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**FACULTY OF PHYSICAL SCIENCES**

**DEPARTMENT OF CHEMISTRY**

**PHYSICOCHEMICAL ANALYSIS OF ROOF RUNOFF IN THE OBUASI AREA**

**By**

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DECLARATION

I hereby declare that this submission is my own work towards the M.Sc and that, to the best of my knowledge, it contains no materials previously published by another person nor material which has been accepted for the award of any other degree of the university, except where due acknowledgement has been made in the text.

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Student name & ID                      Signature                      Date

Certified By

.....  
Supervisor(s) Name                      Signature                      Date

Certified By

.....  
Head of Dept. Name                      Signature                      Date

## DEDICATION

This thesis is dedicated to my parents Mr. Daniel Kojo Issiw Appiah and Mrs. Sarah Appiah who have been my backbone in my achievements and also to Miss Dzigbodi Agama for her enormous support in these hard times.

Thanks a lot and God richly bless you all.

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## ABSTRACT

Life is dependent on water. Water exists in nature in many forms- clouds, rain, snow, ice, and fog; however, strictly speaking, chemically pure water does not exist for any appreciable length of time in nature. These impurities may give water a bad taste, color, odor, or cloudy appearance (turbidity), and cause hardness, corrosiveness, staining, or frothing.

Quality of Water in the Obuasi area has been questioned due to the mining activities as well as ore treatment methods being used in the area. Residents are in dire need of other fresh water alternatives and roof runoffs harvesting has become very common. There is therefore the need to ascertain the quality of this alternative in order not to create another problem in trying to solve one.

In this work, 75 roof runoffs samples from three selected areas (Wawasi, Ramia and Antobuasi) in the Obuasi area were sampled during five raining events between May and August 2007 from Aluminium, Aluzinc, Asbestos, Clay tiles and one collected from the skies to serve as control.

The samples were analysed for physical parameters such as; pH, Alkalinity, Electrical conductivity, Total Dissolved Solids, Total Suspended Solids, Turbidity. Anions such as; Sulphates, Chlorides, Nitrites, Phosphates were also analysed.

For each of the samples collected Six trace metals were determined. Metals were fractionated into dissolved and particulate fractions. Metals analysed include; Iron, Lead,

Zinc, Aluminium, Chromium and Cadmium using Varian 220 Atomic Absorption Spectrophotometer.

It was observed that the general quality of the water sampled from roofing material were seriously affected by the kind of roofing material being used with respect to the sampling area. It was also observed that most of the metals were particulate in nature and it contributed to over 60% of the total metal concentration.

Except for pH, Pb Turbidity and Chromium all the parameters recorded values that were below the WHO guidelines for drinking water. The pH had a good correlation between Iron and Zinc but had a poor correlation with Lead, Aluminium, Chromium and Cadmium.

Generally roof runoff can be recommended for washing utensils, flushing toilets laundry but not drinking and possibly cooking.

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## CHAPTER ONE

### 1.0 INTRODUCTION

Water is a precious natural resource. Whilst there appear to be an abundant water supply, 97% of the over 1.4 billion  $\text{cm}^3$  of water on Earth is sea-water, 2.7% of the remaining 3% is permanently bound up in ice at the poles. This leaves only 0.3% of the Earth's water resources as available fresh water. This available water moves in a permanent cycle through evaporation and rainfall (Waterfall, 2004).

Over 30 per cent of the rural population in Ghana does not have access to safe drinking water. Nationally, 22 per cent of the population still lack access to safe water (Allison, 2007).

Residents of the Obuasi town have relied mainly for their water supply on sources such as hand dug-wells, ponds, streams and springs. Most of these sources particularly the surface water sources are polluted and are the main sources of water-borne diseases in the area. The area also hosts one of the largest gold mines in Ghana, which has been in operation for the past 110 years (Third World Network, 2006).

Akabzaa *et al* (2003) indicated that the impact of gold mining on the environment is severe because of the chemical processes involved in the extraction of gold from its ores.

In addition to its underground mine whose ores are processed at the Biological Oxidation (BIOX) plants for gold recovery, AngloGold Ashanti (AGA) also recover gold

from open-pit surface mining using the 'heap leach' method, which involves reaction of large quantities of sodium cyanide on huge piles of earth and crushed rocks for gold recovery (Akabzaa *et al.*, 2003).

Since gold recovery in the mine mainly involve the use of large volumes of water, this has necessitated the construction of run-off dams (tailing dams) to contain run-off residues from the ore-extraction process. The slurry that initially run into the dam is decanted and the water is treated at a detoxication plant before being discharged into the environment. The leftover wastes are called *tailings* and often contain pollutants such as arsenic and cyanide (Carboo *et al.*, 1997). Environmental monitoring data obtained from water quality, mineralogical and geochemical studies have revealed that water sources that receive the effluents from the tailing dams in the study area are mostly acidic, falling outside the Environmental Protection Agency (EPA) and World Health Organisation (WHO) range of standards (Carboo *et al.*, 1997).

Other research reports have shown that many other streams and rivers in Obuasi have been polluted as a result of spillage and leakage from tailing dams, denying thousands the local people access to adequate clean water (Third world network, 2006).

Cyanide leakage due to flooding and dam failure which occurred in 1996 and 1998 near Dokyiwa further compounded an already pressing problem of pollution of underground water and surface water. This lead to the repartration of the inhabitants of villages such as Badukrom and Attakrom (Third world network report, 2006).

According to Third World Network Africa, an effluent discharged in November 2005 from AGA's Pompora Treatment Plant into the Kwabrafo stream, a tributary of the Jimi River which is the main supply of pipe borne water to communities within its concession, also caused some level of contamination and deprived villages and towns such as Sansu, Odumase, Akofuom, Jimiso Kakraba of their fresh water supplies (Gordon, 2004).

Akabzaa *et al.*, (2003) observed high values of Mg, Ca, SO<sub>4</sub>, and HCO<sub>3</sub> in samples from streams immediately down stream of mining and processing facilities at Kwabrafosu, Binsere and Dokyiwa. These Studies have indicated the immense pollution of streams and groundwater hence the need to resort to other sources of potable water supply to satisfy the day to day domestic water needs of the inhabitants of Obuasi and other communities around.

Studies conducted by researchers have indicated that one of the most growing domestic water resource is harvesting of rainwater and the major harvesting source is the roof top (Engmann 1993). Scientists in Ghana have advocated for the use of harvested rainwater. Though many individuals are convinced that it is the best alternative, no research has been conducted to ascertain the impact of the roofing material on the quality of the harvested rain water. Other researchers have indicated that urbanization and increase in mining activities have made roof runoff a major problem both from the point of view of quantity and quality (Thomas and Greene 1993; Kennedy *et al.*, 2001; Polkowska *et al.*, 2001; Ayenimo *et al.*, 2006).

Though the call for rainwater harvesting started in recent times the practice started many decades ago in many homes in Ghana (Novieku, 1980). The Interest in rainwater harvesting from roofs has grown in the Obuasi Municipality. Its use in households has changed from its function as mere water buck up to its current status of ultimate water source for all kind of household chores. Its utilization is now a healthier option along with more 'traditional' water supply technologies such as boreholes, streams and hand dug wells particularly available in the area and are conceived to be polluted. The increased interest in rainwater harvest has therefore necessitated more research into the quality of the harvested rainwater especially from the type of roofs in the Obuasi area.

## **1.1 STATEMENT OF PROBLEM**

Rainwater which has been projected to be purer and needs less purification might have other contamination sources apart from what is being brought with it from the skies. These contamination sources may be as a result of the roofing materials which is used for rainwater harvesting (Polkowska *et al.*, 2001).

The effective catchments area and the material used in constructing the catchment surface influence the collection efficiency and water quality (Polkowska *et al.*, 2001). Deposition of various pollutants from the atmosphere on rooftops significantly affects the quality of runoff water. Particulate deposition is greatest with a longer drought period. The level of pollution of runoff waters can be related with the type of roofing material, which is a source of many inorganic and organic pollutants. Also the shape of the roof, inclination, etc affects the amount and quality of pollutants in roof runoffs. Acidic rain in heavy

industrial areas could also contribute to the deposition of heavy metals through scavenging of atmospheric particulate matter and enhanced weathering of roofing materials and their final incorporation into roof runoffs (Polkowska *et al.*, 2001).

This present study attempts to create awareness of contamination threats posed by some commonly used roofing materials for rainwater harvesting in Ghana and particularly in the Obuasi area. The research will also attempt to further to prescribe the best type of roofing material for rainwater harvesting.

### **1.2.1 RESEARCH OBJECTIVES**

The specific objectives of this project are to determine:

1. The physicochemical properties of roof runoff such as pH, Alkalinity, Electrical Conductivity, Turbidity, Total Dissolved Solids, Total suspended Solids, Nitrites, Phosphates, Chloride and Sulphate from the Obuasi municipality.
2. Total, dissolve and particulate concentrations of some heavy metals in the roof runoff samples.
3. The type of the roofing materials is suitable for rainwater harvesting in the Obuasi area.

### 1.3 JUSTIFICATION OF RESEARCH OBJECTIVES

Water quality from roof catchments is a function of the type of roof material, climatic conditions, and the surrounding environment (Vasudevan *et al.*, 2001). Rooftops play an important role as a pathway that contaminants travel between a source (the atmosphere) and the harvested water from roof runoff. They are efficient collectors of particulate fallout from the atmosphere and efficient deliverers of those contaminants to runoff during rainfall (Forster, 1999; Davis, 2001).

The roofing materials can also be a source of contamination through the leaching of roofing materials. Metal roofs have been repeatedly shown to be a source of zinc (Yaziz *et al.*, 1989; Good, 1993; Quek and Forster, 1993; Steuer, 1997), and others have reported roofing materials to be a source of copper (Good, 1993) and cadmium (Forster, 1999 and Mason *et al.*, 1999). However, the heavy metals in the atmosphere deposited as aerosols mainly from human activities have a very small falling velocity, and are easily transferred by wind even from the point sources and rain at long distances from the point of their emission (Forster, 1999 and Davis *et al.*, 2001).

In general, the roofing material is a major influencing factor on trace metal concentrations especially when acidic rain is present. Roof guttering also to a large extent contribute to trace metal concentration. Trace metals such as lead, Zinc, Iron, and Aluminium are noted to be associated with metallic roofs. Cadmium and Chromium have been identified as major metal components in asbestos and clay tiles roofs (Forster, 1999 and Davis *et al.*, 2001).

Roofs mainly found in the Obuasi area are metal sheets, clay tiles and asbestos. The effects of some of the other environmental factors such roof leachates, atmospheric pollutants, particulates on roofs, crawling animals, bird droppings etc could also be enhanced if rain water harvesting is integrated into community environmental self-help strategies as being advocated by some researchers. Also the acid rain likely to be experienced in the area due to mining activities could release metals into runoffs and affect its quality.

Pollution of traditional surface water resources no doubt restricts the diversity of water supply options for the Obuasi area. Rain water still remains a good alternative but there is therefore a clear indication that roof runoffs which are the supposed alternative for the polluted traditional water sources in the area may also be contaminated. It is therefore imperative to analyse harvested rainwater from roofs to determine its quality and whether harvesting rainwater from the Obuasi area with such immense mining activity should be encouraged.

## **CHAPTER TWO**

### **2.0 LITERATURE REVIEW**

Rainwater harvesting is the capture, diversion, and storage of rainwater for a number of different purposes. It includes different ways of collecting rainwater from rooftops, land surfaces or rock catchments. Captured rainwater is then stored either in small containers such as jars and pots or more complex ones such as underground or sand dams and large size tanks and reservoirs (Waterfall, 2004).

### **2.1 HISTORY OF RAINWATER HARVESTING AND UTILISATION**

Rainwater harvesting and utilisation systems have been used since ancient times and evidence of roof catchment systems date back to early Roman times. Roman villas and even whole cities were designed to take advantage of rainwater as the principal source of drinking water and for domestic uses since at least 2000 B.C (UNEP, 2006).

In the Negev desert in Israel, tanks for storing runoff from hillsides for both domestic and agricultural purposes have allowed habitation and cultivation in areas with as little as 100 mm of rain per year (UNEP, 2006). The earliest known evidence of the use of rainwater technology in Africa came from northern Egypt, where tanks ranging from 200-2000 m<sup>3</sup> have been used for at least 2000 years – many are still operational today.

The technology also has a long history in Asia, where rainwater collection practices have been traced back almost 2000 years in Thailand (UNEP, 2006).

### **2.1.1 RAINWATER HARVEST (RWH) AND UTILISATION AROUND THE WORLD**

RWH systems have served as a major source of water in many countries. Below are some examples;

#### **2.1.1.1 Singapore**

Almost 86% of Singapore's population live in high-rise buildings. Light roofing is placed on the roofs to act as catchment. Collected roof water is kept in separate cisterns for non-potable uses such fire-fighting drills and toilet flushing. This water accounts for 28% to 33% of the total water used in the country, resulting in savings of approximately \$ 390,000 per annum (UNEP, 2006).

#### **2.1.1.2 Tokyo, Japan**

In Tokyo, rainwater harvesting and utilisation is promoted to mitigate water shortages, control floods, and secure water for emergencies (UNEP, 2006). The Ryogoku Kokugikan Sumo-wrestling Arena, built in 1985 in Sumida City, is a well-known facility that utilises rainwater on a large scale. The 8,400 m<sup>2</sup> rooftop of this arena is the catchment surface of the rainwater harvest system. Collected rainwater is drained into a huge underground storage tank and used for toilet flushing and air conditioning (UNEP, 2006). Following the example of Kokugikan, many new public facilities have begun to introduce rainwater utilisation systems in Tokyo. At the community level, a simple and

unique rainwater utilisation facility, “Rojison”, has been set up by local residents in the Mukojima district of Tokyo to utilise rainwater collected from the roofs of private houses for garden watering, fire-fighting and drinking water in emergencies (UNEP, 2006).

To date, about 750 private and public buildings in Tokyo have introduced rainwater collection and utilisation systems. Rainwater utilisation is now flourishing at both the public and private levels.

### **2.1.1.3 Brazil**

Over the past decade, many NGOs and local organisations in Brazil have focused their work on the supply of drinking water using rainwater harvesting, and the irrigation of small-scale agriculture using sub-surface impoundments. Rainwater harvesting and utilisation is now an integral part of educational programs for sustainable living in the semi-arid regions of Brazil (UNEP, 2006). The rainwater utilisation concept is also spreading to other parts of Brazil, especially urban areas. A further example of the growing interest in rainwater harvesting and utilisation is the establishment of the Brazilian Rainwater Catchment Systems Association, which was founded in 1999 and held its 3rd Brazilian Rainwater Utilisation Symposium in the fall of 2001 (UNEP, 2006).

Other rainwater harvesting systems exist in many cities for numerous reasons and purposes. In Indonesia rainwater harvesting has caused a decrease in the groundwater recharge in their major cities (UNEP, 2006). In the Capiz Province, of the Philippines rainwater systems have been built on credit for farmers to sustain their farms in order to improve their lives and also have enough to repay their loans. In Bangladesh it serves as an alternative source of drinking water for Arsenic affected areas (UNEP, 2006).

#### **2.1.1.4 Africa**

Although in some parts of Africa rapid expansion of rainwater catchment systems has occurred in recent years, progress has been slower than Southeast Asia. This is due in part to the lower rainfall and its seasonal nature, the smaller number and size of impervious roofs and the higher costs of constructing catchment systems in relation to typical household incomes. Nevertheless, rainwater collection is becoming more widespread in Africa with projects currently in Botswana, Togo, Mali, Malawi, South Africa, Namibia, Zimbabwe, Mozambique, Sierra Leone and Tanzania among others. Kenya is leading the way. Since the late 1970s, many projects have emerged in different parts of Kenya, each with their own designs and implementation strategies (UNEP, 2006).

### **2.2 USES OF RAINWATER**

Harvested rainwater can be used in several ways. If the water quality is controlled, it can be used as drinking water. Other domestic uses such as cooking, washing and cleaning are also possible. Moreover, rainwater can be used to keep sanitation facilities clean and hygienical. Beside domestic uses, rainwater can also be used to improve (small scale) agriculture, cattle breeding and even small scale industries (Thompson *et al.*, 2001).

### **2.3 TYPES OF CATCHMENT FOR RAINWATER HARVESTING**

Rainwater harvesting can be categorised according to the type of catchment surface used. These categories are; Roof Catchment Systems, Rock Catchment Systems and Ground Catchment Systems (UNEP, 2006).

## **2.4 ROOF CATCHMENT SYSTEMS**

According to Gould and Nissen-Petersen (1999) Roofs of buildings or houses are the most convenient and common method of providing a catchment area to harvest rainfall. A wide variety of materials are used to build roofs. Traditionally homes in ancient times were constructed with galvanized iron roofs. Changes in technology have come up with new types of roofing materials examples are aluminium/zinc alloy, Non metallic roofing tiles and Asbestos (Pringle, 1998). The roofing materials can be generally grouped into metal roofing and non metal roofing (Kennedy *et al.*, 2001).

### **2.4.1 Metal Roofing**

Metal roofing is the most common material used on the roofs in many homes, commercial and industrial premises (Kennedy *et al.*, 2001). Metal roofs come in a number of different forms including long run roofing (corrugated, trapezoidal, trough section/ concealed fix), tile, shakes and flat sheets. According to Pringle, 1998, galvanized steel was the most commonly used form of profiled metal roofing prior to the development of zinc/aluminium alloy coatings. These roofs consist of mild steel coated with zinc. The long run roofing is typically fixed in place using lead-headed nails.

Zinc/Aluminium alloy coatings were developed in the 1980's and are now the most common coating for mild steel roofs. The coating uses zinc 45% and aluminium 55% in the combination to provide sacrificial protection (zinc) and barrier (aluminium). Zinc/aluminium alloy and galvanized coated mild steel are the most commonly used metals for roofs (Kennedy *et al.*, 2001).

Aluminium, stainless steel, Copper, Lead and Zinc can also be used for roofing. With the exception of Lead, these can be rolled or pressed to form tiles. These materials are usually left unpainted, but can be painted. Materials such as lead have been used traditionally on historical building roof surfaces in European cities. Copper sheets are used to make copper shingles (Kennedy *et al.*, 2001).

#### **2.4.2 Non Metal Roofing Material**

Slate roofs include a wide range of geological materials that are classed as roofing slate. They include Asbestos, siltstone, mudstone, shale, marl and limestone (Kennedy *et al.*, 2001). Asbestos roofs are mainly seen in the form of slates. And can be identified by their flaky nature. Clay roofing tiles are gradually becoming more common and do not require added colouring. In recent times pigment can be added to colour tiles or inorganic oxide coloured cement slurry can be applied to the tile surface. It is also called terracotta (Kennedy *et al.*, 2001). Concrete tiles are also common in recent times. They are made of sand or Portland cement. They are sometimes covered with a base primer coating which comprises acrylic polymer, pigments, fillers and biocide which forms the top coat (Kennedy *et al.*, 2001). Fibre cement sheets are often used on industrial or commercial buildings. They consist of treated cellulose fibres mixed with cement and sand. They can be used as a replacement for asbestos cement sheeting (Kennedy *et al.*, 2001). Wooden shingles and shake roofs have historically been fairly rare. Shingles are sawn on both faces whereas shakes are sawn on the reverse and then split on the front face to produce a more irregular appearance. Shakes and Shingles are made of western red cedar (Kennedy *et al.*, 2001)

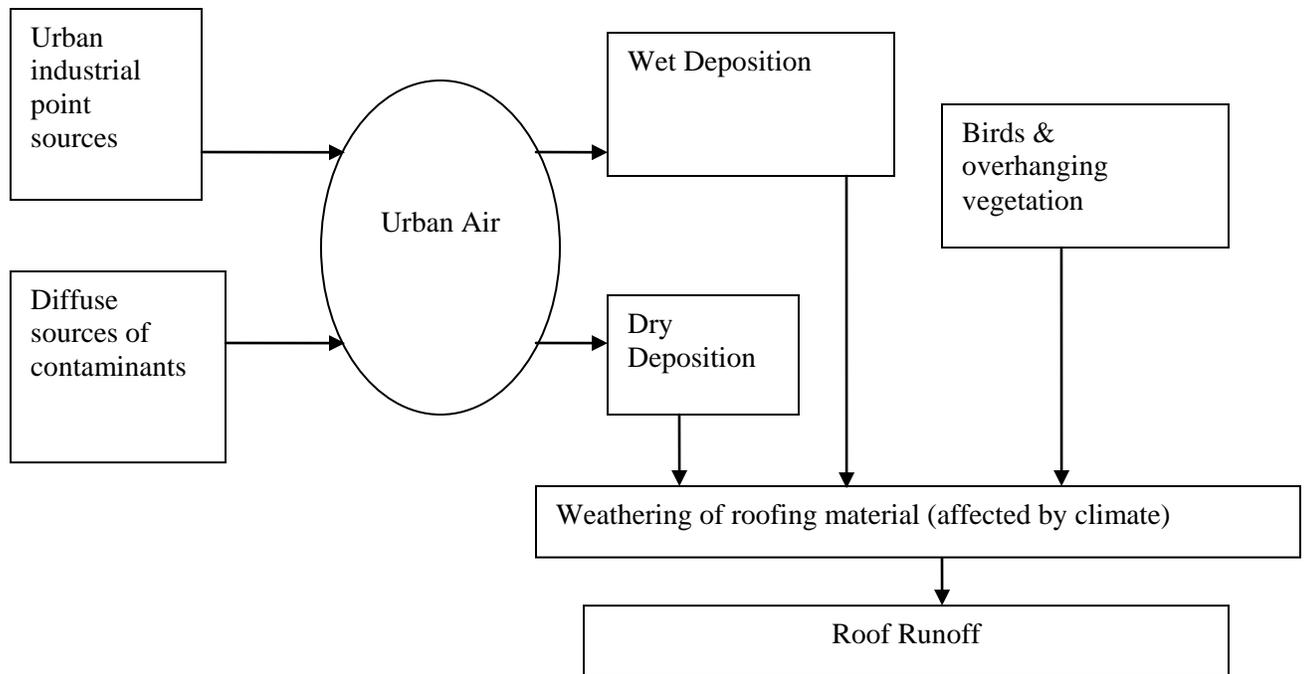
## **2.5 FACTORS AFFECTING ROOF RAINWATER COLLECTION**

Gould and Nissen-Petersen also pointed out that one of the most critical factors determining the efficiency of rainwater collection is the placing of guttering to route the water to the storage system. They also noted that the water collecting efficiency of the systems can be seriously reduced by factors such as the proportion of the roof utilised by the gutters.

The relative efficiency of any roof harvesting scheme will depend on the estimates of water demand to be satisfied, rainfall totals, the distribution of rainfall and the ability to store harvested water (UNEP, 2006).

## **2.6 SOURCES OF CONTAMINATION**

Contaminants in roof runoff come from three main sources: dry deposition, wet deposition and weathering of roof material (Kennedy *et al.*, 2001). Fig 2 shows the processes involved and how they are related.



**Fig 2.1: Sources of contamination and processes contributing to roof runoff quality.**

### 2.6.1 Dry Deposition

Dry deposition is the process where atmospheric particles (aerosols) settle via gravity or are deposited by impact (e.g., via wind) onto the surface of roofs. The deposition rates of these particles depend on particle size, meteorological conditions, concentrations of the pollutants in the atmosphere (Pryor *et al.*, 2000).

Dry depositions can be a source of contaminants as particulate aerosols are emitted by a variety of sources such as motor vehicles, house fires, boilers, non-mobile engines and generators, incinerators, industrial processes hence the materials deposited on the roof can be affected by proximity to major roads and other point sources (Kennedy *et al.*, 2001).

Roof gutters accumulate dust and dirt over time as a consequence of material being deposited on the roof and washing down into the gutter. Data provided by P. Kennedy and Kingett Mitchell from a number of roof gutters located adjacent to a lead smelter in Waione street, Petone, Wellington indicated that Lead and Antimony (Sb) concentrations were highest in the immediate vicinity of the lead smelter and decline rapidly with increasing distance from the smelter. The sediments also had significant concentrations of zinc (Kennedy *et al.*, 2001).

### **2.6.2 Wet Deposition (Rain)**

Wet deposition is the process where aerosols and soluble trace gases are removed from the atmosphere by dissolution and incorporation into water droplets (either in clouds or falling raindrops). Wet deposition also removes gases from the atmosphere. The concentration of these substances in the rainwater depends on the solubility of each individual particle (Kennedy *et al.*, 2001).

### **2.6.3 Roof Material**

Weathering of roofing materials occurs all time, but the rate of weathering depending on the age, the type of roofing material and climatic conditions. In humid areas, dry depositions on the roof surface reacts with the moisture and increase the corrosion rate of the roofing material (Pringle, 1998). During rainfall events, the weathered roof particles are washed from the roof surface into the roof runoff. Depending on the composition of the roofing material, these particles can alter the pH of the runoff, and elevate the concentration of suspended solids, trace metals and organic compounds (Pringle, 1998).

The inclination and direction of the roof also affects the runoff quality (Odnevall *et al.*, 2000). Flat and gentle sloping roofs result in a slow flow of water over the roof surface when compared to roofs with steep inclines. A slower water flow means that smaller particles and lesser amounts of weathered products may be picked up in the runoff. This is because the longer residence of the runoff on the roof can increase the dissolution of contaminants into the rainwater (Odnevall *et al.*, 2000). The roof direction affects runoff quality as roofs facing the prevailing wind are affected more by the climatic conditions. This increases the dry deposition rates and results in increased build up of particulates on the roof in humid areas (Odnevall *et al.*, 2000). This in turn will increase the rate of corrosion and weathering of the roofing material (Pringle, 1998).

## **2.7 FACTORS AFFECTING GENERAL RAINWATER QUALITY**

The three main sources of contaminants discussed above after delivering their particulates onto the roof runoff cause the decline in the quality parameters of the runoff. Below are some of the general qualities affected.

### **2.7.1 Dissolved Gases**

As a raindrop falls and comes in contact with the atmosphere, it dissolves naturally occurring carbon dioxide to form a weak acid. The collection of water from metallic roofs when acidic rain is present should be cautioned as more corrosion and leaching of metals from roofs will occur under hot weather conditions (Kohler *et al.*, 1997). The term 'acid rain' or 'acid deposition' denotes rainwater with pH 5.6 or less. Although the

concentration of both NO<sub>2</sub> and SO<sub>2</sub> is normally much lower than that of atmospheric CO<sub>2</sub>, which is mainly responsible for natural rain pH, it is now recognised that, for the most part, acid deposition is caused by the presence of large quantities of dissolved NO<sub>2</sub> and SO<sub>2</sub> (Kohler *et al.*, 1997).

### **2.7.2 Particulate matter**

Particulate matter refers to smoke, dust, and soot suspended in the air (Kohler *et al.*, 1997). Fine particulates can be emitted by industrial and residential combustion, vehicle exhaust and sandstorms. As rainwater falls through the atmosphere, it can incorporate these contaminants. Rainwater harvested from roofs can contain animal and bird faeces, mosses and lichens, windblown dust, particulates from urban pollution, pesticides, and inorganic ions from industrial emissions. The particles are classified as either primary, those emitted directly into the atmosphere; and secondary, those formed or modified in the atmosphere from condensation (Kohler *et al.*, 1997).

### **2.7.3 Chemical compounds**

Compounds present in the atmosphere are subject to photochemical reactions and global transport over longer distances. During this process, drops of rain dissolve and wash out gases and aerosol which are products of natural and artificial activities from the atmosphere (Davis *et al.*, 2001).

Thomas and Greene, (1993) also noted that high levels of pesticides have been found in rainwater in Europe with highest concentrations occurring in the first rain immediately

after a dry season, in agricultural areas. In industrial areas, rainwater samples can have slightly higher values of suspended solids concentration and turbidity due to the greater amount of particulate matter in the atmosphere (Forster, 1999).

#### **2.7.4 Other factors affecting harvested rain**

According to a United States General Administration, zinc coating on galvanized iron and steel develops a natural carbonate on its surface by exposure to the atmosphere and by the action of rainwater. This coating, however, is usually not thick enough to protect the metal from further corrosion. The carbonate can become brittle and crusty and eventually split, exposing fresh zinc for corrosion. Since the zinc coating on the iron or steel is very thin, it can corrode up to the base metal exposing the base to the atmosphere as well.

Some studies in the U.S.A have examined the importance of various urban roof fractions as sources of metals (Astruc *et al.*, 1979; Sartor *et al.*, 1992; Dannecker *et al.*, 1990; Xanthopoulos *et al.*, 1993) but little attention was particularly paid to roof runoffs. A study by the U.S. Environmental Protection Agency (USEPA, 1990) identified sources of lead and Zn in roof runoff in an urban setting. Bannerman (1991) related increases in Zinc and lead concentrations in roof runoff to increase in areas with high traffic densities. Pitt and Barron (1989) also studied important sources of dissolved metals in the urban roof systems. Similar studies on roof runoffs were carried out in Australia by Thomas and Greene, 1993, and in Washington by Good, 1993.

## 2.8 PHYSICAL PARAMETERS TO BE ANALYSED

### 2.8.1 pH

The pH of rain water represents the concentration of the free hydrogen ions in it. The principal chemicals that produce acid precipitation are  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{CO}_2$ . Human activities are responsible for the production of these atmospheric pollutants. Acid rain is the word used for describing rainfall that has a pH level of less than 5.6 (Radojevic and Harrison, 1992). The chemical reactions that lead to acid rain begin as energy from sunlight in the form of photons which hit ozone molecules to form free oxygen and single reactive oxygen atoms. These oxygen atoms react with water molecules to produce electrically charged, negative, hydroxyl radicals which are responsible for oxidizing  $\text{SO}_2$  and  $\text{NO}_2$  to sulfuric and nitric acids (Radojevic and Harrison, 1992).

When acid waters come into contact with certain chemicals and metals, they often make them more toxic. For example, fish that can tolerate pH values as low as 4.8 will die at pH 5.5 if the water contains 0.9 mg/L of iron (USEPA, 2006). If acid rain water (environment) mixes with small amounts of certain metals such as Aluminum, Lead or Mercury, more contamination of the water occurs and health concerns far exceeding the usual dangers of these substances occurs. The balance of positive hydrogen ions ( $\text{H}^+$ ) and negative hydroxide ions ( $\text{OH}^-$ ) in water determines how acidity or basicity of the water. This means the water molecule is either missing an electron or has an extra electron. Since electrons have a negative charge, an extra one in the  $\text{OH}^-$  molecule makes it  $\text{OH}^-$ , and a missing one in the H-molecule gives it a "missing-minus" charge — in other words,

positive — and makes it  $H^+$ . When analysts measure pH, they are determining the balance between these ions (USEPA, 2006).

### **2.8.2 Electrical Conductivity**

According to the California Water Quality Resources Board (CWQRB, 2005), Conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum cations (ions that carry a positive charge). Organic compounds like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low conductivity when in water. Conductivity is also affected by temperature: the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 °C. Conductivity is measured in microsiemens per centimeter ( $\mu\text{s}/\text{cm}$ ). Distilled water has conductivity in the range of 0.5 to 3  $\mu\text{s}/\text{cm}$ . Industrial waters can range as high as 10,000  $\mu\text{s}/\text{cm}$  (Pushard, 2005).

### **2.8.3 Turbidity**

Turbidity is the measure of the fine suspended matter and its ability to impede light passing through water, this is mostly caused by colloidal matter. It is measured in Nephelometric Turbidity Unit (NTU) (Shelton, 2000). The level of total coliform bacteria and the grade of turbidity in rainwater collected from the rooftop are affected by dry spell, and especially the intensity of rainfall. The longer the dry period in between rainfall events, greater is the amount of turbidity in the rainwater (Shelton, 2000). The more the

intensity of rainfall, the more efficient is the cleaning process and greater is the presence of pollutants in the runoff. The most accurate way to determine water's turbidity is with an electronic turbidimeter. The turbidimeter has a light source and a photoelectric cell that accurately measures the light scattered by suspended particles in a water sample. Turbidity can be measured by filtering a water sample and comparing the filter's color (how light or dark it is) to a standard turbidity color chart (Shelton, 2000).

#### **2.8.4 Alkalinity**

Alkalinity is not a pollutant. It is the total measure of the substances in water that have "acid-neutralizing" ability. Alkalinity should not be confused with pH. pH measures the strength of an acid or base; alkalinity indicates a solution's power to react with acid and neutralize it (USEPA, 2006). The main sources of natural alkalinity are rocks, which contain carbonate, bicarbonate, and hydroxide compounds. Borates, silicates, and phosphates may also contribute to alkalinity (CWQRB, 2005).

#### **2.8.5 Total Dissolved Solids (TDS)**

It is a measure of the total ions in solution. In dilute solution TDS and EC are reasonably comparable and the TDS of a water sample based on the measured EC value can be calculated using the following equation:  $TDS (mg/L) = 0.5 \times EC (\mu s/cm)$ . The above relationship can also be used to check the acceptability of water chemical analyses. It does not apply to raw wastewater or high-strength industrial wastewater. As the solution become more concentrated ( $TDS > 1000 \text{ mg/L}$ ,  $EC > 2000 \mu s/cm$ ), the proximity of the

solution ions to each other depresses their activity and consequently their ability to transmit current, although the physical amount of dissolved solids is not affected. At high TDS values, the ratio TDS/EC increases and the relationship tends toward  $TDS = 0.9 \times EC$ .

Carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, calcium, magnesium, sodium, potassium, iron, manganese contribute to the TDS in a solution. They do not include gases, colloids or sediments. The TDS can be estimated by measuring the specific conductance of the water. Dissolved solids in natural waters range from less than 10mg/L for rainwater to more than 100,000 mg/L for brines (Shelton, 2000).

#### **2.8.6 Total Suspended Solids (TSS)**

According to the CWQRB, TSS provides an actual weight of the particulate material present in the sample. In water quality monitoring situations, a series of more labor intensive TSS measurements can be paired with relatively quick and easy turbidity measurements to develop a site-specific correlation. Once satisfactorily established, the correlation can be used to estimate TSS from more frequently made turbidity measurements, saving time and effort. Because turbidity readings are somewhat dependent on particle size, shape, and color, this approach requires calculating a correlation equation for each location (Shelton, 2000).

TSS of a water sample is determined by pouring a carefully measured volume of water (typically one liter; but less if the particulate density is high, or as much as two or three

liters for very clean water) through a pre-weighed filter of a specified pore size, then weighing the filter again after drying to remove all water. The gain in weight is a dry weight measure of the particulates present in the water sample expressed in units derived or calculated from the volume of water filtered (typically milligrams per liter or mg/L) (Shelton, 2000).

## **2.9 ANIONS TO BE ANALYSED**

### **2.9.1 Nitrite**

According to the USEPA (2006), Nitrate is the more stable oxidized form of combined nitrogen in most environmental media. Most nitrogenous materials in natural waters tend to be converted to nitrate, and, therefore, all sources of combined nitrogen (particularly organic nitrogen and ammonia) should be considered as potential nitrate sources. Nitrates occur naturally in mineral deposits (generally sodium or potassium nitrate), in soils, seawater, freshwater systems, the atmosphere, and in biota. Lakes and other static water bodies usually have less than 1.0  $\mu\text{g/L}$  of nitrate-nitrogen. Groundwater levels of nitrate-nitrogen may range up to 20  $\mu\text{g/L}$  or more, with higher levels characteristically occurring in shallow aquifers beneath areas of extensive development. Major sources of nitrates or nitrite in drinking water include fertilizer, sewage, and feedlots (USEPA, 2006).

The toxicity of nitrate in humans is due to the body's reduction of nitrate to nitrite (Pushard, 2005). This reaction takes place in saliva of humans at all ages and in the gastrointestinal tract of infants during the first three months of life. The toxicity of nitrite is demonstrated by cardiovascular effects at high dose levels and methemoglobinemia at

lower dose levels. Methemoglobinemia, "Blue-Baby Disease," is an effect in which hemoglobin is oxidized to methemoglobin, resulting in asphyxia (Pushard, 2005).

Infants up to three months of age are the most susceptible subpopulation with regard to nitrate. This is due to the fact that in the adult and child, about 10 percent of ingested nitrate is transformed to nitrite, while 100 percent of ingested nitrate can be transformed to nitrite in the infant (Knepp and Arkin, 1973).

### **2.9.2 Phosphates**

According to the (USESB, 2003), Phosphates come from fertilizers, pesticides, industry, and cleaning compounds. Natural sources include phosphate-containing rocks and solid or liquid wastes. Phosphates enter waterways from human and animal wastes (the human body releases about a pound of phosphorus per year), phosphate-rich rocks, wastes from laundries, cleaning, industrial processes, and farm fertilizers. Phosphates also are used widely in power plant boilers to prevent corrosion and the formation of scale (United States Geographical survey).

Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Ortho forms are produced by natural processes and are found in wastewater. Poly forms are used for treating boiler waters and in detergents; they can change to the ortho form in water. Organic phosphates are important in nature and also may result from the breakdown of organic pesticides which contain phosphates (USESB, 2003)

### **2.9.3 Chlorides**

The Secondary Maximum Contaminant Level (SMCL) of 250 mg/l for chloride is the level above which the taste of the water may become objectionable to the consumer. In addition to the adverse taste effects, high chloride concentration levels in the water contribute to the deterioration of domestic plumbing, water heaters, and municipal waterworks equipment. High chloride concentrations in the water may also be associated with the presence of sodium in drinking water. For the preceding reasons, the SMCL for chloride represents a desirable and reasonable level for protection of the public welfare (Shelton, 2000).

### **2.9.4 Sulphates**

The aesthetic objective for Sulphates in drinking water is 500 mg/L. Sulphates, which occur naturally in numerous minerals, are used in the mining and pulping industries and in wood preservation (Shelton, 2000). Large quantities of Sulphates can result in catharsis and gastrointestinal irritation. The presence of Sulphates above the aesthetic limit can result in noticeable taste. Some sensitive individuals may find the taste objectionable at lower Sulphates concentrations (USES, 2003).

## **2.10 TRACE METALS TO BE ANALYSED**

Trace metals are metals in extremely small quantities, almost at the molecular level, that reside in or are present in animal and plant cells and tissue. They are a necessary part of good nutrition, although they can be toxic if ingested excess quantities (Forte *et al.*, 1990). Trace metals include iron, magnesium, zinc, copper, chromium, nickel, cobalt, vanadium, arsenic, molybdenum, and selenium. Trace metals are depleted through the expenditure of energy by a living organism. They are replenished in animals by eating plants, and replenished in plants through the uptake of nutrients from the soil in which the plant grows (Forte *et al.*, 1990). Human vitamin pills and plant fertilizers both contain trace metals as additional sources for trace metals (Antonovics *et al.*, 1971).

### **2.10.1 Aluminium**

Aluminium is a soft, lightweight metal with a normally dull silvery appearance caused by a thin layer of oxidation that forms quickly when the metal is exposed to air. Aluminium oxide has a higher melting point than pure aluminium (Forte *et al.*, 1990). Aluminium has a tensile strength of about 49 megapascals (MPa) in a pure state and 400 MPa as an alloy. Aluminium is about one-third as dense as steel or copper; it is malleable, ductile, and easily machined and cast. It has excellent corrosion resistance and durability because of the protective oxide layer. Aluminium is one of the few metals which retain full silvery reflectance, even in finely powdered form, which makes it a very important component of silver paints (Antonovics *et al.*, 1971).

It has been established that aluminium is a neurotoxin, although the basis for its toxicity is unknown. It recently has been shown to alter the function of the Blood-Brain Barrier (BBB), which regulates exchanges between the central nervous system (CNS) and peripheral circulation (Amundsen *et al.*, 1992). The BBB owes its unique properties to the integrity of the cell membranes that comprise it. Aluminum affects some of the membrane-like functions of the BBB. It increases the rate of transmembrane diffusion and selectively changes saturable transport systems without disrupting the integrity of the membranes. Such alterations in the access to the brain by nutrients, hormones, toxins, and drugs could be the basis of CNS dysfunction. Aluminum is capable of altering membrane function at the BBB; many of its effects on the CNS as well as peripheral tissues can be explained by its actions as a membrane toxin (Andrews *et al.*, 1989).

Aluminum is one of the most abundant elements found in the environment. Therefore, human exposure to this metal is common and unavoidable. However, intake is relatively low because this element is highly insoluble in many of its naturally occurring forms. The significance of environmental contact with aluminum is further diminished by the fact that less than 1 % of that taken into the body orally is absorbed from the gastrointestinal tract (Antonovics *et al.*, 1971).

The average human intake is estimated to be between 30 and 50 mg per day. This intake comes primarily from foods, drinking water, and pharmaceuticals. Based on the maximum levels reported in drinking water, less than 1/4 of the total intake comes from water. Some common food additives contain aluminum. Due to certain additives, cheese

and cornbread are two major contributors to high aluminum exposures in diets. With regard to pharmaceuticals, some common over-the-counter medications such as antacids and buffered aspirin contain aluminum to increase the daily intake significantly (Aurand and Hoffmeister, 1980). Certain aluminum compounds have been found to be an important component of the neurological damage characteristics of Alzheimer's Disease (AD) (Graves *et al.*, 1980). Much research over the last decade has focused on the role of aluminum in the development of this disease. At this point, its role is still not clearly defined. Since AD is a chronic disease which may take a long time to develop, long-term exposure is the most important measure of intake (Parmeggiani, 1983).

### **2.10.2 Iron**

According to Antovics *et al.*, 1971, Metallic iron occurs in the free state and is widely distributed and ranked in abundance among all the element in the earth's crust, next to aluminium. The principal ore of iron is hermatite, other important ores are goethite, magnetite, siderite and bog iron (limonite) (Ralph, 1998).

Iron has the chemical symbol Fe; it is a silvery, malleable and ductile metallic transition element with atomic number 26 and relative atomic weight of 55.847. It belongs to group VIII of the periodic table and in the same group with element like: Ruthenium (Ru), Osmium (Os), etc. It is in period IV just as arsenic (As), copper (Cu), and Zinc (Zn) (Ralph, 1998). Pure iron melts at about 1535 °C (about 2795 °F), boils at 27500 °C (4982 °F) and has a specific gravity of 7.86. The metal exists in three different forms; ordinary or  $\alpha$ -iron (alpha iron),  $\gamma$ -iron (gamma iron), and  $\delta$ -iron (delta iron). The internal

arrangement of the atoms in the crystal lattice changes in the transition from one form to another. The transition from  $\alpha$ -iron to  $\delta$ -iron occurs at 910 °C (Charalambous, 1984).

Chemically, iron is an active metal. It combines with the halogens (fluorine, chlorine, bromine, iodine and astatine) sulfur, phosphorus, carbon, and silicon. It displaces hydrogen from most dilute acids. It burns in oxygen to form ferric oxide,  $\text{Fe}_3\text{O}_4$ . When exposed to moist air, iron become corroded forming a reddish-brown, flaky, hydrated ferric oxide commonly known as rust. The formation of rust is an electrochemical phenomenon in which the impurities present in iron form an electrical “couple” with the iron metal. A small current is set up, water from the atmosphere providing an electrolyte in the form of a salt to accelerate the reaction. In this process the iron metal is decomposed and reacts with oxygen in the air to form rust. The reaction proceeds faster in those places where rust accumulates, and the surface of the metal becomes pitted.

The basic biochemical role of iron in humans is to permit the transfer of oxygen and carbon dioxide from one tissue to another. It accomplishes this primarily as part of both haemoglobin and myoglobin which are iron containing proteins in the blood and muscle (Cook *et al.*, 1972). It is also part of several other compounds and enzymes that are also essential for the uptake and release of oxygen and carbon dioxide. Since these reactions are involved in the release of energy within the cell, iron is essential for energy metabolism. It is also important in blood formation. However, there is considerable evidence that iron functions include catalyzing the conversion of beta-carotene to vitamin A. Although iron is necessary for the growth of microorganisms, it is an essential part of

enzymes and immune substances needed to destroy invading infection organisms (Cook *et al.*, 1972, Sabadell and Axtmann, 1975).

There are two kinds of iron in the diet, with respect to the mechanism of absorption. These are heme-iron and non-heme iron, (Halberg, 1982). Before iron can be absorbed, two conditions must exist, first, the iron must be separate from its organic complex, secondly, and almost always the ferric iron must be reduced to ferrous iron. Although the body can absorb both the reduced ferrous ( $\text{Fe}^{2+}$ ) and the oxidized ferric ( $\text{Fe}^{3+}$ ) iron, absorption is greater when iron is available in the ferrous form (Fifield and Haines, 1996). This change is accomplished in the presence of acid that is available either from hydrochloric acid, which is a normal secretion in the stomach, or from vitamin C (ascorbic acid), which is available from many fruits as dietary iron. The absorption of iron occurs primarily in the upper part of the small intestine, usually the duodenum (Gutlirie, 1989). An average adult human has 4.2 g of iron, mostly combined in proteins of various kinds. These play roles in the transport of oxygen in proteins of various kinds and also in the blood it enhances redox reactions used to generate metabolic energy by the body (Charalambous, 1984)

Generally, about 2-15 % of ingested iron is absorbed from the gastrointestinal tract whereas elimination is only about 0.01 % per day (percent body burden or amount absorbed). Normally, excess ingested iron is excreted, and some is contained within shed intestinal cells and in bile and urine and even smaller amounts in sweats, nails and hair. Total iron excretion is usually in order of 0.5 mg/day (Charalambous, 1984). Acute iron

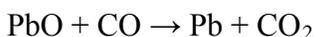
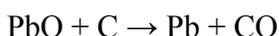
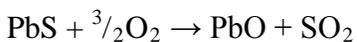
toxicity is nearly always due to accidental ingestion of iron containing medicines and most often occurs in children. Severe toxicity occurs after ingestion of more than 0.5 g of iron or 2.5 g of iron sulphate ( $\text{FeSO}_4$ ). Toxicity becomes manifest with vomits being bloody owing to ulceration of the gastrointestinal tract; stools become black. These are followed by signs of shocks and metabolic acidosis, liver damage and hepatic cirrhosis. An intake of 7-35 g is lethal (Mayer, 1979).

### **2.10.3 Lead**

Lead is available in several forms including foil, granules, ingots, powder, rod, shot, sheet, and wire (Watkins *et al.*, 1983). Small and large samples of lead foil, sheet, and wire (and lead alloy in ingot form) can be purchased from metal shops. Its principal ores are galena ( $\text{PbS}$ ), cerusite ( $\text{PbCO}_3$ ), Anglesite ( $\text{PbSO}_4$ ) and Jamesonite [ $\text{Pb}_4\text{FeSb}_6\text{S}_{14}$ ]. Galena, the principal primary ore of lead is by far the most important and widely distributed. It occurs in many geological formations e.g. veins in the Cambrian clay, slates in bed or nests within the sandstones and limestone (Watkins *et al.*, 1983)

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Alloys include pewter and solder. Tetraethyl lead ( $\text{PbEt}_4$ ) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds (Guthrie, 1989).

There is usually little need to make lead metal in the laboratory as it is so cheap and readily available. Lead is isolated from its sulphide, PbS. The process involves burning in a restricted air flow followed by reduction of the resulting oxide PbO with carbon (Watkins *et al.*, 1983).



This product formed is lead usually contaminated with metals such as antimony, arsenic, copper, gold, silver, tin, and zinc. Lead can cause a variety of adverse health effects in humans. At relatively low levels of exposure, these effects may include interference in red blood cell chemistry, delays in normal physical and mental development in babies and young children, slight deficits in the attention span, hearing, and learning abilities of children, and slight increases in blood pressure of some adults. Lead has been classified in EPA's Group B2 (probable human carcinogen), based upon evidence of kidney tumors in rats by the oral route (Antonovics *et al.*, 1971).

#### **2.10.4 Zinc**

Zinc ranks 24<sup>th</sup> in abundance among the elements in the earth crust. It never occurs free in nature, but is found as zinc oxides (ZnO) in the mineral zincite; as zinc silicate (ZnO.SiO.2H<sub>2</sub>O), in the mineral franklinite; and as zinc sulphides (ZnS) in the mineral sphalerite, or zinc blend. The ores most commonly used as a source of zinc are

smithsonite and sphalerite (Sabadell and Axtmann, 1975). Zinc has a chemical symbol Zn, with atomic number 30 and relative atomic weight 65.38. It is a member of group (XII) of the periodic table of elements just as cadmium and mercury. It is in period (IV) of the periodic table and in the same period with copper, nickel, manganese and iron. Pure zinc is a crystalline metal, insoluble in hot and cold water but soluble in alcohol, acids and alkalis. It is extremely brittle at ordinary temperatures, but becomes malleable between 120 °C and 150 °C (248 F and 302 F) and can be rolled into sheets between heated rollers (Shelton, 2000). Zinc is unaffected by dry air, in moist air, it is oxidized and becomes coated with a carbonate film that protects it from further corrosion. Zinc melts at about 420 °C (about 693 F), boils at about 907 °C (about 1180 F) and has a specific gravity of 7.14. There are five stable isotopes (mass number 64, 66, 67, 68 and 70) and six radioactive isotopes are known. Chemically, it is a reactive metal, combining with oxygen and other non-metals and reacting with dilute acids to release hydrogen gas. It also dissolves in alkaline medium to give zincates. Most of its compound contain  $Zn^{2+}$  ion. It is amphoteric, forming zincates with bases (Shelton, 2000).

The human body contains between 2 g - 25 g of zinc with three quarters of this amount concentrated in the skeleton. A high concentration of zinc also appear in the skin, hair and testes. In the blood most of the zinc occurs in the red blood cells, platelets and the blood serum. Zinc is found in biological systems only in the +2 valence state. This is due to the extra stability associated with filled d-orbital electronic configuration (Ar)  $3d^{10}$ . This also accounts for the differences between zinc and its congeners with unfilled d-orbital such as iron, copper and Arsenic ( $As^{2+}$ ,  $Fe^{2+}$  and  $Cu^{2+}$ ) (USESB, 2003). Biological

redox functions of zinc are largely based on its presence in zinc metalloenzymes. Zinc absorption occurs mostly in the duodenum and proximal jejunum (upper part of the small intestine) (Sheldon, 2000).

The absorption process is active, energy dependent and apparently mediated by specific zinc transport (binding) ligands. The absorption plays an important role in homeostatic regulation. Zinc is transported in blood plasma mostly by albumin (60-70) and by macroglobulin and free amino acids (Sheldon, 2000). Only a small portion of dietary zinc is absorbed from the intestine, the major fraction passing out through the faeces. The Pancreas account for 25% of total excretion whilst sweat losses are generally minor but can be appreciable in tropical climate or under physical stress (USES, 2003). Zinc deficiency related to diet was first characterized in humans by Prasad and co-workers in adolescent boys from the Nile delta. The principal features of the deficiency were growth failure and delayed sexual maturation. After treatment with zinc the patients grew taller and matured sexually. Zinc deficiency in boys and girls studied in Iran responded similarly to treatment. Dwarfism related to zinc deficiency has been reported in Turkey, Morocco and Portugal, the United States as well as China (Watkins *et al.*, 1983).

Zinc is one of the most important trace metals for life. An adult human of average weight of 70 kg has 2.3 g of zinc, mostly forming part of specialized enzymes such as dehydrogenase and other proteins. Zinc is nutritionally essential metal and its deficiency can result in a wide spectrum of clinical effects depending on age, stage of development, and deficiencies of related metals. Excessive exposure to zinc is relatively uncommon

and requires heavy exposure. Daily intakes 150-600mg and 6g are considered toxic and lethal to human. Zinc does not accumulate with exposure, but the body content is modulated by homeostatic mechanisms that principally on absorption and liver levels (Underwood, 1977; NRCC 1981)

### **2.10.5 Cadmium**

Cadmium is found in very low concentrations in most rocks, as well as in coal and petroleum. Mostly cadmium is found in combination with zinc (WHO, 1992). Cadmium uses include electroplating, nickel-cadmium batteries, paint and pigments, and plastic stabilizers (WHO, 1992). It is introduced into the environment from mining smelting and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. The remaining cadmium emissions are from fossil fuel use, fertilizer application, and sewage sludge disposal. Cadmium may enter drinking water as a result of corrosion of galvanized pipe. Landfill leachates are also an important source of cadmium in the environment (Wester *et al.*, 1992). Acute and chronic exposure to cadmium in animals and humans results in kidney dysfunction, hypertension, anemia, and liver damage (Wester *et al.*, 1992). The kidney is considered to be the critical target organ in humans who are chronically exposed to cadmium by ingestion. Cadmium has been classified in EPA's Group B1 (probable human carcinogen), based upon evidence of carcinogenicity in humans through inhalation exposure. However, since cadmium has not been shown to be carcinogenic through ingestion exposure, the metal is

regulated based upon chronic toxicity data. Because of cadmium's potential adverse health effects and widespread occurrence in raw waters, it is regulated (Weast, 1974).

#### **2.10.6 Chromium**

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases (Sheldon, 2000). Chromium is present in the environment in several different forms. The most common forms are chromium (0), chromium (III), and chromium (VI). No taste or odor is associated with chromium compounds. Chromium (III) occurs naturally in the environment and is an essential nutrient. Chromium (VI) and chromium (0) are generally produced by industrial processes. The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. Chromium enters the environment through a number of routes and in many forms (CWQRB, 2005).

In air, chromium compounds are present mostly as fine dust particles which eventually settle over land and water. Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. Fish do not accumulate much chromium in their bodies from water (Andrews *et al.*, 1989). Individuals can be exposed to Chromium through; eating food containing chromium (III), Breathing contaminated workplace air or skin contact during use in the workplace, drinking contaminated well water and Living near uncontrolled hazardous waste sites containing chromium or industries that use chromium (Van-Gronsveld, 1995).

Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat. Breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum (Stokinger, 1981). Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted (Thornton, 1996). Several studies have shown that chromium (VI) compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer. The World Health Organization (WHO) has determined that chromium (VI) is a human carcinogen (Thornton, 1996).

The Department of Health and Human Services (DHHS) has determined that certain chromium (VI) compounds are known to cause cancer in humans. The EPA has determined that chromium (VI) in air is a human carcinogen. It is not known if exposure to chromium will result in birth defects or other developmental effects in people. Birth defects have been observed in animals exposed to chromium (VI). It is likely that health effects seen in children exposed to high amounts of chromium will be similar to the effects seen in adults (Stokinger, 1981).

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Description of the Study Area

The Obuasi town is located between longitudes 5°35' N and 5°65' N, and latitudes 6°35' W and 6°90' W. It generally has an undulating terrain with more of hills rising above 500 m above sea level and covers a total area of 162.4 km<sup>2</sup> as in fig 3.1 (Obuasi Municipal Assembly, 2006 ).

The municipality experiences semi-equatorial climatic conditions with a double maximum rainfall regime. Mean annual rainfall range between 125 cm and 175 cm. Temperatures are uniformly high all year with the hottest month being March when 30 °C is usually recorded. Mean average annual temperature is 25.5 °C. Relative humidity is 75 % - 80 %. Most of the local residents are engaged in farming and mining. The area has a population of about 115,564 according to the 2000 census (Obuasi Municipal Assembly, 2006 ).

The natural environment of the municipality has been degraded. There has been extreme pollution of local rivers and streams with pollution levels up to 38 times above maximum permissible limits, with high levels of arsenic, iron, manganese and other heavy metals, other forms of degradation such deforestation, and air pollution has also taken place (Action aid report, 2006)



## **3.2 EQUIPMENTS AND REAGENTS**

### **3.2.1 Equipments used:**

1. Vacuum/pressure pump
2. Vacuum filtration apparatus
3. pH meter
4. Conductivity meter
5. Atomic Absorption Spectrophotometer (Varian 220)
6. Merck Colorimeter
7. 5500 photometer

### **3.2.2 Reagents Used**

1. Analar grade Nitric Acid by BDH Laboratory supplies, Britain
2. Hydrochloric acid by BDH Laboratory supplies, Britain
3. Ammonium chloride by BDH Laboratory supplies, Britain
4. Concentrated Ammonium solution by BDH Laboratory supplies, Britain
5. Sodium Carbonate by Fisons Laboratory, Britain
6. Silver Nitrate by BDH Laboratory supplies, Britain
7. Potassium Dichromate by Fisons Laboratory, Britain
8. Sodium hydroxide by BDH Laboratory supplies, Britain
9. Tetra oxo Sulphate (VI) Acid by BDH Laboratory supplies, Britain
10. Anhydrous Sodium Sulphate by BDH Laboratory supplies, Britain
11. Glycerol by BDH Laboratory supplies, Britain
12. Sodium Chloride by BDH Laboratory supplies, Britain

13. Barium Chloride by BDH Laboratory supplies, Britain
14. Potassium dihydrogen Orthophosphate by BDH Laboratory supplies, Britain
15. Chloroform by BDH Laboratory supplies, Britain
16. Ammonium Molybdate Fisons Laboratory, Britain
17. Ascorbic acid by BDH Laboratory supplies, Britain
18. Analar Grade Potassium Antimonyl Tartarate by BDH Laboratory supplies, Britain
19. Sulphanilamide by BDH Laboratory supplies, Britain
20. N (-1 Naphthyl) ethylene-diamine by BDH Laboratory supplies, Britain
21. Sodium Nitrite by BDH Laboratory supplies, Britain
22. Potassium Chloride by BDH Laboratory supplies, Britain
23. Phenolphthalein Indicator Fisons Laboratory, Britain
24. Methyl Orange Indicator Fisons Laboratory, Britain

### **3.3 PROCEDURES**

#### **3.3.1 Sampling Areas**

Three sampling areas were chosen based on the availability of roofing materials under study. The presence of mining activities was also taken into consideration. These areas are Ramia, Wawasi and Antobuasi all within the Obuasi community. Consideration was also given to the AGA's environmental departments sampling Scheme for pollution abatement facilities as in fig 3.2. Ramia is at the western part of the Anyinam Township, which has the Kwasi Mensah Shaft and the Sulphur Treatment Plant (STP). Wawasi also has the Cote D'or Shaft, Adansi shaft and Ellis Turner Shaft (ETS). The Pompora



### **3.3.2 Preparation of sampling containers**

In order to obtain accurate results from the sampling programme, sampling procedures were adopted to eliminate or minimise potential contamination of the samples. Sample containers were soaked in nitric acid overnight and were washed with distilled water, rinsed with de-ionized water and dried in a drying cabinet. Some of the dry containers were selected, filled with distilled water and the pH tested, when it is between 6 to 7 then it is ready for use, otherwise the sampling container is washed and the pH tested again. This served as quality control (Anon, 1992). Sample containers were labelled to enhance record keeping. Samples collected from the Wawasi area were labelled as follows; WSAL, WAA, WCT, WAZ and WCO for Aluminium, Asbestos, Clay tiles, Aluzinc roofing materials and control respectively. Those sampled from the Antobuasi area were coded as follows; ASAL, AAA, ACT, AAZ and ACO for Aluminium, Asbestos, Clay tiles, Aluzinc roofing materials and control respectively. Those sampled from the Ramia area were also coded as follows; RSAL, RAA, RCT, RAZ and RCO for Aluminium, Asbestos, Clay tiles, Aluzinc roofing materials and control respectively.

### **3.3.3 Sampling**

Rainwater was collected on different raining events from the different roofing materials in the selected communities in Obuasi. Sampling was done between the months of May and August 2007. The selected roofing materials were Aluminium, Aluzinc, Asbestos, and Clay tiles. Also Rainwater was collected directly from the skies and used as control. The samples were collected ten minutes after the start of the rain into 1 L acid leached polythene containers. This was done to minimize pollution due to atmospheric sources.

A total of 75 samples were collected from 5 rain events within the three selected communities in the Obuasi area. For each roofing material, three water samples were collected from different locations within each community.

### **3.3.4 Preparation of samples**

Samples collected were immediately analysed for pH. Samples were kept under reduced temperature conditions in ice packed ice chests and transported to the laboratory. The samples for metal determination were acidified with concentrated Nitric acid to a pH of 2 and kept in the refrigerator; this was done to prevent the precipitation of metals (Anon, 1992; APHA, 1992).

For the analysis of dissolved metals, samples were prepared by shaking each sample well to ensure adequate homogeneity and filtered through nitrate membrane filters of pore size 0.4  $\mu\text{m}$  using the vacuum filtration. The filtrates were then collected in well cleaned test tubes and sent to the AAS room for analysis for dissolved metals. A blank was prepared without the samples. To develop the standard calibration curve for each one of the metals to be analyzed (Anon, 1992; APHA, 1992). 1, 3 and 5 mg/L standard solutions were prepared from 1000 mL stock solution of Iron, Lead, Zinc, Cadmium, Aluminium and Chromium.

## **3.4 METHODOLOGY**

The following physical water quality parameters were also determined in the samples.

### **3.4.1 pH**

The pH was determined in the samples immediately after sampling using a pH meter. The procedure included the following.

#### **3.4.1.1 Calibration of pH meter.**

Three main buffer solutions of pH 4.01, 7.00, and 9.2 were used to calibrate the pH meter. One buffer tablet each was dissolved in a 100 mL volume of deionised water to prepare a 4.01 and 7.00 buffer solution. The 9.2 buffer solution was prepared by dissolving a sachet of buffer tablet in 500 mL deionised water. New buffer solutions were prepared for each set of rainwater sample collected (AGA Environmental Laboratory manual, 2007).

#### **3.4.1.2 Measurement of pH in water using Fisherbrand Hydrus 100 pH meter**

Before the measurement of the pH a manual calibration of the instrument with two buffers with three pH units apart was conducted. The CAL key was pressed to calibrate and the AUTO calibration procedure was followed (AGA Environmental Laboratory manual, 2007). The Meter automatically displayed MEASURE. The pH of the samples were measured by reading the values that displayed on the screen after the READY signal has disappeared.

### **3.4.2 Determination of Total Dissolved Solids Using Hi 9032 Microprocessor Bench Conductivity Meter**

The instrument was calibrated before the measurements were started. By pressing the TDS key the display will show “TDS” to confirm the measurement mode. The meter automatically defaults the TDS factor value to 0.5 (Shown on the secondary display) every time it was turned on. The TDS factor was changed to the value of the solution, by pressing the FTR key. The TDS factor value will start blinking on the screen. The desired value was obtained by pressing the numeric keys and then the ENTER key to confirm the value. The stored value was displayed and it stopped blinking. Once the measurement reading stabilizes the measurement was complete. The conductivity button on the instrument was pressed to display its value which was then recorded on the data sheet.

### **3.4.3 Determination of Total Suspended Solids (TSS) In Water**

The Total Suspended Solids were determined by the following steps;

#### **3.4.3.1 Set Up for filtration Apparatus**

- i) A 300 mL funnel was attached to a filter holder by means of an anodized aluminium spring clamp.
- ii) A neoprene stopper was inserted in the stem of the filter holder, and the unit plugged into the neck of the filtration flask.
- (iii) The side arm of the filtration flask was then connected to another flask by using a ½ silicone rubber hose and a stopper.

(iv) Finally, this second flask was connected to a vacuum/pressure pump using a ½” silicone rubber hose and a stopper.

#### **3.4.3.2 Determination of Total Suspended Solids**

(i) A vacuum filtration apparatus was set up as described above. A 0.4 µm pore size filter paper was placed on the Teflon-faced glass filter holder and made wet by filtering about 20 mL distilled water through it using the vacuum filtration.

(ii) The wet filter paper was removed carefully using a pair of forceps, and placed on a watch glass. The watch glass and its contents were put in an electric oven for 15 minutes to dry.

(iii) The filter paper together with the watch glass were removed from the oven and placed in a desiccator for about 1 hour to cool.

(iv) The filter paper was marked, weighed on an analytical balance, and its weight was recorded.

(v) The sample was shaken to obtain a homogenous mixture, and thereafter, a reasonable quantity is measured in a graduated glass cylinder. The volume of the sample was recorded.

(vi) The sample was put into the funnel and vacuum filtration was applied.

(vii) The contents of the measuring cylinder were rinsed with distilled water and poured into the funnel, which was later on rinsed with three portions of 20 mL distilled water whilst vacuum filtration continued until the last drop of the filtrate was seen.

(viii) The filter paper, with the solids, was removed using a pair of forceps and put on a clean dry watch glass and placed in an oven for 2 hours.

(ix) The filter paper was then removed from the oven and then placed in a desiccator to cool.

(x) The weight of the filter paper with the solids was then taken on an analytical balance and the value recorded.

### Calculation

$$\text{Mg TSS/L} = \frac{(w_1 - w_2) \times 10^6}{V_s}$$

Where;

$w_1$  = weight of the filter paper and solids, in grams

$w_2$  = weight of the filter paper only, in grams.  $V_s$  = volume of the test sample, in ml

### 3.4.4 Alkalinity

#### 3.4.4.1 Preparation of reagents

##### a. 0.1 M of HCl

A 2.1 mL solution of concentrated HCl was added to a 200 ml of distilled water in a 1000 ml volumetric flask. To this mixture was added more distilled water until it got to the 1000 ml mark.

##### b. 0.05 M $\text{Na}_2\text{CO}_3$ Solution

One liter of sodium carbonate solution was prepared by dissolving a 4.5g of dried  $\text{Na}_2\text{CO}_3$  in double distilled water and transferred into a 1 L volumetric flask. The solution was made to the mark with distilled water.

**c. Standard HCl**

The approximate 0.1 M HCl prepared was titrated against 40 mL of 0.05 M Na<sub>2</sub>CO<sub>3</sub> diluted with 60 mL of water. The acid was added until a pH of 5 was attained. The solution was boiled for 5 minutes and cooled in a dessicator at room temperature.

$$N = \frac{A \times B}{53 \times C}$$

Where;

A = weight in grams of Sodium Carbonate.

B = volume of Sodium Carbonate solution taken for titration

**3.4.4.2 Method for Determining Alkalinity**

A 50 mL sample was measured into a conical flask. Two drops of methyl orange indicator was added and the resulting mixture titrated against the standard 0.1 M HCl solution to the first permanent pink colour at pH 4.5. A reagent blank was performed without the sample.

The following equation was used in the calculation.

$$\text{Alkalinity mg (CaCO}_3\text{)/L} = \frac{A \times N \times 50,000}{\text{VOL OF SAMPLE}}$$

Where;

A = volume of acid used

N = Normality of the acid used

### **3.5.0 PREPARATION OF SAMPLES FOR AAS**

The analytical scheme proposed by Hart and Davies, was adopted and modified to partition metals into two different fractions of dissolved and particulate metals (Hart and Davies, 1981).

#### **3.5.1 Dissolved metals**

250 mL of the runoff samples was filtered through 0.45 µm cellulose membrane filter paper. The filtrate obtained was analyzed for dissolved metals using the flame AAS. A blank was prepared without the samples. For the standard calibration curve, 1, 3 and 5 mg/L standard solutions were prepared.

#### **3.5.2 Particulate and Total metal concentration**

The samples for total metal determination were digested by adding 20 mL each of concentrated HNO<sub>3</sub> to 200 mL samples and heated on a heating mantle till the volume decreased to 50 mL. The samples were filtered and analyzed for the total metals using the flame AAS. A blank was prepared for each metal analysed by taking the reagents through the procedure except that the sample was omitted. Triplicate determinations were made for each metal determined.

The concentrations (mg/L) of six metals Al, Zn, Pb, Fe, Cd and Cr were measured in the samples and the blanks with AAS. A calibration curve was obtained with standard solutions of 1, 3 and 5 mg/L for all the metals (Milner and Peterside, 1984).

## **3.6 SULPHATE DETERMINATION**

### **3.6.1 Preparation of Reagents**

#### **i. Stock Sulphate Solution**

A 1.479 g of anhydrous sodium sulphate salt was dissolved in double distilled water and diluted to 1000 mL. This stock solution contains 1000  $\mu\text{g/mL}$  of sulphate from which the various standard solutions can be prepared.

#### **ii. Conditioning Reagent**

A 50 mL aliquot of glycerol was mixed with a solution containing 30 mL of concentrated HCl, 30 mL of distilled water, 100 ml 95% ethanol and 7.5 g of sodium chloride.

### **3.6.2 Preparation of calibration curve**

Solutions of concentration 1  $\mu\text{g/mL}$ , 2  $\mu\text{g/mL}$ , 3  $\mu\text{g/mL}$  and 4  $\mu\text{g/mL}$  were prepared from the 1000  $\mu\text{g/L}$  sodium sulphate stock solution prepared. To each of these was added 10 mL of conditioning reagent and 0.3 g of barium chloride. The standards were allowed to stand for 45 minutes. The respective absorbance of the solutions at 440 nm were determined. From this data, a graph of absorbance versus concentration was plotted (APHA, 1992).

### **3.6.3 Method of Sulphate Determination**

A 10 mL of conditioning reagent was added to 25 mL of sample. Followed by 0.3 g of  $\text{BaCl}_2$ . The mixture was then diluted to 100 mL with double distilled water. Prepared samples were allowed to stand for 45 minutes. The concentrations of the samples were

determined using the colorimeter at 440 nm. A blank without BaCl<sub>2</sub> was prepared and run at the same wavelength.

### **3.7 PHOSPHATE DETERMINATION**

#### **3.7.1 Preparation of Reagents**

##### **i. Stock orthophosphate solution**

Potassium dihydrogen orthophosphate was dried at 110 °C and 0.4393 g of dry salt was weighed and dissolved in 1 L of double distilled water. The stock was preserved with 5 ml of chloroform and stored in a glass stoppered flask. The strength of this stock solution is 100 µg Orthophosphate-Phosphorus per litre.

##### **ii. 0.25 M Concentrated H<sub>2</sub>SO<sub>4</sub>**

An aliquot of 70 mL of analar grade concentrated H<sub>2</sub>SO<sub>4</sub> was slowly added to 30ml of double distilled water in a 500 mL volumetric flask. The flask was cooled under tap water and the solution made to the mark with distilled water.

##### **iii. Ammonium Molybdate solution (0.8 %)**

A weighed 40 g of Analar grade ammonium molybdate was dissolved in 500 mL of distilled water into a 600 mL beaker. After cooling, the solution was transferred into a 1 L volumetric flask and made to the mark with double distilled water. The solution was put into a plastic bottle and stored in a refrigerator.

**iv. Ascorbic acid (0.01 M)**

A 1.8 g of analar grade ascorbic acid was dissolved in 10 mL of distilled water. This solution was prepared freshly before use.

**v. Antimony solution (0.3%)**

A 0.3 g of analar grade potassium antimonyl tartrate was dissolved in 50 mL of distilled water and made up to 100 mL and was stored in a glass stoppered bottle

**vi. Single combined reagent**

This was prepared by mixing together 50 mL of 2.5 M H<sub>2</sub>SO<sub>4</sub>, 5 mL of Potassium Tartrate, 15 mL Ammonium Molybdate and 30 mL Ascorbic acid solution into a 250 mL volumetric flask.

**3.7.2 Preparation of calibration curve**

Standard solutions of 1, 2, 3 and 4 µg/mL was prepared from the 100 µg/L of orthophosphate-phosphorus stock solution. To these was added 2 mL of combined reagent. The absorbance of the solutions after 10 minutes were taken at 660 nm against a blank solution. A curve of absorbance versus concentration was plotted using a 5500 photometer (APHA, 1992).

### **3.7.3 Method (indirect determination)**

#### **1. Ascorbic acid method (orthophosphate phosphorus)**

To 50 mL of water sample was added 2 mL of combined reagent. The mixture was allowed to stand for 10 minutes after which the absorbance of the sample was taken against a reagent blank using the 5500 photometer. The concentration was obtained by comparing values with a calibration curve. A blank analysis was performed with all the reagents without sample for all the analysis.

### **3.8 DETERMINATION OF CHLORIDE (TITRIMETRIC METHOD)**

Chloride was determined by titration with silver nitrate (titrant) and using  $K_2CrO_4$  (potassium chromate) as indicator.

#### **3.8.1 Preparation of Reagents**

##### **i. 0.0282 N Silver Nitrate**

4.7851 g of  $AgNO_3$  was dissolved in distilled water and made up to 1 L with distilled water.

##### **ii Potassium Chromate, 5 % (W/V).**

5.0 g  $K_2CrO_4$  was dissolved in 100 mL distilled water in a 100 mL volumetric flask.

#### **3.8.2 Procedure**

$AgNO_3$  solution was standardised with standard 0.01 N NaCl solutions. 100 mL of the sample was then placed into a 250 mL conical flask. 3 drops of potassium chromate

indicator was added to the contents of the flask. The contents of the flask were titrated against the silver nitrate solution, with constant stirring, to the end point which was indicated by a permanent red colour.

**Calculation;**

$$\text{Chloride (mg/L)} = \text{Titre value} \times 10$$

### **3.9 DETERMINATION OF NITRITE**

#### **3.9.1 Preparation of Reagents**

##### **i. Preparation of Standard Sodium Nitrite Solution**

A 1.232 g of sodium nitrite was weighed and dissolved with distilled water into a 100 mL volumetric flask and then diluted to the mark. The concentration of the standard prepared is 250 µg/L nitrite.

##### **ii. 0.1 M NaOH**

An amount of 4 g of sodium hydroxide pellets was weighed and dissolved in a small volume of distilled water before transferring to a 100 mL volumetric flask where it was diluted to the mark.

##### **iii. Colour Developing Reagent**

A 300 mL distilled water, 50 mL concentrated Phosphoric acid, 7.5 g of sulphanilamide ( $\text{H}_2\text{N}-\text{C}_6\text{H}_4\text{SO}_4\text{NH}_2$ ) and 0.375 g of naphthyl-1, 1-amide were mixed together and diluted to the mark in a 500 mL volumetric flask.

### **3.9.2 Preparation of the Calibration curve**

Aliquots of 0.1, 0.2, 0.3 and 0.4 mL of the stock solution were measured into different 100 mL volumetric flasks. To these 2 mL of 0.1 M NaOH was added followed by the addition of 1, 2, 3, and 4 mL of colour developing reagent respectively. The mixtures were diluted to the 100 mL mark forming 0.25 µg/L, 0.50 µg/L, 0.75 µg/L and 1.00 µg/L of standard nitrite solution respectively (APHA, 1992). A straight line graph of absorbance at 543 nm versus concentration passing through the origin was obtained for the prepared standard solutions.

### **3.9.3 Method for determining Nitrite**

An aliquot of 2 mL of 0.1 M NaOH solution and 1 mL of colour developing reagent was added to a sample. The mixture was allowed to stand for 20 minutes. The nitrite concentration was determined at wavelength 543 nm of absorbance using a 5500 photometer. A blank analysis was performed with all the reagents without sample for all the analysis.

### **3.10.0 RECOVERY ANALYSIS**

Recovery of Pb, Fe, Zn, Cd, Al and Cr were determined by adding increasing amounts of the respective metals in solution to samples, which were analysed by using the AAS.

Table 3.1 Recovery of Lead (Pb)

Conc. Of Pb, mg/L	Pb Recovered, mg/L	% Recovery
0.2	0.191	95.5
0.5	0.487	97.4
1.0	0.998	99.8

**Mean % recovery is 97.6**

Table 3.2. Recovery of Iron (Fe)

Conc. Of Fe, mg/L	Fe Recovered, mg/L	% Recovery
0.2	0.191	95.5
0.5	0.490	98
1.0	0.992	99.2

**Mean % recovery is 97.6**

Table 3.3. Recovery of Zinc (Zn)

Conc. Of Zn, mg/L	Zn Recovered, mg/L	% Recovery
0.2	0.199	99.5
0.5	0.495	99
1.0	0.980	98

**Mean % recovery 98.8**

Table 3.4. Recovery of Cadmium (Cd)

Conc. Of Cd, mg/L	Cd Recovered, mg/L	% Recovery
0.2	0.186	93
0.5	0.501	100.2
1.0	0.966	96.6

**Mean % recovery is 96.6**

Table 3.5 Recovery of Aluminium (Al)

Conc. Of Al, mg/L	Al Recovered, mg/L	% Recovery
0.2	0.198	99
0.5	0.488	97.6
1.0	0.999	99.9

**Mean % recovery is 98.8**

Table 3.6 Recovery of Chromium (Cr)

Conc. Of Cr, mg/L	Cr Recovered, mg/L	% Recovery
0.2	0.194	97
0.5	0.499	99.8
1.0	0.997	99.7

**Mean % recovery is 98.8**

### **3.11 STATISTICAL ANALYSIS**

The data obtained in this study were subjected to statistical analyses using Microsoft Excel software. Linear regression and correlation analysis were used to determine the correlation between the metals in water samples from a particular roofing material.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

A total of seventy five rainwater samples were taken from three communities in the Obuasi area and they were subjected to physicochemical analyses. The following physical parameters were analyzed; pH, Electrical conductivity, TDS, TSS, Turbidity, and Alkalinity. The mean and standard deviation of the measured values from five rain events are presented in table 4.1, and general periodic sampling results are presented in tables 4.15 -4.19.

Anions determined include Chloride ( $\text{Cl}^-$ ), Sulphate ( $\text{SO}_4^{2-}$ ), Phosphate ( $\text{PO}_4^{3-}$ ) and Nitrite ( $\text{NO}_3^-$ ). The mean and standard deviation values for the selected areas are presented in tables 4.2, and general periodic sampling results are presented in tables 4.15-4.19.

Levels of lead (Pb), Iron (Fe), Zinc (Zn), Cadmium (Cd), Aluminum (Al) and Chromium (Cr) were determined in the rainwater samples. The water samples had trace metals in both dissolved and particulate forms. Results obtained were compared with work done by other researchers on rainwater harvest in different areas as well as the World Health Organisation (WHO) recommended standards for drinking water. Their means and standard deviation values are recorded in tables 4.3 and general periodic sampling results are recorded in tables 4.21- 4.25.

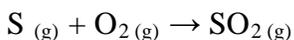
#### 4.1.0 ANALYSIS OF PHYSICAL WATER QUALITY PARAMETERS

##### 4.1.1 pH

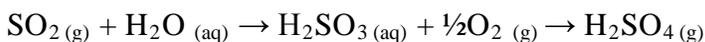
Rainwater pH is an important factor in assessing roof runoff quality, as acidic rainwater has the potential to dissolve a larger proportion of trace metal contaminants on roof tops. Data collected by Ayres *et al.*, (1986), Nichol *et al.*, (1997) and Halstead. (2000) indicated that rainwater water harvested from heavy industrial areas in New Zealand had very low pH especially in areas that have some mining activities. Rainwater in the Obuasi area is mostly acidic. Research Conducted by Foli *et al.*, (2001) indicated that during the wet season (rainfall period), average pH in the area is about 5.6.

Control samples collected from the area within the period of study had low values for pH meaning they were acidic. Values ranged from 4.5 - 4.8 as seen in table 4.19. The mean pH values for the control samples was  $4.67 \pm 0.47$ , This low values may be due to wet atmospheric depositions of gases, such as CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> in the atmosphere produced as a result of the mining of the sulphite ore and extractive processes used in the area which can easily be dissolved and incorporated in the rain droplets and can easily affect the rain pH (Settle and Patterson, 1985; Ayres *et al.*, 1986; Arimoto *et al.*, 1990; Nichol *et al.*, 1997; Halstead *et al.*, 2000). The SO<sub>2</sub> and As<sub>2</sub>O<sub>3</sub> commonly present in the atmosphere in the area are as a result of oxidation of Sulphur (S) and Arsenic (III) from the Arsenopyrite present in the ore (Amonoo-Neizer and Busari, 1980; Gaisie, 1986;

Jetuah, 1997). The above situation may be represented by the following reaction mechanism;



The SO<sub>2</sub> gas is then hydrolysed to form H<sub>2</sub>SO<sub>4</sub> as in the equation;



Also, the effects of intense acid deposition from gases discharged from roaster plants at the Pompora Treatment Plant in the past as well as the use of strong acids during the treatment of ore can also contribute to the low pH value recorded at the Wawasi and Ramia areas. The pH for the Obuasi area ranged between 4.8 - 6.3 for the various roofing materials. Mean values of  $6.1 \pm 0.15$ ,  $5.7 \pm 0.35$ ,  $5.3 \pm 0.26$ ,  $5.97 \pm 0.14$  were recorded for aluminium, asbestos, clay tiles and Aluzinc roofing materials respectively, as in table 4.15.

The pH values of the samples from the roofs were higher (more basic) than the control samples. The highest pH value of 6.4 was recorded from Aluminium roofing materials in the Ramia area as in table 4.15 whilst the lowest value of 4.8 was recorded from Clay tiles in the Ramia area as in table 4.17. The clay materials used to make the roofing tiles may have some FeSO<sub>4</sub><sup>3+</sup> which have the ability to form stable compounds with some cations and precipitate as particles onto the roofs. The general increase in the pH of the roofing materials might be to the replacement of H<sup>+</sup> ions by metal ions during the interaction of the runoffs with the roofs.

**Table 4.1. Mean values and standard deviation of Physical Parameters in Roof****Runoff**

SAMPLE	PH	COND ( $\mu\text{s}/\text{cm}$ )	TDS (mg/L)	TSS (mg/L)	TURB (NTU)	ALK (mg/L)
RSAL	$6.3 \pm 0.06$	$41.9 \pm 3.00$	$20.8 \pm 1.78$	$7.8 \pm 3.11$	$50.5 \pm 8.89$	$10.8 \pm 3.03$
WSAL	$6.1 \pm 0.28$	$32.5 \pm 17.48$	$16.0 \pm 7.76$	$12.4 \pm 6.88$	$69.4 \pm 8.30$	$10.8 \pm 3.03$
ASAL	$5.9 \pm 0.11$	$35.1 \pm 7.66$	$18.2 \pm 4.84$	$6.8 \pm 1.92$	$48.3 \pm 12.37$	$9.2 \pm 3.03$
WAA	$5.8 \pm 0.38$	$21.8 \pm 14.61$	$11.1 \pm 7.24$	$5.8 \pm 4.44$	$89.3 \pm 37.99$	$8.4 \pm 6.61$
RAA	$5.6 \pm 0.31$	$34.6 \pm 37.82$	$17.4 \pm 19.25$	$9.4 \pm 5.32$	$66.2 \pm 45.77$	$7.6 \pm 3.90$
RCO	$4.7 \pm 0.51$	$18.2 \pm 13.28$	$11.8 \pm 5.30$	$8.8 \pm 5.36$	$34.7 \pm 5.76$	$10.8 \pm 3.90$
WCO	$4.5 \pm 0.39$	$22.4 \pm 11.11$	$12.9 \pm 4.75$	$8.4 \pm 4.04$	$50 \pm 19.14$	$5.6 \pm 3.58$
ACO	$4.8 \pm 0.51$	$20.5 \pm 16.10$	$19.2 \pm 5.62$	$17.8 \pm 7.12$	$38.4 \pm 9.32$	$3.2 \pm 1.10$
RCT	$5.3 \pm 0.34$	$16.9 \pm 5.80$	$8.4 \pm 2.83$	$8.4 \pm 2.70$	$97.4 \pm 32.48$	$8.8 \pm 5.76$
WCT	$5.3 \pm 0.18$	$17.4 \pm 7.19$	$7.7 \pm 3.03$	$5.0 \pm 3.46$	$96.6 \pm 29.31$	$8.8 \pm 3.35$
RAZ	$5.9 \pm 0.15$	$28.5 \pm 10.94$	$14.1 \pm 5.46$	$4.2 \pm 2.86$	$43.8 \pm 14.02$	$10.8 \pm 4.60$
WAZ	$6.0 \pm 0.11$	$47.2 \pm 30.32$	$12.3 \pm 15.97$	$20.3 \pm 26.95$	$87.5 \pm 68.19$	$11.6 \pm 3.85$
AAZ	$6.0 \pm 0.16$	$15.2 \pm 4.60$	$8.2 \pm 2.35$	$4.2 \pm 1.64$	$63.0 \pm 26.97$	$13.6 \pm 4.34$

Asbestos roofing material, recorded a mean pH value of  $5.8 \pm 0.28$  for Wawasi whilst Ramia and Antobuasi recorded mean values of  $5.3 \pm 0.05$  and  $5.3 \pm 0.11$  respectively as in table 4.1. Clay tiles recorded a mean of  $5.3 \pm 0.18$  and  $5.3 \pm 0.34$  at Wawasi and Ramia as indicated in table 4.1. For Aluzinc roofing sheets a mean of  $5.9 \pm 0.15$  was recorded at Ramia whilst a mean of  $6.0 \pm 0.11$  and  $6.0 \pm 0.16$  were recorded for Wawasi

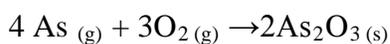
and Antobuasi respectively as shown in table 4.1. Aluminium roofing sheets had a mean of  $6.3 \pm 0.06$ ,  $6.1 \pm 0.28$ , and  $5.9 \pm 0.11$  at Ramia, Wawasi and Antobuasi respectively as shown in table 4.1. The low pH values recorded for asbestos and clay tiles roofing materials instead of the metal sheets (Aluzinc and Aluminium roofing materials) contrasts to Quek and Forster (1993), which discovered that pH of roof runoff, is mainly affected by alkaline particles from the weathering of roofs containing cement such as Clay tiles and asbestos and makes runoff more alkaline.

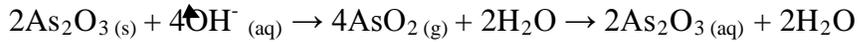
#### 4.1.2 Alkalinity

Studies performed by Verma *et al.*, (2000), and Beaz *et al.*, (1997) demonstrated that for a complete quantification of rainwater acidity, the measurement of alkalinity is recommended. In view of this alkalinity was determined for the samples.

Except for values recorded for control samples collected in the Ramia area, Control samples generally had lower alkalinity values than samples from all the roofing materials in all the communities as represented in table 4.19. Mean alkalinity values recorded in the control samples were  $10.8 \pm 3.90$ ,  $5.6 \pm 3.58$  and  $3.2 \pm 1.10$  units for Ramia, Wawasi and Antobuasi respectively.

Arsenic oxide ( $As_2O_3$ ) is very common in the Obuasi area which According to Marsden and House (1992) is acidic and may react with metal hydroxides (metallurgic reagents) to form aqueous Arsenic Oxide ( $As_2O_3$ ) as in the reaction;





The reaction products formed can consume  $\text{OH}^-$  from the water medium and could therefore generally reduce alkalinity in the area. Hence, the low alkalinity values recorded for the control samples.

There was however a poor correlation between pH and Alkalinity ( $R^2 = 0.4374$ ). The highest values of alkalinity were obtained from the Aluzinc roofing material in the Ramia and Antobuasi areas as indicated in table 4.18. A mean value of  $10.8 \pm 3.03$ ,  $10.8 \pm 3.03$ ,  $9.2 \pm 3.03$  units was recorded for Aluminium roofing materials from Ramia, Wawasi and Antobuasi respectively. Also mean values of  $8.4 \pm 6.07$ ,  $7.6 \pm 3.90$  units were recorded (table 4.1) for asbestos roofing materials from Wawasi and Ramia respectively.

With the Clay tiles roofing material from Ramia and Wawasi, mean values of  $8.8 \pm 5.76$  and  $8.8 \pm 3.35$  were recorded as indicated in (table 4.17). Aluzinc roofing material recorded mean values of  $10.8 \pm 4.60$ ,  $11.6 \pm 3.85$  and  $13.6 \pm 4.34$  units at Ramia, Wawasi and Antobuasi respectively as shown in table 4.18.

In general, the roofing materials had a significant effect on alkalinity. The alkalinity recorded for the control samples were significantly low when compared with values recorded by the roofing materials except that of the clay tiles and asbestos roofing materials.

Alkalinity values were all below the USEPA 1999 and WHO 2003 guidelines for drinking water.

#### **4.1.3 Electrical Conductivity (EC)**

The electrical conductivity (measure of overall ionic constituent concentration) values recorded in roof runoff samples were considerably higher than that of the control samples. This may be due to the contributions from soluble inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate ions and some cations deposited on the roofing materials by dry depositions as well as the absorption of heat by the roofing materials, since sampling occurred in between rain events with a considerable amount of high temperature recorded during the dry spell (Thomas and Greene, 1993).

The clay tiles roofing materials recorded lower EC values than the control samples. All the other roofing materials recorded higher values than the control sample. This low values recorded for the runoff from clay tiles may be due to initial dissolution of deposited aerosols by the rain water followed by continuous dissolution and washing away of clay materials with further rain events which seemed to buffer the effects the acidic water on the release of the ions. Mean EC values recorded for control samples in the area were;  $18.24 \pm 13.28$ ,  $22.38 \pm 11.11$  and  $40.49 \pm 16.10$   $\mu\text{s}/\text{cm}$  for Ramia, Wawasi and Antobuasi respectively.

The highest value of  $101.4$   $\mu\text{s}/\text{cm}$  was recorded in samples from Asbestos roofing material in the Ramia area and the least value of  $9.8$   $\mu\text{s}/\text{cm}$  was recorded in samples from clay tiles roofing in the Wawasi area as shown in tables 4.16 and 4.17 respectively.

Thomas and Greene (1993); Foster (1996), indicated that Conductivity has been found to be highest in runoff from roofs with rougher surfaces such as asbestos and clay tiles than smoother ones like the metal sheets. This assertion did not conform to that found out in this work which recorded higher electrical conductivity values rather for metal sheets. Mean values for aluminium roofing material recorded for the area was;  $41.9 \pm 3.01$ ,  $32.5 \pm 17.48$  and  $35.1 \pm 7.66$   $\mu\text{s}/\text{cm}$  for Ramia, Wawasi and Antobuasi respectively as reported in table 4.15. For Aluzinc roofing material the mean values recorded were;  $28.5 \pm 10.94$ ,  $47.2 \pm 30.32$  and  $15.2 \pm 4.60$   $\mu\text{s}/\text{cm}$  for Ramia, Wawasi and Antobuasi respectively as shown in table 4.18. This may be due to the acidic nature of the rainwater in the Obuasi area as well as the mining activities that contribute a lot atmospheric depositions of ions onto the smoother surface that are easily washed into the runoffs.

Mean values recorded for Asbestos roofing material was;  $21.8 \pm 14.61$  and  $34.6 \pm 37.82$   $\mu\text{s}/\text{cm}$  for Ramia and Wawasi respectively as reported in table 4.16. Mean values for Clay tiles were;  $16.9 \pm 5.80$  and  $17.4 \pm 7.19$   $\mu\text{s}/\text{cm}$  for Ramia and Wawasi respectively as reported in table 4.16. There was however a poor correlation between pH and conductivity ( $R^2=0.1323$ ) as in appendix 1. The values obtained for electrical conductivity for all the roofing materials were far below the WHO 2003 guidelines for drinking water.

#### **4.1.4 Total Dissolved Solids**

Values recorded for the total dissolved solids (TDS) in the control samples were generally higher than those collected from the clay tiles and Aluminium roofing materials

as shown in table 4.15 to 4.18. This may be due to the presence of ions such as sulphates and phosphates from phosphate containing compounds used to prevent corrosion and enhance the formation of scale in pipes and power plant boilers used in the Gold production plants. Contributions from fertilizers used in the farming communities in the area may also affect the TDS value (Pushard, 2005).

The mean TDS values in control samples for the area were;  $11.78 \pm 5.30$ ,  $12.92 \pm 4.75$  and  $19.23 \pm 5.62$  mg/L from runoff from Ramia, Wawasi and Antobuasi respectively. The highest value for TDS was recorded for samples collected from the asbestos roofing materials in the Ramia area with a value of 51.45 mg/L, whilst the lowest value was recorded for clay tiles samples collected from the Wawasi area with a value of 5.1 mg/L. The high value of TDS in the control samples could be attributed to the atmospheric composition of gases and particulates (mainly iron and sulfur) that are dissolved in the raindrops. These components have been known to increase the TDS in rainwater (Kohler et al., 1997). The mean values in runoffs from aluminium roofing material were;  $20.8 \pm 1.78$ ,  $16 \pm 7.76$  and  $18.2 \pm 4.84$  mg/L Ramia, Wawasi and Antobuasi respectively (table 4.15).

The asbestos roofing material recorded mean values of,  $11.09 \pm 7.24$  and  $17.39 \pm 19.25$  mg/L for Ramia and Wawasi respectively as reported in table 4.5. TDS values of  $8.4 \pm 2.83$  and  $7.7 \pm 3.03$  mg/L were also recorded as mean for Clay Tiles roofing materials from Wawasi and Ramia respectively as reported in table 4.17. Aluzinc roofing material recorded  $14.1 \pm 5.46$ ,  $12.26 \pm 15.97$  and  $8.2 \pm 2.35$  mg/L at Ramia, Wawasi and Antobuasi respectively as presented in table 4.18. TDS increased with increasing EC as

recorded in the tables 4.1. There was a poor correlation between pH & TDS, TDS & total aluminium and TDS & total iron ( $R^2 = 0.04, 0.18$  and  $0.002$ ). However there was a good positive correlation between EC & TDS ( $R^2 = 0.61$ ) as recorded in appendix 1.

#### **4.1.5 Total Suspended Solids**

The TSS values for the control samples were relatively higher than those collected from the roofs. Thomas & Greene (1993) found that site characteristics contributed to elevated suspended solids concentrations, with activities such as earthmoving and heavy mining activities which increase the dust and particulate matter in the atmosphere. This statement is consistent with that shown by Forster (1998) who also demonstrated that local emissions contributes to increased particulate matter present in rainwater. The highest value for TSS was recorded for Aluzinc samples in the Wawasi area with a value of 67 mg/L as shown in table 4.18 whilst the lowest value of 1 mg/L was recorded for Asbestos roofing materials in the Wawasi area as indicated in table 4.16.

The mean TSS values in control samples were;  $8.8 \pm 5.36$ ,  $8.4 \pm 4.04$ ,  $17.8 \pm 7.12$  recorded for Ramia, Wawasi and Antobuasi respectively as shown in table 4.19; Aluminium roofing in Ramia, Wawasi and Antobuasi recorded  $7.8 \pm 3.12$ ,  $12.4 \pm 6.88$  and  $6.8 \pm 1.92$  respectively as indicated in table 4.15. Asbestos roofing material in Wawasi and Ramia recorded  $5.8 \pm 4.44$  and  $9.4 \pm 5.32$  respectively as indicated in table 4.16. Clay Tiles in Ramia and Wawasi recorded  $8.4 \pm 2.70$  and  $5 \pm 3.46$  units as presented in table 4.17. Aluzinc roofing in Ramia, Wawasi and Antobuasi recorded  $4.2 \pm 2.86$ ,  $20.3 \pm 26.95$  and  $4.2 \pm 1.64$  respectively as presented for table 4.18.

All the TSS values were far below the WHO 2003 guidelines. There was a poor correlation between TSS and Turbidity ( $R^2 = 0.00002$ ) as in appendix 1.

#### **4.1.6 Turbidity**

The turbidity values for both control and roof runoffs far exceeded the WHO 2003 permissible levels for drinking water. Turbidity is mostly affected by a dry spell; the higher turbidity values obtained can be associated with the breaks between the rainfalls during the sampling period. The particulate contribution due to immense mining activities in the area contributed to the particulate materials in the atmosphere as well as on the roofs and hence the higher values recorded for turbidity in the runoffs.

The mean values for Turbidity of  $50.5 \pm 8.89$ ,  $69.4 \pm 8.30$  and  $48.3 \pm 12.37$  NTU were recorded for aluminium roofing from Ramia, Wawasi and Antobuasi respectively as shown in table 4.15. Samples from asbestos roofing material recorded the mean values of  $89.27 \pm 37.99$  and  $66.2 \pm 45.77$  NTU were recorded at Wawasi and Ramia respectively as shown in table 4.16. With the clay tiles roof water samples recorded mean values of  $97.4 \pm 32.48$  and  $96.6 \pm 29.31$  NTU at Ramia and Wawasi respectively as shown in table 4.17. The Aluzinc roofing material had mean values of  $43.8 \pm 14.02$ ,  $87.5 \pm 68.19$  and  $63 \pm 26.97$  NTU recorded in samples from Ramia, Wawasi and Antobuasi respectively as shown in table 4.18.

## 4.2 ANALYSIS OF ANIONS

**Table 4.2. Mean values and standard deviation for Anions in roof runoff and control samples**

SAMPLE	Cl <sup>-</sup> (mg/L)	SO <sup>-2</sup> <sub>4</sub> (mg/L)	PO <sup>3-</sup> <sub>4</sub> (mg/L)	NO <sup>-</sup> <sub>3</sub> (mg/L)
RSAL	35.2 ± 19.88	63 ± 12.17	0.42 ± 0.20	0.72 ± 0.12
WSAL	21.2 ± 9.78	32.1 ± 4.55	0.22 ± 0.16	0.81 ± 0.39
ASAL	40.4 ± 18.51	29.3 ± 8.11	0.41 ± 0.28	0.67 ± 0.18
WAA	46.8 ± 13.83	16.1 ± 3.30	0.33 ± 0.15	0.2 ± 0.03
RAA	46.0 ± 19.65	31.2 ± 12.64	0.51 ± 0.14	0.43 ± 0.31
RCO	37.6 ± 21.70	19.7 ± 1.66	0.16 ± 0.05	0.27 ± 0.21
WCO	38.4 ± 10.53	17.8 ± 5.60	0.16 ± 0.07	0.26 ± 0.25
ACO	31.5 ± 3.79	10.1 ± 1.62	0.08 ± 0.04	0.22 ± 0.14
RCT	30.9 ± 11.61	21.8 ± 9.04	0.41 ± 0.23	0.77 ± 0.25
WCT	27.2 ± 12.22	8.0 ± 1.42	0.34 ± 0.18	0.68 ± 0.17
RAZ	33.6 ± 6.23	33.9 ± 3.65	0.41 ± 0.22	0.87 ± 0.05
WAZ	65.6 ± 36.64	38.2 ± 3.58	1.3 ± 0.68	0.43 ± 0.15
AAZ	36.8 ± 7.29	35.5 ± 3.41	0.52 ± 0.29	0.67 ± 0.18

Major anions such as Chlorides, Nitrites, Sulphates and Phosphates concentrations in roof runoffs and rainwater has been reported by Forster (1998). Forster explained that the occurrence of these ions in rainwater may be due to weathering of the roof surface. Contrary to this assertion, Thomas & Greene (1993) reported that the nitrite

concentrations in roof runoff are generally not affected by the roof type, but by the environment. Agricultural activities have been recognized to increase nitrate concentrations. Forster (1998) explained that nitrites present in roof runoffs may be due to bird faeces deposited on the roofs which serves as a direct source of nitrites into roof runoffs.

Generally the concentrations of Chlorides, Sulphates, Phosphates and Nitrites values in the roof runoffs were higher than that of the control samples (tables 4.15 - 4.19). All the parameters analysed were below the WHO guidelines for rainwater systems. Since the pH was lower in control samples it was expected that the sulphates, nitrites and chlorides that affect acidity should be high for the control samples, but that was not the case in this work. It can therefore be said that all the roofs contributed some amount of the afore mentioned ions. This may be attributed to depositions due to their atmospheric concentrations due to vehicular, mining and agricultural activities which deposited such aerosols onto the roofs during the dry periods and were consequently washed into the runoffs.

The values for anions ranged between 21.2 - 65.6 mg/L, 8.0 - 63 mg/L, 0.08 -1.30 mg/L, 0.20 – 0.87 mg/L for Chlorides, Sulphates, Phosphates and Nitrites respectively.

The control samples had the lowest set of anion concentration with mean values ranging between 31.5 – 37.6, 10.1 – 19.7, 0.22 – 0.27 mg/L for Chlorides, Sulphates and Nitrites. Comparing work done elsewhere in Egypt by Daifullah and Shakour (2003), the chloride

values obtained in this work were higher as compared to 0.64 mg/L, Sulphate values were relatively similar as compared to 5.12 – 24.17 mg/L, and Nitrites are lower as compared to 0.4 mg/L – 33.43 mg/L.

The chloride ion may originate from human activities. Such as refuse incineration of PVC, which produces HCl in gas phase (Sigg *et al.*, 1987)? It may also originate from some small scale industries. The heavy presence of mining in the area and metallurgical treatment of the ore contributes some amount of chloride ions (Sigg *et al.*, 1987). The mean values recorded for Chlorides in the area were;  $32.27 \pm 16.0573$ ,  $46.4 \pm 16.74$ ,  $29.05 \pm 11.91$ ,  $45.3 \pm 16.72$  and  $35.83 \pm 13.67$  mg/L for Aluminium, Asbestos, Clay tiles, Aluzinc and the Control samples respectively. The values obtained in this work were higher than that done by Thomas & Greene (1993). There was an insignificant correlation between pH and Chloride ion concentration ( $R^2 = 0.02$ ). This means that the chloride ions do not directly influence the pH of the runoffs.

Sulphate constitutes the major anion component in rainwater. It is generally accepted that sulphate is formed in the atmosphere by chemical conversion from  $SO_2$  which is discharged into the atmosphere from natural and anthropogenic sources.  $SO_2$  is gradually converted to aerosols matter by oxidation as it is carried by air currents downwind from its sources. The sulphate recorded mean values of;  $41.467 \pm 8.28$ ,  $23.65 \pm 7.97$ ,  $14.9 \pm 5.23$ ,  $35.867 \pm 3.5460$  and  $15.867 \pm 2.9583$  mg/L for Aluminium, Asbestos, Clay tiles, Aluzinc and Control samples respectively. There was a significant positive correlation between the pH and Sulphate concentration ( $R^2 = 0.53$ ). This means that the sulphate ions

did influence the pH of the runoffs. This may be due to the fact that sulphates are major components in the ores mined in the Obuasi area; most of them are converted back to sulphuric acid through atmospheric reactions. Sulphates in this work were generally higher than those obtained in Egypt by Daifullah *et al.*, (2003) which recorded between 5.2 – 24.17 mg/L and in Nigeria by Ayenimo *et al.*, (2006) which recorded 1.94 – 9.10 mg/L.

Nitrites similar to sulphates are the result of oxidation of nitrogen dioxide. Nitrogen dioxide is mostly of atmospheric origin. The nitrites in the area also had mean values of  $0.733 \pm 0.23$ ,  $0.315 \pm 0.17$ ,  $0.725 \pm 0.21$ ,  $0.657 \pm 0.13$  and  $0.25 \pm 0.20$  mg/L for Aluminium, Asbestos, clay tiles, Aluzinc roofing materials and control samples respectively. This indicates that nitrite may be introduced by the direct dissolution of nitrogen dioxide followed by oxidation of nitrogen dioxide to nitrite particles which are deposited on the roofs and dissolve in the runoff. There was an insignificant correlation between pH & the nitrite concentration ( $R^2 = 0.37$ ), and also between Alkalinity & Nitrite concentration ( $R^2 = 0.30$ ). This means that the nitrite ions did not influence the acidity or the alkalinity of the runoffs.

The mean values for Phosphates in the area were;  $0.35 \pm 0.21$ ,  $0.42 \pm 0.14$ ,  $0.38 \pm 0.20$ ,  $0.74 \pm 0.40$  and  $0.13 \pm 0.05$  mg/L for Aluminium, Asbestos, Clay tiles, Aluzinc roofing materials and the control samples respectively.

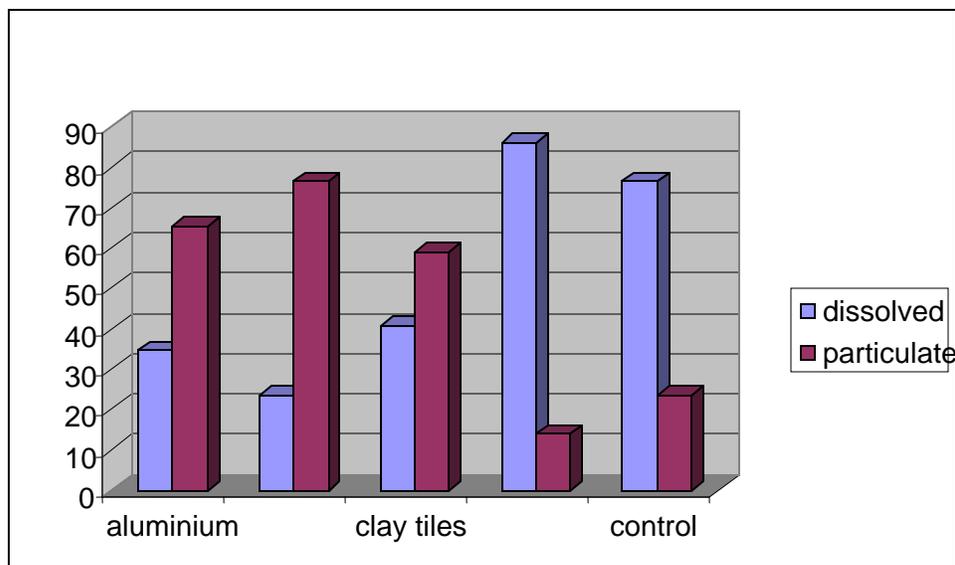
### **4.3 ANALYSIS OF TRACE METALS IN ROOF RUNOFF SAMPLES.**

In general, the type of roofing material is a major factor on trace metal concentrations in roof runoffs. For example galvanized iron roofs tend to have a high concentration of zinc than Lead. Also roof guttering to a large extent contribute to trace metal concentration in the roof runoffs (Ayenimo *et al.*, 2006). Trace metals such as lead, Zinc, Iron, and Aluminium are noted to be associated with metallic roofs. Cadmium and Chromium has been identified as major metal components in asbestos and clay tiles roofs (Ayenimo *et al.*, 2006). For each roofing material dissolved and particulate metals forms of metals that were selected for this work were determined.

#### **4.3.1 Partitioning of Metals into Dissolved and Particulate Fractions**

Selected metal concentration in the roof runoff samples from the different roofing materials were measured as dissolved and particulate forms. Results of total metal concentrations (table 4.3).

With aluminium roofing sheets 65.4% of the total metal content were particulate in nature. Aluzinc roofing sheets had 14% of the total metal concentration being particulate metals whilst 86% were in the dissolved form. Asbestos roofing had 76.5 % of the total metal concentration being particulate metals whilst 23.5 % were dissolved metals. Clay tiles had 59.1 % of the total metals concentration being particulate metals whilst 40.9 % were dissolved metals. Control samples had 23.5 % of the total metal concentrations being particulate whilst 76.5 % occurred in the dissolved forms.



**Fig 4: Levels of dissolve and particulate metals in runoff samples**

It was observed that for most of the runoff analysed had higher concentration of their metals in the particulate forms. As shown in Fig 4.

This conforms to work done by Davis and Burns (1990) who found that most metals especially lead present in roof runoffs are particulate in kind. He attributed their origin to debris, bird feaces and atmospheric dry depositions from heavy industrial activities. Foli (2006) also noted that the buffering activity of carbonates used in metallurgical treatment of the ore reduces metal mobility in the Obuasi area. This also confirms and explains why though low in dissolved fractions, metal concentration is high in particulate forms in the area.

### **4.3.2 Total Trace Metals Concentration in Roof Runoff samples**

Acid deposition can increase the levels of dissolved metals. The acidic nature of the rainwater in the area can effectively leach metals into runoff and affect its quality. Comparing the total metal concentration from the roof runoff and that of the control, it was observed that Zn, Al and Cr metal concentrations in samples from the roofing materials were much higher than that of the control. All the six selected trace metals analysed are characteristic of crustal suspended solid pollutants of anthropogenic origin present in most mining areas (Rao, 1992).

Al and Fe are of natural origin and are contained in highly insoluble particles mostly aluminosilicates. They are also present in weakly soluble hydroxide form (Iturbe and Lopez, 2002). Cd, Cr, Pb exist in aerosols, in nimble form, soluble in water and are dispersed in the environment. The opposite happens with Al and Fe (Ayenimo *et al.*, 2006). The proximity of source metals also reflects the concentration values in the various areas. Areas close to the point sources such as Wawasi and Ramia invariably have higher concentrations of trace metals than Antobuasi as in table 4.3.

**Table 4.3 Mean values and Std. Deviation for total metal concentration in samples**

SAMPLE	Pb (mg/L)	Fe (mg/L)	Zn (mg/L)	Cd (mg/L)	Al (mg/L)	Cr (mg/L)
RSAL	0.14 ± 0.232	0.04 ± 0.05	0.94 ± 0.19	BDL	0.78 ± 0.17	0.08 ± 0.04
WSAL	0.10 ± 0.08	0.07 ± 0.03	0.66 ± 0.41	BDL	0.41 ± 0.21	0.05 ± 0.01
ASAL	0.11 ± 0.06	0.01 ± 0.00	0.63 ± 12.2	BDL	0.07 ± 0.02	0.03 ± 0.01
WAA	0.20 ± 0.02	0.05 ± 0.09	0.34 ± 0.37	0.01 ± 0.1	0.07 ± 0.01	0.30 ± 0.16
RAA	0.20 ± 0.05	0.04 ± 0.01	0.42 ± 0.37	BDL	0.04 ± 0.03	0.11 ± 0.02
RCO	0.17 ± 0.02	0.10 ± 0.02	0.09 ± 0.04	BDL	0.02 ± 0.01	0.02 ± 0.01
WCO	0.19 ± 0.04	0.12 ± 0.05	0.13 ± 0.07	BDL	0.04 ± 0.01	0.06 ± 0.03
ACO	0.18 ± 0.01	0.10 ± 0.02	0.09 ± 0.07	BDL	BDL	BDL
RCT	0.24 ± 0.06	0.07 ± 0.03	0.20 ± 0.14	0.01 ± 0.06	0.08 ± 0.10	0.27 ± 0.04
WCT	0.23 ± 0.05	0.06 ± 0.03	0.09 ± 0.05	0.01 ± 0.02	0.04 ± 0.03	0.24 ± 0.02
RAZ	0.18 ± 0.06	0.02 ± 0.06	0.42 ± 0.17	BDL	0.40 ± 0.14	0.13 ± 0.03
WAZ	0.17 ± 0.05	0.05 ± 0.06	0.89 ± 0.15	BDL	0.30 ± 0.04	0.08 ± 0.08
AAZ	0.16 ± 0.04	0.01 ± 0.00	0.45 ± 0.30	BDL	0.08 ± 0.03	0.05 ± 0.04

- BDL=below detectable limits of 0.01mg/L

Total Pb concentrations in the roof runoffs from the Obuasi area were above the WHO standards. Values range was between 0.10-0.24 mg/L as presented in table 4.3. The mean value for the control samples was higher than that obtained from aluminium sheets and Aluzinc roofing materials but less than those obtained for Asbestos and clay tiles. These values conform to the high values for Pb in rainwater harvested from asbestos roofing materials as reported by Kennedy and Gadd (2001). Most lead compounds are generally insoluble in water (Davies and Burns, 1999), and this may be responsible for their great association with particulate matter, which contributes largely to the total Pb concentration

recorded in this work. There was a poor correlation between pH and Pb ( $R^2 = 0.11$ ). Meaning the pH did not affect the concentration of lead in the runoffs.

Fe concentration for the water samples collected within the sampling area ranged between 0.01 - 0.07 mg/L as reported in table. The values obtained for the metals were all below the WHO guidelines for drinking water of 1 mg/L as in appendix. Nonetheless, those obtained for the control was higher than for Aluminium roofing materials, Asbestos roofing material and Aluzinc roofing material. The mean concentration recorded were  $0.04 \pm 0.03$ ,  $0.045 \pm 0.05$  and  $0.25 \pm 0.04$  mg/L for Aluminium, Asbestos and Aluzinc roofing materials respectively. The presence of iron could be attributed to the arsenopyrite ore being mined in the area which contributes to the atmospheric depositions of Fe thus making all the roofing materials having some amount of iron in the roof runoff. There was a significant positive correlation between pH and total iron concentration ( $R^2 = 0.68$ ). Meaning the pH affected the total iron concentration of the runoffs.

The Zn concentration in the area ranged from 0.05 to 0.74 mg/L as presented in table 4.3. These values were below the WHO guidelines, 2004 of 3 mg/L. Values obtained for the control was lower than those obtained for all the roofing sheets. Mean values and standard deviation recorded were  $0.74 \pm 4.27$ ,  $0.38 \pm 0.37$ ,  $0.145 \pm 0.10$  and  $0.59 \pm 0.21$  mg/L for Aluminium, Asbestos, Clay Tiles and Aluzinc roofing materials respectively. The metal sheets (Aluminium and Aluzinc) recorded higher values than the other roofing materials. This may be due to leaching of zinc from the galvanised iron sheet being used

since galvanized iron sheets tend to have a high concentration of zinc. There is a significant positive correlation between the pH and the total Zinc concentration ( $R^2 = 0.72$ ). Also there was a good significant positive correlation between TDS and total Zn concentration ( $R^2 = 0.66$ ). This may indicate that the  $Zn^{2+}$  ions in the solution contribute a great deal to the total ionic constituent of the sample which was initiated by the release of Zn by acidic runoff flowing on the roof.

Values obtained for Cadmium were below detectable limit of 0.01mg/L of the instrument used for analysis limits and hence will not be discussed in this work. The control samples recorded some trace amount of 0.02 mg/L in Wawasi and Antobuasi.

Aluminium concentration in the rainwater sampled from the area ranged between 0.01 - 0.92 mg/L as in appendix 1. Samples from asbestos, clay tiles and the control had values below the WHO guidelines. Samples collected from Aluzinc and Aluminium roofing materials had values above the WHO guidelines. Mean values recorded for the area was  $0.42 \pm 0.14$ ,  $0.04 \pm 0.02$ ,  $0.07 \pm 0.09$ ,  $0.23 \pm 0.07$ , and  $0.02 \pm 0.01$  mg/L for aluminium, asbestos, clay tiles, aluzinc and the control for the Obuasi area respectively. The control sample recorded the least of the values whilst the aluminium roofing material had the highest value. Meaning the roofing materials contribute to the total aluminium concentration in the harvested water. There was a poor correlation between pH and total aluminium concentration ( $R^2 = 0.34$ ). Meaning the pH did not affect the total aluminium concentration in the runoffs.

Chromium concentration in rainwater samples collected from the area recorded values that ranged from 0.01 - 0.12 mg/L. All the roofing materials recorded higher Cr concentration than the control. The highest value was recorded for asbestos roofing material whilst that of the control recorded the least. The mean values and standard deviation recorded in the area are  $0.04 \pm 0.02$ ,  $0.305 \pm 0.09$ ,  $0.285 \pm 0.03$ ,  $0.095 \pm 0.05$  and  $0.03 \pm 0.01$  mg/L for aluminium, asbestos, clay tiles, aluzinc and control respectively. These results do not conform to that of Ayenimo et al., who found out that Cr concentration is greater in runoffs from ceramic tiles than asbestos. There was a poor correlation between pH and Cr concentration ( $R^2=0.01$ ) as well alkalinity and Cr concentration ( $R^2=0.0006$ ). Meaning that pH also had no effect on the release of Cr into the runoff.

#### **4.3.3 Correlation between total metals concentration from the various Roofing materials**

Correlation between the six metals under study was conducted to ascertain whether they have any relationship apart from occurring in the runoffs. The total metal concentrations for the six metals were used considering the type of roofing material and the sampling area.

Due to the presence of mining activities a lot of trace metals can be found in nimble forms in the area. This might be due to the ore types being mined, the metallurgical processes used to separate the precious metals from the ores, the type of roof under

consideration, the guttering, particulates on the roof and natural origin of the metals. Metals that show significant positive correlations mean that the concentration of the former affects the latter and vice versa (Davies and Burns, 1999).

With regards to correlation between metals in runoff samples collected over aluzinc roofing materials from the Ramia area, it was observed that there was a significant positive correlation between Lead and Cadmium ( $R^2=0.59$ ), Lead and Iron ( $R^2=1$ ) and Aluminium and Chromium ( $R^2=0.61$ ). Lead and cadmium usually occurs together (Davies and Burns, 1999). Their occurrence here may be due to the activities of mining in the area. All the other metals did not show a good correlation (table 4.4). This means, in Ramia the concentration of lead on the Aluzinc roofing affected the concentration of cadmium and Iron, the concentration of aluminium also affected the concentration of Chromium. Samples collected from Aluminium roofing materials also had a significant positive correlation between Lead and Iron ( $R^2=0.52$ ), Lead and Aluminium ( $R^2=0.77$ ), Iron and Zinc ( $R^2=0.54$ ) and Aluminium and Cadmium ( $R^2=0.77$ ) (table 4.5) The control samples from the Ramia area, was observed to have a significant positive correlation between Iron and Zinc ( $R^2=0.63$ ), Iron and Cadmium ( $R^2=0.64$ ), Iron and Aluminium ( $R^2=0.50$ ) and Zinc and Aluminium ( $R^2=0.75$ ), as in table 4.6. The samples from clay tiles in the Ramia area also had a significant positive correlation between Lead and Zinc ( $R^2=0.66$ ) and Lead and Cadmium ( $R^2=0.76$ ).

As shown in table 4.7. With Asbestos roofing in the Ramia area had a good correlation between Iron and Lead ( $R^2=1$ ). Lead and Zinc ( $R^2=0.60$ ) and Aluminium and Chromium ( $R^2=0.47$ ) as in table 4.8.

<b>Table 4.4 Correlation between metals in roof runoff from Aluzinc roofing materials in Ramia</b>						
	Pb	Fe	Zn	Cd	Al	Cr
Pb	<b>1</b>	<b>1</b>	0.0004	<b>0.5845</b>	0.0012	0.2521
Fe	<b>1</b>	<b>1</b>	0.2203	0.0667	0.0176	0.0027
Zn	0.0004	0.2203	<b>1</b>	0.0963	0.001	0.0578
Cd	<b>0.5845</b>	0.0667	0.0963	<b>1</b>	0.0176	0.0027
Al	0.0012	0.0176	0.001	0.0176	<b>1</b>	<b>0.6092</b>
Cr	0.2521	0.0027	0.0578	0.0027	<b>0.6092</b>	<b>1</b>

<b>Table 4.5 Correlation between metals in roof runoff from Aluminium roofing materials in Ramia</b>						
	Pb	Fe	Zn	Cd	Al	Cr
Pb	<b>1</b>	<b>0.52</b>	0.1859	0.0833	<b>0.7698</b>	0.3769
Fe	<b>0.52</b>	<b>1</b>	<b>0.5429</b>	0.1274	0.2068	0.3185
Zn	0.1859	<b>0.5429</b>	<b>1</b>	-	0.0003	0.0038
Cd	0.0833	0.1274	-	<b>1</b>	<b>0.7698</b>	0.3768
Al	<b>0.7698</b>	0.2068	0.0003	<b>0.7698</b>	<b>1</b>	0.2275
Cr	0.3769	0.3185	0.0038	0.3768	0.2275	<b>1</b>

<b>Table 4.6 Correlation between metals in roof runoff from Control samples in Ramia</b>						
	Pb	Fe	Zn	Cd	Al	Cr
Pb	<b>1</b>	0.1801	0.0034	0.4384	-	0.0217
Fe	0.1801	<b>1</b>	<b>0.6343</b>	<b>0.6336</b>	<b>0.5043</b>	0.0194
Zn	0.0034	<b>0.6343</b>	<b>1</b>		<b>0.7452</b>	0.3511
Cd	0.4384	<b>0.6336</b>	-	<b>1</b>	-	-
Al	0.0008	<b>0.5043</b>	<b>0.7452</b>	-	<b>1</b>	-
Cr	0.0217	0.0194	0.3511	-	-	<b>1</b>

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	0.0563	<b>0.6609</b>	<b>0.7634</b>	0.1871	0.0114
<b>Fe</b>	0.0563	<b>1</b>	0.2639	0.0136	0.2398	0.021
<b>Zn</b>	<b>0.6609</b>	0.2639	<b>1</b>	-	0.0353	0.1913
<b>Cd</b>	<b>0.7634</b>	0.0136	-	<b>1</b>	0.1913	-
<b>Al</b>	0.1871	0.2398	0.0353	0.0215	<b>1</b>	-
<b>Cr</b>	0.0114	0.021	0.1913	-	-	<b>1</b>

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	<b>1</b>	<b>0.5947</b>	0.1995	0.0162	0.3144
<b>Fe</b>	<b>1</b>	<b>1</b>	0.0006	0.1429	0.0147	0.2649
<b>Zn</b>	<b>0.5947</b>	0.0006	<b>1</b>	-	0.0451	0.1418
<b>Cd</b>	0.1995	0.1429	-	<b>1</b>	0.0147	0.2649
<b>Al</b>	0.0162	0.0147	0.0451	0.0147	<b>1</b>	<b>0.4682</b>
<b>Cr</b>	0.3144	0.2649	0.1418	0.2649	<b>0.4682</b>	<b>1</b>

In Wawasi area, runoff from the aluzinc roofing materials had a significant positive correlation between Lead and Iron ( $R^2=1$ ), Lead and Zinc ( $R^2=0.70$ ), Iron and Aluminium ( $R^2=0.48$ ), Aluminium and Zinc ( $R^2=0.70$ ), Chromium and Zinc ( $R^2=0.7044$ ) and Aluminium and Chromium ( $R^2=0.73$ ) as reported in table 4.9.

The control samples from the Wawasi area, also had a significant positive correlation between Iron and Aluminium ( $R^2=0.53$ ) as reported in table 4.10. The Clay tiles roofing materials in the Wawasi area also observed a significant positive correlation between Iron and Chromium ( $R^2=0.50$ ), Zinc and Aluminium ( $R^2=0.95$ ) as reported in table 4.11.

Asbestos roofing also had a significant positive correlation between Iron and Lead ( $R^2=1$ ), Aluminium and Iron ( $R^2=0.69$ ), Iron and Chromium ( $R^2=0.88$ ) and Aluminium and Chromium ( $R^2=0.62$ ).

**Table 4.9 Correlation between metals in roof runoff from Aluzinc roofing materials in Wawasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	<b>1</b>	<b>0.7044</b>	0.2433	0.2433	0.0872
<b>Fe</b>	<b>1</b>	<b>1</b>	-	-	<b>0.4801</b>	0.0872
<b>Zn</b>	<b>0.7044</b>	-	<b>1</b>	-	<b>0.7044</b>	<b>0.7044</b>
<b>Cd</b>	0.2433	-	-	<b>1</b>	-	0.0872
<b>Al</b>	0.2433	<b>0.4801</b>	<b>0.7044</b>	-	<b>1</b>	<b>0.7341</b>
<b>Cr</b>	0.0872	0.0872	<b>0.7044</b>	0.0872	<b>0.7341</b>	<b>1</b>

**Table 4.10 Correlation between metals in roof runoff from Control samples in Wawasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	0.018	-	-	-	-
<b>Fe</b>	0.018	<b>1</b>	-	-	<b>0.5272</b>	-
<b>Zn</b>	0.0342	0.001	<b>1</b>	-	0.03442	0.0342
<b>Cd</b>	0.0833	-	-	<b>1</b>	0.1818	0.2774
<b>Al</b>	0.0261	<b>0.5272</b>	-	0.1818	<b>1</b>	0.0244
<b>Cr</b>	0.0833	-	0.042	0.2774	0.0224	<b>1</b>

**Table 4.11 Correlation between metals in roof runoff from Clay Tiles in wawasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	0.3446	0.0021	-	0.0291	0.026
<b>Fe</b>	0.3446	<b>1</b>	0.1325	0.2857	0.0684	<b>0.4972</b>
<b>Zn</b>	0.0021	0.1325	<b>1</b>	-	<b>0.951</b>	0.0446
<b>Cd</b>	-	0.2857	-	<b>1</b>	0.0215	0.0833
<b>Al</b>	0.0291	0.0684	<b>0.951</b>	0.0215	<b>1</b>	0.2632
<b>Cr</b>	0.026	<b>0.4972</b>	0.0446	0.0833	0.2632	<b>1</b>

**Table 4.12 Correlation between metals in roof runoff from Asbestos in Wawasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	<b>1</b>	0.2822	0.1409	0.0691	0.1609
<b>Fe</b>	<b>1</b>	<b>1</b>	0.1376	0.0367	0.6923	<b>0.8761</b>
<b>Zn</b>	0.2822	0.1376	<b>1</b>	-	0.0014	0.0329
<b>Cd</b>	0.1409	0.0367	-	<b>1</b>	-	-
<b>Al</b>	0.0691	<b>0.6923</b>	0.0014	-	<b>1</b>	<b>0.6233</b>
<b>Cr</b>	0.1609	<b>0.8761</b>	0.0329	-	<b>0.6233</b>	<b>1</b>

Considering Aluzinc roofing from the Antobuasi area, there was a significant positive correlation between Lead and Zinc ( $R^2=0.46$ ), Lead and Aluminium ( $R^2=0.55$ ), Iron and Zinc ( $R^2=0.46$ ), Iron and Aluminium ( $R^2=0.55$ ), Zinc and Aluminium ( $R^2=0.46$ ), Zinc and Chromium ( $R^2=0.46$ ) as reported in table 4.13.

**Table 4.13 Correlation between metals in roof runoff from Aluzinc roofing materials in Antobuasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	-	<b>0.4553</b>	-	<b>0.5473</b>	0.15
<b>Fe</b>	-	<b>1</b>	<b>0.4553</b>	0.0667	<b>0.5521</b>	0.15
<b>Zn</b>	<b>0.4553</b>	<b>0.4553</b>	<b>1</b>	-	<b>0.4553</b>	<b>0.4553</b>
<b>Cd</b>	-	0.0667	0.0963	<b>1</b>	0.0176	-
<b>Al</b>	<b>0.5473</b>	<b>0.5521</b>	<b>0.4553</b>	0.0176	<b>1</b>	0.15
<b>Cr</b>	0.15	0.15	<b>0.4553</b>	-	0.15	<b>1</b>

**Table 4.14 Correlation between metals in roof runoff from Control samples in Antobuasi**

	<b>Pb</b>	<b>Fe</b>	<b>Zn</b>	<b>Cd</b>	<b>Al</b>	<b>Cr</b>
<b>Pb</b>	<b>1</b>	0.0144	-	-	-	0.1644
<b>Fe</b>	0.014	<b>1</b>	0.3089	-	-	-
<b>Zn</b>	-	0.3089	<b>1</b>	-	-	-
<b>Cd</b>	-	0.1082	-	<b>1</b>	-	-
<b>Al</b>	-	<b>1</b>	-	-	<b>1</b>	-
<b>Cr</b>	0.1644	0.0766	-	-	-	<b>1</b>

Considering the aluminium roofing sheet the concentration of Pb affected the concentration of Fe and Al, the concentration of Fe also affected the concentration of Zn and Al. Finally the concentration of Cd also affected the concentration of Al. There was also an effect of a significant magnitude on the concentrations of Fe, Zn, Cr and Al by Pb in runoff from Aluzinc roofing materials. In the same Aluzinc roofing the concentrations of Cr, Fe and Zn were also affected by the concentration of Al and then the concentration of Zn also affected the concentrations of Cr and Fe. With regards to clay tiles, the concentration of Pb affected the concentrations of Zn, Cd and Fe. Also the concentration of Fe affected the concentrations of Cr and Al and finally the concentration of Al affected the concentrations of Zn and Cr in the roof runoff. With regards to Asbestos roofing in the Obuasi area, concentration of Pb affected Fe and Zn whilst the concentration of Al affected Cr.

Generally for the asbestos roofing and the aluminium roofing in the Wawasi area there was no significant positive correlation between the metals. Also for control samples, aluminium, clay tiles and asbestos roofing in the Antobuasi area there was no significant positive correlation between the metals.

## CHAPTER FIVE

### 5.0 CONCLUSION

In comparison to the control samples, the Aluminium roofing material caused the pH of the runoff sample to increase by 1.5 making the runoff more basic. The aluminium roofing material recorded higher concentrations in all the parameters than the control samples except for Iron and Cadmium. Average values recorded in these samples were below the WHO guidelines for drinking water, except for pH, Turbidity, Aluminium, Lead, and Chromium. Thus 31.25 % of parameters analysed in samples from the aluminium roofing material were above the WHO guidelines for drinking water whilst 68.75 % were below.

In comparison to the control samples, it was observed that, runoff samples collected from asbestos roofing material recorded higher values in all the parameters analysed except for Total Dissolved Solids, Sulphates and Iron. Most of the values recorded were below the WHO guidelines for drinking water except that of pH, Turbidity, Lead and Chromium. About 25 % of the parameters analysed were above the WHO guidelines whilst 75 % of the sample were below. The highest value for pH, Turbidity, Lead and Chromium were 5.6, 89.27 NTU, 0.20 mg/l and 0.52 mg/l respectively.

In the clay tiles roofing materials higher values in most of the parameters when compared with the control sample was recorded but pH, Turbidity, Sulphate and Iron had lower values in the roof runoffs. Most of the parameters had values which were below the

WHO guidelines for drinking water except for pH, Turbidity, Lead and Chromium were above this value. The highest values recorded for parameters above the WHO guidelines are 5.3, 97.4 NTU, 0.24 mg/l and 0.41mg/l for pH, Turbidity, Lead and Chromium.

Runoff samples from the aluzinc roofing materials recorded higher values in most of the parameters analysed when compared with the control samples except that of pH, TDS, Chloride, Sulphate and Lead. The values obtained were below the WHO guideline for drinking water except that of pH, Turbidity, Lead and Chromium. This represents 25 % of the total parameters analysed and 75 % was below the WHO guidelines. The highest values recorded for these parameters were 5.9, 87.5 NTU, 0.18 mg/l and 0.17 mg/l for pH, Turbidity, Lead and Chromium respectively.

The physicochemical data obtained in this study clearly indicates that, the extensive use of harvested rainwater from roofs as advised by some people can be harmful especially when it is used as an alternative source of water for domestic purposes. Most of these values obtained for trace metals might be comparably low but as already established trace metals have a cumulative effect, its continuous intake over a long period can be harmful.

It can be concluded that the type of roofing material has a direct impact on the quality of roof runoff, and care must be taken in it's over reliance. It was also found that metal roofing sheets are better than the other roofing since it retains less particulates and dirt which were the major contributors of pollutants in the runoff.

The orders in which the roofs are liable of releasing metals into the runoffs are: Cr (ceramic > asbestos > metal sheet), and Zn and Al (metal sheet > asbestos > ceramic tiles). Asbestos and clay tiles roofing materials pose more environmental risk than other roofs investigated in this study, hence should not be used to harvest rainwater for domestic purposes.

### **5.1 Recommendation**

The roofing materials have an impact on the quality of the runoffs but most of the parameters measured in the runoffs were below the WHO limit for drinking water. Since most of the physicochemical parameters analysed in the roof runoff have health implications, care must be taken in advocating for its use for cooking and drinking. Its normal use in households as washing and for flushing toilets can be maintained.

Since turbidity was always high in all the samples, I will recommend that the water should be allowed to settle and properly decanted before it can be used, Since most of the metals were particulate in nature.

Lead contribution due to the roofing gutters can be reduced if the gutters are frequently cleaned and the use of lead guttering discontinued. The frequent cleaning of the gutters will also reduce the contribution of sulphate, Chlorides, nitrates and phosphates.

Further work should be conducted to further ascertain the correlation of the metals and to actually explain some of the observations made in terms of their occurrence. Also some studies indicate that there is a link between acid rain and respiration problems in sensitive populations such as children and asthmatics. So further work should be done in the area to ascertain if this situation is also common in the area.

Also Further work should be conducted on the biological contamination contributed to the runoff by these roofing materials.

**TABLE OF RESULTS**

<b>Table 4.15 Physical parameters and Anions for runoff from Aluminium Roofing</b>										
	<b>PHYSICAL PARAMETERS</b>						<b>ANIONS</b>			
<b>CODES</b>	<b>PH</b>	<b>Cond</b>	<b>TDS</b>	<b>TSS</b>	<b>Turb</b>	<b>Alk</b>	<b>Cl</b>	<b>So<sub>4</sub><sup>2-</sup></b>	<b>P<sub>0</sub><sub>4</sub></b>	<b>N<sub>0</sub><sub>3</sub><sup>-</sup></b>
RSAL 1	6.3	37.95	18.7	5	61	14	24	72	0.38	0.62
RSAL 2	6.3	40.85	20.35	10	53	8	36	68	0.7	0.71
RSAL 3	6.3	44.3	21.2	9	47.61	10	68	58	0.44	0.68
RSAL 4	6.4	41.05	20.05	4	37.12	14	32	44	0.14	0.66
RSAL 5	6.4	45.5	23.5	11	54	8	16	73	0.42	0.92
STD	0.055	3.01	1.78	3.1145	8.89	3.03	19.88	12.17	0.20	0.12
MEAN	6.3	41.9	20.8	7.8	50.5	10.8	35.2	63	0.42	0.72
WSAL 1	6.4	22.9	11.25	16	72	14	12	39	0.14	0.01
WSAL 2	6.4	21.8	11.3	4	65	8	25.6	34	0.1	0.92
WSAL 3	5.8	63.3	29.65	19	82	10	14	31	0.2	0.83
WSAL 4	5.9	24.8	13.2	17	68	8	18.4	30	0.18	0.41
WSAL 5	6.2	29.85	14.6	6	60	14	36	27	0.5	0.87
STD	0.28	17.48	7.76	6.88	8.30	3.03	9.78	4.55	0.16	0.39
MEAN	6.1	32.5	16	12.4	69.4	10.8	21.2	32.1	0.22	0.81
ASAL 1	6.0	21.7	11.65	4.0	57.0	6.0	40.0	20.0	0.66	0.93
ASAL 2	5.9	35.9	18.1	6.0	62.0	8.0	62.0	23.0	0.64	0.68
ASAL 3	6.1	38.4	15.96	7.0	41.5	8.0	38.0	30.0	0.12	0.53
ASAL 4	5.9	40.02	20.91	8.0	31.0	14.0	50.0	40.0	0.11	0.47
ASAL 5	5.8	39.5	24.4	9.0	50	10.0	12.0	34.0	0.53	0.73
STD	0.11	7.66	4.84	1.92	12.37	3.03	18.51	8.11	0.28	0.18
MEAN	5.9	35.1	18.2	6.8	48.3	9.2	40.4	29.3	0.41	0.67

	PHYSICAL PARAMETERS						ANIONS			
CODES	PH	Cond	TDS	TSS	Turb	Alk	Cl	So4 <sup>2-</sup>	P0 <sub>4</sub>	N0 <sub>3</sub> <sup>-</sup>
WAA1	5.2	13.1	7.1	7	142	4	42	16.8	0.13	0.22
WAA2	6.2	21.8	11.2	1	95	14	52	11	0.47	0.14
WAA3	6	11.15	5.55	2	37.35	4	32	19	0.29	0.21
WAA4	5.7	16.12	8.1	12	75	4	68	17.6	0.48	0.22
WAA5	5.9	46.95	23.5	7	97	16	40	18.9	0.29	0.19
STD	0.38	14.61	7.24	4.44	37.99	6.07	13.82	3.30	0.15	0.03
MEAN	5.8	21.8	11.09	5.8	89.27	8.4	46.8	16.1	0.33	0.2
RAA1	5.1	101.4	51.45	17	38.79	6	50	23	0.66	0.11
RAA2	5.6	18.4	8.9	4	117	8	78	46	0.42	0.82
RAA3	5.7	27	13.45	5	115	16	28	16	0.39	0.48
RAA4	5.9	14.15	7.15	9	24.6	8	40	42	0.42	0.12
RAA5	5.8	11.8	6	12	35.64	8	34	29	0.66	0.63
STD	0.31	37.82	19.25	5.32	45.77	3.90	19.65	12.64	0.14	0.31
MEAN	5.6	34.6	17.39	9.4	66.2	7.6	46	31.2	0.51	0.43

	PHYSICAL PARAMETERS						ANIONS			
CODES	PH	Cond	TDS	TSS	Turb	Alk	Cl	So4 <sup>2-</sup>	P0 <sub>4</sub>	N0 <sub>3</sub> <sup>-</sup>
RCT 1	4.8	21.2	10.5	13	152	18	24	30.4	0.17	0.73
RCT 2	5.5	12.85	6.45	6	74	8	26	27.6	0.62	0.61
RCT 3	5.7	12.3	6.2	7	100	2	46	26.8	0.2	0.48
RCT 4	5.2	24.9	12.35	8	88	8	18.4	13	0.42	0.9
RCT 5	5.4	13.1	6.55	8	73	8	40	11	0.66	1.11
STD	0.34	5.80	2.83	2.70	32.48	5.76	11.61	9.04	0.23	0.25
MEAN	5.3	16.9	8.4	8.4	97.4	8.8	30.9	21.8	0.41	0.77
WCT 1	5.1	24.3	6.5	7	148	14	36	8.7	0.22	0.67
WCT 2	5.3	15.4	7.8	2	78	10	14	6.4	0.43	0.58
WCT 3	5.4	9.8	5.1	2	93	8	28	10	0.6	0.53
WCT 4	5.6	25.6	12.8	10	84	6	16	8.1	0.21	0.96
WCT 5	5.3	11.9	6.1	4	80	6	42	7	0.21	0.66
STD	0.18	7.19	3.03	3.46	29.31	3.35	12.22	1.42	0.18	0.17
MEAN	5.3	17.4	7.7	5	96.6	8.8	27.2	8	0.34	0.68

**Table 4.18. Physical Parameters and Anions from Runoff from Aluzinc roofing**

CODES	PHYSICAL PARAMETERS						ANIONS			
	PH	Cond	TDS	TSS	Turb	Alk	Cl	So <sub>4</sub> <sup>2-</sup>	P <sub>0</sub> <sub>4</sub>	N <sub>0</sub> <sub>3</sub> <sup>-</sup>
RAZ 1	6	40.15	19.5	4	31.54	18	34	37.5	0.62	0.9
RAZ 2	6.1	21.16	10.8	2	59	6	38	31.2	0.11	0.86
RAZ 3	5.9	20.15	10.4	4	52	10	40	34	0.28	0.79
RAZ 4	5.7	20.35	9.35	2	49.79	8	24	36.6	0.63	0.92
RAZ 5	6	40.85	20.65	9	26.43	12	32	28.8	0.42	0.88
STD	0.15	10.94	5.46	2.86	14.02	4.60	6.23	3.65	0.22	0.05
MEAN	5.9	28.5	14.1	4.2	43.8	10.8	33.6	33.9	0.41	0.87
WAZ 1	6.1	23.75	11.65	25	67	16	62	42.8	0.52	0.52
WAZ 2	5.9	29.4	15.1	6	62	14	36	37	1.25	0.41
WAZ 3	6	25.04	12.05	6	61	6	42	38.1	1.23	0.6
WAZ 4	6.2	35.2	18.05	3	39.49	12	60	33.2	1.1	0.21
WAZ 5	6	95.4	49.45	67	208	10	128	40.1	2.4	0.43
STD	0.11	30.32	15.97	26.95	68.19	3.85	36.64	3.58	0.69	0.15
MEAN	6	47.2	12.26	20.3	87.5	11.6	65.6	38.2	1.3	0.43
AAZ1	6.3	19.2	11.5	7	108	10	48	34.8	0.8	0.86
AAZ2	5.9	10.65	6.4	4	62	8	30	34.5	0.64	0.66
AAZ3	6	11.85	6.25	3	43	18	34	38.7	0.34	0.43
AAZ4	6.2	20.95	9.9	4	63	16	32	30.6	0.12	0.82
AAZ5	6	13.3	7.1	3	41	16	40	38.8	0.72	0.58
STD	0.16	4.60	2.35	1.64	26.97	4.34	7.29	3.41	0.29	0.18
MEAN	6	15.2	8.2	4.2	63	13.6	36.8	35.5	0.52	0.67

**Table 4.19 Physical parameters and Anions for Control Samples**

CODES	PHYSICAL PARAMETERS						ANIONS			
	PH	Cond	TDS	TSS	Turb	Alk	Cl	So <sub>4</sub> <sup>2-</sup>	P <sub>0</sub> <sub>4</sub>	N <sub>0</sub> <sub>3</sub> <sup>-</sup>
RCO 1	4.4	13.4	9	7	38.79	14	62	21.8	0.22	0.62
RCO 2	4.5	10.4	6.3	16	24.6	8	24	21.2	0.1	0.11
RCO 3	4.5	7.15	11.8	2	35.64	16	56	18.7	0.14	0.23
RCO 4	4.5	40.5	20.4	12	37.35	8	36	19	0.16	0.11
RCO 5	5.6	19.75	11.4	7	37.12	8	10	18	0.2	0.27
STD	0.50	13.28	5.30	5.36	5.76	3.90	21.70	1.66	0.048	0.21
MEAN	4.7	18.24	11.78	8.8	34.7	10.8	37.6	19.7	0.16	0.27
WCO 1	4.9	15.3	9.4	4	31	10	36	24.4	0.12	0.16
WCO 2	4.3	18.6	11.3	14	41.5	8	38	20	0.28	0.11
WCO 3	4.2	16.7	9.8	5	39.5	2	56	14	0.11	0.42
WCO 4	4.9	42.05	21	9	59	2	28	10.2	0.16	0.01
WCO 5	4.1	19.25	13.1	10	79	6	34	20	0.13	0.62
STD	0.39	11.11	4.75	4.04	19.14	3.58	10.53	5.60	0.07	0.25
MEAN	4.5	22.38	12.92	8.4	50	5.6	38.4	38.4	0.16	0.26
ACO 1	4	38.85	19.45	6	26.43	2	14	8	0.1	0.1
ACO 2	5.4	38.6	19.2	21	43	4	32	10.1	0.09	0.17
ACO 3	4.8	59.6	23.4	19	41	4	28	11.2	0.02	0.31
ACO 4	4.9	49.2	24.1	18	31.54	2	34	12	0.11	0.42
ACO 5	4.9	16.2	10	25	49.79	4	18	9	0.08	0.09
STD	0.51	16.10	5.62	7.12	9.33	1.10	8.79	1.62	0.036	0.14
MEAN	4.8	40.49	19.23	17.8	38.35	3.2	31.5	10.2	0.08	0.22

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