

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY  
DEPARTMENT OF ENVIRONMENTAL SCIENCE, COLLEGE OF SCIENCE

LEVELS OF HEAVY METALS AND OIL AND GREASE IN THE RIVERS PANMU AND  
ANKODEE

A THESIS SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL SCIENCE,  
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MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE

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 material 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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## DEDICATION

I dedicate this thesis to my lovely wife Mrs Doris Amankona and our son Bryant Kwaku Yeboah Amankona. I am blessed to have you guys.

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To the Almighty God I humbly give thanks for His infinite Mercies, Grace and Blessings He has showered upon me from my birth till today. To Him be all the Glory!

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## ABSTRACT

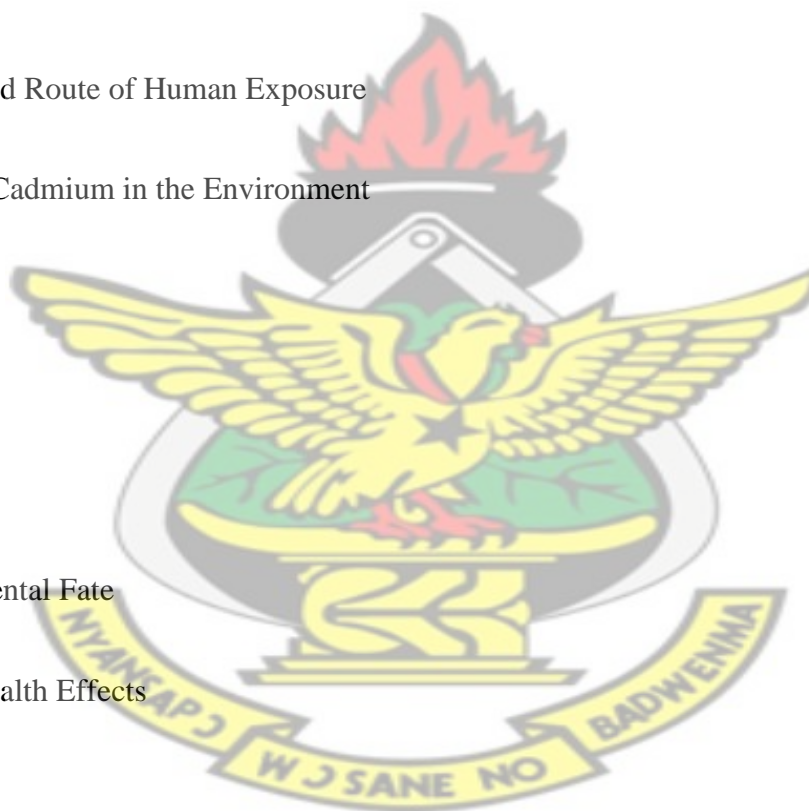
This study measured levels of the heavy metals; Iron, Copper, Lead and Cadmium as well as Oil and Grease in river water and sediment of the Rivers Panmu and Ankodee in the Dormaa Ahenkro Municipality in the Brong Ahafo, Ghana from January to March, 2012. Atomic Absorption Spectrophotometry (AAS) was used in the determination of heavy metals in both water and sediment samples while Partition Gravimetric Method was used in the determination of oil and grease in the water samples. Six water and sediment samples were collected from four different sites along the courses of the rivers Panmu and Ankodee within the Dormaa Ahenkro Township. Generally, levels of heavy metals in sediment samples exceeded levels in the water column. Levels of heavy metals in both water and sediment samples were high and exceeded the World Health Organisation (WHO) health-based guideline values and United States EPA sediment quality guideline for heavily polluted sites, respectively. Iron levels were extremely high compared to the other heavy metals. Oil and Grease levels were however below the Ghana EPA guidelines for effluent discharge into natural water bodies. The Rivers Panmu and Ankodee are heavily contaminated with heavy metals as refuse dumps, fuel service stations and the various scrap metal fabrication workshops are located in their watersheds.

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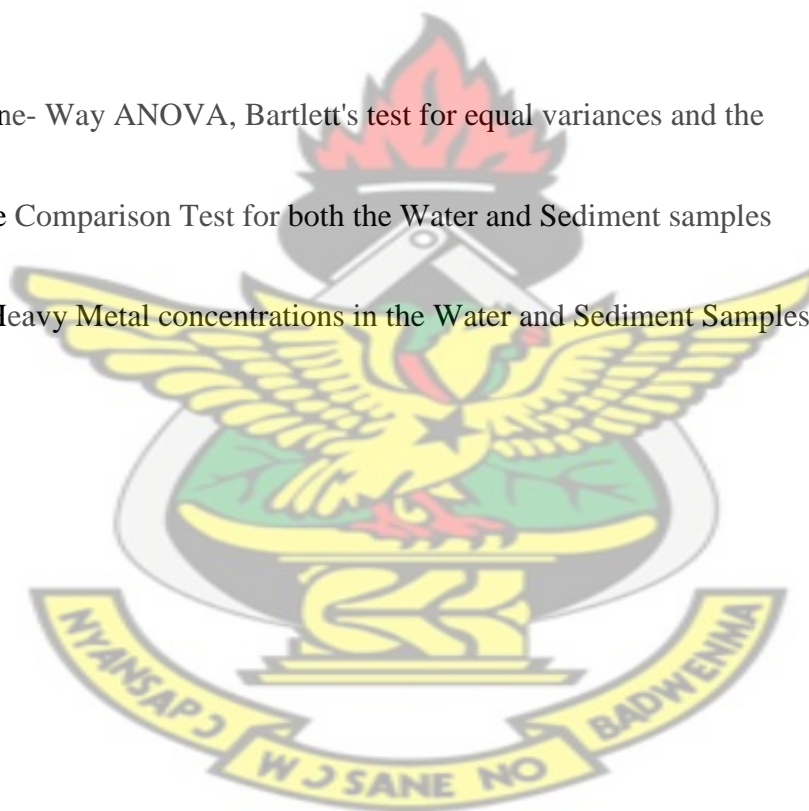
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A map showing the Ankodee and Panmu Rivers and the sampling sites.

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## LIST OF ABBREVIATIONS

**AAS** Atomic Absorption Spectrophotometry

**ANOVA** Analysis of Variance

**AROI** Acceptable Range of Oral Intake

**APHA** American Public Health Association

**ATSDR** Agency for Toxic Substances and Disease Registry

**BDL** Below Detection Limit

**CEC** Cation Exchange Capacity

**DEFRA** Department for Environment Food and Rural Affairs

**EA** Environment Agency

**IARC** International Agency for Research on Cancer

**IPCS** International Programme on Chemical Safety

**OECD** Organization for Economic Co-operation and Development

**PVC** Polyvinyl Chloride

**USEPA** United States Environmental Protection Agency

**MWH** Ministry for Works and Housing

**WHO** World Health Organisation

**WRC** Water Resources Commission



## CHAPTER ONE

### 1.0 INTRODUCTION

#### 1.1 BACKGROUND

Heavy metal contamination in rivers is one of the major water quality issues in many fast growing towns and cities, because maintenance of water quality and sanitation infrastructure did not increase along with population and urbanization growth, especially for developing countries like Ghana (Ahmad *et al.*, 2010). Rivers in urban areas have therefore been associated with water quality problems because of the practice of discharging untreated domestic and industrial effluents into the water bodies which leads to the increase in the level of heavy metals in them (Rim-Rekeh *et al.*, 2006; Khadse *et al.*, 2008; Juang *et al.*, 2009; Venugopal *et al.*, 2009; Sekabira *et al.*, 2010).

In Ghana, one of the earliest studies on heavy metal contamination (Amasa, 1975) examined various matrices, including drinking water, from the Obuasi gold mining area and found that arsenic concentrations occurred above normal values. Pelig Ba *et al.*, (1991) assessed the level of contamination of drinkable ground-water from the Accra plains and upper regions of Ghana and found that in some areas Pb, Cr and Fe concentrations exceeded the WHO guideline limits for drinking water. Studies of heavy metal contaminations in mining areas in Ghana have also revealed high levels of arsenic comparable to other arsenic-endemic areas of the world in urine of inhabitants of Tarkwa (Asante *et al.*, 2007), and some villages near Obuasi (Smedley *et al.*, 1996) in Ghana, again arsenic contamination has been reported in groundwater samples in Obuasi and Bolgatanga (Smedley, 1996).

The recent extensive uncontrolled human activities in the study area have together generated considerable waste and affected the quality of water, especially surface water in the study area.

## **1.2 PROBLEM STATEMENT**

Ghana Water Policy, with a vision for 2025, have as its objective; to promote an efficient management system and environmentally sound development of all water resources of the country (MWH, 2002). To achieve this, freshwater resources must be protected and conserved (MWH, 2005). However, Ghana is currently experiencing a relatively high level of pollution of her rivers, the main causes being the discharge of untreated wastewater from human settlements into the rivers (Ansa- Asare, 2001).

Though lakes and rivers provide a vast majority of environmental goods and services, including fish, these services depend on the integrity of aquatic ecosystems, widely deteriorating water quality and reduced quantities of water that are needed to sustain these ecosystems (WRC, 2004; MWH, 1998).

Rivers in the Dormaa Municipality, especially, the Panmu and Ankodee rivers are used as refuse dumps. The waste dumped around the rivers ranges from putrescible to non-putrescible, metal scraps, waste from electrical gadgets like old computer monitors, system units etc. Among these, are also some human activities along the course of the rivers: mechanics, artisans, fuel service stations, car washing bays, among others, along the course of the river. Grease and oil and other heavy metal pollutants could easily end

up in the rivers and streams especially, these activities are done close to the rivers. Since these pollutants can deteriorate the water quality in those rivers there is therefore the need to investigate the levels of pollutants such as heavy metals in these water bodies

### **1.3 OBJECTIVES**

#### **1.3.1 GENERAL OBJECTIVES**

The main objective of this study was to assess the concentrations of heavy metals and oil and grease in the Panmu and Ankodee rivers

#### **1.3.2 SPECIFIC OBJECTIVES**

The specific objectives are

- To assess the levels of cadmium, iron, lead and copper in water and sediment in the Panmu and Ankodee Rivers
- To assess the levels of grease and oil in the Rivers Panmu and Ankodee
- To identify the effects of the operations of artisans, mechanics etc. on the Rivers Panmu and Ankodee

## 1.4 JUSTIFICATION OF THE STUDY

Heavy metal contaminations are important due to their potential toxicity in the environment and human beings (Gueu *et al.*, 2007; Lee *et al.*, 2007; Adams *et al.*, 2008; Vinodhini and Narayanan, 2008). Some heavy metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for the life processes in animals and plants while many other metals such as Cd, Cr, Pb and Co have no known physiological activities in biota (Kar *et al.*, 2008; Suthar and Singh, 2008; Aktar *et al.*, 2010). Metals are non-degradable and can accumulate in the human body system, causing damage to the nervous system and other internal organs (Lee *et al.*, 2007; Lohani *et al.*, 2008). However, the rivers play a major role in assimilation or transporting municipal and industrial wastewater and runoff from agricultural and mining land (Singh *et al.*, 2004).

The present study aimed to envisage the water quality status of Rivers Panmu and Ankodee with respect to its heavy metal concentrations along the course of the rivers where various anthropogenic activities were observed, in the Dormaa Ahenkro town in the Dormaa Municipality of the Brong Ahafo Region of Ghana. Unfortunately, these rivers serve as a source of drinking and irrigation water for some communities (Zongo "B", Ahantrase e.t.c) downstream.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 HEAVY METALS

Humans have been exposed to heavy metals toxins for a long time. The heavy industrialization of the world has increased the overall environmental load of heavy metal toxins to such an extent that they are present in virtually every area of the biosphere. These metallic contaminants enter the food chain by plant roots uptake from the soil, direct foliate absorption and are incorporated into edible tissue or through the food preparation and storage processes. These elements increase the natural concentration in organisms causing toxic effects in deterioration of general health (Sanayei *et al.*, 2009). The determination of traces of heavy metals in rivers / surface waters has assumed considerable importance in recent years (ATSDR, 2007).

Heavy metal is a term referred to any metallic element that has a relatively high density and is toxic or poisonous even at low concentrations. Heavy metals have atomic weight between 63.546 and 200.590 and a specific gravity greater than 4.0 (Kennish, 1992). They are natural components of the earth crust. It is estimated that 50-75% of heavy metals released annually into the world's environment comes from human activities (anthropogenic sources). Most heavy metals are known toxicants, causing cancer, mental retardation, growth defects, reproductive defects and poor development of both the life of plant and animal. Most are neurotoxins which bio-accumulate through the food chain and through drinking of water and consumption of fish contaminated by these heavy metals (Adimado & Baah, 2002).



Living organisms require little amounts of some heavy metals including copper, iron, zinc etc, thereby been referred to as micronutrients or trace elements, but heavy metals of particular concern to the environment are cadmium, lead, mercury etc. (Kennish, 1992).

Heavy metals are found in soil, air and in water. In both soil and water, however, they exist in complexes rather than as insoluble compounds and in simple, more soluble forms that are readily available (USEPA, 1997). Lead, boron and nickel are used, sometimes, as additive to gasoline, while superphosphate fertilizers and limestone usually contain small amounts of cadmium, manganese, copper, zinc and nickel (Kennish, 1992).

In Ghana, one of the earliest studies on heavy metal contamination (Amasa, 1975) examined various matrices, including drinking water, from the Obuasi gold mining area and found that arsenic concentrations occurred above normal values. A study (Akoto-Bamford, 1990) in which heavy metal pollution from gold mining activities was assessed by analyzing gold ore, tailings, sediments and water for some selected heavy metals revealed the presence of all the elements in sediments within a concentration range of 0.08 to 49 000  $\mu\text{g g}^{-1}$ , whereas only iron and zinc were detected in water at levels of 0.08–2.4 ( $\mu\text{g ml}^{-1}$ ).

Pelig Ba *et al.*, (1991) assessed the level of contamination of drinkable ground-water from the Accra plains and upper regions of Ghana and found that in some areas Pb, Cr and Fe concentrations exceeded the WHO guideline limits for drinking water. Studies of heavy metal contaminations in mining areas in Ghana have also revealed high levels of arsenic comparable to other arsenic-endemic areas of the world in urine of inhabitants of Tarkwa (Asante *et al.*, 2007), and some villages near Obuasi (Smedley *et al.*, 1996) in



Ghana, while arsenic contamination has been reported in groundwater in Obuasi and Bolgatanga (Smedley, 1996). Mercury has also been reported in surface soil and cassava (*Manihot esculenta*) in Dunkwa (Golow and Adzei, 2002), and in human blood, human urine and fish (Adimado and Baah, 2002) in southwestern Ghana. Many chemicals including those from less known e-wastes also enter the environment and chemical pollution remains a major environmental issue in Ghana.

The long period of mining and the more recent extensive surface mining operations have together generated considerable waste and affected the quality of water, especially surface water in the mining areas. Even communities relatively distant from mining and processing facilities are adversely affected due to offsite migration of these pollutants. Communities in Obuasi such as Sansu, Bidiem, Anyinam, Akatakyieso, Odumase, and Tutuka are directly impacted by surface mining and processing activities (Akabzaa et al., 2007).

## 2.2 ENVIRONMENTAL EFFECTS

Elder (1988), reports that, some heavy metals are stable, hence, cannot be degraded and thus become potential environmental contaminants to plants and animals. They tend to accumulate in soils and sediments.

A lot more metals are essential to life; they only become toxic when exposure exceeds some threshold beyond which adverse impact is impending. Some organisms are able to regulate the metal concentrations in their tissues (Elder, 1988). Fish and crustacean can

excrete essential metals such as copper, zinc and iron that are present in excess (Galloway, 1989; Huckabee and Blaylock, 1972)

Research has shown that aquatic plants and bivalves are not able to successfully regulate metal accumulation in polluted environments. In estuarine systems, bivalves often serve as bio-monitor organism in areas of suspected pollution of heavy metals (Kennish, 1992). In comparison to freshwater fish and invertebrates, aquatic plants are equally less sensitive to metals such as mercury, copper, zinc and lead. Metal uptake rates will vary according to the organism in question. Zooplankton and phytoplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to absorb metals is largely dependent on the physical and chemical characteristics of the metals (Kennish, 1992; USEPA, 1987). Research have revealed that heavy metals enter the systems of aquatic organisms through free metal ion that are absorbed through respiratory surfaces, body surfaces which are readily diffused into the blood stream. Also, metals are absorbed onto food and particulates which may be ingested as well as free ions ingested with water (Collison and Shrimp, 1972).

According to Casey *et al* (1986), entry of some of these metals into the food chain may occur in areas of high degree of contamination for example, in mining areas. Irrigation water may transport dissolved metals into agricultural soils. Cadmium, which is a toxic element and usually accumulates in plant roots and shoots, has reportedly caused havoc to people who consumed locally grown rice on cadmium contaminated paddy fields (Young, 2005).

## 2.3 CADMIUM

### 2.3.1 INTRODUCTION

Cadmium, in its elemental form, occurs naturally in the earth's crust. Pure cadmium is a very soft, silvery-white metallic element. It is so soft that it can be cut with a knife and has no definite odour or taste. Cadmium is not usually found in the environment as a metal but as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide) (IPCS, 1992). Cadmium may change forms, but the cadmium metal itself does not disappear from the environment. Naturally-occurring isotopes are <sup>106</sup> (1.22%), <sup>108</sup> (0.88%), <sup>110</sup> (12.39%), <sup>111</sup> (12.75%), <sup>112</sup> (24.07%), <sup>113</sup> (12.26%), <sup>114</sup> (28.86%), and <sup>116</sup> (7.50%) (Weast, 1974).

Soils and rocks contain varying amounts of cadmium, generally in small amounts but sometimes in larger amounts (for example in some fossil fuels or fertilizers). Cadmium ores are rare. Most cadmium is produced as a by-product from extraction of zinc, lead, or copper ores. Greenockite (CdS) is the only mineral of any consequence that contains cadmium (IPCS, 1992).

Cadmium does not corrode easily and has many uses in industry and consumer products, mainly in nickel-cadmium batteries, pigments used mostly in plastics, metal coatings, plastic stabilizers in polyvinyl chloride (PVC), and some metal alloys (Cook and Morrow, 1995; Thornton, 1992). Cadmium compounds are also used in printing, in textiles, in television phosphors, photography, lasers, as a neutron absorber in nuclear reactors, in photovoltaic cells, and other semiconducting cadmium

compounds in a variety of electronic applications (Chang, 2005; Elinder, 1985; OECD, 1994).

Cadmium has no essential biological function and is extremely toxic to humans. In chronic exposure, it accumulates in the body, particularly in the kidneys and the liver (Williams *et al.*, 1999). These properties, along with its common usage make cadmium one of the commonest environmental metal poisonings. Acute poisoning from inhalation of fumes and ingestion of cadmium salts can also occur and at least one death has been reported from self-poisoning with cadmium chloride (Baldwin and Marshall, 1999).

### **2.3.2 SOURCES AND ROUTE OF HUMAN EXPOSURE**

Cadmium is widely distributed in the Earth's crust (0.1-0.5 mg/g), the atmosphere (1-5 ng/m<sup>3</sup>), marine sediment (~1 mg/g) and sea water (~0.1 mg/g) (IPCS, 1992). Cadmium emissions arise from two major sources; natural sources and man-made or anthropogenic sources. Even though the average cadmium concentration in the earth's crust is generally placed between 0.1 and 0.5 ppm, much higher levels may accumulate in sedimentary rocks. Marine phosphates and phosphorites have been reported to contain levels as high as 500 ppm (Cook and Morrow, 1995; WHO, 1992) and are thus undesirable to use as fertilizers (Taylor, 1997). Weathering and erosion of parent rocks result in the transport by rivers of large quantities of cadmium to the world's oceans (OECD, 1994; WHO,

1992). Volcanic activity and forest fires have also been reported as natural sources of cadmium emissions (Nriagu, 1980). Large amounts of cadmium enter the environment from human activities such as mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges, cement production and waste incineration (Elinder, 1985; WHO, 1992).

Estimates of cadmium emissions to the atmosphere from human and natural sources have been carried out at the world-wide, regional, and national levels (IPCS, 1992). According to Nriagu (1979b), about 10-15% of total airborne cadmium emissions arise from natural processes, the major source being volcanic action. Anthropogenic cadmium emissions to air arise, in decreasing order of importance, from the combustion of fossil fuels, iron and steel production, non-ferrous metals production and municipal solid waste combustion. Atmospheric cadmium occurs mainly in the forms of cadmium oxide and cadmium chloride which are ultimately dispersed by the wind (Cook and Morrow, 1995).

Cadmium emissions to water arise, in decreasing order of importance, from phosphate fertilisers, non-ferrous metals production, and the iron and steel industry (OECD, 1994; IPCS, 1992). Mining represent a major source of cadmium release to the aquatic environment. Contamination can arise from mine drainage water, waste water from the processing of ores, overflow from the tailings pond, and rainwater run-off from the general mine area. The release of these effluents to local water-courses can lead to extensive contamination downstream of the mining operation (IPCS, 1992). Cadmium is however, a natural, usually minor constituent of surface and groundwater (ATSDR,1999a). The atmospheric fall-out of cadmium to fresh and marine waters



represents a major input of cadmium at the global level (Nriagu and Pacyna, 1988). Acidification of soils and lakes may result in enhanced mobilization of cadmium from soils and sediments and lead to increased levels in surface and ground waters (WHO, 1992).

The application of phosphate fertilizers and atmospheric deposition are significant sources of cadmium input to arable soils in some parts of the world; sewage sludge can also be an important source at the local level (IPCS, 1992). Cadmium in soil tends to be more available when the soil pH is low. Cadmium is taken up and retained by aquatic and terrestrial plants and is concentrated in the liver and kidney of animals that eat the plants (Elinder, 1985).

Humans normally absorb cadmium into the body either by ingestion or inhalation. Dermal exposure (uptake through the skin) is generally not regarded to be of significance (Lauwerys, 1986). Human exposure to cadmium can result from consumption of food especially grain and leafy vegetables, which readily absorb cadmium from the soil (Williams *et al.*, 1999), drinking water, or incidental ingestion of soil or dust contaminated with cadmium; from inhalation of cadmium-containing particles from ambient air; from inhalation of cigarette smoke, which contains cadmium taken up by tobacco; or from working in an occupation involving exposure to cadmium fumes and dust (Elinder, 1985). A daily intake of 2-4 mg cadmium was estimated from smoking one packet of cigarettes per day (WHO, 1992). For non-smokers, ingestion of food is the largest source of cadmium exposures. Most drinking water contains only very low levels of cadmium and is usually not an important route of exposure, although water may leach cadmium from



plumbing (ATSDR, 2005).

### **2.3.3 LEVELS OF CADMIUM IN THE ENVIRONMENT**

#### **2.3.3.1 AIR**

Ambient air cadmium concentrations have generally been estimated to range from 0.1 to 5 ng/m<sup>3</sup> in rural areas, from 2 to 15 ng/m<sup>3</sup> in urban areas, and from 15 to 150 ng/m<sup>3</sup> in industrialised areas (Elinder, 1985; OECD, 1994; WHO, 1992). Thornton (1992) suggested that coal and oil used in classical thermal power plants are responsible for 50% of the total cadmium emitted to the atmosphere.

Volcanic activity and forest fires has been estimated to release to the atmosphere 820 metric tons (Nriagu, 1980; OECD, 1994; WHO, 1992) and 1 to 70 metric tons per year (Nriagu, 1980) respectively. Emission rates of cadmium from solid waste incinerators have been found to range from 20 to 2,000 µg/m<sup>3</sup> from the stacks of traditional incinerators and from 10 - 40 µg/m<sup>3</sup> from advanced incinerators (IARC, 1993b).

#### **2.3.3.2 WATER**

Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations,

leakage from landfills and contaminated sites, and the dispersive use of sludge and fertilisers in agriculture. Weathering and erosion of parent rocks result in the transport by rivers of large quantities, recently estimated at 15,000 metric tonnes per annum, of cadmium to the world's oceans (OECD, 1994; WHO, 1992).

Cadmium contamination can result from entry into aquifers of mine drainage water, waste water, tailing pond overflow, and rainwater runoff from mine areas (IARC, 1993b). The upper Clark Fork River in Montana is contaminated with large amounts of cadmium from past mining activities between 1880 and 1972. While mining wastes are no longer released into the river, an estimated 14.5 million m<sup>3</sup> of tailings have been incorporated into the riverbed, floodplain, and reservoir sediments (Canfield *et al.*, 1994). Some data shows that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0.1 ppm cited for fresh waters (Cook and Morrow, 1995). Surficial sediments collected from 18 locations in three major tributaries to Newark Bay, New Jersey, had a mean cadmium concentration of 10±6 mg/kg (ppm) dry weight (Bonnevie *et al.* 1994).

Rivers containing excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50km, from the source and is highly persistent in water, with a half-life of about 200 days (WHO, 1992). Atmospheric fallout of cadmium to aquatic systems is another major source of cadmium in the aquatic environment (IARC, 1993; Nriagu and

Pacyna, 1988).

### 2.3.3.3 SOIL

Cadmium in soils is derived from both natural and anthropogenic sources. The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but some rocks such as sedimentary rocks are known to contain about 0.1 to 25 ppm of cadmium. Naturally, high levels of 200 to 14,000 ppm have been estimated for zinc ores and around 500 ppm for typical lead and copper ores. The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm of cadmium. Anthropogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertiliser application. The use of cadmium-containing fertilisers (10-200 ppm) and sewage sludge (1-1000 ppm) is most often quoted as the primary reason for the increase in the cadmium content of soils over the last 20 to 30 years in Europe (Cook and Morrow, 1995; Jensen and Bro-Rasmussen, 1992). Wet and dry deposition of cadmium from the atmosphere may also contribute sizable amounts of cadmium to soil in the areas surrounding sources of atmospheric emissions, such as incinerators and vehicular traffic, which may release cadmium from burned fuel and tire wear (EPA, 1985). Fossil fuels are known to contain 0.5 to 1.5 ppm cadmium (Cook and Morrow, 1995).

#### 2.3.4 ENVIRONMENTAL FATE

Cadmium emitted to the atmosphere from combustion processes is usually associated with very small particulates that are in the respirable range ( $<10\text{ }\mu\text{m}$ ) and are subject to long-range transport with atmospheric residence time of about 1-10 days before deposition occurs (Keitz, 1980). Indeed, it is often assumed that  $< 10\%$  of such emissions are deposited locally, the remainder being available for long-range transport (Krell and Roeckner, 1988). Total deposition rates have been measured at numerous localities worldwide and values have generally been found to increase in the order: background  $<$  rural  $<$  urban  $<$  industrial (IPCS, 1992).

Cadmium is more mobile in aquatic environments than most other heavy metals (e.g., lead). In polluted or organic-rich waters, adsorption of cadmium by humic substances and other organic complexing agents plays a dominant role in transport, partitioning, and remobilization of cadmium. Cadmium concentration in water is inversely related to the pH and the concentration of organic material in the water (Callahan *et al.*, 1979). Cadmium has a relatively long residence time in aquatic systems. In Lake Michigan, a mean residence time of 4-10 years was calculated for cadmium (Wester *et al.*, 1992). Studies have indicated that concentrations of cadmium in sediments are at least one order of magnitude higher than in the overlying water. Cadmium concentrates in freshwater and marine animals to concentrations hundreds to thousands of times higher than in the water (Callahan *et al.*, 1979).

Rivers contaminated with cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, by the dumping of dredged sediments, or through

flooding (Forstner, 1980; Tsuchiya, 1978). Forstner (1980) reported soil cadmium concentration of 70 mg/kg in agricultural land adjacent to Neckar River, Germany, which received dredge sediments for soil improvement and Tsuchiya (1978) reported soil contamination due to irrigation in Japan.

The most important soil factors influencing plant cadmium accumulation are soil pH and cadmium concentration (Page *et al.*, 1981; Herrero and Martin, 1993). Factors such as cation exchange capacity and the contents of the hydrous oxides of manganese and iron, organic matter, and calcium carbonate also influence distribution of cadmium in soil and soil solution. Increases in these parameters result in decreased availability of cadmium to plants owing to a reduction of the level of cadmium in the soil solution (IPCS, 1992). Contamination of soil by cadmium is of concern because the cadmium is taken up efficiently by plants and, therefore, enters the food chain for humans and other animals (ATSDR, 1999a; IPCS, 1992).

### **2.3.5 HUMAN HEALTH EFFECTS**

Cadmium can enter the blood by absorption from the stomach or intestines after ingestion of food or water, or by absorption from the lungs after inhalation. However, once cadmium enters the body, it is very strongly retained and low doses may build up significant cadmium levels in the body if exposure continues. The amount of cadmium needed to cause an adverse effect in an exposed person depends on the chemical and physical form of the element. In general, cadmium compounds that dissolve easily in water (e.g., cadmium chloride), or those that can be dissolved in the body (e.g., cadmium



oxide), tend to be more toxic than compounds that are very hard to dissolve (e.g., cadmium sulphide) (IPCS, 1992).

An acute intake of cadmium causes testicular damage and may affect female reproductive cycle. Within a few hours of exposure, there is necrosis and degeneration of the testes with complete loss of spermatozoa. This is due to a reduction in the blood supply to these organs (Timbrell, 1995). Acute inhalation of cadmium may initially cause irritation of the upper respiratory tract, although symptoms may be delayed for 4-8 hours. Dyspnoea, chest pain and muscle weakness may also occur. Pulmonary oedema, bronchitis, chemical pneumonitis, respiratory failure and death may occur within days of exposure.

Long-term exposure may result in progressive pulmonary fibrosis and impaired lung function (WHO, 1992). Acute ingestion of cadmium produces severe gastrointestinal irritation, which is manifest as severe nausea and vomiting, abdominal cramps and diarrhoea. A lethal dose of cadmium for ingestion is estimated to be between 0.35 and 8.90 g (Hu, 1998).

Chronic oral exposure to cadmium leads to renal failure, characterised by proteinuria due to renal tubular dysfunction. The accumulation of cadmium in the kidney affects renal vitamin D metabolism, which subsequently disturbs calcium balance that may lead to osteomalacia and osteoporosis (DEFRA and EA, 2002a). This, as well as the increased excretion of calcium and phosphorus may result in bone disease characterized by bone and joint aches and pains, a syndrome, first described in Japan, where it was termed the itai-itai ("ouch-ouch") disease. Symptoms of this disease



include weak bones that lead to deformities, especially of the spine, or to more easily broken bones. It is often fatal. (ATSDR, 1999a)

Long term exposure to cadmium can cause anaemia, loss of sense of smell, fatigue and/or yellow staining of teeth. Chronic inhalation of cadmium causes loss of renal tubular function, leading to proteinuria and impairs lung function by causing bronchitis, obstructive lung disease and in some cases interstitial fibrosis (IPCS, 1992). Chronic obstructive airway disease has been associated with long-term high-level occupational exposure by inhalation (OECD, 1994; WHO, 1992). Cadmium (especially cadmium Oxide) is also known to be carcinogenic, and in studies has been linked with cancers in the lungs and prostate (Williams *et al.*, 1999).

## 2.4 LEAD

Lead is a heavy metal, low melting point, bluish-gray metal that naturally in the crust of the earth. Nonetheless, it is rarely found naturally as a metal. It is usually found combined with two or more other elements to form lead compounds. Metallic lead is resistant to corrosion (that is, not easily attack by water and oxygen). When exposed to air or water, thin films of lead compounds are formed that protect the metal from further attack (ATSDR, 2006; IPCS, 2001).

Lead is easily moulded and shaped. Lead can be combined with other metals to form alloys. Lead and alloys of lead are commonly found in pipes, storage batteries, weights, shot and ammunitions, cable covers, and sheets used to shield humans from radiations.

The largest use for lead is in storage batteries in cars other vehicles. Lead compounds are used as pigments in paints, dyes, and ceramic glazes and in caulk. Tetraethyl lead is used in gasoline for off-road vehicles and airplanes. Lead is used in ammunition, which is the largest non-battery end use, has remained fairly constant in recent years. However, the use of lead in bullets as well as in fishing sinkers is being reduced because of its harm to the environment. Most lead by industry comes from mined ores (“primary”) or from recycled scrap metal or batteries (“secondary”). However, most lead today is “secondary” lead obtained from lead-acid batteries (ATSDR, 2007)

Because of health concerns, lead from gasoline, paints and ceramic products, caulking, and pipe solder has been dramatically reduced in recent years (ATSDR, 2006).

Lead occurs naturally in the environment but, most of the high levels found throughout the environment come from anthropogenic activities such as its uses. Environmental levels of lead have increased more than 1,000 fold over the past three centuries as a result of human activity (WHO, 2000). The greatest increase occurred between the years 1950 and 2000, and reflected increasing worldwide use of leaded gasoline. Lead can enter the environment through releases from mining lead and other metals, and from factories that make or use lead, lead alloys, or lead compounds. Lead is released into the air during burning coal, oil, or waste. Before the use of leaded gasoline was banned, most of the lead released into the environment came from vehicle exhaust. Before the 1950s, lead was used in pesticides applied to fruit orchards. Once lead gets into the atmosphere, it may travel long distances if the lead particles are very small. Lead is removed from the air by rain and by particles falling to land or into surface water. Sources of lead in dust and soil include lead that falls to the ground from the air, and

weathering and chipping of lead-based paint from buildings, bridges, and other structures. Landfills may contain waste from lead ore mining, ammunition manufacturing, or other industrial activities such as battery production. Disposal of lead-containing products contribute to lead in municipal landfills. Past uses of lead such as its use in gasoline are a major contributor to lead in soil, and higher levels of lead in soil are found near roadways. Most of the lead in inner city soils comes from old houses with paint containing lead and previous automotive exhaust emitted when gasoline contained lead. Once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil. That is why past uses of lead such as lead in gasoline, house paint, and pesticides are so important in the amount of lead found in soil (ATSDR, 2006).

Small amounts of lead may enter rivers, lakes, and streams when soil particles are moved by rainwater.

Small amounts of lead from lead pipe or solder may be released into water when the water is acidic or "soft". Lead may remain stuck to soil particles or sediment in water for many years. Movement of lead from soil particles into groundwater is unlikely unless the rain falling on the soil is acidic or "soft". Movement of lead from soil will also depend on the type of lead compound and on the physical and chemical characteristics of the soil. Sources of lead in surface water or sediment include deposits of lead-containing dust from the atmosphere, waste water from industries that handle lead (primarily iron and steel industries and lead producers), urban runoff, and mining piles (WHO, 2000).

Some lead compounds are changed into other forms of lead by sunlight, air, and water. However, elemental lead cannot be broken down (Bruhn and Franke, 1976).

The levels of lead may build up in plants and animals from areas where air, water, or soil are contaminated with lead. If animals eat contaminated plants or animals, most of the lead that they eat will pass through their bodies (ATSDR, 2006).

#### **2.4.1 SOURCES AND ROUTE OF EXPOSURE OF LEAD TO HUMANS**

Lead is commonly found in soil especially near roadways, older houses, old orchards, mining areas, industrial sites, near power plants, incinerators, landfills, and hazardous waste sites. People living near hazardous waste sites may be exposed to lead and chemicals that contain lead by breathing air, drinking water, eating foods, or swallowing dust or dirt that contain lead. People may be exposed to lead by eating food or drinking water that contains leads (WHO, 1990).

However, not much lead can get into the body through the skin. In the home, one may be exposed to lead if one takes medicines that contain lead compounds. Lead compounds are found in cosmetics, types of hair colorants, cosmetics, and dyes containing lead acetate. Exposure to lead occurs in many occupations, workers in lead smelting and refining industries, brass/bronze foundries, rubber and plastic industries, soldering, steel welding and cutting operations, battery manufacturing plants, and lead compound manufacturing industries may be exposed to lead (Amoo *et al.*, 2005). Construction and demolition workers and people who work at municipal waste incinerators, pottery and ceramics industries, radiator repair shops, and other industries that use lead solder may also be exposed. Painters who sand or scrape old paint may be exposed to lead in dust. Families of workers may be exposed to higher levels of lead when workers bring home

lead dust on their work clothes. Individuals may also be exposed to lead in the home if you work with stained glass as a hobby, make lead fishing weights or ammunition, or if you are involved in home renovation that involves the removal of old lead-based paint (Anderson, 1995).

#### **2.4.2 HUMAN HEALTH EFFECTS**

The effects of lead are the same whether it enters the body through breathing or swallowing. The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults to lead at work has resulted in decreased performance in some tests that measure functions of the nervous system (WHO, 1992). Lead exposure may also cause weakness in fingers, wrists, or ankles. Lead exposure also causes small increases in blood pressure, particularly in middle-aged and older people. Lead exposure may also cause anaemia (ATSDR, 1999; WHO, 1990). At high levels of exposure, lead can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High-level exposure in men can damage the organs responsible for sperm production (ATSDR, 2007). Kidney tumours have developed in rats and mice that had been given large doses of some kind of lead compounds. The International Agency for Research on Cancer (IARC) has determined that inorganic lead is probably carcinogenic to humans. However, the IARC determined that organic lead compounds are not classifiable as to their carcinogenicity in humans based on inadequate evidence from studies in humans and in animals. Potential health effects in humans from exposures



during the period from conception to maturity at 18 years of age. Studies have shown that children are more vulnerable to lead poisoning than adults. Children are exposed to lead all through their lives. They can be exposed to lead in the womb if their mothers have lead in their bodies. Babies can swallow lead when they breast feed, or eat other foods, and drink water that contains lead. Babies and children can swallow and breathe lead in dirt, dust, or sand while they play on the floor or ground. These activities make it easier for children to be exposed to lead than adults (WHO, 1992). The dirt or dust on their hands, toys, and other items may have lead particles in it. In some cases, children swallow non-food items such as paint chips; these may contain very large amounts of lead, particularly in and around older houses that were painted with lead-based paint. The paint in these houses often chips off and mixes with dust and dirt. Some old paint contains as much as 50% lead. Also, compared with adults, a bigger proportion of the amount of lead swallowed will enter the blood in children (ATSDR, 2007).

#### **2.4.3 SOURCES OF LEAD TO AQUATIC ENVIRONMENT**

Lead enters the aquatic environment through surface runoff and deposition of airborne lead. Adsorption to sediments occurs rapidly and almost quantitatively. The uptake and accumulation of lead by aquatic organisms from water and sediments are influenced by various environmental factors. These must be taken into consideration when evaluating the hazards of environmental contamination by lead (ATSDR, 2007).



## 2.5 IRON

Iron is a silvery-white or greyish metal. It makes up 5 percent of the Earth's crust and is second in abundance to aluminium among the metals and fourth in abundance behind oxygen, silicon, and aluminium among the elements (Allen and Casterline, 2001). Iron, which is the chief constituent of the Earth's core, is the most abundant element in the Earth as a whole (about 35 percent) and is relatively plentiful in the Sun and other stars (Underwood, 2001).

Iron is a very active metal hence rarely exists as a free metal in the earth but occurs combined in its ores. It readily combines with oxygen in moist air forming rust. The most common ores of iron are hematite, limonite, magnetite, siderite, and taconite which is a mixture of hematite and silica. The naturally occurring isotopes of iron are iron-54, iron-56, iron-57, and iron-58 (Lahey, 1975).

Man-made sources of iron are from mining and refining of other metals such as copper, that may contain iron ores, agriculture and other industrial activities such as textile, paints, ceramics, leather, insecticide water purification and sewage treatment systems; photography, wood preservative and even in dietary supplementation (Hallberg, *et al.*, 1997).

The combination of rice, beans, and meat consumed with fresh citrus fruit provides an excellent source of absorbable iron (Gillooly *et al.*, 1983).

### 2.5.1 IMPORTANCE OF IRON

Iron is one of the most important trace elements required and is widely distributed throughout the body. The total iron content of the body varies with sex, age, nutrition and state of health and species. The estimated dosage for adult males is 10mg per day and 18 mg per day for females (Allen and Casterline, 2001).

Iron is also essential element carrying oxygen and forming part of the oxygen-carrying proteins-haemoglobin in red blood cells and myoglobin in muscles. It is also a component of various enzymes and is concentrated in bone marrow, liver, kidney and spleen.

### 2.5.2 DEFICIENCY OF IRON

The deficiency of iron is based on the absorption and the rate at which it is lost. In terms of iron intake, fortified products and pharmaceutical supplements are important sources of iron in addition to the usual diet (Bothwell and Charlton, 1982). The actual amount of iron absorbed depends on the iron requirements, the presence of inhibitors and enhancers of iron absorption in the diet (Allen and Casterline, 2001). On the other hand, iron is lost in sweat and during menstruation, both of which can vary significantly among individuals. Significant amounts of iron can also be lost due to parasitic infections such as malaria, hookworm and schistosomiasis (Allen and Casterline, 2001). Iron requirements are also increased during periods of rapid growth, such as during pregnancy, early childhood and adolescence (Allen and Casterline, 2001).

Young children and women of reproductive age especially during pregnancy have increased requirements for iron, placing them at increased risk of deficiency and related adverse consequences (Allen and Casterline, 2001). Severe iron deficiency results in anaemia, and red blood cells that have a low haemoglobin concentration. Iron deficiency in pregnant women results in premature babies or babies with low birth weight (Innis *et al.*, 1997).

In young children, iron deficiency can manifest in behavioural abnormalities (including reduced attention) reduced cognitive performance and slow growth. In adults, severe iron deficiency impairs physical work capacity (Innis *et al.*, 1997).

Symptoms of iron deficiency may include fatigue, poor stamina, intestinal bleeding, excessive menstrual bleeding, nervousness, heart palpitations and shortness of breath. It may also cause the mouth corners to crack, brittle hair, and difficulty in swallowing and digestive disturbances (Petersen and Parkinson, 1996).

### **2.5.3 TOXICITY AND HEALTH EFFECTS OF IRON**

Iron is a heavy metal of concern, particularly because ingesting dietary iron supplements may acutely poison young children (e.g., as few as five to nine 30-mg iron tablets for a 30-lb child).

Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption (Hallberg *et al.*, 1997). Most overdoses appear to be the result of children

mistaking red-coated ferrous sulphate tablets or adult multivitamin preparations for candy.

High iron content in the body has been linked to cancer and heart disease. Excessive iron intake causes genetic abnormality. Iron supplements are the leading cause of deaths in children and as little as 600 mg of iron in children can be fatal. High iron intake for a long period can result in liver and heart damage, diabetes and skin diseases (Underwood, 2001).

Large iron supplementation may also contribute to the hardening of the arteries, heart diseases and reduced zinc absorption. In infants, an increase in the daily intake of iron might saturate the lactoferrin secreted into the intestines and suppress the capacity of the protein to contribute to the body's protection against infection (Bothwell and Charlton, 1982).

## 2.6 COPPER

Copper has a natural abundance of approximately 60 mg/kg in the earth's crust and  $2.5 \times 10^{-4}$  mg/litre in the sea (Lide and Frederikse, 1993).

Copper is found in a wide variety of mineral salts and organic compounds such as cuprite ( $\text{Cu}_2\text{O}$ ), malachite ( $\text{Cu}_2\text{CO}_3 \cdot \text{Cu}(\text{OH})_2$ ), azurite ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), and bornite ( $\text{Cu}_5\text{FeS}_4$ ). The most important sources of copper are chalcocite, chalcopyrite and malachite (Weant, 1985). Copper can also be found naturally in the elemental or metallic form. The metallic form is very stable to dry

air at low temperatures but undergoes a slow reaction in moist air to produce a hydroxycarbonate or hydroxysulfate that forms a greenish-grey amorphous film over the surface which protects the underlying metal from further attack (Cotton and Wilkinson, 1989). In compounds, copper usually has a valence of +2 but can exist in the metallic, +1 and +3 valence states. Copper is distributed along with other metals through the environment by precipitation into rivers which transport the particles as they flow. Depending on the flow dynamics, these particles settle out and form sedimentary deposits. An important source of copper in aquatic sediments is from dead organisms which settle out and contribute both copper and organic material. This also contributes to a significant source in the oceans.

Nriagu (1989) estimated mean worldwide emissions of copper from natural sources as follows: windblown dusts,  $0.9-15 \times 10^3$  tonnes; forest fires,  $0.1-7.5 \times 10^3$  tonnes; volcanic particles,  $0.9-18 \times 10^3$  tonnes; biogenic processes,  $0.1-6.4 \times 10^3$  tonnes; sea salt spray,  $0.2-6.9 \times 10^3$  tonnes.

Average background concentrations of copper in air in rural areas range from 5 to 50 ng/m<sup>3</sup>. Copper levels in seawater of 0.15 µg/litre and in freshwater of 1.0-20 µg/litre are found in uncontaminated areas (Nriagu, 1979b). Background levels of copper in uncontaminated sediments range from 800 to 5000 mg/kg (dry weight), from 2 to 740 mg/kg (dry weight) in marine sediments with median copper concentrations in uncontaminated soil reported to be in average of 30 mg Cu/kg within a range of 2-250 mg/kg (Bowen, 1985). Copper is found as a natural component of foods eaten by humans and animals (ATSDR, 2004).



Anthropogenic sources of copper include emissions from mines, smelters and foundries producing or utilizing copper, zinc, silver, gold and lead (ATSDR, 2004). Copper can also be released into the atmosphere through the burning of coal and from municipal waste incinerators. Other anthropogenic sources of copper include its use as an antifouling agent in paints, agriculture (fertilizers, algicides, feed supplements) and animal and human excreta (animal manure and human sewage sludge). Copper is also intentionally released into some water bodies to control the growth of algae (Slooff *et al.*, 1989; ATSDR, 2004).

## **2.6.1 ENVIRONMENTAL TRANSPORT AND DISTRIBUTION**

### **2.6.1.1 WATER**

Several processes influence the fate of copper in aquatic systems. These include complexation to inorganic and organic ligands, sorption to metal oxides, clays, and particulate organic material, bioaccumulation and exchange between sediment and water (Stiff, 1971; Callahan *et al.*, 1979).

Much of the copper discharged to water is in particulate form and tends to settle out, or be adsorbed by organic matter, hydrous iron, manganese oxides and clay in the sediment or water column (Callahan *et al.*, 1979).

The copper (Cu) ion is unstable in aqueous solution, tending to disproportionate to copper (II) and copper metal unless a stabilizing ligand is present (Callahan *et al.*, 1979). The only cuprous compounds stable in water are insoluble ones such as the sulfide, cyanide



and fluoride. In its copper (II) state, copper forms coordination compounds or complexes with both inorganic and organic ligands. Ammonia and chloride ions are examples of species that form stable ligands with copper. Copper also, forms stable complexes with organic ligands such as humic acids. In seawater, organic matter is generally the most important complexing agent. Samples collected from the surface waters (< 200 m) of the northeast Pacific revealed that over 99.7% of the total dissolved copper was associated with organic complexes. At depths of 1000 m approximately 50-70% of the copper was in the organically complexed form. Copper complexation gave rise to very low cupric ion activities in surface waters, around 1 pg Cu<sup>2+</sup>/litre. The authors reported that two classes of copper-binding ligands were identified: an extremely strong ligand at low concentrations dominated in surface waters and a weaker class of ligand at higher concentrations was found throughout the water column (Coale and Bruland, 1988).

#### 2.6.1.2 SOIL

In the terrestrial environment, a number of factors influence the fate of copper in the soil. These include the nature of the soil, soil pH, organic matter content, the soil redox potential, the presence of oxides, the base status of the soil and its cation exchange capacity (CEC), the rate of litter decomposition and the proportions of clay to silt to sand particles (ATSDR, 2004). The residence time of copper in the soil is also a function of overall climate and of the vegetation present at a site.

Most copper deposited on soil are strongly adsorbed to the upper layer soil. It can be bound to the organic matter, as well as being adsorbed by carbonate minerals and

hydrous iron and manganese oxides (Lehmann and Harter, 1984). Copper binds more strongly than most other metals and is less influenced by pH (Assaad and Nielsen, 1984). The greatest amount of leaching of copper occurs from sandy soils, compared with clays and peats, whereas acidic conditions favour copper leaching to the groundwater from top soil (Petruzzelli *et al.*, 1988).

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## 2.6.2 LEVELS OF COPPER IN THE ENVIRONMENT

### 2.6.2.1 WATER

Copper is widely distributed in water because it is a naturally occurring element. Nriagu (1979b) reported average copper levels in seawater ranging from 0.15 µg/litre in open ocean to 1.0 µg/litre in polluted near-shore waters; levels in fresh water were 1.0-20 µg/litre. Other reports indicate that copper concentrations in seawater are highly variable, ranging from 0.005 µg/litre in the Black Sea (Haraldsson and Westerlund, 1988) to 40 µg/litre in estuaries in southwest Spain (Cabrera *et al.*, 1987). Additional variation in copper concentrations is related to depth and the area in the ocean examined. Surface concentration in the North Pacific Ocean drops from 0.1 µg Cu/litre (1.2 nmol/kg) in the California Current to 0.03-0.04 µg Cu/litre (0.4-0.5 nmol/kg) in the central oceanic region, and increases to 0.24 µg Cu/litre (3 nmol/kg) in deep waters (Boyle *et al.*, 1977; Bruland, 1980). In the North Atlantic Ocean surface waters display values of copper from 0.07 µg/litre (1.1 nmol/kg) to 0.11 µg/litre (1.7 nmol/kg), whereas concentration of the metal increases to 0.13-0.26 µg/litre (2-4 nmol/kg) in deep waters (Moore, 1978).

### 2.6.2.2 SOIL

Median copper concentrations in uncontaminated soil were reported to be 30 mg/kg (range 2-250 mg/kg) (Bowen, 1985). Shacklette and Boerngen (1984) analysed soil samples from various locations in the USA, and found that copper concentrations in soils ranged from below 1 to 700 mg/kg with an average of 25 mg/kg. Kabata-Pendias and Pendias (1984) reviewed worldwide literature on copper in uncontaminated surface soils and reported mean concentrations ranging from 6 to 80 mg/kg (dry weight).

Copper can accumulate in soils from the long-term application of fertilizers or fungicides. Reuther and Smith (1952) analysed soils from mature Florida citrus groves and found that copper oxide levels in the topsoil increased with grove age. Copper oxide levels of 247mg/kg and 93 mg/kg (dry weight) were measured at depths of 0-8 cm and 8-15 cm, respectively. At depths of > 15 cm, copper oxide levels of 18 mg/kg were measured. Copper oxide levels in adjacent untreated soil ranged from 1 to 2 mg/kg. Christie and Beattie (1989) reported an accumulation of copper in soil from the application of pig slurry (50-200 m<sup>3</sup>/ha per year). EDTA-extractable copper concentrations of up to 85.2 mg/kg were recorded; levels in control soils ranged from 4.4 to 5.4 mg/kg.

Paoletti *et al.* (1988) found that in Italy vineyard soil to which copper-containing fungicide had been applied contained mean copper concentrations of 89.8 mg/kg (dry weight). Soils from other locations contained mean levels ranging from 44.0 to 52.1 mg/kg. Holmgren *et al.* (1993) analysed surface soil samples from agricultural regions throughout the USA. Copper concentrations ranged from 0.3 to 495 mg/kg (dry weight).

Copper levels were higher in the organic soil areas of Florida, Oregon and the Great Lakes, reflecting the use of copper fertilizers and fungicides.

Copper can also accumulate at areas near copper smelting factories. Hunter *et al.* (1987a) reported mean surface soil copper concentrations of 15.1, 543 and 11 000 mg/kg at a control site, 1 km from a copper refinery (Merseyside, United Kingdom) and at the refinery, respectively. Almost all of the copper contamination was held at the surface of the mineral soil.

### 2.6.3 IMPORTANCE/ USES OF COPPER

The unique combination of properties of copper, including durability, ductility, malleability and electrical and thermal conductivity, determine its uses in a vast range of applications. Worldwide, the largest use of copper is in electrical wire and cable and other electronic applications, which can account for as much as 65% ( $9.75 \times 10^6$  tonnes) of total annual copper consumption.

Rolled copper is also extensively used in architectural applications for roofing, rainwater goods and cladding, while rolled copper and brass are also used for vehicle radiators. Overall, the major industrialized countries consume over  $1.5 \times 10^6$  tonnes of rolled product per year. Approximately 15% ( $2.25 \times 10^6$  tonnes) of copper is used annually in building and construction, including plumbing, architectural applications such as roofing, guttering and flashing, and in fixtures and fittings. Copper is also used in the manufacture of goods for transport equipment, air-conditioning and refrigeration as well as general and

light engineering uses such as machine parts, and process equipment, coinage, ordnance and consumer goods, such as domestic appliances as well as production of bronze and brass alloys.

Copper is an essential element for all biota. Copper was identified in plant (Bucholtz, 1816) and animal (Harless, 1847) systems in the nineteenth century and postulated to be a biological catalyst in the early twentieth century (McHargue, 1925). Subsequent nutritional studies demonstrated that copper is necessary for optimal growth of plants and animals (McHargue, 1927a, b; Arnon and Stout, 1939; Woolhouse, 1983). Copper is also essential for the utilization of iron in the formation of haemoglobin (ATSDR, 2004); hence its involvement in anaemia prevention.

#### **2.6.4 DEFICIENCY OF COPPER**

The lower limit of the Acceptable Range of Oral Intake (AROI) is 20 µg/kg body weight per day. In children, this figure is 50 µg /kg body weight per day.

Characteristic clinical features of copper deficiencies in infants are anaemia refractory to iron, and low copper plasma levels (WHO, 1996). Copper deficiency has been considered to be the likely cause of the anaemia in children (Cordano *et al.*, 1964). It has been shown that copper deficiency is associated with increased incidence of infection and impaired weight gain in infants recovering from malnutrition (Castillo-Duran and Uauy, 1988). Copper deficiency is associated with altered immunity in humans (Prohaska and Failla,



1993). Low copper intake has also been demonstrated to diminish glucose tolerance (Klevay *et al.*, 1986) and alter cardiac rhythm (Lukaski *et al.*, 1988).

The role of copper deficit in altered neurodevelopment has been postulated on the basis of the high copper content of the brain, especially of the basal ganglia. The existence of a prenatal critical phase in central nervous system (CNS) development during which copper deficiency can cause CNS damage has been suggested (Danks, 1988). This could explain the severe mental deficiency associated to prenatal tissue deficit found in Menkes disease while postnatally acquired nutritional copper deficiency is not accompanied by neurological abnormalities.

#### **2.6.5 TOXICITY AND EFFECTS ON HUMANS**

The upper limit of the AROI in adults is about 2-3 mg/day (ATSDR, 2004). Acute toxicity due to ingestion of copper is infrequent in humans and is usually a consequence of the contamination of beverages (including drinking-water) or from accidental or deliberate ingestion of high quantities of copper salts (ATSDR, 2004). Symptoms including vomiting, lethargy, acute haemolytic anaemia, renal and liver damage, neurotoxicity, increased blood pressure and respiratory rates and in some cases, coma and death have all been reported from copper toxicity (ATSDR, 2004). Other symptoms associated with copper toxicity include nausea, abdominal pain, headache, dizziness, vomiting and diarrhea (Knobeloch *etal.*, 1994).

## 2.7 OIL AND GREASE

Oil and grease are petroleum- derived materials. The term oil refers to a lubrication fluid, while grease is lubrication solid (Sawyer *et al*, 1994).

In the vehicle oil and grease are used in such operations as engine oil, transmission fluid, power steering fluid, brake fluid, and radiator fluid. During undercarriage or engine cleaning these fluids mixes with the water used. Oil and grease harm aquatic life, mainly by smothering or preventing oxygen transfer to the water. Oil and grease may contain additives such as lead. Lead residues are deposited in exhaust of cars and are collected by water during washing. Exposure to lead may result in toxic biochemical effects on aquatic organisms and humans who consume fishes (Sawyer *et al*, 1994).

## 2.8 ANALYTICAL METHODS OF ANALYSIS OF HEAVY METALS

Heavy metals may be determined satisfactorily by Atomic Absorption Spectroscopy (AAS), Neutron Activation Analysis, Polarography or Colorimetric methods. The instrumental methods are preferable because they are rapid and do not require extensive separations (Batley, 1989)

Atomic Spectroscopy is used for the qualitative and quantitative determination of about 70 elements. Sensitivity of atomic methods lie typically in the part per million (ppm) to parts per billion (ppb) range. In addition, these methods are rapid, convenient and usually selective (Batley, 1989). Atomic Spectroscopy falls into three classes commonly designed as absorption, fluorescence and emission and routinely available instrument

can perform both absorption and emission experiments with equal ease (Ahuja and Jespersen, 2006).

Spectroscopy determination of atomic species can be performed only on a gaseous medium in which the individual atoms or sometimes elementary ions are well separated from one another. Consequently the first step in all atomic spectroscopic procedures is atomization, a process in which a sample is volatilized and decomposed to produce an atomic gas (Ahuja and Jespersen, 2006).

### **2.8.1 GENERAL PRINCIPLE OF ATOMIC ABSORPTION SPECTROSCOPY**

When a solution containing metal ions is introduced as a fine droplet into the gas stream entering the burner, the metal ions are reduced to neutral atoms by electron capture (atomization). The light beam is then directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized elements in the flame. Because each metal has its own characteristic absorption wavelength, a source lamp (hollow cathode lamp) composed of that element is used. This makes the method relatively free from spectral or radiation interferences. Thus the amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample (Alloway and Ayres, 1998).

### 2.8.1.1 INSTRUMENTATION

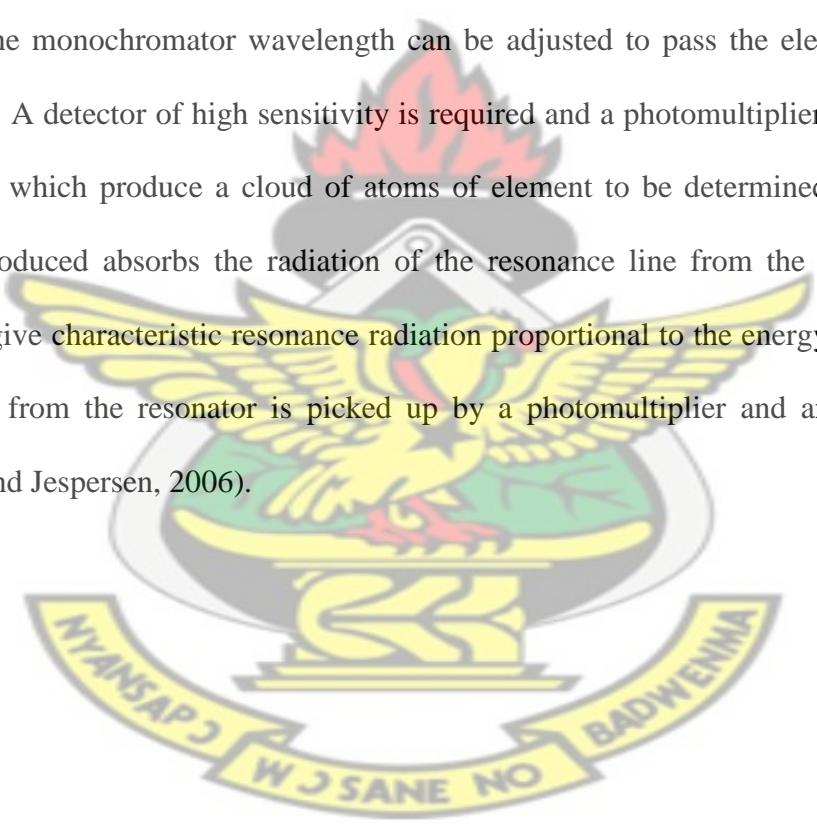
Atomic absorption spectrophotometer consist of a source of light emitting the line spectrum of an element (hollow cathode lamp), a device for vapourizing the element usually a flame, a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated amplifying and electronic measuring equipment.

*Hollow Cathode Lamp:* The hollow cathode lamp consists of a tungsten anode and a cylindrical cathode sealed in a glass tube that is filled with neon or argon at a pressure of 1 to 5 torr. The cathode is constructed of the metal whose spectrum is desired or serve to support a layer of that metal. When a high enough voltage is applied between the anode and cathode, the filter gas becomes ionized and positive ions are accelerated towards the cathode. They strike the anode with enough energy to sputter metal atoms from the cathode into the gas phase (Harris Laitinen, 1975). Each hollow cathode lamp is specific for a particular element and individual lamps are available for the estimation of over seventy elements. Most of these are for single elements (mono-cathode lamp), there are some multi-element cathode lamps for the estimation of group of elements (Alloway and Ayres, 1998).

*Burner:* there are two types of burners, the turbulent-flow or total consumption burners and laminar-flow or premix burners. In the turbulent flow burner, the sample is drawn up the capillary and nebulized by the venturic action. A typical sample flow rate is 1-3 ml/min. the advantage of this burner is the introduction of relatively large and representative sample into the flame. Its disadvantage includes short path length through

flame and problem of clogging of the tip. The premix burner, nebulize the sample by the flow of oxidant gas past a capillary tip (Ahuja and Jespersen, 2006). Premix burners provide relatively quiet flame and a long path length. These properties tend to enhance sensitivity and reproducibility. The mixing chamber of premix burners contains a potentially explosive mixture which can be ignited by flashback if the flow rates are not sufficient (Alloway and Ayres, 1998).

*Monochromator and Detector:* A sensitive narrow band pass monochromator is essential so that the monochromator wavelength can be adjusted to pass the element resonance line only. A detector of high sensitivity is required and a photomultiplier with a suitable amplifier which produce a cloud of atoms of element to be determined. The cloud of atoms produced absorbs the radiation of the resonance line from the hollow cathode lamp to give characteristic resonance radiation proportional to the energy absorbed. The radiation from the resonator is picked up by a photomultiplier and amplifier system (Ahuja and Jespersen, 2006).





## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 STUDY AREA

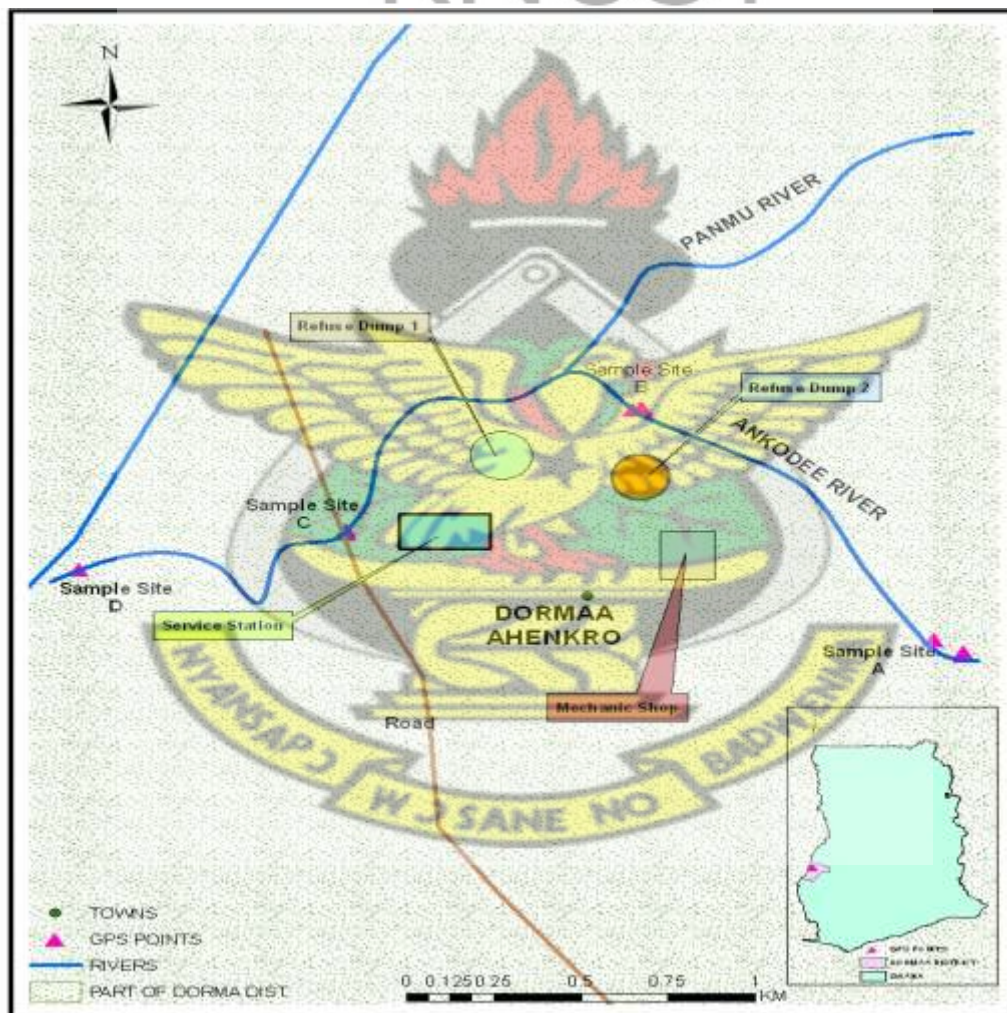
The Study was carried out in the Dormaa Ahenkro Municipality in the Brong Ahafo Region of Ghana. The Dormaa Municipal is located at the Western part of the Brong Ahafo Region. It lies within longitudes 3° West and 3° 30' West and latitudes 7° North and 7°30' North. Jaman and Berekum Districts bound the district on the north, on the east by the Sunyani Municipality, in the South and southeast by Asunafo and Asutifi Districts respectively, in the southwest by Western Region and in the West and northwest by la Cote d'Ivoire. The Municipal Capital is Dormaa Ahenkro, located about 80 kilometres west of the regional capital, Sunyani.

The Municipal has a total land area of 1,368km<sup>2</sup>, which is about 3.5% of the total land area of Brong Ahafo Region and about 0.6% of that of Ghana. It has 345 settlements, one traditional authority and two constituencies, namely: Dormaa East and Dormaa West.

The Rivers Panmu and Ankodee run through the main town of Dormaa Ahenkro with settlements and economic activities notably artisans; mechanics, fuel service stations and metal scrap dealers along the course of the river.

### 3.2 SAMPLING SITES

Sample site A was located close to the source of the stream Ankodee, site B was close to a number of artisanal activities, mechanic shops and a refuse dump. Site C was an area just a little after the stream Ankodee joins the river Panmu which was drained by the town's gutters. Site D was located far downstream, about 300m away from the main town which had no visible anthropogenic activities nearby. (Figure 3.1).



**Fig. 3.1** A map showing the Ankodee and Panmu Rivers and the sampling sites and anthropogenic activities.

Bimonthly water and sediment samples were collected from four different sampling points along the course of the rivers. All samples were collected in triplicate from each (four) sampling site within a three month sampling period between January and March, 2012.

### 3.3 WATER SAMPLING

Water samples were collected in 500mL polyethylene bottles which have been washed with 5% nitric acid, distilled water and oven dried. At each sampling point, the bottles were rinsed three times with the stream water before collection of the sample. Each bottle was immersed at about 8 cm below the water surface. The collected water samples were acidified with 5mL of Conc.  $\text{HNO}_3$ . This was done to preserve the water samples and as an initial step to bring the particulate metals into solution (APHA, 1992). Samples were labeled and placed in ice chests at a temperature of 4°C and transported to the laboratory for analysis within 48 hours.

### 3.4 SEDIMENT SAMPLING

Sediment samples were collected with a plastic scoop. The scoop was used to scoop soil sample from the stream bed and placed in sterile food bags. Samples were transported to the laboratory in an ice chest with ice packs. In the laboratory, the sediment samples were air dried at room temperature in an open dust free environment for three days. Organic debris and other unwanted materials were handpicked from the samples. The

dried sediment samples were ground and sieved using 2mm sieve. Samples were then stored at a temperature of 4 °C awaiting digestion.

Water and sediment samples were analyzed at the Faculty of Renewable and Natural Resources' Laboratory of the Kwame Nkrumah University of Science and Technology, Kumasi and Anglogold Ashanti Laboratories, Obuasi.

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### 3.5 DIGESTION OF SOIL SAMPLES

A 1g of soil was weighed and placed into 300 mL volumetric flask and 10 mL of  $\text{HNO}_3$  and  $\text{HClO}_4$  mixture with ratio 9: 4 was added and the contents well mixed by swirling thoroughly (Motsara and Roy, 2008; Okalebo and Gathua, 1993). The flask with contents was then placed on a hotplate in the fume chamber and heated at 85 °C and then raised to 150 °C. Heating continued until the production of brown  $\text{NO}_2$  fumes ceased. The contents were further heated until volume was reduced to 3 – 4 mL and became colourless or yellowish. This was done to reduce interference by organic matter and to convert metal associated particulate to a form (the free metal) that can be determined by the Atomic Absorption Spectrophotometer (AAS). Contents were cooled and volume made up with distilled water and filtered through No. 1 filter paper. The resulting solution was preserved at 4 °C, ready for AAS determination.



### 3.6 DIGESTION OF WATER SAMPLES

The sample was thoroughly mixed by shaking and 100 mL transferred into a conical flask. A 10 mL concentrated  $\text{HNO}_3$  and a few boiling chips were added (APHA, 1992). The mixture was then heated until the volume was reduced to about 20-40 mL and complete digestion was indicated by either a light coloured or clear solution. Contents were washed down with double distilled water and then filtered. The filtrate was transferred into 100 mL volumetric flask and topped up to the 100 mL mark with double distilled water prior to transfer into washed plastic containers and stored at 4 °C, ready for AAS analysis (APHA, 1992).

### 3.7 OIL AND GREASE DETERMINATION (Partition- Gravimetric Method)

Two hundred millilitres (200 mL) of the water sample was measured into a flask and acidified with Hydrochloric acid to pH 2 and transferred into a separatory funnel. The sampling bottle was carefully rinsed with 30 mL petroleum ether and solvent washings were added to separatory funnel. The separatory funnel was then shaken vigorously for 2 minutes and corked. The separating funnel was inverted and the pressure released through the bottom. The shaking was repeated and the pressure released until there was no more pressure built up in the separatory funnel. The separatory funnel was opened and hung upright to allow solvent to separate from the water sample. The solvent layer was drained through a funnel containing solvent moistened filter paper into a clean-tarred evaporating dish when the layer separates. The extraction was repeated twice more with 30 mL solvent each.



The extracts were combined in a tarred flask and the filter paper washed with additional 20 mL solvent. The solvent was distilled from a distilling flask on a water bath at 70°C till the flask was mainly due to oil and grease

#### CALCULATION

$$\text{Oil \& Grease (mg/ L)} = (A - B) \times 100 / \text{mL of sample}$$

Where A = total gain in the weight of the flask in grams

B = Solvent blank

#### 3.8 ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS) ANALYSIS

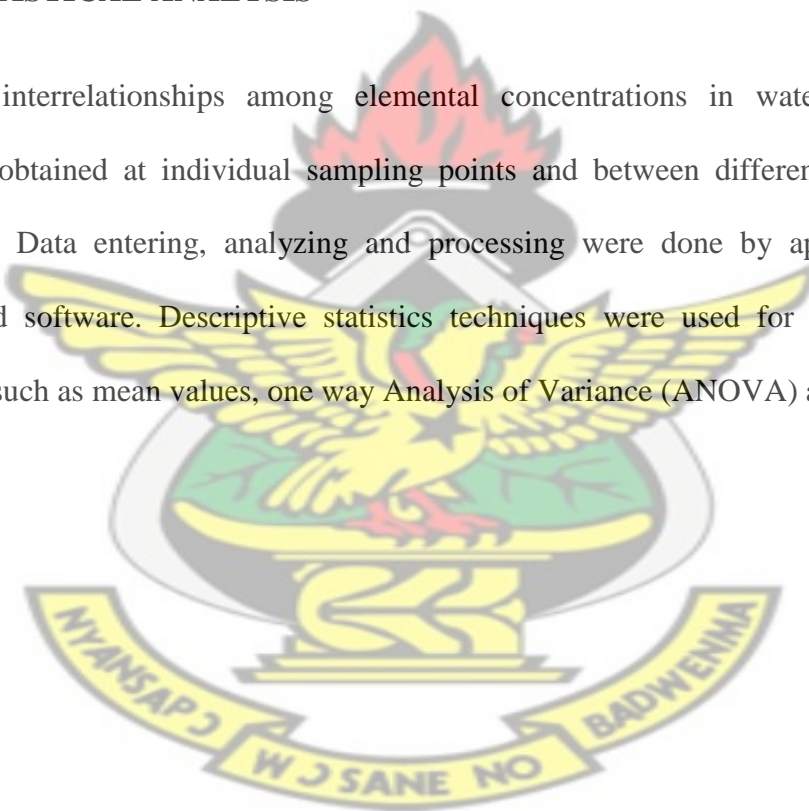
AAS 220 model was used in determining the concentration lead, cadmium, iron and copper in the digested samples. The acetylene gas and compressor were fixed and compressor turned on and the liquid trap blown to rid off any liquid trapped. The Extractor was turned on and the AAS 220 power turned on (AOAC, 2006). The capillary tube and nebulizer block were cleaned with cleansing wire and opening of the burner cleaned with an alignment card. The worksheet of the AAS software on the attached computer was opened and the hollow cathode lamp inserted in the lamp holder. The lamp was turned on; ray from cathode aligned to hit target area of the alignment card for optimal light output, then the machine was ignited. The capillary was placed in a 10 mL graduated cylinder containing deionized water and aspiration rate measured, and set to 6 mL per minute. The analytical blank was prepared, and a series of calibration solutions of

known amounts of analyte element (standards) were made. The blank and standards were aspirated in turn and their responses measured. A calibration graph was plotted for each of the solutions, after which the sample solutions were aspirated and measured. Lead, cadmium, iron and copper concentrations from the sample solutions were determined from the calibration, based on the absorbance obtained for the unknown (AOAC, 2006).

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### **3.9 STATISTICAL ANALYSIS**

Various interrelationships among elemental concentrations in water and sediment samples obtained at individual sampling points and between different elements were analysed. Data entering, analyzing and processing were done by application of the GraphPad software. Descriptive statistics techniques were used for quantitative data analysis such as mean values, one way Analysis of Variance (ANOVA) and bar charts.



## CHAPTER FOUR

### RESULTS

#### 4.1 Heavy Metals Concentrations in Water and Sediment Samples from the Rivers Panmu and Ankodee

Table 4.1: Overall Mean Heavy Metal Concentrations in the Water Samples

	Fe (mgL <sup>-1</sup> )	Cu (mgL <sup>-1</sup> )	Pb (mgL <sup>-1</sup> )	Cd (mgL <sup>-1</sup> )	O&G(mgL <sup>-1</sup> )
<b>Sampling Stations</b>					
Site A	4.36±3.34	0.019±0.014	0.011±0.018	0.025±0.020	0.719±0.789
Site B	10.15±2.46	0.073±0.065	0.003±0.007	0.012±0.006	0.002±0.004
Site C	13.07±4.21	0.019±0.018	0.021±0.035	0.035±0.031	0.006±0.010
Site D	12.39±1.65	0.024±0.016	BDL	0.008±0.008	0.002±0.004

**BDL**= Below detection limit

Table 4.2: Overall Mean Heavy Metal Concentrations in the Sediment Samples

	Fe (mg/kg)	Cu (mg/kg)	Pb(mg/kg)	Cd (mg/kg)
<b>Sampling Stations</b>				
Site A	14772±13590	6.66±7.32	2.40±5.14	0.58±0.66
Site B	34629±10288	550.80±555.7	275.30±638.00	0.61±0.70
Site C	21799±14491	7.25±8.19	0.81±1.68	0.48±0.55
Site D	21782±16605	12.43±06.59	2.09±3.24	2.03±0.83

Generally, heavy metals concentrations in the River water samples were lower compared to that in the sediment samples. Total iron concentrations recorded at sampling sites A, B, C and D over the sampling period were high and varied from  $4.36 \pm 3.34$  mg/L to  $13.07 \pm 4.21$  mg/L (Figure 4.1). There were statistically significant differences ( $P < 0.05$ ) in iron concentrations at the various sampling sites (Appendix I).

Iron concentrations in the sediment samples were also high and varied from  $14772 \pm 13590$  mg/kg to  $34629 \pm 10288$  mg/kg (Figure 4.2). Statistically, there were no significant differences ( $P < 0.05$ ) in iron concentrations at the different sites (Appendix I).

Sample site A was located at close to the source of the stream Ankodee, site B was close to a number of artisanal activities, mechanic shops and a refuse dump. Site C was an area just a little after the River Ankodee joins the River Panmu which was drained by the town's gutters. Site D was located far downstream, some distance away from the main town which had no visible anthropogenic activities nearby.

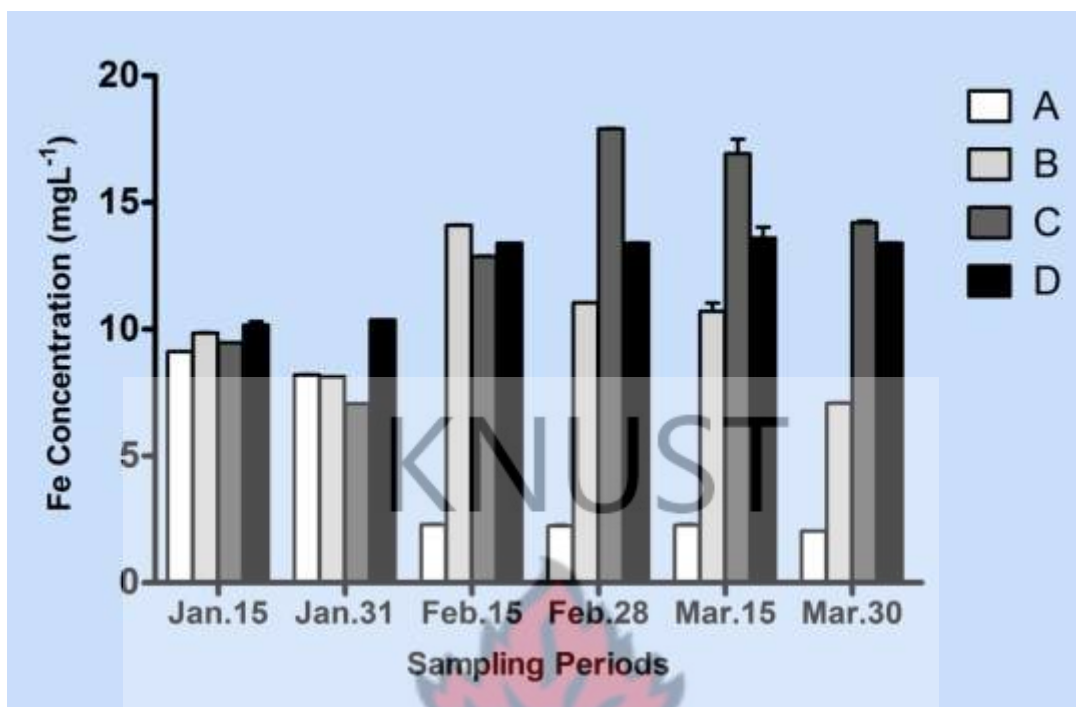
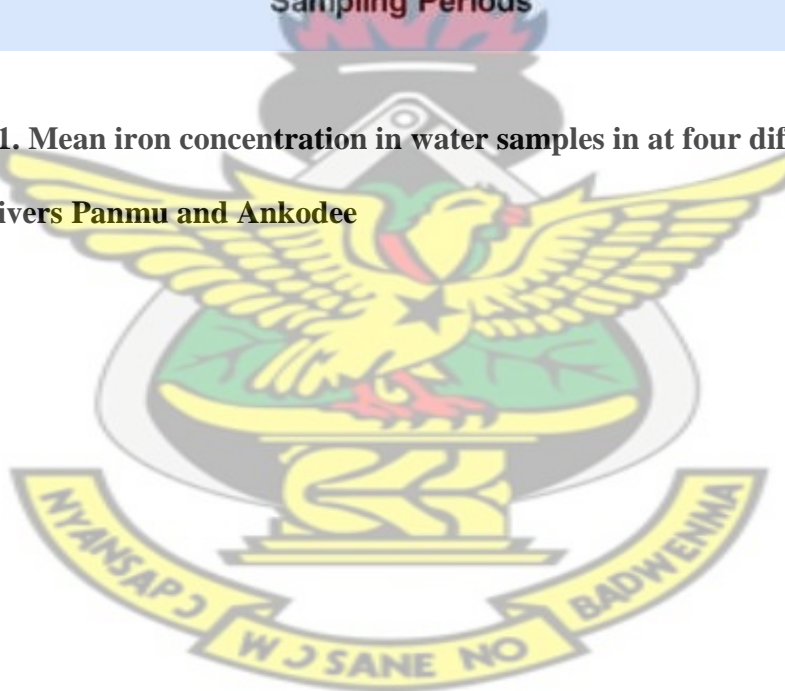
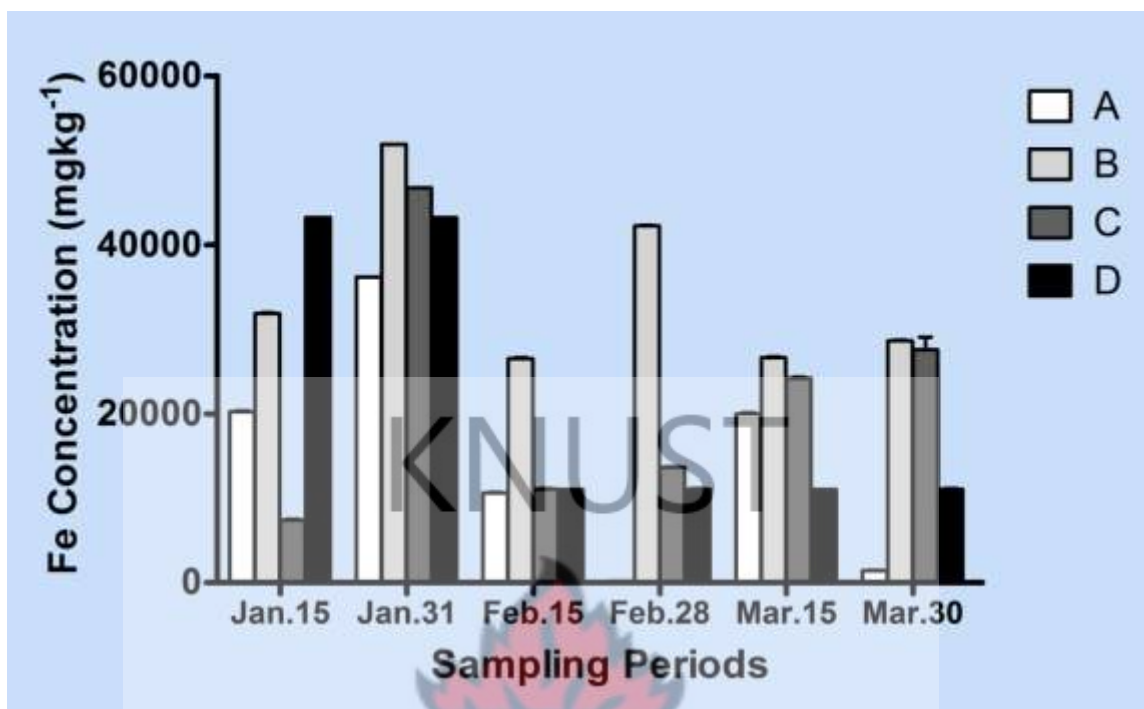


Figure 4.1. Mean iron concentration in water samples in at four different sampling sites on Rivers Panmu and Ankodee







**Figure 4.2. Mean iron concentrations in Sediment samples at four different sampling sites on Rivers Panmu and Ankodee**

Comparably, concentrations of Copper, Lead and Cadmium were low in the river water samples and ranged from  $0.019 \pm 0.014$  mg/L to  $0.073 \pm 0.065$  mg/L for Copper,  $0.003 \pm 0.007$  mg/L to  $0.021 \pm 0.035$  mg/L for lead and  $0.008 \pm 0.008$  mg/L for cadmium, respectively (Table 4.1). Lead concentrations at site D were below detection limit (BDL) (Figure 4.3, 4.4, 4.5).

Statistically, there were no significant differences ( $P < 0.05$ ) in the mean concentrations of lead and cadmium at the different sampling sites (Appendix I). However, there were statistically significant differences ( $P < 0.05$ ) in copper concentrations at the four different sampling sites (Appendix I).

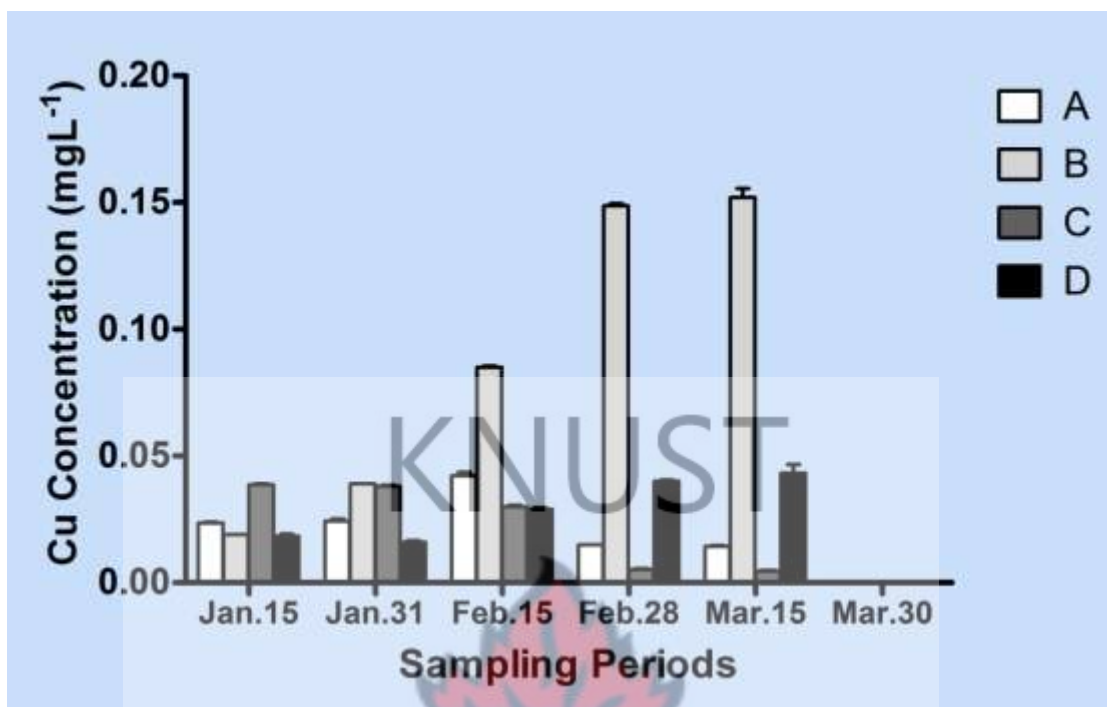
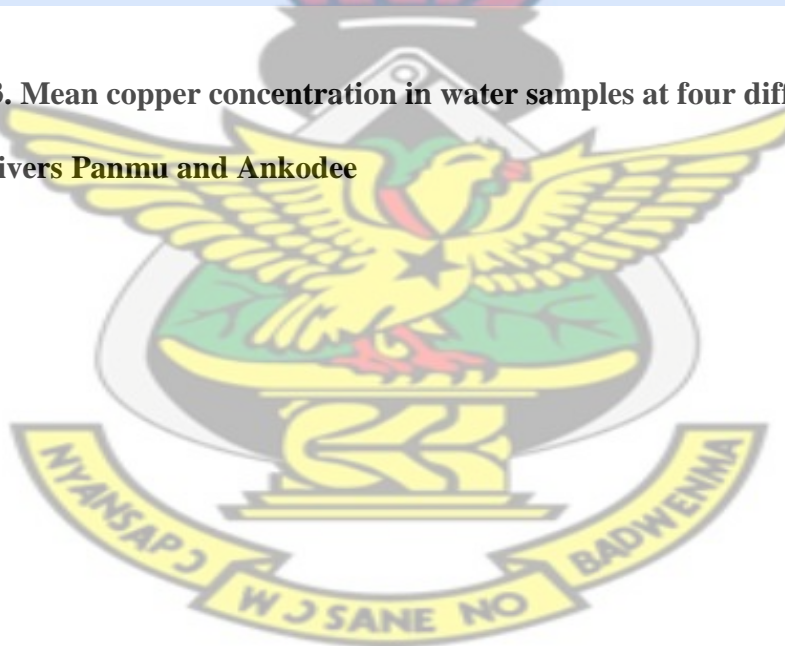
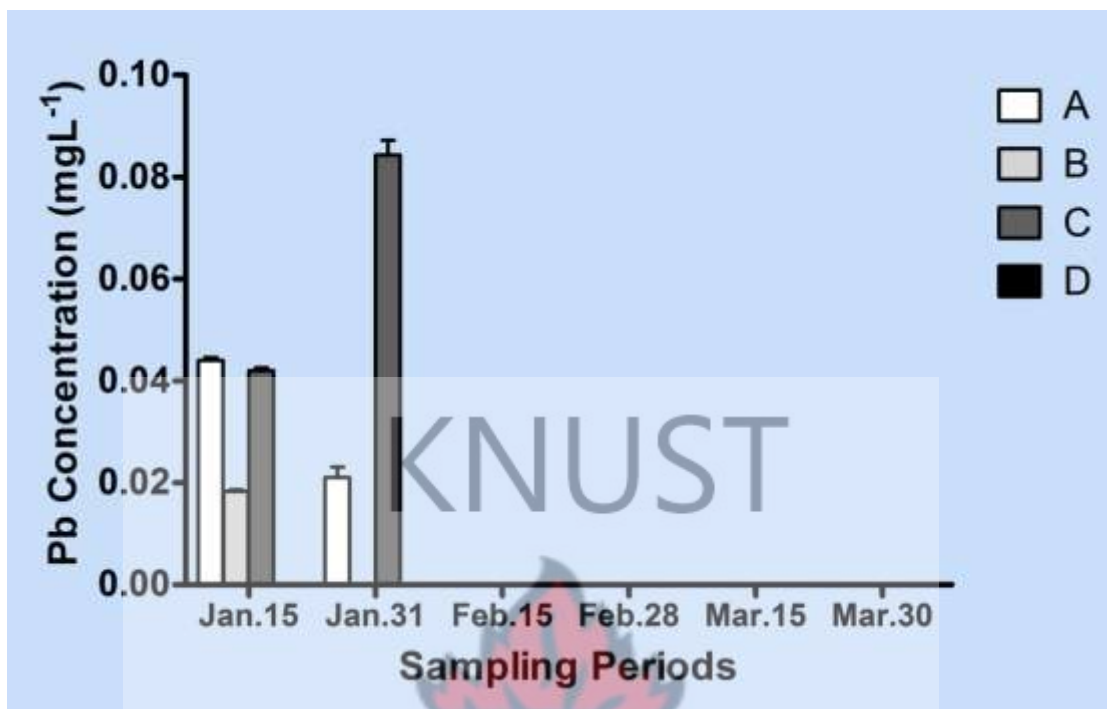
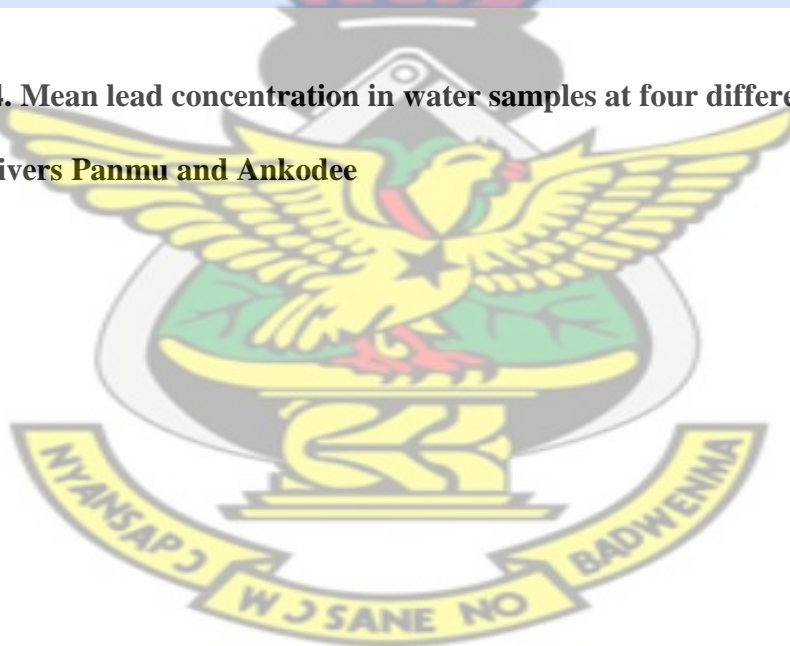


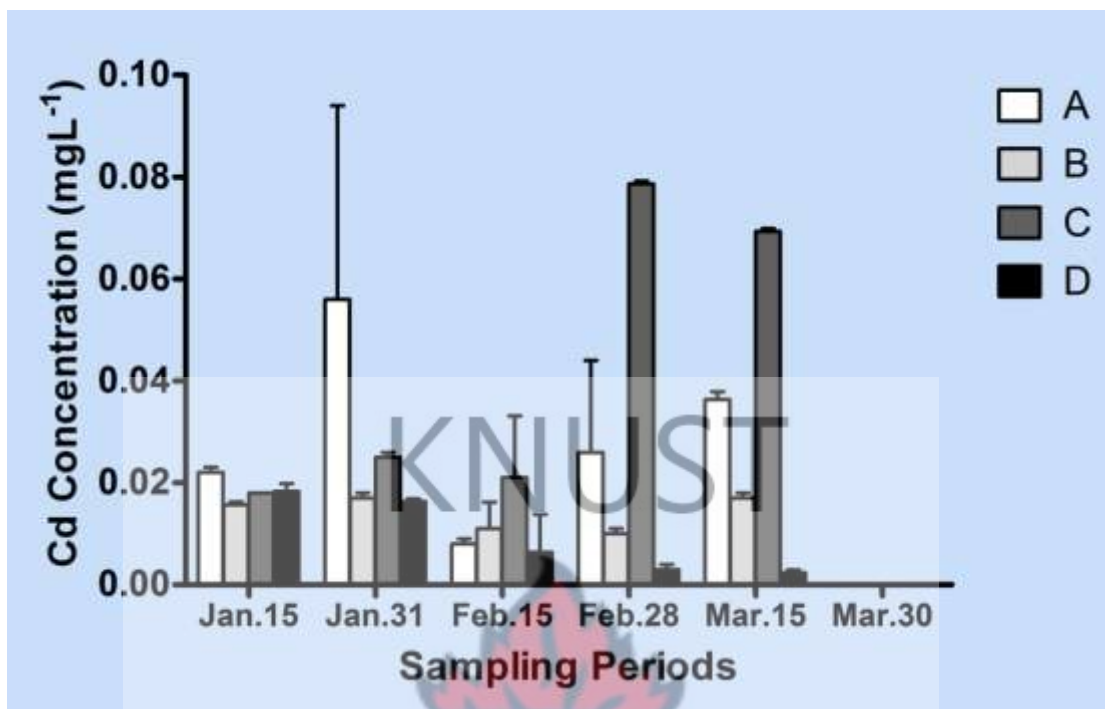
Figure 4.3. Mean copper concentration in water samples at four different sampling sites on Rivers Panmu and Ankodee





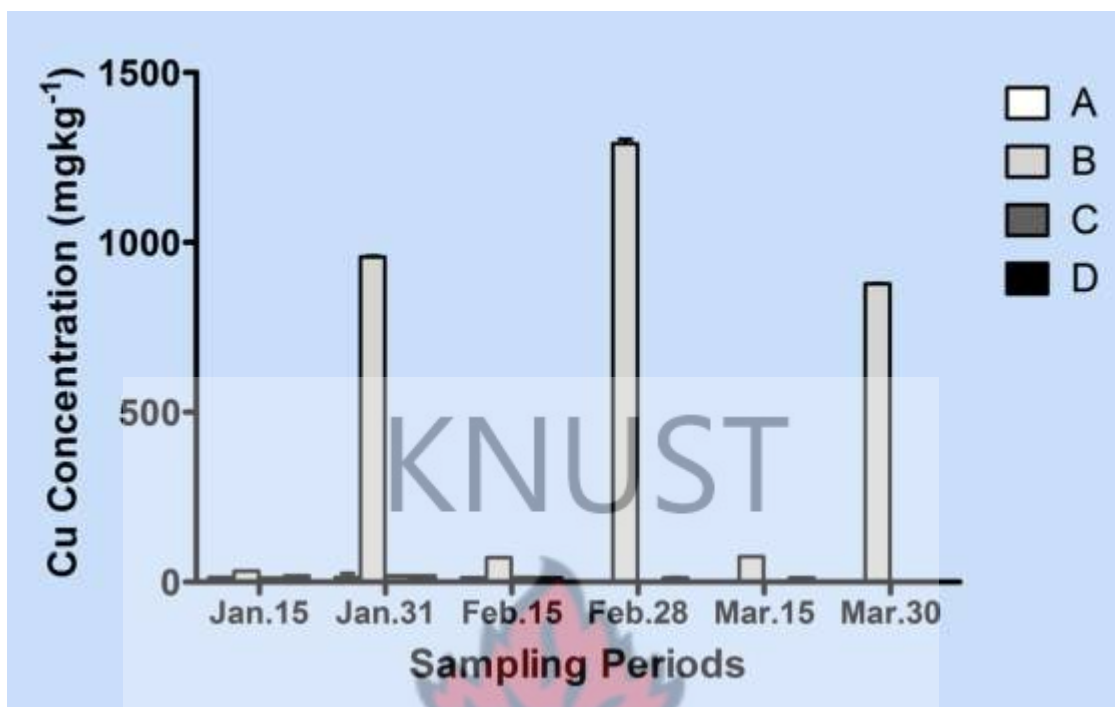
**Figure 4.4. Mean lead concentration in water samples at four different sampling sites on Rivers Panmu and Ankodee**





**Figure 4.5. Mean cadmium concentration in water samples at four different sampling sites on Rivers Panmu and Ankodee**

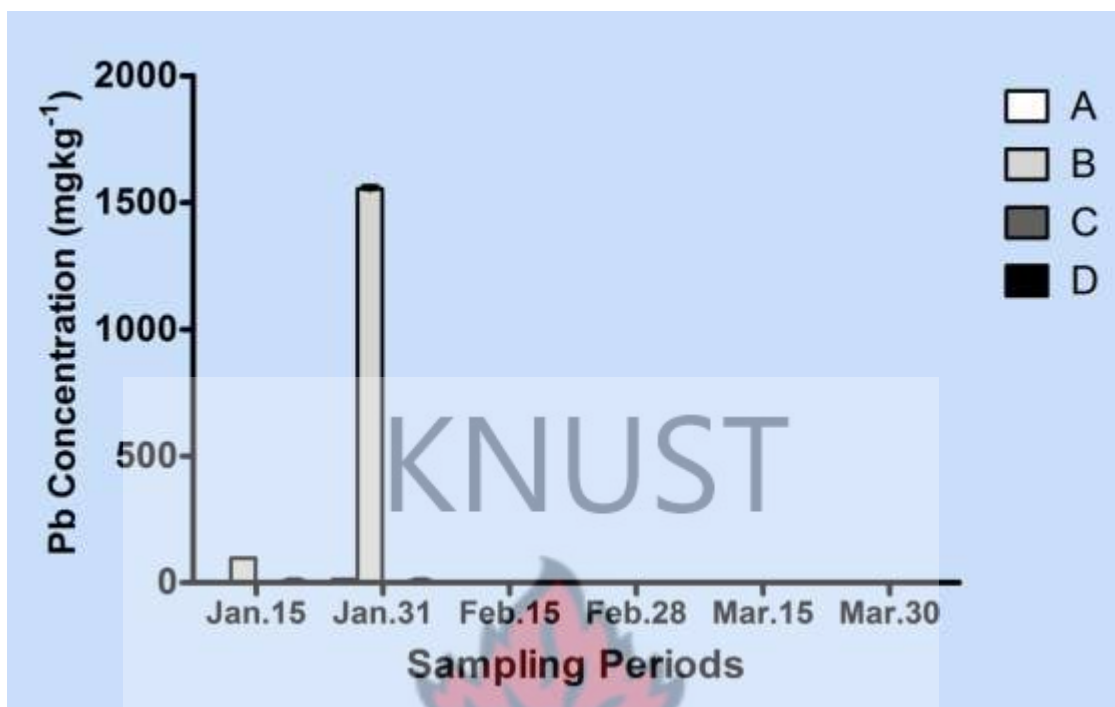
Mean heavy metals concentration in the sediment samples were however high compared to that in the water column varying from  $6.66 \pm 7.32$  mg/kg to  $550.80 \pm 555.70$  mg/kg for copper,  $0.81 \pm 1.68$  mg/kg to  $275.30 \pm 638.00$  mg/kg) for lead and  $0.48 \pm 0.55$  mg/kg to  $2.03 \pm 0.83$  mg/kg for cadmium (Figure 4.6, 4.7, 4.8) (Table 4.1, 4.2).



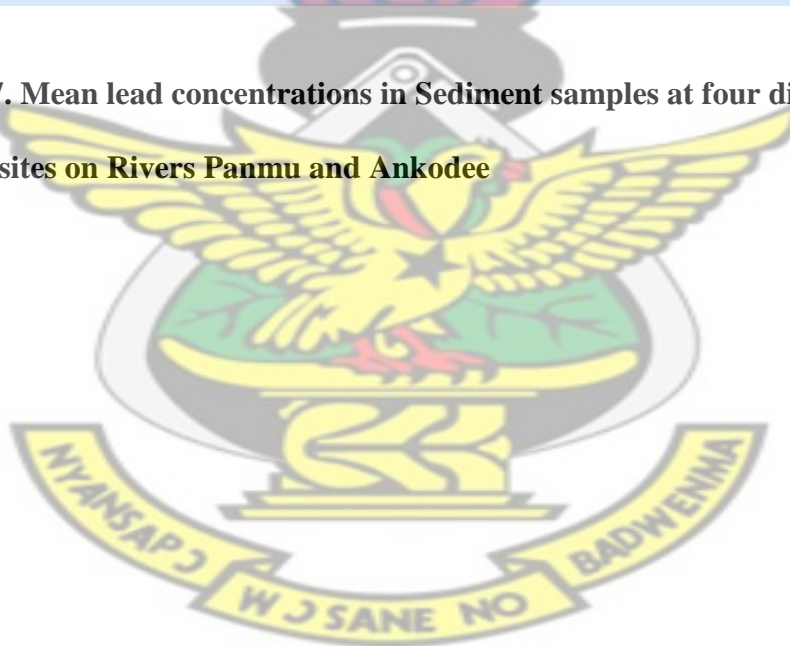
**Figure 4.6. Mean copper concentrations in Sediment samples at four different sampling sites on rivers Panmu and Ankodee**

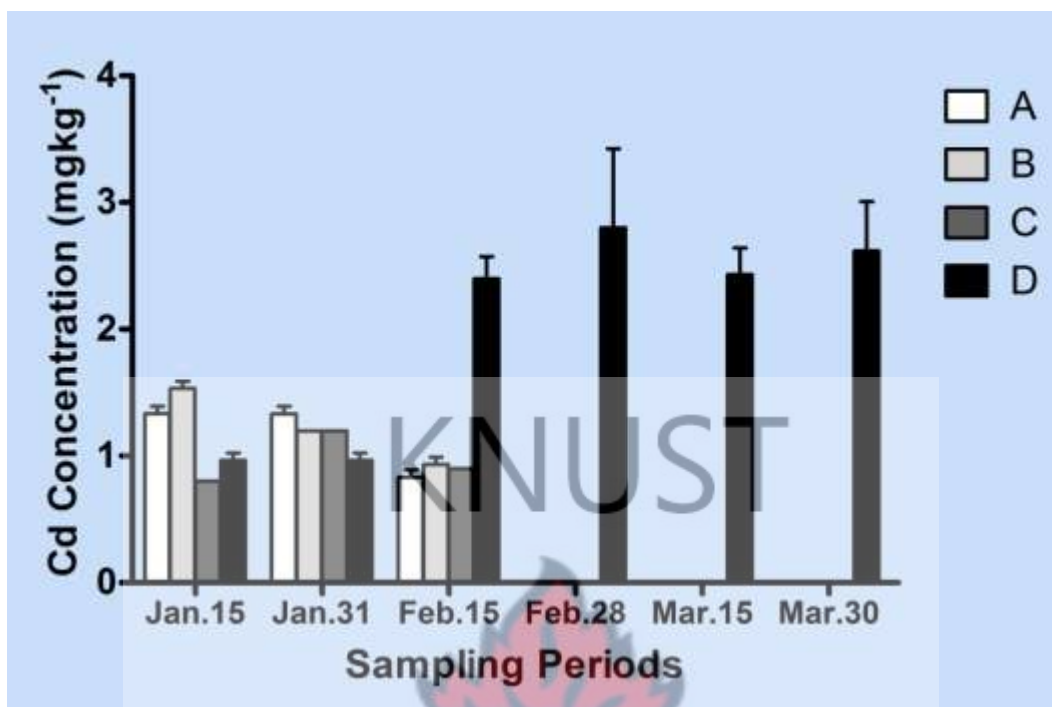
Apart from January samples, lead could not be detected in sediments samples collected over the sampling period. There were no statistically significant differences ( $P < 0.05$ ) in the mean concentration of lead at the various sampling sites (Appendix I). However, there were statistically significant differences ( $P < 0.05$ ) in mean cadmium and copper concentrations (Appendix I).





**Figure 4.7. Mean lead concentrations in Sediment samples at four different sampling sites on Rivers Panmu and Ankodee**

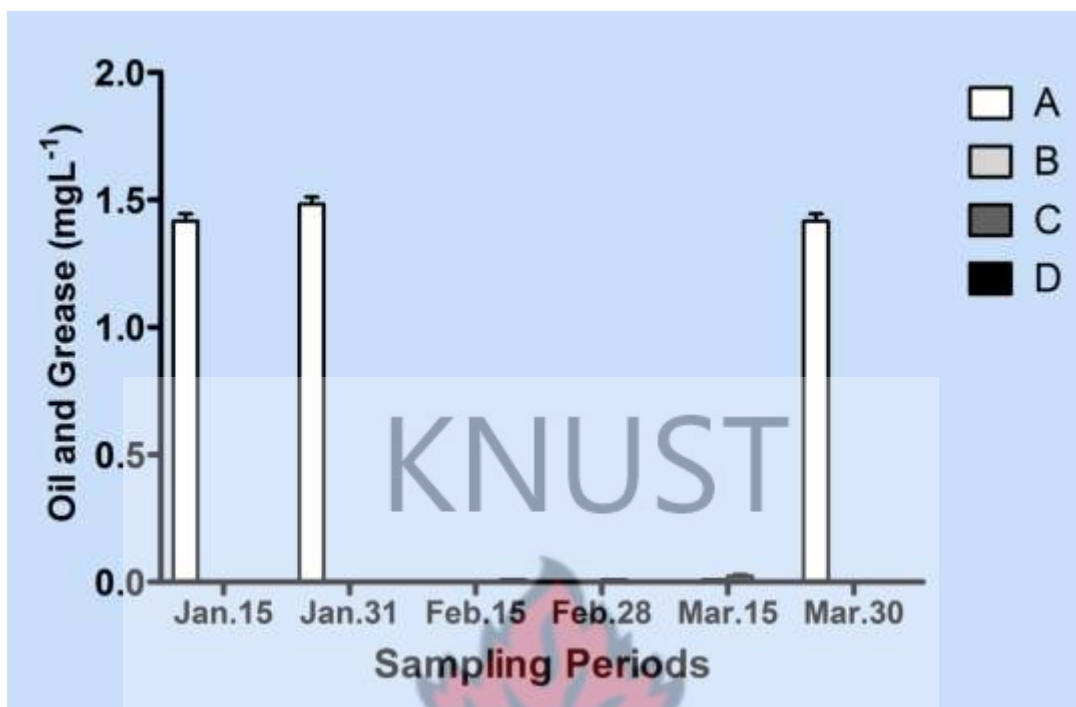




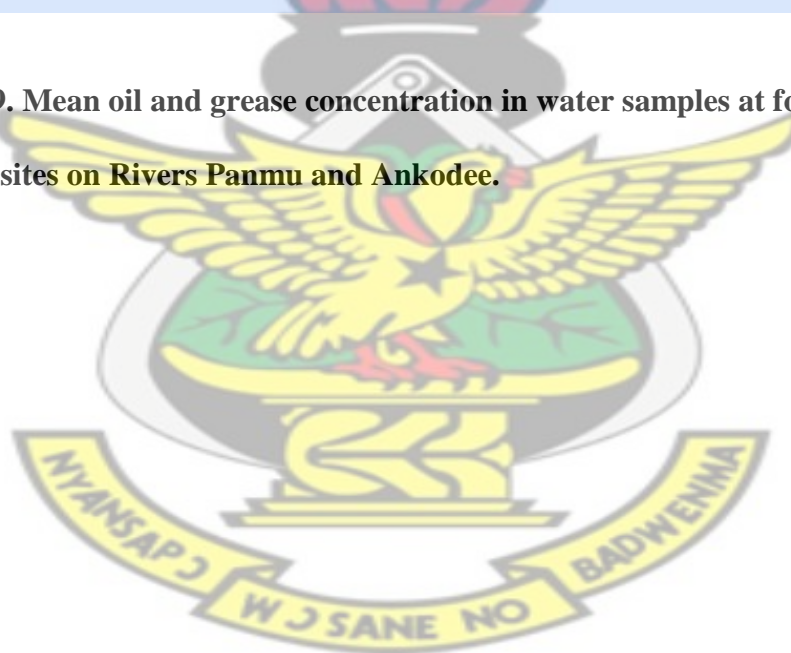
**Figure 4.8. Mean cadmium concentrations in Sediment samples at four different sampling sites on Rivers Panmu and Ankodee**

#### **4.2 Mean concentration of Oil and Grease in water samples from Rivers Panmu and Ankodee**

Mean oil and grease concentrations in Rivers Panmu and Ankodee were very low over the period of the study (Figure 4.9). Grease and oil recorded  $0.719 \pm 0.789$  mg/L as the highest concentration and  $0.002 \pm 0.004$  mg/L as the lowest at sites A and D, respectively. Concentrations at almost all the different sampling sites were below detection limit except at site A (Table 4.1). There were statistically significant differences ( $P < 0.05$ ) between the mean concentration of oil and grease recorded at the various sampling sites (Appendix I).



**Figure 4.9. Mean oil and grease concentration in water samples at four different sampling sites on Rivers Panmu and Ankodee.**



## CHAPTER FIVE

### DISCUSSION

The study has shown that generally, the rivers Panmu and Ankodee within the Dormaa Municipality are heavily contaminated with iron as the concentrations were high (4.36 – 13.07mg/L) when compared with the WHO (2011) human health-based guideline value of  $0.3\text{mgL}^{-1}$  (Appendix II). These high iron concentration levels at the sampling sites A, B, C and D in the river water may be due to the activities along the course of the Rivers Panmu and Ankodee. However, concentrations in the sediments ( $14772 \pm 13590 - 34629 \pm 10288 \text{ mg/kg}$ ) were extremely high as compared to that in the water column, suggesting the nature of the geology as well as the anthropogenic activities being responsible for the high iron levels. The sediments are also known to be important sinks for various pollutants like heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions and in interactions between water and sediment (Rashed, 2004). It was observed, during the study, that livestock wade and drink from the river. This development makes the high Iron levels in the sediment samples worrying because the particulate-bound metals can disassociate from its particle to become soluble in the water column (Wetzel, 2001; Brönmark and Hansson, 2005) increasing the metal levels in the water.

In comparison, concentrations of Copper, Lead and Cadmium were, generally, low in the water column compared to the higher levels in the sediment samples. Concentrations of copper in the water column were low ( $0.019 \pm 0.014 \text{ mg/L} - 0.073 \pm 0.065 \text{ mg/L}$ ) relative to ( $6.66 \pm 7.32 \text{ mg/kg} - 550.08 \pm 555.70 \text{ mg/kg}$ ) for the sediment samples. The level of

Copper recorded in the rivers Panmu and Ankodee during the study, generally, fell below the WHO (2011) health-based guidelines for human consumption of 2 mg/L whereas that of the sediment sample could be compared to heavily polluted sites with copper because the levels of copper, generally, exceeded the USEPA levels of > 50 mg/kg for heavily polluted sites (Appendix III).

Similar to the trends exhibited by the mean concentrations of copper and cadmium, mean concentrations of lead in the river water samples ( $0.003 \pm 0.007$  mg/L –  $0.021 \pm 0.035$  mg/L) were low when compared to that in the sediment samples ( $0.810 \pm 1.68$  mg/kg –  $275.30 \pm 638.00$  mg/kg). The levels of lead recorded in the sediment samples were comparable to sites heavily polluted with lead with levels far exceeding the USEPA sediment quality guideline for heavily polluted sites of > 60mg/kg. However, levels in the water column were slightly above the WHO (2011) health-based guideline for human consumption of 0.01mg/L (Appendix II). The high levels may have been the activities of the garages, around the rivers Panmu and Ankodee, such as recharging of automobile batteries which contains lead, also contribute some lead pollutants into the Rivers.

Cadmium levels pattern in both the water column and the sediment samples were not different from that of Copper and Lead in the Rivers Panmu and Ankodee. Levels of cadmium in the river water samples were found to be generally higher than the WHO (2011) health-based guidelines for human consumption of 0.03mg/L (Appendix II) with  $0.008 \pm 0.008$  mg/L and  $0.035 \pm 0.031$  mg/L being the lowest and highest levels recorded, respectfully. Unlike the water samples, sediment levels fell within the range of  $0.48 \pm 0.55$  mg/kg to  $2.03 \pm 0.83$  mg/kg which fell below the USEPA sediment quality guideline of 5mg/kg (Appendix II). The high levels of Cadmium could be due to its release into the



Rivers from the waste dumps and from fertilizer application by vegetable farmers, especially at sample site D among other activities. Surface runoffs from vegetable farms contain some concentrations of Cadmium (Opaluwa *et al.*, 2012).

The higher concentrations of heavy metals (Cu, Pb and Cd) in the sediment of the Rivers Panmu and Ankodee may be due to the refuse dumps, fuel service stations and the various scrap metal fabrication workshops located in the watersheds of the Rivers. Surface runoff that is carried in gutters that is channeled into the river may also contribute to higher levels of heavy metals in the River sediments. As heavy metals flow into the River they adsorb to particulate matter and become heavier, settling at the bottom of the lake. This may have contributed to higher levels of heavy metals in the sediments than in the overlying surface water. The results were consistent with earlier research carried out by Depinto and Martin (1980) and Adomako *et al* (2008). According to Adomako *et al* (2008), concentrations of the heavy metals in sediments are higher than that in water and this might be due to the fact that metals can be either transported with the water or suspended sediment stored within Riverbed bottom sediment. Again, suspended sediments and other solids are stored in river sediment after they aggregated to form larger denser particles that settle at the bottom of the water.

Fostener and Wittmann (1981), believes that, sediments can play a useful role in the assessment of metal contamination because in stable environments, metals are preferentially transferred from the dissolved to the particulate phase. Consequently, metal concentration in sediments may be generally higher than the overlying water. This assertion may probably, also account for the higher contamination load or concentration recorded in sediments during the study. The higher concentration of heavy metals in the

Rivers Panmu and Ankodee sediment is worrying as this may result in reduction in the benthic biodiversity. However, heavy metals were low at the surface water as a result of adsorption of the metals onto the particulate matter which becomes heavier and consequently settled at the bottom of the rivers (Adomako *et al.*, 2008).

Water pollution, especially from vehicle washing activities among others, is of significance in the study area because of the other uses the Ankodee and Panmu Rivers serve. The two water bodies serve as irrigation water sources for agricultural activities especially vegetable farming and concerns are often raised by people regarding vegetables irrigated with water from these potentially polluted streams regarding the health of consumers. Some riparian communities, especially those located downstream of the water bodies and the informal settlements in the peri-urban areas also depend on the water bodies as their sources of drinking water. Incidents of water quality-related problems have been reported in certain areas and communities that depend on the streams for some forms of livelihood. Lead and Cadmium from the surface runoffs, due to the application of fertilizers in vegetable farming along the course of the rivers Panmu and Ankodee can also have toxic effects on both aquatic plants and animals due to their toxicity. They can bio-accumulate in the aquatic species and then have an impact all the way through the food chain.

Oil and grease was mainly detected in the water sample at site A, the source of the Ankodee River. Concentration varied from  $0.002 \pm 0.004$  mg/L to  $0.719 \pm 0.789$  mg/L. The measurable oil and grease over the sampling period were found to be generally lower than the Ghana EPA guideline for effluent discharge into natural water bodies of 5mg/L

(Appendix II). The higher level of oil and grease at the source of the Ankodee River may have come from a nearby vehicle fuel service station with a Lube and Washing Bay.

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## CHAPTER SIX

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 CONCLUSIONS

The following conclusions were made at the end of the study:

- All the levels of the heavy metals studied in the water and sediment samples were higher and above the WHO and USEPA guidelines standards, respectively.
- Sediment samples recorded higher heavy metals than the water samples.
- Relative to the other metals studied, Iron recorded the highest levels in both the water and sediment samples
- Grease and oil levels were generally, low and below Ghana EPA standards
- It could therefore, be concluded that the Rivers Panmu and Ankodee in the Dormaa Ahenkro Municipality are polluted with the heavy metals; Iron, Copper, Cadmium and Lead.

#### 6.2 RECOMMENDATIONS

1. The mechanics shops, artisans etc. along the course of the river should be relocated by the Town authorities.

2. Further investigations should be conducted to find out the presence of plant nutrients, microbes and other physico- chemical parameters that can provide insight and explanation to the level of the heavy metals found, due to the siting of refuse dump along the course of the rivers.
3. Further study should be conducted to assess pollution of the Panmu and Ankodee Rivers by other heavy metals not considered in this study.
4. There should be educational campaign by organizations such as the Ghana Water Company Limited, the Environmental Protection Agency and the Public Health Divisions of the Ghana Health Service to create awareness of the consequences of heavy metals accumulation in the Rivers.





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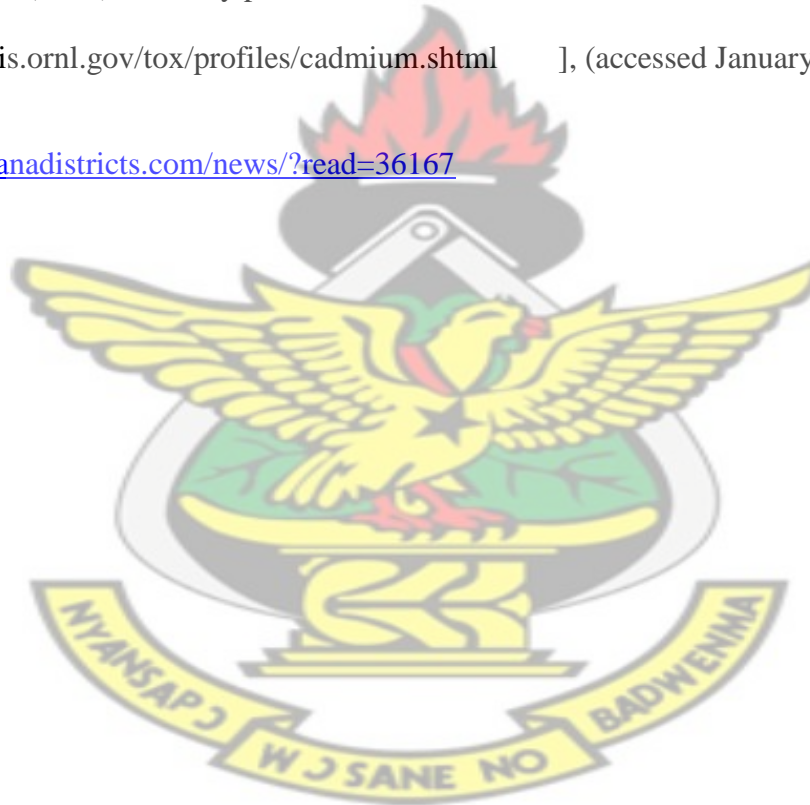
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## APPENDICES

**APPENDIX I:** Results of the One- Way ANOVA, Bartlett's test for equal variances and the Tukey's Multiple Comparison Test for both the Water and Sediment samples

Table 1a: ANOVA for Iron in the water from the different sampling sites

Table Analyzed	Fe Water				
One-way analysis of variance					
P value	0.0003				
P value summary	***				
Are means signif. different? (P < 0.05)	Yes				
Number of groups	4				
F	9.966				
R squared	0.5992				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	4.085				
P value	0.2524				
P value summary	ns				
Do the variances differ signif. (P < 0.05)	No				
ANOVA Table	SS	df	MS		
Treatment (between columns)	281.9	3	93.96		
Residual (within columns)	188.6	20	9.428		
Total	470.4	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-5.790	4.619	Yes	*	-10.75 to -0.8290
A vs C	-8.713	6.951	Yes	***	-13.67 to -3.752
A vs D	-8.028	6.404	Yes	**	-12.99 to -3.067
B vs C	-2.923	2.332	No	ns	-7.884 to 2.039
B vs D	-2.237	1.785	No	ns	-7.199 to 2.724
C vs D	0.6852	0.5466	No	ns	-4.276 to 5.647



Table 1b: ANOVA for Copper in the water from the different sampling sites

Table Analyzed	Cu Water				
One-way analysis of variance					
P value	0.0416				
P value summary	*				
Are means signif. different? (P < 0.05)	Yes				
Number of groups	4				
F	3.295				
R squared	0.3307				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	16.52				
P value	0.0009				
P value summary	***				
Do the variances differ signif. (P < 0.05)	Yes				
ANOVA Table	SS	df	MS		
Treatment (between columns)	0.01257	3	0.004191		
Residual (within columns)	0.02544	20	0.001272		
Total	0.03801	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-0.05400	3.709	No	ns	-0.1116 to 0.003630
A vs C	0.0005000	0.03434	No	ns	-0.05713 to 0.05813
A vs D	-0.004500	0.3091	No	ns	-0.06213 to 0.05313
B vs C	0.05450	3.743	No	ns	-0.003130 to 0.1121
B vs D	0.0495	3.400	No	ns	-0.008130 to 0.1071
C vs D	-0.005000	0.3434	No	ns	-0.06263 to 0.05263

Table 1c: ANOVA for Lead in the water from the different sampling sites

Table Analyzed	Pb Water				
One-way analysis of variance					
P value	0.3031				
P value summary	ns				
Are means signif. different? (P < 0.05)	No				
Number of groups	4				
F	1.296				
R squared	0.1628				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)					
P value					
P value summary	ns				
Do the variances differ signif. (P < 0.05)	No				
ANOVA Table	SS	df	MS		
Treatment (between columns)	0.001589	3	0.0005295		
Residual (within columns)	0.008169	20	0.0004085		
Total	0.009758	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	0.007778	0.9427	No	ns	-0.02488 to 0.04043
A vs C	-0.01022	1.239	No	ns	-0.04288 to 0.02243
A vs D	0.01083	1.313	No	ns	-0.02182 to 0.04349
B vs C	-0.0180	2.182	No	ns	-0.05066 to 0.01466
B vs D	0.003056	0.3703	No	ns	-0.02960 to 0.03571
C vs D	0.02106	2.552	No	ns	-0.01160 to 0.05371

Table 1d: ANOVA for Cadmium in the water from the different sampling sites

Table Analyzed	Cd Water				
One-way analysis of variance					
P value	0.0834				
P value summary	ns				
Are means signif. different? (P < 0.05)	No				
Number of groups	4				
F	2.565				
R squared	0.2778				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	13.57				
P value	0.0036				
P value summary	**				
Do the variances differ signif. (P < 0.05)	Yes				
ANOVA Table	SS	df	MS		
Treatment (between columns)	0.002854	3	0.0009514		
Residual (within columns)	0.007420	20	0.0003710		
Total	0.01027	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	0.01294	1.646	No	ns	-0.01818 to 0.04407
A vs C	-0.01061	1.349	No	ns	-0.04173 to 0.02051
A vs D	0.0170	2.162	No	ns	-0.01412 to 0.04812
B vs C	-0.02356	2.996	No	ns	-0.05468 to 0.007567
B vs D	0.004056	0.5158	No	ns	-0.02707 to 0.03518
C vs D	0.02761	3.511	No	ns	-0.003512 to 0.05873

Table 1e: ANOVA for Oil and Grease in the water from the different sampling sites

Table Analyzed	O&G Water				
One-way analysis of variance					
P value	0.0099				
P value summary	**				
Are means signif. different? (P < 0.05)	Yes				
Number of groups	4				
F	4.953				
R squared	0.4263				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	112.3				
P value	P<0.0001				
P value summary	***				
Do the variances differ signif. (P < 0.05)	Yes				
ANOVA Table	SS	df	MS		
Treatment (between columns)	2.310	3	0.7700		
Residual (within columns)	3.109	20	0.1555		
Total	5.419	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	0.7178	4.459	Yes	*	0.08068 to 1.355
A vs C	0.7139	4.435	Yes	*	0.07679 to 1.351
A vs D	0.7178	4.459	Yes	*	0.08068 to 1.355
B vs C	-0.003889	0.02416	No	ns	-0.6410 to 0.6332
B vs D	0.0000	0.0000	No	ns	-0.6371 to 0.6371
C vs D	0.003889	0.02416	No	ns	-0.6332 to 0.6410

Table 1f: ANOVA Iron in the sediment from the different sampling sites

Table Analyzed	Fe Sed				
One-way analysis of variance					
P value	0.1297				
P value summary	ns				
Are means signif. different? (P < 0.05)	No				
Number of groups	4				
F	2.120				
R squared	0.2412				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	1.041				
P value	0.7912				
P value summary	ns				
Do the variances differ signif. (P < 0.05)	No				
ANOVA Table	SS	df	MS		
Treatment (between columns)	1234000000	3	411300000		
Residual (within columns)	3881000000	20	194100000		
Total	5115000000	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-19860	3.492	No	ns	-42370 to 2653
A vs C	-7007	1.232	No	ns	-29520 to 15500
A vs D	-7010	1.233	No	ns	-29520 to 15500
B vs C	12850	2.259	No	ns	-9660 to 35360
B vs D	12850	2.259	No	ns	-9663 to 35360
C vs D	-3.049	0.0005361	No	ns	-22510 to 22510



Table 1g: ANOVA Copper in the sediment from the different sampling sites

Table Analyzed	Cu Sed				
One-way analysis of variance					
P value	0.0054				
P value summary	**				
Are means signif. different? (P < 0.05)	Yes				
Number of groups	4				
F	5.706				
R squared	0.4612				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	94.25				
P value	P<0.0001				
P value summary	***				
Do the variances differ signif. (P < 0.05)	Yes				
ANOVA Table	SS	df	MS		
Treatment (between columns)	1322000	3	440800		
Residual (within columns)	1545000	20	77250		
Total	2867000	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-544.2	4.796	Yes	*	-993.3 to -95.06
A vs C	-0.5884	0.005185	No	ns	-449.7 to 448.5
A vs D	-5.772	0.05087	No	ns	-454.9 to 443.3
B vs C	543.6	4.791	Yes	*	94.47 to 992.7
B vs D	538.4	4.745	Yes	*	89.29 to 987.5
C vs D	-5.183	0.04568	No	ns	-454.3 to 443.9

Table 1h: ANOVA Lead in the sediment from the different sampling sites

Table Analyzed	Pb Sed				
One-way analysis of variance					
P value	0.3578				
P value summary	ns				
Are means signif. different? (P < 0.05)	No				
Number of groups	4				
F	1.138				
R squared	0.1458				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	122.1				
P value	P<0.0001				
P value summary	***				
Do the variances differ signif. (P < 0.05)	Yes				
ANOVA Table	SS	df	MS		
Treatment (between columns)	336600	3	112200		
Residual (within columns)	1972000	20	98610		
Total	2309000	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-272.9	2.129	No	ns	-780.3 to 234.5
A vs C	1.594	0.01244	No	ns	-505.8 to 509.0
A vs D	0.3111	0.002427	No	ns	-507.1 to 507.7
B vs C	274.5	2.141	No	ns	-232.9 to 781.9
B vs D	273.2	2.131	No	ns	-234.2 to 780.6
C vs D	-1.283	0.01001	No	ns	-508.7 to 506.1

Table 1i: ANOVA Cadmium in the sediment from the different sampling sites

Table Analyzed	Cd Sed				
One-way analysis of variance					
P value	0.0024				
P value summary	**				
Are means signif. different? (P < 0.05)	Yes				
Number of groups	4				
F	6.791				
R squared	0.5046				
Bartlett's test for equal variances					
Bartlett's statistic (corrected)	0.8406				
P value	0.8397				
P value summary	ns				
Do the variances differ signif. (P < 0.05)	No				
ANOVA Table	SS	df	MS		
Treatment (between columns)	9.795	3	3.265		
Residual (within columns)	9.616	20	0.4808		
Total	19.41	23			
Tukey's Multiple Comparison Test	Mean Diff.	q	Significant? P < 0.05?	Summary	95% CI of diff
A vs B	-0.02778	0.09813	No	ns	-1.148 to 1.093
A vs C	0.1000	0.3533	No	ns	-1.020 to 1.220
A vs D	-1.447	5.112	Yes	**	-2.568 to -0.3268
B vs C	0.1278	0.4514	No	ns	-0.9927 to 1.248
B vs D	-1.419	5.014	Yes	*	-2.540 to -0.2990
C vs D	-1.547	5.466	Yes	**	-2.668 to -0.4268

## APPENDIX II: Mean monthly Heavy Metal concentrations in the Water and Sediment Samples

Table 2a: Monthly Water Samples

water	Fe (mgL <sup>-1</sup> )	Cu (mgL <sup>-1</sup> )	Pb (mgL <sup>-1</sup> )	Cd (mgL <sup>-1</sup> )	O&G (mgL <sup>-1</sup> )
<b>Sampling Site A</b>					
Jan.15	9.12±0.001	0.024±0.001	0.044±0.001	0.022±0.001	1.417±0.029
Jan.31	8.20±0.012	0.024±0.001	0.021±0.004	0.056±0.038	1.483±0.029
Feb.15	2.30±0.010	0.042±0.002	0.000±0.000	0.008±0.001	0.000±0.000
Feb.28	2.24±0.061	0.015±0.000	0.000±0.000	0.026±0.018	0.000±0.000
Mar.15	2.27±0.062	0.014±0.001	0.000±0.000	0.036±0.002	0.000±0.000
Mar.30	2.03±0.009	0.000±0.000	0.000±0.000	0.000±0.000	1.417±0.029
<b>Sampling Site B</b>					
Jan.15	9.86±0.001	0.019±0.000	0.018±0.001	0.016±0.001	0.000±0.000
Jan.31	8.12±0.003	0.039±0.000	0.000±0.000	0.017±0.001	0.000±0.000
Feb.15	14.10±0.03	0.085±0.000	0.000±0.000	0.011±0.005	0.000±0.000
Feb.28	11.04±0.00	0.149±0.002	0.000±0.000	0.010±0.001	0.000±0.000
Mar.15	10.70±0.57	0.152±0.002	0.000±0.000	0.017±0.001	0.010±0.000
Mar.30	7.08±0.035	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000
<b>Sampling Site C</b>					
Jan.15	9.46±0.001	0.039±0.006	0.042±0.001	0.018±0.000	0.000±0.000
Jan.31	7.06±0.001	0.039±0.001	0.084±0.000	0.025±0.001	0.000±0.000
Feb.15	12.88±0.001	0.085±0.001	0.000±0.000	0.021±0.012	0.000±0.000
Feb.28	17.92±0.001	0.149±0.001	0.000±0.000	0.079±0.001	0.010±0.000
Mar.15	16.91±1.001	0.152±0.001	0.000±0.000	0.069±0.001	0.023±0.006
Mar.30	14.21±0.099	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000

### Sampling Site D

Jan.15	10.17±0.23	0.018±0.002	0.000±0.000	0.018±0.002	0.000±0.000
Jan.31	10.36±0.00	0.016±0.001	0.000±0.000	0.016±0.001	0.000±0.000
Feb.15	13.40±0.02	0.029±0.001	0.000±0.000	0.006±0.008	0.010±0.000
Feb.28	13.40±0.02	0.040±0.001	0.000±0.000	0.003±0.001	0.000±0.000
Mar.15	13.60±0.073	0.043±0.006	0.000±0.000	0.002±0.001	0.000±0.000
Mar.30	13.40±0.02	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000

WHO (2011)	0.3	2	0.01	0.003	*
EPA Ghana					5

\* No health-based guideline value proposed

Table 2b: Monthly Sediment Samples

Sediment	Fe	Cu	Pb	Cd
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### Sampling Site A

Jan.15	20244.33±107.58	13.63±0.11	1.60±0.10	1.33±0.06
Jan.31	36171.77±0.40	13.97±11.92	12.80±0.20	1.33±0.05
Feb.15	10622.77±59.09	12.37±0.15	0.000±0.00	0.83±0.06
Feb.28	161.90±0.700	0.00±0.00	0.00±0.00	0.00±0.00
Mar.15	19989.67±132.66	0.00±0.00	0.00±0.00	0.00±0.00
Mar.30	1435.17±44.80	0.00±0.00	0.00±0.00	0.00±0.00



**Sampling Site B**

Jan.15	31870.00±107.58	32.70±0.10	96.90±0.10	1.53±0.06
Jan.31	51888.23±0.897	957.10±2.90	1554.73±4.56	1.20±0.00
Feb.15	26517.80±105.41	72.07±0.21	0.00±0.00	0.93±0.06
Feb.28	42240.27±75.98	1290.83±12.98	0.00±0.00	0.00±0.00
Mar.15	26643.03±101.77	74.43±0.72	0.00±0.00	0.00±0.00
Mar.30	28613.73±90.76	877.90±1.61	0.00±0.00	0.00±0.00

**Sampling Site C**

Jan.15	7430.00±110.00	12.10±0.10	4.20±0.10	0.80±0.00
Jan.31	46760.33±2.88	18.13±0.12	0.63±0.06	1.20±0.00
Feb.15	11075.33±56.86	13.27±0.15	0.00±0.00	0.90±0.00
Feb.28	13656.97±71.91	0.00±0.00	0.00±0.00	0.00±0.00
Mar.15	24174.90±1.001	0.00±0.00	0.00±0.00	0.00±0.00
Mar.30	27577.83±1514.76	0.00±0.00	0.00±0.00	0.00±0.00

**Sampling Site D**

Jan.15	43219.33±0.57	18.00±0.00	6.67±0.15	0.97±0.06
Jan.31	43219.33±0.57	18.00±0.00	0.63±0.05	0.97±0.06
Feb.15	11047.33±0.57	12.96±0.15	0.00±0.00	2.40±0.17
Feb.28	11080.67±57.45	12.67±0.51	0.00±0.00	2.80±0.63
Mar.15	11047.00±0.00	12.97±0.15	0.00±0.00	2.43±0.21
Mar.30	11080.67±57.45	0.00±0.00	0.00±0.00	2.62±0.39

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Table 2c: USEPA Guidelines for Sediments (mg/kg Dry Weights)

Metal	Not Polluted	Moderately Polluted	Heavily Polluted
Pb	<40	40-60	>60
Cd	-	-	>6
Cu	<25	25-50	>50
Fe	-	-	-

- No health-based guideline value proposed

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