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IMPACT OF GOLD MINING ACTIVITIES ON THE WATER QUALITY OF THE LOWER PRA RIVER

BY

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A THESIS SUBMITTED TO THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF GHANA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PHILOSOPHY DEGREE IN CHEMISTRY

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DECLARATION

I, Offei Samuel K. Dwamena of the Chemistry Department of the University of Ghana, do hereby declare that this thesis ‘Impact of Gold Mining Activities on Water Quality of the Lower Pra River’ is the outcome of research work undertaken by myself under the supervision of Prof. V. K. Nartey and Dr. R. K. Klake and that it has neither in part nor in whole been presented for another degree in this University or elsewhere except for references to works of other researchers which have been duly acknowledged.

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DEDICATION

To the glory of God

And

My family

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ACKNOWLEDGEMENT

With a heart full of thanks I am grateful to God for bringing me this far. It is His grace and strength that has kept me strong and active to this day.

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ABSTRACT

This study was conducted to assess the extent of Mercury (THg) contamination at four locations within the Shama-Mporhor Wassa catchment area of the Lower Pra River. Water, fish and sediment samples were taken twice with the longitudinal transect method at Daboase, Beposo, Bokorkope and Shama during the minor rainy season in October and at the apex of the dry season in March. Careful investigation of the Shama-Mporhor Wassa catchment area revealed that two of the locations Daboase and Beposo had been continuously impacted by the activities of Artisanal Gold miners (AGM). From the study, Total Mercury (THg) levels were found to have persisted in River water several kilometers downstream the second Artisanal Gold mining (AGM) location at Shama estuary for both seasons. Ten trace elements Mercury (Hg), Selenium (Se), Copper (Cu), Chromium (Cr), Lead (Pb), Iron (Fe), Manganese (Mn), Nickel (Ni), Zinc (Zn) and Cadmium (Cd) were determined in water, fish and sediment samples using the Atomic Absorption Spectroscopy (AAS) equipped with both Hydride Generation (HGAAS) for Selenium (Se) and Cold Vapour (CVAAS) for Total Mercury (THg). The levels of Total Mercury (THg) were largely above the WHO and USEPA guidelines for drinking water (1µg/L) and sediments (200 µg/Kg) respectively for the four locations investigated. Total Mercury (THg) exceeded the WHO, 2011 guideline value of 0.5 mg/Kg for fish species *Clarias submarginatus* but was below the guideline value for *Xenomystus nigri*. Mean concentration of Cd and Fe exceeded the WHO, 2011 guideline values for drinking water for the wet season. The other trace elements Zn, Ni, Cu, Cr, Se, Mn, and Pb had their mean concentration below the WHO, 2011 guideline values for drinking water. Apart from the mean concentration of Cd that exceeded the Canadian Interim Sediment Quality (ISQG) guideline value of 0.6 mg/Kg for the wet season, Cr, Cu, Zn, Ni and Pb were below their respective guideline values for both seasons. Statistical parameters such as the Coefficient of Variation and the Paired Sampled T- test were used to investigate the spatial and temporal variation of trace elements, water physico-chemical parameters and nutrients. Physico-chemical parameters such as total alkalinity, pH and Biochemical Oxygen Demand (BOD) were affected by seasonal variations as evident from the Paired Sampled T- Test. Environ metrics model Principal Component Analysis (PCA) proved to be an effective tool for identifying the possible sources (natural and anthropogenic) of trace elements and their relationship with water physico-chemical parameters. The model showed that Total Suspended Solids (TSS) had a major role to play in the distribution of Total Mercury (THg) and Selenium (Se) across the four locations in the study area. Generally, the Lower Pra River was found to be polluted and of poor water quality in terms of Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and microbes such as *E. coli*, Total Coliform (TC), Fecal Coliform (FC), and Total Heterotrophic Bacteria (THB). Microbial contamination was also found to be connected to human activities along the banks of the river.

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ACRONYMS

AGM	Artisanal Gold Mining Activities
APHA	American Public Health Association
AWWA	American Water Works Association
BAF	Bioaccumulation Factors
BOD	Biochemical Oxygen Demand
Co.V	Coefficient of Variation
CRM	Canadian Reference Material
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
EDTA	Ethylenediaminetetra-acetic Acid
EPA	Environmental Protection Agency
FC	Faecal Coliform
HMWC	High Molecular Weight Complex
ISQG	Canadian Interim Sediment Quality Guidelines
PCA	Principal Component Analysis
QC	Quality Control
TC	Total Coliform
TDS	Total Dissolved Solids
THB	Total Heterotrophic Bacteria
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
WEF	Water Environmental Federation
WHO	World Health Organization

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TABLE OF CONTENTS

University of Ghana http://ugspace.ug.edu.gh

University of Ghana http://ugspace.ug.edu.gh

CHAPTER THREE 51

University of Ghana http://ugspace.ug.edu.gh

University of Ghana http://ugspace.ug.edu.gh

LIST OF TABLES

University of Ghana http://ugspace.ug.edu.gh

LIST OF FIGURES AND PLATES

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CHAPTER ONE

1.0 INTRODUCTION

1.0.1 Background to study

Environmental pollution is one of the major problems nations are facing around the world. In recent times this problem has become more difficult in light of increasing population and industrialization. This increase in population has brought about massive urbanization, industrialization and the depletion of natural resources (Chamie, 2004).

Industrial waste may contain contaminants that destroy or alter the environment we inhabit. Many countries ignore industrial waste management since it is expensive. Heavy metals are by-products from many industrial processes and varying amounts are released into the atmosphere, marine and freshwater environment. They affect not only the ecosystems, but also human life through Bio-accumulation and Bio-augmentation in the food chain. They are present in environmental compartments such as water (fresh water and marine systems), soil or sediments and biota but are mostly hazardous when they enter the food chain (Robson and Neal, 1997). Heavy metals are toxic even at very low concentrations (Volesky, 1990; Alkorta *et al.*, 2004).

Mineral elements are required by living organisms for growth and development. Mineral elements can be divided into two main groups: essential and non-essential minerals. Each of these groups can be further divided into major (macro) and trace (micro) elements. An essential element is one required for maintenance of life and its deficiency results in an impairment of a function from optimal to suboptimal (Mertz, 1981; Nyarko, 2012). Essential elements needed in large quantities are referred to as macro-element examples are: Hydrogen (H), Carbon (C), Nitrogen (N), Oxygen (O), Magnesium (Mg), Carbon (C), Sodium (Na), Phosphorous (P), Sulfur (S) and Potassium (K).

Essential elements are usually bound to proteins and in abnormal quantities are deemed toxic to the organism. These elements include Copper (Cu), Vanadium (V), Magnesium (Mg), Calcium (Ca), Phosphorous (P), Sulfur (S), Potassium (K), Boron (B), Manganese (Mn), Iron (Fe), and Zinc (Zn). Non-essential elements are neither beneficial nor harmful if present in sufficiently low amounts but their deleterious effect begins to show with the gradual accumulation in biological tissues. Examples are heavy metals such as Cadmium (Cd), Mercury (Hg), Arsenic (As), Lead (Pb) among others. These metals are said to be cumulative poisons (Nyarko, 2012).

Harrison and De Mora, 1996 reported of a complex relationship between the total concentration of heavy metals in the environment and its ability to cause toxic effect in organisms. Two constraints they identified are the speciation of the element and the condition of the organism. Elemental speciation especially it's partitioning between host association in aqueous and particulate phase influences bioavailability. Most heavy metals are damaging to marine organisms in their organometallic form. Mercury is a classic example which is mostly bioavailable and toxic as methyl mercury (CH_3Hg^+). The environmental location and conditions affect the potentially toxic substance in the organism. Specific environmental conditions such as temperature, dissolved oxygen, chemical oxygen demand and pH affect metal-organism interaction.

The release of Mercury (Hg) into the environment can be through natural means such as volcanic eruption and weathering as well as a variety of anthropogenic sources such as mining, burning of fossil fuel, and combustion of municipal and medical waste (Oduro *et al.*, 2012; Jackson and

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Jackson, 1995). Due to its persistence and high mobility, Mercury (Hg) exhibits an age related accumulation and strong bio-magnification in the food web (Nigro and Leonzio, 1996).

Artisanal small-scale gold mining (AGM) is the single largest contributor to intentional discharge of mercury (Hg) to the environment with a global estimate of 650-1000 tons of mercury (Hg) released per annum (AMAP/UNEP, 2008). The only source of contamination for areas not known for having direct mercury input is through atmospheric deposition. It is therefore, normally transported from likely sources of emission such as mining and smelter sites to locations remote from the pollution centers (Schroeder and Munthe, 1998).

Artisanal Gold miners use simple primitive technology to extract gold from soils and river sands. This process begins with the dredging of river sand and centrifugal separation of the crushed gold ore to produce a concentrate. The concentrate is mixed with mercury in amalgamation drums. Mercury binds to gold in a solution known as an amalgam and this solution is separated from the concentrate matrix by panning (Telmer and Veiga, 2006). Mercury is then recovered from the amalgam by roasting it in partially enclosed retorts or even in the open air. Pure gold produced contains up to 5% mercury (Hg). Mercury not recovered properly adds to atmospheric release especially in towns where Artisanal gold mining (AGM) activities occur.

Public concern over mercury pollution reached its peak in the 1970’s following a number of incidents where the discharge of elemental mercury into water bodies was linked to fatalities and severe health problems in local residents (Jackson and Jackson, 1995). The effect of mercury (Hg) pollution may therefore not just be limited to the geographical location of the discharge point (local pollutant) but several kilometers radius (global pollutant) of the point of original discharge (Harada *et al*., 2001). Mercury (Hg) concentration in sediments have been found to

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have a strong correlation with soil organic matter since this element in question has the tendency to bind with humate ligands. An abundant organic matter environment favors mercury methylation due to bacteria action (Pak and Bartha, 1998; Gilmour *et al.*, 1992).

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

The antagonistic phenomenon between selenium (Se), both an essential and a toxic trace element and mercury (Hg) was first reported by Parizek and Ostadalova, 1967. Several mechanisms have been proposed for mercury (Hg) and selenium (Se) interaction. The most prominent is the formation of an inorganic and (or) protein Hg-Se complex although this complex formation remains unclear. Numerous other studies have been conducted between the two elements in mammals and the findings tend to support an antagonistic effect between selenium (Se) and mercury (Hg).

Since most of the studies have been conducted on mammals with an almost 1:1 Hg/Se molar ratio established in various mammalian organs, the study of Hg and Se especially in fish food and in aquatic environment will provide more information on the antagonistic effect of Se on Hg especially the bioaccumulation of Hg in the presence of Se in Hg contaminated water bodies.

1.1 PROBLEM STATEMENT

The Pra river system, the longest in south western Ghana, takes its source from the Kwahu plateau and flows 240 km into the Gulf of Guinea through its estuary at Shama (Ayibotele and Nerquaye-Tetteh, 1989, Oduro *et al.,* 2012). The river is divided into two parts which is the Upper and Lower Pra. The upper part of the main Pra river watercourse and its main tributaries are known to have direct input of mercury due to Artisanal Gold Mining (AGM) operators popularly known as galamsay operators and the mode of extraction of gold is through amalgamation (Bonzongo *et al.*, 2003; Spiegel, 2009; Donkor *et al.*, 2006[a, b]).

According to Donkor *et al.*, 2006[b], the communities along the lower reaches of River Pra were widely acclaimed to have no direct Hg input source since these areas were not known for AGM activities. From their studies, traces of Hg were found in sediments and in River water at areas of the lower catchment regions of the Lower Pra River not known for AGM activities. There is even a greater worry as these AGM operators pollute the water body with their effluent and destroy the entire ecosystem. When they are done, they migrate to new areas along the watershed to continue their activities.

Presently AGM activities are found in areas such as Beposo and Daboase located in the lower region of the Lower Pra catchment area and previously not known for AGM operations. In their operations, they make use of mobile rigs which constitute rafts with mechanized dredging equipment mounted on them. They also heap piles of sand into the river which aids in their operations (Oduro *et al.*, 2012).

The discharges of Hg from mining effluent into the river along with other contaminants affect the water quality thereby increasing the cost of water treatment at the water treatment plant located at Daboase. In June of 2013, the Minerals' Commission together with the Ghana Military raided certain AGM sites especially at Beposo and Daboase in the Shama and Mpohor Wassa district respectively in an attempt to clamp down on the activities of illegal gold miners (Ghana News Agency, 2013).

Selenium (Se) has been known to have an antagonistic effect on Hg from polarography studies where investigations into the standard redox potential of mercurous salts and various organic selenium compounds in unbuffered systems clearly exhibited this phenomenon (Feroci *et al.*, 2005). However few studies have been conducted in natural systems especially in aquatic environments on this phenomenon. The investigation of both Se and Hg in various aquatic components will shed more light on the relationship between the two elements (possible antagonism) and the relationship the two elements have with other trace elements.

This study firstly is aimed at assessing the levels of Hg pollution in the Lower Pra Shama - Mpohor Wassa catchment area river water to explore the possible impact of Hg pollution on water supply and secondly to investigate the possible antagonistic effect of Se on the toxicity of Hg in various aquatic components such as fish, sediments and river water.

1.1.1 Research hypothesis

This study was carried out on the bases of the following hypothesis

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

  Ha : Hg is not used by AGM operators in the extraction of gold

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

  Ha : Hg is not known to travel several kilometers from source of pollution
- Ho : Se plays an important role in the antagonism of Hg

  Ha : Se does not play an important role in the antagonism of Hg
- Ho : Water physicochemical parameters differs significantly with seasonal changes

  Ha : Water physicochemical parameters do not differ significantly with seasonal changes

1.1.2 Study objectives

The main objective of the study are to determine the concentration levels of Hg and Se in water, fish, and sediment samples from the lower catchment regions of the Lower Pra River and how these elements if present affect each other.

Specifically, the study seeks to:

- Determine the concentration of Mercury (Hg) together with Selenium (Se), Cadmium (Cd), Lead (Pb), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Chromium (Cr), and Zinc (Zn) in the major environmental compartments: water, sediment and fish
- Assess the relationship of Hg and Se on other elements and certain Physico-Chemical parameters like pH in the study area
- Assess the spatial and temporal variation of trace elements and water Physico-Chemical parameters along the water course
- Investigate the levels of microbial contamination in water as a potential cause of waterborne diseases

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- Determine the overall quality of water as source for direct consumption and for the water treatment plant situated at Daboase

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 DEFINITION AND PROPERTIES OF HEAVY METALS

Different definitions have been proposed for the term heavy metals – some based on density or specific gravity, some on atomic number or weight and some on chemical properties or toxicity. Bjerrum, 1936 defined heavy metal as metals with elemental densities above 7 g/cm^3 whereas Morris, 1992 based his definition on greater than 5 g/cm^3.

The terminology is sometimes applied indiscriminately and it is not unusual to find a list of heavy metals that includes elements like aluminum (Atomic mass 26.98 gmol^{-1} and specific gravity of 2.7). Some studies have used the terms trace or toxic elements in place of heavy metals. Glanze, 1996 reported of 35 metals of environmental concern due to occupational or residential exposure; 23 of these were "heavy metals": antimony (Sb), arsenic (As), bismuth (Bi), cadmium (Cd), cerium (Ce), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), gold (Au), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), tellurium (Te), thallium (Tl), tin (Sn), uranium (U), vanadium (V) and zinc (Zn).

Heavy metals exist either in the solid phase or in solution as free ions and are associated with several soil components which determines their bioavailability (Track *et al.*, 2006). They have variable oxidation states, paramagnetic and form colored complex ions. Heavy metals are non-biodegradable, non-thermodegradable, possess long biological half-lives and residence times.

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2.2 SOURCES OF HEAVY METALS

A natural source of heavy metals into the environment is volcanic eruption through volcanic ash. Nriagu, 1990 reported that volcanic activity is one major source of atmospheric cadmium and it is estimated to contribute about 820 metric tons each year. Heavy metals occur as constituents of primary and secondary minerals through the process of inclusion, adsorption and solid solution formation termed as co-precipitation (Sposito, 1989). Atmospheric depositions as a result dust storms and wild forest fires are other natural source of heavy metal pollution (Nriagu, 1990; Nadiu *et al.,* 1997).

Anthropogenic sources of heavy metals include Agricultural activities such as pesticide, fertilizer, herbicide application, and contaminated irrigation water sources. Also industrial activities such as mining and smelter, the use of lead and manganese as anti-knock agents in gasoline, exhaust fumes from cars (Nriagu, 1990; Kakulu, 2002), heavy metal additives in building materials like paints, aerosol and sewage discharge, among others, contribute to the pollution load in the environment (Manoj *et al.,* 2012).

2.3 AN ENVIRONMENTAL CLASSIFICATION OF METALS

A more recent attempt at classifying environmentally important metals has been made by Richardson and Nieboer, 1980. Their system builds on the earlier concepts of Ahrland *et al.*, 1958 but takes into account bonding due to both covalent and ionic interactions. The covalent index $X^2_m r$ (X_m = metal ion electronegativity, r = ionic radius of metal) is a reflection of the ability of the metal to accept electrons from a donor ligand. This is the chemical parameter used in differentiating between classes A, B and borderline metals as suggested by Ahrland *et al.*, 1958. Values for the index are smallest for class A and largest for class B ions. The ionic index

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Z^2/r measures the possibility of ionic bond formation and thus more highly charged species tend to be found on the right-hand side of the diagram.

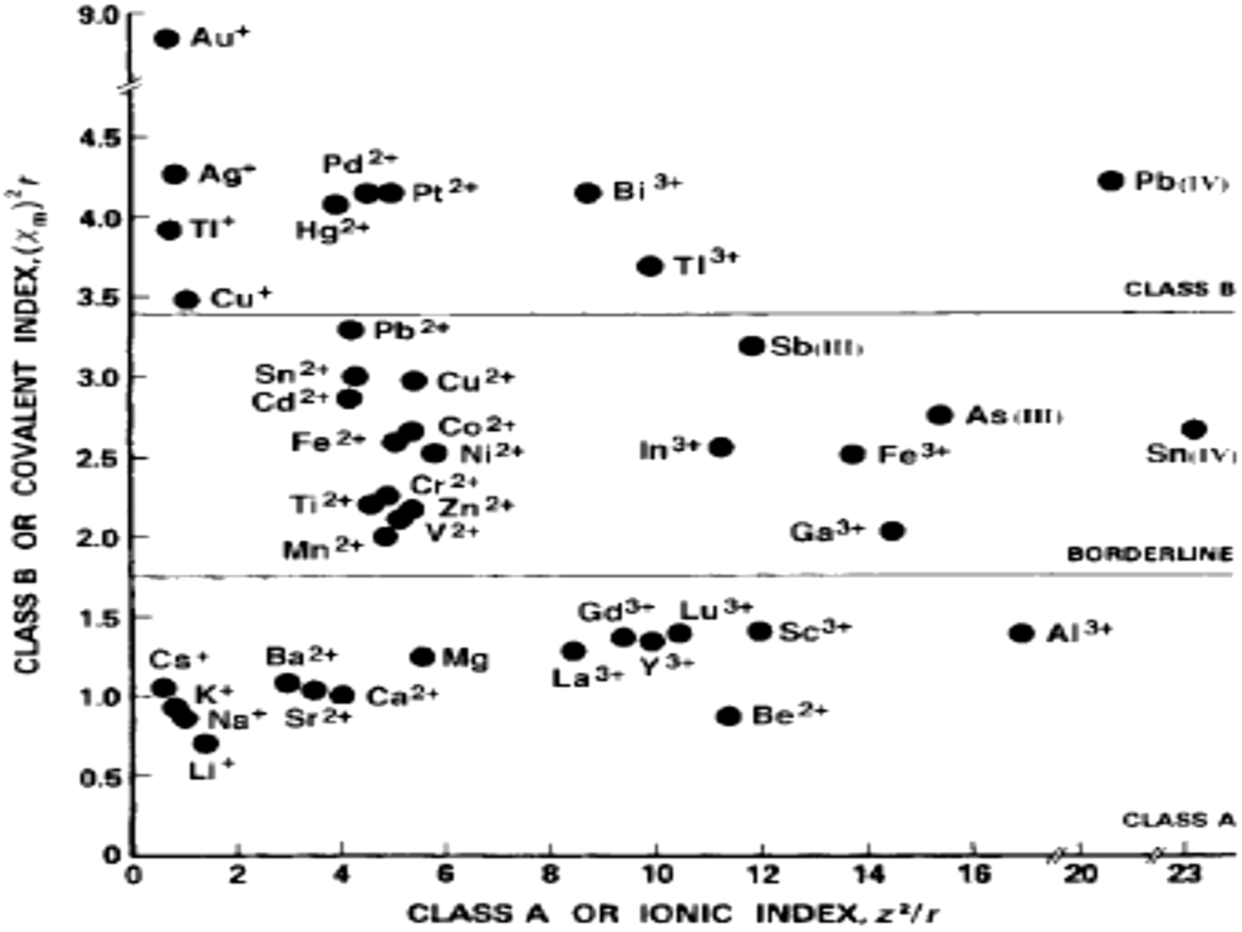


Figure 2.1: Environmental classification of metals courtesy Nieboer and Richardson, 1980. Subdivisions are based on Ahrland *et al.*, 1958, classification indicated by horizontal lines.

Elements such as potassium (K) and calcium (Ca) which serve as macro-nutrients for micro-organisms, plants and animals are found in class A. When dissolved in water and in their interaction with complexing ligands, they are usually found to be associated with oxygen electron donors. Most biological micronutrients such as manganese (Mn), copper (Cu), and zinc (Zn) are found in the borderline group. Borderline ions form stable complexes with a variety of electron donor atoms such as oxygen, nitrogen, and sulfur. Class B metals include several that are known to be toxic to organisms. Toxicity increases in the order Class A< borderline < Class B metals.

While Class B ions have a stronger affinity for sulfur donor atoms, they also form more stable complexes with oxygen-donating compounds than do borderline and Class A metals (Figure 2.1). The ability to form methylated derivatives that are stable in aqueous solutions is another feature that is characteristic of metals in this class (eg mercury (Hg)). Methyl derivatives of Class A metals decompose in water and the same is true of most of most borderline metals.

2.4 OVERVIEW OF RESEARCH OF MERCURY IN GHANA

Artisanal gold mining (AGM) is one such anthropogenic activity that has resulted in the use of an enormous amount of metallic mercury (Appoh, 2010). A lot of studies have been carried out worldwide to investigate the impact of AGM operations on the environment in locations known to have gold deposits. Several studies have been carried out on mercury in Ghana particularly in areas known for gold mining. Most of the researches have been based on rivers and streams particularly in the southwestern belt of Ghana due to the alluvial deposits of gold by these water bodies.

For instance Donkor *et al.*, 2006[b] and Oduro *et al.*, 2012 all studied total mercury (THg) in the Lower Pra River which serves as source for drinking water for communities along the basin. Donkor *et al.*, 2006[b] reported that THg levels in drinking water were below the WHO guideline values of 1000 ng/L but were above the standard of 12 ng/L set by the USEPA for the protection against chronic effect to aquatic wildlife. Oduro *et al.*, 2012 reported of THg levels in drinking water above the WHO guideline limits in communities where the studies were carried out. Bannerman *et al.*, 2003 reported of THg and Arsenic (As) contaminations in water and sediments in gold mining regions in the Ankobra river basin. Hayford *et al.*, 2008 investigated the presence of toxic elements including THg in samples of cassava, plantain and soil from mining communities around Tarkwa. They reported that THg levels in cassava, plantain and soil were higher than the permissible values proposed by the FAO for food and the WHO for soil.

Some studies have also been conducted on fish species, human head hair, urine and blood in gold mining areas. Voegborlo *et al.*, 2010 assessed both THg and methyl mercury (MeHg) in human head hair to evaluate the extent of human exposure to mercury. They reported that 97% of Hg in the human head hairs was in its toxic form which is MeHg. THg was also assessed in muscles of fish by Ntow and Khwaja, 1988 from various coastal towns and Agorku *et al.*, 2009 from water reservoirs for hydroelectric power generation. Both studies reported that THg levels in fish muscles were below WHO limit of 0.5 µg/g since the aquatic environment have not been significantly impacted with mercury.

In spite of all these studies, there is still a need for a continuous environmental assessment of mercury and this time around its interaction with selenium since the relationship between the two elements remains unclear to several researchers and hence the result obtained will provide an insight at a possible relationship between the two elements.

2.5 MERCURY

2.5.1 Chemical fate

Mercury is generally found at very low concentrations generally less than 10ng/g in crustal materials such as granites, feldspars and clays (Davis *et al.*, 1997), and in the range of 40 to 200ng/g in soils and sediments that are not directly impacted by anthropogenic discharges (NRC, 2002). Mercury is found generally in aquatic systems in its organic form (about 95 to 99%) and in sediments rather than the dissolved phase.

Mercury (Hg) occurs in traces in ore deposits and together with sulfur as Cinnabar (HgS). Anthropogenic sources of mercury (Hg) include various industrial discharges and abandoned mines, coal combustion and medical waste incineration. Inorganic mercury exists in three known oxidation states: as elemental mercury (Hg°), as mercurous ion (Hg^{+}) and as mercuric ion (Hg^{2+}). The oxidation state of mercury in an aqueous environment is depends on the redox potential, the pH, and the nature of the anions and other chemical forms present with which mercury may form stable complexes (Reimers *et al.*, 1974). Mercurous compounds (Hg^{+}) are not common as they are rapidly oxidized to mercuric forms (Hg^{2+}) by hydrolysis (Booer, 1944).

The presence of organic matter in the sediments can either enhance or retard mercury mobility by either forming soluble organic complexes or the precipitation of mercury as mercuric sulfides (HgS). In highly anaerobic systems, the mercuric sulfide may be reduced to elemental mercury and sulfide, whereas under alkaline conditions with high levels of sulfides the more soluble mercuric disulfide complex (HgS_2^{2-}) may exist.

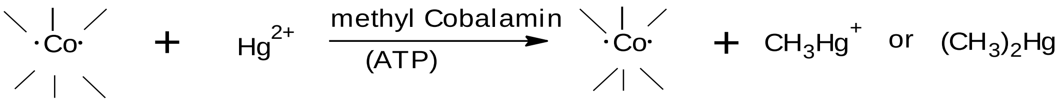
In general, the sediment water interface tends to accumulate inorganic mercury, and both pore water and the water column are possible sites for mercury methylation since these sites are rich in organic ligands (NRC, 2002). An important characteristic of mercury is its low solubility as a result of its high probability to coagulate, i.e., to be removed from the soluble aqueous phase. This occurs through a number of physicochemical processes such as precipitation as mercuric sulfide, co-precipitation with hydrated iron and manganese oxides and complexation with organic matter. The solubilization /coagulation of mercury depends on the forms of mercury present, the amounts and nature of the organic and inorganic matter present, as well as on the environmental conditions, e.g., pH, chloride levels (NRC, 2002).

Balogh *et al.,* 1998 showed that total mercury levels in water are strongly correlated with total suspended solids concentrations, suggesting that mercury can remain suspended in the water column attached to colloidal and particulate matter. Pak and Bartha, 1998, reported that in aquatic systems, dissolved mercury can be partitioned between inorganic and organic forms largely controlled by rates of methylation and demethylation by microorganisms.

Organic mercury complexes remain important influences on the mobility and bioavailability of mercury. Dissolved mercury in natural water systems exists mostly in organic forms and a high level of mercury in fish tissues is observed by Gill and Bruland, 1990. Mercury methylation is a biologically mediated process between dissolved inorganic mercury and, primarily, sulfate reducing bacteria (Driscoll *et al*., 1994). Factors affecting methylation of mercury aquatic system include the amount of dissolved inorganic mercury and physicochemical characteristics of the aquatic system such as pH, organic matter, dissolved sulfate and sediment sulfide (Pak and Bartha, 1998). For example, mercury methylation activity in sediments was found to be positively correlated with the level of organic matter (Driscoll *et al*., 1994).

Methylation occurs under anaerobic conditions via a pathway which involves the transfer of a methyl group from methylcobalamin, a derivative of vitamin B_{12} to the mercury atom under reducing conditions.

[1]



Courtesy Nutifafa, 2007

The relative abundance of methylated mercury species is of particular concern since these compounds are highly toxic, bioavailable and can enter the food chain by direct uptake from solution (Driscoll *et al*., 1994). Methyl mercury is unique since the methyl group induces lipophilicity whiles Hg (II) has a tendency to bind with sulfhydryl (or selenol) groups (Craig, 1986; Carty and Malone, 1979). The bond between mercury and the methyl group is stable, while methyl mercury is membrane permeable and thiol reactive, properties which contribute to the toxicity, long biological half-time, and the tendency toward bioaccumulation of mercury in aquatic organisms (NRC, 2002).

The organomercuric salts exhibit properties and reactions similar to those of inorganic mercuric salts, and thus do not bioaccumulate as well as methyl mercury. Organomercuric compounds other than methyl mercury species are volatile, thermally unstable, light sensitive and decompose by ultraviolet radiation to elemental mercury and free radicals (NRC, 2002).

2.5.2 Mercury in mine effluents and receiving waters

Effluent from mines most likely contains dissolved inorganic species of mercury. Depending on the pH two species of inorganic mercury may exist. At high pH, hydrated mercuric oxide ($HgO \cdot H_2O$) is the dominant form whiles mercuric chloride ($HgCl_2$) exists at low pH and aerobic conditions. However, at high concentrations of chlorides (and low pH), the very stable and water-soluble mercuric tetrachloride complex ($HgCl_4$) will form. A variety of biogeochemical conditions may influence the behavior of mercury in the receiving environment. The formation and dissolution of inorganic Hg solids is controlled by redox and pH conditions and redox conditions in particular occur over a wide range in surface water environments (NRC, 2002).

2.5.3 Interactions with Other Mineral Element

Dissolved mercury adsorbs strongly to sediment and suspended solids including organic material and Fe or Mn oxy-hydroxides (Balogh *et al.*, 1998). Gagnon and Fisher (1997) reported the binding strength of mercury to sediments to be very high at near neutral pH values and little desorption (less than 10%) at lower or acidic pH values (pH <5). The tendency of inorganic mercury and mercury bound organic complexes to adsorb onto these iron oxy-hydroxide surfaces decreases mercury mobility in water (Schutler, 1997).

2.5.4 Mercury environmental cycle

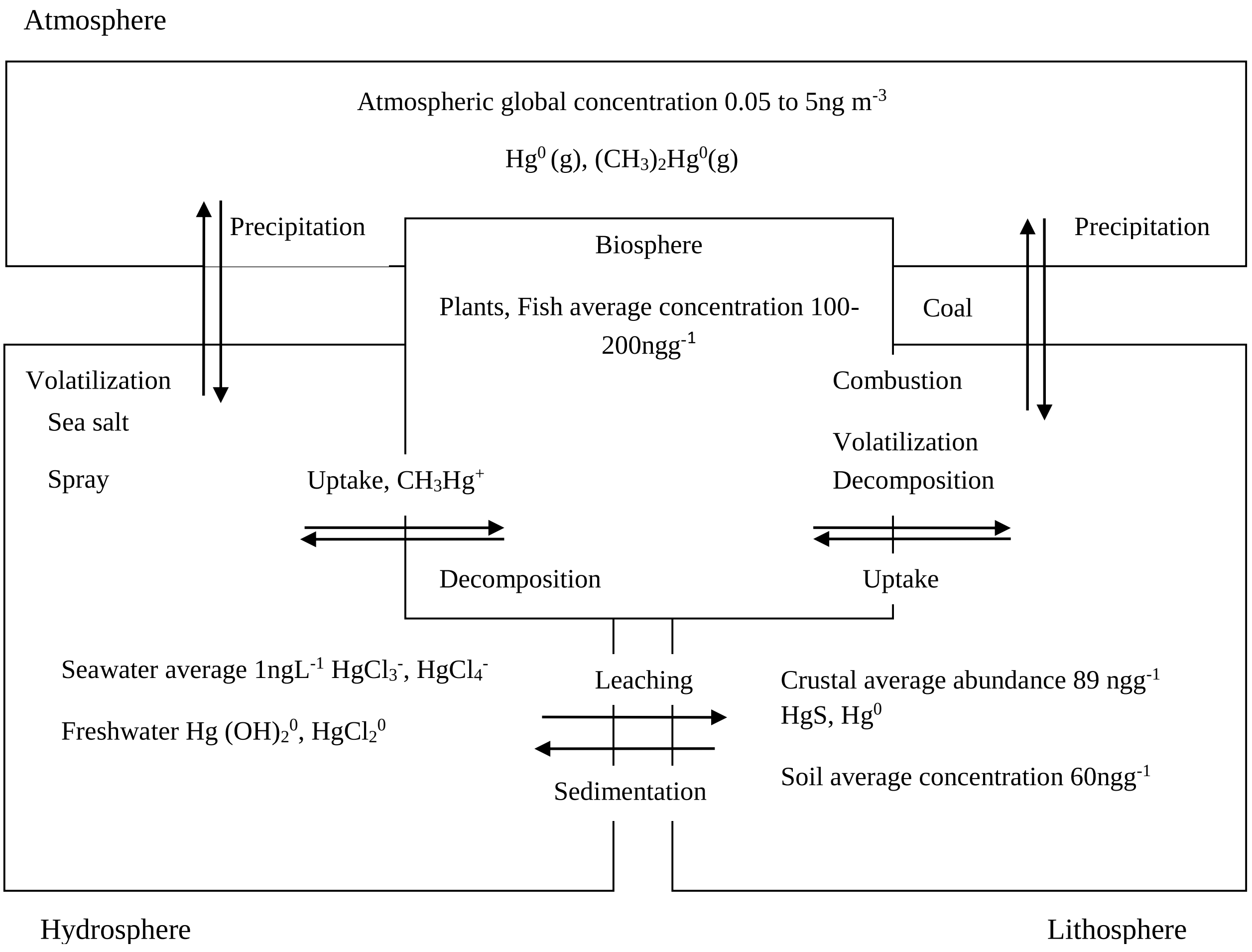


Figure 2.2: Major components of the environmental cycle of mercury (Mason *et al.*, 1994; Mason and Sheu, 2002)

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2.6 SELENIUM

Total selenium concentrations in natural waters have been reported to be in the range of 0.1 to 1.5 mg/L (Demayo *et al.*, 1979). Natural selenium concentrations in solids range from 0.05 mg/g in ultramafic to felsic igneous rocks, up to 0.08 mg/g in limestone and as high as 0.6 mg/g in shale's (Faure, 1991). Selenium is a metalloid and resembles sulfur in many of its properties and often occurs together with or substituted for sulfur in soils and rocks. For example, selenide can substitute for sulfides in pyrite and is known to accumulate to 300 mg/g in sedimentary pyrite.

Selenate can also substitute for sulfate in very hydrous sulfate salts such as jarosite, but does not substitute for sulfate in less hydrous sulfate salts such as gypsum. Anthropogenic sources of selenium include copper, lead and nickel refining and sulfuric acid manufacturing. Selenium is an essential element, with a recommended daily intake of 1.7 mg/Kg body weight for infants, and 0.9 mg/kg body weight for adults. Most of the natural human intake arises from food (approximately 75%) with the remainder coming mainly from drinking water (WHO, 1996).

2.6.1 General Fate Information

Selenium exists in four oxidation states in the natural environment - selenide (Se^{2-}), elemental selenium (Se^{0}), selenite (Se^{4+}) and selenate (Se^{6+}). Selenium cycling in the environment is controlled by biogeochemical processes. Microbial methylation is an important pathway of the biogeochemical selenium cycle (Doran, 1982). Organic forms of selenium include seleno amino acids, methyl selenides, methyl seleninic esters, methyl selenones, and methylselenonium ions (Cooke and Bruland, 1987). These organic compounds occur as products of bio-methylation and are more volatile than inorganic forms of selenium (Atkinson *et al.*, 1990). Bacterial selenium methylation occurs in temperate lake sediments (Chau *et al.*, 1976) and is stimulated by organic carbon and temperature (Chau *et al.*, 1976; Doran, 1982; Thompson-Eagle and Frankenberger, 1990a, 1990b).

The greatest proportion of total selenium in lakes and streams can normally be found in the sediments, reflecting a net removal of selenium from the water column (Cutter, 1989; Lemly and Smith, 1987). Cutter (1985, 1989) examined sedimentary selenium by sequential extraction of sediments. The selenide (Se^{2-}) plus elemental selenium (Se^0) fraction (calculated as the difference between 'total' selenium and (selenite plus selenate) accounted for more than 93% of sedimentary selenium in five lakes. Sequential extraction has also shown that more than 90% of the sedimentary selenium is associated with organic matter and is identified as Se^{-2} plus Se^0, while less than 10% of the sedimentary selenium is associated with iron and manganese oxides (Cutter, 1989).

Rudd *et al.*, 1980 studied selenium scavenging by sediments and demonstrated that selenium sedimentation was effectively halted by sealing off the bottom of an experimental mesocosm from the sediments. These results suggest further that selenium can be effectively scavenged by natural sediments and that sediments are an important sink for selenium loadings from mining. Dissolved inorganic selenium occurs in mining effluents as both selenite (Se^{4+}) and selenate (Se^{6+}) oxidation states. Inorganic selenium speciation is controlled by redox conditions, pH, and complexation with metals and interactions with solids such as sorption processes.

Selenate (SeO_4^{2-}) predominates under alkaline oxidizing conditions whilst under moderately oxidizing conditions, the selenious acid species selenite (SeO_3^{2-}) and biselenite ($HSeO^{3-}$) predominate. Elemental selenium (Se^0) is relatively stable at all pH values in waters that are free of oxidizing and reducing agents (Faust and Aly, 1981). Selenide, primarily as hydrogen selenide

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(HSe^-) can form in environments with a large reservoir of free electrons, such as organic rich sediments.

An important process regulating the dissolved concentration and mobility of inorganic selenium is adsorption onto solid surfaces (Balistrieri and Chao, 1990). Selenite (Se^{4+}) efficiently adsorbs onto both iron and manganese oxides. Selenite (Se^{4+}) adsorption decreases with increasing pH and is further inhibited by the presence of dissolved phosphate, silicate, and molybdate (Balistrieri and Chao, 1990). Selenate (Se^{6+}) rather adsorbs weakly to clays and Fe oxy-hydroxides and does not adsorb to manganese oxides. Selenate adsorption (Se^{6+}) is further limited by competitive effects with sulfate at neutral pH. Therefore, sorption reactions can reduce concentrations of dissolved selenite but do not significantly influence selenate concentrations, particularly in sulfate rich waters.

2.6.2 Selenium and Mercury in Organisms: Interactions and Mechanisms

There are numerous possible mechanisms for the interaction between mercury and selenium. In principle, the interaction may be direct or indirect (or a combination). A direct interaction may involve formation of complexes between some chemical form of selenium and some chemical form of mercury, the simplest possibility being mercury selenide (Hg-Se), although different complexes may be anticipated.

Also, selenium and mercury may compete for binding sites in proteins (most probably thiols) or other compounds. A competition may occur at the "receptor sites" where mercury and selenium exert their toxic effects, but a complex binding or a competition at other binding sites may also affect the metabolism (absorption, distribution, biotransformation or excretion) which may affect the "receptor site" concentration secondarily (Skerfving, 1978).

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An indirect interaction may involve effects by one compound on any metabolic function affecting the other. A competition may occur on the "receptor sites" where mercury and selenium exert their toxic effects, but a complex binding or a competition at other binding sites may also affect the metabolism (absorption, distribution, biotransformation or excretion) which may affect the "receptor site" concentration secondarily. There are numerous possibilities. Enzyme systems performing biotransformation of one compound may be affected by the other, or membrane function may be impaired by one compound, causing an alteration of membrane passage of the other (Skerfving, 1978).

Parizek and Ostadalova, 1967 reported the toxicity of Hg^{2+} to be reduced when Hg^{2+} doses of 0.002 mmol/Kg body weight was administered to rats followed by the same dose of selenite (SeO_3^{2-}) one hour later. It was observed by Burk *et al.*, 1974 that the intravenous co-administration of rats with mercuric chloride and sodium selenite resulted in an increased presence of Hg and Se in the bloodstream and this was caused by the presence of a single compound with a Hg:Se molar ratio of 1:1. Burk *et al.*, 1974 and later Naganuma and Imura, 1980 proposed that both elements bind to a single plasma protein to form high molecular weight complexes (HMWC).

Burk *et al.*, 1974 and Naganuma *et al.*, 1984 proposed that the interaction between Hg^{2+} and selenite which occurred primarily in the blood stream resulted in HMWC assimilation by the liver (Imura and Naganuma, 1985). HMWC might undergo proteolytic processes to form insoluble inert Hg-Se complexes that subsequently accumulate in liver tissue (Nagamuna and Imura, 1981). Selenoprotein-*P* in plasma was found to bind Hg and Se when Hg^{2+}, selenite (SeO_3^{2-}), and glutathione (GSH) were added to serum of rats. This complex is described as {(Hg-Se)n}m-Selenoprotein-*P*, where *n* is the number of atoms forming the colloidal mercuric-selenide complex and m as the number of binding sites for the mercuric selenide complexes on Selenoprotein-*P* (Yoneda and Suzuki, 1997).

After entering the bloodstream selenite is rapidly taken up by erythrocytes and reduced by glutathione (GSH) to selenide (HSe^-), which effluxes and reacts in plasma with albumin bound Hg^{2+} (Gailer *et al.*, 2000) to form the {(Hg-Se)n}m-Selenoprotein-*P* complex in blood. Extended studies showed that the (Hg-Se) complex had a five molecule GSH bounded to it and this made it water soluble. Two molecules of -GSH could be stripped off, and therefore the final complex would be $\{(Hg\text{-}Se)_{100}(GS)_3\}_{35}$-selenoprotein-*P* (Yang *et al.*, 2008).

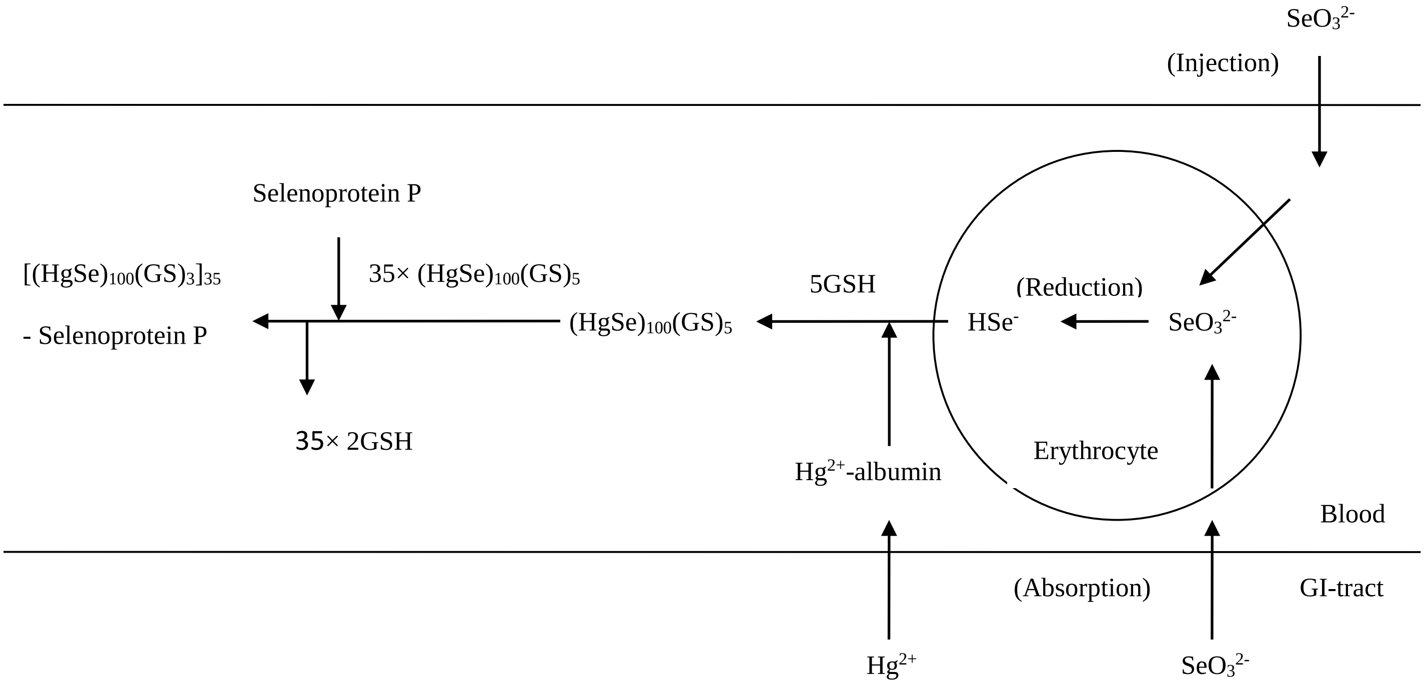


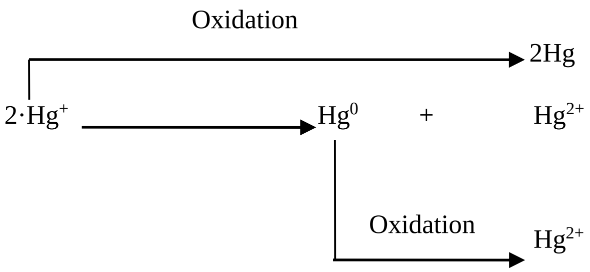
Figure 2.1: An illustration of the possible mechanism of interaction between selenite and Hg^{2+} in blood courtesy Yang *et al.*, 2008

A synergistic toxicity between dimethylselenide ($(CH_3)_2Se$) and Hg^{2+} has also been reported when selenite was given 1hr before Hg^{2+}, causing the death of a rat (Parizek 1980; Naganuma *et* *al.*, 1984). The dead animal showed symptoms of dimethylselenide intoxication, and the death was thought to be caused by the synergistic effect of Hg^{2+} and dimethylselenide generated from selenite metabolism. Dimethylselenide in the presence of Hg^{2+} have been shown to be more than 10000 times toxic than when administered alone (Parizek, 1980).

Three other Se compounds, selenite, selenocystine, and selenomethionine, have been less frequently used than selenite (SeO_3^{2-}) in studies on the antagonism with Hg^{2+}. Since all of the above forms of selenium could be transformed to Se^{2-}, a metabolic intermediate generated in vivo and which will interact with Hg^{2+} to form Hg-Se complexes (Yang *et al.*, 2008). Methyl mercury might undergo hemolysis in the body to form $^{\cdot}CH_3$ radicals and inorganic Hg (Hg^0 and Hg^{2+}), which lead to the generation of reactive oxidative species (ROS) and the inhibition of oxidative enzymes (Ganther 1978; Atchison and Hare, 1994; Garg and Chang, 2006).

The formation of the non-bioavailable Hg-Se complex affects selenium availability for selenoprotein synthesis. Sufficient selenium should not only guarantee the amount needed for selenoprotein synthesis, but also bind to Hg^{2+} released from CH_3Hg^+ breakdown to form Hg-Se *in vivo*. Selenium could be a scavenger of inorganic mercury resulting from the demethylation of methyl mercury (CH_3Hg^+). It was proposed by Watanbe, 2002 that Se^{2-} can co-exist close to CH_3Hg^+ and react with the demethylated Hg^{2+} to form Hg-Se complex. Reaction mechanisms for the breakdown of methyl mercury (CH_3Hg^+) by radical attack are summarized below:

[2] $CH_3Hg^+ \longrightarrow \cdot CH_3 + \cdot Hg^+$



[3] $\xrightarrow{\text{Oxidation}} 2Hg$

[4] $2\cdot Hg^+ \longrightarrow Hg^0 + Hg^{2+}$

[5] $\xrightarrow{\text{Oxidation}} Hg^{2+}$

[6] $\text{Selenocompounds} \xrightarrow{\text{Metabolism}} Se^{2-}$

[7] $Se^{2-} + Hg^{2+} \longrightarrow HgSe \longrightarrow \text{deposits}$

[8] $\text{Selenocompounds [with – SeH groups]} + Hg^{2+} \longrightarrow \text{Hg- selenocompounds} + 2H^+$

Yang *et al.*, 2008

Selenium may be actively involved in the demethylation process. Magos *et al.*, 1979 reported of a decomposition of $(CH_3Hg)_2Se$ resulted in the loss of mercury (Hg) and the formation of HgSe. Iwata *et al.*, 1982 reported of a gradual demethylation to generate inorganic mercury (Hg) when methyl mercury chloride (CH_3HgCl) was incubated with GSH and sodium selenite. Similar observations were reported when L-cysteine, 2-mercatoethanol or sodium selenite was used. Reactions are summarized below:

[9] $SeO_3^{2-} \xrightarrow{\text{Reduction (by GSH, L-cysteine, 2- mercatoethanol) or } Na_2S} Se^{2-}$

[10] $Se^{2-} + 2CH_3Hg^+ \longrightarrow CH_3Hg\text{-}Se\text{-}HgCH_3 \longrightarrow HgSe + CH_3HgCH_3$

In vivo tests showed that CH_3Hg^+ may act as a methyl donor for the methylation of selenium, rendering it demethylated. Yamane *et al.*, 1977 found that the carbon atom in the ^{14}C-labeled CH_3Hg^+ appeared to end up as a $^{14}CH_3\text{-}Se\text{-}^{14}CH_3$ compound in rats treated with methylated

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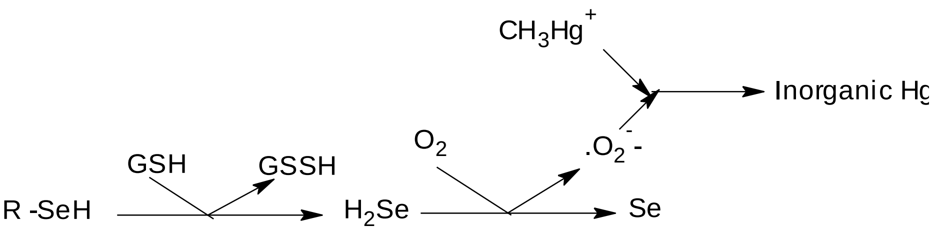
chloride and sodium selenide. Se^{2-} and compounds with –SeH groups produces superoxide radicals (Spallholz, 1994), which may attack CH_3Hg^+ to form inorganic mercury. It is not expected that selenium at normal levels inside the cell would produce significant levels of radicals to initiate demethylation. However higher levels of superoxides are produced when selenium is supplemented in diet leading to toxicity.

[11]



The methylation of Hg^{2+} in the environment to CH_3Hg^+ mainly happens in aquatic and wetland systems and the most important factors that influence this process include temperature, pH, organic material content, redox conditions, microbiological activity, salinity and sulfide concentration (Ullrich *et al.*, 2001). Recent field studies on aquatic organisms by Belzile *et al.*, 2006 and Chen *et al.*, 2001 at different trophic levels have shown that both Hg and CH_3Hg^+ concentrations decreased with increasing concentrations of total dissolved selenium in lake waters and total selenium in tissues of the studies biota.

Possible mechanisms to explain the interactions in aquatic systems include:

[12] $Hg^{2+} + Se^{2-} \longrightarrow HgSe$

[13] $Hg^0 + Se^0 \longrightarrow HgSe$

It is possible for Hg^{2+} to react first with Se^{2-} ions to form the inert Hg-Se complex (eqn 12). Mercuric selenide is also expected to form when Hg^0 and Se^0 come into contact (eqn 13). In consequence, the methylation of mercury (Hg) in aquatic systems would be stopped or at least greatly reduced if precipitation occurs. Se^{2-} (or HSe^{-}) and Se^{0} is generated in aquatic systems through the metabolisms mediated by microorganisms (Heider and Bock, 1993; Losi and Frankenberger, 1997; Hockin and Gad, 2003). Elemental selenium can also be produced abiotically, for example by the reduction of selenite under anoxic conditions in the presence of Fe^{2+} or dissolved sulfide (Trulong *et al.*, 2005).

Photolysis is one of the most significant abiotic demethylation processes in the environment reported by Ullrich *et al.*, 2001 and sulfides were found to stimulate such a process. Methyl mercury (CH_3Hg^{+}) in the form of CH_3HgS^{-}, $(CH_3Hg)_2S$, and CH_3Hg-thiol complexes can decompose much faster under U.V. radiation to generate mercuric sulfides (HgS) precipitate.

Other forms such as methyl mercury hydroxide (CH_3HgOH) or methyl mercury chloride cannot undergo decomposition due to their weak absorption capacity (Baughman *et al.*, 1973).

$$[14]\ HS + 2CH_3Hg^{+} \longrightarrow H_3CHg\text{-}S\text{-}HgCH_3 \longrightarrow H_3C\text{-}Hg\text{-}CH_3 + HgS$$

Studies have also found that organisms living in lakes with higher concentration of selenium (Se) assimilated higher concentration of selenium (Se) in their body (Chen *et al.*, 2001; Belzile *et al.*, 2006). However, there was no biomagnification of se along the aquatic food chain but rather a decrease in concentration was noticed due to biomass dilution (Yang *et al.*, 2008). Ganther and Corcoran, 1969 found that selenite (SeO_3^{2-}) can react with –SH groups of ribonuclease, to form –S-Se-S bond. This prevents CH_3Hg^{+} from binding to these blocked sites therefore promoting its excretion.

2.7 CADMIUM

2.7.1 Chemical fate

Cadmium (Cd) is a soft, ductile, silver-white metal that belongs together with zinc (Zn) and mercury (Hg) to group IIb in the Periodic Table. It has relatively low melting (320.9 °C) and boiling (765 °C) points and a relatively high vapour pressure. The average concentration in the earth's crust is about 0.2 mg/Kg widely distributed in rocks, sediments and soils (Manson and Moore, 1982). Cadmium (Cd) is rapidly oxidized in air into cadmium oxide. Cadmium (Cd) is widely distributed in the earth's crust and rarely found as a pure metal.

Cadmium (Cd) and zinc (Zn) frequently undergo geochemical processes together. Cadmium (Cd) is also an inevitable by-product of zinc (Zn), lead (Pb) and copper extraction (ATSDR, 1999). Cadmium (Cd) exists in water as hydrated ion, as inorganic complexes such as carbonates (CO_3^{2-}), hydroxides (OH^-), chlorides (Cl^-) or sulfates (SO_4^{2-}), or as organic complexes with humic acids (Sauve *et al*., 1999).

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

Non-ferrous metal smelting contributes approximately 76% of the anthropogenic cadmium (Cd) emissions, while fossil fuel combustion accounts for the remaining 24% (Nriagu, 1980).

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

2.7.2 Toxicity of Cadmium (Cd)

Cadmium (Cd) bioaccumulates in terrestrial and aquatic species. Accumulation half-life is in order of years to decades (Eisler, 1985; Norberg *et al*., 1985; WHO, 1992[a, b]). Bioaccumulation primarily takes place in target organs such as the kidney and liver (Nordberg *et al.*, 1985). In fish, the gill is the target organ of toxicity under conditions of acute waterborne exposure.

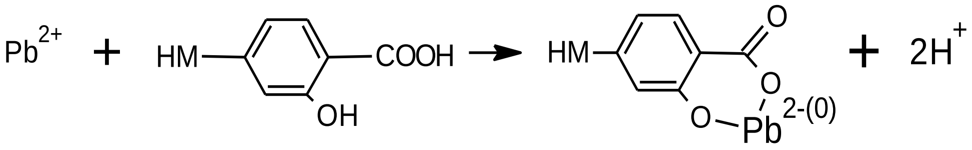
The toxicity and bioaccumulation of cadmium is a function of free ion activity (Sprague, 1985) and is therefore affected by interactions with other inorganic elements particularly calcium (Ca), magnesium (Mg), zinc (Zn), copper (Cu), and iron (Fe) (Spivey-Fox, 1988). More importantly the toxicity of cadmium (Cd) ultimately involves the disruption of calcium (Ca) metabolism.

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

2.8 LEAD

2.8.1 Chemical fate

The atomic number of lead (Pb) is 82 and atomic mass is 207.2 g/mol. It has a melting point of 327 °C, a boiling point of 1755 °C and a density of 11.34 g/cm^3 at 20 °C. The main lead (Pb) mineral is galena (PbS), which contains 86.6 % lead. Other common varieties are cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Lead (Pb) is a class B metal and therefore has the ability to form stable complexes with oxygen-donating compounds.

[15] 

Lead (Pb) has many industrial and commercial uses. For instance, it is used in metal products, cables and pipelines to improve durability, additives in paints, and in pesticides. It is a major constituent of the lead-acid car batteries. It is used as a coloring element in ceramic glazes as projectiles and in some candles to treat the wick. It is the traditional base metal for organ pipes, and it is used as electrodes in the process of electrolysis. One of its major uses is in the glass of computer and television screens, where it shields the viewer from radiation.

Balba *et al.,* 1991 reported that automobiles (leaded gasoline), industrial wastewater (lead mining and smelting) and pesticides are the major anthropogenic sources of lead (Pb) in the environment.

2.8.2 Toxicity of lead

Exposure to lead (Pb) can have a wide range of effects on a child's development and behavior. Growing evidence suggests that lead (Pb) in a child's body, even in small amounts, can cause disturbances in early physical and mental growth and later in intellectual functioning and academic achievements. There is accumulated epidemiological evidence, which indicates that lead (Pb) exposure in early childhood causes discernible deficit in cognitive development during childhood years (Tong *et al.*, 2000) resulting in lower Intelligent Quotient (IQ)(Adeyeye, 1993). Particularly, dangerous to all forms of life are the organic lead (Pb) compounds. As a result of their comparatively high affinity for proteins, the lead (Pb) ions consumed bond with the haemoglobin and the plasma protein of the blood. This leads to inhibition of the synthesis of red blood cells and thus of the vital transport of oxygen. If the bonding capacity here is exceeded, lead (Pb) passes into the bone-marrow, liver and kidneys.

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

2.9 IRON

2.9.1 Chemical fate

Iron (Fe) is a lustrous, ductile, malleable, silver-gray metal belonging to group VIII of the periodic table. It is known to exist in four distinct crystalline forms. Iron (Fe) rusts in dump air, but not in dry air. It dissolves readily in dilute acids. Iron (Fe) is chemically active and forms two

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major series of chemical compounds, the bivalent iron (II) (Fe^{2+}), or ferrous compounds and the trivalent iron (III) (Fe^{3+}), or ferric compounds.

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

Iron (Fe) is essential to most life forms and to normal human physiology. It is an integral part of many proteins and enzymes that maintain good health. Dallman, 1986 explains that in humans, iron (Fe) is an essential component of proteins involved in oxygen transport. Andrews, 1999 and Bothwell *et al.*, 1979 indicate its essentiality in the regulation of cell growth and differentiation.

2.9.2 Toxicity of Iron (Fe)

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

Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an X-ray change. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer

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development in workers exposed to pulmonary carcinogens. In recent years, excess iron (Fe) intake and storage, especially in men, has been implicated as a cause of heart disease and cancer. Overdose has been reported by Corbett, 1995 to be one of the leading causes of fatality from toxicological agents in children younger than 6 years.

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Table 2.1: Summary on the literature review of some trace metals and macro elements

Elements	Physical/Chemical properties	Sources/Uses	Toxicity
Manganese (Mn) A-54.93 $gmol^{-1}$ Z-23	Pinkish gray, hard to melt but easily oxidized, melting point of 1247 ˚C, boiling point of 2061 ˚C, density of 7.43 g/cm^3 at 20 ˚C	Occurs as Pyrolusite (MnO_2)/ Rhodochrosite ($MnCO_3$), Component in alloys and additive in fuels	Respiratory disorders, Parkinson diseases, Hallucinations and forgetfulness, symptom's such as schizophrenia
Copper (Cu) A-63.55 $gmol^{-1}$ Z-29	Melting point of 1083 ˚C, boiling point of 2595 ˚C, density of 8.9 g/cm^3at 20 ˚C	Naturally as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), used for electrical equipment, industrial machinery	Dermatitis, liver cirrhosis, neurological disorders, renal diseases etc.
Chromium (Cr) A-51.99 $gmol^{-1}$ Z-24	Melting point of 1907 ˚C, boiling point of 2672 ˚C, density of 7.19 g/cm^3 at 20 ˚C	Naturally through volcanic eruptions as chromite ($FeCr_2O_4$), components in alloys and metal ceramics	Allergic dermatitis, skin lesions, respiratory problems and tumor formations
Nickel (Ni) A-58.71 $gmol^{-1}$ Z-28	Silvery-white, hard, malleable and ductile metal, melting point of 1453 °C, boiling point of 2913 °C, density of 8.9 g/cm^3 at 20 °C	Occurs with sulfur as millerite, with arsenic as niccolite, component in alloys for gas turbines and rocket engines	Skin rash, swelling of the brain and liver and various type of cancers
Zinc (Zn) A-65.37 $gmol^{-1}$ Z-30	Lustrous bluish-white metal, melting point of 420 °C, boiling point of 907 °C, density of 7.11 g/cm^3 at 20 °C	Occurs as zinc sulfides (sphalerite), used in the galvanization of steel and also a major component in alloys	Arteriosclerosis, disturbs protein metabolism, stomach cramps and skin irritations
Sodium (Na) A-22.98 $gmol^{-1}$ Z-11	Soft metal, melting point of 97.81°C, density of 0.971 at 25 °C, produces yellow flame.	Associated with many minerals in the earth crust, natural brines, many industrial uses	High levels in soil affects plant growth, heart failure, neurological damage,
Potassium (K) A-39.0983 $gmol^{-1}$ Z-19	Melting point of 63.65 °C, density of 0.862 g/cm^3 at 20 °C, Produces violet flame	Associated with aluminosilicate minerals such as feldspar, many industrial applications	Elevated levels will lead to death by heart failure

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2.10 WATER

2.10.1 Importance of good water quality

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

The largest demand and use of water worldwide is for industrial and agricultural purposes. Agricultural uses of water are mainly through irrigation and in the application of agro-chemicals. Water for agriculture continues to increase worldwide due to high demand for food. Water is used in industries mainly for power generation, transportation of waste materials and in many industrial products such as beverages and solvents for chemicals.

Water pollution has impacted negatively on the economy of many developing countries especially in the area of human health and ecosystem disruption. Any physical, biological or chemical change in water quality that adversely affects living organisms or makes water unsuitable for desired use could be considered as being polluted. Sedimentation from erosion and poisoned springs contribute to natural sources of water contaminant. Anthropogenic sources of water contaminant include sewage from industries, pesticides and other agro-chemical runoff from farmlands and faecal pollution. Faecal pollution of drinking water has frequently caused water borne diseases such as cholera which has decimated several populations.

Water quality is a term used to describe water's physical, chemical and biological characteristics. The term is usually used to describe water's suitability for a particular purpose (i.e., drinking water, recreation and aquatic life) (USGS, 2005). For freshwater systems, stream flow affects many issues related to water quality and quantity such as pollutant concentration and water temperature (Richter, 2003).

Urbanization, industrialization and various modern agricultural practices has greatly affected our environment and the quality of water. The assessment of water quality is therefore the best in ensuring that it is safe for its intended user, particularly uses which may affect human health and the health of aquatic systems.

2.10.2 Freshwater Physico-Chemistry

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

Extreme changes in water Physico-Chemistry can have adverse effects on aquatic systems and organisms. Physico-Chemical parameters to investigate are temperature, dissolved oxygen (DO), biochemical oxygen demand (BOD), pH, electrical conductivity/salinity (EC), total dissolved and suspended solids (TDS and TSS), microbial activity and dissolved ions (water nutrients).

2.10.3 Dissolved oxygen (DO)

Oxygen is essential to all forms of aquatic life. The amount of oxygen in water is known as dissolved oxygen. Dissolved oxygen (DO) is critical for sustenance of aquatic life in order for aerobic species to be able to survive and carry out their ecological functions. The oxygen content of natural water varies with temperature, salinity and atmospheric pressure.

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Under natural freshwater conditions, DO concentrations ranges from 15 mg/L at 0˚C to 8 mg/L at 25˚C (Manaham, 1991). Lack of DO can lead to anaerobic decomposition of organic matter, resulting in unpleasant odours that are indicative of formation of hydrogen sulfides (H_2S) and ammonium (Schindler, 1981). Dissolved oxygen (DO) determination is a fundamental part of water quality assessment since oxygen is involved in or directly influences nearly all chemical and biological processes within water bodies (Fianko, 2003).

2.10.4 Total Alkalinity

It measures the presence of carbonates, bicarbonates, phosphates and hydroxides and also a measure of the buffering capacity of an aquatic ecosystem (Fianko, 2003). Phosphate and orthophosphates contribute to 0.1 % of total alkalinity. At a specific pH, carbonate/bicarbonate ions can be formed from the dissociation of carbonic acid.

Alkalinity is controlled by carbonate/bicarbonate species, and is represented as mg/L $CaCO_3$ (Dallas and Day, 2004). Alkalinity is important for fish and other aquatic life in fresh water system because it buffers pH changes. Alkalinity components such as carbonate/bicarbonate species will complex toxic heavy metals thereby reducing their toxicity significantly (Fianko, 2003). The WHO in their 2011 report has no stated guideline value for alkalinity because high concentrations of carbonate/bicarbonate species in drinking water does not pose any health concern (WHO, 2011). However EPA's secondary drinking water regulations limits alkalinity only in terms of TDS (500 mg/L) and to some extent by the limitation on pH.

2.10.5 Biochemical oxygen demand (BOD)

Biochemical oxygen demand, or BOD, measures the amount of oxygen consumed by microorganisms in decomposing organic matter in water bodies. BOD also measures the chemical oxidation of inorganic matter (i.e., the extraction of oxygen from water via chemical reaction) (USEPA, 2013). The rate of oxygen consumption in a water body is affected by a number of variables: temperature, pH, the presence of certain kinds of microorganisms, and the type of organic and inorganic material in the water.

High concentrations of oxidizable materials lead to anoxic conditions-stagnant water that does not support higher life forms such as fish. BOD directly affects the amount of dissolved oxygen in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in a water body. This means less oxygen is available to higher forms of aquatic life. The consequences of high BOD are the same as those for low dissolved oxygen: aquatic organisms become stressed, suffocate, and die. Water of poor quality has high BOD.

2.10.6 Electrical conductivity

Electrical conductivity (EC) estimates the amount of total dissolved salts/solids (TDS), or the total amount of dissolved ions in the water. Dissolved salts or ions are electrically charged and their ionic strength determines water conductivity. The EC in freshwater ecosystems is regulated by rocks' mineral composition, size of the watershed and other sources of ions (Hudson-Edwards *et al*., 2003; Nielsen *et al*., 2003). A bigger watershed means relatively more water flow and more contact with soil will result in more salt/ion extraction from the sediment hence contributing to high electrical conductivity (Vega *et al.*, 1998). Wastewaters from industries, sewage treatment works and septic tanks, and non-point sources from settlements and agriculture are other sources that contribute to in-stream EC (Roelofs, 1991; Nielsen *et al*., 2003).

2.10.7 Turbidity and suspended matter in the hydrosphere

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

The American Public Health Association (APHA), 1989 explains turbidity as a representation of the optical property of water that causes light scattering or absorption. Light scattering results from suspended matter (clay, silt, organic and inorganic matter, plankton and other microorganisms). Turbidity is caused by runoffs from non-point (e.g. irrigation schemes) and point sources (e.g. STW effluent). Higher turbidity can affect benthic, invertebrates and fish communities (Wood and Armitage, 1997).

2.10.8 Total hardness

Hardness of water is a measure of the mineral content especially calcium and magnesium mainly in combination with bicarbonate (HCO_3^-), sulfates (SO_4^{2-}) and chloride (Cl^-). Other divalent or trivalent ions can contribute to hardness such as iron (Fe), barium (Ba), and/or strontium (Sr) though their contributions are small and difficult to define. Because the concentrations of Ca^{2+} and Mg^{2+} are usually much greater than the concentrations of other group 2 ions, hardness can be equated to the total calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions present.

Limestone is a mixture of calcium and magnesium carbonate, $CaCO_3$ and $MgCO_3$. Surface or ground water often contains CO_2 and thereby making the water slightly acidic by the formation of carbonic acid (USEPA, 2013). Slightly acidic groundwater reacts with the basic limestone, and a neutralization reaction occurs resulting in the formation of soluble Ca^{2+}, Mg^{2+} bicarbonates which will contribute to water hardness. It is normally expressed as mg $CaCO_3$ per litre. There are two types of water hardness; permanent and temporary hard water. Permanent hardness in water is hardness due to the presence of the chlorides (Cl^-), nitrates (NO_3^-) and sulfates (SO_4^{2-}) of calcium (Ca^{2+}) and magnesium (Mg^{2+}), which will not be precipitated by boiling.

For temporary hardness, calcium (Ca^{2+}) and magnesium (Mg^{2+}) form salt with bicarbonates (HCO_3^-). These compounds are unstable and will decompose when heated. Boiling the water will cause the precipitation of calcium and magnesium carbonate which also removes the hardness. Hardness is used to determine how usable water resources are for drinking and domestic purposes. Hard water forms fur and scales in boiler and leaves scum in clothes in addition to wasting of soap. The WHO recommends that hardness should not exceed 200 mg/L $CaCO_3$ but levels of 50-100 mg/L $CaCO_3$ are generally acceptable (WHO, 2011).

2.10.9 The effect of nutrients on freshwater ecosystems

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

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eutrophication in freshwater systems, a process called cultural eutrophication (Campbell *et al.*, 1992).

2.10.9.1 Nitrogen cycle

In the hydrosphere and on land, nitrogen (N) in various forms is an essential nutrient for plant and animals and excessive concentrations of inorganic species in the hydrosphere leads to eutrophication. Nitrogen undergoes a number of processes in terrestrial, aquatic and atmospheric environments which includes nitrogen fixation, denitrification, ammonification and nitration.

2.10.9.2 Nitrogen fixation

Atmospheric nitrogen is relatively unreactive, and is converted to NH_3/NH_4^+ by nitrogen fixing microorganisms. The conversion requires breaking of strong N≡N triple bond therefore a large energy input is required. However, in freshwaters, nitrogen can occur in different forms which include dissolved molecular nitrogen, organic compounds from proteins, recalcitrant anthropogenic compounds and inorganic nitrogen (ammonia, nitrite and nitrate) (Dowd *et al.*, 2000; Wetzel, 2001; Kubiszewski *et al.*, 2008).

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

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2.10.9.3 Denitrification

It occurs mostly in stagnant fresh water and in deep, organic-rich Sea waters. Several biochemical reactions occur where oxidized nitrogen anions are biochemically reduced to nitrogen:

[16] $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Nitrate (NO_3^-) is able to act as electron acceptor for the oxidation of organic matter. Heterotrophic bacteria such as species of Pseudomonas and Achromobacter facilitate the process. Ammonium can be oxidized by Planctomycete species (anammox bacteria) (Kuenen, 2008), using nitrite as the electron acceptor.

[17] $NH_4^+ + NO_2^- + HCO_3^- + H^+ \rightarrow N_2 + NO_3^- + H_2O + CH_2O_{0.5}N_{0.15}$

2.10.9.4 Ammonification

When organic matter decomposes in water and soil, the nitrogen is first released in a reduced form as ammonium ions or ammonia, depending on the ambient pH. This conversion of nitrogen from organic to inorganic forms is a type of mineralization called ammonification. Carbon nitrogen bonds are reactive and ammonification is therefore a rapid reaction:

[18] $2CH_3NHCOOH + 3O_2 + 2H_3O^+ \rightarrow 2NH_4^+ + 4CO_2 + 4H_2O$

2.10.9.5 Nitrification

Ammonium ion, present in water or in soil as a result of ammonification is subjected to oxidation in an aerobic environment. The optimum environmental pH for nitrification is between 6.5 and 8, and reaction rate decreases when pH falls below 6. The reaction takes place in two steps and the process is mediated by autotrophic bacteria:

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[19] $2NH_4^+ + 3O_2 + 2H_2O \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 4H_3O^+$

[20] $2NO_2^- + O_2 + H_2O \xrightarrow{\text{Nitrobacter}} 2NO_3^-$

Overall reaction:

[21] $NH_4^+ + 2O_2 + H_2O \rightarrow NO_3^- + 2H_3O^+$

The consequence of nitrification is the release of hydroxonium ions into the local environment causing the local environment to be acidified. Inorganic nitrogen in freshwater within the range 0.5 – 2.5 mg/L has been reported to result in eutrophication. Concentrations above this range lead to species loss, and hence decreased biodiversity, and stimulate excessive algal and aquatic plant growth. Any inorganic nitrogen concentrations > 10 mg/L can result in the significant loss of species diversity and lead to water becoming toxic to animals and humans (DWAF, 1996; Bongumusa, 2010).

2.10.9.6 Sulfur in freshwater

Sulfur chemistry has a major influence on the process in all the compartments of the Earth's environment. In the atmosphere, oxidation reactions convert lower oxidation state species into sulfate, sulfate aerosols and sulfuric acid. Sulfur in the hydrosphere is present in many inorganic and organic forms and exhibits oxidation states from -2 to +6. The most important reduced and oxidized mineral forms of the element are sulfides, including pyrite (FeS_2), and sulfates, including gypsum ($CaSO_4 \cdot 2H_2O$). The concentration in unimpacted fresh water is much less than 0.12 $mmol^{-1}$ but none the less one of the principal ionic species in lakes and rivers. In reducing environment sulfur is obtained in the -2 oxidation state.

In organic matter, sulfur exists as both carbon-bonded and oxygen-bonded forms:

C-bonded	$R\text{-}CH_2SH$	hydrosulfide	in amino acids
	$R_3C\text{-}S\text{-}S\text{-}CR_3$	disulfide	

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O-bonded	S=O	sulfoxide
	R-OSO_2OH	sulfonic acid

When organic matter undergoes microbial decomposition, the sulfur-containing groups within the organic compounds are simultaneously transformed. Sulfides are mainly formed during the decomposition of organic matter and it is easily oxidized under aerobic conditions. Chemoautotrophic bacteria such as *Thiobacillus thiooxidans* is responsible for sulfide oxidation and is found in most oxygen-containing waters, sediments, and soils. The reaction also produces hydroxonium ions and is also an acidifying process.

[22] $HS^- + 2O_2 + H_2O \rightarrow SO_4^{2-} + H_3O^+$

In an organic-rich, reducing aquatic environment, sulfate is readily reduced to species in the -2 or, less commonly, 0 oxidation state. Many marine, estuarine, and fresh water sediments as well as waterlogged soils contain sulfate-reducing bacteria. The sulfide species generated are toxic to aquatic life; they may also react with metals present in the sediment/soil, such as iron (II), to produce insoluble sulfides that are components of marine shales.

[23] $SO_4^{2-} + 2\{CH_2O\} + H_3O^+ \rightarrow HS^- + 2CO_2 + 3H_2O$

[24] $2SO_4^{2-} + 3\{CH_2O\} + 4H_3O^+ \rightarrow 2S^0 + 3CO_2 + 9H_2O$

2.10.9.7 Phosphorous in freshwater

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

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

[25] $P_3O_{10}^{5-} + 2H_2O \rightarrow 3PO_4^{3-} + 4H^+$

Orthophosphate/soluble reactive phosphate (SRP), H_2PO_4 and HPO_4^{-2} are the only soluble forms of inorganic phosphorus and hence are readily available to aquatic life. Orthophosphate is taken up by algae, cyanobacteria, heterotrophic bacteria and larger aquatic plants and forms the basics of aquatic food chain. Phosphorus enhances aquatic plants and algal growth (Manaham, 1991). Concentrations of dissolved phosphorus below 0.005 mg/L stimulate moderate levels of species diversity, low productivity, rapid nutrient cycling, and no algal and aquatic plant growth. Phosphorus concentrations between 0.005 and 0.025 mg/L PO_4^{3-} can enhance species diversity; promote moderate primary production, algal and water plant growth. Concentrations above 0.025 mg/L result in decreased species diversity, high productivity, and high growth of nuisance aquatic plants and algal blooms (Camargo *et al.*, 2007). Phosphorus concentrations are used to measure ecosystem eutrophication with the concentration of 0.1 mg/L PO_4^{3-} indicative of a eutrophic system (Campbell *et al.*, 1992).

2.10.10 Microbial Quality of Drinking Water

There is the need to determine the microbial quality of drinking water since the microbial quality affects the overall quality of the water. Waterborne diseases are caused by enteric pathogens such as bacteria, viruses and parasites that are transmitted by faecal oral route. Water supplies that are unprotected are susceptible to microbial and other external contamination from surface runoff, human/animal faecal pollution and unsanitary collection methods. Faecal contamination of water is common in communities with poor sanitation.

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The survival of microorganisms such as bacteria in a given environment depends on many factors such as temperature, pH, electrolyte concentration and nutrient supply. Detection of each pathogenic microorganism in water is extremely difficult and instead indicator organisms are routinely used in the assessment of microbial quality of water (Grabow, 1996). They include the heterotrophic plate count (THB), total coliform bacteria (TC), faecal coliform bacteria (FC), *E. coli,* faecal enterococci, *C. perfringens* and male specific F-RNA bacteriophages. Four indicator organisms are considered for this study which includes THB, TC, FC, and *E. coli*.

2.10.10.1 Total heterotrophic bacteria (THB)

Heterotrophic microorganisms are naturally present in the environment and can be found in soil, sediment, food, water and in human and animal faeces. Heterotrophs include bacteria, yeast and molds that require organic carbon for growth. Although generally harmless, some are considered as opportunistic and could have viral characters and could affect the health of consumers (Lye and Dufour, 1991). They also survive in biofilms inside water distribution systems, reservoirs and household storage containers. The pour plate, membrane filtration or the spread plate methods are used routinely with Yeast-extract agar, Plate count agar, Tryptone Glucose agar or R2A agar, and incubation periods 5 to 7 days at room temperature (25 °C) (APHA AWWA WEF, 1995).

2.10.10.2 Total coliform bacteria (TC)

Total coliform bacteria are defined as aerobic or facultative anaerobic, gram negative, non-spore forming, rod shaped bacteria, which ferments lactose and produce gas at 35 °C (APHA AWWA WEF, 1995). They include bacteria of known faecal origin such as *E. coli* as well as others which do not originate from faecal sources such as *klebsiella sp*., *Citrobacter sp*., and *Enterobacter sp.*

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The recommended test for total coliform is membrane filtration using mEndo agar and incubation at 35 to 37 °C for 24 hours to produce colonies with golden-green metallic shine. The presence of total coliform in water samples gives an indication of bacteria such as *klebsiella sp* which are causal agents for diseases such as typhoid fever, dysentery and cholera (APHA AWWA WEF, 1995).

2.10.10.3 Faecal coliform (FC)

Faecal coliform bacteria are gram negative bacteria. They are also called thermo-tolerant coliforms or presumptive *E. coli*. They are considered to be a more specific indicator of the presence of faeces (Maier *et al.*, 2000). The recommended test for faecal coliform is membrane filtration using mFC agar and incubation at 44.5 °C for 24 hours to produce blue colored colonies. They are generally used to indicate unacceptable microbial water quality and could be used as an indicator in the place of *E. coli* (APHA AWWA WEF, 1995).

2.10.10.4 Escherichia coli (*E. coli*)

E. coli is used as a preferred indicator of faecal pollution. It is a gram negative bacterium and they are found in the intestines of warm blooded animals and humans. *E. coli* is used to indicate recent faecal pollution of water samples. Testing for the enzyme β-glucuronidase is one confirmatory test for the presence of *E. coli*. Also growth media containing the fluorogenic substrate 4-methyl-umbelliferyl-β-D-glucuronidase (MUG) is used in the isolation and identification of *E. coli* from water samples. *E. coli* and related bacteria possess the ability to transfer DNA via bacterial conjugation, transduction or transformation, which allows genetic material to spread horizontally through an existing population (APHA AWWA WEF, 1995).

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2.11 ANALYTICAL METHOD FOR DETERMINATION OF HEAVY METALS

A variety of analytical techniques have been employed in the determination of the heavy metals. These techniques included Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X−ray fluorescence (XRF), Electron Microprobe (EM) Flame Photometry (FP) and Instrumental Neutron Activation Analysis (INAA).

These instruments accurately measure elements in environmental samples to parts per billion (ppb) concentrations i.e. µg L^{-1} and µg Kg^{-1} in liquids and solids samples respectively. Before any element is determined with any of these instruments, pre-treatment with acidic extraction or acidic oxidation digestion and in some cases chelation may be required. The significance of pre-treatment is that all elemental species are converted into the inorganic form for easier detection and measurement. One advantage of INAA is the ability to measure trace amounts of elements without destroying the sample. FP uses flame atomic emission and a filter to quantify Li, Na, K and Ca in liquid samples (Xudong *et al.*, 2011).

AAS is a technique in which the absorption of light by free gaseous atoms in a flame or furnace is used to measure the concentration of atoms. In analyzing any given metal, a lamp is chosen that produces a wavelength of light that is absorbed by that element. Sample solutions are aspirated to a nebulizer system. The sample then mixes with an oxidant gas drawn under pressure into a burner to form aerosol. The flame which uses either air-acetylene or nitrous-oxide acetylene operates at a temperature of 2400 ^{o}C and 2800 ^{o}C respectively.

Within the flame, the aerosol undergoes processes such as evaporation of the solvent and excitation of the gaseous metallic element. If any gaseous atoms of the given element are present in the flame, they absorb light produced by the lamp before it reaches the detector (photomultiplier tube). The amount of light absorbed is proportional to the concentration of metal ions following Beer-Lambert law. Absorbance values for unknown samples are compared to calibration curves prepared by running known standards. Elements like mercury (Hg) and selenium (Se) need specialized compartments like the Cold Vapour AAS and the Hydride Generation AAS respectively for their analysis.

2.11.1 Hydride Generation Atomic Absorption Spectrometry (HGAAS)

Elements like selenium (Se) may exist in solution as oxyanions and may not undergo complete atomization. Their hydrides however decompose very easily into the atoms. Problems encountered with the conventional AAS such as interferences, poor reproducibility and poor detection limits are however corrected. The gaseous hydride is then swept (by inert gas) into a sampling cell in the light path of the AA for atomization by the flame. The oxidation state of the metalloid is very important during the hydride generation. For example, selenium (Se) requires an oxidation state (IV) selenite for successful hydride generation. Higher oxidation states give erratic results. Samples are first oxidized with HNO_3 to the Se (VI), and then reduced to selenium (Se) (IV) by boiling with HCl, before reacting with borohydride. Hydride generation pre-concentrates the metalloid thus removing interfering species and improving detection limit.

2.11.2 Cold Vapour Atomic Absorption Spectrometry (CVAAS)

Most atoms for atomic spectroscopy analysis cannot exist in the free, ground state at room temperature; therefore, samples must be heated in order to liberate atoms for analysis. Hg however exists as free atoms at room temperature and can be analysed by AAS without employing a flame or graphite furnace to atomize it. The Hg in the sample is oxidised to Hg^{2+}, the reduced to Hg^0.

[26] $Hg^{2+} + 2e \rightarrow Hg^0$

The free Hg atoms are swept into an absorption cell for absorbance measurement and therefore no need for a flame. Reducing agents used are: $SnCl_2$ / $NaBH_4$ + HCl. The reaction quantitatively releases Hg from solution which is carried by a stream of argon into the AA for absorbance measurement (Xudong *et al.*, 2011).

2.12 FISH SPECIES

Fish species were identified as *Xenomystus nigri* (African knife fish) and *Clarias submarginatus* (Mudfish). *Xenomystus nigri* is a predator fish which belongs to the *Notopteridae* family. It feeds on meaty food such as bloodworm, insect, crustacean and small snails. It grows up to (30 cm) in the wild (Günther, 1868).

It is flat and elongated with an arched back. It has a continuous fin along the underside formed by a joining of the caudal and anal fin. It is a graceful swimmer which prefers still waters and where its fin allows it to move both forwards and backwards. These fish species have no dorsal fins. They are freshwater fish which are mainly found in West Africa and prefer water conditions of temperatures ranging from 22 ºC to 28 ºC and pH ranges of 6-8 (Günther, 1868).

Clarias submarginatus (Mudfish) is a demersal fish which belongs to the *Clariidae* family. It is a freshwater fish also found in West Africa. It grows up to a maximum length of 16 cm. The head is short and rather rounded in dorsal outline with eyes dorsally located. Its frontal fontanelles are

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extremely short and oval-shaped and also have its occipital fontanelle oval-shaped. The tooth plates are relatively broad. Its pectoral spines are slightly curved with long and slender gill rakers which are distantly set. It also has well developed suprabranchial organ (Peters, 1882).

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CHAPTER THREE

3.0 METHODOLOGY

3.1 DESCRIPTION OF STUDY AREA

3.1.1 Pra River Catchment

The Pra River system is the longest in South Western Ghana. This river takes its source from the Kwahu plateau and flows through a distance of 240 km into the Gulf of Guinea through its estuary at Shama. The river has a drainage area of 23188 km^2 and an estimated mean annual discharge of 214 m^3s^{-1} (Akrasi and Ansah-Asare, 2008). The river is divided into two main catchment regions namely the Upper Pra which is located in the Eastern Region and the Lower Pra which flows through the Central and the Western regions.

The Upper Pra starts from the Kwahu plateau and flows to join the Birim River at around Akroso. The Lower Pra River is formed from the Upper Pra River and its two major adjoining tributaries, the Birim and Offin River flowing from the eastern and western parts of the middle belt region of the country respectively. The Lower Pra River flows through towns like Twifo Praso in the Central Region and Daboase in the Western Region until it enters the sea through its estuary at Shama in the Western Region. People living at the banks of the river depend on this river body for their livelihood through fishing, transportation and farming activities.

3.1.2 Climate and Geology of the Catchment Area

The geology in this region is pre-cambrian and is classified into the Birimian and Tarkwaian formations (Junner, 1940; Kesse, 1985). The area is quite humid (relative humidity 60–95%) with annual rainfall in the range of 1500 – 2000 mm. The average minimum and maximum temperature ranges from 21 °C to 32 °C. The basin is always strongly under the influence of the moist south-west monsoons during the rainy season and as a result there is a pro-longed rainy season from April through to October/November each year. The primary vegetation consists of moist semi-deciduous forest and the soil type is mainly the forest ochrosol (Brammer, 1962).

Figure 3.1: Map of the Lower Pra River and its adjoining tributaries. The areas in the violet, green and red captions represents the upper stream, mid-stream and downstream catchment regions of the Lower Pra River respectively. The part of the Lower Pra River under study is captured in the red caption.

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3.1.3 Catchment Divisions

The Lower Pra River is divided into three main catchment regions which are the upper stream regions, the middle portions and the lower stream regions. The upper stream catchment of the Lower Pra River stretches from the point where the Offin River joins with the Upper Pra River at Awisam through Twifo Praso to areas around Enyinabrim. The middle portion of the Lower Pra River stretches from downstream Enyinabrim to areas around Sekyere Herman. Most of the areas in the middle portions are un-navigable due to the large forest reserve in the area and the rocky nature of the river bed.

The lower stream areas stretch from Daboase (DB) through Beposo (BP) to the estuary where the river enters the sea. Towns in the upper stream catchment have been reported for artisanal illegal small scale gold mining (AGM) and their activities affect the communities in the lower catchment region. However in this study, the lower catchment region is isolated for monitoring since the activities of illegal gold miners have reached towns further downstream such as Beposo (BP) and Daboase (DB).

3.1.4 Site Selection for Monitoring

An investigation was carried out in the Shama district of the lower stream catchment region to isolate towns noted for illegal gold mining operations. From the investigation, four towns along the watershed were considered. Three towns selected were in the Shama district whiles one other town was selected further upstream in the Mpohor Wassa East district.

Two of these towns, Beposo (BP) and Daboase (DB) were noted for illegal gold mining operations as at October 2012 whilst two more towns, Bokorkope (BK) and Shama (SH) estuary selected further downstream are not known for recent illegal gold mining but have a history of illegal gold mining. Samples were taken from the main river because there were no adjoining tributaries in the area of study. The distance of the river from Daboase to Shama is about 20 km.

Site 1 Daboase: Upstream Lower Catchment Region (N 05° 08´ 29.0´´, W 001° 39°´ 09.5´´)

This site is located in the Daboase Township in the Mpohor Wassa East district. The major anthropogenic activity that takes place in this area is the illegal mining of gold by galamsay operators. Their activity bothers on piling of heaps of sand and using of a mobile rig on the water bed for winning the metal from the heaps. The local water works that supplies the water in the Western Region is situated in this area. The water body is turbid and muddy on sight since the operators wash their heaps direct into the river.

Plate 3.1: A section of the Lower Pra River at Daboase which is a current AGM site. Piles of sand located at the center of the river which aids in AGM operations.

Site 2 Beposo: Midstream Lower Catchment Region (N 05° 07´ 24.5´, W 001° 36°´ 59.8´)

This site is located 5 km downstream site one. The site is impacted by a lot of anthropogenic activities especially the illegal mining of gold. The processes and equipment used are the same as stated in site one. Unlike site one, people live on the banks of the river here and depend on the river so much for their livelihood. Important landmarks here are the bridge which connects Accra to Takoradi with very high vehicular traffic and a busy market.

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Plate 3.2: A section of the Lower Pra River at Beposo which is a current AGM site

Site 3 Bokorkope: Midstream Lower Catchment Region (N 05° 04´ 22.2, W 001° 37°´ 00.8)

This site is located 6 km downstream site two. This site is located in a forest with rural settlement mainly engaged in farming and fishing. There is no recent known illegal gold mining activity. The flow rate and direction of flow of the river is however interesting depending on the tide at the Shama estuary. The flow of river water in this particular location is against the direction of water current during high ocean tides.

Plate 3.3: A section of the Lower Pra River at Bokorkope currently not known for AGM operations

Site 4 Shama Estuary: Downstream Lower catchment region (N05°00´49.2, W001°37°´50.0)

The Lower Pra River enters the Gulf of Guinea at this location. It is a typical fishing community characterized by a lot of anthropogenic activities such as the discharge of effluents either from homes or small artisan shops into the river. Recent illegal gold mining is absent at this site. The estuary at Shama is a coastal plain estuary. Coastal plain estuary is formed by the sea level rising and filling an existing river valley. It is also classified as a well-mixed estuary due to strong tidal mixing and low river flow that mix the sea water throughout the shallow estuary. Mixing is so complete that the salinity is the same top to bottom and decreases from the ocean to the river (Tufour *et al.*, 2007).

Plate 3.4: A section of the Lower Pra River at Shama estuary which is a coastal plain estuary

3.2 SAMPLING

Sampling was done twice in the month of October during the minor rainy season and at the apex of the dry season in March to represent the dry and wet seasons of the southern belt of the country. Water, Sediments and Fish species were sampled at the four sites. For each sampling site, water samples were collected at different points up to a kilometer headwater upstream from isolated sampling locations (Donkor *et al.*, 2006[a, b]).

Water was collected at about 30 cm below water surface with the aid of an improvised water sampler. Water samples were collected into acid (2 mL Conc. HNO_3) pre-treated poly-teflon bottles using the ultra-clean free-metal sampling protocol (EPA, 1996). Sediment was sampled from the riverbed and this was done by divers. Both dried and wet fish samples were obtained

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from natives living at the banks of the river. In the study area it was observed that fish is consumed after smoking with wood fire and this process allows the villagers to store large amounts of fish (Donkor *et al.*, 2006^{b}).

3.2.1 Sample Collection

Sediments were sampled in triplicates, collected into acid pre-treated poly-ethylene bags and then aggregated to form a composite sample. Fish samples were collected into pre-treated poly-ethylene bags, sealed and placed in an ice chest together with water and sediment samples and brought to the lab for further preparation and analysis.

For water samples, physicochemical parameters such as temperature, pH and electrical conductivity were recorded on the field using a Hanna's portable dual purpose pH-conductivity meter which was pre-calibrated in the laboratory. Azide modification of the Winkler method was used to fix oxygen on the field for dissolved oxygen analysis (DO). Water samples for biochemical oxygen demand (BOD) were collected into BOD 300mL dark bottles with the same azide modification/Winkler principle.

Water samples for other parameters such as hardness, alkalinity, total solids (TS, TSS, and TDS) and water nutrients were fetched into different treated poly-ethylene bottles (1.5 L), stored under ice and analyzed immediately upon arrival at the laboratory. Water samples for microbial studies were collected into sterilized bottles and frozen prior to analysis.

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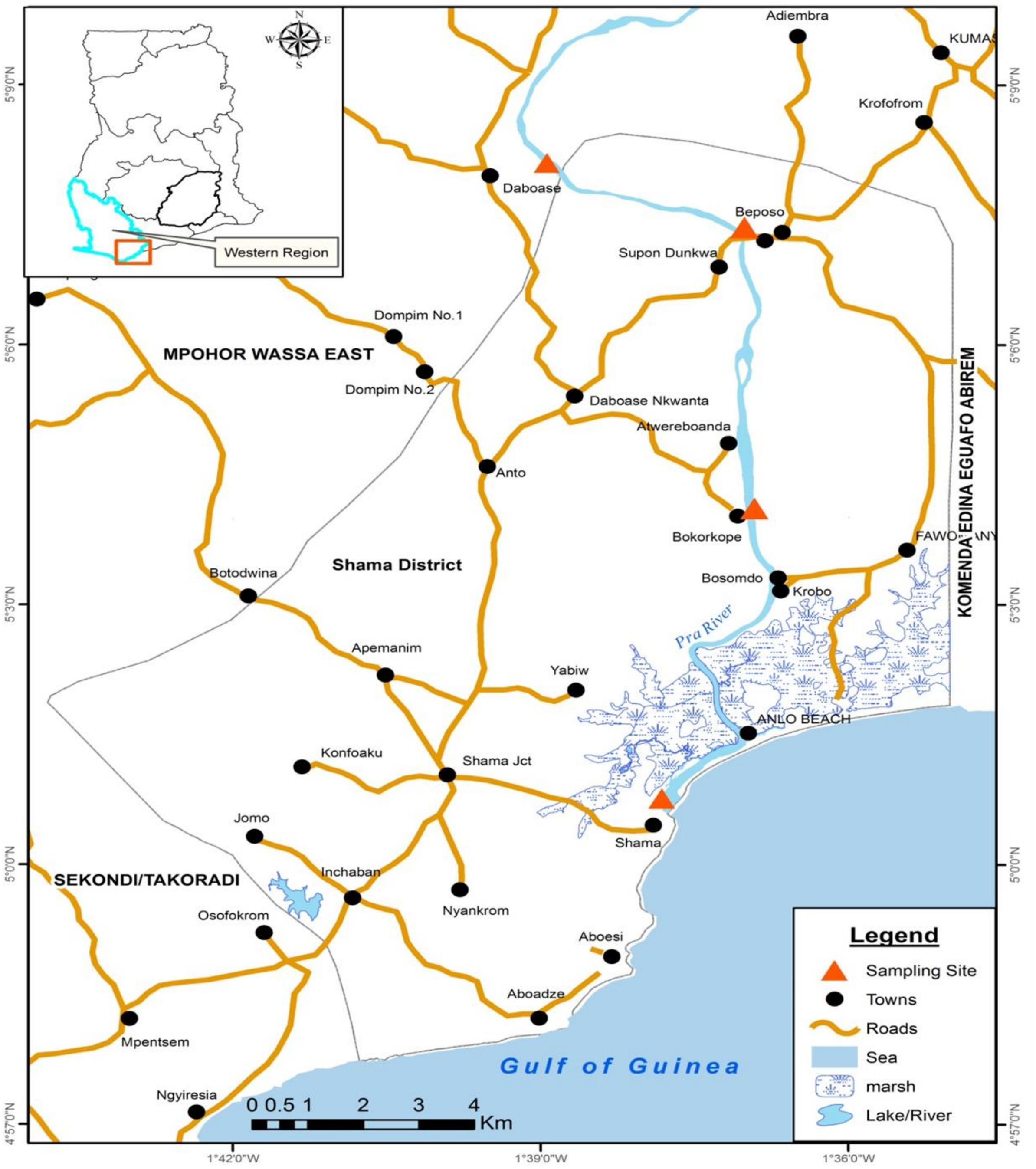

Figure 3.2: Map showing the four sampling sites at the lower catchment regions of the Lower Pra River. Samples were taken from locations at Daboase, Beposo, Bokorkope and Shama in the Shama and Mpohor Wassa East district of the western region. The distance of River water understudy is about 20 km.

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3.2.2 Sample Preparation

3.2.2.1 Cleaning of Glassware

Glassware were treated by washing under deionised running water, soaking and boiling in nitric acid bath (20 % v/v) overnight and dried in an oven.

3.2.2.2 Water Samples

Approximately 100 mL of sampled water which had already been acidified with Conc. HNO_3 during sampling was further acidified and transferred into a beaker and gently heated for five minutes on a hot plate. The solution was then filtered with Whatman no. 42 filter paper and made up to the 100 mL mark with deionized water for analysis.

3.2.2.3 Sediment Samples

Sediments were air dried and broken down into finer particles using a porcelain mortar and pestle and then passed through a 2 mm sieve. The < 2 mm fine sample was further ground with pestle and mortar and passed through a 325 μm mesh sieve. Approximately 1 g of each sediment sample was digested with 20 ml acid mixtures (3:7 v/v) HNO_3:$HClO_4$ and (9:3:1 v/v) HNO_3: HCl: H_2O_2 (EPA, 1995) on a hot plate.

3.2.2.4 Fish Samples

Fish samples were identified at the Department of Oceanography and Fisheries at the University of Ghana, Legon. Fish species were classified as *Clarias submarginatus* and *Xenomystus nigri*. Dried fish samples were first washed, further oven dried, and milled. Approximately 0.5 g of each dried fish sample was digested with 10 mL (5:2 v/v) HNO_3 / H_2O_2. Fresh fish from the freezer was partly thawed then lengths and weights were recorded. Steel scissors and forceps were used to remove the skin and a steel knife was further used to dissect the fish into various parts.

Fish tissues were homogenized on a steel plate and ground in a porcelain mortar. Approximately 0.5 g of fresh fish sample was digested using the same procedure as done for the dried fish sample. After digestion, the digestate was allowed to cool completely and then diluted, filtered and made up to the 100 mL mark with de-ionized water in a volumetric flask (Ntow and Khwaja, 1988).

3.2.3 Instrumental Models

Heavy metals such as Cd, Cu, Pb, Zn, Ni, Fe, Cr and Mn in the filtrate of digested samples were analyzed with Atomic Absorption Spectrophotometer (Model AAnalyst 400, Perkin Elmer Inc., Norwalk, CT, USA and VARIAN, AA240FS, product of USA/AUSTRALIA) present at the Ghana Atomic Energy Commission (GAEC), Kwabenya and AGILENT 270 FS present at the Water Research Institute (WRI), Council for Scientific and Industrial Research (CSIR) located at Airport Residential Area, Accra. The instrument was calibrated manually with prepared standard solution of concentrations 1 mg/L, 2 mg/L, and 5 mg/L of the respective salts of heavy metals. An air/acetylene flame mixture was used for volatilizing the sample. However for Hg and Se, AAS equipped with both cold vapour (CVAAS) and hydride generation (HGAAS) compartments was used. Alkali metals Sodium (Na) and Potassium (K) were analyzed using the Flame photometer.

3.2.4 Analysis of Soil Physicochemical Parameters

3.2.4.1 Soil pH

Approximately 20 g of the sieved air-dried soil sample was put into a 100 mL beaker and 50 mL distilled water added. The suspension was agitated vigorously for 5 min using a mechanical shaker and then allowed to settle for 2 hours. The pH was measured with the Hanna pH meter. For precise measurements, the pH meter was pre-calibrated using a two point calibration with standard buffer solutions of 4.0 and 9.0.

3.2.4.2 Electrical Conductivity

Approximately 50 mL distilled water was added to 20 g of the sieved air-dried soil sample in a 100 mL beaker. The suspension was mixed vigorously for 5 min. using a mechanical shaker and then allowed to settle for 2 hours. The conductivity meter was calibrated with 0.01 M KCl standard solution. The conductivity measurement was taken after the electrodes of the conductivity meter were immersed into the suspension.

3.2.5 Physicochemical Parameters of Water

Parameters such as pH, conductivity, and temperature were recorded at the field with the Hanna's portable dual purpose pH-conductivity meter. Parameter such as dissolved oxygen (DO), biochemical oxygen demand (BOD), water hardness, total alkalinity, total dissolved and suspended solids (TDS & TSS) and water nutrients were also determined using various titrimetric and volumetric analysis in the laboratory. Microbial activity such as total coliform (TC), faecal coliform (FC), total heterotrophic bacteria (THB) and *E. coli* counts were determined at the microbiology laboratory at CSIR, Water Research Institute.

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3.2.5.1 Dissolved Oxygen (DO)

Water sample for dissolved oxygen determination was collected into 300 mL BOD bottles. The BOD bottle was carefully immersed into the water so that water gently fills the bottle without creating bubbles. Approximately 2 mL of Winkler I (480 g $MnSO_4 .4H_2O$ in distilled water filter and dilute to 1 L) is introduced by submerging the tip of the pipette into the sampled water. This was followed by the introduction of Winkler II (Alkali-iodide-azide reagent; 500 g NaOH, 150 g KI, 10 g NaN_3 in 40 mL of distilled water diluted to 1 L).

The formation of reddish brown precipitate indicates the fixing of oxygen in the sampled water. The stopper was then placed into the BOD bottle. Prior to titration, 2mL of conc. H_2SO_4 was introduced to dissolve the precipitate and to liberate iodine. Approximately 100 mL of water sample was titrated against 0.015 M standardized thiosulfate solution (APHA AWWA WEF, 1998).

3.2.5.2 Biochemical Oxygen Demand (BOD)

Dilutions must result in a sample with a residual DO (after 5 days of incubation) of at least 1 mg/L and a DO uptake of at least 2 mg/L. Approximately 40 ml of water sample was diluted with aerated water into a 1 L volumetric flask. Mixed diluted water sample was siphoned into three separate BOD 300 ml bottles, and stoppered to prevent entry of air. The initial dissolved oxygen was determined on one bottle whilst the other two were incubated at 27 °C for five days. BOD was computed as the difference between the DO for day-1 and day-5 per the decimal volumetric fraction of sample used (APHA AWWA WEF, 1998).

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3.2.5.3 Total Water Hardness

Ethylenediaminetetra-acetic acid (EDTA) di-sodium salt (3.723 g di-sodium salt of EDTA was dissolved in distilled water and diluted to 1 L) of 0.01 M stock solution was standardized with standard calcium carbonate ($CaCO_3$) solution. About 2 mL of buffer solution (16.9 g NH_4Cl dissolved in 143 mL conc. NH_4OH and diluted to the 250 mL) was added gradually to 10 mL of water sample to give it a pH between 10.0 and 10.1. Two drops of Eriochrome Black T indicator were added to the water sample to give a reddish tinge colour. The water sample was titrated against standardized EDTA solution to a blue colour endpoint (APHA AWWA WEF, 1998).

3.2.5.4 Total Alkalinity

Stock solution of 0.01 M HCl was standardized against 0.05 M of Na_2CO_3 with methyl orange as the indicator. Two to three drops of bromocresol green indicator were added to 10 mL sampled water and then titrated against standardized HCl from blue to yellow colour change at the endpoint (Vogel, 1978).

3.2.5.5 Total Suspended Solids (TSS)

Filter paper (Whatman 42) was placed on to a filter assembly and washed with deionized water. The filter paper was placed in an aluminum dish and dried in an oven at 80 °C for 30 minute, cooled in a desiccator and weighed to achieve a constant weight. The filtration apparatus was assembled using the washed dried and weighed filter paper and was made wet in order to seat it. Sampled water was stirred with a magnetic stirrer and while stirring, 100 mL water sample was measured on to the filter apparatus using a pipette and then suctioned. The filter paper was washed with distilled water and suction was continued for about a minute. The filter paper was

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then carefully removed, placed into an aluminum dish, dried, cooled and reweighed (APHA AWWA WEF, 1998).

3.2.5.6 Total Dissolved Solid (TDS)

The same procedure as stated for TSS determination was followed except that the total filtrate was transferred to a weighed evaporating dish and evaporated to dryness in an oven at around 100 °C. The evaporating dish was cooled in a desiccator and reweighed (APHA AWWA WEF, 1998).

3.2.5.7 Microbial Studies

Microbial parameters consisting of, Total Coliform (TC), Faecal Coliform (FC), *E. coli*, and Total Heterotrophic Bacteria (THB) were carried out at the Water Research Institute (WRI), CSIR at Achimota. The American Public Health Association (APHA) protocols 9222A, 9222D, 9260F, and 9215B were employed in the analysis of TC, FC, *E. coli*, and THB respectively.

3.2.5.8 Sodium (Na) and Potassium (K)

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

3.2.5.9 Quality Control

Appropriate quality control procedures and precautions were taken to avoid contamination and ensure the reliability of the data. Samples were carefully handled to avoid contamination. Analytical grade reagents were used in this study. Deionized water was used throughout the study. Standard solutions of heavy metals were used to calibrate instruments. Various reagent blanks were prepared and measurements were done to account for interferences by other species and traces of analyte found in reagents (impurities) used for sample preservation, preparation and analysis. For validity of analytical procedure, certified reference material (CRM) Estuarine Sediment 1646A and SO-1 reference soil from the Canadian reference material project were analyzed against sediment samples. All samples were analyzed in triplicates and the results averaged. Results of certified and measured values of standard reference material SO-1 soil and Estuarine Sediment 1646A are presented in Tables 3.1 and 3.2 respectively.

Table 3.1: Certified and measured values for standard reference material SO-1 soil

Element	Certified values/ mg/Kg	Measured values/ mg/Kg
Cd	-	-
Cr	160.1 ± 0.1	155.0 ± 0.8
Cu	61 ± 2	52.0 ± 0.7
Fe	6.00 ± 0.07	5.5 ± 0.8
Mn	0.089 ± 0.04	0.066 ± 0.009
Ni	139 ± 2	121 ± 5
Pb	21 ± 2	17 ± 1
Zn	146 ± 4	144.0 ± 0.6

Hg	0.022 ± 0.005	0.023 ± 0.009
Se	-	-

Table 3.2: Certified and measured values for standard reference material 1646 A

Element	Certified values/ mg/Kg	Measured values/ mg/Kg
Cd	0.148± 0.007	0.142 ± 0.009
Cr	-	-
Cu	10.0± 0.3	9.0 ± 0.1
Fe	2.01± 0.04	1.98 ± 0.05
Mn	235 ±3	224 ± 2
Ni	2.3± 0.2	1.8 ± 0.5
Pb	12 ±1	1 ± 2
Zn	49 ±2	42.7 ± 0.9
Hg	0.040 ±0.003	0.037 ± 0.007
Se	0.19 ±0.03	0.18 ± 0.01

Percentage recoveries on reference material 1646A and SO-1 ranged from 78% to 99% and 74% to 104.5% respectively. Recoveries above 70% show the reproducibility of the analytical method in this project.

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3.3 DATA ANALYSIS

Statistical analysis was performed using the statistical package SPSS (v 16.0, SPSS Inc., Chicago, IL, USA) and Microsoft Excel 2010 (Microsoft Corp.).

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CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

The results of field and laboratory analyses are presented in the form of figures and tables in this section. Tabulated mean results of the parameters studied are presented alongside safe limits where necessary. Statistical analysis and models such as descriptive and discriminant analysis, one-way ANOVA, Pearson correlation and regression analysis, and principal component analysis (PCA) (environmetrics) were applied to the results obtained to highlight the relationship between elements and other parameters as well as to identify the various sources of these elements.

4.1.1 Physical Parameters of Water and Sediments

4.1.1.1 Temperature

The results of various physical parameters for water and sediment samples are presented in Tables 4.1A and 4.1B. Recorded mean temperature of water for the wet season was 28.6 °C. Temperature ranged from 27.5 °C to 29.5 °C for river water in the study area for the wet season. Maximum temperature for the wet season was recorded at Bokorkope with the minimum temperature recorded at Shama (Table 4.1B). There was a rise in temperature in the dry season with recorded mean value of 31.3 °C and a range from 30.8 °C to 32.0 °C. Minimum temperature of water in the dry season was recorded at Daboase with the maximum temperature recorded at Shama. Cooling effect from rainfall resulted in lower temperature readings in the wet season (Table 4.1B).

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4.1.1.2 Conductivity

Recorded mean conductivity of water in the wet season was 25.85 ms/cm. Minimum conductivity (11.60 ms/cm) was recorded at Daboase while a maximum conductivity (36.90 ms/cm) was recorded at Bokorkope. In the dry season, minimum conductivity of 152 µS/cm was recorded at Daboase with an overall mean conductivity of 2386.13 µS/cm recorded for the study area (Table 4.1B). Mean sediment conductivity was higher in the dry season (544.83 µS/cm) than in the wet season (133.125 µS/cm). Sediment conductivity generally increased moving downstream along the water course in the dry season with the highest reading of 1548 µS/cm recorded at Shama (Table 4.1B).

4.1.1.3 pH

The water samples recorded a mean pH value of 7.2 in the wet season and a value of 7.7 in the dry season (Table 4.1A). The pH of river water was fairly neutral for the two seasons. The highest pH in the wet season was recorded at Shama with a value of 7.38 and the lowest of 6.98 recorded at Daboase. The highest pH in the dry season was recorded at Beposo with a value of 8.31 with minimum pH of 6.73 recorded at Daboase. There was a general increase in pH moving downstream for the wet season. The pH of river water for both seasons were within the WHO and USEPA safety limits of 6.5-8 and 6.5-8.5 respectively. The pHs of sediments for both seasons were below the value of 7 and classified as acidic (Table 4.1A). Maximum pH values of 6.0 and 6.1 were both reported at Shama for the wet and dry seasons respectively.

Table 4.1A: pH Distributions in Water and Sediments Samples

Locations	River Water		Sediments	
	Wet Season	Dry Season	Wet Season	Dry Season
Daboase	6.98±0.01	6.73±0.07	5.56±0.01	4.7±0.8
Beposo	7.01±0.01	8.31±0.01	5.77±0.05	5.46±0.05
Bokorkope	7.23±0.01	7.51±0.01	5.53±0.01	4.1±0.3
Shama	7.38±0.01	8.23±0.01	6.0±0.1	6.1±0.4
Mean	7.150	7.695	5.725	5.085
SD (3 Sig)	0.164	0.638	0.204	0.756
Range	6.98-7.38	6.73-8.31	5.53-6.00	4.1-6.1
Mean ± SD (1 Sig)	7.2±0.2	7.7±0.6	5.2±0.2	5.1±0.8

*WHO safe limits 6.5-8, USEPA 6.5-8.5

Table 4.1B: Physical Parameters of Water and Sediment Samples

	Wet Season			Dry Season		
Location	Temp /°C	Water Cond./ mS/cm	Sediment Cond./ µS/cm	Temp /°C	Water Cond./ µS/cm	Sediment Cond./ µS/cm
Daboase	29.0	11.6	146.0	30.8	152.0	53.3
Beposo	28.5	33.0	101.4	31.0	1394.5	164.3
Bokorkope	29.5	36.9	72.1	31.4	>3999	413.8
Shama	27.5	21.9	213.0	32.0	>3999	1548.0
Max.	29.5	36.9	213.0	32.0	>3999	1548.0
Min.	27.5	11.6	72.1	30.8	152.0	53.3
Mean	28.63	25.85	133.13	31.3	2386.13	544.83

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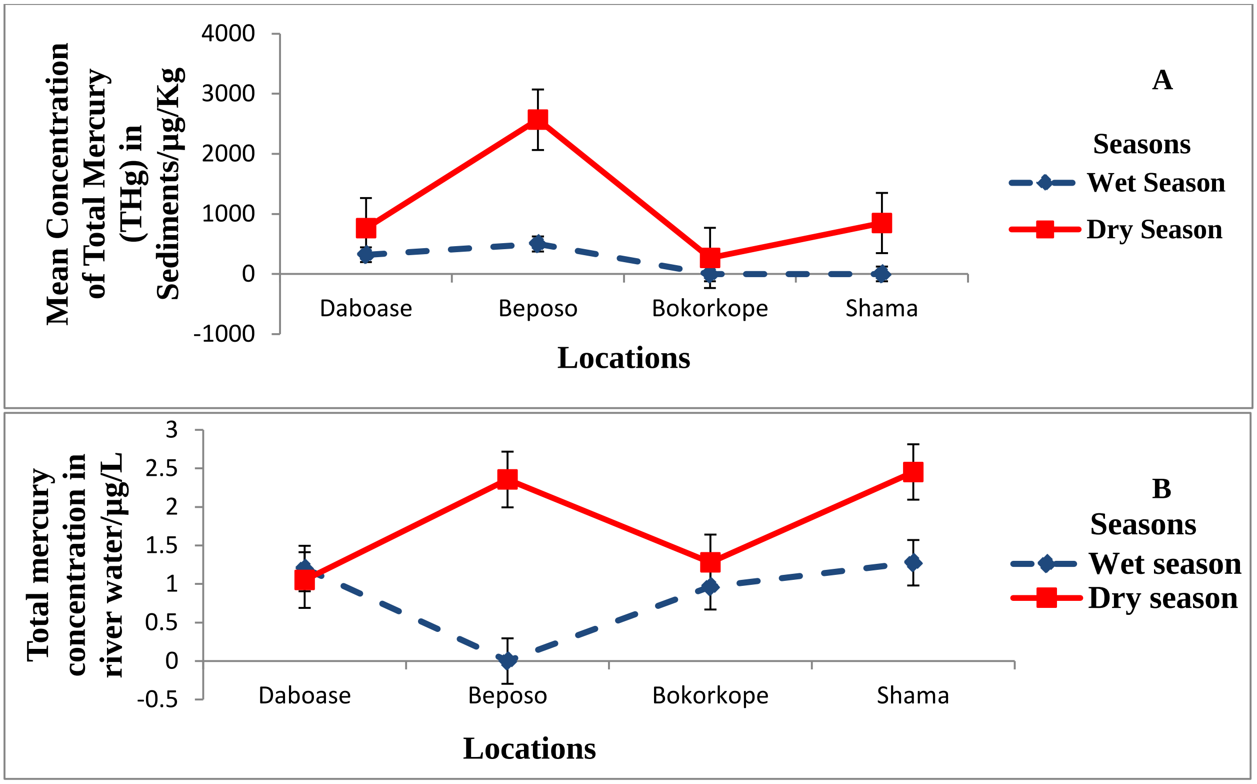
4.2 DISTRIBUTION OF MERCURY AND SELENIUM IN WATER AND SEDIMENTS

4.2.1 Mercury levels

The distributions of THg in water and sediment for the four locations are illustrated in Figures 4.1A and 4.1B. THg concentration in sediment and River water showed an unusual pattern for both seasons moving downstream from the first AGM site at Daboase. In the wet season, mean THg concentration of 1.2 µg/L was recorded in the water at Daboase. THg concentrations were below detection limits in the river water at Beposo, an AGM site 6 km downstream Daboase. Mean THg concentration of 0.97 µg/L was recorded 6 km further downstream at Bokorkope which had increased to 1.3 µg/L over a distance of 8 km at Shama (Figure 4.1B).

In the dry season, the highest concentration of THg was recorded at Shama (2.4 µg/L) 20 km from the first AGM site at Daboase. Minimum concentration of 1.1 µg/L was recorded at Daboase. Concentration of THg in water was generally higher in the dry season for the four locations with an overall mean concentration of 1.7 µg/L compared to 0.7 µg/L for the wet season.

Both AGM sites at Daboase and Beposo recorded THg concentration of 302 µg/Kg and 500 µg/Kg in the sediments respectively for the wet season. However THg concentrations were below the detection limits in the sediments at Bokorkope and Shama for the wet season. THg concentration in sediments was generally higher in the dry season with minimum concentration of 297 µg/Kg recorded at Bokorkope and a maximum concentration of 2568 µg/Kg recorded at Beposo. An overall mean concentration of THg in sediments was 205 µg/Kg in the wet season compared to an overall mean concentration of 1111 µg/kg in the dry season for the four locations (Appendix B18).



Figures 4.1A-B: Mean concentrations of Total Mercury (THg) in sediments (A) and water (B) for both Dry and Wet season for the four locations. Sampling locations not drawn to scale. Error bars set at 1 standard deviation.

4.2.2 Selenium levels

The distributions of Se in water and sediment samples for the four locations are illustrated in Figures 4.2A and 4.2B. Selenium levels in river water gradually decreased over a distance of 12 km downstream Daboase with a minimum average concentration of 0.65µg/L recorded at Bokorkope. There was a marginal rise in the concentration of Se 8 km further downstream Bokorkope at Shama (0.7 µg/L). The maximum average concentration of Se in the wet season was recorded at Daboase (1.1 µg/L) with an overall mean concentration of 0.7 µg/L for the study area. Selenium levels were relatively higher in water for the dry season than the wet season with maximum average concentration recorded at Shama (12 µg/L) and minimum average concentration recorded at both Daboase (5 µg/L) and Bokorkope (5 µg/L) (Figure 4.2B).

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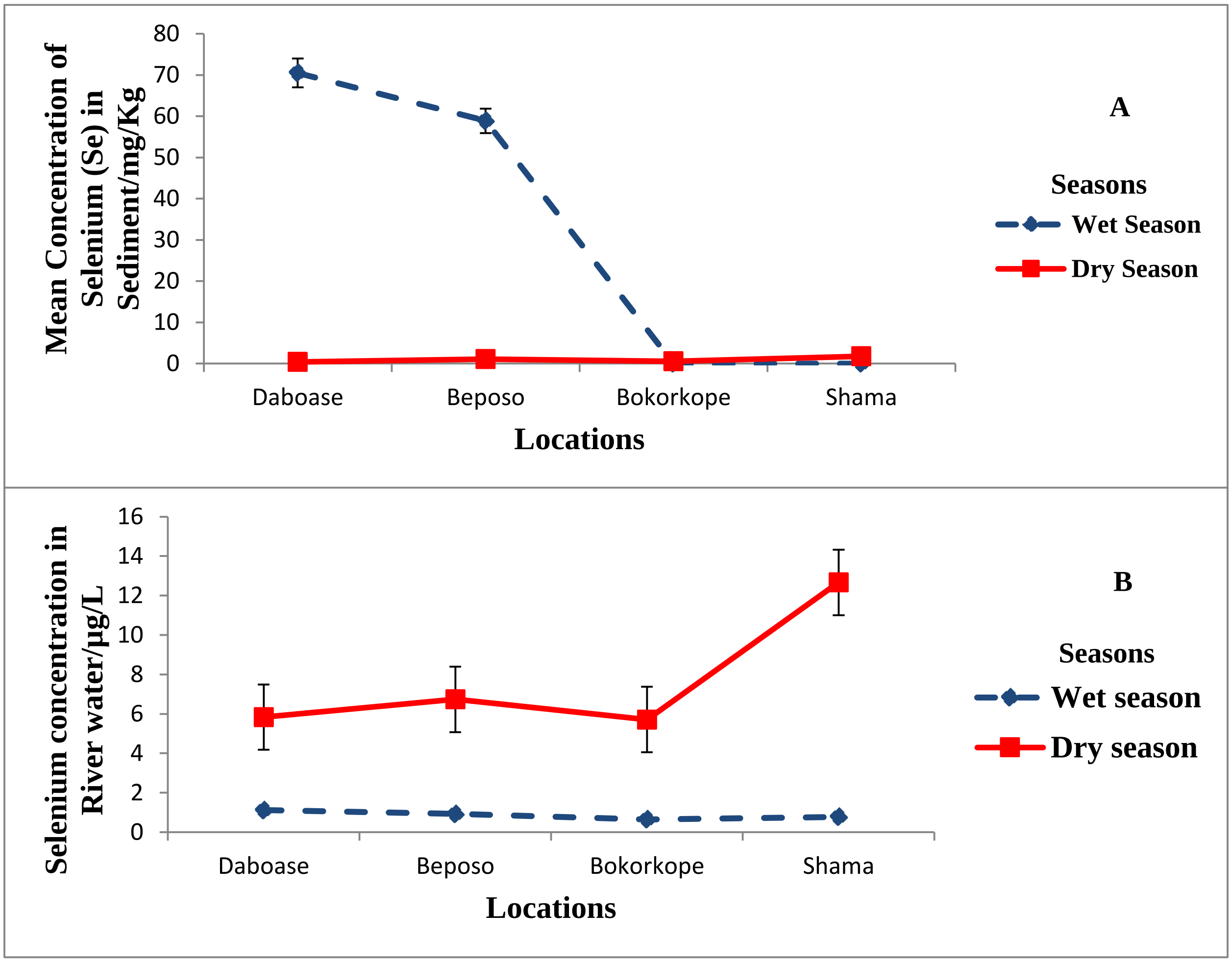
Selenium levels in sediments were abundantly high in the two AGM sites Beposo and Daboase with overall mean concentrations of 58 mg/Kg and 70 mg/Kg respectively for the wet season. Selenium was below detection limit further downstream at Bokorkope and Shama. The least concentration of selenium in sediments for the dry season was recorded at Daboase (0.4 mg/Kg) with the highest recorded at Shama (1.8 mg/Kg). Selenium profile in sediments was similar for the two seasons both showing a wide distribution along the water course (Figure 4.2A).

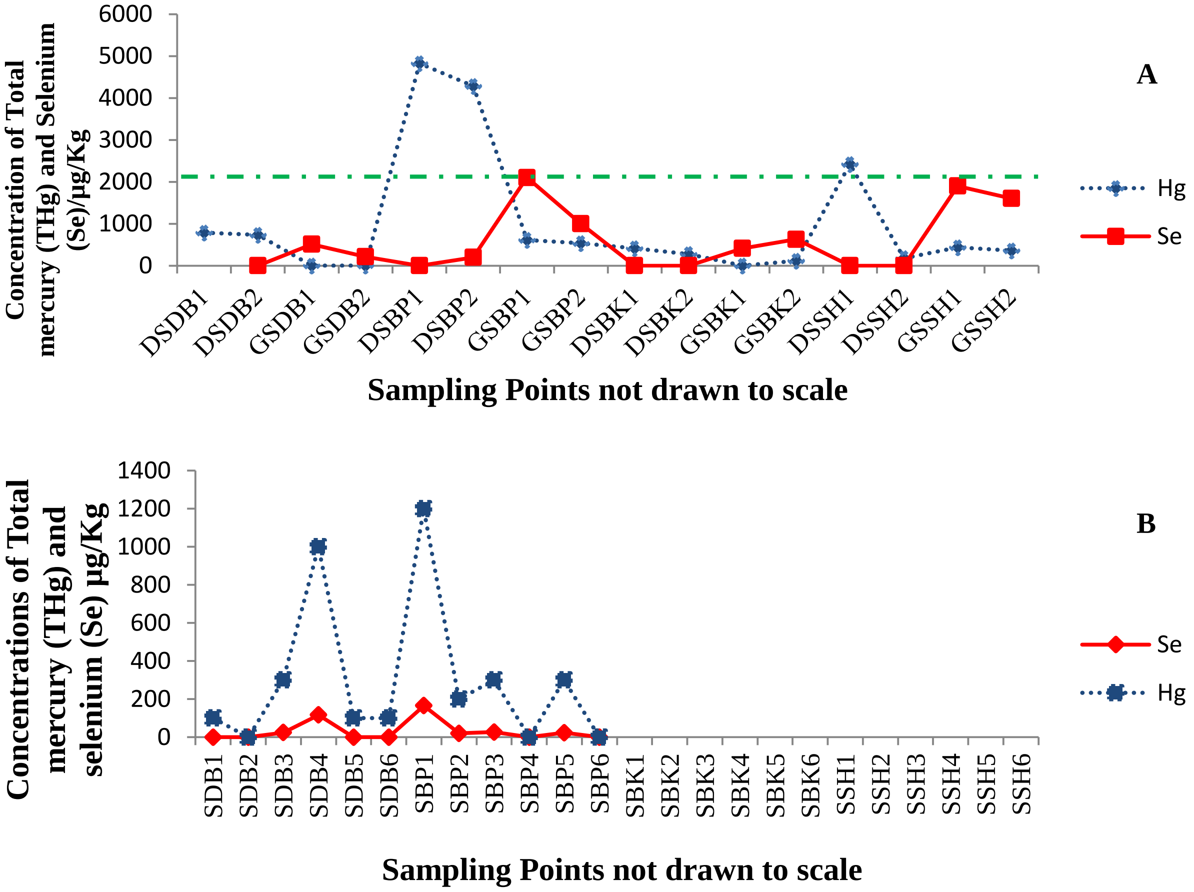


Figures 4.2A-B: Mean concentrations of Selenium (Se) in sediments (A) and water (B) for both Dry and Wet season for the four locations in the Study Area. Sampling locations not drawn to scale. Error bars are set at 1 standard deviation.

4.3 MERCURY AND SELENIUM INTERACTION IN AQUATIC ECOSYSTEM

4.3.1 Sediments

Selenium concentration in sediments was generally higher than mercury in the wet season with the highest concentrations of Se reported at individual sampling sites SBP1 and SDB4 (Figure 4.3B). However in the dry season, there were some sampling sites with THg concentrations higher than Se. Sampling sites DSDB1, DSDB2, DSBP1, DSBP2, DSBK1, DSBK2, DSSH1, and DSSH2, all reported higher levels of THg than Se (Figure 4.3A). Figures 4.3A and 4.3B illustrate the THg-Se concentrations in sediment for dry and wet seasons respectively.



Figures 4.3A-B: Line charts showing the longitudinal distribution of THg-Se concentrations in Riverbed sediments for both seasons. Broken green line in Fig. 4.3A set at the maximum concentration of Se. DSDB1-GSSH2 are the sampling sites of sediments for the dry season (A). SBP1-SSH6 are the sampling sites of sediments for the wet season (B). DB-Daboase, BP-Beposo, BK-Bokorkope, SH-Shama

Figures 4.4A and 4.4B are the projected scatter diagrams from the two line charts of individual sampling point of sediments for both seasons. The regression analysis and Pearson correlation studies differed for the two seasons. There was a strong positive relationship between THg and Se for the sediments in the wet season (n = 24, r^2 = 0.9781, r = 0.989) (Figure 4.4B) and a weak inverse relationship between the two in the dry season (n = 16, r^2 = 0.072, r = - 0.269) (Figure 4.4A). The relationship between THg and Se were significant for both seasons which is indicative of the possible association between both elements in sediments (Jin *et al.*, 1999).

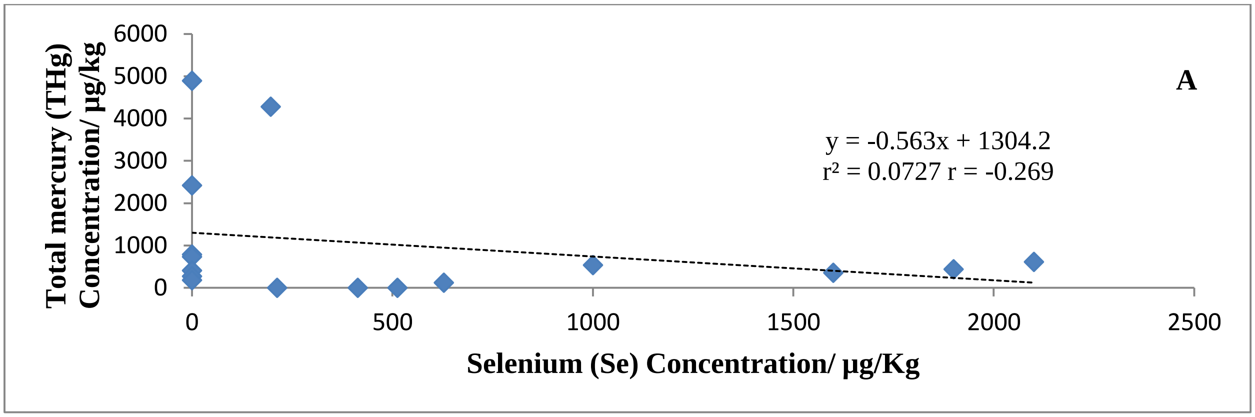


Figure 4.4A: Scatter plot diagram showing THg as a function of Se for individual sampling points of sediment for Dry Season

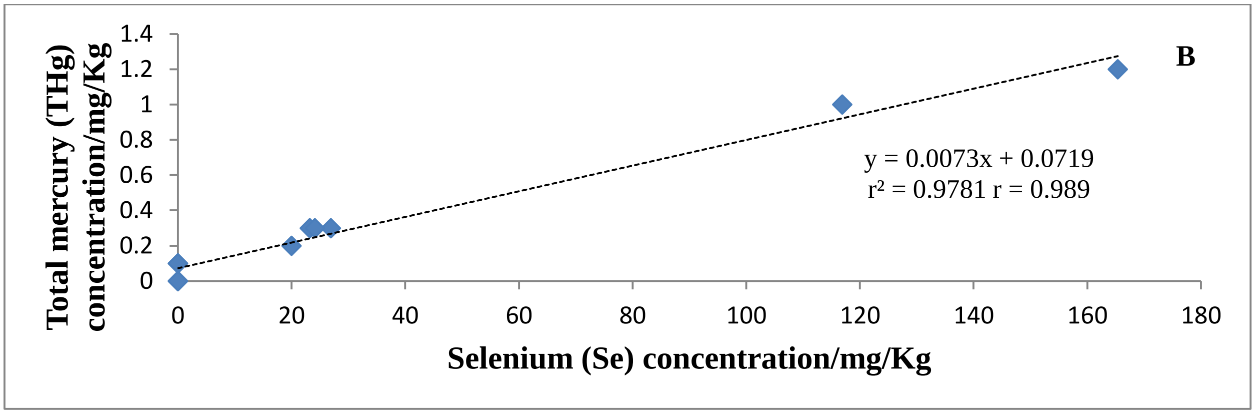
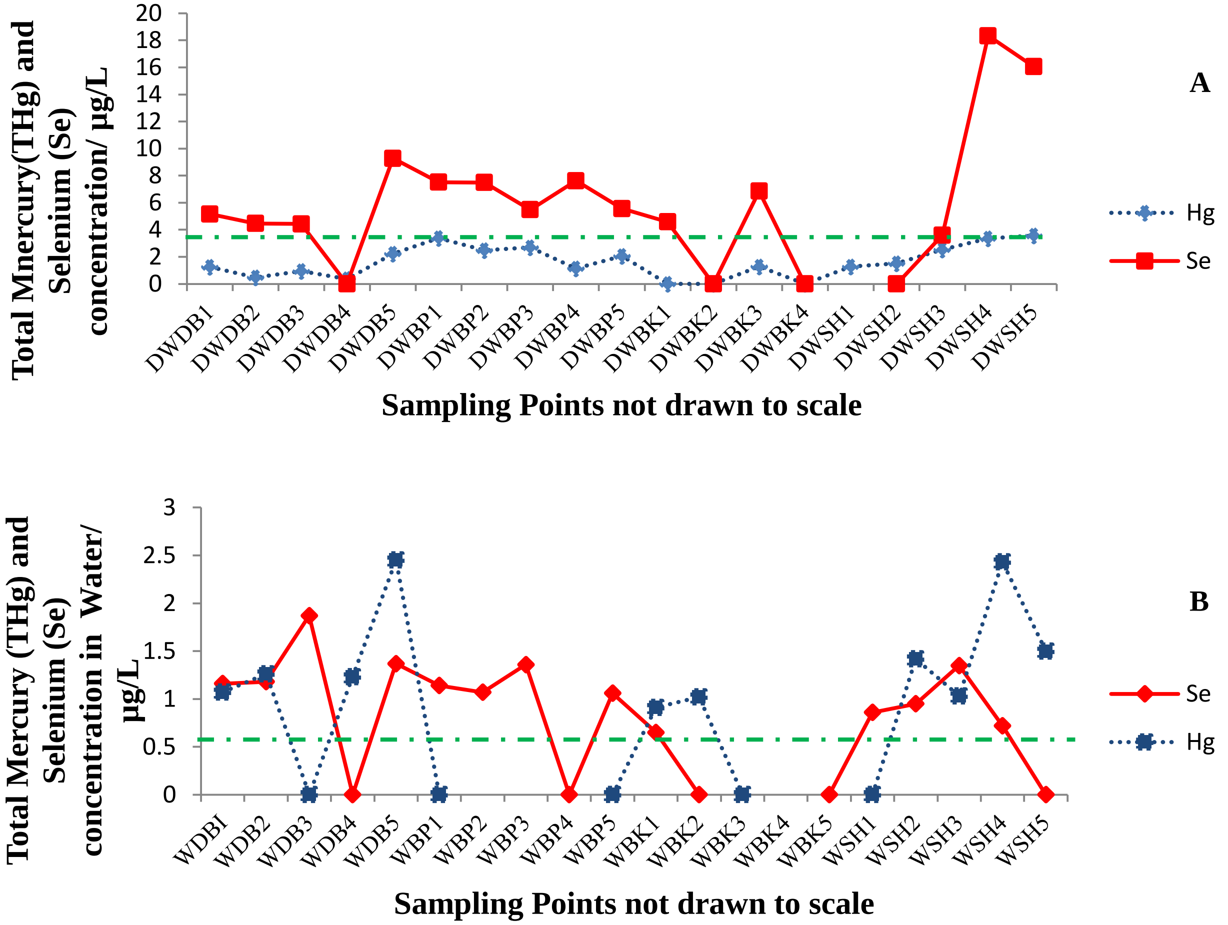


Figure 4.4B: Scatter plot diagram showing THg as a function of Se for individual sampling points of sediment for Wet Season

4.3.2 River water

Selenium concentrations in water samples were generally higher than THg for the two seasons. Total mercury concentrations were higher for individual sampling sites WDB2, WDB5, WBK1, WBK2, WSH2, WSH4 and WSH5 in the wet season (Figure 4.5B). Individual sampling points DWDB2, DWSH1 and DWSH2 had THg concentration higher than Se for the dry season (Figure 4.5A). Line charts for THg-Se concentrations in water for both seasons are illustrated in the Figures 4.5A and 4.5B below.



Figures 4.5A-B: Line charts showing the longitudinal distribution of THg-Se concentration in surface water for both seasons. Broken green line in Fig. 4.5A set at the maximum concentration of THg. Broken green line in Fig. 4.5B set at the minimum detected concentration of Se. GWDB1-GWSH2 are the sampling sites of water for the dry season (A). WBP1-WSH6 are the sampling sites of surface water for the wet season (B). DB-Daboase, BP-Beposo, BK-Bokorkope, SH-Shama

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Figures 4.6A and 4.6B are the scatter diagrams from the line charts of individual sampling sites of surface water for both seasons. A strong positive relationship was observed for THg and Se in the dry season for water (n = 19, r^2 = 0.5246, r = 0.724) (Figure 4.6A). In Figure 4.6A, an increase in mercury across the individual sampling sites is characterized by a decrease in selenium. However no relationship was observed for THg and Se in the wet season for water (n = 20, r^2 = 0.0895, r = 0.0635) (Figure 4.6B). Clearly the regression and correlation studies showed that the relationship between the two elements differed for both seasons.

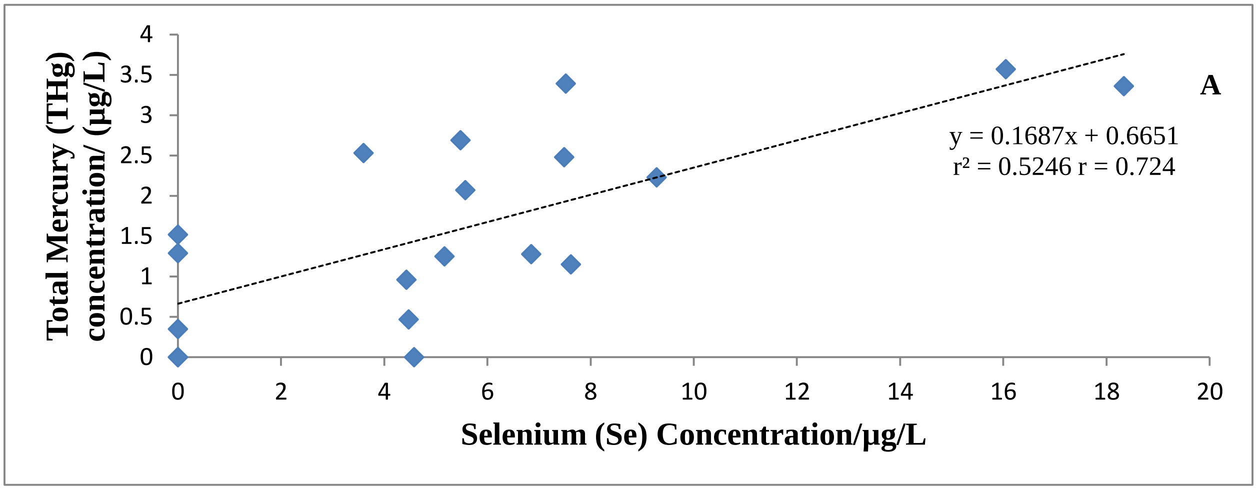

Figure 4.6A: THg - Se correlation curves of individual sampling sites of water for Dry Season

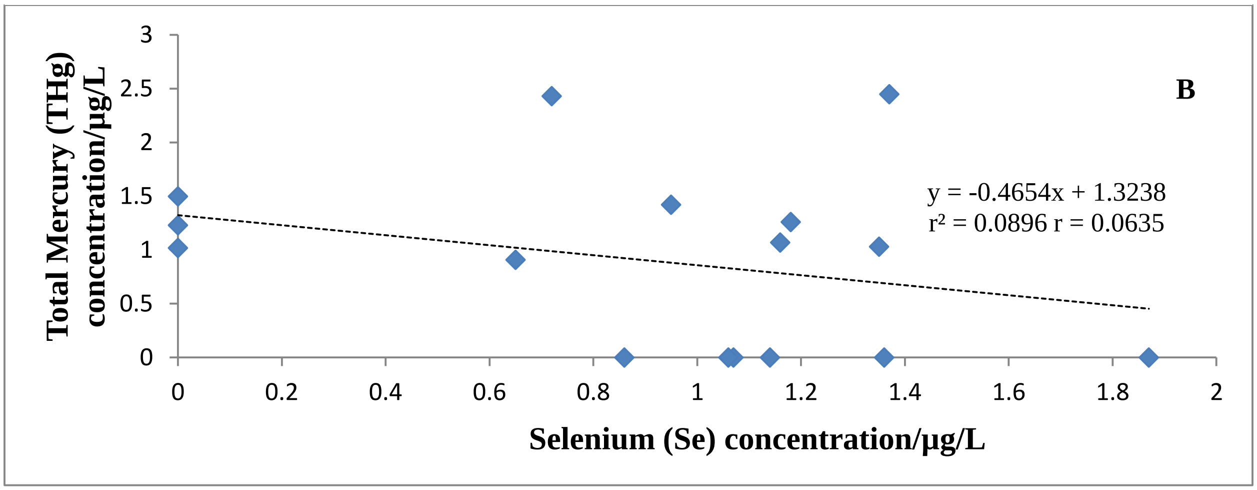

Figure 4.6B: THg - Se correlation curves of individual sampling sites of water for Wet Season

4.4 TRACE ELEMENTS IN FISH SPECIES

Ten trace elements Hg, Se, Cd, Cu, Fe, Mn, Pb, Cr, Ni, and Zn were measured in different tissue parts of *Xenomystus nigri* and in the dorsal tissues of *Clarias submarginatus* (Mudfish). Cu and Cd were below the detection limit in Mudfish (Table 4.2). Fe recorded the highest average concentration in Mudfish (372 mg/Kg dry weight). Zn recorded an average concentration of 105 mg/kg dry weight for dorsal tissues of Mudfish. Mn recorded an average concentration of 55 mg/kg dry weight for Mudfish. Ni, Pb, Hg and Se recorded average concentrations of 12 mg/Kg, 33 mg/Kg, 1 mg/Kg and 155 mg/Kg dry weight respectively in dorsal tissues of Mudfish (Table 4.2). Trace elements were in decreasing order of:

Fe > Se > Zn > Mn > Pb > Ni > Cd > Hg > Cu ≈ Cd

Mn and Cu were below the detection limit in different tissues of *Xenomystus nigri*. Fe recorded the highest average concentration in *Xenomystus nigri* (7 mg/Kg wet weight). Hg and Se recorded an average concentrations of 315 µg/Kg and 786 µg/Kg wet weights in *Xenomystus nigri* respectively. Pb, Cd, Cr, Zn and Ni recorded average concentrations of 3.4 mg/Kg, 0.62 mg/Kg, 0.8 mg/Kg, 1.1 mg/Kg and 2.0 mg/Kg wet weights in *Xenomystus nigri* (Table 4.3).

Trace elements were in decreasing order of:

Fe > Pb > Ni > Zn > Cr > Se > Cd > Hg > Mn ≈ Cu

Concentrations of trace elements in Mudfish were relatively higher than in *Xenomystus nigri* (Tables 4.2 and 4.3). The mode of preservation of *Clarias submarginatus* such as air drying or smoking with wood fire by locals may have accounted for elevated levels of trace elements since trace elements are introduced into the fish tissues through these processes.

Table 4.2: Concentrations of trace elements in the dorsal tissues of *Clarias submarginatus* (Mudfish)

CODES/ mg/Kg	Fe	Mn	Pb	Cu	Cd	Cr	Zn	Ni	Hg	Se
F1	455.8	56	12.4	BDL	0.4	BDL	90	BDL	1.6	197.4
F2	332.8	55.8	64	BDL	BDL	BDL	108	BDL	0.2	BDL
F3	336.6	56.2	12.6	BDL	0.2	BDL	121.4	0.2	2.2	347.8
F4	336.6	55.2	68.4	BDL	2.4	BDL	106.8	2.2	0.2	17.8
F5	386.8	55.6	17.6	BDL	2.2	BDL	103.8	BDL	1.2	172.6
F6	387.2	52.4	21.4	BDL	0.6	BDL	104.2	33.6	0.4	41.8
Max.	455.8	56.2	68.4	-	2.4	-	121.4	33.6	2.2	347.8
Min.	332.8	52.4	12.6	-	BDL	-	90	BDL	0.2	BDL
Mean	372.633	55.2	32.7	-	1.16	-	105.7	12	0.9667	155.48
S.D	43.804	1.29	23.89	-	0.94	-	9.177	15.29	0.7608	119.09
Mean ±SD	372±44	55±1	33±24	-	1.1±0.9	-	105±9	12±15	1.0±0.8	155±119

* BDL- below detection limit, detection limit Cu- 0.2 mg/Kg, Cd-0.2 mg/Kg, Ni-0.2 mg/Kg, Se-0.2 mg/Kg

Fish Species: Mudfish (*Clarias submarginatus*) (Peters, 1882) n=8 (mg/Kg dry weight)

Fish length (6±1) cm, Fish weight (23±7) g, dorsal part muscle tissues

Table 4.3: Concentrations of trace elements in the different tissues of *Xenomystus nigri*

SAMPLE ID/(mg/Kg)	Fe	Mn	Pb	Cu	Cd	Cr	Zn	Ni	Hg/ (µg/Kg)	Se/ (µg/Kg)
F_{1Dr}	12.8	BDL	BDL	BDL	BDL	1.2	BDL	2.8	248	278
F_{2In}	2.8	BDL	BDL	BDL	BDL	0.2	BDL	2.0	BDL	330
F_{3Dr}	12.6	BDL	BDL	BDL	BDL	1.3	1.2	2.6	38	324
F_{4V}	BDL	BDL	BDL	BDL	BDL	BDL	0.4	0.6	460	822
F_{5Ts}	BDL	BDL	3.5	BDL	0.6	BDL	BDL	1.4	BDL	1136
F_{6V}	BDL	BDL	BDL	BDL	0.7	BDL	BDL	BDL	500	BDL
F_{7In}	2.8	BDL	BDL	BDL	BDL	0.2	BDL	2.2	BDL	242
F_{8V}	BDL	BDL	BDL	BDL	0.6	BDL	1.8	2.0	500	624
F_{9Dr}	13.6	BDL	BDL	BDL	BDL	1.2	BDL	2.6	144	1076
F_{10Ts}	2.4	BDL	3.2	BDL	0.6	BDL	BDL	BDL	BDL	2242
Max	13.6	-	3.5	-	0.6	1.3	1.8	2.8	500	2242
Min	BDL	-	BDL	-	BDL	BDL	BDL	BDL	BDL	BDL
Mean	7.83	-	3.35	-	0.625	0.82	1.13	2.025	315	786
S.D.	5.17	-	0.15	-	0.043	0.51	0.57	0.681	182.54	608.226
Mean± S.D	7±5	-	3.4±0.2	-	0.62±0.04	0.8±0.5	1.1±0.6	2.0±0.7	315±183	786±608

* BDL- below detection limit, detection limit Fe-1.2 mg/Kg, Mn-0.4 mg/Kg, Cu- 0.2 mg/Kg, Cd-0.2 mg/Kg, Ni-0.2 mg/Kg, Pb-0.2 mg/Kg, Cr-0.2 mg/Kg, Zn-0.2 mg/Kg, Se-2 µg/Kg, Hg-2µg/Kg

Fish species: *Xenomystus nigri* (Günther, 1868) n=4, (mg/Kg, µg/Kg wet weight)

Fish length (25.7±0.9) cm, Fish weight (174±2) g

4.4.1 Bioaccumulation factor (BAF) in fish species

The bioaccumulation factor of the fish was calculated as follows:

BAF= C_{fish} /C_{water}

C_{fish} and C_{water} refer to the concentration of a metal in fish and water respectively. Bioaccumulation of trace metals was observed in the dorsal tissues of Mudfish (*Clarias submarginatus*) and in various tissue parts of *Xenomystus nigri*. Cu was not detected in either fish species. Mn and Cr were not detected in the tissues of *Xenomystus nigri* and Mudfish.

Calculated BAF showed that Se and Ni bioaccumulated the highest in Mudfish and *Xenomystus nigri* respectively.

BAF in a decreasing order of trace metals in Mudfish was;

Se (1.75E5) > Pb (3667.7) > Zn (1875) > Hg (1346.1) > Mn (1100) > Ni (600) > Cd (183.3) > Fe (62) Cu ≈ Cr

BAF in a decreasing order of trace metals in *Xenomystus nigri* was;

Ni (1666.7) > Cr (160) > Cd (156) > Hg (95.87) > Se (93.07) > Zn (78.57) > Pb (68) > Fe (10) > Mn ≈ Cu

4.4.2 Mercury-Selenium concentrations and Bioaccumulation Factors (BAF) in fish parts

The concentration of THg-Se and BAF of fish tissues in both Mudfish and *Xenomystus nigri* are presented in Tables 4.2 to 4.5. Selenium (Se) concentration was relatively higher than THg concentration in the tissue parts of both fish species. F2 recorded the lowest concentration for both THg and Se in Mudfish (Table 4.2). F3 recorded the highest concentration and BAF of THg and Se in Mudfish with BAF of 3.07E3 and concentrations of 2.2 mg/Kg for THg and BAF of 4.71E5 and concentrations of 347.8 mg/Kg for Se (Tables 4.2 and 4.5).

Mercury had bioaccumulated the highest in the ventral tissue than the dorsal tissue in *Xenomystus nigri* (Figure 4.8). Mercury was however below the detection limit in the internal organs and tail section tissues of *Xenomystus nigri* (Figure 4.8). Highest concentration and BAF was recorded in ventral tissue parts F6v and F8v (500 µg/Kg, 261.7) (Table 4.4). Selenium had bioaccumulated the highest in the tail section tissues F10ts (2242 µg/Kg, 295) and was below the detection limit in F6v (Figure 4.8). Both mercury (Hg) and selenium (Se) showed a wide distribution in different tissues of *Xenomystus nigri* with Coefficient of variation (CoV/%) of 58% and 77% respectively and a wide distribution of 80% and 76% respectively for the dorsal tissue of Mudfish.

Table 4.4: Bioaccumulation Factors (BAF) in the tissue parts of *Xenomystus nigri*

Fish parts	Hg	Se	Log BAF Se	Log BAF Hg
F1Dr	129.84	36.57	1.56	2.11
F2In	0	43.42	1.63	-
F3Dr	5	42.60	1.63	0.69
F4V	240.8	108.15	2.03	2.38
F5Ts	0	149.47	2.17	-
F6V	261.7	0	-	2.41
F7In	0	31.84	1.50	-
F8V	261.7	82.10	1.91	2.41
F9Dr	59.68	141.57	2.15	1.77
F10Ts	0	295	2.46	-

Table 4.5: Bioaccumulation Factors in the dorsal tissue parts of *Clarias submarginatus*

Fish parts	Hg/E3	Se/E3	Log BAF Se	Log BAF Hg
F1	2.23	267.84	2.427	0.348
F2	0.27	0	0	-0.568
F3	3.07	471.9	2.673	0.487
F4	0.28	24.15	1.380	-0.554
F5	1.67	234.19	2.369	0.223
F6	0.56	56.71	1.753	-0.253

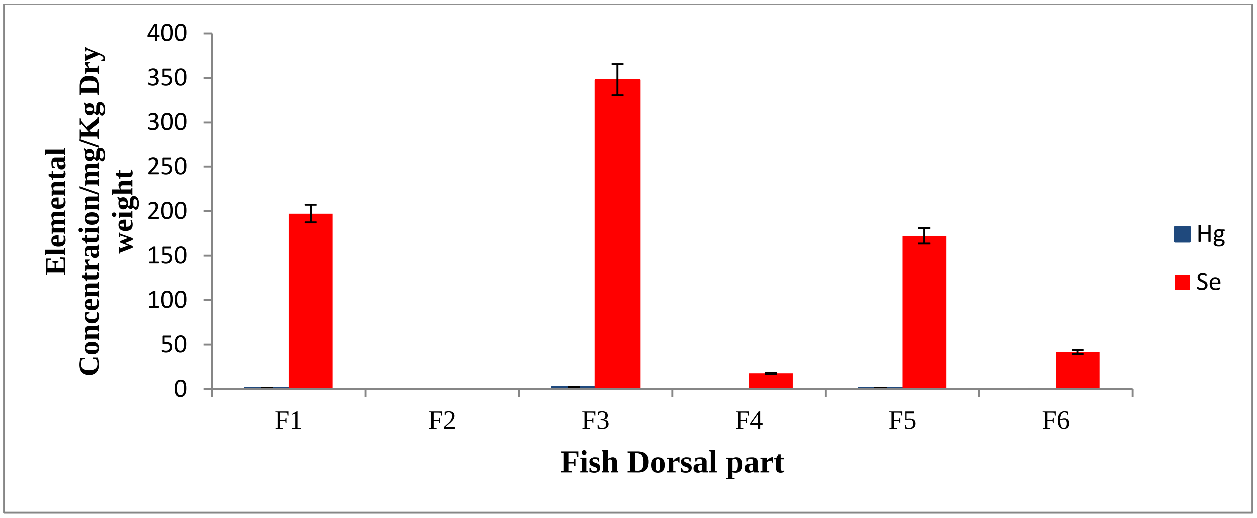

Figure 4.7: Mercury (THg) and Selenium (Se) Concentrations in the dorsal tissues of Mudfish (*Clarias submarginatus*)

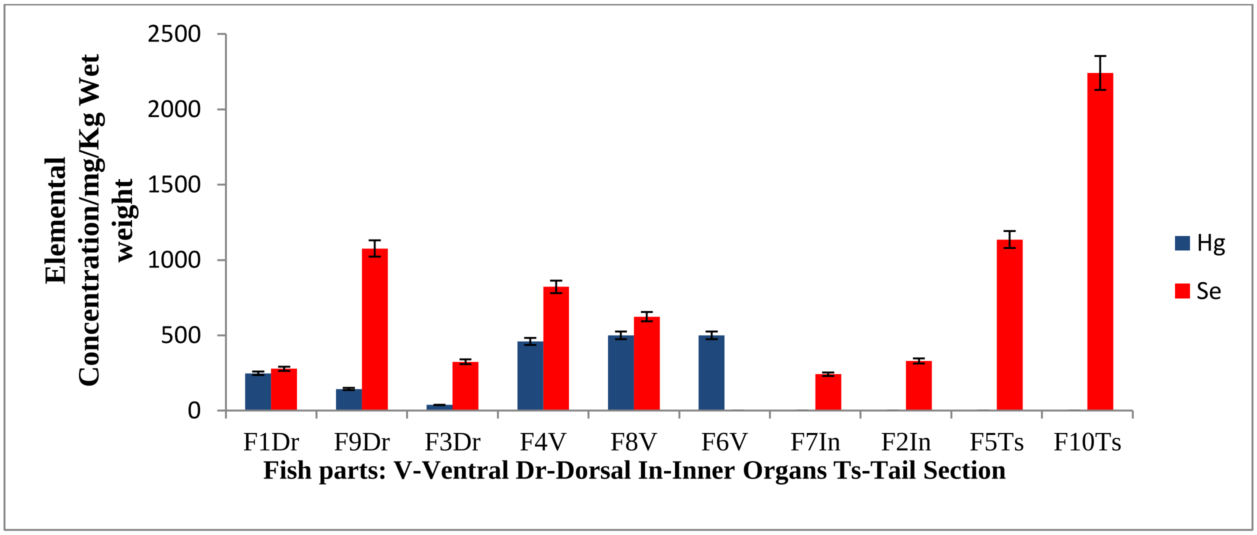

Figure 4.8: Mercury (THg) and Selenium (Se) Concentrations in the different tissues of *Xenomystus nigri*. Fish parts: V-Ventral, Dr-Dorsal, In-Inner Organs, Ts-Tail Section

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4.4.3 Mercury and Selenium molar ratios

A 1:1 molar ratio between Se and Hg has been reported in organs (mainly liver) of some mammals (Koerman *et al.*, 1975). For a protective effect of selenium to be noticed in the detoxification of mercury, threshold concentrations of selenium must be reached especially in fish parts. The selenium/mercury (Se/Hg) molar ratio was obtained by using the molecular weight (200.59 for Hg and 78.9 for Se). Average (Hg/Se) molar ratios in *Xenomystus nigri* (0.196) were higher than in Mudfish (0.003) (Tables 4.6 and 4.7). Average (Se/Hg) molar ratios in Mudfish (261.09) were higher than in *Xenomystus nigri* (5.116) (Tables 4.6 and 4.7).

Table 4.6: Total Mercury-Selenium molar ratio in Fish Species (Mudfish)

Codes	Hg(µmol/Kg)	Se(µmol /Kg)	Hg:Se	Se:Hg
F1	8	2498.70	0.0032	312.33
F2	1	-	-	-
F3	11	4402.53	0.0025	400.18
F4	1	225.30	0.0044	225.30
F5	6	2184.80	0.0027	364.13
F6	2	529.11	0.0037	264.50
Average	4.833	1968.088	0.0033	261.09

Table 4.7: Total Mercury-Selenium molar ratios in *Xenomystus nigri*

Codes	Hg(µmol/Kg)	Se(µmol /Kg)	Hg:Se	Se:Hg
F1Dr	1.24	3.51	0.35	2.83
F2In	0	4.17	-	-
F3Dr	0.19	4.1	0.05	21.57
F4V	2.3	10.4	0.22	4.7
F5Ts	0	14.3	-	-
F6V	2.5	0	-	-
F7In	0	3.06	-	-
F8V	2.5	7.89	0.31	3.136
F9Dr	0.72	13.62	0.05	18.91
F10Ts	0	28.37	-	-
Average	0.945	8.942	0.196	5.1146

From Tables 4.6 and 4.7 total mercury-selenium ratios (Hg/Se, Se/Hg) varied for the two fish species. The highest Se:Hg molar ratio in *Xenomystus nigri* was recorded for F3Dr (21.57) which corresponded to the lowest Hg:Se molar ratio 0.05. The 1:1 molar ratio complex as reported in marine mammals is not supported by the data in Tables 4.6 and 4.7.

4.4.4 Relationship between Total Mercury and Selenium in fish species

Regression analysis and Pearson’s correlation for THg and Se in the two fish species showed a strong direct association in mudfish and a weak association and an inverse relationship in the different tissues of *Xenomystus nigri*. Mercury was positively correlated with Selenium in the dorsal tissues of Mudfish ($r^2 = 0.98$, $r = 0.99$) (Figure 4.10) and negatively correlated in the fish tissues of *Xenomystus nigri* ($r^2 = 0.0987$, $r = -0.314$) (Figure 4.9). Logarithm transformation of bioaccumulation factors was applied to normalize the data set for regression analysis. This was because the data set was not normally distributed. Logarithm transformation of the bioaccumulation factors also gave similar trends in both Mudfish ($r^2 = 0.55$, $r = 0.74$) (Figure 4.12) and *Xenomystus nigri* ($r^2 = 0.121$, $r = -0.349$) (Figure 4.11). An increase in THg was characterized by the increase in Se in Mudfish. An increase in Se corresponded to a decrease in THg across the different tissues of *Xenomystus nigri*. An increase in the bioaccumulation of Se was characterized by a decrease in the bioaccumulation of Hg across the different tissues in *Xenomystus nigri*.

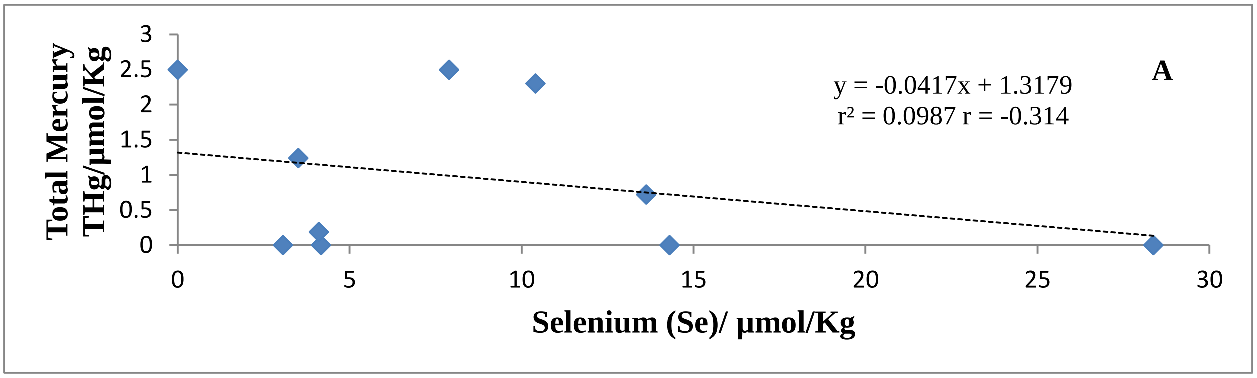

Figure 4.9: Scatter diagram showing the molar concentrations of THg as a function of the molar concentrations of Selenium (Se) across the different tissues of *Xenomystus nigri*

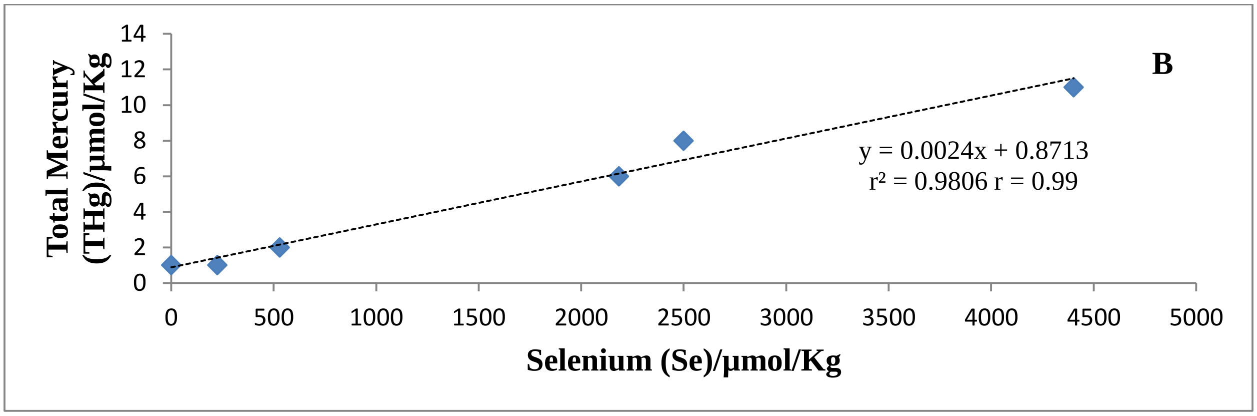

Figure 4.10: Scatter diagram showing the molar concentrations of THg as a function of the molar concentrations of Selenium (Se) in the dorsal tissues of Mudfish (*Clarias submarginatus*)

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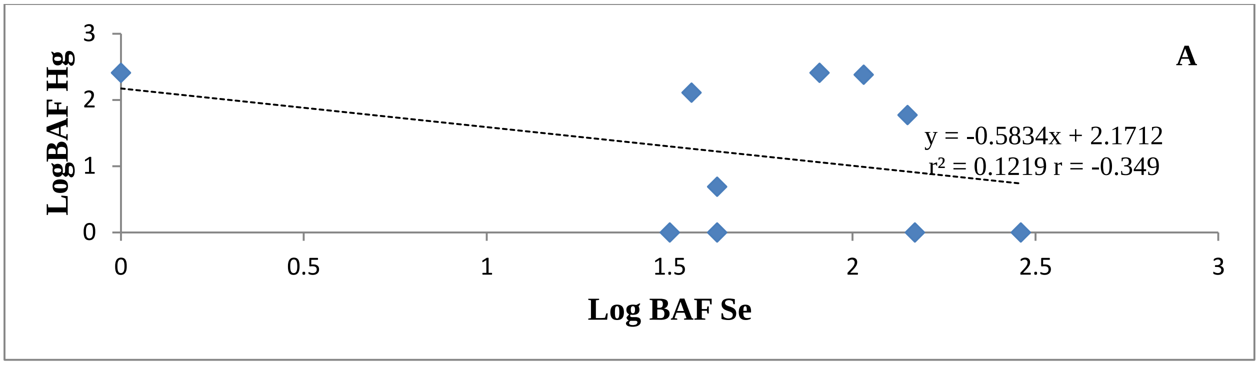

Figure 4.11: Scatter diagram showing the logarithm transformation of BAF of THg as a function of the BAF of Se in the different tissues of *Xenomystus nigri*

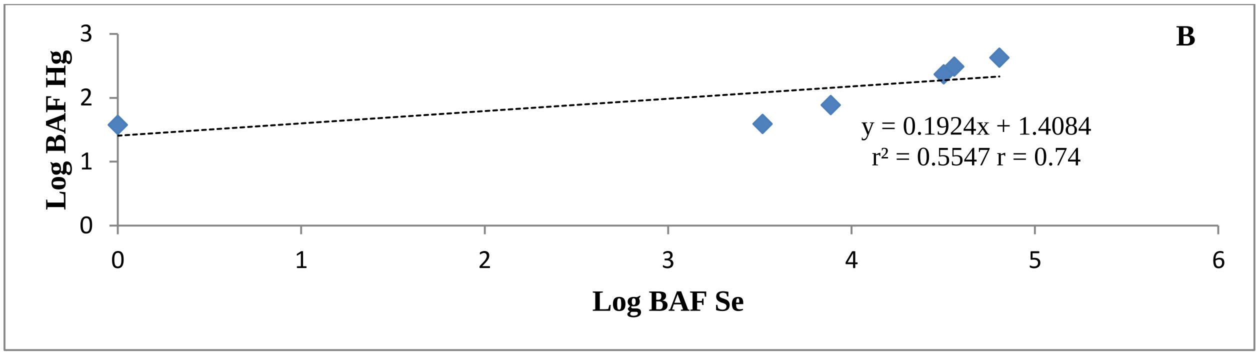

Figure 4.12: Scatter diagram showing the logarithm transformation of BAF of THg as a function of the BAF of Se in the dorsal tissues of Mudfish (*Clarias submarginatus*)

4.4.5 Selenium association with other elements in fish tissues (Cd, Fe, Zn)

Apart from mercury, it has been found that selenium also interacts with other heavy metals in certain biological systems (Parizek, 1978; Feroci *et al.*, 2005). Its presence either reduces the availability of other heavy metals such as cadmium (Cd) whiles its deficiency causes an overload of iron (Fe) and an unbalanced *in vivo* distribution of other elements such as zinc (Zn), magnesium (Mg), copper (Cu) and calcium (Ca) (Chareonpong-Kawamoto *et al.*, 1995). Regression analysis between selenium and heavy metals (Cd, Fe, Zn) in the tissue parts of Clarias ($0.03 \leq r^2 \leq 0.08$) and *Xenomystus nigri* ($0.0133 \leq r^2 \leq 0.109$) all resulted in virtually no significant relationships (Figures 4.13A-C and 4.14A-C).

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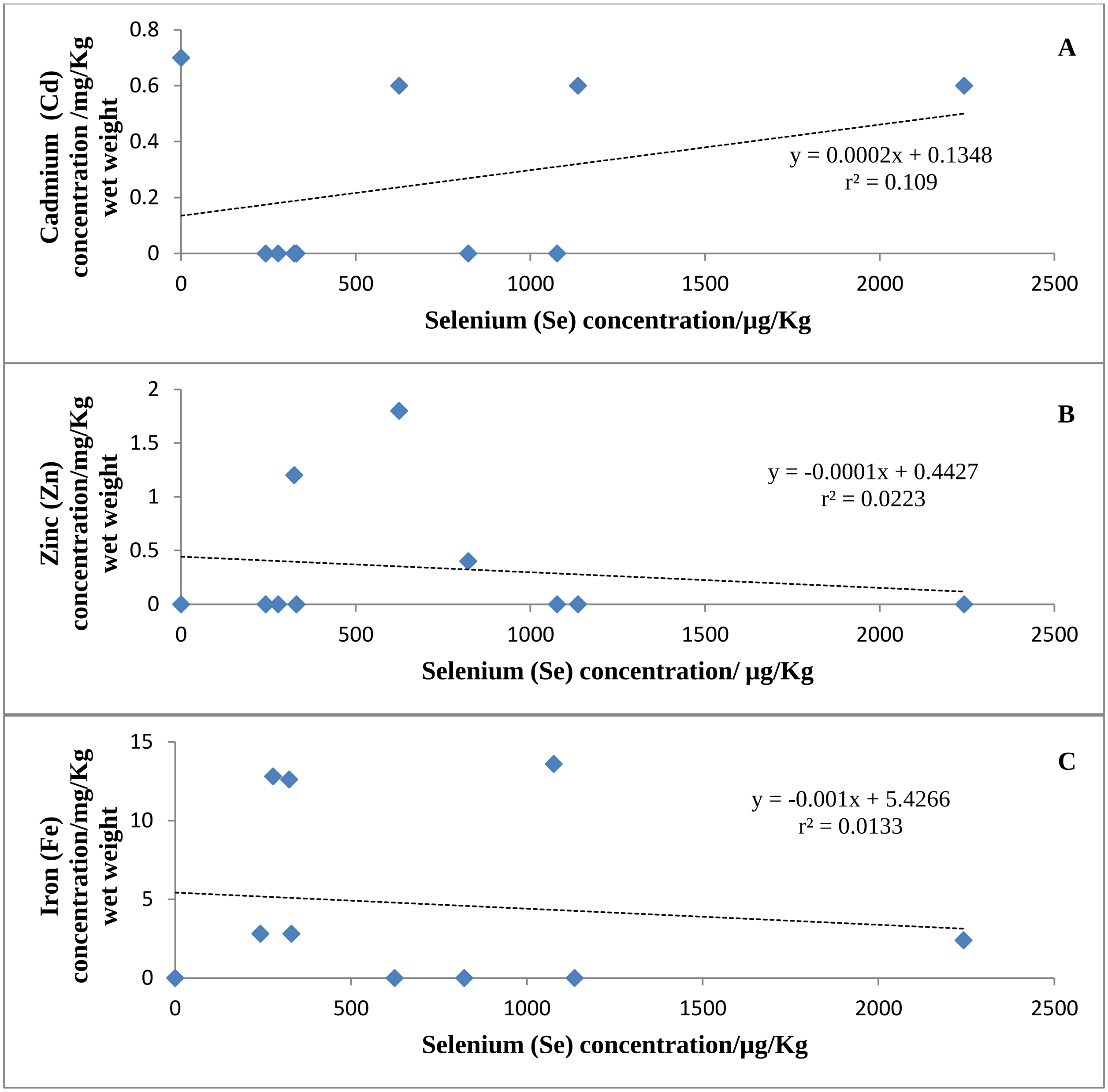
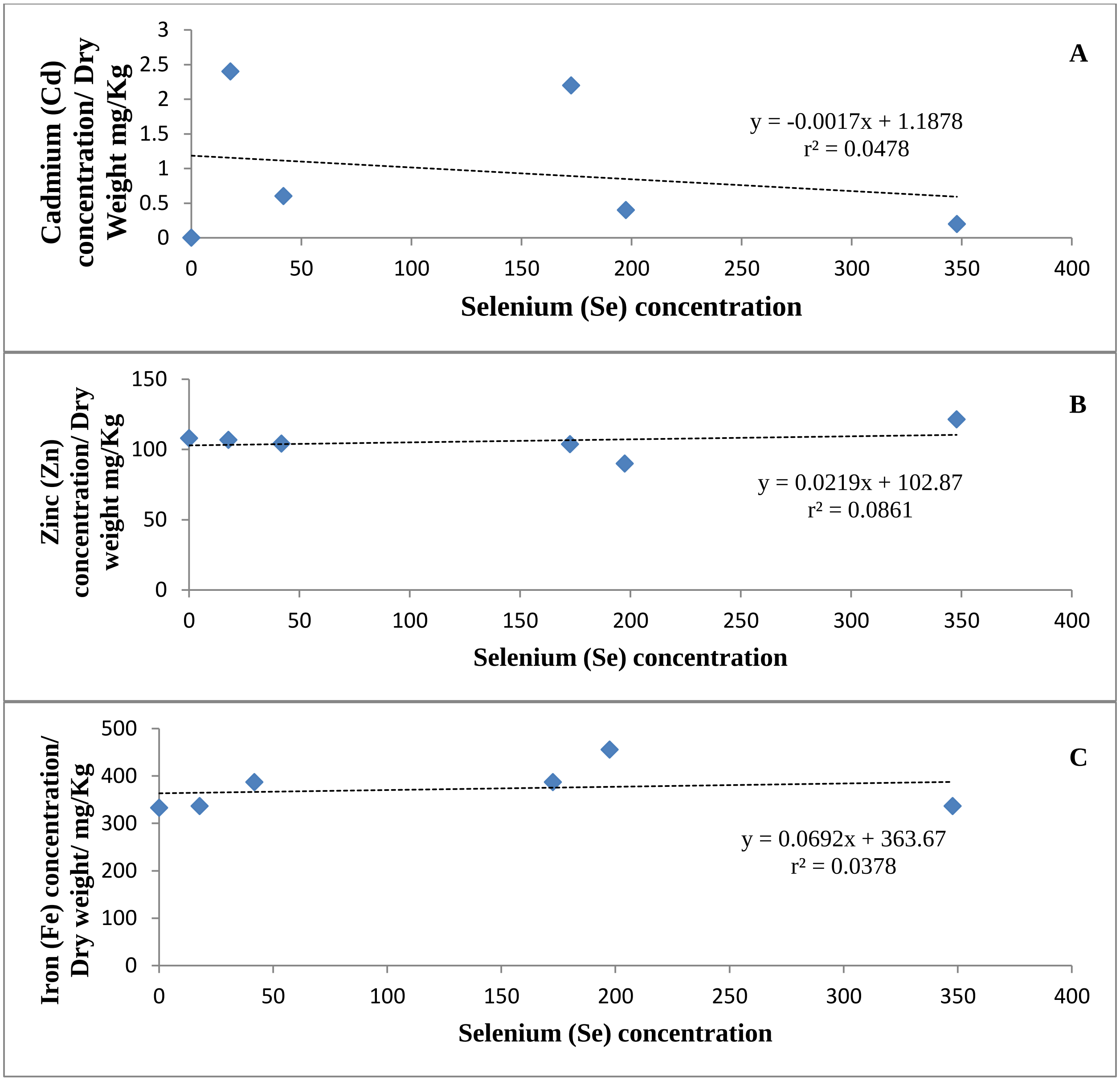
Xenomystus nigri



Figures 4.13 A-C: Scatter diagram showing a plot of Fe, Zn and Cd as a function of Se in various tissue parts of *Xenomystus nigri*. Figure A – Cd against Se, Figure B – Zn against Se, Figure C- Fe against Se. Fe, Cd, and Zn are the dependent variables. Se is the independent variable

Mudfish (*Clarias submarginatus*)



Figures 4.14A-C: Scatter diagram showing a plot of Fe, Zn and Cd as a function of Se in the dorsal tissues of Mudfish (*Clarias submarginatus*). Figure A – Cd against Se, Figure B – Zn against Se, Figure C- Fe against Se. Zn, Cd, and Fe are the dependent variable. Se is the independent variable.

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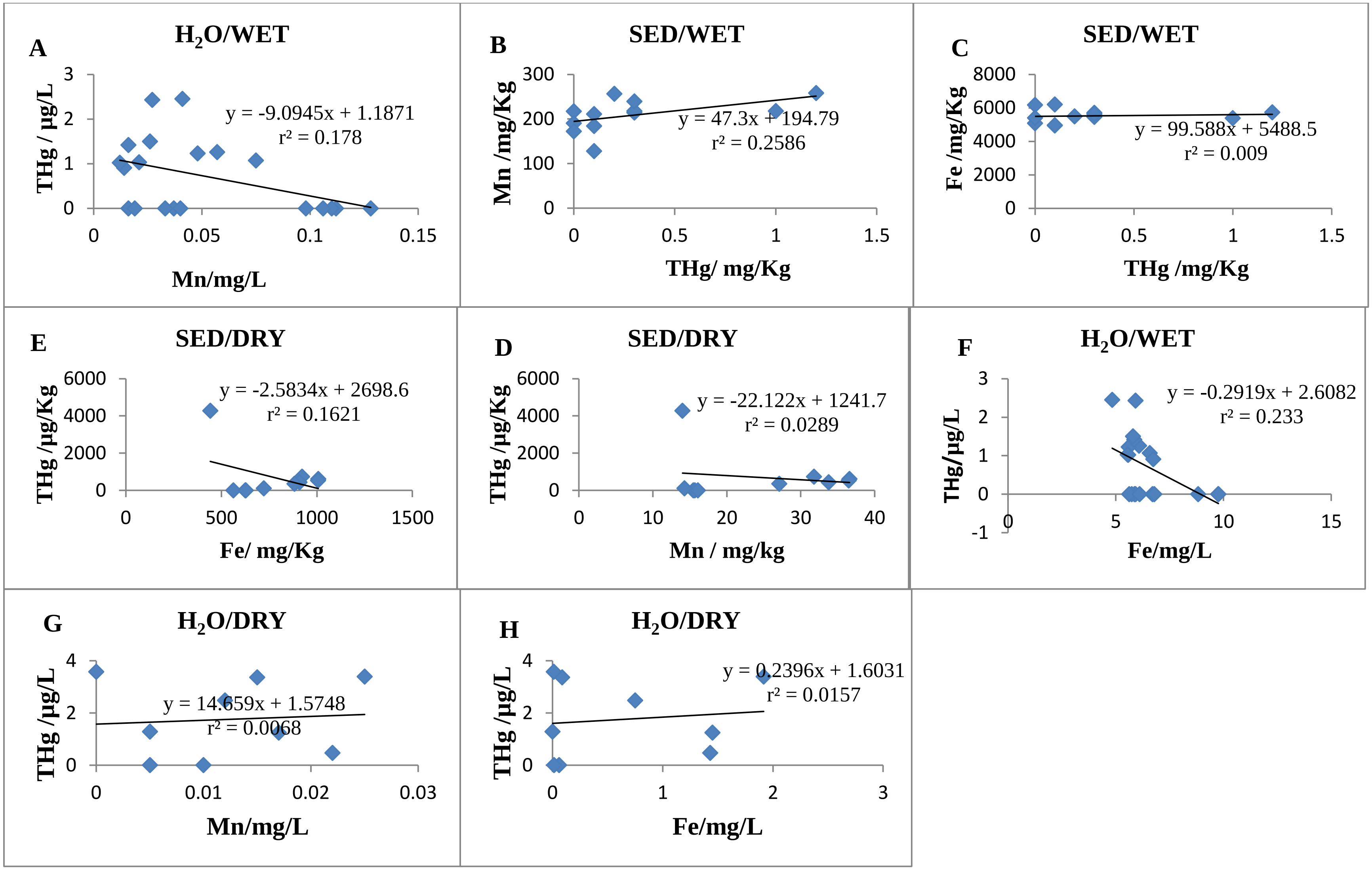
4.5 MERCURY (THg) RELATIONSHIP WITH IRON (Fe) AND MANGANESE (Mn)

Dissolved mercury has been found to adsorb strongly to Fe- or Mn-oxyhydroxides (Balogh *et al.*, 1998). A statistically significant positive relationship was found between THg and aqueous total Fe in water and sediment (Warner *et al.*, 2005). The relationship between Fe and THg in sediment for both seasons was statistically insignificant in this study ($0.009 \leq r^2 \leq 0.16$) (Figures 4.15C and 4.15E). The same could be said of Fe and THg in River water ($0.0153 \leq r^2 \leq 0.233$) (Figures 4.15F and 4.15H). A weak relationship was observed between Mn and THg for sediments ($0.0289 \leq r^2 \leq 0.2586$) (Figures 4.15B and 4.15D) and river water ($0.0068 \leq r^2 \leq 0.178$) (Figures 4.15A and 4.15G) for both seasons. THg relationship with Fe and Mn although statistically not significant varied in river water and sediments for the two seasons.

4.6 SELENIUM RELATIONSHIP WITH IRON (Fe) AND MANGANESE (Mn)

Selenium species depending on pH adsorb onto oxides of Mn and Fe (Ballistrieri and Chao, 1990). Statistically significant relationships were observed for Se with Fe and Mn in sediments for both seasons. A moderately positive relationship was observed between Se and Mn ($0.2708 \leq r^2 \leq 0.4251$) in sediments for both seasons (Figures 4.16A and 4.16B). A moderately strong relationship between Se and Fe was observed for sediments in the dry season ($r^2 = 0.4251$) (Figure 25D) with a weak relationship in the wet season ($r^2 = 0.0128$) (Figure 4.16E). Weak relationships were observed in River water for both seasons between Se and Fe ($0.007 \leq r^2 \leq 0.06$) (Figures 4.16C and 4.16F) and between Se and Mn ($0.016 \leq r^2 \leq 0.095$) (Figures 4.16G and 4.16H). Statistically significant relationship between Se and Fe/Mn suggests an association in sediments than in River water.



Figures 4.15A-H: Scatter diagrams showing the correlation curves of THg with Mn and Fe in sediments and water for dry and wet seasons. Figures: A-THg vrs Mn water wet season, B- Mn vrs THg sediments wet season, C-Fe vrs THg sediments wet season, D-THg vrs Mn sediments dry season, E-THg vrs Fe sediments dry season, F-THg vrs Fe water wet season, G-THg vrs Mn water wet season, H-THg vrs Fe water dry season

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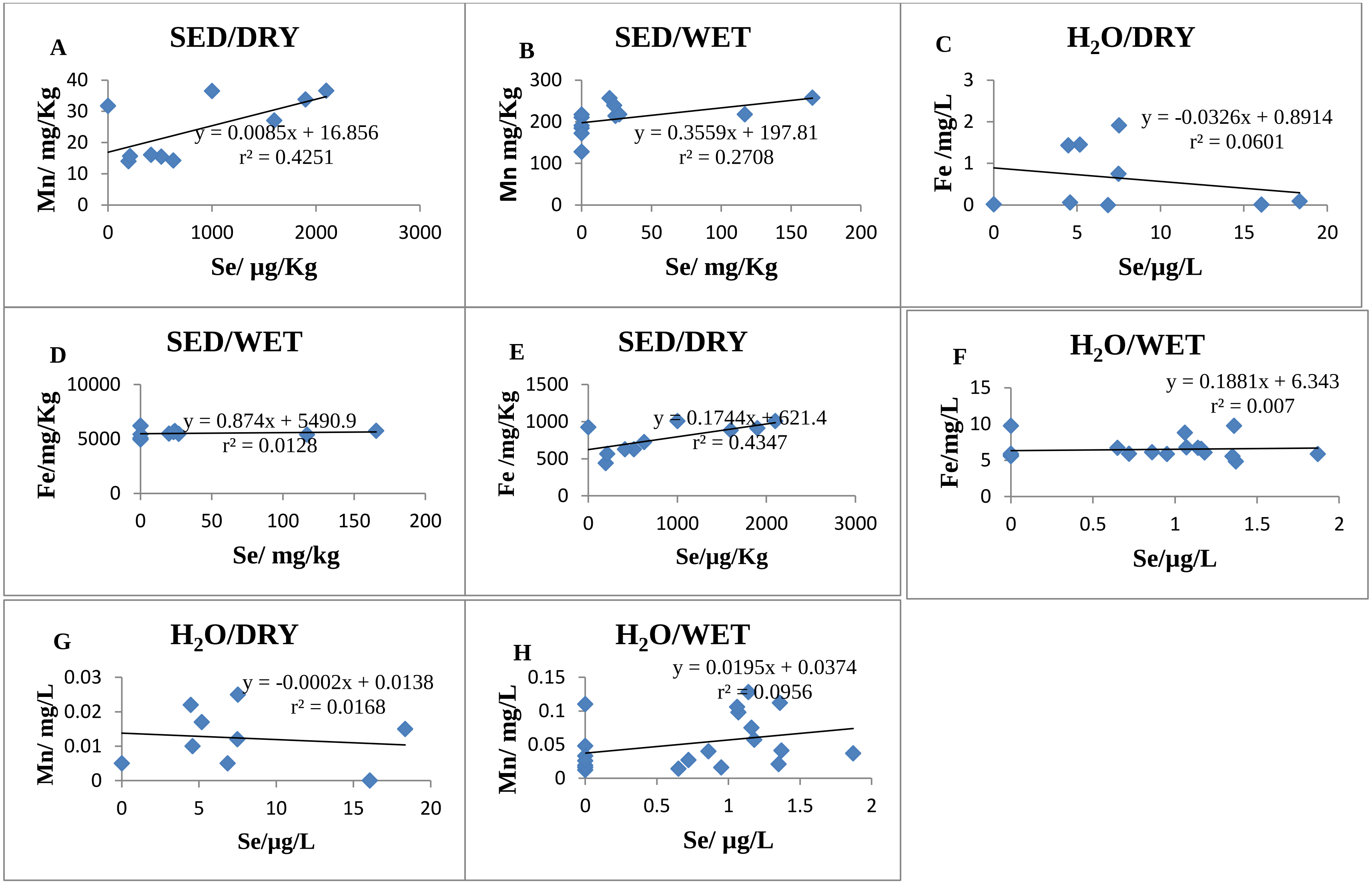

Figures 4.16A-H: Scatter diagrams showing the correlation curves of Mn and Fe with Se in sediments and water for dry and wet seasons. Figures: A- Mn vrs Se sediment dry season, B- Mn vrs Se sediment wet season, C- Fe vrs Se water dry season, D- Fe vrs Se sediment wet season, E- Fe vrs Se sediment dry season, F-Fe vrs Se water wet season, G-Mn vrs Se water wet season, H-Mn vrs Se water wet season

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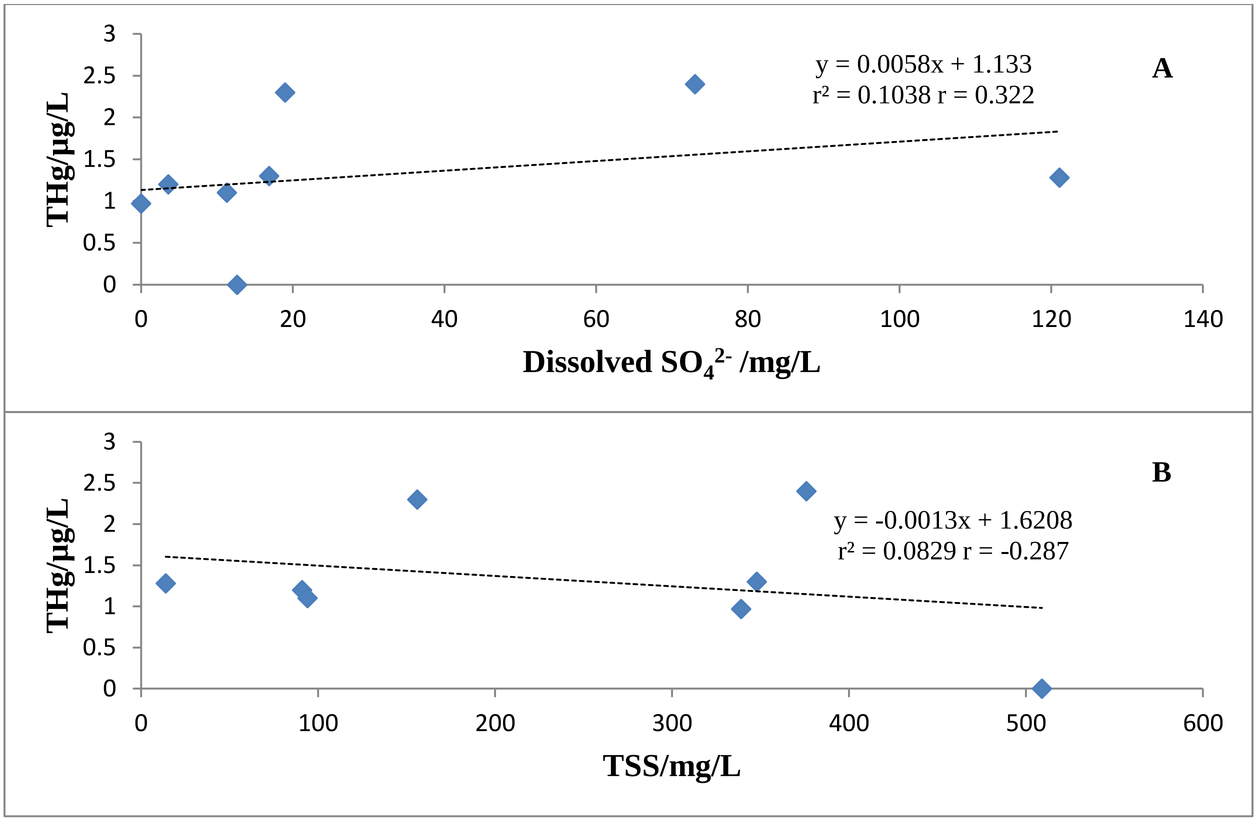
4.7 MERCURY RELATIONSHIP WITH TSS AND SULFATE

Mercury being a soft metal (B class) shows a pronounced preference for ligands of sulfur especially attached to dissolved organic matter (DOM) (Ravichandran, 2004). In this study, there was a weak positive relationship ($r^2 = 0.1038$, $r = 0.322$) between dissolved sulfates and THg in River water (Figure 4.17A). Mercury methylation is particularly aided by sulfur reducing bacteria and a weak positive correlation highlights the affinity of mercury to sulfur containing compounds. TSS on the other hand had a weak inverse relationship ($r^2 = 0.08$, $r = -0.287$) with THg contrary to what was observed by Balogh *et al.*, 1998 and Warner *et al.*, 2005 (Figure 4.17B).



Figures 4.17A-B: Scatter diagram of averaged THg of locations as a function of Dissolved SO_4^{2-} (A) and TSS (B) in water for the two seasons. TSS is a physicochemical parameter whilst SO_4^{2-} is a water nutrient.

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4.8 OTHER HEAVY METAL DISTRIBUTIONS

4.8.1 Sediments

Eight other metals namely Fe, Mn, Pb, Cr, Cu, Ni, Cd, and Zn were determined in sediments. Fe was the most abundant in sediments for the two seasons. Overall mean concentration of Fe in sediments was 5738 mg/Kg in the wet season and 773 mg/Kg in the dry season. Minimum average level of Fe in the wet season was recorded at Beposo (5470 mg/kg) whiles the highest levels was reported at Shama (6388 mg/Kg). Minimum level in the dry season was recorded at Bokorkope (675 mg/Kg) whiles the highest was recorded at Shama (895 mg/Kg) (Figure 4.18A).

Overall mean concentration of Mn in sediments in the dry season (24 mg/Kg, range: 15.2-30 mg/Kg) was far less than what was recorded for the wet season (213 mg/Kg, range: 156-274 mg/Kg). Bokorkope and Shama recorded the minimum average concentration and highest average concentration respectively for the sampling locations for both seasons (Figure 4.18B). Overall mean concentration of Pb in the dry season was 8 mg/Kg (range: 0.9-13.6 mg/Kg) which was generally less than the overall mean concentration for the wet season (14 mg/Kg, range: 7-31 mg/Kg). The highest average concentrations of Pb for both seasons was recorded at Shama (Figure 4.18C).

Overall mean concentration of Cu in the study area in the wet season was 2.8 mg/Kg (range: 2-4 mg/Kg) which had increased to 5 mg/Kg (range: 2.6-7 mg/Kg) in the dry season with concentrations for each location generally higher in the dry season than in the wet season (Figure 4.18F). Zn was generally higher for all four locations in the wet season (55 mg/Kg, range: 41-82 mg/Kg) than in the dry season (4 mg/Kg, range: 3.1-7.4 mg/Kg). The highest average concentration of Zn was recorded at Shama for both seasons (Figure 4.18E).

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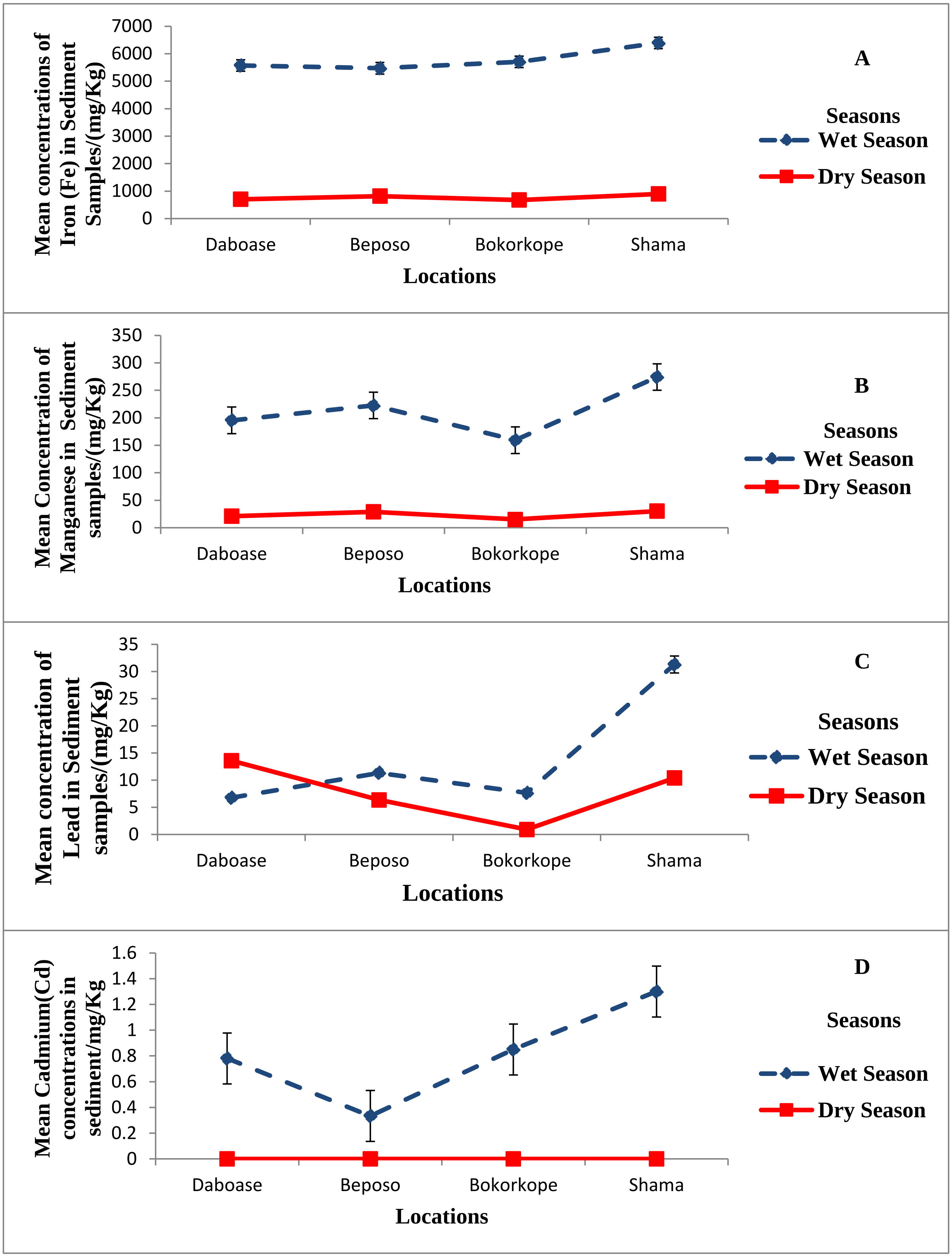
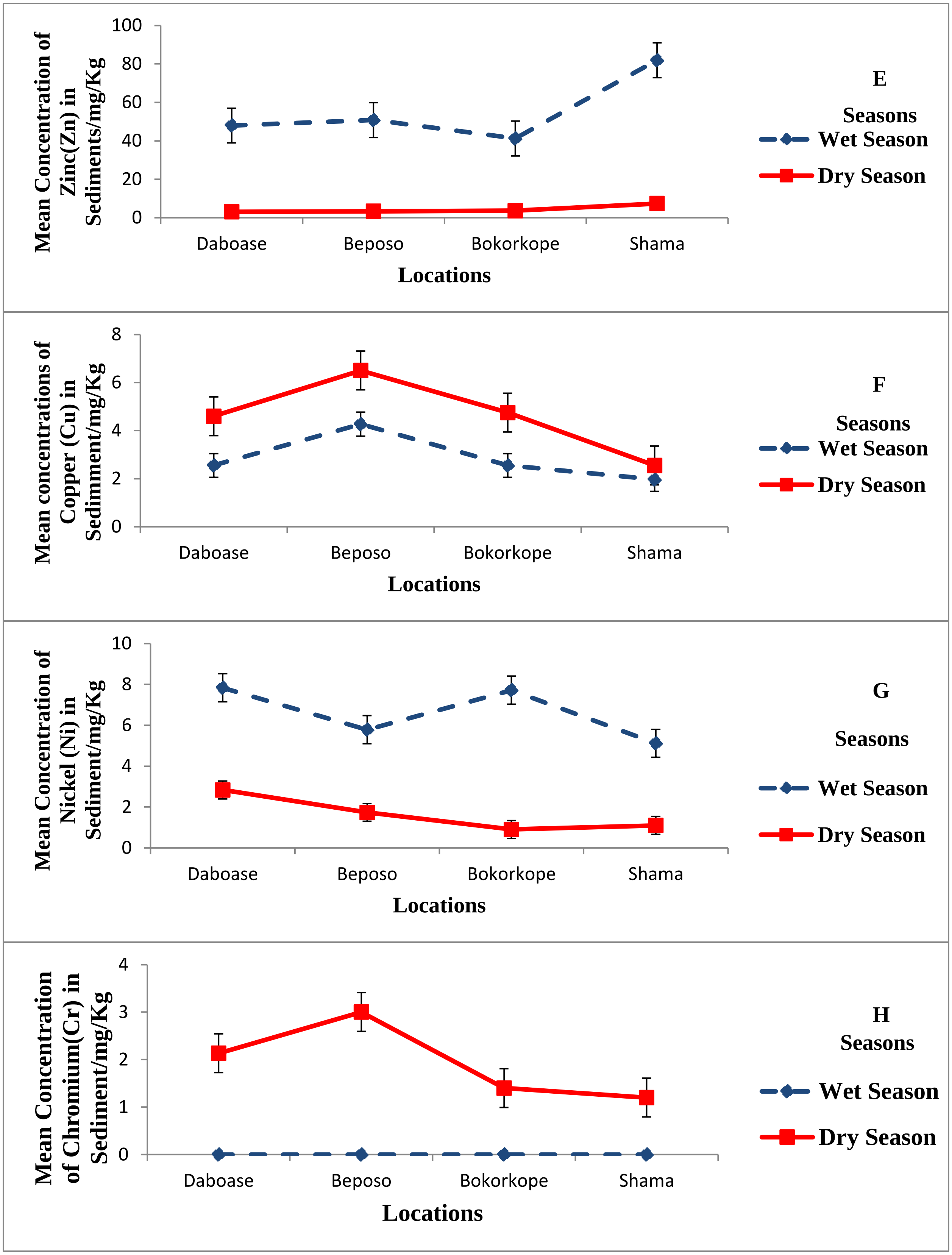
Ni in sediments were generally high in the wet season than the dry season with an overall mean concentrations of 7 mg/Kg (range: 5-8 mg/Kg) in the wet season and 1.6 mg/Kg (range: 0.9-2.8 mg/Kg) in the dry season (Figure 4.18G).

Cr concentrations was below the detection limit in sediments for the wet season but the dry season recorded an overall mean concentration of 1.9 mg/Kg (range: 1.2-3 mg/Kg) (Figure 4.18H). Cd on the other hand was below detection limit in sediment for the dry season but recorded an overall mean concentration of 0.8 mg/Kg (range: 0.3-1.3 mg/Kg) in the wet season (Figure 4.18D). Heavy metals was in the decreasing order of Fe > Mn > Zn > Pb > Ni > Cu > Cd > Cr in the wet season and a decreasing order of Fe > Mn > Pb > Cu > Zn > Ni > Cr > Cd in the dry season.



Figures 4.18A-D: Distribution of Pb, Cd, Mn, and Fe in sediments. Sampling locations are not drawn to scale. Error bars are set at 1 standard deviation. Fig. A - Fe, B - Mn, C - Pb, D - Cd



Figures 4.18E-H: Distribution of Zn, Cr, Ni, and Cu in sediments. Sampling locations are not drawn to scale. Error bars are set at 1 standard deviation. Fig. E - Zn, F - Cu, G - Ni, H - Cr

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4.8.2 Water samples

The overall mean concentration of 6 mg/L (range: 5.6-9 mg/L) was recorded for Fe in the wet season with an overall mean concentration of 0.7 mg/L (range: 0.04-1.44 mg/L) recorded for the dry season. The minimum average concentration of Fe for wet season was recorded at Daboase (5.6 mg/L) and for the dry season was recorded at Bokorkope (0.04 mg/L) respectively (Figure 4.19H). The maximum average concentration of Fe for wet season was recorded at Beposo (9 mg/L) and for the dry season was recorded at Daboase (1.44 mg/L) (Appendix B1). Concentrations of Fe were generally higher for the wet season than the dry season for all locations (Figure 4.19H).

Maximum average concentration of Mn in the wet season was recorded at Beposo (0.11 mg/L) with a reported mean of 0.05 mg/L (range: 0.022-0.11 mg/L) in the wet season and a dry season mean concentration of 0.013 mg/L (range: 0.007-0.020 mg/L) (Appendix B4).

Overall mean concentration of Pb was 0.009 mg/L (range: BDL-0.02 mg/L) in the wet season with a recorded mean of 0.05 mg/L (range: BDL-0.082 mg/L) in the dry season. Pb was largely below the detection limit at Daboase for both seasons but a recording of the metal was made at sampling site WDB1 at Daboase in the wet season with a value of 0.007 mg/L (Appendix B5).

Overall mean concentrations of Cu for both seasons were comparable with mean values of 0.026 mg/L (range: 0.021-0.036 mg/L) and 0.02 mg/L (range: 0.006-0.038 mg/L) for the dry and wet season respectively (Figures 28C). Recordings of copper were made at particular sampling sites WBP1 at Beposo (0.006 mg/L) and WBK5 at Bokorkope (0.006 mg/L) in the wet season (Appendix B7). Cd was largely below the detection limit in the dry season but recordings of 0.004 mg/L were made at two sites DWBK 1 and DWBK 2 (Appendix. B7).

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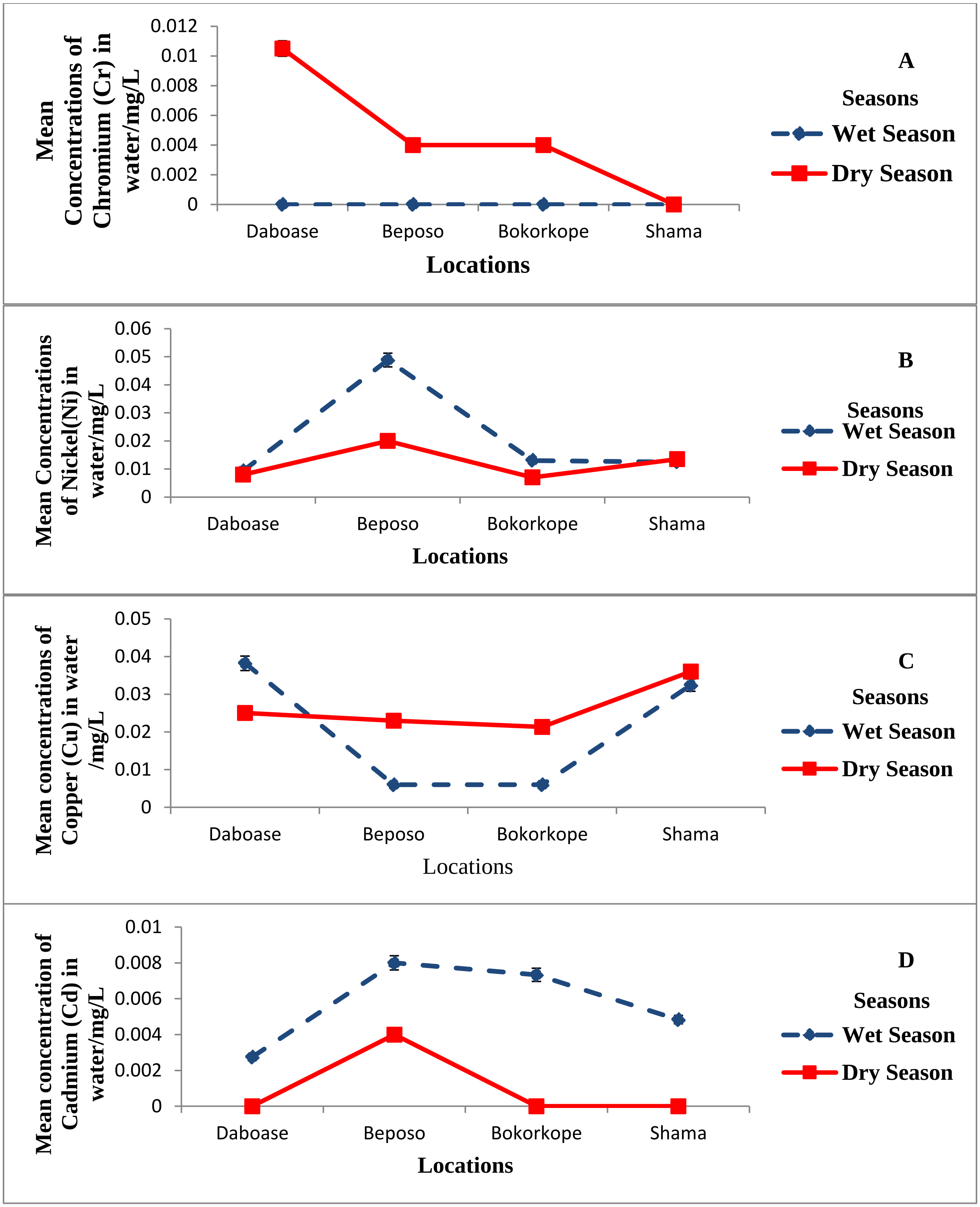
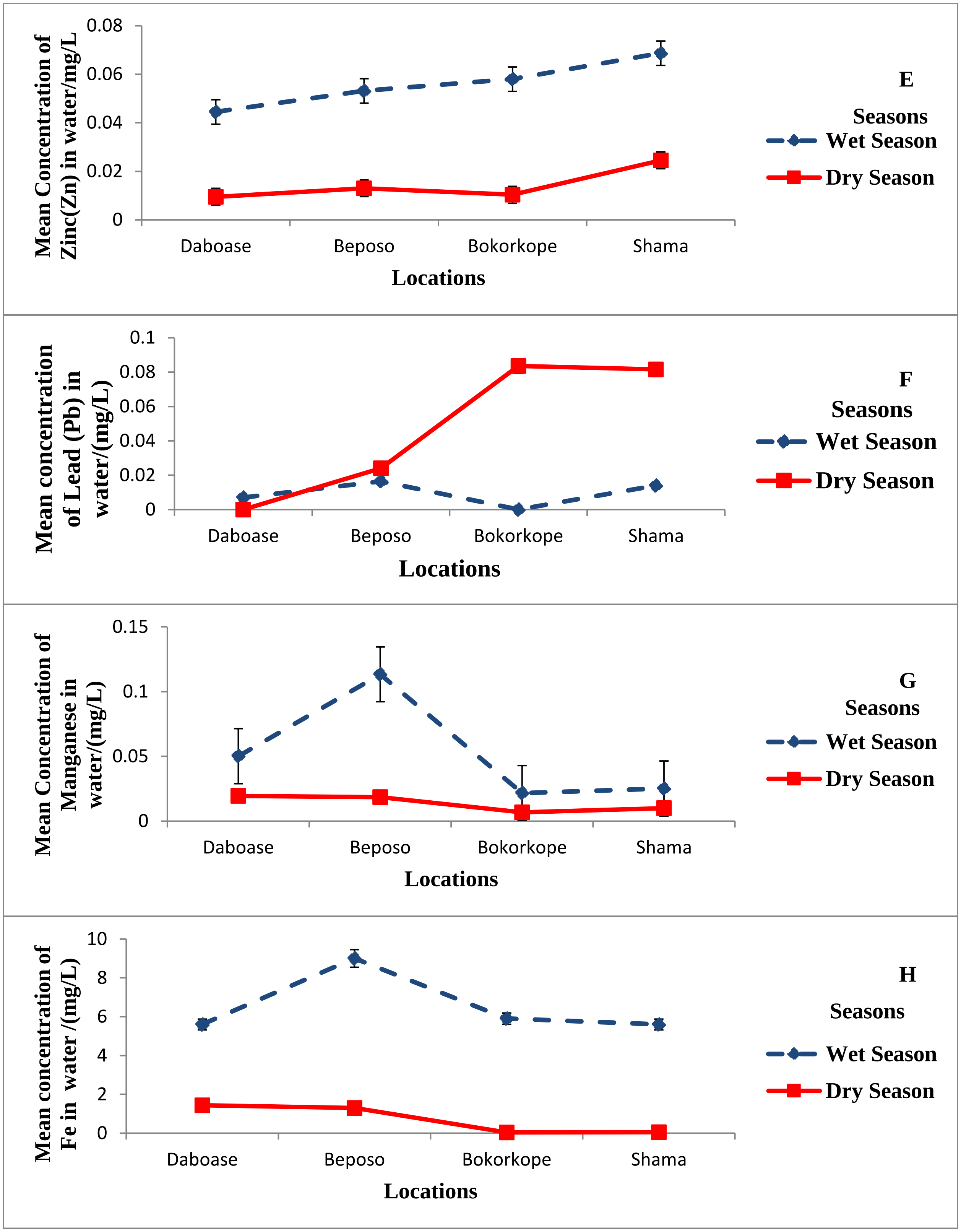
Zn recorded an overall mean concentration of 0.056 mg/L (range: 0.04-0.07 mg/L) for the wet season and an overall mean concentration of 0.014 mg/L (range: 0.0095-0.0245 mg/L) in the dry season far less than what was recorded for the wet season (Appendix B11, Figure 4.19E). Mean maximum concentration of the metal was recorded at Shama in the wet (0.07 mg/L) and dry season (0.0245 mg/L) (Appendix B11).

Concentrations of Ni in river water for the four locations were generally higher in the wet season than the dry season with an overall mean concentrations of 0.02 mg/L (range: 0.009-0.013 mg/L) recorded for the wet season and 0.012 mg/L (range: 0.007-0.002 mg/L) recorded for the dry season (Appendix 13, Figure 4.19B). Concentrations of Ni were highest at Shama for the two seasons (Figure 4.19B).

Cr was largely below the detection limit in the wet season but particular recordings were made at sampling sites at Beposo (0.004 mg/L) and Bokorkope (0.004 mg/L) in the dry season (Appendix B15). Heavy metal levels were in the decreasing order of Fe > Zn > Mn > N i≈ Cu > Pb > Cd > Cr in the wet season and a decreasing order of Fe > Pb > Cu > Zn > Mn > Ni > Cr > Cd in the dry season.



Figures 4.19A-D: Distribution of Cr, Ni, and Cu, Cd in water. Sampling locations are not drawn to scale. Error bars are set at 1 standard deviation. Fig. A - Cr, B - Ni, C - Cu, D - Cd



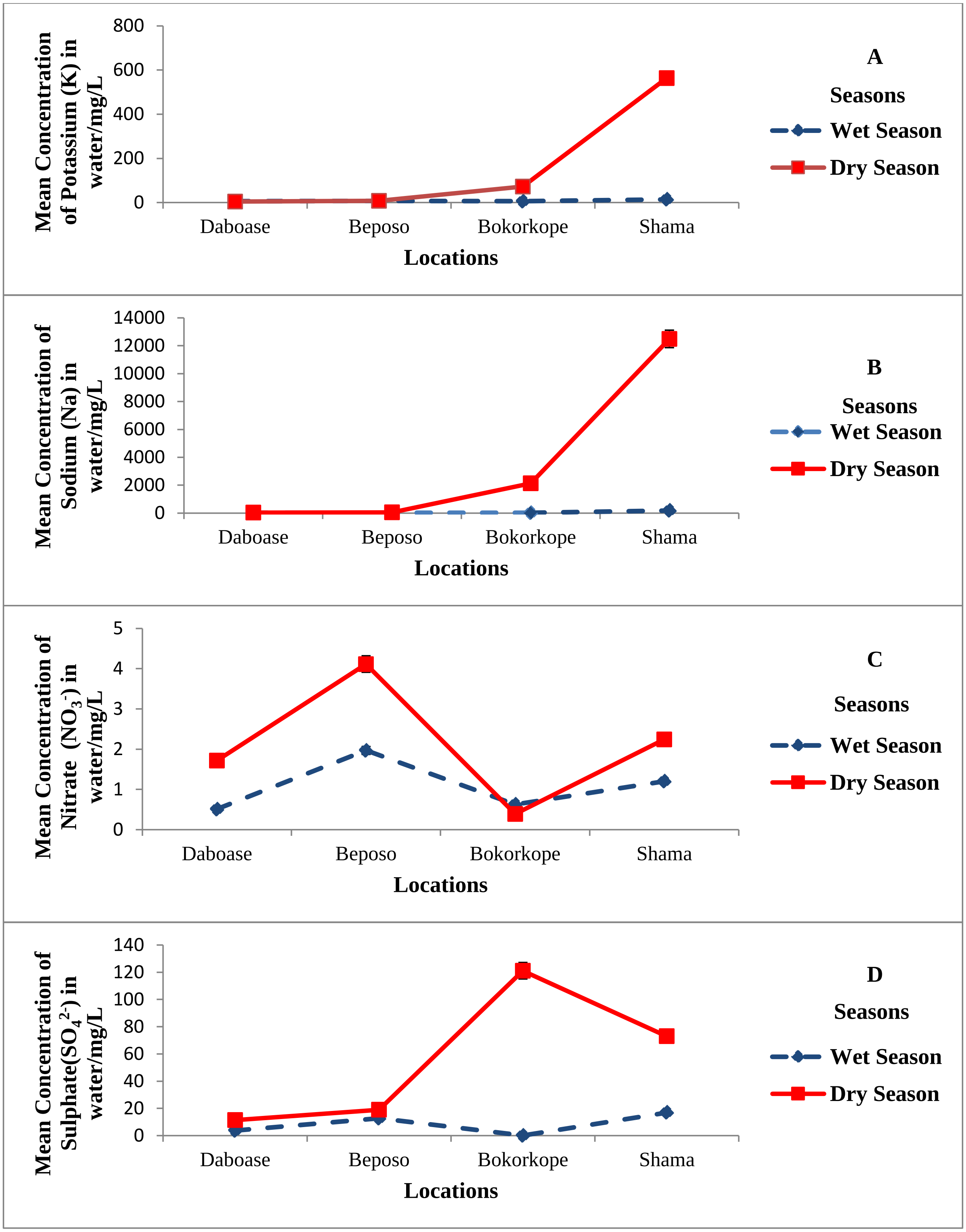
Figures 4.19E-H: Distribution of Zn, Pb, Mn and Fe in water. Sampling locations are not drawn to scale. Error bars are set at 1 standard deviation. Fig. E – Zn, F – Pb, G – Mn, H - Fe

4.9 WATER NUTRIENTS AND MACRO ELEMENTS (IONS)

Three water nutrients PO_4^{3-}, SO_4^{2-} and NO_3^- and two macro elements were Na^+ and K^+ determined in this study. Four of the ions Na^+ ,K^+, SO_4^{3-} and NO_3^- had their overall mean concentrations for the study area higher in the dry season than in the wet season. Overall mean concentration of PO_4^{3-} for the dry and wet season were comparable with values of 0.28 mg/L for the wet season and 0.2 mg/L for the dry season (Appendix C4). Na^+ had a minimum concentration of 19.9 mg/L recorded for Bokorkope in the wet season and the highest of 12,490 mg/L recorded for Shama in the dry season (Appendix C1, Figure 4.20B).

Minimum concentration of K^+ for the dry season was recorded at Daboase (4.3 mg/L) with the highest concentration of 563 mg/L recorded at Shama also in the dry season for the entire study period (Appendix C2, Figure 4.20A). Mean concentration of NO_3^- in the wet season was 1.1 mg/L (range: 0.509-1.969 mg/L) which had increased to 2 mg/L (range: 0.392-4.113 mg/L) in the dry season. Minimum concentration of 0.041 mg/L PO_4^{3-} was recorded for Shama in the dry season with maximum concentration of 0.499 mg/L recorded at Beposo also in the dry season for the entire study period (Appendix C4, Figure 4.20E). SO_4^{2-} levels were higher for all four locations in the dry season than in the wet season with mean concentration of 56 mg/L (range: 11.304-121.118 mg/L) for the dry season and 11 mg/L (range: BDL-16.894 mg/L) for the wet season (Appendix C5, Figure 4.20D).

Ions were in the increasing order $PO_4^{3-} < NO_3^- < K^+ < SO_4^{2-} < Na^+$ for the wet season and an increasing order of $PO_4^{3-} < NO_3^- < SO_4^{2-} < K^+ < Na^+$ for the dry season.


A
Mean Concentration of Potassium (K) in water/mg/L
800
600
400
200
0
Daboase
Beposo
Bokorkope
Shama
Locations
Seasons
Wet Season
Dry Season
B
Mean Concentration of Sodium (Na) in water/mg/L
14000
12000
10000
8000
6000
4000
2000
0
Daboase
Beposo
Bokorkope
Shama
Locations
Seasons
Wet Season
Dry Season
C
Mean Concentration of Nitrate (NO$_3^-$) in water/mg/L
5
4
3
2
1
0
Daboase
Beposo
Bokorkope
Shama
Locations
Seasons
Wet Season
Dry Season
D
Mean Concentration of Sulphate(SO$_4^{2-}$) in water/mg/L
140
120
100
80
60
40
20
0
Daboase
Beposo
Bokorkope
Shama
Locations
Seasons
Wet Season
Dry Season

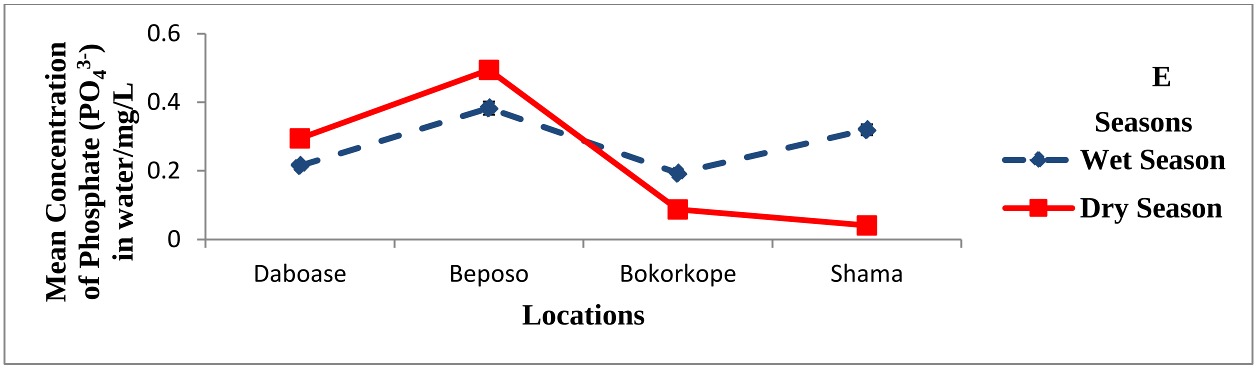


Figure 4.20A-E: Distribution of ions PO_4^{3-}, NO_3^-, K^+, SO_4^{2-}, and Na^+ in water. Sampling locations are not drawn to scale. Fig. A – K^+, B – Na^+, C – NO_3^-, D – SO_4^{2-}, E – PO_4^{3-}

4.10 STATISTICAL ANALYSIS

4.10.1 Coefficient of Variation (Co.V/%)

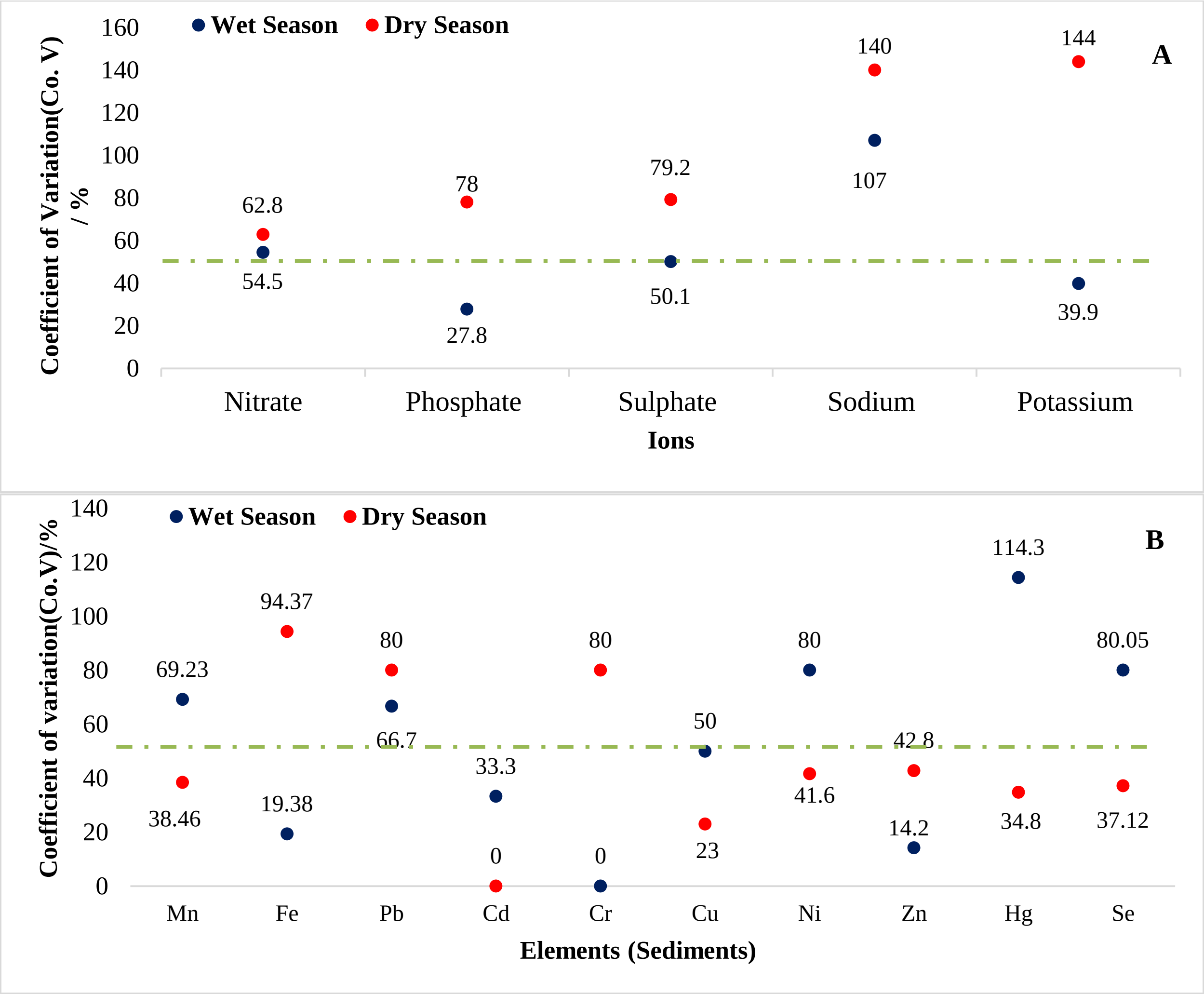
Coefficient of variation is employed to determine the nature of distribution and patterns of dispersion of studied elements and ions along the watercourse. It was calculated as follows:

Co.V = Standard Deviation/Mean

It is expressed as the relative standard deviation which is in percentages. All elements in a population are considered including outliers for coefficient of variation. Distributions are classified close or narrow and wide or scattered when Co.V is below or above 50% respectively. For studied ions, Na^+ recorded a wide or scattered distribution in the river water moving downstream for both seasons with Co.V of 107% and 140% for wet and dry seasons respectively. The other ions NO_3^- (62.8%), PO_4^{3-} (78%), SO_4^{2-} (79.17%) and K^+ (140%) also recorded scattered or widely dispersed moving downstream for the dry season (Figure 4.21A).

PO_4^{3-} (27.8%) and K^+ (39.9%) however had a close distribution in river water moving downstream for the wet season (Figure 4.20A). In sediments, Pb (71.42%, 62.5%), Hg (104.9%, 78.12%), and Se (84.3%, 58.3%) all recorded scattered distribution for the wet and dry seasons respectively moving downstream. All the other elements recorded Co.V below 50% and were very narrowly distributed in sediments moving downstream for the four locations. Hg recorded the highest Co.V in sediment for both seasons (Figure 4.21B).

Fe (94.37%) and Cr (80%) all recorded scattered distributions moving downstream the four locations for the dry season. Hg (114.3%), Se (80.05%), Ni (80%), and Mn (69.23%) were widely dispersed in river water along the watercourse for the wet season. Pb was widely dispersed in the river water along the watercourse for the two seasons with Co.V of 66.7% and 80% for wet and dry seasons respectively (Figure 4.21C).



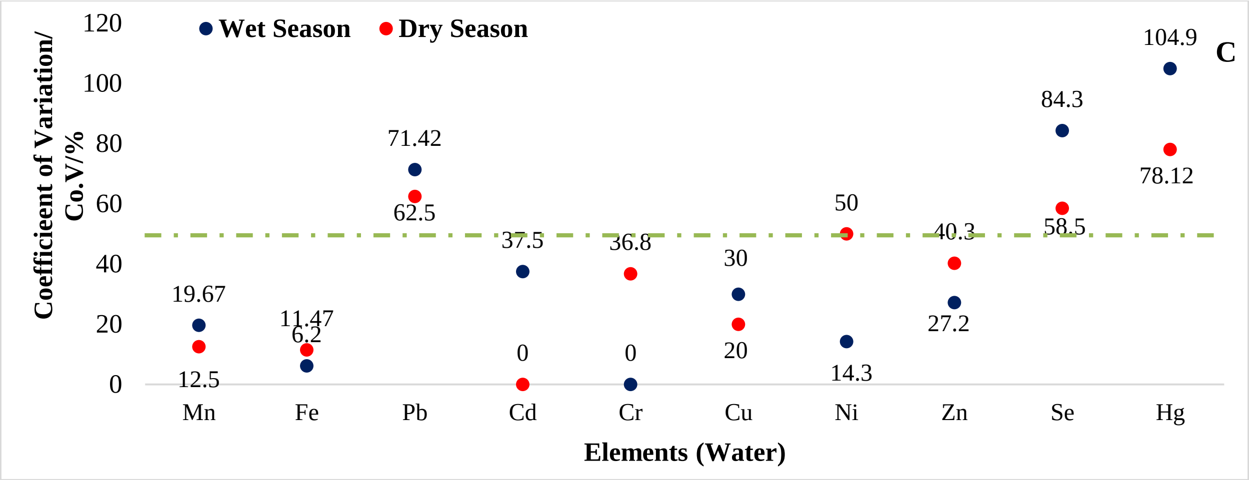


Figure 4.21A-C: Coefficient of variations of studied elements and ions along the watercourse. Broken green line set at 50% limit of variation. Figure 4.21A – Co.V for ions, Figure 4.21B – Co. V for elements in sediments, Figure 4.21C – Co. V for elements in water. Affum *et al.*, 2008

4.10.2 pH versus Heavy metal content (One way ANOVA)

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

For water, there were significant variations ($P < 0.05$) between the group means of Pb ($P = 0.00$), Zn ($P = 0.001$), Mn ($P = 0.000$), Fe ($P = 0.00$), Ni ($P = 0.00$), Hg ($P = 0.00$) and Se ($P = 0.011$) with site-pH ($0.00 \leq P \leq 0.011$) (Appendix D2). Site-pH does not account for any significant variation ($P > 0.05$) between the group means of Cu ($P = 0.428$) and Cr ($P = 0.477$) for river water (Appendix D2).

For sediments, there were significant variations ($P < 0.05$) between the group means of Pb ($P = 0.018$), Cu ($P = 0.001$), Zn ($P = 0.00$), Mn ($P = 0.00$), Fe ($P = 0.00$) and Hg ($P = 0.012$) with site-pH ($0.00 \leq P \leq 0.018$) (Appendix D3). No significant variations ($P > 0.05$) were observed for Se ($P = 0.419$), Cr ($P = 0.742$), Cd ($P = 0.578$), and Ni ($P = 0.065$) with pH ($0.065 \leq P \leq 0.742$) (Appendix D3). It was observed from this study that pH affected the distribution patterns and mobility of heavy metals like Pb, Mn, Fe and Hg in both sediments and water along the sampling sites. pH also affected the variations of Se in water along the sampling sites.

4.10.3 Paired Sample T-Test

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

Ho: Water physicochemical and ion parameters differ significantly with seasonal changes

Ha: Water physicochemical and ion parameters did not differ significantly with seasonal changes

For ions, it was observed that NO_3^-, Na^+, K^+, SO_4^{2-} had paired values of ($0.002 \leq P \leq 0.049$) and were significant ($P < 0.05$). PO_4^{3-} had a paired value of ($P = 0.329$). Hence the measured values were not significant. The null hypothesis is rejected when $P < 0.05$ and accepted when $P > 0.05$. The null hypothesis is rejected for NO_3^-, Na^+, K^+, SO_4^{2-} but is accepted for PO_4^{3-}.

For physicochemical parameters, it was observed that dissolved oxygen had a paired value $P = 0.015$ which was significant. Physicochemical parameters such as temperature, total hardness, total alkalinity, pH, BOD, TSS and TDS had their paired values above the level of significance ($P > 0.05$) were insignificant ($0.108 \leq P \leq 0.291$). The null hypothesis is rejected for dissolved oxygen and it is accepted for the other Physico-Chemical parameters.

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4.10.4 Other Physico-Chemical Parameters of Water

4.10.4.1 Total Alkalinity

Total Alkalinity was closely dispersed along the watercourse with Co.V of 28.36% and 10.18% for wet and dry seasons respectively. Maximum average level for the wet season was recorded for Daboase with a value of 91 mg/L and a minimum average value of 47 mg/L recorded for Shama. The minimum average concentration of 34 mg/L was recorded in the dry season for the first three locations along the watercourse with a gradual rise to 42.5 mg/L recorded at Shama (Appendix A5, Figure 4.22A). The current guidelines for total alkalinity have not been established but overall average levels were below the WHO, 1996 guideline value of 400 mg/L and the EPA's secondary regulation of 500 mg/L for drinking water (Appendix A5, Figure 4.22A).

4.10.4.2 Total Hardness

River water was classified as moderately hard to very hard (61 mg/L-180 mg/L) along the watercourse for both seasons (USEPA, 2005). There was a general increase in the level of hardness moving downstream the four locations for both seasons. The minimum hardness level was recorded at Daboase with a value of 53 mg/L and a maximum level of 105 mg/L recorded at Shama in the wet season (Appendix A4). In the dry season, minimum hardness level was recorded at Beposo with a value of 51 mg/L and a maximum value of 2970 mg/L recorded at Shama. Total hardness was widely dispersed along the watercourse for the four locations in the dry season with Co.V of 127.5% and narrowly distributed in the wet season with Co.V of 28.9% (Appendix A4, Figure 4.22C).

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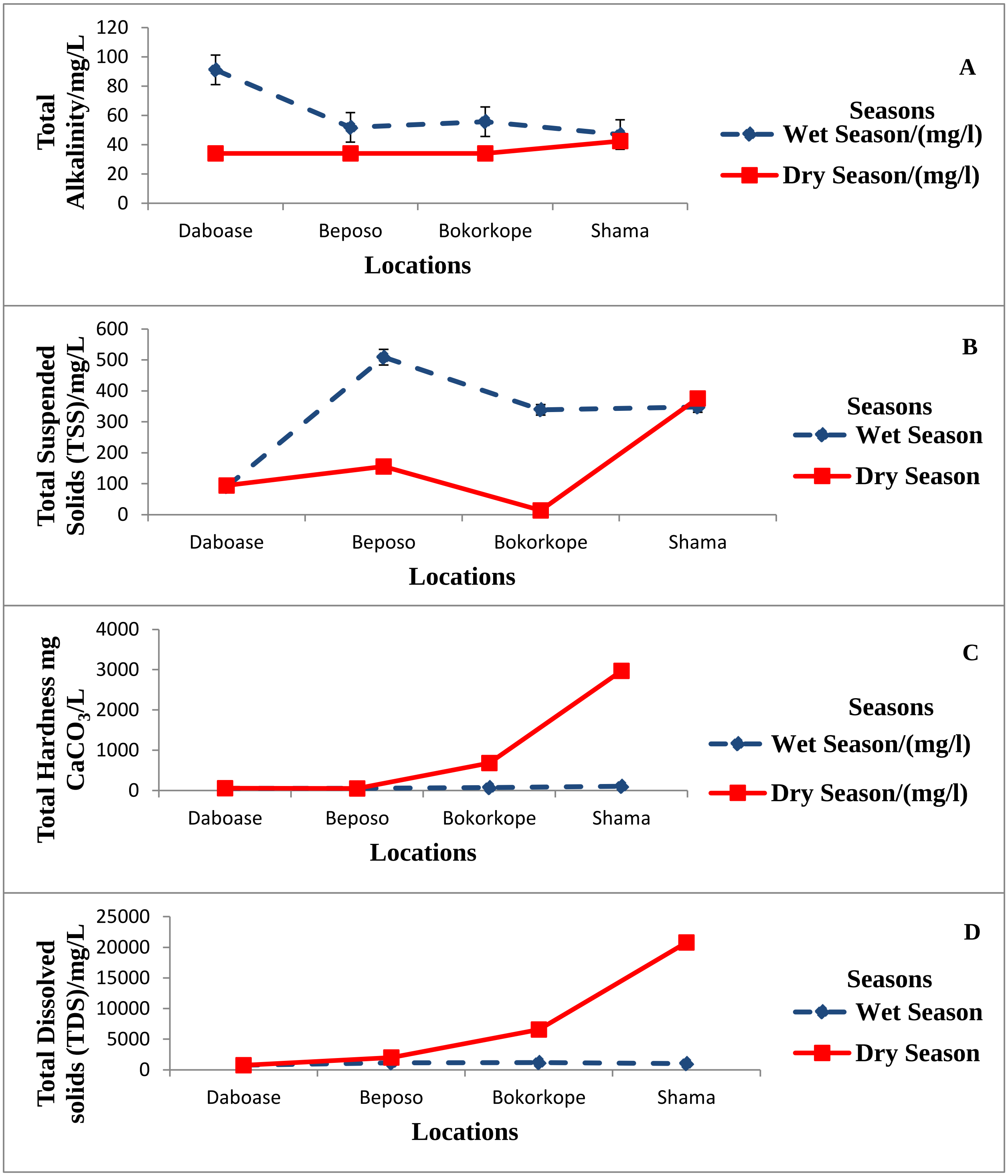
4.10.4.3 Total Suspended Solids (TSS)

Total suspended solids (TSS) were narrowly dispersed along the watercourse of the four locations in the wet season with Co.V of 46.4%. This was not the case for the dry season as TSS distribution was scattered along the watercourse with Co. V of 84%. The wet season recorded an average TSS of 322 mg/L (range: 91-509 mg/L) whiles the dry season recorded average levels of 160 mg/L (range: 14-376 mg/L) (Appendix A6). Shama recorded the highest TSS for the dry season (376 mg/L) whilst Beposo recorded the highest for the wet season (509 mg/L) (Appendix A6, Figure 4.22B).

4.10.4.4 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) were generally higher than total suspended solids (TSS) in both seasons. Overall mean concentration of 1,012 mg/L TSS was recorded in the wet season and the dry season recording an overall mean concentration value of 7527 mg/L. TDS was narrowly dispersed throughout the watercourse in the wet season with a Co.V of 15.8% (Appendix A8). There was a gradual rise in TDS for the first three locations with a sharp rise recorded at Shama with an average concentration of 20,764 mg/L for the dry season (Appendix A8, Figure 4.22D). TDS recorded a wide distribution along the watercourse in the dry season with Co.V of 94.4% (Appendix A8). Water is regarded as unpalatable when TDS concentration is greater than 1,200 mg/L. Water with TDS concentration below 600 mg/L is considered as good for drinking (WHO, 1984) (Figure 4.22D).



Figures 2.22A-D: Distribution of Physicochemical parameters in the Study Area. Sampling locations are not drawn to scale. Figure A- Total Alkalinity, Figure B-TSS, Figure C-Total Hardness and Figure D- TDS

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4.10.5 Principal Component Analysis (PCA)

Principal component analysis was performed to identify the possible sources of environmental variables (Heavy metals, Water nutrients, Physicochemical parameters). The major aim of the PCA is the auto-scaling of data to better describe the relationship between variables. First, the mean is subtracted from each data dimension to produce a data set whose mean is zero from which the co-variance matrix is extracted. Eigen values are calculated from Eigen factors which are derived from the co-variance matrix. Eigen vectors are unit vectors with their length equal to one. Therefore the selection of the number of principal components is based on the Kaiser criterion with Eigen value higher than one (Ackah, 2012; Manoj *et al.*, 2012).

Three principal components were selected since all the other components with Eigen values less than one are regarded as less significant. The three components selected were subjected to varimax rotation with Kaiser-normalization and then three components (factors) are extracted. The factor loadings are the correlation coefficients between variables and factors. Factor loading values greater than 0.75, between 0.75-0.5, and 0.5-0.3 are classified strong, moderate and weak based on their absolute values. Variables with factor loadings above 0.5 within same principal component group (PC1, PC2 or PC3) are associated and this strongly suggests that they have a similar source (Ackah, 2012; Manoj *et al.*, 2012).

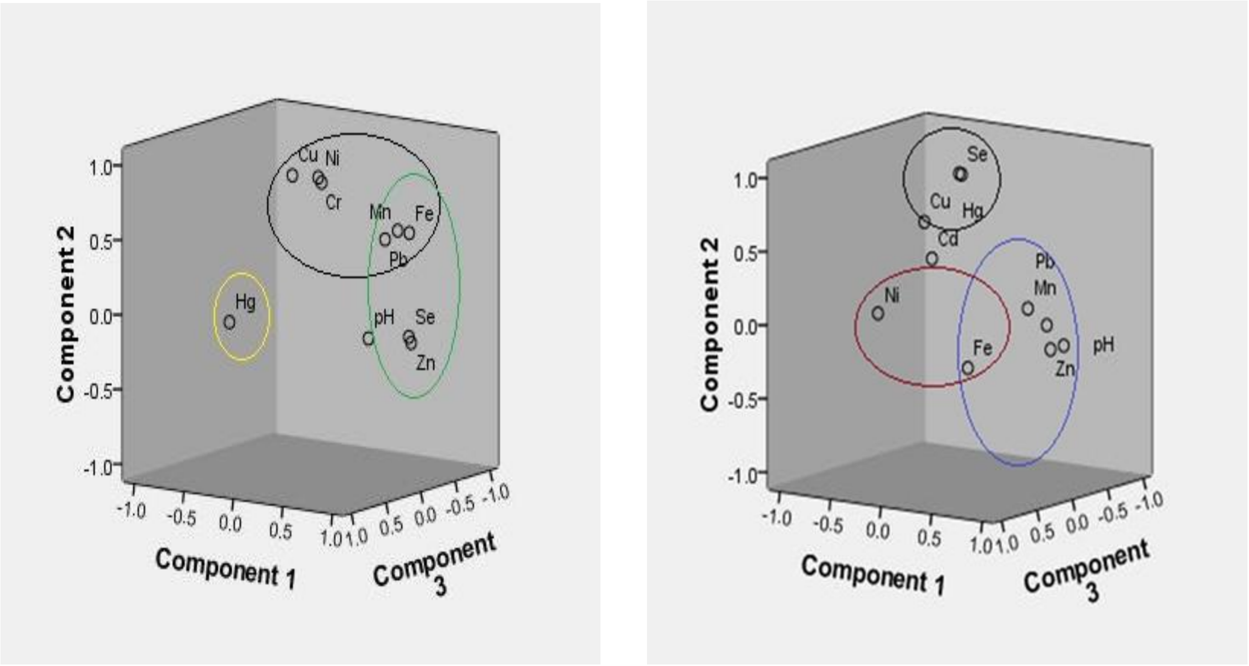
The cumulative variance is the percentage of data variability that was accounted for during the data reduction processes. For plot 1, the three components extracted accounted for 88% of all data variation with only a 12% loss of information (Appendices E1 and F1). Plot 2 accounted for 80% of all the data variation with a 20% loss of data (Appendices E2 and F2). Plot 3 accounts for 86% of all data variation with a 14% loss of data (Appendices E3 and F3). Plot 4 accounted for 86% of all data variation with a 14% loss of data (Appendices E4 and F4).

For plot 1, PC1 with variance of 41.35% comprises Pb, Mn, Se, Zn, and Fe. PC2 with a 31.95% variance consists of Pb, Cr, Mn, Cu, Fe, and Ni. PC3 with a 14.74% variance comprises Hg (Appendices E1 and F1). Pb, Mn, and Fe belonging to both PC1 and PC2 implies that they are coming from both natural and anthropogenic sources or from similar anthropogenic sources in the study area. Atmospheric deposition could be coming from traffic sources as well as the natural and artificial weathering of rocks since the study area is known for alluvial deposits. AGM activities at the study site may be accounting for only Hg in sediments for the study area for the dry season.

For plot 2, PC1 with 36.39% variance comprises Pb, Mn, Zn, and Fe. PC2 with 26.85% variance consists of Cu, Hg and Se with high factor loadings. PC3 with 17.5% variance is made up of Fe and Ni (Appendices E2 and F2). Fe and Ni in PC3 could be accounted for by natural input since it is accompanied by Fe. Both PC1 and PC2 are from different anthropogenic input especially for PC2 which are mostly from mining effluents from AGM sites. Fe in both PC1 and PC2 is indicative of mixed sources of input into sediments in the wet season (Appendices E2 and F2).

For plot 3, PC1 with 37% of the total variance comprises Zn, Hg, TSS, TDS, Se, Ni, Na, K, and Cu (Appendices E3 and F3). PC1 showed that TSS and TDS were associated with the distribution of Hg and Se in the river water and sediments for the dry season. TSS and TDS were also associated with other elements such as Zn, Na, K and Ni. Total variance of 32.62% for PC2 comprises Fe, Mn, Cr, NO_3^-, and PO_4^{3-} which indicated natural sources of weathering evident by the alluvial deposits which are carried in river water. Total variance of 16.37% for PC3 comprises Hg and NO_3^-. Hg in PC1 and PC2 is mainly attributed to the effluents that are discharged from the AGM sites into the river in the dry season.

Plot 3 and Plot 4 were similar for PC1 which affirms the fact that both TSS and TDS were responsible for the distribution of THg and Se in the study area although THg showed a weak inverse correlation with TSS (Figure 4.17B). PC2 for plot 4 with 32.5% of total variance comprises Pb, Cr, Na and TDS. PC3 with 15.45% of total variance comprises PO_4^{3-}, Hg, and NO_3^-. Hg in PC1 and PC3 highlights the various sources of effluents discharged into the river from AGM sites for the wet season which is the same as in the dry season (Appendices E3 and E4, F3 and F4).



PLOT 1 **PLOT 2**

Figures 4.23: Principal component analysis diagram showing the rotated factor loadings of the principal component (PC1, PC2 and PC3) to a descriptor space of three dimensions. Plot 1 is for sediments for the dry season. Plot 2 is for sediments for the wet season.

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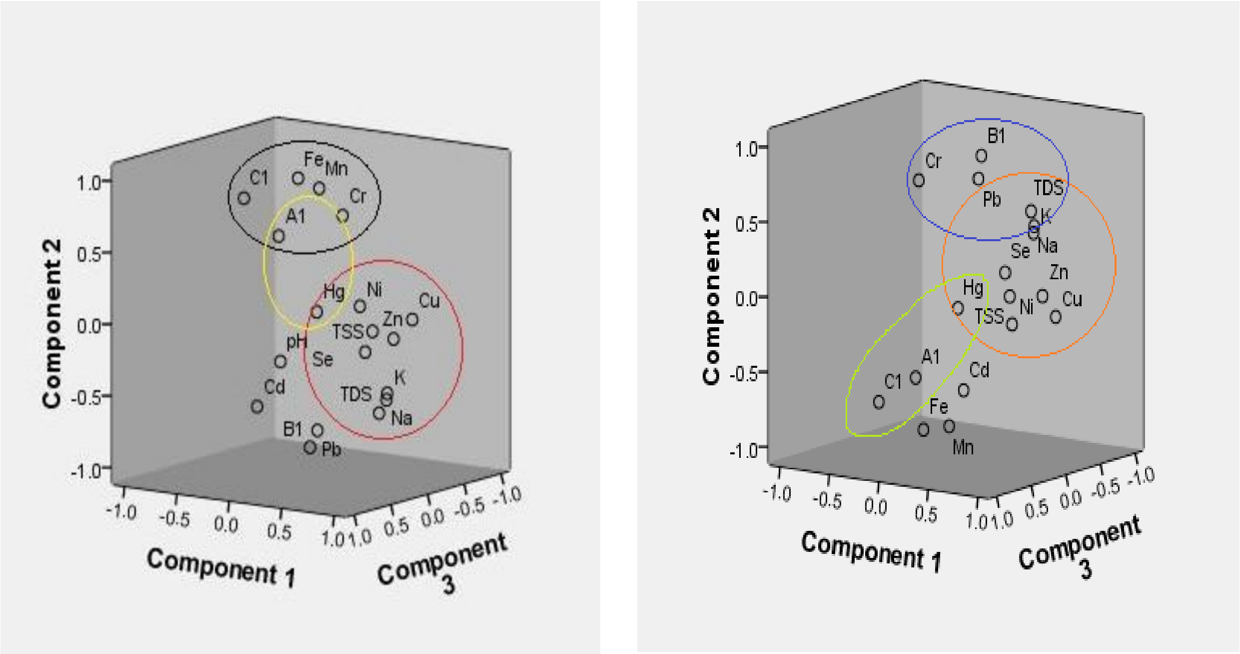

PLOT 3

PLOT 4

Figures 4.24: Principal component analysis diagram showing the rotated factor loadings of the principal component (PC1, PC2 and PC3) to a descriptor space of three dimensions. Plot 3 is for river water for the dry season. Plot 4 is for river water for the wet season. A1, B1, and C1 are for water nutrients NO_3^-, SO_4^{2-}, and PO_4^{3-} respectively.

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4.11 DISCUSSION

This study highlights the relationship between total mercury (THg) and selenium (Se) in various aquatic components, their association with other heavy metals and other physicochemical parameters at the lower catchment regions of the Lower Pra River.

Concentrations of THg and Se were determined in sediments, fish species and river water for the minor wet season of 2012 and the dry season of 2013. From the studies, THg and Se were found in sediments and river water at sites isolated for AGM activities. Dilution of THg was not observed as concentrations were higher in water and sediments about 20 km further downstream from the first AGM sites at Shama estuary for both seasons. THg was widely dispersed from point source in the wet season for river water and widely dispersed in sediments for both season.

Some factors that may have accounted for these observations include atmospheric deposition and resuspension of mercury particulates from point source, river flow factors and anthropogenic input. The entire Lower Pra River catchment is noted for AGM activities and the operators are known to move from one location to the other for their operations. Mercury is used by these operators because its use is accessible and highly effective in the capture of gold. Mercury is released into the river through mining effluent or emitted into the atmosphere when the mercury-gold amalgam is heated or roasted. Mercury together with other mine tailings pollutes the river which serves as source for drinking water.

Also persistent and historic mining accounts for levels of mercury in locations not noted for AGM activities (Donkor *et al.*, 2006[a, b]; Oduro *et al.*, 2012). THg levels in sediments and in river water were relatively higher in this study compared to previous studies conducted by Donkor *et al.*, 2006[a, b] and Oduro *et al.*, 2012. The high THg levels may be attributed to the fact that AGM

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activities in the Lower Pra river basin have intensified particularly last year accounting for higher levels of THg observed in this study. Concentrations of THg generally exceeded the USEPA 2004 permissible limit of 200 µg/Kg for sediments and 1 µg/L for drinking water for most of the sampling sites except for Borkorkope. THg was largely below the detection limit in sediments and in river water for the wet season in this location. This is because the location was not largely impacted by a lot of anthropogenic activities.

THg had no significant relationship with TSS, Fe and Mn although other studies by Warner *et al.*, 2005 and Balogh *et al.*, 1998 suggested otherwise. THg in river water had a significant relationship with dissolved sulfate highlighting a possible methylation process. Methylation is favored under anoxic conditions in the presence of sulfur reducing bacteria.

Studies on two fish species *Xenomystus nigri* and *Clarias submarginatus* (Mudfish) showed that THg had bioaccumulated in the tissue parts of the two fish species (Tables 4.4 and 4.5). Mercury had bioaccumulated in the dorsal tissues of Mudfish and in the dorsal and ventral tissues of *Xenomystus nigri*. THg content in the ventral tissues was relatively higher than in the dorsal tissues of *Xenomystus nigri* (Figure 4.8 and Table 4.3).

From the studies, length and weight did not affect the THg content for the two fish species. *Clarias submarginatus* (Mudfish) which were smaller in length and in weight had higher THg content in their tissues than that of *Xenomystus nigri* (Table 4.2 and 4.3). Studies conducted on various fish species by Ntow and Khjawa found no correlation between THg content and size, weight and length of fish species under investigation. THg content and rate of accumulation differs for every fish species since various fish species have different migratory and feeding habits as well as different metabolic and excretion rates (Ntow and Khwaja, 1988).

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Bioamplification in food chain increases the concentration of mercury especially methylmercury which is the most abundant in fish species (Voegborlo *et al.*, 2010). The highest concentrations of mercury in the food chain is observed in the secondary and tertiary trophic levels (Dix, 1891; Hamilton, 1971) and at these levels mercury toxicity is greatly felt.

Other elemental content such as Cd, Mn, Pb, Fe, Zn, Se and Ni were generally higher in Mudfish than in *Xenomystus nigri* (Table 4.2 and 4.3). Copper was not detected in the two fish species. The higher elemental content in Mudfish is due to the mode of preservation for the Mudfish. The local indigenes in the area preserve fish by smoking and drying and this could have accounted for the elevated mineral content.

Correlation and regression studies between THg and Se for river water showed a moderately strong positive correlation for the two elements for the dry season (n = 24, r^2 = 0.521, r = 0.724) and a no relationship for the wet season (n = 24, r^2 = 0.0895, r = 0.0635) (Figures 4.6A and 4.6B). This implied that THg increased as Se increased in river water in the dry season but no pattern was observed for the wet season. For sediments, there was a weak inverse relationship between the two elements in the dry season (n = 16, r^2 = 0.072, r = -0.269) and a moderately direct correlation in the wet season (n = 24, r^2 = 0.978, r = 0.989) (Figures 4.4A and 4.4B). This implied that as THg increases across the sediment in the dry season there was a slight decrease in Se and in the wet season an increase in THg was accompanied with an increase in Se.

Although Se appeared generally higher than THg in most of the individual sites that were examined, the patterns of correlation were not definite but statistically significant relationships between the two elements in sediments and in river water for both seasons suggests the possible association between the elements. The antagonism between Se and Hg however remains unclear.

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There was a near perfect correlation between THg and Se for dorsal tissue parts of mudfish (r^2 = 0.98, r = 0.99) and a weak inverse relationship between the two elements in the various fish tissue parts in *Xenomystus nigri* (r^2 = 0.0987, r = - 0.314). The logarithm transformation of the bioaccumulation factors also gave the same results (Figure 4.11 and 4.12). In *Xenomystus nigri*, an increase in the molar ratios of Se in fish tissue parts was characterized by a decrease in the molar ratios of THg (Figure 4.9).

Se contamination in river water accounted for elevated Se levels in fish and it was evident from the calculated bioaccumulated factors. A near 1:1 Hg:Se/Se:Hg molar ratio has been observed in organs of marine mammals suggesting a possible antagonism taking place between the two elements (Koeman *et al.*, 1975; Caurant *et al.*, 1996) but this molar ratio was not supported in this studies. Se:Hg were in average ratios of 261:1 for mudfish and 5:1 for *Xenomystus nigri* (Tables 4.6 and 4.7). Higher Se:Hg molar ratios in fish species have been reported in walleyes by Yang *et al.*, 2010 suggesting the antagonistic effect of Se on Hg. Yang *et al.*, 2010 suggested that threshold concentrations of Se must be reached before a clear protective role of Se on Hg can be noticed. Se:Hg molar ratios have been found to decrease along the food web due to biomass dilution (Chen *et al.*, 2001).

From the study, several questions remained unanswered. Although Se is an essential element for living organisms, other forms of this element can be toxic and can magnify the toxicity of mercury (Parizek, 1980). Since there is a small difference between essential and toxic levels of Se (Feroci *et al.*, 2005) and this differs with various fish species, the particular form of Se will provide more insight on an antagonism or a synergism phenomenon.

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Both Hg/Se speciation in fish will give more insight as to the antagonistic nature of Se on THg. Se is also known to have certain other interactions with elements such as Cd, Zn and Fe. Feroci *et al.*, 2005 conducted polarographic studies on Hg, Cd, and Zn with different selenium compounds. From the studies, it was found out that THg interacts more significantly with Se and oxy-selenium compounds and that Zn and Cd displayed very weak interactions. The observation made by Feroci *et al.*, 2005 was largely supported by the regression studies of Se on Zn and Cd in fish species as no significant relationship was established (Figures 4.13A-C and 4.14A-C).

One way ANOVA studies showed that pH had an effect on the linear variation of THg in sediments and in river water along the watercourse ($p < 0.05$) (Appendices D2 and D3). pH in sediments were found to be acidic for both seasons thus highlighting the acidic nature of effluents released from AGM sites into the river body. The effluents released from AGM sites include oxides of nitrogen and sulfur which tend to lower pH (Figure 4.23 and 4.24). This affects the acid-base balance of water body thereby having an adverse effect on aquatic life (Fianko, 2003).

Principal Component Analysis (PCA) was used to identify the sources of pollution, apportion to natural, anthropogenic or mixed contributions. PCA results showed that THg in mining effluent was accompanied by Se and Cu and they adsorb onto sediments evident in plot 2 (Figure 4.23). Fe and Mn can be accounted for by mixed sources either through natural or artificial weathering contributing mainly to alluvial nature of the study area. Fe and Mn were found to be accompanied by TSS and TDS in plot 3 (Figure 4.24). Sand winning by AGM operators and quarrying of rocks is found to increase the TSS and TDS of the river water by introducing dissolved and suspended particulates which are mainly rich in Fe and Mn. Fe and Mn was also accompanied by water nutrients such as phosphate from phosphorous bearing rocks evident in plot 3 (Figure 4.23). Pb was found to be accompanied by Mn and Fe either from mixed natural and anthropogenic sources as displayed in plot 1 (Figure 4.23) or mainly from anthropogenic sources displayed in plot 2 (Figure 4.23).

Average concentration of Cd in river water for the wet season exceeded the WHO guideline value of 0.003 mg/L for drinking water whilst concentrations levels were largely not detected in the dry season. Average concentrations of Fe also exceeded the WHO value of 0.3 mg/L in the wet season. Average concentration of Pb was close to the WHO guideline value of 0.01 mg/L in the wet season and far exceeded the guideline value for the dry season. Levels of Ni, Cu, Cr, Se, Mn, and Zn were all below the WHO guideline for value for both seasons (Appendices B1-B20) (WHO, 2011).

Average levels of Pb in *Xenomystus nigri* (3.4 mg/Kg) and in Mudfish (33 mg/Kg) exceeded the WHO guideline value of 2 mg/Kg for fish (Tables 4.2 and 4.3). Average Cr levels in *Xenomystus nigri* (0.8 mg/Kg) was close to the guideline limit of 1 mg/Kg. Cd, Hg and Zn all had average concentrations below the WHO guideline limit of 2 mg/Kg, 500 µg/Kg and 50 mg/Kg respectively for *Xenomystus nigri* but were above the WHO guidelines for Mudfish (Tables 4.2 and 4.3) (WHO, 2011).

Overall mean concentration of Cd in sediments for wet season (0.8 mg/Kg) exceeded the Canadian Interim Sediment Quality (ISQG) threshold effect level (TEL) guideline value of 0.6 mg/Kg. Overall mean concentrations of Pb, Zn, Ni, Cr and Cu were below the ISQG threshold effect guideline values for the two seasons (Appendices B1-B20) (Burton, 2002).

Safe drinking water is defined by WHO as that water having acceptable quality in terms of its physical, chemical and bacteriological parameters. Bacteriological parameters, especially *E. coli* and total coliform (TC) have been used to determine the general quality of drinking water worldwide. Microbial investigations carried out further upstream at Daboase and further downstream at Shama revealed that total coliform (TC), total heterotrophic bacteria (THB), faecal coliform (FC) and *E. Coli* counts were above the WHO guideline value for drinking water. Based on WHO risk categories, river water was classified as low to intermediate risk for purposes of drinking (Appendices A1 to A3). Higher microbial population in these two sites highlights the disposal of faecal matter into the river and this affects water quality. Microbial contamination of water sources for drinking purposes results in the outbreak of waterborne diseases such as Cholera, Typhoid fever, Dysentery, Vibrio illness and many others.

Biochemical Oxygen Demand (BOD) and Dissolved Oxygen (DO) are important parameters in the determination of water quality. BOD and DO investigations were carried out at the first and the last sampling locations, Daboase and Shama. These two towns selected were highly populated with human activities affecting the general water quality of the river. DO recorded at Shama was 13.11 mg/L in the dry season and 6.60 mg/L in the wet season. DO recorded at Daboase was 13.22 mg/L and 6.40 mg/L in the dry and wet seasons respectively. BOD recorded at Daboase was 6.60 mg/L in the dry season and 3.50 mg/L in the wet season. Shama recorded BOD of 4.84 mg/L in the dry season and 2.66 mg/L in the wet season (Appendices A1 to A3).

BOD was above the WHO guideline value of 3 mg/L for drinking water for the two locations for both seasons. DO on the other hand was below the recommended WHO, 2011 guideline value of 7 mg/L in the wet season and above the guideline value in the dry season. DO concentrations below 7 mg/L can have an effect on aquatic life through oxygen starvation. This is because oxygen is needed in a biochemical process like respiration. Higher BOD could be as a result of higher organic matter content in effluents either from domestic purposes or from mines that are

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discharged into the river water from these two communities. Microbes introduced into the water utilize more of the DO in the breakdown of organic matter thereby decreasing the DO concentration. Concentration of DO was higher the dry season because the AGM activities had been abandoned due to the raids by the military and minerals commission at the two isolated AGM site (Appendices A1 to A3).

There was an elevated level of TSS and TDS in water due to the winning of sand by AGM operators. TSS was higher in the wet season than the dry season (Figure 4.21B) because of runoffs during rainfall. TDS and ions such as Na^+ and K^+ were found to be very high in river water at downstream locations Bokorkope and Shama especially for the dry period. Elevated levels of TDS, Na^+ and K^+ at these locations were due to the influx of seawater inland. This could be attributed to the differences in tides at the estuary, flow rate and direction of river current which are affected by the differences in seasons.

Water nutrients PO_4^{3-}, NO_3^- and SO_4^{2-} had their overall mean concentrations lower than the WHO, 2011 guideline values for drinking water for both seasons (Appendices C1 to C5). The dry season generally recorded higher values of NO_3^- and SO_4^{2-} than the wet season (Figures 4.20A-E). PO_4^{3-} recorded higher values in the dry season than the wet season for the first two AGM sites (Figure 4.20E). Excessive evaporation of river water leading to pre-concentration of ions in the dry season could have accounted for elevated nutrients levels in water.

A survey conducted by the Water Research Institute (WRI) in 2011 on the surface water quality at selected towns including Daboase reported total alkalinity, total hardness, TDS and DO at levels of 40 mg/L, 52 mg/L, 58.9 mg/L and 6.49 mg/L respectively. Average concentration of total hardness for both seasons was higher in this study at Daboase than what was reported in the

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survey (Appendix A4). Total alkalinity was higher in the wet season for this study than what was reported (Appendix A5). TDS was higher in this study for the two seasons than what was reported in the survey at Daboase (Appendix A7). Levels of DO at Daboase in this study for the wet season were comparable to what was reported in the survey but was higher than what was reported in the survey for the dry season (Appendix A3)

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CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

- THg largely exceeded the WHO guideline value for drinking water for both seasons and exceeded the USEPA guideline value for sediments in the dry season for the four locations which is an indication that amalgamation with mercury is the technique used by illegal gold miners.
- THg levels were higher in sediments and in river water for this study than in other studies carried out by Donkor *et al.,* 2006[a, b] and Oduro *et al.,* 2012 in other selected sites along the Lower Pra River and this as a result of the intense activities of illegal gold miners especially in the lower catchment regions of the Lower Pra River.
- THg levels were detected in river water at Shama estuary which was the last sampling location, several kilometres from Daboase which was the second selected location for sampling and known for AGM activities as at the time of study.
- A strong association characterized by a weak inverse and a strong direct relationship was observed between THg and Se in *Xenomystus nigri* and *Clarias submarginatus* respectively but an antagonism effect of Se on THg was not clearly established. The null hypothesis in this case could not be supported.
- It was observed from the Principal Component Analysis (PCA) that TSS had a role in the distribution of THg and Se for the four locations in the study area. Furthermore TSS accounted for the scattered distributions of Pb, THg and Se across the longitudinal transect for both seasons evident from the co-efficient of variation in Figure 4.21C and Principal

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Component Analysis (PCA) plot 3 and 4 which show the association between TSS, Pb, THg and Se.

- From the paired sampled T-test, physicochemical parameters such as temperature, total hardness, total alkalinity, pH, BOD, TSS and TDS were affected by the changes in seasons which validates the null hypothesis.
- Human activities along the banks of the river and the inflow of effluents from domestic and AGM activities appear to have great impact on the quality of water as source for drinking.

5.2 RECOMMENDATIONS

- Elemental speciation will provide more insight on the antagonistic nature of Se on Hg. Further information provided by the speciation of the two elements will be helpful in the long term treatment of mercury contaminated systems with selenium.

- Other methods of Gold extraction that are safer and that cause minimum impact on the environment should be encouraged other than mercury amalgamation.

- Activities of small scale miners must be monitored by the Environmental Protection Agency (EPA) to ensure their compliance to environmental regulations.

- Miners must be educated on the irreversible health problems associated with mercury poisoning.

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APPENDICES

APPENDIX A

A1: Wet Season Microbial Studies

Location	TC/ CFU/100ml	FC/CFU/100ml	*E. coli*/CFU/100ml	THB/CFU/100ml
Daboase	120	4	558	780
Shama	7	1	392	5616

A2: Dry Season Microbial Studies

Location	TC/ CFU/100mL	FC/CFU/100mL	*E. coli*/CFU/100mL	THB/CFU/100mL
Daboase	90	45	16	37
Shama	66	52	28	73

n=1, for each location, where n is the number of samples

WHO, 2011 Guideline values: 0 CFU/ 100ml, 0 CFU/100 ml (conformity), 1-10 CFU/100ml (low risk), 10-100 CFU/100ml (intermediate risk), 100-1000 CFU/ml (high risk)

A3: DO and BOD

Location	Dissolved Oxygen (DO) (mg/L)		Biochemical Oxygen Demand (BOD)(mg/L)	
	Dry Season	Wet Season	Dry Season	Wet Season
Daboase (Upstream)	13.22	6.40	6.60	3.50
Shama (Downstream)	13.11	6.60	4.84	2.66

n = 1 DO for each location, n = 3 BOD for each location WHO, 2011: BOD – 3 mg/L; DO – 7 mg/L

APPENDIX A

A4: Total Hardness

Location	Wet Season/(mg/L)	Dry Season/(mg/)
Daboase	53±7	59±6
Beposo	57±13	51±6
Bokorkope	71±8	683±17
Shama	105±12	2970±104
Mean	71.5	940.65
SD	20.72722	1199.525
Co. V/%	28.9	127.5
Range	53-105	51-2970
Mean± SD corrected to nearest whole number	72±21	941±1200

n = 3 for each location *WHO 2011 – 200 mg/L

A5: Total Alkalinity

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	91±53	34±7
Beposo	52±27	34±9
Bokorkope	56±39	34±7
Shama	47±5	42.5±5
Mean	61.445	36.125
SD	17.43775	3.680608
Co. V/%	28.36	10.18
Range	47-91	34-43
Mean± SD corrected to nearest whole number	61±17	36±4

n = 3 for each location

A6: Total Suspended Solids

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	91±12	94±4
Beposo	509±167	156±47
Bokorkope	339±97	14±5
Shama	348±98	376±62
Mean	321.75	160
SD	149.4111	134.4842
Co. V/%	46.4	84
Range	91-509	14-376
Mean± SD corrected to nearest whole number	322±149	160±134

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APPENDIX A

A7: Total solids (TSS + TDS), n = 3 for each location

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	848±79	846±93
Beposo	1641±312	2162±204
Bokorkope	1503±229	6598±472
Shama	1346±210	21140±2407
Mean	1334.5	7686.5
SD	299.6452	8054.409
Co. V/%	22.45	104.78
Range	848-1503	846-21140
Mean± SD corrected to nearest whole number	1335±300	7687±8054

***WHO 2011 – 1500 mg/L**

A8: Total Dissolved Solids

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	757±67	752±89
Beposo	1132±145	2007±157
Bokorkope	1164±132	6584±467
Shama	998±112	20764±2345
Mean	1012.75	7526.75
SD	160.252	7106.032
Co. V/%	15.8	94.4
Range	757-1164	752-20764
Mean± SD corrected to nearest whole number	1013±160	7527±7106

***WHO – 600 mg/L**

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APPENDIX B
Heavy Metal Analysis

B1: Mean Concentration of Iron (Fe) in River Water

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	5.6±0.7	1.44±0.01
Beposo	9±1	1.3±0.6
Bokorkope	5.9±0.4	0.04±0.02
Shama	5.6±0.6	0.05±0.04
Min	5.6	0.04
Max	9	1.44
Co.V/%	19.38	94.37
Range	(5.6-9)	0.04-1.44
Mean ± SD Nearest whole number	6±1	0.7±0.6

***WHO 2011 – 0.3 mg/L**

B2: Mean Concentration of Iron (Fe) in Sediment samples

Location	Wet season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	5567±515	704±157
Beposo	5470±207	818±266
Bokorkope	5703±710	675±47
Shama	6388±333	896±13
Min	5470	675
Max	6388	895
Co.V/%	6.20	11.47
Range	5470-6388	675-895
Mean ± SD Nearest whole number	5738±360	773±89

B3: Mean Concentration of Manganese (Mn) in Sediment samples

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	195±32	21±8
Beposo	223±32	29±11
Bokorkope	156±36	15.2±0.9
Shama	274±26	30±3
Min	156	15.2
Max	274	30
Co.V/%	19.67	11
Range	156-274	15.2-30
Mean ± SD Nearest whole number	213±42	30±3

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B4: **Mean Concentration of Manganese (Mn) in River Water**

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.007	BDL
Beposo	0.02±0.01	0.02±0.01
Bokorkope	BDL	0.08±0.04
Shama	0.014±0.009	0.082±0.006
Min	BDL	BDL
Max	0.02	0.082
Co.V/%	66.7	80
Range	BDL-0.02	BDL-0.082
Mean ± SD Nearest whole number	0.009±0.006	0.05±0.04

***Detection limit 0.006 mg/L *WHO 2011 – 0.4 mg/L**

B5 **Mean Concentration of lead (Pb) in River Water**

Location	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.05±0.01	0.020±0.003
Beposo	0.11±0.01	0.019±0.007
Bokorkope	0.022±0.009	0.007±0.002
Shama	0.025±0.006	0.010±0.007
Min	0.022	0.007
Max	0.11	0.020
Co.V/%	69.23	38.46
Range	0.022-0.11	0.007-0.020
Mean ± SD Nearest whole number	0.05±0.04	0.013±0.005

***Detection limit – 0.001 mg/L *WHO 2011 – 0.01 mg/L**

B6: **Mean Concentrations of Lead (Pb) in Sediment samples**

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	7±3	13.6
Beposo	11±8	6±4
Bokorkope	8±5	0.9
Shama	31±19	10±2
Min	7	0.9
Max	31	13.6
Co.V/%	71.42	62.5
Range	7-31	0.9-13.6
Mean ± SD Nearest whole number	14±10	8±5

***ISQG – 35 mg/Kg**

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B7: Mean Concentration of Cadmium (Cd) in River Water

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.003±0.002	BDL
Beposo	0.008	0.004±0.002
Bokorkope	0.007±0.003	BDL
Shama	0.005	BDL
Min	0.003	BDL
Max	0.007	0.003
Co.V/%	33.3	-
Range	0.003-0.007	BDL-0.004
Mean ± SD	0.006±0.002	-
Nearest whole number		

***Detection limit – 0.002 mg/L**

B8: Mean Concentration of Cadmium (Cd) in Sediment samples

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	0.8±0.7	BDL
Beposo	0.3±0.2	BDL
Bokorkope	0.9±0.7	BDL
Shama	1.3	BDL
Min	0.3	-
Max	1.3	-
Co.V/%	37.5	-
Range	0.3-1.3	-
Mean ± SD	0.8±0.3	-
Nearest whole number		

***Detection limit – 0.2 mg/Kg *ISQG – 0.6 mg/Kg**

B9: Mean Concentration of Copper in River Water

Locations	Wet Season(mg/L)	Dry Season/(mg/L)
Daboase	0.038±0.001	0.025±0.003
Beposo	0.006	0.023±0.004
Bokorkope	0.006	0.021±0.007
Shama	0.032±0.004	0.036±0.004
Min	0.006	0.021
Max	0.038	0.036
Co.V/%	50	23
Range	0.006-0.038	0.021-0.036
Mean ± SD	0.02±0.01	0.026±0.006
Nearest whole number		

***WHO 2011 – 2 mg/L**

B10: Mean concentration of Copper (Cu) in Sediment

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	3.0± 0.8	5 ±2
Beposo	4 ±1	7± 1
Bokorkope	3 ±1	4.75± 0.05
Shama	2.0± 0.6	2.6± 0.2
Min	2	2.6
Max	4	7
Co.V/%	30	20
Range	2-4	2.6-7
Mean ± SD Nearest whole number	2.8± 0.9	5± 1

***ISQG – 37.3 mg/Kg**

B11: Mean Concentration of Zinc (Zn) in River samples

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.04±0.01	0.0095±0.0005
Beposo	0.05±0.02	0.013±0.003
Bokorkope	0.058±0.003	0.010±0.007
Shama	0.07±0.02	0.0245±0.0005
Min	0.04	0.0095
Max	0.07	0.0245
Co.V/%	14.2	42.8
Range	0.04-0.07	0.0095-0.0245
Mean ± SD Nearest whole number	0.056±0.009	0.014±0.006

***WHO 2011 – 3 mg/L**

B12: Mean Concentration of Zinc (Zn) in Sediment samples

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	47±6	3.1±0.8
Beposo	51±5	3.3±0.9
Bokorkope	41±7	3.65±0.05
Shama	82±8	7.4±0.3
Min	41	3.1
Max	82	7.4
Co.V/%	27.2	40.3
Range	41-82	3.1-7.4
Mean ± SD Nearest whole number	55±1	4±2

***ISQG – 123 mg/Kg**

B13: Mean Concentrations of Nickel (Ni) in River Water

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.009 ±0.006	0.008
Beposo	0.05 ±0.02	0.02
Bokorkope	0.013	0.007 ±0.001
Shama	0.013± 0.007	0.014± 0.004
Min	0.009	0.007
Max	0.013	0.02
Co.V/%	80	41.6
Range	0.009-0.013	0.007-0.02
Mean ± SD Nearest whole number	0.02±0.02	0.012±0.005

***WHO 2011 – 0.07 mg/L**

B14: Mean Concentration of Nickel (Ni) in Sediment

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	8±4	2.8±0.9
Beposo	6±2	1.7±0.7
Bokorkope	8±5	0.9±0.2
Shama	5±3	1.1±0.5
Min	5	0.9
Max	8	2.8
Co.V/%	14.3	50
Range	5-8	0.9-2.8
Mean ± SD Nearest whole number	7±1	1.6±0.8

***ISQG – 18 mg/Kg**

B15: Mean Concentrations of Chromium (Cr) in River Water and Sediments

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	BDL	0.010±0.003
Beposo	BDL	0.004
Bokorkope	BDL	0.004
Shama	BDL	BDL
Min	-	BDL
Max	-	0.010
Co.V/%	-	80
Range	-	BDL-0.010
Mean ± SD Nearest whole number	-	0.005±0.004

***Detection limit – 0.001 mg/L *WHO 2011 - 0.05 mg/L**

B16: Mean Concentrations of Chromium (Cr) in Sediments

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	BDL	2±2
Beposo	BDL	3±1
Bokorkope	BDL	1.4
Shama	BDL	1.2±0.2
Min	-	1.2
Max	-	3
Co.V/%	-	36.8
Range	-	1.2-3
Mean ± SD Nearest whole number	-	1.9±0.7

***Detection limit – 0.1 mg/Kg *ISQG-37.3 mg/Kg**

Mercury and Selenium concentration in Sediments and River Water along the Water shed

B17: Sediments (Selenium (Se))

Locations	Wet Season/(mg/Kg)	Dry Season/(mg/Kg)
Daboase	70±46	0.4 ±0.2
Beposo	58±61	1±0.8
Bokorkope	-	0.5±0.1
Shama	-	1.8±0.2
Min	BDL	0.4
Max	70	1.8
Co.V/%	83.44	55.55
Range	BDL-70	0.4-1.8
Mean ± S.D	65±54	0.9±0.5

***Detection limit – 0.1 mg/Kg**

B18: Total Mercury (THg)

Locations	Wet Season/(µg/Kg)	Dry Season/(µg/Kg)
Daboase	320± 349	762±25
Beposo	500±406	2568±2004
Bokorkope	-	297±120
Shama	-	849±913
Min	BDL	297
Max	500	2568
Co.V/%	104.9	78.12
Range	BDL-500	297-2568
Mean ± S.D	205±215	1111±869

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***Detection limit – 1 µg/Kg *USEPA – 200 µg/Kg *ISQG – 0.17 mg/Kg**

B19: Total Mercury (THg) River water

Locations	Wet Season/(µg/L)	Dry Season/(µg/L)
Daboase	1.2±0.8	1.1±0.7
Beposo	BDL	2.3±0.7
Bokorkope	0.97±0.06	1.28
Shama	1.3±0.8	2.4±0.9
Min	BDL	1.1
Max	1.3	2.4
Co.V/%	114.3	34.8
Range	BDL-1.3	1.1-2.4
Mean ± S.D	0.7±0.8	1.7±0.6

***Detection limit – 0.01 µg/L USEPA - 1µg/L**

B20: Selenium (Se)

Locations	Wet Season/(µg/L)	Dry Season/(µg/L)
Daboase	1.1±0.6	5±2
Beposo	0.9±0.4	7±1
Bokorkope	0.65	5±1
Shama	0.7±0.4	12±6
Min	0.65	5
Max	1.1	12
Co.V/%	80.05	37.12
Range	0.65-1.1	5-12
Mean ± S.D	0.7±0.6	8±3

***WHO 2011 – 0.04 mg/L**

APPENDIX C

Concentrations of Water Nutrients along the Water shed

C1: **Sodium (Na)**

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	27.8	21.4
Beposo	23.8	44
Bokorkope	19.9	2130
Shama	180	12490
Min	19.9	21.4
Max	180	12490
Co.V/%	107	140
Range	19.9-180	21.4-12490
Mean ± SD Nearest whole number	63±68	3671±5163

***WHO 2011 – 200 mg/L for Na^+**

C2: **Potassium (K)**

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	6.3	4.3
Beposo	7.5	7.6
Bokorkope	5.8	72.1
Shama	14.2	563
Min	5.8	4.3
Max	14.2	563
Co.V/%	39.9	144
Range	5.8-14.2	4.3-563
Mean ± SD Nearest whole number	8±3	162±233

***WHO 2011 – no value listed**

C3: **Nitrate (NO_3^-)**

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.509	1.72
Beposo	1.969	4.113
Bokorkope	0.629	0.392
Shama	1.204	2.242
Min	0.509	0.392
Max	1.969	4.113
Co.V/%	54.5	62.8
Range	0.509-1.969	0.392-4.113

Mean ± SD Nearest whole number	1.1±0.6	2±1

*** WHO 2011 – 50 mg/L**

C4: Phosphate (PO_4^{3-})

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	0.215	0.295
Beposo	0.383	0.494
Bokorkope	0.193	0.088
Shama	0.32	0.041
Min	0.193	0.041
Max	0.383	0.494
Co.V/%	27.8	78
Range	0.193-0.383	0.041-0.494
Mean ± SD Nearest whole number	0.28±0.08	0.2±0.2

*** WHO 2011 – 0.3 mg/L**

C5: Sulfate (SO_4^{2-})

Locations	Wet Season/(mg/L)	Dry Season/(mg/L)
Daboase	3.602	11.304
Beposo	12.671	19.006
Bokorkope	<0.001	121.118
Shama	16.894	73.043
Min	<0.001	11.304
Max	16.894	121.118
Co.V/%	50.1	79.17
Range	<0.001-16.894	11.304-121.118
Mean ± SD Nearest whole number	11±6	56±44

***Detection limit – 0.001 mg/L WHO 2011 – 500 mg/L**

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APPENDIX D

D1:

Statistical Analysis

Paired Samples Test

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Nitrates (Wet) - Nitrates (Dry)	-1.039000E0	.886072	.255787	-1.601983	-.476017	-4.062	11	.002
Pair 2	Phosphates (Wet) - Phosphate (Dry)	.048250	.163714	.047260	-.055769	.152269	1.021	11	.329
Pair 3	Sulphate (Wet) - Sulphate (Dry)	-2.339533E1	24.572381	8.190794	-42.283337	-4.507330	-2.856	8	.021
Pair 4	Sodium (Wet) - Sodium (Dry)	-3.608475E3	5323.311607	1536.707695	-6990.745831	-226.204169	-2.348	11	.039
Pair 5	Potassium (Wet) - Poatssium (Dry)	-1.533000E2	240.214438	69.343935	-305.924973	-.675027	-2.211	11	.049

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D2: **ANOVA (One way)**

		Sum of Squares	df	Mean Square	F	Sig.
Pb	Between Groups	.022	6	.004	56.303	.000
	Within Groups	.002	23	.000		
	Total	.024	29			
Cd	Between Groups	.000	4	.000	3.187	.034
	Within Groups	.000	21	.000		
	Total	.000	25			
Cu	Between Groups	.001	7	.000	1.081	.428
	Within Groups	.001	13	.000		
	Total	.002	20			
Zn	Between Groups	.013	7	.002	5.169	.001
	Within Groups	.009	25	.000		
	Total	.022	32			
Cr	Between Groups	.000	3	.000	2.248	.447
	Within Groups	.000	1	.000		
	Total	.000	4			
Mn	Between Groups	.042	7	.006	54.208	.000
	Within Groups	.003	24	.000		
	Total	.044	31			
Fe	Between Groups	236.132	7	33.733	46.618	.000
	Within Groups	17.366	24	.724		
	Total	253.498	31			
Ni	Between Groups	.006	7	.001	4.700	.010
	Within Groups	.002	12	.000		
	Total	.008	19			

*0.05 significant level

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

D3: **ANOVA**

		Sum of Squares	df	Mean Square	F	Sig.
Pb	Between Groups	2723.089	7	389.013	3.118	.018
	Within Groups	2869.990	23	124.782		
	Total	5593.079	30			
Cd	Between Groups	.931	3	.310	.689	.578
	Within Groups	4.958	11	.451		
	Total	5.889	14			
Cu	Between Groups	63.741	7	9.106	5.137	.001
	Within Groups	46.087	26	1.773		
	Total	109.827	33			
Zn	Between Groups	24510.996	7	3501.571	80.673	.000
	Within Groups	1128.510	26	43.404		
	Total	25639.506	33			
Cr	Between Groups	4.533	3	1.511	.429	.742
	Within Groups	17.627	5	3.525		
	Total	22.160	8			
Mn	Between Groups	293978.861	7	41996.980	43.802	.000
	Within Groups	24928.628	26	958.793		
	Total	318907.489	33			
Ni	Between Groups	205.144	7	29.306	2.224	.065
	Within Groups	342.672	26	13.180		
	Total	547.815	33			
Fe	Between Groups	1.804E8	7	2.578E7	105.716	.000
	Within Groups	6339973.912	26	243845.150		
	Total	1.868E8	33			

*0.05 significant level

One way ANOVA for Sediment with pH as the factor variable

D4: **Paired t-test comparing the TSS-TDS of Dry Season to the Wet Season**

Paired Samples Test

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	WET SEASON TSS - DRY SEASON TSS	1.61750E2	205.24355	102.62178	-164.83830	488.33830	1.576	3	.213
Pair 2	WET SEASON TDS- DRY SEASON TDS	-6.51400E3	9148.91655	4574.45827	-21071.96783	8043.96783	-1.424	3	.250

D5: **Paired Samples Test comparing pH of wet season to the dry season**

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	H_2O pH Wet Season H_2O pH Dry Season	.54500	.67461	.33731	-.52846	1.61846	1.616	3	.205
Pair 2	Soil pH Wet Season - Soil pH Dry Season	-.62500	.66536	.33268	-1.68373	.43373	-1.879	3	.157

D6: **Paired t-test for DO/BOD Wet and Dry season**

Paired Samples Test

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	DO/Wet - DO/Dry	-6.66500	.21920	.15500	-8.63446	-4.69554	-43.000	1	.015
Pair 2	BOD/Wet - BOD/Dry	-2.64000	.65054	.46000	-8.48485	3.20485	-5.739	1	.110

D7: Paired t-test for Total Alkalinity, Total Hardness and Total Solids (TS) with Seasonal variations

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Total Hardness/Wet - Total hardness/Dry	-8.69250E2	1361.42802	680.71401	-3035.58578	1297.08578	-1.277	3	.291
Pair 2	TS/Wet - TS/Dry	-6.35200E3	9249.16735	4624.58367	-21069.48923	8365.48923	-1.374	3	.263
Pair 3	Total Alkalinity/Wet - Total Alkalinity/Dry	2.53750E1	22.37325	11.18663	-10.22584	60.97584	2.268	3	.108

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APPENDIX E

E1: **Rotated Component Matrix[a] PLOT 1**

	Component		
	1	2	3
Soil-Pb	**.774**	**.536**	.047
Soil-Cr	.245	**.884**	.235
Soil-Mn	**.781**	**.573**	-.121
Soil-Hg	-.109	.058	**.987**
Soil-Se	**.895**	-.127	-.089
Soil-Zn	**.876**	-.177	-.224
Soil-Cu	-.119	**.884**	.119
Soil-Fe	**.738**	**.523**	-.358
Soil-Ni	-.094	**.829**	-.273
pH	**.847**	-.076	.393

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 4 iterations.

E2: **Rotated Component Matrix[a] PLOT 2**

	Component		
	1	2	3
Pb	**.775**	.012	-.122
Cd	-.349	.353	-.105
pH	**.939**	-.111	-.128
Mn	**.875**	.194	.287
Cu	-.015	**.721**	.478
Zn	**.939**	-.111	.058
Hg	-.013	**.980**	-.010
Se	.029	**.981**	.014
Fe	**.600**	-.172	**.743**
Ni	-.167	.147	**.917**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 5 iterations.

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E3: **Rotated Component Matrix[a] PLOT 3**

	Component		
	1	2	3
Fe	-.151	**.948**	-.042
Mn	-.002	**.882**	-.118
Cr	-.150	**.600**	-.647
Zn	**.901**	-.038	.159
Cd	-.546	-.685	-.046
Hg	**.579**	.203	**.745**
TSS	**.872**	.048	.405
TDS	**.797**	-.559	.207
pH	.331	-.148	**.888**
Se	**.819**	-.099	.430
Ni	**.636**	.175	.239
Na	**.852**	-.463	.186
K	**.870**	-.414	.201
Cu	**.917**	.065	-.073
Nitratre	.177	**.684**	**.690**
Pb	.282	-.716	.314
Sulphate	-.080	-.930	-.103
Phosphate	-.389	**.842**	.357

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 5 iterations.

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E4: **Rotated Component Matrix[a] PLOT 4**

	Component		
	1	2	3
Fe	-.145	-.913	.260
Pb	.281	**.778**	.076
Cr	-.549	**.636**	-.248
Cu	**.934**	-.103	-.108
Cd	-.175	-.741	-.363
Ni	**.682**	-.141	.161
Zn	**.923**	.060	.065
Se	**.801**	.256	.432
Na	**.837**	**.517**	.062
K	**.854**	.477	.096
TSS	**.857**	.106	.444
TDS	**.788**	**.607**	.036
Nitrate	.190	-.444	**.854**
Sulphate	-.062	**.821**	-.457
Phosphate	-.374	-.703	**.581**
Hg	**.578**	.050	**.794**
Mn	.017	-.892	.122

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 5 iterations.

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APPENDIX F

F1: Principal Component Analysis (PCA) Elemental variables of sediments for Dry Season (PLOT 1)

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.744	47.441	47.441	4.744	47.441	47.441	4.135	41.349	41.349
2	2.622	26.217	73.658	2.622	26.217	73.658	3.196	31.958	73.308
3	1.439	14.392	88.051	1.439	14.392	88.051	1.474	14.743	88.051
4	.573	5.734	93.784						
5	.312	3.115	96.900						
6	.255	2.553	99.453						
7	.034	.341	99.793						
8	.013	.129	99.922						
9	.008	.078	100.000						
10	1.798E-16	1.798E-15	100.000						

Extraction Method: Principal Component Analysis.

F2: Principal Component Analysis (PCA) Elemental Variables of Sediments for Wet Season (PLOT 2)

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.763	37.629	37.629	3.763	37.629	37.629	3.639	36.391	36.391
2	2.804	28.042	65.671	2.804	28.042	65.671	2.683	26.825	63.217
3	1.505	15.047	80.718	1.505	15.047	80.718	1.750	17.501	80.718
4	.886	8.857	89.575						
5	.544	5.444	95.019						
6	.236	2.356	97.375						
7	.130	1.299	98.673						
8	.092	.917	99.590						
9	.034	.339	99.929						
10	.007	.071	100.000						

Extraction Method: Principal Component Analysis.

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F3: Principal Component Analysis Dry Season River water Elemental Variables and Physicochemical parameters (PLOT 3)

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.367	46.485	46.485	8.367	46.485	46.485	6.661	37.007	37.007
2	5.387	29.926	76.411	5.387	29.926	76.411	5.872	32.624	69.631
3	1.827	10.151	86.562	1.827	10.151	86.562	3.048	16.931	86.562
4	1.060	5.888	92.450						
5	.844	4.687	97.137						
6	.253	1.407	98.544						
7	.149	.830	99.373						
8	.113	.627	100.000						
9	3.199E-16	1.777E-15	100.000						
10	2.591E-16	1.439E-15	100.000						
11	1.241E-16	6.897E-16	100.000						
12	8.963E-17	4.980E-16	100.000						
13	5.333E-17	2.963E-16	100.000						
14	-1.686E-17	-9.369E-17	100.000						
15	-1.033E-16	-5.737E-16	100.000						
16	-2.677E-16	-1.487E-15	100.000						
17	-3.502E-16	-1.946E-15	100.000						
18	-5.443E-16	-3.024E-15	100.000						

Extraction Method: Principal Component Analysis.

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F4: Principal Component Analysis Wet Season River water Elemental Variables and Physicochemical parameters (PLOT 4)

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.960	46.826	46.826	7.960	46.826	46.826	6.562	38.601	38.601
2	5.331	31.362	78.188	5.331	31.362	78.188	5.528	32.519	71.121
3	1.427	8.391	86.579	1.427	8.391	86.579	2.628	15.459	86.579
4	1.048	6.164	92.743						
5	.763	4.487	97.231						
6	.247	1.456	98.686						
7	.128	.752	99.438						
8	.095	.562	100.000						
9	4.368E-16	2.570E-15	100.000						
10	2.974E-16	1.749E-15	100.000						
11	1.742E-16	1.025E-15	100.000						
12	3.265E-17	1.920E-16	100.000						
13	-6.044E-17	-3.555E-16	100.000						
14	-8.314E-17	-4.891E-16	100.000						
15	-2.498E-16	-1.469E-15	100.000						
16	-4.528E-16	-2.664E-15	100.000						
17	-7.090E-16	-4.171E-15	100.000						

Extraction Method: Principal Component Analysis.

APPENDIX G

Chemical Reactions and Calculations

Total Alkalinity:

Calculation

mg $CaCO_3$ / L = $\frac{A \times t \times 1000}{\text{ml of sample}}$

Where A = mL standard acid used

t = titer of standard acid, mg $CaCO_3$/ mL

Chemical Reactions

$HCO_3^- + H^+ \rightarrow H_2CO_3$

$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$

$HCO_3^- + CO_3^{2-} + 3H^+ \rightarrow 2H_2CO_3$

Total Hardness:

Calculation

(EDTA) as mg $CaCO_3$/ L = $\frac{A \times B \times 1000}{\text{ml of sample}}$

Where A = mL titration for sample

B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant

Chemical Reactions

Y is the disodium salt of EDTA ($Na_2H_2C_{10}H_{12}N_4O_8$)

$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$

$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$

$MgY^{2-} + Ca^{2+} \rightarrow CaY^{2-} + Mg^{2+}$

Total Solids (TS) Dried at 100˚C - 105˚C:

Calculation

$$\text{mg Total Solids (TS)/ L} = \frac{(A-B)\times 1000}{\text{sample volume, ml}}$$

Where A = weight of dried residue + dish, mg

B = weight of dish, mg

Total Dissolved Solids (TDS) Dried at 100˚C:

Calculation

$$\text{mg Total Dissolved Solids (TDS)/ L} = \frac{(A-B)\times 1000}{\text{sample volume, ml}}$$

Where A = weight of dried residue + dish, mg

B = weight of dish, mg

Total Suspended Solids (TSS) Dried at 100˚C:

Calculation

$$\text{mg Total Suspended Solids (TSS)/ L} = \frac{(A-B)\times 1000}{\text{sample volume, ml}}$$

Where A = weight of dried residue + dish, mg

B = weight of dish, mg

Na and K (Flame Photometric Method) (APHA AWWA WEF, 1998):

Calculation

From the calibration curve mg Na/L or K/L = (mg Na/L or K/L in portion) × D

Where D = dilution ratio

$$D = \frac{\text{ml sample} + \text{ml water}}{\text{ml sample}}$$

Sulphate (SO_4^{2-}) (Turbidimetric Method) (APHA AWWA WEF, 1998):

Calculation

$$\frac{\text{mg } SO_4^{2-}}{L} = \frac{\text{mg } SO_4^{2-} \times 1000}{\text{ml sample}}$$

Concentration range for calibration curve: 5mg/L to 40 mg/L of Sodium Sulphate (Na_2SO_4)

Nitrate (NO_3^-) (UV Spectrophotometric Method) (APHA AWWA WEF, 1998):

Calculation

$$\frac{\text{mg } NO_3^-}{L} = \frac{\text{mg } NO_3^- \times 1000}{\text{mL Sample}}$$

Concentration range for calibration curve: 1mg/L to 7mg/L of $NO_3^- - N$ prepared by diluting to 50 mL the following volumes of intermediate solution: 1.00, 2.00, 4.00,…., 35mL.

Phosphate (PO_4^{3-}) (Ascorbic Acid Method) (APHA AWWA WEF, 1998):

Calculation

$$\frac{\text{mg } PO_4^{3-}}{L} = \frac{\text{mg } PO_4^{3-} \times 1000}{\text{mL Sample}}$$

Concentration range for calibration curve: 2 mg/L to 10 mg/L of PO_4^{3-} prepared by serially diluting 50 mL of anhydrous KH_2PO_4.

Dissolved Oxygen (DO) (Azide Modification of Winkler Method)

Chemical Equations

$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$

$2Mn(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2MnO(OH)_2$ Oxidation of Mn (II) to Mn (III)

$2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 6H_2O$ Oxidation of I^- to I_2

$I_2 + I^- \leftrightarrow I_3^-$

Standardization with Potassium Iodate (KIO_3)

$IO_3^- + 8H^+ + 6H^+ \rightarrow 3I_3^- + 3H_2O$

$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$ Oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$, reduction of I_3^- to I^-

Biochemical Oxygen Demand (BOD)

Calculation

$$BOD_5, \frac{mg}{L} = \frac{D_1 - D_2}{P}$$

D1 = DO of diluted sample immediately after preparation, mg/L,

D2 = DO of diluted sample after 5 days incubation at 27℃, mg/L,

P = decimal volume fraction of sample used

Microbial Activity

Total Coliforms (TC) (APHA 9222A, Membrane Filter Technique)

Calculation of Coliform Density

$$\frac{\text{CFU}}{100\text{mL}} = \frac{\text{Coliform Colonies Counted} \times 100}{\text{mL Sample Filtered}}$$

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Total Heterotrophic Bacteria (THB) (APHA 9215B, Pour Plate Procedure)

Calculation of Coliform Density

$$\frac{\text{CFU}}{1\text{mL}} = \frac{\text{Colonies Counted}}{\text{Actual volumes of samples in dish,mL}}$$

Faecal Coliform (FC) (APHA 9222D, Membrane Filter Technique)

Calculation of Coliform Density

$$\frac{\text{FC}}{1\text{ g dry weight}} = \frac{\text{Colonies Counted}}{\text{Dilution Factor}\times(\%\text{ Dry Solids})}$$

***E. coli* (APHA 9260F, Modification of Standard Total Coliform (TC) Fermentation Technique)**

Calculation of Coliform Density

$$\frac{\text{CFU}}{100\text{mL}} = \frac{\text{Coliform Colonies Counted}\times 100}{\text{mL Sample Filtered}}$$