externally flame-heated, tube confined H_2 - O_2 or air flames) and a graphite furnace of the type used for EAAS.

3.2.2.2.3 ADVANTAGES OF AAS

Despite the numerous setbacks disccused earlier, the AAS has advantages over other methods. The main advantages include:

1) High sensitivity for wide range of metals, including many which are difficult or impossible to determine by flame photometry.
2) It is highly specific.
3) Any one metal can normally by determined in the presence of large amounts of other substances.
4) It is rapid and requires small sample volume.
5) The small amount of pretreatment and handling of samples normally minimizes the risk of contamination.

3.2.2.2 OTHER-METHODS

Other methods in use for the determination of arsenic include Atomic Emission Spectrocopy (AES), X-ray Fluorescence (XRF), Neutron Activation Analysis (NAA), Differential

Pulse Polarography, Anodic Stripping Voltametry and Isotope Dilution Mass Spectrometry. All these have detection limits in the nanogram range[82].

An enzyme method reported by Goode and Mathews[90] gave reasonable results in the 0.02 to 2.0mg/kg range. An Electron Spectroscopic method (ESM) with detection limit within the ppb range[94] and Direct Current Plasma Atomic Emission Spectrscopy (DCP-AES)[89] have also been reported.

CHAPTER 4

EXPERIMENTAL

This chapter describes the reagents used, the various methods and other auxilliary materials employed in this work. The chemicals and standards used in the experiments and mentioned in this chapter were obtained from BDH, London, and unless otherwise stated were all of analytical grade. They were used without further purification

4.1 CHEMICALS AND REAGENTS

Calgon solution: Prepared for particle size analysis. 50.0g of sodium hexametaphosphate was dissolved in distilled water and diluted to 1 litre.

Digestion accelerator: Prepared for the determination of total Nitrogen. 10g K_2SO_4, 1g $CuSO_4.5H_2O$ and 0.1g Selenium were mixed together.

Mixed indicator Used for the determination of Total Nitrogen. 0.13g of methyl red added to 0.066g methylene blue dissolved in 100ml 95% ethanol.

Silver sulphate solution: Prepared for the determination of Organic Carbon. 1.25g of Ag_2SO_4 was dissolved in 100ml conc. H_2SO_4.

Reagents A and B: Used for the determination of Total Phosphorus.

Reagent A: 12.0g of ammonium molybdate and 0.2908g of antimony potassium tartrate were dissolved in 250ml and 100ml distilled water respectively. The two solutions were added to 1000ml of 5M sulphuric acid in a 2 litre volumetric flask, mixed thoroughly and made to the mark. It was stored in Pyrex glass bottle in the dark.

Reagent B: 1.056g of ascorbic acid was dissolved in 200ml of reagent A. This reagent should be prepared as required as it does not keep for more than 24 hours.

Reductant solution: Used for the determination of total Arsenic. Prepared by dissolving 3% $NaBH_4$ in 1% NaOH.

4.2 SAMPLING

The sampling area, called the Kwabrafo-Pompo-Jimi network, forms part of the mineral concession of the Obuasi Goldmines. The Jimi is the major river in the catchment area with the Pompo river as its main tributary. The Kwabrafo stream joins the Pompo river at points M and N (see MAP 1).

The sampling points were selected to coincide with those of the Environmental Laboratory of the mines and cover the distance from the Upper Freshwater Dam (UFD) downstream to the Pompo Treatment Plant (PTP) and the Jimi river.

Fifteen (15) points were selected for sampling. These are Y, A, B, C, D, E , F, I, K and L. The remaining sampling points are R, M, N, O and P. Samples could not be collect-

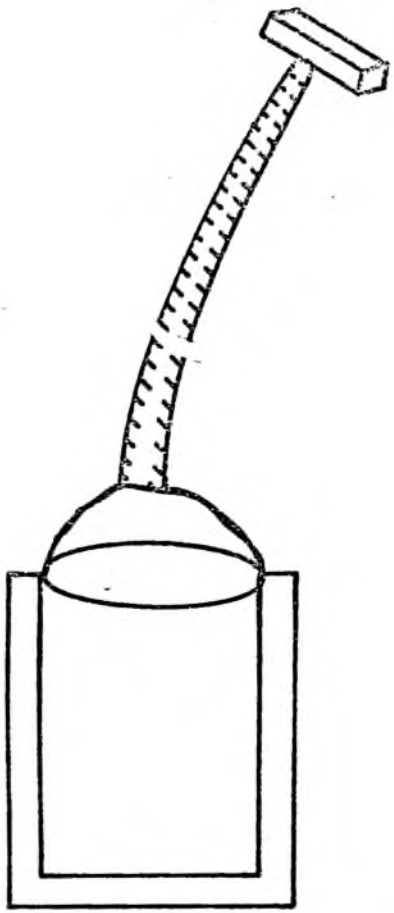


FIG. 3 WATER COLLECTION APPARATUS

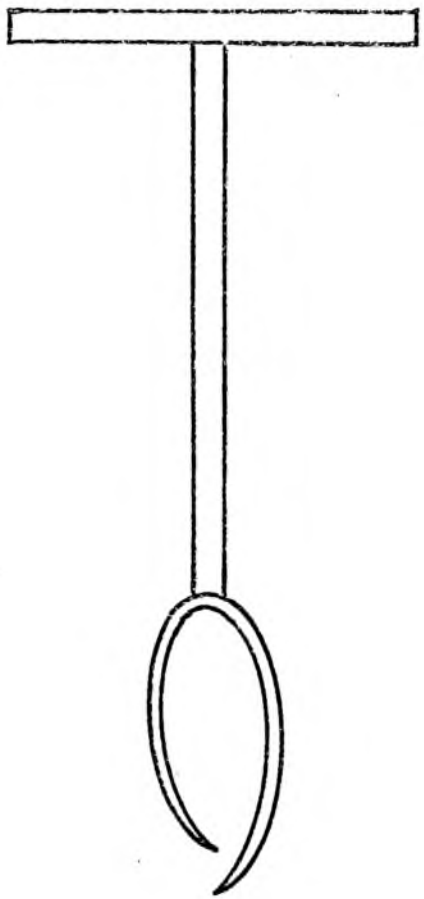


FIG. 4 DUTCH AUGER SAMPLER

ed from G, H, J and Q because they were either inaccessible or too deep. Periodically effluents from the PTP are discharged directly into the Kwabrafo stream through Point C.

Sampling was done on two occasions. The first sampling was from 5th - 6th November 1992 and the second one from 14th - 19th June 1993. Water samples were collected by using a plastic bottle with its cork tied to a long rope (fig. 3). The plastic bottle was fitted into a weighted bamboo stem which had a graduated rope attached to it. At the sampling point the apparatus was thrown into the stream. At a depth of 30cm below the water surface the rope tied to the cork was pulled to open the bottle for water to fill. The apparatus was then drawn out and the water poured into a preconditioned (see Appendix) 1-litre bottle to make it full. At each point three samples were taken.

Sediments were taken at the same points as the water samples using a Dutch auger sampler (fig. 4). At each point samples were taken from the surface and where possible some from a depth of about 30cm, this is because in the sediment trace metals are partitioned among various sinks.

4.3 SAMPLE TREATMENT

4.3.1 WATER SAMPLES

The water samples were filtered using a preconditioned Millipore filter unit equipped with a 0.45 µm membrane filter paper (GELMAN INSTRUMENT COMPANY, LONDON) and a

vacuum pump. The first 100 - 200ml was discarded. The membrane filter paper was replaced after the filtration of about 200ml of water. This was necessary because the pores of the membrane filter paper got blocked by particulate matter during filtration. Also the open end of the cup was covered with a Whatman filter paper to minimize contamination from the air. The filtrate was stored in a refrigerator at 10°C in the same polythene bottles used for sampling, but before this was done, the bottles were rinsed several times with deionized-distilled water and then with some of the filtrate.

4.3.2 SEDIMENT SAMPLES

The sediment samples were oven dried at a temperature of 40°C for 48 hours and ground. The grinding was done using a clean agate mortar and a pistil and sieved through 85 mesh sieve. They were then stored in polythene bags at room temperature in a clean cupboard. Portions of the finely ground samples were taken for the analyses.

4.3.3 TREATMENT OF SAMPLE CONTAINERS

In order to avoid contamination of samples for trace metal determinations during sampling, handling and storage, instrumental and working conditions are carefully selected.

Apart from the polythene bottles used in sampling and

storage, Pyrex glassware were used exclusively. The polythene bottles were cleaned with distilled acetone to remove grease and fat residues. They were then rinsed successively with deionised-distilled water, 10ml conc. HCl, then four times with water. Subsequently, dilute HCl (1:50) was introduced into them and left for two days at room temperature. They were then washed thoroughly with water and until needed, filled with acidified (0.01M HCl) water and stored.

In case of water samples, the bottles were washed several times with the water to be collected.

4.4 ANALYTICAL PROCEDURES

The following general procedures were used in the various determinations.

4.4.1 pH DETERMINATION[48]

The pH of the water samples and the sediment samples were determined using a Corning pH-meter and a Crison pH-meter respectively. The pH of the sediment was measured in water and in 0.01M KCl solution.

In water the pH of the sediment was determined by weighing 20g sediment sample into a 100ml beaker and 20ml of deionized distilled water added. The suspension was stirred for 30 minutes with a magnetic stirrer and allowed to stand for 30 minutes. pH measurement was made by dipping the glass electrode into the partly settled suspension after the pH

meter (Crison Ltd, London) had been calibrated with buffer solutions of pH 4.0 and 9.0 according to the manufactures directive.

In the case of 0.01M KCl 10g of sediment sample was weighed into a 50ml beaker to which were added 20ml of 0.01M KCl solution. The suspension was stirred for 30 minutes with a magnetic stirrer and allowed to stand for 30 minutes. The electrode was inserted into the partly settled suspension and the pH read off as indicated.

4.4.2 DETERMINATION OF REDOX POTENTIAL[92]

A 10g sample of sediment was suspended in 50ml water to give a ratio of 1 : 5 and stirred with a magnetic stirrer for 30 minutes. The suspension was then filtered clear by suction.

Redox potential measurements were carried out on the solution using a model 933.3 Bioblock Scientific conductivity meter regulated at 25°C. The conductivity cell consists of platinum and calomel electrodes connected to a voltmeter.

4.4.3 DETERMINATION OF ORGANIC CARBON

The determination was based on the method of Walkley and Black[48]. 1gm of sediment sample was weighed into a 250ml Erlenmeyer flask. With a pipette 10ml 1M $K_2Cr_2O_7$ solution were added into the soil in the flask and swirled gently to disperse the soil. 20ml conc. sulphuric acid were

then added to the content of the flask, swirled gently at first for 1 minute and then more vigorously afterwards for 2 minutes. The mixture was allowed to cool for 30 minutes after which were added 200ml deionized-distilled water, 10ml of orthophosphoric acid and finally 2ml barium diphenylamine sulphate indicator. The content was titrated against 0.2M ferrous ammonium sulphate solution until the colour changes to blue then to a green endpoint.

A blank titration was carried out in the same manner without the sediment sample. All determinations were carried out in triplicate.

$$\% \text{ Organic Carbon} = \frac{(10.0 - XM) \times 0.3}{W}$$

where X = volume (ml) of ferrous ammonium sulphate solution required for titration.

M = molarity of ferrous ammonium sulphate solution.

W = weight of soil sample.

For the calculation of percentage organic matter in the soil, the percentage organic carbon value is multiplied by the factor 1.724.

% Organic matter = % Organic carbon x 1.724.

4.4.4 DETERMINATION OF TOTAL NITROGEN

Kjeldahl method was employed in this determination[48]. 1gm of sediment sample was weighed into a 300ml Kjeldahl flask, 2ml deionized - distilled water were added to moisten

the sediment. 2gm of digestion acceleration mixture and 20ml of conc sulphuric acid were added. The mixture was heated for 2 hours until the digest became whitish. It was cooled, transferred with distilled water into a 100ml volumetric flask and made to the volume. 5ml aliquot was put into a Markham distillation apparatus, 5ml of 50% sodium hydroxide and 50ml of deionized-distilled water were added.

It was distilled and the distillate collected into 50ml of 2% boric acid to which had been added 2 drops of the mixed indicator solution. The distillate was titrated with 0.02M HCl from green to reddish end point.

The percentage Nitrogen was calculated using the formula:

$$\% N = \frac{0.02M \times V \times 100 \times 14}{W \times A \times 100} \times 100$$

where V = Titre volume (of HCl used)

W = weight of sediment used

A = volume of aliqout taken.

4.4.5 PARTICLE SIZE ANALYSIS

Day's method was adopted[93]. 40g of sediment sample was placed into a dispensing cup to which were added 100ml of Calgon solution and 400ml of distilled water. The soil suspension was agitated using a Klaxon electric mixer for 20 minutes to break down the soil aggregates.

The soil suspension was then transferred into a sedi-

mentation cylinder with the help of distilled water from a wash-bottle, and made to the 1 litre mark with distilled water. A plunger was inserted into the cylinder and moved up and down to mix the contents thoroughly and the time carefully noted with a stop watch. It was allowed to stand undisturbed and a hydrometer carefully dipped into the suspension. The hydrometer scale was read at the top of the meniscus exactly after 5 minutes and 5 hours to correspond to the weight of silt and clay per litre and the weight of clay per litre respectively.

Since hydrometer reading is affected by temperature, if the temperature of the solution deviated from 20°C it was corrected for by adding 0.3g of a unit for every one degree above 20°C, and 0.3g of unit subtracted from every one degree drop below 20°C.

The suspension was poured directly from the sedimentation cylinder onto 85 mesh sieve and the effluent discarded. The residue on the sieve was agitated thoroughly by running tap water into it directly from a rubber tube leading from the tap. When most of the fine material had been washed through the sand particles were transferred into an aluminum cup, dried in an oven at a temperature of 40°C to dryness and the weight recorded.

A blank was done in the same manner but without the soil sample. The blank reading was subtracted from soil sample readings.

Calculation of the percentage clay, silt and sand was done as follows:

$$\% \text{ Silt + Clay} = \frac{\text{corrected 5 min reading}}{\text{oven dry weight of soil}} \times 100$$

$$\% \text{ Clay} = \frac{\text{corrected 5 hour reading}}{\text{oven dry weight of soil}} \times 100$$

$$\% \text{ Sand} = 100 - (\% \text{ silt} + \% \text{ Clay})$$

4.4.6 DETERMINATION OF TOTAL PHOSPHORUS[94]

1gm of sediment sample was digested with a mixture of 10ml concentrated HNO_3 and 20ml $HClO_4$ for 2 hours until the solution appeared colourless and the dense white fumes of the perchloric acid ceased. The digest was cooled, diluted with distilled water and filtered through a Whatman filter paper into 100ml volumetric flask.

20ml of the filtrate were put in a cuvette, 2 drops of p-nitrophenol indicator added and 4M aqueous ammonia added dropwise until the solution turned yellow. 8ml of Reagent B were added, made to mark with distilled water and mixed thoroughly.

The intensity of the colour was measured at 660nm wavelength using a Spectronic 20 colorimeter.

Prior to sample measurement the Colorimeter was calibrated using phosphorus standards of 1ppm, 2ppm, 4ppm, 6ppm and 10ppm. A blank determination was also carried out. All measurements were done in triplicate.

4.4.7 FLAME PHOTOMETRIC DETERMINATION OF SODIUM AND POTASSIUM[48]

2.5g of sediment sample was digested with 100ml 1M HCl for 30 minutes. After cooling and diluting with deionized -distilled water it was filtered over a Whatman filter paper into a 250ml volumetric flask. The residue was washed with four-15ml portions of 0.1M HCl. The filtrate was cooled and diluted to the mark.

Portions of this were taken for measurement on a ANA-KL flame Photometer (Japan). A blank determination was carried out. All measurements were done in triplicate.

The flame photometer was calibrated before the measurement of the samples. For sodium the following standard solutions were used: 0.5ppm, 2.0ppm, 4.0ppm, 6.ppm, 8.0ppm and 10.0ppm. Standard solution used for the calibration of potassium were: 5.0ppm, 10.0ppm, 15.0ppm, 20.0ppm and 25.0ppm.

4.4.8 ATOMIC ABSORPTION SPECTROPHOTOMETRIC (AAS) MEASUREMENTS

Determination of the concentrations of the heavy metals Al, Fe, Mn, Au and As was done by AAS. For the Arsenic Hydride generation technique was employed. The principle and instrumentation have been dilated upon in Chapter 3.

This section therefore deals with instrumental conditions as well as calibration of the instrument.

For the water samples, measurement of Arsenic was per-

formed at the Environmental Laboratory of the Ashanti Goldfield Corporation (Gh) Ltd (AGC), Obuasi, using Smith-Hieftje 11/12 background correction AAS equipment. The sediments and all other measurements were carried out at Ghana Standards Board Laboratory (Headquarters), Accra, Using Perkin-Elmer 2280 AAS equipment.

Water Samples

For the measurement of Al, Mn, Fe and Au, the filtered water sample was directly aspirated into the Perkin-Elmer 2280 AAS equipment using individual hollow cathode lamps. The Parameters for the various elements were taken from the operation manual. Table 4 summarises these parameters.

For the Arsenic measurement aliquots of 1 - 5ml depending on the Arsenic level in the sample were put into a reaction cup and 10ml 1.5% HNO_3 added. Hydride generation was achieved using a Perkin-Elmer Atomic Vapour Accessory (AVA) operated manually. The system was flushed for 30 seconds with nitrogen at a flow rate of 2.5 l min^{-1}. About 5 - 10mls of sodium tetrahydroborate(III) solution were then delivered to the reaction cup and after a reaction time of 0.5min the volatile hydrides were flushed into the atom cell by nitrogen gas. The atom cell (quartz cell) assembly wa mounted on a 10cm one slot burner head and heated by the standard air -acetylene flame. The absorbance was then read from the readout display.

Table 4: ANALYTICAL CONDITIONS FOR THE AAS MEASUREMENT OF As, Al, Fe, Mn, Au.

ELEMENT	WAVELENGTH (nm)	SLIT WIDTH (nm)	BURNER HEAD	FLAME	FLAME FLOW RATE		LIGHT SOURCE	LAMP CURRENT (mA)	LINEAR RANGE
					FUEL	OXIDANT			
Arsenic	193.7	0.7	10cm (1 slot)	C_2H_2,Air	20	50	HCL	16	50ng
Aluminum	309.3	0.7	5cm (1 slot)	C_2H_2,N_2O	45	30	HCL	25	100.0ppm
Manganese	279.5	0.2	10cm (3 slot)	C_2H_2,Air	30	50	HCL	20	2.0ppm
Iron	248.3	0.2	10cm (3 slot)	C_2H_2,Air	30	50	HCL	30	2.0ppm
Gold	328.1	0.7	10cm (3 slot)	C_2H_2,Air	30	50	HCL	10	40.0ppm

Sediment Samples

a) Determination of Arsenic

1g sediment sample was digested with 8ml of H_2SO_4/HNO_3 (1:1). The mixture was heated on a sand bath for 30 minutes until the acid fumed. The beaker was rotated gradually during heating to prevent caking of the acid-soil mixture. Heating was continued with rotation at intervals until the soil became light grey in colour i.e. when all the organic matter had been oxidized. 8ml of 70% $HClO_4$ were added and the digestion continued for 1½ hours after which the acid-soil mixture became almost white. The digestate was diluted and filtered over Whatman filter paper into a 100ml volumetric flask and diluted to the mark with deionized-distilled water. Aliquots of 1 - 5ml of this solution was used for As determination as described above. All determinations were done in triplicate.

The atomic absorption spectrometer was calibrated and the calibration checked before measurement involving the unknowns. A standard arsenic solution containing 0.001ppm As gave an absorbance of 0.52 when measured, as was obtained from the calibration curve.

Distilled water (arsenic free) was aspirated into the flame after the measurement of each sample in order to remove all traces of this sample before proceeding to the next solution.

The total arsenic concentrations of the sample solutions were calculated using the following equation:

$$\text{Total Arsenic Concentration} = \frac{Asp \times Vstd \times Cstd \times Vd}{Astd \times Va} \times Vp$$

where Asp = Absorbance of sample solution

Astd = Absorbance of standard solution

Cstd = Concentration of standard solution

Vstd = Volume of standard solution

Vd = Dilution volume (sample solution)

Va = Volume of aliquot taken

Vp = Volume of sample prepared

In the above calculation:

Astd = 0.52

Cstd = 0.001ppm

Vstd = 10ml

Vd = 100ml

Vp = 100ml.

b) Determination of Fe, Al and Mn by the dithionite-citrate Method[95]

1g sediment sample was weighed into a 50ml centrifuge tube. 25ml sodium citrate solution and 0.4g of dithionite were added. It was stoppered and fixed in a shaker (GRIFFIN, LONDON) and shaken overnight. It was centrifuged for 15 minutes at a rate of 500rpm and then filtered to remove suspended materials and stored in a plastic vial pending analysis by AAS.

An air-acetylene flame is suitable for the determination of Fe and Mn and a nitrous-oxide - acetylene flame for Aluminium.

Calibration curves were plotted for the various elements from which the concentrations of the unknowns were determined from their measured absorbance.

c) Determination of Gold

1g of sediment sample was digested with 10ml aqua regia (3HCl : $1HNO_3$) for 1½ hours until no brown fumes evolved. It was diluted with distilled water and filtered over Whatman filter paper, the residue washed with 10ml deionized-distilled water and the filtrate collected.

Excess 6M NaOH solution were added to the filtrate to precipitate any Fe (III) present. It was filtered and washed as above. The filtrate was acidified to pH 1.50 with 6M HCl using a pH meter. The filtrate was extracted with 4-methyl pentan-2-one (methyl isobutyl ketone, MIBK).

Prior to sample measurements the AAS was calibrated using gold standards of concentrations 0.2ppm, 0.4ppm, 0.6ppm, 0.8ppm and 1.0ppm. These prepared standards were extracted into MIBK and aspirated after the equipment had been set to the manufacturers specification (see table 4). A blank of MIBK was aspirated before the organic phases (samples). All measurements were done in triplicate. The Measurement was done using 2280 Perkin-Elmer AAS equipment.

4.4.9 LEACHING OF ARSENIC

At the time of sampling AGC had curtailed the discharge of effluents from the Pompo Treatment Plant (PTP) into Kwabrafo stream. Also with the installation of the Arsenic Recovery Plant in July 1992 virtually no AsO_3 is discharged into the atmosphere. It is therefore of interest to find out how long it will take for the high As concentration of the sediment to decrease to acceptable levels, if the environment is left on its own. For that reason sediment samples were leached for several weeks with deionized-distilled water (pH 6) and simulated river water containing 3.0ppm Al, 1.0ppm Mn and 1.5ppm Fe. The solution was prepared by taking 3.0ml of a 1000ppm Al, 1.0ml of a 1000ppm Mn solution and 1.5ml of a 1000ppm Fe solution and diluting to 1000ml.

Two methods were employed for the leaching:

In METHOD A the experiment was carried out by suspending 2.0g of sediment sample in 100ml deionized-distilled water (pH 6) in 150ml plastic bottle. After stirring for 30 minutes

the suspension was allowed to stand undisturbed at room temperature. 1ml portions of the clear supernatant water were taken for total As measurement on weekly basis. Portions for measurement were filtered over a Millex-FG_{50} unit (MILLIPORE, USA).

In the METHOD B the experiment was set up in the same manner as indicated above for method A, but after each sampling the leachant was decanted from the sediment and replaced with a fresh one.

Determination of total As was done as described earlier in this chapter. The AAS was calibrated using As standards of 10.0ppb, 25.0ppb, 50.0ppb and 75.0ppb. and 100ppb. All measurements were done in triplicate.

4.5 REPRODUCIBILITY

All the determinations were done in triplicate. To ascertain the precision of the various measurements, however, some of the samples were randomly selected and the experiments with them repeated five times. From these the mean, standard deviation and the coefficient of variation are calculated. The reproducibility was checked from time to time during the analyses.

For the total arsenic, samples from points R, B, B30cm, D and N were selected. Heavy metal analysis were performed on the same samples.

Samples for the various leaching tests were selected

from points Y and B30cm. The results are reported in tables 17 and 18.

CHAPTER 5

RESULTS AND DISCUSSION

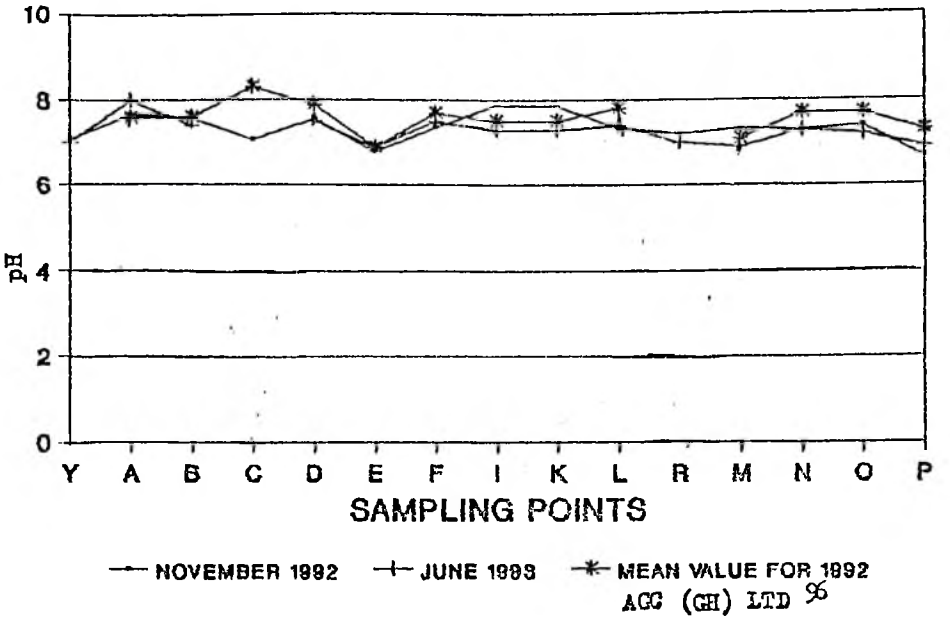
The discussion of the experimental results is divided into two parts:

1) Water 2) Sediments.

5.1 WATER

The Gyimi and its tributary, the Pompo, are the major rivers in the catchment area of the mineral concession. At the Pompo Treatment Plant (P.T.P.), effluents from the mines are sometimes discharged directly into the Kwabrafo stream (Map 1) which joins the Pompo stream between the sampling points L and N.

The pH of the natural water is affected by the presence of such inorganic species as hydroxides, carbonates, bicarbonates, ammonium, silicates and phosphates which tend to increase the pH. The presence of carbon dioxide, oxides of sulphur, nitrogen and the halides, the presence of un-ionised portion of weakly ionizing acids like carbonic and tannic acids as well as hydrolysing salts like ferrous salts lower the pH[97]. Water with low pH can cause action on rock structure and also leach ions from the soil to appreciable extent to cause undesirable amounts in the water[98]. Water with high pH redissolves amphoteric metals for example aluminium and lead[98]. The pH values for the water are presented in Table 5 and illustrated graphically in Fig 5.



ACC (GH) LTD 96

FIG.5: COMPARISON OF pH VALUES FOR THE VARIOUS SAMPLING POINTS

These are mean values of three determinations.

TABLE 5: pH of the water samples collected in November 1992 and June 1993 compared to values obtained by AGC (Gh) Ltd

SAMPLING POINTS	NOV. 1992	JUNE 1993	MEAN VALUES FOR 1992 AGC(GH) LTD(96)
Y	7.08	7.00	N.A.
A	7.66	8.00	7.60
B	7.58	7.40	7.60
C	7.07	N.A.	8.30
D	7.56	7.50	7.90
E	6.80	6.90	6.90
F	7.37	7.50	7.70
I	7.88	7.30	7.50
K	7.86	7.30	7.50
L	7.34	7.40	7.80
R	7.20	7.00	N.A.
M	7.33	6.90	7.10
N	7.30	7.30	7.70
O	7.40	7.20	7.70
P	6.65	6.90	7.30

N.A. - value not available.

Generally, the pH of the water is slightly above 7 at most points, with little variations. The highest pH value (for the 1992 collection) is 7.88 (Point I) and the lowest value is 6.55 (Point P). These values obtained compare favourably with the mean pH values recorded by the Environmental Laboratory of the Ashanti Goldfields Corporation (Gh) Limited for year 1992.

At these pH values heavy metals such as iron, aluminium, manganese etc. are known to form various hydrous compounds which can affect the As concentration due to their ability to adsorb and co-precipitate arsenic.

The As concentration of the water samples are presented in Table 6.

TABLE 6: Mean concentration of As in the water samples

SAMPLING POINTS	CONCENTRATION (ppm) NOVEMBER 1992 COLLECTION	JUNE 1993 COLLECTION
Y	7.56	0.40
A	5.51	0.13
B	3.00	4.00
C	20.00	N.A.*
D	9.46	4.00
E	9.60	1.45
F	7.29	1.71
I	5.64	1.97
K	6.41	1.97
L	6.67	2.76
R	0.00	0.00
M	0.35	0.00
N	5.10	1.84
O	3.50	1.58
P	2.00	0.40

* No sampling was done at this point

There is great disparity between the two sets of values; the Nov. 1992 set has invariably the higher values. This is probably due to the fact that the discharge from the PTP into the Kwabrafo stream and which accounted for the high arsenic levels in the water was stopped shortly after the November 1992 sampling. The effluent was recycled for use in the running operations of the PTP in a mechanism known as 'zero effluent sumps' devised to treat all waste water[2].

At both sampling periods no detectable As was found at

Point R on the Pompo stream. This is expected because Point R is a village called Mampamhwe about 14 kilometers east of Obuasi and so well out of the general north-westerly wind direction. The zero As content at Point R is also accounted for by the fact that the Pompo is flowing downstream from a distance of about 14 kilometers before it meets the Kwabrafo, the most polluted stream in the catchment area. Even though there is mixing of the two streams, it can be argued that the rate at which Arsenic is diluted in the Pompo far exceeds the rate at which As diffuses upstream. This is further supported by the fact that Point M at a distance of about 2 kilometers downstream the Kwabrafo stream has the lowest As concentration of 0.35ppm (November 1992 collection) and zero Arsenic content (June 1993 collection) respectively.

The arsenic concentrations of points Y, A and B above the entry Point of the PTP (Point C) as expected are relatively low. Here As contamination is probably due to arsenic fallout on the vegetation and rain-washed into the dam. Also contamination could be due to erosion and weathering of rocks and soils. At the PTP the As concentration increases dramatically to 20.00ppm, decreases sharply to a value of 9.49ppm (Point D) and 9.60ppm (Point E) and decreases gradually downstream to a value of 2.00ppm (Point P). This decreasing trend is corraborated by values obtained by the Environmental Laboratory of the AGC (GH) Ltd. in table 7.

TABLE 7: The concentration of As in the water samples analysed by the Environmental Laboratory AGC(GH) LTD[96]

SAMPLING POINTS	CONCENTRATION (PPM) MEAN VALUES 1992	MAY 1993	JUNE 1993
Y	N.A.	< 0.02	0.40
A	2.00	1.10	0.13
B	2.30	4.70	4.00
C	35.00	189.00	N.A.
D	13.00	18.20	4.00
E	9.60	< 0.02	1.45
F	7.30	3.10	1.71
I	6.20	4.70	1.97
K	6.20	4.40	1.97
L	6.60	4.90	2.76
R	--	--	--
M	0.23	< 0.02	0.00
N	4.90	4.00	1.84
O	4.10	3.30	1.58
P	1.50	< 0.02	0.40

Note: 1) No analysis was done at point Y in 1992.
2) There was a leakage from the PTP in May 1993 hence the very high value for Point C.

This trend may be the result of dilution and possibly sorption[99]. Arsenic sorption is known to be supported by hydrous oxides such as $Al(OH)_2^+$, $Fe(OH)_2^+$ and $Mn(OH)_2^+$ which is probably present at the prevailing pH. Arsenic ions interact with these active water components and the interaction normally may be between the positive charges on the $Al(OH)_2^+$ and $Fe(OH)_2^+$ groups as well as protonated doubly coordinated hydroxyl groups with arsenic ions. Hydrous oxides and alumo-silicate clays in suspension may contribute to arsenic sorption through surface reactions[99] such as

$$M\text{-}OH + H_2AsO_4^- \rightleftharpoons M\text{-}HAsO_4^- + H_2O$$

Sorption sites may be activated in acid media by the reaction:

$$M\text{-}OH + H^+ \rightleftharpoons M\text{-}OH_2^+$$

$$M\text{-}OH_2^+ + H_2AsO_4^- \rightleftharpoons M\text{-}H_2AsO_4 + H_2O$$

So sorption will be expected to decrease with increasing pH. Beyond pH 10 sorption process becomes less significant[99]. However, sorption due to Ca^{2+} ions is known to predominate at higher pH (pH > 11) as a result the formation of the stable $Ca_3(AsO_4)_2$ which determines the sorption of As.

The concentration of heavy metals Al, Fe and Mn believed to influence As sorption are presented in Table 8.

TABLE 8: The mean concentration of heavy metals in the water samples

SAMPLING POINTS	MEAN CONCENTRATION (ppm)							
	Mn		Al		Fe		Au	
	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993
Y	0.02	0.04	0.45	0.75	0.14	0.20	0.10	0.20
A	0.08	0.12	1.13	1.10	0.16	0.30	0.30	0.35
B	1.20	1.10	1.16	1.55	0.20	0.25	0.10	0.15
C	1.02	0.90	3.83	2.90	0.34	0.30	0.10	0.20
D	0.58	0.75	1.08	1.10	0.14	0.20	0.20	0.30
E	0.12	0.30	2.00	2.25	0.13	0.30	0.15	0.20
F	0.14	0.20	2.34	3.10	0.22	0.20	0.10	0.35
I	0.52	0.90	3.30	2.90	0.34	0.45	0.20	0.22
K	0.47	0.65	1.53	1.70	0.16	0.20	0.20	0.25
L	0.45	0.50	2.73	2.70	0.07	0.10	0.15	0.20
R	0.02	0.05	2.00	2.20	0.55	0.50	0.00	0.00
M	0.02	0.15	1.00	1.10	0.24	0.35	0.10	0.10
N	0.19	0.40	2.93	2.95	0.20	0.20	0.10	0.20
O	0.42	0.35	2.28	3.90	0.18	0.35	0.20	0.21
P	0.04	1.10	0.55	0.75	1.26	2.00	0.10	0.15

These metals form complexes with As compounds in aqueous systems between the pH range of 4.0 - 7.8[55]. The complexes formed include $AlAsO_4.2H_2O$, $FeAsO_4.2H_2O$ and $Mn_3(AsO_4)_2$. It can therefore be argued that at the prevailing pH these are the probable species responsible for As removal from the streams.

Another factor that may explain the decreasing trend of As concentration is the self-cleansing action of water. Water has a self-cleansing mechanism not only for As but also for a number of other metals. Arsenite and arsenate form insoluble salts with cations (usually Fe) that are dissolved or suspended in water, these particles gradually settle onto the sediment[74] thus increasing the As content of the sediment.

With the exceptions of Points R (0.00ppm) and M (0.35ppm) the arsenic concentrations for all the sampling points are above 0.50ppm which is the WHO International Standard for drinking water, and water for agricultural purposes and production of aquatic life of 1.00ppm[103].

Among the other metals determined was gold (Table 8). The values obtained are relatively low, the highest being 0.35ppm. Gold was measured to find out if the values obtained could form the basis for exploration from the sediments.

5.2 SEDIMENTS

Seventeen (17) sediment samples were collected, eleven (11) of the samples were collected at the surface of the river bed and six (6) were collected at an average depth of 30cm from the surface.

The pH values in water and 0.01M KCl solution are presented in Table 9. As expected[8], all the pH values measured in KCl solution are lower than the pH values measured in distilled water.

The pH (0.01M KCl) for most sampling points is around 6 ranging from 4.62 to 6.90. The following figures gleaned from several sources[68] show that the pH of submerged soils and sediments and their interstitial solution is about 7:

Submerged Soils:	6.7 - 7.2
Solutions of Submerged Soils:	6.5 - 7.0
Freshwater Sediment:	6.0 - 7.0
Sea Sediment:	6.2 - 7.7
Marsh Soils:	5.0 - 7.0

Comparison of the pHs of water and sediments indicate that the pH values of sediments are lower than those of the corresponding waters. Biney[101] found similar results for freshwater and coastal ecosystems in Southern Ghana. No clear pattern could be identified in the differences between the pH of sediments both in water and KCl and that of the water. This may be explained by the differences in the composition of sediments from different areas over which the

TABLE 9: The mean pH in water and 0.01M KCl solution and the Eh of the sediment samples

SAMPLING POINTS	pH (H_2O)		pH (KCl)		Eh (V)	
	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993
Y	5.12	5.22	4.90	4.92	0.10	0.09
A	6.50	6.54	5.47	5.46	0.15	0.14
B	7.72	7.69	6.38	6.36	0.10	0.10
B30cm	5.36	5.30	4.62	4.60	0.20	0.11
D	6.86	6.84	6.05	6.06	0.10	0.12
F	7.04	7.03	6.65	6.67	0.30	0.29
F30cm	6.84	6.85	6.54	6.55	0.20	0.21
I	7.46	7.44	6.44	6.42	0.15	0.14
I30cm	6.75	6.70	6.25	6.20	0.10	0.12
K	6.58	6.56	6.50	6.51	-0.10	-0.11
K30cm	6.84	6.86	6.74	6.75	-0.15	-0.16
L	6.75	6.74	6.22	6.20	0.35	0.35
L30cm	6.59	6.60	6.40	6.40	0.20	0.22
M	6.50	6.52	6.10	6.11	0.40	0.41
M30cm	5.89	5.91	5.52	5.50	0.30	0.29
N	6.89	6.85	6.21	6.22	0.20	0.18
R	7.50	7.49	6.90	6.91	0.25	0.24

streams flow. Thus while the sediment at Point Y is acidic (4.99) the water in contact with the sediment at that point is neutral (7.08).

Soil redox potential (Eh) is affected by the pH of the soil. According to Ponnamperuma et al[68] the Eh of reduced soil solutions ranges from 0.2 to 0.0V and rarely drops below -0.05V. By contrast, reduced soils, lakes and oceans muds give potentials of 0.00V to 0.03V with occasional plunges to values as low as -0.4V. High positive Eh values are characteristic of oxidizing conditions while low and negative Eh values are found in reducing environment.

The redox potential of the sediment ranges between -0.10V to 0.40V (Table 9). From Table 9 the Eh values of samples taken at the surface are relatively higher than at a depth of 30cm, the only exceptions being points B and B30cm, where their values are 0.10V and 0.20V respectively. From the values obtained it can be said that reducing conditions prevail in the sediments. Conditions in which an Eh of less than 300mV may occur, for example, during flooding, favour the reduction of arsenate, in which case arsenite content becomes significant.

The total As concentration of the various points are presented in Table 10. In general the concentration of As in the sediment is far greater than those of the water. This is expected because of the self-cleaning ability of water for arsenic and a number of other metals. Arsenate and arsenite from insoluble precipitates with Fe, Ca, Al, Pb and Mn compounds found in natural waters. They may also get adsorbed or coprecipitated onto clay particles[19] hence increasing the concentration in the sediment.

TABLE 10 The mean concentration of Arsenic in the sediments

SAMPLING POINTS	MEAN CONCENTRATION (PPM)	
	NOV. 1992 COLLECTION	JUNE 1993 COLLECTION
Y	15.38	16.00
A	17.31	15.50
B	20.81	21.65
B30CM	48.08	47.50
D	50.00	48.50
F	45.61	42.60
F30CM	38.94	37.90
I	25.48	27.90
I30CM	22.12	21.40
K	43.75	40.30
K30CM	38.46	37.30
L	34.14	32.50
L30CM	29.33	28.70
M	24.04	23.62
M30CM	17.79	15.61
N	33.65	43.80
R	2.00	2.10

The arsenic content for the samples for both sinks range from 2.00ppm (Point R) to 50.00ppm (Point D) with coefficients of variation below 3% (see table 11).

Table 11. Reproducibility of the total As-concentration

SAMPLE	CONCENTRATION (ppm)	x	±	σ	CV (%)
R1	1.92				
R2	2.02				
R3	1.92				
R4	1.92				
R5	1.83	1.92		0.06	3.3
B1	20.57				
B2	20.57				
B3	20.49				
B4	20.48				
B5	20.60	20.53		0.06	0.3
B30-1	46.15				
B30-2	46.15				
B30-3	46.25				
B30-4	46.35				
B30-5	46.15	46.21		0.05	0.1
D1	47.40				
D2	47.30				
D3	47.40				
D4	47.40				
D5	47.30	47.36		0.05	0.1
N1	32.96				
N2	32.71				
N3	32.68				
N4	32.68				
N5	32.67	32.69		0.02	0.06

Comparing the range of 2ppm to 5ppm recommended for uncontaminated soils[14] with the above range of 2.00ppm to 50.00ppm, it can be said that the sediments contain considerable amounts of arsenic which is likely to pose toxicity problems should inhabitants consume fishes and other food materials in and around the streams. Such high values can be attributed to the constant befoulding of the Obuasi environ-

ment by the smoke and other effluents from the gold treatment plant since no meaningful amounts of arsenic containing pesticides or weedicides are used in the area for farming purposes. In addition the mountains of tailing heaped in the catchment area are constantly washed into the streams which makes the river bed rich in tailings, reaching beyong a depth of 30cm at some points. This is evidenced by the fact that the lowest value of As was obtained at Point R (Mampamhwe, 14 kilometers away) where there is no arsenic contamination of the water. It has been reported that agricultural soils with known history of As pesticide or herbicide application may contain more than 550ppm of As[19]. Another observation is that the As concentration decreased with distance away from the treatment plant at the PTP for both sampling periods.

Comparing the November 1992 results with that of the June 1993, it can generally be said that for most sampling points the values of November 1992 are higher than the June 1993 values. This trend may be attributed to the fact that at the time of sampling (June 1993) discharge of effluents from the PTP into the Kwabrafo stream, had been stopped about six months earlier (in January). It can be argued that the arsenic had been washed with other materials into the stream and carried away.

In sediments, trace metals are partitioned among various sinks; this partitioning depends on such physicochemical variables as the nature and concentration of ligands in

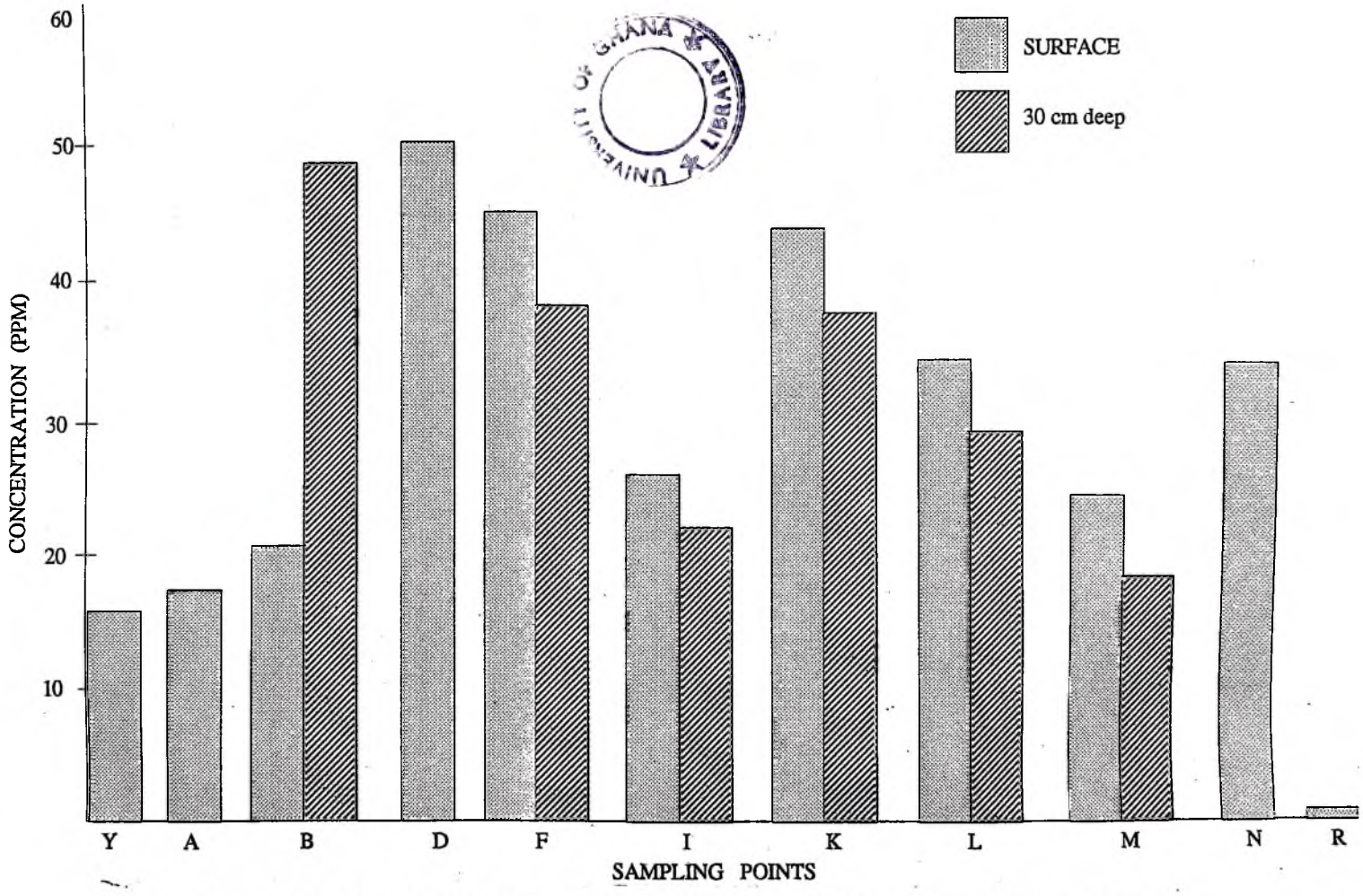


FIG 6: COMPARISON OF ARSENIC IN THE SEDIMENT AT VARIOUS SINKS (i. e. Surface and 30 cm deep)

the water, the nature and concentration of solid substrate, the pH and the redox potential[6]. Sampling of As was therefore done at two sinks – at the surface and at 30cm deep.

At Y, A, D, N and R only surface samples could be taken because the streams were too deep and dangerous. The variation of arsenic in the various sinks is illustrated in Fig. 6. At the points where samples were taken from both sinks, the surface invariably had the higher As concentration. Earlier studies carried out in some mining areas of Ghana gave similar results[5]. The very high values at points B and D reflect the effect of discharge from the PTP (Point C where no sample could be collected for lack of sediments).

Factors known to influence As availability and mobility are soil texture, organic matter contents, concentration of hydrous oxides of Fe and Al, soil pH, Mn and P conentrations.

Clay minerals are products of rock weathering and have marked effects on both physical and chemical properties of soils. Their contribution to soil chemical properties results from their comparatively large surface area, and permanent surface negative charges. The soil textural class is dependent on the percentages of clay, silt and sand-sized particles. Clays rarely occur in pure form in soils, they usually have humic colloids and hydrous oxide precipitates linked to them. It is known that As has a slow downward mobility especially when the sediment has high clay

content(19), that is sandy or low clay soils have less affinity for arsenic and hence As becomes more mobile. Table 12 shows the percentages of clay, silt and sand fractions of the various samples, whiles Table 13 shows the mean concentrations in the sediments

TABLE 12: The mean percentage composition of clay, silt and sand in the sediment

SAMPLING POINTS	% CLAY		% SILT		% SAND	
	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993
Y	35.39	34.75	15.79	16.58	46.18	45.94
A	30.13	28.20	13.16	15.20	49.80	48.90
B	32.50	33.00	18.42	17.56	49.21	49.78
B30cm	40.40	40.60	18.40	19.20	43.82	42.15
D	41.50	39.65	26.30	28.00	29.40	30.28
F	38.30	36.96	23.08	24.25	36.00	39.00
F30cm	37.76	38.82	15.79	16.80	46.32	46.90
I	23.97	23.50	12.82	13.10	63.08	62.65
I30cm	22.50	22.95	7.69	10.35	60.40	57.50
K	42.10	39.80	10.56	11.50	46.56	48.40
K30cm	41.92	40.15	20.51	19.40	31.30	32.75
L	27.87	26.48	10.52	12.75	55.70	54.62
L30cm	27.60	27.90	13.20	14.00	60.40	58.74
M	35.10	32.75	31.60	28.32	34.90	40.10
M30cm	27.20	26.55	23.70	22.90	48.70	49.85
N	32.50	33.15	26.30	23.40	38.50	40.95
R	40.40	38.95	21.10	20.87	35.60	37.20

TABLE 13. The mean concentration of heavy metals in the sediment samples

SAMPLING POINTS	MEAN CONCENTRATION (ppm)							
	Mn		Al		Fe		Au	
	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993
Y	0.017	0.028	63.50	59.10	1.00	1.25	0.60	0.67
A	0.805	0.910	31.25	30.75	1.38	1.40	0.60	0.50
B	1.160	1.350	58.50	55.10	1.06	1.75	0.65	0.75
B30CM	1.105	1.215	51.50	49.15	0.90	0.80	0.25	0.45
D	0.900	1.000	42.00	43.50	1.40	1.75	0.40	0.58
F	1.050	1.175	67.25	62.10	1.76	1.80	0.65	0.60
F30CM	0.550	0.750	22.00	22.20	1.26	1.30	0.20	0.30
I	0.340	0.320	80.00	79.52	1.14	1.34	0.50	0.75
I30CM	0.270	0.300	68.00	67.50	1.00	1.20	0.40	0.50
K	0.750	0.800	28.10	28.20	1.66	1.55	0.55	0.65
K30CM	0.440	0.475	34.75	35.00	1.26	1.30	0.20	0.35
L	0.670	0.550	42.70	43.10	1.10	1.25	0.80	0.82
L30CM	0.410	0.510	48.50	49.10	1.00	1.15	0.56	0.67
M	0.300	0.400	25.00	25.60	1.52	1.75	0.40	0.45
M30CM	0.230	0.350	40.50	39.90	1.06	1.20	0.30	0.40
N	0.880	0.955	54.00	55.10	1.40	1.50	0.89	1.00
R	0.950	1.115	40.50	40.90	0.96	1.00	0.70	0.89

There is considerable amount of clay in the sediment ranging between 22.50% - 41.92% indicating a probable slow downward mobility. Mobility, however, does not depend only

on the amount of clay content present, but also on the type of clay. Even though a clay may be present in small quantities yet its adsorptive capacity may be high and ionic mobility will be low[102].

An inspection of Table 13 reveals that generally surface samples have higher Al, Fe and Mn values than samples taken at 30cm depth. At the prevailing pH these metals form hydroxo compounds (in aqueous medium) which are able to complex with As compounds and precipitate out of solution hence increasing the As concentrations at the surface. The same effect would discourage the downward mobility of As.

Soils contain organic matter and nutrients, although the amount and type vary considerably, table 14. Colloidal soil organic matter has a major influence on the chemical properties of soils. Organic matter is classified into 'non-humic' and 'humic' substances[8]. It mainly consits of amino acids, carbohydrates, organic acids, fats and waxes, with a wide variety of functional groups including carboxyl, carbonyl, phenolic hydroxyl, ester and possibly quinone and methoxy groups[8], available for bonding with As species. Downward migration is greatly limited due to strong sorption of As on organic matter[103], a factor that increases the retention time of As. This factor contributes to the slow downward mobility of As, hence the higher content of As at the surface.

TABLE 14: The concentration of nutrients in the sediment samples

SAMPLING POINTS	% N		% ORGANIC C		P_2O_5 (ppm)		K (ppm)		Na (ppm)	
	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993	NOV. 1992	JUNE 1993
Y	2.208	2.500	2.21	2.50	4.00	3.90	6.60	8.10	2.80	8.20
A	3.384	3.492	3.38	3.20	2.55	3.00	1.90	2.15	7.50	9.10
B	2.784	2.810	2.78	2.00	5.00	4.90	3.60	4.10	7.12	6.50
B30cm	3.012	2.950	3.01	4.10	3.25	4.10	2.30	2.10	7.45	7.35
D	3.180	3.310	3.18	2.90	3.00	3.20	2.90	3.40	8.25	7.90
F	3.492	3.480	3.49	2.58	2.70	2.90	3.20	3.00	8.12	9.20
F30cm	3.504	3.715	3.50	3.40	3.00	3.15	2.80	2.65	8.25	9.00
I	2.172	2.300	2.70	2.90	2.90	3.10	2.60	3.10	7.60	7.95
I30cm	2.088	2.218	2.90	3.50	4.15	3.85	2.90	2.60	8.12	8.30
K	2.016	2.235	2.02	1.75	3.10	3.50	4.80	4.45	21.50	24.10
K30cm	2.256	3.100	2.26	3.10	3.50	3.80	6.30	6.95	23.50	22.50
L	2.220	2.110	2.22	2.10	4.50	4.00	3.30	2.50	7.80	7.70
L30cm	2.928	3.215	2.93	2.80	5.60	6.10	2.70	3.20	7.60	7.10
M	3.996	4.105	4.00	4.15	5.00	4.85	1.50	2.00	7.85	6.95
M30cm	3.960	3.655	3.96	3.80	5.56	6.00	1.30	2.70	7.55	8.10
N	3.216	4.216	3.22	3.10	4.00	3.80	2.20	3.20	8.25	8.50
R	4.500	5.000	3.10	3.30	2.80	3.00	3.50	2.95	10.20	9.90

5.3 LEACHING OF ARSENIC

The results of the leaching experiments are presented in tables 15, 16, 17 and 18. The values indicate that generally very little amount of arsenic was leached from the sediments by distilled water. The results show further that in the static method (table 15) the rate of arsenic leaching at the initial stages was high, but this decreased rapidly in subsequent weeks. The fraction of arsenic leached however remained very small, generally far under 1% in most cases even after 20 weeks of leaching (table 16). This is also illustrated graphically in fig 7.

TABLE 15: Cumulative rate of leaching of arsenic in deionised-distilled water

TIME (WEEKS)	LEACH RATE (ppb/wk)															
	Y	A	B	B30CM	D	F	F30CM	I	I30CM	K	K30CM	L	L30CM	M	M30CM	N
1	11.00	12.00	41.70	20.80	38.90	48.60	32.00	30.60	32.00	24.00	26.40	41.70	31.90	16.60	4.00	32.00
2	4.00	5.70	8.80	8.60	3.60	2.40	4.00	9.10	3.50	5.00	4.10	2.50	3.60	3.60	5.50	2.00
3	3.50	1.80	3.50	6.55	3.00	3.00	2.00	4.30	1.50	6.50	1.50	4.70	5.00	1.80	1.70	2.10
4	3.50	3.30	4.10	2.05	5.00	6.20	8.00	2.85	12.50	1.85	3.45	0.40	4.50	1.90	4.30	2.50
5	4.00	4.30	3.10	2.80	2.40	2.60	1.00	6.15	6.10	3.60	1.45	5.90	4.10	2.00	1.50	3.40
6	3.90	1.55	5.10	1.40	3.75	1.10	2.20	3.00	2.30	3.05	2.20	0.90	2.50	1.10	4.95	1.60
7	2.55	1.95	2.70	3.60	4.25	1.45	6.40	1.90	2.10	4.10	4.15	0.80	2.00	2.30	1.05	2.70
8	4.65	2.80	1.00	5.10	3.60	2.09	2.20	2.00	2.30	5.90	2.85	2.80	4.30	3.30	1.60	1.20
9	2.80	5.25	5.09	7.80	2.40	2.01	6.20	6.30	2.00	4.10	1.30	2.30	1.10	3.60	2.10	1.50
10	5.20	1.25	3.20	1.20	2.50	7.85	1.00	2.70	2.40	1.10	1.60	2.90	8.35	1.10	0.20	4.40
11	1.70	2.95	3.95	2.05	1.85	2.60	2.10	2.30	2.20	4.20	4.60	2.80	1.00	2.00	0.10	0.60
12	2.20	1.45	0.15	0.85	1.75	0.20	1.10	3.00	1.60	1.60	0.30	3.00	1.55	6.20	0.90	0.20
13	1.10	0.10	1.80	0.20	2.90	0.90	0.80	2.40	3.10	3.05	2.45	3.40	2.50	2.00	1.20	2.20
14	0.80	2.45	2.80	1.45	4.10	1.00	0.20	0.40	3.40	2.48	1.00	0.80	2.60	1.80	6.30	2.10
15	0.02	6.15	0.25	0.45	2.10	2.10	0.20	1.20	2.30	0.80	1.10	0.10	1.00	0.10	0.60	3.90
16	3.60	1.00	1.85	1.30	0.35	0.20	3.10	1.90	1.40	0.30	0.45	0.15	0.40	0.20	1.00	1.90
17	3.50	0.10	0.50	0.20	0.45	0.66	0.50	0.40	1.75	0.40	0.10	0.75	0.50	0.25	0.40	2.10
18	3.40	0.10	0.40	0.30	1.10	1.44	0.90	0.40	0.15	0.30	2.10	0.10	0.90	0.95	0.20	0.90
19	3.20	0.30	3.60	0.20	1.00	1.50	1.30	0.10	0.30	0.15	0.20	0.40	0.40	0.80	0.30	1.00
20	3.30	0.40	1.15	0.30	1.70	0.40	0.10	1.10	0.10	0.75	0.60	0.20	0.20	0.50	1.60	0.40

TABLE 16. Cumulative percentage amount of arsenic leached

(in deionised-distilled water)

TIME (WEEKS)	AMOUNT OF ARSENIC LEACHED (%)																
	Y	A	B	B30CM	D	F	F30CM	I	I30CM	K	K30CM	L	L30CM	M	M30CM	N	R
1	0.069	0.077	0.193	0.044	0.080	0.114	0.084	0.110	0.143	0.056	0.071	0.128	0.111	0.070	0.026	0.092	0.305
2	0.094	0.114	0.233	0.062	0.088	0.120	0.095	0.142	0.186	0.072	0.082	0.136	0.124	0.086	0.061	0.098	0.438
3	0.116	0.126	0.249	0.076	0.094	0.127	0.100	0.158	0.206	0.088	0.086	0.150	0.141	0.093	0.072	0.104	0.533
4	0.136	0.147	0.268	0.080	0.104	0.141	0.121	0.168	0.219	0.093	0.095	0.152	0.157	0.101	0.099	0.113	0.683
5	0.163	0.175	0.283	0.086	0.109	0.147	0.124	0.190	0.248	0.102	0.099	0.167	0.171	0.110	0.109	0.123	0.805
6	0.187	0.185	0.306	0.089	0.117	0.150	0.130	0.200	0.262	0.109	0.105	0.170	0.180	0.114	0.141	0.127	0.850
7	0.203	0.197	0.318	0.096	0.126	0.153	0.147	0.208	0.271	0.119	0.116	0.172	0.187	0.124	0.147	0.135	0.904
8	0.232	0.215	0.323	0.107	0.133	0.158	0.153	0.208	0.280	0.134	0.124	0.181	0.202	0.137	0.158	0.139	1.009
9	0.249	0.249	0.346	0.124	0.138	0.163	0.169	0.237	0.300	0.144	0.127	0.188	0.206	0.157	0.171	0.143	1.095
10	0.282	0.257	0.361	0.126	0.143	0.181	0.172	0.247	0.312	0.147	0.131	0.197	0.235	0.157	0.172	0.155	1.143
11	0.293	0.276	0.379	0.130	0.145	0.186	0.177	0.255	0.322	0.151	0.144	0.205	0.238	0.165	0.173	0.157	1.255
12	0.306	0.286	0.380	0.132	0.151	0.188	0.180	0.266	0.329	0.166	0.145	0.214	0.244	0.191	0.179	0.158	1.376
13	0.313	0.286	0.388	0.133	0.156	0.190	0.182	0.274	0.344	0.176	0.151	0.255	0.252	0.200	0.186	0.164	1.438
14	0.318	0.302	0.401	0.136	0.165	0.192	0.183	0.276	0.360	0.179	0.154	0.227	0.261	0.207	0.227	0.170	1.448
15	0.318	0.342	0.402	0.137	0.169	0.197	0.183	0.280	0.371	0.181	0.157	0.228	0.265	0.208	0.231	0.181	1.471
16	0.341	0.348	0.411	0.139	0.170	0.198	0.191	0.287	0.377	0.182	0.158	0.228	0.266	0.209	0.237	0.187	1.524
17	0.363	0.349	0.411	0.140	0.171	0.199	0.193	0.288	0.385	0.183	0.158	0.230	0.268	0.210	0.240	0.193	1.667
18	0.384	0.350	0.415	0.140	0.173	0.203	0.195	0.290	0.386	0.184	0.164	0.231	0.271	0.214	0.241	0.194	1.714
19	0.404	0.352	0.427	0.141	0.175	0.206	0.198	0.290	0.387	0.184	0.164	0.232	0.274	0.216	0.243	0.198	1.810
20	0.425	0.350	0.434	0.141	0.177	0.207	0.199	0.294	0.388	0.186	0.166	0.233	0.276	0.216	0.253	0.199	1.857

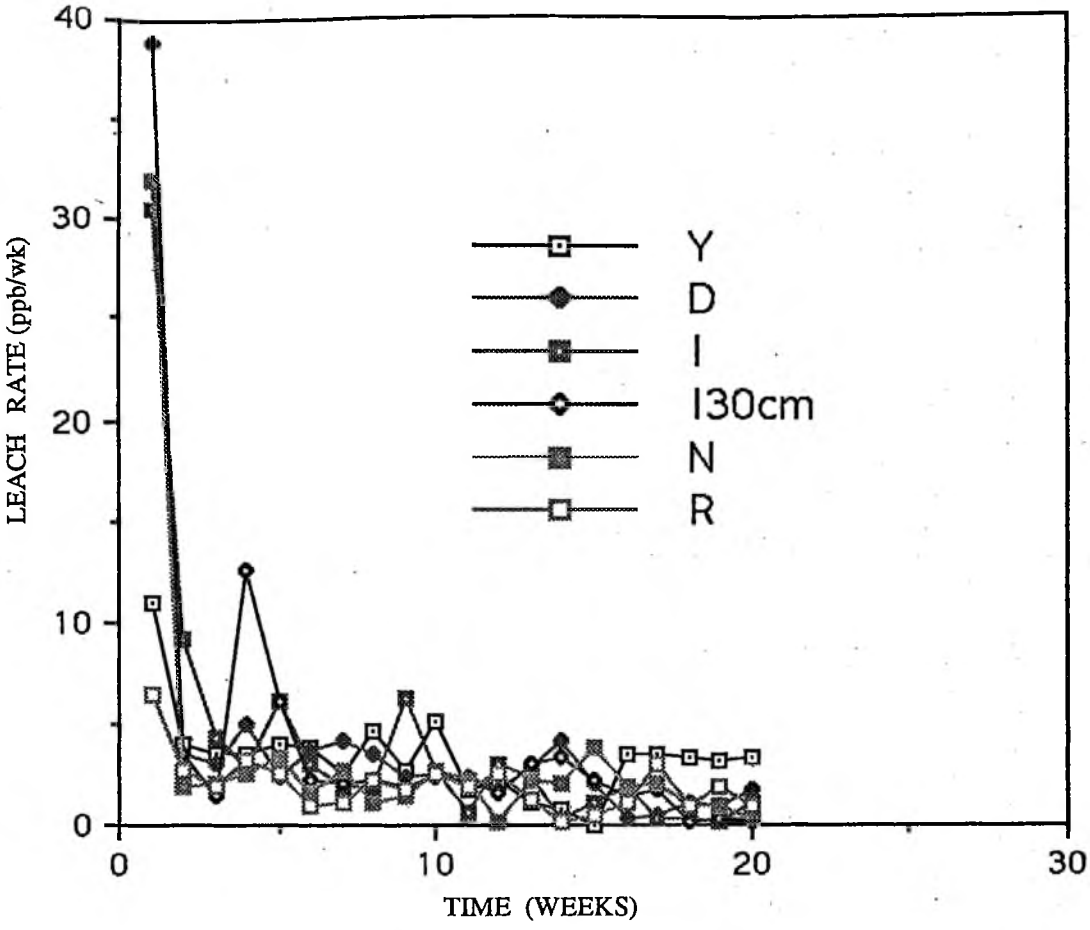


FIG. 7: **CUMMULATIVE LEACH RATE FOR ARSENIC IN SEDIMENT (LEACHANT: DEIONIZED - DISTILLED WATER)**

In the method by which the leachant was renewed periodically (table 17) the rate of leaching was higher but also decreased slowly with time. Here too the fraction leached after several weeks is insignificantly small (see fig 8).

TABLE 17 Differential Rate of Leaching of Arsenic in Deionised-distilled Water

	LEACH RATE [ppb/wk]																
TIME (WEEKS)	Y	A	B	B30CM	D	F	F30CM	I	I30CM	K	K30CM	L	L30CM	M	M30CM	N	R
1	11.50	12.00	41.80	20.60	38.50	48.90	32.20	30.50	32.10	24.10	26.20	41.90	31.90	17.00	4.20	32.50	6.30
2	12.00	12.50	42.00	42.50	38.30	50.15	32.50	29.50	34.10	25.10	24.60	40.90	28.50	18.00	6.50	30.00	6.65
3	13.50	14.00	42.50	24.00	38.20	40.00	20.70	25.60	30.20	24.90	20.00	40.00	21.20	16.50	8.00	24.50	7.50
4	11.50	10.20	35.10	20.10	37.50	35.00	20.00	22.10	28.50	24.10	16.70	30.80	20.90	12.00	7.40	20.00	6.40
5	10.00	9.55	28.00	19.00	25.20	34.20	16.80	21.10	19.20	20.00	15.00	25.10	18.70	10.50	7.00	18.00	6.00
6	9.20	9.00	25.00	17.75	20.50	20.00	15.15	20.00	14.50	18.75	14.60	21.70	16.00	8.00	6.90	18.70	-
7	8.00	9.10	20.00	17.00	17.90	13.70	10.00	17.50	14.00	18.90	13.20	10.20	13.70	8.15	6.00	15.00	-
8	7.00	8.00	16.00	15.00	17.00	12.00	10.10	14.00	11.00	18.00	13.00	9.50	12.00	-	-	12.50	-
9	-	-	12.10	11.45	14.10	10.30	8.00	10.00	9.00	16.50	12.00	9.00	10.90	-	-	13.10	-
10	-	-	10.00	10.50	10.70	7.46	-	9.50	8.50	12.15	9.00	-	8.00	-	-	10.00	-
11	-	-	8.95	7.65	9.00	-	-	7.45	8.50	11.20	-	-	-	-	-	-	-
12	-	-	-	-	8.00	-	-	-	8.20	10.00	-	-	-	-	-	-	-

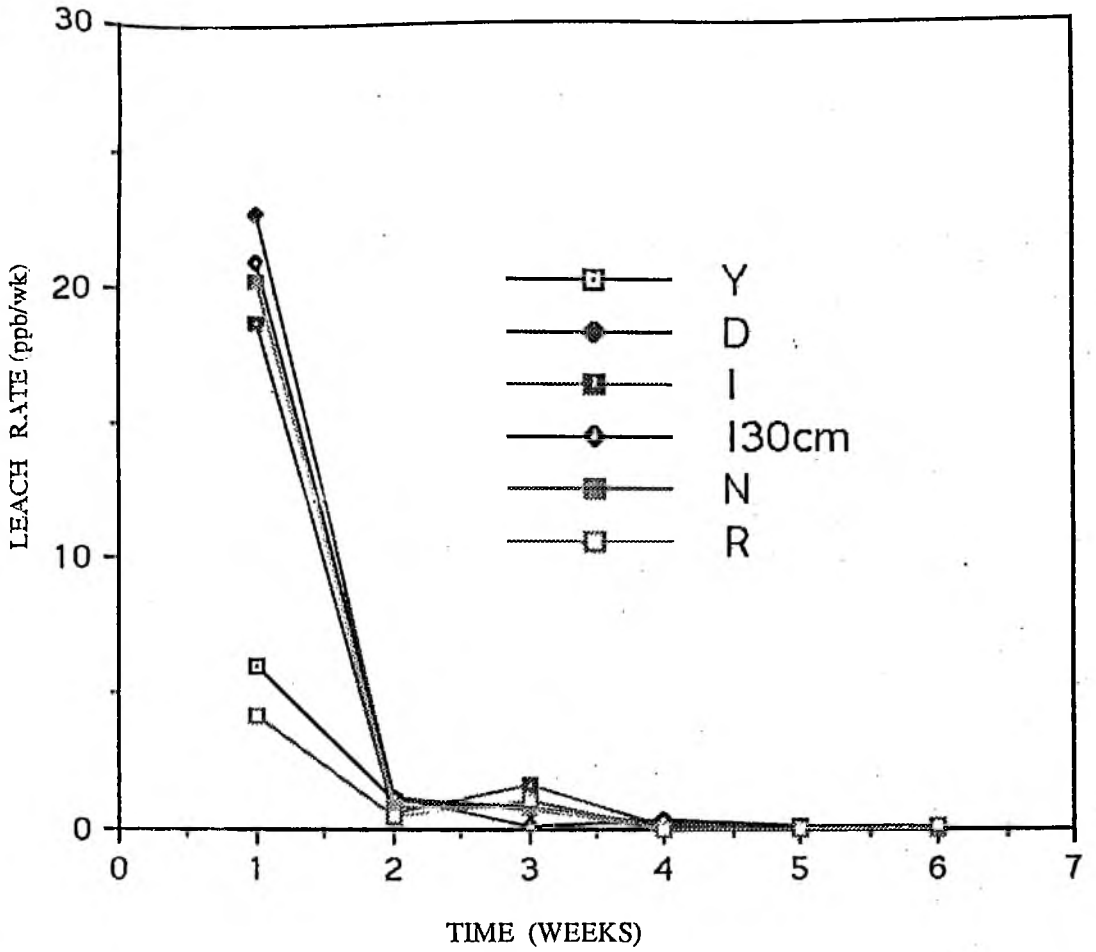


FIG 8: CUMMULATIVE LEACH RATE FOR ARSENIC IN SEDIMENT (LEACHANT: SIMULATED RIVER WATER)

The results of the leaching experiments performed with simulated river water as leachant are given in table 18 and illustrated graphically in fig. 9. These indicate that arsenic leaching is greatly suppressed compared to the leaching in distilled water.

TABLE 18: Cumulative rate of leaching of arsenic in simulated river water

TIME (WEEKS)	LEACH RATE OF ARSENIC (ppb/wk)															
	Y	A	B	B30CM	D	F	F30CM	I	I30CM	K	K30CM	L	L30CM	M	M30CM	N	R
1	6.00	7.00	25.70	16.80	22.75	32.30	20.00	18.70	21.00	15.60	16.90	27.70	19.20	10.15	3.00	20.20	4.20
2	1.10	0.50	1.30	0.70	1.25	1.55	1.10	0.60	1.20	1.40	0.90	1.40	1.50	1.20	1.10	0.80	0.50
3	0.90	1.40	2.00	0.80	0.70	1.05	0.85	1.70	0.60	0.90	1.30	1.00	1.30	0.75	0.65	0.90	1.10
4	0.10	0.30	0.15	0.17	0.20	0.10	0.05	0.10	0.35	0.02	0.10	0.10	0.05	0.07	0.15	0.05	0.00
5	0.05	0.12	0.05	0.13	0.10	0.00	0.05	0.07	0.10	0.08	0.05	0.02	0.15	0.08	0.02	0.05	0.02
6	0.05	0.05	0.10	0.08	0.10	0.07	0.05	0.03	0.11	0.02	0.03	0.08	0.15	0.15	0.08	0.04	0.10

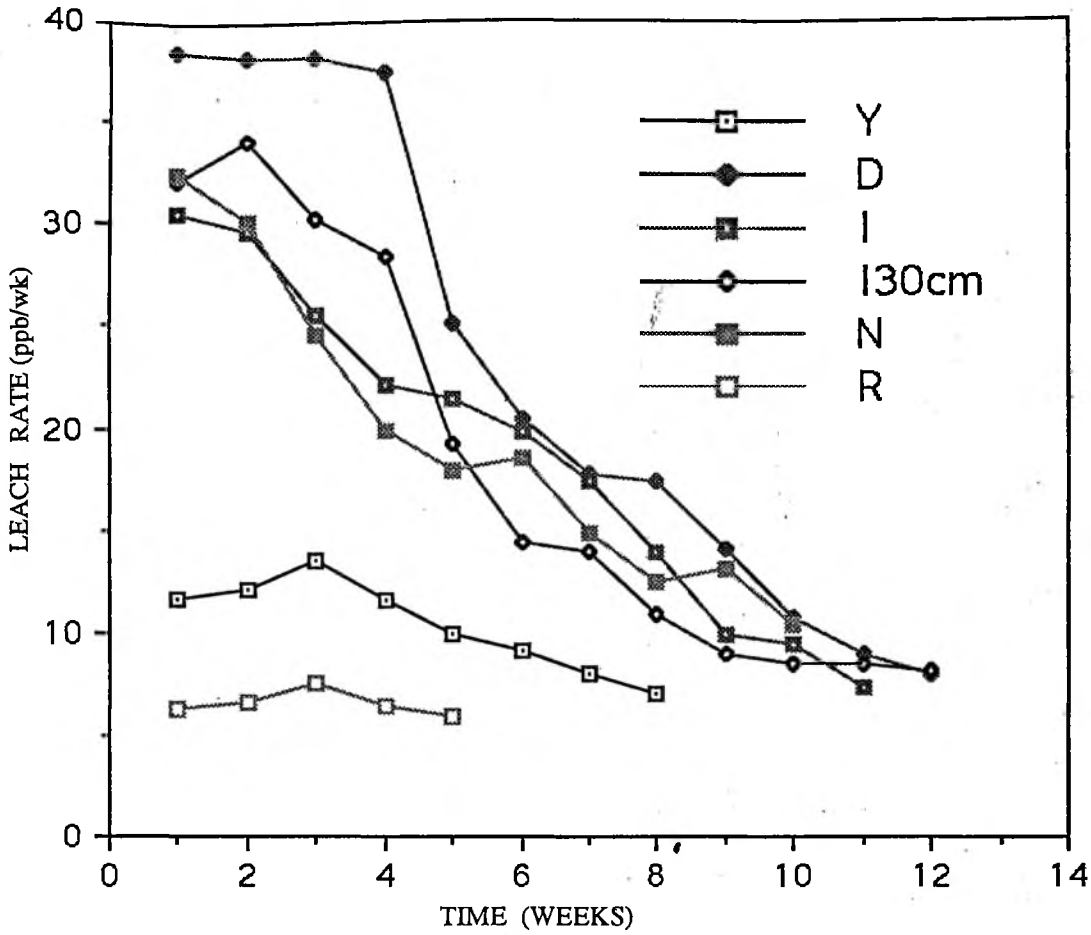


FIG 9: **DIFFERENTIAL LEACH RATE OF ARSENIC IN SEDIMENT (LEACHANT: DEIONIZED - DISTILLED WATER)**

These results are not quite unexpected. Arsenic is known to have low leachability as a result of the strong adsorptive capability of sediments and soils for it. It may be leached from coarse-textured soil, if the soil is low in reactive Al and Fe, however it is quite immobile in fine-textured soil[48]. Also since arsenic forms compounds of varying degrees of solubility with elements such as Fe, Ca, Mg and is adsorbed or occluded by hydrous oxides of Fe and Al, their presence would tend to suppress the leaching. But it is also known that phosphate ions tend to mobilize As because of competition for same adsorptive sites[19,]. It can thus be inferred that in the presence of phosphate ions, leaching of arsenic will be enhanced. However, the results show that even though PO_4^{3-} is present, leaching was suppressed. This may be due to formation of compounds that do not easily release arsenic.

The reproducibilities of the leaching results (table 19) are in all cases better than 10%. For heterogenous materials like the sediment lower reproducibilities are expected because the system is seldom in equilibrium[104]. So many processes may be occuring simultaneously to different extents. These may include, dissolution, exchange, diffusion etc.

Table 19. Reproducibility of the Arsenic leachability

(Leachant : Deionized-distilled water)

TIME (Weeks)	SAMPLE	AMOUNTS OF ARSENIC LEACHED (ppb)					x ± σ		CV (%)
		Exp. I	Exp. II	Exp. III	Exp. IV	Exp. V			
1	Y	11.00,	11.58,	12.25,	11.80,	11.45	11.62	0.50	4.3
1	B30	20.80,	21.90,	22.60,	21.70,	23.80	22.16	1.12	5.1
5	Y	26.80,	27.30,	25.50,	26.00,	27.90	26.65	0.97	3.6
5	B30	42.50,	40.80,	41.50,	40.80,	40.90	41.30	1.36	3.2
10	Y	46.50,	45.10,	47.80	45.20,	49.00	46.72	2.95	6.3
10	B30	59.90,	65.50,	58.70,	63.00,	58.20	61.06	3.65	5.9

5.4 CONCLUSION

From the above discussions the following conclusions can be drawn:

The streams in the catchment area of the Obuasi Gold-fields are polluted with arsenic, with the Kwabrafo stream being the most polluted. This is expected because it is the direct entry point of the effluents from the PTP. These streams are unhealthy for both domestic and industrial purposes. The pollution is caused by the smoke and other effluents from the PTP.

The sediments are more polluted than the streams down to at least 30cm deep. In areas where samples could be taken from both sinks, the surface appear to have higher arsenic concentration. The arsenic concentration in the water decreases with distance away from the PTP.

The rate of leaching of the arsenic from the sediment is so low that it is not likely that the ecosystem there can redeem itself, even if all discharges from the PTP were stopped and no further action taken.

The gold contents of both water and sediments are below 1ppm and it is not clear whether they can be useful for exploration.

5.5 RECOMMENDATIONS

In the light of the above conclusions, the following recommendations are made:

1) The Ashanti Goldfields Corporation (AGC), the mining company at Obuasi, should start a comprehensive programme of desilting all polluted streams within the mineral concession.

2) The Company, as a matter of urgency should adopt one of the many recycling processes available to recycle or clean the flue dust with the aim of reducing, if not completely eliminating its arsenic content before discharging into the atmosphere. This has actually been tackled with the installation of the Arsenic Recovery Plant (ARP). With it, several tonnes of arsenic trioxide, which otherwise would have gone into the atmosphere are being trapped. Its effectiveness is yet to be studied.

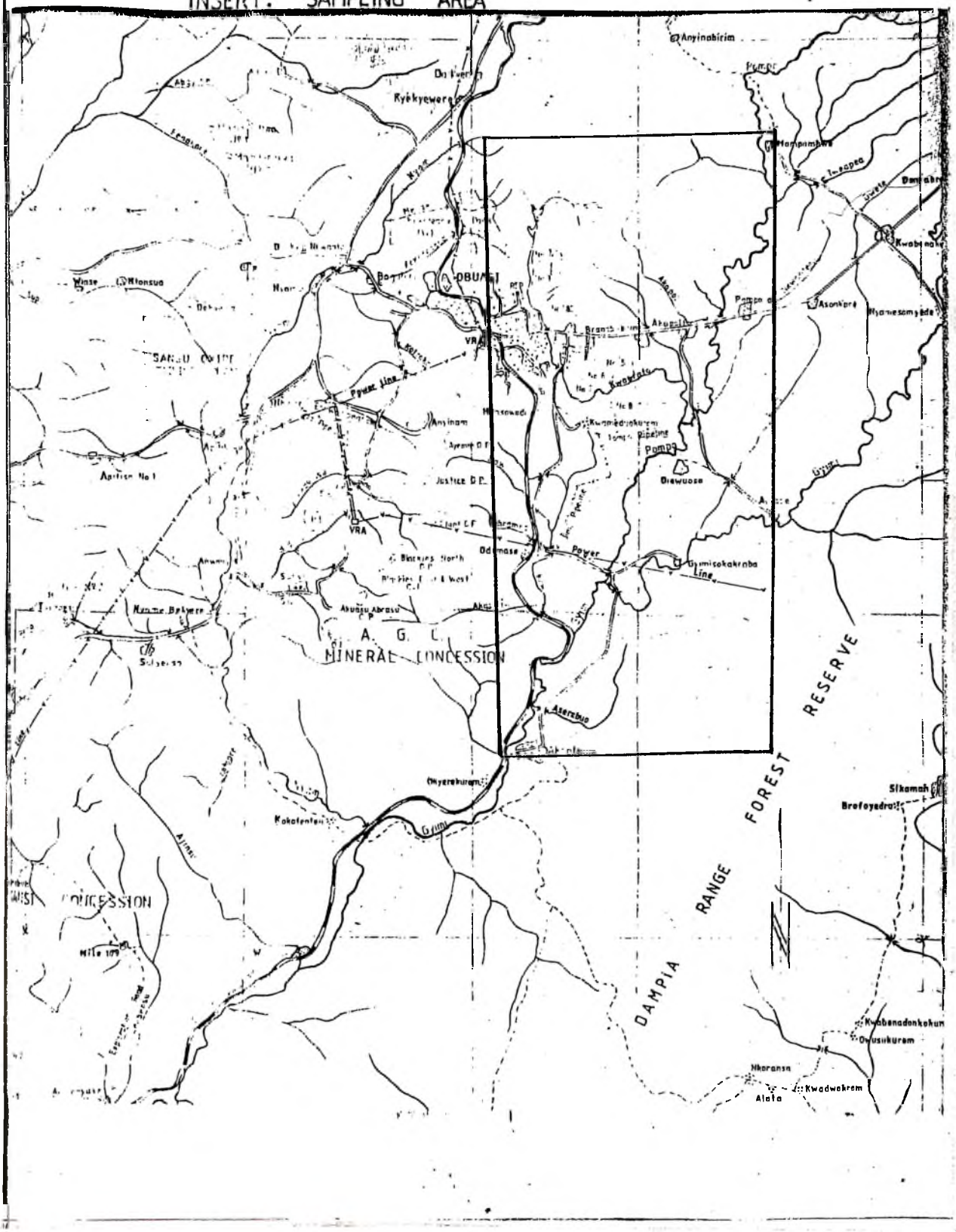
3) Programmes to continuously monitor the arsenic levels in finger nails, hair, blood and urine of Obuasi residents should be instituted with the aim of assessing the human poisoning in the area.

4) The type of study presented in this project should be extended to other mining and industrial communities in the country.

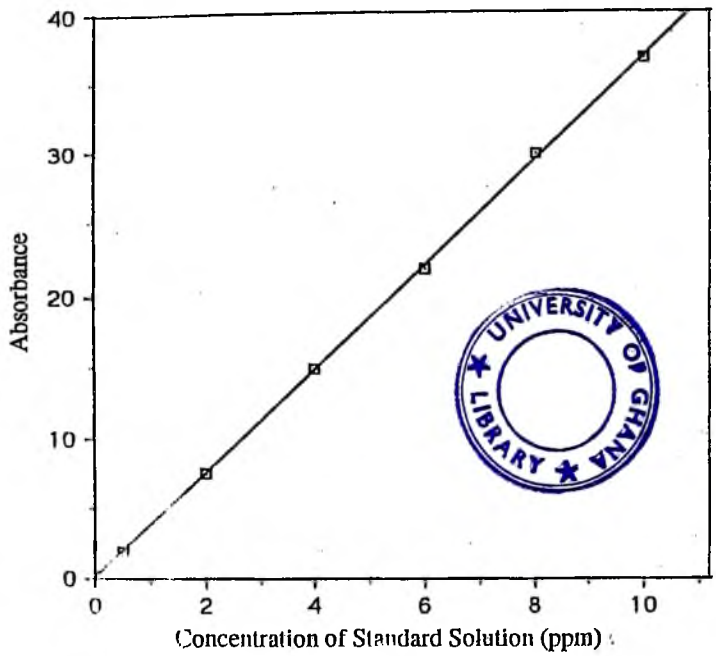
APPENDIX: I Map of Obuasi showing sampling area
========
II Calibration curves

APPENDIX I

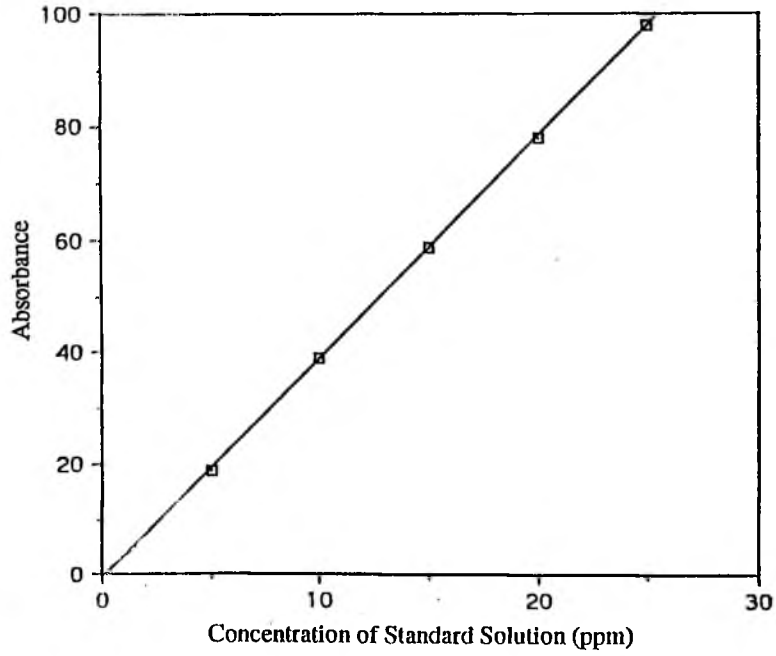
MAP OF OBUASI SHOWING PART OF AGC MINERAL CONCESSION



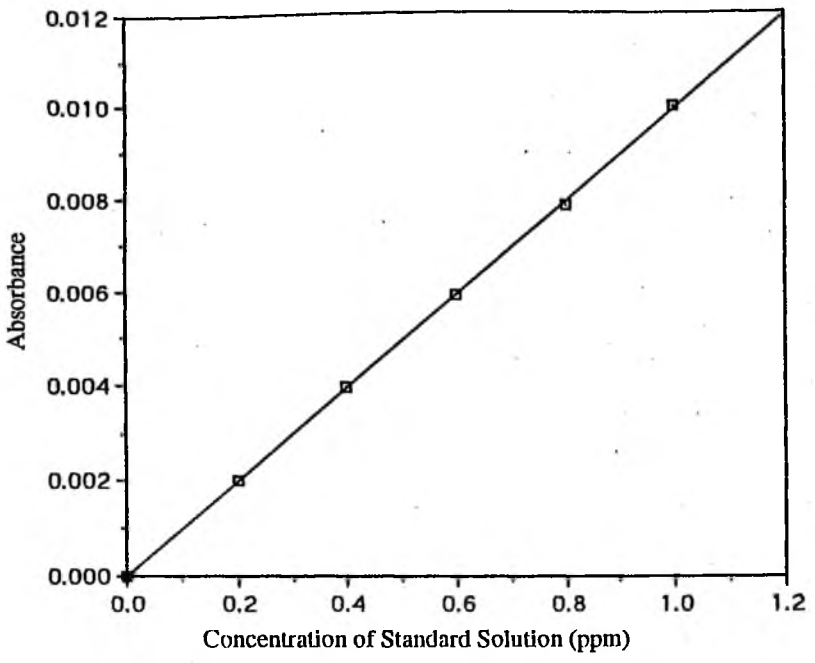
APPENDIX II



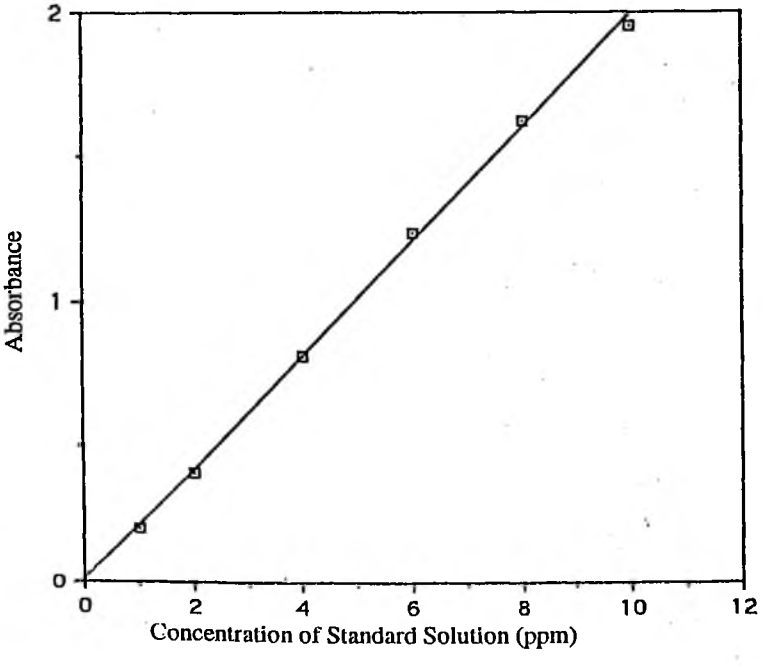
A. GRAPH 1: CALIBRATION CURVE FOR DETERMINATION OF SODIUM IN SEDIMENT



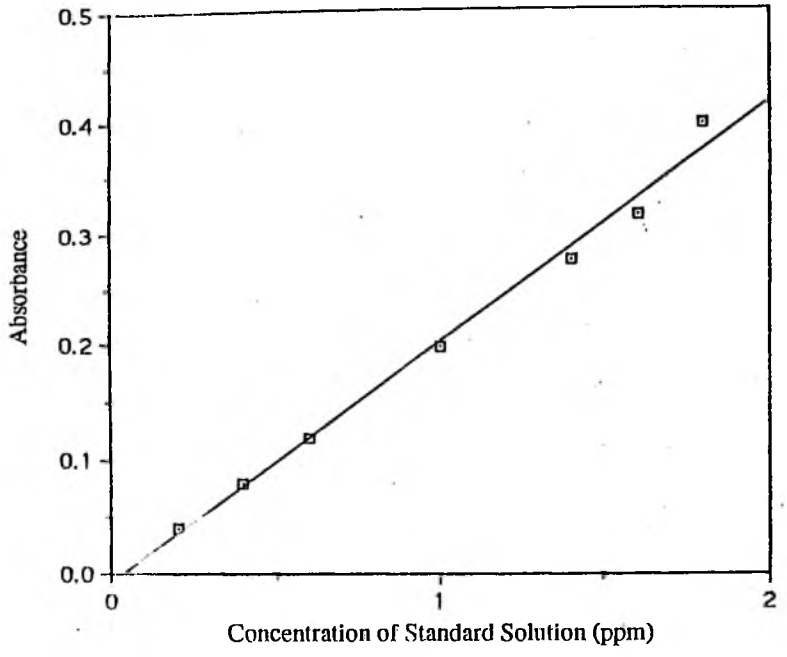
B. GRAPH 2: CALIBRATION CURVE FOR DETERMINATION OF POTASIUM IN SEDIMENT



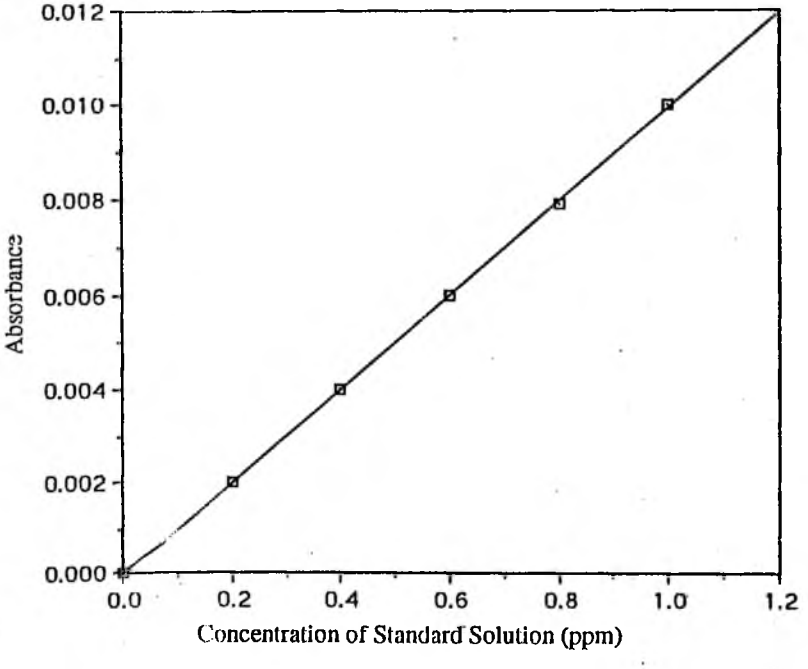
C. **GRAPH 3: CALIBRATION CURVE FOR DETERMINATION OF GOLD**



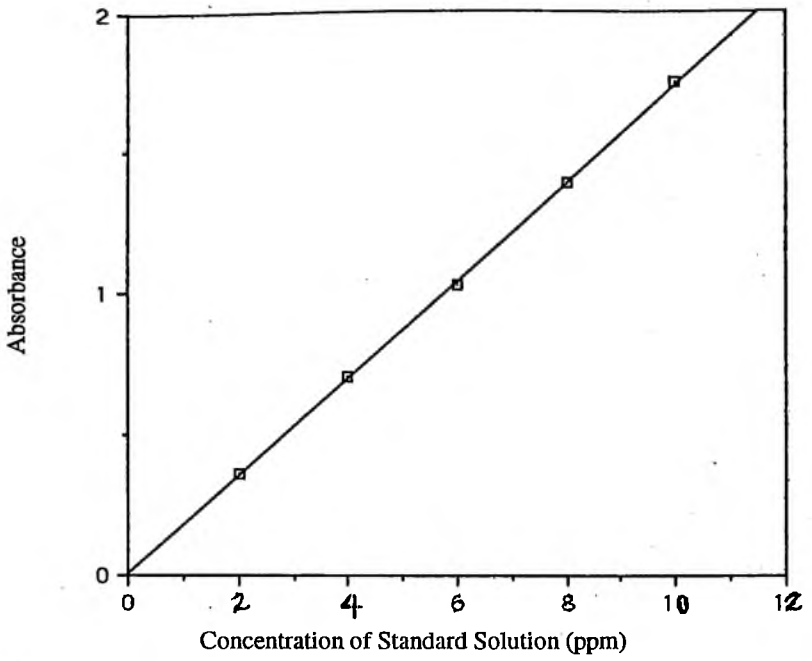
D. **GRAPH 4: CALIBRATION CURVE FOR DETERMINATION OF PHOSPHOROUS IN SEDIMENT**



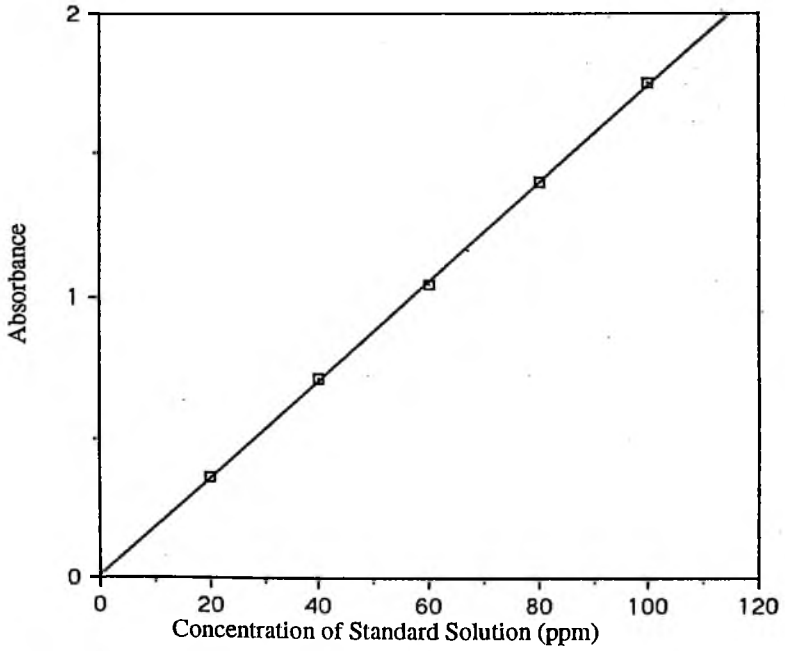
E. GRAPH 5: CALIBRATION CURVE FOR DETERMINATION OF IRON IN (WATER AND SEDIMENT



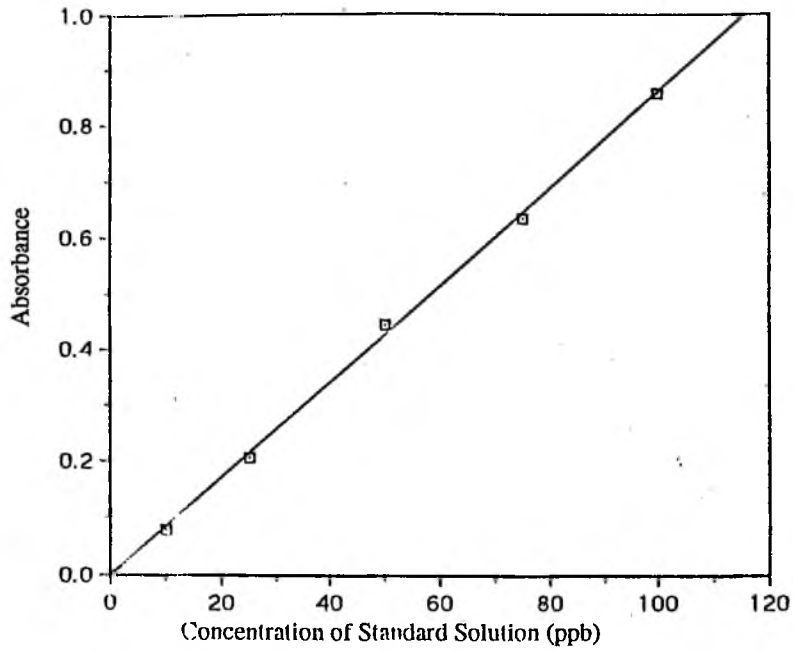
F. GRAPH 6: CALIBRATION CURVE FOR DETERMINATION OF MANGANESE (WATER AND SEDIMENT)



G. **GRAPH 7: CALIBRATION CURVE FOR DETERMINATION OF ALLUMINIUM IN WATER**



H. **GRAPH 8: CALIBRATION CURVE FOR DETERMINATION OF ALUMINIUM IN SEDIMENT**



I. GRAPH 9: CALIBRATION CURVE FOR DETERMINATION OF LEACHING OF ARSENIC (SEDIMENT)

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