

UNIVERSITY OF GHANA



**IMPACT OF GOLD MINING ACTIVITIES ON THE BIRIM RIVER IN THE AKYEM
ABUAKWA AREA IN THE EASTERN REGION OF GHANA.**

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**THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF GHANA, LEGON IN
PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MPhil
CHEMISTRY DEGREE.**

MAY, 2018

DECLARATION

I hereby declare that this thesis is the outcome of research undertaken by Adomako Kyei Clement under the supervision of the under listed lecturers towards the award of MPhil Chemistry degree in the Department of Chemistry, University of Ghana, and has neither in part nor in whole been presented for another degree elsewhere. Reference to other people's work have been duly acknowledged.

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DEDICATION

This work is dedicated to my two fathers;

Samuel kyei Baffour, who brought me into this world

and

Rev. S.O K. Marfo, who took it upon himself to “raise me up”



ACKNOWLEDGEMENTS

I am grateful to my supervisors, Prof. Vincent Nartey and Dr. Raphael Klake for their patience, guidance and invaluable contributions throughout the work. My sincere thanks also goes to Dr Arthur at Cocoa Research Institute of Ghana -Tafo, for his support right from the inception to the culmination of this work. He has been very inspirational in this work.

I am greatly indebted to my father, Samuel Kyei, who will go through anything to raise a pesewa to sponsor my education. I never anticipated a master's degree this early. Grandpa S.O.K, your prayers have been answered. I pray that you all live long to enjoy the fruits from the seed you sowed in me.

I, also, thank all CRIG-TAFO officials in the Eastern region for the hospitality and immeasurable assistance given me during sampling, most especially Sammy and Divine (soil science division at CRIG). May God bless you abundantly.

My sincere gratitude also goes to the Laboratory Technicians of ECOLAB, and of the Chemistry and Soil Science Departments of the University of Ghana especially Mr Prince Owusu, Mr Sarquah (ECOLAB), Mr Bob-Essien (Chemistry), Mr Julius A. Nartenor and Mr Bernard Anipa (Soil Science) for the assistance given me during the laboratory analysis. To my friends and fellow MPhil students, I say thank you for the roles you played in my life. The assistance from Acheampong Charles and Michael Kyene is highly appreciated.

My praises go to the Almighty God who does everything beautiful in his own time.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
AGM	Artisanal Gold Mining
CRIG	Cocoa Research Institute of Ghana
CVAAS	Cold Vapour Atomic Absorption Spectrophotometer
EC	Electrical Conductivity
EPA	Environmental Protection Agency
Fig	Figure
GPS	Global Positioning System
Igeo	Geo-Accumulation Index
TA	Total Alkalinity
TDS	Total Dissolved Solids
TH	Total Hardness
TSS	Total Suspended Solids
UG	University of Ghana
USEPA	United States of America Environmental Protection Agency



ABSTRACT

This study was conducted to assess heavy metal contamination (Hg, Fe, Ni, As, Mn, Pb, Cd, Zn) in water and sediment samples from the Birim River in the Akyem Abuakwa Area. Water and sediment samples were taken from ten different Sites within the Akyem Abuakwa area in September 2015 (wet season) and January 2016 (dry season). Heavy metal concentrations were determined using atomic absorption spectrophotometer (AAS) equipped with cold vapour (CVAAS) for total mercury. In the wet season, mean concentrations of heavy metals in the water samples were 0.47 µg/L (Hg), 1.75 mg/L (Fe), 0.03 mg/L (Ni), 0.01 mg/L (As), 0.40 mg/L (Mn), 0.02 mg/L (Pb), 0.02 mg/L (Cd) and 0.18 mg/L (Zn) while in the dry season, the mean concentrations were 0.34 µg/L (Hg), 1.28 mg/L (Fe), 0.05 mg/L (Ni), 0.01 mg/L (As), 0.44 mg/L (Mn), 0.01 mg/L (Pb), 0.01 mg/L (Cd) and 0.38 mg/L (Zn). Levels of heavy metals (As, Ni, Pb,) were below the WHO guideline values for drinking water while metals such as (Hg, Mn, Fe, Cd) were all above the EPA and WHO recommended safety guideline limit for drinking water. All the metal concentrations in the sediment were higher than that of the water samples in both dry and wet seasons. The concentrations of all the metals studied were below USEPA guideline values. Results of Pollution Indices computed namely, contamination factors (Cf), Geo-Accumulation Index (I-Geo) Pollution load Index showed no pollution for all metals studied except mercury and iron which showed moderate pollution. There was no correlation between the pH and heavy metals in the water samples. However the metal concentrations in the river sediments showed a significant difference with pH.

Ions in the water (K^+ , Na^+ , SO_4^{2-} , PO_4^{3-} and NO_3^-) showed seasonal variations. Also physico-chemical parameters such as total dissolved solids, total suspended solids, total alkalinity, total

hardness, electrical conductivity and temperature showed seasonal variations in their concentration levels. The high levels of metals such as Mn, Fe, Cd and Hg indicates that artisanal gold mining has adverse impact on the Birim River.

Keywords: Birim River, water, sediment, heavy metals, seasonal variation, Contamination factors, Geo- Accumulation Index, Pollution load Index



CHAPTER ONE

INTRODUCTION

1.1 Background to Study

Environmental pollution is a major problem nations are facing around the world. In recent times this problem has become more challenging in light of increasing population and industrialization (Chamie, 2004).

Ghana for some time has been considered as being one of the leading producers of gold worldwide.

Gold mining has a lot of pollution issues, which includes the release of anthropogenic pollutants into the environment. The most affected environment is the water environment. Many rivers found in the areas of gold mining have been shown to be polluted (Chamie, 2004).

Industrial wastes contain pollutants that may destroy the environment we inhabit. Many countries ignore industrial waste management since it is expensive. Heavy metals are by-products from industrial activities and different amounts are discharged into freshwater and the environment. They affect both the ecosystem, and human life through Bio-accumulation in the food chain. They are present in environmental compartments such as water (fresh water and marine systems), soil or sediments and biota but are mostly dangerous when they enter the food chain (Robson and Neal, 1996). Trace metals are harmful even at very low levels (Volesky, 1990).

Mineral elements are required by living organisms for growth and development. Such minerals are known as essential minerals. Essential elements are needed for continuity of life (Mertz, 1981; Nyarko, 2012).

Essential elements needed in large quantities are referred to as macro-elements. Examples are: Carbon (C), Nitrogen (N), Magnesium (Mg), Carbon (C), Sodium (Na), Phosphorous (P), Sulphur (S) and Potassium (K).

Essential elements are usually bound to proteins and in abnormal quantities are considered toxic to the organism. These elements include Copper (Cu), Magnesium (Mg), Phosphorous (P), Sulphur (S) and Potassium (K). Non-essential elements are neither beneficial nor harmful if present in sufficiently low amounts but their harmful effect begins to show with the gradual accumulation in biological tissues. Examples of such elements include Cadmium, Mercury and Lead, just to mention a few. These metals are said to be cumulative poisons (Nyarko, 2012).

Harrison and De Mora (1996) reported of a complex correlation existing between concentration of metals found in the ecosystem and their ability to cause toxic effect in organisms. Two constraints they identified are the speciation of the element and the condition of the organism. Elemental speciation, especially its partitioning between host association in aqueous and particulate phase influences bioavailability. Most heavy metals are damaging to marine organisms in their organometallic form. Mercury is a classic example which is mostly bioavailable and toxic as methyl mercury (CH_3Hg^+).

Discharge of mercury into water bodies could occur through the activities of illegal mining, and also combustion of medical waste (Oduro *et al.*, 2012; Jackson and Jackson, 1995). Small-scale gold mining, popularly known as ‘galamsey’ is the major contributor to intentional discharge of mercury into water bodies. The only avenue of contamination for areas not known for having direct mercury input is through atmospheric deposition. (Schroeder and Munthe, 1998).

Artisanal Gold mine workers use primitive technology to extract gold from soils and river sands. The process begins with the dredging of river sand and centrifugal separation of the crushed gold ore to produce a concentrate. The concentrate is mixed with mercury in amalgamation drums. Mercury binds to gold in a solution known as an amalgam and this solution is separated from the concentrate matrix by panning (Telmer and Veiga, 2008). Mercury is then recovered from the amalgam by roasting it in partially enclosed retorts or even in the open air. Pure gold produced contains up to 5% mercury (Hg). Mercury not recovered properly adds to atmospheric release especially in towns where Artisanal gold mining (AGM) activities occur.

The impact of mercury pollution is not restricted to the point of release but several kilometers of the point of original discharge (Harada *et al.*, 2001). Mercury (Hg) concentration in sediments have been found to have a strong correlation with soil organic matter since this element in question has the tendency to bind with humate ligands. An abundant organic matter environment favors mercury methylation due to bacteria action (Pak and Bartha, 1998).

Several studies have reported that the level of one element always has an impact on the presence of other elements (Feroci *et al.*, 2005). Parizek (1978) proposed a direct or indirect interaction (or combination) for complexes of some elements (i.e., Hg and Se). Direct interactions are mainly test-tube type reactions of the elements in question without the involvement of living matter. In other cases, a metabolic conversion of at least one of the interacting elements (compounds) would have to occur within the organism to make the interaction possible. An indirect interaction may involve effects by one element or compound on any metabolic function affecting the other. Membrane function may be impaired by one element or compound, causing an alteration of membrane passage of the other. This

eventually results in change of the toxic form of the element or compound at the receptor sites (Skerfving, 1978).

1.2 Problem Statement

The Birim River system, which flows through the eastern region, is a tributary of the River Pra in Ghana. It is found in the east of Atewa district. The Birim River is known to have direct input of mercury due to Artisanal Gold Mining (AGM) operations popularly known as ‘galamsay’ which mode of extraction of gold is through amalgamation (Bonzongo *et al.*, 2003; Spiegel, 2009). From previous studies conducted by Asamoah (2012) and Gyampoh (2013), traces of Hg were found in sediments and the river at areas known for AGM activities. There is even a greater worry as these AGM operators pollute the water body with their effluent and destroy the entire ecosystem. When they are done, they migrate to new areas along the watershed to continue their activities.

Currently AGM activities are found in areas such as Efisa, Adadientem, Akyem Adukrom, Asikam, Obronikrom, Osino and Abomosu located in the Akyem Abuakwa District in the Eastern region. In their operations, they make use of mechanized dredging equipment which are mounted on mobile rigs. They also heap piles of sand into the river which aids in their operations (Oduro *et al.*, 2012). The discharges of Hg from mining run-off into the river along with other pollutants affect the water quality.

This research seeks to determine the levels of Hg pollution in the Birim River and to explore the possible impact of Hg pollution on water and sediment samples.

1.3 Research Hypothesis

The study was carried out on the basis of the following hypotheses:

Ho: Hg is used by AGM operators in the extraction of gold.

Ho: Hg is known to travel several kilometers from source of pollution.

Ho: Water physicochemical parameters differ significantly with seasonal changes.

1.4 Study Objectives

1.4.1 Aim

The research seeks to assess the levels of trace metals in sediment samples, and water samples from the Birim River.

1.4.2 Specific Objectives

The research seeks to:

- Determine the concentrations of Mercury, Zinc, Lead, Nickel, Cadmium, Arsenic, Iron and Manganese in the water and sediment samples.
- Compare levels of trace metal contamination with those of Environmental Protection Agency (EPA-Ghana) and World Health Organization guideline limits for metals.
- Assess levels of physicochemical parameters.
- Use pollution indices to assess the extent of pollution in the sediment samples.
- Make recommendations based on the outcome of the research.



Figure 1.1: Section of Birim River, destroyed by galamsey activities.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition and Properties of Heavy Metals

Different definitions have been suggested for the term heavy metals. Bjerrum (1936) defined heavy metal as metals with elemental densities above 7 g/cm^3 whereas Morris (1992) based his definition on densities greater than 5 g/cm^3 .

The terminology is sometimes applied indiscriminately, such as the unusual inclusion of aluminum as a heavy metal (Atomic mass 26.98 g/mol^{-1} and specific gravity of 2.7). Some studies have used the terms trace or toxic elements in place of heavy metals. Glanze (1996) reported of 35 metals of environmental concern due to occupational or residential exposure; among these metals are mercury, cadmium, Arsenic, iron, lead, manganese, nickel, zinc.

Metals exist either in the solid phase or in solution as free ions and are associated with several soil components which determines their bioavailability.

2.2 Sources of Heavy Metals

Volcanic eruption through volcanic ash is one natural way heavy metals get into the environment. Nriagu (1990) reported that volcanic activity is one major source of atmospheric cadmium and it is estimated to contribute about 820 metric tons each year. Atmospheric depositions are as a result of dust storms and wild forest fires are other natural source of heavy metal pollution (Nriagu, 1990).

Anthropogenic sources of heavy metals include Agricultural activities such as pesticide, fertilizer, herbicide application, and contaminated irrigation water sources. Other sources include mining and the use of lead and manganese as anti-knock agents in gasoline and exhaust fumes from cars (Nriagu, 1990; Kakulu, 2002).

Heavy metal additives in building materials like paints, aerosol and sewage discharge, among others, contribute to the pollution load in the environment. (Manoj *et al.*, 2012).

2.3 Overview of Research of Mercury in Ghana

The use of a large amount of mercury is as a result of Artisanal gold mining (AGM) (Appoh, 2010). A lot of research has been carried out to assess the impact of AGM operations on the environment in locations known to have gold deposits. Lots of research works have been done on mercury in areas particularly known for gold mining.

Most of the researches have been based on rivers and streams particularly in the southwestern belt of Ghana due to the alluvial deposits of gold by these water bodies. For instance, Donkor *et al.* (2006) and Oduro *et al.* (2012) studied total mercury in Lower Pra River which serves as a source of drinking water for communities along the Pra basin. Donkor *et al.* (2006) reported that mercury concentration in drinking water was below the WHO guideline values of 1000 ng/L but were above the standard of 12 ng/l set by WHO guideline limits for drinking water. Oduro *et al.* (2012) reported of high THg concentration in drinking water in communities where the studies were carried out. Hayford *et al.* (2008) assessed the presence of toxic elements including mercury in soils from mining communities around Tarkwa. They reported that mercury in the soil was higher than the permissible values by the Food and Agricultural Organization for food and the World Health Organization for soils.

There is still a need for a continuous environmental assessment of mercury and its related health effects in spite of all these studies.

2.4 MERCURY

2.4.1 Chemical Fate

The concentrations of Mercury are generally found to be very low in materials such as granites (Davis *et al.*, 1997). Mercury (Hg) occurs in traces in ore deposits together with sulphur as Cinnabar (HgS). Anthropogenic sources of mercury (Hg) include various industrial discharges and abandoned mines, coal combustion and medical waste incineration.

The sediment interface has a tendency to accrue inorganic mercury (Donald , 2010).

Dissolved mercury in natural water systems exists mostly in organic forms and a high level of mercury in fish tissues was observed by Gill and Bruland (1990).

2.4.2 Mercury in Mine Effluents and Receiving Waters

Effluent from mining sites mostly contains dissolved mercury. Depending on pH, two species of mercury may exist. At high pH, hydrated mercuric oxide ($\text{HgO} \cdot \text{H}_2\text{O}$) is the dominant while mercuric chloride (HgCl_2) exists at low pH and aerobic conditions. There is formation of mercuric tetrachloride complex (HgCl_4) at high concentrations of chlorides (and low pH). The formation and dissolution of inorganic Hg solids is controlled by redox and pH conditions and redox conditions in particular occur over a wide range in surface water environments (Donald, 2010).

2.5 CADMIUM

2.5.1 Chemical Fate

Cadmium (Cd) is a group IIb metal in the periodic table with a low melting point of (320.9 °C) and boiling point of 765 °C. It has an average concentration of 0.2 mg/kg in the earth's crust and is largely distributed in sediments soils and rocks, (Manson and Moore, 1982). Cadmium

(Cd) is rapidly oxidized in air into cadmium oxide. Cadmium (Cd) and Zinc (Zn) frequently undergo geochemical processes together (ATSDR, 1999). Cadmium (Cd) exists in water as hydrated ion, as inorganic complexes such as carbonates (CO_3^{2-}), hydroxides (OH^-), chlorides (Cl^-) or sulfates (SO_4^{2-}), or as organic complexes with humic acids (Sauve *et al.*, 1999).

Cadmium (Cd) may enter aquatic systems through weathering, erosion of soils and bedrock, and atmospheric deposition or direct discharge from industrial operations. Much of the cadmium (Cd) entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment (WHO, 1992a, and b). Once cadmium (Cd) enters sediments, it can react with sulphur and form relatively insoluble cadmium sulfides (CdS). Partitioning of cadmium (Cd) between the adsorbed-in-sediment state and dissolved-in-water state is, therefore, an important factor in the bioavailability of cadmium.

Non-ferrous metal smelting contributes approximately 76% of the anthropogenic cadmium (Cd) emissions, while fossil fuel combustion accounts for the remaining 24% (Nriagu, 1990).

Cadmium (Cd) also has a long residence time in the atmosphere which aids its long range atmospheric transport. Anthropogenic emissions of cadmium are usually associated with the release of nitrogen and sulphur oxides. Cadmium (Cd) concentration in freshwater is typically inversely related to pH (Breder, 1988) and may be retained for longer periods in the water column of acidified lakes relative to non-acidified lakes. Cadmium (Cd) is normally partitioned to the particulate phase and rapidly deposited to sediments (Breder, 1988).

2.5.2 Toxicity of Cadmium (Cd)

Cadmium is generally accumulated in aquatic and terrestrial species mostly in target organs such as the kidney and liver (Nordberg *et al.*, 1985). The accumulation and toxicity of

cadmium is as a result of free ion activity (Sprague, 1985) and is therefore affected by interactions with other elements such as Zinc (Zn), Calcium (Ca) and Iron (Fe). More importantly the toxicity of Cadmium (Cd) ultimately involves the disruption of Calcium (Ca) metabolism.

Low-dose exposure to elevated Cadmium (Cd) over a long period can cause adverse health effects such as gastrointestinal, hematological, musculoskeletal, renal and respiratory effects. Cadmium (Cd) poisoning may lead to cardiac failure cancers, osteoporosis, proteinuria, emphysema and cerebrovascular infarction associated with long term exposure to Cadmium (Cd) (Hallenbeck, 1894), cataract formations in the eyes (Ramakrishma *et al.* 1995) and kidney diseases (Jarup *et al.*, 2000). Cadmium (Cd) has been classified as a carcinogen (Achanzar, 2001), developmental toxicant (Turgut *et al.*, 2005) and reproductive toxicant (Correa, 1996).

2.6 LEAD (Pb).

2.6.1 Chemical Fate

Lead (Pb), a group (IV) element is a class B metal which has the ability to form stable complexes with oxygen-donating compounds (Balba *et al.*; 1991). It has many industrial and commercial uses. For instance, it is used in metal products, cables and pipelines to improve durability, additives in paints, and in pesticides. It is used as a coloring element in ceramic glazes as projectiles and in some candles to treat the wick. It is the traditional base metal for organ pipes, and it is used as electrodes in the process of electrolysis. One of its major uses is in the glass of computer and television screens, where it shields the viewer from radiation. It is also used in the production of lead-acid batteries for automobiles (Balba *et al.* 1991). Balba *et al.* (1991) reported that automobiles (leaded gasoline), industrial wastewater (lead mining

and smelting) and pesticides are the major anthropogenic sources of lead (Pb) in the environment.

2.6.2 Toxicity of Lead

Exposure to lead (Pb) can have a wide range of effects on a child's development and behavior. Growing evidence suggests that lead (Pb) in a child's body, even in small amounts, can cause disturbances in early physical and mental growth and later in intellectual functioning and academic achievements. There is accumulated epidemiological evidence, which indicates that lead (Pb) exposure in early childhood causes discernible deficit in cognitive development resulting in lower Intelligent Quotient (IQ) (Adeyeye, 1993).

Particularly, dangerous to all forms of life are the organic lead (Pb) compounds. As a result of their comparatively high affinity for proteins, the lead (Pb) ions absorbed bond with the haemoglobin and the plasma protein of the blood. This leads to inhibition of the synthesis of red blood cells and thus of the vital transport of oxygen. If the bonding capacity here is exceeded, lead (Pb) passes into the bone-marrow, liver and kidneys (Ogwuebu and Muhanga, 2005).

In adult, lead (Pb) may accumulate in bone and lie dormant for years, and then pose a threat later in life during events such as pregnancy, lactation, osteoporosis and hyperparathyroidism which mobilizes stores of lead (Pb) (Mushak *et al*; 1989). Lead (Pb) toxicity causes reduction in haemoglobin synthesis, disturbance in the functioning of kidney and chronic damage to the central and peripheral nervous systems (Ogwuebu and Muhanga, 2005).

2.7 IRON

2.7.1 Chemical Fate

Iron (Fe) is a lustrous, ductile, malleable, silver-gray metal belonging to group VIII of the periodic table. It is known to exist in four distinct crystalline forms. Iron (Fe) rusts in damp air, but not in dry air. It dissolves readily in dilute acids. Iron (Fe) is chemically active and forms two major series of chemical compounds, the bivalent iron (II) (Fe^{2+}), or ferrous compounds and the trivalent iron (III) (Fe^{3+}), or ferric compounds (Dallman, 1986).

Iron (Fe) is believed to be the tenth most abundant element in the universe. Iron (Fe) is also the most abundant (by mass, 34.6%) element making up the Earth; the concentration of iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Most of this iron (Fe) is found in various iron oxides, such as the minerals hematite, magnetite, and taconite (Morgan and Anders, 1992). The earth's core is believed to consist largely of a metallic iron (Fe)-nickel (Ni) alloy. Iron is the most common metal in use today due to its abundance and strength. They form part of machine tools, automobiles, building and machine parts. They are also used as catalyst in many processes, food containers and screwdrivers.

Iron (Fe) is vital to most life forms and to normal human physiology. Dallman, (1986) explained that in humans, iron (Fe) is an essential constituent of proteins involved in oxygen transport. Andrews (1999) and Bothwell *et al.* (1979) indicate its essentiality in the regulation of cell growth and differentiation.

2.7.2 Toxicity of Iron (Fe)

Iron (Fe) is needed in the body in small amount to help cell growth, differentiation and also to boost the immune system. It forms the bases of many proteins and enzymes. It is an important component of proteins both in the regulation of cell growth, oxygen transport and a major component of haemoglobin and myoglobin (Dallman, 1986).

Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. Excessive iron (Fe) intake and storage, especially in men, has been considered as a cause of heart disease and cancer in recent years (Bothwell *et al.*, 1979).

2.8 WATER

2.8.1 Importance of good water quality

Water is man's most important resource and from history it has been the key to most civilization's development. Water defines population growth and is a key factor in human settlements. Society will enjoy good health basically from disease and toxin free water sources. Modern civilization classifies natural bodies of fresh water according to intended use, for example public water supply, fish propagation, recreation, transportation, agriculture and industrial or domestic use (Khan, 1988).

The largest demand and use of water worldwide is for industrial and agricultural purposes. Agricultural uses of water are mainly through irrigation and in the application of agro-chemicals. Water for agriculture continues to increase worldwide due to high demand for food (Khan, 1988). Water is used in industries mainly for power generation, transportation of waste materials and in many industrial products such as beverages and solvents for chemicals. Water pollution has impacted negatively on the economy of many developing countries especially in

the area of human health and ecosystem disruption. Any physical, biological or chemical change in water quality that adversely affects living organisms or makes water unsuitable for desired use could be considered as being polluted (Khan, 1988).

Sedimentation from erosion and poisoned springs contribute to natural sources of water contaminant. Anthropogenic sources of water contaminant include sewage from industries, pesticides and other agro-chemical runoff from farmlands and faecal pollution. Faecal pollution of drinking water has frequently caused water borne diseases such as cholera which has decimated several populations (Schulten *et al.* 1997).

Urbanization, industrialization and various modern agricultural practices has greatly affected the environment and the quality of water. The assessment of water quality is therefore the best in ensuring that it is safe for its intended user. (Khan, 1988).

2.8.2 Freshwater Physico-Chemistry

Aquatic communities, species and their way of life are directly influenced by the Physico-chemistry of the hydrosphere they inhabit. Physico-Chemical parameters include physical parameters such as pH, temperature, turbidity, total dissolved and suspended solids (TDS and TSS) and chemical parameters as alkalinity and hardness (Banahene, 2005).

Extreme changes in water Physico-Chemistry can have adverse effects on aquatic systems and organisms. Physico-Chemical parameters to investigate are temperature, pH, electrical conductivit (EC), total dissolved and suspended solids (TDS and TSS), and dissolved ions (water nutrients) (Banahene, 2005).

2.8.3 Total Alkalinity

It measures the presence of carbonates, bicarbonates, phosphates and hydroxides and also a measure of the buffering capacity of an aquatic ecosystem (Banahene, 2005). Phosphate and orthophosphates contribute to 0.1 % of total alkalinity. Alkalinity is measured by carbonate compounds denoted as mg/L CaCO_3 (Dallas and Day, 2004). It is important for fish and other aquatic life in fresh water system because it buffers pH changes. Its components such as carbonate/bicarbonate complexes toxic metals thereby decreasing their toxicity significantly (Banahene, 2005). The WHO in their 2011 report has no stated guideline value for alkalinity because a high concentration of bicarbonate species in drinking water does not pose any health concern (WHO, 2011). However, EPA's secondary drinking water regulations limits alkalinity only in terms of TDS (500 mg/L) and to some extent by the limitation on pH.

2.8.4 Electrical Conductivity

Electrical conductivity (EC) determines the level of total dissolved solids (TDS), in water sample. Dissolved salts or ions are electrically charged and their ionic strength determines water conductivity. In freshwater ecosystems, electrical conductivity is controlled by rocks' mineral composition, other sources of ions (Hudson-Edwards *et al.*, 2003; Nielsen *et al.*, 2003). A bigger watershed means relatively more water flow and more contact with soil will result in more salt/ion extraction from the sediment hence contributing to high electrical conductivity (Vega *et al.*, 1998).

2.8.5 Turbidity and Suspended Matter in the Hydrosphere

Suspended material consists of typical soil minerals and organic matter, especially those in the fine (clay-size) fraction. The elements present in such inorganic and organic structures usually include relatively high concentrations of alkali and alkaline earth metals, aluminum (Al), and iron (Fe), along with smaller amounts of other metals depending on the particular materials involved. Some elements of interest particularly those found in traces are associated with sediments as adsorbed species on the interface of the fine particles. The interface absorbed metals are more available than structural elements; for example, when a sediment-bearing river discharges water into an estuary, most of the adsorb ions are displaced by sodium ions via an ion-exchange reaction and become part of the solution phase (Wood and Armitage, 1997).

2.8.6 Total Hardness

Hardness of water is the amount of the mineral content especially calcium and magnesium mainly in combination with bicarbonates (HCO_3^-), sulphates (SO_4^{2-}) and chloride (Cl^-). Other divalent or trivalent ions can contribute to hardness such as iron (Fe), barium (Ba), and/or strontium (Sr) though their contributions are small and difficult to define. Because the concentrations of Ca^{2+} and Mg^{2+} are usually much greater than the concentrations of other group II ions, hardness can be equated to the total calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions present. Limestone is a mixture of calcium and magnesium carbonate, CaCO_3 and MgCO_3 . Surface or ground water often contains CO_2 and thereby making the water slightly acidic by the formation of carbonic acid (H_2CO_3) (USEPA, 2013). Slightly acidic groundwater reacts with the basic limestone, and a neutralization reaction occurs resulting in the formation of soluble Ca^{2+} , Mg^{2+} bicarbonates which will contribute to water hardness. It is normally

expressed as mg CaCO_3 per litre. There are two types of water hardness; permanent and temporary hard water. Permanent hardness in water is hardness due to the presence of the chlorides (Cl^-), nitrates (NO_3^-) and sulphates (SO_4^{2-}) of calcium (Ca^{2+}) and magnesium (Mg^{2+}), which will not be precipitated by boiling. For temporary hardness, calcium (Ca^{2+}) and magnesium (Mg^{2+}) form salt with bicarbonates (HCO_3^-). These compounds are unstable and will decompose when heated. Boiling the water will cause the precipitation of calcium and magnesium carbonate which also removes the hardness. Hardness is used to determine how usable water resources are for drinking and domestic purposes. Hard water forms fur and scales in boiler and leaves scum in clothes in addition to wasting of soap.

2.9. THE EFFECT OF NUTRIENTS ON FRESHWATER ECOSYSTEMS

Nutrients such as nitrates (NO_3^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) exist as either inorganic anionic species or a part of very huge organic structures in freshwaters. Nutrients attached to organic compounds are broken down through a series of biochemical reactions and released into the aquatic environment. Nutrients occur in small amounts in a healthy freshwater system but in large quantities, they can cause water pollution problems. Domestic sewage, industrial waste and storm drainage into water bodies contribute to an overload of nutrients in freshwater systems. Higher nitrates (NO_3^-) and phosphates (PO_4^{3-}) nutrients contribute to the acceleration of natural eutrophication in freshwater systems, a process called cultural eutrophication (Campbell *et al.*, 1992).

2.9.1 Nitrogen Cycle.

In the hydrosphere and on land, nitrogen (N) in various forms is a vital component for plant and animals and excessive concentrations of it in the hydrosphere leads to eutrophication.

Nitrogen undergoes a number of processes in terrestrial, aquatic and atmospheric environments which includes nitrogen fixation, denitrification, ammonification and nitrification.

2.9.2 Nitrogen Fixation

Atmospheric nitrogen is relatively unreactive, and is converted to $\text{NH}_3/\text{NH}_4^+$ by nitrogen fixing microorganisms. The conversion requires breaking of strong $\text{N}\equiv\text{N}$ triple bond therefore a large energy input is required. However, in freshwaters, nitrogen can occur in different forms which include dissolved molecular nitrogen, organic compounds from proteins, recalcitrant anthropogenic compounds and inorganic nitrogen (ammonia, nitrite and nitrate) (Dowd *et al.*, 2000; Wetzel, 2001; Kubiszewski *et al.*, 2008).

The availability of atmospheric ammonia is mainly due to nitrogen fixing bacteria that use unreactive nitrogen to form ammonia that normally fall into freshwaters, thus increasing ammonium concentrations in water (Bowden, 1987; Roscher *et al.*, 2008). Cyanobacteria are responsible for most nitrogen fixation in freshwater systems due to their heterocysts (specialized nitrogen fixation cells). Marine organisms like the blue-green algae, azotobacter, and clostridium also contribute to nitrogen fixation.

2.9.3 Sulphur in Freshwater

Sulphur chemistry has a major influence on the process in all the compartments of the Earth's environment. Sulphur in the hydrosphere is present in many inorganic and organic forms and exhibits -2 to +6 oxidation states. The most important reduced and oxidized mineral forms of the element are sulphides, including pyrite (FeS), and sulphates, including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The concentration in unimpacted fresh water is much less than 0.12 mmol but

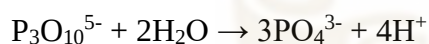
nonetheless one of the principal ionic species in lakes and rivers. In reducing environment sulphur is obtained in the -2 oxidation state. In organic matter, sulphur exists as both carbon-bonded and oxygen-bonded forms:

C-bonded	R-CH ₂ SH	hydrosulphide in amino acids
	R ₃ C-S-S-CR ₃	disulphide
O-bonded	S=O	sulphoxide
	R-OSO ₂ OH	sulphonic acid

2.9.4 Phosphorous in Freshwater

Phosphorous naturally occurs in wastewater as phosphates. They are categorized as orthophosphate, condensed phosphate (pyro-, meta- and polyphosphate) and organically bound -phosphates. It naturally occurs by the breaking of phosphate bearing rocks. Anthropogenic activities contribute to elevated phosphorus in freshwaters through agricultural runoffs, domestic and industrial sewages (Baron *et al*; 2003).

Polyphosphate when they enter water bodies are slowly transformed into phosphate ions (orthophosphate).



Orthophosphate/soluble reactive phosphate (SRP), H₂PO₄ and HPO₄⁻² are the only soluble forms of inorganic phosphorus and hence are readily available to aquatic life. Orthophosphate is taken up by algae, cyanobacteria, heterotrophic bacteria and larger aquatic plants and forms the basics of aquatic food chain. Phosphorus enhances aquatic plants and algal growth (Manaham, 1991).

Concentrations of dissolved phosphorus below 0.005 mg/L stimulate small levels of species diversity, low productivity, rapid nutrient cycling, and no algal and aquatic plant growth. Phosphorus concentrations ranging between 0.05 and 0.25 mg/L PO_4^{3-} can enhance species diversity; promote moderate primary production, algal and water plant growth. Concentrations above 0.025 mg/L result in decreased species diversity, high productivity, and high growth of nuisance aquatic plants and algal blooms (Camargo *et al.*, 2007). Phosphorus concentrations are used to measure ecosystem eutrophication with the concentration of 0.1 mg/L PO_4^{3-} indicative of a PO_4^{3-} eutrophic system (Campbell *et al.*, 1992).

2.10 ANALYTICAL METHODS FOR SAMPLE ANALYSIS

Elements in water and soil sediments can be determined in the laboratory using the following fixed laboratory assays: Atomic Absorption Spectroscopy (AAS), X-ray fluorescence (XRF), Electron Microprobe (EM), Flame Photometer (FP) and Instrumental Neutron Activation Analysis (INAA). These instruments accurately measure elements in environmental sample to parts per billion (ppb) concentrations i.e. $\mu\text{g L}^{-1}$ and $\mu\text{g kg}^{-1}$ solid samples respectively (Melamed, 2005). The choice of a particular technique, however, depends on factors such as speed of analysis, availability of the instrument, technical expertise of the analyst or technician and the cost of analysis among others (Skoog *et al.*, 1998). In this study, ICP-AES was used to analyse the total concentrations of Cd, Cr, Fe, Mn, Ni, Pb and Zn whereas, for the concentrations of exchangeable bases, AAS (for Ca and Mg) and FP (for Na and K) were used. Before any element is determined with any of these instruments, pre-treatment of sample with acidic extraction (acidic oxidation digestion) or with target reagents is required. The significance of pre-treatment is that all elemental species is converted into the inorganic

form for easier detection and measurement. These laboratory assays measure elements accurately but they are expensive to operate and maintain.



CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter describes the study area, sampling procedures and various analytical methods used in this research.

3.2 STUDY AREA

The sampling areas are all found in the East Akim Municipality located in Eastern Region of Ghana. It has an approximate land area of 725 km². It has Kibi (Kyebi) as its district capital 55 km from Koforidua and 105 km from Accra. It has coordinates of 06° 10' N 00°33'W/6.167°N 0.550W (Asomaning, 1992).

3.2.1 Economic Activities

The municipality has about 50 per cent of its 11,677 natives settling in the rural areas. Some of the indigenes are engaged in small scale farming as well as pastoral farming. The main source of livelihood for the people is the mining of gold called 'galamsey'. Illegal miners have trooped into the municipality of late due to the high levels of gold found in the surrounding villages in the Kibi municipality (Asante *et al.* 2005).

3.3 THE BIRIM RIVER

The Birim River is one of the main tributaries of the Pra River in Ghana and is the country's most important diamond-producing river, flowing through most of the width of the Eastern region. The river rises in the east of the Atiwa Range, flows north through the gap between this range and the Kwahu plateau, then runs roughly south- west until it joins the river Pra.

The surrounding lowlands are about 180-200 m above sea level. The Birim river gravels hold gold which has long been extracted through panning or Placer mining used in making ornaments and for trans-Saharan trade long before the Europeans discovered the Gold Coast (Asante *et al.* 2005). The communities around the river use the water extensively for drinking and other domestic purposes without prior treatment.





Figure 3.1: Map of river Birim showing the sampling sites with reference to Apapam as the source of the river.

3.4 DATA COLLECTION

The research was undertaken in the Akyem Abuakwa Traditional Area. These included observation of sampling sites, sample collection, preparation and analysis of data/results.

3.5 REAGENTS

All reagents used were of analytical grade obtained from BDH, UK. They were used without further purification.

3.6 SAMPLES AND SAMPLING PROCEDURE

Sampling of the water started at the beginning of October to November, 2015 representing the wet season and January to early February 2016 representing dry season at ten (10) different sites. (Efisa, Adadientem, Obronikrom, Asikam, Akyem Adukrom, Osino, Anyinam, Abomosu, Bunso, upstream of Apapam which served as a control). The samples taken included water and sediments from the Birim, river. The surface water samples and river sediments were collected simultaneously at the ten different sites along the river course. Plastic bottles which had been pre – washed with detergent and tap water, and later rinsed with 1:1 concentrated hydrochloric acid. Two bottles of the water samples were taken at each sampling site of which one was acidified with 10% nitric acid for the analysis of heavy metals whilst the other was used for the physicochemical analysis .With the sediment samples, two sediment samples, weighing 200 grams were also collected at each sampling site and emptied into polyethylene bags.

The samples were picked at about four kilometers interval except for the one in Apapam which was picked at source of the river.

The sampling areas were mapped by a Global Positioning System (GPS) device. All samples were labelled and described on the field, packed and transported to the Soil Science Division Laboratory of Cocoa Research Institute of Ghana (CRIG)-Tafo in the Eastern Region for analysis. In all one hundred and ten (110) water samples, one hundred and ten (110) sediment were obtained.

3.6.1 Sample Preparation

3.6.2 Water Samples

A 100 mL of the sampled water which had already been acidified with Concentrated HNO_3 during sampling was further acidified and transferred into a beaker and heated for 5 to 10 minutes on heating mantle. The solution was then filtered with Whatman No.42 filter paper into a 500 mL volumetric flask and made up to the volumetric mark with deionized water for analysis of the trace metals (Iron, Nickel, Arsenic, Manganese, Lead, Cadmium, Zinc, and Mercury)

3.6.3. Sediment Samples

Sediments were dried in the open for 21 days. The samples were powdered and sieved through 160 μm sieve mesh. 2 g of each sediment samples were weighed digested in a digestion bomb with 15 mL of HNO_3/HCl (1:3 v/v) and digested in a microwave digestion system.

3.7.0 ANALYSIS OF WATER PHYSICOCHEMICAL PARAMETERS

Temperature and pH were determined on site field

3.7.1 Temperature

Thermometer was used in determining the temperature of the water samples on the field.

3.7.2 pH

The pH metre for the determination was first calibrated using a pH 4, 7 and 9 buffer; and the probe stored in 4M KCl saturated with AgCl three hours prior to the sampling. 100 cm³ of distilled water was measured in a beaker and the tip of the probe was immersed into it. The stable pH readings were recorded to the nearest 0.1 unit. The electrode was used in determining the pH of the other samples after it had been rinsed and wiped with a clean tissue.

3.7.3 Electrical Conductivity

The conductivity meter model Phywe 13701.93 was first calibrated with a 0.1M KCl solution. By the help of the calibration button, the conductivity of the 0.1M KCl solution was set to 14.2 millisiemens/cm at 30° C. The electrode was then rinsed thoroughly using deionized water. The electrode was then dipped gently into the sample to be measured and a stable reading was recorded. The probe of the conductivity metre was always kept in distilled water.

3.7.4 Total Dissolved Solids (TDS)

To assess the total dissolved solids, an empty evaporating dish was cleaned and dried in an oven at the temperature of (103-105) °C and weighed to a constant weight. A 200 cm³ volume of water sample was filtered through 0.45 µm pore size filter paper into the dish. The dish and its content was re-weighed, then heated at a temperature of 105 °C. The water sample was left to evaporate to dryness. The dish and its contents were cooled in a desiccator and heated again at 105°C to a constant weight. The difference in weight between the empty dish and the dish

with its content, was used to calculate the total dissolved solid (mg/L). (APHA AWWA WEF, 1998)

3.7.5 Total Suspended Solids (TSS)

Filtration apparatus with a whatman No. 42 filter paper weighed was put on a filter flask. 200 cm³ of the water sample was mixed thoroughly and poured into a graduated cylinder. The cylinder was rinsed into the filtration apparatus with three successive 10 cm³ portions of distilled water, allowing complete drainage between each rinsing. Suction continued until filtration of the final rinse was completed. The filter with the residue on it was then dried in an oven at 103-105° C for 1 hour. This was then followed with cooling of the filter in a desiccator to room temperature. The filter with the residue was then weighed and the total suspended solids (TSS) recorded.

3.7.6 Sulphate Ions

A conditioning reagent was prepared by measuring exactly 25 cm³ glycerol into a beaker. 10 cm³ concentrated HCl was then added followed by 50 cm³ of 95 % isopropyl alcohol. 7 g sodium chloride solution was then added to the solution and made up to the 250 cm³ volumetric flask mark.

Standard sulphate solution was prepared by dissolving 2 g anhydrous Na₂SO₄ in water in a 100 cm³ volumetric flask and made to the mark. Six (6) 100 cm³ glass stoppered standard flask (four for standards, one for the sample and one for the blank) were filled with 10 cm³, 20 cm³, 30 cm³, 40 cm³, for the first four bottles. To the fifth standard flask, 20 cm³ of the sampled water was added. The sixth standard flask serving as a blank was filled with distilled water. A

5 cm³ volume of the conditioning reagent was added to each of the flasks and made up to the 100 cm³ mark with distilled water. The ultraviolet - visible spectrometer was used to determine the absorbance for each of them.

3.7.7 Nitrate Ions

For nitrate determination, a stock solution (100 mg/L NO₃-N) was prepared by dissolving 2 g KNO₃ in 1000 cm³ distilled water preserved with 2 cm³ CHCl₃. An intermediate nitrate solution was prepared by diluting 5 cm³ of the stock solution. A series of NO₃ -N calibration standards in the range of 0.50 – 2 mg/L were made from the intermediate nitrate solutions and made up to 10 cm³ each. A volume of 10 cm³ of filtered sample was measured into test tube with 1 mL of 30 % (W/W) NaCl. A 5 mL volume of 6.5 M H₂SO₄ was then added with swirling after which a 0.25 cm³ brucine reagent was added. The solution was heated in a water bath for 25 minutes at 95 °C. The same was done for the blanks and standards except brucine which was not added to the blank since it gives a yellow colour as indication of nitrate in the sample. The heated solution was allowed to cool to room temperature and absorbance read on a uv-spectrophotometer at 410 nm wavelength. The standards were treated just like the sample. A calibration curve of absorbance against concentration was plotted. Concentration of the sample was then read from the curve.

3.7.8 Phosphate ions

A 3.5 g of ammonium molybdate and 0.045 g of potassium antimonyl tartrate were weighed into a 500 cm³ volumetric flask and 10.0 cm³ of concentrated H₂SO₄ added. A 0.1 M ascorbic acid was made by dissolving 3.52 g of the salt in 200 cm³ distilled water. The molybdate-

antimony reagent and the ascorbic acid were added in the ratio of 1:4 and this is referred to as the combined reagent. To 10 cm³ of the filtered sample, 4 cm³ of the combined reagent were added and mixed well and allowed to stand for 10 minutes. A UV spectrophotometer at 880 nm was used to determine the absorbance of each sample and the blank (reference). The same was done for the standard of 50 mg/L prepared from anhydrous KH₂PO₄. Concentration of samples was calculated from the calibration curve.

3.7.9 Sodium (Na) and Potassium (K) ions

Determinations of these metals were done photometrically using the Advance Technical Service (ATS) Flame Photometer (FP). The intensities of sodium (Na) and potassium (K) were measured at wavelengths of 598 nm and 766.5 nm respectively after calibrating the instrument with serially diluted standards prepared from salts of the two elements. Five drops of Ionization Suppressor Cesium Chloride (CsCl) were added to the solution to minimize the ionization of sodium (Na) and potassium (K) after which the solution was aspirated into the flame for readings to be taken.

3.7.10 Total hardness

A 100 cm³ volume of the water sample was transferred into a 500 cm³ conical flask. 2 cm³ of aqueous ammonia was added followed by 2 drops of methyl orange indicator and then mixed thoroughly. A pink colouration formed was a confirmation of the presence of salts of magnesium and calcium. The solution was then titrated with standard EDTA solution. The titration was continued drop-wise to a blue end point.

3.7.11 Total Alkalinity

50 cm³ of the water sample was pipetted into a conical flask and 2 drops of methyl orange added. It was then titrated against 0.02 M HCl standard solution to a pale pink end point.

3.8 Contamination factor and degree of contamination

The assessment of sediment contamination was carried out using the contamination factor and degree of contamination. In the version suggested by Hakanson (1980), they enable an assessment of sediment contamination through reference of the concentrations in the surface layer of bottom sediments to preindustrial levels (average shale).

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \quad (2)$$

where C_f^i is the contamination factor of the element of interest, C_{0-1}^i is the concentration of the element in the sample, C_n^i is the background concentration in this study (Taylor, 1969).

C_f^i is defined according to four categories: $C_f < 1$ represents low contamination factor, $1 \leq C_f < 3$, moderate contamination factor, $3 \leq C_f < 6$ considerable contamination factor and $C_f \geq 6$ very high contamination factor. The sum of the contamination factors of all the elements in the sample gives the degree of contamination as indicated in the equation below:

$$C_{deg} = \sum C_f^i \quad (3)$$

Four categories have been defined for the degree of contamination as follows; $C_{deg} < 8$ represents low degree of contamination, $8 \leq C_{deg} < 16$ moderate degree of contamination, $16 \leq$

$C_{deg} < 32$ considerable degree of contamination and $C_{deg} > 32$ very high degree of contamination.

3.9 Statistical analysis and data treatment

A statistical analysis was carried out using SPSS 20 (SPSS Inc.). Relationships between various variables were determined using the Pearson correlation coefficients (r). Regression models were performed by stepwise selection with a significance level of $p < 0.05$ for variables to remain in the predictive equations. Other statistical analyses including mean, standard error (SE), maximum, minimum and coefficient of variation (CV), and step - wise linear regressions were carried out using SPSS 20.0 and Microsoft excel. Independent T-test was also performed using SPSS 20.0.

3.10 Quality assurance (QA) and quality control (QC)

All experiments have been performed in duplicates including reagent blanks. Additionally, a certified reference material (IAEA-7) has been analyzed ($n = 4$) in conjunction with the samples to verify the accuracy and precision of the analytical procedure for total metal concentration. The recovery values of metals of the certified reference material were all greater than 85% of the certified values provided by IAEA-7.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

This chapter reveals the explanation of results of both field and laboratory analyses in both tables and figures. The parameters discussed were considered whether they were below or above pollution level using different conditions most importantly the WHO guideline limits for the assessment. The results and discussions were grouped into two seasons which cover the wet and dry seasons. Generally, seasonal variation was observed in the concentration of physico-chemical parameters. The dry season recorded higher concentrations for the physico-chemical parameters compared to that of the wet season. This general trend could be attributed to runoffs, discharge of waste chemicals into the river, dissolved minerals and excessive evaporation of water from the surface water which resulted in an increase in concentration of ions. Based on the objectives of the study, the results are discussed under their corresponding headings. Statistical analyses such as, one-way ANOVA, was applied to the results (using SPSS ver. 16.0) to highlight the relationship between elements and other parameters as well as to identify the various sources of these elements.

4.1 Temperature

Tables 1 and 2 show the results of the physical parameters (temperature and pH) of water samples respectively. The recorded mean temperature of the water samples for the wet season was 28.5 °C, ranging from values of 26.0 °C to 29.5 °C with the maximum temperature recorded at Bunso (downstream) and the minimum temperature recorded at Apapam (upstream).

There was a rise in the values of temperature recorded in the dry season with a mean value of 31.50 °C. The temperature ranged from 30.50 °C to 32.0 °C. Minimum temperature of the

water in the dry season was recorded at Apapam (upstream) with the maximum recorded at Bunso (downstream). The lower temperatures recorded in the wet season may be as a result of cooling effect of rainfall.

Table 4.1: Comparison of Mean Temperature Values for the Water Samples during the Wet and Dry Seasons

Sampling sites	(°C)	
	Wet season	Dry season
Apapam	26.00	30.5
Efisa	28.00	32.00
Adadientem	27.50	32.00
Obronokrom	29.00	31.00
Asikam	28.50	31.50
Akyem adukrom	29.00	30.50
Bunso	29.50	30.5
Anyinam	27.50	32.00
Osino	27.50	31.50
Abomosu	28.50	31.00
Mean	28.05	31.50

4.2 pH

A mean pH value of 7.21 was recorded for the water sample in the wet season and a mean value of 7.86 in the dry season. The pH of the river water for the wet season was fairly

neutral whilst that of the dry season was slightly basic. The maximum pH value for the wet season was recorded at Bunso (downstream) with a value of 7.48 with the minimum recorded at Apapam (Upstream) with a value of 6.92. Adadientem recorded the highest pH value of 8.32 with the lowest recorded at Apapam with a value of 6.71 for dry season. There was an increase in the pH values from upstream to downstream for the wet season. Both wet and dry seasons had their pH values within the WHO and USEPA safety limit of 6.5 - 8.0 and 6.5 - 8.5 respectively.

Table 4.2: Comparison of Mean pH Values for the Water Samples during the Wet and Dry Seasons

Apapam	6.92	6.71
Efisa	7.23	7.41
Adadientem	7.38	8.32
Obronokrom	7.01	8.21
Asikam	7.31	7.51
Akyem adukrom	7.10	8.10
Bunso	7.48	8.23
Anyinam	7.01	8.31
Osino	7.23	7.56
Abomosu	7.38	8.23
Mean	7.21	7.86

4.3 DISTRIBUTION OF MERCURY IN WATER AND SEDIMENT SAMPLES

Concentration of mercury in water samples taken during both seasons, the wet (September, 2015) and dry (February, 2016) seasons are shown in table 4.2 and 4.3 (Appendix D) and presented comparatively in figure 4.1.

4.3.1 MERCURY IN WATER SAMPLES

All the mercury concentrations measured in the dry season were higher than those in the wet season. A mean concentration of ($0.333 \mu\text{L}$) was recorded in the wet season while the dry season recorded an average value of ($0.569 \mu\text{L}$). The increase in the total mercury concentration in the dry season may be as a result of two reasons. The first may be attributed to an increased mining activities during the dry season with an increases in mercury use and the second may be as a result of evaporation of the surface water during the dry season resulting in increased mercury concentrations. However there was no indication of rampant mining operations during the research period. The high levels of mercury may therefore be as a result of evaporative effects on the surface water. The concentrations of mercury in both seasons were below the world health organization guideline value of ($1.0 \mu\text{g/L}$) for drinking water (WHO, 1996).

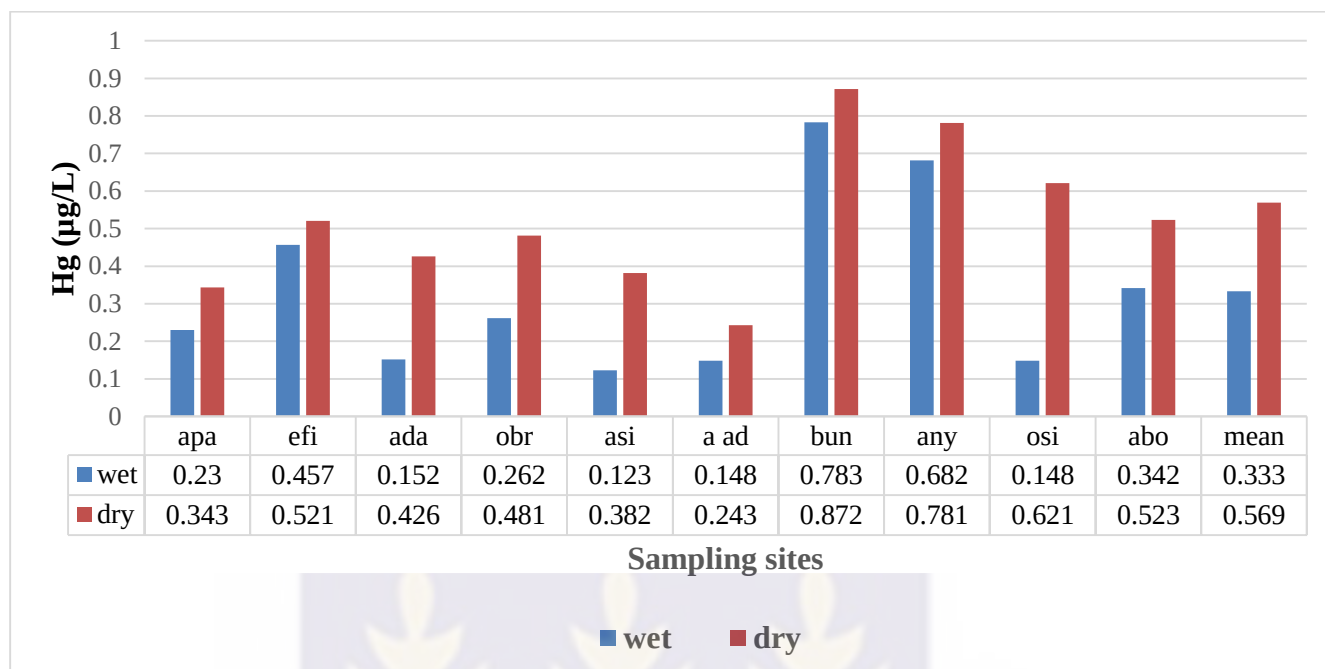


Figure 4.1: Total Mercury Concentrations of water samples

4.4 TOTAL MERCURY IN WATER SEDIMENT.

Total mercury concentrations on the surface sediment samples for both seasons are given in tables 4.4 and 4.5 (**Appendix E**) and presented comparatively in figure 4.2.

Concentrations of mercury measured in the dry season were higher than the corresponding wet season concentrations. There was an increase in mercury concentrations in the River sediment moving downstream. The wet season recorded an average mercury concentration of 0.938 mg/kg ranging from 0.412 mg/kg to 1.712 mg/kg and an average concentration of 1.899 mg/kg, ranging from 0.821 mg/kg to 4.870 mg/kg in the dry season. Two reasons may account for these seasonal changes in the total mercury concentrations. Firstly, mining activities may have increased during the dry season with an increased use in mercury and the second been evaporation of the surface water leading to increased mercury concentrations in the water and sediments. There was however no evidence of increased mining operations and so the high

levels of mercury during the dry season can only be as a result of evaporation. There is also minimal mixing of the river during the dry season which reduces the mercury in bottom layers of sediments from moving to the surface to be volatilized, possibly resulting in higher total mercury levels in the sediments. All the mercury concentrations of the upstream and downstream sediments during both seasons exceeded the US EPA guideline value (0.2 mg/kg) for sediment.

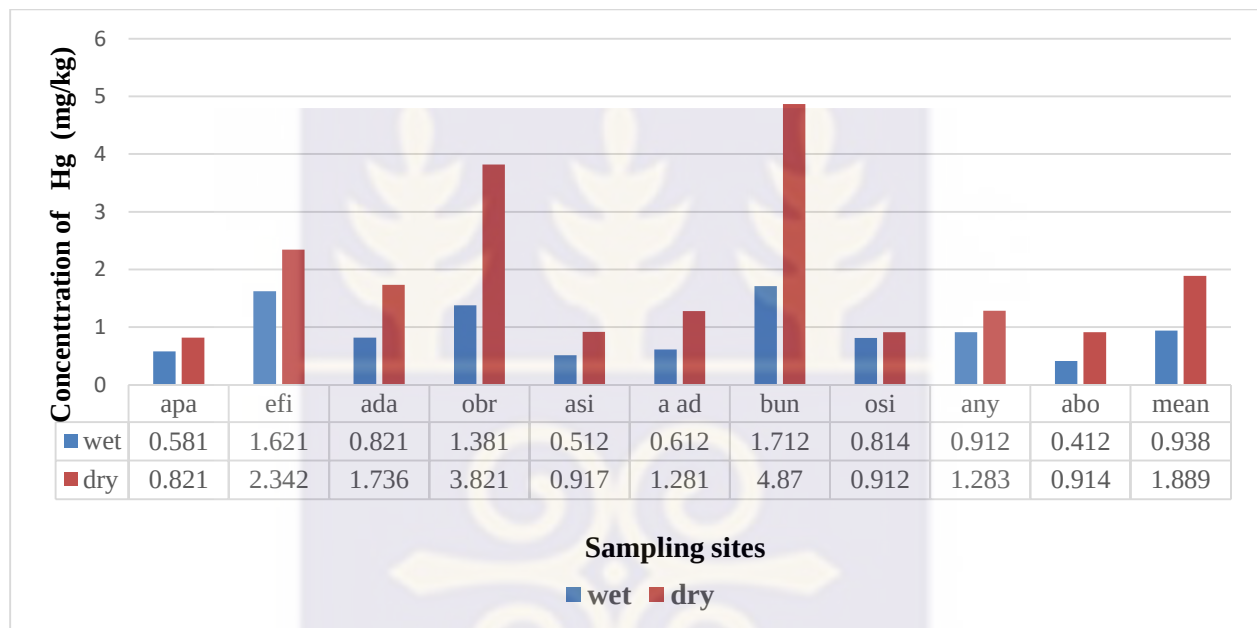


Figure 4.2: Total Mercury Concentrations of water Sediment Samples

4.5 OTHER HEAVY AND TRACE METALS IN WATER AND SEDIMENT SAMPLES

4.5.1 Manganese in Water Samples

Manganese is commonly found in natural water. It has the tendency of causing unsight stains and problems that are normally associated with neurological damage (Kondakis et al, 1989).

A mean concentration of 0.406 mg/L, ranging between 0.11 mg/L (Apapam) and 0.81 mg/L (Abomosu) was recorded during the wet season. However, during the dry season a mean concentration of 0.43 mg/L ranging between 0.14 mg/L (Apapam) and 0.90 mg/L (Abomosu) was recorded.

The Mn concentrations observed during both seasons were higher than the recommended limit of 0.01 mg/L for drinking water (WHO, 2011).

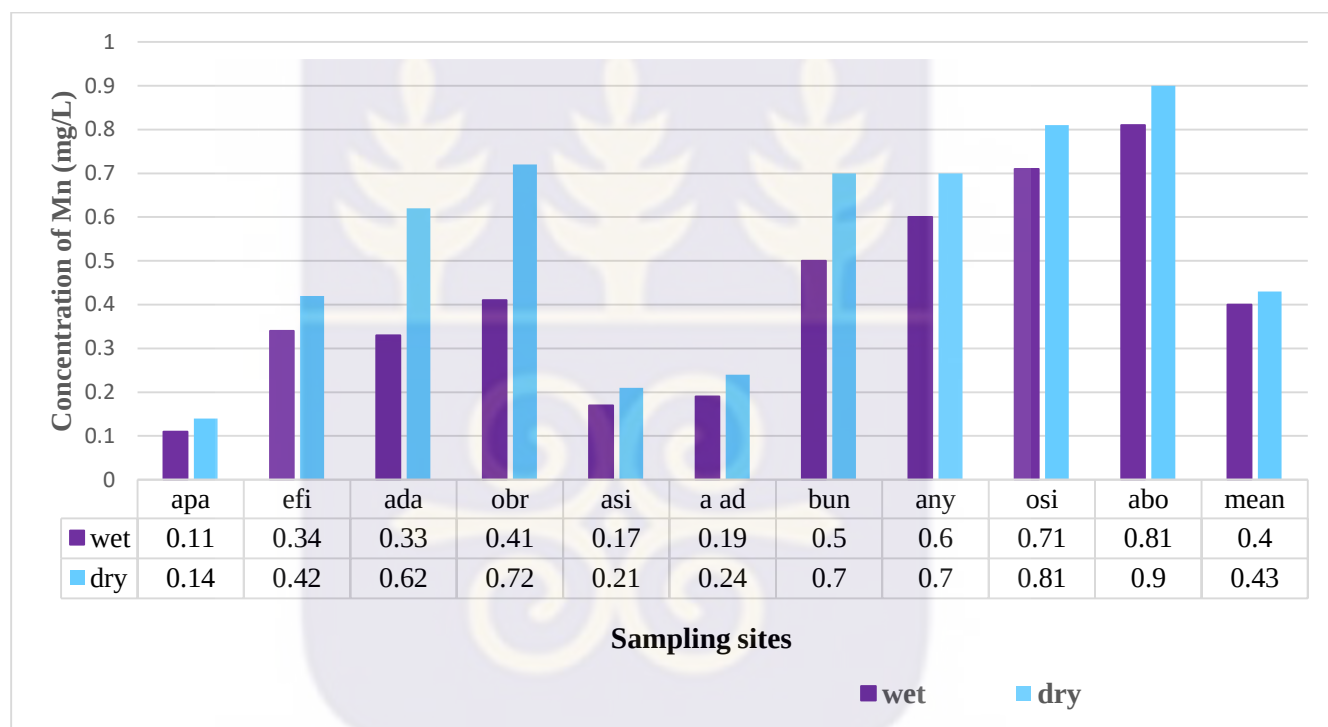


Figure 4.3: Comparison of mean manganese concentrations in water samples during wet

4.5.2 Manganese in water sediments

The mean manganese (Mn) concentration for the sediment in the wet season was found to be 20.20 mg/kg, ranging from 18.31 mg/kg (Efisa) to 22.06 mg/kg (Bunso). A mean concentration of 20.45 mg/kg was recorded during the dry season. This ranged from 18.46

mg/kg (Efisa) to 22.63 mg/kg (Bunso). The mean values of manganese in the sediment for both seasons were below the USEPA sediment guideline value of 30 mg/kg, (USEPA, 1999).

There was a mean contamination factor (C_f) of 0.02 (Appendix F and G) which remained constant throughout all the sampling sites for both seasons. C_f values below 1 is an indication of no pollution, hence the sediment was not polluted with respect to Mn.

The Geo-accumulation index value during the wet season (Appendix C) was -6.08 which ranged from -5.63 (Apapam) to -6.28 (Efisa). For the dry season, the mean Geo-accumulation index was -6.13 ranging from -6.03 (Asikam) to -6.28 (Adadientem), (Appendix I). From the Muller classification (Appendix J) the mean and range values for both seasons fell into category 0 indicating no pollution by manganese.

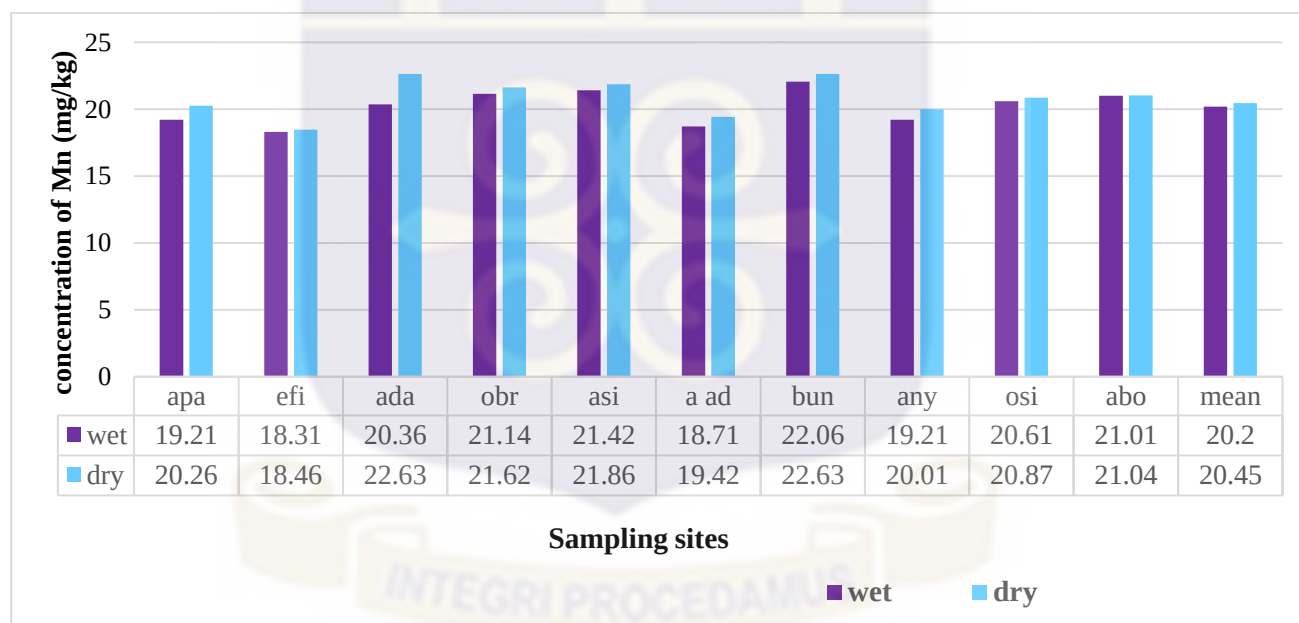


Figure 4.4: Comparison of mean manganese concentrations in water Sediment samples during wet and dry seasons.

4.5.3. Iron in water samples

Iron though is vital elements in human nutrition, its occurrences at higher concentration in an aquatic system can cause major pollution and health issues (Akan 2012). The overall mean concentration of Iron at the ten sampling sites was 1.75 mg/L and ranging from 0.86 mg/L (Apapam) to 2.39 mg/L (Abomosu) in the wet season. However, in the dry season a mean concentration of 1.28 mg/L ranging between 0.62 mg/L (Apapam) and 1.92 mg/L (Akyem Adukrom) was recorded.

Concentration of Fe were generally relatively higher during the wet season than in the dry season at all sampling sites. Iron levels recorded in all the sampling sites were higher than the recommended limit of 0.01mg/ L for drinking water (WHO, 2011). This implies the Birim River may be contaminated with iron (Fe).

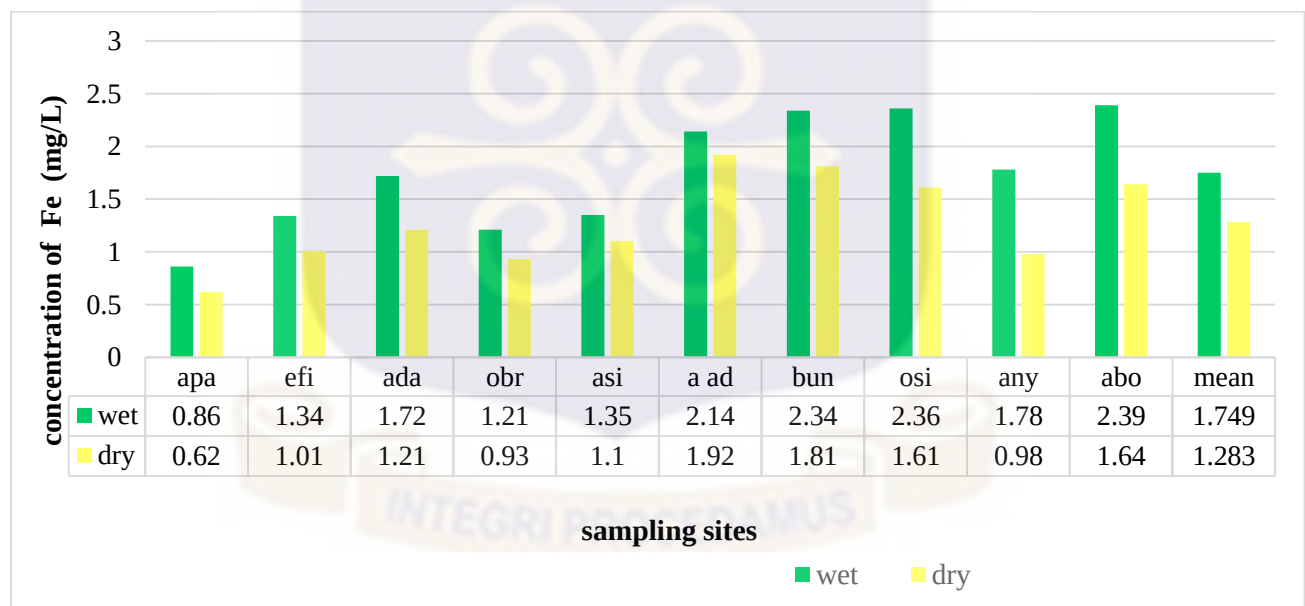


Figure 4.5: Comparison of mean Iron concentrations in water samples during wet and dry seasons.

4.5.4 Iron in water sediments

The mean Iron (Fe) concentration in the sediments in the wet season was 25.11 mg/kg and ranged between 11.51 mg/kg (Apapam) and 40.21 mg/kg (Bunso). The mean concentration during the dry season was 27.09 mg/kg, ranging from 12.23 mg/kg (Apapam) to 42.64 mg/kg (Bunso). The mean values of Iron in the sediment for both seasons were all below the USEPA (1991) sediment guideline value of 30 mg/kg.

The mean sediments contamination factor of Fe was 5.34 and ranged between 2.45 (Apapam) and 8.56 (Bunso) during the wet season (Appendix F) and a mean value of 5.78 season ranging from 2.6 (Apapam) to 9.07 (Bunso) during the dry season (Appendix G).

All the C_f values for both seasons were greater than 2 indicating moderate contamination (Appendix F and G). The sediments from Bunso, Osino, Anyinam and Abomosu (Appendix E) which are downstream Apapam had their C_f values greater than 6, indicating very high contamination. Martin and Meybeck (1979). The wet season recorded a mean Geo accumulation index (Geo-I) of 1.68 ranging from 0.71 (Apapam) to 2.51(Bunso) whilst the dry season had a mean value of 1.79, ranging from 0.79 (Apapam) to 2.60 (Bunso). The two mean values for both seasons fell within category 2 (Appendix J) of the Muller's classification indicating moderate pollution by Iron (Fe).

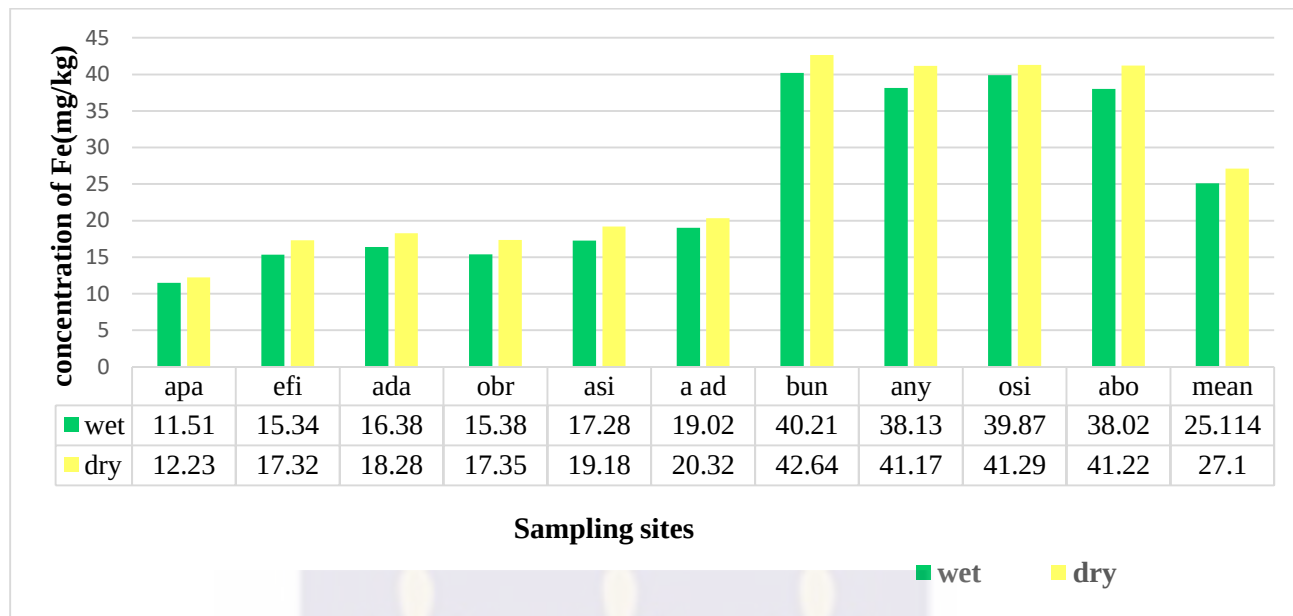


Figure 4.6: Comparison of mean Iron concentrations in water Sediment Samples during wet

4.5.5 Lead in water Samples

Lead has a lot of health problems worldwide (Makokha, 2004). It has serious adverse health impacts which usually affect children (WHO, 1995), where it has been explicitly related to neuro-behavioural and developmental issues. The overall mean concentration of Pb at the ten sampling sites was 0.25 mg/L and ranged between 0.06 mg/L (Apapam) and 0.82 mg/L (Akyem Adukrom) in the wet season and an overall mean concentration of 0.37 mg/L, ranging from 0.08 mg/L (Apapam) to 0.96 mg/L (Obromikrom) in the dry season. There was an increase (from 0.08 to 0.957 mg/L) in the concentrations of Pb downstream.

The concentrations of Pb during both seasons were all above the recommended limit of 0.01mg/ L in drinking water (WHO, 2011).

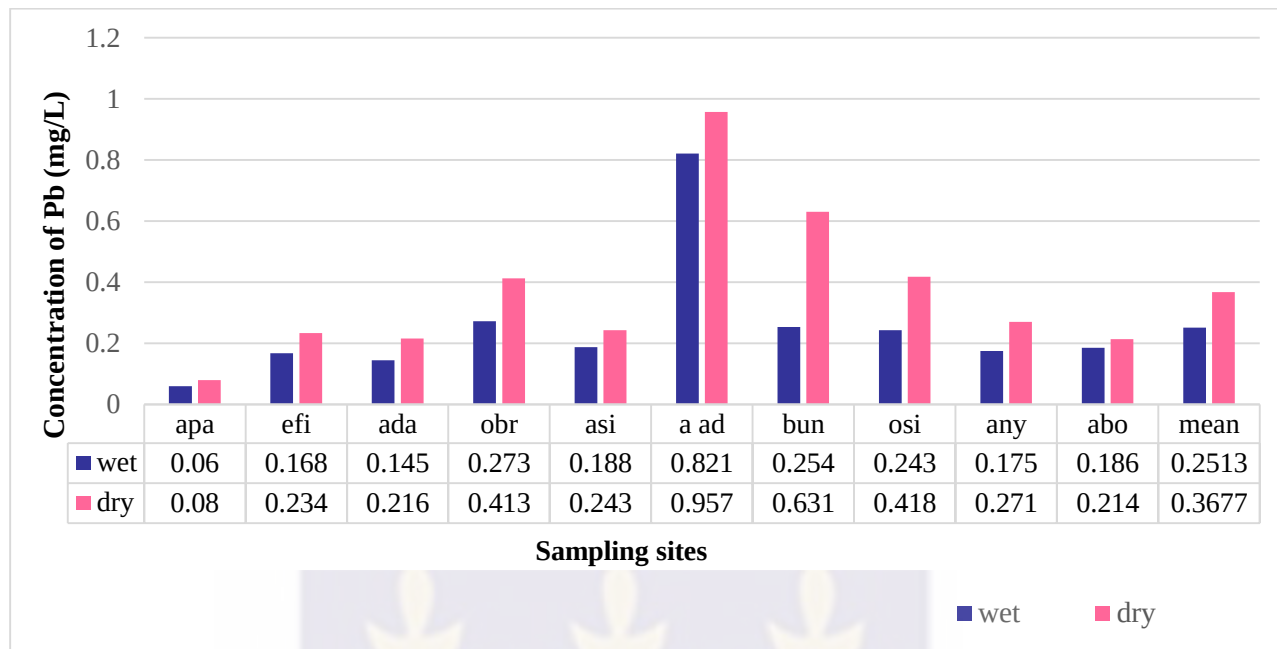


Figure 4.7: Comparison of mean Lead concentrations in water samples during wet and dry seasons.

4.5.6 Lead in water Sediment Samples

The mean Lead (Pb) concentration in the sediment was 2.14 mg/kg in the wet season, ranging from 1.45 mg/kg (Efisa) to 3.72 mg/kg (Bunso). The dry season recorded a mean value of 2.29 mg/kg which ranged from 1.31 mg/kg (Efisa) to 4.22 mg/kg (Bunso). The mean Pb concentration in the sediment observed in this study were lower than the recommended limit of 40 mg/kg for lead in sediment (WHO, 2011). The mean contamination factor (C_f) for Pb in the sediment during the wet season was 0.26, ranging from 0.12 (Efisa) to 0.29 (Bunso). In the dry season, a mean value of 0.18 was recorded ranging from 0.1 (Efisa) to 0.34 (Bunso). All the C_f values for both seasons were less than 1 indicating low contamination by Pb.

The wet season recorded a mean value of -3.22 for the Geo-accumulation Index (Geo-I) ranging from -2.33 (Bunso) to -3.69 (Efisa). During the dry season, a mean value of -3.16 was recorded ranging from -2.15 (Bunso) to -4.08 (Asikam). All the sampling sites recorded a

negative value with respect to Geo- accumulation index hence no pollution by Pb according to the Muller classification since this falls under category 0. (Appendix J)

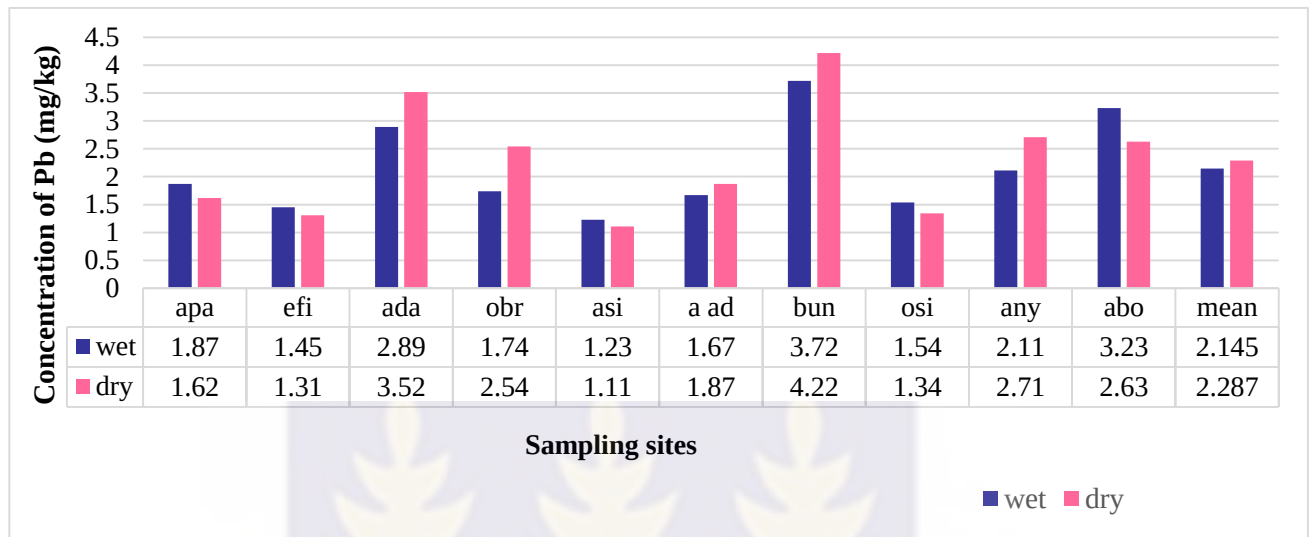


Figure 4.8: Comparison of mean Lead concentrations in water sediment samples during wet and dry seasons

4.5.7 Nickel concentration in water Samples

The mean concentration of Ni in water for the ten sampling sites were generally lower in the dry season than the wet season with a mean value of 0.038 mg/L (range: 0.02- 0.06 mg/L) during the wet season and 0.019 mg/L (range: 0.01-0.04 mg/L) during the dry season.

The levels of Ni were all below the WHO guideline value of (0.002 µg/L) for drinking water (WHO, 2011).

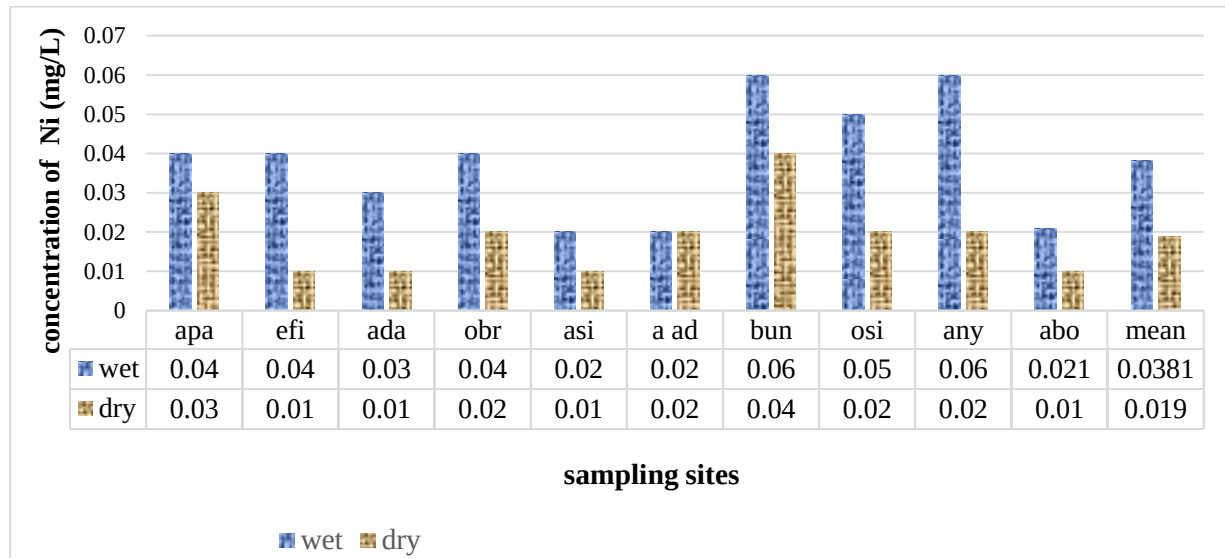


Figure 4.9: Comparison of mean Nickel concentrations in water samples during wet and dry seasons.

4.5.8 Nickel in water Sediment Samples

The mean Ni concentration in the sediments was 7.82 mg/kg in the wet season, ranging from 6.34 mg/kg (Efisa) to 9.03 mg/kg (Bunso). The dry season had a mean value of 8.24 mg/kg which ranged between 6.94 mg/kg (Adadientem) and 9.24 mg/kg (Bunso). The mean concentrations for each season was lower than the suggested limit of 18 mg/kg for Ni in sediment. (WHO, 2011). The mean contamination factor (C_f) for Nickel in the sediment during the wet season was 0.1, ranging from 0.08 (Efisa) to 0.12 (Bunso). In the dry season, a mean contamination factor value of 0.11 was recorded which ranged from 0.09 (Adadientem) to 0.12 (Bunso). All the C_f values for both seasons were less than 1 indicating low contamination of Ni as proposed by (Hankanson, 1980).

The overall mean value of Nickel for Geo-accumulation Index (Geo-I) was -3.85 Nickel and ranged between -3.64 (Bunso) and -4.15 (Efisa). During the dry season, Nickel had a mean value of -3.87 which ranged between -3.61 (Bunso) and -4.02 (Adadientem).

All the sampling sites had negative values for Geo-accumulation Index for both seasons indicating no pollution by Ni as proposed by Muller. (Appendix J)

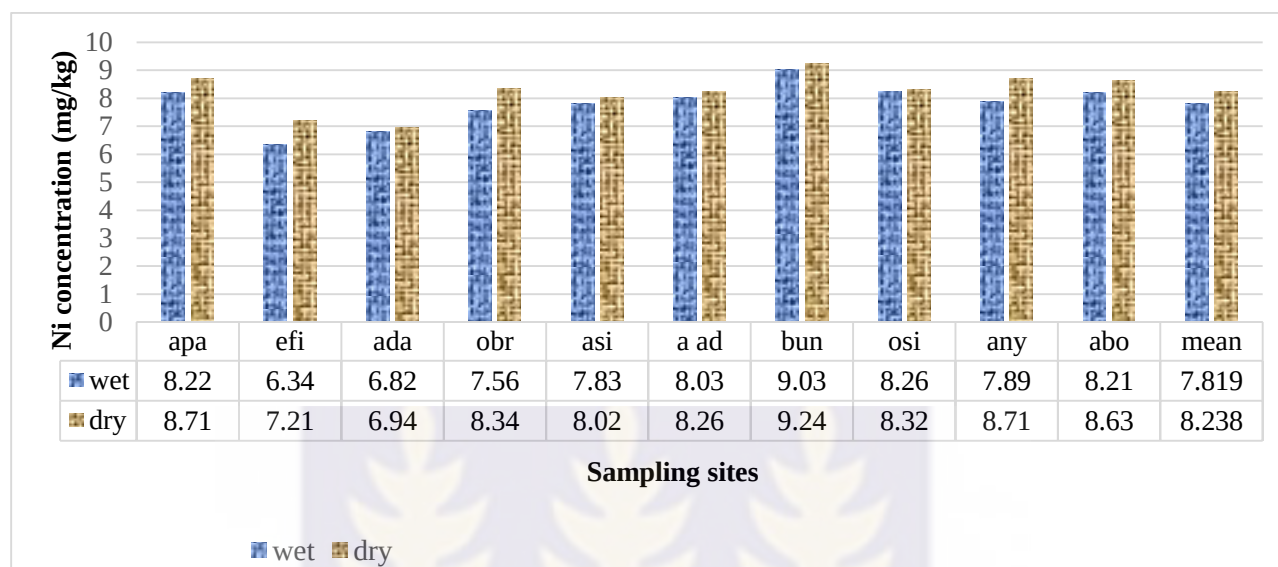


Figure 4.10: Comparison of mean Nickel concentrations in water sediments during wet and dry seasons.

4.5.9 Cadmium Concentrations in water Samples

The overall mean concentration of Cd at the ten sampling sites was 0.05 mg/L and ranged from 0.02 mg/L (Asikam) to 0.009 mg/L (Abomосу) during the wet season. However, during the dry season, Cd concentrations in all ten sampling sites ranged from 0.04 mg/L (Obronikrom) to 0.09 mg/L (Bunso) with an overall mean concentration of 0.07 mg/L. The concentration of Cd for the dry season were all greater than that of the wet season for the various sampling sites. For the wet season, the level of Cd in the water samples were all above the WHO guideline for safety drinking water except Asikam and Obronikrom (0.02 mg/L) as compared to the WHO value of 0.03 mg/L, (WHO 2004). In the case of the dry season, the Cd level were all above the WHO safety limit of Cd for drinking water.

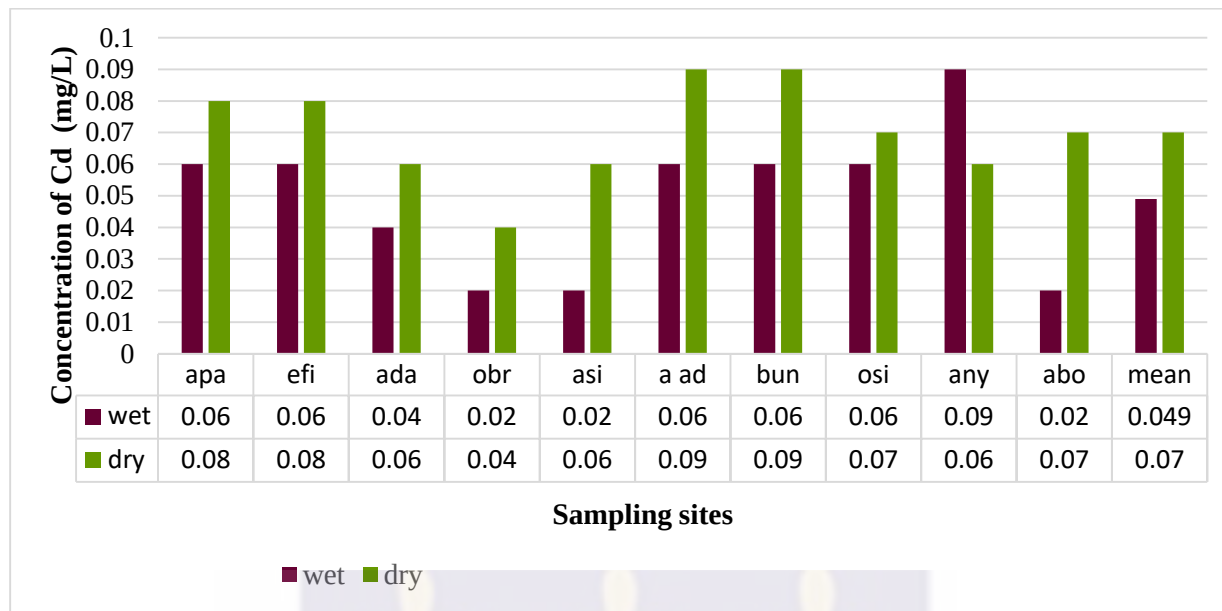


Figure 4.11: Comparison of mean Cadmium concentrations in water samples during wet and dry seasons.

4.5.10 Cadmium (Cd) Concentration in water Sediments.

The overall average concentration of Cadmium at all sampling locations in the sediment in the wet season was 0.12 mg/kg ranging from 0.04 mg/kg (Asikam) to 0.21 mg/kg (Bunso) whilst the dry season recorded a mean value of 0.16 mg/kg ranging from 0.05 mg/kg (Oboronikrom) to 0.31 mg/kg (Bunso). The mean values during both seasons for Cd metal were all below the USEPA sediment quality guideline of 0.6 mg/kg.

The mean contamination factor for Cd in the sediment was 1.47 and ranged between 0.71 (Oboronikrom) and 3.00 (Bunso) in the wet season and a mean of 0.79 ranging between 0.39 (Akyem Adukrom) and 1.55 (Bunso) during the dry season. The C_f values during the dry season were greater than 1 suggesting moderate contamination by Cd. (Appendix G)

The Geo-accumulation Index values (I-Geo) for Cd ranged from -0.51 (Bunso) to -2.91 (Asikam) in the wet season with a mean value of -1.24 ranging from -0.05 (Bunso) to -2.58

(Abomосу) during the dry season. The Geo-accumulation values for all the sampling sites were negative. This from the Muller classification falls into category 0 indicating no pollution by cadmium (Appendix J)

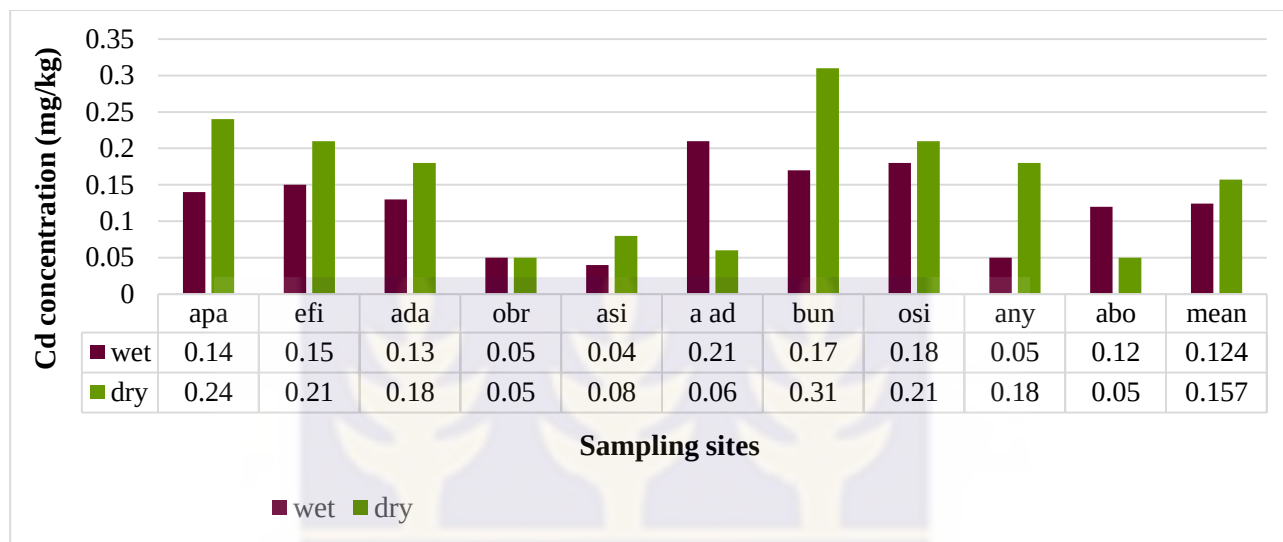


Figure 4.12: Comparison of mean Cadmium concentrations in water Sediment samples during wet and dry seasons.

4.5.11 Zinc concentrations in water samples

The overall mean concentration of Zn for the ten sampling locations was 0.178 mg/L ranging between 0.143 mg/L (Apapam) to 0.199 mg/L (Anyinam) during the wet season. However, in the dry season the Zn concentrations ranged from 0.231 mg/L (Apapam) to 0.521 mg/L (Bunso) with overall mean value of 0.380 mg/L. The levels of Zn in the water samples were below the WHO guidelines for safety water of metals (3 mg/L) in both seasons, (WHO, 2011).

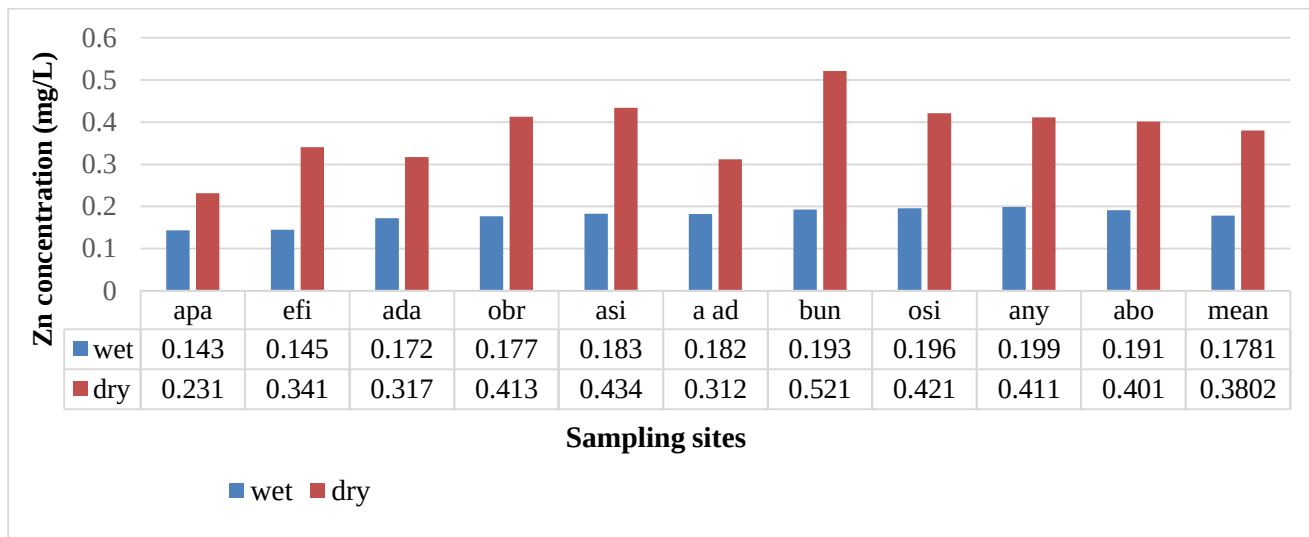


Figure 4.13: Comparison of mean Zinc concentrations in water samples during wet and dry seasons.

4.5.12 Zn concentrations in water Sediment Samples

The mean Zinc (Zn) concentration in the sediments in the wet season was 0.48 mg/kg ranging between 0.128 mg/kg (Anyinam) and 0.814 mg/kg (Bunso). The mean concentration in the dry season was 0.633 mg/kg which ranged from 0.354 mg/kg (Osino) to 1.212 mg/kg (Bunso). The mean values of Zn in the sediment for both seasons were all below the USEPA (1991) sediment quality guideline of 123 mg/kg.

The mean contamination factor of Zinc was 0.0064 and ranged from 0.004 (Anyinam) to 0.012 (Bunso) during the wet season and a mean value of 0.0089 during the dry season with a range of 0.005 (Anyinam) to 0.017 (Bunso).

All the C_f values for both seasons were less than 0 indicating low contamination.

The Geo-accumulation Index values (I-Geo) for Zn ranged from -7.02 (Bunso) to -9.77 (Anyinam) with a mean value of -7.85 in the wet season and the dry season ranging from -6.44 (Bunso) to -8.23 (Osino) with a mean value of -7.48. The Geo-accumulation values for

all the sampling sites were negative. This from the Muller classification falls into category 0, indicating no pollution by Zn. (Appendix J)

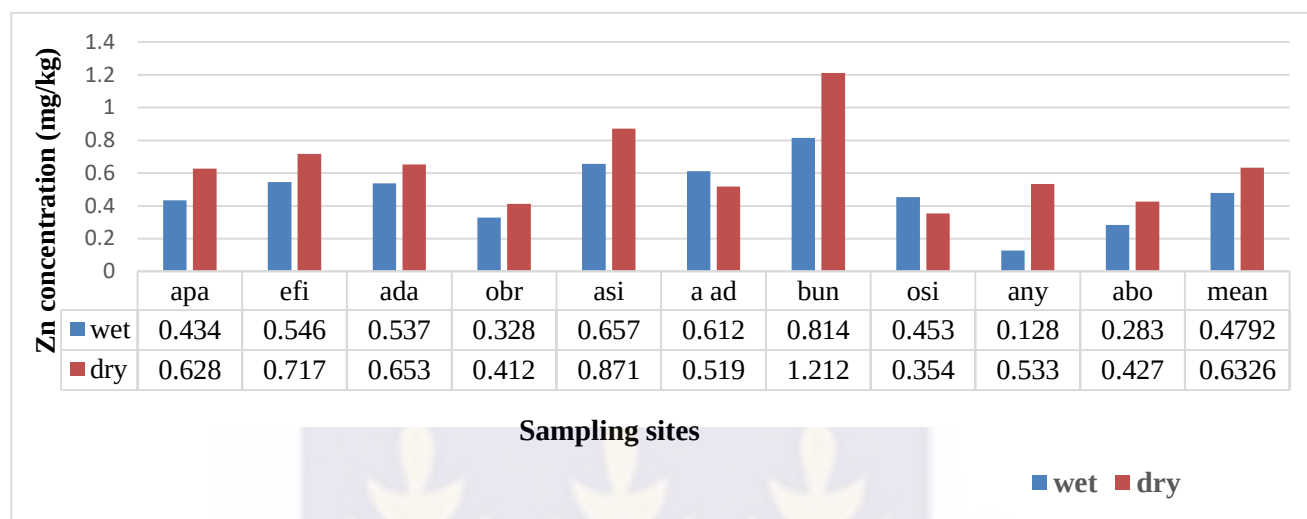


Figure 4.14: Comparison of mean Zinc concentrations in water Sediment samples during wet and dry seasons.

4.5.13 Arsenic concentrations in water Samples

The levels of As in the wet season were relatively higher than the dry season. The overall mean concentration of As at the ten sampling sites was 0.011 mg/L and ranged between 0.01 mg/L (Apapam) and 0.02 mg/L (Oboronikrom) in the wet season. However, in the dry season, the As concentrations ranged between 0.002 mg/L (Apapam) and 0.009 mg/L (Oboronikrom) with a mean concentration of 0.01 mg/L. With the exception of Oboronikrom, 5 km downstream Apapam, all the other sampling sites had As levels within the WHO guidelines of safety limit of drinking water of As, 0.01 mg/L (WHO, 2011).

Oboronikrom recorded a value of 0.02 mg/L which exceeded the WHO guideline of As for drinking water. This may be due to the rampant mining activities in the area compared to the others.

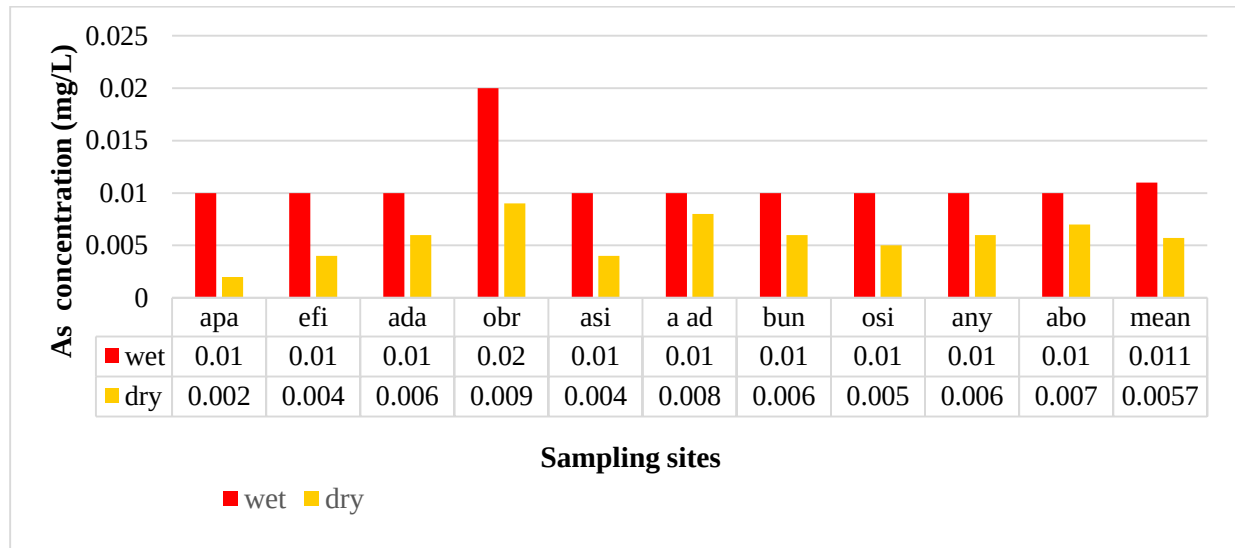


Figure 4.15: Comparison of mean Arsenic concentrations in water samples during wet and dry seasons.

4.5.14 Arsenic levels in water Sediment Samples

The overall average concentration of Arsenic at the sampling locations in the sediments during the wet season was 0.0188mg/kg, ranging between 0.006 mg/kg (Apapam) to 0.100 mg/kg (Oboronikrom) whilst the dry season had a mean value of 0.022 mg/kg and ranged from 0.008 mg/kg (Apapam) to 0.110 mg/kg (Oboronikrom). The mean values for both seasons for As metal were all below the USEPA sediment guideline value of 0.2 mg/kg.

The mean Contamination factor (C_f) for As in the sediments was 0.01 ranging from 0.003 (Apapam) to 0.012 (Bunso) in the wet season and a mean value of 0.018 ranging from 0.004 (Apapam) to 0.061 (Oboronikrom and Akyem Adukrom) in the dry season. All the C_f values were less than one suggesting low contamination by As.

The Geo-accumulation Index values (I-Geo) for As ranged from -4.75 (Oboronikrom) to -8.81 (Apapam) in the wet season with a mean of -7.88 and ranged from -3.12 (Bunso) to -8.39 (Apapam) in the dry season with a mean of -6.88. The Geo-accumulation values for all the

sampling sites were negative. This from the Muller classification falls into category 0 indicating no pollution by As. (Appendix J)

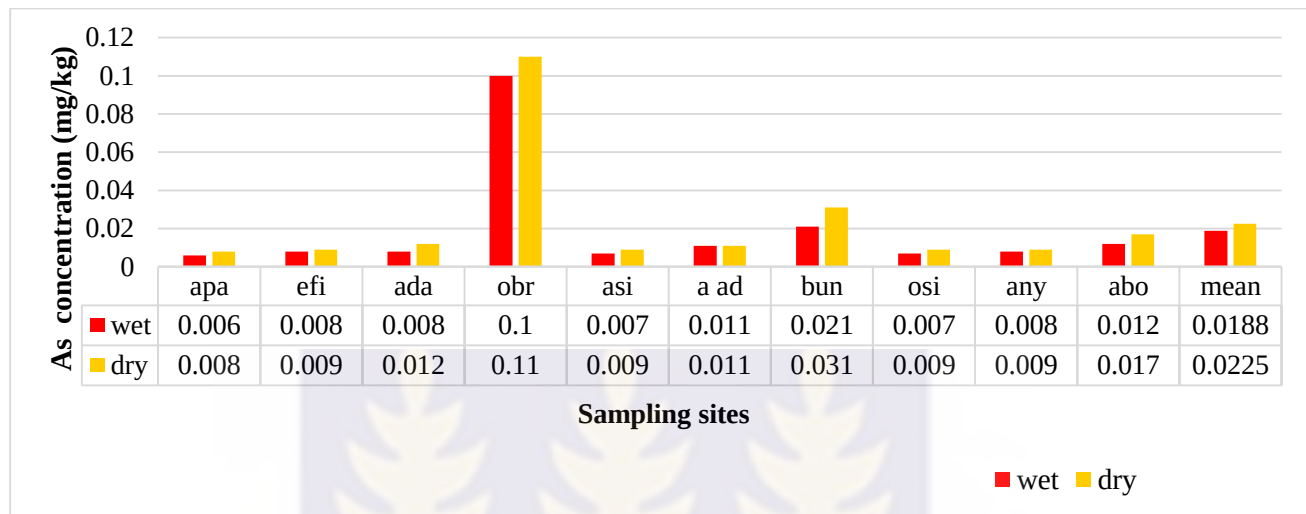


Figure 4.16: Comparison of mean Arsenic concentrations in water Sediment samples during wet and dry seasons.

4.6 POLLUTION LOAD INDEX (PLI)

Pollution Load Index (PLI) was used to determine the contamination status of the sediments found in the Birim River. The PLI for the Birim River was evaluated based on the following equation:

$$PLI = (CF_1 * CF_2 * CF_3 * CF_4)^{1/n}$$

Where n represents the number of metals.

PLI value > 1 is an indication of pollution and PLI value < 1 shows no pollution (Seshan et al., 2010). The results of the Pollution Load Index (PLI) are shown in Appendix F. The values for all the sites for both the dry and wet seasons are less than 1 which indicates that the River Birim is not contaminated with the heavy metals measured.

4.7. PHYSICO-CHEMICAL PARAMETERS OF WATER SAMPLES

4.7.1 Electrical Conductivity

The overall average conductivity of water at the ten sampling sites was 125.55 $\mu\text{S}/\text{cm}$ in the wet season ranging between (112.70 $\mu\text{S}/\text{cm}$ (Apapam) and 138.50 $\mu\text{S}/\text{cm}$ (Bunso) (Appendix A). However, in the dry season, an average conductivity of the water samples for all the ten sampling sites was 155.95 $\mu\text{S}/\text{cm}$ ranging between 150.3 $\mu\text{S}/\text{cm}$ (Apapam) and 169.64 $\mu\text{S}/\text{cm}$ (Bunso) (Appendix B). Water conductivity largely increased moving downstream along the water course for both wet and dry seasons.

According to Koning and Roos, (1999), an unpolluted stream must have an electrical conductivity value of 350 $\mu\text{S}/\text{cm}$.

The electrical conductivity for the water samples were all below the recommended value of 1500 $\mu\text{S}/\text{cm}$ for clean drinking water (WHO, 2011).

4.7.2 Total Suspended solids (TSS).

The overall mean concentration for the ten sampling sites was 21.89 mg/L which ranged between 6.3 mg/L (Apapam) and 40.2 mg/L (Abomosu). Though the values observed during both seasons were lower when compared to EPA-Ghana guidelines of 50.00 mg/L but when compared to WHO limit of 20.00 mg/L, then there is an alarming situation for the water quality so far as TSS is concerned (Appendices A and B).

High TSS values could be due to land-use practices such as excavation, discharge of raw sewage and domestic waste which brings large quantities of silt and debris into the streams (Cloern, 1987).

4.7.3 Total Dissolved Solids (TDS).

TDS is the most common indicator of polluted water (Tay, 2007). The Total Dissolved Solids (TDS) recorded for both seasons were all higher than the Total Suspended Solids. The overall mean concentration of TDS for the ten sampling was 61.32 mg/L in the wet season (Appendix A). However, in the dry season TDS concentrations for the ten sampling sites was 51.97 mg/L (AppendixB). These values were not worrying when compared to the WHO, 2011 recommended limit of 1000 mg/L in drinking water. However, in Ghana, it is of much concern since the EPA - Ghana recommended guideline value for TDS in drinking water is less than 50mg/L (EPA - Ghana, 1994).

4.7.4 Total Hardness

The average range concentration of total hardness of all the water samples for both seasons fell below both EPA-Ghana and WHO 2011 recommended safety guideline limit value of 500mg/L in drinking water. There was a general increase in the level of hardness concentration moving downstream for the ten locations for both seasons. The minimum total hardness concentration was 32.3 mg/L at Apapam (upstream) and the maximum concentration of 48.3 mg/L at Abomosu in the wet season (Appendix A). In the dry season, the minimum hardness concentration was 31.4 mg/L at Apapam and the maximum concentration of 47.1 mg/L at Abomosu (Appendix B). Total hardness was narrowly dispersed along the watercourse for the ten sampling sites in both the wet and dry season with Co.V of 10.87% and 15.95% respectively (Appendices A and B).

4.7.5 Total Alkalinity

The overall mean concentration of total alkalinity at the ten sampling sites was 39.10 mg/L ranging between 29.6 mg/L at Apapam and 47.4 mg/L at Bunso in the wet season (Appendix A). In the dry season, the overall mean concentration of total alkalinity was 35.86 mg/L , ranging from 27.6 mg/L (Apapam) to 41.5 mg/L (Bunso) (Appendix B). During the dry season, there was a decrease in the total alkalinity concentration. The current guidelines for total alkalinity have not been established but overall mean levels were below the WHO,1996 guideline value of 400 mg/L and the EPA's secondary regulation of 500 mg/L for drinking water.

4.8 WATER NUTRIENTS AND MACRO ELEMENTS.

Three water nutrients NO_3^- , PO_4^{3-} SO_4^{2-} and two macro elements K^+ and Na^+ were determined in this study. All the ions had their overall mean concentration in the dry season greater than that of the wet season.

4.8.1 Phosphate ion concentrations in river water

In most surface water, the phosphorous content ranges from 0.005 to 0.020 mg/L (Chapman, 1992). High levels of phosphate in water bodies is a sign of pollution which is largely responsible for eutrophication (MacCutheon et al., 1983).

Overall mean concentration of PO_4^{3-} for the wet and dry seasons were 0.50 mg/L and 0.66 mg/L respectively (Appendices A and B). EPA-Ghana has a permissible limit value of phosphate concentration of 2.0 mg/L. All the mean concentration of the water samples was below the EPA-Ghana permissible limit of phosphate, with the highest recorded at Bunso (downstream) with a value of 0.82 mg/L and Adadientem (mid-stream) having the least value

of 0.12 mg/L during the wet season (Appendix A). The same pattern was observed in the dry season with a highest value of 0.92 mg/L at Bunso (downstream) and the least value 0.42 mg/L at Apapam (upstream) (Appendix B) but these values were higher compared to WHO value of 0.3 mg/L.

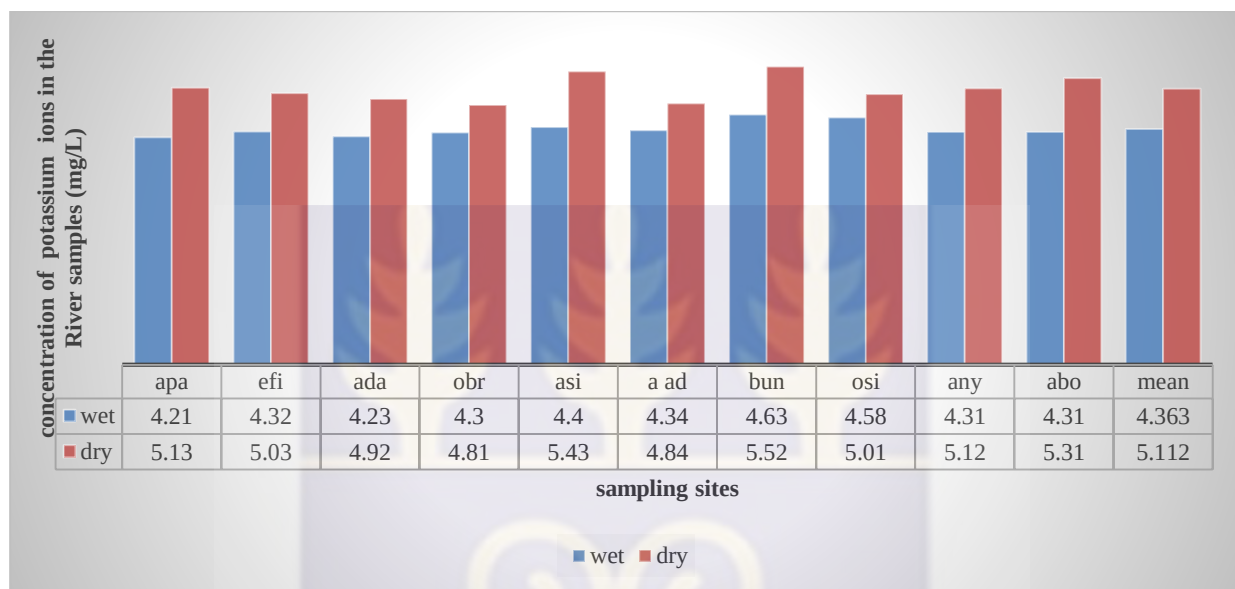


Figure 4.17: Comparison of mean Concentration of phosphate ions in water Samples during Wet and Dry seasons.

4.8.2 Sodium ion concentrations in water samples

Na^+ had a mean concentration of 6.66 mg/L with the minimum value of 6.21 mg/L at Anyinam and highest value of 7.02 mg/L at Bunso during the wet season (Appendix A). The overall mean concentration of Na^+ at the ten sampling sites was 7.01 mg/L and ranged between 6.71 mg/L (Anyinam) and 7.18 mg/L (Akyem Adukrom) during the dry season (Appendix B).

The overall mean concentration of Na^+ at the ten sampling sites was 4.36 mg/L and ranged between 4.21 mg/L (Apapam) and 4.63 mg/L (Bunso).

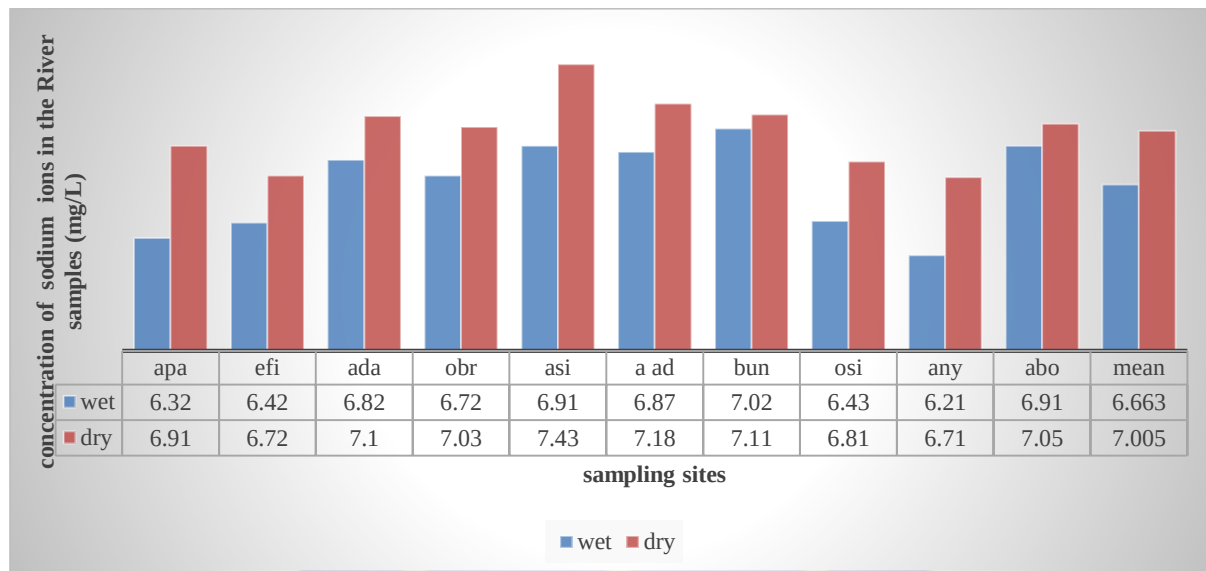


Figure 4.18: Comparison of mean Sodium ions (Na^+) concentrations in water samples during wet and dry seasons

4.8.3 Potassium (K^+) ion concentrations in water samples

The overall mean concentration of K^+ at all sampling sites was 4.36 mg/L and ranged from 4.21 mg/L (Apapam) to 4.63 mg/L (Bunso) in the wet season (Appendix A). However, in the dry season, K^+ concentration in the ten sampling sites ranged from 4.81 mg/L (Obromikrom) and 7.18 mg/L (Akyem Adukrom) (Appendix B)



Figure 4.19: Comparison of mean Potassium ion (K^+) concentrations in water samples during wet and dry seasons.

4.8.4 Nitrate ion (NO_3^-) concentrations in water samples

A mean concentration of 0.11 mg/L which ranged from 0.06 mg/L (Adadientem) to 0.19 mg/L (Osino) was recorded during the wet season (Appendix A). The mean concentration for the dry season had a slight increase from the 0.11mg/L to 0.14 mg/L having the minimum and highest values of 0.08 mg/L and 0.25 mg/L recorded at Asikam and Abomosu respectively (Appendix B).

Mean NO_3^- concentrations for both seasons were below the WHO's (2004) recommended limit of 10.00 mg/L.

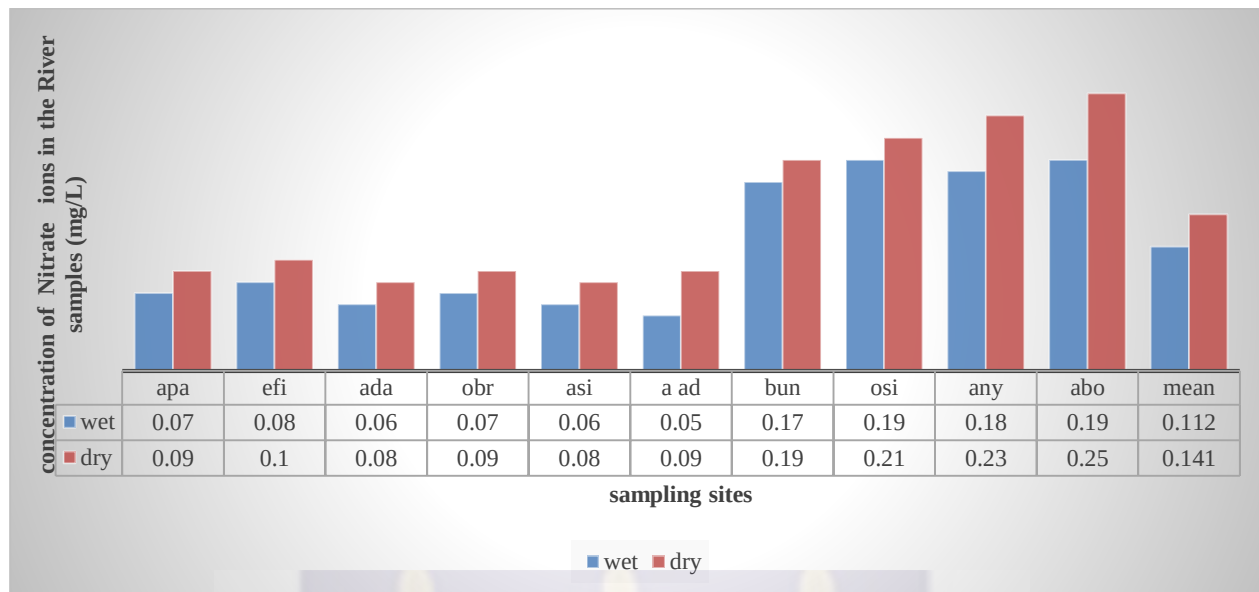


Figure 4.20: Comparison of mean Nitrate ion (NO_3^-) concentrations in water samples during wet and dry seasons.

4.8.5 Sulphate ion (SO_4^{2-}) ion concentrations in River samples

Sulphate ion (SO_4^{2-}) concentration levels were higher for all the ten sampling sites in the dry season than in the wet season with the mean concentration of 4.85 mg/L (range: 4.53 -5.23 mg/L) for the dry season and 4.14 mg/L (range: 3.78-4.87 mg/L) for the wet season (Appendices A and B)

The ion concentrations for both seasons were in increasing order of:



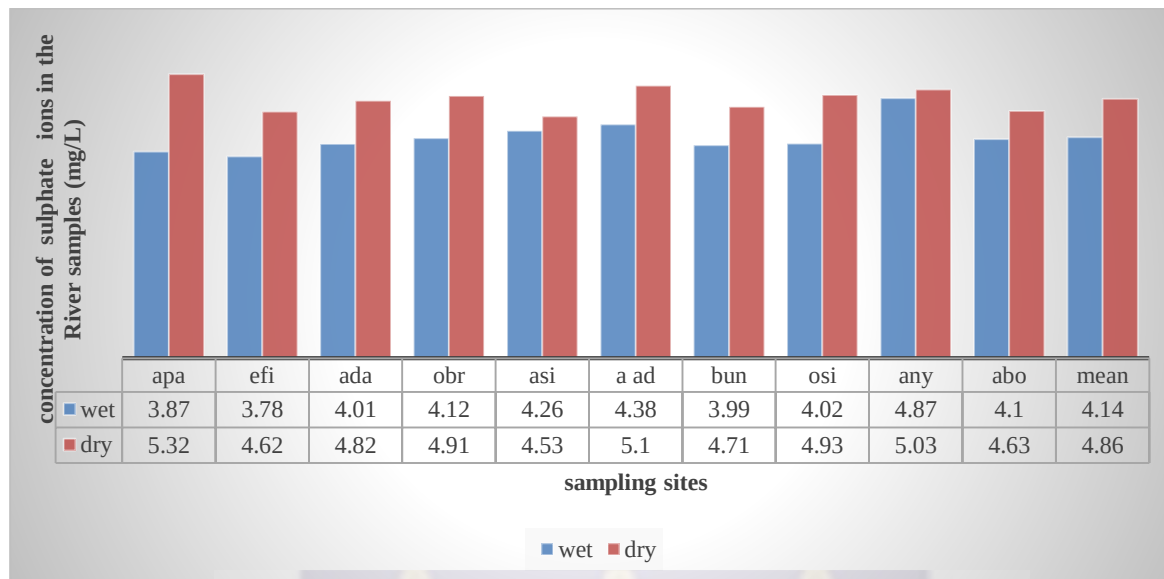


Figure 4.21: Comparison of mean Sulphate ion (SO_4^{2-}) concentrations in water samples during wet and dry seasons.

Table 4.3: Mean concentrations of water nutrients in the river samples during the wet season.

Location	(mg/L)				
	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+
Apapam	0.09	0.42	5.32	6.91	5.13
Efisa	0.10	0.55	4.62	6.72	5.03
Adadientem	0.08	0.58	4.82	7.10	4.92
Obronikrom	0.09	0.51	4.91	7.03	4.81
Asikam	0.08	0.49	4.53	7.43	5.43
Akyem Adukrom	0.09	0.54	5.10	7.18	4.84
Bunso	0.19	0.92	4.71	7.11	5.52
Osino	0.21	0.96	4.93	6.81	5.01
Anyinam	0.23	0.82	5.03	6.71	5.12
Abomosu	0.25	0.83	4.63	7.05	5.31
Mean	0.14	0.66	4.85	7.00	5.11
SD	0.07	0.19	0.22	0.22	0.24
Co.V%	49.52	28.79	4.54	3.10	4.69

Table 4.4: Mean concentrations of water nutrients in the river samples during the dry season.

Location	(mg/L)				
	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Na ⁺	K ⁺
Apapam	0.07	0.35	3.87	6.32	4.21
Efisa	0.08	0.44	3.78	6.42	4.32
Adadientem	0.06	0.12	4.01	6.82	4.23
Obronikrom	0.07	0.32	4.12	6.72	4.30
Asikam	0.06	0.38	4.26	6.91	4.40
Akyem Adukrom	0.05	0.41	4.38	6.87	4.34
Bunso	0.17	0.82	3.99	7.02	5.63
Osino	0.19	0.84	4.02	6.43	4.58
Anyinam	0.18	0.72	4.87	6.21	4.31
Abomosu	0.19	0.61	4.10	6.91	4.31
Mean	0.11	0.50	4.14	6.67	4.36
SD	0.06	0.24	0.31	0.28	0.14
Co.V%	54.54	48.0	7.48	4.20	3.21

4.9 Statistical Analysis

4.9.1 Coefficient of Variation (Co. V %)

Coefficient of variation was employed to determine the nature of distribution and pattern of dispersion of the studied elements and ions along the watercourse. It was calculated as follows:

Co. V= standard Deviation/Mean.

It is expressed as relative standard deviation which is in percentage. All elements in the population are considered including outliers for coefficient of variation.

Distribution are classified close or narrow and wide or scattered when Co.V is below or above 50% respectively.

For the studied ions Na^+ (4.2%), K^+ (3.2%), SO_4^{2-} (7.48%), PO_4^{3-} (48%) there was a close distribution in river water moving downstream the wet season. There was however a wide distribution in the river water moving downstream for NO_3^- ion (54. 54%). There was a close distribution for all the ions moving downstream the watercourse during the dry season.

Thus Na^+ (3.1%), K^+ (4.69%), SO_4^{2-} (4.54%), PO_4^{3-} (28.79%) NO_3^- (49.52%)

For the heavy metals in the water samples, there was a close distribution of all the metals except for Mn and Hg which were widely distributed during the wet season. Thus, Fe (31.26%), Ni (37.52%), As (22.06%), Pb (34.09%), Cd (41.33%), Se (48.89%), Zn (11.15%), Mn (62.40 %) and Hg (114.72 %). The distribution during the dry season followed the same pattern as was observed in the wet season with Mn and Hg recording a wide distribution. Thus, Fe (33.77%), Ni (19.16%), As (36.14%), Pb (35.71%), Cd (23.47%), Se (37.12%), Zn (21.35%), Mn (78.26 %) and Hg (527.57 %). Hg recorded the highest Co.V in the water samples for both seasons.

Cu (53.39%) recorded a scattered/widely distribution moving downstream for the sediment samples for the wet season. The other metals however showed a close distribution moving downstream for the sediment samples. Thus, Fe (1.72%), Ni (9.16%), As (36.72%), Pb (0.23%), Cd (1.69%), Zn (17.09%), Mn (1.68 %) and Hg (20.41 %), Cu (53.39%).

As (66.67%), and Cd (56.25%) and Hg however recorded a closely distribution for Co.V during the dry season for the sediment sample moving downstream of the river. The other metals recorded a narrowly distribution in the sediment samples during the dry season. Thus Fe (46.62%), Ni (8.49%), As (66.67%), Pb (44.98%), Cd (56.25%), Zn (41.27%), Mn (6.94 %) and Hg (150 %), Cu (21.77%).

4.9.2 pH versus Heavy Metal content (One-way ANOVA)

Analysis of variance (ANOVA) is a technique used to compare the means of multiple unrelated groups. One way (ANOVA) was performed to find out if pH has any significant effect on the linear variation of trace elements along the watercourse. Trace elements were entered as dependent variables and the pH for the sites were entered as a factor variable. The significant level was set at 95% confidence level. Variations are significant if ($P < 0.05$) and not significant if ($P > 0.05$).

For the water samples, there was no significant variations ($P > 0.05$) between the metal groups with the pH sites since significant P values were all greater than 0.05. Thus Fe ($p = 0.596$), Ni ($p = 0.880$), Cd ($p = 0.710$), Mn ($p = 0.574$), As (0.895), Pb ($p = 0.122$), Hg ($p = 0.937$) and Zn ($p = 0.885$), (Appendix K)

For the sediment, samples there were significant variations ($p < 0.05$) between the group means of Ni ($p = 0.014$), As ($p = 0.005$), Mn ($p = 0.005$) and Hg ($p = 0.004$) with site –pH ($0.004 < p < 0.04$), (Appendix L). No significant variations ($p > 0.05$) were observed for Fe ($p = 0.780$), and Zn ($p = 0.576$) with pH ($0.076 < p < 0.780$). It was observed that pH has no effect on the distribution patterns and mobility of heavy metals in water samples. However, pH had effect on the distribution pattern and mobility of heavy metals like Ni, As, Mn and Hg in the sediment samples.

4.9.3 Paired Sample T- Test

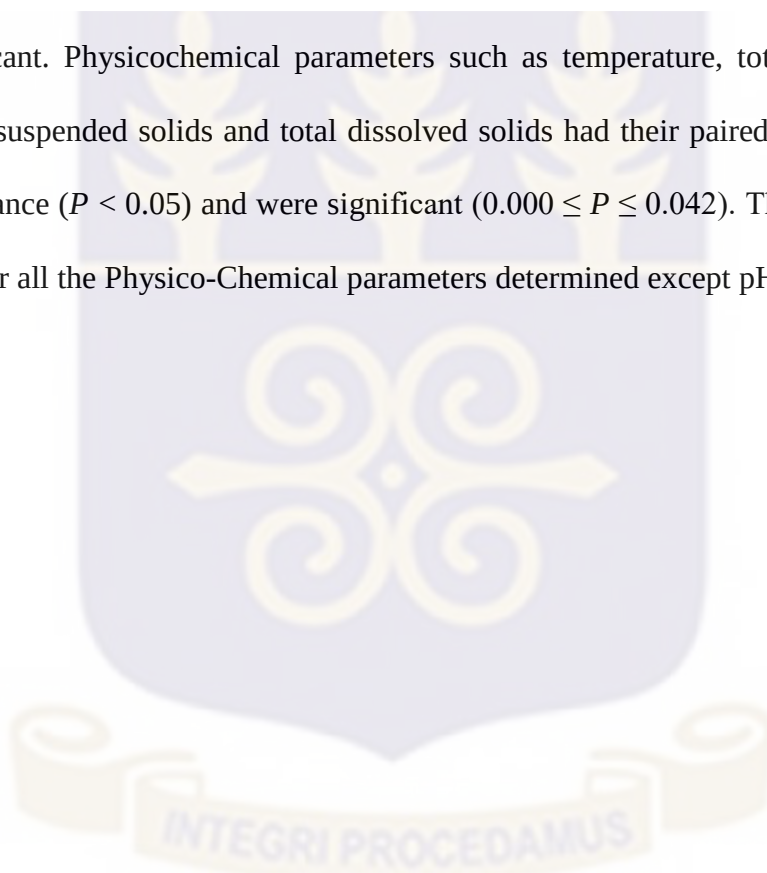
A paired sample t-test was used to compare the means of the physicochemical and nutrients data for the wet and dry seasons. Physicochemical data for both seasons were entered as paired variables with the confidence interval set at 95% confidence interval. The hypothesis was set as:

Ho: Water physicochemical and water nutrient parameters did not differ significantly with seasonal changes.

Ha: Water physicochemical and ion parameters differ significantly with seasonal changes.

For the ions, it was observed that all the ions (Na^+ , K^+ , PO_4^{3-} , NO_3^- , SO_4^{2-}) had paired values of ($0.000 \leq P \leq 0.002$) and were significant ($P < 0.05$). The null hypothesis is rejected when $P < 0.05$ and accepted when $P > 0.05$. The null hypothesis is therefore rejected for all the ions determined.

For physicochemical parameters, it was observed that pH had a paired value $P = 0.859$ which was not significant. Physicochemical parameters such as temperature, total hardness, total alkalinity, total suspended solids and total dissolved solids had their paired values below the level of significance ($P < 0.05$) and were significant ($0.000 \leq P \leq 0.042$). The null hypothesis is rejected for for all the Physico-Chemical parameters determined except pH.



CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Though ten sampling sites were considered, the sites were grouped into three main categories thus upstream (Apapam), midstream (Efisa - Akyem Adukrom) and downstream Bunso – Abomoso. From the results, concentration for most of the metals recorded higher values moving downstream. From the study, metals such as manganese, Iron as well as Cadmium (Cd) had their mean concentrations in the river samples higher than the estimated WHO guideline limit for drinking water. This means that the Birim River is polluted with respect to these metals. The other metals (Zn, As, Pb, Ni,) had their mean concentrations below the minimum permissible limit of E.P.A-Ghana and WHO guideline value of drinking water. The various pollution indices also showed that there was no pollution in the sediment samples except for Iron (Fe) which showed moderate pollution as shown by the Geo-accumulation index values.

Study of mercury content of the water samples at the various sampling sites along River Birim revealed that, some sampling sites had mean values above WHO 2006 permissible background value of $1\mu\text{g/L}$ while others recorded mean values that were below GEPA standard. Similar trend of mercury concentration was seen in the River sediments. Mercury does not have a natural source in the municipality. It is introduced into the environment during gold processing. Mercury was used to recover gold from ore minerals by the process of amalgamation hence the high values. From literature, mercury is more stable in sediments than in air (Kpekata, 1974). Therefore, the values in water samples are taken as an indicator which shows that there is probably more mercury in the studied areas in other forms. The

occurrence of mercury in this river confirms findings that mercury is a major pollutant associated with gold panning in Ghana and elsewhere. (Kpekata, 1974).

The traces of mercury in the Birim poses serious health risk to users of the river due to the toxicity/poisonous nature of mercury.

Currently only the upstream at Apapam of the Birim River can be considered clean and safe for drinking. The water nutrients for both seasons also had their levels below the permissible guideline limit for various nutrients in water samples.

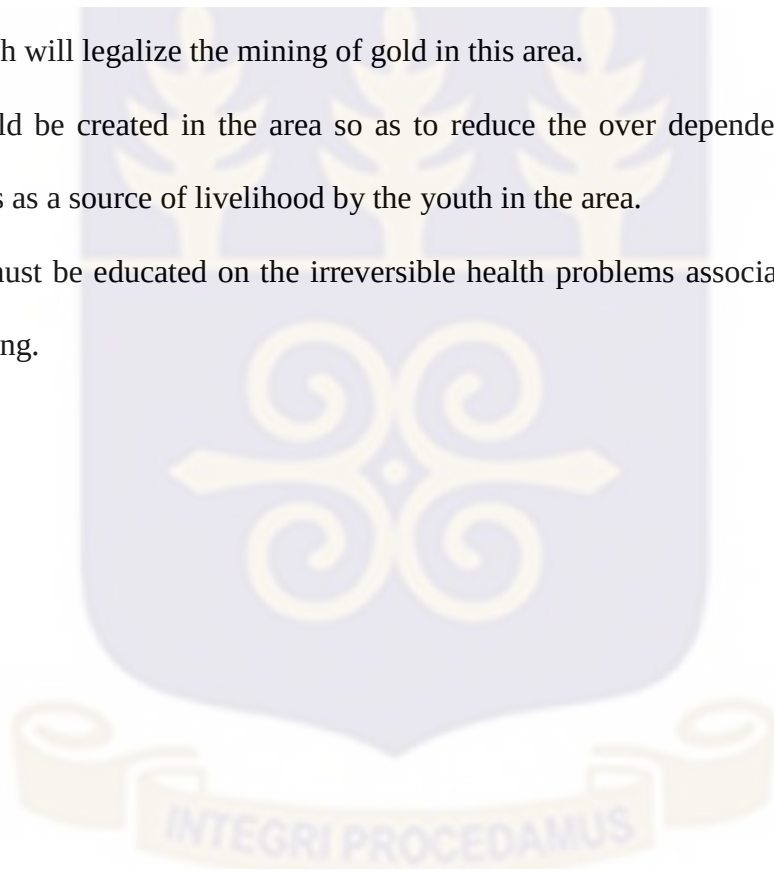
From the physico chemical parameter such as total alkalinity, total dissolved solids, total suspended solids, pH and electrical conductivity, the mean values obtained were all below the WHO 2011 safety guideline for drinking water hence the water is not polluted with respect to these parameters. However, due to the color of the river, it makes it unattractive for domestic usage due to the rampant usage of the water for the washing of these metals during the panning processes. There was no relationship between the pH and the trace metals in the water samples. However, there was significant variation between the pH and the river sediments from the one-way anova analysis (Appendix L)

From the paired sampled T-test all the physicochemical parameters such were affected by seasonal changes.

In light of the above findings it could be concluded that Artisanal Gold Mining activities in Kibi and its surrounding villages has negative consequences on the water quality of River Birim. This is as a result of the high levels of Manganese, Iron, Cadmium and Mercury which exceeded the EPA and WHO levels.

5.2 RECOMMENDATIONS

- Laws must be passed to control the mining activities of the artisanal gold mining so as to preserve the only left drinking water from Apapam (upstream).
- Mining companies, Government, Mineral Commission, Water Resources Commission, Ghana Water Company Limited and the District Assemblies should adopt a method or technology that will remove any high levels of toxic chemicals from the water bodies in the study area.
- The government and chiefs in the area must come together in order to draw policies and legal framework which will legalize the mining of gold in this area.
- More jobs should be created in the area so as to reduce the over dependence of the illegal mining activities as a source of livelihood by the youth in the area.
- Illegal miners must be educated on the irreversible health problems associated with mercury and lead poisoning.



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APPENDICES

APPENDIX A

Mean concentration of water nutrients and other physico-chemical parameters values in the wet season.

LOCATION	pH	EC	TEM	TSS	TDS	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Na ⁺	K ⁺	TH	TA
		(µs/cm)	°C					(mg/L)				
Apapam	6.92	112.70	26.00	8.50	83.40	0.07	0.35	3.87	6.32	4.21	32.30	29.60
Efisa	7.23	120.40	280	9.30	80.60	0.08	0.44	3.78	6.42	4.32	40.50	30.10
Adadientem	7.38	124.60	27.5	9.70	89.70	0.06	0.12	4.01	6.82	4.23	41.60	32.40
Obronikrom	7.01	127.40	290	17.30	79.30	0.07	0.32	4.12	6.72	4.30	41.70	37.30
Asikam	7.31	120.40	28.5	16.40	50.30	0.06	0.38	4.26	6.91	4.40	42.30	41.30
AkyemAdukrom	7.10	126.40	290	18.30	42.60	0.05	0.41	4.38	6.87	4.34	43.50	42.70
Bunso	7.48	138.50	29.5	39.60	47.60	0.17	0.82	3.99	7.02	4.63	46.60	47.40
Osino	7.01	130.10	270	39.80	45.90	0.19	0.84	4.02	6.43	4.58	46.20	42.30
Anyinam	7.23	131.60	27.5	40.30	47.30	0.18	0.72	4.87	6.21	4.31	47.30	43.30
Abomosu	7.38	123.40	28.5	42.30	46.50	0.19	0.61	4.10	6.91	4.31	48.30	44.60
Mean	7.21	125.55	28.05	24.15	61.32	0.11	0.50	4.14	6.67	4.36	43.03	39.10
SD	0.18	6.24	1.07	14.49	19.15	0.06	0.24	0.31	0.28	0.14	4.65	6.36
Co.V %	2.49	4.97	3.81	60.00	31.23	54.54	48.00	7.48	4.20	3.21	10.87	16.27

EC- Electrical conductivity, TH- Total Hardness, TA-Total Alkalinity, TSS- Total Suspended Solids, TDS-Total Dissolved Hardness

TEM- Temperature

APPENDIX B

Mean concentration of water nutrients and other physico-chemical parameters values in the dry season.

LOCATIONS	pH	EC ($\mu\text{s}/\text{cm}$)	TEM $^{\circ}\text{C}$	TSS	TDS	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+	TH	TA
								(mg/L)				
Apapam	6.7	150.3	30.5	6.3	60.6	0.09	0.42	5.23	6.91	5.13	31.40	27.60
Efisa	7.41	161.6	32	7.2	70.5	0.1	0.55	4.62	6.72	5.03	39.60	28.30
Adadientem	8.32	167.9	32	8.4	71.3	0.08	0.58	4.82	7.10	4.92	40.30	29.60
Obronikrom	8.21	194.3	31	15.6	62.4	0.09	0.51	4.91	7.03	4.81	41.20	32.40
Asikam	7.51	148.4	31.5	14.3	43.7	0.08	0.49	4.53	7.43	5.43	41.10	38.30
A.Adukrom	8.1	140.5	30.5	17.7	41.5	0.09	0.54	5.10	7.18	4.84	42.70	40.70
Bunso	.23	169.6	30.5	35.1	40.3	0.19	0.92	4.71	7.11	5.52	45.50	41.50
Osino	8.31	144.3	32	36.8	42.1	0.21	0.96	4.93	6.81	5.01	45.80	38.70
Anyinam	7.56	137.8	31.5	37.3	43.6	0.23	0.82	5.03	6.71	5.12	46.30	41.30
Abomosu	8.23	144.8	31	40.2	43.7	0.25	0.83	4.63	7.05	5.31	47.10	40.20
Mean	7.858	155.95	31.25	21.89	51.97	0.14	0.66	4.85	7.005	5.11	42.10	35.86
SD	0.54	18.32	0.63	13.84	19.15	0.07	0.19	0.22	0.22	0.24	4.64	5.72
Co.V %	6.87	11.75	2.03	63.24	36.85	49.52	28.79	4.54	3.10	4.69	11.02	15.95

APPENDIX C

Overall Concentration and Geo – accumulation index for heavy metals concentrations in sediments of River Birim in the Wet Season

LOCATIO N	Overall Concentration (mg/kg)									Geo – accumulation index (Geo-I)								
	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As
Apapam	11.51	0.43	1.87	8.22	0.14	6.12	19.2	0.005	0.006	0.71	-7.93	-3.33	-3.77	-1.09	-3.75	-5.63	-4.58	-8.81
Efisa	11.34	0.54	1.45	6.34	0.15	6.56	18.3	0.005	0.008	1.12	-7.60	-3.69	-4.15	-1.00	-3.65	-6.28	-4.58	-8.39
Adadientem	16.38	0.53	2.89	6.82	0.13	7.69	20.3	0.006	0.008	1.22	-7.63	-2.69	-4.04	-1.21	-3.39	-6.13	-4.32	-8.39
Obronikrom	15.38	0.32	1.74	7.56	0.05	6.75	21.1	0.007	0.100	1.13	-8.36	-3.42	-3.89	-2.58	-3.61	-6.07	-4.09	-4.75
Asikam	17.28	0.65	1.23	7.83	0.04	8.91	21.4	0.007	0.007	1.29	-7.34	-3.93	-3.84	-2.91	-3.21	-6.05	-4.09	-8.59
A.Adukrom	19.02	0.61	1.67	8.03	0.06	5.87	18.7	0.097	0.011	1.43	-7.43	-3.49	-3.81	-2.32	-3.81	-6.25	-0.31	-7.93
Bunso	40.21	0.81	3.72	9.03	0.21	10.8	22.0	0.008	0.021	2.51	-7.02	-2.33	-3.64	-0.51	-2.92	-6.01	-3.91	-7.01
Osino	38.13	0.45	1.54	8.26	0.17	8.71	19.2	0.097	0.007	2.44	-7.87	-3.61	-3.77	-0.82	-3.24	-6.21	-0.39	-8.59
Anyinam	39.87	0.12	2.11	7.89	0.18	9.65	20.6	0.007	0.008	2.50	-9.77	-3.15	-3.83	-0.74	-3.09	-6.11	-4.09	-8.39
Abomosu	38.02	0.28	3.23	8.21	0.05	8.87	21.0	0.006	0.012	2.43	-8.55	-2.54	-3.78	-2.58	-3.21	-6.08	-4.32	-7.81
Mean	25.11	0.47	2.15	7.82	0.12	8.02	20.2	0.025	0.019	1.68	-7.95	-3.22	-3.85	-1.58	-3.39	-6.08	-3.47	-7.87

APPENDIX D**Mean concentration of heavy metals in the water sample during the wet season****(mg/L)**

Location	Fe	Ni	As	Mn	Pb	Cd	Hg(μ g/L)	Zn
Apapam	0.86	0.04	0.01	0.01	0.008	0.06	0.7	0.143
Efisa	1.34	0.04	0.01	0.34	0.016	0.06	0.79	0.145
Adadientem	1.72	0.03	0.01	0.33	0.014	0.04	0.81	0.172
Obronikrom	1.21	0.04	0.02	0.41	0.027	0.02	0.92	0.177
Asikam	1.35	0.04	0.01	0.17	0.018	0.02	BDL	0.183
Akyem Adukrom	2.14	0.02	0.01	0.19	0.019	0.06	BDL	0.182
Bunso	2.34	0.02	0.01	0.50	0.008	0.08	1.5	0.193
Osino	2.36	0.01	0.01	0.60	0.025	0.06	BDL	0.196
Anyinam	1.78	0.02	0.01	0.71	0.024	0.06	BDL	0.199
Abomosu	2.39	0.03	0.01	0.81	0.017	0.09	BDL	0.191
mean	1.75	0.03	0.01	0.40	0.018	0.055	0.472	0.178
SD	0.55	0.01	0.002	0.25	0.006	0.002	0.541	0.019
Co.V %	31.26	37.52	22.06	62.40	34.09	41.33	114.72	11.15

Mean concentration of heavy metals in water sample during the dry season (mg/L)

LOCATION	Fe	Ni	As	Mn	Pb	Cd	Hg(μ g/L)	Zn
Apapam	0.62	0.0004	0.002	0.042	0.006	0.008	BDL	0.231
Efisa	1.01	0.0004	0.004	0.052	0.013	0.008	BDL	0.341
Adadientem	1.21	0.0004	0.006	0.621	0.011	0.006	BDL	0.317
Obronikrom	0.93	0.0005	0.009	0.721	0.021	0.004	0.009	0.413
Asikam	1.10	0.0004	0.004	0.213	0.014	0.006	BDL	0.434
Akyem Adukrom	1.92	0.0003	0.008	0.191	0.015	0.009	0.009	0.312
Bunso	1.81	0.0005	0.006	0.123	0.006	0.009	0.01	0.521
Osino	1.61	0.0004	0.005	0.700	0.021	0.007	0.009	0.421
Anyinam	0.98	0.0005	0.006	0.821	0.020	0.006	BDL	0.411
Abomosu	1.64	0.0006	0.007	0.901	0.013	0.009	BDL	0.401
mean	1.28	0.00044	0.006	0.439	0.014	0.007	0.009	0.3802
SD	0.43	0.001	0.002	0.343	0.005	0.002	0.005	0.081
Co.V %	33.77	19.16	36.14	78.26	35.71	23.47	527.57	21.35

APPENDIX E**Mean concentration of heavy metals in sediment samples in the wet season (mg/kg)**

LOCATION	Fe	Ni	As	Mn	Pb	Cd	Hg	Cu	Zn
Apapam	11.51	8.22	0.006	19.21	1.87	0.14	0.005	0.14	0.43
Efisa	15.34	6.34	0.008	18.31	1.45	0.15	0.005	0.15	0.54
Adadientem	16.38	6.82	0.008	20.36	2.89	0.13	0.006	0.13	0.53
Obronikrom	15.38	7.56	0.100	21.14	1.74	0.05	0.007	0.05	0.32
Asikam	17.28	7.83	0.007	21.42	1.23	0.04	0.007	0.04	0.65
Akyem	19.02	8.03	0.011	18.71	1.67	0.06	0.097	0.06	0.61
Adukrom	40.21	9.03	0.021	22.06	3.72	0.21	0.008	0.21	0.81
Bunso	38.13	8.26	0.007	19.21	1.54	0.17	0.097	0.17	0.45
Osino	39.87	7.89	0.008	20.61	2.11	0.18	0.007	0.18	0.12
Anyinam	38.02	8.21	0.012	21.01	3.23	0.05	0.006	0.05	0.28
mean	25.11	7.82	0.02	20.20	2.15	0.12	0.02	0.12	0.47
SD	0.43	0.76	0.002	0.34	0.01	0.002	0.01	0.06	0.08
Co.V %	1.72	9.72	10.64	1.68	0.23	1.69	20.41	53.39	17.09

Mean concentration of heavy metals in sediment samples (mg/kg) in the dry season.

LOCATION	Fe	Ni	As	Mn	Pb	Cd	Hg	Cu	Zn
Apapam	12.23	8.71	0.008	20.26	1.62	0.24	0.007	6.23	0.62
Efisa	17.32	7.21	0.009	18.46	1.31	0.21	0.008	7.01	0.71
Adadientem	18.28	6.94	0.012	18.36	3.52	0.18	0.008	8.23	0.65
Obronikrom	17.35	8.34	0.11	21.62	2.54	0.05	0.009	7.56	0.41
Asikam	19.18	8.02	0.009	21.86	1.11	0.08	0.009	9.32	0.87
Akyem	20.32	8.26	0.011	19.42	1.87	0.06	0.01	6.05	0.51
Adukrom	42.64	9.24	0.031	22.63	4.22	0.31	0.009	11.54	1.21
Bunso	41.17	8.32	0.009	20.01	1.34	0.21	0.01	9.65	0.35
Osino	41.17	8.71	0.009	20.87	2.71	0.18	0.114	10.65	0.53
Anyinam	41.22	8.63	0.017	21.04	2.63	0.05	0.012	9.67	0.42
mean	27.09	8.24	0.03	20.45	2.29	0.16	0.02	8.59	0.63
SD	12.63	0.70	0.02	1.42	1.03	0.09	0.03	1.87	0.26
Co.V %	46.62	8.49	66.67	6.94	44.98	56.25	150	21.77	41.27

APPENDIX F**Overall Contamination factor for heavy metal concentrations in sediments of River Birim in the Wet Season**

LOCATION	Overall Concentration (mg/kg)									Contamination factor (Cf)								
	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As
Apapam	11.51	0.43	1.87	8.22	0.14	6.12	19.21	0.005	0.006	2.45	0.006	0.15	0.11	2.00	0.11	0.02	0.06	0.003
Efisa	11.34	0.54	1.45	6.34	0.15	6.56	18.31	0.005	0.008	3.26	0.007	0.12	0.08	2.14	0.12	0.02	0.06	0.004
Adadientem	16.38	0.53	2.89	6.82	0.13	7.69	20.36	0.006	0.008	3.49	0.007	0.23	0.09	1.86	0.14	0.02	0.08	0.004
Obronikrom	15.38	0.32	1.74	7.56	0.05	6.75	21.14	0.007	0.100	3.27	0.004	0.14	0.10	0.71	0.12	0.02	0.09	0.056
Asikam	17.28	0.65	1.23	7.83	0.04	8.91	21.42	0.007	0.007	3.68	0.009	0.98	0.10	0.57	0.16	0.02	0.09	0.004
A.Adukrom	19.02	0.61	1.67	8.03	0.06	5.87	18.71	0.097	0.011	4.05	0.008	0.13	0.11	0.86	0.11	0.02	1.21	0.006
Bunso	40.21	0.81	3.72	9.03	0.21	9.87	22.06	0.008	0.021	8.56	0.012	0.29	0.12	3.00	0.19	0.02	0.10	0.012
Osion	38.13	0.45	1.54	8.26	0.17	8.71	19.21	0.097	0.007	8.11	0.006	0.12	0.11	0.24	0.16	0.02	1.21	0.004
Anyinam	39.87	0.12	2.11	7.89	0.18	9.65	20.61	0.007	0.008	8.48	0.001	0.17	0.11	2.57	0.18	0.02	0.09	0.004
Abomosu	38.02	0.28	3.23	8.21	0.05	8.87	21.01	0.006	0.012	8.09	0.004	0.26	0.11	0.71	0.16	0.02	0.08	0.007
Mean	25.11	0.47	2.15	7.82	0.12	8.02	20.20	0.025	0.019	5.34	0.006	0.26	0.10	1.47	0.15	0.02	0.31	0.010

APPENDIX G

Overall Contamination factor for heavy metals concentrations in sediments of River Birim in the dry Season

LOCATIO N	Overall Concentration (mg/kg)									Contamination factor (Cf)								
	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As
Apapam	12.23	0.62	1.62	8.71	0.24	6.23	20.26	0.007	0.008	2.60	0.009	0.13	0.12	1.20	0.11	0.02	0.09	0.004
Efisa	17.32	0.71	1.31	7.21	0.21	7.01	18.46	0.008	0.009	3.69	0.010	0.10	0.10	1.05	0.13	0.02	0.10	0.005
Adadientem	18.28	0.65	3.52	6.94	0.18	8.23	18.36	0.008	0.012	3.9	0.009	0.29	0.09	0.90	0.15	0.02	0.10	0.007
Obronikrom	17.35	0.41	2.54	8.34	0.05	7.56	21.62	0.009	0.110	4.28	0.006	0.20	0.11	0.25	0.14	0.02	0.10	0.061
Asikam	19.18	0.87	1.11	8.02	0.08	9.32	21.86	0.009	0.009	3.69	0.012	0.09	0.11	0.40	0.17	0.02	0.11	0.005
A.Adukrom	20.32	0.51	1.87	8.26	0.06	6.05	19.42	0.010	0.011	4.32	0.007	0.15	0.11	0.30	0.11	0.02	0.13	0.061
Bunso	42.64	1.21	4.22	9.24	0.31	11.5	22.63	0.009	0.031	9.07	0.017	0.34	0.12	1.55	0.21	0.02	0.11	0.017
Osion	41.17	0.35	1.34	8.32	0.21	9.65	20.01	0.010	0.009	8.76	0.005	0.11	0.11	1.05	0.18	0.02	0.13	0.005
Anyinam	41.17	0.53	2.71	8.71	0.18	10.6	20.87	0.114	0.009	8.76	0.008	0.22	0.12	0.90	0.19	0.02	1.43	0.005
Abomosu	41.22	0.42	2.63	8.63	0.05	9.67	21.04	0.012	0.017	8.77	0.006	0.21	0.12	0.25	0.18	0.02	0.15	0.009
Mean	27.09	0.63	2.29	8.24	0.16	8.59	20.45	0.019	0.023	5.78	0.009	0.18	0.11	0.79	0.16	0.02	0.25	0.018

APPENDIX H

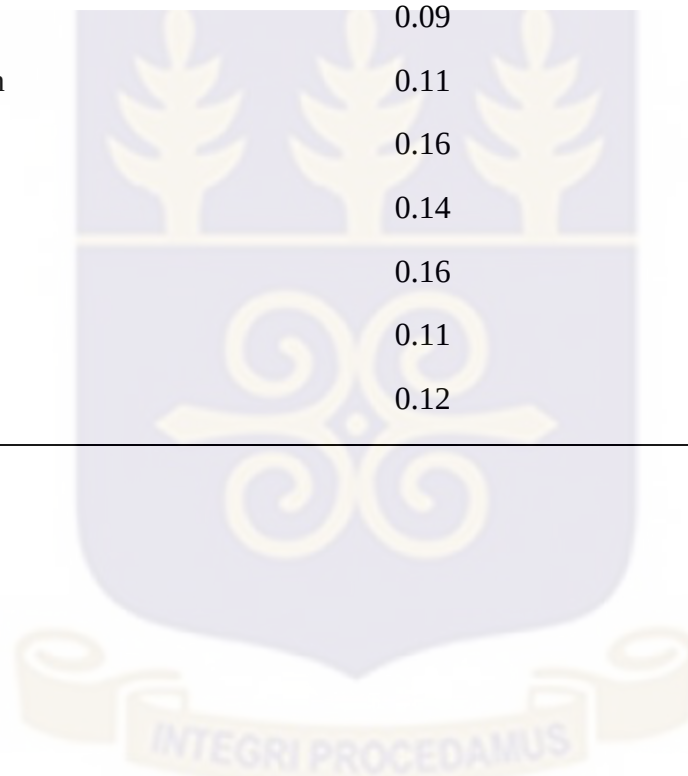
Pollution Load Index of the various sampling sites for sediment during the wet season.

LOCATIONS	Pollution load Index
Apapam	0.085
Efisa	0.087
Adadientem	0.100
Obronikrom	0.079
Asikam	0.110
Akyem Adukrom	0.125
Bunso	0.157
Osion	0.113
Anyinam	0.204
Abomosu	0.104
mean	0.116

Pollution Load index (PLI) for the dry season for sediment samples

LOCATIONS	Pollution load Index
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Apapam	0.09
Efisa	0.09
Adadientem	0.11
Obronikrom	0.11
Asikam	0.09
Akyem Adukrom	0.11
Bunso	0.16
Osion	0.14
Anyinam	0.16
Abomosu	0.11
mean	0.12



APPENDIX I

Overall Geo-accumulation Index (Geo-I) for heavy metals concentrations in sediments of River Birim in the dry Season

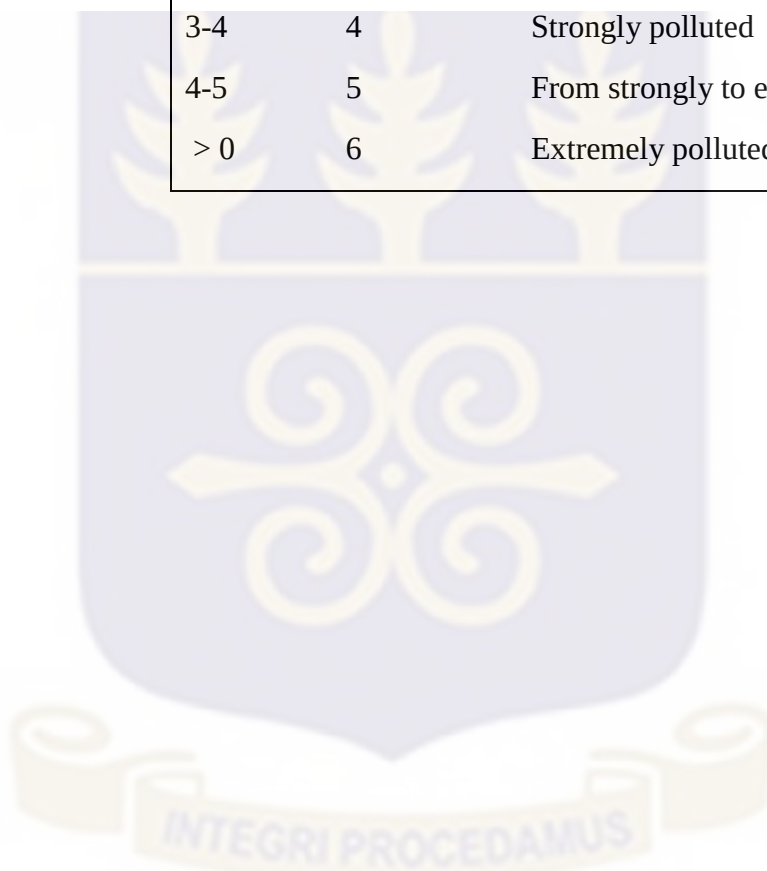
LOCATIO N	Overall Concentration (mg/kg)									Geo-accumulation Index (Geo-I)								
	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As	Fe	Zn	Pb	Ni	Cd	Cu	Mn	Hg	As
Apapam	12.23	0.62	1.62	8.71	0.24	6.23	20.26	0.007	0.008	0.79	-7.40	-3.53	-3.69	-0.32	-3.73	-6.14	-4.09	-8.39
Efisa	17.32	0.71	1.31	7.21	0.21	7.01	18.46	0.008	0.009	1.29	-7.21	-3.84	-3.96	-0.51	-3.56	-6.27	-3.91	-8.23
Adadientem	18.28	0.65	3.52	6.94	0.18	8.23	18.36	0.008	0.012	1.38	-7.34	-2.41	-4.02	-0.74	-3.32	-6.28	-3.91	-7.81
Obronikrom	17.35	0.41	2.54	8.34	0.05	7.56	21.62	0.009	0.110	1.30	-8.00	-2.88	-3.75	-2.58	-3.45	-6.04	-3.74	-4.62
Asikam	19.18	0.87	1.11	8.02	0.08	9.32	21.86	0.009	0.009	1.44	-6.92	-4.08	-3.81	-1.91	-3.15	-6.03	-3.74	-8.23
A Adukrom	20.32	0.51	1.87	8.26	0.06	6.05	19.42	0.010	0.011	1.53	-7.69	-3.33	-3.77	-2.32	-3.77	-6.19	-3.58	-4.62
Bunso	42.64	1.21	4.22	9.24	0.31	11.54	22.63	0.009	0.031	2.60	-6.44	-2.15	-3.61	0.05	-2.84	-5.98	-3.74	-3.12
Osion	41.17	0.35	1.34	8.32	0.21	9.65	20.01	0.010	0.009	2.55	-8.23	-3.81	-3.76	-0.74	-3.09	-6.15	-3.74	-8.23
Anyinam	41.17	0.53	2.71	8.71	0.18	10.65	20.87	0.114	0.009	2.55	-7.63	-2.79	-3.69	-0.74	-2.95	-6.09	-0.07	-8.23
Abomosu	41.22	0.42	2.63	8.63	0.05	9.67	21.04	0.012	0.017	2.55	-7.97	-2.83	-3.70	-2.58	-3.09	-6.08	-3.32	-7.31

Mean	27.09	0.63	2.29	8.24	0.16	8.59	20.45	0.019	0.023	1.79	-7.48	-3.17	-3.78	-1.24	-3.29	-6.13	-3.38	-6.88
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Muller's Classification for the Geo- Accumulation Index

I –Geo	Value Class	Sediment quality
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 0	6	Extremely polluted



APPENDIX K**One way ANOVA for water samples with pH as the factor variable.**

		ANOVA (One way)				
		Sum of Squares	df	Mean Square	F	Sig.
Fe	Between Groups	1.710	6	.285	.872	.596
	Within Groups	.980	3	.327		
	Total	2.690	9			
Ni	Between Groups	.000	6	.000	.338	.880
	Within Groups	.001	3	.000		
	Total	.001	9			
As	Between Groups	.000	6	.000	.313	.895
	Within Groups	.000	3	.000		
	Total	.000	9			
Mn	Between Groups	.375	6	.063	.927	.574
	Within Groups	.202	3	.067		
	Total	.578	9			
Pb	Between Groups	.000	6	.000	4.518	.122
	Within Groups	.000	3	.000		
	Total	.000	9			
Cd	Between Groups	.000	6	.000	.634	.710
	Within Groups	.000	3	.000		
	Total	.000	9			
Hg	Between Groups	.411	4	.103	-	-
	Within Groups	.000	0			
	Total	.411	4			
Zn	Between Groups	.001	5	.000	.290	.885
	Within Groups	.002	2	.001		
	Total	.003	7			

*0.05 significant level

One way ANOVA for water samples with pH as the factor variable.

APPENDIX L**One way ANOVA for sediment with pH as the factor variable.**

		ANOVA (One way)				
		Sum of Squares	df	Mean Square	F	Sig.
Fe	Between Groups	908.262	6	151.377	.507	.780
	Within Groups	895.867	3	298.622		
	Total	1804.129	9			
Ni	Between Groups	53.226	6	8.871	21.741	.014
	Within Groups	1.224	3	.408		
	Total	54.450	9			
As	Between Groups	.008	6	.001	44.274	.005
	Within Groups	.000	3	.000		
	Total	.008	9			
Mn	Between Groups	373.536	6	62.256	45.665	.005
	Within Groups	4.090	3	1.363		
	Total	377.626	9			
Pb	Between Groups	8.100	6	1.350	6.568	.076
	Within Groups	.617	3	.206		
	Total	8.717	9			
Cd	Between Groups	.039	6	.006	4.754	.114
	Within Groups	.004	3	.001		
	Total	.043	9			
Hg	Between Groups	.417	6	.069	49.186	.004
	Within Groups	.004	3	.001		
	Total	.421	9			
Zn	Between Groups	.190	5	.038	.892	.576
	Within Groups	.128	3	.043		
	Total	.317	8			

*0.05 significant level

One way ANOVA for sediment with pH as the factor variable.

APPENDIX M

Paired t-test comparing the physico-chemical parameters of Dry Season to the Wet Season

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	DS_pH - WS_pH	-.14700	2.54541	.80493	-1.96788	1.67388	-.183	9	.859
Pair 2	DS_EC - WS_EC	3.04000E 1	17.85174	5.64521	17.62964	43.17036	5.385	9	.000
Pair 3	DS_TEM - WS_TEM	- 9.85000E 1	131.49546	41.58252	-192.56618	-4.43382	-2.369	9	.042
Pair 4	DS_TSS - WS_TSS	-2.26000	1.06375	.33639	-3.02096	-1.49904	-6.718	9	.000
Pair 5	DS_TDS - WS_TDS	-9.35000	7.49685	2.37071	-14.71292	-3.98708	-3.944	9	.003
Pair 6	DS_NO ₃ - WS_NO ₃	.02900	.01524	.00482	.01810	.03990	6.018	9	.000
Pair 7	DS_PO ₄ - WS_PO ₄	.16100	.11416	.03610	.07934	.24266	4.460	9	.002
Pair 8	DS_SO ₄ - WS_SO ₄	.71100	.33739	.10669	.46965	.95235	6.664	9	.000

Paired t-test comparing the physico-chemical parameters of Dry Season to the Wet Season

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 9 DS_Na ⁺ - WS_Na ⁺	.34200	.16040	.05072	.22726	.45674	6.742	9	.000
Pair 10 DS_K ⁺ - WS_K ⁺	.74900	.21620	.06837	.59434	.90366	10.955	9	.000
Pair 11 DS_TH - WS_TH	-.93000	.29833	.09434	-1.14341	-.71659	-9.858	9	.000
Pair 12 DS_TA - WS_TA	-3.24000	1.42377	.45023	-4.25850	-2.22150	-7.196	9	.000