KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

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ACCUMULATION OF TOXIC AND ESSENTIAL ELEMENTS IN CLAMS AND SEDIMENTS FROM THE VOLTA ESTUARY

BY

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DECLARATION

"I declare that Accumulation of Toxic and Essential Elements in Clams and Sediments from the Volta Estuary is my own work and that, to the best of my knowledge**,** it has not been submitted for any degree or examination at any other university and that all the sources I have used or quoted have been indicated and acknowledged by complete references".

…… ……

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(Head of Department)

DEDICATION

This is dedicated to my parents Mr. Kwesi Baffoe and Madam Beatrice Ama Akyeamah and also to my senior brothers Edward Prempeh Wilson and Frank Yeboah who have supported me in every way in my academic pursuit.

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ABSTRACT

The clams (*Galatea paradoxa*) and sediments were collected from the Volta Estuary in Ghana for six months' period at Ada and Aveglo. They were analysed for six different elements (Cd, Cr, Cu, Hg, Ni, and Se) using Flame Atomic Absorption Spectrometer (AAS) and Automatic mercury analyzer Model HG 5000. A total of one hundred and eighty (180) clams were analysed over the period.

The mean elements concentrations in the tissues of the G. *paradoxa* from Ada sampling site ranged from: Cd: 0.09 -0.17 mg/kg; Cr: 3.42 – 20.51 mg/kg; Cu: 0.55 – 3.10 mg/kg; Hg: 0.05 – 0.12 mg/kg; Ni: 5.49 – 27.96 mg/kg and Se: 0.34 – 0.49 mg/kg. That of o sediments were: Cd: 0.09 mg/kg; Cr: 15.03 mg/kg; Cu: 89.94 mg/kg; Hg: 0.06 mg/kg; Ni: 47.16 mg/kg and Se: 0.41 mg/kg. For Aveglo the mean metal concentrations in clam tissues were: Cd: 0.07 - 0.14 mg/kg; Cr: 2.01 –24.10 mg/kg; Cu: 0.79 – 3.65 mg/kg; Hg: 0.04 – 0.09 mg/kg; Ni: 10.25 – 28.14 mg/kg and Se: 0.13 – 0.29 mg/kg and the sediment samples recorded the mean metal concentrations as: Cd: 0.07 mg/kg; Cr: 16.28 mg/kg; Cu: 75.66 mg/kg; Hg: 0.04 mg/kg; Ni: 51.25 mg/kg and Se: 0.38 mg/kg.

The analysis of the elements concentrations in the tissues of the different clams in relation to body size for the Ada sampling site shows significant difference ($p < 0.05$) for Cd and Cu in the various clam sizes. The mean concentrations of Cr, Hg, Ni and Se exhibited significant differences ($p>0.05$) in concentration between some clam sizes at Ada sampling site. The test for difference in mean concentrations of Cd and Cr showed significant differences ($p < 0.05$) between the various clam size classes at the Aveglo sampling site. Nevertheless, there was no significant differences ($p > 0.05$) showed between the mean concentrations of Cu, Hg, Ni and Se for some clam sizes.

The evaluation of the risk associated with consumption of clams from the Volta estuary using WHO/FAO Standards for Bivalves, the Tolerable daily Intake (TDI), the rate of shellfish consumption (RSC), Risk Quotients (RQs) and the levels of concerns (LOCs) suggest that the normal consumption rates should be safe with regards to Cd, Cu, Hg, Ni and Se in the clam tissues except for Cr in medium to large clam sizes whose concentrations exceeded the WHO/FAO Standards for Bivalves legal limits

The mean elements concentration of Cu in sediments for both Ada and Aveglo exceeded the NOAA Effects Range – Low (ERL) value of 20.9 mg/kg and CSQG Threshold Effects Level (TEL) value of 52.3 mg/kg whilst Ni at both sampling sites exceeded the NOAA Effects Range – Low (ERL) of 20.9 mg/kg. Sediment metal concentrations for Cd, Cr, Hg and Se were below the various effect ranges at all sites. The geoaccumulation index indicates practically unpolluted sediments as far as elements Cd, Cr, Hg, Ni and Se are concerned except for Cu.

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LIST OF ABBREVIATIONS AND UNITS

µg/g dw	: Microgram per gram dry weight
ANOVA	: Analysis of variance
AVFs	: Acid-Volatile sulfides
CF	: Contamination Factors
BSAF	: Biota - Sediment Accumulation Factors
CIFA	: Committee for Inland Fisheries of Africa
CSQG	: Canadian Sediment Quality Guideline
CRM	: Certified Reference Material
DNA	: Deoxyribonucleic Acid
DWAF	: Department of Water Affairs and Forestry
EAF	: East Africa Marine Pollution and Research Programme
ERL	: Effects Range-Low
ESAADI	: Estimated Safe and Adequate range of Daily Dietary Intake Levels
FAAS	: Flame Atomic Absorption Spectrophotometer
FAO	: Food and Agriculture Organisation
GESAMP	: The Group of Experts on Scientific Aspects of Marine Environmental Protection
HCL	: Hydrogen Cathode Lamp
IAEA	: International Atomic Energy Agency
IOC	: Intergovernmental Oceanic Commission
IQ	: Intelligence Quotient
LDPE	: Low-density polyethylene
LOC	: Level of Concern
MDH	: Minnesota Department of Health

NAS/NRC : National Academy of Science of the National Research Council

NOAA : National Oceanic and Atmospheric Administration

PLI : Pollution Load Index

ND : None Detected

RQ : Risk quotient

RSC : Rate of Shellfish Consumption

TDI : Tolerable Daily Intake

TEL : Threshold Effects Level

UNECE : United Nations Economic Commission for Europe

UNEP : United Nations Environment Programme

USEPA : United States Environmental Protection Agency

VRA : Volta River Authority

WHO : World Health Organisation

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Heavy metals in the environment are of great social concern both globally and locally due to their serious effects on animal and human health. The detrimental effects of metals on aquatic ecosystems necessitate the continuous monitoring of their accumulation in key species, since it affords indication of temporal and spatial extent of the process and impact on organism's health (Kotze *et al.*, 1999). The levels of heavy metals can be analysed in water samples, sediment samples and biota. Assessing water quality in terms of metal contamination, and also to identify pollution sources, can be inconclusive due to fluctuations in dissolved constituents within short time intervals (Forstner, 1980). Metal concentrations found in water are usually very low, resulting in analytical difficulties (Rainbow, 1995).

Sediments form an essential and integral part of aquatic systems and an important repository for metal pollutants that enters rivers, lakes and the sea. They provide the substrate for organisms and through interaction with the overlying waters play an essential role in the aquatic ecosystem (Burden et al., 2002). Exposure of sediment-dwelling organisms to metals may then occur via uptake of interstitial waters, ingestion of sediment particles via the food chain (Luoma, 1989). In polluted aquatic systems sediments are increasingly recognized as the most important sink for contaminants and a future source of pollutants (Ikenaka et al., 2005). However, measuring concentrations of pollutants in water and sediments alone does not provide information on the potential impact of pollution on resident organisms (Lovett–Doust et al., 1994).

Benthic organisms, in particular, have direct contact with sediment, and the contaminant level in the sediment may have greater impact on their survival than do aqueous concentrations (Malins, 1984). Biomonitoring as indicative of the presence of pollutants is defined as the use of bio-organisms to obtain quantitative information on certain characteristics of the biosphere (Wolterbeek, 2002). Development of indicators of exposure is thus critical to evaluate risk from heavy metals and they are necessary as early warning systems for environmental deterioration (Anon, 1983). Biomonitors generally accumulate trace metals to concentrations that are relatively easy to measure (Rainbow and Phillips, 1993). It has the conceptual advantage that biotic responses may provide more direct measures of the biological significance of environmental contaminants (Markert, 1993). Essential characteristics required of biomonitors include the capacity to accumulate pollutants without being killed by the encountered levels, sufficiently long-lived, abundant in the study area and of reasonable size to provide enough tissues for analysis. Clams are particularly biomonitors by virtue of their distribution, large body size and high population density (Phillips, 1976, Ahn, 2005, De Astudillo et al., 2005, Kanakaraju et al., 2008). The *Galatea paradoxa* (Born, 1778) considered in this study fulfills most of the characteristics and is also filter feeder.

In Ghana, many clams have been identified but the one with the significant interest is the *Galatea paradoxa,* which is harvested mainly for consumption. The Volta estuary is presently the main habitat of *Galatea paradoxa* with Ada and Aveglo being the most populated areas. The clam constitutes an important and affordable protein source to the riparian communities around the Volta River (Amador, 1997). They are harvested for food and sold to earn income for living (Gordon and Amatekpor, 1999).

1.2 Problem Statement

Humans are encouraged to consume more sea foods, because they are good sources of proteins, minerals and fibers which are beneficial to their health. However, many shell fish including *G. paradoxa* contain both essential and toxic metals over a wide range of concentrations. The contamination of natural waters by heavy metals negatively affects aquatic biota and poses considerable environmental risks and concerns (Cajaraville et al., 2000; Ravera, 2001). Heavy metal contamination of foodstuffs and fish products may occur due to the addition of fertilizers and metal - based pesticides, irrigation with contaminated water, industrial emissions, transportation, harvesting process, storage and sale.

The major tributaries to the Volta Lake such as the White Volta, Black Volta and the Oti River originate outside Ghana, where a lot of agricultural and mining activities take place which are potential sources of heavy metals. The construction of the Akosombo Dam on the lake and perennial flooding of farm lands serves as major contributors of these contaminants in the lake which moves downstream into the estuary.

Contamination of fish species with heavy metals poses a threat, because high content of heavy metals in fish is associated with (etiology) of a number of diseases, especially cardiovascular, kidney, nervous system and bones. Monitoring programmes and research on heavy metals in aquatic environmental samples have become widely important due to concerns over accumulation and toxic effects in aquatic organisms and to humans through the food chain (Otchere, 2003).

1.3 Justification

Heavy metals are considered as one of the most hazardous substances that could accumulate in biota. Aquatic ecosystems polluted with heavy metals may therefore

threaten human nutrition and health directly. Seafood sources are susceptible to heavy metal contamination and the *Galatea paradoxa* is no exception, hence high levels of heavy metals in fish species posses a direct threat to other organisms in the food web including humans. The increasing demand of food safety has stimulated research regarding the risk associated with consumption of seafood's which can accumulate heavy metals.

The toxicity of a metal is usually defined in terms of the concentration required to cause an acute response or a sub-lethal response (Smith, 1986). In the human body, the metallic toxicants attack the proteins notably the enzymes (Ademoroti, (1996) and their toxic effects are cumulative and cause slow poisoning of the system over a period of time (Nriagu, 1988; Ukpebor et al., 2005).

In recent times, there has been an increase in agricultural and industrial activities along the catchment area of the Volta Lake (Obirikorang, 2010). The increase in agricultural activities such as cultivation of vegetables, fish farming, groundnut cultivation, in areas like Ada, Agave, Aveglo, etc with application of various agrochemicals such as fertilizers, pesticides on these farms contribute immensely to heavy metal accumulation in top soil layers and also their subsequent transport into rivers through surface run-offs.

The *Galatea paradoxa* happens to be one of the fishery resources and an important source of nutrition in the area and is consumed by people in the area of study and beyond. Hence, in view of the toxicological importance of this edible clam, it is therefore imperative for studies to be conducted to examine levels of heavy metals in sediments and tissues of G. *paradox* from the Volta Estuary, and to verify whether their concentrations in the clams are within permissible limits for human consumption in comparison to WHO

tolerable daily intake (TDI) and safety reference standards for the consumption of bivalves and molluscs.

1.4 Objectives of the Study

The main objective of this study is to determine the concentration of some heavy metals in clams and sediments from the Volta Estuary in order to ascertain the level of pollution from Ada and Aveglo.

The specific objectives of this study are:

1. To measure the concentration of some heavy metals (Cd, Cr, Cu, Hg, Ni and Se) in sediments and *Galatea paradoxa* from the study area.
2. To determine the relationship between sediment metal concentration and *Galatea paradoxa* tissue metal concentration.
3. To assess the risk of consuming the clam *Galatea paradoxa* from the Volta estuary.

CHAPTER TWO

LITERATURE REVIEW

2.1 Contamination and Pollution of the Environment

In recent times, significant attention has been paid to the problem of environmental contamination by a wide variety of chemical pollutants including heavy metals (Eldemerdash and Elegamy, 1999). The contamination of fresh waters with a wide range of pollutants has become a matter of concern over the last few decades (Vutukuru, 2005; Dirilgen, 2001; Voegborlo *et al.,* 1999; Canli *et al.,* 1998). Contamination and pollution of the environment involves the disturbance of the natural ecological state of the environment by natural activities such as volcanic eruptions, tsunamis etcetera with human activities aggravating the situation. The two terms are distinguishable by the severity of the effect: pollution induces the loss of potential resources (Goldberg, 1992) and contaminant exposures in natural systems can be highly variable. The exponential growth of human population along the river and estuarine areas around the world has caused the deterioration of the environmental quality of the coastal areas (Bertolotto et al., 2005). Urban and industrial activities contribute to the input of significant amounts of pollutants into the marine environment and directly affect the coastal systems in which they are often deposited (Maanan, 2007). The agricultural drainage water containing pesticides and fertilizers and effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge quantities of inorganic anions and heavy metals (ECDG, 2002).

Contaminants can affect aquatic ecosystems in many different ways and to varying degrees. Manifestation of these effects can be experience at all levels of biological organization: cellular, organ, whole organism, and population levels. Important chemical

and physical properties of the contaminant include its volatility, solubility, partitioning onto solids, and its stability or persistence (Pierce *et al.*, 1998). These contaminants once introduced into surface waters rapidly adsorb to suspended sediment and organic matter and are in this manner scavenged from the water column through flocculation, coagulation and sedimentation (Huh et al., 1992, Honeyman and Santschi, 1988, Hatje et al., 2003).

The natural aquatic systems may extensively be contaminated with heavy metals released from domestic, industrial and other man-made activities (Velez and Montoro, 1998; Conacher *et al.*, 1993). Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms (Farombi *et al.*, 2007; Vosyliene and Jankaite, 2006; Ashraj, 2005).

2.2 Heavy Metal Pollution in Sediments

River sediments serve as a sink and reservoir for a variety of environmental contaminants and provide foodstuffs for bottom dweller living organisms. The behavior and distribution of metals in marine sediments is influenced by hydrodynamics, anthropogenic discharges, and biogeochemical processes (Zwolsman et al., 1997). The analysis of sediment is a useful method of studying aquatic pollution with heavy metals (Batley, 1989). Major indicators of pollution in aquatic environments are contaminated sediments that can be defined as soils, sand, organic matter, or minerals accumulated at the bottom of a water body (USEPA, 1998).

Studies on the distribution of trace metals in sediments and other media are of great importance in the context of environmental pollution (Howari, 2005). Metals in the aquatic environment can be categorized into three basic reservoirs namely: water, sediment and biota. Metal levels in each of these three reservoirs are dominated by a

complex dynamic equilibrium governed by various physical, chemical and biological factors (Murray and Murray, 1973). Among these three reservoirs, sediment is the major repository for metals, in some cases, holding over 99% of the total amount of metal present in the system (Renfro, 1973). Under certain conditions, contaminants found in sediments can be released to waters and thus, sediments can be important sources of the contaminants in waters (Allen, 1995). The concentration of heavy metals in sediments can be influenced by variation in their texture, composition, reduction/oxidation reactions, adsorption/desorption, and physical transport or sorting in addition to anthropogenic input (Basaham and El-Sayed, 1997). Also at high alkalinity and pH, the metals, particularly lead and cadmium, precipitate by forming complexation products, resulting in an array of chemical speciation of metals that dramatically influence metal toxicity (Van Aardt and Booysen, 2004; Van Aardt and Venter, 2004).

Potentially, toxic compounds, especially heavy metals, are adsorbed on mineral or organic particles either in their organic or inorganic forms (Forstner and Wittman, 1983, Kabata-Pendias and Pendias, 2000). However, to assess the environmental impact of contaminated sediments, information on total concentrations is not sufficient and of particular interest is the fraction of the total heavy metal content that take part in further biological processes (Jain, 2004; Nwuche and Ugoji, 2010).

2.3 Heavy Metal Accumulation in Organisms

The accumulations of heavy metals in water, sediments and fish species from natural and artificial sources and subsequent consequences represent important environmental pollution problems. Bioavailability and bioaccumulation of heavy metals in aquatic environments is gaining tremendous global attention. The lakes have a complex and fragile ecosystem, as they do not have self-cleaning ability and, therefore, readily accumulate pollutants (Lokeshwari and Chandrappa, 2006a). Metals are non-

biodegradable and once they enter aquatic ecosystem remains in water as suspended colloids and in the process forming complex compounds with inorganic and organic ligands. They however, tend to accumulate in the course of time in bottom sediments or are taken up by aquatic organisms, at different trophic levels of the food chain.

Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air (Lokeshwari and Chandrappa, 2006b). Heavy metals are known to accumulate in living organisms (Karatas et al., 2006). These heavy metals are taken up by aquatic animals directly through the epithelium of the skin, gills and elementary canals while some parts are accumulated in food organisms and are incorporated into the body of aquatic animals by nutrition (Chandra, 1999). Food safety issues and potential adverse health risks make this one of the most serious environmental concerns (Cui et al., 2004). Heavy metals accumulated in organisms may be further become concentrated in successive trophic levels of food webs by a process called biomagnification. The accumulation of heavy metals continuously in living organism at critical levels from contaminated environment may results in serious illnesses leading to death and increase mortality rates. Due to the deleterious effects of metals on aquatic ecosystems, it is necessary to monitor their bioaccumulation in key species, because this will give an indication of the temporal and spatial extent of the process, as well as an assessment of the potential impact on organism health (Fernandes *et al*., 2006). Marine organisms, in general, accumulate contaminants from the environment and therefore have been extensively used in marine pollution monitoring programmes (Linde *et al*., 1998; Mora *et al*., 2004).

Factors known to influence metal concentrations and accumulation in these organisms include metal bioavailability, season of sampling, hydrodynamics of the environment,

size, sex, and changes in tissue composition and reproductive cycle (Boyden and Phillips, 1981). Seasonal variations have been related to a great extent to seasonal changes in flesh weight during the development of gonadic tissues (Joiris *et al.*, 1998, 2000). Element concentrations in molluscs at the same location differ between different species and individuals due to species-specific ability/capacity to regulate or accumulate trace metals (Reinfelder *et al.*, 1997; Otchere *et al*., 2003).

Trophic transfer of trace elements along marine food webs has been recognized as an important process influencing bioaccumulation and geochemical cycling of many elements (Fisher and Reinfelder, 1995). The trophic level is thus important; suggesting that bioaccumulation of trace elements may be due to the feeding habits of organisms in each level (Turner and Swick, 1983). Under certain environmental conditions, heavy metals might accumulate up to a toxic concentration and cause ecological damage (Sivaperumal *et al*., 2007).

2.4 Effects of Heavy Metal Contamination in Sediments

Heavy metals are preferentially transferred from the dissolved to the particulate phase and these results in the elevation of metal concentrations in estuaries and marine sediments. Therefore, concentrations often exceed those in overlying water by several orders of magnitude (Langston, 2000). Since sediments can accumulate heavy metals, concentrations can be high and become potentially toxic (Williamson et al., 2003). Exposure and uptake of even a small fraction of sediment-bound metal by organisms could have significant toxicological significance, in particular where conditions favor bioavailability. In addition, increased metal concentrations in pore water may contribute significantly to sediment toxicity (Langston, 2000).

Evidence of fatal effects of metal-polluted sediments can be assessed by the absence of sensitive species or by the development of resistance mechanisms and adaptation in tolerant forms such like efficient excretory features in organisms. Binning and Baird (2001) reported that many of the metals have no known biological function in the marine environment, but can act together with other chemical species to increase toxicity. The potential effects of accumulating levels of heavy metals can be estimated by comparing the concentrations of contaminants of interest present in sediments with sediment quality guidelines (SQGs) (Williamson et al., 2003).

2.5 Heavy Metal Pollution in Water

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000). Water pollution by heavy metals is an important factor in both geochemical cycling of metals and in environmental monitoring. According to Mateu *et al*., (1996) trace metal levels can be indicators of the concentrations of other pollutants to which they are potentially related. Among the inorganic contaminants of the river water, heavy metals are getting importance for their non-degradable nature and often accumulation through tropic level causing a deleterious biological effect (Jain, 1978).

The main sources of heavy metal pollution to life forms are invariably the result of anthropogenic activities (Kennish, 1992; Francis, 1994). The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal (Santos et al., 2005). Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates (Amman, *et al*., 2002) from different industries, example: tannery, steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and

pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings (Lantzy and Mackenzie, 1979; Nriagu, 1979; Ross, 1994) and sustaining aquatic biodiversity (Ghosh and Vass, 1997; Das, *et al*., 1997).

Acid rain resulting from dissolved hydrogen sulphide, sulphur dioxide and oxides of nitrogen has contributed to alterations of soil and freshwater acidity. As a consequence there is an increase in the bioavailability of many heavy metals to freshwater biota (Sprenger and McIntosh, 1989).

Rivers are a dominant pathway for metals transport (Miller *et al.*, 2003; Harikumar *et al.*, 2009) and heavy metals become significant pollutants of many riverine systems (Dassenakis *et al.,* 1998). During their transport, the heavy metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Dassenakis *et al.,* 1998; Akcay *et al.,* 2003; Abdel- Ghani and Elchaghby, 2007) which affect their behavior and bioavailability (Nicolau *et al.,* 2006; Nouri *et al.,* 2011). The overall behavior of heavy metals in an aquatic environment is strongly influenced by the associations of metals with various geochemical phases in sediments (Morillo *et al*., 2004). Heavy metals can even have effects on different aspects of water use, such as oxygen consumption by organisms in the environment (Ahern and Morris, 1999), water permeability (Rasmussen et al., 1995) and osmoregulation (Ahern and Morris, 1998).

2.6 Monitoring Heavy Metals in the Environment

A good knowledge of the distribution of heavy metals in water and sediments plays a key role in detecting the sources of pollution in aquatic systems (Forstner and Wittmann, 1981; Idodo-Umeh and Oronsaye, 2006). The characteristics of water, such as acidity or

amount of organic matter are known to be important factors in determining the fate of heavy metals in lakes (Verta et al. 1990, Mannio et al. 1993, Skjelkvåle et al. 2001). The pollutant concentrations in the water only indicate the situation at the time of sampling, (Ravera *et al*., 2003). For example a lower degree of contamination would be measured after a high discharge due to erosion of the river bed sediments (Forstner, 1980). Increased inputs of metals in such forms available for association with sediments result in increases in metal concentrations in sediments (Luoma, 2000). Metal concentration in sediments are not only determined by metal inputs but also effected by other complex factors such like sediment characteristics and reactions at particle surfaces that influence the quantity of metal adsorbed, and reduction/oxidation reactions (Luoma, 2000). In other words, the metals there are not fixed in a permanent manner and can be released back into the water column at the time of an environmental change, such as the pH, the potential redox (PE) the presence of the micro organisms and hydrodynamics (James, 1978; Fôrstner, 1987). Also dead organisms in sediments may carry the heavy metals with them, either taken in by the organism while alive or sorbed on to the animal before or after death (Fergusson, 1990). Hence, sediments can be used to monitor heavy metal pollution in aquatic ecosystems. Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and are deposited onto the sediments (Guzman and Garcia, 2002). After reaching the water environment from different sources, the metals are adsorbed on the inorganic and organic particles and incorporated in the accumulated sediments, and it results in an elevation of their concentrations in the bottom sediments (Jeon et al., 2002).

During the past few decades, many species have been studied to determine their potential as a biomonitoring organism, and mollusca have become a popular choice for heavy metal monitoring (Phillips, 1980; Wilson, 1980; Bryan *et al*., 1985; Hung *et al.*, 2001).

Among animal species, fishes are the inhabitants that cannot escape from the detrimental effects of these pollutants (Olaifa *et al.*, 2004; Clarkson, 1998; Dickman and Leung, 1998). Fish are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic systems (Farkas *et al.*, 2002; Yousuf and El-Shahawi, 1999).

2.7 Biomonitoring of Heavy metal Contaminants in the Environment

Biomoniotors are organisms or systems of an area that can be used to evaluate variations in the bioavailabilities of any parameters, including heavy metals in the aquatic environment. The use of biomonitors offers time integrated measures of those portions of the ambient metal load that are of direct ecotoxicological relevance (Rainbow, 1995). Monitoring is conducted for two primary reasons: (1) to establish a baseline that represents the current status of the environment; and (2) to detect changes over time that are outside the natural variation of the baseline (Hicks and Bridges, 1994). The detrimental effects of metals on aquatic ecosystem necessitate the continuous monitoring of their accumulation in key species, since it affords indication of temporal and spatial extent of the process and impact on organism's health (Kotze *et al.*, 1999).

Sediments have frequently been analysed to identify sources of trace metal in the aquatic environment because of the high accumulation rates exhibited (Forstner *et al*., 1981). Sediments were considered an important indicator for environmental pollution; they act as permanent or temporary traps for material spread into the environment (DeGregori *et al*., 1996). Sediment analysis allows contaminants that are absorbed by particulate matter, which escape detection by water analysis, to be identified.

2.8 Biomonitoring Biota

Biomonitoring is a regular systematic use of living organisms to evaluate changes in environmental or water quality in laboratory or field conditions, by assessing either

bioaccumulation, biological effect, health (occurrence of disease) and/or ecosystem integrity (Van Der Oost *et al*., 2003). The biota used for biomonitoring may be placed into three broad categories based on the overall biomonitoring objectives (NRC, 1991; Johnson et al., 1993; Beeby, 2001). Monitoring species are used to determine an activity or environmental condition on the basis of measurable changes in physical, chemical, or biological structures. Indicator species are used to measure environmental conditions on the basis of the species absence or abundance within the environment of interest. Lastly, sentinel species are used to evaluate and provide early warning of adversely changing environmental conditions on the basis of observed levels of pollutants in their tissues (Rabinowitz et al., 1999; van der Schalie et al., 1999; Beeby, 2001).

According to Phillips and Rainbow (1993) an ideal biomonitor should fulfill several requisites: should be sessile or sedentary in order to be representative of the study area; should be abundant in study areas, easy to identify and sampled at all times of year, and should have sufficient tissue for analysis of the contaminant of interest; should be hardy, tolerating wide ranges of contaminant concentration, thereby permitting the design of transplant experiments and laboratory studies of contaminant kinetics; and should be strong accumulators of the relevant trace metal.

Furthermore, small mammals as a group were proposed as biomonitors of contamination (Talmage and Walton, 1991) and animals, in general for monitoring environmental quality (Buck, 1979). Monitoring of annual harvests provides measures of overall lake productivity and the condition of the fishery, while contaminant measurements of lake trout tissue provide information regarding ecological and human exposure to hazardous chemicals as well as tracking contaminant levels in the lake ecosystems (e.g., DeVault et al., 1985, Mac and Edsall, 1991).

2.9 Bioindicators

The term bioindicator has been applied to living organisms whose characteristics are used to point out the presence or absence of environmental conditions which cannot be feasibly measured for other species or the environment as a whole (Landres et al., 1988). A wide range of indicator species have been used to assess the uptake of metal pollutants (Funes *et al.*, 2006; Berglund *et al.*, 2007; Elia *et al.*, 2007). Bioindicators make a broad and intangible concept such as biodiversity or ecosystem monitoring, manageable by breaking it down into a specific set of quantifiable indicators (Noss, 1990). The use of bioindicators for environmental safety implies a thorough knowledge of their biological function in order to avoid misinterpretation, which could lead to conclusions that abnormalities were caused by environmental parameters when in fact they were normal variations (Lagadic *et al.*, 2000). So, if animals living in polluted environments accumulate spatially and temporally heavy metals in their tissues they can be used as bioindicators of environmental pollution (Talmage and Walton, 1991). By monitoring organisms in addition to physical/chemical attributes a temporal aspect is inherently introduced since organisms incorporate past, as well as present, conditions (Rosenburg and Resh, 1996). Inference through biological indicators replaces direct measurement when such measurements are not possible, too expensive/difficult, or too direct (Landres et al., 1988, Caro and O.Doherty, 1999).

Bioindicators are frequently used to measure the exact concentrations of pollutants in the biological organisms at different trophic levels of organization. Information obtained from such monitoring programs has been useful in establishing environmental and health guidelines and underscores the relevance of the use of bioindicators in monitoring environmental contaminants. Various species of living organisms such as fish, plants,

butterflies, ants etc have been potentially used as bioindicator organisms in the past for measuring various types of pollutants at different situations and has proved futile.

2.9.1 Using Bivalves as Bioindicator Organisms

Bivalve shellfish have been used for decades as bioindicators of aquatic contamination with heavy metals and pesticides (O'Connor, 2002). In recent years, shellfish have also been recognised worldwide as bioindicators of aquatic contamination with fecal origin bacteria, viruses, and parasites (Fayer et al., 1998; Freire-Santos et al., 2000; Pommepuy et al., 2004). There are several attributes that make mussels superior than the other organisms for use as 'sentinel' or 'indicator' organisms in environmental monitoring programs throughout the world (Phillips, 1980; Farrington et al., 1987; Tanabe, 2000). Phillips (1980), Gosling (1992) and Farrington and Trip (1995) have explained many of the advantages in using mollusks, especially bivalves as bioindicators of contaminant loads in coastal and estuarine systems. It may be appropriate to mention some of them here.

1. Species of bivalves such as mussels and oysters are having a wide geographical distribution and are dominant members of estuarine and coastal communities. Since the same species of bivalves can be collected from wide geographic locations, the problems in comparing data obtained from different species are eliminated. This will be an important parameter especially in tropical areas with a wide biodiversity.
2. They are sedentary and are therefore better than mobile species like fin fishes as integrators of chemical contamination in a given area.
3. They are relatively tolerant to a wide range of environmental conditions such as salinity, season, sampling position in the water column, size, reproductive condition etc. Since these animals are sedentary, most of the problems that may

arise due to these variables can be relatively simply eliminated during the sampling procedure (Phillips, 1980).

4. Bivalves are relatively tolerant to a wide range of environmental contaminants, including moderately high levels of many types of contaminants. They can exist in habitats contaminated by variety of pollutants at the same time.
5. A correlation always exists between the pollutant content in the organism and the average pollutant concentration in the surrounding habitat. Almost always the bioconcentration factors of POPs in bivalve mollusks are many-fold.
6. Bivalves like mussels and oysters always occur in wide and stable populations and hence can be sampled repeatedly in different seasons.
7. Many bivalves are reasonably long-lived (e.g. 1 to 8 years) and so specimens of various sizes (year-classes) can be sampled easily for comparison.
8. Most of them are of reasonable size, providing adequate tissue for analysis.
9. Bivalves are suspension feeders (filter-feeders) that pump several liters of water every hour and concentrate many chemicals in their tissues, by factors of 10 to 105, relative to the concentrations in water. This makes the measurement of contaminants easier.
10. In comparison with many other animals in the same trophic level, bivalves have a very low level drug metabolizing enzyme activities. Therefore the contaminant concentrations in the tissues of bivalves more accurately reflect the magnitude of environmental contamination. At the same time, unlike in larger animals like marine mammals and birds, which are also used as bioindicators, bioaccumulation in mussels adequately reflects the changing levels in the environment (Phillips, 1980; Farrington et al., 1987; Cossa, 1988).

11. Most bivalves are of commercial interest and a measure of chemical contaminants in them is of public interest

2.10 Heavy Metal Uptake by Bivalves

Heavy metals in aquatic environment are absorbed by bivalves either directly through the gills in the process of respiration or indirectly with food particles (Clark, 1997). Benthos species of fish, through their association with sediment substrate, can directly uptake metals by ingestion of sediment particles or indirectly through consumption of benthic invertebrates (Bervoets and Blust, 2003). According to Phillips and Rainbow (1994), who reviewed the uptake of metals from particulates, there are two distinct ways in which metals can be taken up; namely through direct ingestion of particles with a subsequent uptake from digestive gland and/or uptake *via* pinocytosis in the gills of bivalves. During the process of respiration large volumes of water pass through the gills of bivalves and the large surface area of the gills facilitate the absorption of heavy metals (Tinsley, 1979). Tinsley (1979) has shown that bivalves are primary consumers, and therefore the chances of accumulating heavy metals through food chain are very remote. However, Phillips (1977) suggests that uptake from food in the most important route of entry, as dissolved concentration of heavy metals in water is very low.

Colloidal particles represent an important food source for deposit and suspension feeding benthic organisms (Griscom et al., 2000). Since clams are benthic filter feeders, they are a meaningful indicator of the bioavailability of toxic metal contamination in the estuary (Luoma et al., 1983). These animals ingest metal-enriched particles directly (Luoma et al., 1983). This is due to their intimate contact with the contaminated sediments and exceedingly high pumping activity and their responses are often proportional to ambient pollutant concentrations (Wang and Guo, 2000). Uptake of metals from these particles is

a function of the particle metal concentration, feeding rates, and biogeochemical factors (Griscom et al., 2000).

2.10.1 Effects of Heavy Metal Accumulation in Bivalves

Some bivalves have the ability to neutralize the toxicity of heavy metals and to store materials at cellular levels of the body tissues (Frazier, 1976; Viarengo, 1985). However, a number of adverse effects of heavy metals on the health and productivity of bivalves have been reported in literature (Krogh and Scanes, 1996). The physiology, reproduction and development of bivalves can be affected by sub-lethal levels of heavy metal toxicity in the environment (van Roon, 1999). For example, morphological changes, such as the greening and thinning of shells, or retardation of growth have been observed in oysters when they were exposed to sub-lethal levels of heavy metal concentrations in the surrounding environment (Nielsel and Nathan, 1975). Mance (1987), observed abnormal development in the adult and larvae of *Crassostrea gigas* when they were exposed to higher concentrations of cadmium, copper, lead and zinc under experimental conditions. Olvier et al., (2002), observed changes in the behavioural, physiological and biochemical patterns of bivalves as a response to a heavy metal pollutant in the environment.

As the concentration of a metal increases, the accumulation of the metal and its damage effect increase (Cain and Louma, 1986; Buschiazzoa *et al.*, 2004). Elevated metal concentrations in estuaries may have a direct toxic effect on macro-invertebrates and their predators (e.g. fish), or have an indirect effect on natural community structure, by reducing prey item diversity (negative effect) or reducing competition within a species (positive effect), resulting in a trophic cascade (Fleeger et al., 2003; Chapman, 2004). Elevated environmental metal concentrations have also been linked to increased concentrations of stress proteins and decreased concentrations of lipids in benthic macroinvertebrates (Panfoli et al., 2000; Hamer et al., 2004). A development of thin

watery translucent tissues and abnormal shells were observed in *Crassostrea gigas* when they were exposed to contaminated environments (Okazaki and Panietz, 1981). In addition, heavy metals can affect enzymatic and hormonal activities, as well as growth rate and increase mortality (Bubb and Lester, 1991).

2.11 Using Chemical Methods to Monitor Aquatic Environment

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Camusso *et al.*, 1995), which generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976). Hence, analyses of animal tissues, sediments and water chemically can provide the necessary data and information on the concentrations of heavy metals present in specific aquatic media. Chemical analysis of water, sediments, plants or animal tissues are widely used to detect the impact of anthropogenic contaminants in marine and estuarine environments (Phillips, 1977). However, some limitations have been observed in some of these analytical methods (Phillips, 1977).

2.11.1 Analysing Heavy Metals in Water

One of the problems of measuring heavy metals concentration in water samples is that the concentrations may be too low to detect (Phillips, 1977); O' Connor, 1998). Measuring these very low amounts in water requires pre-concentration processes (Rainbow, 1995). The other problems associated with detecting heavy metal in water include, that the concentration vary very rapidly due to environmental factors such as seasonal changes, time of the day, amount of fresh water runoff (Phillips, 1977; Rainbow, 1995). The characteristics of water, such as acidity or amount of organic matter are known to be important factors in determining the fate of heavy metals in lakes (Verta et al., 1990, Mannio et al., 1993, Skjelkvåle et al., 2001). The pollutant concentrations in the water only indicate the situation at the time of sampling. (Ravera *et al*., 2003), thus the results

obtained is not enough to be used as an index of pollution. However, this data provide only a quantitative assessment of the total metals present in the aquatic environment at the time of sampling (Rainbow, 1995). The measured heavy metal concentration in water would not represent the biological important fraction of the heavy metals (Rainbow, 1995). Many authors found that by simply monitoring contaminants in natural waters, they were unable to integrate the overall environmental conditions and their impacts on aquatic life and further found difficulty in quantifying very low contaminant concentrations commonly found in natural waters (Phillips and Rainbow, 1994; Narbonne, 2000). However, information obtained through this method could be inaccurate, as heavy metals tend to be dispersed into the aquatic environment or distributed into the biota (Barsyte-Lovejoy, 1999; Kennish, 2000; Issam *et al.*, 2003).

2.11.2 Analysing Heavy Metals in Sediments

A good knowledge of the distribution of heavy metals in water and sediments plays a key role in detecting the sources of pollution in aquatic systems (Forstner and Wittmann, 1981; Idodo-Umeh and Oronsaye, 2006). As an alternative method to monitor the heavy metal in aquatic environment, the chemical analysis of sediments has some advantages over that of water (O' Connor, 1998). Both organic and inorganic ion composition in sediments influences metals adsorption on it (Luoma, 1989). Increased inputs of metals in such forms available for association with sediments result in increases in metal concentrations in sediments (Luoma, 2000). When the organic component of the sediments increases, its metals content will increase in a linear fashion (van Roon, 1999). Gaw, 1997, found a positive relationship between the organic matter content and heavy metal of the sediments. However, the organic matter content is not the major factor that control heavy content in the estuarine sediments (Martincic, Kwotal et al., 1990). The biological oxidation of organic carbon changes to form iron, manganese and sulphur in

sediments which in turn increase the binding of trace metals to sediments (van Roon, 1999).

Heavy metal measurements obtained by sediments analysis depend on the rate of particle sedimentation and the rate of heavy metal deposition (Phillips, 1977). Sampling time and location may also have influence on the final results (Phillips, 1977). Sediments act as a natural absorbent for a number of contaminants, including heavy metals (Samoiloff, 1989), and the concentration of heavy metals in sediments is always higher that the concentration in water (Rainbow, 1995). Hence, sediments provide a concentrated pool of metals for analysis in aquatic environments (Luoma, 1989).

2.11.3 Analysing Heavy Metals in Animal Tissues

The universally acceptable biological approach to monitoring environmental pollution is the chemical analysis of body tissues of organisms to detect the level of contaminants in the environment (Samoiloff, 1989). Studies conducted in coastal areas proved that coastal organisms have the ability to accumulate heavy metals, such as mercury and cadmium, up to high levels even when those metals are in hardly detectable concentrations in water (Penny, 1984). They can also offer time–integrated measures of the bioavailable levels of heavy metals which is a feature that makes them superior when compared to water or sediment samples (Rainbow, 1995).

The chemical analyses of plant and animal tissues to measure heavy metal concentration in aquatic habitats can be used to avoid limitations in water and sediment analysis (Phillips, 1977). Bioaccumulated heavy metals can be measured either using the whole animal or individual tissue samples on a dry or wet weight basis (Fisher and Reinfelder, 1995). This approach provides a measurement of contaminants levels, as well as, the real effects of contaminants on organisms either singularly or cumulatively (Thomas, 1975;

Samoiloff, 1989). More accurate values can be obtained for the heavy metal concentrations in aquatic environment using plants or animals samples, because tissues of these organisms are not or less subjected to contamination during the process of analysis, and provide time integrated measures of metal contamination (Rainbow, 1995). Changes in heavy metal concentrations in these organisms indicate changes in pollution levels in the environment (Phillips and Rainbow, 1992). These types of organisms, known as biomonitors, can used to monitor the environmental factors over time (Phillips and Rainbow, 1992).

The greatest advantage of using animals to monitor the environment is that the measured concentrations of contaminants are directly related to the bioavailability of contaminants (Phillips and Rainbow, 1992). Using organisms to analyse contaminants, such as metals, provides a direct assessment, more comprehensive and realistic measurement of the bioavailability in the aquatic environment (Samoiloff, 1989; Silvia, Rainbow et al., 2001). However, the disadvantage of using organisms to monitor the environment is that they cannot indicate precisely which environmental factor or condition is responsible for the contamination (Lenihan and Flecther, 1978). Biomonitors generally accumulate trace metals to concentrations that are relatively easy to measure (Rainbow and Phillips, 1993).

2.12 Relationship between Heavy Metals in Sediments and Organisms.

Sediments are an important sink of a variety of pollutants, particularly heavy metals and may serve as an enriched source for benthic organisms (Wang *et al*., 2005). Sediments accumulate contaminants and may act as long-term stores for metals in the environment (Spencer and MacLeod, 2002). Exposure of sediment-dwelling organisms to metals may then occur via uptake of interstitial waters, ingestion of sediment particles and via the food chain (Luoma, 1989). As bivalves live in the water sediment interphases, they have a

potential to bioaccumulate heavy metals from the contaminated sediments and water (Huanxin, Lejun et al., 2000).

Samoiloff (1989) indicated that the heavy metals in sediments usually enter the body systems of animals through, contact with sediments, ingestion of sediments by the organisms and absorption of contaminants from sediments to water body which is used by the organisms. The heavy metal concentration in bivalve tissues gives a more reliable measurement of heavy metal concentration in sediments than in the water (Shulkin, Presley et al., 2003). The concentration of heavy metals contaminants detected by the analysis of bivalve tissues is not directly proportionate to the concentration of the heavy metals in the sediments, but is related only to extractable metal forms in sediments (Shulkin, Presley et al., 2003).

2.13 Heavy Metals

Heavy metals occur naturally as they are components of the lithosphere and are released into the environment through volcanism and weathering of rocks (Fergusson, 1990). The natural sources of heavy metals include soil, earthquakes, dust, volcano gas, forest fire. However, large-scale release of heavy metals to the aquatic environment is often a result of human intervention (Mance 1987, Denton et al., 1997) or as byproducts of different human activities (Brown et al., 1979; Vesk et al., 1997). Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are also obvious sources of heavy metals into rivers, estuaries and coastal waters (Mance, 1987). If the concentrations theses contaminants reach high enough levels in the environment, they become toxic to aquatic organisms and humans as well through food chain.

Heavy metals are defined by Alloway (1995) as “elements which have an atomic density greater than 6 g/cm3.” The metals that are of most concern are: cadmium, chromium,

cobalt, copper, iron, lead, manganese, mercury, nickel and zinc. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems **(**Evanko et al., 1997). Heavy metals have unique characteristics including; they do not decay with time, they can be beneficial to living organisms at certain levels but can be toxic when exceeding specific thresholds, they are always present at a background level of non-anthropogenic origin, their input in soils being related to weathering of parent rocks and pedogenesis and, they often occur as cations which strongly interact with the soil matrix, consequently, heavy metals in soils can become mobile as a result of changing environmental conditions. This situation is referred to as "Chemical timing bomb" (Facchinelli et al., 2001).

The heavy metals identified as having the greatest potential toxicity to humans resulting from ingestion of contaminated fish and shellfish are mercury (Hg), arsenic (As) and cadmium (Cd) (USEPA, 2000). Metals exert toxic effects if they enter into biochemical reactions in the organism and typical responses are inhibition of growth, suppression of oxygen consumption and impairment of reproduction and tissue repair (Duffus, 2002). In trace amounts, some heavy metals (e.g. Cu, Fe, Ni, Zn) are essential in maintaining human body metabolism whereas others like (Cd, Hg, Pb) are non-essential and toxic even in trace amounts. These essential metals can also produce toxic effects when the metal intake is excessively elevated (Tüzen, 2003).

2.14 Toxicity of Heavy Metals

Heavy metal is one of the most serious environmental pollutants because of its high toxicity, abundance and ease of accumulation by various plant and animal organisms (Idris, et al. 2004). The presence of metals in water and soils can pose a significant threat to human health and ecological systems. Heavy metal toxicity represents an uncommon, yet clinically significant, medical condition. Although several adverse health effects of

metals have been known for a long time, exposure to heavy metals continues, and has even increasing in some parts of the world, in particular in less developed countries (Jarup, 2003). There are documented cases of many different metals causing toxicity issues (e.g. Grasmanis and Leeper, 1966; Godbold and Huttermann, 1985; Merry et al., 1986; Kelly et al., 1990). The toxicity of heavy metals has been reported to follow the general order of Zn < Pb <Ag < Cd < Cu < Hg, which may vary depending on environmental conditions and species (Rai et al., 1981). Increase in the concentration of any metabolite can demonstrate either increased production or decreased utilisation by the reactions for which it is a substrate or product (Burke et al., 1990). If unrecognized or inappropriately treated, heavy metal toxicity can result in significant morbidity and mortality.

Many metals are essential to biochemical processes in correct concentrations but at higher doses, heavy metals can cause negative health effects such as irreversible brain damage. Heavy metals such as cadmium, mercury, lead, copper, and zinc, are regarded as serious marine pollutants because of their toxicity, tendency to be incorporated into food chains, and ability to remain in an environment for a long time (Puyate et al., 2007). Heavy metals are especially toxic due to their ability to bind with proteins and prevent DNA replication (Kar et al., 1992). Some metals such as lead and mercury easily cross the placenta and damage the brain (Levine et al., 2006). Heavy metals block functional groups of proteins, displace and/or substitute essential metals, induce conformational changes, denature enzymes and disrupt cells and organelle integrity (Hall, 2002). In addition, heavy metals can affect enzymatic and hormonal activities, as well as growth rate and increase mortality (Bubb and Lester, 1991). The macro – micro toxic mode of actions of metals can results in growth reduction, foliar symptoms and anatomically as cellular symptoms. Essential elements (*e.g.* manganese, iron, zinc, copper and selenium)

are physiologically present in the living organisms, since they are important in many molecular and cellular functions, and are thus often regulated by efficient homeostatic mechanisms (Hoffman *et al.*, 2001).

2.14.1 Cadmium (Cd)

Cadmium (Cd) is a soft, malleable silver-white metal with low melting point which occurs naturally in the earth's crust. Naturally it occurs in the form of CdS, $CdCO_3$. The aqueous chemistry of cadmium is, for most part, dominated by Cd^{2+}, $CdCO_3$(s) (otavite), and $Cd(OH)_2$(s) (Faust and Aly, 1998). Cadmium occurs as a minor component in most zinc ores and therefore is a by-product of zinc production (West et al., 1987). Sources of Cd include wastes from Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilisers are used since Cd is a common impurity in phosphate fertilisers (Stoeppler, 1991).

Cadmium enters aquatic systems through aerial deposition or runoff and accumulates in bed sediments by association with particulate matter, such as organic matter and iron and manganese hydroxides, or by precipitating out of solution with carbonate or sulphide (Landrum and Robbins, 1990; Burton, 1992). Factors such as pH, redox conditions and complexing agents in the water influence the release cadmium from sediments. Cadmium is less mobile under alkaline conditions (Fergusson, 1990). Cadmium can accumulates easily living organisms via the food chain. Several other cultivated plants, most notably cereals, also tend to take up Cd from the soil (Järup, 1998). Shellfish can contain 200-2000 μg/kg Cd (Galal-Gorchev, 1991) without themselves been poisoned.

Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering et al., 1994), and it is a Group 1 human carcinogen (IARC, 1993). Cadmium is extremely toxic to most plants and animal species particularly in the form of free

cadmium ions (Denton et al., 1997). Thus, has no biological usefulness in living organisms and is even toxic in small quantity. Cadmium is one of the most toxic environmental and industrial pollutants because it can damage, all important organs (ATSDR, 2008) and inhalation of air borne particles containing cadmium is considered an industrial hazard. Depending on the size of the particles, airborne Cd is absorbed from the respiratory tract to 2-50% (Chaney et al., 2004). Absorbed Cd is transported via the blood to the main target organs such as lung, kidney, liver, bones, brain, testis, even to the placenta (Casalino et al., 2002; Méndez-Armenta et al., 2003; Morselt et al., 1991; Wier et al., 1990).

In a published acute case of intoxication due to Cd inhalation, the victim had first respiratory signs which transformed over 3-6 months to a Parkinson-like state (stiffness of the limbs, bradykinesia, muscle stiffness) that did not improve on antiparkinsonian medication (Okuda et al., 1997). Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small air sacs of the lungs become distended and eventually destroyed reducing lung capacity (Ansari et al., 2004). Cadmium has the potential to disrupt endocrine function by behaving like sex hormones (Stoica et al., 2000). A study has shown that even low doses and short term exposure to cadmium can cause specific DNA damage in breast tissue and may be a possible mechanism of action of cadmium on the cell cycle of human mammary cell lines (Roy et al., 2004).

2.14.2 Copper (Cu)

Copper is reddish coloured, takes on a bright metallic luster, and is malleable, ductile, and a good conductor of heat and electricity (second only to silver) (West et al., 1987). Most copper (Cu) compounds found in air, soil and water are strongly attached to dust or embedded in minerals (MDH, 2006). Inputs of copper into the natural waters come from

various source including mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Denton et al., 1997). It is used as a building material, and a constituent of various metal alloys (West et al., 1987). Algaecides and antifouling paints are identified as major contributors of copper to harbor areas whereas coastal waters are generally receiving inputs from rivers and atmospheric sources (Denton et al., 1997).

The physico-chemical and hydro-dynamic characteristics, as well as the biological state of the water determine speciation of copper in natural waters (Moore and Ramamoorthy, 1984). In the pH range of most of the natural waters (6.5-9.5) the predominant copper species is $CuCO_3$ (Grooters, 1998). In aquatic solutions, Cu (II) ions are more stable than in other oxidation states (Wong, 2004), and thus the predominant toxic specie of copper. Copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ (LaGrega et al., 1994). Copper ions can potentially bioaccumulate in certain aquatic organisms. When the copper concentration in the environment exceeds a certain level, microbial diversity, populations and activities are affected (Flemming and Trevors, 1989; Landner and Reuther, 2004; Boivin, 2005). Hence, the copper content in the environment, such as in the soil, water and sediment, needs to be considered in environmental management/ monitoring programmes (Bulter and Davies, 2004; Swedish EPA, 2000; Brils, 2008).

Copper is an essential element for living organisms, including humans, and small amounts is necessary in diets to ensure good health (Vitosh *et al*., 1994; MDH, 2006). Copper serves as a cofactor for many proteins involved in respiration, iron metabolism, and free radical eradication (Valko et al., 2005). However, exposure to higher doses can cause various adverse health effects. Long term exposure to copper results in nose irritation, mouth, and eyes, and cause headache, and diarrhea (Finkelman, 2005). Copper has also been associated with liver damage and kidney disease (MDH, 2006).

2.14.3 Chromium (Cr)

It is a steel-gray, lustrous, hard metal that takes high polish (West et al., 1987). Chromium occurs naturally in rocks, soils, animals and plants (ATSDR, 2008) in any of the oxidation states from -2 to +6 (but not zero; Klasing et al., 2005). Major coastal marine contributors of chromium are dominated by input from rivers, urban runoff, domestic and industrial wastewaters and sewage sludge (Denton et al., 1997). The application of Cr includes: wood preservatives, fungicides in the agriculture, algicides, porcelain and glassmaking, stainless steel cookware or tattoos (Cohen and Costa, 2007), and these has contributed to its presence in the environments due to improper disposal methods and excessive usage.

Chromium (Cr) basically exists in the natural environment in two oxidation states, Cr^{3+} and Cr^{6+}, as result they vary variable in chemical properties leading to differences in speciation and toxicity. The chemical toxicity of chromium depends on the state in which it exists in the environment. Cr^{3+} is a nutritionally essential trace element and non-toxic but if the concentrations of chromium exceed the recommended threshold values it may become toxic to human health. Environmental Cr^{6+} originates almost totally from human activities, such as metallurgical processes, manufacturing of Portland cement, sewer sludge and waste incineration, etc. (Cohen and Costa, 2007). It is more toxic than Cr^{3+}; it is a strong oxidant, a carcinogen, allergen and an acute irritant both in humans and animals (Barceloux, 1999a). Cr^{3+} is a component of the glucose tolerance factor, thus regulating glucose, protein and fat metabolism (Mertz, 1969; Klasing et al., 2005).

In soils high in pH and phosphorus a significant proportion of Cr forms hydroxides and phosphates rather that organic complexes (Bartlett and Kimble, 1976b). Hexavalent chromium forms occur to a much lesser extent as compared to trivalent forms and the addition of Cr^{4+} to soils usually results in complete reduction to Cr^{3+} by soil organic

matter (Bartlett and Kimble, 1976a). Chromium reduction is enhanced under anaerobic conditions, such as within waterlogged soils (Bloomfield and Pruden, 1980; Bartlett, 1991; Losi et al., 1994). Waterlogged soils may also enhance chromium reduction because of increased CO_2 trapping, which tends to lower soil pH (Losi et al., 1994). However, if Cr^{6+} does occur to some extent its solubility is low in most soil pH conditions (6-8), thus limiting mobility (Bartlett and Kimble, 1976a). Levels of chromium in marine sediments range from 2.4 μg/g at unpolluted sites to 749 μg/g at grossly contaminated sites (Denton et al., 1997).

Health effects of chromium depend on chemical forms of exposure (Calder, 1988). Respiratory symptoms were also described after exposure of workers to chromite ore (containing Cr^{3+}), and increase in the number of complaints and clinical signs was reported in parallel with the increased number of respirable Cr^{3+} and Cr^{6+} particles (ATSDR, 2008). Although ingested Cr^{3+} is considered non-toxic, hypoactivity, mydriasis, lacrimation and body weight loss was reported as signs of acute Cr toxicity (ATSDR, 2008). Based on recent findings, (Levina and Lay, 2008) suggested to pay more attention to the toxic effect of trivalent Cr compounds. Chromium is carcinogenic to humans and long term exposure has been associated with lung cancer in workers exposed to levels in air that in the order of 100 to 1000 times higher than usually found in the environment (Finkelman, 2005).

2.14.4 Mercury (Hg)

Mercury (Hg) is an element that has generated a lot of global concern despite its applications but with no relevant uses within biological systems of organisms. The natural emissions are released during outburst from volcanoes, forest fires, degrading of minerals and by degasification from land and water surfaces (Gochfeld, 2003; Jitaru and Adams, 2004; UNEP Chemicals, 2002). Other sources are the chloro-alkali industry where $HgCl_2$

is used as a cathode in the production, non-ferrous metal production, cement production and other industries, waste disposal, from crematoriums due to old amalgams in teeth and by primary Hg production (Jitaru and Adams, 2004; Pacyna et al., 2006).

The ultimate source of mercury to most aquatic ecosystems is deposition from the atmosphere, primarily associated with rainfall (Kwaansa- Ansah et al., 2012). Mercury has three variable oxidation numbers; 0 elemental mercury, +1 mercurous and +2 mercuric. In the environment, Hg may undergo transformations among its various forms and among its oxidation states (Young, 2005). Toxic Hg compounds are found in all three of the oxidation states, but the most toxic Hg compound is found as mercuric Hg (Clarkson and Magos, 2006). The most toxic Hg compounds is considered to be the organomercurials and especially methyl mercury (CH_3Hg^+), often referred to as MeHg, and dimethylmercury (Clarkson and Magos, 2006; Gochfeld, 2003).

Mercury is mostly present in the aquatic environment in the inorganic form, with some transformed to the most bioavailable and toxic methylmercury which accumulates in aquatic organisms with long live span. The primary sink for mercury in the aquatic ecosystem is bottom sediments where the inorganic form undergoes methylation to the organic form which can enter the food chain or can be released back to the atmosphere by volatilization (Kwaansa- Ansah et al., 2012). In the environment Hg can be methylated and demethylated by several different pathways, but it is generally accepted that methylation is principally a biological process where sulphate reducing bacteria (SRB) are the most important methylators (Mason and Benoit, 2003). In marine environments the concentration of methylmercury in organisms at the top of the aquatic food chain can be up to 100 000 times larger than in the surrounding waters (WHO, 1990). Mercury is potentially accumulated in organisms and sediments, and subsequently transferred to man through the food chain (Chen, et al. 2009).

The general human population is primarily exposed to mercury *via* food, where fish is the major source of methyl mercury exposure (Järup, 2003). Mercury has no necessary function in any living organism and is considered as a non-essential metal, is among the most toxic elements to man and many higher animals (Steinnes, 1995; Landner and Lindestrom, 1998). MeHg forms water-soluble complexes in body tissues attached to thiol (-SH) groups in proteins, certain peptides, and amino acids and is highly mobile in the body (Clarkson and Magos, 2006).

Severe damage to the central nervous system and other vital organs can occur as result of continuous exposure to organic mercury forms. Although any exposure to organic mercury compounds will contribute to the body burden of mercury, exposure during pregnancy or the postnatal period has the most significant consequences (Young, 2005). Its effect on the central nervous system makes it especially toxic to developing fetuses (Clarkson and Magos, 2006). Exposure of the foetus of humans to mercury can also cause late development of speech, late walking, memory shortfall in attention and autism (Zahir *et al*., 2005). Chronic exposure due to consumption of methyl mercury in fish and other seafood with subsequent neurotoxicity is a human health concern (Goyer and Clarkson, 2001).

2.14.5 Nickel (Ni)

Nickel is ubiquitous in the biosphere and ranks 24th in crustal abundance of all elements (Eisler, 1998). The major source of discharge to natural waters is municipal wastewater followed by smelting and the refining of nonferrous metals (Denton et al., 2001). Furthermore, nickel is one of the most common metals in surface waters (USEPA, 1986). Nickel is also released into the environment from natural processes including the weathering and leaching of rock and in soi1 dust (Environment Canada, 1994). Nickel released from metal mining, milling, and smelting operations enters aquatic systems

through atmospheric deposition, liquid effluents, and leachates **(**Chau and KuIikovsky-Cordeiro, 1995).

Nickel occurs in aquatic systems as dissolved species or as soluble salts adsorbed onto or associated with clay minerals, iron and manganese oxides, or organic matter (WHO, 1991; Aquamin, 1996). In the bottom sediments of estuaries nickel deposition may occur as result of many processes such as precipitation, complexation, adsorption on particles, and for further uptake by biota. . Because of microbial activity or changes in physical and chemical parameters, including pH, ionic strength, and particle concentration, sorption processes may be reversed, leading to release of nickel from the sediment (Di Toro et al., 1986). Nickel is moderately soluble in soil water and as is typically true for metals, increases at low pH (McGrath, 1995). Within aquatic systems, nickel typically occurs as soluble salts adsorbed onto, or associated with, clay particles, organic matter, and other substances (Eisler, 1998). Freshwater fish inhabiting contaminated systems are exposed to Ni, primarily through the ingestion of contaminated food and sediments (Dallinger and Kautzky, 1985). Nickel concentrations in sediments that exceed this concentration are predicted to cause frequent adverse effects in aquatic organisms (Environrnent Canada, 1994).

In mammals and humans nickel metabolism has been described in great detail (Eisler, 1998; WHO, 1991). Other studies suggest that nickel may serve as a cofactor for activation of calcineurin, a calmodulin-dependent phosphoprotein phosphatase, that has importance as a brain and skeletal muscle enzyme regulator (Sunderman and Oskarsson, 1991; Nielsen, 1993). Additionally, it might be involved in cyclic nucleotide gated channel functions (Gordon and Zagotta, 1995) and recent evidence suggests that there is a collaborative relationship between vitamin B-12 metabolism and nickel (Stangl et al., 2000). The effects of nickel deficiency include delayed gestation period, fewer offspring,

anaemia, skin eruptions, reduced hemoglobin and hematocrit values, and reduced activity of several enzymes (WHO, 1991).

Some of the most serious health effects due to exposure to nickel include reduced lung function some nickel compounds are reported to be carcinogenic to humans and metallic nickel may also be carcinogenic (Finkelman, 2005). Carcinogenic actions of nickel compounds are thought to be mediated by oxidative stress, DNA damage, epigenetic effects, and the regulation of gene expression by activation of certain transcription factors (Leonard et al., 2004). Inhalation of nickel during refining of ore produces respiratory tract cancer, and allergic contact dermatitis to nickel alloys is common (Goyer and Clarkson, 2001).

2.14.6 Selenium

There are various selenium species, including elemental selenium (0), selenide (-2), selenite (+4), selenate (+6) and organic selenium such as selenomethionine and selenocysteine (Tamari, 1998; Barceloux, 1999b). The main anthropogenic sources include ceramic, pharmaceutical, photoelectric cell, pigment, rectifier, rubber, semiconductor, and steel industries (Barceloux, 1999b). Selenium is also recovered from the sludge accumulating in sulphuric acid plants and from electrostatic precipitator dust collected during the processing of copper and lead (Earnshaw and Greenwood, 1997).

Selenium is almost always present in water and soil at some concentration and the presence of selenium represents a combination of naturally occurring forms as well as the forms that were put back into the environment by human activity (Palmer, 1998). Animals and humans are exposed to environmental selenium via dermal contact, the inhalation of air and via the ingestion of water, plants and animals that have a diet that

contains food produced on soil containing selenium (Fordyce, 2005). However, food is the main exposure pathway of selenium (WHO, 2008).

Selenium is an essential micronutrient to humans and other biological organisms. Selenium, an essential dietary trace mineral, is a critical component of numerous selenoproteins in humans (Levander, 1987; Brown and Arthur, 2001). Selenoproteins are important components of several antioxidant systems (e.g., glutathione peroxidase) that actively protect against damage from free radicals and reactive oxygen species (Holben and Smith, 1999; Brown and Arthur, 2001). However, it becomes toxic at more elevated levels (Kuo and Jiang, 2008). The toxicity of most Se species is low and depends mainly on the chemical form (Barceloux, 1999b). Selenite, selenate and selenomethionine are among the most acutely toxic selenium compounds (Högberg and Alexander, 1986). Acute symptoms such as vomiting have been observed, but so far no serious cases of toxicity have been recorded (Johansson *et al*., 1997).

2.15 Impacts of Heavy Metal Accumulation to Human Health

Humans have always depended on aquatic resources for food, medicines and materials as well as recreational and commercial purposes such as fishing and tourism (Chopra et al., 2009). There are two basic routes from the environment that the metal can take in order to interact with the organism, direct contact via the aqueous compartment or through ingestion of metal contaminated food (Langston and Spence, 1995).

Toxicants including heavy metals in fish species are prime interest due to their potential effects on organisms that feed on them and the fishes themselves. Consumption of such aquatic food enriched with toxic metal may cause serious health hazards through food chain magnification (Miretzky et al., 2004). Effects of metals on organisms must be considered within a context of physical and chemical influences affecting transport and

fate, as well as vulnerabilities that are unique to individuals, species, populations, and communities (Peakall and Burger, 2003; Fairbrother *et al.*, 2007). Essential elements (*e.g.* manganese, iron, zinc, copper and selenium) are physiologically present in the living organisms, since they are important in many molecular and cellular functions, and are thus often regulated by efficient homeostatic mechanisms (Hoffman *et al.*, 2001). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage while also posing a risk to human health (Adams *et al.*, 1992; Grimanis *et al.*, 1978).

In organisms, the dose-response relationship for essential elements reflect the fact that at very low intakes of the metal, biological effects may appear due to deficiencies, whereas at high intake, effects may be due to an over-dosage (Fairbrother *et al.*, 2007). Metal toxicity is the adverse effect that the uptake of the metal has on an organism (Mason and Jenkins, 1995). Metals such as lead, cadmium, mercury and arsenic, which have no known function in living organisms, are toxic even at very low doses and may displace or substitute for essential metals and interfere with proper functioning of enzymes and associated cofactors (Hoffman *et al.*, 2001). The chronic effect of lead on man includes neurological disorders, especially in the foetus and in children. This can lead to behavioral changes and impaired performance in IQ tests (Lansdown, 1986; Needleman, 1987). The effect of Cd toxicity in man includes kidney damage (Friberg *et al*., 1986; Herber *et al*., 1988) and pains in bones (Tsuchiya, 1978). Exposure of the foetus of humans to mercury can also cause late development of speech, late walking, memory shortfall in attention and autism (Zahir *et al*., 2005).

In organisms, the dose-response relationship for essential elements reflect the fact that at very low intakes of the metal, biological effects may appear due to deficiencies, whereas at high intake, effects may be due to an overdosage (Fairbrother *et al.*, 2007). Toxic

substances may knock down immune; reproductive, nervous and endocrine systems in animals and these effects can be at organ, tissue and cell level (Geeraerts and Belpaire, 2009). Disturbed neurotransmission also belongs to the toxic spectrum of certain neurotoxic heavy metals (Braga et al., 1999; Takeda et al., 2003).

2.16 Indices for Sediment and Organism Pollution Assessment

There are several common methodologies used in analysing pollution intensities in organisms and the environments such as; Contamination Factor (CF), Pollution Load Index (PLI), Geoaccumulation Index (Igeo) and Bio- sediment Accumulation Factors (etc). According to Tomlinson *et al*., (1980), indices enable quality of the environment to be easily understood by non-specialist. They are also used to compare the pollution status of different areas of the environment (Tomlinson *et al*., 1980).

2.16.1 Pollution Load Index (PLI)

The PLI of a sampling point, community or an area is obtained by deriving Contamination Factors (CFs), using background concentrations or baseline or concentration of the element of interest in an unpolluted area (Tomlinson *et al*, 1980; El-Sammak and Abdul-Kassim, 1999; Adomako *et al*., 2008).

Contamination Factor (CF) is the ratio of concentration of an element in a sample and background concentration. The CF's for different elements at the sampling site will vary, and a site's pollution load index may then be calculated by multiplying the contamination factors and deriving the Nth root of the N factors (Tomlinson *et al*., 1980). Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al*., 1980; Cabrera *et al*., 1999). Pollution Load Index is used to find out the mutual pollution effect at different stations by the different elements in soils and sediments (El-Sammak and Abdul-Kassim, 1999). This type of

measure has however been defined by some authors in several ways, for example, as the numerical sum of eight specific contamination factors (Hakanson, 1980), whereas, (Abrahim, 2005) assessed the site quality as the arithmetic mean of the analysed pollutants. The calculated PLI values were compared to description of sediment quality by (Tomlinson et al., 1980) to verify the pollution levels of the two sampling sites.

2.16.2 Geoaccumulation Index

The geoaccumulation index (Igeo) has been used since the late 1960s, and has been widely employed in European trace metal studies (Yaqin *et al*., 2008). The Igeo values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al*., 2008). Geoaccumulation Index is calculated using the formula;

$$Igeo = Log_2(Cn/1.5 \times Bn)$$

Cn is the measured content of element in sediment, and Bn the element's content in "average shale" (background concentration) (Turekian and Wedepohl, 1961) and 1.5 is a constant. The constant 1.5 allows for analyses of natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Teng *et al*., 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008).

The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al*., 2004). The geoaccumulation index consists of 7 classes (Grzebisz *et al*., 2002; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008) [Table 4.7].

2.16.3 Biota – Sediment Accumulation Factor (BSAF)

Biota – Sediment Accumulation Factor (BSAFs) is the ratio metal concentrations in an organism to its corresponding sediment metal concentrations, represented by the equation below. The various clam sizes obtained for each sampling period was treated as a unit.

$$\text{BSAF.} = \frac{\text{Concentration of heavy metal in the organism}}{\text{Concentration of heavy metal in sediments}} \quad \text{(Thomann } et\ al.\text{, 1995)}$$

Where BSAF = Biota – Sediment Accumulation Factor in kilogram tissue per kilogram sediment (*kg tiss/kg sed*). Concentration of metal in the organism tissues reported in milligrams per kilogram tissue (*mg/kg tiss*); and Concentration of the same metals in the ambient environment, sediment in this case reported in milligrams per kilogram sediment (*mg/kg sed*).

2.17 Distribution of the Clam Population

The bivalve mollusk, fishing industry is an important fishery resource in the world. It serves as an essential source of animal protein and a cherished nutritional delicacy for many people around the globe. In 2000 landings of clams from capture fisheries and aquaculture operations totaled 14,204, 152 tones (Michael and Niel, 2004). The freshwater bivalve mollusc, *Galatea paradoxa* (Born, 1778) (=*Egeria radiata* (Lamarck, 1804) is stenotopic, being restricted in its mega-scale occurrence to few large West African rivers namely: Volta River in Ghana, Nun and Cross Rivers in Nigeria, and Sanaga River in Cameroon (King and Udoidiong, 1991). Limited information about the prevalence and commercial exploitation of this clam is available from only a few countries, including Ghana, Nigeria and Cameroon, despite its extensive distribution in the wider West African region (Obirikorang, 2010).

In Ghana, many clams have been identified but the one with the significant interest is the clam *Galatea paradoxa* (Born, 1778) which is presently harvested mainly for

consumption. It has been harvested for food and sold to earn income for living (Gordon and Amatekpor, 1999). However, there is a growing concern about the continued decline in clam population in the Volta River in recent times. Until the creation of the Akosombo dam in 1963, picking this clam was the main occupation and also served as the source of livelihood for the people at the lower Volta especially Ada-Foah (Yankson, 2004).

The construction of the Akosombo dam has lead to a decrease in the perennial floods and increase in the formation sandbars at the estuary despite some desiltation. The effect of this was that saline water, which during high tide flowed upstream into the river channel, has completely ceased (UNEP, 2002). The resultant effect is the change in the water chemistry and other ecological factors leading a decline clam population and livelihood of the indigenes within the catchment area of the Volta basin. The increase in recreational activities, industrialization and economic development following the construction of the dam, with their resultant pollution of the lake has adversely affected fishery resources in the lake and clams are no exception. Thus, the daily livelihood of people who depended on fishing and clam harvesting has been seriously affected.

This rejuvenation in the clam industry does not, however, compare with what it used to be with respect to size of fishing grounds, the number of people involved and the present catches are just a fraction of the pre-dam periods (Amador, 1997) when the clam industry stretched between Akuse and Sogakope (Lawson, 1963). Before the construction of the dam at Akosombo, clam picking was mainly the predominant activity in the lower Volta estuary (Gyasi, 1999). Its exploitation in most rivers is largely devoid of management and conservation strategies and these have resulted in over-exploitation leading to a decline in abundance and sizes of clams caught (Amador, 1997).

The economic importance of clams cannot be underestimated as their flesh is consumed for their nutritional importance and their shells used for other purposes. Calculated on a dry matter basis, the average protein content of smoked clam fish is 46.5% (Kwei, 1965). Bivalve shells can be put to a wide range of uses including preparation of paint, terrazzo, concrete for building, poultry feed ingredient as a source of calcium, liming of agricultural lands, treatment of burns, etc.(Yankson, 1990; Obodai and Yankson, 1999).

2.18 Previous Work on Heavy Metal Pollution in the Study Area

Some works have been carried out on heavy metal concentrations in the bivalve *Galatea paradoxa* in Volta Lake, which includes (Obirikorang, 2010) at Ada and Aveglo and (Tay et. al., 2004).

Table 2.1: *Overview of trace metal concentrations in the whole soft tissue of Bivalves specie Galatea paradoxa collected in the waters of the Volta Lake. (All values are expressed in μg/g dw).*

		Heavy Metal Concentration (μg /g dw)			
AREA	REFERENCE	Fe	Zn	THg	Mn
Volta River, Ada, Ghana	Obirikorang, 2010	71-316	13-43	0.028-0.056	49-867
Volta River,Aveglo, Ghana	Obirikorang, 2010	123-539	16-49	0.037-0.074	73-206
Volta River, Ghana	Tay et. al., 2004	74.9	89.4		116.7

Source:Obirikorang (2010)

According to (Obirikorang, 2010), the concentrations of Mn, Fe, Zn and Hg in the Volta clams are within acceptable limits and therefore, are safe for human consumption according to WHO safety reference standard for bivalves and molluscs (2000).

CHAPTER THREE

MATERIALS AND PROCEDURES

3.1 Study Area

The sampling locations were in Volta Lake estuary in Ghana. Ada and Aveglo were chosen for clam and sediment collection. The two locations are currently the most active fishing grounds of the clams in Ghana. The site locations are shown in (Figure 3.1). The samples were collected for a period of six months at two months interval.

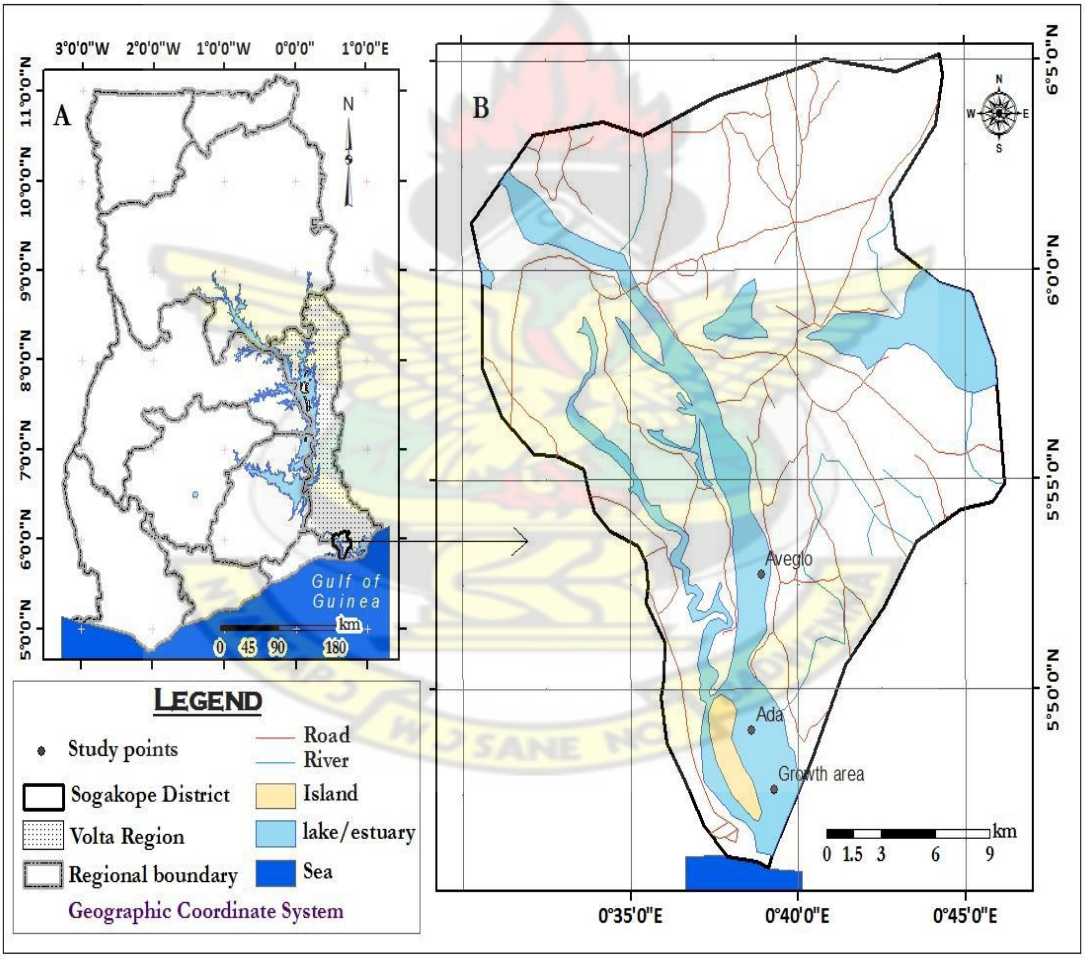

Figure 3.1: *Clam sampling locations at Ada and Aveglo in the Volta estuary in Ghana. Source: Obirikorang, 2010*

3.2 SAMPLE COLLECTION AND PREPARATION

3.2.1 Clam Samples

Clams and sediment samples were collected between September, 2011 and February, 2012. The clam samples were collected from Ada and Aveglo from fishermen's catch. The clam samples were soaked in river water in insulated cooler chests which has been washed with 10% nitric acid and deionized water to prevent possible contaminations. The samples were transported to the laboratory at Kwame Nkrumah University of Science and Technology (KNUST), Kumasi within 24 hours of collection for processing.

In the laboratory at KNUST, the clams were categorized into three groups representing the most abundant size groups with 10 individuals for each group based on shell length using venier caliper to nearest 0.1 mm as follows: small (25mm – 40mm), medium (41mm – 55mm), and large (above 55mm) per the procedure described by (Obirikorang, 2010). A total of 180 clam samples covering the three dominant *Galatea paradoxa* species were obtained. The clams were rinsed with distilled water to remove any remaining sediment outside or inside the shell and weighed. The various clam size classes were purged of ingested organic and inorganic particles before being analysed for heavy metal accumulation by keeping each size class in distilled water for a 24- hour depuration (Obirikorang, 2010). After the depuration process, a sterile stainless steel knife was used to dislodge and remove the soft tissue of each clam from the shell (Chiu *et al*., 2000). The removed flesh of each individual clam from each group was weighed to the nearest 0.0001 g. Samples of each size class were stored in air-tight, acid-washed clean white-polyethylene bags for heavy metals analyses.

3.2.2 Sediment Samples

Sediment samples were collected from a canoe at the same point the clams were collected using Erkman grab according to the standard procedure described by the (USEPA, 1994). The samples were bagged in clean dark-polyethylene bags and properly labelled and stored in insulated cooler chest. The sample bags and the insulated chest were washed with 10% nitric acid and deionized water to prevent possible contaminations.

Portion of the sediment samples were air dried at room temperature for seven days to constant weight. Unwanted particles such as organic debris and large stone particles were removed. The dried samples were homogenized by grinding using mortar and pestle, sieved through 2 mm mesh and stored in acid pre-wash polythene bags.

2.2.3 Digestion of Samples

The frozen clams were homogenized using a mortar and a pestle. About 0.5g of the homogenized clam paste and the sediment samples were weighed into a 50 ml digestion tube together with 1ml of distilled water, 2.0 ml acid mixture of (HNO_3-$HClO_4$) (1:1 v/v) and 5.0 ml sulphuric acid (H_2SO_4) were added and digested for 30 minutes at 200 ±5 ºC in a fume chamber. After the digestion it was allowed to cool down to room temperature. The digested samples were filtered into 50 ml volumetric flasks and distilled water was added to the mark. The content of the 50 ml volumetric flask was transferred into pre-washed, labelled, and acid-cleaned bottles with vials.

3.3 Total Mercury (THg) Measurement

Total mercury concentrations were determined in the digests by an Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd., Japan) using on cold vapour atomic absorption spectrophotometry. The wavelength of the mercury lamp used was 253.7 nm. In the cold vapour method, 5 ml of the digested solution was put in to the

reaction vessels; 0.5 ml of 10% (w/v) $SnCl_2.2H_2O$ in 1 M HCl was used as a reducing reagent in the mercury analysis. The responses were recorded and the peaks height used to calculate the concentrations of mercury.

3.4 Analysis of Heavy Metals

Digested samples were analysed at the Ecological Laboratory at University of Ghana, Legon to determine the concentrations of Cd, Cr, Cu, Ni and Se using Flame Atomic Absorption Spectrophotometer (FAAS). The operating conditions Cd, Cr, Cu, Ni and Se for analysis by FAAS are indicated in Table 3.1. Calibration of the instrument was carried out with standard solutions of concentrations, 1 ppm, 2 ppm and 4 ppm.

Table 3.1: *Wavelengths and detection limits for the studied heavy metals*

Element	Wavelength (nm)	Slit width (nm)	Lamp	Detection limit (mg/L)	Gas
Cd	228.80	2.7/1.35	HCL	0.005	Acetylene
Cu	324.75	2.7/0.8	HCL	0.0015	Acetylene
Cr	357.87	2.7/0.8	HCL	0.003	Acetylene
Ni	232.00	1.8/1.35	HCL	0.006	Acetylene
Se	196.00	2.7/0.7	HCL	0.100	Acetylene

HCL: Hydrogen Cathode Lamp

3.5 Quality Assurance

Analyses of blank and replicate samples were carried out for quality assurance purposes. Certified reference material (Dogfish muscle, DOLT- 4) and TORT-2 from the National Research Council (NCR) in Canada were used to assess the accuracy and precision of the analytical methods. The blank solution was prepared by adding 2 ml of nitric acid and perchloric acid (HNO_3- $HClO_4$) mixture in the ratio of 1:1; 5 ml sulphuric acid (H_2SO_4) to

1 ml of distilled water in a digestion tube. The content was heated for 30 minutes at a temperature of 200 ±5 ºC. The Certified Reference Materials (CRMs) were brought into solution following the same analytical procedure and the solutions were analysed in the same manner as the samples during the analysis.

3.6 STATISTICAL ANALYSES AND CALCULATION OF POLLUTION INDICES

3.6.1 Statistical Analysis

Statistical analysis of data was carried out using SPSS 17.0 statistical package program. One way ANOVA (Analysis of Variance) was performed for statistically significant difference in the mean value of heavy metal concentrations in different class sizes of clam tissues for the two sampling sites. The concentrations of all metals in clam tissues and sediments were expressed in mg/kg.

3.6.2 Calculation of pollution indices

The pollution Load Index (PLI), Contamination Factor (CF), Geoaccumulation Index and Bio-sediment Accumulation Factors (BSAFs) were computed using Microsoft Excel 2007 version. Tomlinson et al. (1980) and Cabrera et al. (1999) method was used in computing the overall pollution load indices (PLIs) of the sediment. The CF's for different elements at the sampling site will vary, and a site's pollution load index may then be calculated by multiplying the contamination factors and deriving the Nth root of the N factors (Tomlinson *et al*., 1980). Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al*., 1980; Cabrera *et al*., 1999). The PLI was calculated using the equations below:

$$PLI_{sampling\ site} = (CF_{Cd} \times CF_{Cu} \times CF_{Cr} \times CF_{Hg} \times CF_{Ni} \times CF_{Se})^{1/6}$$

CF: Contamination factor, Cd: cadmium, Cu: copper: Cr: chromium, Hg: mercury, Ni: nickel, Se: selenium

3.6.3 Contamination factor (CF)

The level of contamination of heavy metals in sediments is expressed in terms of a contamination factor (CF). Contamination Factors (CFs) are derived, using background concentrations or baseline or concentration of the element of interest in an unpolluted area (Tomlinson *et al*, 1980; El-Sammak and Abdul-Kassim, 1999; Adomako *et al*., 2008). It is expressed by the equation;

$$\text{CF.} = \frac{\text{C metal}(mg/\text{kg})}{\text{C background value (mg/kg)}}$$

where the contamination factor CF < 1 means low contamination; 1 ≤ CF < 3 indicates moderate contamination; 3 ≤ CF ≤ 6 represents considerable contamination and CF > 6 means very high contamination. C metal sample concentration and C background is background concentration.

3.6.4 Geoaccumulation Index

Geoaccumulation Index (Igeo) quantitative approach was used to quantify the degree of anthropogenic contamination in sediments from the Volta Estuary. The Igeo values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al*., 2008). The Igeo for each analysed metal was calculated using the formula;

$$\text{Igeo} = \text{Log}_2 (\text{Cn}/1.5 \times \text{Bn}),$$

where Igeo is the Geoaccumulation Index, Cn is the measured content of element in sediment, and Bn the element's content in "average shale" (background concentration) (Turekian and Wedepohl, 1961) and 1.5 is a constant.

3.6.5 Biota – Sediment Accumulation Factor (BSAF)

Biota – Sediment Accumulation Factor (BSAFs) were calculated from dividing tissue metal concentrations by the corresponding sediment metal concentrations, as represented in the equation below. The various clam sizes obtained for each sampling period was treated as a unit.

$$\text{BSAF.} = \frac{\text{Concentration of heavy metal in the organism}}{\text{Concentration of heavy metal in sediments}}$$ (Thomann *et al*., 1995)

3.7 Health Risk Assessment Associated with the Consumption of Clams from Ada and Aveglo

The health risk posed by the consumption of *Galatea paradoxa* from the Volta estuary of the metals under studied was assessed in comparison to that carried out by (Fung *et al.*, 2004). Risk quotient (RQ) was calculated as the ratio between concentration of trace element in the *Galatea paradoxa* and the level of concern (LOC) for that metal (Fung *et al.*, 2004). 2004). Thus, the level of concern (LOC), which is a threshold concentration of a chemical above which a hazard to human health may exist, was calculated as the ratio of Tolerable Daily Intake (TDI) and the Rate of Shellfish Consumption (RSC) (Fung *et al.*, 2004).

$$\text{Level of Concern (LOC)} = \frac{\text{Tolerable Daily Intake (TDI)}}{\text{Rate of Shell Fish Consumption (RSC)}}$$

$$\text{Risk Quotient (RQ)} = \frac{\text{Concentration of element in clam}}{\text{Level of Concern (LOC)}}$$

Data on average national rate of shellfish consumption (RSC) was calculated from the Daily Food Supply per capita from Fish and Fishery Products of the FAO (FAOSTAT 2004) which estimates the daily food supply from fish and fishery products in Ghana to

be 62.6 g/person/day. The national daily rate of shellfish consumption was estimated to be 0.95 g/person/day (Obirikorang, 2010).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Metal Concentrations in Clams and Sediments

The mean of the various metal concentrations determined in clam tissues from Ada and Aveglo sampling sites expressed in mg of metal per kg of clams on wet weight basis are reported in Table 4.1. The results for the metal concentrations recorded in sediment samples from the two sampling sites are expressed in mg of metal per kg of sediment (dry weight) are reported in Table 4.2. The measured concentrations of the elements raw data in individual clam tissue samples from the two sampling areas are given in Appendix 2.

Cadmium (Cd) concentrations in *Galatea paradoxa* across the two sampling sites ranged between 0.07 and 0.17 mg/kg. Samples from Ada sampling location recorded the lowest average Cd concentration of 0.09 mg/kg in February, 2012 in large clams, 0.15 mg/kg in medium class sized and a higher mean value of 0.17 mg/kg in small sized clams were all recorded in September, 2011 respectively.

Samples from Aveglo sampling point recorded the lowest average Cd level of 0.07 mg/kg in large clams; 0.13mg/kg for the medium, and 0.15 mg/kg for the small clams. These results were registered in November, 2011.

The mean chromium (Cr) levels in clam tissues from the studied areas ranged between 2.01 and 24.10 mg/kg. The least value of 2.01 mg/kg and the highest value of 24.10 mg/kg were obtained in small and large clams in February, 2012 and the medium had a high mean of 16.91 mg/kg in September, 2011 for Aveglo. The Ada site recorded both the lowest and highest values of 3.42 mg/kg and 20.51 in November, 2011. The medium category had a high value of 19.28 mg/kg was obtained in September, 2011.

Means copper (Cu) concentration recorded at the two sampling locations ranges from 0.55 mg/kg to 3.65 mg/kg respectively. The mean Cu concentrations in clam tissues recorded at the Ada sampling point were 0.55 m/kg and 2.84 mg/kg for small and medium clam sizes sampled in November, 2011, and 3.10 mg/kg in large clam size. However, concentrations of 0.79 mg/kg, 2.81 mg/kg were recorded in small and medium clam sizes in September, 2011 and 3.65 mg/kg in large clam sizes was observed in February, 2012 at Aveglo.

Mean mercury (Hg) concentrations in clam tissues from the studied areas ranged between 0.04 and 0.12 mg/kg. A low value of 0.05 mg/kg and a high value of 0.12 mg/kg respectively were obtained in small and large clam tissues in September, 2011. The medium clam size recorded the highest mean Hg levels of 0.08 mg/kg in February, 2012 samples at Ada. Mean Hg levels in samples from the Aveglo site ranged from 0.04mg/kg to 0.09 mg/kg respectively in the small and large clams in September, 2011 and November, 2011 whilst the medium sized clams had an average Hg concentration of 0.07 mg/kg in February, 2012.

Mean nickel (Ni) concentrations recorded at the sampling sites ranged between 5.49 and 28.14 mg/kg. Ada recorded the highest average Ni concentration of 27.96 mg/kg in medium size clams sampled in September, 2011; followed by the 23.70 mg/kg obtained in the large clams in September, 2011 whilst the small clams registered the least mean level of 5.49 mg/kg. The Aveglo sampling station registered the highest nickel levels of 28.14 mg/kg in medium class sized clam in September, 2011 whilst the large clam sized recorded 25.65 mg/kg in September, 201. Also, the small clam recorded the least value of 10.25 mg/kg in September, 2011 for the Aveglo station.

The selenium *(Se)* concentrations ranged between 0.13mg/kg and 0.49 mg/kg at the two sampling locations. The Ada sampling site registered the highest concentration of 0.49 mg/kg in small clams in November, 2011; 0.40 mg/kg in the medium clams in November, 2011 and 0.34 mg/kg for large clams in September, 2011.

The Aveglo sampling station recorded the highest value of 0.29 mg/kg for the small clams in November, 2011. The medium clams recorded a mean value of 0.27 mg/kg in November, 2011 whilst the large clams registered a low value of 0.13 mg/kg in September, 2011.

Table 4.1: *Mean ± Standard Deviation (SD) of heavy metals concentration (mg/kg) in clam tissues from the Volta Estuary Ada.*

ADA SAMPLING SITE

PERIOD	SIZE	Cd	Cr	Cu	Hg	Ni	Se
Sept.,2011	SN	0.17±0.02	3.49±1.56	1.16±0.75	0.05±0.02	5.49±1.88	0.43±0.13
	DD	0.15±0.05	19.28±7.46	1.87±1.70	0.07±0.03	27.96±5.25	0.39±0.14
	TZ	0.12±0.04	19.76±4.64	3.08±2.45	0.12±0.04	23.70±6.87	0.34±0.09
Nov.,2011	SN	0.16±0.04	3.42±1.98	0.55±0.22	0.07±0.02	9.34±2.24	0.49±0.10
	DD	0.12±0.04	17.14±6.85	2.84±1.63	0.07±0.02	20.28±9.68	0.40±0.24
	TZ	0.10±0.04	20.51±2.57	2.72±1.45	0.09±0.02	25.64±6.80	0.35±0.13
Feb., 2012	SN	0.16±0.02	4.30±2.21	0.89±0.81	0.06±0.02	9.52±3.81	0.46±0.09
	DD	0.13±0.04	16.42±8.48	0.91±0.89	0.08±0.04	25.22±5.99	0.34±0.13
	TZ	0.09±0.02	18.94±3.53	3.10±1.62	0.06±0.03	24.67±6.90	0.37±0.08

SN – Small, DD – Medium, TZ – Large

Table 4.2: *Mean ± Standard Deviation (SD) of heavy metals concentration (mg/kg) in clam tissues from the Volta Estuary Aveglo.*

		AVEGLO SAMPLING SITE					
PERIOD	**SIZE**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Se**
Sept.,2011	GA	0.13±0.03	2.05 ±0.67	0.79±0.84	0.04±0.02	10.25±2.62	0.27±0.07
	MV	0.12±0.04	16.91±6.03	2.81±1.79	0.06±0.05	28.14±4.83	0.24±0.09
	FL	0.10±0.05	19.31±6.25	3.57±1.26	0.09±0.05	24.30±4.79	0.13±0.06
Nov.,2011	GA	0.15±0.02	3.69±2.13	0.85±0.79	0.04±0.02	10.41±4.93	0.29±0.12
	MV	0.13±0.04	13.06±7.31	2.30±2.81	0.05±0.02	25.51±6.12	0.27±0.07
	FL	0.07±0.03	19.49±3.15	2.82±2.26	0.07±0.02	25.65±3.65	0.19±0.22
Feb.,2012	GA	0.14±0.02	2.01 ±0.55	0.88±0.81	0.05±0.02	11.71±4.79	0.23±0.10
	MV	0.10±0.04	12.23±4.62	1.27±0.69	0.07±0.03	27.04±5.22	0.25±0.07
	FL	0.08±0.03	24.10±4.22	3.65±3.81	0.08±0.04	25.06±3.31	0.18±0.17
WHO/FAO(1984)		**1.0**	**13.0**	**20.0**	**0.5**	**80.0**	**0.5***

GA – Small, MV – Medium, FL – Large

4.1.1 Metals Concentration in Sediment Samples

The cadmium concentrations obtained over the sampling period did showed slight variation. The lowest and highest concentrations recorded at Ada were 0.06 and 0.12 mg/kg in November, 2011 and February, 2012. The Aveglo sampling station recorded concentrations of 0.05 and 0.09 mg/kg respectively in February, 2012 and November, 2011.

The concentration of chromium in sediments from the two sampling sites ranged between 12.68 and 19.86 mg/kg. The Ada sampling station recorded the lowest concentration of 12.68 mg/kg in November, 2011 whilst Aveglo registered the highest value of 19.86 mg/kg in September, 2011.

However, the copper concentration over the period ranged between 63.22 and 106.75 mg/kg. Copper concentration in sediments at Ada recorded the highest results of 106.75 mg/kg whereas Aveglo recorded the least concentration of 63.22 mg/kg. These results were all registered in November, 2011.

The concentrations of mercury in sediments recorded indicated a minimum of 0.03 mg/kg and a maximum value of 0.08 mg/kg in November 2011 at Aveglo and Ada respectively.

The nickel concentrations ranged between 39.36 and 64.11 mg/kg from the two locations. The Aveglo station registered both the minimum and the maximum concentrations of 39.36 mg/kg and 64.11 mg/kg in November and September, 2011 respectively, whilst the Ada station showed a least and a maximum concentrations of 43.55 and 51.03 mg/kg in the months of February, 2012 and November, 2011 respectively.

With selenium concentration in the sediment samples ranged between 0.36 and 0.43 mg/kg. The Ada sampling site recorded a least and a high values of 0.39 and 0.43 mg/kg in September, 2011 and November, 2011 respectively. The sampling location at Aveglo recorded its minimum and maximum values of 0.36 and 0.41 mg/kg in November, 2011 and September, 2011 respectively during sampling period.

Table 4.3: *Concentrations of heavy metals in sediment from the Volta Estuary (Ada and Aveglo), during the study, (mg/kg) dw.*

PERIOD	SITE	Cd	Cr	Cu	Hg	Ni	Se
SEPT., 2011	ADA	0.10	17.45	94.81	0.04	46.89	0.39
	AVE	0.07	19.86	88.04	0.06	64.11	0.41
NOV.,2011	ADA	0.06	12.68	106.75	0.08	51.03	0.43
	AVE	0.09	15.94	63.22	0.04	39.36	0.36
FEB.,2012	ADA	0.12	14.96	68.29	0.07	43.55	0.40
	AVE	0.05	13.05	75.71	0.03	50.27	0.38

AVE – Aveglo

4.2 Impacts of Heavy Metal in Sediments on Aquatic Life.

Heavy metal concentrations are variable in sediments in Ghana thus, it was important to determine whether the concentrations found pose a threat to aquatic life. This was assessed firstly by comparison with sediment quality criteria.

Since Ghana has no established sediment quality guidelines at this time, the US National Oceanic and Atmospheric Administration (NOAA) and Canadian guidelines were used as interim measures to assess whether the concentrations of heavy metals in sediments could have adverse biological impacts (Table 4.4).

The threshold effects level (TEL) and Effects Range-Low (ERL) (Long *et al.,* 1995) for a particular sediment parameter are the concentrations below which adverse biological effects are expected to occur only rarely. TEL is generally recommended as the proposed interim Canadian Sediment Quality Guidelines (Anonymous, 2002), whiles ERL values are used in the NOAA Guidelines (Long *et al.,* 1995). Sediment results showed that copper and nickel at all sites sampled in the Volta estuary exceeded either the TEL or of Canadian Sediment Quality Guideline and ERL of NOAA Guidelines. This indicates that the existing concentrations of the two metals in these sediments are sufficiently high to cause adverse biological effects.

Table 4.4: *Guideline values for heavy metals of NOAA Guidelines and Canadian Sediment Quality Guidelines*

Metal	NOAA Guidelines		Canadian Guidelines		*Mean sediments metal concentrations(mg/kg)*	
	ERL	ERM	TEL	PEL	ADA	AVEGLO
Cadmium	1.2	9.6	0.7	4.2	0.09	0.07
Chromium	81	370	52.3	160	15.03	16.28
Copper	34	270	18.7	108	89.85	75.66
Mercury	0.15	0.71	0.13	0.7	0.06	0.04
Nickel	20.9	51.6	--	--	47.16	51.25
Selenium	--	--	--	--	0.41	0.38

Effects Range-Low: ERL; Effects Range-Median. ERM; Threshold Effect Level: TEL; Probable Effect Level: PEL. (mg/kg dry wt).

4.3 Total Metal Concentration and Distribution in Clams and Sediments

The values for clam tissue and sediment metal concentrations are presented on a bar chart in figures 4.1 and 4.2 respectively. The highest metal concentrations in sediment were observed for Cu and Ni, whereas Cd, Hg, and Se recorded higher concentrations in clam tissues at the Ada sampling site. Moreover, Cr metal concentration in sediment and the highest tissue metal concentration were almost the same at the Ada sampling station.

However, at the Aveglo sampling site high metal concentrations were observed for Cd, Cr, and Hg in clam tissues whiles Cu, Ni and Se exhibited higher concentrations in sediments.

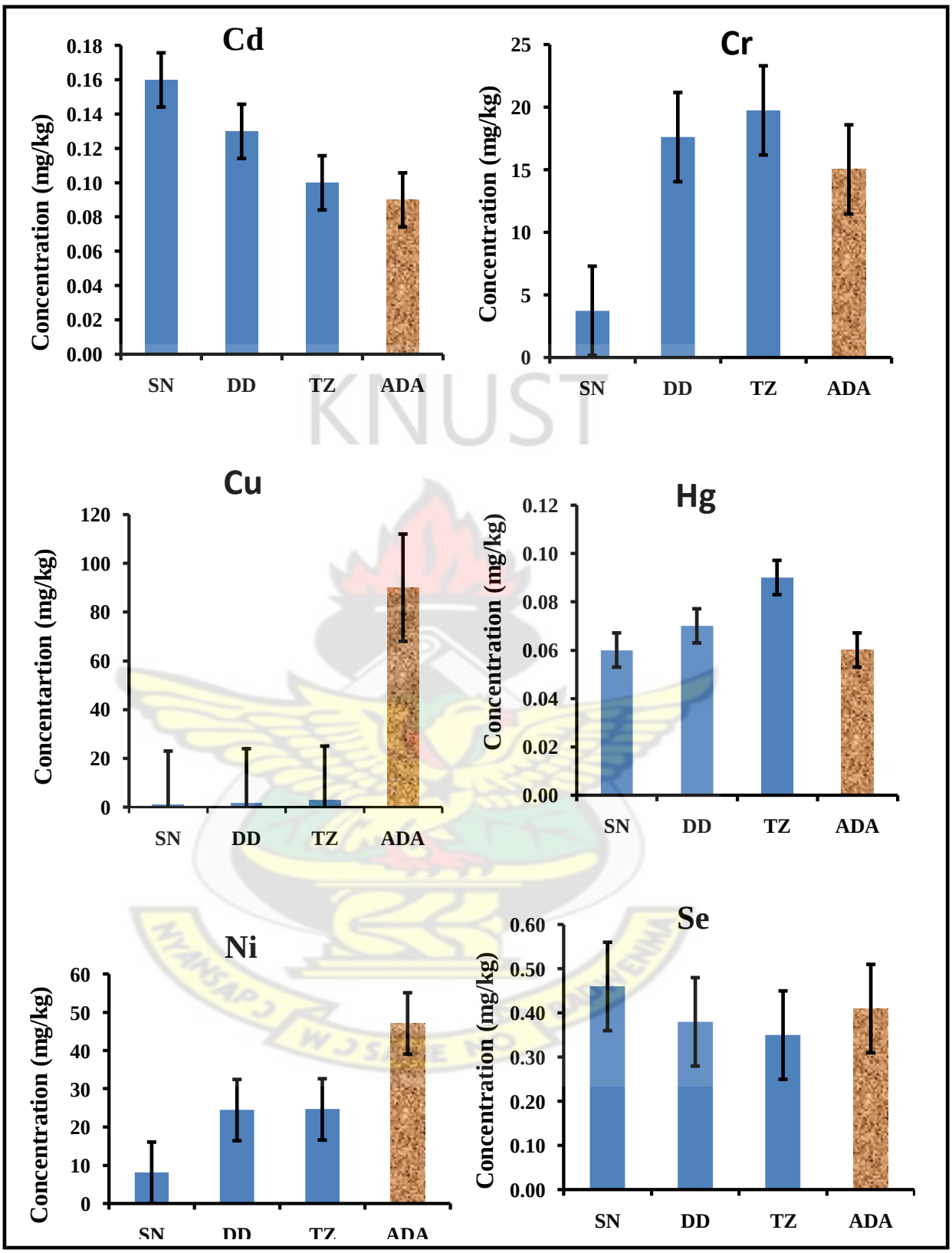

Figure 4.1: *Mean ± Standard Deviation (S.D) of Cd, Cr, Cu, Hg, Ni and Se Concentrations in Clam Tissues and Sediment at Ada. Clams: SN- Small, DD – Medium, TZ – Large and Ada – Sediment.*

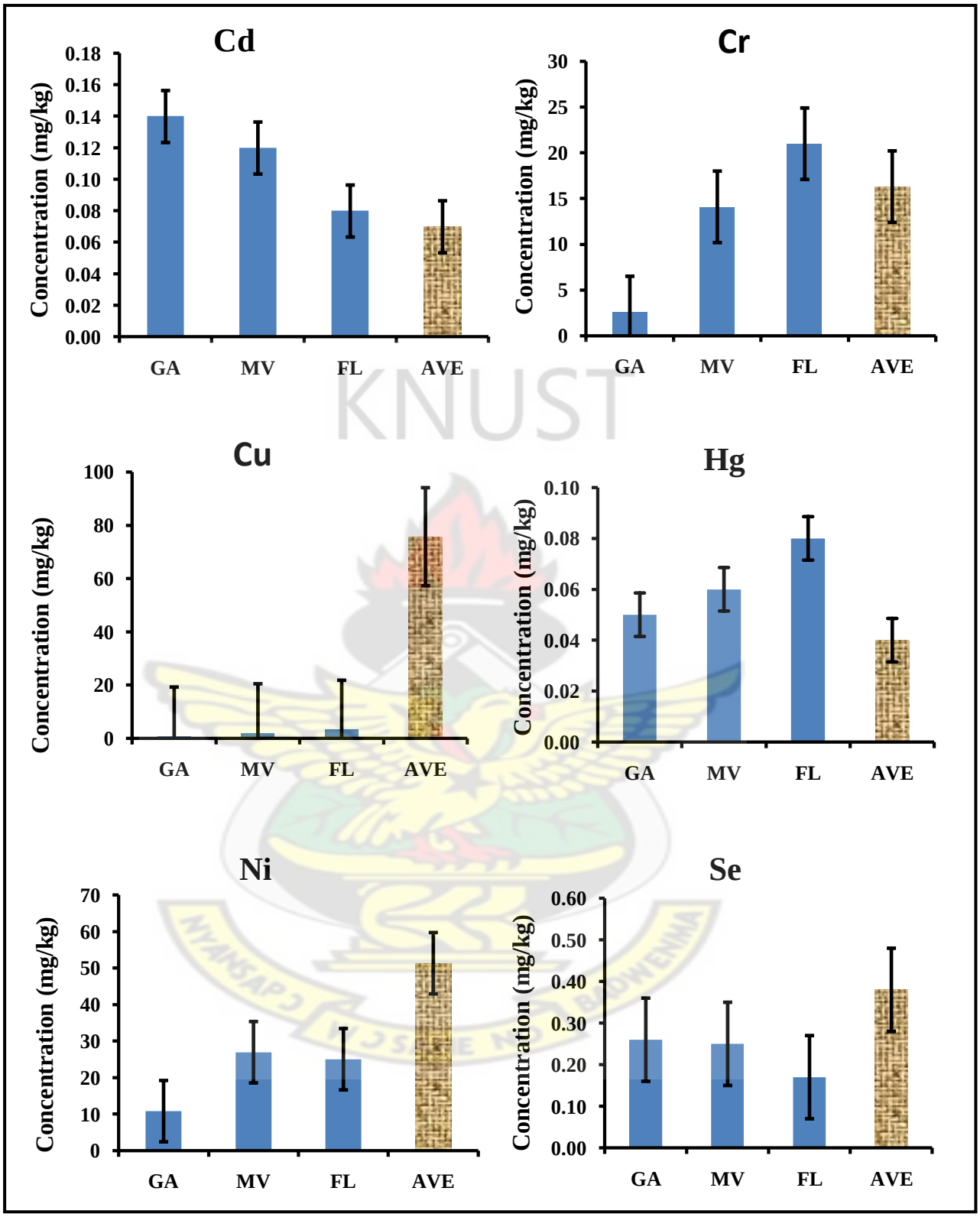

Figure 4.2: *Mean ± Standard Deviation (S.D) of Cd, Cr, Cu, Hg, Ni and Se Concentrations in Clam Tissues and Sediment at Aveglo. Clams: GA-Small,* MV – Medium, FL – Large and AVE – Sediment.

4.4 Variation in Heavy Metal Concentrations in Relation to Clam Size

The variations in heavy metal concentrations in the tissues of the *G. paradoxa* in relation to body size were carried out to investigate whether metal uptake, storage and accumulation varied with clam sizes. The concentrations of the six studied heavy metals in the whole soft tissues of the three clam size classes were subjected to one way ANOVA to compare the tissue concentrations of all the possible pairs of size classes; i.e. Small *vs.* Medium, Small *vs.* Large and Medium *vs.* Large for significant differences between the compared classes and to determine whether or not there are significant differences in the concentrations of the studied heavy metals as far as clam size was concerned.

The variations in levels of Cadmium and Copper among different clam size classes obtained from for the Ada sampling stations over the sampling period were significantly different ($p<0.05$). However, Chromium, Nickel and Selenium exhibited no significant difference ($p>0.05$) in mean concentrations between clam sizes (TZ and DD). Moreover, Total Mercury (THg), exhibited no significant difference in concentration between the means of (SN-Small and DD - Medium) and (DD – Medium and TZ - Large) in clams collected at Ada.

Moreover, mean concentrations of Cadmium and Chromium showed significant differences among the various clam size classes at the Aveglo sampling site. Nevertheless, copper and nickel showed no significant difference ($p > 0.05$) between the clam sizes (MV- Medium and FL - Large) whereas Total Mercury (THg) and selenium exhibited no significant difference ($p > 0.05$) in clam size (GA - Small and MV - Medium). Figure 4.3 and 4.4 below represents the mean concentrations recorded during the period of study at Ada and Aveglo.

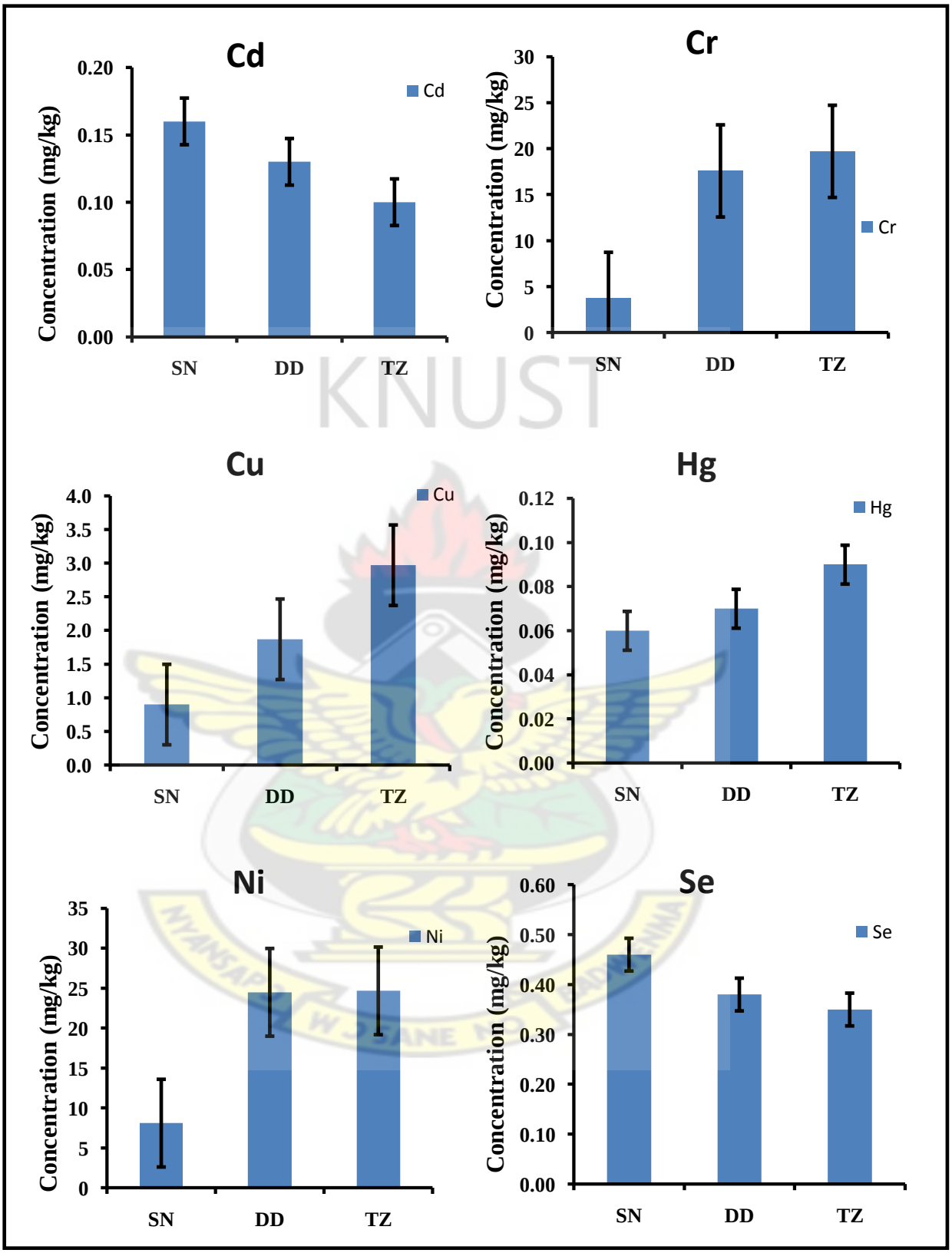

Figure 4.3: *Mean ± Standard Deviation (S.D) of heavy metals Cd, Cr, Cu, THg, Ni and Se in various calm sizes during the period of study at Ada. Clams: SN- Small, DD – Medium, TZ – Large*

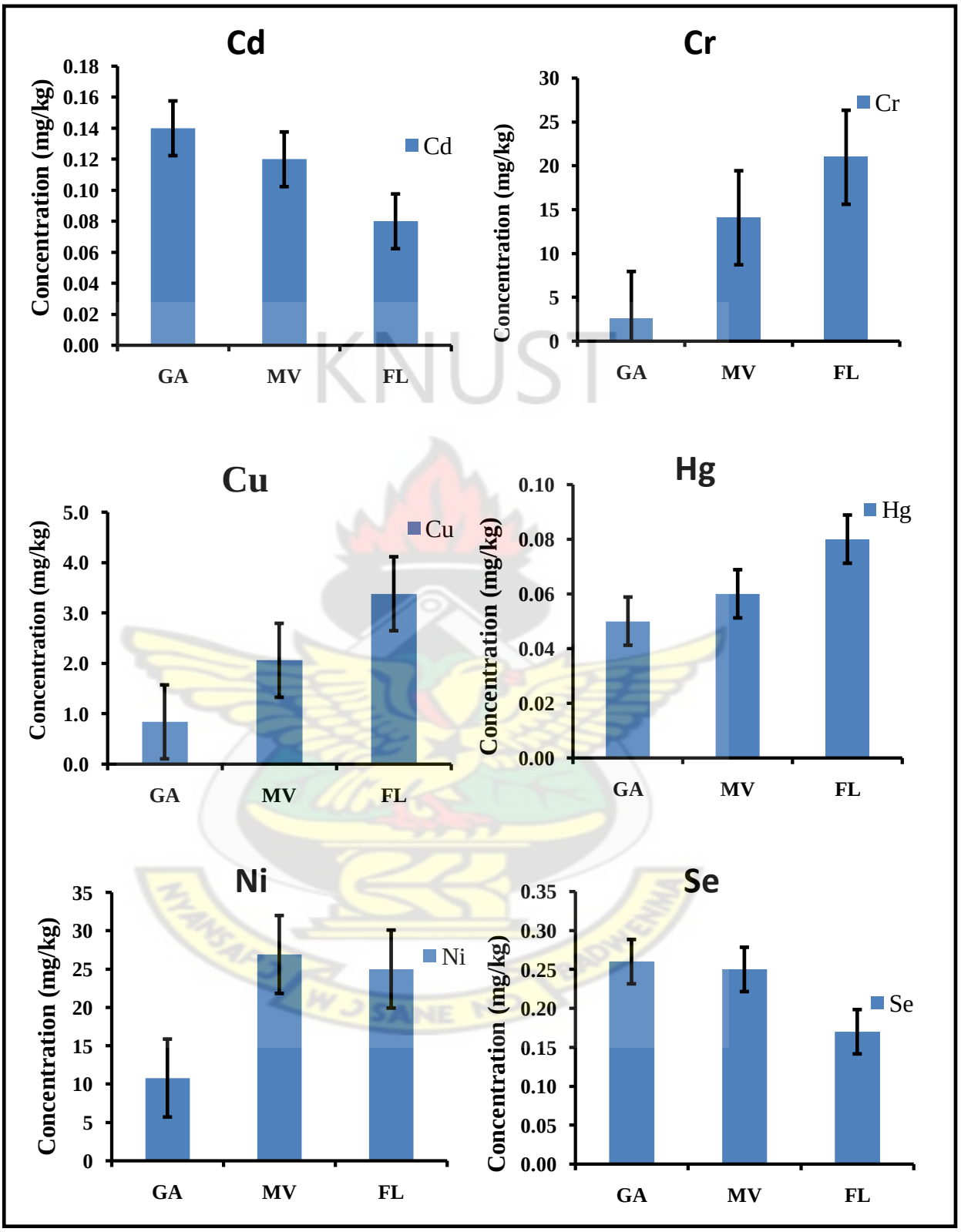

Figure 4.4: *Mean ± Standard Deviation (S.D) of heavy metals Cd, Cr, Cu, THg, Ni and Se in various clam sizes during the period of study at Aveglo. Clams: GA - Small, MV – Medium, FL – Large*

4.5 Human Consumption Levels

Heavy metals may accumulate to toxic levels which can lead to ecological damage. The accumulation of heavy metals from water column by bivalve molluscs has been shown to be relatively rapid and to reflect ambient exposure levels closely (Mauri, 2004; Yap, 2004; Usero et al; 2005, Wang, 2005). Hence, polluted aquatic environments would result in contaminated fish species which could threaten human health upon consumption.

Based on the standards by either the FAO/WHO, the US Food and Drug Administration (http://vm.cfsan.fda.gov), or the National Research Council (NRC) of the US National Academy of Sciences (NAS), the Tolerable Levels of Intake (TDI) and Estimated Safe and Adequate range of Daily Dietary Intake Levels (ESAADI) listed in Table 4.5, were used to calculate the relevant level of concern (LOC) for each metal due to the absence of available data on health criteria for these metals in Ghana. The LOC which is a threshold concentration of a chemical above which a hazard to human health may occur were evaluated and compared to the maximum concentrations obtained for the various metals analysed in this study.

It must be stated that the rate of exposure for heavy metals from shellfish consumption is a reflection of the national average shellfish consumption. The data may not be suitable for estimating exposures of particular individuals living along the coastal settlements and locations of active shellfish production, where more shellfish is consumed as expressed earlier by (Obirikorang, 2010).

Table 4.5: *Risk analysis for the minimum and maximum concentrations of metals present in the clam samples from Ada and Aveglo*

Metal	Min. conc. (ug/g)	Max. conc. (ug/g)	PDTI or ESAADI (ug/p/d)	RSC (g/p/d)	LOC1 (ug/g)	LOC2 (ug/g)	RQ_{wcs} 1-For (Min. conc.)	RQ_{wcs} 2- For (Max. conc.)
Cd	0.07	0.17	55[a]	0.95		57.89		0.0029
Cr	2.01	24.10	50 – 200[b]	0.95	52.63	210.52	0.0382	0.1145
Cu	0.55	3.65	2000 - 3000[b]	0.95	2105.26	3157.89	0.0003	0.0012
THg	0.04	0.12	33 – 43[c]	0.95	34.74	45.26	0.0012	0.0027
Ni	5.49	28.14	300[d]	0.95		315.79		0.0891
Se	0.13	0.49	50 - 200[e]	0.95	52.63	210.52	0.0025	0.0023

Legend:

TDI-Tolerable Daily Intake (in µg/person/day)

ESAADI-Estimated Safe and Adequate range of Daily Dietary Intake levels (in µg/person/day) for all foods set by the National Research Council of the National Academy of Sciences of the USA

RSC- Rate of Shellfish Consumption for Ghana calculated from the Daily Food Supply per capita from Fish and Fishery Products of the FAO (FAOSTAT, 2004- http:// apps.fao.org)

LOC1-Level of Consumption (in µg/g) calculated from the lowest value of TDI or ESADDI range

LOC2-Level of Consumption (in µg/g) calculated from the highest value of TDI or ESADDI range

RQwcs- Risk Quotient for worst-case scenario: 1-For lowest value of TDI or ESADDI range

2-For highest value of TDI or ESADDI range

[a]–Provisional Tolerable Daily Intake of cadmium (FAO/WHO, 2003); calculated from the PTWI for 60 kg human ($PTWI_{Cd}$=7 µg/kg body weight/week).

[b]–Estimated Safe and Adequate range of Daily Dietary Intake levels (in μg/person/day) for Cr, Cu and Ni set by the National Research Council of the National Academy of Sciences of the USA.

[c]–Provisional Tolerable Daily Intake of total mercury; set by FAO/WHO.

[d]-US Food and Nutrition Board (1980); Safe and Adequate range of dietary Selenium Intake.

4.6 Pollution Index Analysis of Sediment Samples

All the sediment samples had contamination factors (CFs) less than one (1) for Cd, Cr, Hg, Ni, and Se (Table 4.6). The only metal which recorded contamination factor greater than 1 throughout the sampling period and at all the sampling points was Cu. The Ada sampling point recorded CF values of Cu as 2.11, 2.37, and 1.52 whereas the Aveglo sampling point had CF values for Cu as follows 1.96, 1.40 and 1.68. The values were recorded in the order September, 2011; November, 2011 and February, 2012 respectively. As seen in Table 4.6, the two sampling points had Cu contamination factors (CFs) above 1. This implies that these sites are polluted with Cu. The likely sources may be mainly from anthropogenic activities.

The sampling points showed variations in the PLI values. Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al*., 1980; Cabrera *et al*., 1999).

However, all the sampling points had PLI values less than 1.0. The Ada sampling area registered PLI values of 0.43, 0.44 and 0.45. The Aveglo sampling point recorded PLI values of 0.46, 0.37 and 0.34 respectively.

Table 4.6: *Contamination Factors (CFs) and Pollution Load Indices (PLI) of heavy metals in sediments from the two sampling sites.*

		CFs						
PERIOD	SITE	Cd	Cr	Cu	Hg	Ni	Se	PLI
Sept., 2011	ADA	0.33	0.19	2.11	0.10	0.69	0.65	0.43
	AVE	0.23	0.22	1.96	0.15	0.94	0.68	0.46
Nov., 2011	ADA	0.20	0.14	2.37	0.20	0.75	0.72	0.44
	AVE	0.30	0.18	1.40	0.10	0.58	0.60	0.37
Feb., 2012	ADA	0.40	0.17	1.52	0.18	0.64	0.67	0.45
	AVE	0.17	0.15	1.68	0.08	0.74	0.63	0.34

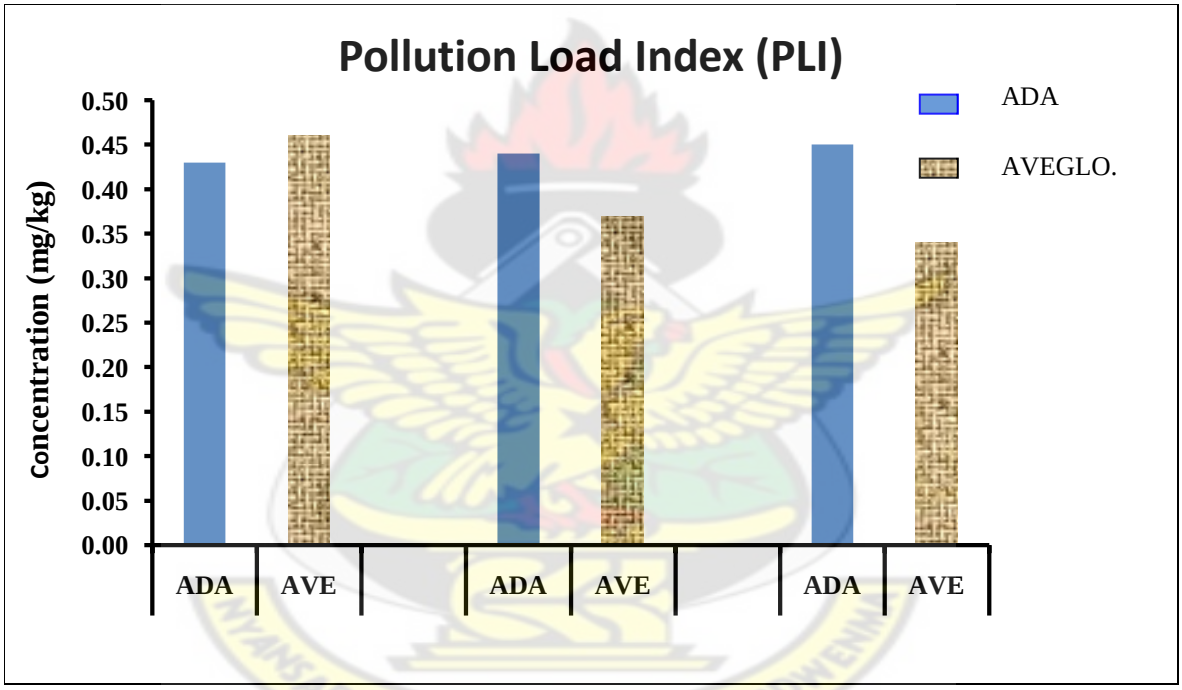

Figure 4.5: *A comparison of PLI values for sediments in the Ada and Aveglo.*

4.6.1 Geoaccumulation Index

The results for individual elemental geoaccumulation (Igeo) values for each sampling point are presented in Table 4.8. The sediments were classified using the table of seven classes of Geoaccumulation index values used by (Grzebisz *et al*., 2002, Lokeshwani and Chandrappa *et al*., 2007 and Yaqin *et al*., 2008) (Table 4.7).

The Igeo values indicated in (Table 4.8) for Cd, Cr, Hg, Ni, and Se were less than zero (0) for all the sampling points indicating practically unpolluted sediments. However, Igeo values for Cu were within the range <0 - 1.0 for all the sampling points, thus indicating an unpolluted to a moderately polluted sediment.

Table 4.7: *The seven classes of Geoaccumulation index values*

Igeo value	Igeo Class	Intensity of pollution
<0	1	Practically unpolluted
>0 -1	2	Unpolluted to moderately polluted
>1 - 2	3	Moderately polluted
>2 - 3	4	Moderately to strongly polluted
>3 - 4	5	Strongly polluted
>4 - 5	6	Strongly to very strongly polluted
>5	7	Very strongly polluted

Table 4.8: *Geoaccumulation Index (Igeo) of metals analyzed in sediment samples*

PERIOD	SITE	Cd	Cr	Cu	Hg	Ni	Se
SEPT.2011	ADA	-2.17	-2.95	0.49	-3.91	-1.12	-1.21
	AVE	-2.68	-2.77	0.38	-3.32	-0.67	-1.13
NOV., 2011	ADA	-2.91	-3.41	0.66	-2.91	-1.00	-1.07
	AVE	-2.32	-3.08	-0.09	-3.91	-1.37	-1.32
FEB., 2012	ADA	-1.91	-3.17	0.02	-3.10	-1.23	-1.17
	AVE	-3.17	-3.37	0.17	-4.32	-1.02	-1.24

4.6.2 Biota-Sediment Accumulation Factors (BSAFs) for Clams in the Ada and Aveglo Sampling Sites.

Biota – Sediment Accumulation Factor (BSAFs) shown in Table 4.9 were calculated from dividing tissue metal concentrations by the corresponding sediment metal concentrations. The average values for the BSAFs for all metals were less than 1 except for cadmium and mercury. This indicates that these metals accumulate at a slower rate in the clam. The interactions between the metal geochemistry and animal physiology determine the differences in the bioavailability among heavy metals (Wang *et al*, 2002).

Basically, BSAFs is the chemical distribution between biota and sediment thus, can vary between or within ecosystems both temporally and spatially. The relationship between concentrations of the studied contaminants in the clam tissues and sediments was not distinctive, supporting the fact that several variables control both the bioavailability and accumulation of heavy metals in the individuals exposed to contamination (Ansari *et al.*, 2004). Measured bioaccumulation factors are essential for predicting toxic effects on organisms and assessment of the ecological risk of chemical contaminants in the environments.

Table 4.9: *Average Biota-sediment accumulation factors (BSAFs) for G. paradoxa from Ada and Aveglo*

Element	Site	Tissue Metal Conc.	Sediment Conc.	BSAF
Cd	ADA	0.13	0.09	1.44
	AVE	0.11	0.07	1.57
Cr	ADA	13.70	15.03	0.91
	AVE	12.54	16.28	0.77
Cu	ADA	1.95	89.95	0.02
	AVE	2.31	75.66	0.03
Hg	ADA	0.07	0.06	1.17
	AVE	0.06	0.04	1.50
Ni	ADA	19.09	47.16	0.40
	AVE	20.90	51.25	0.41
Se	ADA	0.40	0.41	0.98
	AVE	0.23	0.38	0.61

4.7 Metals in Sediments and Clams

Comparative evaluation of metal concentrations in clams from the Volta estuary with WHO/FAO standards shows that the level of the metals studied were below WHO/FAO standards except for chromium which recorded higher concentrations in medium and large clams. Although the occurrence of copper and nickel in medium and large clams were high they were below the standard limits. This indicates that as the weight of *Galatea paradoxa* increases there is a proportional increase in the amount of chromium, copper, mercury and nickel accumulated in their tissues. This shows that there is an

increase in bioaccumulation over a period and that the *Galatea paradoxa* has a capacity of storing these metals in its body over time. This agrees with similar observation made for *E. radiata by* (Das *et al*., 2007). On the hand, for cadmium and selenium as the weight of *Galatea paradoxa* increased the amount of these heavy metals bioaccumulated in their soft tissues decreases. Based on the observations from this work metals can be divided into two groups: metals whose bioaccumulation depend on the size/weight; and metals showing decreasing bioaccumulation with size/ weight. This agrees with observation by Popham and D'Auria (1983), they found Zn concentrations to be independent of size in an uncontaminated area, but positively correlated with size in a polluted area.

The sediment analysis showed that copper at all sites sampled in the Volta estuary exceeded the TEL of Canadian Sediment Quality Guideline and ERL of NOAA Guidelines. Similarly, presented in Table 4.5, nickel concentrations at the two sites, exceeded either TEL or ERL values. This indicates that the existing concentrations of these metals in sediments are sufficiently high to cause adverse biological effects. Although there are no NOAA Guidelines for selenium the values were lower than 0.6 mg/kg the average shale level reported by (Turekian and Wadepohl, 1961), suggesting that the levels are not high enough to cause adverse environmental hazard.

4.8 Relationship between Metal Concentrations in Sediments and the Tissues of the Different Clam Size Classes.

There was no distinctive relationship between metal concentrations in sediments and tissues metal concentration. The observed cadmium, chromium and mercury concentrations in clam tissues were lower than those in sediments whiles copper, nickel and selenium to some extent showed high metal concentrations in sediments than clam tissues. Therefore, the mechanism for cadmium, chromium and mercury accumulation in clam tissues may differ from those of copper, nickel and selenium. Some studies have

established relationships between the metal concentration in sediments and bivalves for various heavy metals (Philips and Yim, 1981). Also in a study conducted in Tasmania, (Forstner and Wittman, 1979), a linear relationship between cadmium and copper in *Crassostrea gigas* and the concentration of same elements in sediments was observed. But (Huanxin et al., 1999.), found no simple linear relationship between metal concentrations in sediments and bivalves.

The results of analysis of sediment metal concentration and the whole soft tissue of the clams showed no definite relationship. Therefore, it maybe be suggested that, heavy metal accumulation in clams may not be directly or solely derived from sediments (Huanxin et al., 1999). Other sources of heavy metals in bivalve tissues may be derived from living or dead suspended particles and from dissolved metals in the water (Huanxin et al., 1999).

4.9 Relationship between Heavy Metal Concentrations in the Tissues of the Clams and Body Size

Comparing the different clam size classes (small vs. medium, small vs. large and medium vs. large) from the two sampling stations using one way ANOVA, significant differences ($p<0.05$) were observed for cadmium and copper concentrations in the tissues of the compared clam class sizes at Ada. The test for significance in mean concentrations of cadmium and chromium showed significant difference among their various clam sizes at the Aveglo sampling site. Although, the other metals exhibited no significant differences in relation to body size in some instances, it was observed that the *Galatea paradoxa* accumulate heavy metals irrespective of body.

Positive relationships between metal concentrations in whole body tissues and body size have been reported occasionally from a variety of bivalves and gastropods (Boyden 1974, 1977, Cossa, 1989, Odzak *et al.,* 1994). In this study body burdens of metals like

chromium, copper, mercury and to some extent nickel increase with body size of the *Galatea paradoxa* indicating a positive metal – size relationship. Hence, these positive relationships observed in some mollusc species have been explained in terms of extremely slow rates of elimination of a metal from the body of an organism with non-regulatory uptake (Langston and Zhou, 1987a, 1987b).

However, Cd and Se concentrations in clams tissues decreased with increasing body size which is an indication that large clam sizes appears to have some regulatory mechanism to regulate to some extent the accumulation of these metals. This is probably due to the well known effect of 'dilution' of trace metal concentration due to enlargement of the body weight (Cossa, 1989; Phillips and Rainbow, 1993). Thus, it is an indication that metals vary in their rates of accumulation in *Galatea paradoxa.*

Although no distinctive source of pollution within the catchment area of the estuary was established, the variability of heavy metal concentrations can also be caused by changes in the physiological conditions of the clams (Phelps *et al*., 1985; Ferreira *et al*., 2004) and environmental parameters including temperature, pH, salinity, oxygen concentrations (Phillips, 1976; Luoma and Bryan, 1982). Therefore, given the variations in natural sources of metals in the Volta Lake and natural factors affecting their accumulation in clams, the variations of results in the Volta clam are to be expected.

4.10 Human Health Implications from the Consumption of Clams from the Volta Estuary

Calculation of the risks associated with consumption of the clams from the Volta estuary was carried out to ascertain whether it poses a threat to the health of human consumers. It is noteworthy that, the evaluation of Risk Quotient for worst-case scenario (RQwcs) provides a convenient way of examining chemicals that may require a more refined

analysis. For cases where RQ<1 the chemicals involved are unlikely to cause harm to human consumers (Fung *et al.*, 2004). The RQ's of all the metals were lower than "1.0", suggesting that probably no health associated problems might be encountered, at least not for moderate shellfish consumers.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results of this study indicate that the clam *Galatea paradoxa* is a useful organism to be used for monitoring heavy metal pollution of the environment. Also, the ability of the clam to accumulate cadmium, chromium, copper, total mercury, nickel and selenium shows that the *Galatea paradoxa* can be used to reflect longer term exposure to environmental contamination by these metals. However, the use of the clams as monitors of heavy metal contamination in local coastal waters will require further investigations to develop appropriate mechanisms for their use.

The accumulation and uptake of metals by benthic organisms is greatly affected by many factors (metal - sediment chemistry, type of organism, temperature, chelating agents and others), and it is almost impossible to predict bioaccumulation using simple models with a single or few indicators. The concentrations of essential and non – essential elements obtained in the tissues of the clams and sediment samples varied significantly at both sampling sites with no distinctive relationship was established between sediment metals concentration and clam tissue metals concentration. This indicates that the clam *Galatea paradoxa* tends to regulate the levels of these heavy metals in their tissues, and may not reflect the levels in sediments from which they are exposed.

The health risk associated with the consumption of the clam species with regards to the five metals (Cd, Cr, Cu, Ni and Se) is minimal. Although the concentration of chromium in medium and large clams was higher than the WHO/ FAO standard, the evaluation of

the Risk Quotient was lower than one (RQ<1) suggesting that probably no health associated problems might be encountered, at least not in moderate shellfish consumers.

Sediment results showed that copper at all sites sampled in the Volta estuary exceeded the TEL of Canadian Sediment Quality Guideline and ERL of NOAA Guidelines. Similarly, nickel concentrations at the two sampling sites, exceeded their respective TEL or ERL values. This is an indication that the existing concentrations of these metals in the sediments are sufficiently high to cause adverse biological effects.

5.2 Recommendations

In view of the results obtained in this study, it is recommended that:

1. There should be an effort to protect Volta Lake especially the estuary from pollution to reduce environmental risks and this study may provide valuable data for future research on the Volta estuary. This is to minimize shellfish and fish food contamination which will in turn reduce clinical poisoning in humans who consume *Galatea paradoxa* and other fishery products from the Volta estuary.
2. In regards to this result of Cr concentration over WHO/FAO legal limits in medium and large clam sizes, more extensive investigation is required to confirm this result further.
3. Future studies should be made to compare metal concentrations in the shell of the organism to the soft tissues and sediments. A holistic study which would encompass the collection and measurement of metals in the water column, sediments, soft and hard tissues of the benthic organisms studied and also a look at the possible sources of heavy metals in the estuary.

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APPENDIX 1: Physical Measurements of the clam size classes

September 2011, Ada

Size Class	Length (mm)	Width (mm)	Weight (g)	Wet Weight (g)
SMALL (SN)	32.3	21.6	24.07	2.12
	27.9	21.7	16.54	0.57
	24.1	19.3	11.87	0.39
	34.6	23.9	26.57	2.03
	29.8	23.6	18.64	1.64
	32.5	24.3	21.02	1.97
	26.4	20.7	16.65	0.49
	37.5	28.4	23.72	2.78
	35.8	25.6	24.66	2.14
	25.7	19.1	15.76	0.27
MEDIUM (DD)	54.8	44.4	49.27	5.93
	43.1	38.5	45.88	4.34
	41.8	35.8	31.43	3.45
	50.7	40.1	41.12	4.89
	51.9	42.8	40.23	4.65
	48.5	34.8	23.12	2.35
	42.6	30.4	26.55	2.89
	49.7	35.2	30.62	3.88
	53.2	42.9	43.21	5.03
	49.6	37.6	31.44	3.73
LARGE (TZ)	76.9	70.6	68.93	14.69
	67.4	59.7	62.65	12.18
	56.2	42.8	45.17	6.45
	60.7	49.7	53.48	7.36
	68.4	57.2	62.09	10.87
	62.8	55.6	51.83	8.12
	64.8	53.9	56.44	8.95
	88.1	80.8	81.56	18.27
	59.3	47.1	45.72	6.88
	63.5	52.9	60.04	10.23

November 2011, Ada

Size Class	Length (mm)	Width (mm)	Weight (g)	Wet Weight (g)
SMALL (SN)	28.8	22.8	17.66	0.67
	30.7	19.9	26.55	1.09
	29.6	22.4	18.84	1.59
	26.6	17.1	14.65	0.81
	29.8	22.8	30.97	1.95
	30.5	23.1	25.44	1.08
	29.7	22.4	18.66	1.69
	28.1	21.3	27.58	2.55
	27.8	21.1	16.57	1.41
	33.9	25.7	22.89	2.46
MEDIUM (DD)	44.6	32.9	28.94	3.44
	54.6	43.8	42.56	6.01
	42.8	31.5	26.23	3.12
	51.3	42.5	38.17	6.11
	54.1	45.1	42.09	4.27
	46.8	35.7	28.35	4.56
	50.5	40.3	36.76	5.45
	49.1	39.5	31.88	4.81
	47.6	36.2	29.39	3.37
	45.7	34.4	30.15	4.23
LARGE (TZ)	57.6	46.2	56.88	8.74
	65.1	57.4	60.23	11.24
	66.5	58.8	65.46	12.18
	74.7	50.9	48.91	13.84
	87.8	74.3	93.59	18.39
	55.3	42.2	40.59	8.06
	69.9	60.7	61.10	10.55
	59.1	51.1	47.33	6.76
	60.4	49.9	54.72	7.96
	86.2	78.6	81.63	20.61

February 2012, Ada

Size Class	Length (mm)	Width (mm)	Weight (g)	Wet Weight (g)
SMALL (SN)	31.5	20.9	23.55	1.99
	30.9	21.6	22.54	1.29
	38.7	31.8	26.57	3.89
	39.5	30.1	24.06	2.79
	38.5	29.6	23.73	2.45
	32.9	21.7	25.09	2.24
	27.6	21.1	15.55	0.49
	35.1	26.5	20.75	2.67
	26.4	20.9	16.57	0.38
	37.3	29.7	28.66	2.87
MEDIUM (DD)	48.7	38.5	29.74	5.89
	49.7	40.8	44.69	4.99
	54.9	44.3	39.15	3.15
	53.8	41.7	37.48	5.07
	50.8	43.4	46.94	8.79
	41.6	30.2	24.56	2.68
	54.6	46.1	41.22	6.53
	48.7	39.6	31.21	4.06
	43.9	35.2	48.06	7.28
	52.1	45.4	45.98	9.12
LARGE (TZ)	67.1	56.5	69.81	10.55
	63.6	52.1	79.57	18.69
	64.5	55.1	59.55	11.02
	58.9	46.9	66.14	13.43
	70.4	63.8	86.86	15.47
	81.8	74.7	101.37	26.58
	64.1	58.7	56.34	9.94
	76.2	64.9	78.01	22.26
	63.8	52.2	57.33	9.72
	59.2	47.1	70.56	12.74

September 2011, Aveglo

Size Class	Length(mm)	Width(mm)	Weight (g)	Wet Weight (g)
SMALL (GA)	28.5	24.8	10.70	1.28
	37.9	30.1	22.35	2.45
	34.7	28.6	18.61	1.78
	31.8	25.1	12.25	1.56
	36.9	29.5	21.25	2.23
	36.1	28.9	21.02	3.02
	27.9	22.9	10.79	1.07
	32.1	26.6	16.53	1.98
	38.2	30.3	25.66	4.31
	37.5	29.8	20.89	2.68
MEDIUM (MV)	45.9	37.7	33.62	4.85
	49.3	39.6	44.11	5.03
	48.6	38.1	41.37	4.99
	53.2	44.3	50.68	8.52
	47.1	35.7	34.77	2.69
	42.4	32.6	27.56	2.32
	49.8	36.8	40.68	5.74
	52.4	45.8	48.43	8.47
	47.6	37.4	44.70	6.31
	43.3	34.9	42.93	4.74
LARGE (FL)	87.2	79.3	72.43	16.22
	58.4	46.6	48.06	10.45
	61.5	49.9	52.24	11.89
	56.9	43.5	40.37	7.71
	58.7	47.1	70.01	9.35
	63.8	51.8	51.80	8.44
	66.4	55.8	72.56	9.69
	59.5	47.6	77.45	10.50
	84.6	76.7	101.09	13.26
	64.1	53.1	49.37	9.54

November 2011, Aveglo

Size Class	Length(mm)	Width(mm)	Weight (g)	Wet Weight (g)
SMALL (AV)	30.5	23.8	14.40	1.64
	24.7	19.8	12.99	0.76
	36.6	22.9	17.52	2.01
	37.2	29.6	19.25	2.32
	37.7	23.1	25.01	2.65
	34.9	28.9	18.15	1.86
	36.9	21.7	22.29	2.45
	35.4	28.6	18.99	2.32
	33.5	28.7	15.89	1.99
	26.8	22.8	13.97	0.64
MEDIUM (MV)	46.6	35.5	42.42	3.90
	47.8	36.1	41.82	5.78
	50.5	42.8	48.69	4.39
	41.6	35.3	41.20	4.78
	45.8	33.1	42.09	3.61
	48.8	38.4	39.85	3.34
	43.3	32.5	36.13	4.02
	54.1	43.1	48.70	8.96
	55.7	46.8	39.66	6.38
	52.4	45.7	43.22	7.77
LARGE (FL)	60.7	49.5	87.16	10.51
	86.6	76.7	100.48	25.39
	57.1	46.1	60.15	8.67
	84.5	76.8	107.31	20.06
	58.1	43.3	40.96	7.83
	65.8	55.6	60.34	8.36
	64.9	52.9	48.45	11.09
	62.4	50.2	49.93	9.66
	58.8	47.4	52.46	13.65
	80.2	74.1	92.73	17.39

February 2012, Aveglo

Size Class	Length(mm)	Width(mm)	Weight (g)	Wet Weight (g)
SMALL (GA)	28.0	21.7	15.94	1.12
	35.5	26.9	24.30	2.98
	39.8	33.8	25.25	3.35
	38.2	32.6	22.78	3.04
	25.8	17.8	12.01	0.99
	36.9	29.6	17.23	2.34
	26.7	20.5	13.78	1.08
	37.1	31.7	20.67	2.05
	38.8	32.7	25.04	2.54
	39.3	30.6	24.83	3.24
MEDIUM (MV)	51.4	44.5	53.76	8.35
	47.2	35.9	36.72	5.14
	45.2	34.7	19.03	2.86
	52.1	45.9	32.56	5.94
	47.4	36.3	25.50	2.72
	42.6	31.1	18.88	2.53
	46.6	34.9	24.65	3.61
	50.8	44.2	39.01	4.99
	49.5	38.6	40.78	5.15
	45.2	36.7	39.84	4.33
LARGE (FL)	59.8	47.9	55.61	15.04
	81.4	71.3	92.74	19.65
	67.1	56.8	53.12	15.18
	59.9	48.6	64.01	12.22
	70.5	59.9	80.5	16.98
	68.6	58.5	42.33	8.13
	86.9	75.4	87.16	14.62
	77.4	54.8	71.9	17.34
	56.9	45.8	60.9	12.87
	61.7	52.5	50.72	9.33

APPENDIX 2: Concentration of various metals (mg/kg) in individual clam size species.

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (TZ)
September, 2011	Cadmium (Cd)	0.14	0.05	0.05
		0.19	0.10	0.15
		0.20	0.18	0.14
		0.18	0.12	0.13
		0.17	0.18	0.12
		0.17	0.19	0.13
		0.18	0.18	0.11
		0.16	0.17	0.06
		0.15	0.17	0.16
		0.18	0.18	0.10
November, 2011		0.18	0.12	0.07
		0.08	0.07	0.06
		0.14	0.16	0.08
		0.19	0.05	0.14
		0.10	0.08	0.03
		0.18	0.14	0.14
		0.17	0.14	0.11
		0.17	0.11	0.16
		0.18	0.14	0.12
		0.17	0.16	0.05
February, 2012		0.16	0.16	0.08
		0.17	0.13	0.06
		0.13	0.16	0.09
		0.18	0.13	0.12
		0.14	0.06	0.05
		0.15	0.17	0.07
		0.18	0.14	0.12
		0.14	0.15	0.10
		0.18	0.08	0.10
		0.12	0.10	0.07

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (TZ)
September, 2011	Copper (Cu)	1.20	3.51	4.36
		0.07	4.38	2.95
		ND	ND	ND
		2.51	ND	1.21
		ND	0.60	4.88
		1.29	ND	ND
		ND	ND	0.31
		0.88	0.21	6.96
		1.46	1.70	ND
		0.74	0.81	0.90
November, 2011		ND	ND	2.83
		0.40	5.20	3.00
		ND	ND	2.35
		ND	4.52	ND
		0.74	3.01	3.83
		ND	2.65	1.90
		0.35	3.21	0.21
		0.83	1.00	2.44
		ND	0.50	ND
		0.41	2.59	5.21
February, 2012		0.33	0.73	2.87
		0.30	0.10	3.50
		1.62	0.14	1.56
		0.12	ND	0.90
		0.41	2.80	4.53
		1.91	ND	5.72
		ND	0.40	ND
		0.40	0.60	3.81
		ND	1.51	1.21
		2.01	1.01	3.84

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (TZ)
September, 2011	Chromium (Cr)	3.95	26.63	24.59
		2.44	24.51	22.00
		2.34	2.59	15.54
		6.88	21.81	18.70
		3.99	21.01	20.98
		3.62	9.36	20.55
		3.34	21.51	22.19
		3.00	19.65	25.33
		4.40	21.71	9.53
		0.93	24.00	18.20
November, 2011		0.66	22.17	17.86
		3.28	23.50	21.14
		6.31	8.58	23.51
		1.86	24.53	18.88
		5.11	15.20	24.98
		4.41	22.10	20.40
		2.74	17.32	17.78
		6.10	13.23	20.75
		1.43	4.00	22.35
		2.30	20.72	17.46
February, 2012		3.61	2.79	19.84
		3.75	20.40	19.12
		6.31	18.80	17.15
		7.98	12.00	14.62
		2.34	18.80	20.68
		6.91	1.70	24.50
		3.08	18.20	17.96
		1.77	20.25	20.30
		1.88	27.80	12.66
		5.39	23.50	22.57

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (TZ)
September, 2011	Mercury (Hg)	0.04	0.10	0.16
		0.03	0.09	0.11
		0.03	0.10	0.09
		0.09	0.07	0.07
		0.07	0.05	0.12
		0.06	0.04	0.07
		0.05	0.08	0.15
		0.05	0.05	0.14
		0.08	0.05	0.09
		0.04	0.11	0.18
November, 2011		0.08	0.06	0.07
		0.07	0.11	0.16
		0.04	0.05	0.08
		0.08	0.08	0.04
		0.09	0.09	0.13
		0.04	0.04	0.05
		0.09	0.07	0.08
		0.11	0.08	0.06
		0.05	0.04	0.09
		0.06	0.06	0.12
February, 2012		0.04	0.04	0.06
		0.05	0.06	0.08
		0.07	0.09	0.06
		0.06	0.07	0.05
		0.06	0.14	0.04
		0.08	0.05	0.13
		0.04	0.06	0.02
		0.05	0.04	0.08
		0.05	0.16	0.03
		0.09	0.06	0.07

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (TZ)
September, 2011	Nickel (Ni)	7.12	31.11	35.12
		4.73	28.11	28.40
		3.16	27.94	17.92
		9.81	31.15	18.21
		5.30	29.13	24.50
		4.34	24.18	18.40
		5.21	14.54	15.94
		4.33	30.83	33.61
		6.31	32.17	19.39
		4.56	30.47	25.51
November, 2011		9.00	8.92	20.90
		8.31	33.44	31.53
		7.58	10.96	33.84
		6.35	30.21	17.54
		10.36	25.60	32.50
		7.80	15.50	19.05
		11.11	21.62	20.55
		14.36	23.80	18.44
		9.44	4.98	31.36
		9.11	27.81	30.70
February, 2012		8.60	26.93	19.64
		12.91	29.13	32.17
		13.61	32.01	18.11
		15.00	22.50	20.03
		10.33	12.22	31.19
		7.00	24.53	34.21
		4.64	21.36	17.22
		5.90	27.87	26.48
		5.00	32.60	17.20
		12.16	23.00	30.49

Ada

Month	Metal	Small (SN)	Medium (DD)	Large (FL)
September, 2011	Selenium (Se)	0.31	0.06	0.31
		0.57	0.26	0.29
		0.56	0.46	0.50
		0.31	0.44	0.30
		0.39	0.37	0.38
		0.19	0.52	0.38
		0.52	0.53	0.30
		0.50	0.48	0.18
		0.44	0.32	0.39
		0.51	0.45	0.40
November, 2011		0.58	0.61	0.37
		0.57	0.07	0.29
		0.45	0.60	0.28
		0.60	0.09	0.42
		0.30	0.07	0.06
		0.46	0.63	0.51
		0.55	0.55	0.35
		0.39	0.39	0.48
		0.60	0.53	0.40
		0.42	0.50	0.31
February, 2012		0.40	0.45	0.43
		0.51	0.11	0.35
		0.44	0.40	0.34
		0.45	0.33	0.56
		0.40	0.25	0.32
		0.35	0.52	0.31
		0.60	0.28	0.37
		0.54	0.49	0.36
		0.58	0.39	0.39
		0.35	0.18	0.26

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Cadmium (Cd)	0.14	0.13	0.07
		0.10	0.11	0.16
		0.13	0.14	0.14
		0.16	0.03	0.14
		0.12	0.16	0.10
		0.11	0.18	0.13
		0.16	0.15	0.02
		0.14	0.07	0.05
		0.08	0.10	0.04
		0.14	0.13	0.15
November, 2011		0.15	0.13	0.04
		0.16	0.14	0.05
		0.13	0.08	0.07
		0.14	0.13	0.03
		0.12	0.17	0.09
		0.16	0.17	0.06
		0.13	0.18	0.08
		0.14	0.09	0.05
		0.15	0.15	0.12
		0.17	0.10	0.08
February, 2012		0.14	0.07	0.08
		0.16	0.04	0.03
		0.09	0.08	0.11
		0.16	0.06	0.04
		0.15	0.13	0.12
		0.15	0.14	0.09
		0.11	0.18	0.07
		0.16	0.14	0.05
		0.13	0.10	0.12
		0.14	0.08	0.10

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Copper (Cu)	ND	ND	5.90
		0.90	2.03	2.78
		ND	ND	3.94
		2.10	4.70	2.47
		1.41	ND	1.91
		ND	ND	2.08
		ND	ND	4.32
		0.04	4.60	3.77
		0.20	2.10	4.63
		0.09	0.60	3.90
November, 2011		0.21	ND	3.52
		ND	0.60	7.60
		2.31	1.22	ND
		ND	ND	3.63
		0.63	1.25	ND
		0.90	7.60	1.90
		ND	0.40	0.74
		0.96	4.80	2.28
		ND	ND	0.31
		0.11	0.23	2.59
February, 2012		0.21	0.76	1.52
		ND	1.90	6.00
		0.16	1.00	1.34
		ND	ND	10.51
		1.10	1.32	2.05
		ND	ND	2.66
		0.65	ND	9.93
		ND	2.50	0.63
		2.36	0.61	1.74
		0.82	0.83	0.11

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Chromium (Cr)	2.79	18.56	22.33
		1.65	21.05	20.78
		2.00	6.11	17.93
		1.93	24.91	14.58
		3.15	22.86	19.46
		1.77	7.96	16.24
		1.02	16.73	16.75
		1.69	16.90	29.37
		2.86	14.63	27.70
		1.66	19.40	7.99
November, 2011		1.75	8.30	17.81
		2.18	12.74	23.44
		2.13	16.56	16.00
		6.72	16.00	17.08
		7.93	14.24	18.00
		2.64	16.07	21.96
		4.56	0.74	24.79
		3.83	21.56	18.76
		3.16	2.18	15.88
		2.00	22.22	21.21
February, 2012		1.35	13.71	23.74
		1.90	14.40	30.88
		2.35	2.74	21.90
		2.00	16.83	26.83
		2.91	14.29	27.00
		1.79	11.96	21.86
		1.31	5.00	23.72
		1.50	13.50	25.12
		2.20	14.30	14.82
		2.75	15.60	25.15

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Mercury (Hg)	0.09	0.06	0.08
		0.03	0.02	0.11
		0.04	0.05	0.06
		0.08	0.04	0.15
		0.02	0.06	0.08
		0.04	0.15	0.06
		0.09	0.06	0.04
		0.03	0.14	0.06
		0.05	0.03	0.04
		0.03	0.02	0.18
November, 2011		0.08	0.03	0.09
		0.02	0.04	0.05
		0.07	0.05	0.06
		0.04	0.06	0.07
		0.03	0.03	0.06
		0.02	0.08	0.09
		0.02	0.05	0.04
		0.04	0.04	0.08
		0.08	0.06	0.09
		0.03	0.07	0.03
February, 2012		0.03	0.04	0.07
		0.04	0.05	0.08
		0.06	0.07	0.15
		0.05	0.03	0.14
		0.09	0.05	0.04
		0.04	0.08	0.07
		0.05	0.12	0.06
		0.07	0.06	0.07
		0.05	0.10	0.06
		0.06	0.08	0.09

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Nickel (Ni)	7.00	26.72	29.81
		13.21	29.32	17.18
		6.71	31.81	25.00
		10.43	32.01	23.90
		11.52	31.74	24.23
		9.33	22.31	15.26
		8.21	21.43	25.81
		12.21	33.91	26.90
		14.53	30.78	30.10
		9.31	21.39	24.83
November, 2011		5.11	30.60	21.90
		3.89	32.30	27.82
		18.22	22.00	21.70
		17.39	20.80	30.80
		13.76	22.10	25.11
		12.43	22.32	19.92
		10.33	15.94	30.21
		7.80	31.03	27.86
		7.91	23.32	25.83
		7.26	34.73	25.31
February, 2012		18.81	30.41	24.56
		9.22	21.95	30.25
		16.71	21.72	21.64
		7.15	35.29	27.61
		7.19	28.59	22.88
		7.09	31.32	19.27
		6.93	25.08	26.39
		15.33	32.00	28.61
		16.85	19.56	24.35
		11.79	24.45	25.00

Aveglo

Month	Metal	Small (GA)	Medium (MV)	Large (FL)
September, 2011	Selenium (Se)	0.37	0.28	0.08
		0.20	0.23	0.18
		0.32	0.12	0.15
		0.33	0.10	0.21
		0.15	0.18	0.20
		0.27	0.32	0.05
		0.32	0.38	0.13
		0.32	0.25	0.07
		0.20	0.23	0.06
		0.24	0.34	0.19
November, 2011		0.34	0.19	0.27
		0.44	0.37	0.08
		0.08	0.24	0.26
		0.32	0.27	0.06
		0.20	0.25	0.77
		0.22	0.21	0.10
		0.25	0.39	0.10
		0.21	0.17	0.12
		0.47	0.33	0.08
		0.32	0.24	0.10
February, 2012		0.12	0.21	0.14
		0.37	0.25	0.05
		0.12	0.25	0.21
		0.25	0.11	0.15
		0.41	0.35	0.07
		0.27	0.31	0.64
		0.23	0.18	0.09
		0.25	0.34	0.10
		0.18	0.24	0.15
		0.11	0.30	0.22

APPENDIX 3: Results of the one way ANOVA for significance in metal concentrations in the three clam size classes

Ada: Cadmium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	30	4.851	0.1617	0.000691
DD	30	3.978	0.1326	0.001779
TZ	30	2.97	0.099	0.00134

ANOVA Test for Difference in Means SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.012702	1	0.012702	10.28493	0.002184	4.006873
Within Groups	0.071632	58	0.001235			
Total	0.084334	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.058969	1	0.058969	58.05814	2.66E-10	4.006873
Within Groups	0.05891	58	0.001016			
Total	0.11788	59				
Are means significantly different?(P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.016934	1	0.016934	10.85764	0.001681	4.006873
Within Groups	0.090461	58	0.00156			
Total	0.107396	59				
Are means significantly different?(P<0.05)					Yes	

Ada: Copper

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	20	17.981	0.89905	0.486253
DD	22	41.18	1.871818	2.498694
TZ	24	71.28	2.97	3.1428

ANOVA Test for Difference in Means between SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8.486486	1	8.486486	5.500759	0.024055	4.084746
Within Groups	61.71138	40	1.542785			
Total	70.19787	41				
Are means significantly different?(P<0.050					Yes	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	46.78728	1	46.78728	24.10437	1.43E-05	4.072654
Within Groups	81.5232	42	1.941029			
Total	128.3105	43				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	15.73702	1	15.73702	5.550221	0.022999	4.061706
Within Groups	124.757	44	2.835386			
Total	140.494	45				
Are means significantly different? (P<0.05)					Yes	

Ada: Chromium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	30	112.11	3.737	3.65238
DD	30	528.37	17.61233	55.67571
TZ	30	592.12	19.73733	13.00342

ANOVA Test for Difference in Means between SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2887.873	1	2887.873	97.35264	5.09E-14	4.006873
Within Groups	1720.515	58	29.66404			
Total	4608.388	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3840.16	1	3840.16	461.1198	2.75E-29	4.006873
Within Groups	483.0182	58	8.3279			
Total	4323.178	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	67.73438	1	67.73438	1.972488	0.165517	4.006873
Within Groups	1991.695	58	34.33956			
Total	2059.429	59				
Are means significantly different? (P<0.05)					No	

Ada: Mercury

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	30	1.84	0.061333	0.00044
DD	30	2.21	0.073667	0.000955
TZ	30	2.68	0.089333	0.001751

ANOVA Test for Difference in Means between SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.002282	1	0.002282	3.27215	0.075649	4.006873
Within Groups	0.040443	58	0.000697			
Total	0.042725	59				
Are means significantly different? (P<0.05)					No	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.01176	1	0.01176	10.73578	0.001777	4.006873
Within Groups	0.063533	58	0.001095			
Total	0.075293	59				
Are means significantly different? P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.003682	1	0.003682	2.72079	0.104455	4.006873
Within Groups	0.078483	58	0.001353			
Total	0.082165	59				
Are means significantly different? (P<0.05)					No	

Ada: Nickel

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	30	243.44	8.114667	10.71756
DD	30	734.62	24.48733	61.98377
TZ	30	740.15	24.67167	44.43295

ANOVA Test for Difference in Means between SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4020.963	1	4020.963	110.6159	4.63E-15	4.006873
Within Groups	2108.339	58	36.35066			
Total	6129.302	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4112.014	1	4112.014	149.1197	1.14E-17	4.006873
Within Groups	1599.365	58	27.57525			
Total	5711.378	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.509682	1	0.509682	0.009579	0.922371	4.006873
Within Groups	3086.085	58	53.20836			
Total	3086.595	59				
Are means significantly different? (P<0.05)					No	

Ada: Selenium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
SN	30	13.84	0.461333	0.011509
DD	30	11.33	0.377667	0.030094
TZ	30	10.59	0.353	0.009484

ANOVA Test for Difference in Means between SN and DD

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.105002	1	0.105002	5.047808	0.028479	4.006873
Within Groups	1.206483	58	0.020801			
Total	1.311485	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between SN and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.176042	1	0.176042	16.77202	0.000132	4.006873
Within Groups	0.608777	58	0.010496			
Total	0.784818	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between DD and TZ

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.009127	1	0.009127	0.461197	0.299766	4.006873
Within Groups	1.147767	58	0.019789			
Total	1.156893	59				
Are significantly different?(P<0.05)					No	

Aveglo: Cadmium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	30	4.129	0.137633	0.000516
MV	30	3.588	0.1196	0.001712
FL	30	2.44	0.081333	0.001453

ANOVA Test for Difference in Means between GA and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.004878	1	0.004878	4.377193	0.04081	4.006873
Within Groups	0.064636	58	0.001114			
Total	0.069514	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.047545	1	0.047545	48.27477	3.58E-09	4.006873
Within Groups	0.057124	58	0.000985			
Total	0.104669	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.021965	1	0.021965	13.87682	0.000444	4.006873
Within Groups	0.091806	58	0.001583			
Total	0.113771	59				
Are means significantly different? (P<0.05)					Yes	

Aveglo: Copper

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	17	14.28	0.84	0.610975
MV	19	39.11	2.058421	3.912358
FL	28	94.76	3.384286	6.827329

ANOVA Test for Difference in Means between GA and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13.31971	1	13.31971	5.646897	0.023261	4.130018
Within Groups	80.19805	34	2.358766			
Total	93.51776	35				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	68.47408	1	68.47408	15.16837	0.000338	4.067047
Within Groups	194.1135	43	4.514267			
Total	262.5876	44				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	19.89813	1	19.89813	3.514737	0.067325	4.056612
Within Groups	254.7603	45	5.661341			
Total	274.6585	46				
Are means significantly different? (P<0.05)					No	

Aveglo: Chromium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	30	77.48	2.582667	2.269731
MV	30	422.05	14.06833	38.77446
FL	30	629.08	20.96933	25.80121

ANOVA Test for Difference in Means between GA and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1978.808	1	1978.808	96.42331	6.07E-14	4.006873
Within Groups	1190.281	58	20.52209			
Total	3169.089	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5071.043	1	5071.043	361.3019	1.37E-26	4.006873
Within Groups	814.0574	58	14.03547			
Total	5885.1	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA: Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	714.357	1	714.357	22.12465	1.62E-05	4.006873
Within Groups	1872.694	58	32.28783			
Total	2587.051	59				
Are means significantly different? (P<0.05)					Yes	

Aveglo: Mercury

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	30	1.47	0.049	0.00052
MV	30	1.82	0.060667	0.001034
FL	30	2.35	0.078333	0.001297

ANOVA Test for Difference in Means between GA and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.002042	1	0.002042	2.628172	0.110407	4.006873
Within Groups	0.045057	58	0.000777			
Total	0.047098	59				
Are means significantly different? (P<0.05)					No	

ANOVA Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.012907	1	0.012907	14.20828	0.000385	4.006873
Within Groups	0.052687	58	0.000908			
Total	0.065593	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.004682	1	0.004682	4.016617	0.049731	4.006873
Within Groups	0.067603	58	0.001166			
Total	0.072285	59				
Are means significantly different? (P<0.05)					Yes	

Aveglo: Nickel

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	30	323.63	10.78767	17.22526
MV	30	806.93	26.89767	28.62443
FL	30	750.04	25.00133	14.96053

ANOVA Test for Difference in Means between GA and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3892.982	1	3892.982	169.815	7.07E-19	4.006873
Within Groups	1329.641	58	22.92484			
Total	5222.622	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3030.425	1	3030.425	188.3082	7.26E-20	4.006873
Within Groups	933.3879	58	16.09289			
Total	3963.813	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	53.9412	1	53.9412	2.475221	0.121093	4.006873
Within Groups	1263.964	58	21.79248			
Total	1317.905	59				
Are means significantly different? (P<0.05)					No	

Aveglo: Selenium

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
GA	30	7.88	0.262667	0.00971
MV	30	7.63	0.254333	0.00615
FL	30	5.08	0.169333	0.025365

ANOVA: Test for Difference in Means between AD and MV

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001042	1	0.001042	0.131362	0.718341	4.006873
Within Groups	0.459923	58	0.00793			
Total	0.460965	59				
Are means significantly different? (P<0.05)					No	

ANOVA: Test for Difference in Means between GA and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.130667	1	0.130667	7.450713	0.008382	4.006873
Within Groups	1.017173	58	0.017537			
Total	1.14784	59				
Are means significantly different? (P<0.05)					Yes	

ANOVA: Test for Difference in Means between MV and FL

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.108375	1	0.108375	6.877765	0.011131	4.006873
Within Groups	0.913923	58	0.015757			
Total	1.022298	59				
Are means significantly different? (P<0.05)					Yes	

APPENDIX 4: Background concentrations (ppm) of studied metals.

Metal	Cd	Cr	Cu	Hg	Ni	Se
WA*	0.3	90	45	0.4	68	0.6

*World average shale reported by Turakian and Wedepohl (1961)