

**ASSESSMENT OF HEAVY METAL CONTAMINATION OF THE DENSU
RIVER, WEIJA FROM LEACHATE**

BY

ESI SAAWA DADZIE

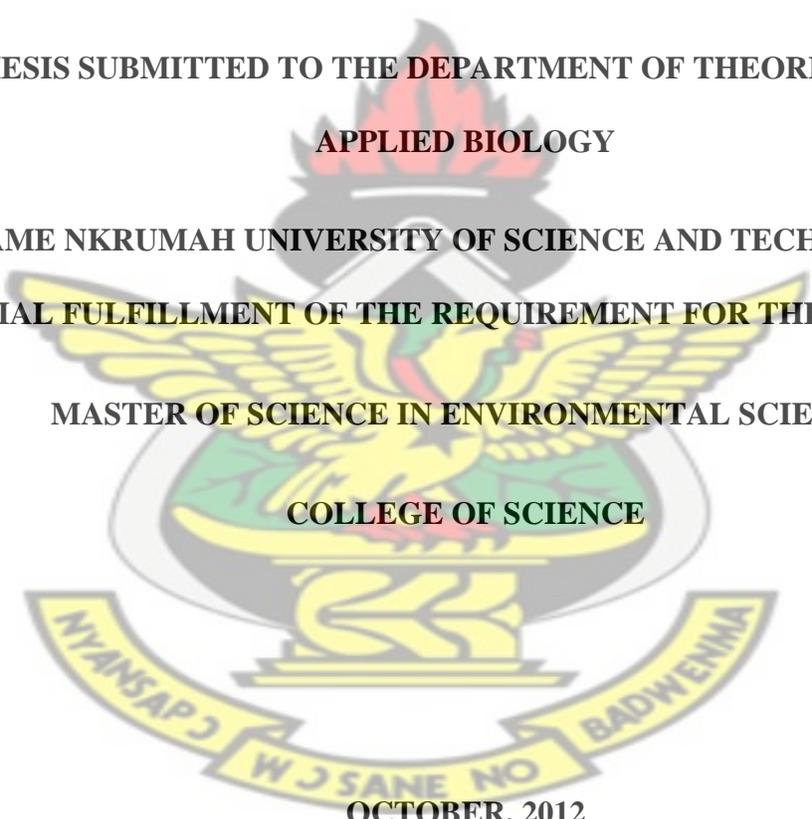
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COLLEGE OF SCIENCE

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DECLARATION

I hereby declare that this submission is my own work towards the MSc. 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.

SIGNATURE: DATE:

DADZIE ESI SAAWA (PG4171710)

(STUDENT NAME & ID)

CERTIFIED BY:

SIGNATURE: DATE:

PROF. K. OBIRI-DANSO

(SUPERVISOR)

CERTIFIED BY:

SIGNATURE: DATE:

.....

(HEAD OF DEPARTMENT)

ABSTRACT

The effect of leachate seepage from a landfill site on the quality of an urban river, Densu, that is the one of the main sources of water abstracted for treatment for most residents in the Accra Metropolitan area was determined by measuring the levels of heavy metals (As, Pb, Hg, and Cd) in the seepage and in the river itself using Atomic Absorption Spectrometry methods. Heavy metal concentration upstream before leachate contamination was low and within WHO limits. The mean concentrations of arsenic, lead, mercury and cadmium were 0.026mg/l, 0.957mg/l, 0.025mg/l and 0.005mg/l, respectively in the leachate. Mean heavy metal concentration, two hundred metres downstream from the leachate discharge point (where water is drawn for domestic and drinking purpose) was 0.008mg/l for arsenic, 0.393mg/l for lead, 0.001mg/l for mercury while cadmium was not detected. Lead exceeded the WHO acceptable limit of 0.01mg/l for drinking water. Mean levels in the corresponding sediment samples were 0.015mg/kg for arsenic, <0.001mg/kg for lead, 0.004mg/kg for mercury and cadmium 0.151mg/kg. Contamination factors computed were less than one ($CF < 1$) for arsenic and lead in the sediments which imply low contamination and moderate contamination for cadmium ($1 \geq CF \geq 3$). Seepage of leachate from the landfill site into Densu must be monitored to ensure the quality of River Densu especially when it is being used as a drinking water source by downstream communities.

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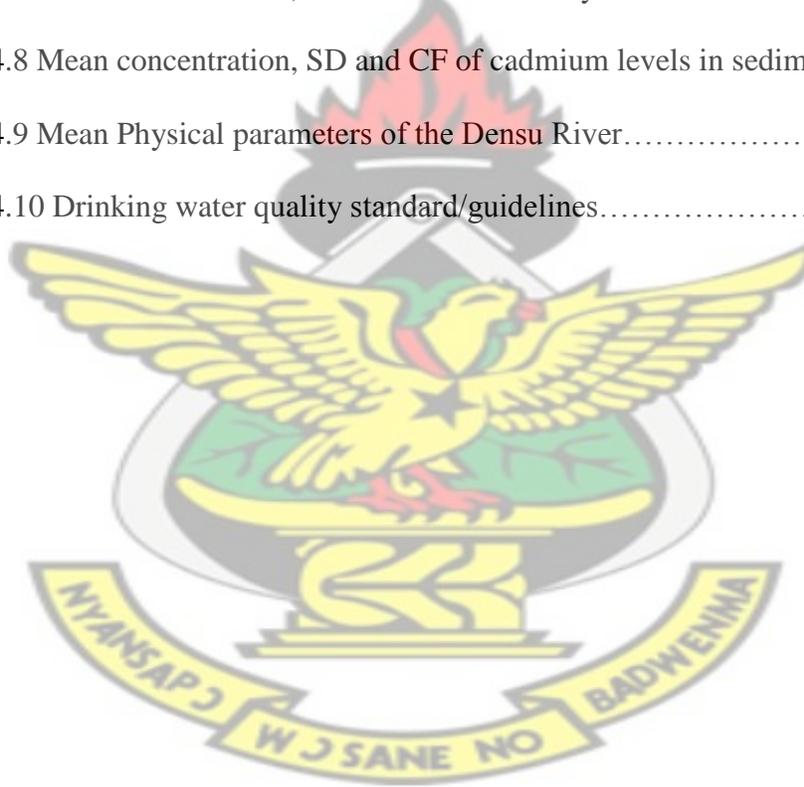
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DEDICATION

I dedicate this work to the Almighty God who made all things possible and to all men and women of God who have given my life a meaning.

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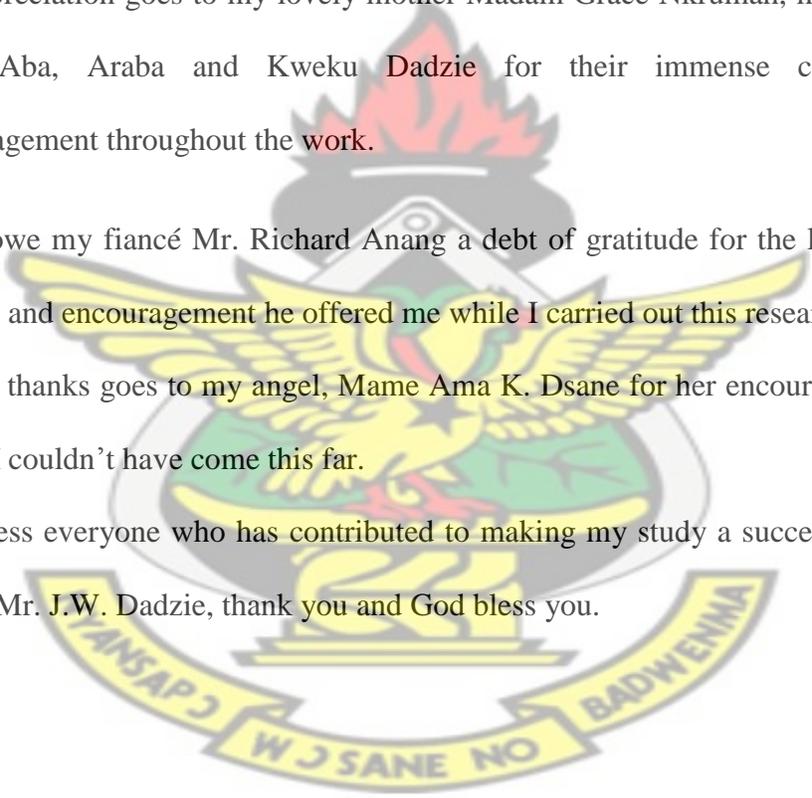
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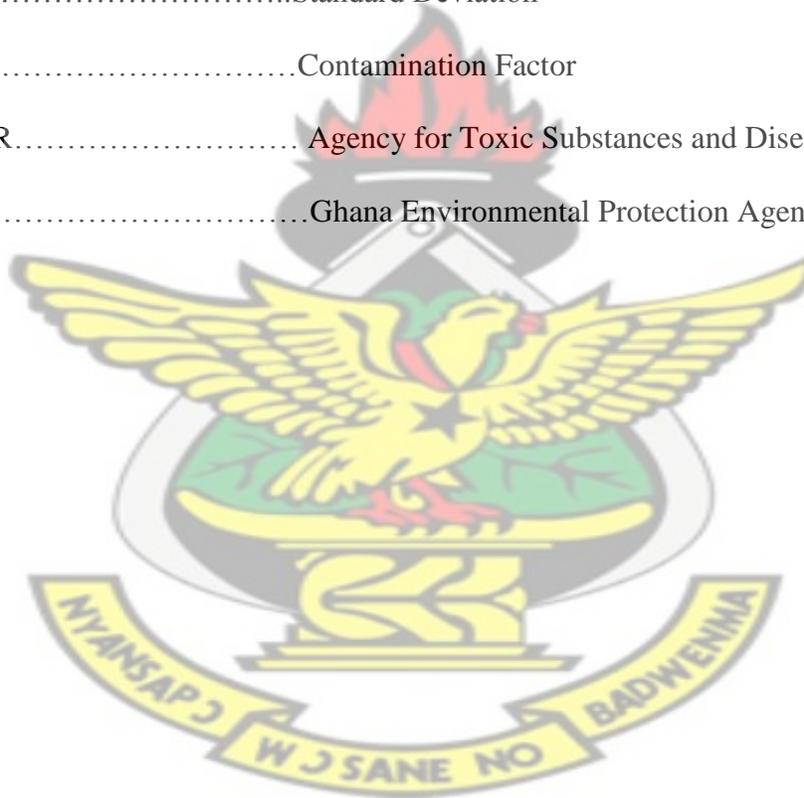
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LIST OF ABBREVIATIONS

WHO.....	World Health Organization
EPA.....	Environmental Protection Agency
AAS.....	Atomic Absorption Spectrophotometer
APHA.....	American Public Health Association
TDS.....	Total dissolved solids
USEPA.....	United State Environmental Protection Agency
SD	Standard Deviation
CF.....	Contamination Factor
ATSDR.....	Agency for Toxic Substances and Disease Registry
GEPA.....	Ghana Environmental Protection Agency



CHAPTER ONE

1.0 INTRODUCTION

Ghana aims at achieving an efficient and effective management system for the sustainable development of water resources and to ensure full socio-economic benefits for present and future generations by 2025. However, water management is still a major developmental challenge as human activities have resulted in the dwindling of freshwater resources, increased pollution load, health and transportation problems and reduced ecosystem resilience which pose significant threat to sustainable development (Roosbroeck *et al.*, 2006).

Densu serves as a major fishing and drinking water resource for people living along the banks of the entire stretch of the river in Ghana. Rapid urbanization and industrialization in many developing countries have given rise to contamination of water resources. The fast expansion of urban, agricultural and industrial activities spurred by rapid population growth and the change in consumer habits have produced vast amounts of solid wastes. Unfortunately, managing this waste has been a challenge for many countries. In Ghana, technical, financial and institutional constraints have compounded this problem. Also, improperly designed solid waste disposal facilities and landfill sites have further contributed to contamination of surface and underground water resources. Akoteyon *et al.* (2011) investigated the heavy metal contamination of groundwater around a landfill site in Alimosho area of Lagos State, Nigeria and concluded that the leachates from the landfill have impacted on the groundwater

resources of the sampled wells in the study area based on the direction of groundwater flow.

There are more than twenty heavy metals, but four are of particular concern to human health and the environment namely Lead (Pb), Cadmium (Cd), Mercury (Hg), and Arsenic (As), (ATSDR, 2011). They are toxic and can cause damaging effects even at very low concentrations. The Agency for Toxic Substances and Disease Registry (ATSDR) in Atlanta, Georgia, (a part of the U.S. Department of Health and Human Services) compiled a Priority List called the "Top 20 Hazardous Substances." The heavy metals arsenic (1), lead (2), mercury (3), and cadmium (7) appear on this list.

Heavy metals are produced from a variety of natural and anthropogenic activities like mining, disposal of effluents (Amman *et al.*, 2002) from industries, and indiscriminate use of fertilizers and pesticides in agriculture. Sarpong *et al.*, (2009) investigated the spatial distribution of levels of arsenic, lead and cadmium in River Subin, in Kumasi. High heavy metal concentrations were recorded in the river water samples and these levels were all above the World Health Organization acceptable limit for domestic water use in irrigation and therefore considered unsuitable for use in vegetable farming.

In an aquatic ecosystem, heavy metal pollution can result from atmospheric deposition, geological weathering or through the discharge of waste. Metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, while many other metals like Cd, Cr and Pb have no known physiological activity, but have been proved to be detrimental beyond certain limits (Marschner, 1995; Bruins *et al.*, 2000).

An environmental concern is contamination of the River Densu by leachates from a decommissioned waste dump site. According to Christensen *et al.* (1998), municipal waste dump leachates are highly concentrated complex effluents which contain dissolved organic matters; inorganic compounds, and heavy metals. Watananugulkit *et al.* (2003) assessed the impact of leachate on the quality of surface water and ground water around the On-Nuch disposal site center in Bangkok. The impact of the leachate indicated that the surface water was more polluted than ground water. Drinking water containing high levels of these essential metals, or toxic metals such as arsenic, cadmium, chromium, lead, and mercury may be hazardous to health (Salem *et al.*, 2000).

Despite the truism that every human on this planet needs drinking water to survive and that water can contain many harmful constituents, there are no universally recognized and accepted international standards for drinking water. Even where standards do exist, and are applied, the permitted concentration of individual constituents may vary by as much as ten times from one set of standards to another. Many developed countries in Europe and the USA have specific standards to be applied in their own country. Countries without a legislative or administrative framework for such standards, the World Health Organization published guidelines is often used. Where standards do exist most are expressed as guidelines or targets and very few have any legal basis or are subject to enforcement. The European Drinking Water Directive and the Safe Water Act in the USA are two exceptions where there is a requirement to legally comply with specific standards.

This project seek to monitor the surface water in Weija, Accra considering the spatial variations in heavy metal content and also to evaluate the status of the river water quality with respect to drinking purposes.

1.1 PROBLEM STATEMENT

Densu, a major river in southern Ghana, is the main source of water abstracted for treatment to persons living in west Accra and its environs. Rapid urbanization and industrialization in the nation's capital have given rise to contamination of this water source. Landfill leachate rich in heavy metals discharges into the Densu River at Oblogo, Weija. Among the inorganic contaminants of the river water, heavy metals are of great concern because of their non-degradable nature and their potential to accumulate through trophic level causing a deleterious effect. Arsenic, lead, mercury and cadmium are among the "Top 20 Hazardous Substances" listed by the Agency for Toxic Substances and Disease Registry (ATSDR) which are of great concern to human health and the environment. Therefore, monitoring these metals is important for safety assessment of the environment and human health.

1.2 JUSTIFICATION OF THE STUDY

The rapid population growth along the Densu River has necessitated proper conservation and efficient utilization of freshwater bodies for sustainable development. This is necessary because there has been accelerated deterioration of water quality within Weija-Oblogo because of increased domestic, municipal and agricultural activities. Effluent discharge, urbanization and deforestation are the main causes of environmental degradation within the catchment (Karikari *et al.* 2006; Hagan *et al.*,

2011). As a result of these anthropogenic influences on the River Densu (as source of drinking water), it becomes imperative that investigation of levels of pollution of the Densu River be carried out regularly.

1.3 OBJECTIVE OF THE STUDY

The objective of this project is to assess the level of Lead (Pb), Cadmium (Cd), Mercury (Hg), and Arsenic (As) in the Densu River to ascertain its water quality vis a vis leachate discharge from a decommissioned landfill.

The specific objectives are to investigate:

1. Levels of Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd) in the landfill leachate.
2. Levels of Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd) in the Densu River and sediment just at the point of leachate entry.
3. Levels of Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd) in River Densu and its sediments at a distance of a hundred and two hundred metres upstream from the leachate discharge point.
4. Levels of Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd) in River Densu and its sediments at a distance of a hundred and two hundred metres downstream from the leachate discharge point.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 WATER QUALITY

Water quality refers to the chemical, physical and biological characteristics of water. It involves the process of evaluation of the physical, chemical and biological nature in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic system. The most common standards used to assess water quality relate to health of ecosystems, safety of human contact and drinking water. Water quality depends on the local geology and ecosystem, as well as human uses such as use of water bodies as sink (Johnson *et al.*, 1997).

The parameters for water quality are determined by the intended use. Water quality tends to be focused on water that is treated for human consumption, water for industrial use, or in the environment. Water contaminants that may be present in untreated water include microorganisms such as viruses and bacteria; inorganic contaminants such as salts and metals; organic chemical contaminants from industrial processes and petroleum use; pesticides and herbicides; and radioactive contaminants. Water Quality Standards have been established to regulate substances that potentially affect human health, environment and aesthetic qualities of water. The World Health Organization (WHO) guideline for Drinking Water Standards, United States Specification for Drinking Water and European Union Specification for Drinking Water are among the recognized water quality standards.

Dissolved minerals may affect suitability of water for a range of industrial and domestic purposes. The most familiar of these is the presence of ions of calcium and magnesium which interfere with the cleaning action of soap, and can form hard sulphate and soft carbonate deposits in water heaters or boilers. Hard water may be softened by removing these ions.

Environmental water quality, also called ambient water quality, relates to water bodies such as lakes, rivers, and oceans. Water quality standards for surface waters vary significantly due to different environmental conditions, ecosystems, and intended human uses. Toxic substances and high populations of certain microorganisms can present a health hazard for non-drinking purposes such as irrigation, swimming, fishing, rafting, boating and industrial uses. These conditions may also affect wildlife, which use the water for drinking or as a habitat. Modern water quality laws generally specify protection of fisheries especially endangered species and recreational use (Roosbroeck *et al.*, 2006).

2.2 ANTHROPOGENIC IMPACTS ON WATER QUALITY

With the advent of industrialization and increasing populations, the range of requirements for water has increased together with greater demands for higher quality water. Water has been considered, the most suitable medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns, etc.). These activities have undesirable, effects on the natural environment. Also, uncontrolled land use, urbanization, deforestation, accidental (or unauthorized) release of chemical substances and discharge of untreated wastes or

leaching of noxious liquids from solid waste deposits have impacted negatively on the quality of water resources (UNESCO, 2003).

2.3. PHYSICAL INDICATORS OF WATER QUALITY

2.3.1. CONDUCTIVITY

Conductivity is a measure of the ability of water or solution to carry an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids. Organic compounds do not conduct electrical current very well and therefore have a low conductivity when in water. Conductivity is also affected by temperature, the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degrees Celsius. Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Discharges to streams can change the conductivity depending on their make-up. Conductivity is measured in micro siemens per centimeter ($\mu\text{s}/\text{cm}$).

2.3.2. TOTAL DISSOLVED SOLIDS

Total Dissolved Solid represents the total concentration of dissolved substances in water. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution all have an influence on conductivity. Total dissolved solids (in mg/l) may be obtained by multiplying the conductance by a factor which is commonly between 0.55 and 0.75. This factor is determined for each water body, but remains approximately constant provided the ionic proportions of the water body remain stable. The multiplication factor is close to 0.67

for waters in which sodium and chloride dominate, and higher for waters containing high concentrations of sulphate (WHO, 1996).

2.3.3. TURBIDITY

Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids). Turbidity in open water may be caused by growth of phytoplankton, human activities which lead to high sediment levels entering water bodies during rain storms (USEPA, 2005).

2.3.4. COLOR, ODOR AND TASTE

Physically, the color of water is affected by factors like the light source, absorption and scattering of light, as well as suspended materials in the water. Quality drinking water should be colorless (WHO, 2008) Color and turbidity determines the depth to which light penetrates in water systems. Odors and tastes in water are associated with the presence of variety of substances which include living microscopic organisms or decaying matter. Taste responses are often difficult to differentiate from odor responses because the senses of taste and smell are closely interrelated. Odors can be caused by volatile substances in concentrations too small to be detected by ordinary analytical techniques.

2.4. CHEMICAL INDICATORS OF WATER QUALITY

2.4.1 pH

The pH value of a water source is a measure of its acidity or alkalinity. It is a measurement of the activity of the hydrogen atom, because the hydrogen activity is a

good representation of the acidity or alkalinity of water. For drinking water, the WHO guidelines set the pH in the range of 6.5-8.5 (WHO, 2008).

Human activities like industrial operations and toxic waste disposal have effect on the pH of water sources. A change in the pH of water can have consequences on aquatic life which are extremely sensitive to changes in water temperature and composition.

2.4.2. HARDNESS

Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include Ca^{2+} and Mg^{2+} . These ions enter water supply by leaching from minerals within an aquifer. Hardness is most commonly expressed as mg/l of CaCO_3 . The following equilibrium reaction describes the dissolving or formation of calcium carbonate scales:



Calcium carbonate scales formed in water-heating systems are called lime scale (Weingärtner, 2006; Nitsch *et al.*, 2005).

Temporary hardness of water is caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations (Ca^{2+} , Mg^{2+}) and carbonate and bicarbonate anions (CO_3^{2-} , HCO_3^-). The presence of the metal cations makes the water hard. However, unlike the permanent hardness caused by sulphate and chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the process of lime softening. Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium

carbonate out of solution, leaving water soft (Nitsch *et al.*, 2005). Permanent hardness cannot be removed by boiling. Despite the name permanent, the hardness of the water can be easily removed using an ion exchange column.

2.4.3. SULPHATES

Sulphates occur naturally in drinking water. They have a detoxifying effect on the liver and stimulate the function of the gall bladder and thus aid the digestive function as well. In high doses, they have a laxative effect. Health concerns regarding sulphate in drinking water have been diarrhea which may be associated with the ingestion of water containing high sulphate levels. Sulphate in drinking water has a secondary maximum contaminant level of 250 milligrams per liter (mg/L), based on aesthetic effects (i.e., taste and odor). The presence of sulphate in drinking-water may also cause noticeable taste and may contribute to the corrosion of distribution systems. (WHO, 2008; USEPA, 2012).

2.4.4. NITRATES

Nitrates and nitrites are nitrogen-oxygen chemical units which combine with various organic and inorganic compounds. Nitrates (NO_3) are essential source of nitrogen (N) for plants. The greatest use of nitrates is as a fertilizer; nitrates taken into the body are converted to nitrites. Nitrate levels in drinking water can also be an indicator of overall water quality. Elevated nitrate levels may suggest the possible presence of other contaminants such as disease-causing organisms from sewage, pesticides, or other inorganic and organic compounds that could cause health problems.

The US Environmental Protection Agency has set the Maximum Contaminant Level (MCL) of nitrate as nitrogen ($\text{NO}_3\text{-N}$) at 10 mg/L (or 10 parts per million) for the safety of drinking water. Nitrate levels at or above this level have been known to cause a potentially fatal blood disorder in infants under six months of age called methemoglobinemia or "blue-baby" syndrome (USEPA, 2012).

2.4.5. PHOSPHATES

Phosphates are the naturally occurring form of the element phosphorus, found in many phosphate minerals. Natural waters have a phosphorus concentration of approximately 0.02 parts per million (ppm) which is a limiting factor for plant growth. The concentration of phosphates above 100 mg/liter may adversely affect the coagulation processes in drinking water treatment plants. The addition of large quantities of phosphates to waterways accelerates algae and plant growth in natural waters; enhancing eutrophication and depleting the water body of oxygen.

In biological systems, phosphorus is found as a free phosphate ion in solution and is called inorganic phosphate. An important occurrence of phosphates in biological systems is as the structural material of bone and teeth. These structures are made of crystalline calcium phosphate in the form of hydroxyapatite. Manmade sources of phosphate include human sewage, agricultural run-off from farms, sewage from animal feedlots, pulp and paper industry, vegetable and fruit processing, chemical and fertilizer manufacturing, and detergents (Hochanadel , 2010; Laws, 1993).

2.5. BIOLOGICAL INDICATORS

Coliform bacteria are commonly used bacterial indicator of sanitary quality of foods and water. They are defined as rod-shaped Gram-negative non-spore forming bacteria which can ferment lactose with the production of acid and gas when incubated at 35-37°C (APHA, 1995). Coliforms can be found in the aquatic environment, in soil and on vegetation; they are universally present in large numbers in the feces of warm-blooded animals. Coliforms are themselves not normally causes of serious illness, they are easy to culture and their presence is used to indicate that other pathogenic organisms of fecal origin may be present. Fecal pathogens include bacteria, viruses, or protozoa and many multicellular parasites.

2.6. HEAVY METALS

Heavy metals are chemical elements with a specific gravity at least 5 times that of water. The specific gravity of water is 1 at 4°C. Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metals with a specific gravity 5 or more times that of water are cadmium (8.65), iron (7.9), lead (11.34), and mercury (13.546) (Lide, 1992).

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these elements (eg, iron, copper, manganese, and zinc) or some forms of them are commonly found naturally in foodstuffs, fruits and vegetables, and in commercially available multivitamin products. Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in parenteral

nutrition mixtures, and the use of lead as a radiation shield around x-ray equipment (Roberts, 1999). Heavy metals are also common in industrial applications.

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the human body via food, water, air, or absorption through the skin in agriculture, manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure is common in adults and ingestion the most common route in children (Roberts, 1999). Children may develop toxic levels from normal hand-to-mouth activity (ie, coming in contact with contaminated soil or eating objects that are not food such as dirt or paint chips). Less common routes of exposure include a radiological procedure, inappropriate dosing or monitoring during intravenous (parenteral) nutrition, a broken thermometer or a suicide or homicide attempt (Lupton, 1985; Smith, 1997).

Heavy metals once released into the environment can remain in waterways for decades or even centuries, in concentrations that are high enough to pose a health risk. Several methods are used to clean up the environment from these kinds of contaminants, but most of them are costly and difficult to get optimum results. Currently, phytoremediation is an effective and affordable technological solution used to extract or remove inactive metals and metal pollutants from contaminated soil and water. This technology is environmental friendly and potentially cost effective (Bieby *et al.*, 2011).

2.7 ARSENIC

Arsenic is a chemical element with the symbol As, atomic number 33 and relative atomic mass 74.92. It has a specific gravity 5.73, melting point of 817°C (at 28 atmospheres). It boils at 613°C and a vapor pressure of 1 mmHg at 372°C. Arsenic is a semi metallic element, odorless and tasteless (Mohan *et al*, 2007.). Arsenic is number one on the ATSDR's toxic and hazardous substances “Top 20 List,” and is the most common cause of acute heavy metal poisoning in adults.

2.7.1 EXPOSURE ROUTES FOR ARSENIC TO THE ENVIRONMENT

Arsenic can be found naturally on earth in small concentrations. It occurs in soil and minerals and it may enter air, water and land through wind-blown dust and water runoff. Arsenic in the atmosphere comes from various sources, volcanoes release about 3000 tonnes per year and microorganisms release volatile methylarsines to the extent of 20,000 tonnes per year, but human activity is responsible for much more 80,000 tonnes of arsenic per year are released by the burning of fossil fuels. Arsenic occurs in various organic forms in the environment (Matschullat, 2000). Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation (Reimer *et al*, 2010).

Arsenic is a highly toxic element that exists in various species, despite its notoriety as a deadly poison, arsenic is an essential trace element for some animals, although the necessary intake may be as low as 0.01 mg/day. The toxicity of arsenic depends on its species, the pH, and redox conditions, surrounding mineral composition, and microbial activities affect the form (inorganic or organic) and the oxidation state of arsenic.

In general, inorganic compounds of arsenic are regarded as more highly toxic than most organic forms which are less toxic (Andrianisa *et al.*, 2008).

Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. The arsenic cycle has broadened as a consequence of human interference. Large amounts of arsenic end up in the environment and in living organisms.

Arsenic is released into the environment by the smelting process of copper, zinc, and lead, as well as the manufacturing of chemicals and glasses. Arsine gas is a common byproduct produced by the manufacturing of pesticides that contain arsenic. Arsenic may be also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. (Roberts, 1999; ATSDR, 2011). Arsenic cannot be destroyed once it enters the environment, and can therefore spread and cause health effects to humans and animals on many locations on earth.

2.7.2 HEALTH EFFECTS OF ARSENIC

Arsenic poisoning from naturally occurring arsenic compounds in drinking water remains a problem in many parts of the world. Residents who consumed water that had arsenic level greater than 5 µg/L for ten years or longer were more likely to report a diagnosis of skin cancer, adult onset diabetes, and cardiovascular disease than age-matched residents who drank water that contained no detectable arsenic (Knobeloch, 2002).

Arsenic from drinking water can cause severe skin diseases including skin cancer; lung, bladder, and kidney cancers, and perhaps other internal tumors; peripheral vascular disease; hypertension; and diabetes. It also seems to have a negative impact on reproductive processes (infant mortality and weight of newborn babies) (Hopenhayn, 2006). Arsenic is classified as an established human carcinogen by the International Agency for Research on Cancer. Epidemiologic studies have provided substantial evidence for the association of arsenic in drinking water with cancers of the skin (non-melanoma), lung and bladder. Limited epidemiologic evidence also suggests a possible association of arsenic in drinking water with cancers of the liver, kidney, and prostate (International Agency for Research on Cancer, 1987).

Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. Levels of arsenic in food are fairly high, however, levels of arsenic in fish and seafood may be higher, because fish absorb arsenic from the water they live in. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies. Arsenic is not absorbed very well through the skin. Therefore, exposure from skin contact alone, such as bathing in arsenic-contaminated water, is unlikely to cause health problems (Fact sheet, 2003).

2.8 LEAD

Lead (Pb), has an atomic number 82, atomic weight 207.19, and a specific gravity of 11.34. It is a bluish or silvery-grey metal with a melting point of 327.5°C and a boiling point at atmospheric pressure of 1740°C. It has four naturally occurring isotopes with atomic weights 208, 206, 207 and 204 (in decreasing order of abundance) (Wikipedia).

Lead is number two on the ATSDR's "Top 20 List" of toxic and hazardous substances. Lead accounts for most cases of pediatric heavy metal poisoning (Roberts, 1999). Lead exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace metals. Most of the lead in the environment is in the inorganic form and exists in several oxidized states (Jackson *et al.*, 2005).

2.8.1. EXPOSURE ROUTES FOR LEAD TO THE ENVIRONMENT

The main sources of lead entering an ecosystem are atmospheric lead (primarily from automobile emissions), paint chips, used ammunition, fertilizers and pesticides and lead-acid batteries or other industrial products. The transport and distribution of lead from major emission sources, both fixed and mobile are mainly through air. Lead in the air has come from a variety of sources. Leaded gasoline is the major source of dispersing lead into the human environment. When leaded gasoline is burned, it emits small particles of lead into the air, where they remain for extended periods of time. The lead particles eventually fall out into soil and dust, creating a large amount of lead to continue to poison generations unless covered or removed.

The dispersive nature of leaded gasoline and its long-term effects, the ease with which lead enters the body after it is emitted by motor vehicles, and the vulnerability of at-risk

urban populations, especially children, combine to make elimination of leaded gasoline (Kinder, 2011).

The manufacture of paint containing high concentrations of lead for interior and exterior residential surfaces, toys, and furniture was banned in 1978 by the Consumer Product Safety Commission. Although lead-containing paint was banned for residential use in the United States in 1978, residential paint on older buildings is the most frequent source of lead exposure in young children. Aside from lead paints, lead is emitted into the air from industrial emissions. These industrial sources included smelters, refineries, incinerators, power plants, manufacturing operations, recycling efforts, and hundreds of other sources. Some old homes may have lead water pipes, which can then contaminate drinking water (Kinder, 2011).

Lead in the environment binds strongly to particles, such as soil, sediment and sewage sludge. Because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. It does not bioaccumulate in most organisms, but can accumulate in biota feeding primarily on particles, e.g. mussels and worms. These organisms often possess special metal binding proteins that remove the metals from general distribution in the organism; in humans, lead may accumulate in the bones.

Soil and plants can be contaminated by lead from car exhaust, dust, and gases from various industrial sources. It is found in trace amounts in various foods, notably fish, which are heavily subject to industrial pollution. Most of the lead taken into the human body is removed through urine; however, there is still risk of buildup, particularly in children. (Salem *et al.*, 2000)

Lead is a dangerous element; it is harmful even in small amounts. Lead enters the human body in many ways. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline.

2.8.2 EFFECT OF LEAD ON AQUATIC LIFE

Lead is one the most stable ionic species present in the environment, and is thought to be the form in which the maximum bioaccumulation of lead occurs in aquatic organisms. Lead occurs in a wide range of physical and chemical forms that influence the behavior of fish adversely at concentration higher than normal. One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. However, the toxicity of lead depends upon many factors including fish age, pH and hardness of the water (Nussey *et al.*, 2000). Young stages of fish are more susceptible to lead than adults or eggs. Typical symptoms of lead toxicity include spinal deformity and blackening of the tail region. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment. In aquatic invertebrates, adaptation to low oxygen conditions can be hindered by high lead concentrations.

2.8.3 HEALTH EFFECT OF LEAD

Exposure to lead is cumulative over time. High concentrations of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys (Jennings *et al.*, 1996). This damage commonly results in behavior and learning problems (such as hyperactivity), memory and concentration problems, high blood pressure, hearing problems, headaches, slowed growth, reproductive problems in men

and women, digestive problems, muscle and joint pain. Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Not only does lead poisoning stunt a child's growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children (USGAO). Children are susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity and hypertension (Salem *et al.*, 2000).

According to Salem *et al.*, (2000), strong relationship between contaminated drinking water with heavy metals from some of the Great Cairo Cities, Egypt and chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anemia was identified in their study. These diseases were apparently related to contaminant drinking water with heavy metals such as Pb, Cd, Cu, Mo, Ni, and Cr. Renal failure was related to contaminant drinking water with lead and cadmium, liver cirrhosis to copper and molybdenum, hair loss to nickel and chromium, and chronic anemia to copper and cadmium. Studies of these diseases suggested that abnormal incidence in specific areas was related to industrial wastes and agriculture activities that have released hazardous and toxic materials in the groundwater and thereby led to the contamination of drinking water in those areas.

2.9 MERCURY

Mercury is a naturally occurring metal that is present in several forms. Metallic mercury is shiny, silver-white, odorless liquid. Mercury, which has the lowest melting point (-39°C) of all the pure metals, is the only pure metal that is liquid at room temperature. However, due to its several physical and chemical advantages such as its low boiling point (357°C) and easy vaporization, mercury is still an important material in many industrial products (Chang *et al.*, 2009). Mercury is number three on ATSDR's "Top 20 List" of toxic and hazardous substances. Mercury is generated naturally in the environment from degassing of the earth's crust, from volcanic emissions.

It exists in several forms: elemental or metallic mercury, inorganic mercury compounds, and organic mercury compounds. The most reduced is Hg^0 metal with the other two forms being ionic of mercurous ion and mercuric ion Hg^{2+} , in oxidizing conditions especially at low pH. Hg^+ ion is not stable under environmental conditions since it dismutates into Hg^0 and Hg^{2+} .

2.9.1 EXPOSURE ROUTES FOR MERCURY TO THE ENVIRONMENT

Environmental contamination due to mercury is caused by several industries, petrochemicals and also by agricultural sources such as fertilizer and fungicidal sprays (Resae *et al.*, 2005) Some of the more common sources of mercury found throughout the environment include but may not be limited to the household bleach, acid, and caustic chemicals (e.g., battery acid, household lye, muriatic acid (hydrochloric acid), sodium hydroxide, and sulfuric acid), instrumentation containing mercury (e.g., medical instruments, thermometers, barometers and manometers), dental amalgam

(fillings), latex paint (manufactured prior to 1990), batteries, electric lighting (fluorescent lamps, incandescent wire filaments, mercury vapor lamps, ultraviolet lamps), pesticides, pharmaceuticals (e.g., nasal sprays, cosmetics, contact lens products), household detergents and cleaners, laboratory chemicals, inks and paper coatings, lubrication oils, wiring devices and switches, and textiles. Though mercury use in many of the above items being produced now is restricted or banned, there are still some existing, older products in use (Musselman, 2004). Mining operations, chloralkali plants, and paper industries are significant producers of mercury (Goyer, 1996). Atmospheric mercury is dispersed across the globe by wind and returns to the earth in rainfall, accumulating in aquatic food chains.

Terrestrial plants are generally insensitive to the harmful effects of mercury compounds; however, mercury is known to affect photosynthesis and oxidative metabolism by interfering with electron transport in chloroplasts and mitochondria. Mercury also inhibits the activity of aquaporins and reduces plant water uptake (Sas-Nowosielska *et al.*, 2008).

2.9.2 HEALTH EFFECT OF MERCURY

Mercury and its compounds are cumulative toxins and in small quantities are hazardous to human health. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier and has effect on the brain (Resae *et al.* 2005). Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment. Although its potential for toxicity in highly contaminated areas such as Minamata Bay, Japan, in the 1950's

and 1960's, is well documented, research has shown that mercury can be a threat to the health of people and wildlife in many environments that are not obviously polluted. (USGS, 2000)

The US National Research Council, in its 2000 report on the toxicological effects of methylmercury, pointed out that the population at highest risk is the offspring of women who consume large amounts of fish and seafood. The report went on to estimate that more than 60,000 children are born each year at risk for adverse neuro developmental effects due to in utero exposure to methylmercury. In its 1997 Mercury Study Report to Congress, the U.S. Environmental Protection Agency concluded that mercury also may pose a risk to some adults and wildlife populations that consume large amounts of fish that is contaminated by mercury. Mercury is a persistent environmental pollutant with bioaccumulation ability in fish, animals, and human beings. Mercury salts and organomercury compounds are among the most poisonous substances in our environment (Chang *et al.*, 2009).

2.10 CADMIUM

Cadmium is a chemical element with the symbol Cd and atomic number 48. Cadmium is number seven on ATSDR's toxic and hazardous substances "Top 20 list," and a byproduct of the mining and smelting of lead and zinc. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with zinc. Geologic deposits of cadmium can serve as sources to groundwater and surface water, especially when in contact with soft, acidic waters. There is no evidence indicating its essentiality to humans (Hogan, 2010).

2.10.1 EXPOSURE ROUTES FOR CADMIUM TO THE ENVIRONMENT

Cadium is introduced into the environment from paint and pigments, and plastic stabilizers, mining and smelting operations and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. Cadmium can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that contain cadmium are used in agriculture. Cadmium emissions are also from fossil fuel use and cigarettes. It may enter drinking water as a result of corrosion of galvanized pipe. Cadmium dispersed in the environment can persist in soils and sediments for decades.

2.10.2 HEALTH EFFECTS OF CADMIUM

Webb (1979) reported that geochemical implications of cadmium in human health related to bone and renal disease in populations exposed to industrially contaminated drinking water. Lung and renal dysfunction are reported in industrial workers exposed to air-borne cadmium. In low doses, cadmium can produce coughing, headaches, and vomiting. In larger doses, cadmium can accumulate in the liver and kidneys, and can replace calcium in bones, leading to painful bone disorders and to a renal failure. The kidney is considered to be the critical target organ in humans chronically exposed to cadmium by ingestion (EPA, 1999).

An epidemic occurrence of the Itai-Itai disease was observed in the Jinzu river basin (Japan) in the 1940s. Japanese mining operations contaminated the Jinzū River with cadmium and traces of other toxic metals. As a consequence, cadmium accumulated in

the rice crops growing along the riverbanks downstream of the mines. Some members of the local agricultural communities consuming the contaminated rice developed itai-itai disease and renal abnormalities, including proteinuria and glucosuria (Nogawa *et al.*, 2004). The victims of this poisoning were almost exclusively post-menopausal women with low iron and other mineral body stores. Similar general population cadmium exposures in other parts of the world have not resulted in the same health problems because the populations maintained sufficient iron and other mineral levels. Thus, while cadmium is a major factor in the itai-itai disease in Japan, most researchers have concluded that it was one of several factors (Kirk-Othmer, 1994).

A summary of current knowledge on Cadmium and its effect on health by (Benard, 2008) reveals that cadmium once absorbed, is efficiently retained in the human body, in which it accumulates throughout life. It is primarily toxic to the kidney, especially to the proximal tubular cells, the main site of accumulation. It can also cause bone demineralization, either through direct bone damage or indirectly as a result of renal dysfunction. In the industry, cadmium is hazardous both by inhalation and ingestion and can cause acute and chronic intoxications. Excessive exposures to airborne cadmium may impair lung function and increase the risk of lung cancer.

The most salient toxicological property of cadmium is its exceptionally long half-life in the human body. Once absorbed, it irreversibly accumulates in the human body, in particularly in kidneys and other vital organs such the lungs or the liver. In addition to its extraordinary cumulative properties, cadmium is also a highly toxic metal that can

disrupt a number of biological systems, usually at doses that are much lower than most toxic metals (Nordberg *et al.*, 2007).

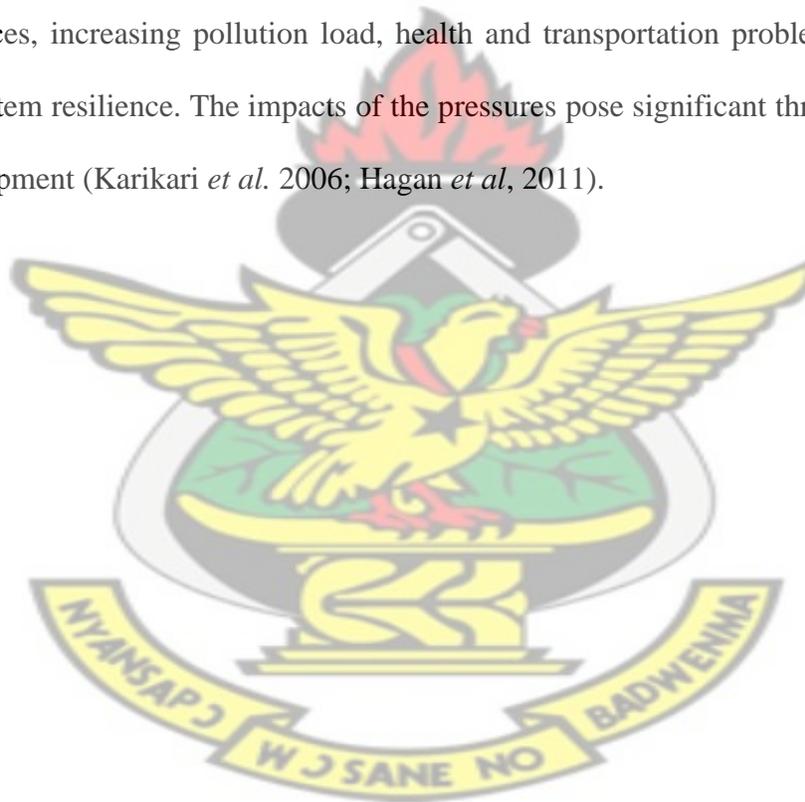
2.11 SURFACE WATER IN GHANA

Surface water covers five percent of total area of the country. Surface water is one of the major water resources which provide fresh water for industrial and domestic use, irrigation as well as livelihoods for a number of people who are engaged in fishing along its banks and also an important transportation link between southern and northern Ghana. Water bodies in Ghana include the largest man-made lake in the world, the Lake Volta (4% of the total land area), the natural lake, Bosumtwi, Densu River and others. Rainwater harvesting serves as the major source of surface water for many rural communities during the rainy season. Small-scale and illegal artisanal mining have adverse impacts on the environment. Mercury pollution is a threat on water bodies due to illegal artisanal mining. Several communities in mining areas have their water sources polluted. In mining areas in Obuasi and Prestea, high levels of arsenic have been recorded in ground waters and high cyanide level at Sumang. High arsenic levels of 40.5-1290mg/L have been observed in the Pra Basin (Roosbroeck *et al.*, 2006; Karikari *et al.* 2006).

Rivers and lagoons located near industrial areas are dying as a result of the discharge of untreated industrial and domestic effluent leading to nutrient enrichment and odor. Untreated domestic waste water is discharged into the nearest lagoon or the Gulf of Guinea via water ditches on the roadsides which could impact negatively on the quality of the water body. Climatic variability has also modified freshwater resources. The outbreak of diseases indicates lack of drinkable water and means of sanitation. Cholera

is endemic in Greater Accra and Central regions at the peak of the rainy and dry seasons. The incidence of guinea worm is linked to safe water availability and it is endemic to the Northern, Volta and Brong Ahafo regions (Roosbroeck *et al.*, 2006).

Fresh water resources of Ghana are at risk of scarcity because of inappropriate management, high rates of logging, fuel wood extraction, poor agricultural practices, surface mining and desertification leading to increasing poverty and sensitivity to human and natural disasters. These have resulted in the dwindling of freshwater resources, increasing pollution load, health and transportation problems and reducing ecosystem resilience. The impacts of the pressures pose significant threat to sustainable development (Karikari *et al.* 2006; Hagan *et al.*, 2011).



CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 STUDY AREA

The Densu River, a major source of water for treatment and supply of pipe borne water to the Accra metropolis takes its source from the Atewa-Atwiredu mountain ranges in the Eastern region of Ghana. It has a catchment area of 2564km² and 116km long, and its basin lies between latitudes 5°30' N to 6°20' N and longitude 0°10' W to 0°35'W and shares its boundary with the Odaw and Volta basins to the east and north, respectively, the Ayensu and Okrudu to the west and the Birim basin to the northwest. The basin is underlain by crystalline rocks, comprising five formations, namely Birimian, super group intruded by Granites, Togo series, and Dahomeyan and Accraian sediments (Amuzu, 1975).

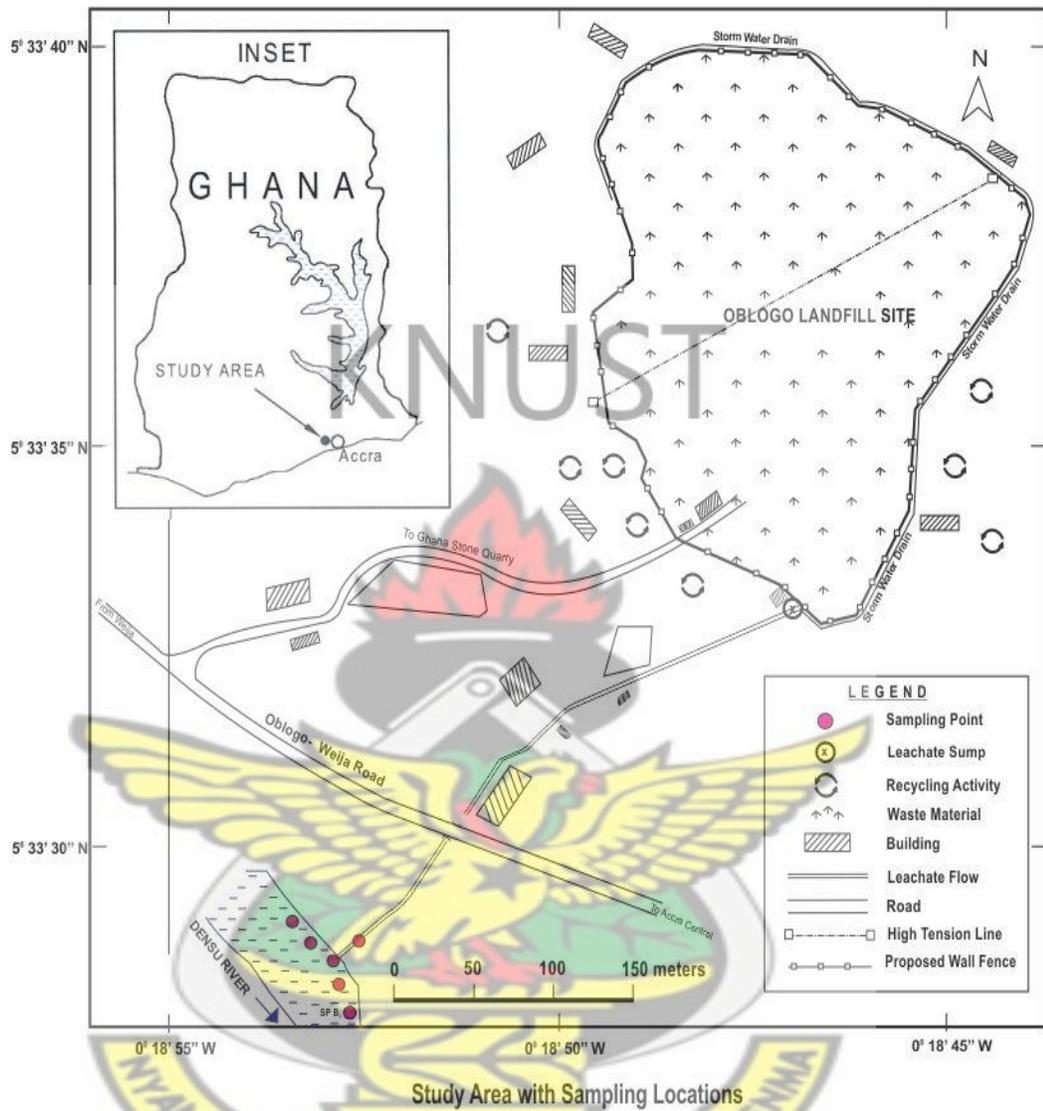
The recipient downstream of the Densu River in Accra is the Weija reservoir which is one of the main sources of water supply for the city of Accra. Accra is one of the most populated and fast growing Metropolis in Ghana with a population of one million eight hundred and forty-eight thousand six hundred and fourteen (1,848,614) people (Ghana Statistical Services, 2010). Oblogo landfill, an abandoned stone quarry which was used in early 2002 as a landfill, was one of the main recipients of waste from the city of Accra-Ghana. It is situated north of an ecologically important wetland where the Densu River runs through. Leachate from the landfill flows down slope directly south to enter the Densu River. Communities around the Densu River abstract water from the river for human and animal consumption.

3.1.1 SAMPLING SITES

Five sampling sites along the Densu River in Weija were selected for the study (as shown in Figure 3.1 and 3.2) , a hundred and two hundred metres upstream from the leachate entry site, a hundred and two hundred metres downstream from the leachate entry site and just at leachate entry into the river.

3.1.2 SAMPLING

Water and sediment samples were collected monthly from each of the five sampling sites from January to March 2012. Samples were collected along the river with the aid of a canoe. Water samples were collected at the water surface using 350ml HDPE (high density polyethylene) bottles. Water sampling bottles were rinsed twice with the water before sampling was done at each site. Sediment samples were also collected in plain sterile polyethylene bags using a plastic pipe to scoop sediment. The bags were sealed and transported together with the water samples in an ice chest to the laboratory. Five water and five sediment samples were collected from each site (duplicate water samples on each sampling occasion was taken for on-site measurement of pH, Total Dissolved Solids (TDS) and Electrical Conductivity using a portable meter) monthly during the study period. A sample of the leachate was also taken. Water and leachate samples were acidified with concentrated nitric acid, well labeled, kept over ice in ice chest according to the standard method (APHA, 1995) to maintain them at a temperature below 4 °C during transfer from the field to the laboratory.



Source: Journal of Water Resource and Protection, 2012,

Figure 3.1: A map of the study area showing the sampling sites.

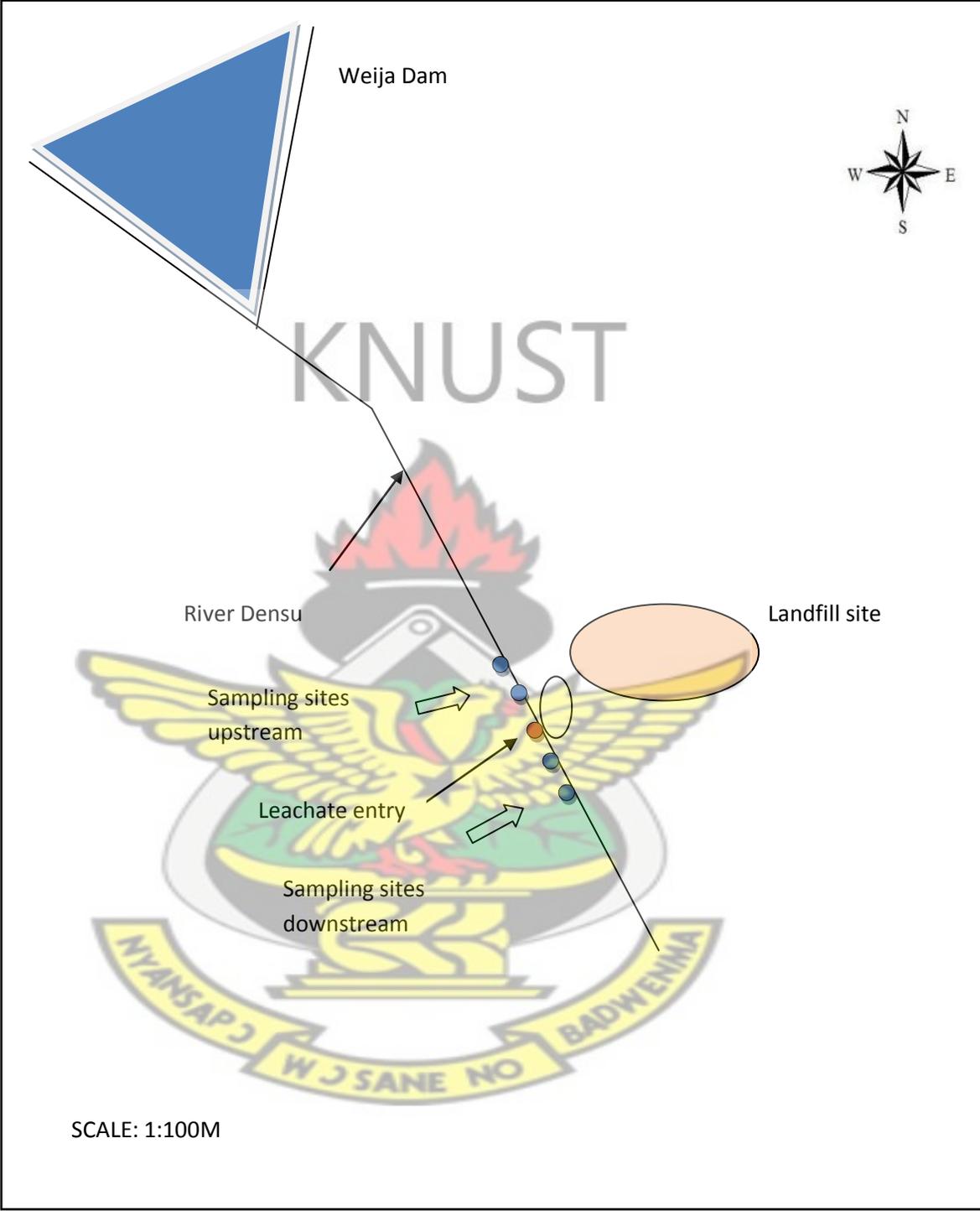


Figure 3.2: The study area showing sampling sites

3.1.3 SAMPLE PREPARATION

Sediment samples were air dried for a week in a clean environment with organic debris picked from the samples. The samples were crushed with a mortar and pestle and sieved using 0.5mm mesh size.

They were sealed and labeled in polyethylene bag awaiting digestion prior to metals analysis. Water and leachate samples for metal analysis were filtered through a funnel with a Whatman No. 41 filter paper.

3.1.4 MEASUREMENT OF pH, CONDUCTIVITY AND TDS

The physical parameters were determined by probe method on the field. Temperature, pH, Electrical Conductivity (EC) and TDS (Total Dissolved Solids) were determined with a portable Hanna HI98129/30 pH meter.

3.2 SAMPLE ANALYSES

3.2.1 DIGESTION PROCEDURE FOR WATER

Metal digestion was done using the Milestone Acid digestion method. Five millilitre of each water sample was pipetted into 20ml teflon tube. Concentrated acids of 6ml nitric acid (HNO_3 , 65%), 3ml of hydrochloric acid (HCl , 37%) and 0.25ml hydrogen peroxide (H_2O_2) were added to each sample. A blank was prepared using 6ml HNO_3 (65%), 3ml of HCl (37%) and 0.25ml H_2O_2 . The samples were placed in an ETHOS 900 microwave digester for thirty minutes. After digestion, the samples were allowed to cool to room temperature and the solutions then diluted to 20 ml with distilled water. The liquid extract was then used for the determination of arsenic, lead, cadmium and

mercury using VARIAN AA240FS Fast Sequential Atomic Absorption Spectrometer under the recommended instrument parameters (Table 3.1). The same digestion process carried out on the leachate samples. Two standard reference materials - IAEA 356 from the National Institute of Standards and Technology, USA, and NIVA SLP 0838 PROVE I from Norway were used for the validation of the analytical results.

The concentration of each metal was calculated using the formula below:

Final concentration (mg/l) = concentration of metal x dilution factor x nominal volume/Sample volume (ml).

The same digestion process carried out on the water samples was repeated for the leachate samples.

3.2.2 DIGESTION PROCEDURE FOR SEDIMENT

Sediment samples (1.5g) were weighed into a 20 ml teflon tube and concentrated acids of 6 ml nitric acid (HNO₃, 65%), 3 ml of hydrochloric acid (HCl, 37%) and 0.25ml hydrogen peroxide (H₂O₂) were added to each sample. The samples were placed in an ETHOS 900 microwave digester for thirty minutes and solution allowed to cool to room temperature. About 5 ml of distilled water was added to each sample and then filtered through a funnel with a Whatman No. 41 filter paper into 20 ml teflon tube. The solution was then diluted to 20 ml with distilled water. The liquid extract was then used for the determination of arsenic, lead, cadmium and mercury using VARIAN AA240FS Fast Sequential Atomic Absorption Spectrometer under the recommended instrument parameters (Table 3.1).

The concentration of each metal was calculated using the formula :

Final concentration (mg/kg) = concentration of metal x dilution factor x nominal volume/Sample weight (g).

Table 3.1 Recommended instrument parameters for Atomic Absorption Spectrometer

Element	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Fuel	Support
Lead	217	1	5	acetylene	air
Cadmium	228.8	0.5	4	acetylene	air
Arsenic (bihydrate)	193.7	0.5	10	acetylene	air
Mercury	253.7	0.5	4	No flame	air

3.3 CONTAMINATION FACTOR

The contamination factor (CF) which gives an indication of the level of contamination, was computed for the sediments using the concentration of the heavy metals and their corresponding values in the world average shale reported by Turekian *et al* (1961). The level of contamination of sediment by a metal is often expressed in terms of a contamination factor calculated as follows,

Contamination Factor (CF) = Metal content in the sediment/Background level of metal

Where $CF < 1$ refers to low contamination, $1 \geq CF \geq 3$ means moderate contamination, $3 \geq CF \geq 6$ indicates considerable contamination, and $CF > 6$ indicates very high contamination.

3.4 STATISTICAL ANALYSIS

The data obtained from the chemical analysis were subjected to descriptive statistical analysis (mean, range and standard deviation at 95% confident limit).

CHAPTER FOUR

4.0 RESULTS

4.1. QUALITY OF LEACHATE FROM LANDFILL

Leachate from the Oblogo landfill site, an abandoned stone quarry which since 2002 has been used as a landfill, was detected to be high in heavy metals concentration. Mean concentrations of arsenic, lead, mercury and cadmium were 0.026mg/l, 0.957mg/l, 0.025mg/l and 0.005mg/l, respectively (Table 4.1, 4.2, 4.3 and 4.4). These levels of heavy metals contained in the leachate from the landfill site seeps into the River Densu.

Table 4.1 Mean concentration (mg/l), Standard Deviation(SD) and Range of Arsenic in the River water

Sampling Site	Mean \pm SD	Range
Leachate	0.026 \pm 0.006	0.021-0.032
Just at leachate entry	0.015 \pm 0.008	0.010-0.024
200m upstream	0.003 \pm 0.005	<0.001-0.008
100m upstream	0.007 \pm 0.006	<0.001-0.012
100m downstream	0.012 \pm 0.007	0.004-0.017
200m downstream	0.008 \pm 0.006	0.001-0.014

4.2 QUALITY OF RIVER DENSU UPSTREAM

Heavy metal concentration in River Densu, two hundred and a hundred metres upstream before it gets polluted by the leachate from the landfill site was low; arsenic

concentration two hundred metres upstream was 0.003mg/l but increased to 0.007mg/l at a hundred metres.

A similar trend was observed for lead; two hundred metres upstream was <0.001mg/l and at hundred metres upstream off the leachate entry point was 0.008mg/l (Table 4.2).

Mean mercury concentration in the river at hundred and two hundred upstream was below detection limit of <0.001 (Table 4.3). Cadmium was also below the detection limit of <0.002mg/l at both points (Table 4.4). These heavy metal concentrations in the Densu before entry of the leachate were within the WHO, EU and USEPA stipulated limits for drinking water.

Mean arsenic levels in the river sediment samples at a distance of two hundred metres before the leachate entry was <0.001mg/kg. This concentration however increased to 0.018mg/kg at a hundred metres distance (Table 4.5). Lead levels in the sediments at

Table 4.2 Mean concentration (mg/l), Standard Deviation (SD) and Range of lead in the River water

Sampling Site	Mean± SD	Range
Leachate	0.957±0.041	0.912-0.994
Just at leachate entry	0.839±0.047	0.798-0.891
200m upstream	<0.001	-
100m upstream	0.008±0.007	<0.001-0.014
100m downstream	0.564±0.121	0.436-0.676
200m downstream	0.393±0.144	0.244-0.532

Below detection limit, <0.001

hundred metres had a mean concentration of 0.607mg/kg. Mercury at a hundred metres distance was 0.009mg/kg whilst that of cadmium was 0.124mg/kg (Table 4.6).

4.3 QUALITY OF RIVER DENSU AT LEACHATE ENTRY POINT

At the point where the leachate from the landfill site enters the Densu River, arsenic concentration in the river itself was 0.015mg/l which was almost a fifty percent decrease compared to arsenic levels in the actual leachate (0.01-0.024mg/l) (Table 4.1). Similarly, mean lead and mercury concentrations were 0.839mg/l and 0.014mg/l (Table 4.2 and 4.3). Cadmium was however not detected (below detection limit of <0.002mg/l) at the point (Table 4.4).

Heavy metal concentrations in the sediment samples were generally higher than in the overlying water. This trend was observed in all the sampling sites with low levels of metals in the river water corresponding to high levels in sediment. Mean arsenic, lead, mercury and cadmium in sediment samples were 0.066, 0.759, 0.044 and 0.178mg/kg, respectively (Table 4.5- 4.8).

Table 4.3 Mean concentration (mg/l), Standard Deviation and Range of Mercury in the River water

Sampling Site	Mean± SD	Range
Leachate	0.025±0.004	0.022-0.029
Just at leachate entry	0.014±0.003	0.011-0.016
200m upstream	<0.001	-
100m upstream	<0.001	-
100m downstream	0.007±0.002	0.004-0.009
200m downstream	0.001±0.002	<0.001-0.004

Below detection limit, <0.001

4.4 DOWNSTREAM QUALITY OF RIVER DENSU

Further downstream after the entry of leachate, mean concentration of arsenic at a hundred metres from the leachate entry was 0.012mg/l and decreased to 0.008mg/l at a distance of two hundred metres. This decrease in concentration was about one and half times the concentration at a distance of two hundred metres. Mean lead concentration was 0.564mg/l at a distance of a hundred metres and a range of 0.436-0.676mg/l. This concentration decreased at a distance of two hundred metres to 0.393mg/l with a range of 0.244 to 0.532mg/l (Table 4.2). The concentration of lead downstream far exceeds the WHO, EU and USEPA stipulated limits of 0.01, 0.01 and 0.015mg/l respectively for drinking water (Table 4.10).

The mean concentration of mercury in the river water at a hundred metres distance was 0.007mg/l with a range of 0.004 to 0.009mg/l. This decreased to 0.001mg/l at two hundred metres distance (Table 4.3). Cadmium was below detection limit of <0.002mg/l at both distances of a hundred and two hundred metres (Table 4.4).

Table 4.4 Mean concentration (mg/l), Standard Deviation (SD) and Range of Cadmium in the River water

Sampling Site	Mean \pm SD	Range
Leachate	0.005 \pm 0.005	<0.002-0.010
Just at leachate entry	<0.002	-
200m upstream	<0.002	-
100m upstream	<0.002	-
100m downstream	<0.002	-
200m downstream	<0.002	-

Mean arsenic levels in sediment samples at a distance of a hundred metres was 0.031mg/kg. The concentration however decreased to 0.015mg/kg at two hundred metres distance (Table 4.5). Mean lead concentration in sediment samples was 15.77mg/kg at hundred metres which decreased to <0.001 mg/kg at two hundred metres with mercury recording 0.004mg/kg and cadmium 0.151mg/kg at two hundred metres.

4.5 PHYSICAL PARAMETERS OF RIVER DENSU

The river water is near neutral with a pH range of 7.61 to 7.74 for samples upstream and downstream whilst the leachate recorded a pH of 8.80. (Table 4.9) The pH of the river water was within the range of 6.5- 8.5 stipulated for drinking and domestic purpose (WHO, 1993). Electrical Conductivity (EC) ranges from 950 to 985 μ s/cm which exceeded the WHO limit of 700 μ s/cm with the leachate recording 1589 μ s/cm.

Table 4.9 Mean physical parameters of the Densu River water

Sampling Site	pH	EC (μ s/cm)	TDS (mg/l)
Leachate	8.8	1589	2950
Just at leachate entry	7.74	985	482
200m upstream	7.61	962	469
100m upstream	7.64	950	464
100m downstream	7.69	982	479
200m downstream	7.64	974	476

The range of Total Dissolved Solids (TDS) was from 464 to 482mg/l and 2950mg/l for leachate. Total Dissolved Solids (TDS) of the river water was within the WHO

guideline value of 1000mg/l except the leachate. There was no floating material in the water sample indicating absence of oil and grease.

Table 4.5

Mean concentration (mg/kg), Standard Deviation (SD) and Contamination factor (CF) of Arsenic levels in sediment		
Sampling Site	Mean \pm SD (mg/kg)	CF
200m upstream	<0.001	0.000
100m upstream	0.018 \pm 0.008	0.001
Just at leachate entry	0.066 \pm 0.004	0.005
100m downstream	0.031 \pm 0.008	0.002
200m downstream	0.015 \pm 0.027	0.001

Below detection limit, <0.001

Table 4.6

Mean concentration (mg/kg), Standard Deviation(SD) and Contamination factor (CF) of Lead in sediment		
Sampling Site	Mean (mg/kg)	CF
200m upstream	<0.001	0.000
100m upstream	0.607 \pm 0.541	0.030
Just at leachate entry	0.759 \pm 0.045	0.038
100m downstream	15.778 \pm 3.377	0.789
200m downstream	<0.001	0.000

Table 4.7
Mean concentration (mg/kg), Standard Deviation (SD) and Contamination factor(CF) of Mercury in sediment

Sampling Site	Mean (mg/kg)	CF
200m upstream	<0.001	NA
100m upstream	0.009±0.008	NA
Just at leachate entry	0.044±0.008	NA
100m downstream	0.009±0.008	NA
200m downstream	0.004±0.005	NA

Below detection limit, <0.001

NA-Not Available

Table 4.8
Mean concentration (mg/kg), Standard Deviation(SD) and Contamination factor (CF) of Cadmium in sediment

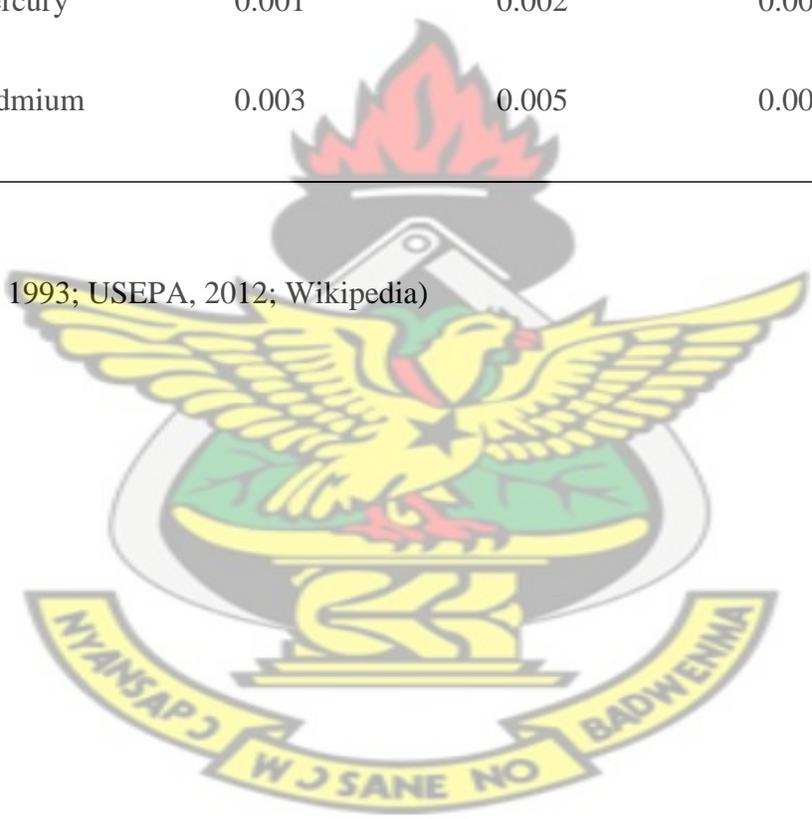
Sampling Site	Mean (mg/kg)	CF
200m upstream	0.066±0.041	0.220
100m upstream	0.124±0.021	0.413
Just at leachate entry	0.178±0.012	0.593
100m downstream	0.471±0.028	1.570
200m downstream	0.151±0.077	0.503

Table 4.10. Drinking water quality standards/guidelines

in mg/l

Element	WHO	USEPA	EU
Arsenic	0.01	0.01	0.01
Lead	0.01	0.015	0.01
Mercury	0.001	0.002	0.001
Cadmium	0.003	0.005	0.005

(WHO, 1993; USEPA, 2012; Wikipedia)



CHAPTER FIVE

5.0 DISCUSSION

This study has shown that leachate from the Oblogo landfill site substantially increases the heavy metal concentration in the Densu River. Levels of arsenic, lead, mercury and cadmium in the leachate were high and did exceed the permissible levels set by the WHO, EU and USEPA.

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5.1 QUALITY OF RIVER DENSU UPSTREAM

Mercury and cadmium levels at a hundred and two hundred metres upstream before the leachate discharge point were low and below detectable limit of $<0.001\text{mg/l}$ and $<0.002\text{mg/l}$ respectively (Table 4.3 and 4.4). Arsenic and lead were detectable probably from the diffusion of leachate within the water and also the channelling of residential waste water into the river. Similarly, the concentration of heavy metals in the sediments upstream was generally low with the contamination factor less than one ($\text{CF}<1$).

According to Karikari *et al.* (2006) the Densu River could be generally classified as a good source of water supply along most of its stretches though areas around Nsawam Bridge fall into the poor water quality category (Amuzu, 1975). Due to the growing population densities, progressive industrialization and intensification of agricultural activities, the Densu River is presently one of the most polluted rivers in the country (WRC, 2000). Karikari *et al.* (2006) also reported that the heavy metal levels in the Densu River were below their background levels and WHO guideline (Cu, Zn, Pb) hence there was no danger with respect to these metals. However, Hagan *et al.* (2011) reported iron (Fe) levels in the Densu River to be above the WHO standard for drinking

water which may have adverse effects on the health of users of the water without treatment over a long period of time. It also reported lead levels to be above the WHO limits in the river after leachate discharge.

The pH and TDS of the river water were within the WHO, EU and USEPA permissible limits. However, high EC was an indication of higher ionic concentration probably resulting from the underlying geology of the area and strong anthropogenic activities.

5.2 QUALITY OF LANDFILL LEACHATE

The leachate recorded high pH, TDS and conductivity values with mean concentration of arsenic, lead, mercury and cadmium recording 0.026mg/l, 0.957mg/l, 0.025mg/l and 0.005mg/l, respectively.

Comparing this study to Nyame *et al.*, (2012), leachate in this present study had lower conductivity and TDS, with generally low metal levels except lead. The metal levels were above the WHO guideline values. An earlier work by Osei *et al.*, (2011) showed that the landfill leachate at Oblogo had relatively high metal levels which were attenuated by the sediments in the wetland. The landfill was therefore not well located as it generates nuisances and leachate which was deteriorating the Densu river quality.

Municipal landfill leachates which are highly concentrated complex effluents contain dissolved organic matter; inorganic compounds, such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides and heavy metals such as cadmium, chromium, copper, lead, nickel, zinc among others which could impact negatively on the environment when left untreated. The discharge of untreated leachate either directly or indirectly through runoffs, into water bodies may result in high BOD

level and low level of dissolved oxygen an indication that the water may not support aquatic life sufficiently.

Heavy metals present could pose a health hazard to users of these contaminated water bodies (Christensen *et al.*, 1998; Akoteyon *et al.*, 2011).

5.3 QUALITY OF RIVER DENSU DOWNSTREAM

The leachate flow into the Densu River resulted in elevated levels of heavy metals in the water. However these levels decreased with increasing distance downstream from the leachate entry point through dilution (Nyame *et al.*, 2012). The heavy metal levels at hundred metres after the entry of leachate were 0.012, 0.546, 0.007 and <0.002mg/l for arsenic, lead, mercury and cadmium respectively and these were within the WHO, EU, USEPA and GEPA limits for drinking water except lead (Figure 5.1, 5.2 and 5.3). Following further dilution downstream and deposition, at two hundred metres, 0.008, 0.393, 0.001 and <0.002mg/l for arsenic, lead, mercury and cadmium respectively were recorded. Lead levels exceeded the standard limit of 0.01 mg/l stipulated by WHO. Communities around this sampling site use the water for drinking and crop irrigation.

In a report on four notable water bodies that flows through the Accra Metropolis, all were found to be flowing through some solid waste dump sites namely Lafa, Bale, Densu (Oblogo) and Gbegbe Lagoon (Glefe) (Nartey *et al.*, 2012). Among the water bodies, Densu recorded the lowest lead concentration which was within the WHO limit. However, this research detected high lead levels which could be attributed to accumulation in the water body.

Heavy metal poisoning particularly lead and cadmium has been reported to give rise to chemical syndromes; cadmium accumulation is associated with hypertension, osteomalacia and itai-itai disease (Nogawa *et al.*, 2004) and lead poisoning has been found to be associated with permanent brain damage, behavioral disorders and impaired hearing. The major effects of mercury poisoning manifest as neurological and renal disturbances because it can easily pass the blood-brain barrier and affect the brain (Resae *et al.*, 2005). Arsenic in drinking water can cause severe skin diseases including skin cancer as well as lung, bladder, and kidney cancers, and perhaps other internal tumors, peripheral vascular disease, hypertension and diabetes. It also has a negative impact on reproductive processes (infant mortality and weight of newborn babies) (Hopenhagen, 2006).

Heavy metal levels in the sediment samples were higher than the overlying water. This is because sediments are a major depository of metals, in some cases holding up to 99% of the total amount of metals present in a system (Ademoroti, 1996; Garbarino *et al.*, 1995). Secondly, heavy metals dissociate from its complexes and come into solution at low pH while at high pH, little or no heavy metals dissociate but rather settle to the bed of the river water body in the form of a heavy metal complex (Sarpong *et al.*, 2009). The study recorded higher levels of heavy metal concentration in areas where the water pH was high or basic. Although the metal levels in sediment were high, the contamination factors computed were less than one ($CF < 1$) except cadmium which recorded 1.57. Arsenic and lead contamination in sediments in River Densu were low at all the sampling sites whilst cadmium was moderate. (The world average shale

concentration of elements by Turekian *et al.*, (1961) was used as background values however, it was unavailable for mercury.

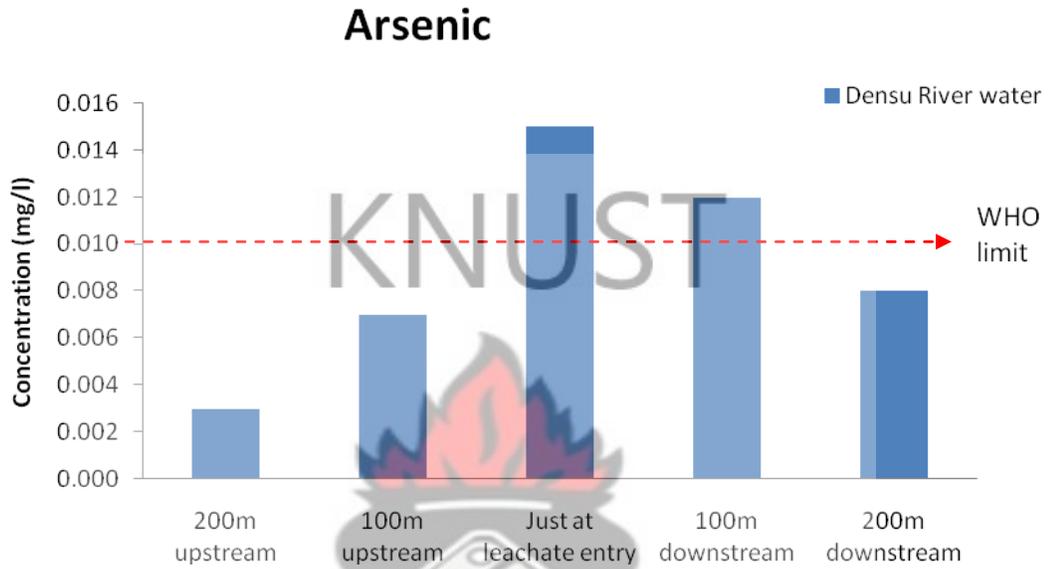


Figure 5.1 Arsenic level in the Densu River

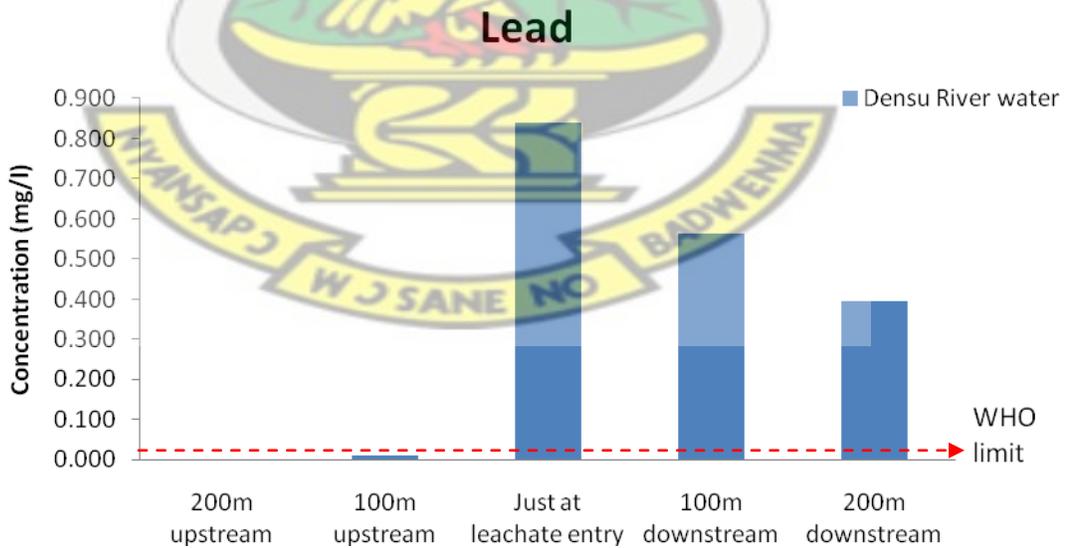


Figure 5.2 Lead level in the Densu River

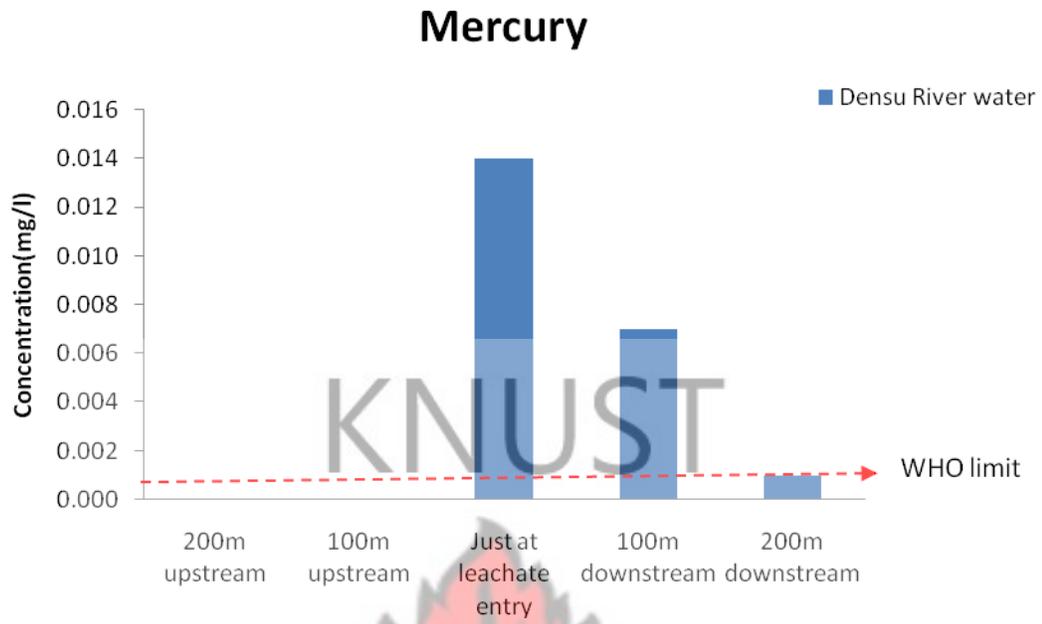
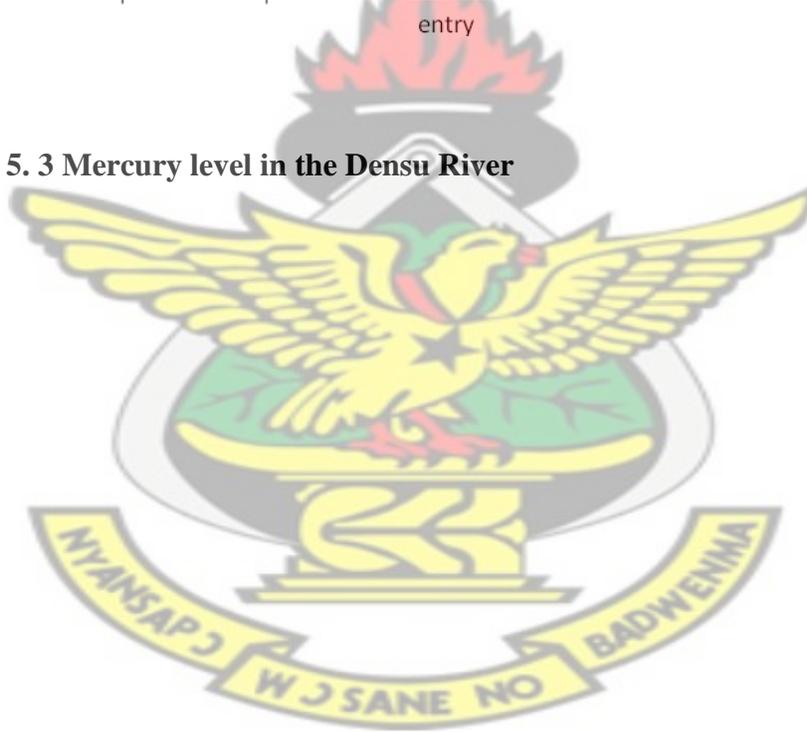


Figure 5.3 Mercury level in the Densu River



CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

Mean heavy metals concentration in the River Densu upstream before the leachate discharge point was generally very low and below detection limit. However, levels of heavy metals in the leachate and the river downstream were very high. Heavy metals concentration in the river sediments was moderate for cadmium and low for arsenic and lead. The study has shown that levels of arsenic, cadmium and mercury in the River Densu conform to the WHO maximum permissible limits. The research findings made it clear that the contamination of this water body with these heavy metals was primarily due to the leachate discharged.

6.2 RECOMMENDATION

Densu serves as a major fishing, drinking and irrigation water resource for people living along the banks of the entire stretch of the river in Ghana. Apparently anthropogenic activities threaten the sustainability of this resource, hence the need for proper monitoring and enforcement of water resource management regulations by the authorities concerned to ensure the quality of the Densu River. There should be increased environmental sanitation education by district assemblies in communities along the bank to prevent contamination of this water resource and subsequent transmission of water-related diseases.

REFERENCES

- Abbasi, S. A., Abbasi, N., Soni, R., (1998). Heavy metal in the environment, 1st. Ed., Mital Publication, New Delhi, India, pages 6-9
- Ademoroti, C. M. A (1996), Environmental Chemistry and Toxicology. Fodulex press Ltd. Ibadan, pp. 79-121.
- Adomako, D., Nyarko, B. J. B., Dampare, S. B., Serfor-Armah Y., Fianko, J. R. and Akaho, E. H. K. (2008). Determination of toxic elements in waters and sediments from Subin in the Ashanti Region of Ghana. *Environ. Monit. Assess*; 141:165-175.
- Agbozu, I.E., Ekweozor A. and Opuene, K.(2007). Survey of heavy metals in the catfish (Synodontisclarias), *International Journals of Environmental Science and Technology*.4: 93-97.
- Akoteyon, I.S., Mbata, U.A. and Olalude, G.A.(2011). Investigation of heavy metal contamination in groundwater around landfill site in a typical sub-urban settlement in Alimosho, Lagos-Nigeria. *Journal of Applied Sciences in Environmental Sanitation*. 6(2): 155 – 163.
- Amman, A. A.; Michalke, B.; Schramel, P., (2002). Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. *Anal. Biochem.*, 372: 448-452.
- Amuzu A.T., (1975). Survey of water quality of the River Densu. A research report presented to the Water Resources Research Unit of the CSIR, Accra, Ghana, 556.114 (667) pp. 56
- Anomanyo, E.D., (2004). Integration of municipal solid waste management in Accra (Ghana): Bioreactor treatment technology as an integral part of the management process. M.Sc. Thesis, Lund University, Lund, Sweden.24
- Andrianisa H.A , Ito A., Sasaki A, Aizawa J., and Umita T.,(2008), Biotransformation of arsenic species by activated sludge and removal of bio-oxidised arsenate from wastewater by coagulation with ferric chloride, *Water Research*, 42(19): 4809–4817.
- APHA (1995). Standard methods for the examination of water and waste water, 19th. Ed, American Public Health Association, American Water Works Association & Water Environment Federation, Washington, DC.
- ATSDR,(2011) Agency for Toxic Substances and Disease Registry , 4770 Buford Hwy NE Atlanta, GA 30341.(Oct 2011 update). (<http://www.atsdr.cdc.gov/SPL/index.html>). (Accessed: 2012 August 3)
- Benard A, (2008), Cadmium and its adverse effect on health, Department of Public Health, *Indian J Med Res* , India, p 557-564

Bernard A. (2004), Renal dysfunction induced by cadmium: biomarkers of critical effects. *Biometals; Indian J Med Res*, 17 : 519-23.r

Bieby V.T., Abdullah S. R .S Basri H , Idris M, Anuar N, and Mukhlisin M. ,(2011). A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation, *International Journal of Chemical Engineering* 1: Bangin , Malaysia

Bruins, M. R.; Kapil, S.and Oehme, F. W., (2000). Microbial resistance to metals in the environment. *Ecotox. Environ.Safe.* 45: 198-207

Chang T.C, You S. J., Yu B. S., Chen C. M., and Chiu Y. C.,(2009). Treating high-mercury-containing lamps using full-scale thermal desorption technology, *Journal of Hazardous Materials*, 162(2-3): 967–972.

Christensen, J. B., Jensen D. L., Gron C., Filip Z. and Christensen T. H., (1998): Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater, *Water Res.*, 32: 125-135.

Dickson, K.B. and Benneh .G. (1980). A New Geography of Ghana, Longman Group Ltd., London. Page 48

EPA, U.S. (1999): Drinking water and Health. EPA816-k-99-001.<http://www.doh.wa.gov/epa/water.htm>(Assessed: 2011 March 7)

Fact Sheet, (2003). Arsenic in the environment ,Washington State Department of Health : <http://www.doh.wa.gov/ehp/factsheets.htm> . (Assessed: 2011 March 11).

FAO (1992). Committee for Inland Fisheries of Africa. Report of the third session of the Working Party on Pollution and Fisheries. Accra, Ghana, p 25-29,

Fernandes C, Fontainhas-Fernandes A., Peixoto F. and Salgado M.A (2007). Bioaccumulation of heavy metals in *Liza saliens* from the Esomriz-Paramos coastal lagoon, Portugal. *Ecotox. Environ. Saf.* 66: 426-431.

Ghana Statistical Service (2010). Ghana Population and Housing Census 2010, http://www.statsghana.gov.gh/docfiles/2010phc/Census2010_Summary_report_of_final_results.pdf (Assessed: 2012 March 15).

Giguere A, Campbell P.G, Hare L, McDonald D.G, and Rasmussen J.B (2004). Influence of lake chemistry and fish age on cadmium, copper and zinc concentrations in various organs of indigenous yellow perch (*Perca flavescens*). *Cand. J. Fish. Aquat. Sci.* 61: 702-716.

Goyer, R.A.(1996). Toxic effects of metals: mercury. Casarett and Doull's Toxicology: The Basic Science of Poisons, Fifth Edition 1996. New York: McGraw-Hill.

Gupta A, Rai D.K, Pandey R.S, and Sharma B (2009). Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. *Environ. Monit. Assess.* 157: 449-458.

Hagan G.B., Ofosu F.G., Hayford E.K., Osa E.K. and Oduro-Afriyie K. (2011), Heavy Metal Contamination and Physico-Chemical Assessment of the Densu River Basin in Ghana, *Research Journal of Environmental and Earth Sciences* 3(4): 385-392,

Hochanadel, D. (2010). Limited amount of total phosphorus actually feeds algae, study finds. *Lake Scientist*. <http://www.lakescientist.com/2010/limited-amount-of-total-phosphorus-actually-feeds-algae-study-finds>.

Hogan, C.M. (2010). Encyclopedia of Earth, National Council for Science and the Environment, Washington DC.

Hopenhayn, C. (2006). Mineralogical Society of America, Arsenic in Drinking Water: Impact on Human Health, *Int. J. Environ. Res. Public Health* 3 (4): 316–22.

International Agency Research Cancer Monographs on the Evaluation of the carcinogenic Risks to Humans, Beryllium, Cadmium, mercury and Exposures in the Glass manufacturing Industry, Vol. 58. World Health Organization, Lyon, France, (1993).

International Agency for Research on Cancer; (1987). (IARC) Monographs on the Evaluation of the Carcinogenic Risk to Humans: Arsenic and arsenic compounds, Lyon.

Jackson, R.N., Baird D. and Els S.. (2005). The effect of the heavy metals, lead (Pb²⁺) and zinc (Zn²⁺) on the brood and larval development of the burrowing crustacean *Callianasskraussi*. *Water S.A.*, 31(1): 107-116.

Jain, V. K., (1978). Studies on effect of cadmium on the growth pattern of phaseolusaurius varieties, *JIBS*, 57-84.

Järup L, Berglund M, Elinder C.G, Nordberg G, and Vahter M.(1998), Health effects of cadmium exposure - a review of the literature and a risk estimate. *Scand J Work Environ Health*; 24(Suppl 1) : 1-51.

Jennings, G., D.; Sneed, R., E.; Clair, M., B., St., (1996), Metals in drinking water, North Carolina Cooperative Extension service Publication no.: AG-473-1.

Johnson, F. M., (1998). The genetic effects of environmental lead., *Mutat. Res.*, 410: 123-140.

Johnson, D.L., Ambrose S.H., Bassett T.J., Bowen M.L., Crummey D.E., Isaacson J.S., Johnson D.N., Lamb P., Saul M., and Winter-Nelson A.E. (1997). Meanings of environmental terms. *Journal of Environmental Quality*. 26: 581-589.

Johnson, C. L., (2004). The environmental Sources toxicities, and prevention exposure. *Pediatr Ann.* 33(7), 437-442

Kar, D.; Sur, P.; Mandal, S. K.; Saha, T.; Kole, R. K., (2008). Assessment of heavy metal pollution in surface water. *Int. J. Environ. Sci. Tech.*, 5(1): 119-124.

Karikari, A.Y. and O.D. Ansa-Asare, (2006). Physicochemical and microbial water quality assessment of the Densu River of Ghana. *West Afr. J. Appl. Ecol.*,10: 87-100.

Kinder Carolyn, Lead Contamination In Our Environment, <http://www/sources/lead/environment.html> (Assessed 2012 July 26)

Kirk-Othmer Encyclopedia of Chemical Technology, (1994), (4-th edition).John Wiley & Sons., New York:

Knobeloch Lynda ,(2002), Health Effects of Arsenic Contaminated Drinking Water, Association of arsenic-contaminated drinking-water with prevalence of skin cancer in Wisconsin's Fox River Valley. *J. Health Popul Nutr* 24 (2): 206–13. [PMID 17195561](#).

Laws E.A (1993). Aquatic Pollution. 2nd Ed. John Wiley & Sons, Inc., New York, NY. pp 148-149.

Lide, D. CRC, Handbook of Chemistry and Physics, 1992, 73rd Edition. Boca Raton, FL: CRC Press.

Lupton, G.P., Kao, G.F., Johnson, F.B., Graham, J.H.and Helwig, E.B. (1985) Cutaneous mercury granuloma. A clinicopathologic study and review of the literature. *J. Am. Acad. Dermatol.* Feb; 12(2, Pt. 1): 296-303

Maitera O. N, OgugbuajaV. O. and Barminas J. T. , Determination of trace metal levels in water and sediments of River Benue in Adamawa state, Nigeria *Journal of Ecology and the Natural Environment* 3(4): 149-156.

Marschner, H., (1995). Mineral nutrition of higher plants, Academic Press, London

Matschullat, Jörg (2000). Arsenic in the geosphere — a review. *The Science of the Total Environment* 249 (1–3): 297–312.

Mohan D. and Pittman Jr. C. U.,(2007) Arsenic removal from water/wastewater using adsorbents—a critical review, *Journal of Hazardous Materials*, 142(1-2): 1–53.

Musselman J. F (2004) Sources of Mercury in Wastewater, Pretreatment corner, Bangin, Malaysia , *International Journal of Chemical Engineering*,4 :(31)

Nartey V. K., Hayford E. K. and Ametsi S. K., (2012) Assessment of the Impact of Solid Waste Dumpsites on Some Surface Water Systems in the Accra Metropolitan Area, Ghana, *Journal of Water Resource and Protection*, 4: 605-615.

National Ground Water Association,(2001). Arsenic, What you need to know <http://www.ngwa.org/ASSETS/A0DD107452D74B33AE9D5114EE6647ED/Arsenic.pdf>.(Assessed 2011 June 8)

Nitsch C., Hans-Joachim H., Marsen H, and Schliüssler H. (2005). Cleansing Agents, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim. doi:10.1002/14356007.a07_137

Nogawa, K., Kobayashi, E., Okubo, Y., and Suwazono, Y. (2004). Environmental cadmium exposure, adverse effects and preventative measures in Japan. *Biometals* 17 (5): 581.

Nordberg G, Nogawa K, Nordberg M, Friberg L.(2007). Cadmium.In: *Handbook on toxicology of metals*, (4) p. 65-78.

Nussey, G.,Vuren V.J.H.J. and Preez H.H.(2000). Bioaccumulation of chromium, manganese, nickel and lead in the tissues of the moggel, (*Labeoumbratus*) from Witbankdam. Mpumalanga. *Water S.A.*, 26 (2): 264-284.

Nyame K. F, Tigme J, Kutu M. J, Armah K.T (2012), Environmental Implications of the Discharge of Municipal Landfill Leachate into the Densu River and Surrounding Ramsar Wetland in the Accra Metropolis, Ghana. *Journal of Water Resource and Protection*, 4, 622-633 (<http://www.SciRP.org/journal/jwarp>)

Ogundiran, O. O.; Afolabi, T. A., (2008). Assessment of the physicochemical parameters and heavy metals' toxicity of leachates from municipal solid waste open dumpsite. *Int. J. Environ. Sci. Tech.*, 5 (2): 243-250.

Osei J., Osaе S.K.,Fianko J.R., Adomako D., Laar C., Anim A.K., Ganyaglo S.Y.,Nyarku M. And Nyarko E.S., (2011).Nuclear Chemistry and Environmental Research Centre, GAEC, Legon, Ghana. *Research Journal of Environmental and Earth Sciences* 3(6): 633-636.

Reimer, K.J.; Koch, I., Cullen, W.R. (2010). Organoarsenicals. Distribution and transformation in the environment. *Metal ions in life sciences* (Cambridge: RSC publishing) 7: 165–229.

Resaeе, J. Derayat, S. B. Mortazavi, Y. Yamini, and M. T. Jafarzadeh, (2005) Removal of Mercury from chlor-alkali industry wastewater using *Acetobacterxylinum* cellulose, *American Journal of Environmental Sciences*, 1(2): 102–105.

Roberts, J.R. (1999) Metal toxicity in children. In Training Manual on Pediatric Environmental Health: Putting It into Practice Jun. Emeryville, CA: Children's

Environmental Health Network (<http://www.cehn.org/cehn/trainingmanual/pdf/manual-full.pdf>).

Roosbroeck P. Van , Amlalo D. S. , (2006) , Country Environmental Profile of Ghana, final draft, Ref MWH 47501 004.001 rev.0, (http://ec.europa.eu/development/icenter/repository/Ghana-CEP_2006.pdf Accessed 2012 July 3)

Salem, H. M., Eweida, A., and Azza, F. (2000). Heavy metals in drinking water and their environmental impact on human health, *Center for Environmental Hazards Mitigation*, p 542- 556.

Sas-Nowosielska A, R. Galimska-Stypa, R. Kucharski, U. Zielonka, E. Małkowski, and L. Gray,(2008) Remediation aspect of microbial changes of plant rhizosphere in mercury contaminated soil, *Environmental Monitoring and Assessment*, 137(1-3): 101–109.

Smith, S.R., Jaffe, D.M., and Skinner M.A, (1997). Case report of metallic mercury injury. *Pediatr. Emer. Care*; 13: 114-6.

Turekian, K.K, Wedepohl, K.H (1961) Distribution of the elements in some major units of the earth's crust. *Bulletin of Geological Society of America*, 72:175-192.

Tsuji, L. J. S.; Karagatzides, J. D., (2001). Chronic lead exposure, body condition and testis mass in wild Mallard Ducks, *B. Environ. Contam. Tox.*, 67: 489-495.

USEPA (2005). Washington, D.C. National Management Measures to Control Nonpoint Source Pollution from Urban Areas., Chapters 7 and 8. Document No. EPA 841-B-05-004.)

USEPA (2012) Basic Information about Nitrate in Drinking Water , Regulated Drinking Water Contaminants , EPA 841-B-012-007..)

USGAO (2000). Health Effect of lead in drinking water. U.S. General Accounting Office reports, *Center for Environmental Hazards Mitigation*, Atlanta.

USGS (2000), Mercury in the Environment, Fact Sheet 146-00 <http://www.usgs.gov/themes/factsheet/146-00/index.html>, (Accessed, 2011 June 2)

UNESCO (2003). Water for people, water for life: *UN world water development report, executive summary*. Paris: United Nations Educational, Scientific and Cultural Organization

Watananugulkit R., Intim C. , Patnukao P, and Premchit T. (2003) Assessment of Impact on Water Quality of Leachate at On-nuch Disposal Site Center in Bangkok 10330, Thailand.

Webb, M. (ed.) 1979a: The geochemistry, Biochemistry and Biology of Cadmium. Elsevier/Noyth Holland Biomedical Press, Amesterdam.

Weingärtner H. (2006). Water, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim. doi:[10.1002/14356007.a28_001](https://doi.org/10.1002/14356007.a28_001)

Wikipedia, the free encyclopedia, Lead, <http://en.wikipedia.org/wiki/lead>, (Assessed 2011 September 3)

Wikipedia, the free encyclopedia, Arsenic <http://en.wikipedia.org/wiki/arsenic>, (Assessed 2011 September 5)

Wikipedia, the free encyclopedia, Mercury <http://en.wikipedia.org/wiki/mercury>, (Assessed 2011 September 3)

Wikipedia, the free encyclopedia, cadmium, <http://en.wikipedia.org/wiki/cadmium> (Assessed 2011 September 12)

WHO (1973), World Health Organization technical report series No. 532, Geneva.

WHO, 1993, Guidelines for Drinking-water Quality, Geneva

WHO (1996) ,Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring -Second Edition, 651 pages, printed in Great Britain at the University Press, Cambridge, ISBN 0 419 21590 5 (HB) 0 419 21600 6 (PB)

WHO (2008). Guidelines for Drinking Water Quality, 3rd ed. Vol 1. Incorporating the first and Second Addenda, WHO, Geneva (2008): ISBN 978 92 4 154761 1

WHO (2001) Regional Office for Europe, Air Quality Guidelines, chapter 6.7, Lead, Copenhagen, Denmark, 2nd edition, <http://www.euro.who.int/document/aicq/lead.pdf>. (Assessed 2011 June 8)

APPENDIX A

RAW DATA OF METALS IN RIVER DENSU AND LANDFILL LEACHATE

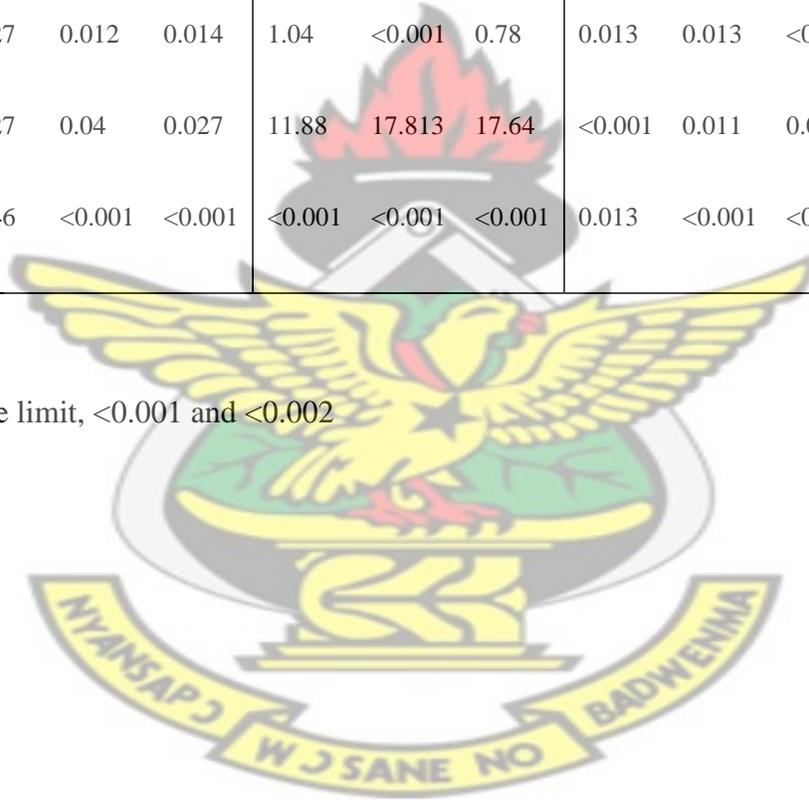
METALS IN WATER (mg/L)	As			Pb			Hg			Cd		
	JAN	FEB	MAR	JAN	FEB	MAR	JAN	FEB	MAR	JAN	FEB	MAR
Leachate	0.032	0.021	0.025	0.964	0.994	0.912	0.024	0.029	0.022	0.01	<0.002	0.004
Leachate entry	0.024	0.012	0.01	0.828	0.891	0.798	0.016	0.011	0.014	<0.002	<0.002	<0.002
200m upstream	<0.001	0.008	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002	<0.002
100m upstream	0.008	0.012	<0.001	0.014	0.01	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002	<0.002
100m downstream	0.017	0.015	0.004	0.58	0.676	0.436	0.007	0.009	0.004	<0.002	<0.002	<0.002
200m downstream	0.010	0.014	0.001	0.244	0.404	0.532	<0.001	0.004	<0.001	<0.002	<0.002	<0.002



RAW DATA OF METALS IN DENSU RIVER SEDIMENT

METALS IN SEDIMENT (mg/kg)	As			Pb			Hg			Cd		
	JAN	FEB	MAR	JAN	FEB	MAR	JAN	FEB	MAR	JAN	FEB	MAR
Leachate entry	0.067	0.069	0.062	0.707	0.785	0.785	0.04	0.053	0.038	0.173	0.192	0.169
200m upstream	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.067	0.107	0.025
100m upstream	0.027	0.012	0.014	1.04	<0.001	0.78	0.013	0.013	<0.001	0.12	0.147	0.106
100m downstream	0.027	0.04	0.027	11.88	17.813	17.64	<0.001	0.011	0.015	0.44	0.48	0.493
200m downstream	0.046	<0.001	<0.001	<0.001	<0.001	<0.001	0.013	<0.001	<0.001	0.24	0.106	0.108

Below detectable limit, <0.001 and <0.002



APPENDIX B

PHOTOGRAPHS OF LEACHATE DISCHARGE INTO THE DENSU RIVER AT OBLOGO, WEIJA.



