ASSESSMENT OF HEALTH RISKS DUE TO TOXIC METALS AND NATURALLY OCCURRING RADIOACTIVE MATERIALS IN THE BIRIM RIVER IN EAST AKIM MUNICIPALITY OF THE EASTERN REGION GHANA

BY

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THIS THESIS IS SUBMITTED TO UNIVERSITY OF GHANA, LEGON DEPARTMENT OF NUCLEAR SCIENCES AND APPLICATIONS GRADUATE SCHOOL OF NUCLEAR AND ALLIED SCIENCES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PHILOSOPHY DEGREE IN NUCLEAR AND ENVIRONMENTAL PROTECTION

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DECLARATION

I hereby declare that this thesis is the result of research work undertaken by Prosper Kwame Klu in the Department of Nuclear Sciences and Applications, University of Ghana. And with the exception of references to other people's work which have duly been acknowledged, this Thesis is the result of my own research work and no part of it has been presented for another degree in this University or elsewhere.

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The preparation of this project was supervised in accordance with the guidelines of the supervision of Thesis work laid down by the University of Ghana.

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Date Date

DEDICATION

This research is dedicated to my beloved mother Flora Adiase, wife Cynthia Ofinibo, and son Senam Apeh Klu-Akoto, for their unfailing love, support and prayers throughout the course of this thesis.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
A_{Sp}	Activity concentration
CDI_{derm}	Chronic Daily Intake Dermal
CDI_{ing}	Chronic Daily Intake Ingestion
CR	Carcinogenic Risk
DCF	Dose Conversion Factor
EC	Electrical Conductivity
GAEC	Ghana Atomic Energy Commission
H_{ex}	External Hazard Index
H_{in}	Internal Hazard Hndex
H_{ing}	Annual Effective Dose
HPGE	High Purity Germanium
HQ	Hazard Quotient
IAEA	International Atomic Energy Agency
ICRP	International Commission for Radiological Protection
MCA	Multi-Channel Analyser
MDA	Minimum detectable activity

NORM	Naturally Occurring Radioactive Materials
SCA	Single Channel Analyser
SF	Carcinogenic Slope Factor
SPSS	Statistical Package for Social Sciences
TDS	Total Dissolved Solids
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
USEPA	United States Environmental Protection Agency
UV	Ultra-Violet
WHO	World Health Organisation
PCA/FA	Principal Component Analysis/Factors Analysis
PCBs	Polychlorinated Biphenyls

LIST OF SYMBOLS

A	Average titre
As	Arsenic
B	Blank solution
Bq/kg	Becquerel per kilogram
Bq/L	Becquerel per litre
$\mathbf{C_{calib}}$	Calibration concentration
Cd	Cadmium
Cl	Chlorine
$\mathbf{C_{NO3-}}$	Concentration of nitrate
Cu	Cupper
$\mathbf{D_f}$	Dilution factor
Fe	Iron
g	Gram
K	Potassium
mg	Milligram
$\mathbf{mgL^{-1}}$	Milligram per Litre
mL	Millilitre
Mn	Manganese
mSv	millisievert (10^{-3} Sievert)
M	Molarity of $AgNO_3$
nGy/h	nano Gray per hour
$\mathbf{^oC}$	Degree Celcius

Pb	Lead
Th	Thorium
U	Uranium
Zn	Zinc
μ	Micro
μScm^{-1}	Micro Siemens per Centimeter
‰	Per million

ABSTRACT

A detailed study has been carried out to determine the health risk associated with the level of trace metals and naturally occurring radioactive materials in the Birim River in East Akim Municipality of the Eastern Region of Ghana. The river runs through several communities in the municipality and serves as the main source of drinking water, irrigation and for domestic purposes. However, small-scale mining activities in the area are deteriorating the quality of the river water. Results of the study show that water from the Birim River is polluted with respect to Hg, As and Fe. The most polluted sampling points were Adadientem and Kibi. Turbidity levels in water samples were between 2 – 708 NTU. Results from Principal Component Analysis/Factors Analysis (PCA/FA) analyses in November suggest high loading of phosphate (0.934) and chloride (0.802). High level of Hg was recorded in sediment samples from Adadietem (Ad-1) (0.4 mg/kg), KTC-6, (0.775 mg/kg), Kyebi Training College (KDS-5), (0.55 mg/kg), Bonsu-Accra Road (B-AR-10) (0.575 mg/kg) and Bonsu Bridge (BB-8) (0.4 mg/ kg) while at all the sampling points, high levels of As and Fe were recorded. As levels ranged between 8.40 mg/kg and 16.25 mg/kg while mean Fe levels were 821.62 – 837.81 mg/kg. Health risk assessment shows that Fe, Mn, As, Zn and Hg metals were the main contributors for ingestion and dermal exposures to the human environment in the river. The levels of Hazard Quotient (HQ_{ing}) for As was greater than one, indicating that it could have harmful effects on human health. This is an indication that risk may occur via the ingestion of contaminated water in the municipality. As, Fe, Hg, Mn and Cr were found to be the main contributors to non-carcinogenic risk (HI) from the Birim River in Kibi Municipality. Carcinogenic risk (CR_{ing}) was found to be associated with the slight elevated value of As. The calculated average activity concentration of ^{232}Th was higher than WHO guidance level of 1.0 Bq/L in water. The mean annual effective doses of the two periods in the various communities had values lower than the WHO recommended value of 0.10 mSv/year. Cancer risk to adult in water for November and February is 2.25×10^{-6} and hereditary effect is 4.41×10^{-7}. Estimated results of the lifetime risk among adult member of the Kibi Municipality are within the range of acceptable risk values recommended by USEPA.

CHAPTER ONE

INTRODUCTION

1.0 BACKGROUND TO THE STUDY

The Birim River is a very useful river in the Akim Municipality in the Eastern Region of Ghana. It runs through several communities in the municipality and serves as the main source of drinking water, irrigation, fishing and for domestic purposes. The Birim River Basin has been identified to be rich in minerals such as gold, diamond, manganese and bauxite. This has attracted many artisanal miners to the area to scout for these natural resources especially gold. The gold mining operations consequently turn out large volumes of solid and liquid wastes in the form of waste dams; slime dams, tailings dams, which could contain elevated levels of metals which are toxic into the river. The mining activities also enhance the levels of naturally occurring radioactive materials (NORM) into the environment which may end up into the river (Faanu, 2011) causing pollution which may lead to various health problems

Gold mining contributes significantly to Ghana's Economic Recovery Programme, but it is at a great environmental cost as exploitation of the gold puts stress on water, soil, vegetation and poses human health hazards (Amonoo-Neizer and Amekor, 1993). Gold mining in recent times is regarded as a significant source of Hg, Pb and trace metal contamination of the environment owing to activities such as mineral exploitation, smelting, disposal of the tailings and waste waters around mines (Essumang et al., 2007; Hanson et al., 2007; Obiri, 2007; Singh et al., 2007).

Some trace metals such as chromium, copper, iron, zinc, mercury, nickel, lead, arsenic and manganese are considered to be very toxic. These elements are not biodegradable hence making them potentially harmful to most organisms including man (Wakida et al., 2008; Zare and Ebadi, 2005; Ahmed and Hussein, 2004). Even though, some trace elements such as Zn, Fe and Cu are essential for the growth and well-being of man and other living organisms others such as Pb, Hg and Cd are not essential for any metabolic activity in living organism and exhibit toxic properties even when present at very low concentration.

Naturally Occurring Radioactive Materials (NORMs) are present in several types of materials. They are present in the atmosphere, aquatic and terrestrial environments in varying concentrations (NRPA, 2004). The presence of the NORMs may be due to any of the primordial radionuclides or radioactive elements as they occur in nature, such as radium, uranium, thorium, potassium, and their radioactive decay products, that are disturbed as a result of human activities such as gold mining (Faanu, 2011). The distribution of long-lived radioactive elements such as ^{238}U, ^{232}Th and ^{40}K depends on the type of rocks formation under the earth's crust (Mujahid and Hussain 2011).

As a result of human activities, (mining, milling and processing of uranium ores and mineral sand, manufacture of fertilizers etc) higher concentrations of natural radioactivity may arise causing surface water pollution. The contamination of rivers and other surface waters are due to surface runoff of rainwater transporting leached radionuclides from cities, mines water, soil weathering and agricultural areas (Pujol and Sanchez, 2000). The knowledge of natural radioactivity present in surface waters and sediments will enable one to assess any possible radiological hazard to humankind as a result of water and sediment use. Potential health hazards from trace metals and NORMs, in water have been considered worldwide and there is therefore the need to assess the level of chromium, copper, iron, zinc, mercury, nickel, lead, arsenic and manganese as well as the level of ^{238}U, ^{232}Th and ^{40}K in the Birim River in East Akim Municipality.

1.1 STATEMENT OF THE PROBLEM

Although, the emergence of Gold mining contributes significantly to Ghana’s Economic Recovery Programme, it is at a great environmental cost as exploitation of the gold puts stress on water, soil, vegetation and poses human health hazards. Availability of clean water leads to good health, development and prosperity. Unpolluted rivers provide drinking water, fish and wildlife habitats, recreational opportunities and economic benefits for local communities.

River Birim, which was the main source of drinking water for the people of Kibi and the surrounding communities in recent times, has been polluted by artisanal mining activities which has led to severe scarcity of drinking water in the community. Water from the river has become brown in colour due to deposition of tailings and other dissolved pollutant. Chemicals used in mining processes cause pollution to the environment. The mercury that is used to amalgamate the gold and the cyanide for extraction is discharged into rivers and streams, thus contaminating the water bodies and killing the aquatic organisms. People who consume such contaminated water and aquatic organisms are prone to serious health hazards. The current state of Birim River compelled the inhabitants in the area to depend on bagged water as their source of drinking water instead of the river water denying thousands of people access to their source of drinking water. Osafo, 2011 and Asamoah, 2012 have studied the physicochemical parameters and the concentration of some trace metals in the river but the human health effect on the ingestion and dermal contact of the water was not assessed, as well as activity concentration of naturally occurring radioactive materials.

It is against this background that a study of the trace metals and natural radioactivity levels in the river is important to determine the extent of pollution of the Birim River.

1.2 PURPOSE OF THE STUDY

The primary aim of this study is to evaluate the potential human health risk associated with ingestion of trace metals and naturally occurring radioactive material in Birim River at Kibi and its environs.

1.2.1 Specific objectives

1. To determine the physicochemical parameters of the river water.
2. To assess the activity concentration of Uranium-238, Thorium-232 and Potassium- 40, and the levels of trace metals in the river water and sediments.
3. To estimate the human health risk on the ingestion and dermal contact of the water.

1.3 RELEVANCE AND JUSTIFICATIONS

In many developing countries including Ghana, data on radionuclide concentrations in river water is not enough. Consequently, there is general lack of awareness and knowledge on the radiological hazards and exposure levels by exposed people, legislators, regulators and operators. This study seeks to create awareness on the radiological hazards and exposure levels to people, legislators, and regulators in the East Akim Municipality. This work will also provide baseline data on the level of human exposure to toxic metals and radioactivity in the East Akim Municipality.

CHAPTER TWO

LITERATURE REVIEW

2.1 SURFACE WATER QUALITY

“Water quality” is a term used here to express the suitability of water to sustain various uses or processes. People have specific water quality requirements for drinking water, recreation, agriculture and industry; although the specific water quality requirements vary by sector (Meybeck et al., 1996). Any particular use will have certain requirements for the physical, chemical or biological characteristics of water (Meybeck et al., 1996).

Water quality relates to the composition of water as affected by natural processes and human activities. Without human influences, water quality would be determined by the weathering of bedrock minerals and by the atmospheric processes of evapotranspiration. The deposition of dust and salt by wind and natural leaching of organic matter and nutrients from soil, by hydrological factors that lead to runoff, and by biological processes within the aquatic environment that can alter the physical and chemical composition of water (UNEP/GEMS, 2006). As a result, water in the natural environment contains many dissolved substances and non-dissolved particulate matter. Dissolved salts and minerals are necessary components of good quality water as they help maintain the health and vitality of the organisms that rely on this ecosystem service. Quality of water depends not only on the chemical, biological and physical condition of the water but also on its radiological condition. In addition, the quality relates to specific use, and is usually measured in terms of constituent concentrations. The level of water quality is based upon the evaluation of measured parameters, which then are compared to water quality standards, objectives or criteria.

2.2 WATER QUALITY INDICES (WQI)

A water quality index provides a single number (like a grade) that expresses overall water quality at a certain location and time based on several water quality parameters (Abrahão, et al., 2007; Mitchell and Stapp, 2000). Water quality index can also refers to two or more parameters that are used to indicate how healthy or save water is for use by man and other living organisms (Svobodova et al., 1993). The objective of an index is to turn complex water quality data into information that is understandable and useable by the public. The WQI will be used to describe quality of water in terms of the concentration and state (i.e. dissolved or particulate) of some or all of the organic and inorganic materials that may be present in the water as well as certain physical characteristics of the water.

2.3. SURFACE WATER POLLUTION

Water pollution occurs when contaminants are released into the water degrading the quality of the water for users. Water pollution includes all of the waste materials that cannot be naturally broken down in water. Pollution, in certain circumstances, can be caused by nature itself, such as when water flowing through soils with high acidities. However, more often than not, human actions are responsible for the pollutants that enter the water (World Water Council, 2000).

2.4 Sources of Water Pollution

The major sources of water pollution can be classified as point and non-point sources. Point source is a pollution input that can be related to a single outlet. Untreated, or inadequately treated sewage disposal is one of the major point source of pollution to the world's waters. Other important point sources include mines and industrial effluents. Some point sources are characterized by a relatively constant discharge of the polluting substances over time, such as domestic sewers, whereas others are occasional or fluctuating discharges, such as leaks and accidental spillages. Non-point sources cannot be ascribed to a single point or a single human activity, they may be due to many individual point sources to a water body over a large area, for instance Agricultural run-off and urban run-off from city streets and surrounding areas.

2.4.1 Industrial sources (Mining)

Industrial waste is generated by manufacturing or industrial processes. Industrial activities create huge pollution. Many industrial facilities use fresh water to carry away waste from their plants into rivers, lakes and oceans. The characteristics of the pollutants released by industrial establishments vary greatly, both within and among industries. These toxic chemicals and pollutants can cause air pollution that can lead to acid rain and drain into rivers and lake to course water pollution and damage to our environment and us. Water can become contaminated with radioactive materials from nuclear establishments like uranium mines and toxic materials from chemical manufacturing plants.

Mining activities emit several metal waste and sulphides into the environment. Industrial waste contains pollutants such as lead, mercury, sulphur, asbestos, nitrates and many other harmful chemicals. Many industries do not have proper waste management system and release the waste in the fresh water which goes into rivers, canals and later in to sea (http://www.conserve-energy-future.com/sources-and-causes-of-water-pollution.php). The toxic chemicals have the capability to change the chemistry of water, increase the amount of minerals and cause eutrophication leading to ageing of the water.

2.4.2 Municipal sources

Urban runoff from city streets and surrounding areas (which is not channelled into a main drain or sewer) is also another source of water pollution. Likely contaminants include derivatives of fossil fuel combustion, bacteria, metals (particularly lead) and industrial organic pollutants, particularly Polychlorinated Biphenyls (PCBs). Another route of water pollution by municipal sources is disposal of solid waste in open surface and sometimes along banks of streams and rivers (Amerasinghe, et al., 2013). Rain runoff then carries the refuse into receiving water bodies either nearby or far off. This results in the introduction of toxic materials into the aquatic ecosystem.

2.4.3 Agricultural sources

Agriculture, consisting of crop cultivation, commercial livestock and poultry farming is another major contributor to water pollution. Agricultural run-off, including soil erosion from surface and sub-soil drainage transfer organic and inorganic soil particles, nutrients, pesticides and herbicides to adjacent water bodies (Amerasinghe, et al., 2013). The chemical fertilizers that are used by the farmers are also washed off by runoff waters into nearby water bodies. The polluting fertilizers can increase the amount of nitrates and phosphate in the water, which can lead to the process of eutrophication. These chemicals are particularly dangerous to life in the aquatic ecosystem where they can be building up over a period of time (http://www.conserve-energy-future.com/sources-and-causes-of-water-pollution.php).

2.5 Effect of Water Pollution

The effects of water pollution are varied and depend on the type and kind of contaminant. The effects of water pollution can be considered under the three categories (Dix, 1981);

i) **Physical effect:** This effect alters the physical appearance or state of the water. Examples include suspended solid particles that cause water turbidity and oil covering surface of water. From the above it is evident that there is some real financial implications that will result from water pollution. It can cost a lot more to purify drinking water with high turbidity.

ii) **Toxic chemical effect:** Animals, including aquatic ones die when water is poisoned for various reasons. Animals are stressed and their populations are endangered through pesticide water pollution. For instance, toxins emitted by algae growth can cause stomach aches and rashes. Excess nitrogen in drinking water also poses serious risks to infants.

iii) **Pathogenic effect:** Microorganisms such as bacteria and viruses, which are introduced in to water through untreated sewage, may present a health hazard to humans. In countries that have poor screening and purification practices, people often get water-borne disease outbreaks such as cholera and tuberculosis. In developed countries, even where there are better purification methods, people still suffer from the health effects of water pollution.

2.6 TRACE METALS (ELEMENTS) AND THEIR SOURCES

Trace elements are elements, which may be metal, non-metal, or metalloids that normally occur in the environment at low concentrations (<1 mg/L) (Duffus, 2002). Trace metals such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc normally occur at very low concentrations in the environment. Some trace metals are essential for life whiles others are very toxic even at low concentration. For example, iron is an essential element for many living things and in human blood, iron transports oxygen around the body. Concentration of metals in the environment increase when they are released from the geology (Laar, 2013). These releases can occur through natural processes or through human activities. Natural processes include breakdown of rocks, and volcanic activity.

Human activities that release trace metals into the environment include mining, smelting, burning of coal, and waste disposal. The tar sands, diamond, and metal mining can release trace metals into the surrounding environment. This often occurs when contaminated waste is not properly disposed of or when a lot of dust from the mine site blows around. For the most part, human contributions of trace metals to the environment have even exceeded the natural inputs.

2.6.1 SELECTED TRACE METALS

2.6.1.1 Mercury (Hg)

Mercury occurs naturally in the environment and exists in several forms. These forms can be organized under three headings: metallic mercury (also known as elemental mercury), inorganic mercury, and organic mercury (ATSDR, 1999). Metallic mercury is a shiny, silver-white metal that is a liquid at room temperature. It is the elemental or pure form of mercury.

Inorganic mercury compounds occur when mercury combines with elements such as chlorine, sulphur, or oxygen. These mercury compounds are also called mercury salts. Most inorganic mercury compounds are white powders or crystals, except for mercuric sulphide (also known as cinnabar) which is red and turns black after exposure to light.

When mercury combines with carbon, the compounds formed are called "organic" mercury compounds or organomercurials. The most common organic mercury compound in the environment is methylmercury (also known as monomethylmercury). Other organic mercury compounds are dimethylmercury and phenylmercury. Like the inorganic mercury compounds, both methylmercury and phenylmercury exist as "salts" (for example, methylmercuric chloride or phenyl mercuric acetate). When pure, most forms of methylmercury and phenylmercury are white crystalline solids. Dimethylmercury, however, is a colourless liquid (ATSDR, 1999).

The solubility of mercury compounds in water varies: elemental mercury vapour is insoluble, mercury (II) chloride is readily soluble, mercury (I) chloride is much less soluble and mercury sulphide has a very low solubility. Methylation of inorganic mercury is an important process in water and occurs in both fresh water and seawater (IPCS, 1989). Bacteria (Pseudomonas spp.) isolated from mucous material on the surface of fish and soils were able to methylate mercury under aerobic conditions. Some anaerobic bacteria that possess methane synthetase are also capable of mercury methylation (Wood &Wang, 1983). Once methylmercury is released from microbes, it enters the food-chain as a consequence of rapid diffusion and tight binding to proteins in aquatic biota. Environmental levels of methylmercury depend on the balance between bacterial methylation and demethylation (IPCS, 1990).

Mercury has been used as cathode in the electrolytic production of chlorine and caustic soda, in electrical appliances (lamps, arc rectifiers, mercury cells), in industrial and control instruments (switches, thermometers, barometers), in laboratory apparatus and as a raw material for various mercury compounds (WHO, 2005). The mercury compounds are used as fungicides, antiseptics, preservatives, pharmaceuticals, electrodes and reagents. Gold mining operations use mercury to extract gold from ores through amalgamation (Carrico, 1985). Mercury has also been widely used in dental amalgams (IPCS, 2003).

2.6.1.2 Health effects

Mercury is toxic and has no known function in human biochemistry and physiology. Mercury will cause severe disruption of any tissue with which it comes into contact in sufficient concentration (WHO, 2005). The two main effects of mercury poisoning are neurological and renal disturbances (WHO, 2005). Exposure to high levels of mercury can damage the brain and the kidneys. The most susceptible group to the effect is the foetuses. This is because methyl mercury can easily cross the placenta resulting in exposure and toxicity to the developing brain. This impaired development of motor and language skills as well as blindness and deafness (Femer, 2001; Jarup, 2003).

2.6.1.3 Arsenic (As)

Arsenic is classified chemically as a metalloid, having both properties of a metal and a non-metal; however, it is frequently referred to as a metal (ATSDR, 2007). Arsenic exists in oxidation states of −3, 0, +3 and +5. It is distributed throughout Earth’s crust, most often as arsenic sulphide or as metal arsenates and arsenides.

In water, As is most likely to be present as arsenate, with an oxidation state of +5 if the water is oxygenated. However, under reducing conditions (<200 mV), it is more likely to be present as arsenite, with an oxidation state of 3 (IPCS, 2001). Arsenic is introduced into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition (IPCS, 1981; Hindmarsh & McCurdy, 1986). In well oxygenated surface waters, arsenic(V) is generally the most common arsenic species present (Irgolic, 1982; Cui & Liu, 1988); under reducing conditions, such as those often found in deep lake sediments or groundwater, the predominant form is arsenic(III) (Welch et al., 1988; WHO, 2011). An increase in pH may increase the concentration of dissolved arsenic in water (WHO, 2011).

Arsenicals are used commercially and industrially as alloying agents in the manufacture of transistors, lasers and semiconductors, as well as in the processing of glass, pigments, textiles, paper, metal adhesives, wood preservatives and ammunition. They are also used in the hide tanning process and to a limited extent, as pesticides, feed additives and pharmaceuticals (WHO, 2011).

Elemental arsenic is used as an anti-friction additive to metals used for bearings, and to strengthen lead-acid storage battery grids. In the past, the predominant use of arsenic was in agriculture. The uses of lead arsenate as a growth regulator on citrus, calcium arsenate as a herbicide on turf, sodium arsenite as a fungicide on grapes. The use of arsenic acid as a desiccant on okra for seed and cotton were voluntarily stopped in the late 1980s and the early 1990s (USEPA, 2006).

2.6.1.4 Health effects

Arsenic has not been demonstrated to be essential in humans (IPCS, 2001). The acute toxicity of arsenic compounds in humans is predominantly a function of their rate of removal from the body. Arsine is considered to be the most toxic form, followed by the arsenites (arsenic (III)), the arsenates (arsenic (V)) and organic arsenic compounds. Lethal doses in humans range from 1.5 mg/kg of body weight (diarsenic trioxide) to 500 mg/kg of body weight (Buchet & Lauwerys, 1982). Acute arsenic intoxication associated with the ingestion of well water containing1.2 and 21.0 mg of arsenic per litre has been reported (Feinglass, 1973). Early clinical symptoms of acute intoxication include abdominal pain, vomiting, diarrhoea, muscular pain and weakness, with flushing of the skin. Signs of chronic arsenicism, including dermal lesions such as hyperpigmentation and hypopigmentation, peripheral neuropathy, skin cancer, bladder and lung cancers and peripheral vascular disease, have been observed in populations ingesting arsenic-contaminated drinking-water (Zaldivar, 1980; Zaldivar & Ghai, 1980). Dermal lesions were the most commonly observed symptom, occurring after minimum exposure periods of approximately 5 years. Effects on the cardiovascular system were observed in children consuming arsenic-contaminated water (mean concentration 0.6 mg/l) for an average of 7 years (Zaldivar, 1980; Zaldivar & Ghai, 1980).

2.6.1.5 Cadmium (Cd)

Cadmium concentration in natural surface water and groundwater is usually <1μg/L. Cadmium exists as the hydrated ion or as ionic complexes with other inorganic or organic substances in surface water (ATSDR, 2012).

Cadmium is emitted to soil, water, and air by non-ferrous metal mining and refining, manufacture and application of phosphate fertilizers, fossil fuel combustion, and waste incineration and disposal. Cadmium from polluted soil and water can accumulate in agricultural crop sand aquatic organisms, thus entering the food supply (ATSDR, 2012).

In the environment, cadmium exists in only one oxidation state (+2) and does not undergo oxidation- reduction reactions. Soluble forms of cadmium can migrate in water. (WHO, 2011)

Insoluble forms of cadmium settle and adsorb to sediments. Cadmium's fate in soil depends on several factors such as pH of the soil and the availability of organic matter. The dominant use of cadmium is in active electrode materials in Ni-Cd batteries (USGS, 2008). Cadmium is also used as pigments for plastics, ceramics, and glasses; stabilizers for polyvinyl chloride (PVC) against heat and light; engineering coatings on steel and some nonferrous metals; and components of various specialized alloys (Elinder 1992; IARC 1993; Thornton 1992; USGS 2008). Cadmium salts have been used in a limited capacity as a fungicide for golf courses and home lawns (EPA 2006b). Cadmium chloride is used in photography, photocopying, dyeing, calico printing, vacuum tube manufacture, pigment manufacture, galvanoplasty, lubricants, ice-nucleation agents, and in the manufacture of special mirrors (Herron 2003).

2.6.1.6 Health Effects

Low dose of cadmium exposure for several years which might occur through daily ingestion of cadmium contaminated food or drinking water can cause kidney tubular dysfunction and osteoporosis (Jarup et al., 1998). High exposure to cadmium fumes may occur in some occupational settings such as plastics and ceramics industries that use cadmiun, which can cause acute bronchitis or even chronic disease, such as emphysema or pulmonary fibrosis and lung cancer (Goyer and Clarkson, 2001; Davison et al., 1988)

2.6.1.7 Lead (Pd)

Lead is commonly found in soil especially near roadways, older houses, old orchards, mining areas, industrial sites, near power plants, incinerators, landfills, and hazardous waste sites. People living near hazardous waste sites may be exposed to lead and chemicals that contain lead by breathing air, drinking water, eating foods, or swallowing dust or dirt that contain lead. People may be exposed to lead by eating food or drinking water that contains lead. Drinking water in houses containing lead pipes may contain lead, especially if the water is acidic (ATSDR, 2007).

Lead is malleable and therefore easily moulded and shaped. Lead can be combined with other metals to form alloys. Lead and lead alloys are commonly found in pipes, storage batteries, weights, shot and ammunition, cable covers, and sheets used to shield us from radiation. The largest use for lead is in storage batteries in cars and other vehicles. Lead compounds are used as a pigment in paints, dyes, and ceramic glazes and in caulk.

2.6.1.8 Health Effects

Acute lead poisoning causes headache, irritability, abdominal pain and various symptoms related to disruptions in the proper functioning of the nervous system. This condition is known as lead encephalopathy (Jarup, 2003). The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults to lead at work has resulted in decreased performance in some tests that measure functions of the nervous system. Lead exposure may also cause weakness in fingers, wrists, or ankles and increase in blood pressure, particularly in middle-aged and older people. At high levels of exposure, lead can severely damage the brain and kidneys in adults or children and ultimately cause death (ATSDR, 2007).

2.6.1.9 Zinc (Zn)

Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of mining, purifying of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes. Domestic wastewater and run-off from soil containing zinc can discharge zinc into surface water. Most of the zinc in lakes or rivers settles on the bottom, however, a small amount may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases (ATSDR, 2005). Zn toxicity in water is affected by hardness, pH, temperature, dissolved oxygen, and alkalinity.

Metallic zinc has many uses in industry. A common use for zinc is to coat steel and iron as well as other metals to prevent rust and corrosion; this process is called galvanization. Metallic zinc is also mixed with other metals to form alloys such as brass and bronze, are components of dry cells, and can also combine with other elements such as chlorine, oxygen, and sulphur, to form zinc compounds. Zinc sulphide and zinc oxide are used to make white paints, ceramics, and other products. Zinc oxide is also used in producing rubber. Zinc compounds, are used in preserving wood and in manufacturing and dyeing fabrics. Zinc compounds are used by the drug industry as ingredients in some common products, such as vitamin supplements and others (USGS, 2003)

2.6.1.10 Health Effects

Low levels of Zn are essential for maintaining good health; too little and too much Zn is harmful to health. Inhalation or contact with decomposition products, vapours, or substance may cause death or severe injury. Signs of deficiency include growth retardation, hair loss, diarrhoea, delayed sexual maturation, eye and skin lesions (slow wound healing), damaged immune system, and loss of appetite. Taking large amounts, even for a short time, causes stomach cramps, nausea, and vomiting; chronic use can cause anaemia, pancreas damage, and lower levels of high density lipoprotein cholesterol (the good form of cholesterol). Breathing zinc dust or fumes causes ‘metal fume fever’ (ATSDR, 2005).

2.6.1.11 Copper (Cu)

Copper (Cu) is a shiny reddish-brown metal found in rock, soil, water, sediment, and air. Its average concentration in the earth's crust is about 50 parts copper per million parts soil (ppm). Copper also occurs naturally in all plants and animals. It is an essential element for all known living organisms including humans and other animals at low levels of intake (ATSDR, 2004). The major sources of copper in the environment include the mining industry, copper smelting and refining industry, industry producing products from copper such as wires and pipes, and fossil fuel combustion (Kalantari and Ebadi, 2006). Other sources of release into the environment are in the agricultural sector where copper is used against plant disease and treatments applied to water bodies to eliminate algae, through waste dumps, domestic waste water, combustion of waste phosphate fertilizer production, and natural sources such as, decaying vegetation (Atafar et al., 2010).

Copper is one of the most important metals because of its durability, ductility, malleability, and electrical and thermal conductivity. It is used primarily as the metal or in alloys. Its alloys, including brass, bronze, and gun metal and are important commodities. Also Cu is used in electrical circuits, household plumbing materials, coins and compounds to treat plant diseases (mildew); wood, leather, and fabric preservatives (USGS, 2002). Moreover, Cu is important in telecommunications, power utilities, in-plant equipment, air conditioning, automotive electrical, automotive nonelectrical, business electronics, and industrial valves and fittings (Jolly and Edelstein, 1987; ATSDR, 2004).

2.6.1.12 Health Effects

Metallic Cu has little toxicity, but Cu's soluble salts are poisonous. Low levels of Cu are essential for maintaining good health. Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in haemoglobin formation, drug xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the cross-linking of collagen, elastin, and hair keratin, and the antioxidant defence mechanism. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anaemia, leukopenia, and osteoporosis. After nutritional requirements are met, several mechanisms prevent copper overload. High levels can cause harmful effects such as skin allergies and irritation of the nose, mouth, eyes, nausea, diarrhoea, vomiting, and stomach cramps. Short periods of exposure can result in gastrointestinal disturbance; long periods can result in kidney/liver damage. It may decrease fertility in adults. Breathing Cu-containing dust or skin contact in mining Cu or processing ore can cause death and liver/kidney disease (Uauy et al., 1998; Olivares et al., 2000; Cordano, 1998; ATSDR, 2004).

2.6.1.13. Iron (Fe)

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5% outer crust. Elemental iron is rarely found in nature, as the iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen and sulphur-containing compounds to form oxides, hydroxides, carbonates, and sulphides. Iron is most commonly found in nature in the form of its oxides (Elinder, 1986; Knepper, 1981). Iron is released into natural waters such as rivers, springs and lakes by the process of weathering and leaching. In fresh water, iron is also an important nutrient for algae and other organisms. Iron is predominant in all freshwater environments because it is highly abundant within the earth's crust and often reaches significant level of concentration in water and sediment than other trace metals (WHO, 1996; Vuori, 1995). Concentrations of iron in drinking-water are normally less than 0.3 mg/litre but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution.

Iron is a natural constituent in plant and animals hence a most crucial element for growth and survival of almost all living organisms. Liver, kidney, fish, and green vegetables contain iron (Valko et al., 2005; Yip, 2001). Iron is used for many purposes all over the world. It is used as constructional material, for drinking-water pipes in the assembly of cars in the production of galvanized sheet metal and electromagnets. Iron oxides are used as pigments in paints and plastics. Other compounds are used as food colours and for the treatment of iron deficiency in humans. Various iron salts are used as coagulants in water treatment.

2.6.1.14 Health Effects

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability and range from about 10 to 50 mg/day (Elinder, 1986; Knepper, 1981). Iron mediated reactions support most of the aerobic organisms in their respiration process. If it is not shielded properly, it can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism. Iron poisoning has always been a topic of interest mainly to pediatricians. Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron-containing products (Albertsen, 2006). Iron overdose causes gastro intestinal bleeding, vomiting and diarrhoea (Osweiler et al., 1985). Acute exposure to iron also results in hypotension, lethargy, tachycardia, hepatic necrosis, metabolic acidosis and sometimes death. Excess iron uptake is a serious problem in developed and meat eating countries and it increases the risk of cancer.

2.6.1. 15 Manganese (Mn)

Manganese is a naturally occurring substance found in many types of rocks and soil. Pure manganese is a silver-coloured metal; however, it does not occur in the environment as a pure metal. Rather, it occurs combined with other substances such as oxygen, sulphur, and chlorine. Manganese can exist in 11 oxidative states; the most environmentally and biologically important manganese compounds are those that contain Mn^{2+}, Mn^{4+} or Mn^{7+} (USEPA, 1994).

The primary source of manganese is food and manganese-containing nutritional supplements. Also, heavy tea drinkers may have a higher intake of manganese than the average person. Certain occupations like welding or working in a factory where steel is made may increase your chances of being exposed to high levels of manganese (ATSDR, 2012).

Manganese is used principally in steel production to improve hardness, stiffness, and strength. It is used in carbon steel, stainless steel, high-temperature steel, and tool steel, along with cast iron and super alloys (ATSDR, 2012). Manganese occurs naturally in most foods and may be added to food or made available in nutritional supplements. Manganese is also used in a wide variety of other products, such as fireworks, dry-cell batteries, fertilizer, paints, a medical imaging agent and cosmetics. It may also be used as an additive in gasoline to improve the octane rating of the gas. Small amounts of manganese are used in a pharmaceutical product called mangafodipir trisodium (MnDPDP) to improve lesion detection in magnetic resonance imaging of body organs (ATSDR, 2012; IPCS, 1999).

2.6.1.16 Health effects

Manganese is a trace element and is necessary for good health. In the case of high level of exposure of inhaled manganese, neurological effects are experience in humans (Canavan et al., 1934; Cook et al., 1974; ATSDR, 2012). The syndrome known as “manganism” is caused by exposure to very high levels of manganese dusts or fumes and is characterized by a “Parkinson-like syndrome”, including weakness, anorexia, and muscle pain, apathy, and slow speech, monotonous tone of voice, emotionless “mask-like” facial expression and slow, clumsy movement of the limbs. In general, these effects are irreversible. Some motor functions may already be affected following chronic exposure to levels of manganese of ≤ 1 mg/m^3.Loss of sex drive and sperm damage has also been observed in men exposed to high levels of manganese in workplace air (ATSDR, 2012).

2.6.1.17 Chromium (Cr)

Chromium is a naturally-occurring element found in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds. The three main forms of chromium are: chromium (0), chromium (III), and chromium (VI) (ATSDR, 2012).

Chromium is released to the environment from natural and anthropogenic sources, with the largest release occurring from industrial releases. The industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production.

The distribution of compounds containing chromium (III) and chromium (VI) depends on the redox potential, the pH, the presence of oxidizing or reducing compounds, the kinetics of the redox reactions, the formation of chromium (III) complexes or insoluble chromium (III) salts, and the total chromium concentration. In soil, chromium (III) predominates. Chromium (VI) can easily be reduced to chromium (III) by organic matter, for example, and its occurrence in soil is often the result of human activities (WHO, 2003). Chromium in water mostly originates from surface runoff, deposition from air or release from wastewaters. It is transported in water as suspended materials and deposited in estuaries and lagoons but it is more frequently removed from the water column by the process of sedimentation (Towill, 1978). In water, chromium (III) is a positive ion that forms hydroxides and complexes, and is adsorbed at relatively high pH values. In surface waters, the ratio of chromium (III) to chromium (VI) varies widely, and relatively high concentrations of the latter can be found locally. In general, chromium (VI) salts are more soluble than those of chromium (III), making chromium (VI) relatively mobile. In air, chromium is present in the form of aerosols. Both trivalent and hexavalent chromium are released into the air (WHO, 2003).

Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, and in photography, and for chrome alloy and chromium metal production, chrome plating, and corrosion control (WHO, 2003).

2.6.1.18 Health Effects

Small amounts of chromium (III) are needed for human health (Stoecker, 2001). High exposures to chromium results in the irritation of the lining of the nose, runny nose, asthma, cough shortness of breath, wheezing and skin rashes. The concentrations of chromium in air that can cause these effects may be different for different types of chromium compounds, with effects occurring at much lower concentrations for chromium(VI) compared to chromium (III) (ATSDR, 2012). The International Agency for Research on Cancer (IARC) has determined that chromium (VI) compounds are carcinogenic to humans (IARC, 1980). Mixed results have been found in studies of populations living in areas with high levels of chromium (VI) in the drinking water (ATSDR, 2012).

2.7 TRACE METAL DISTRIBUTION IN RIVER WATER AND SEDIMENT

Metals can be dispersed in soil, water, and air. Metals in aquatic environment dispersed in surface water, and sediment, by settling in sediment and suspending as particles in surface water. In surface and ground water, sediment and air, bioavailability is a complex function of many factors including total concentration and speciation (physical-chemical forms) of metals, mineralogy, pH, redox potential, temperature, total organic content (both particulate and dissolved fractions), and suspended particulate content, as well as volume of water, water velocity, and duration of water availability, particularly in arid and semi-arid environments. Many of these factors vary seasonally and temporally, and most factors are interrelated (Luoma, 1989). The dissolved fraction of trace metals in aquatic environment consists of carbonate complexes, whose abundance increases with pH, and metals in solution, including metal cation and anion complexes and hydrated ions whose solubilities are affected strongly by pH and tend to increase with decreasing pH (Elder, 1989).

2.7.1 Water

The occurrence of high concentrations of trace metals in water has been of a great interest to environmental scientists. Among the inorganic contaminants of water, trace metals are non-degradable in nature and often accumulate through tropic levels causing a deleterious biological effect to humans and organisms that depend on the water (Qishlaqi and Moore, 2007). The occurrence of elevated levels of trace metals in water can be a good indication of pollution attributed to anthropogenic influence rather than natural enrichment processes like geological weathering. Trace metal concentration have been found to be generally low in water compared with their concentrations in sediments (Ozturk et al., 2009; Asaolu et al., 1997; Adeyeye, 1994).

2.7.2 Sediment

Trace metal concentration in sediments usually exceed those of the overlying water by several orders of magnification (Van Aardt and Erdmann, 2004). According to Mwamburi (2003) trace metal distribution in sediments can reflect the current and historical situation of the water system and can be used to detect the presence of contaminants that do not remain soluble after discharge in to surface water. Studies from Demirak et al (2006) also recorded elevated levels of metals in stream sediments than the corresponding overlying water.

Sediments act as a carrier and a source of pollutants, because trace metals can release back into the water column as a result of sediment agitation and changes in environmental condition. Physicochemical properties including total concentration and speciation (physical-chemical forms) of metals, mineralogy, pH, redox potential, temperature, total organic content of sediments also affect the concentration and availability of trace metals in the sediments (Qishlaqi and Moore, 2007)

2.7.3 Bio-availability

Bioavailability is the proportion of total metals that are available for incorporation into biota. Total metal concentrations do not necessarily correspond with metal bioavailability. In surface water and sediment, bioavailability of trace metals is characterized with many factors including total concentration and speciation of metals.

2.8 Naturally Occurring Radioactive Materials (NORMs)

NORMs are materials which may contain any of the primordial radionuclides or radioactive elements uranium – 238, thorium – 232, potassium – 40 that occur in nature and their radioactive decay products. Long-lived radioactive elements of interest include uranium-238, thorium-232 and potassium-40, and any of their radioactive decay products, such as radium and radon. These elements have always been present in the earth’s crust and within the tissues of all living species. NORM is found in a wide variety of bulk commodities, process wastes and commercial items, sands, clays and soils, rocks, coal, groundwater, oil as well as gas, metal ores and non-metal minerals, including fertilizer raw materials such as rock phosphate and apatite. Metal ores that have been found to be associated with NORM include tin, tantalum, niobium, rare earths, copper and gold.

Higher concentrations may arise as a result of human activities such as mining and mineral processing. In most NORM, several or all of the radioactive isotopes of the three primordial decay series (^{235}U, ^{238}U and^{232}Th) are present in small concentrations in the natural matrix. Artificially concentrated NORM is sometimes called TENORM, an acronym for ‘technologically enhanced naturally occurring radioactive material (ICRP, 2000; UNSCEAR, 2000; IAEA; 2005). NORM is widely distributed, and gives rise to a natural radiation background that varies depending on location and altitude, that is the properties of the underlying rocks and of the soil in a location (Merdanoglu and Altinsoy, 2006). According to UNSCEAR 2000 report, the levels of exposure living species to NORMs vary by a factor of 3 (UNSCEAR, 2000). There appears to be no scientific evidence relating general variations in this natural background to health effects. Average activity concentrations of some of the naturally occurring radionuclides, including a number of very long-lived singly occurring radionuclides such as potassium-40 (^{40}K), rubidium-87 (^{87}Rb) and indium-115 (^{115}In) in the undisturbed environment world-wide, are given (UNSCEAR, 2000). The presence of these radionuclides in the environment gives rise to natural background radiation.

In addition to the NORMs from terrestrial and cosmogenic sources, technologically enhanced naturally occurring radioactive materials (TENORM) and man-made (artificially produced) radionuclides have been introduced into the environment due to the proliferation of different nuclear applications. These sources can contribute to the levels of natural background radioactivity at a given location.

2.8.1 Sources of Natural Radiation

All living organisms are continually exposed to ionizing radiation from natural sources. The levels of exposure vary depending on location and altitude. Radiation comes from outer space, from the ground and even from within our own bodies. Radiation is all around us and has been present since the birth of this planet. The main sources of exposure are: cosmic rays that come from outer space and from the surface of the sun and terrestrial radionuclides that occur in the earth crust. NORM also occurs in building materials, air, water, foods and, in the human body (Faanu, 2011; Ademola, 2008).

It is thus important to carry out an assessment of the doses resulting from the natural sources since it has been identified as the largest contributor to the collective dose of the world population. Cosmic radiation has been identified to be intense at higher altitudes whilst the concentration of uranium and thorium in soils are higher in localised areas. The exposure to radiation from concentration of ^{40}K in foods has been found to be fairly constant and uniform for individuals everywhere in the world (UNSCEAR, 2000).

It has been reported that the concentration of natural radioactivity in the environment is a function of geology and other physical characteristics of the soil or geological formation. The major source of radioactivity in the environment comes from the uranium, thorium, and actinide series are all abundant in the earth crust. Human activity like nuclear weapon testing and the application of radionuclides in nuclear power plants and the medical industry in recent times have introduced man-made radionuclides into the environment. Other human activities like mining have also enhanced the concentration of natural radioactivity.

2.8.1.1 Terrestrial Radionuclides

Terrestrial radionuclides are primordial radionuclides which have been on earth since the formation of the earth. These radionuclides have very long decay half-lives, comparable to the age of the earth (Lilley, 2001; Klement, 1982). They are ubiquitous in the earth's crust, and are consequently assumed to represent a primordial inventory. They include: ^{40}K with a half-life of 1.28×10^{9} years, ^{232}Th with a half-life of 1.41×10^{10} years, and ^{238}U with a half-life of 4.47×10^{9} years. Other primordial radionuclides of secondary importance include: ^{235}U with a half-life of 7.04×10^{8} years and ^{87}Rb with a half-life of 4.70×10^{10} years. Of these radionuclides, thorium and uranium lead a series of several radionuclides, many of which contribute to human radiation exposure. The target radionuclides of interest are ^{226}Ra, ^{238}U, ^{232}Th and their daughter nuclides in the decay series and ^{40}K (Faanu, 2011).

2.8.1.2 Cosmogenic Radionuclides

Cosmogenic radionuclides are produced continuously by the interaction of nucleons released from cosmic radiation with target nuclei in the earth atmosphere, mostly upper atmosphere (Eisenbud and Gesell, 1997). There are several cosmogenic radionuclides with a range of half-lives from minutes to millions of years; however, only four of them contribute a significant measurable dose of radioactivity to humans (Eisenbud and Gesell, 1997). Typically, they include: ^{3}H, ^{7}Be, ^{14}C and ^{22}Na. (UNSCEAR, 2000). The most significant cosmogenic radionuclide is ^{14}C which can be taken up by plants and then enter the food chain (Watson et al., 2005).

2.8.1.3 Artificial Radionuclides

Since the discovery of radioactivity man has explored the potentials of this phenomenon. Man is changing his world through the knowledge of radioactivity. Thus, from military to medical uses, production of energy, detection of fire and prospecting for minerals have all made use of radioactivity. As a result, the radionuclides are released in to the environment. According to Klement, (1982) most of the radionuclides have been released into the environment due to the use of radiation sources by man for various purposes. Detectable quantities of man-made radionuclides are widely distributed in the atmosphere, particularly as a result of nuclear weapons testing and the Chernobyl reactor accident in 1986 and Fukushima Daiichi nuclear accident in 2011 (Klement, 1982; Watson, et al., 2005; Lilley, 2001). A significant radionuclide produced from these sources is ^{137}Cs with half-life of 30.7 years. This nuclide has been globally dispersed and deposited through rain and dry deposition on terrestrial surfaces (Watson, et al., 2005).

However, the environmental levels of released radionuclides are slowly declining and some of them are below the limits of detection.

2.9 Fate and Distribution of Radionuclides in the Environment

The fate and distribution of radionuclides in the environment is very much depending on the chemical and physical form of the radionuclides (USEPA, 2006). Naturally occurring radionuclides are created in the upper atmosphere and are found in the Earth's crust. They are found in certain types of rocks that contain trace amounts of the radioactive isotopes of uranium, thorium and/or actinium. As these rocks weather, the resulting clays and other materials may transmit radionuclides into water and sediment. In the Earth's crust, radioactive isotopes released from the Uranium and Thorium series are immediately dissolved into surrounding aquifers or readily absorbed by surrounding soil particles like clay which has a high absorption and ion exchange capacity (Aldahan et al., 2006). Solomon et al., (2002) also found that clays have higher concentration of radioactive isotopes than found in sand-stones. Groundwater can rise to surface waters through fault and springs and carry along with it considerable amounts of dissolved elements including radioisotopes. Radon can also find their way to aquifers and the surface of the earth through geological fault and cracks (Agalga, 2012).

According to Almgren (2008) the vertical distribution of radionuclides in soil highly affects the radiation dose to humans and animals. Radionuclides with low mobility that are present in the uppermost layers of the soil for a long time, contributes to higher external doses. The radionuclides in the upper layers also enhance plants uptake as a result of increased root transport of the radionuclides. The presence of radionuclides in uppermost and upper layers of the soil increases internal doses through food intake.

The sources of radioactivity in aquatic environment includes NORMs from the soil, fallout from the atmosphere, runoff from watershed that have received atmospheric deposition as well as radioactive effluents from medical, industrial, and nuclear facilities released either accidentally or routinely (Blaylock et al., 1993). There are various factors that affect the fate, transport and distribution of radionuclides in aquatic environments. This includes hydrogeological, mineralogical and geochemical properties of the geometrical medium.

The variability of radionuclides in river environment depends on the transport pathways, human activity, sediment load and climatic conditions (Aldahan et al., 2006). Also, depending upon the element and the chemical form, radionuclides may accumulate in bottom sediment or remain in the water column in the dissolve state. This causes bioaccumulation of radionuclides in the biota. Studies conducted on the presence of natural radionuclide in surface water have reveal the present of some concentration of ^{238}U, ^{232}Th and ^{40}K with some level of contamination from ^{137}Cs and other radionuclides (Mazzilli et al., 1998; Afaf et al, 2011; Ismail et al, 2009).

Ingestion is one of the main ways of uptake of naturally occurring radionuclide this is done through drinking water and food. Radionuclides in surface water normally end up contaminating aquatic foods such as fish and shrimps, and finally ended up in the bottom sediment (Wallner et al, 2008). In Ghana, data on the levels of natural radioactivity in surface water is scanty. Therefore various studies on the presence of NORMs in domestic water, underground water surface water and saline water have been made mostly in the southern part of Ghana (Faanu et al., 2011; Darko et al., 2010; Kansana et al., 2012). The hazard associated with radionuclide are widely known and studied, hence the assessment of naturally occurring radionuclides in the environment is key in order to take appropriate measures to prevent the hazards that is associated with it.

2.10 Gross Alpha and Beta Emitters

Uranium-238 and radium-226 emit alpha particles. These and other alpha emitters occur naturally as radioactive contaminants, but several such as plutonium and americium also come from man-made sources. They may occur in either groundwater or surface water. At high exposure levels, alpha emitters may cause cancer (Mortazavi and Karamb 2005). Beta and photon emitters are primarily man-made radioactive contaminants associated with operating nuclear power plants, facilities that use radioactive material for research or manufacturing, or facilities that dispose of radioactive material. Some beta emitters occur naturally (strontium-90). Beta and photon emitters primarily occur in surface water. At high exposure levels, beta and photon emitters are believed to cause cancer in humans (Mortazavi and Karamb, 2005).

2.11 Effect of Radiation on Human

Naturally occurring radioactive materials, account for about 80% of man’s exposure to natural radiation and is the second leading cause of cancer following tobacco (USEPA, 2006; UNSCEAR, 2000). Long-term exposure to Uranium through inhalation has several health effects such as chronic lung diseases, acute leucopoenia anaemia and necrosis of the mouth. Radium causes, bone, cranial and nasal tumours (Ramasamy et al, 2009).

Thorium exposure can cause lung, pancreas, hepatic, bone, kidney cancers and leukemia (Taskin et al., 2009; USEPA, 2006).

2.12 METHODS AND INSTRUMENTATION FOR ASSESSMENT OF NORMS

There are many different types of methods and instruments available for measuring ionizing radiation in environmental samples. The methodology that should be used depends on the type of site, the stage of the project that is being investigated, the levels to which the contamination is to be determined at the site and the specificity of the analysis needed (USEPA, 2006). Some of the instruments include: Liquid Scintillation Counting, Gas Extraction, Gamma Spectrometry and Alpha Spectrometry.

The basic requirement of the instruments is that, the radiation interacts with the detector in such a manner that the magnitude of the instrument's response is proportional to the radiation effect or the radiation property being measured (Cember, 1996; IAEA, 1989). For the detector to respond, the radiation must have undergone one of the following interactions: Photoelectric effect, Compton scattering and Pair production.

2.12.1 Liquid Scintillation Counting

In this method, samples are mixed with the counting material and counted by the conventional liquid scintillation counters used for naturally occurring radioactive materials analysis. This method lends itself to large scale counting with automation and gives a rapid analysis of NORMs.

Liquid Scintillation Counting is the most common technique for the measurement of radioactivity of low energy beta emitters. Such emitters (H-3, C-14, Ca-45, etc) are difficult to detect using portable survey instruments since the beta may not be able to penetrate the thin window of the gas filled detector. In liquid scintillation counting, the sample is dissolved in a counting solution. The energy of the beta is absorbed by solvent molecules causing them to become excited. This excitation energy is transferred to a 4-10 rssc radiation detectors & survey instruments 8/99 scintillator resulting in a flash of light or "scintillation" when the scintillator molecules return to the ground state. The number of scintillations emitted is proportional to the energy of the beta particle. A photomultiplier tube (PMT) is used to detect and amplify the light photons from the sample. The emitted light causes the emission of photoelectrons from the PMT which are multiplied by the PMT into a measurable electrical pulse. The height (amplitude) of the pulse is proportional to the number of photons which interact in the PMT. Therefore, the pulse height at the output of the PMT is proportional to the energy of the beta particle in the sample. These pulses can be analyzed to provide the energy of the beta particle and the rate of beta emission in the sample. It is also possible to count very low energy gamma emitters by liquid scintillation since most of the gammas are absorbed in the counting solution.

2.12.2 Gas Extraction

Gas extraction method of detecting NORM is more sensitive especially in water and is suitable at lower concentrations. In this method the NORM are extracted as a gas and count the emitted alpha particles in ZnS scintillation cell. Here, helium is bubbled through the water, striping the NORM. The mixture of gases then passed through a cold trap, for example activated charcoal at liquid nitrogen temperature that traps NORM while the helium passes through. The trap is then warmed and NORM is transferred into a Lucas counting cell by stripping with a small amount of helium.

2.12.3 Gamma Spectrometry

High-resolution gamma spectrometry has been used widely in the determination of radionuclides in environmental samples. Naturally occurring radioactive materials concentration can be determined by counting gamma rays from NORM daughter decay using standard gamma-ray spectroscopy techniques with an HpGe or NaI detector. According to Cardoso et al (2011), it is possible to determine directly the gamma emitters of the sample, obtaining a qualitative and quantitative identification of the radionuclides present in the sample. Several works (Ramasamy et al., 2009; Darko et al., 2005; Ateba et al, 2010; Turhan et al, 2009; Sowmya et al, 2010) have all used this method to evaluate various environmental sample for naturally occurring radionuclides.

2.12.4 Alpha Spectrometry

Naturally occurring radioactive materials (NORMs) concentration can also be determined using alpha spectrometry. The basic alpha spectroscopy system includes: an alpha spectrometer (vacuum chamber and amplifier electronics), alpha detector(s) and analog to digital converter (ADC), multichannel analyser (MCA), computer software, and a print device. The basic principle of this method is that alpha emitting sample are placed on the sample holder in the alpha spectrometer and a vacuum is pulled on the spectrometer vacuum chamber. When alpha particles are emitted by the sample the alpha detectors produce electronic signals that are analysed by the MCA to generate a digital spectrum that is equivalent to the energy of the alpha particles. The spectrum is then analysed by computer software that identifies and quantifies the alpha energies.

CHAPTER THREE

MATERIALS AND METHODS

3.1 The study Area

The study was conducted in the East Akim Municipality of the Eastern Region of Ghana. The study area is located between latitude 0°23'40W, 0°36'30W and longitude 6°16'50 N, 6°9'30N in the East Akim Municipality of the Eastern Region of Ghana. The Municipality has a total land area of approximately 725 km^2. It used to be the second largest of the 15 districts in the Eastern Region until 2004 when the Atiwa district was carved out of it. The district capital, Kibi, is 55 km from Koforidua, 105 km from Accra and 179 km from Kumasi (Asomaning, 1992; Asamoah, 2012; Osafo, 2011). The municipality is bounded by six administrative districts, namely the Atiwa District to the north, West Akim Municipal to the north-west, Fanteakwa District to the east, New Juaben Municipal to the south, Yilo Krobo District to the south-east and Suhum Kraboa Coaltar District to the west (http://eastakim.ghanadistricts.gov.gh).

3.1.1Topography, Geology and Drainage

The land is generally undulating and rises about 240-300 metres above sea level with the highest point being the Atiwa Ranges rising over 350 metres above sea level (http://eastakim. ghanadistricts.gov.gh). The underlying rocks are the Birimmian formation. Also found are masses of granite which occur in parallel belts. The major soil dominating is the Atiwa series which are mainly red, well drain, deep gravel-free silty loams and silty-clay loams. These rock groups contain several mineral deposits including gold, diamond, bauxite and kaolin (http://eastakim. ghanadistricts.gov.gh).

The municipality is drained by rivers such as the Birim, Pra, Kua, Adenchaensu, Densu and Berepong but the main river used by many people is the Birim. The Birim River takes its source from north of Apapam, and passes through Kibi, Pano and Bunso. The main occupation of the inhabitants of the Municipality is farming. Many people are also engaged in small-scale mining activities known as galamsey, mostly along the banks and inside of the Birim River. The activities of the galamsey have affected the river to such an extent that the water is no longer useful (http://eastakim.ghanadistricts.gov.gh).

3.1.2 Climate

East Akim Municipality lies in the west semi-equatorial zone characterized by double rainfall maxima. The two rainfall seasons are interspersed by a dry season. The main rainy season occurs in June and October. The first rainy season is from March to June and the second from September to December. The mean annual rainfall is between 1250-1750 mm (http://eastakim. ghanadistricts.gov.gh). The dry seasons occurs from December to February. Temperature is found to be fairly uniform ranging between 26^{o}C in August and 30^{o}C in March. Relative humidity is generally high throughout the year, ranging between 70 – 80 % in the dry season and 75–80 % in the wet season (Ansa-Asare and Asante, 2000; Asamoah, 2012; Osafo, 2011).

3.1.3 Economic Activities

The municipality has an agro-based economy with most communal rural communities practicing rain-fed agriculture. This account for 58% of the municipality's workforce followed by the service sector with 21.5%, commerce 11% and industry 9.5% (http://eastakim. ghanadistricts.gov.gh). To support their livelihoods the rural population exploits natural resources in the vicinity of their settlements. Agriculture still constitutes the leading employer and covers a total land area of about 159 acres, involving irrigated market gardening, wildlife hunting, and wood harvesting. Gold prospecting also covers a total land area of about 343 acres. It must be emphasized that the activities of these illegal miners is posing serious threat to the environment in the municipality and River Birim (Ansa-Asare and Asante, 2000; Asamoah, 2012).

3.2.1 Desk study

In order to achieve the objectives of the study, a desk-study was carried out to assess the general research work done in the study area pertaining to the mining activities and the impact on the Birim River. This task involved literature review and collection of topographical maps. Availability of equipment at Ghana Atomic Energy Commission (GAEC) and Geological Survey Department was assessed.

3.2.2 Sampling site selection

Reconnaissance field work was carried out prior to actual sampling, in order to identify the type of kits that were required for the sampling task and selection of sampling points. The sampling sites selected were Apapam, Afiesa, Adadientem Akura, Kibi, Asikem and Bonsu which are along the Birim River (Fig. 3.1). The choice of sampling sites was due to their strategic location, the bulk of human activities as well as population densities. Sampling location for surface water targeted the Birim River and its tributaries Topographic and geological maps, as well as aerial photographs and satellite images of the project area were acquired and studied. Lineaments were inferred and areas of intense anthropogenic activity were demarcated for surface water monitoring.

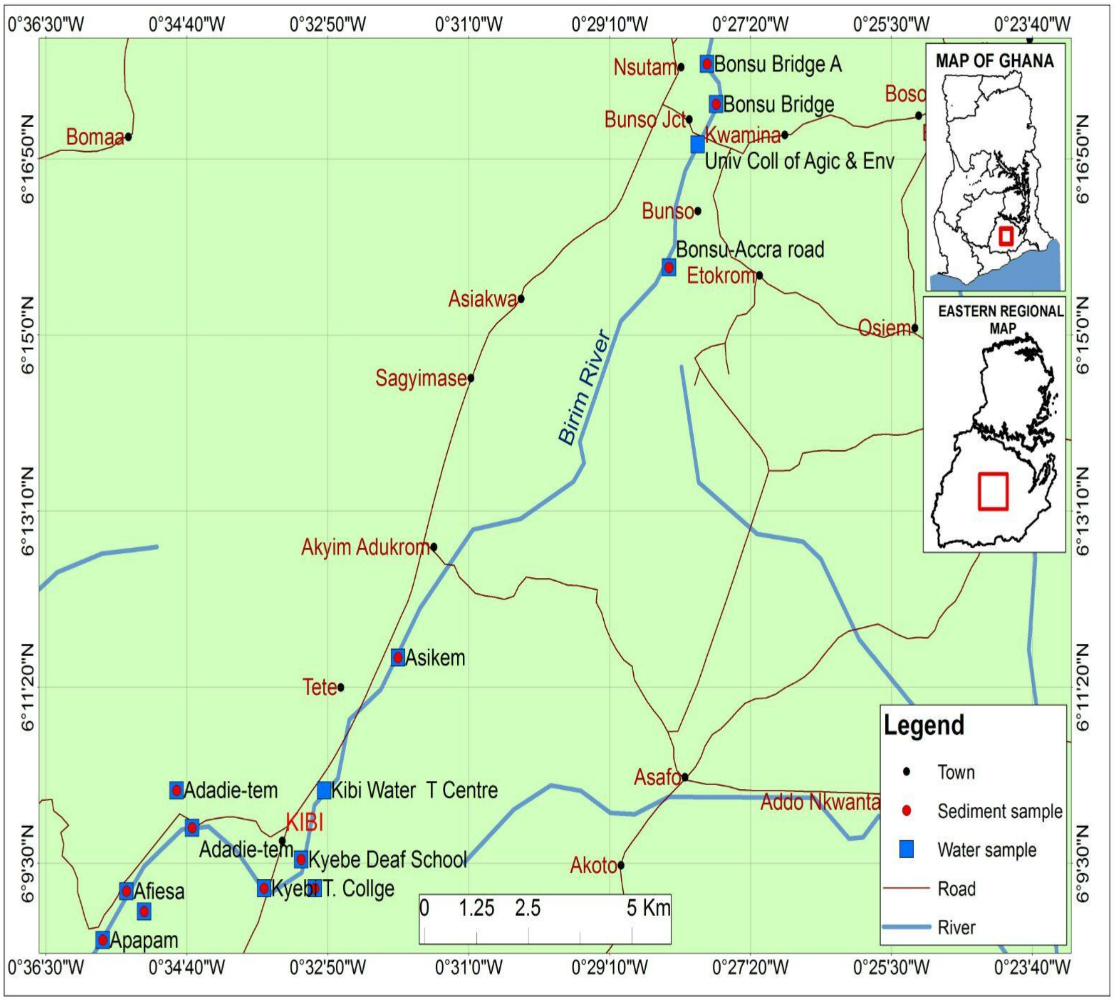


Fig. 3.1: Map of River Birim showing the sampling sites

3.2.3 Treatment of sample containers

New high density polyethylene (HDPE) containers were used. The polyethylene bottles were immersed in a warm liquid soap bath for two days and then rinsed with de-ionized water, immersed in 10 % HNO_3 at room temperature for three days. Bottles were again rinsed three times with de-ionized water, and then immersed in 50 % HNO_3 bath at 90 °C for 24 hours. Bottles were further rinsed with de-ionized water and dried overnight in a clean oven at 60 °C. The bottles were then removed from the oven and allowed to cool, capped tightly and double bagged in re-sealable new polyethylene bags (USEPA, 1983).

3.2.4 Sampling

Surface water and sediment from the Birim River and its tributaries in the East Akim Municipality were sampled individually between November 2014 and February 2015. Surface water samples were taken from a depth of 20-30 cm into acid cleaned 1-L high-density polyethylene bottles (HDPE) with strict adherence to the sampling protocol as described by APHA (1998) standard methods. Surface water samples were filtered in the field using Sartorius polycarbonate filtering apparatus (Gottingen, Germeny) and 0.45µm cellulose acetate membrane filters. At each point, 4 samples were taken for physical parameters, anions, and trace metals, analysis. Water samples for trace metal analysis were acidified to pH < 2 using analytical grade 1% v/v HNO_3 acid after filtration. The samples were carried on ice in an ice cooler from the field and stored in a refrigerator at 4°C prior to analysis.

Using a bottom grab sampler about 100 g of sediments was collected at the top 10 g of the bottom sediments from the point where water samples were taken. The samples were placed in clean plastic bags which were tightly sealed and stored in an ice chest and transported to the laboratory.

3.2.5 Field analysis

Water samples collected were analyzed by both classical and automated instrumental standard methods prescribed for the analysis of water and wastewater (APHA, 1998). Water temperature, electrical conductivity (EC), total dissolved solids (TDS), turbidity and pH were measured at each sampling site using portable (field-type) instruments

(HACH conductivity meter (Colorado, USA) and Metrohm model 691-pH meter (Herisau, Switzerland).

3.2.6 Laboratory Analysis

Major anions measured in water samples were chloride, nitrate, sulphate and phosphate.

3.2.6.1 Determination of Chloride

The chloride content in the water samples was determined titrimetrically using the Argentometric method (APHA, 1998). A portion of 25 mL aliquot of the water sample was placed in a 250 mL conical flask, followed by the addition of two drops (~ 1.0 mL) of potassium chromate ($K_2Cr_2O_4$) indicator. The contents of the conical flask were thoroughly mixed by swirling. The mixture was then titrated against the standardized 0.0141 M $AgNO_3$, till the colour of the water changed to pinkish red (signifying the end point of the titration) and the titre value recorded. For each water sample, two replicate titrations were performed. The amount of chloride in the unknown water samples was determined using Equation 3.1

$$Cl^{-}\,(mg/L) = \frac{(A - B) \cdot N \cdot 35.45 \cdot 100}{V_{sam}} \tag{3.1}$$

where: A is the average titre, B is the titre value for the blank solution; N is the molarity of $AgNO_3$ (0.0141 M), and 35.45 is the relative atomic mass of chlorine.

3.2.6.2 Determination of Phosphate (PO_4^{3-})

The ascorbic acid method was used to determine the level of phosphate in the water samples. Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form an antimonyl-phosphomolybdate complex, which is reduced to intensely blue coloured molybdenum by ascorbic acid. The absorbance of the molyddenum blue is measured at a wavelength of 880 nm on a UV-Visible spectrophotometer.

An aliquot (10 mL) of the water sample was transferred into a 20 mL test tube and to each test tube; 2 mL of the combined reagent was added to each test tube, and left for 5 minutes. During this period, the blue colour of antimonyl-phosphomolybdate complex was developed in each test tube. Aliquot (10 mL) of each blue-coloured solution was transferred into a 1 mL cuvette; the cuvette was inserted into the spectrophotometer (Shimadzu, Australia) and the absorbance measured at a wavelength of 880 nm. Quantification was by external calibration using standard solutions with different concentrations (0.00, 0.20, 0.40, 0.60, 0.80, 1.00 mg/L) and subjected to the same procedure after which a calibration curve is plotted.

3.2.6.3 Determination of Sulphate (SO_4^{2-})

The turbidimetric method was employed. The method is based on the reaction of sulphate ion (SO_4^{2-}) with barium chloride ($BaCl_2$) under acidic conditions to precipitate barium sulphate ($BaSO_4$). The absorbance of the white $BaSO_4$ suspension is measured at a wavelength of 420 nm on a UV-Visible spectrophotometer.

Calibration

10 mL of the standard SO_4^{2-} calibrant solutions were quantitatively transferred into separate test tubes. To each test tube, 1 mL of the acid salt solution (i.e 25g of NaCl, 2 mL of HCl and 100 mL of distilled water), 0.5 mL of glycerol solution (conc.) and 0.5 g $BaCl_2$ were added. The resulting cloudy solution was shaken for 60 sec and left for 5 min.

Aliquot (2 mL) of the cloudy solution was transferred into 1 cm cell and the absorbance of the coloured solution measured at a wavelength of 420 nm on the UV-Visible spectrophotometer. The absorbance of each calibrant solution was plotted against the concentration (0.00, 15.00, 20.00, 25.00, 30.00, 35.00 mg/L) of the calibrants. A straight line graph was obtained and the concentrations of SO42- in the water samples were deduced from the graph.

An aliquot (10 mL) of the water sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to obtain the absorbance of each water sample at a wavelength of 420 nm on the UV-visible spectrophotometer. The concentration of SO_4^{2-} in each water sample was obtained from the calibration graph.

3.2.6.4 Determination of Nitrate (NO_3^-)

The method is based on the reaction of the nitrate ion with brucine sulphate in a H_2SO_4 solution at a temperature of 100 °C. The yellow colour of the resulting complex is measured at a wavelength of 410 nm (Rump and Krist, 1988).

Calibration

A 5 mL portion of each calibrant solution was pipetted into separate 20 mL test tube. To each test tube, 1 mL of 30% NaCl was added, followed by the addition of 5 mL of 6.5 M H_2SO_4. The test tubes were swirled to ensure thorough mixing of the reagents. 0.5 mL of the brucine-sulfanilic acid reagent was added to the content of each tube (except blank). The test tubes were then placed on a rack and lowered into a water bath at 95 ºC for 25 minutes. At the end of the 25 minutes, the rack of test tubes was removed from the bath and immersed in ice. An appropriate aliquot of the yellow coloured calibrant solutions was transferred into a 1 cm cell. The cell was placed into the spectrophotometer and the absorbance of the solution measured at a wavelength of 410 nm.

A standard graph of absorbance of standards against concentration (0.00, 0.20, 0.40, 0.60, 0.80, 1.00 mg/L) of standards was plotted.

About 5 mL aliquot of the water samples were transferred into separate 20 mL test tube and the same procedure as used for the establishment of the calibration curve was followed to obtain the absorbance of each water sample at a wavelength of 410 nm on the UV-visible spectrophotometer. The concentration of NO_3^- in each water sample was deduced from the calibration graph. The concentration was calculated from the relation

$$C_{NO_3^-} = C_{Calib.} \cdot D_f \tag{3.2}$$

where: $C_{NO_3^-}$ is the nitrate concentration, C_{calib} is the concentration from the calibration curve and D_f is the dilution factor.

3.3 Determination of dissolved metals

The Varian AA-240FS Atomic Absorption Spectrophotometer (Varian, California, USA) with operational conditions in Table 3.1 was used to carry out trace metal analyses. The data obtained were averages of triplicate analysis. The concentrations of dissolved metals in the samples were verified using calibration curves for each element. All reagents used were of analytical grade and equipment pre-calibrated appropriately prior to measurement.

Table 3.1: Operational Working Conditions (AAS)

Element (Metal)	Wavelength/ nm	Lamp Current/ nA	Slit Width/ nm	Fuel	Support
Zinc (Zn)	213.9	5	1.0	acetylene	air
Mn	279.5	5	0.2	acetylene	air
Iron(Fe)	248.3	5	0.2	acetylene	air
Cadmium (Cd)	228.8	4	0.5	acetylene	air
Lead(Pb)	217.0	5	1.0	acetylene	air
Chromium(Cr)	357.9	7	0.2	acetylene	air
Copper (Cu)	324.7	4	0.5	acetylene	air
As(By Hydride)	193.7	10	0.5	acetylene	argon
Hg(By Hydride)	253.7	4	0.5	argon	air

3.3.1 Sediment sample preparation and analysis

Sediment samples were dried at ambient air for a week and in the oven to a constant weight at 105^{o}C to ensure that all has been driven away. Dry sediment samples were crushed and ground using ceramic mortar and pestle. The homogenized sample was sieved through a 5 mm mesh size sieve. The powdered samples were placed in a clean plastic zip lock bags and stored until analysis.

Pulverized dried sediment (1g) was sieved and weighed with a digital weighing balance into a clean Teflon beaker. Aqua regia of 25 ml, in the ratio of 1:3 (HCl-HNO_3) was added to the weighed sample and then digested for 3 hours on a hot plate. After digestion samples were left to cool to room temperature and then filtered using 0.45 µm filter paper into volumetric flask and the beakers rinsed with de-ionized water and made up to the final volume. Varian AA240FS AAS (Palo Alto, California, USA) was used to determine the levels of Cd, Mn, Fe, Zn, Cu, Hg, As, Pb and Cr in the sediment samples. The equipment was pre-calibrated appropriately with standard solutions prior to measurement. The concentration of mercury was however determined with the cold vapour atomic absorption method. The analyses were carried out in the instrumental analysis laboratory of the department of Chemistry Ghana Atomic Energy Commission. Replicate analyses were carried out for each determination to ascertain reproducibility. Total trace metals concentrations from analysis by atomic absorption spectrophotometer were calculated in mg/L for water samples and mg/kg for the sediments using values deduced from the calibration curve.

3.3.2 Quality Control/Quality Assurance

Quality assurance measures applied in the laboratory included rigorous contamination control procedures (strict washing and cleaning procedures), monitoring of blank levels of solvents, equipment and other materials, analysis of procedural blanks, monitoring of instrument response, linearity and quality of analysis (APHA, 1998). During analysis, blanks and duplicates were included and re-calibration standards run frequently to check the integrity of the calibration. Analysis of all blank samples showed no inherent bias in the method of analysis for trace elements and water quality parameters of interest. Replicate samples were collected immediately after the routine samples in the field using the same collection methods and equipment. All differences measured in concentrations between replicate pairs were within the precision of the method for all analytes of interest.

3.4. Calculation of Chronic Daily Intake (CDI)

The hazards caused by trace metals can be divided into two groups for calculating numerical estimates of risk: carcinogenic and non-carcinogenic. In the risk assessments, CDI of contaminants in drinking water are estimated from different exposure scenarios through ingestion, inhalation and dermal contact pathways (Chowdhury and Champagne, 2009; USEPA, 1998).

The chronic daily intake (CDI) through ingestion of some trace metals, in water was calculated according to Equation 3.3.

For non-carcinogenic risk

$$\text{Chronic Daily Intake } (CDI_{ing}) \text{ mg/kg day} = \frac{Cw \times IR \times EF \times EP}{BW \times AT} \tag{3.3}$$

C_w = concentration of trace metals in water (mg/L)

EP = exposure period (70 year)

IR= average water ingestion rate (2 L/day)

EF = exposure frequency (365 days/year)

BW = body weight (60 kg)

AT = averaging time (25,550 days)

Table 3.2 Parameters for estimating dermal exposure assessment of trace metals used in this study (USEPA, Wu. et al., 2009; Liang et al., 2011; Naveedullah et al, 2013).

Exposure factors	**unit**	**values**
Concentration of metals in water (CW)	mg/L	-
Water ingestion rate (IR)	L/day	2
Exposure frequency (EF)	days/year	365
Exposure duration (ED)	year	30
Average body weight (BW)	kg	70
Averaging time (AT)	days	25550
Exposed skin area (SA)	cm^2	18,000
Exposure time (ET)	h/day	0.6
Dermal permeability coefficient (Kp)		
Hg	cm/h	0.001
Zn	cm/h	0.0006
Cu	cm/h	0.001
Mn	cm/h	0.001
Fe	cm/h	0.001
Cd	cm/h	0.001
Cr	cm/h	0.002
Pb	cm/h	0.004
As	cm/h	0.001

$$CDI_{dem} \text{ in mg/kg day} = \frac{Cw \times SA \times EF \times ET \times Kp \times ED}{BW \times AT} \qquad (3.4)$$

where; CDI_{derm} = Chronic Daily Intake, SA= Exposed skin area, ET= Exposure time, Kp = Dermal permeability coefficient, ED = Exposure duration, BW = Average body weight, AT= Averaging time, EF = Exposure frequency and CW = Concentration of metals in water

3.4.1 Calculation of Hazard Quotient (HQ_{ing}) and (HQ_{derm})

For non-carcinogenic risk**,** the hazard quotient (HQ) for non-carcinogenic risk was calculated by the following equation,

$$\text{Hazard Quotient } (HQ_{\ ing}) = \frac{CDIing}{RfD} \tag{3.5}$$

$$HQ_{\ derm} = \frac{CDIdem}{RfD} \tag{3.6}$$

where, according to USEPA database the oral toxicity data reference dose values (Rfd) are 8.0×10^{-01}, 1.4×10^{-01}, 5.0×10^{-03}, 3.0×10^{-04}, 3.0×10^{-01}, 1.5×10^{-03}, 3.5×10^{-03}, 5×10^{-04} and 3×10^{-04} mg/kg day for Fe, Mn, Cu, Hg, Zn, Cr, Pb, Cd and As respectively.

3.4.2 Calculation of Hazard Indices (HI)

$$\text{Hazard Index } (HI) = HQ_{\ ing} + HQ_{\ derm} \tag{3.7}$$

For carcinogenic risk (CR) Indices

Carcinogenic risks through ingestion of waters are typically predicted by the following equation

$$CR_{ing} = CDI_{\ ing} \times SF \tag{3.8}$$

CDI_{ing} = chronic daily intake via ingestion (mg/kg day); SF = the carcinogenic slope factor of the contaminant (mg/kg/day).

In order to show the life time carcinogenic risk to the local people, CR_{ing} values were calculated for As due to the available carcinogenic slope. The SF_{ing} value used in this work for As is $1.5\times10^{+0}$ (USEPA, 2010).

Under most regulatory programs, a CR value over 1.00×10^{-06} indicates potential carcinogenic risk (USEPA, 2010). Estimated dose below or at the reference dose is generally considered acceptable and safe level of exposure over life time.

3.5 DETERMINATION OF ACTIVITY CONCENTRATION OF RADIONUCLIDES

3.5.1 Water Sampling and Sample Preparation

Water samples for radionuclides analysis were collected into plastic bottles and acidified on site with a drop of 1M HNO_3 to prevent radionuclides from adhering to the sides of the container. The bottles were filled to the brim without any head space to prevent trapping of CO_2 gas. For activity concentration measurement, the water samples were also transported to the laboratory and prepared into 1 litre Marinelli beakers and appropriately labelled. The samples were not filtered prior to preparation and counting for the presence of $NORM_S$ using HPGe Gamma Spectrometer.

3.5.2 Sediment Sampling and Sample Preparation

Sediments were taken at the middle of the river where samples have not been disturbed. Seventeen sediment samples were collected using a geological auger (Dormer, Australia). The samples were kept in polythene bags and labelled appropriately and taken to the laboratory. At the laboratory, sediments were air dried for a week and oven dried at $110^{o}C$ till a constant dry weight was obtained, the samples were then pulverized and 1 kg of it was measured into a 1 litre marinelli beaker tightly sealed and left for a period of 30 days to attain secular equilibrium prior analysis.

3.5.3 The Gamma Ray Spectrometer

3.5.3.1 Calibrations

Prior to the measurements, the detector and measuring assembly were calibrated for energy and efficiency to enable quantitative analysis of the samples to be performed. The energy and efficiency calibrations were performed using mixed radionuclide calibration standard homogenously distributed in the form of solid water, serial number NW 146 with approximate volume 1000 mL and density 1.0 g cm^{-3} in a 1.0 L Marinelli beaker. The standard was supplied by Deutscher Kalibrierdienst (DKD-3), QSA Global GmBH, Germany and contains radionuclides with known energies and activities (^{241}Am (59.54 keV), ^{109}Cd (88.03 keV), ^{57}Co (122.06 keV), ^{139}Ce (165.86 keV), ^{203}Hg (279.20 keV), ^{113}Sn (391.69 keV), ^{85}Sr (514.01 keV), ^{137}Cs (661.66 keV), ^{60}Co (1173.2 keV and 1332.5 keV) and ^{88}Y (898.04 keV and 1836.1 keV) in a 1000 mL Marinelli beaker was used.

3.5.3.2 Energy Calibration

The energy calibration was performed by matching the principal gamma ray peaks observed in the spectrum of the standard to the channel numbers. The formulae relating the energy and the channel number was expressed as

$$E = A_o + A_1 \bullet CN \tag{3.9}$$

where; E is the energy, CN is the channel number for a given radionuclide, and A_0 and A_1 are calibration constants for a given geometry. A graph of energy against channel number was plotted as shown in Figure 3.2

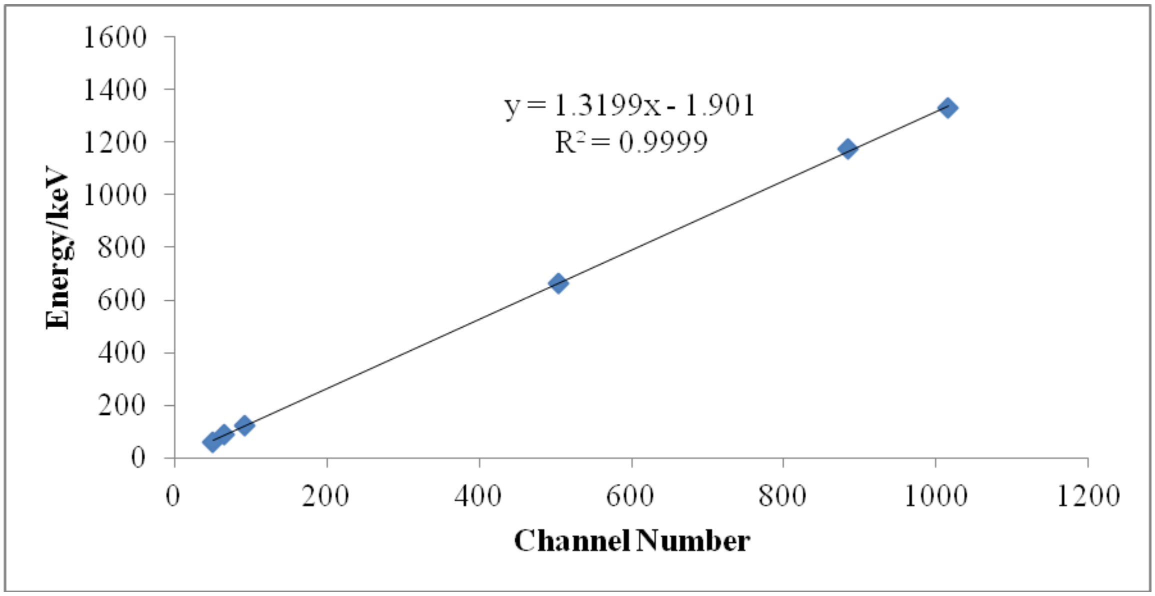


Figure 3.2 Energy calibration for 1000 mL Marinelli geometry

3.5.4 Efficiency Calibration

The efficiency calibration was performed by acquiring a spectrum of the standard until the count rate of total absorption could be calculated with a statistical uncertainly of <1% at a confidence level of 95%. The net count rate was determined at the photo peaks for all the energies to be used for the calculation of the efficiency. The efficiency was then related to the count rate and the activity of the standard by

$$\eta = \frac{N_T - N_B}{P_E . A_{STD} . T_{STD}} \tag{3.10}$$

where; P_E is the gamma ray emission probability for the energy E, η is the efficiency of the detector, N_T is the total count under a photo peak in a peak range, N_B is the background counts, A_{STD} is the activity of the calibration standard for a given radionuclide in Bq at the time of measurement and T_{STD} is the counting time.

The efficiency is related to the energy by the expression.

$$In\ \eta\ (E) = B_o + B_1 InE + B_2\,(InE)^2 \qquad (3.11)$$

where; B_0, B_1, B_2 are calibration constants for a given geometry and the other symbols have the usual meaning given earlier in the passage. The efficiency calibration curve is shown in Fig.3.3.

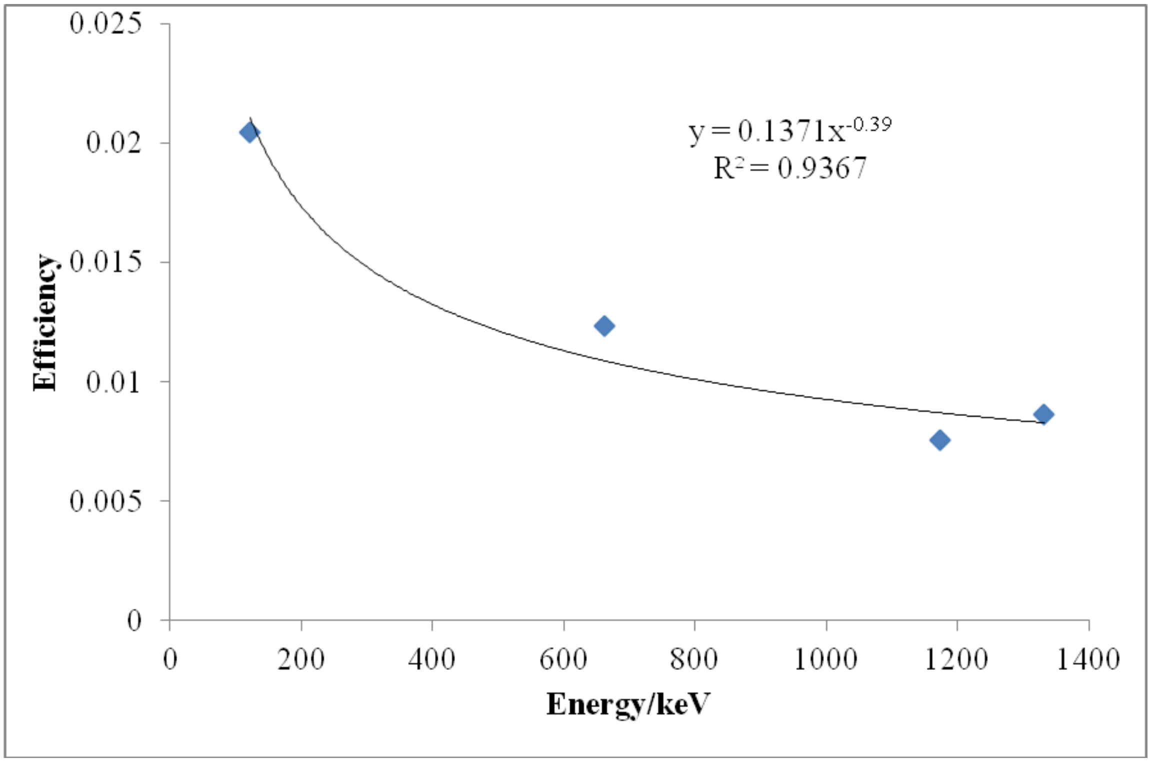


Figure 3.3 Efficiency calibration curve for 1 L geometry

From the efficiency calibration curve the following expression was obtained:

$$In\ \eta = 0.137 - 0.39\ In\ E_\gamma \quad (\text{for } E_\gamma > 100 \text{ keV}) \qquad (3.12)$$

3.5.5 Sample Measurement and Analysis of Spectra

The activity concentrations of the water and sediment samples were determined by a non-destructive analysis using a computerized gamma ray spectrometry system with high purity germanium (HPGe). The relative efficiency of the detector system was 25%, and resolution of 1.8 keV at 1.33MeV of ^{60}Co. The gamma spectrometer is coupled to conventional electronics connected to a multichannel analyzer card (MCA) installed in a desk top computer. A software program called MAESTRO- 32 was used to accumulate and analyse the data manually using spread sheet (Microsoft Excel) to calculate the natural radioactivity concentrations in the samples. The detector is located inside a cylindrical lead shield of 5 cm thickness with internal diameter of 24cm and height of 60cm. The lead shield is lined with various layers of copper, cadmium and Plexiglas, each 3mm thick. A counting time of 36,000 seconds (10hrs) was used to acquire spectral data for each sample**.** The activity concentrations of the uranium-series were determined using γ-ray emissions of ^{214}Pb at 351.9 keV (35.8%) and ^{214}Bi at 609.3 keV (44.8%) for ^{226}Ra, and for the ^{232}Th-series, the emissions of ^{228}Ac at 911 keV (26.6%), ^{212}Pb at 238.6 keV (43.3%) and ^{208}Tl at 583 keV (30.1%) were used. The ^{40}K activity concentration was determined directly from its emission line at 1460.8 keV (10.7%). The γ-ray emission of ^{137}Cs was determined at 661.66 keV.

3.5.6 Calculation of Activity Concentration

The specific activity concentrations (A_{sp}) of ^{238}U, ^{232}Th, and ^{40}K in Bq/L for the water and Bq/kg for sediment samples were determined using the following expression

$$A_{sp} = \frac{N_{sam}}{P_E . \varepsilon . T_c . M} \qquad (3.13)$$

where;

N_{sam} - net counts of the radionuclide in the sample

P_E - gamma ray emission probability (gamma yield)

ε - total counting efficiency of the detector system

T_c - sample counting time

M - mass of sample (kg) or volume (L)

Minimum Detectable Activity

The minimum detectable activity (MDA) of the γ-ray measurements were calculated according to the formula:

$$\text{MDA (Bqkg}^{-1}\text{)} = \frac{\sigma\sqrt{B}}{\varepsilon PTW} \qquad (3.14)$$

where; σ is the statistical coverage factor equal to 1.645 confidence level 95%, B is the background counts for the region of interest of a certain radionuclide, T is the counting time in seconds, P is the gamma yield for any particular element, W is the weight of the empty Marinelli beaker and ε is the efficiency of the detector.

The minimum detectable activity (MDA) derived from background measurements was approximately 0.11 Bq kg^{-1}for ^{226}Ra , 0.10 Bq kg^{-1} for ^{232}Th and 0.15 Bq kg^{-1} for ^{40}K. Concentration values below these detection limits have been taken in this work to be below the minimum detection limit (MDL).

3.6 CALCULATION OF ABSORBED DOSE RATE (D)

Absorbed dose is a measure of the energy deposited in a medium by ionizing radiation per unit mass. The S. I. units of absorbed dose is joules per kilogram and represented by gray (G). Effects of gamma radiation are normally expressed in terms of the absorbed dose rate in air, which originate from radioactive sources in the soil. The activity concentrations in sediments correspond to the total absorbed dose rate in air at 1m above the ground level. The values of the absorbed dose rate (D) due to the river sediment were calculated using the following equation from UNSCEAR (2000).

$$D\ (nGyhr^{-1}) = 0.0417C_K + 0.462C_u + 0.604C_{Th} \tag{3.15}$$

where; D(nGyhr^{-1}) represents the total air absorbed dose rate due to the specific activity concentration C_k, C_u, and C_{Th} (Bqkg^{-1}) for ^{40}K,^{238}U and ^{232}Th respectively at 1m above the ground.

3.6.1 Calculation of Hazard Indices

The external hazard index (H_{ex}) and Internal hazard index (H_{in}) values was calculated using the following equation from Beretka and Mathew, (1985).

$$H_{ex} = \frac{Cu}{370} + \frac{CTh}{259} + \frac{Ck}{4810} \tag{3.16}$$

$$H_{in} = \frac{Cu}{185} + \frac{CTh}{259} + \frac{Ck}{4810} \tag{3.17}$$

where; C_u, C_{Th}, C_k are the activity concentrations of ^{238}U, ^{232}Th and ^{40}K in Bqkg^{-1}, respectively.

3.6.2 Annual Effective Dose

The average annual effective dose was calculated from the absorbed dose rate by applying the dose conversion factor of 0.7 Sv/Gy and an outdoor occupancy factor of 0.2 (UNSCEAR, 2000) .

$$E_{\gamma} = D_r \times 0.2 \times 8760 \times 0.7. \qquad (3.18)$$

Where: E_{γ} is the average annual effective dose and D_r is the absorbed dose rate in air.

For the water samples, the committed effective doses were estimated from the activity concentrations of each individual radionuclide and applying the yearly water consumption rate for adults of 730 L/year. The dose conversion factors of ^{238}U, ^{232}Th and ^{40}K were taken from the IAEA (1996) and using Eq. (3.19) to calculate.

$$H_{ing}(w) = \sum_{j=1}^{3} DCF_{\text{ing}} \left({}^{238}U, {}^{232}Th, {}^{40}K\right) \times A_{sp} \times I_w \qquad (3.19)$$

Where, H_{ing} is annual effective dose of the water. DCF_{ing} is dose conversion factors by ingestion of selected radionuclides in water samples by adult members of the public, living in the study areas were taken to be 4.5×10^{-8} Sv/Bq for ^{238}U, 6.2×10^{-9}Sv/Bq for ^{40}K and 2.3×10^{-7} Sv/Bq for ^{232}Th from IAEA (1996), ICRP (1996), UNSCEAR (2000) and WHO (2004). A_{Sp} is activity concentration of each selected radionuclide in water samples and $\mathbf{I_w}$ is daily water consumption rate considered to be 2 L/day.

3.6.3 The Risk to Population Estimation

The risk to population was then estimated using the recommended risk coefficients in ICRP (1990) report and assumed 70 years lifetime of continuous exposure of population to low level radiation. According to the ICRP methodology:

$$\text{Cancer Risk} = \text{Total Annual Effective Dose (Sv)} \times \text{Cancer Risk Factor} \qquad (3.20)$$

$$\text{Hereditary Effects} = \text{Total Annual Effective Dose (Sv)} \times \text{Hereditary Effect Factor} \qquad (3.21)$$

Cancer Risk Factor = 0.05 Sv^{-1}

Hereditary Effect Factor = 0.01Sv^{-1} (IAEA, 1996; ICRP, 1990).

3.7 Data Analysis

Data analyses were performed with SPSS 22.0 and Microsoft office excel software. In this study, a single factor analysis of variance was performed to determine the significance of variability in water quality variables at the 5% level of significance. Principal component analysis (PCA) and factors analysis (FA) as used in several studies such as (Samsudin et al., 2011; Jayawardana et al., 2012; Attua et. al., 2014;), were applied for data reduction and pattern recognition in order to decipher the variance in the dataset and reveal the sources of component factors. The agglomerative hierarchical cluster analysis (AHCA) was performed based on the normalized data, using Ward's method to minimize the error sum of squares between clusters (Khan, 2008), and Euclidean distance as a measure of similarity between the interdependent variables.

The Kaiser-Meyer-Olkin (KMO) test was performed to examine the suitability of the dataset (Adomako et al., 2011) before a linear discriminant analysis (LDA) was performed using the standardized dataset to assess group validity of water samples. In order to identify the variables that are most important in discriminating among the groups, a step-forward discriminant analysis with cross-validation was carried out using probabilities of F-to-enter-of 0.05 and F-to-remove of 0.10. As in most applications of PCA regarding factors eligible for extraction, the eigen value greater than 1 rule was employed in this study.

CHAPTER FOUR

RESULTS AND DISCUSSION

In this chapter, the results obtained in the study are presented in the form of tables, and figures followed by detailed discussion of the results.

4.1 PHYSICO-CHEMICAL PARAMETERS

The physico-chemical constituent's results of the Birim River are presented in Table 4.1a and 4.1b The results are compared with World Health Organization (WHO) guidelines for drinking water (WHO, 2004), and the international average for fresh water since some communities at upstream of the Birim River use the untreated water for domestic purposes. The concentrations that are above the guideline values are identified and discussed.

Table 4.1.a: Physicochemical parameters for water in November

	Turbidity (NTU)	pH	Salinity ‰	TDS /(mg/L)	Temp. /0C	EC /(μS/m)	(Cl-)/ (mg/L)	(SO42-)/(mg/)	(NO3-)/ (mg/L)	(PO43-)/(mg/L)
Apapam	139.00	7.45	0.00	65.00	25.4o	108.00	11.99	0.50	0.19	0.12
Afiesa	2.00	7.46	0.00	73.00	28.30	120.70	9.99	0.78	0.03	0.13
Adadie-tem	21.00	7.64	0.00	69.00	28.50	114.90	17.99	3.16	0.37	0.22
Kyebi T. college	135.00	7.61	0.00	73.00	29.50	121.50	9.99	2.27	0.26	0.16
Kyebi Deaf School	97.00	7.52	0.00	84.00	31.00	139.10	9.99	2.34	0.22	0.14
Kyebi water T. center	122.00	7.59	0.00	88.00	29.60	146.30	11.99	1.39	0.09	0.12
Asikem	202.00	7.68	0.00	86.00	29.80	143.70	9.99	3.83	0.17	0.17
Bonsu-Accra Road	395.00	7.73	0.00	70.00	29.80	117.10	11.99	1.85	0.13	0.16
Uni. College of Agric & Env.Studis	708.00	7.63	0.00	71.00	30.00	118.50	13.99	2.53	0.25	0.15
Bonsu Bridge	291.00	7.66	0.00	71.00	29.00	118.00	9.99	2.17	1.38	0.17
Min	**2.00**	**7.45**	**0.00**	**65.00**	**25.40**	**108.00**	**9.997**	**0.502**	**0.03**	**0.12**
Max	**708.00**	**7.73**	**0.00**	**88.00**	**31.00**	**146.30**	**17.99**	**3.829**	**1.38**	**0.22**
average	**211.20**		**0.00**	**75.00**	**29.09**	**124.78**	**11.80**	**2.0823**	**0.31**	**0.15**
WHO	**5**	**6.5-8.5**		**500**		**1500**	**250**	**200**	10.00	**< 0.300**

Temp (Temperature) EC (Electrical Conductivity) TDS (Total Dissolved Solids)

Table 4.1.b: Physico-chemical parameters for water in February

PARAMETERS	Turbidity (NTU)	pH	Salinity ‰	TDS /(mg/L)	Temp./ ^{0}C	EC /(μS/m)	(Cl^-)/ (mg/L)	(SO_4^{2-})/(mg/L)	(NO_3^-)/(mg/ L)	(PO_4^{3-})/(mg/L)
Apapam	75.00	7.60	0.00	65.00	25.80	110.00	9.99	12.56	3.49	0.75
Afiesa	15.00	7.60	0.00	72.00	30.00	119.90	17.99	30.26	6.71	0.00
Adadie-tem	26.00	6.90	0.00	69.00	28.70	123.20	15.99	35.34	6.88	0.00
KyebiTtraining college	46.00	8.20	0.00	74.00	29.00	126.50	7.99	33.05	7.64	0.00
Kyebi Deaf School	25.00	8.30	0.00	86.00	31.20	139.10	11.99	10.10	2.97	0.55
Afiesa	26.00	8.00	0.00	90.00	29.90	146.30	13.99	31.57	6.59	0.00
Asikem	25.00	7.00	0.00	88.00	30.50	145.20	13.99	8.295	2.85	0.50
Bonsu - Accra Road	49.00	7.30	0.00	73.00	29.80	120.30	15.99	104.85	3.20	0.60
Bonsu Bridge	27.00	8.30	0.00	74.00	30.20	121.00	17.99	10.26	2.97	0.62
Min	**15.00**	**6.90**	**0.00**	**65.00**	**25.8**	**110.00**	**7.99**	**8.30**	**2.85**	**0.00**
Max	**75.00**	**8.30**	**0.00**	**90**	**31.2**	**146.30**	**17.99**	**104.90**	**7.64**	**0.75**
Average	**34.89**		**0.00**	**76.78**	**29.46**	**127.94**	**13.99**	**30.70**	**4.81**	**0.34**
WHO	**5.00**	**6.5-8.5**		**500**		**1500**	**250**	**200**	**10.00**	**< 0.30**

Temp (Temperature) EC (Electrical Conductivity) TDS (Total Dissolved Solids)

Table 4.2: The linear Correlation Matrix for physicochemical parameters and anions at 95 % in November

		Turbidity	Chloride	Sulphate	Nitrate	Phosphate.	pH	EC	Temp	TDS
Correlation	Turbidity	1.00								
	Chloride	0.105	1.00							
	Sulphate	0.194	0.229	1.00						
	Nitrate	0.155	-0.089	0.172	1.00					
	Phosphate	0.029	**0.556**	**0.766**	0.345	1.00				
	pH	**0.480**	0.201	**0.681**	0.300	**0.637**	1.00			
	EC	-0.184	-0.359	0.337	-0.242	-0.198	0.110	1.00		
	Temperature	0.280	-0.173	**0.578**	-0.004	0.239	**0.511**	**0.623**	1.00	
	TDS	-0.204	-0.368	0.317	-0.241	-0.213	0.081	**0.999**	**0.616**	1.00

Correlation Matrix for February phosp. (phosphate)

		pH	EC	Temp.	TDS	Turbidity	Cl^-	Sulphate	Nitrate
Correlation	pH	1.00							
	EC	**0.544**	1.00						
	Temp.	-0.061	0.250	1.00					
	TDS	**0.557**	**0.973**	0.199	1.00				
	Turbidity	-0.180	**-0.551**	-0.148	**-0.522**	1.00			
	Cl^-	-0.006	-0.076	-0.428	-0.032	**-0.600**	1.00		
	Sulphate	0.004	-0.238	0.043	-0.224	0.200	0.209	1.00	
	Nitrate	0.322	-0.010	0.428	-0.148	-0.209	-0.121	0.083	1.00

4.1.1Physical characteristics

The river water temperature and pH were typical of fresh waters. Temperature of samples in November ranged from 25.4^{o}C to 31^{o}C and in February, it ranges from 25.8^{o}C to 31.1^{o}C. pH varies between 7.45 and 7.73 in November. In February it varies from 6.90 to 8.30 with (Table 4.1a and 4.1.b). The highest (pH 7.73 and 8.30) were recorded in samples from Bonsu-Accra Road and Bonsu Bridge, Kyebi Deaf School in November and February respectively. The surface water was generally neutral to slightly alkali. The pH values recorded were within the recommended limit of 6.5- 8.5 for drinking water (WHO, 2003). The observed variation in pH may be attributed to the differences in the geology and chemistry of the river water. That is, it might be due the presence of dissolved carbonates and bicarbonates present in the water, which are known to affect pH of almost all surface water (Chapman, 1992). pH generally plays an important role in metal bioavailability, toxicity and leaching capability (DWAF, 1998). Therefore, such pH values in the river could increase the amount of dissolved metals in the water.

The turbidity of the sampled river water ranged from 2 NTU to 708 NTU with a mean of 211.2 NTU in November and 15 NTU to 75 NTU with mean value of 34.9 NTU February. About 94.7% of the sampled water studied recorded values that have far exceeded the WHO guideline value of 5 NTU (WHO, 2004). The highest value (708 NTU) was recorded in November at University College of Agric & Env. Studies. The lowers turbidity value was recorded at Afiesa with value of 2 NTU.

Most parts the river at Adadientem and Kibi portion where panning is taking place release a lot of tailing directly in to the river. This mostly causes the river to be clouded by suspended sediments as indicated by the brown colour of the river. The relatively higher turbidity values could also be attributed to additional land runoff and soil erosion from other mining areas in the municipality. Poor farm practices along the river also produce large quantities of topsoil ending up in the river. Elevated turbid water may impact micro-biological contamination (Fianko, 2010).

The results also indicate that surface water from the Birim River in East Akim Municipality was soft and fresh since the total dissolved solids (TDS) of 100.% of the water samples did not exceed 500 mg/L (Kattan, 1995). The TDS recorded was between 65 and 88 mg/L in with an average of 75 mg/L November. TDS in February varies from

65 to 90 mg/L with a mean of 76.8 mg/L, while EC measured was124.78 µS/cm, with the lowest value of 108.00 µS/cm at Apapam and the highest of 146.30 µS/cm at Kyebi Water Treatment Center in November. In February, the mean EC was measured to be 127.94 µS/cm in the range 110.00-146.30 µS/cm, the highest at Afiesa. The conductivity of most freshwaters ranged from 10 to 1000 µScm^{-1} (Chapman, 1992). The electrical conductivity (EC) and TDS of the Birim river water gradually increased from Apapam at upstream and remained fairly constant at Kibi where a lot of mining activities are taking place. EC values at Afiesa, Asikem, Kyebi Deaf School and Kyebi Training College, along the Birim River was a bit higher than others and this may be attributed to the fact that many particles may be introduced into the river water and dissolved into solution because of frequent panning at these sampling points. Electrical conductivity is related to the concentration of TDS. This was evidence from the Correlation Matrix where EC correlated strongly with TDS with $r = 0.999$ and $r = 0.973$ in November and February respectively (Table 4.2). With these low conductivity values, it is not surprising that the TDS, which is an index of the amount of dissolved solids in water, which also determine the degree of salinity, would be low. The salinity for the river water at all the sampling points was below the detection limit in both November and February in Birim River at Kibi traditional area. Overall, the physical characteristic registered in this study compared favourably with that of other rivers in Ghana (Ansa-Asare and Asante, 2005).

4.2. The Major Anions

Chloride (Cl^-)

Examination of the chloride concentration in the water revealed considerable variations. The chloride values in the river water ranged from 7.998 to 17.994 mg/L (Table 4.1a). The mean values for November and February are 11.796 mg/L and 13.995 mg/L. All the measured values in this study are lower than the USEPA guideline permissible level of 250 mg/L. The sources of chloride in river runoff from are domestic activities and waste. The decomposition of organic matter may be a contributing factor. The highest value of chloride (17.994 mg/L) observed was at Adadietem in November and this is an area that is very close to houses. The high concentration at this point might be due to runoff from homes. In February, the chloride concentration increase steadily downstream at Bonsu. The Birimian formation is made up of quartzite, tuff schists, phyllite and argillite. These are likely to be the sources of the chloride as well. There is a very strong and significant positive correlation between chloride, phosphate (r =0.556) in November chloride and turbidity in February (Table 4.2).

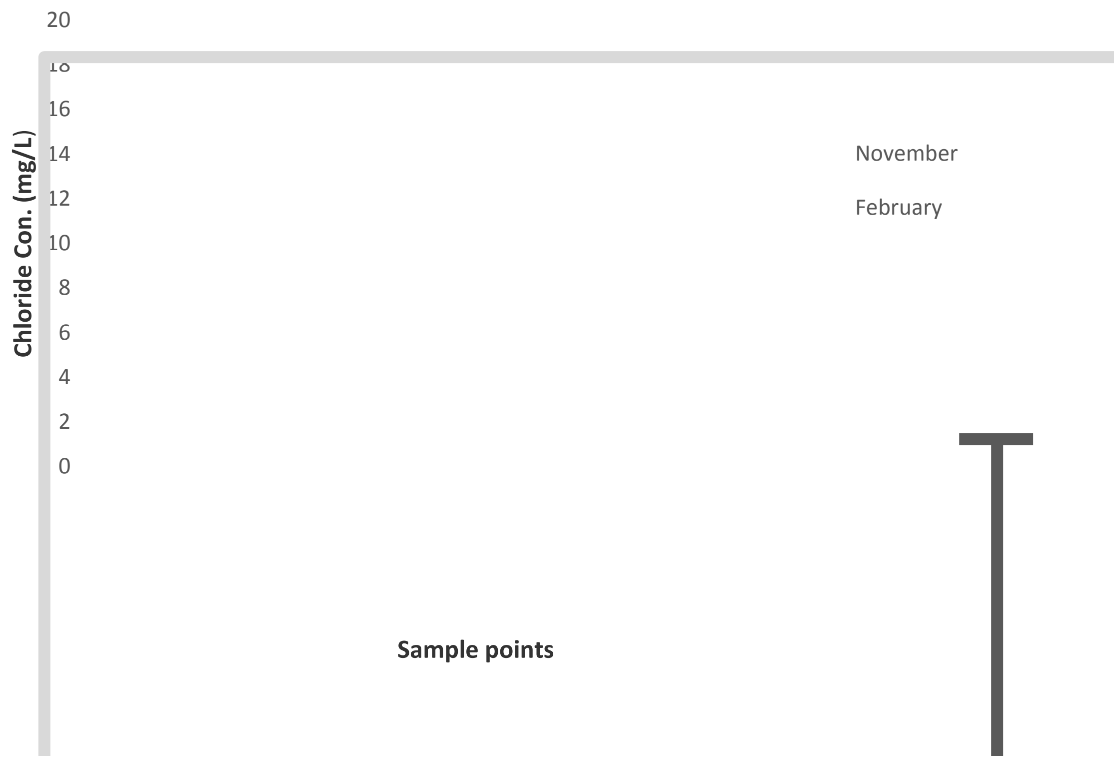


Fig. 4.1 Comparison of Cl^- concentration in water sample for November and February

4.2.1 Nitrate, Phosphorus and Sulphate

Nitrate and phosphorus occur in water as NO_3-N and PO_4-P respectively and both are useful for plant growth (Chapman, 1992). However, excess phosphorus concentrations of 0.015 mg/L and nitrogen of about 0.3 mg/L are known to promote algal bloom (Klein, 1962; WHO 2003). In this study, levels of NO_3-N and PO_4-P in water samples ranged between 0.033-1.378 mg/L and 0.116-0.217 mg/L respectively in November whilst in February NO_3^- and PO_4^{3-} range from 2.848-7.643 mg/L and 0.00-0.75 mg/L respectively. The mean values for NO_3^- and PO_4^{3-} in November are 0.308 mg/L and 0.153 mg/L and in February NO_3^- and PO_4^{3-} have mean values of 4.81 and 0.603 mg/L respectively. The highest value for NO_3^- at Kyebi Training College is 7.643 mg/L in February and in November, the highest value recorded was 1.378 mg/L at Bonsu Bridge (BB-8).

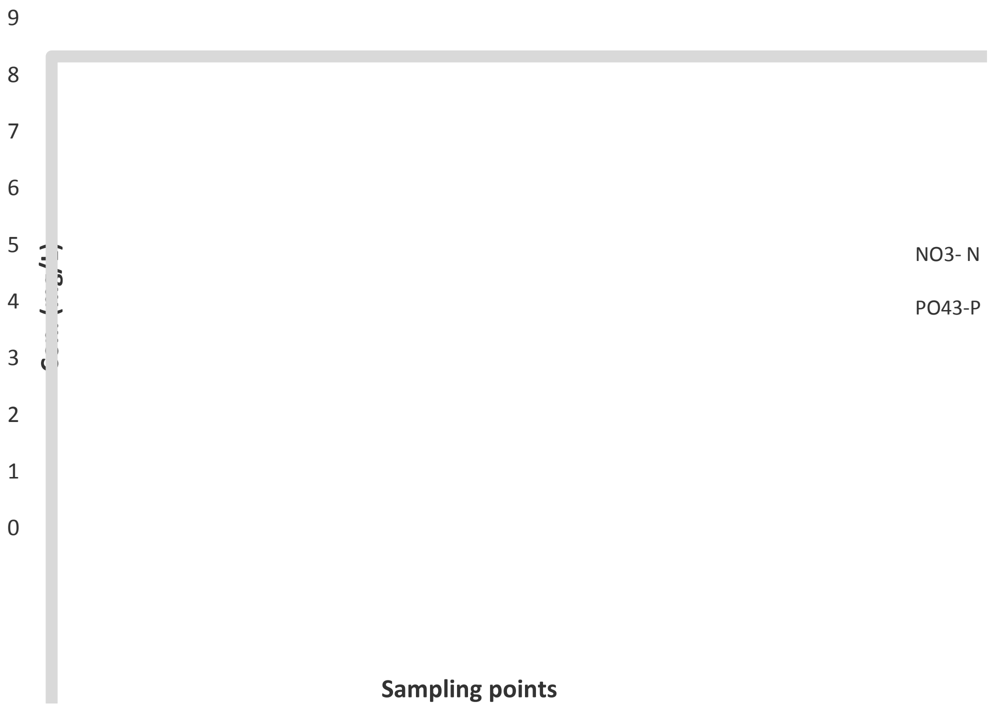


Fig. 4.2a Levels of NO$_3^-$-N and PO$_4$-P for water samples in February

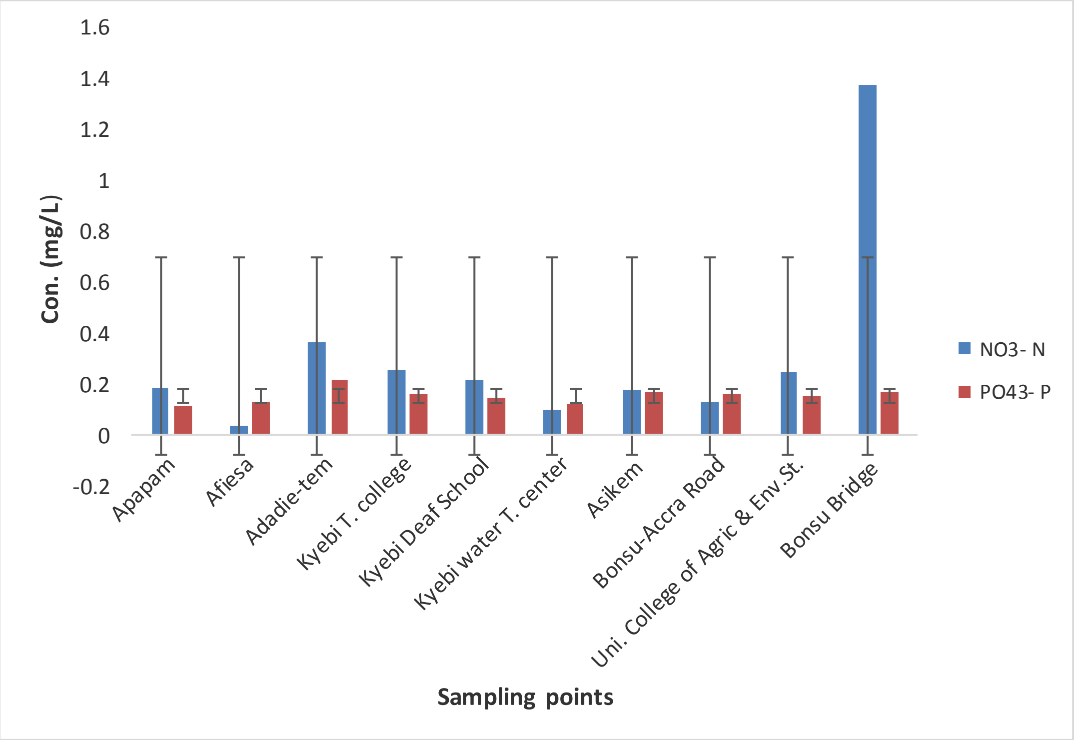


Fig. 4.2b Levels of NO$_3^-$-N and PO$_4$-P for water samples in November

The nitrogen levels could be attributed to agricultural and other anthropogenic activities. Thus, heavy precipitation and denitrification rate influencing the nitrate content in the water and this might be responsible to the high level in February (Fig.4.2a). Furthermore, the temporal variability in nitrogen levels in the study could be largely explained by variability in water discharge, resulting from the discharge of untreated effluent from municipal, domestic, agricultural and small scale agro-industries.

Moreover, most nitrogen found in surface water came from land drainage, sewage and dilution of waste water effluents coming from homes and food processing discharges (Fianko, 2010). Compared to the permissible limit in drinking water of 10.0 mg/L for nitrate, all values recorded in the water samples from the sample points are below the permissible limit.

A natural range of 0.005-0.02 mg/L for phosphorus (Chapman, 1992), compared with the range obtained in this study shows that phosphorus is around or just above the range (0.116-0.217 mg/L and 0.00-0.75 mg/L) in both November and February. Though no aquatic weeds were found in sampled river, the range of phosphorus nutrient in the river makes it vulnerable for evasion of aquatic plants (Asante et al., 2008). The main natural source of phosphate in many water samples is due to the weathering of phosphorus-bearing rocks and the breakdown of organic matter (Branom and Sarkar, 2004). Domestic wastewaters (particularly those containing detergents), industrial effluents and fertilizer run-off contribute to elevated levels in surface waters. However, phosphate minerals often do not last long in readily available form and tend to quickly combine with other minerals in the water. At high pH (alkaline water), phosphorus is often present as calcium phosphates.

The minimum sulphate concentration recorded was 0.502 mg/L at Apapam while a maximum of 3.829 mg/L was observed at Asikem in November. February recorded a minimum of 10.262 mg/L at sampling point Bonsu Bridge (BB-8A14) and a maximum of 104.852 mg/L at Bonsu-Accra Road ($B\text{-}A_R\text{-}10B$) (Fig.4.3). The mean sulphate concentration in February was 30.70 mg/L and that of November was 2.08 mg/L. The observed levels in this study are far lower than the WHO guideline value of 200 mg/L. There is a very strong and significant positive correlation between sulphate and temperature, sulphate and phosphate, and sulphate and pH ($r = 0.578$, $r = 0.766$ and $r = 0.681$) respectively (Table 4.2).

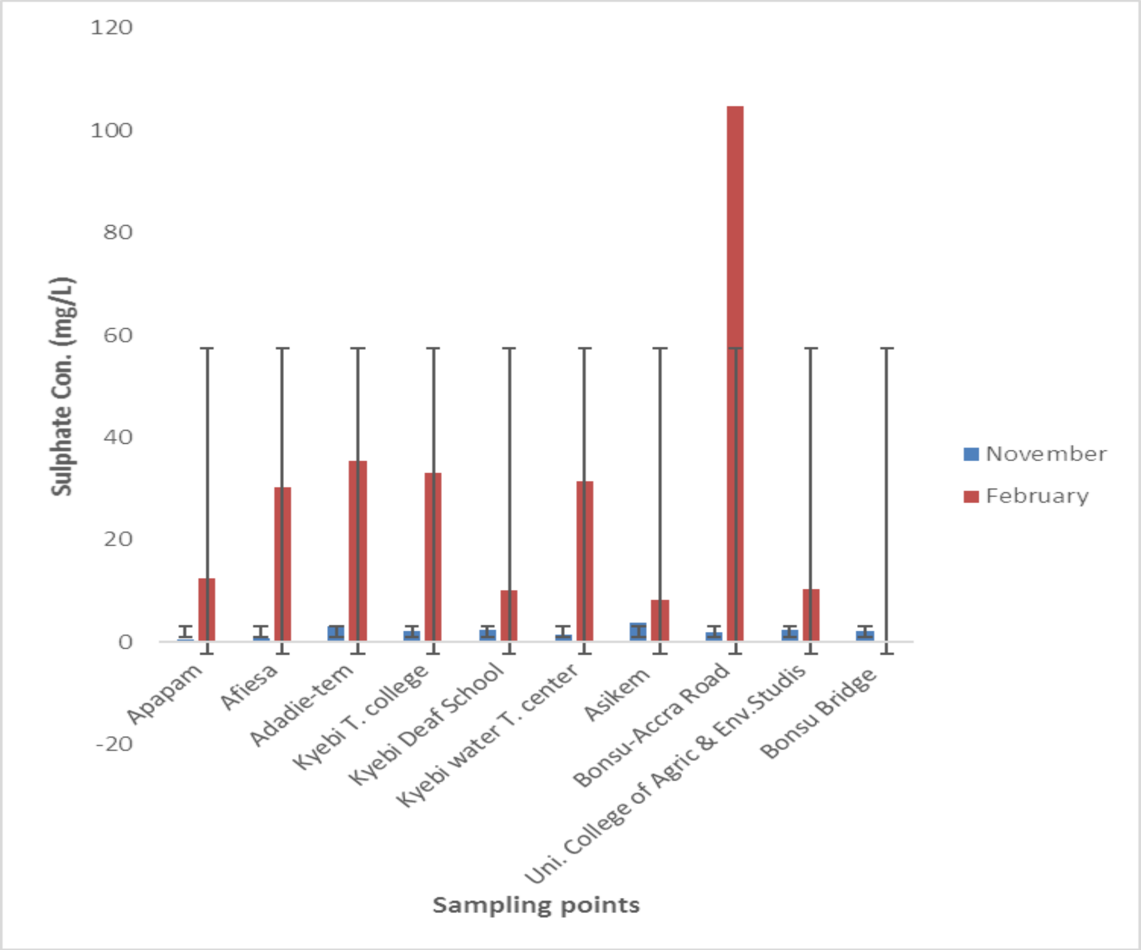


Fig. 4.3 Levels of SO_4^{2-} for water samples in November and February

4.2.2 Principal Component/Factor Analysis for Physicochemical Parameters (Source identification)

A Kaiser-Meyer-Olkin (KMO) test produced a significant of 0.569 suggesting the basis of the factor analysis and interpretation. At an eigenvalue greater than 1.0, PCA extracted three significant components for November and four for February. Components which were of eigenvalues <1.0 were considered insignificant and therefore omitted from further analysis.

Table 4.3. Loadings of experimental variables on principal components for November and February

Variables	Component for November				variables	Component for February			
	1	2	3			1	2	3	4
Phosphate	**0.934**	0.000	0.096		pH	**0.881**	0.088	-0.015	**0.466**
Chloride	**0.802**	0.358	-0.251		EC	**0.874**	-0.094	0.066	-0.257
sulphate	**0.708**	-0.530	0.149		Temperature	-0.006	0.135	**0.858**	-0.223
EC	-0.120	**-0.948**	-0.247		TDS	**0.897**	-0.085	-0.052	-0.258
TDS	-0.135	**-0.942**	-0.261		Turbidity	-0.240	**0.859**	-0.267	0.234
Temperature	0.130	**-0.818**	0.270		Chloride	-0.134	**-0.910**	-0.266	0.217
Turbidity	-0.098	0.026	**0.815**		Sulphate	-0.075	-0.027	0.047	**0.776**
Nitrate	0.019	0.173	**0.650**		Nitrate	-0.018	-0.099	**0.827**	0.375
PH	**0.499**	-0.329	**0.547**		Eigenvalue	2.863	1.717	1.363	1.040
Eigenvalue	3.166	2.770	1.221		% Total variance	35.784	21.465	17.041	13.003
% Total variance	35.179	30.779	13.567		Cumulative % variance	35.784	57.249	74.290	87.293
Cumulative % variance	35.179	65.958	79.526						

Table 4.3 indicates that nearly 79.526% of total variance in water is explained by the first three in November and 87.293% total variance in water is explained by the first four in February Principal Component (PCs). Classification of factor loading is thus ‘strong’, ‘moderate’ and ‘weak’, corresponding to absolute loading values of > 0.75, 0.75-0.50 and 0.50-0.30, respectively (Liu et al, 2003). Corresponding, variable loadings, eigenvalues and variances of the components extracted are presented in Table 4.3for both November and February, and strong loading values have been highlighted.

For November, Principal Component (PC1), which explained 35.179% of the total variance, had strong positive loadings on Phosphate (0.934) and chloride (0.802) and moderate loading on Sulphate (0.708) and had weak loadings on pH (0.499). This factor indicates that during this period, the surface runoff originated from the fields containing high load of solids from waste disposal source (Shrestha and Kazama, 2007). The presence of dissolved carbonates from the mining tailings and bicarbonates present in the water (Chapman, 1992).

Principal Component (PC2), which explained 30.779% of the total variance, had strong negative loadings on EC (-0.948), TDS (-0.942), and temperature (-0.818). This component is associated with electrical conductivity of water contributed by inorganic ions in solution and facilitated by temperature. In addition, this component represents non-point pollution from soluble rock salts alongside the transport of sediment into rivers through surface run-off.

Principal Component (PC3), which explained 13.567% of total variance, had strong positive loading of turbidity (0.815), and moderate loading on nitrate (0.650) and pH (0.547). This component also represents pollution from surface run-off of tailings as well as soluble rocks alongside the transport of sediment into rivers.

In February, Principal Component 1 (PC1) contains strong positive loading of TDS (0.897), pH (0.881) and EC (0.874) explaining 35.784% of the total variance. This is also associated with electrical conductivity of water contributed by inorganic ions in solution and pollution from surface run-off of tailings as well as soluble rocks alongside the transport of sediment into rivers.

PC2 showed a strong positive loading on turbidity (0.859) and strong negative loadings on Chloride (-0.910) explaining 21.465% of the total variance. Factor 2 is interpreted to represent the contamination of surface water from runoff originated from the fields containing high load of solids from waste disposal source and the communities (Shrestha

Kazama, 2007) in addition to, pollution from surface run-off of tailings as well as soluble rocks alongside the transport of sediment into rivers.

PC3 in February contains moderate loadings of temperature (0.858) and nitrate (0.827) and explains an additional 17.041% of total variance. Moreover, PC4 loaded strongly on sulphate (0.776) weakly on pH (0.466) and nitrate (0.375). The likely contaminants are organic solids and wastes, especially from domestic, commercial and agricultural origins, which reach the river by surface run-off in February. The respective communalities show that all the variables were described to an acceptable level.

4.3 Trace Element Concentration in the Water

The levels of trace metals in water in the study area were generally low with majority of the below detection limit. The elemental occurrence in November was Fe>Mn>As>Zn>Hg. Cd, Pb, Cu and Cr ware not detected. In February, the occurrence was in the order Fe>Mn>As>Zn>Cu>Cr>Hg. Cd and Pb ware also not detected. The concentration of Fe in November ranged from 0.41 mg/L to 3.700 mg/L with a mean value of 1.27 mg/L. In February, the range of concentration was 0.13 to 0.88 mg/L with a mean of 0.49 mg/L (Appendix I and II). The highest level of Fe concentration was, detected at Kyebi Training College at Kibi. This might be due to intense mining activities that were going on in the area and the water velocity was slow at the time of sampling, suggesting serious exposure of the rocks to water due to the mining activities and further showing that iron concentration increases with exposure of mafic minerals. The concentration of Fe in all the sampling points at the study area in both November and February are slightly higher than the WHO guideline level of 0.3 mg/L except Adadientem and Asikem of values 0.14 mg/L and 0.13 mg/L respectively in February.

Fe and Mn in the study area are associated with the Birimian rock system, containing high amounts of iron and manganese. Therefore mining in the area will enhance weathering and leaching of Fe and Mn into the Birim River.

Manganese concentrations varied from 0.025 mg/L to 0.140 mg/L with a mean of 0.071 mg/L and 0.025 mg/L to 0.400 mg/L with a mean of 0.150 mg/L in November and February respectively, (Appendixes I and II). A comparison of Mn concentration in water samples for November and February from the study area with the WHO permissible guideline values revealed that, Kyebi Training College, Bonsu-Accra Road, Kyebi Deaf School, Kyebi water Treatment Centre and Asikem recorded values of dissolved Mn that were around the recommended value of 0.100 mg/L (Appendix I and II). Concentrations from other sampling points were lower than the permissible guideline value. Mean concentration of Mn in both periods are also found to be around WHO value (Fig.4.3) Manganese can be found in rocks such as granites, schists and sandstones but in minute quantities. Manganese ores in commercial quantities exists as oxides and hydroxides as pyrolusite (MnO_2), psilomelane, manganite (MnO_2H), braunite (Mn_2O_3) and hausmannite (Mn_3O_4). Minute occurrences include carbonate and silicate ores (Kesse, 1985).

The high concentration of Fe and Mn in the study area is from the enhance weathering of the Birimian rock system by small-scale miners. Other sources of iron in the study area include the occasional discharge of mining waste, acid mine drainage which may increase iron and Mn levels in the surface water. High levels of Fe and Mn recorded in water samples in the study area, pose significant health hazard to inhabitants. Exposure to high levels of iron in drinking water can result in iron storage disease where the liver becomes cirrhotic (Foulkes, 1986).

A one-sample t-test that was, performed clearly shows a significant level between the WHO value and the mean Fe concentration at a 95% confident level for both November and February analysis (Appendix XVIII).

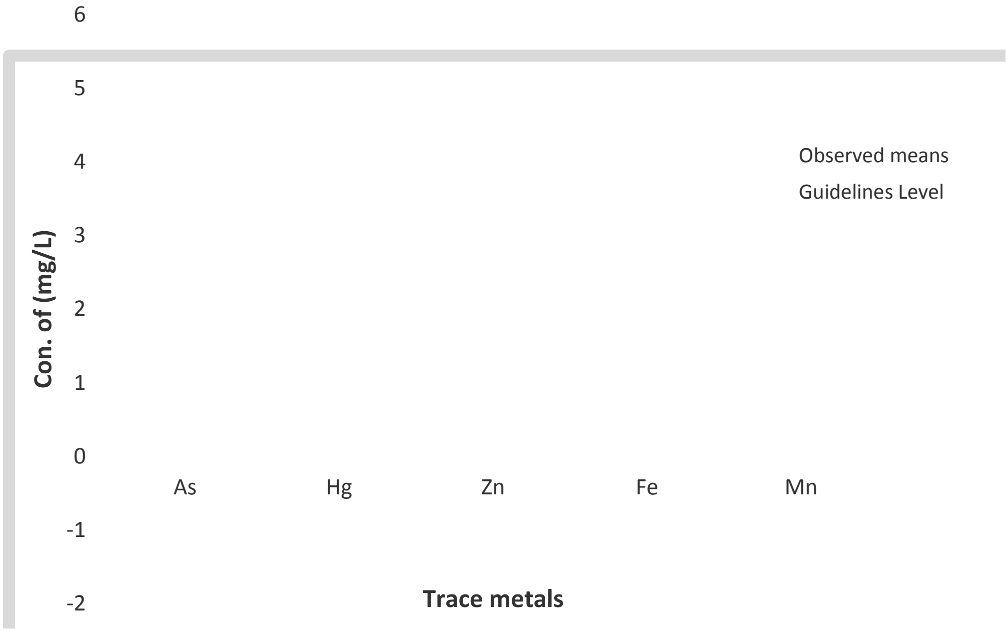


Fig. 4.4a Comparison of observed mean concentrations of trace metals in water samples in November in the study area with the WHO guideline levels.

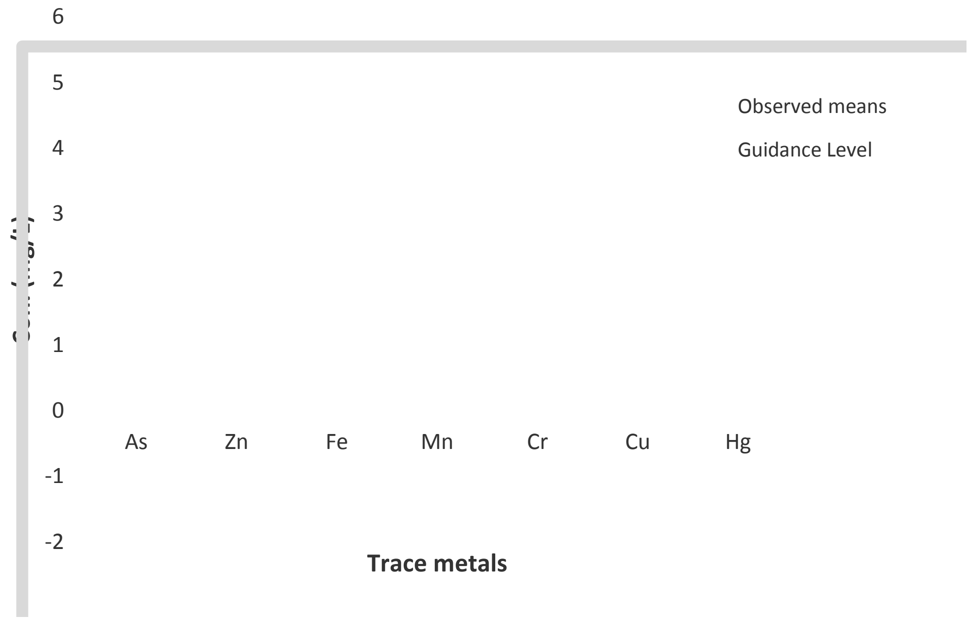


Fig. 4.4b comparison of observed mean concentrations of trace metals in water samples in February in the study area with the WHO guideline levels.

Concentrations of As and Hg in water samples collected in both November and February were low. The mean arsenic concentration of the river water in November is 0.0387 mg/L, ranges from 0.0200 to 0.0580 mg/L. In February, the mean concentration is 0.0318 mg/L in the rage 0.0138 to 0.0475 mg/L. The highest As concentration (0.0580 mg/L and 0.0475 mg/L) in November and February was detected at Kyebi Training College (Appendix I and II). This might be due to intense mining activities at this point. The concentration of As in all the sampling points at the study area both in November and February are slightly higher than the WHO guideline level of 0.01 mg/L (Appendix I and II). Fig 4.4a and 4.4b also show a comparison of mean concentration with the WHO level.

Arsenic is found in the deep bedrock materials as well as the shallow glacial materials and alongside the gold ores such as arsenopyrites (FeAsS) (Coakley, 1996). Arsenic is usually present in the environment in inorganic form. The inorganic arsenic easily dissolves and enters underground and surface waters. The presence of arsenic in the environment may be attributed to one of the following sources: residual arsenic from farmer pesticidal use, smelter emission from ores of gold such as arsenopyrites from the sulphur treatment plant. Thus, during ore crushing and panning by the small scale gold miners, arsenopyrite like Arsenic is released into the environment and it finally finds its way into sediments and surface water (Asamoah, 2012). The high levels of arsenic concentrations measured in River Birim at Kibi Traditional area in this study can therefore suggest that symptoms associated with arsenic intoxication would be higher for residents in the study area through the use of the water.

A one-sample t-test that was performed shows a significant level between the WHO value and the mean As concentration at a 95% confident level for both November and February analysis.

Analysis of mercury content of the water samples at the various sampling points along River Birim in November and February revealed that, some sampling points such as BB-8, Kyebi Deaf School, Bonsu-Accra Road and Kyebi water Treatment Centre recorded values of 0.0025, 0.005, 0.0038, 0.005 mg/L respectively in November. Bonsu Bridge, Kyebi Deaf School, Bonsu-Accra Road and Kyebi water Treatment Centre recorded values of 0.0025, 0.0025, 0.0013 and 0.0025 mg/L in February. The values recorded at these sampling points might be because of huge mining tailings that were observed been discharge into the river and settling at downstream at Bonsu-Accra Road and Bonsu Bridge. The mean value of mercury in November and February are 0.00125 mg/L with the highest value of 0.0050 mg/L and 0.00098 mg/L with the highest value of 0.0025 mg/L respectively in the river**.** The mean value in November is slightly above WHO recommended levels and that of February is around the recommended level of 0.001 mg/L Fig. 4.3a and 4.3b.

Mercury is introduced into the environment during gold processing. Mercury is used to recover gold from ore minerals by the process of amalgamation hence the levels at those points may be attributed to the processing of gold which is a widespread activity along the river. A one-sample t-test was performed to confirm the significant level of the WHO value with the mean Hg value at a 95% confident level. The test shows that we cannot confidently say that the mean Hg concentration in the River is above the WHO level but rather around WHO level. Mercury is a very poisonous metal hence its presence in the Birim River even in minute quantities poses serious health risk to users of water from the river.

Concentration of Zn in Birim River was measured and was found to be generally low. In November the levels recorded varied from 0.0025 to 0.0110 mg/L while in February, it ranged from 0.0100 to 0.0388 mg/L. The highest value (0.0388 mg/L) was recorded at Kyebi Training College in February (Appendix I and II). This is where most of the mining activities are taking place and the water is flowing slowly. However, all the recorded concentrations were lower than the WHO guideline level of 5 mg/L (Fig. 4.3). Zinc is one of the most common elements in the earth's crust and its ore sphalerite (ZnS) usually occurs in association with lead (Kesse, 1985). Most of the zinc in water bodies, such as lakes or rivers, settles on the bottom. However, small amounts may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases. Most of the zinc in soil is bound to the soil and does not dissolve in water.

Chromium and Cu were recorded only in February and the mean concentration of Cr is 0.0038 mg/L. The highest Cr concentration (0.0088 mg/L) was recorded at Kyebi Deaf School (Appendix I and II). Very low levels of copper were observed in samples from Afiesa, Apapam, Kyebi Training College, Kyebi Deaf School and Bunso Bridge. The mean value of copper recorded was 0.0072 mg/L, which is far lower than the WHO guidelines limit of 2 mg/L for drinking water (Appendix I and II). Lead and Cd were below detection limit during the two periods of sampling and so pose no health problem. However, the low concentration of these metals notwithstanding continuous consumption of water containing them over a period of time could result in ailments since they are often cumulative.

Analysis of variance was carried out on the trace metals concentrations measured in the water sample to ascertain whether differences exist among the trace elements. The mean difference is significant at a 95% confidence level (Appendix: XIV). Post Hoc Tests shows that there is no significant different among As, Cd, Cu, Mn, Pb, Cr, Hg and Zn. However, there is a significant difference between Fe, and the other trace metals (Appendix: XIV).

4.3.1 Trace Element Concentration in Sediment

Table 4.4 shows mean concentrations of nine trace elements (Cd, Pb, Fe, Zn, Mn, Cu, Cr, Hg and As) assessed in sediment from River Birim at twelve sampling points in Kibi Municipality (Apapam, Afiesa, Adadie-tem, Kyebi, Asikem, Bonsu) sited in artisanal mining areas along the river and Bunso downstream.

Table 4.4 The mean of November and February concentration of trace metal in sediment (mg/kg)

Sample Code	Mean Hg	Mean As	Mean Cd	Mean Pb	Mean Zn	Mean Cu	Mean Fe	Mean Mn	Mean Cr
Apapam	0.17	10.90	<0.002	1.23	5.43	4.60	834.29	160.75	20.48
Afiesa	0.13	12.45	<0.002	0.88	5.48	4.50	829.72	140.85	6.70
Afiesa3A	0.15	12.65	<0.002	0.35	7.40	4.10	837.81	256.35	14.40
Adadietem	0.40	10.30	<0.002	0.40	4.85	2.15	828.25	79.90	25.65
Adadietem A	0.20	10.35	<0.002	0.80	7.40	8.15	844.54	106.65	14.55
Kyebi T. college	0.78	16.25	<0.002	0.60	7.25	6.73	834.16	167.05	5.75
Kyebi Deaf School	0.55	12.90	<0.002	1.95	2.55	3.00	821.62	184.95	6.05
Kyebi Deaf School A	0.15	12.85	<0.002	0.90	18.67	6.30	826.64	161.30	9.40
Asikem	0.10	8.40	<0.002	1.35	3.60	4.48	831.53	85.45	10.18
Bonsu-Accra Road	0.58	12.55	<0.002	1.05	5.25	5.88	823.12	181.28	8.30
Bonsu Bridge	0.40	11.65	<0.002	0.75	3.80	5.15	832.72	209.20	6.35
Bonsu Bridge A14	0.15	11.65	<0.002	2.40	6.80	7.05	831.28	238.35	9.10

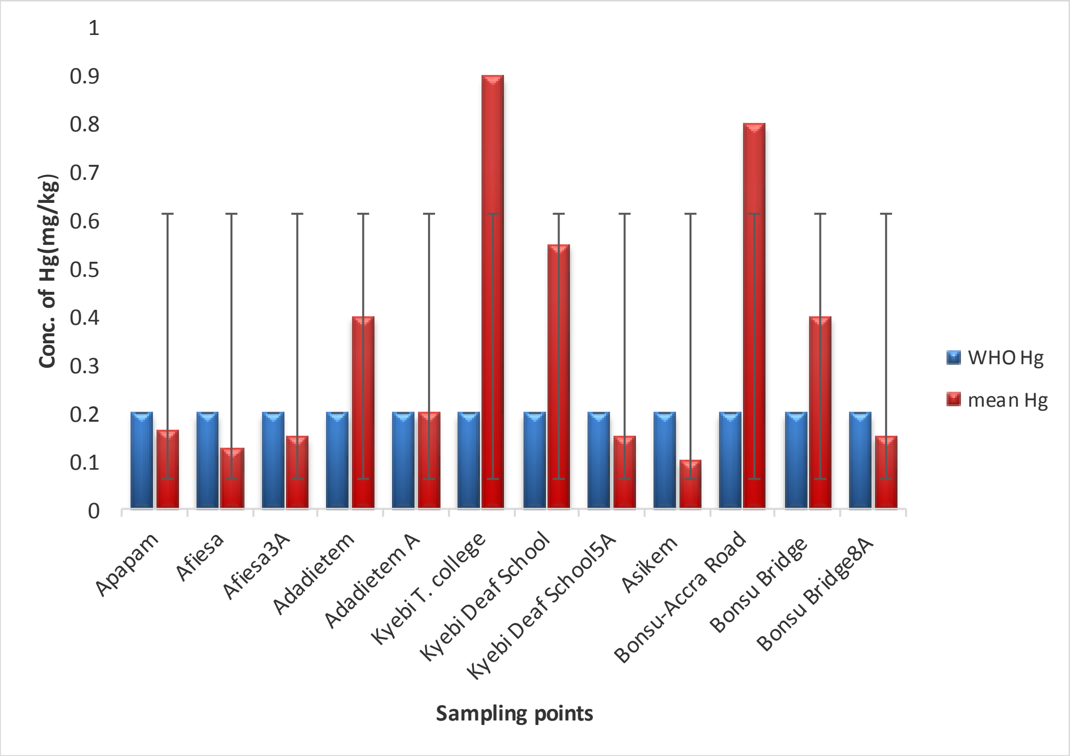


Figure 4.5 Mean Hg level in sediments at the sampling points with WHO level.

Significant levels of mercury (Hg) were determined in sediment samples from Adadietem, Kyebi Training College, Kyebi Deaf School, Bonsu-Accra Road and Bonsu Bridge. The mean concentrations registered (0.4, 0.775, 0.55, 0.575 and 0.4 in mg/ kg respectively) were found to be above the maximum acceptable level (Fig.4.5). The high levels of Hg concentration in these areas might be said to come from human influence such artisanal gold mining activities (Carrico, 1985). The mining activities are predominant in these areas of study. Mercury compounds are used in gold mining operations to extract gold from ores through amalgamation (Carrico, 1985).

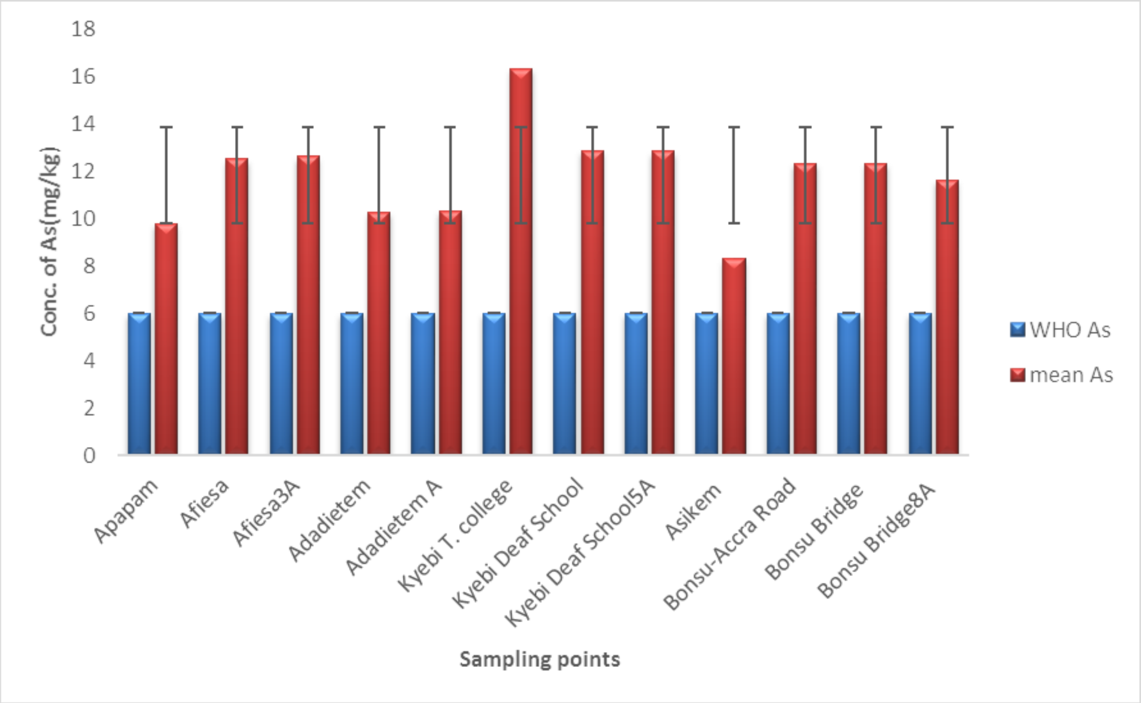


Figure 4.6 Mean As level in sediment at the sampling points with WHO level

Arsenic may get into water through dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition (IPCS, 1981; Hindmarsh & McCurdy, 1986). Arsenic introduced into water adhere to particulate matter in the water which later sinks to become part of the sediment. The mean As concentration in the sediments was found to be above the maximum acceptable level (6.00 mg/kg) in the river sediments (WHO, 2004) at all the sampling points in the study area (Fig 4.6). Irrespective of whether mining has taken place or not, arsenic bearing ores can be oxidized to produce As in water and settle in the sediment. However, mining activities increases the surface area of rocks and exposes rocks to rapid weathering therefore increasing the levels of As in the sediment. This might be probable cause of the high level of As in the river sediment at the study area. Arsenic has not been demonstrated to be essential in humans (IPCS, 2001). The high level of concentration of As in the sediment might make the river unsafe for aquatic organisms and human use.

The mean sediment concentrations of Cd, Pb, Cr, Fe, Zn, Mn, and Cu in the artisanal mining areas of Kibi municipality in River Birim were all found to be generally low, that is, below the maximum acceptable levels of 0.60, 31.0, 26.0, 20,000, 120.0, 460.0 and 16.0 mg/kg respectively for water sediment Table 4.4. And also in Appendix III and IV.

The frequent use of Hg by artisanal gold miners to extract the gold from the ore (Donkor et al., 2006), and the occurrence of As, as an impurity in gold ore (Eisler, 2004) might have led to the slightly high contamination of the As and Hg in the sediments.

4.3.2 Human Health Risk Assessment

A comprehensive risk assessment was performed in an attempt to quantify the carcinogenic and non-carcinogenic risks, associated with ingestion and dermal contact of the river contaminated with trace metals.

In November, the levels of Chronic Daily Intake (CDI_{ing} and CDI_{derm}) from the river were seen in the order: Fe>Mn>As>Zn>Hg and Fe>Mn>As>Zn>Hg respectively while in February, the order was Fe>Mn>As>Zn>Cu>Cr>Hg and Fe>Mn>As>Zn>Cu>Cr>Hg respectively (Table 4.5).

Table 4.5 Summary of health risk assessment for metals in water samples from the study area through ingestion and dermal absorption pathways, during November and February.

Element	RfD_{ing}/(mg/kg day)	RfD_{derm}/(mg/kg) day	CDI_{ing}	CDI_{derm}	HQ_{ing}	HQ_{derm}	HI	CR_{ing}
Hg	3.0×10^{-4}	2.40×10^{-4}	4.17×10^{-5}	8.27×10^{-5}	0.1389	0.3444	0.4833	NA
As	3×10^{-04}	2.85×10^{-04}	0.0013	0.0026	4.3000	8.9787	13.2787	0.0019
Cd	5×10^{-04}	2.5×10^{-05}	0.0000	0.0000	0.0000	0.0000	0.0000	NA
Pb	3.5×10^{-03}	4.2×10^{-05}	0.0000	0.0000	0.0000	0.0000	0.0000	NA
Zn	3.0×10^{-01}	6.0×10^{-02}	0.0002	0.0002	0.0007	0.0041	0.0048	NA
Cu	5.0×10^{-03}	8.0×10^{-03}	0.0000	0.0000	0.0000	0.0000	0.0000	NA
Fe	8.0×10^{-01}	1.40×10^{-01}	0.0424	0.0841	0.5297	0.6004	1.1300	NA
Mn	1.4×10^{-01}	9.60×10^{-04}	0.0024	0.0047	0.0169	4.9041	4.9210	NA
Cr	1.5×10^{-03}	7.5×10^{-05}	0.0000	0.0000	0.0000	0.0000	0.0000	NA

February

	RfD_{ing}/ (mg/kg day)	RfD_{derm}/(mg/kg) day	CD_{Iing}	CDI_{derm}	HQ_{ing}	HQ_{derm}	HI	CR_{ing}
Hg	3.0×10^{-04}	2.40×10^{-04}	3.26×10^{-05}	6.47×10^{-05}	0.1086	0.2694	0.3780	NA
As	3×10^{-04}	2.85×10^{-04}	0.0011	0.0021	3.5358	7.3830	10.9188	0.0016
Cd	5×10^{-04}	2.5×10^{-05}	0.0000	0.0000	0.0000	0.0000	0.0000	NA
Pb	3.5×10^{-03}	4.2×10^{-05}	0.0000	0.0000	0.0000	0.0000	0.0000	NA
Zn	3.0×10^{-01}	6.0×10^{-02}	0.0007	0.0009	0.0024	0.0147	0.0170	NA
Cu	5.0×10^{-03}	8.0×10^{-03}	0.0002	0.0005	0.0482	0.0598	0.1080	NA
Fe	8.0×10^{-01}	1.40×10^{-01}	0.0162	0.0321	0.0202	0.2291	0.2494	NA
Mn	1.4×10^{-01}	9.60×10^{-04}	0.0049	0.0097	0.0349	10.083	10.1178	NA
Cr	1.5×10^{-03}	7.5×10^{-05}	0.0001	0.0005	0.0839	6.6612	6.7452	NA

NA: not applicable

The result indicated that Fe, Mn, As, Zn and Hg were the main contributors for ingestion and dermal exposures to the human environment in the river. Iron in the study area is associated with the Birimian rock system. The Birimian rock system contains high amounts of iron and other toxic chemicals such as manganese.

In this study Hazard Quotient (HQ_{ing}) for Cd, Pb, Fe, Zn, Cu, and Hg metals during November and February were less than 1 (Table 4.5), which indicates that these metals could pose no or minimal minimum hazard to local residents (Naveedullah et al., 2013). However, As in November and February have mean level greater than 1 hence it could have harmful effects on human health when the water is ingested (Moore, 1984). The HQ_{derm} values for November and February were also found to be less than 1 for Cd, Pb, Fe, Zn, Cu, and Hg, which means that the dermal adsorption of the metals in the river may have little or no health threat. While As, Mn and Cr mean values in November and February were more than 1 indicating that the dermal adsorption of As, Mn and Cr metals in the river may have harmful effect or health threat on the people in the environment.

The Hazard Index (HI) estimated in the study in November were for As, Fe, and Mn. These were 8.9787, 1.1301, and 4.9210, respectively (Table 4.5) but in February HI was calculated for As, Mn, and Cr which yielded values of 10.9188, 10.1178 and 6.7452 respectively. All Hazard Index (HI) values were greater than 1 which is an indication that As, Fe, Mn and Cr are the main pollutants that threatens human health in River Birim at Kibi Municipality. HI values for Hg, Zn, Cu registered in November and February were less than 1, which clearly indicates that there is no cumulative potential adverse health risks in the water samples via direct ingestion or dermal contact to the inhabitants of the area with respect to Hg, Zn Cu, Cd and Pb.

For carcinogenic risk (CR_{ing}), As was found to have values of 0.00194 in November and 0.0016 in February. In most cases, the results slightly exceeded the target remedial goal of 1.0×10^{-06}. This indicated that the carcinogenic risk for As was found to be higher to the inhabitants via ingestion route of water from the river. These metals are mostly found in many types of rocks and soil and are introduce into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition (IPCS, 1981; Hindmarsh & McCurdy, 1986)

4.4 URANIUM, THORIUM AND POTASSIUM IN THE WATER

The mean activity concentrations of ^{238}U, ^{232}Th and ^{40}K in the water samples are as shown in Tables 4.6a and 4.6b. The mean values for ^{238}U, ^{232}Th and ^{40}K in November are 1.741 Bq/L in a range of 0.821-2.176 Bq/L, 2.406 Bq/L in a range 1.439-3.638 Bq/L and 63.694 Bq/L in a range of 56.382-75.321 Bq/L respectively.^{238}U, ^{232}Th and ^{40}K in the water samples in February were observed to have mean values of 1.526 Bq/L in a range of0.832-2.314 Bq/L, 2.300 Bq/L in a range of 1.623-3.176 Bq/L and 61.609 Bq/L in a range of 48.112-71.523 Bq/L respectively.

Table 4.6a. Average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in water in the study area in November as well as calculated absorbed dose rate, Cancer Risk, Hereditary Effects, Hazard Index and the estimated annual effective doses.

	Activity concentration (Bq/L)			Absorbed dose rate	Hazard Indices		Annual effective dose		
Sampling points	**U-238**	**Th-232**	**K-40**	**(nGy h^{-1})**	**H_{ex}**	**H_{in}**	**(mSv)**	**Cancer Risk**	**Hereditary Effects**
Apapam	1.79	2.79	63.68	5.172	0.0289	0.0337	0.00082	4.08×10^{-05}	8.16×10^{-06}
Afiesa	1.87	1.93	62.13	4.621	0.0254	0.0305	0.00067	3.34×10^{-05}	6.67×10^{-06}
Adadie-tem	1.43	2.84	62.02	4.964	0.0277	0.0316	0.00081	4.02×10^{-05}	$8.0\times10^{-06}5$
Kyebi T. college	2.12	2.05	75.32	5.363	0.0293	0.0351	0.00076	3.78×10^{-05}	7.56×10^{-06}
Kyebi Deaf School	1.19	1.48	61.08	3.987	0.0216	0.0248	0.00056	2.82×10^{-05}	5.63×10^{-06}
Kyebi water T. center	1.83	2.75	69.38	5.399	0.0299	0.0349	0.00082	4.18×10^{-05}	8.36×10^{-06}
Asikem	2.18	2.85	64.90	5.433	0.0304	0.0363	0.00084	4.22×10^{-05}	8.44×10^{-06}
Bonsu-Accra Road	2.49	3.64	61.30	5.904	0.0335	0.0403	0.00097	4.85×10^{-05}	9.7×10^{-06}
Uni. Coll. of Agric & Env. Studis	0.82	2.29	56.38	4.113	0.0228	0.0250	0.00067	3.33×10^{-05}	6.66×10^{-06}
BonsuBridge	1.69	1.44	60.75	4.181	0.0227	0.0273	0.00057	2.86×10^{-05}	5.72×10^{-06}
Mean	**1.74**	**2.41**	**63.69**	**4.914**	**0.0272**	**0.0319**	**0.00075**	**3.75×10^{-05}**	**7.49×10^{-06}**
Range	**0.82-2.18**	**1.44-3.64**	**56.38-75.32**	**3.987-5.904**	**0.0216-0.0335**	**0.0248-0.040**	**0.00056-0.00097**	**2.82×10^{-05}-4.85×10^{-05}**	**5.63×10^{-06}-9.70×10^{-06}**
Guidelines levels	**10.0**	**1.0**	**N/A**				**0.1**		

Table 4.6b Average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in water in the study area in February as well as calculated absorbed dose rate, Cancer Risk, Hereditary Effects, Hazard Index and the estimated annual effective doses.

Sampling points	Activity concentration (Bq/L)			Absorbed dose rate (nGy h^{-1})	Hazard Indices		Annual effective dose (mSv)	Cancer Risk	Hereditary Effects
	U-238	Th-232	K-40		H_{ex}	H_{in}			
Apapam	0.92	1.62	68.44	4.260	0.0230	0.0255	0.00061	3.06×10^{-05}	6.13×10^{-06}
Afiesa	2.04	2.44	48.11	4.424	0.0249	0.0305	0.00069	3.47×10^{-05}	6.95×10^{-06}
Adadietem	1.44	2.42	54.51	4.404	0.0246	0.0285	0.00070	3.51×10^{-05}	7.01×10^{-06}
Kyebi T. college	2.14	2.09	74.32	5.355	0.0293	0.0351	0.00076	3.79×10^{-05}	7.58×10^{-06}
Kyebi Deaf School	1.14	2.16	63.54	4.482	0.0246	0.0277	0.00069	3.44×10^{-05}	6.88×10^{-06}
Afiesa	1.26	3.11	58.54	4.905	0.0276	0.0310	0.00083	4.14×10^{-05}	8.29×10^{-06}
Asikem	0.83	3.18	71.52	5.285	0.0294	0.0316	0.00088	4.42×10^{-05}	8.84×10^{-06}
Bonsu-Accra Road	2.32	1.78	52.76	4.346	0.0241	0.0304	0.00061	3.07×10^{-05}	6.14×10^{-06}
Bonsu Bridge	1.64	1.88	62.71	4.511	0.0248	0.0292	0.00065	3.27×10^{-05}	6.54×10^{-06}
Mean	**1.53**	**2.3001**	**61.609**	**4.663**	**0.0258**	**0.0299**	**0.00072**	**3.58×10^{-05}**	**7.15×10^{-06}**
Range	**0.83-2.32**	**1.623-3.18**	**48.11-71.52**	**4.260-5.355**	**0.0230-0.0294**	**0.025-0.0351**	**0.0006-0.00088**	**3.06×10^{-05} 4.40×10^{-05}**	**6.13×10^{-06}- 8.84×10^{-06}**
Guidelines levels	**10.0**	**1.0**	**N/A**				**0.1**		

The mean values of ^{238}U, ^{232}Th and ^{40}K as shown in Table 4.6a and 4.6b were generally low. In both November and February, the activity concentration of ^{238}U is lower than WHO guidance level of 10.0 Bq/L and ^{232}Th is higher than WHO guidance level of 1.0 Bq/L at all the sampling points. The calculated average activity concentration of ^{232}Thwas higher than as compared to WHO guidance level. This could be due to the relatively low solubility of ^{232}Th as compared to ^{238}U. Moreover, this may also come from the fact that, the water samples were not filtered prior to analysis. Thorium is normally transported with particulate matter and become deposited in water bodies (Adukpo, et al., 2014).

4.4.1 Analysis of variance for NORM

The idea is to see if there exist differences in mean for the variance substances.

Table 4.7 Post-hoc test: Comparison of the means of the concentrations of uranium, Thorium and Potassium in the water sample

Multiple Comparisons

(I) Chemical	(J) Chemical	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
U	Th	-0.6656000	1.3754478	0.879	-4.075910	2.744710
	K	-61.9538000*	1.3754478	0.000	-65.364110	-58.54349
Th	U	0.6656000	1.3754478	0.879	-2.744710	4.075910
	K	-61.2882000*	1.3754478	0.000	-64.698510	-57.87789
K	U	61.9538000*	1.3754478	0.000	58.543490	65.364110
	Th	61.2882000*	1.3754478	0.000	57.877890	64.698510

*. The mean difference is insignificant at p> 0.05 and significant at P<0.05 level (2-tailed)

From Table 4.7, it is clear that the mean concentrations of ^{238}U and ^{40}K and ^{232}Th and ^{40}K are significantly different whereas ^{238}U and ^{232}Th are not. This implies that ^{238}U and ^{232}Th may exist together in varying concentrations in the river water samples.

4.4.2 Radiological Risk Assessment in the Water Sample

The mean annual effective dose from the water was calculated to be 0.000749 mSv in a range of 0.00056-0.00097 mSv in November (Table 4.6a). In February, annual effective dose in Table 4.6b shows a range of 0.000613-0.000884 mSv with average values of 0.000715 mSv in water sample.

The WHO guideline value of annual effective dose in water has been set at 0.10 mSv/year (WHO, 2004). The mean annual effective dose in this study is far lower than the recommended annual effective dose in drinking water. Generally, the mean annual effective doses of the two periods in the various communities had values lower than the WHO recommended value of 0.10 mSv/year.

The calculated values of the external hazard index (H_{ex}) and internal hazard index (H_{in}), for water samples studied were below the safe limit of one (Table 4.6a and 4.6b). The results show that the H_{ex} and H_{in} for water samples are below the limit of unity, meaning that the radiation dose is below, the permissible limit of 0.1 mSv/year recommended by WHO (2004) in both two periods of sampling (Table 4.6a and 4.6b). The values of the radiation hazard parameters from this current study are not high compared to the world averages and the recommended values and therefore unlikely to cause radiological health risks to the people living in the study area using the water.

The radiological cancer risks for population as well as hereditary effects were also evaluated by using the ICRP risk assessment methodology (ICRP, 1991; 2007).

The results of the evaluated cancer risk to adult per year in the river water ranged from 2.82×10^{-05}-4.85×10^{-05} with average value of 3.75×10^{-05} in November and 3.06×10^{-05}-4.42×10^{-05} with average value of 3.58×10^{-05} in February. This means that in terms of cancer risk to adult in November and February, approximately 4 out of 100,000 may suffer from some form of cancer risk.

Hereditary effect range from 5.63×10^{-06}-9.7×10^{-06} with a mean of 7.49×10^{-06} in November, whiles in February it ranged from 6.13×10^{-06}-8.84×10^{-06} with mean value of7.15×10^{-06}. This indicates that, approximately 7 out of 1,000,000 may surfer hereditary effects in Kibi municipality on the use of the river water.

The negligible cancer risk value recommended by USEPA is in the range of 1.0×10^{-06} to1.0×10^{-04}. That is one person out of 1000,000 or 10,000 suffering from some form of cancer fatality is considering trivial. Comparing, the estimated results of the lifetime cancer risk in the present study with the acceptable risk factor, it can be concluded that, all estimated results of the lifetime risk among adult member of the Kibi municipality are within the range of acceptable risk values recommended by USEPA.

4.5 URANIUM, THORIUM AND POTASSIUM IN THE WATER SEDIMENT

Table 4.8a and 4.8b shows the activity concentrations of ^{238}U, ^{232}Th and ^{40}K in the sediment samples as well as the calculated absorbed dose rate, Cancer Risk, Hereditary Effects, Hazard Index and the estimated annual effective doses. The mean value of the activity concentrations of ^{238}U in November is 22.92 Bq/kg and that in February is 23.74 Bq/kg in the range of 6.55-95.05 Bq/kg and 6.25 -92.05 Bq/kg respectively. For ^{232}Th in November and February the mean activity concentration are 24.69 Bq/kg and 25.128 Bq/kg respectively, in range of 15.90-33.54 Bq/kg and 16.00-32.24 Bq/kg. In November and February, mean activity concentration for ^{40}K is 246.13 Bq/kg and 236.21 Bq/kg in range of 140.97-355.96 Bq/kg and 146.52-352.87 Bq/kg. All the mean values found in this study are lower than the worldwide average activity concentrations for ^{238}U, ^{232}Th and ^{40}K in soil samples from various studies around the world of values 35, 30 and 400 Bq/kg respectively, (UNSCEAR, 2000). The highest values for ^{238}U, ^{232}Th and ^{40}K were measured in sediment samples taken from Bonsu-Accra Road, Asikem and Bonsu Bridge downstream (Tables 4.8a and 4.8b). This is due to settling of more runoff tailing at downstream.

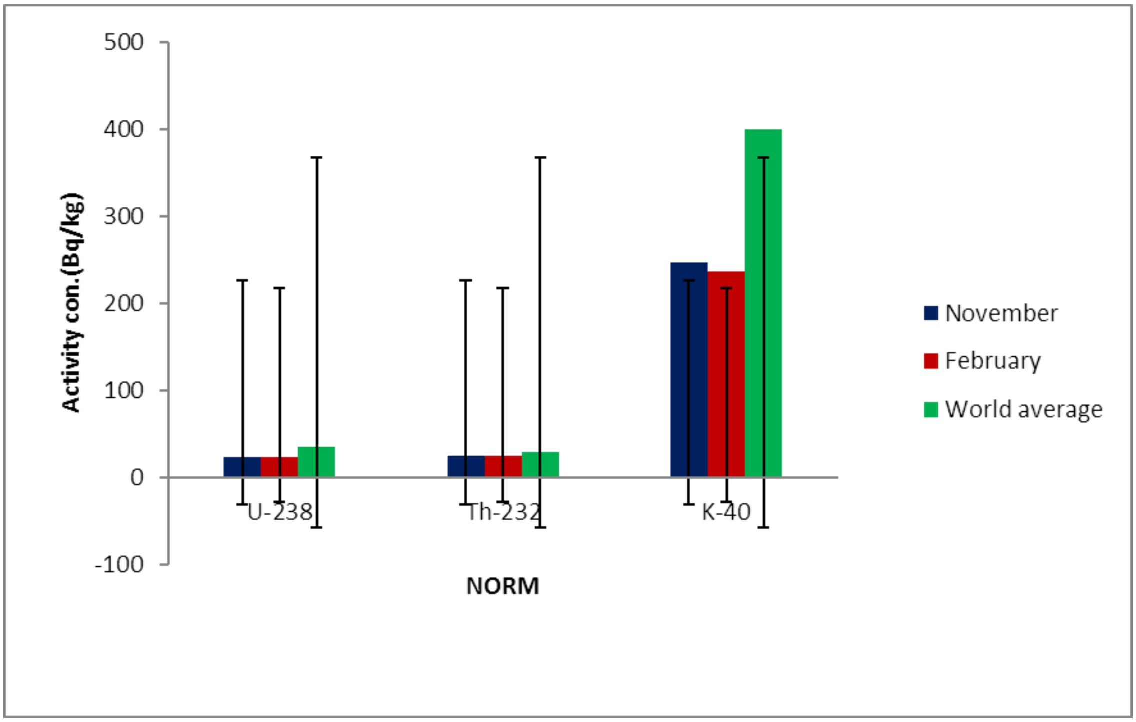


Figure 4.7 Comparison of the mean activity concentration of ^{238}U, ^{232}Th and ^{40}K in sediments in November and February in this study with the world average values

Figure 4.7 is a comparison of the mean activity concentration of ^{238}U, ^{232}Th and ^{40}K in sediments in November and February in this study with the world mean values. The values compared well with published world average values and were all below the world average values. The activity concentrations of the river sediment at all the sampling points in the study area in November and February were also compared and the results shown in Figure 4.8a and 4.8b

Table 4.8a Average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in sediments and their toxicity indices in November.

Sampling points	**U-238 (Bqkg^{-1})**	**Th-232 (Bqkg^{-1})**	**K-40 (Bqkg^{-1})**	**Absorbed dose rate (nGyh^{-1})**	**Annual effective dose (mSv)**	**Cancer Risk**	**Hereditary Effects**	**Hazard Index**	
								H_{ex}	**H_{in}**
Apapam	8.30	18.85	140.97	21. 10	0.03	1.29×10^{-06}	2.59×10^{-07}	0.125	0.147
Afiesa	12.35	26.04	146.52	27.54	0.04	1.69×10^{-06}	3.38×10^{-07}	0.164	0.198
Adadietem	18.89	29.24	308.38	39.25	0.05	1.87×10^{-06}	3.75×10^{-07}	0.228	0.279
Kyebi T. college	20.27	21.25	236.80	32.07	0.04	1.97×10^{-06}	3.94×10^{-07}	0.186	0.241
Kyebi Deaf School	6.55	22.64	235.45	26.52	0.03	1.63×10^{-06}	3.26×10^{-07}	0.154	0.172
Asikem	9.97	33.54	340.05	39.04	0.05	2.40×10^{-06}	4.79×10^{-07}	0.227	0.254
Bonsu-Accra Road	95.05	15.91	204.91	62.07	0.08	3.80×10^{-06}	7.62×10^{-07}	0.361	0.618
Bonsu Bridge	11.99	30.07	355.96	38.54	0.05	2.37×10^{-06}	4.73×10^{-07}	0.223	0.255
Mean	**22.92**	**24.69**	**246.129**	**35.77**	**0.04**	**2.13×10^{-06}**	**4.26×10^{-07}**	**0.209**	**0.270**
Range	**6.55-95.05**	**15.91-33.54**	**140.97-355.96**	**21.10-62.07**	**0.03-0.08**	**1.29×10^{-06}-3.80×10^{-06}**	**2.59×10^{-07}-7.62×10^{-07}**	**0.125-0.361**	**0.147-0.618**
World average	**35.0**	**30.0**	**400.0**						

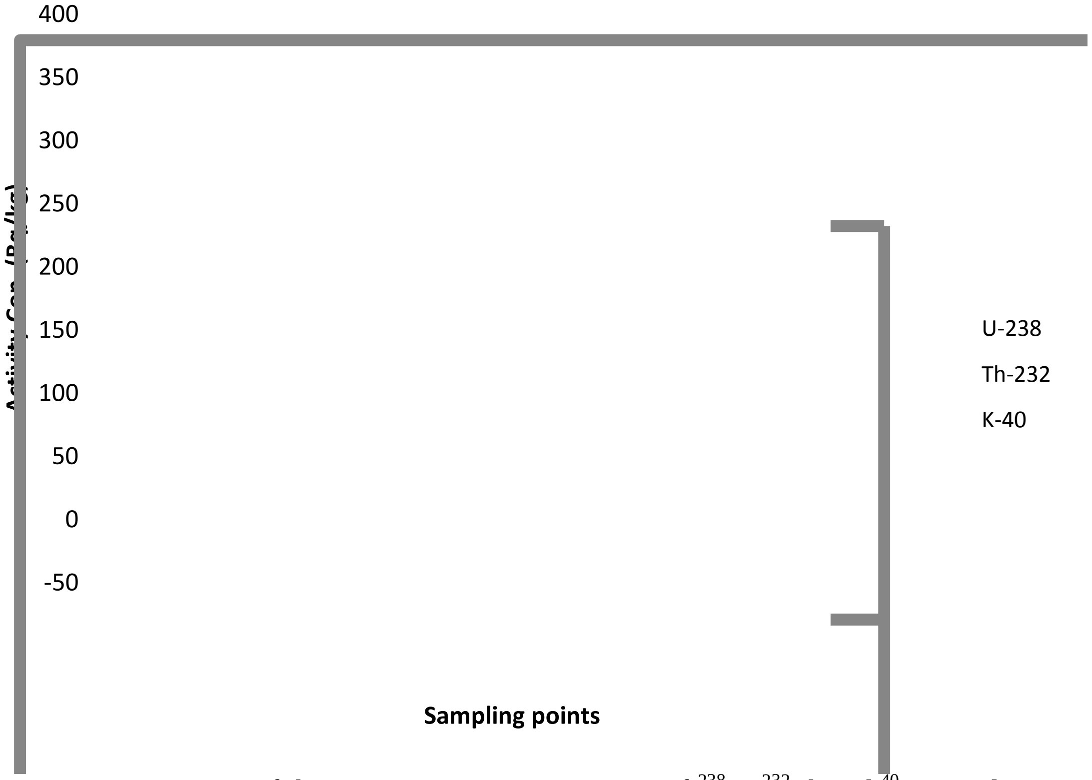


Figure 4.8a Comparison of the mean activity concentration of ^{238}U, ^{232}Th and ^{40}K in sediment at all the sampling points in the study area in November

Table 4.8b Average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in sediments and their hazard indices in February

Sampling points	**U-238 (Bqkg^{-1})**	**Th-232 (Bqkg^{-1})**	**K-40 (Bqkg^{-1})**	**Absorbed dose rate (nGyh^{-1})**	**Annual effective dose (mSv)**	**Cancer Risk**	**Hereditary Effects**	**Hazard Index**	
								H_{ex}	**H_{in}**
Apapam	13.39	29.75	169.99	31.25	0.04	1.92×10^{-06}	3.84×10^{-07}	0.19	0.22
Afiesa	21.35	26.04	146.52	31.70	0.04	1.94×10^{-06}	3.89×10^{-07}	0.19	0.25
Adadietem	18.96	29.13	298.28	38.79	0.05	2.39×10^{-06}	4.76×10^{-07}	0.23	0.28
Kyebi T. college	19.26	19.24	231.70	30.18	0.04	1.85×10^{-06}	3.72×10^{-07}	0.17	0.23
Kyebi Deaf School	6.25	19.64	226.41	24.20	0.03	1.48×10^{-06}	2.97×10^{-07}	0.14	0.16
Afiesa	20.55	26.04	155.32	31.70	0.04	1.94×10^{-06}	3.89×10^{-07}	0.19	0.24
Asikem	8.97	32.24	340.05	37.80	0.05	2.32×10^{-06}	4.64×10^{-07}	0.22	0.24
Bonsu-Accra Road	92.05	16.01	204.71	60.73	0.07	3.72×10^{-06}	7.45×10^{-07}	0.35	0.60
Bonsu Bridge	12.90	28.06	352.87	37.63	0.05	2.32×10^{-06}	4.62×10^{-07}	0.22	0.252
Mean	**23.74**	**25.128**	**236.21**	**36.00**	**0.04**	**2.25×10^{-06}**	**4.41×10^{-07}**	**0.21**	**0.28**
Range	**6.25-92.05**	**16.00-32.24**	**146.52-352.87**	**24.20-30.18**	**0.03-0.07**	**1.48×10^{-06}-3.72×10^{-06}**	**2.97×10^{-07}-7.45×10^{-07}**	**0.14-0.35**	**0.16-0.60**
World average	**35.0**	**30.0**	**400.0**						

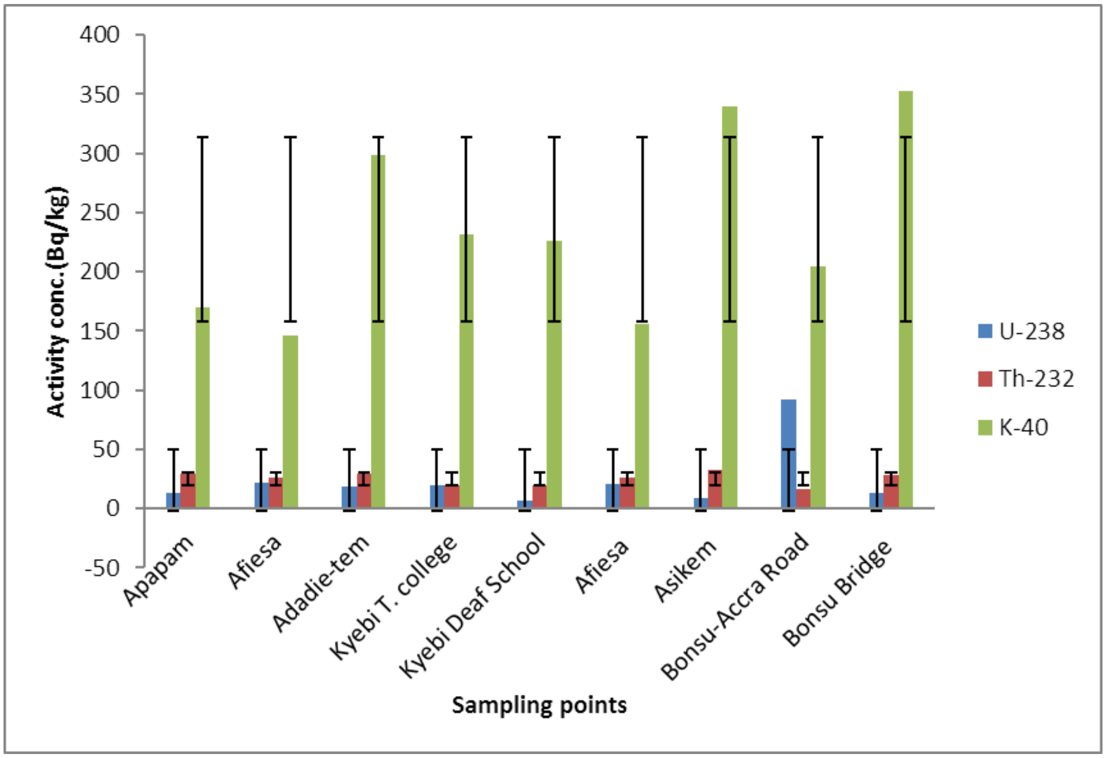


Figure 4.8b Comparison of the mean activity concentrations of ^{238}U, ^{232}Th and ^{40}K in sediment at all the sampling points in the study area in February.

4.5.1 Radiological Risk Assessment in Water Sediment

In the case of the absorbed dose rate and annual effective dose for November in Table 4.8a, it can be observed that the absorbed dose rate varied in a range of 21.09-62.07 nGy h^{-1} with an average of 35.767 nGy h^{-1}, which is lower as compared with the acceptable international value of 59 nGy h^{-1} in sediment (WHO, 2004). The annual effective dose also in November have a mean of 0.0439 mSv and varied in a range of 0.026-0.076 mSv which is within the International Commission for Radiological Protection recommended limit of 1 mSv per year for public exposure (ICRP, 1991). In February, the absorbed dose rate and annual effective dose in Table 4.8b, shows a range of 24.19-30.18 nGy h^{-1} and 0.029-0.074 mSv respectively, with average values of 35.997 nGy h^{-1} for absorbed dose rate and 0.0441 mSv for annual effective dose, which is also lower than ICRP recommended limit.

The calculated values of the external hazard index (H_{ex}) and internal hazard index (H_{in}), for sediment samples studied were below the safe limit of one. The results show that the H_{ex} and H_{in} for sediment samples are below the limit of unity, meaning that the radiation dose is below, the permissible limit of 1mSvy^{-1}recommended by IAEA (2007) in both two batches (Table 4.8a and 4.8b). The values of the radiation hazard parameters from this current study are not high compared to the world averages and the recommended values and therefore unlikely to cause radiological health risks to the people living in the study area.

The radiological cancer risks for population as well as hereditary effects were evaluated by using the ICRP risk assessment methodology (ICRP, 1991; 2007).

The results of the evaluated cancer risk to adult per year in the river sediment ranged from 1.29×10^{-06}-3.80×10^{-06} with mean value of 2.13×10^{-06} in November, and 1.48×10^{-06}-3.72×10^{-06} with average value of 2.25×10^{-06} in February. This means that in terms of cancer risk to adult in November and February, approximately 2 out of 1,000,000 may suffer from some form of cancer risk.

Hereditary effect range from 2.59×10^{-07}-7.62×10^{-07} with a mean of 4.26×10^{-07} in November, whiles in February it ranged from 2.97×10^{-07}-7.45×10^{-07} with mean value of 4.41×10^{-07}. This indicates that, approximately 4 out of 10,000,000 may surfer hereditary effects in Kibi municipality on the use of the sediment.

The negligible cancer risk value recommended by USEPA is in the range of 1.0×10^{-06} to1.0×10^{-04}. That is 1person out of 1000,000 or 10,000 suffering from some form of cancer fatality is considering trivial. Comparing, the estimated results of the lifetime cancer risk in the present study with the acceptable risk factor, it can be concluded that, all estimated results of the lifetime risk among adult member of the Kibi traditional area population are within the range of acceptable risk values recommended by USEPA.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The primary aim of this study was to evaluate the potential human health risk associated with trace metals and naturally occurring radioactive material in Birim River at Kibi and its environs due to the artisanal gold mining activities in the area. This was done by the determination of the physicochemical parameters of the river water. Assessment of the levels of trace metals in the river water and sediment as well as activity concentration of Uranium, Thorium and Potassium was done. Finally, human health risk on the ingestion and dermal contact of the water was estimated.

The study revealed that the water samples from the Birim river is fresh mildly alkaline with minimal inorganic constituents but high turbidity (2.00 – 708.00 NTU). Results from PCA/FA analyses in November suggest high loading of Phosphate (0.934) and Chloride (0.802). High level of Hg was recorded in sediment samples from Adadietem (0.4mg/Kg), Kyebi Training College (KTC-6), (0.775 mg/kg), Kyebi Deaf School (KDS-5), (0.55 mg/kg), Bonsu-Accra Road (B-AR-10) (0.575 mg/kg) and Bonsu Bridge (BB-8) (0.4 mg/kg) while at all the sampling points high levels of As and Fe were recorded. As levels ranged between 8.40 mg/kg and 16.25 mg/kg while mean Fe levels were 821.62 – 837.81 mg/kg. Health risk assessment shows that Fe, Mn, As, Zn and Hg metals were the main contributors for ingestion and dermal exposures to the human environment in the river. The levels of HQ_{ing} for As was greater than one, indicating that it could have harmful effects on human health, This is an indication that risk may occur via the ingestion of contaminated water in the municipality. As, Fe, Hg, Mn and Cr were found to be the main contributors to non-carcinogenic risk (HI) from the Birim River in Kibi municipality. Carcinogenic risk (CR_{ing}) was found to be associated with the slight elevated value of As.

The calculated average activity concentration of ^{232}Th was higher than WHO guidance level of 1.0 Bq/L in water. The mean annual effective doses of the two periods in the various communities had values lower than the WHO recommended value of 0.10 mSv/year. Cancer risk to adult in water for November and February is 2.25×10^{-06} and hereditary effect is 4.41×10^{-07}. Estimated results of the lifetime risk among adult member of the Kibi municipality are within the range of acceptable risk values recommended by USEPA. It can therefore be concluded that water from the Birim River is polluted with respect to Hg, As and Fe with high level of suspended solids. The most polluted sampling points were Adadientem and Kibi.

5.2 RECOMMENDATIONS

Based on the study conducted, the following recommendations are proposed:

(a) Continuous monitoring of the Birim River in the Kibi municipality should be encouraged, especially in Adadietem and Kibi where there is intensive gold mining activities and Apapam the source of the river where new mining have just started.

(b) The study covered only the Kibi municipality at upper basin of River Birim and should be extended to the lower basin. This survey will be important to establish data on the entire catchment of the river.

(c) Determination of naturally occurring radioactive materials should be intensified since mining activities in the area can enhance the levels of NORMs.

(d) The Government, Minerals Commission, Water Resources Commission, Ghana Water Company Limited, Mining companies and the District Assemblies should adopt method or technology that removes high levels of toxic chemicals from the water bodies in the study area. And also the technology that will monitor high levels of naturally occurring radioactive materials in drinking water.

REFERENCES

Abrahão R., Carvalho M., Da Silva Jύnior W. R., Machado, T. T. V., Gadelha C. L. M. and Hernandez, M. I. M. (2007). Use of Index Analysis to Evaluate the Water Quality of Stream Receiving Industrial Effluents, Vol.33, No. 4, pp. 459-465.

Ademola, J. A. (2008). Assessment of natural radionuclide content used in Nigeria. Journal of Radiological Protection vol. 28(4): page 581-588.

Adeyeye, E.I. (1994). Determination of trace heavy metals in *Illisha Africana fish* and inassociated water and soil sediments from some fish ponds. *Intern. J. Environmental Studies* 45:231-238.

Adomako D, Gibrilla A, Akiti TT, Fianko, R., Maloszewski, P. (2011). Hydrogeochemical evolution and groundwater flow in the Densu River Basin, Ghana. Journal of Water Resource and Protection, 3: 548-561. doi:10.4236/jwarp.2011.37065.

Adukpo O. K., Faanu A., Lawluvi, H., Tettey-Larbi L., Emi-Reynolds G., Darko E. O., Kansaana C., Kpeglo D. O., Awudu A. R., Glover E. T., Amoah P. A., Efa A.O., Afaf A. Fakeha, Safiah Q., Hamidalddin, Zain M. Alamoudy, and Ahlam M. A. Al-Amri (2011). Concentration of Natural Radioactivity and their Contribution to the Absorbed Dose from Water Samples from the Western Province, Saudi Arabia JKAU: Sci., Voi. 23(2): page 17-30.

Afaf A. Fakeha, Safiah Q. Hamidalddin, Zain M. Alamoudy, and Ahlam M. A. Al-Amri (2011). Concentration of Natural Radioactivity and their Contribution to the absorbed dose from water samples from the Western Province, Saudi Arabia JKAU: Science. 23(2):17-30.

Agalga, R. (2012). Evaluation of the Concentration of Naturally Occurring Radioactive Materials in the Tono Irrigation Dam and Associated Radiological Hazards. MPhil Thesis, School of Nuclear and Allied Science, University of Ghana.

Agency for Toxic Substances and Disease Registry (ATSDR), (1999). *Toxicological Profile for Mercury* U.S. Department of Health and Human Services. Retrieved on March 4, 2015 from htt://www.atsdr.cdc.gov/toxfaq.html

Agency for Toxic Substances and Disease Registry (ATSDR), (2004). *Toxicological Profile for Copper* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2005). *Toxicological Profile for zinc* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2007). *Toxicological Profile for Arsenic* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2007). *Toxicological Profile for lead* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2012). *Toxicological Profile for Cadmium* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2012). *Toxicological Profile for Manganese* U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Agency for Toxic Substances and Disease Registry (ATSDR), (2012). *Toxicological Profile for* Chromium U.S. Department of Health and Human Services. Retrieved on March 4, 2015

Ahmed A. M. and Hussein M. M., (2004). Residual levels of some heavy metal in fish flesh and water from El-Manzala Lake, *Egypt J King Saud University of Agricultural Sciences. 16* (2): 187-196.

Albertsen, J. (2006). Toxicology Brief: The toxicity of iron, an essential element, Journal, pp 1-5

Aldahan, A., Kkli, A. and Possnert G. (2006). Distribution and Sources of ^{129}I in Rivers of the Baltic Region, Journal of Environmental Radioactivity 88(1): 49-73.

Almgren, S. (2008). Studies on the Gamma Radiation Environment in Sweden with Special Reference to 137Cs; Chalmers Repro Service, Goteborg ISBN 978-91-628-7583-1 pp6

Amerasinghe P., Bhardwaj R. M., Scott C., Jella K., Marshall F. (2013). *Urban wastewater and agricultural reuse challenges in India. International Water Management Institute Report 147.*

American Public Health Authority (APHA) (1998). Standard Methods for the Examination of Water and Waste Water. APHA/AWWA/WEF, Washington DC 20th Edition.

Amonoo-Neizer, E.H. and Amekor, E.M.K. (1993). Determination of total arsenic in environmental samples from Kumasi and Obuasi, Ghana. Environ. Health Perspect. 101: 44-49.

Ansa-Asare O. D. and Asante K. A. (2000). The Water Quality of Birim River in South-East of Ghana.West Afr. J. appl. Ecol. 1: 23-34.

Ansa-Asare, O. D. and Asante, K. A. (2005). Changes in the chemistry of the Weija dam reservoir in Ghana, twenty years after impoundment. West African Journal of Applied Ecology, 8, 35-47 pp.

Armah F.A., Obiri, S., Yawson, D. O., Pappoe, A. (2010) Mining and Heavy Metal Pollution: Assessment of Aquatic Environments in Tarkwa (Ghana) using Multivariate Statistical Analysis. J. Env. Statistics. Vol. 1 (4)

Asamoah, E. (2012) The Impact of Small Scale Gold Mining Activities on The Water Quality of River Birim in the Kibi Traditional Area. MSc Thesis, Kwame Nkrumah University of Science and Technology Kumasi, Ghana

Asante, K. A., Quarcoopome, T., Amevenku, F.Y.K. (2008). Water Quality of the Weija Reservoir after 28 years of Impoundment. West African Journal of Applied Ecology, 13: 171-180.

Asaolu, S. S., Ipinmoroti, K. O., Adeeyinwo, C. E. and Olaofe, O. (1997). Interrelationship of heavy metal concentration in water, sediment and fish samples from Ondo State coastal area, Nigeria *Afr. J. Sci.*, I: 55-61.

Asomaning, G. (1992). Groundwater Resources of the Birim Basin in Ghana. Parasitology International 49 (2): 155-163

Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M. and Mahvi, A. H. (2010). Effect of fertilizer application on soil heavy metal concentration. *Environ Monit Asess* 160:83-89.

Ateba, J.F.B., Ateba, P. O., Ben-Bolie, G. H., Abiama, P. E., Abega, C. R. and Mvondo, S. (2010). Natural Background Dose Measurements in South Cameroon. Radiation Protection Dosimetry. 140(1): page 81-88.

Attua, E. M., Annan,S. T. and Nyame, F. (2014). Water quality analysis of rivers used as drinking sources in artisanal gold mining communities of the Akyem-Abuakwa area: A multivariate statistical approach. Ghana Journal of Geography Vol. 6, Pages 24 – 41

Beretka, I., Mathew, P.I. (1985). Natural radioactivity of Australia building materials, waste and by-products. Health physics 48, 87-95.

Blaylock, B. G., Frank M. L. and O'Neal B. R. (1993). Methodology for Estimating Radiation Dose Rate to Freshwater Biota Exposed to Radionuclides in the Environment. ES/ER-TM-78.Oak Ridge

Borgońo J. M, and Greiber R. (1972). Epidemiological study of arsenicism in the city of Antofagasta. In: Hemphill DD, ed. Trace substances in environmental health, V. A symposium. Columbia, MO, University of Missouri Press, pp. 13–24. Canavan M. M., Cobb S. and Srinker C. (1934). Chronic manganese poisoning. *Archives of Neurology and Psychiatry*, 32:501–512.

Branom J.R., and Sarkar D. (2004). Phosphorus bioavailability in sediments of a sludge-disposal lake. *Environmental Geoscience* 11: 42 - 52

Buchet J.P., Lauwerys R.R. (1982). Evaluation of exposure to inorganic arsenic. Cahiers de médecine du travail, 19:15.

Canavan M. M., Cobb S. and Srinker C. (1934). Chronic manganese poisoning. *Archives of Neurology and Psychiatry*, 32:501–512.

Cardoso, L. X., Souza, S. O., Ferreira, F. C. L., Ferreira, O. C. and Barboza, E. (2011). Determination of the concentration of natural and artificial radionuclides in the soil of the Campus of the Federal University of Sergipe, Scientia Plena 7(1): 1-6

Carrico LC. (1985). Mercury. In: Mineral facts and problems. Bulletin 675. Washington, DC: U.S. Department of the Interior, Bureau of Mines, 499-508.

Cember, H. (1996). Introduction to Health Physics, 3rd Edition, McGraw-Hill, New York

Chapman D (1992). Water quality assessment, A guide to the use of biota, sediments and water in environmental monitoring, University Press, Cambridge, p.585.

Chowdhury, S., P. Champagne (2009). Risk from Exposure to Trihalomethanes During Showering: Probabilistic Assessment and Control. Science of the Total Environment. 407(5):1570-1578.

Coakley, G. J. (1996). The Mineral Industry of Ghana, U.S. Geological Survey.

Cook D. G., Fahn S. and Brait K. A. (1974). Chronic manganese intoxication. *Archives of Neurology*, 30:59–64.

Cordano A. (1998). Clinical manifestations of nutritional copper deficiency in infants and children Am J Clin Nutr 67:1012S-1016S.

Cui C. G. and Liu Z.H. (1988). Chemical speciation and distribution of arsenic in water, suspended solids and sediment of Xiangjiang River, China. The Science of the Total Environment, 77:69–82.

Darko, E. O., Tetteh, G. K. and Akaho, E. H. K. (2005). Occupational radiation exposure to norms in a gold mine, Journal of Radiation Protection Dosimetry, Vol. 114.

Darko, E.O., Faanu, A., Razak, A., Emi-Reynolds, G., Yeboah, J., Oppon, O. C. And Akaho, E. H. K. (2010). Public exposure hazards associated with natural radioactivity in open-pit mining in Ghana, Rad. Prot, Dosim. Vol. 138.

Davis, D.W.; Hirdes, W.; Schaltegger, U.; Nunoo, E.A. (1994). U-Pb age constraints on deposition and provenance of Birimian and gold-bearing Tarkwaian sediments in Ghana, West Africa. Precambrian Research 67: 89-107

Davison, A.G., Taylor, A. and Darbyshire, J. (1988).Cadmium fume inhalation and emphysema. *Lancet 26:663-667.*

Demirak, A., Yilmaz, F., Tuna, A. L. and Ozdemir, N. (2006). Heavy metals in water, sediment and tissues of *Leuciscus cephalus* from a stream in southwestern Turkey. *Chemosphere* 63: 1451-1458.

Dix, H. M. (1981). Environmental pollution. John Wiley & Sons Ltd, New York.

Duffus, J. H. (2002) ‘Heavy metals’-a meaningless term? Pure Appl. Chem., 74(5): 793-807.

Eisenbud, M. and Gesell, T. (1997). Environmental radioactivity from natural, industrial, and military sources. Academic press, San Diego.

El-Arabi, A. M. (2005) Gamma activity in some Environmental Samples in South Egypt. *Indian Journal of pure and Applied Physics, 43(6): page 422-426.*

Elder, J.F. (1989). Metal biogeochemistry in surface-water systems-A review of principles and concepts: U.S. Geological Survey Circular 1013, 43 p.

Elinder C. G. (1986). Iron. In: Friberg L, Nordberg GF, Vouk VB, eds.Handbook on the toxicology of metals, Vol. II. Amsterdam, Elsevier, 276-297.

Elinder C. G. (1992). Cadmium as an environmental hazard. IARC Sci Publ 118:123-132.

Emeka, (2010) Ionizing radiation, man and the environment Inaugural lecture University of Jos Nigeria, UNIJOS Inaugural lecture 43.

EPA. (2006). Revised reregistration eligibility decision for MSMA, DSMA, CAMA, and cacodylic acid, August 10, 2006.Washington, DC: U.S. Environmental Protection Agency.http://www.epa.gov/oppsrrd1/REDs/organic arsenicalsred.pdf. September 12 2006.

Essumang, D., K.; D. K. Dodoo, S. Obiri, J. Y. Yaney, (2007). Arsenic, cadmium, and mercury in Cocoyam (Xanthosoma sagititolium) and Watercocoyam (Colocasia esculenta) in Tarkwa, a Mining Community. Bulletin of Environmental Contamination and Toxicology 79:377-379.

Faanu, A. Ephraim, J. H. and Darko, E. O. (2011). Assessment of Public Exposure to Naturally Occurring Radioactive Materials from Mining and Mineral Processing Activities of Tarkwa Goldmine in Ghana, Springer Science Media B. V. 2010, Environmental Monitoring and Assessment 180: 15-29

Feinglass E.J. (1973). Arsenic intoxication from well water in the United States. *New England Journal of Medicine,* 288:828–830.

Femer, D.J. (2001). Toxicity, heavy metals. eMed. J. 2(5): I.

Fianko, J. R. (2010). The hydrochemistry of groundwater in the Densu river basin, Ghana. Environ Monit Assess. 2010 Aug; 167(1-4): 663-74.

Foulkes, E. C. (1986). Absorption of Cadmium. In: Handbook of Experimental Pharmacology, E. C., Foulkes, (Ed.) Springer Verlag, Berlin. Vol. 80. Pp.1-3.

Goyer, R. A. and Clarkson, T. M (2001). Toxic effects of metals, p. 811-868. In: C.D Klaassen. (ed) Casarett & Doull's toxicology. McGraw-Hill.

Hanson, R., Dodoo, D. K., Essumang , D. K., Blay Jr J., Yankson, K. (2007). The effect of some Selected Pesticides on the Growth and Reproduction of Fresh Water Oreochromis niloticus, Chrysicthys nigrodigitatus and Clarias gariepinus. Bulletin of Environmental Contamination and Toxicology 79:544-547.

Herron N. (2003). Cadmium compounds. Kirk-Othmer encyclopedia of chemical ltechnology. Vol. 4. John Wiley & Sons, Inc., 507-523. http://mrw.interscience

Hindmarsh J.T. and McCurdy R. F. (1986). Clinical and environmental aspects of arsenic toxicity. Critical Reviews in Clinical Laboratory Sciences, 23:315–347.

http://eastakim.ghanadistricts.gov.gh. East Akim Municipality of Eastern Region of Ghana. Accessed 20th March, 2015

http://www.conserve-energy-future.com/sources-and-causes-of-water-pollution.php. Causes of water pollution. Accessed 30th March, 2015

Ibe A. C. and Kullenberg G. (1995). Quality assurance/quality control (QA/QC) regime in marine pollution monitoring programmes: the GIPME perspective. Mar. Pollut. Bull., 31, 209–213.

International Agency for Research on Cancer (IARC) (1980). Some metals and metallic compounds. Lyon, 205-323 Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 23.

International Agency for Research on Cancer (IARC), (1993). Cadmium and certain cadmium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Beryllium, cadmium, mercury and exposures in the glass manufacturing industry. IARC monographs, Vol. 58. Lyon, France: p.119-236.

International Atomic Energy Agency (IAEA) (1996). International basic safety standards for protection against ionizing radiation and for the safety of radiation sources. IAEA, Vienna.

International Atomic Energy Agency (IAEA) (1989). Measurement of Radionuclides in Food and Environment: A Guidebook, IAEA-Technical Reports Series No. 295, Austria.

International Atomic Energy Agency (IAEA) (2005). Naturally Occuring Radioactive Materials (IV), proceedings of an international conference held in Szczyrk, IAEA-TECDOC-1472, Poland.

International Commission of Radiological Protection (ICRP) (1991). 1990 recommendations of the International Commission on Radiological Protection, ICRP

Publication 60, Annals of the ICRP, Elsevier, New York, vol 21(1–3).Industrial, and Military Sources (4th edition), London: Academic Press.

International Commission of Radiological Protection (ICRP) 1996. Age-dependent committed dose conversion coefficient for members of the public from intake of radionuclides. ICRP Publication No. 72 (Oxford: Pergamon Press, annal ICRP 25, 3/

International Commission on Radiological Protection (ICRP) (2000). Protection of the public in situations of prolonged radiation exposure. Publication 82, Annals of the: 29(1), 1-2.

International Organization for Standardization (1985). Water quality-determination of electrical conductivity. Geneva, (ISO 7888).

International Programme on Chemical Safety (IPCS), (1981). Arsenic. Geneva, World Health Organization, (Environmental Health Criteria 18).

International Programme on Chemical Safety (IPCS) (1989). Mercury-environmental aspects. Geneva, World Health Organization, (Environmental Health Criteria 86).

International Programme on Chemical Safety (IPCS) (1990). Methylmercury. Geneva, World Health Organization, (Environmental Health Criteria 101).

International Programme on Chemical Safety (IPCS) (1999). Manganese and its compounds. Geneva, World Health Organization, (Concise International Chemical Assessment Document 12).

International Programme on Chemical Safety (IPCS) (2003). Elemental mercury and inorganic mercury compounds: human health aspects. Geneva, World Health Organization, (Concise International Chemical Assessment Document 50).

International Programme on Chemical Safety (IPCS), (2001). Arsenic and arsenic compounds. Geneva, World Health Organization, (Environmental Health Criteria 224).

Irgolic K. J. (1982). Speciation of arsenic compounds in water supplies. Research Triangle Park, NC, United States Environmental Protection Agency (EPA-600/S1-82-010).

Ismail, A. M., Kullab M. K. and Saq'an S. A. (2009). Natural Radionuclides in Bottled Drinking Water in Jordan and their Committed Effective Doses, Jordan Journal of Physics, Vol. 2(1): 47-57.

Jain V. K. (1978). Studies on effect of cadmium on the growth pattern of phaseolus aurius varieties. Absi. I. Bot. Conf. WHO: World Health Organization technical report JIBS, 57-84.

Jarup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin 68*:167-182.

Jarup, L., Berglund, M., Elinder, C.G., Nordberg, G. and Vahter, M. (1998). Health effect of cadmium exposure: A review of the literature and a risk estimate. *Sound J Work Environ Health* 24:1-52.

Jayawardana DT, Ishiga H, Pitawala H. MTGA (2012). Geochemistry of surface sediments in tsunami-affected Sri Lankan lagoons regarding environmental implications. International Journal of Environmental Science and Technology, 9, 41–55.

Kalantari, M. R. and Ebadi, A. G. (2006). Geochemical Assessment of some heavymetals levels in Neka River sediments – Neka City, Iran. *Journal of Applied Sciences* 6(5): 1017-1019.

Kansana C., Darko, E. O., Schandof, I. C., Adukpo, O. K., Faanu, A., Lawluvi, H. and Kpeglo, O. (2012). Determination of Natural Radioactivity in Saline Water and Salt from Panbros Salt Industry Limited in the Accra Metropolis, Ghana, International Journal of Science and Technology, Volume 2 No. 3.

Kattan, Z. (1995). Chemical and environmental isotope study of fissured basaltic aquifer systems of the Yarmouk Basin. Proceedings of a Symposium on Isotopes in Water Resources Management. Vol 2, Vienna. p.10.

Kesse G.O. (1985). The mineral and rock resources in Ghana. Balkema, Rotterdam, pp13-26.

Khan TA (2008). Cluster analysis and quality assessment of groundwater in and around Aligarh city, U.P India., Proceedings of All India Seminar on Advances in Environmental Science and Technology, Z, H. College of Engineering and Technology, India, pp 109-114.

Klein L (1962). River Pollution: Causes and Effects, Butterworth & Co. (Publishers) Ltd., London. 456pp

Klement, A.W. (1982). CRC Handbook of Environmental Radiation, Florida: CRC Press, Inc.

Knepper W. A. (1981). Iron. In: Kirk-Othmer encyclopedia of chemical technology,Vol. 13. New York, NY, Wiley Interscience, 735-753.

Kuma, J., S.; Younger, P., L. (2004).Water quality trends in the Tarkwa Gold-mining district, Ghana. Bulletin of Engineering Geology and the Environment 63:119-132.

Lar, U. A. (2013). Trace Elements and Health: An Environmental Risk in Nigeria. *Earth Science*. Vol. 2, No. 3, 2013, pp. 66-72.

Liang F., Yang S. G., Sun C. (2011). Primary health risk analysis of metals in surface water of Taihu Lake, China. B. Environ. Contam. Tox. 87, (4), 404.

Lilley, J. (2001), Nuclear Physics: Principles and Applications, Chichester: John Wiley & Sons, Ltd.

Liu, C.W., Lin, K.H. and Kuo, Y. M. (2003). Application of factor analysis in the assessment of groundwater qualityin a Blackfoot disease area in Taiwan. Science in the Total Environment, 313, 77-89.

Luoma, S.N. (1989). Can we determine the biological availability of sediment-bound trace elements? Hydrobiologia, 176/177, 379-396.

Mazzilli, B., Camargo, I. M. C., Oliveira J Nieri A Sampa M. H. O. & Silva B. L.R. (1998). Evaluation of Dose due to Ingestion of Natural Radionuclides of the Uranium Series in Spring Waters. Radiation Research, 150(2): 250-252.

Merdanoglu, B. and Altinsoy (2006) radioactivity concentrations and dose assessmentfor soil samples from Kestanbol granite area, Turkey, Radiation Protection Dosimetry Vol. 121(4): 399-405.

Meybeck, M. and Helmer, R. (1989). The quality of rivers: from pristine state to global pollution. Paleogeog. Paleoclimat. Paleoecol. (Global Planet. Change Sect.), 75, 283-309

Meybeck, M., Chapman, D. and Helmer, R. (1989). Global Freshwater Quality: A First Assessment. Blackwell Reference, Oxford, 306 pp.

Mitchell M. K. and Stapp W. B. (2000). Field Manual for Water Quality Monitoring. Twelfth Edition.

Moore J. W., Ramamoorthy S. (1984) Heavy metals in natural waters: Applied Monitoring Impact Assessement. Springer New York. pp 205-233.

Mortazavi, S. M. J.; Karamb P.A. (2005). "Apparent lack of radiation susceptibility among residents of the high background radiation area in Ramsar, Iran: can we relax our standards?". *Radioactivity in the Environment* 7: 1141–1147.

Mujahid and Hussain (2011) Measurement of Natural Radioactivity from soil samples of Sind, Pakistan Radiation Protection Dosimetry 145(4): 351-355.

Mwamburi, J. (2003). Variations in trace elements in bottom sediments of major rivers in Lake Victoria’s basin, Kenya. *Lakes & Reservoirs: Research and Managements* 8: 5-13.

Naveedullah., Hashmi M.Z., Yu C., Shen H.,Duan D., Shen C., Lou L., Chen Y. (2013) Risk Assessment of Heavy metals Pollution in Agricultural Soils of Siling Reservoir Watershed in Zhejiang Proveince, China. BioMed. Res. Int.

NRPA (2004). Natural Radioactivity in Produced Water from the Norwagian Oil and Gas Industry in 2003, page 10.

Obiri, S. (2007). Determination of heavy metals in boreholes in Dumasi in the Wassa West District of Western Region of the Republic of Ghana. Environmental Monitoring and Assessment 130: 455-463

Olivares M., Araya M., and Uauy R. (2000). Copper hemeostasis in infant nutrition: Deficit and excess. J Pediatr Gastroenterol Nutr 31(2):102-111.

Osafo, E. (2011) The Effect of Small Scale Gold Mining Activities on the Birim Riverin the East Akim Municipality of the Eastern Region, MSc Thesis, Kwame Nkrumah University of Science and Technology Kumasi, Ghana

Osweiler G. D., Carson T. L., Buck W. B. and Van Gelder G. A. (1985). Iron. In: Clinical and diagnostic veterinary toxicology. 3rd edn. Kendall/Hunt Publishing Co., Dubuque, IA, USA, 104–106.

Ozturk, M. Ozozen, G., Minareci, O. and Minareci, E. (2009). Determination of heavy metals in fish, water and sediments of Avsar Dam Lake in turkey. *Iran J. Enron. Health. Sci. Eng.* 6(2): 73-80.

Pujol L and Sanchez C, (2000) Natural and artificial radioactivity in surface water of the Ebro River basin (Northeast Spain), Journal of Environmental Radioactivity 51(2), 181-210.

Qishlaqi, A. and Moore, F. (2007). Statistical Analysis of Accumulation and Sources of Heavy Metals Occurrence in Agricultural Soils of Khoshk River Banks Shiraz, Iran. *American-Eurasian J. Agric. & Environ. Sci.*, 2(5): 565-573.

Ramasamy, V.; Senthil; S., Meenakshisundaram, V. and Gajendran, V. (2009). Measurement of Natural Radioactivity In Beach Sediments From North East Coast of Tamilnadu, India. Research Journal of Applied Sciences, Engineering and Technology 1(2): 54-58.

Rump, H.H.; Krist, H. (1988) Laboratory Manual for the Examination of Water, Wastewater & Soil, VCH, ISBN 0-89573-851-1

Samsudin MS, Juahir H, Zain SM, Adnan N. H (2011). Surface River Water Quality Interpretation Using Environmetric Techniques: Case Study at Perlis River Basin, Malaysia. International Journal of Environmental Protection, 1 (5):1-8.

Shrestha, S. and Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. Environmental Modelling & Software, 22, 464-475

Singh, N.; Koku, J.E.; Balfors, B. (2007). Resolving Water Conflicts in Mining Areas of Ghana through Public Participation a Communication Perspective. Journal of Creative Communications 2: 361-382

Solomon, A.O., Ike E. E., Ashano, E. C. and Jwanbot, D. I. (2002). Natural Background Radiation Characteristics of Basalts on the Jos Plateau and the Radiological Implication of the use of the Rock for House Constraction. African Journal of Natural Sciences, 5(1): 43 – 40.

Sowmya, M. B. Senthilkumar, B. R. R. Seshan, G. Hariharan, R. Purvaja, S. Ramkumar and R. Ramesh (2010). Natural radioactivity and associated dose rate in soil samples from kalpakkam, south, radiation protection dosimetry, 141(3): 239-247

Standard methods for examination of water and waste water (1998). 20th Ed. American Public Health Association. Washington D C. Pp.56-60.

Stoecker, B. J. (2001). Minerals and Trace Elements, 366-370. In: B.A. Bowman and R. M. Russell (eds) *Pressent knowledge in nutrition.* ILSI Press.

Svobodova, Z., Lloyd, R., Machova, J. and Vykusova, B. (1993). Water Quality and fish health. EIFC Technical Paper. No. 54. Rome, FAO. 59p.

Taskin, H., Karavus, M., Ay, P., Topuzoglu, A., Hindiroglu, S. and Karahan, G. (2009). Radionuclide concentration in soil and lifetime cancer risk due to the gamma radioactivity in Kirklareli, Turkey. *Journal of environmental radioactivity*. 100(1): page 49-53.

Thornton I. (1992). Sources and pathways of cadmium in the environment. In: Nordberg GF, Herber RFM, Alessio L, eds. Cadmium in the human environment: Toxicity and carcinogenicity. IARC Scientific Publications No.118. Lyon, France: International Agency for Research on Cancer, 149-162.

Towill, L. E., Shriner, C. R., Drury, J. S., Hammons, A. S. and Holleman, J. W. (1978). Reviews of the environmental effects of pollutants: III chromium U.S. Environmental Protection Agency Rep. 600/1-78-023. 287pp.

Turhan S., Aykamis, A. S. and Kilic, A. M. (2009). Measurement of the natural radioactivity in building materials used in Ankara and assessment of external doses, Journal of Radiological Protection 28(1): page 83-91

U.S. Environmental Protection Agency (EPA) (1998). Toxicological review of hexavalent chromium. Available online at http://www.epa.gov/iris. Retrieved 25, June 2015

U.S. Geological Survey (USGS). (2002). Mineral commodity summary. http://www.usgs.gov/minerals/pubs/commodity/copper. December 8, 2014

U.S. Geological Survey (USGS). (2003). Zinc. Mineral Commodity Summaries. http://minerals.usgs.gov/minerals/pubs/commodity/zinc. June 5, 2013.

U.S. Geological Survey. (USGS), (2008). Cadmium. Mineral commodity summaries. http://minerals.usgs.gov/minerals/pubs/commodity/cadmium/mcs-2008-cadmi.pdf. April 29, 2008.

Uauy, R., Olivares, M. and Gonzalez, M. (1998). Essentiality of copper in humans. *Am J Clin Nutr*. 67: 952S-959S.

United Nations Scientific Committee on the Effects of Atomic Radiation. (UNSCEAR) (2000),"Sources and Effects of Ionizing Radiation", UNSCEAR 2000 Report

Vol.1to the General Assembly, with scientific annexes, United Nations Sales Publication, United Nations, New York.

United Nations Environment Programme/ Global Environment Monitoring system/ water programme (UNEP/GEMS) (2006). Water quality for ecosystem and human health ISBN 92-95039-10-6.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (2000) Exposures from natural sources, 2000 report to general assembly.
Annex B, New York

United Nations Scientific Committee on the Effects of Atomic Radiation, (UNSCEAR) (2000). Report to the General Assembly Vol. 1. Annex B: Exposure from Natural Radiation Sources. United National, New York.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). (1993). Exposures from Natural Sources of Radiation, 1993 Report to General Assembly, Annex A, New York.

US Environmental Protection Agency (EPA) (1983). Methods for chemical analysis of waters and wastes. EPA-600/4-79-020, Cincinnati, Ohio

US Environmental Protection Agency (EPA) (2006) *Volunteer Estuary Monitoring: A Methods Manual.* EPA 842-B-003.Office of Water Washington, DC. Retrieved on June 30, 2010 from http://www.epa.gov/owow/estuaries/monitor/

US Environmental Protection Agency (EPA). (2006b). Technical factsheet on cadmium: Ground water and drinking water. http://www.epa.gov/OGWDW/dwh/t-ioc/cadmium.html. July 28, 2008.

US Environmental Protection Agency (USEPA) (1976). Quality Criteria for Water Use. Environmental Protection Agency, Washington DC.

US Environmental Protection Agency (USEPA) (2006a) Edition of the Drinking Water Standards and Health Advisories

US Environmental Protection Agency (USEPA) (2006b). Technical Report on Technologically Enhanced Naturally Occurring Radioactive Materials from Uranium Mining Vol.1 Mining and Reclamation Background, EPA 402-R-05-007, January 2006.

US Environmental Protection Agency (USEPA) (2010). Risk-Based concentration table. Available at http://www.epa.gov/reg3hwmd/risk/human/index.htm. 28/09/2015

Valko M.M.H.C.M., Morris H, and Cronin MTD. (2005). Metals, toxicity and oxidative stress. *Curr Med Chem* 12(10): 1161-1208.

Van Aardt, W. J. and Erdmann, R. (2004). Heavy metals (Cd, Pb, Cu, Zn) in mudfish and sediments from three hard-water dams of the Mooi River catchment, South Africa. *Water SA*. 30(2): 211-215.

Vuori, K. (1995). Direct and indirect effects of iron on river ecosystems *Ann. Zool Fennici* 32:317-329.

Wakida F. T., Lara- Ruiz, D. Temores- Pena, J., Rodriguez-Ventura, J.G., Diaz, C. and Garcia-Flores, E. (2008). Heavy metals in sediments of the Tecate River, Mexico. *Environ Geol* 54:637-642.

Wallner, G., Herinces, E. and Shahram Ayromlou, (2009) Determination of Natural Radionuclides in Drinking Water from the Waldviertel, Austria, by the Arzona Board of Regents on behalf of the University of Arizona LSC 2008, Advances in Liquid Scintillation Spectrometry edited by J Eikenberg, M Jaggi, H Beer, H Baehrle,page 345-352

Watson, S.J., Jones, A.L., Oatway, W.B. and Hughes, J.S. (2005), "Ionising Radiation Exposure of the UK population: 2005 Review", Health Protection Agency, Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division, Chilton, Didcot, Oxfordshire, OX11 0RQ,UK.

Welch A. H., Lico M. S, and Hughes J. L. (1988). Arsenic in ground water of the western United States. Ground Water, 26:333–347.

WHO/UNEP, GEMS (1989) Global freshwater quality. Oxford, Alden Press.

wiley.com/emrw/9780471238966/kirk/article/cadmherr.a01/current/pdf. April 29, 2008.

Wood J.M. and Wang H.K. (1983). Microbial resistance to heavy metals. Environmental Science and Technology, 17:82a–90a.

World Health Organisation (WHO) (1996). Guidelines for drinking-water quality Iron in drinking-water. 2nd ed.Vol.2 Retrieved on January 25, 2010 from htt://www.who.int.org.

World Health Organisation (WHO) (2003). Chromium in Drinking-water, *Guidelines for Drinking-water Quality* WHO/SDE/WSH/03.04/04. Retrieved on March 4, 2015.

World Health Organization (2004) Guidelines for drinking water quality: radiological aspects, 3rd edn. WHO, Geneva

World Health Organization (WHO) (2003). Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, world Health Organization. WHO/SDE/WSH/03.04

World Health Organization (WHO) (2005). Mercury in Drinking-water, Background document for development of Guidelines for WHO Drinking-water Quality. Retrieved on March 4, 2015 from htt://www.mercuryfinal.org.

World Health Organization (WHO) (2011). Arsenic in Drinking-water Background document for development of Guidelines for WHO Drinking-water Quality. Retrieved on March 4, 2015 from htt://www.arsenic.org.

World Health Organization (WHO) (2011). Cadmium in Drinking-water Background document for development of Guidelines for WHO Drinking-water Quality. Retrieved on March 4, 2015 from htt://www.cadmium.org

World Health Organization (WHO) (2011). Lead in Drinking-water Background document for development of Guidelines for WHO Drinking-water Quality. Retrieved on March 4, 2015 from htt://www.lead.org.

World Water Council (WWC), (2000). Regional consultations: Africa, in World Water Vision, Retrieved on June 5, 2010 from http://www.watervision.org

Wu B., Zhao D. Y., Jia H. Y., Zhang Y., Zhang X. X., Cheng S. P. (2009). Preliminary Risk Assessment of Trace Metal Pollution in Surface Water from Yangtze River in Nanjing Section, China. B. Environ. Contam. Tox. 82, (4), 405

Yip, R. (2001). Iron. In: B. A. Bowman and R. M. Russell (eds) *present knowledge in nutrition.* ILSI Press

Zaldivar, R. (1980). A morbid condition involving cardio-vascular, broncho-pulmonary, digestive and neural lesions in children and young adults after dietary arsenic exposure. Zentralblatt fűr Bakteriologie und Hygiene, Abteilung I: Originale B, 170:44–56.

Zaldivar, R. and Ghai, G. L. (1980). Clinical epidemiological studies on endemic chronic arsenic poisoning in children and adults, including observations onchildren with high and low-intake of dietary arsenic. Zentralblatt fűr Bakteriologie und Hygiene, Abteilung I: Originale B, 170: 409–421.

Zare S. and Ebadi, A. G. (2005). Measurement of Heavy metals in fish from the Tajan River. *Pakistan Journal of Biological Science* 8(10): 1460-1462.

APPENDICES

Appendix I: Concentration of Trace Element in water (November) mg/L

Lacation Description	**Hg**	**As**	**Cd**	**Pb**	**Zn**	**Cu**	**Fe**	**Mn**	**Cr**
Apapam	<0.001	0.020	<0.002	<0.001	0.0025	<0.003	0.410	0.025	<0.006
Afiesa	<0.001	0.035	<0.002	<0.001	0.0038	<0.003	0.808	0.028	<0.006
Adadie-tem	<0.001	0.040	<0.002	<0.001	0.0050	<0.003	2.073	0.045	<0.006
Kyebi T. college	0.005	0.058	<0.002	<0.001	0.0075	<0.003	3.700	0.093	<0.006
Kyebi Deaf School	0.005	0.039	<0.002	<0.001	0.0038	<0.003	1.275	0.069	<0.006
Kyebi water Training center	<0.001	0.038	<0.002	<0.001	0.0050	<0.003	0.848	0.055	<0.006
Asikem	<0.001	0.031	<0.002	<0.001	0.0050	<0.003	0.644	0.058	<0.006
Bonsu-Accra Road	0.0038	0.038	<0.002	<0.001	0.0110	<0.003	1.181	0.086	<0.006
Uni. College of Agric & Env.Studis	<0.001	0.053	<0.002	<0.001	0.0088	<0.003	0.724	0.118	<0.006
Bonsu Bridge	0.0025	0.035	<0.002	<0.001	0.0100	<0.003	1.049	0.135	<0.006

Appendix II: Concentration of Trace Element in water (February) mg/L

Lacation Description	**Hg**	**As**	**Cd**	**Pb**	**Zn**	**Cu**	**Fe**	**Mn**	**Cr**
Apapam	<0.001	0.0138	<0.002	<0.001	0.0188	0.0075	0.6613	0.0250	0.0038
Afiesa	<0.001	0.0275	<0.002	<0.001	0.0250	0.0175	0.6225	0.0788	0.0038
Adadie-tem	<0.001	0.0350	<0.002	<0.001	0.0150	<0.001	0.1375	0.1663	0.0025
Kyebi Training college	0.0025	0.0475	<0.002	<0.001	0.0388	0.0188	0.8600	0.0650	0.0075
Kyebi Deaf School	0.0025	0.0325	<0.002	<0.001	0.0100	0.0088	0.2788	0.1113	0.0088
Afiesa	<0.001	0.0325	<0.002	<0.001	0.0175	<0.001	0.3488	0.4023	<0.001
Asikem	<0.001	0.0313	<0.002	<0.001	0.0250	<0.001	0.1263	0.1350	0.0038
Bonsu - Accra Road	0.0013	0.0275	<0.002	<0.001	0.0138	<0.001	0.4538	0.2550	<0.001
Bonsu Bridge	0.0025	0.0388	<0.002	<0.001	0.0325	0.0125	0.8775	0.0788	0.0038

Appendix III: Concentration of Trace Element in sediment (November) mg/kg

Lacation Description	**Hg**	**As**	**Cd**	**Pb**	**Zn**	**Cu**	**Fe**	**Mn**	**Cr**
Apapam	0.325	9.800	<0.002	0.700	2.500	2.950	822.159	141.10	28.050
Afiesa	0.250	12.550	<0.002	<0.001	3.950	4.150	833.531	135.30	7.050
Adadie-tem	0.400	10.300	<0.002	<0.001	2.200	2.150	828.250	79.900	25.650
Kyebi T. college	0.900	16.350	<0.002	0.600	7.600	7.450	839.252	186.70	5.950
Kyebi Deaf School	0.550	12.900	<0.002	1.950	2.550	3.000	821.620	184.95	6.050
Asikem	0.200	8.300	<0.002	2.700	2.200	4.900	839.117	73.15	10.400
Bonsu-Accra Road	0.800	12.350	<0.002	<0.001	1.850	2.300	808.431	122.25	4.850
Bonsu Bridge	0.400	11.650	<0.002	0.750	3.800	5.150	832.724	209.20	6.350
IAEA-SOIL-7	**0.035**	**12.95**	**1.25**	**60.08**	**10.35**	**10.75**	**25655.0**	**-**	**59**
%RECOVERY	**87.50**	**96.64**	**96.15**	**100. 1**	**94.09**	**97.73**	**99.82**	**-**	**99.0**

Appendix IV: Concentration of Trace Element in sediment (February) mg/kg

Lacation Description	**Hg**	**As**	**Cd**	**Pb**	**Zn**	**Cu**	**Fe**	**Mn**	**Cr**
Apapam	<0.001	12.00	<0.002	1.750	8.350	6.250	846.42	180.40	12.90
Afiesa	0.150	12.65	<0.002	0.350	7.400	4.100	837.81	256.35	14.40
Adadie-tem	0.200	10.35	<0.002	0.800	7.500	8.150	844.54	106.65	14.55
Kyebi T. college	0.650	16.15	<0.002	0.600	6.900	6.000	829.06	147.40	5.55
Kyebi Deaf School	0.150	12.85	<0.002	0.900	18.670	6.300	826.64	161.30	9.40
Afiesa	<0.001	12.35	<0.002	1.7500	7.000	4.850	825.90	146.40	6.35
Asikem	<0.001	8.50	<0.002	<0.001	5.000	4.050	823.94	97.75	9.95
Bonsu-Accra Road	0.350	12.75	<0.002	2.100	8.650	9.450	837.81	240.30	11.75
Bonsu Bridge	0.150	11.65	<0.002	2.400	6.800	7.050	831.28	238.35	9.10
IAEA-SOIL-7	**0.035**	**12.95**	**1.25**	**60.08**	**10.35**	**10.75**	**25655.0**	**-**	**59**
%RECOVERY	**87.50**	**96.64**	**96.15**	**100. 1**	**94.09**	**97.73**	**99.82**	**-**	**99.0**

Appendix V: Activity concentration of U, Th and K in water (November) Bq/L

Lacation Description	**U-238**	**Th-232**	**K-1460**
Apapam	1.792 ± 0.384	2.795 ± 0.449	63.681 ± 2.656
Afiesa	1.866 ± 0.453	1.933 ± 0.385	62.132 ± 2.545
Adadie-tem	1.434 ± 0.384	2.840 ± 0.531	62.021 ± 2.490
Kyebi T. college	2.124±0.322	2.054±0.314	75.321±11.148
Kyebi Deaf School	1.189 ± 0.725	1.475 ± 0.687	61.080 ± 2.656
Kyebi water T. center	1.829 ± 0.459	2.749 ± 0.541	69.379 ± 2.656
Asikem	2.176 ± 0.603	2.850 ± 0.467	64.898 ± 1.273
Bonsu-Accra Road	2.490 ± 0.053	3.638 ± 0.669	61.302 ± 2.877
Uni. College of Agric & Env.Studis	0.821 ± 0.341	2.289 ± 0.788	56.382 ± 1.604
Bonsu Bridge	1.685 ± 0.459	1.439 ± 0.834	60.748 ± 3.209

Appendix VI: Activity concentration of U, Th and K in water (February) Bq/L

Lacation Description	U-238	Th-232	K-1460
Apapam	0.921±0.138	1.623±0.243	68.443±10.266
Afiesa	2.041±0.306	2.441±0.367	48.112±7.217
Adadie-tem	1.443±0.216	2.424±0.364	54.514±8.177
Kyebi T. college	2.144±0.322	2.094±0.314	74.321±11.148
Kyebi Deaf School	1.136±0.170	2.164±0.325	63.542±9.531
Afiesa	1.263±0.189	3.112±0.467	58.546±8.782
Asikem	0.832±0.125	3.176±0.476	71.523±10.728
Bonsu-Accra Road	2.314±0.347	1.783±0.267	52.763±7.914
Bonsu Bridge	1.641±0.246	1.884±0.283	62.714±9.407

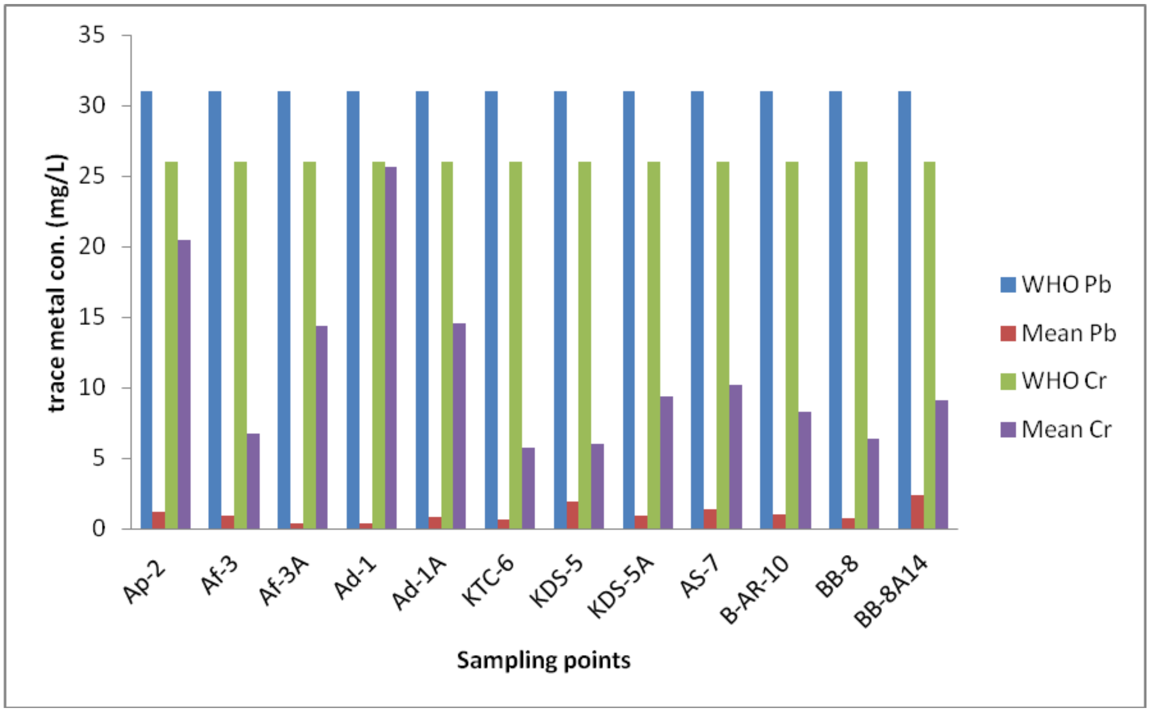
Appendix VII: Activity concentration of U, Th and K in sediment (November) Bq/kg

Lacation Description	U-238	Th-232	K-1460
Apapam	8.299 ± 5.368	18.853 ± 2.829	140.972 ± 4.478
Afiesa	12.347 ± 1.400	26.038 ± 0.987	146.524 ± 4.134
Adadie-tem	18.892 ± 1.554	29.239 ± 1.168	308.375 ± 5.322
Kyebi T. college	20.269 ± 2.341	21.245 ± 1.219	236.802 ± 4.690
Kyebi Deaf School	6.552 ± 0.398	22.644 ± 1.561	235.453 ± 4.823
Asikem	9.969 ± 2.901	33.540 ± 1.845	340.045 ± 5.615
Bonsu-Accra Road	95.050 ± 2.320	15.909 ± 1.964	204.905 ± 4.397
Bonsu Bridge	11.993 ± 1.177	30.065 ± 1.501	355.956 ± 5.662

Appendix VIII: Activity concentration of U, Th and K in sediment (February) Bq/kg

Lacation Description	U-238	Th-232	K-1460
Apapam	13.389 ± 5.368	29.753 ± 2.829	169.992 ± 4.499
Afiesa	21.347 ± 1.400	26.038 ± 0.987	146.524 ± 4.134
Adadie-tem	18.962 ± 1.547	29.129 ± 1.168	298.276 ± 5.411
Kyebi T. college	19.261 ± 2.332	19.242 ± 1.208	231.702 ± 4.681
Kyebi Deaf School	6.252 ± 0.393	19.644 ± 1.561	226.413 ± 4.803
Afiesa	20.547 ± 1.400	26.039 ± 0.987	155.323 ± 4.131
Asikem	8.965 ± 1.998	32.240 ± 1.843	340.045 ± 5.715
Bonsu-Accra Road	92.050 ± 2.320	16.009 ± 1.953	204.708 ± 4.377
Bonsu Bridge	12.903 ± 1.078	28.062 ± 1.500	352.873 ± 5.654

Appendix IX: Comparison of mean Pb and Cr levels in sediments at the sampling points with WHO levels



Appendix X: USEPA database oral toxicity data reference dose values (Rfd)		
Elements	RfD_{ing}/(mg/kg day)	RfD_{derm}/(mg/kg) day
Hg	3.0×10^{-04}	2.40×10^{-04}
As	3×10^{-04}	2.85×10^{-04}
Cd	5×10^{-04}	2.5×10^{-05}
Pb	3.5×10^{-03}	4.2×10^{-05}
Zn	3.0×10^{-01}	6.0×10^{-02}
Cu	5.0×10^{-03}	8.0×10^{-03}
Fe	8.0×10^{-01}	1.40×10^{-01}
Mn	1.4×10^{-01}	9.60×10^{-04}
Cr	1.5×10^{-03}	$\mathbf{7.5}\times10^{-05}$

Appendix XI: Factor analysis of physical parameters for November **(Descriptive Statistics)**

	N	Range	Minimum	Maximum	Mean		Std. Deviation	Skewness	
	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic	Statistic	Std. Error
Turbidity	10	706.000	2.000	708.000	211.200	66.583582	210.5557	1.641	0.687
Chloride	10	7.997	9.997	17.994	11.7963	0.813478	2.572444	1.792	0.687
sulphate	10	3.327	0.502	3.829	2.08230	0.320450	1.013353	0.027	0.687
Nitrate	10	1.345	0.033	1.378	0.30880	0.122322	0.386817	2.834	0.687
Phosphate	10	0.101	0.116	0.217	0.15320	0.009349	0.029563	0.859	0.687
PH	10	0.280	7.450	7.730	7.59700	0.029441	0.093101	-.501	0.687
EC	10	38.300	108.000	146.300	124.780	4.186109	13.23764	0.771	0.687
Temperature	10	5.600	25.400	31.000	29.0800	0.475815	1.504659	-1.705	0.687
TDS	10	23.000	65.000	88.000	75.0000	2.521023	7.972174	0.760	0.687
Salinity	10	0.000	0.000	0.000	0.00000	0.000000	0.000000	.	.
Valid N (listwise)	10								

Appendix XII: **Total Variance Explained (November)**

Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings[a]
Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
3.166	35.179	35.179	3.166	35.179	35.179	2.580
2.770	30.779	65.958	2.770	30.779	65.958	3.009
1.221	13.567	79.526	1.221	13.567	79.526	1.981
0.990	10.997	90.523				
0.350	3.888	94.411				
0.271	3.016	97.427				
0.229	2.539	99.966				
0.003	0.034	100.000				
1.397E-7	1.552E-6	100.000				

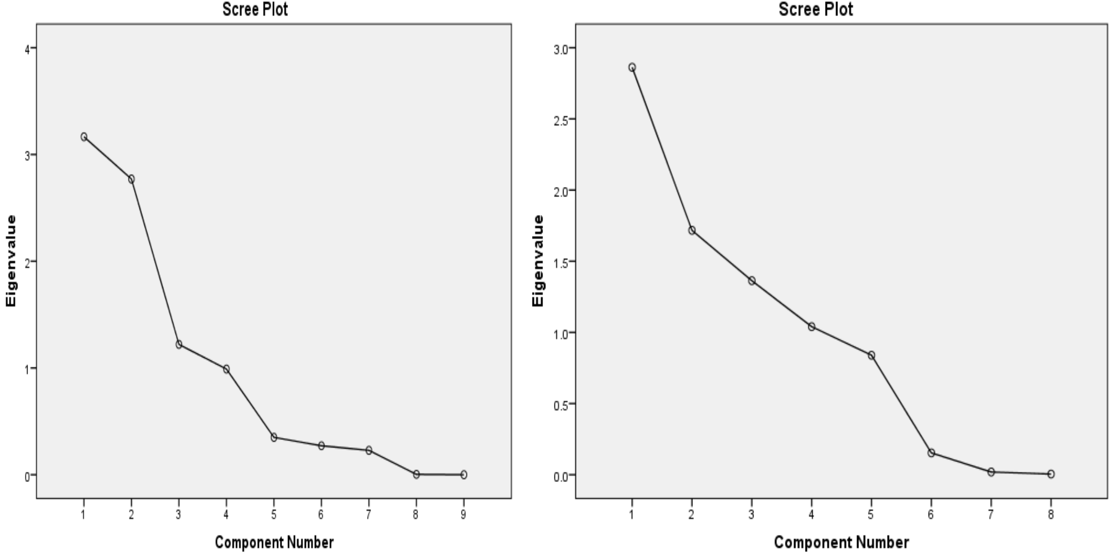
Extraction Method: Principal Component Analysis.

Total Variance Explained (February)

Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings[a]
Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
2.863	35.784	35.784	2.863	35.784	35.784	2.642
1.717	21.465	57.249	1.717	21.465	57.249	1.724
1.363	17.041	74.290	1.363	17.041	74.290	1.660
1.040	13.003	87.293	1.040	13.003	87.293	1.342
0.839	10.492	97.786				
0.153	1.917	99.702				
0.019	0.237	99.939				
0.005	0.061	100.000				

Extraction Method: Principal Component Analysis.

Appendix XIII: Scree Plot for November and February Physical parameters of water.



Appendix XIV; Post Hoc Tests for Trace elements in November

Multiple Comparisons

Dependent Variable: Raw Scores

Tukey HSD

(I) Trace Elements	(J) Trace Elements	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Hg	As	-0.0374500	0.1936872	1.000	-0.587803	0.512903
	Zn	-0.0049900	0.1936872	1.000	-0.555343	0.545363
	Fe	-1.2699500*	0.1936872	0.000	-1.820303	-0.719597
	Mn	-0.0699500	0.1936872	0.996	-0.620303	0.480403
As	Hg	0.0374500	0.1936872	1.000	-0.512903	0.587803
	Zn	0.0324600	0.1936872	1.000	-0.517893	0.582813
	Fe	-1.2325000*	0.1936872	0.000	-1.782853	-0.682147
	Mn	-0.0325000	0.1936872	1.000	-0.582853	0.517853
Zn	Hg	0.0049900	0.1936872	1.000	-0.545363	0.555343
	As	-0.0324600	0.1936872	1.000	-0.582813	0.517893
	Fe	-1.2649600*	0.1936872	0.000	-1.815313	-0.714607
	Mn	-0.0649600	0.1936872	0.997	-0.615313	0.485393
Fe	Hg	1.2699500*	0.1936872	0.000	0.719597	1.820303
	As	1.2325000*	0.1936872	0.000	0.682147	1.782853
	Zn	1.2649600*	0.1936872	0.000	0.714607	1.815313
	Mn	1.2000000*	0.1936872	0.000	0.649647	1.750353
Mn	Hg	0.0699500	0.1936872	0.996	-0.480403	0.620303
	As	0.0325000	0.1936872	1.000	-0.517853	0.582853
	Zn	0.0649600	0.1936872	0.997	-0.485393	0.615313
	Fe	-1.2000000*	0.1936872	0.000	-1.750353	-0.649647

*. The mean difference is significant at the 0.05 level.

Appendix XV; Post Hoc Tests for Trace elements in February

Multiple Comparisons

Dependent Variable: Raw Score
Tukey HSD

(I) Trace Elements	(J) Trace Elements	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
As	Zn	0.0100000	0.0551909	1.000	-0.158774	0.178774
	Fe	-0.4533444*	0.0551909	0.000	-0.622119	-0.284570
	Mn	-0.1145667	0.0551909	0.381	-0.283341	0.054208
	Cr	0.0280444	0.0551909	0.999	-0.140730	0.196819
	Cu	0.0245889	0.0551909	0.999	-0.144185	0.193363
	Hg	0.0308444	0.0551909	0.998	-0.137930	0.199619
Zn	As	-0.0100000	0.0551909	1.000	-0.178774	0.158774
	Fe	-0.4633444*	0.0551909	0.000	-0.632119	-0.294570
	Mn	-0.1245667	0.0551909	0.283	-0.293341	0.044208
	Cr	0.0180444	0.0551909	1.000	-0.150730	0.186819
	Cu	0.0145889	0.0551909	1.000	-0.154185	0.183363
	Hg	0.0208444	0.0551909	1.000	-0.147930	0.189619
Fe	As	0.4533444*	0.0551909	0.000	0.284570	0.622119
	Zn	0.4633444*	0.0551909	0.000	0.294570	0.632119
	Mn	0.3387778*	0.0551909	0.000	0.170003	0.507552
	Cr	0.4813889*	0.0551909	0.000	0.312615	0.650163
	Cu	0.4779333*	0.0551909	0.000	0.309159	0.646708
	Hg	0.4841889*	0.0551909	0.000	0.315415	0.652963
Mn	As	0.1145667	0.0551909	0.381	-0.054208	0.283341
	Zn	0.1245667	0.0551909	0.283	-0.044208	0.293341
	Fe	-0.3387778*	0.0551909	0.000	-0.507552	-0.170003
	Cr	0.1426111	0.0551909	0.151	-0.026163	0.311385
	Cu	0.1391556	0.0551909	0.172	-0.029619	0.307930
	Hg	0.1454111	0.0551909	0.135	-0.023363	0.314185
Cr	As	-0.0280444	0.0551909	0.999	-0.196819	0.140730
	Zn	-0.0180444	0.0551909	1.000	-0.186819	0.150730
	Fe	-0.4813889*	0.0551909	0.000	-0.650163	-0.312615
	Mn	-0.1426111	0.0551909	0.151	-0.311385	0.026163
	Cu	-0.0034556	0.0551909	1.000	-0.172230	0.165319
	Hg	0.0028000	0.0551909	1.000	-0.165974	0.171574
Cu	As	-0.0245889	0.0551909	0.999	-0.193363	0.144185

	Zn	-0.0145889	0.0551909	1.000	-0.183363	0.154185
	Fe	-0.4779333*	0.0551909	0.000	-0.646708	-0.309159
	Mn	-0.1391556	0.0551909	0.172	-0.307930	0.029619
	Cr	0.0034556	0.0551909	1.000	-0.165319	0.172230
	Hg	0.0062556	0.0551909	1.000	-0.162519	0.175030
Hg	As	-0.0308444	0.0551909	0.998	-0.199619	0.137930
	Zn	-0.0208444	0.0551909	1.000	-0.189619	0.147930
	Fe	-0.4841889*	0.0551909	0.000	-0.652963	-0.315415
	Mn	-0.1454111	0.0551909	0.135	-0.314185	0.023363
	Cr	-0.0028000	0.0551909	1.000	-0.171574	0.165974
	Cu	-0.0062556	0.0551909	1.000	-0.175030	0.162519

*. The mean difference is significant at the 0.05 level.

Appendix XVI: November ANOVA test for trace metals in water

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Hg	10	0.001250	0.0021246	0.0006719	-0.000270	0.002770	0.0000	0.0050
As	10	0.038700	0.0106254	0.0033601	0.031099	0.046301	0.0200	0.0580
Zn	10	0.006240	0.0028953	0.0009156	0.004169	0.008311	0.0025	0.0110
Fe	10	1.271200	0.9676777	0.3060066	0.578965	1.963435	0.4100	3.7000
Mn	10	0.071200	0.0366418	0.0115872	0.044988	0.097412	0.0250	0.1350
Total	50	0.277718	0.6516858	0.0921623	0.092511	0.462925	0.0000	3.7000

Appendix XVII : February ANOVA test for trace metals in water

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
As	9	0.031822	0.0091374	0.0030458	0.024799	0.038846	0.0138	0.0475
Zn	9	0.021822	0.0093604	0.0031201	0.014627	0.029017	0.0100	0.0388
Fe	9	0.485167	0.2863855	0.0954618	0.265031	0.705302	0.1263	0.8775
Mn	9	0.146389	0.1170151	0.0390050	0.056443	0.236335	0.0250	0.4023
Cr	9	0.003778	0.0029423	0.0009808	0.001516	0.006039	0.0000	0.0088
Cu	9	0.007233	0.0077358	0.0025786	0.001287	0.013180	0.0000	0.0188
Hg	9	0.000978	0.0012163	0.0004054	0.000043	0.001913	0.0000	0.0025
Total	63	0.099598	0.1995158	0.0251366	0.049351	0.149846	0.0000	0.8775

Appendix XVIII **One-Sample Test for** trace metals in November

Mg/l	T	Df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
					Lower	Upper
As	8.542	9	0.000	0.0287000	0.021099	0.036301
Hg	0.372	9	0.718	0.0002500	-0.001270	0.001770
Zn	-5454.269	9	0.000	-4.9937600	-4.995831	-4.991689
Fe	3.174	9	0.011	0.9712000	0.278965	1.663435
Mn	1.830	9	0.101	0.0212000	-0.005012	0.047412

One-Sample Test for trace metals in February

Mg/l	t	Df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
					Lower	Upper
As	7.165	8	0.000	0.0218222	0.014799	0.028846
Zn	-1595.503	8	0.000	-4.9781778	-4.985373	-4.970983
Fe	1.940	8	0.088	0.1851667	-0.034969	0.405302
Mn	2.471	8	0.039	0.0963889	0.006443	0.186335
Cr	-98.110	8	0.000	-0.0962222	-0.098484	-0.093961
Cu	-772.810	8	0.000	-1.9927667	-1.998713	-1.986820
Hg	-0.055	8	0.958	-0.0000222	-0.000957	0.000913