Assessing the spatial distribution of arsenic concentration from goldmine for environmental management at Obuasi, Ghana

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March, 2007

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by

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Thesis submitted to the International Institute for Geo-information Science and Earth Observation in partial fulfilment of the requirements for the degree of Master of Science in Geo-information Science and Earth Observation, Specialisation: (Environmental Systems Analysis and Management)

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Abstract

Arsenic (As) occurs naturally in the earth's crust and is widely distributed in the environment. Natural mineralization and activities of micro organisms enhance arsenic mobilization in the environment but human intervention has exacerbated arsenic contamination. Although arsenic is useful for industrial, agricultural, medicinal and other purposes, it exerts a toxic effect in a number of organisms. Spatial distribution and assessment of soils in the mining sites of Anglogold Ashanti, Obuasi, were investigated to determine the extent of As contamination.

Obuasi is one of the gold mining areas in Ghana and whose mine sites have been active since the 19th century. Obuasi is a residential town suffering from considerable consequences of poorly regulated mining activities. Several studies show that mining and smelting of gold ores have created soil contamination problems. Fine particles selectively eroded from the mine waste-rock, tailings and slag have the potential to contaminate nearby soils or migrate as sediments in surface waters, enlarging the area affected by the mining activities. Sediments in river channels, reservoirs and floodplains are affected by As derived from mining operations.

In this study, geostatistics were applied to study the hazard posed by arsenic in the area. The ordinary kriging estimates of arsenic were mapped using the soil samples and indicator kriging applied to characterize the hazard posed by arsenic concentration at a threshold value of 20 ppm in the study area. These maps provide a decision support tool to define the areas where remedial action is needed in the light of the risks to humans and the ecosystems.

Soil samples taken from a depth of 0-15 cm contain high arsenic concentrations up to 69.72 ppm, whereas those taken at 15-30 cm contain up to 42.90 ppm. Stream sediments collected within 1 km of the mine sites contain as much as 34253 ppm indicating significant geochemical dispersion of arsenic downstream of the tailings and the retention sumps. Foodcrops and vegetation samples analyzed were found to be < 13 ppm. The pH values of the top-soil were found to be less than 7, showing that soil samples were acidic. This suggests that weathering processes go on in the area.

The results revealed a negative significant relationship between the top-soil arsenic levels and pH of the top-soil ($R^2 = 0.56$, $p < 0.05$). High As values of top-soil correlates with low pH of top-soil. This implies that As mobilized by streams/rivers are very often deposited on land during flooding. About 55% of the soils in the study area are contaminated with As; and high As concentration in plants were found to occur on soils with high As concentration levels. Because farmers preferred to cultivate foodcrops on floodplains or close to rivers/streams it will be appropriate to remediate contaminated soils since chronic ingestion of As in foodcrops or in water is a health hazard.

Acknowledgements

Many people and some institutions have been, in one way or the other, very co-operative in teaching, guiding, correcting and above all stimulating me during all the phases of the research writing and preparing it for submission. I will like to express my appreciation to all of them, since without their help this thesis would not have been what it is now.

I am most grateful, first of all, to the lord who through His Grace and love taught me the principles of life. I have come this far in my studies just by His Grace.

The International Institute for Geo-information Science and Earth Observation (ITC), Netherlands and the University of Mines and Technology (UMaT), Ghana deserve a word of appreciation for enabling me to follow the masters program by providing academic and financial support.

A special word of thanks goes to Dr. Alfred A. Duker my advisor in Ghana and Andre Kooiman the advisor in the Netherlands for their encouraging advice and constructive suggestions. Prof Alfred de Gier, Louise van Leeuwen, Dr. Eric Forkuo and Drs. Boudewijn de Smeth also deserve to be acknowledged for reviewing the text of the thesis. Their comments and suggestions immensely enriched the content of the research work.

I am very grateful to Harriet Sakyiwaa for her continuous support, love and valuable suggestions from the beginning of my studies to the end.

My sincere gratitude goes to my father Mr. A.K. Kumi and siblings (Kofi Kumi, Faustina Kumi, Daniel Kumi, Augustina Kumi and Kwadwo Amankwaa) for their support.

Last but not the least, Vincent Kyere my room mate, Seth Ahiaku of UMaT, all staff of environmental section of Anglogold Ashanti and Prince Asamoah of Ministry of Food and Agriculture, Obuasi deserve a word of appreciation for their support during my field work.

Dedication

This research is dedicated to the memory of my late mother Agnes Ama Owusuaa, Mr. A. K. Kumi-my father, Harriet Abena A. Sakyiwaa and all children born to poor parents.

Jeremiah 29:11

> "For I know the thoughts that I think toward you, says the Lord, thoughts of peace and not of evil, to give you a future and a hope" [Gideons International)

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1. GENERAL INTRODUCTION

1.1. BACKGROUND TO RESEARCH

The development of natural resources involves the manipulation of the environment to achieve specific objectives. Mineral resource is the most exploited natural resource and it involves extraction, grinding, ore concentration and dispersal of tailing (Ferreira da Silva et al., 2004). These activities generate a lot of chemical wastes and cause various degrees of environmental damage and a threat to plants, animals as well as human life. Mining can generate large concentrations of highly soluble inorganic matter, some of which are considered toxic (Mousa Ibrahim, 1997). Generation of chemical waste as a result of mining activity occurs world-wide and may severely affect natural resources such as vegetation, streams and the ecosystem in general (Ramani, 2001).

The composition and processing of ores also determine the nature of pollutants (Eppinger, 1999). After the precious metals which are usually derived from the sulphide ores are extracted, varying concentrations of other undesirable inorganic parameters such as arsenic, copper, lead, zinc, iron, sulphate, cyanide, nitrate, calcium, and magnesium are usually passed into tailings. The tailings, together with the sulphide bearing mine waste rock, are often exposed to the weather, thereby resulting in the mobilisation of metals and other chemical compounds related to ore processing into nearby water-bodies. Elevated concentrations of these elements in the water-bodies pose serious health hazards to host communities. The rate of contamination is likely to increase with increase in treatment of high tonnage material (Cunninghan, 1995).

This research will concentrate on problems related to gold mining in Ghana. Elements associated with gold mining waste includes arsenic(As), cadmium (Cd), copper (Cu), lead (Pb), antimony (Sb) and zinc (Zn), which can dissolve and disperse into surrounding streams due to rain water percolating through the waste (Ferreira da Silva et al., 2004) or dispersed as particles through erosion processes. Impacts of goldmines can be environmentally detrimental. Mining related stream sediment levels have been found in magnitudes higher than those associated with other land-use changes such as agricultural intensification, road building, deforestation and urbanization (Krishnaswamy et al., 2006)

Water and soil is the major path through which toxic trace elements affect plants, animals and man. Heavy metal pollution due to gold mining waste is difficult to control and unless removed or strictly contained in a tailing pond, remains a major source from which metal pollutants can spread into surrounding areas (Jianmin Shu, 1995). Studies conducted in Tanzania (Kishe and Machiwa, 2003), Ireland (McGrath David et al., 2004), China (Liu et al., 2006), Spain (Alvarez et al., 2003) and Morocco (Boularbah et al., 2006) have shown wide variation of heavy metal contamination in soil, sediment, water, fish, and flora. The studies revealed that heavy metal levels were significantly higher than permissible levels.

Ghana is an important gold-producing country with mining operations since the late 19th century and it produces about one third of the world’s yearly gold production (Griffis et al., 2002). The most important mining area is Obuasi in Ashanti region of Ghana. Gold-mining in the area is associated with sulphide mineralization, particularly arsenopyrite and pyrite (Griffis et al., 2002) as well as carbonaceous materials (Asiam, 1996) in such a way that the gold cannot be sufficiently liberated even by fine grinding for cyanide leaching. The sulphide concentrates are, therefore, roasted (Asiam, 1996) to release the occluded gold. During roasting, however, arsenic and sulphidic sulphur are eliminated from the reaction zone as arsenic trioxide fume and sulphur dioxide gas respectively, while the gold is concentrated in the calcine. Consequently, arsenic trioxide and sulphur dioxide have been discharged directly into the Obuasi countryside for the past 50 years and this poor environmental practice has had some adverse impacts on the environs of Obuasi (Asiam, 1996).

Arsenic is mobilized in the local environment as a result of the oxidation of arsenopyrite. High arsenic concentrations have been reported in soils (Amasa, 1975) and rivers (Smedley et al., 1996) close to the mining operations and ore processing plant. At the Obuasi mine, the long period of mining and metallurgic activities have resulted in increased concentrations of physico-chemical parameters in water-bodies, as well as the degradation of agricultural lands (Anon, 1992). For example, from 1947 until 1992, effluents were discharged without precaution, thereby resulting in the degeneration of the environment (Carboo, 1997; Tsidzi, 1993; Tufour, 1997). Exploitation of hitherto low-grade ore as a result of the Ashanti Mine Expansion Programme (AMEP) caused increased mining activities, hence increased chemical contamination at the Obuasi mine (Anon, 2002). AMEP was part of the several responses of the Ghanaian Mining Industry Policy Initiative to promote investment in the sector. Unfortunately, these initiatives were rather weak on the provision of guidelines for the management of the associated negative environmental impacts (Akabzaa, 2000).

The human health effects of arsenic exposure include skin lesions and lung, liver and bladder cancers with circulatory problems. Recent study (Duker et al., 2005a) in part of the Amansie west in Ashanti region showed Buruli Ulcer prevalence in the settlements along arsenic-enriched drainage channels and farmlands. However, very few studies have been conducted in Obuasi to assess the possible impacts of heavy metals, specifically arsenic, from mine waste on water resources, food crops and vegetation cover within the communities surrounding the mine. As a check to limit environmental degeneration, sustainable development through sound environmental management was embraced by the Obuasi mine management, using key policies such as the conduction of Impact Assessment Studies, adherence to environmental guidelines and monitoring (Anon, 1995; Jones, 1995; Lucas, 1996). The Environmental Protection Agency (EPA) Act 490 of 1994 empowers this in Ghana.

1.2. MINING AND METALLURGIC HISTORY OF THE OBUASI MINE

Gold has been mined in the Obuasi area for over a century. The gold was discovered and worked mechanically from alluvium and friable quartz of reefs long before the arrival of Europeans in 1895 (Kumi, 1998). Early mining was from quartz vein outcrops on the surface, which were later accessed by adits and shafts. The first shaft was sunk in 1905 (Ayensu, 1996). This method of mining was changed to conventional cut-and-fill in stopes through sub-level caving in 1969 and then to full-scale mechanisation in 1986. The transformations greatly increased the extraction of ore tonnages (Anon, 2002). Waste generated during the process of mining development is used as stope back-fills, thus limiting fresh underground waste rock from being exposed entirely to the surface conditions.

Open pit activities and major re-treatment of old tailings around the Pompora Treatment Plant (PTP) area evolved massively in the 1980s (Anon, 1992). From 1947-1992, sulphide pre-treatment was solely by pyro-metallurgy, which gradually came to a halt in 2000. Pyro-metallurgical pre-treatment method in the extraction of gold from sulphides is highly diversified and takes advantage of the relative abundance of iron in the ore. Iron (II) compounds are oxidised to iron (III), which is a potential impurity, and the application of lime (as neutraliser) enhances the process in a carbothermal reaction that proceeds at a relatively low temperature (Rankins, 1987). Sulphur oxidises to sulphur dioxide, and then hydrolyses in the presence of water to soluble sulphates, while arsenic (III) oxidises to arsenic (V). The sulphate precipitates as stable solids of iron (III) and arsenic (V) prior to disposal (Marsden, 1992).

Hydrometallurgical pre-treatment involving the use of natural bacteria, and used to catalyse mineral oxidation reactions was first introduced in 1992, and gradually developed to full capacity in 2000. Under hydrometallurgy, Thio- and ferro-oxidan thiobacilli, at a set of temperature-pH conditions, oxidise sulphur and iron species to break down sulphides (Marsden, 1992). The principal mineral extraction method is by the autoclave-carbon in leach (CIL) electro-winning process. An Oxide Treatment Plant (OTP) was installed for the treatment of oxide ore, a Heap Leach Plant (HLP) treated low-grade sulphide, while Tailings Treatment Plant (TTP) was installed for tailings reclamation.

1.3. PROBLEM STATEMENT

Various surveys have been carried out to determine arsenic concentration in various parts of the world (Ahmad et al., 2005; Bortoleto and Cadore, 2005; Erickson and Barnes, 2005; Smedley and Kinniburgh, 2002; Yang et al., 2003). These surveys have served to quantify levels of arsenic in different environments and have provided an understanding of the natural and anthropogenic sources of arsenic concentration in drinking water and soils (Smedley and Kinniburgh, 2002). Arsenic is widely distributed in nature and mainly transported into the environment by water. The main source of arsenic exposure for the general population is ingestion of surface and ground water sources as well as soil materials with high levels of arsenic, especially from mine waste (Smedley et al., 1996).

Humans, animals and plants are exposed to inorganic or organic arsenic through environmental, medicinal, and occupational sources (Yang et al., 2003). Mining activities cause arsenic to be released in high concentrations from oxidized sulphide minerals (Smedley and Kinniburgh, 2002). This may result in high concentrations of arsenic in surface water (Azcue et al., 1994; Smedley et al., 1996; Williams et al., 1996), groundwater (Armienta et al., 1997; Del Razo et al., 1990; Smedley and Kinniburgh, 2002), soil and vegetation (Amasa, 1975).

In spite of the known environmental problems of goldmines in the world, there is enormous pressure to mine Ghana’s mineral resources (Hilson, 2002; Kuma et al., 2002). Mining, in Ghana, normally results in land degradation through loss of vegetation cover, soil erosion (Aryee et al., 2003) and arsenic contamination of both water and soil from poor handling of ore processing tailings and dumped mine waste (Smedley et al., 1996). Some studies have investigated arsenic and its health implications (Duker et al., 2006; Sarkodie et al., 1997; Smedley et al., 1996) in Ghana.

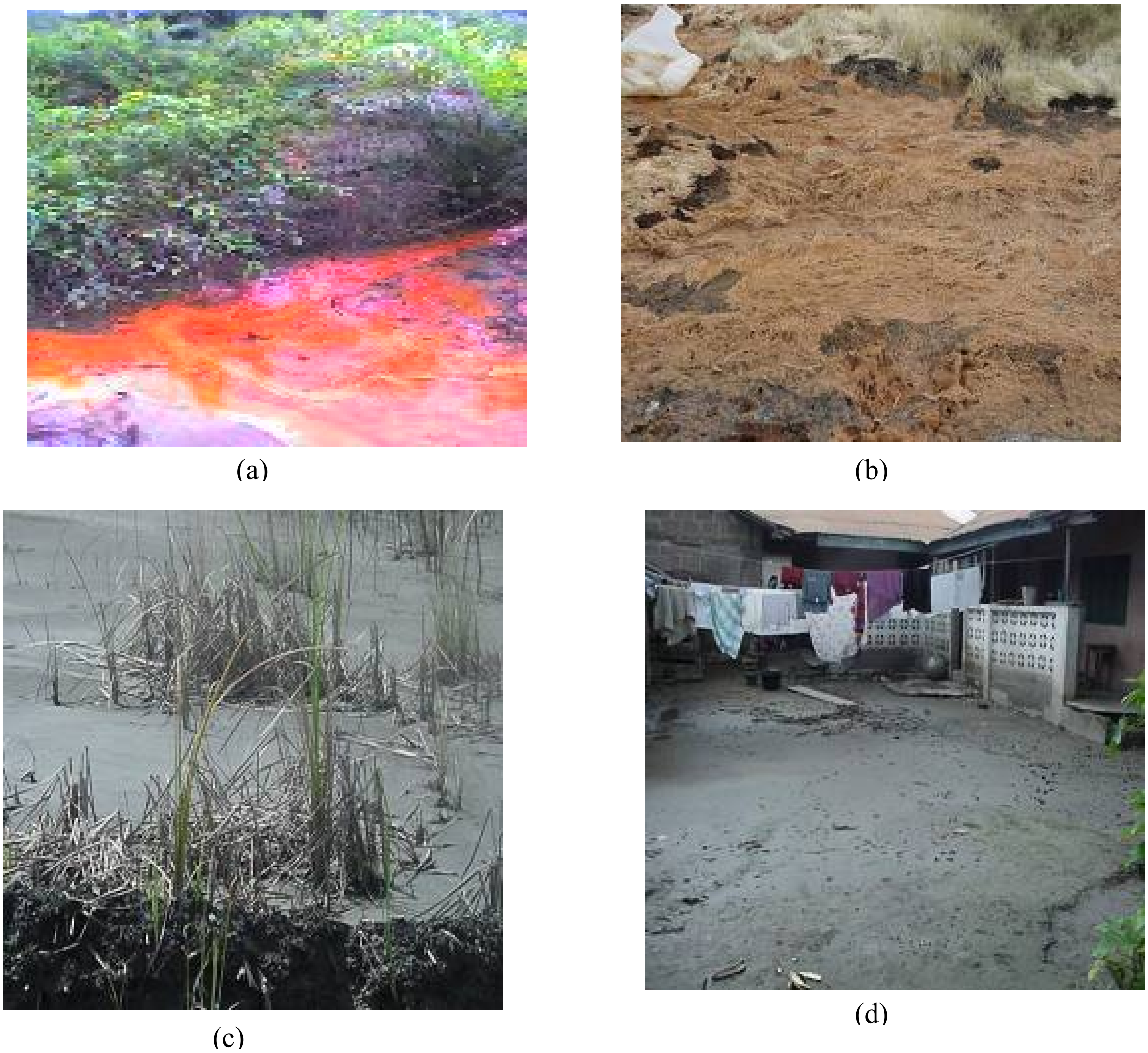
However, these investigations have not estimated the size of the affected area, level of arsenic concentration and its spatial distribution. High concentrations of arsenic in the environment may endanger the health of plants, animals and may also affect the suitability of food crops and portable water for human consumption (Thornton, 1983). Arsenic effects in humans has been reviewed by Duker et al (2005a). The organs mostly affected by arsenic include kidney, skin, liver and circulatory system. Signs usually associated with chronic arsenic toxicity include dermal lesion, skin cancer and vascular diseases (Duker et al., 2005b). These signs have been observed mostly in large groups of people for example in Ghana (Duker et al., 2005b) and Bangladesh (Smith et al., 2000) whose drinking water contains arsenic.

During the year 2005, there were three recorded incidents of tailings spillage, each of which resulted in serious environmental problems at Obuasi;

- In February 2005 two birds died after drinking from a pool of arsenic contaminated water in the area;
- 4,000 000 cubic meters of arsenic contaminated water spilled into the Nyam river as well as active farm lands and
- an overflow of tailings treatment retention sumps into a number of settlements, farm lands and grass land (Anglogold Ashanti, 2005) (Figure 1).

These spillages from the dams would be the cause of reduced production levels of farm products and, redish colour of vegetation in the area as well as the bare nature of some portions of the land.

Following these incidents, environmental protection agency raised a number of concerns about the failure of the company to identify and manage the risks and impact of tailings spillage as well as arsenic contamination which has become almost a daily occurrence (Anglogold Ashanti, 2005). In order to develop mitigation measures and monitor arsenic concentration, it is essential to gain understanding of the size of the affected and/or contaminated area, levels of arsenic concentration, the spatial distribution within the area and its influence on food crops as well as the vegetation cover of the communities fringing the gold mining area.



(a) (b)

(c) (d)

Figure 1: Effects of spillage ;(a) Iron hydroxide precipitates observed in a farm (b) Vegetation poisoned by spills from tailings dam (c) Tailings deposition in grass after a recent spill (d) Silt deposits in a house after a spill

1.4. RESEARCH OBJECTIVES

The proposed objective of the research is to assess the spatial distribution and levels of arsenic concentration from tailings dam and treatment retention sumps on soils, streams, food crops and the vegetation of the communities fringing the tailings and the retention sumps.

1.4.1. Specific Objectives

- To determine the levels of arsenic concentration in soils, streams, food crops and vegetation
- To determine the relationship between the top-soil arsenic and the pH of the top-soil in the area
- To determine the spatial distribution of arsenic concentration
- To determine the size of the area above a specified threshold and/or required treatment of the soil
- To determine the relationship between arsenic levels in soils and in plants

1.5. RESEARCH QUESTIONS

- What is the level of arsenic concentration in soils, streams, food crops and/or vegetation?
- Is the top-soil pH capable of estimating the top-soil arsenic levels in the area?
- How is arsenic levels distributed in the area?
- Which areas require soil treatment and/or contaminated?
- What is the relationship between arsenic levels in soils and in plants?

1.6. RESEARCH APPROACH

The research was conducted in a four phase approach as described below (Figure1).

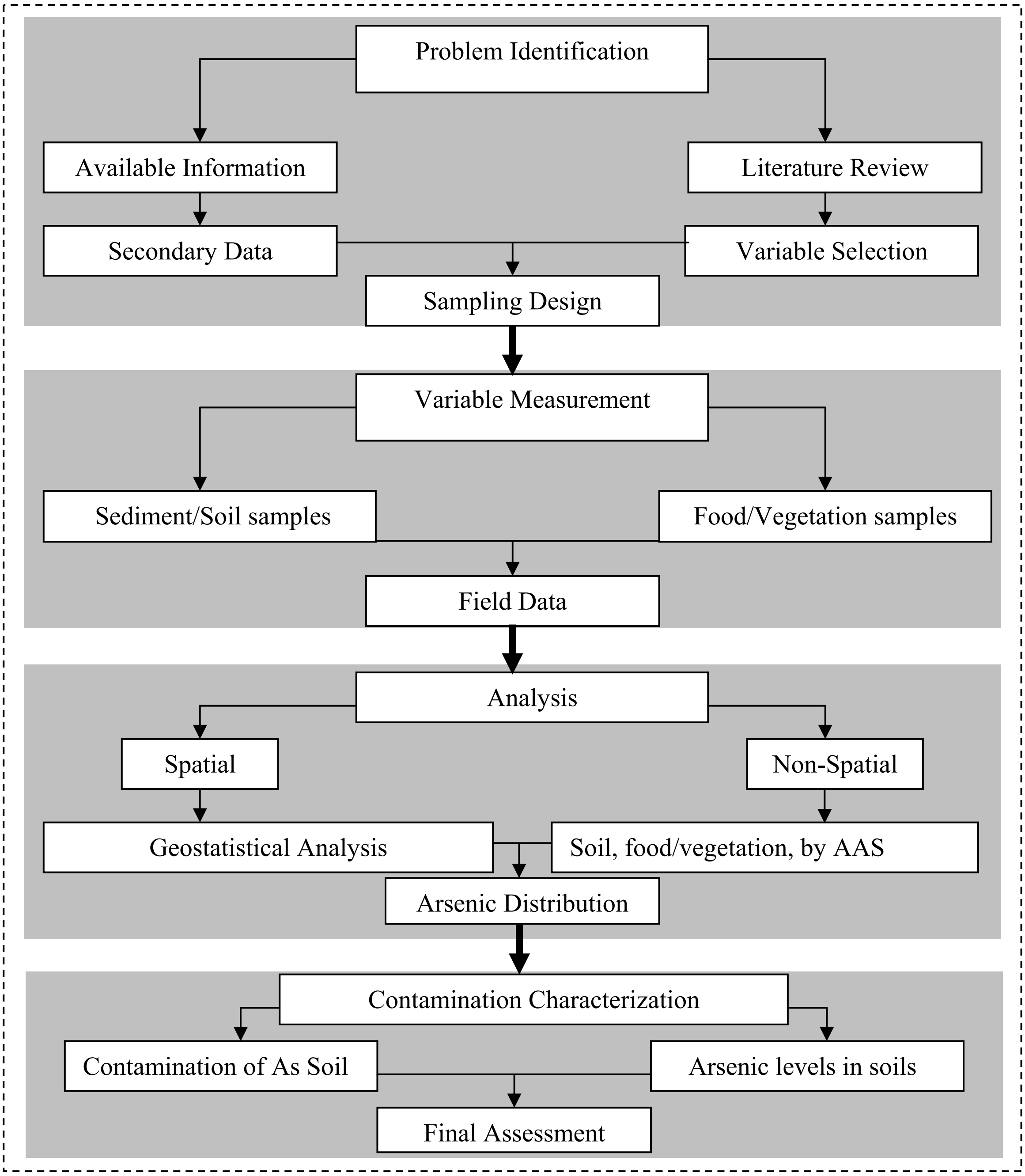


Figure 2: Research approach- Assessing spatial distribution of arsenic levels from goldmine

1.6.1. Preliminary Work

This was the first phase of the research and it spanned through literature review, data shopping for secondary data and how spills from goldmine occur. Available information was studied to ascertain the problem of arsenic concentration from both natural and anthropogenic sources in streams, soils, and its uptake by foodcrops (fruits) and vegetation. Detailed review of various researches on arsenic concentration was carried out to select appropriate environmental variable for assessment. A topographic map covering the study area was derived from a digitized topographic map at a scale of 1: 50,000.

1.6.2. Field Work

The second phase was the measurement of environmental variables. Preliminary survey on the historical overflow of tailings into the communities fringing the mine was conducted. Stream sediments were collected from the middle of the stream while soil samples were taken along the bank of the Nyam River (recipient of the spills) to ascertain the levels of arsenic concentration. Vegetation samples within the affected areas were mapped and foodcrops (fruits trees) samples analysed for arsenic. Farmers within the communities affected by the constant spills from the tailings were interviewed to determine their yields over the years since there was no statistical data on food production from the area.

1.6.3. Analyses

This third phase was the spatial and non-spatial analyses of stream sediment, soil and vegetation samples. The non-spatial included the analysis of arsenic in the stream sediments, soil and vegetation samples using atomic absorption spectrometric (AAS) techniques. The spatial part was the geostatistical analysis of the arsenic levels to determine the spatial distribution of arsenic concentration of soils within the area.

1.6.4. Final Assessment

The final phase of the research was the generation of map of areas using ordinary and indicator kriging that require treatment of the arsenic enriched soils.

1.7. THE STRUCTURE OF THE THESIS

The first chapter introduces the research conducted, describing the mining and metallurgic history of the Obuasi mine, stating the research problem, main and specific objectives to attain, the research questions to deal with and finally a description of the research approach.

Chapter 2 is devoted to the summary of the literature review on arsenic and the environment as well as the concept of geostatistics. The chapter begins with a description of the element arsenic, its geochemical occurrence and origin in soils. It continues with arsenic distribution around the world and concludes with a brief overview of geostatistical analyses using ordinary and indicator kriging.

In chapter 3, the study area is described with regards to its climate, geology, vegetation, occupation of the inhabitants and population. The chapter also gives a vivid account of the methods, software and materials used for the research. The materials and software used are carefully listed whilst the methods for the stream sediments, soils and vegetation samples described. The chapter concludes with the geostatistical analyses of the arsenic levels in soils using ordinary kriging to produce the spatial distribution map and indicator Kriging for the contaminated map.

The results of the research are discussed in chapter 4. The chapter states the descriptive parameters and the data distribution, and then follows with the relationship between the top-soil arsenic and other parameters, arsenic levels in the study area. The relationship between top–soil arsenic and the top-soil pH together with the spatial structure of arsenic levels in soils carefully accounted for in the chapter. The discussions in this chapter are outlined in five main sections:

- Levels of Arsenic concentration
- Top–soil arsenic levels and pH of the top–soil
- Spatial distribution of arsenic
- Arsenic contamination of soils
- Relationship between arsenic levels in soils and plants

Chapter 5 concludes the research with some recommendations whilst the references and the appendices are given in chapters 6 and 7 respectively.

2. CONCEPTS

2.1. ARSENIC AND THE ENVIRONMENT

2.1.1. Introduction

Arsenic (As) is a natural element which behaves like a metal. It is an ubiquitous element found in the soils and rocks, natural waters, atmosphere and organisms. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and dispersal of tailings as well as through other anthropogenic activities. Most environmental arsenic problems are the result of mobilization under natural conditions, but man has had an important impact - through mining activities, combustion of fossils fuel, groundwater table lowering through pumping and through the overuse of pesticides, herbicides, crop desiccants and additive to animal feed (Alloway, 1990).

Arsenic has achieved great notoriety due to its toxic properties of a number of its compounds. Fortunately, there are differences in the toxicity of different compounds and the species that are most commonly found in soils are not the most toxic. The uptake of As by many terrestrial plants is not very much so that, even on relatively high As soils, plants do not usually contain dangerous levels of As (Alloway, 1990).

Arsenic compounds appear to have been used by human for several years. Duker (2005a) provides a general account of As usage and reviews of health effects and metabolic changes in plants, humans and animals. A review of the global cycling of As by Alloway (1990) suggested that natural inputs to the atmosphere were 45 Kt As/yr, where anthropogenic sources added 28 Kt As/yr. In soils the natural levels are dependent on the parent rock type and the normal range is 1–40 ppm with most soil being in the lower half of this range (Alloway, 1990). Levels may be elevated due to mineralization, contamination from industrial activity or from As–based pesticides. Majority of the organo-As-compounds are less toxic than the inorganic As compounds (Duker et al., 2005a).

2.1.2. Arsenic Geochemical Occurrence

Arsenic can be present in soil, air and water as a metalloid and as chemical compounds of both inorganic and organic forms (Alloway, 1990; Matera, 2001; Ortiz Escober, 2005). Arsenic ranks on the twentieth most abundant element in the earth's crust, fourteenth in sea-waters (Ortiz Escober, 2005) and the twelfth in the human body (Mandal, 2002).

Arsenic occurs as a major constituent in over 200 minerals, including elemental arsenic, arsenide sulphides, oxides, arsenates and arsenites (Alloway, 1990). Approximately 60% being arsenates, 20% sulphides and sulphosaltes and the remaining 20% being arsenides, arsenites, and elemental As (Alloway, 1990). The most common of the As minerals is arsenopyrite (FeAsS). Arsenic is found associated with many types of mineral deposits especially those of the sulphides minerals (Duker et al., 2005a).

The concentration of associated As can range from a few parts per million (mg per kg) up to percentage levels. There is relatively little difference in the concentration of As in different rocks types unless the levels have been raised by associated mineralization. Mean values of the order of 3 ppm appears to be those most commonly found for igneous and sedimentary rocks, but the finer grained argillaceous rocks and phosphorites average 10–15 ppm (Alloway, 1990). Higher level of As are often associated with the presence of sulphide minerals such as pyrites (Griffis et al., 2002). Arsenic has often been used as a "pathfinder" or indicator element when geochemical prospecting methods have been utilized to identify mineral deposits (Asiam, 1996)

2.1.3. Origin of Arsenic in Soil Material

Arsenic can enter terrestrial and aquatic environments through both natural geologic and anthropogenic processes. The primary anthropogenic contribution of As to soils are from the combustion of solid waste, application of arsenical pesticides (herbicides, fungicides and insecticides), land application of solid waste/sewage sludges river and irrigation waters, mining and smelting of As – constraining areas such as mining and smelting of As–containing ores, combustion of fossil fuel (especially coal), land filling of industrial wastes, the lease or disposal of chemical wastes agents.

The average As content in the earth's crust was estimated to be about 1.8 ppm (Greenwood, 1984). A similar level of 1.5 ppm was also suggested by Onish (1969) for igneous rocks. Higher As levels were detected in sedimentary rocks and values as high as 13 ppm are common for clay rich rocks (Ortiz Escober, 2005). Since As accumulates due to weathering and translocation in colloid fractions, its concentration is usually higher in soils than in parent rocks (Alloway, 1990; Ortiz Escober, 2005; Yan-chu, 1994). In recent times Smith, et al (1998) Zhang, et al (2002) and Escobar, (2005) suggested that as a result of the variability in these process (weathering), the distribution of As in sedimentary rock is highly variable. Arsenic concentration ranges from 1.7 to 400 ppm in sedimentary rocks, and from 1.3 to 3.0 ppm in the igneous rocks (Ortiz Escober, 2005).

The US national academy of science, medical and biological effects of environmental pollutants (2000) established the average of As content of the Earth's crust as 2.5 ppm. However, more recently, Nagy (2005) has proposed that the total As in the earth's crust ranged from 45 to 3275 ppm. Concentrations of As in non-contaminated soils also range from 0.1 to 40 ppm Kabata – Pedias (1992) and Fitz (2002) suggested a new value of < 1.0 ppm. This makes it clear therefore that the general values for uncontaminated soils are significantly higher than for uncontaminated rocks. Arsenic is also commonly associated with sulphides, e.g. in sulphidic ore deposits. The elevated As level within the gangue minerals associated with an economic ore mineral leads to the risk of wind dispersal and leaching of As from the finely ground spoil tip and over flow of tailings dam materials. This may lead to very high As concentrations close to old and active dumps, though levels drop off rapidly with distance away from the dump site (Alloway, 1990). The rate of decline in As concentration is also influenced by the degree of stabilization of the spoil material affecting the drainage pathways.

The natural pool of As in surface soils arises from the net of geological, hydrological and soil- framing biogeochemical processes (Ortiz Escober, 2005). Under typical soil–forming conditions, the nature of soil As is controlled by the lithology of the parent rock materials, volcanic activity, weathering history, transport, biological activity and precipitation (Ortiz Escober, 2005). Historically, the mining and smelting of trace elements has created soil contamination problems of greatest magnitude (Ortiz Escober, 2005). Fine particles selectively eroded from the mining waste–rock, tailings and slag have the potential to contaminate nearby soils or may migrate as sediments in surface waters, greatly enlarging the area affected by the original mining activities. Secondary contamination often occurs in ground water beneath or down gradient open pits and ponds. Sediments in river channels, reservoirs, and floodplain are also affected by As derived from mining operations (Pierzynski, 2005).

Arsenic compounds have been widely used as pesticides over hundred years, but their use is now declining. The phyto-toxic effects of As compounds made them attractive as herbicide and as desiccant to allow cotton to be easily harvested after defoliation (Matera, 2001; Ortiz Escober, 2005). However, there has been concern about the build-up of As residues in soil and stream sediments which has occurred after the use of large quantities of inorganic As compound (Alloway, 1990). World wide usage of As has been estimated to be 8000 t As/yr as herbicides, 12000 t As/yr as cotton desiccant and 16000 t As/yr in wood preservatives (Alloway, 1990). The rate of application of the pesticides is generally in the range of 2-4 kg As/ha but larger quantities of Dimethylarsnic acid (DMA) may be used with application rates being up to three times greater (Alloway, 1990). In addition small quantities of organo As compounds are used as animal feed additives at rate of 10-50 mg As/kg feed, to promote growth in chickens, turkeys and pigs (Alloway, 1990). The compounds are rapidly excreted, often with little chemical change having apparently taken place thereby migrating as sediments in surface and ground waters as well as on soils. Phosphate fertilizers are also potential source of As.

2.1.4. Arsenic Distribution around the World

Arsenic is a significant contaminant of soils and groundwater in many regions of the world (Figure 3). Depending on the country, exposure to As has come from natural sources, from industrial sources or from food and beverages. High concentration of As in drinking water (above 50 µg/l) have been reported in several countries, including Argentina chile, China, Japan, Napal, Mongolia, USA etc. The world's largest As health issues are the contamination of drinking water aquifers in Bangladesh and west Bengal, India, potentially affecting millions of people (Duker et al., 2005b; Ortiz Escober, 2005; Smedley and Kinniburgh, 2002; Smith et al., 2000). Localized groundwater As problems are being reported by some countries and new cases are continuing to be discovered. Many countries, particularly developing ones, still use the 50µg/l of As standard, because of lack of adequate test facilities for lower As concentrations (Ortiz Escober, 2005). Until recently, As was not traditionally on the list of analysts routinely tested by water-quality laboratories. It is thus possible many water sources with high As might have been missed (Smedley and Kinniburgh, 2002). High As levels in ground water are not necessarily related to areas of high As concentrations in the source rocks or sediments(Ortiz Escober, 2005).

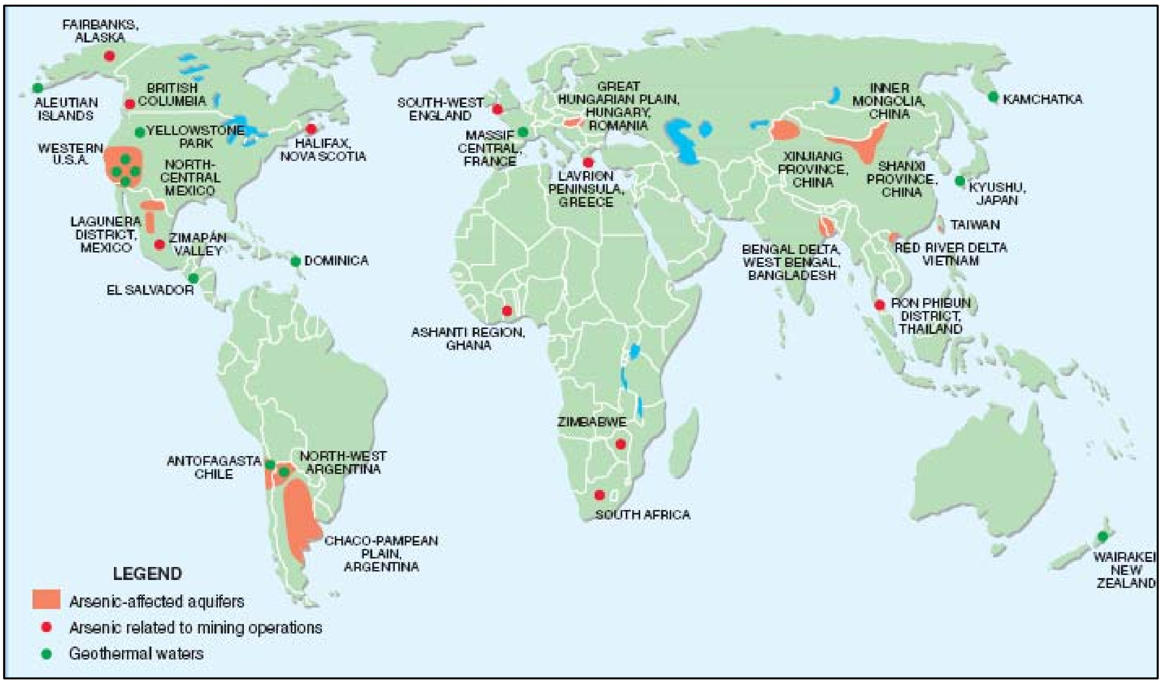


Figure 3: Arsenic Distribution around the world (adapted from Smedley and Kinniburg, 2002)

In Africa, As has only been identified as a water–quality problem in some localized areas associated with sulphide mining activities (Smedley et al., 1996; William, 1994). According to William (1994) 72 mg/l of As was found in acidic waters of a gold mining area in Zimbabwe. Smedley et al (1996) reported As concentrations up to 350 µg/L in streams waters affected by mining pollution in Obuasi area of Southern Ghana. However, no regions in Africa are yet known to have been identified with problems related to groundwater As (Ortiz Escober, 2005).

2.1.5. Mining Related Arsenic Problems in Ghana

Several workers have reported the effects of mining activity on the environment in Ghana. Today Ghana produces one third of the world's gold. The most important mining area is the Ashanti Region of Ghana. The gold in Ghana is associated with sulphides mineralization particularly arsenopyrite (Griffis et al., 2002). Arsenic mobilizes in the environment as a result of arsenopyrite oxidation induced by mining activities (especially dispersal of tailings). Around the town of Obuasi, high As concentrations have been reported in rivers, school compounds, farm lands and settlements close to the mine sites (Smedley et al., 1996). Groundwater in the gold belt of Ghana is thus vulnerable to potential As problems as a result of oxidation of sulphide minerals (Smedley et al., 1996).

2.2. GEOSTATISTICAL ANALYSIS

2.2.1. Overview

Geostatistics has been popularly applied in investigating and mapping soil pollution by heavy metals (Ferreira da Silva et al., 2004; Hooker and Nathanail, 2006; Korre et al., 2002; McGrath David et al., 2004). It provides a method that facilitates quantification of spatial features of heavy metals and enables its spatial interpolation within the environment (Liu et al., 2004; McGrath David et al., 2004). Geostatistics is based on the theory of a regionalized variable, which is distributed in space and shows spatial auto-correlation such that samples close together in space are more alike than those that are further apart (McGrath David et al., 2004). Geostatistics are also described sometimes as a set of techniques/tools used to analyze and predict values of a variable distributed in space or in time. The technique allows to quantitatively deal with spatial variation in large set of data. This is normally carried out in four main stages;

- Exploring of sample data
- Calculating experimental variogram
- Kriging interpolation and determination of the probabilities of exceeding a threshold value

The main distinction with statistics is that in Geostatistics, the variables used are linked to locations. Observations in space are linked to their co-ordinates and each observation has its specific place in space. This is sometimes referred to as regionalized variables. One way to summarize data is the use of graphs of cumulative relative variance for increasing distance. These show the distance at which important increase in variance occur (Saldana, 1998).

Geostatistical technique can be used to analyse spatial variability of a variable at different observation points since each variable that is measured is associated with its observation location x. A variogram γ (h) for variable Zi(x) can then be estimated from the equation:

$$\gamma_i\,(h) = \tfrac{1}{2}\, E[Z_i(x) - Z_i(x + h)]^2\text{-----}[Eqn(1)]$$

where x and x + h are two locations, separated by distance h, at which the regionalized variable is measured, and E denotes the mathematical expectation. The pairs of observations are grouped into a limited number of distance classes and each class contain pairs with approximately the same distance. The variogram in this research were estimated using the program R 2.4. The variogram describes the spatial correlation of a regionalized variable. Three important parameters characterized the variogram: the nugget variance, the sill variance and the range.

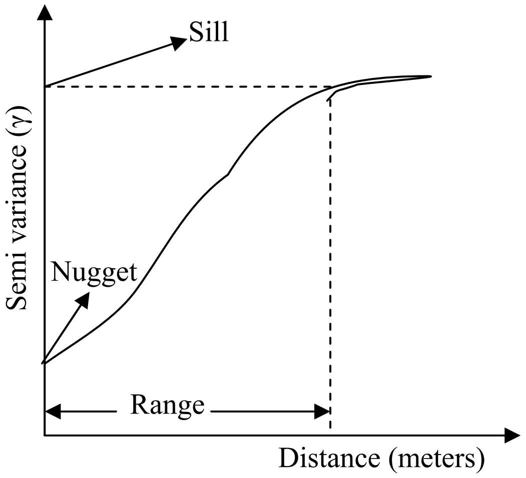


Figure 4: Parameters that characterise variogram model

The nugget is the positive intercept of the variogram with the ordinate and represents unexplained spatially dependent variation or purely random variable. The sill is the value at which transitive variogram level out and the distance at which the levelling occurs is known as the range of the spatial dependence (Burrough, 1998). According to Burrough (1998), variogram models with a clear range and sill are known as transitive models such as Spherical, Exponential (used in this research), Gaussian, Hole effect (wave) and Pure nugget.

The Gaussian describes continuous, gradually varying attributes while the Spherical model describes attributes with abrupt boundaries at discrete and regular spacing (range) and the distance between the abrupt changes is not clearly defined. Attributes characterized by the exponential model and pure nugget model indicates that there is no spatial dependence at the scale of investigation. Model fitting is required for the interpolation procedure and it is the preceding step to the creation of a map. The model fitting in this research was done using the program R 2.4.

2.2.2. Kriging

One of the central factors in spatial variability is to move from point observations towards statements concerning the area. This requires estimation of the prediction of the variable at unvisited locations. This can be achieved through interpolation techniques. The technique allows one to explore your sample data, construct variogram models and produce interpolated surface. A point interpolation (also known as gridding) performs an interpolation on randomly distributed point values and returns regularly distributed point values. An alternative to the point interpolation methods (Nearest point, trend surface, moving average and moving surface) is kriging. Unlike the straightforward deterministic methods such as nearest point, trend surface, moving average and moving surface, it is a statistical method based on the theory of regionalized variables (ILWIS3.0, 2001).

Kriging is a weighted–moving–average interpolation method where the set of weights assigned to samples minimizes the estimation variance, which is computed as a function of the variogram model and locations of the samples relative to each other, and to the point or block being estimated. Kriging has a number of advantages over most other interpolation methods:

Smoothing	Kriging smoothes, or regresses, estimates based on the proportion of total sample variance accounted for by random "noise". The noisier the data set, the less individual samples represent their immediate vicinity, and the more they are smoothed (GEOEAS, 1991).
Declustering	The Kriging weight assigned to a sample is lowered to the degree that its information is duplicated by nearby highly correlated samples. This helps mitigate the impact of over sampling "hot spots" (GEOEAS, 1991).
Anisotropy	When samples are more highly correlated in a particular direction, kriging weights will be greater for samples in that direction. (GEOEAS, 1991)
Precision	Given a variogram representative of the area to be estimated, kriging will compute the most precise estimates possible from the available data. In practices, this is only approximated, as the variogram must itself be estimated from available data. (GEOEAS, 1991)

Various kriging operations such as ordinary kriging, simple kriging, indicator kriging, universal kriging, anisotropic kriging and co-kriging exist. For the purpose of this research ordinary kriging and Indicator kriging was used.

2.2.3. Ordinary Kriging

Ordinary Kriging is a variety of Kriging which assumes that local means are not necessarily closely related to the population mean, and which therefore uses only the samples in the local neighborhood for the estimate. This is the most commonly used method for environmental situations such as mapping risk of soil nutrients deficiency (Lark, 2004), modeling of uncertainty in soil science (Goovaerts, 1999; McGrath David et al., 2004), health related problem (Duker et al., 2005b) etc. Ordinary Kriging involves three main stages namely the calculation of experimental variogram, Modeling variogram and Kriging interpolation.

A variogram is a plot of the variance (one-half the mean squared difference) of paired samples measurements as a function of the distance (and optionally of the direction) between samples. Typically all possible sample pairs are examined, and grouped into classes (lags) of approximately equal distance and direction. Variogram provides a means of quantifying the commonly observed relationship that, samples close together will tend to have more similar values than samples far apart. In fact the computation, interpretation and modeling of the variogram is the "heart" of a geostatistical analysis. It also serves as the interpretation of the spatial correlation structure of the sample data set.

2.2.4. Indicator Kriging

The concept of an indicator variable offers a clever way of adapting the ordinary Kriging procedure so that it can be used to estimate a cumulative probability distribution (Isaaks and Mohan Srivastava, 1989). In using the indicator method, however one does not obtain a complete description of the distribution, but obtains instead an estimation of particular points on the cumulative distribution curve (Isaaks and Mohan Srivastava, 1989). The implication of this is that once the indicator Kriging procedure has done its job, there is still work to be done interpolating the behavior of the distribution between the estimated points. The parametric approach avoids this draw back, at the cost of not permitting as much detail about the pattern of spatial continuity to be injected into the estimation procedure. Parametric method makes rather sweeping assumptions about the nature of the indicator variogram at a specified threshold or cutoff (As > 20 ppm in this research).

3. MATERIALS AND METHODS

3.1. STUDY AREA

The study area (Obuasi) is about 80 km south west of Kumasi, Ghana and is situated at latitude 6° 12' 00″ North and longitude 1° 40' 00″ West (fig 4). It is geologically situated within the principal greenstone belt of Proterozoic (Birimian) age which consist of volcano-sedimentary and igneous formations. This belt extends over a distance of approximately 300 km in a north-east/south-west trend in south-western Ghana (Anglogold Ashanti, 2005). The vegetation in the area is mainly secondary forest, forbs re-growth and swamp. There are two rainy seasons, with the major reaching its maximum in May and June and the minor in October. The month of July, August and early September are generally much drier than the remaining months. The annual rainfall ranges from 130 cm to 230 cm/yr with temperature between 22°C and 32°C. The area has a population of over 100 000 scattered over many small to large villages throughout the area and is mainly drained by the Nyam and Jimi Rivers. Beside mining, the majority of the people are farmers (Griffis et al., 2002)

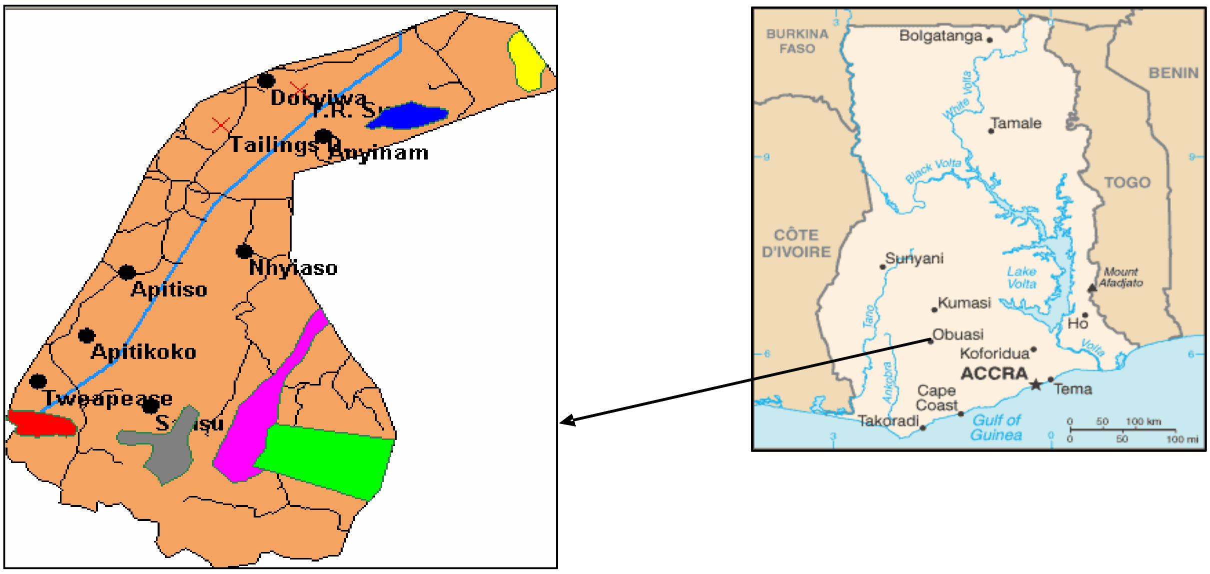


Figure 5: Study area- some communities in Obuasi

Cases of arsenic contamination in drinking water from streams, shallow wells and boreholes have been found in Ghana with the highest levels occurring in the mining community of Obuasi (Smedley et al., 1996). The main sources of arsenic in the area has been attributed to mining activities and natural oxidation of sulphide minerals, predominately arsenopyrite (Amasa, 1975; Amonoo-Neizer, 1994; Asiam, 1996; Smedley et al., 1996). In the case of Obuasi, mine waste dumps have high arsenic content that contaminates the surrounding streams (Foli, 2004) percolating through the waste dumps especially when it rains. The south tailings dam and the treatment retention sump of the Anglogold Ashanti are situated close to a number of communities. These communities, Nhyiaso, Apitiso, Apitikoko, Dokyiwa and Tweapease constantly receive overflows of the tailings and the treatment retention sumps onto their farmlands, houses, river and schools (Anglogold Ashanti, 2005). Whenever there is flooding, the arsenic contaminated water runs into the main river, the Nyam River, on which the five communities depend for drinking, irrigation of foodcrops and other domestic activities.

3.2. MATERIALS AND SOFTWARE

3.2.1. Sample Materials

- 30 cm soil auger
- Polythene bags for soil and stream sediment samples
- Geological hammer
- Topographic map of the study area
- Handheld GPS

3.2.2. Laboratory Equipments

- Atomic Absorption Spectrometer (AAS)
- Hydrochloric acid, concentrated
- Deionised water
- Test-tubes, 10 ml
- Hot plates
- pH metre

3.2.3. Software Used

- Descriptive statistics were produced with R 2.4
- Geostatistical analysis were produced with R 2.4
- Maps were produced with ILWIS (version 3.3)

3.3. RESEARCH METHOD

3.3.1. Soil Samples

An extensive investigation of soil was conducted in the Anglogold mine area. A total of 220 soil samples (Appendix D) were collected along the banks of the Nyam River on a grid system at an interval of 200 m. Samples were however not taken from locations that were difficult to access. Most of the samples were taken from flood prone, i.e. areas flooded whenever there was overflow of tailings and retention sump. Samples were also taken only on one side of the river Nyam due to the restrictions placed on places where samples could be taken (Figure. 5). At each sample point, two samples (0-15 cm (a) and 15-30 cm (b) depth) were taken from within a 10 x 10 m area with the central point giving the defined position for the sample and the position recorded with a GPS. The sampling depths were chosen to determine the effect of the change in soil profile on the arsenic contamination levels. It was to determine whether arsenic levels decreases or increases with depth. It was also taken because that is the depth at which plants obtain their nutrients. All the soil samples were oven-dried at temperature of 50^0C and sieved over a 2 mm sieve. Analyses were performed on the < 2 mm fraction by AAS after a hot acid decomposition for Arsenic (As), and pH.

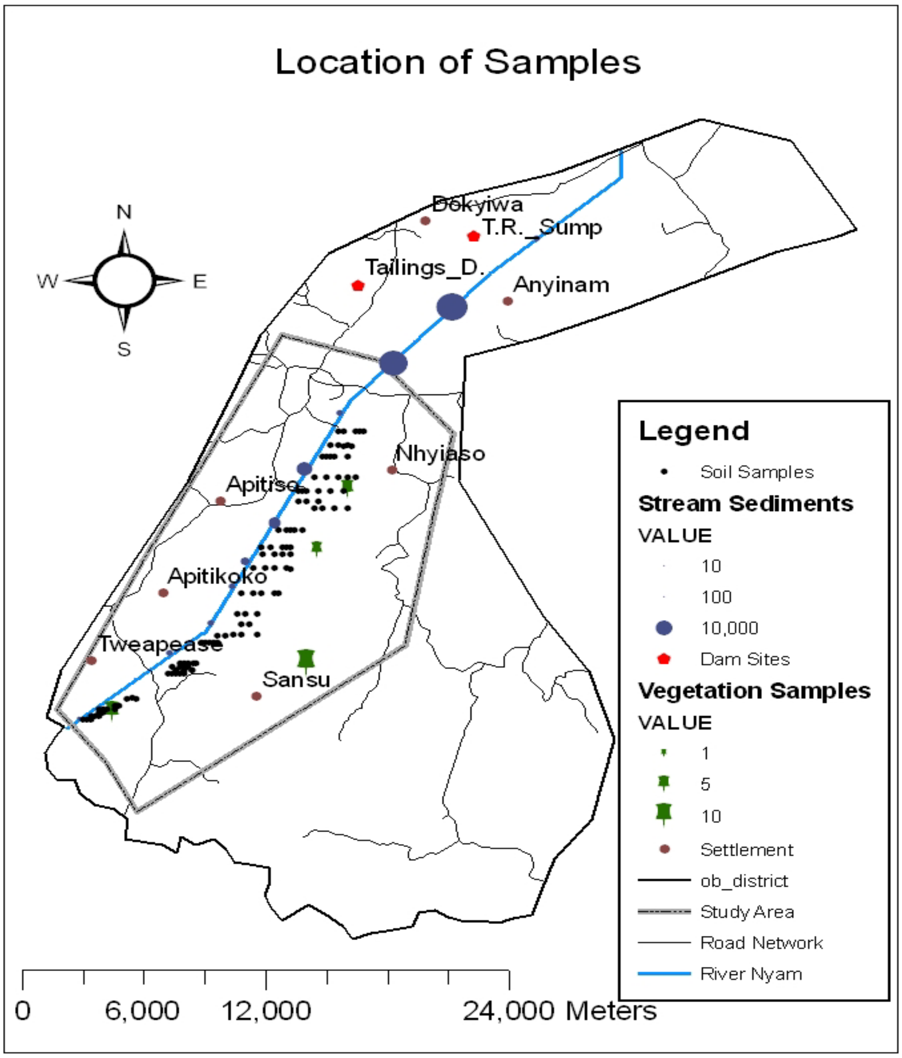


Figure 6: Location of samples

3.3.2. Stream Sediment Samples

A total of 14 stream sediment samples (Appendix B) were collected in the Nyam River at irregular intervals to ascertain the extent of the contamination from both anthropogenic (dam spills) and natural (weathering of parent rocks) processes (Figure. 5). The samples were composed of several grabs of fine sediments. A 2 mm sieve was used to homogenize the sample particles size before packing them into the sample bags. The coordinates of the sample points were recorded. The samples were oven-dried at a temperature of 50^0C and sieved over a 2 mm sieve. Analyses were performed on the < 2 mm fraction for As and pH. The metal was estimated following digestion of the sediment using AAS techniques.

3.3.3. Determination of Arsenic Levels in Soils

About 0.4 g oven-dried soil (passed a 2 mm sieve) was weighed and quantitatively transferred into a 10 ml test-tube. 2 ml hydrochloric acid and 1 ml nitric acid were added. The solution was placed on a hot plate set at 95^0C to heat for an hour. The solution was removed from the plate, cooled and topped to a 10 ml mark with deionised water. It was then filtered and aspirated to determine As levels using AAS.

3.3.4. Determination of Soil pH

About 20 g of oven-dried soil (passed a 2-mm sieve) was weighed into a 50 ml beaker. Distilled water of 20 ml was added and allowed to stand for about 30 minutes. The electrode of the pH meter was inserted into the partly settled suspension for the pH to be measured.

3.3.5. Vegetation Samples

During the soil sampling, a random vegetation survey was also conducted in the affected areas to determine the physical effects of the spills on it. A total of 30 randomly selected plants (grass, oil palm leaves, cocoyam leaves and orange leaves) were sampled (Appendix C). The colour of the vegetation was observed and recorded in the field data sheet and samples analysed for As. The leaves of orange trees, oil palm trees, grass, and cocoyam were thoroughly washed in water and oven-dried at a temperature of 100^0C for 4 days before pulverising. One gram (1 g) of each sample was wet-ashed using 10 ml mixture of concentrated HNO_3 and concentrated H_2SO_4 for an hour. The solution was diluted with distilled water and analysed for arsenic using AAS.

3.3.6. Spatial Distribution Map of Arsenic

For the purpose of this research ordinary kriging and Indicator kriging was used. The spatial structure of the data set did not indicate any direction, thus, anisotropic kriging could not be used. Again since there were no local trend or drift in the data set, universal kriging was eliminated whilst the raw data did not predict other parameter to warrant a co-kriging. The results of the soil samples were tested for skewness and outliers in order to determine normality (Isaaks and Mohan Srivastava, 1989). The data set was evaluated spatially using ordinary kriging to determine the possible migration of arsenic concentration to the surrounding environment.

The study area was stratified into a grid system with a cell size of 10m x 10m. Ordinary point kriging was used. This method of Kriging has been widely used in soil sciences (Goovaerts, 1999; McGrath David et al., 2004; Schroder, 2006; Zhang et al., 1998) with the estimated value calculated as the average, can reduce the variance values, and the variances are used in calculating the distribution map. In this research, an investigation was conducted on the raw data sets (arsenic levels) to determine whether or not the point values are spatially correlated and until which distance from any point this correlation occurs. A point map of the arsenic levels in soils was used for the spatial autocorrelation analysis.

In ILWIS, the spatial correlation operation can be done either as omindirectional or Bidirectional method. The Omindirectional method simply determines all distance between point pairs regardless of any direction. Thus all point pairs that have a certain distance towards each other will be counted in a distance class, where as the bidirectional method counts all point pairs with a certain distance to each other and with a certain direction towards each other. The analysis revealed a strong spatial correlation with omnidirection (Figure 12) confirming the choice of ordinary kriging but not anisotropic kriging.

The next step after the spatial correlation between the point values (arsenic levels) was the modeling of the variogram to determine the spatial structure. An exponential model gave a good fit for the variogram as shown in (Figure 13). The final step in the ordinary kriging process was the calculation of the Kriging estimation (Arsenic distribution map). This was done by specifying the parameters (sill, nugget and range) for the exponential model to interpolate the arsenic levels (Figure 14). In conclusion, the production of the arsenic distribution map followed these processes:

- Calculation of experimental variogram
- Modeling of variogram
- Ordinary Kriging Interpolation.

3.3.7. Arsenic Contamination Map

For the purpose of the arsenic contaminated soils assessment, threshold was defined for maximum permissible soils concentration (As $\succ$ 20 ppm) was used to estimate the arsenic polluted soils map based on the spatial distribution map of arsenic using indicator Kriging. The raw data set (arsenic levels) was classified into two (i.e. high or low). High values indicate arsenic level > 20 ppm represented as 1 and low values indicate arsenic levels < 20 ppm represented as 0 in the operation.

The indicator Kriging was carried out by considering the attribute of the As > 20 ppm or As < 20 ppm as point measurements with values 0 and 1. Omindirectional spatial correction and a variogram model similar to the one obtained above (Figure 13) was used to estimate the contaminated areas of arsenic in the soils. In ILWIS, the indicator Kriging is done using ordinary Kriging operation but with the new attributes of 0 or 1 indicating presence or absence as shown in the arsenic contaminated soil map in (Figure 15).

4. RESULTS AND DISCUSSION

4.1. RESULTS

4.1.1. Descriptive Parameters and Data Distribution

To evaluate the dataset, the representative percentiles were calculated and shown in the table below (Table 1). The concentrations of the top-soil arsenic [As (a)] and the sub-soil arsenic [As (b)] levels extend over several orders of magnitudes. For the top-soil arsenic levels, the minimum, median and maximum values are 0.03, 19.37 and 69.72 ppm respectively. The 90th and 100th percentiles of sub-soil arsenic level is much higher than the upper quartiles (75%) revealing their skewed distributions. However, the maximum 90th and 100th percentiles of the top and sub soils pH levels are almost the same as the upper quartile (75%), revealing their relative normality.

Table 1: Percentiles of the raw data set (n= 110, units in ppm except pH)

Percentile	As(a)	As(b)	pH(a)	pH(b)
0%	0.03	0.20	3.10	4.00
10%	3.34	0.40	4.30	4.90
25%	10.86	1.80	4.70	5.20
50%	19.37	3.70	5.50	5.70
75%	33.79	11.18	6.75	6.40
90%	50.07	21.31	7.01	6.91
100%	69.72	42.90	7.30	7.40

To illustrate the normality of the parameters, summary statistics were calculated and the results shown in Table 2. A careful perusal of the summary results reveals that Arsenic levels decreases with depth. The mean and the median values of the top soil arsenic levels are relatively the same indicating relative normality. To further attest to this, Shapiro-wilk (W) normality test was conducted on the dataset which confirmed the normality since w is close to 1.

Table 2: Summary results of soil data (n= 110, units in ppm except pH)

Summary	As(a)	As(b)	pH(a)	pH(b)
Mean	22.89	8.02	5.62	5.76
Median	19.37	3.70	5.50	5.70
Stand.Dev.	17.11	9.27	1.06	0.81
Maximum	69.72	42.90	7.30	6.91
Shapiro-Wilk normality test	0.914	0.774	0.928	0.963
p-Value	2.69e-06	1.02e-11	1.58e-05	0.004

To illustrate the spatial distribution features, a post–plot of the top soil arsenic (Figure 7) can be identified, showing high levels in the north-east and south-west directions (NE-SW trend) of the area (Figure 6).

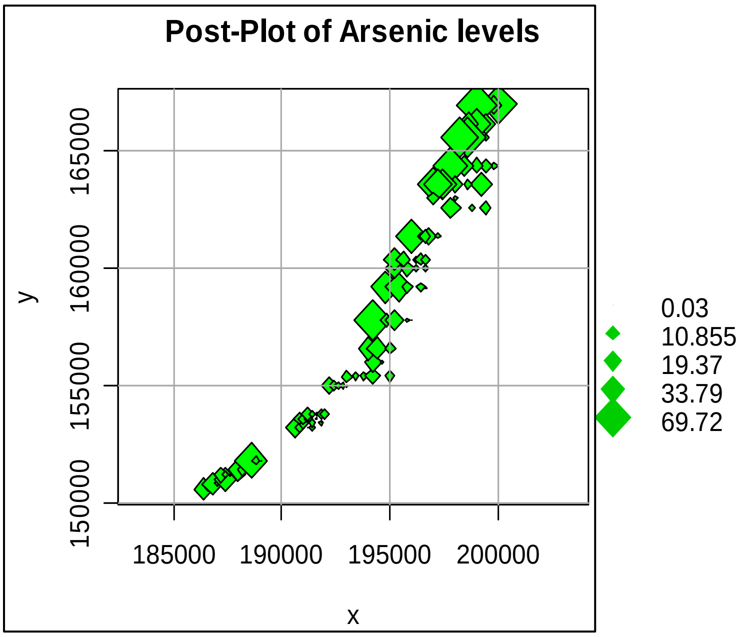


Figure 7: Post-Plot of top-soil arsenic levels

The histogram of the top soil and sub soil pH exhibited a relatively normal distribution (Figure 8). This indicates that possible outliers were not identified and therefore, the dataset do not lead to biased conclusion in statistical and geostatistical analyses. The data distribution confirms the observations by Goovaerts (2001) in the Jura Mountains dataset analyses of heavy metals. The pH values also of both the top and the sub soils passed the normality test (Tables 2) as its w is close to 1. This is presumably due to the pH being already logarithmically transformed H+ concentrations (McGrath David et al., 2004). However, the histograms of the top and sub-soil arsenic levels exhibited a positive skewness (Figures 8 and 9).

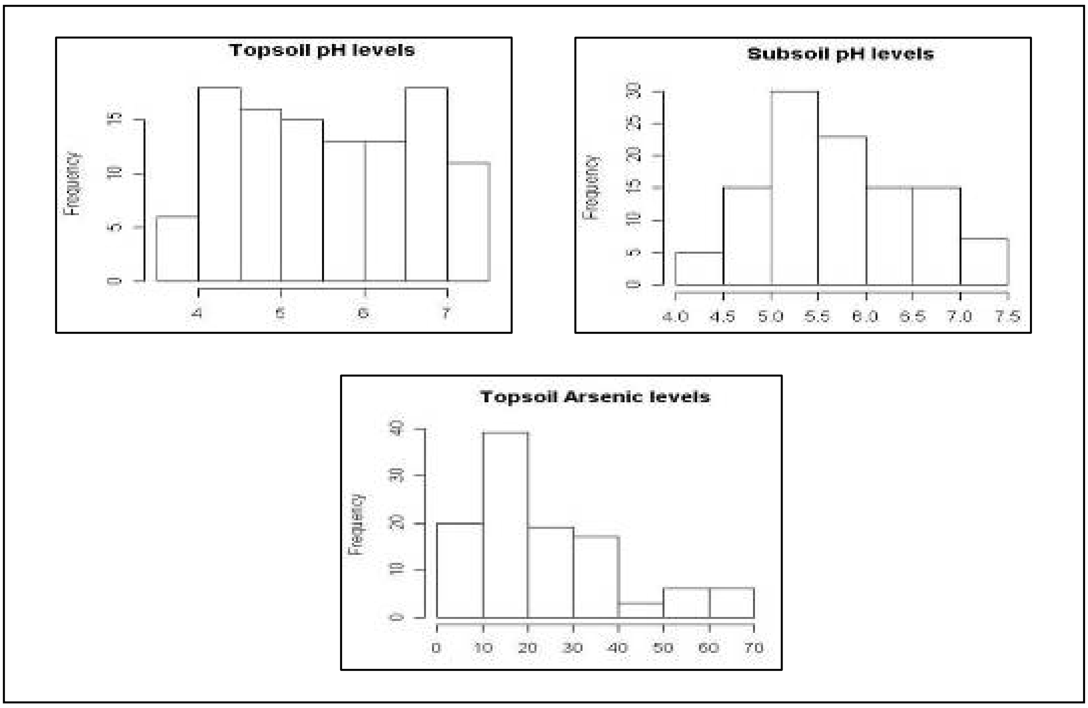


Figure 8: Histogram of top-soil pH, top-soil arsenic and sub-soil pH levels

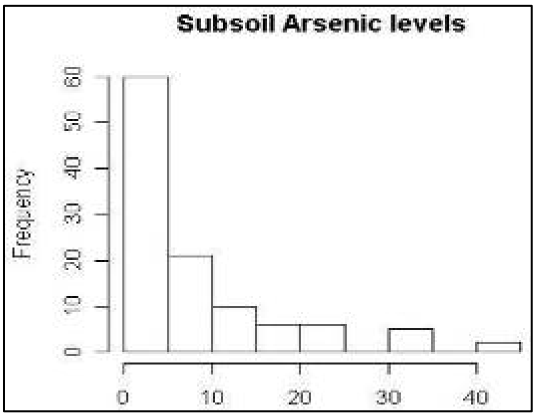


Figure 9: Histogram of top-soil iron and sub-soil arsenic levels

4.1.2. Relationship between Top Soil Arsenic and other Parameters

The correlation coefficients between all the variables were calculated, and the results are shown in Table 3. A positive correlation was observed between the top-soil arsenic and sub-soil arsenic levels at a significance level < 0.01. Relatively weak correlations were shown between the arsenic levels [As (a) and As (b)] and the type of soil (loam or clay).

Table 3: Correlation co-efficient (lower-left side) and their significance levels (upper-right side)

Parameters	As(a)	As(b)	pH(a)	pH(b)	Soil
As(a)	**1**	0.00	0.00	0.00	0.63
As(b)	0.51	**1**	0.00	0.00	0.04
pH(a)	-0.75	-0.38	**1**	0.00	0.36
pH(b)	-0.38	-0.43	0.55	**1**	0.37
Soil	0.05	0.20	-0.09	-0.09	**1**

The pH shows negative correlations with the top-soil arsenic and sub-soil arsenic levels. The strong negative relationship between the top-soil arsenic and the top-soil pH gives a strong indication that further analysis should be conducted to determine whether pH values are capable of estimating arsenic levels in the area. The scatter plots below (Figure 10) shows the type of correlation that exists between the parameters.

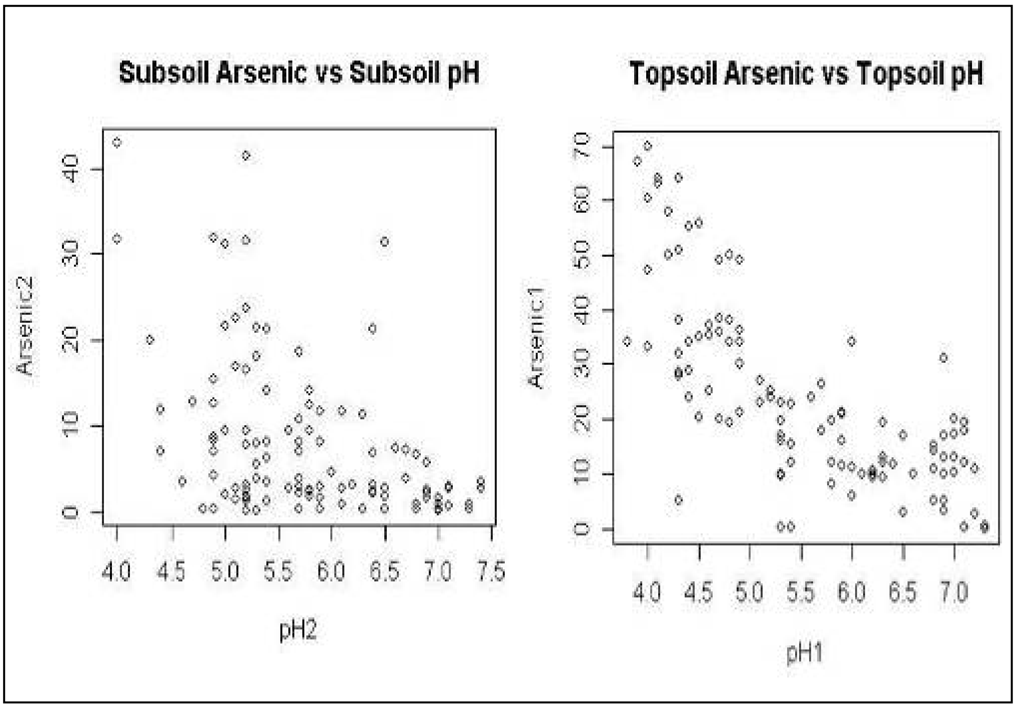


Figure 10: Scatter plot of pH verses arsenic levels

4.1.3. Arsenic Levels in the Study Area

The arsenic levels in the soil ranges from 0.03 to 69.72 ppm with average levels between 18.62 to 27.17 ppm at 99% confidence interval with p-value < 0.05 (Table 4).

Table 4: Best mean estimate of arsenic level at 1% chance of being wrong

Estimates	As(a) ppm	As(b) ppm	pH(a)	pH(b)
99%CI	18.62–27.17	5.71-10.34	5.35-5.88	5.56-5.96
t	-4.355	-24.878	-240.62	-314.95
df	109	109	109	109
p-Value	3.02e-05	<2.2e-16	<2.2e-16	<2.2e-16

The arsenic levels in food crops ranges from 0.01 ppm in sugar cane to 1.83 ppm in Cocoyam (Appendix A).Vegetation samples recorded in the study area showed arsenic levels from 0.01 ppm to 12.89 ppm (Tables 5 & 6). The minimum As levels recorded for grass occurred in Sansu, Nhyiaso and Tweapease whilst the maximum occurred in Apitiso. Sansu recorded the least levels of As in oil palm with the highest occurring at Apitiso. Tweapease and Apitiso recorded high As levels in cocoyam and orange respectively.

Table 5: Summary statistics of As in grass & oil palm, units in ppm

Community	Grass			Oil Palm		
	Min	Mean	Max	Min	Mean	Max
Apitiso	0.28	4.03	**12.89**	0.04	2.72	**7.42**
Nhyiaso	0.01	1.64	4.93	0.01	3.52	5.86
Sansu	0.01	1.74	4.11	0.16	1.37	3.51
Tweapease	0.01	1.02	2.52	0.22	1.47	3.06

Table 6: Summary statistics of As in cocoyam & orange, units in ppm

Community	Cocoyam			Orange		
	Min	Mean	Max	Min	Mean	Max
Apitiso	0.06	1.33	3.48	0.15	3.87	**11.06**
Nhyiaso	0.03	1.14	2.84	0.12	1.59	3.07
Sansu	0.15	2.13	4.68	0.14	1.03	2.56
Tweapease	0.13	2.80	**6.03**	0.01	2.50	7.48

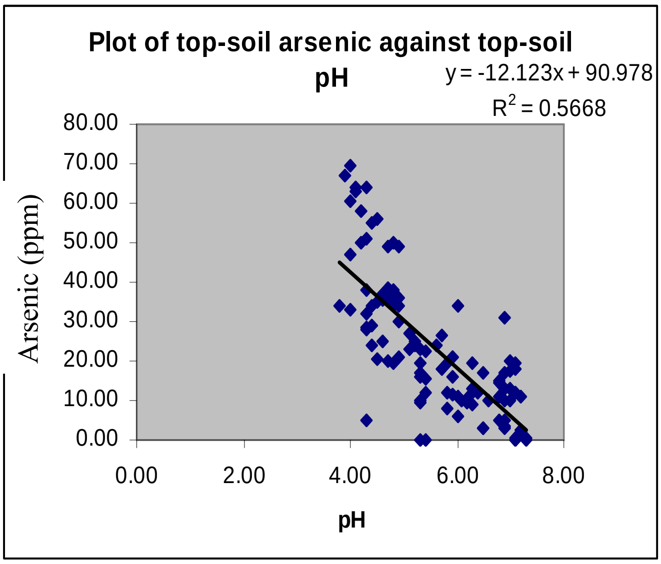
The arsenic levels in stream sediments recorded in the Nyam River at irregular intervals revealed high levels from 50.00 ppm to 34253.00 ppm with an average level of 6488.14 ppm (Table 7). In general the distribution of arsenic was found to decrease with increasing distance form the tailings dam and the treatment retention sumps.

Table 7: Summary results of stream sediments

Parameters	Minimum (ppm)	Maximum (ppm)	Mean (ppm)
As	50.00	34253.00	6488.14
pH	6.30	7.70	7.10

4.1.4. Relationship between the top-soil arsenic and the top-soil pH

The correlation coefficient between the top-soil arsenic and the top-soil pH was further explored and the results are shown in the tables below (Table 8 & 9). There was a strong negative relationship between the arsenic levels and the pH values of the top-soils (Figure 11).



Regression Statistics	
Multiple R	-0.753
R Square	0.567
Adjusted R Square	0.563

Figure 11: Correlation between top-soil arsenic levels and top-soil pH

Table 8: Analysis of variance of arsenic levels and pH values of the top-soils at 95% CI

ANOVA	df	SS	MS	F	Significance F
Regression	1	18094.92213	18094.92	141.2821	2.44409E-21
Residual	108	13832.26342	128.0765		
Total	109	31927.18555			

Table 9: Parameters for the equation predicting arsenic levels of the top-soils

	Coefficients	Standard Error	t Stat	P-value
Intercept	90.97813455	5.828801655	15.60838	1.9E-29
X Variable 1	-12.12259113	1.019886507	-11.8862	2.44E-21

4.1.5. Spatial Structure of Arsenic Levels in Soils

The spatial structure of As is revealed by the variogram cloud and surface shown in Figure 12 and Figure 13. The best correlations were observed in the north east – southwest directions and virtually no correlations in the northwest and southeast directions. This indicates omindirectional and thus no anisotropy.

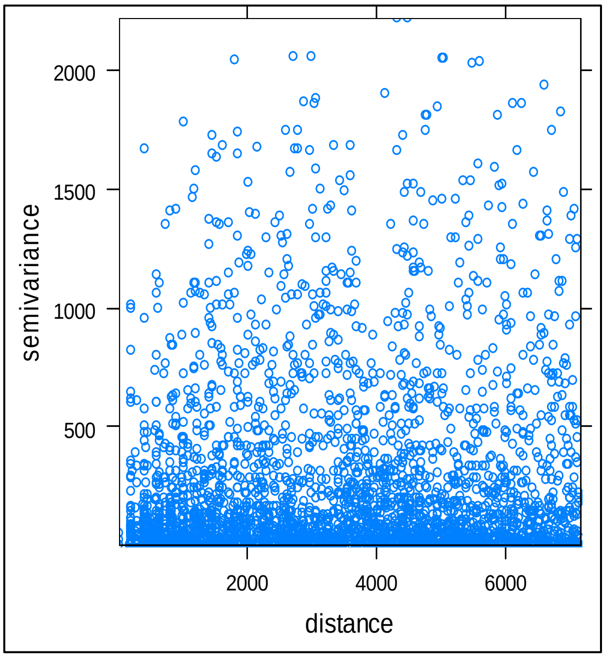


Figure 12: Variogram cloud

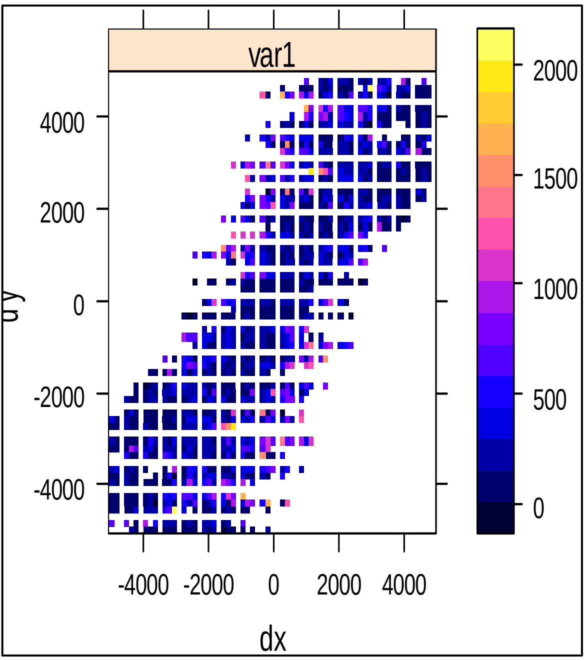
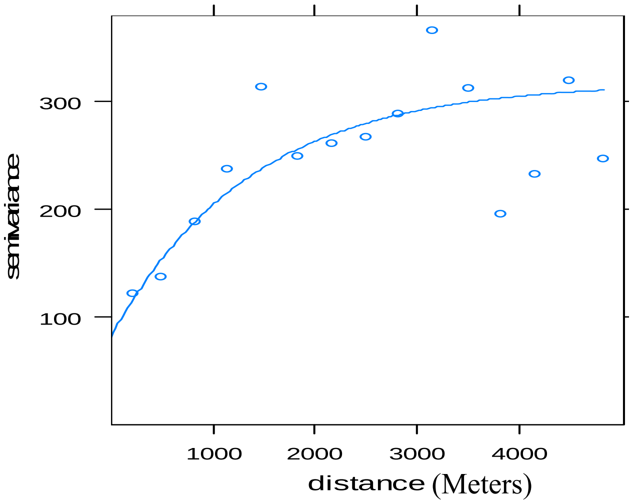


Figure 13: Variogram surface

The Isotropic variogram model of As (Figure 14) exhibits a very good structure, which can be well fitted with an exponential model.



Exponential model

Nugget= 80.93629
Sill= 236.12289
Range= 1362.75

Figure 14: Isotropic variogram model of arsenic

There is a nugget effect of 80.94 showing that the sampling density is adequate to reveal the spatial structures. Furthermore, the range of 1362.75 m implies that the length of the spatial autocorrelation is much longer than the sampling interval of 200m. Therefore, the current sampling design is appropriate for this study and it is expected that a good spatial structure will be shown on the interpolated map (McGrath David et al., 2004). Since the anisotropic feature was not clearly identified in the variogram surface (Figure 13), directional variogram was not computed; rather ordinary kriging interpolation was calculated.

4.1.6. Spatial Distribution Maps

In this research, ordinary Kriging was applied. The number of observations used for calculation was set to 14. For the purpose of contaminated soil assessment, indicator Kriging was used to show high or low levels based on the As distribution map (Figure 15) and a map of As > 20 ppm was produced and is shown in (Figure 16). The value of 20 ppm threshold is based on the maximum estimate of As in soil that could produce toxic symptoms in farm lands / grazing animal and industrial sites (Ortiz Escober, 2005).

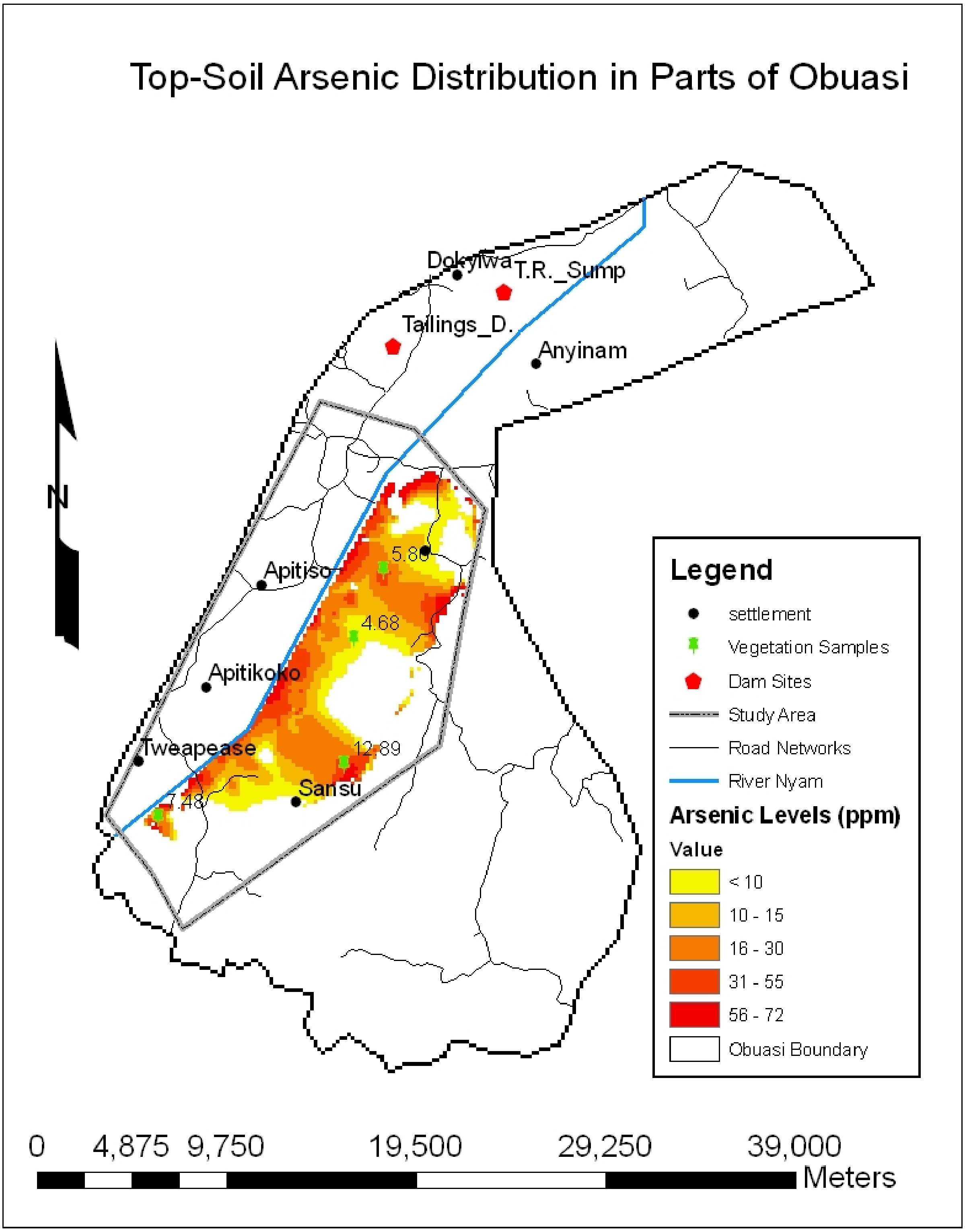


Figure 15: Arsenic distribution map in some parts of Obuasi

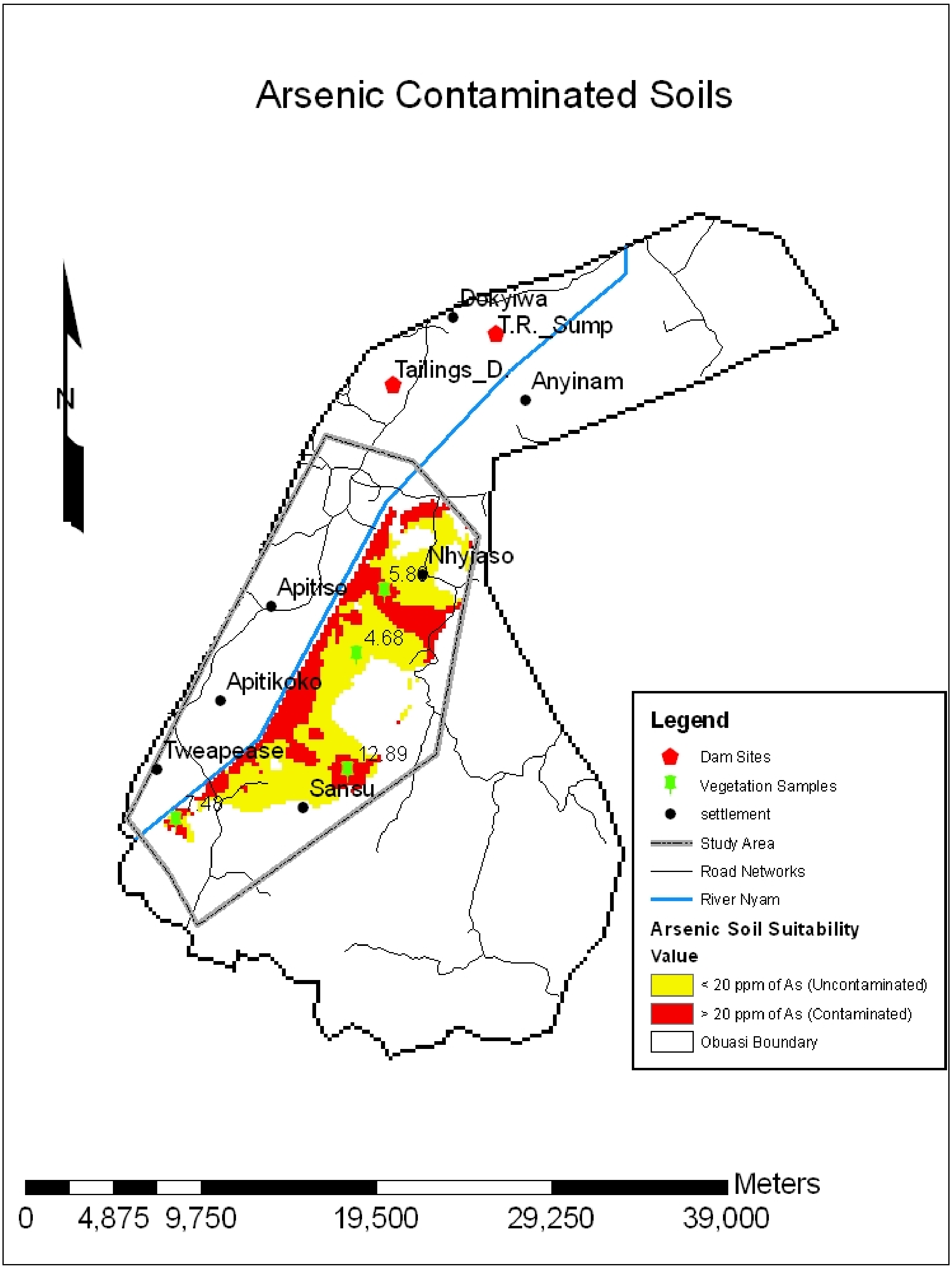


Figure 16: Arsenic soil contaminated map in some parts of Obuasi

4.2. DISCUSSION

4.2.1. Levels of Arsenic Concentration

The results of arsenic levels in stream sediments, soils, food crops, vegetation as well as the pH measurements of the topsoil samples are given in appendices B, D, A, and C respectively. The arsenic levels found in stream sediments were within the range 50.00 – 34253.00 ppm. The extremely high levels of arsenic in the stream sediment of the Nyam stem from the fact that the river is the direct recipient of the discharges from the treatment retention sump and the tailings dam. The high levels of As have rendered the river without life and the community has also been barred from drinking the water. The mining company has since 1998 provided the community with a borehole as their source of drinking water.

The concentration of As found in the soils of the study area ranges from 0.03 ppm to 69.72 ppm. The relatively high arsenic concentrations in the soils may be due to two major observations. It could be the high degree of contamination by the processes of mining operations, such as roasting of ore in the past, solid mechanical dispersal of primary minerals of arsenic as well as secondary minerals formed by weathering in the tailings and contaminated water effluents (Garcia-Sanchez and Alvarez-Ayuso, 2003). The other reason may also be attributed to dissolved arsenic from stream sediment materials washed from the Nyam River. The average level of the arsenic concentrations found in the soils of the five communities is within the range 18 ppm and 27 ppm at 99% confidence interval (Table 4). Furthermore, the pH values of the topsoil were found to be rather low ($pH < 7$) showing that the soil samples were acidic and thus suggesting a weathering process which confirms Asiam's study (Asiam, 1996). It is therefore, unlikely that the source of arsenic found in the soils may only be from the discharges from the tailings dam and the retention sumps. It may also be possible that, arsenic in the past has been introduced into the environment either as air – borne suspended As_2O_3 particles that later settled directly on the soils as well as on surface supports (say leaves) which are eventually washed into the top-soil whenever it rained or through the overflow of tailings and that of the Nyam River. This may possibly affect food crops (including vegetation) grown on such soils.

The As concentration ranging from 0.01 ppm-12.89 ppm were found in vegetation samples collected in the field while that of food crops were within the range 0.01 – 1.83 ppm.. The values in these plants (Appendix A and C) were found to be higher than that permitted by the EPA, Ghana (i.e. ≥ 0.2 ppm). The levels of As in plants may however, be influenced by the likely presence of arsenate in the soils and its stability relationship driven by the pH conditions (Baroni et al., 2004). It is also possible the arsenic concentration in the vegetation could suggest the emission of $As_2 O_3$ in the past from the mine during the roasting of gold bearing arsenopyrite concentrates. From the above discussions, it can be suggested that, the Nyam River has high arsenic concentrations since the discharges from the tailings and treatment retention sumps are directed to it. This eventually dispersed downstream and, in periods of floods coupled with the weathering activities, introduces arsenic into soils of the floodplains on which vegetation and/or food crops are grown.

4.2.2. Top-Soil Arsenic Levels and pH of the Top-Soils

The results revealed a negative significant relationship between the top-soil arsenic levels and pH of the top-soil ($R^2 = 0.56$, $p < 0.05$). From the plot of arsenic levels against the pH values (Figure 11), it can be seen that low levels of pH give rise to higher levels of arsenic. This could imply that the more acidic the soils in the area becomes, the faster the weathering process and this thus give rise to high levels of arsenic since parent rocks contain arsenopyrite. Thus the presence of arsenic in the study area could be attributed to weathering activities and the discharges from the tailings dam or the treatment retention sump and the Nyam River. The availability of the As in soil is affected by changes in pH. In general there is an increase in As toxicity effects on plants as the soils become more acidic, particularly at pHs below 5 when As–binding species such as Fe Oxy-compound become more soluble (Alloway, 1990).

The results confirms Alloway (1990) findings which concluded that, there is an increase in arsenic toxicity on plants as the soils become more acidic, particularly at pHs below 6. The relationship that exists between the arsenic levels and the pH values gives an indication that the pH triggers weathering of rocks. These weathered materials are mobilized by the stream which also in times of flood are dispersed into their flood plains or agriculture lands that are close by. It will therefore be noticed that the trend reduces further from the bank of the river thus giving an indication that the pH values in the study area may be used to estimate the levels of arsenic concentration using the model below:

$$\text{Arsenic Levels} = -12.123pH + 90.978 \ldots\ldots\ldots \text{Eqn (1)}$$

The model is applicable to only the study area.

4.2.3. Spatial Distribution of Arsenic in Soils

The ordinary Kriging map (Figure 15) indicates the spatial distribution of As in the five communities considered for this research. High concentrations of As are located in the north east and south west direction along the bank of the river Nyam. This kind of spatial distribution confirms the direction revealed by the As variogram surface (Figure 13) and the post-plots (Figure 7) of the arsenic levels. Out of the total area of 11961 ha considered for the soil samples, 6805 ha of the soils in the area (57 %) have levels between 0.00-30.00 ppm and 5156 ha of the soils (43 %) in the area have values between 31.00-70.00 ppm. Nhyiaso and the Sansu communities are found to be highly contaminated. However, the levels fairly reduce with an increasing distance away from the mine site and the Nyam River. This result agrees with similar studies conducted in the Obuasi township by Asiam (1996) and Amasa (1975) where they both concluded that arsenic levels in the Obuasi environs decreases gradually with distance from the mine site.

4.2.4. Arsenic Contamination of Soil (Permissible Levels)

The indicator Kriging map (Figure 15) indicates that, the As contents of soils are very high along the bank of the Nyam river due to the processes of mining operations such as gold mine waste, dispersal of primary minerals of As and secondary minerals formed by weathering processes and contaminated water effluents. Out of the total area considered for this research, 6996 ha are above the threshold i.e. >

20 ppm As set for maximum permissible soil concentration (BGS, 2005) . This indicates that 55 % of the area is contaminated with arsenic and thus require treatment of the soil. Nhyiaso and Sansu are found to be part of the 55 % highly contaminated soils. These two communities are mainly farming communities and this has resulted in low yield.

According to Azcue et al (1995), Davies (1980) and Garcia–Sanchez (2003), As concentration in contaminated soils can reach values up to some hundreds of ppm in mining environments. The high percentage of contaminated soils in the area confirm the earlier works conducted in some parts of Obuasi by Amasa (1975), Amonoo–Neizer and Amekor (1994), Asiam (1996) and Smedley (1996). The soils close to the Nyam River presents high As contents than those located at longer distance (500 m – 1000 m). Thus, the As dispersion halo around the river effluents are not very wide. The medium to low pH (3.0 – 6.0) of soil samples favours the As adsorption on Fe Oxyhydroxides by the mechanism of ligand exchange (Garcia-Sanchez and Alvarez-Ayuso, 2003).

A large number of reported studies on the arsenic adsorption on Oxides, Oxyhydroxides and soil show great adsorption capacities of Oxyhydroxides with a maximum adsorption around pH 3.0 – 6.0 (Asiam, 1996; Garcia-Sanchez and Alvarez-Ayuso, 2003; Smith, 1998). Because of the extremely slow solubility of the arsenate at low pH, its persistence on arsenopyrite – bearing rocks and the high As adsorption capacity of Fe Oxyhydroxides in the pH range of the soil, the mobility of As around spoils is low and the areas of contaminated soil are limited to narrow zones (Garcia-Sanchez and Alvarez-Ayuso, 2003) as observed in the map of polluted areas (Figure 16).

4.2.5. Relationship between Arsenic Levels of Soils and Plants

A careful assessment of the vegetation samples result (Tables 5 & 6) indicates that Apitiso and Tweapease generally have high levels of As in plants. This may be due to the locations of the two communities. Apitiso is about 50 m away from the tailings dam while Tweapease is situated downstream of the Nyam. The levels of As in edible plants is generally low, often close to the limit of detection even when the crops are grown on contaminated land (Alloway, 1990).

When compared to As levels of soils at several mining sites, where total As ranged from 2 to 17, 000 ppm and available As from 1 to 390 ppm (Baroni et al., 2004; Bech, 1997; de Koe, 1994; Flynn, 2002; Jung, 2002), the values of As in these soils can be said to be considered intermediate or moderate (Appendix D). Nevertheless, in some farm soils, the arsenic contents exceeded the legal limits for maximum permissible soil concentrations (As > 20 ppm). The high levels arsenic in the vegetation (12.89 ppm) may be explained by the high values of As in the soils of that community contradicting the general observation by Alloway (1990) that, levels of As in plants are generally low even if they are grown on contaminated land.

The results clearly show that when the concentrations or levels of arsenic in the soil are not particularly high, the levels in the plants/vegetation are relatively low. This finding agrees with previous results for grass grown near smelters (Baroni et al., 2004; de Koe, 1994; Otte, 1990; Temple, 1997). However, Alloway (1990), O’ Neill (1995), Pitten et al (1999) observed very different relationship as discussed above.

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSIONS

- The results revealed a negative significant relationship between the top-soil arsenic levels and pH of the top-soil ($r^2= 0.56$, $p < 0.05$). High As values correlates with low pH of the top-soil. This implies that As mobilized by streams/rivers as very often deposited on land during flooding.

- The average levels of arsenic in the area were estimated to be in the range of 18 ppm and 27 ppm at a 99 % confidence interval whilst as high as 12.89 As levels were found in vegetation. About 55 % of the soils in the study area are contaminated with As.

- Within the limitations of the exploratory data analyses and the size of the datasets used in this research, there is a reasonable indication that high levels of As in plants/vegetation occurred on soils with high As levels. The high As concentration from weathered rocks and tailings might have been mobilized by the stream in the study area (Nyam River) and deposited on floodplains and nearby agricultural soils.

- Since farmers preferred to cultivate foodcrops on floodplains or close to the river bank, it will therefore be appropriate to remediate contaminated soils since chronic ingestion of As in foodcrops or in water is a health hazard.

5.2. RECOMMENDATIONS

- In order to fully establish the contamination processes floodplains further downstream of the mining areas should also be studied because the sediments, which are found to be high in arsenic, are also deposited with other stream debris during erosion.

- A stricter environmental monitoring program which among other activities, involves re-vegetating the areas covered by the tailings piles and prohibiting unauthorized and unplanned digging of the tailings by the local people (“Galamsey” operators) can reduce the process responsible for the leaching of arsenic from the tailings piles and their subsequent erosion into the streams(in this case the Nyam River).

- Large geochemical datasets (Soil, Vegetation, Food crops, Stream Sediments and Rock samples) should be collected to cover the whole of Obuasi in order to determine the spatial extent of the arsenic pollution.

- Future works in the area should take into consideration the generation of flood prone areas to determine the actual floodplains to select areas to be sample for more emphasis. The soil As and pH model developed should be validated.

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7. APPENDICES

Appendix A (Food Crop Samples)

Town	Crop	As (ppm)
Tweapease	Orange	0.64
Apitiso	Cassava	0.64
Nhyiaso	Plantain	0.56
Dokyiwa	Cocoyam	1.83
Anyinam	Pineapple	1.28
Sansu	Orange	0.58
Apitikoko	Sugar Cane	0.01

Source: Environmental Department, Anglogold Ashanti

Appendix B (Stream Sediment Samples)

X loc	Y loc	As (ppm)	pH
204587.43	174060.38	34253.00	6.70
201632.43	170886.49	28363.00	7.50
199005.77	168040.94	1861.00	7.70
197364.10	164867.05	9000.00	7.30
195831.88	161802.60	5800.00	7.30
194409.10	159613.72	3361.00	7.30
192657.99	156111.49	1764.00	7.30
190687.99	154360.38	1834.00	7.60
188936.88	152937.60	58.00	6.50
208746.32	178000.38	1625.00	6.90
194190.21	158519.27	151.00	6.50
202726.88	172199.83	50.00	6.30
186200.77	150639.27	750.00	7.10
193752.43	158190.94	1964.00	7.40

Appendix C (Results of Vegetation Samples)

ID	Community	Grass	Oil Palm	Cocoyam	Orange
		As	As	As	As
A1	Apitiso	0.28	3.06	1.70	0.58
A2		1.51	4.93	2.40	1.27
A3		12.89	7.42	0.20	11.06
A4		4.17	1.04	3.48	6.70
A5		5.74	0.04	0.12	4.21
A6		1.03	2.17	0.06	0.15
A7		2.56	0.35	1.36	3.14
N1	Nhiaso	4.93	3.17	1.80	1.91
N2		1.28	4.93	0.14	0.12
N3		0.01	5.86	0.03	2.06
N4		2.63	3.69	2.84	0.15
N5		1.17	1.93	0.04	3.07
N6		0.16	5.04	2.05	1.03
N7		1.30	0.01	1.11	2.79
S1	Sansu	0.21	0.37	1.03	0.97
S2		4.11	2.12	4.00	0.54
S3		2.48	0.67	3.19	2.00
S4		1.27	0.93	4.68	1.57
S5		0.09	1.78	0.15	0.14
S6		0.01	3.51	2.37	2.56
S7		2.19	0.16	0.35	0.29
S8		3.58	1.43	1.24	0.18
T1	Tweapease	0.49	0.64	5.12	3.48
T2		0.58	2.45	3.01	7.48
T3		1.23	3.06	6.03	2.06
T4		2.06	1.73	0.17	0.93
T5		0.12	1.11	1.83	0.01
T6		2.52	0.22	3.59	4.21
T7		0.01	0.37	2.51	0.67
T8		1.17	2.14	0.13	1.12

Appendix D

The table below is the analyzed soil samples for arsenic and pH. The soil type (1 is loam and 2 indicates clay) was also recorded.

Sample id	Coordinate System		Arsenic (As)		pH		Soil Type
	X Loc	Y Loc	a (ppm)	b (ppm)	a	b	
S1	200202.63	167007.23	22.71	11.70	5.40	6.10	1
S2	200000.14	167007.93	63.20	18.60	4.10	5.70	1
S3	199802.15	167004.21	28.00	16.50	4.30	5.20	2
S4	199204.93	167004.31	35.07	12.60	4.50	4.90	2
S5	199000.48	167004.17	69.72	12.80	4.00	4.70	2
S6	199598.52	166198.69	10.06	3.00	6.10	5.70	2
S7	199399.16	166201.84	34.02	3.20	6.00	6.20	1
S8	199204.33	166198.66	28.68	2.80	4.30	5.60	1
S9	198999.99	166201.82	50.09	12.40	4.20	5.80	2
S10	198600.72	166201.88	38.06	21.60	4.30	5.00	2
S11	199402.36	165603.69	11.05	1.40	6.00	5.10	1
S12	198801.56	165600.38	19.47	11.80	6.30	5.90	1
S13	198600.23	165610.16	64.11	31.20	4.30	5.00	1
S14	198395.84	165610.16	49.04	22.50	4.70	5.10	1
S15	198197.82	165603.65	67.22	32.00	3.90	4.90	1
S16	199804.81	164403.22	12.01	9.50	5.10	5.80	1
S17	199402.52	164403.21	21.24	7.00	4.90	4.90	1
S18	199000.16	164406.41	24.07	7.10	5.60	5.70	1
S19	198399.20	164403.22	33.13	8.70	4.00	4.90	1
S20	197802.02	164406.45	60.45	42.90	4.00	4.00	1
S21	199203.95	163602.36	38.41	15.50	4.70	4.90	1
S22	198600.22	163605.57	14.31	2.80	6.80	6.50	1
S23	198000.62	163605.50	25.14	2.90	4.60	5.70	2
S24	197403.43	163602.33	49.1	1.70	4.90	5.90	2
S25	196997.70	163608.86	55.08	21.40	4.40	5.30	2
S26	199401.87	162605.94	20.16	31.50	4.70	5.20	2
S27	198801.36	162605.98	10.99	31.30	5.20	6.50	2
S28	198200.03	162602.65	3.10	11.30	6.50	6.30	2
S29	197804.03	162602.62	34.02	1.80	4.80	5.20	2
S30	197203.69	163605.32	50.07	41.50	4.80	5.20	2
S31	186397.92	150599.74	34.10	21.30	3.80	6.40	2
S32	186586.45	150610.89	10.07	1.30	6.60	5.40	2
S33	186808.25	150599.75	0.12	2.10	5.10	6.90	2
S34	186808.23	150799.36	36.04	21.20	4.70	5.40	2
S35	187007.89	150821.52	9.33	1.60	6.20	6.90	2
S36	187207.43	150821.59	10.11	3.00	6.20	7.10	2

S37	187195.39	151000.69	13.06	5.80	6.30	6.90	1
S38	187403.04	150997.44	38.14	7.90	4.80	5.30	1
S39	187201.39	151201.49	24.01	8.10	5.20	5.40	1
S40	187399.38	151201.46	12.09	14.10	7.10	5.80	2
S41	187600.57	151198.16	3.20	2.40	6.90	5.80	2
S42	187996.56	151201.42	23.09	1.20	5.10	5.40	2
S43	187996.85	151399.45	34.02	1.70	4.90	5.20	2
S44	188194.54	151402.69	19.71	1.30	5.80	5.20	2
S45	188597.53	151797.18	58.01	14.20	4.20	5.40	2
S46	188798.70	151803.60	13.08	4.30	6.90	4.90	2
S47	189006.50	151797.12	0.20	3.10	5.40	5.20	2
S48	190600.30	153201.41	32.07	31.70	4.30	4.00	2
S49	190801.50	153198.24	17.07	23.70	6.90	5.20	2
S50	190999.50	153198.27	0.26	2.10	5.10	6.90	2
S51	191200.70	153204.78	0.36	1.70	5.30	7.00	1
S52	191398.70	153198.29	11.92	8.20	6.40	5.70	1
S53	191006.02	153399.46	11.36	17.00	5.90	5.10	1
S54	191402.05	153399.40	10.04	12.00	5.30	4.40	1
S55	191804.48	153402.75	10.07	9.40	6.90	5.60	1
S56	191006.07	153399.40	18.02	8.20	5.70	5.90	1
S57	191402.04	153399.49	13.11	2.60	6.90	5.80	1
S58	191804.41	153402.76	0.06	3.50	5.30	4.60	1
S59	194200.92	157802.13	64.04	19.90	4.10	4.30	1
S60	194804.65	157802.12	19.33	7.30	5.10	6.70	1
S61	195203.79	157795.65	34.01	9.40	4.40	5.00	1
S62	195807.43	157798.84	6.00	8.30	6.00	4.90	1
S63	196002.26	157802.11	0.08	7.00	5.10	4.40	1
S64	194801.39	159203.26	51.05	6.80	4.30	6.40	1
S65	195401.78	1592006	47.22	7.40	4.00	6.60	1
S66	195800.97	159206.52	21.02	6.60	5.90	6.80	1
S67	196402.85	159203.27	15.03	7.80	6.80	5.20	1
S68	196607.36	159196.78	5.00	0.70	6.80	7.10	1
S69	195207.53	160001.65	31.02	3.40	6.90	7.40	1
S70	195804.75	159998.42	24.06	3.90	4.40	6.70	1
S71	196200.74	160001.65	12.11	3.50	6.30	5.40	1
S72	196603.23	160001.65	10.81	4.70	6.80	6.00	1
S73	195201.00	160407.35	36.18	3.90	4.90	5.70	1
S74	195603.53	160404.12	26.52	3.10	5.70	6.40	1
S75	196204.06	160407.33	10.61	2.90	6.20	5.90	1
S76	196405.28	160400.80	19.64	3.90	5.30	5.30	1
S77	196606.47	160400.80	17.01	2.70	5.30	5.10	1
S78	196002.62	161402.95	55.81	2.50	4.50	5.20	1
S79	196405.15	161402.95	12.09	5.60	5.40	5.30	1
S80	196801.14	161406.14	27.13	9.40	5.10	5.20	1

S81	196602.96	161403.78	21.16	10.80	5.90	5.70	1
S82	197203.39	161403.70	9.59	18.10	5.30	5.30	1
S83	196998.84	163005.71	20.42	6.30	4.50	5.40	2
S84	197401.36	163002.54	3.06	2.10	6.50	5.70	2
S85	197999.25	163005.76	8.08	1.80	5.80	6.50	1
S86	190804.88	153603.90	20.03	2.20	7.00	6.40	1
S87	191002.86	153600.66	17.03	2.80	6.50	6.10	1
S88	191200.74	153600.79	13.1	2.40	7.00	6.40	1
S89	191398.76	153603.98	0.03	2.60	7.30	6.90	1
S90	191600.09	153603.93	3.35	1.80	6.90	5.80	1
S91	191200.75	153801.96	23.01	2.00	5.30	5.00	1
S92	191398.73	153805.18	10.23	2.70	7.00	7.40	1
S93	191603.25	153801.99	5.00	2.70	6.90	7.10	1
S94	191807.72	153798.72	15.35	0.90	5.40	6.80	1
S95	191995.94	153798.76	16.02	0.90	5.30	7.30	1
S96	192202.32	155002.35	29.01	0.40	4.40	4.80	1
S97	192400.33	155002.34	16.03	0.80	5.90	6.10	1
S98	192601.59	155002.34	13.12	0.40	6.30	7.00	1
S99	192802.78	154995.87	9.24	0.40	6.30	6.50	1
S100	193007.25	154995.88	2.68	0.40	7.20	7.30	1
S101	193004.05	155398.39	18.07	0.80	7.10	7.00	1
S102	193403.20	155401.56	13.06	0.40	6.90	6.80	2
S103	193801.26	155404.53	11.97	0.40	5.80	5.90	2
S104	194199.23	155407.71	25.11	0.40	5.20	6.30	2
S105	194999.28	155404.54	17.32	0.20	7.00	7.00	1
S106	194204.17	156001.77	30.01	0.20	4.90	5.30	1
S107	194603.34	155998.48	5.03	0.40	4.30	4.90	1
S108	194002.98	156595.65	37.02	0.20	4.60	5.20	1
S109	194398.86	156602.12	35.48	0.20	4.60	5.30	1
S110	194999.33	156605.40	19.41	0.40	4.80	5.70	1

Appendix E

FIELD OBSERVATION SHEET

Soil Samples **Sheet Number------------------**

Top-Soil ID--------------------------Date-------------------------Sampler--

Sub-Soil ID-------------------- Community--

Sample Site Location

Ghana Metre Grid Easting-----------------------------Northing-----------------------------------

Site Description

Landscape/topography---

Land use

○ Agriculture, specify crop------------------------------ Color----------------ID----------------------------
○ Pasture, grassland, fallow field
○ Forest
○ Wetland
○ Non-Cultivated
○ Others, specify--

Soil Characteristics

Soil type---

Sampling interval (cm): Top-Soil-------------------- Sub-Soil-------------------

Sample Humidity	Top-Soil	Sub-Soil
Wet	O	O
Dry	O	O

Appendix F

FIELD OBSERVATION SHEET

<u>Stream Sediment Samples</u> Sheet Number--------------

Stream Sediment ID--------------Date-----------------Sampler-----------------Community------------------------

Sample Site Location

Ghana Metre Grid Easting---------------------------Northing---------------------------------------

Channel Characteristics

○ Natural
○ Reinforced
○ Man-made (ditch)

Stream Flow

○ Low
○ Normal
○ High

Stream Bed

○ Boulders & gravel
○ Gravel & sand
○ Sand & silt
○ Mud
○ Vegetation

Possible Source of Contamination---

Appendix G

R – Code for data analyses

To read data in R

```
Obs ----- read. CSV (“obs.CSV”)
```

Variable names and format

```
Str (Obs)
```

To save data in R

```
Save (Obs, file = “Obs. R Data”)
```

To recover data in R

```
Load (“Obs. Rdata”)
```

Summary Results

```
Summary (Arsenic 1)
Summary (Arsenic 2)
Summary (pH1)
Summary (pH2)
```

Histogram

```
Hist (Arsenic 1, main = “Top soil Arsenic levels”)
Hist (Arsenic 2, main = “Subsoil Arsenic levels”)
His (PH1, main = “Top soil pH”)
Hist (pH2, main = “Subsoil pH”)
```

Best Estimate of the mean arsenic levels at 99%. C.I.

```
t – test (Arsenic1), mu = 30, Conf. level = .99)
```

Normality test

Shapiro. test (arsenic 1)

Shapiro. test (Arsenic 2)

Shapiro. test (pH1)

Shapiro. test (pH2)

Scatter plots

Plot (Arsenic 1, Arsenic 2); title (“Sub soil vs Topsoil”)

Plot (Arsenic 1, pH1); title (“Topsoil pH vs Top soil arsenic”)

Plot (Arsenic 2, pH2); title (“subsoil pH vs subsoil arsenic”)

Plot (pH1, pH2); title (“subsoil pH vs Top soil Ph”)

Correlation

Cor. (Arsenic 1, Arsenic 2)

Cor. test (Arsenic 1, Arsenic 2)

Cor. (Arsenic1. pH1)

Cor. test (Arsenic 1, pH1)

Cor. (Arsenic 2, pH2)

Cor. test (Arsenic2, ph2)

Cor. (pH1, pH2)

Cor. test (pH1, pH2)

Post – plot of arsenic levels

Plot (x, y, asp = 1, pch = 23, bg = “green”, (ex =3x)

Arsenic 1/max (arsenic 1); grid (lty=1, col = “dark grey”

Or

Bubble (Obs, x col = 1, Y col =2, ZCol = “Arsenic 1, pch = 18

Percentiles of variables

```
Quantile (Arsenic 1, probs = seq (0, 1, by = .1))
Quantile (Arsenic 2, probs = Seq (0, 1, by = .1))
Quantile (pH1, probs = Seq (0, 1, by = .1))
Quantile (pH2, probs = seq (0, 1, by = .1))
```

Explanatory factors (classified predictor)

```
AS1.SL <- lm (arsenic 1~Soil)
Summary (AS1.SL); anova (AS1.SL)
pH1.SL <-lm (Ph1~Soil)
Summary (pH1-SL); anova (pH1. SL)
```

Omni directional variogram

Variogram cloud

```
VC <- variogram (Arsenic 1~1, obs, cloud = T)
Plot (vc)
```

Experimental variogram

```
V1 <- variogram (Arsenic 1 ≈ 1, obs, cut off = 5000))
Plot (V1, pl = T)
```

Isotropic Variogram model

```
V1 <- variogram (Arsenic1~1, obs)
Plot (V1, pl = T, model=vm2)
```

Fitting an Exponential model by observation

```
Vm2 <- vgm (200, “Exp”, 2500, 95)
 Plot (V1, pl = T, model = vm2)
```

Fitting an exponential model by R

```
Vm2.F <- fit. Variogram (V1, Vm2)
Vm2; Vm2. F
Plot (VI, Pl = T, model = Vm2)
Str (Vm2.F)
```

Directional variogram

Variogram surface

```
V <- variogram (Arsenic 1~1, obs, map = T, cute off = 500, width 150)
Plot (V)
OR
Plot (v, Col. regions = bpy. colors (64))
```