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CONCENTRATION OF SOME HEAVY METALS (Cu, Zn, Cd, Hg, As) IN THE WATER AND SEDIMENT OF LAKE TADEE AT ASHANTI MAMPONG IN ASHANTI REGION OF GHANA.

BY:

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DECLARATION

It is hereby declared that this thesis is the outcome of research work undertaken by the author, and that no part has been presented for another degree elsewhere.

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DEDICATION

This research is dedicated to my parents Mr. and Mrs. Dankwah as well as my lovely wife Grace Anane.

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I thank almighty God for his guidance and protection for helping me to finish this research. I wish to express my sincerest thanks and deepest gratitude to my supervisor , Dr. J. I Adam, who, willing, conscientiously and painstakingly read through my script and offered very useful suggestions and advice. My gratitude also goes to Y 2k who is a lecturer at Chemistry Department for reading through my work. Special thanks to my friends, especially John Duodu, Ampofo Nuako, Ben Twum, Ishmeal Amoako Attah, George Owusu, Francis Ajao, Stephen Yeboah. May almighty God bless you all.

ABSTRACT

The aim of this research was to assess the water quality of Lake Tadee with respect to heavy metals pollution. The water and sediment samples were collected from Lake Tadee at Ashanti Mampong in the Ashanti Region of Ghana during October, 2010 and February, 2011. The water and sediment samples were analyzed for Zn, Cu, Cd, Hg and As, using Instrumental Neutron Activation Analysis (INAA). The results of this study showed that there were significant differences in concentrations of the metals in the surface water and bottom sediment of Lake Tadee except mercury in which there was insignificant different. The higher concentrations of heavy metals in the sediment of the Lake Tadee than its overlying water may be due to factors such as changes in temperature, pH, sediment matrix, and redox condition as well as effluent from domestic, municipal and agricultural waste might have contributed to the release of higher contaminants in the bottom of the sediment. The mean concentration of heavy metals (mg/L) in the water ranged from 0.066 to 0.174 for zinc, 0.021 to 0.036 for copper, less than 0.001 to 0.015 for cadmium, and those mercury and arsenic were below detection limits. The concentration (mg/Kg) of the heavy metals in the sediment ranged from 8.683 to 10.041 for zinc, 8.560 to 10.072 for copper, 0.036 to 0.096 for cadmium, 0.553 to 0.658 for arsenic, and that of mercury was below detection limit. Heavy metals concentration in the Lake Tadee was significantly higher than that of Kyiremfa. However, Concentrations of heavy metals in the two water bodies are currently within acceptable limits of USEPA and WHO recommended guidelines. Care must be taken to reduce the amount of pollutants released into the Lake to prevent future increase in heavy metals concentration in the Lake so that its concentrations would not exceed the national and international standards.

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CHAPTER ONE

INTRODUCTION

1.1 BACKRGROUND

Among environmental pollutants, metals are of particular concern, due to their potential toxic effects and ability to bioacccumulate in aquatic ecosystems (Censi *et al.,* 2006). The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination; which are natural processes and anthropogenic activities. The main sources of heavy metals pollution to life forms are invariably the result of anthropogenic activities (Francis, 1994). In the fresh water environment toxic metals are potentially accumulated in sediments (Camouso *et al.,* 1995). These heavy metals generally exist in low levels in water and attain considerable concentration in sediments (Naminga and Wilhm, 1976).

Studies on heavy metals in lakes and sediments have been a major environmental focus especially during the last decade (Praveena *et al*., 2008). Sediments have been reported to form the major repository of heavy metal in aquatic system while both allochthonous and autochthonous influences could make a concentration of heavy metals in the water high enough to be of ecological significance (Oyewo and Don-Pedro, 2003).

Bioaccumulation and magnification is capable of leading to toxic level of these metals in organisms even when the exposure is low. The presence of metal pollutants in fresh water is known to disturb the delicate balance of the aquatic systems. The use of samples that may be contaminated with heavy metals in food may result in accumulation of these metals in human organs and lead to different health problems (Sekhar *et a*l., 2002). Heavy metals may enter the human body through inhalation of

dust, consumption of contaminated drinking water, direct ingestion of soil and consumption of food plants grown in metal contaminated soil (Cambra *et al.*, 1999). Heavy metals may reach and contaminate plants, vegetables and fruits through water and soil during cultivation (Queirolo *et al*., 2000). Copper and zinc are known to be essential and may enter the food materials from soil through environmental contamination (Prasad and Oberleas, 2004).

The adult human body contains about 1.5 to 2 $mgkg^{-1}$ of copper (Dente and Hopkins, 2004) and 33 mg/kg of zinc (Fairweather-Tait, 1998). Mercury and Cadmium are toxic and accumulations exceeding threshold values can affect human health (Steenland and Boffetta, 2000). This study assesses the levels of some heavy metals in sediments and water samples from Lake Tadee which is used for watering vegetables.

1.2 PROBLEM STATEMENT

Studies have been carried out on heavy metals pollution at Lake Bosomtwe (Shanahan, 2006), Fosu Lagoon (Dodoo *et al.*, 2006) and Lake Volta (Gyau *et al.*, 2000) but no work has been done on Lake Tadee which is located in Ashanti Mampong in the Ashanti Region of Republic of Ghana. The water from the lake provides a source of livelihood for vegetable farmers who use water from the lake to grow vegetables such as carrot, cabbage, lettuces and green pepper. Due to anthropogenic activities (dumping of waste), such as washing of cars around the lake and drainage water from the town into the lake, the water could be polluted with heavy metals.

The need for this research is from the fact that, it is generally known that vegetables (cabbage, lettuce and green pepper) are widely grown and largely consumed by most residents in Mampong, Kumasi and other parts of Ghana, hence the upsurge of the

fast food industry in the municipality. Exposure to these heavy metals through the consumption of vegetables has a number of health hazards to human when consumed beyond certain threshold values, thus there is the need to determine the levels of these heavy metals in the water which is used for irrigation.

1.3 MAIN OBJECTIVE

The main objective of this research was to assess the water quality of Lake Tadee with respect to heavy metals.

1.4 SPECIFIC OBJECTIVES

The specific objectives of this research were to assess:

1. The levels of Hg, Cd, Cu, Zn and As in the water and sediment of Lake Tadee.
2. The levels of Hg, Cd, Cu, Zn and As in the water and sediment of Kyerimfa river (control).

1.5 JUSTIFICATION OF THE STUDY

Water is an essential component of living organisms. It forms about 90% of the body fluid. Water from Lake Tadee is used extensively for cultivation of vegetables and for domestic purposes.

Activities around the banks of the lake as well as agricultural and municipal runoffs are likely to deposit heavy metals into the lake. However, there is no known research work on heavy metals occurrence in the lake. It is therefore against this background that the present study seeks to assess the concentration of heavy metals such as Hg, As, Cd, Cu, and Zn in the water and sediment of Lake Tadee in the Ashanti Mampong of Ghana.

CHAPTER TWO

LITERATURE REVIEW

2.1 HEAVY METALS

Heavy metals are elements that have an atomic weight between approximately 63 and 200 (NCSU, 2006). They occur naturally in minerals that are found, in different levels throughout our natural environment. Many of these metals are essential to the health and wellbeing of the organisms that live on our planet, including human.

However, if excess amounts of these atoms are allowed to accumulate in our natural environment, the result can lead to a number of problems including soil contamination, surface and groundwater contamination, loss of aquatic life, and even severe human health effects. The contamination of soils, sediments, water resources and biota by heavy metals is of major concern because of their toxicity, persistence and bioaccumulative nature (Ikem *et al*., 2003). Toxic metals can alter many physiological processes and biochemical parameters, either in blood or in tissues including structural deformations in aquatic animals (Barlas *et al.,* 2005). Being non-biodegradable, they can concentrate along the food chain, producing their toxic effects at points often far away from the source of pollution (Fernandez *et al.,* 2000).

The concentration of metals in surface water depends on several factors like soil dust, local point sources, natural presence in the bedrock and soils, and airborne contribution from long range transport (Frank and Cross, 1974). In addition, conditions in the catchment area of the lake are important for the mobility and availability of metals in the water.

2.2 SOURCES OF HEAVY METALS

Heavy metals are emitted to the environment from a variety of anthropogenic sources to supplement natural background geochemical sources. The amounts of most heavy metals deposited to the surface of the earth are many times greater than depositions from natural background sources. Possible sources include wastewater arising from informal settlements (Jackson *et al.,* 2007), leachates from municipal and industrial landfill sites (Moodley *et al.,* 2007), mining activities, disposal of metal-containing industrial effluents (Phuong *et al*, 1998), municipal wastewater, dry docking companies and petrol filling stations (Shriadah, 1998). Combustion processes are the very important sources of heavy metals, particularly, power generation, smelting, incineration and internal combustion engine (Nriagu, 1988).

2.3 DISTRIBUTION PATHWAYS AND FATE OF HEAVY METALS IN AQUATIC ENVIRONMENT

Once in the aquatic environment, metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota). The metals in the aquatic environment may occur in dissolved, particulate and complexed form. The main processes governing distribution and partition are dilution, dispersion, sedimentation and adsorption/desorption (Biney *et al*., 1994). Nonetheless, some chemical processes could also occur. Thus, speciation under the various complexes and by the physico-chemical properties of the water (pH, dissolved ions and temperature). Adsorption could be the first step in the ultimate removal of metals from water. In the course of distribution, permanent or temporary storage of metals takes place in the sediments of both freshwater and marine environments. Microbial activity and redox processes may change the properties of sediments and affect the

composition of interstitial water. As a result, Iron and Magnesium oxides may be converted to carbonates or sulphides, leading to a decrease in the absorption capacity of the sediments. Reworking of the sediments by organisms will also bring sediments to the surface, where a significant fraction of the metal will be released (Kennish, 1992a).

2.4 HEAVY METALS AND PLANTS

Metallic elements can be found in all living organisms and play a variety of roles: structural elements, components of control mechanism, components of redox systems, stabilizers of biological structures, enzyme activators and so on. Some metals are essential e.g. Cu, Zn and their deficiency will lead to impairment of biological functions. However, further supply of these essential elements does not lead to a growth increase, because beyond certain concentration all essential elements will become toxic (Bargagli, 1998). However, some of heavy metals (Pb, Hg) are non-essential and even toxic to living organisms even under very small concentrations (Rozema *et al*., 2007)

2.4.1 Heavy Metals Tolerance Mechanisms

Heavy metals are absorbed by roots of plants from the soil and, depending on the internal regulating system, plants may show three different types of uptake (Hyde, 2003)

- Excluders have developed the mechanism that selectively takes up only the amount of heavy metals they need.
- Indicators take up and accumulate metals through some mechanisms, such as chelation, localization and chemical inactivation.

However, after a certain level of heavy metal concentration, indicators cannot regulate the uptake and continue to absorb heavy metals until plants die.

- Accumulators accumulate high concentrations of heavy metal from soil, regardless of the heavy metals toxicity.

2.4.2 Heavy Metals Toxicity On Plants

Plant responses to heavy metal toxicity include leaf discolouration, chlorosis, necrosis, dwarfism, gigantism, leaf expansion inhibition and root growth inhibition (Othman, 2001). Within plant cells, excessive amount of certain heavy metals can modify the permeability of the plasma membrane, causing leakage of ions and solutes. Several metals like copper have a high affinity for sulphydryl and carboxyl groups, which lead to a decrease in the plasma lemma ATP-ase activity. In addition, some cell components can be damaged by free radicals formed by metal participation (Moolenaar, 1998).

Excessive heavy metals also have many negative effects on chlorophyll. Some metals have a high affinity for sulphydryl groups and can cause the inhibition of enzyme and chlorophyll synthesis (Bargagli, 1998). Displacements of these essentials elements could decrease the levels of chlorophyll content (Rozema and Verkleij, 1991).

2.5 BENEFICIAL HEAVY METALS

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace metals (e.g. Fe, Cu, Mn and Zn). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits, vegetables and in commercially available multivitamin product (Brown *et al*., 2004).

Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in parental nutrition mixtures (Kennish, 1992b). Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth (National Institute for Occupational Safety and Health, 1999). Many of these products are in our homes and actually add to our quality of life when properly used.

2.6 TOXIC HEAVY METALS

2.6.1 Common Causes of Heavy Metal Toxicity

Heavy metals toxicity can result from either actual or chronic exposure to heavy metals.

Acute exposure can occur as a result of:

- Receiving vaccinations that contain thimerosal (mercury preservative),
- Mishandled metals at a job site,
- Chemical and heavy metals spills (e.g. from a broken mercury thermometer),

Chronic exposure happens over a period of time, and includes:

- Having mercury amalgams (silver fillings) in teeth,
- Living in a home that has lead-based paint,
- Smoking and/or inhaling second-hand smoke,
- Eating foods (such as contaminated fish) that contain high levels of heavy metals,
- Living near a land fill,
- Working in an environment where exposure is prevalent, such as at a dentist's office where amalgam is used to fill cavities (Ozmen *et al*., 2004).

2.7 MERCURY (Hg)

2.7.1 Sources of mercury

2.7.2 Mercury in air

As a natural element, mercury is ubiquitous in the environment approximately 10,000 tons originate from degassing of earth's crust; to this amount approximately 20,000 tons/year is added by anthropogenic activity (Hansen and Dasher, 1997). Mercury emissions from coal smoke are the main source of anthropogenic discharge and mercury pollution in atmosphere. It is estimated that the mercury emissions will increase at a rate of 5% a year (Zhang *et al.,* 2002). When medical devices like thermometer/sphygmomanometer or household items like fluorescent night lamps or thermostats are discarded residual mercury is emitted. Coal-fired electric utilities accounted for 52.7% of USA Hg emissions. Other important contributors to Hg emissions in the USA included municipal waste combustion (5.6%), mercury-cell chlor-alkali plants and hazardous-waste incinerators (4% each), stationary internal combustion engines (ICEs) (3.5%), industrial, commercial and institutional (ICI) boilers (3.3%) and lime manufacturing (3.0%) and medical waste incineration (1%) (Murray and Holmes, 2004). Informal gold mining has used mercury since antiquity. High contamination of Brazilian Amazon (Brazil is world's second largest producer of gold) is indicated by the strong presence of mercury in its biota (Grandjean *et al*., 1995). It is an occupational hazard for dental workers (Rowland and Baird, 1994).

2.7.3 Mercury in water

Mercury in air eventually passes into rivers, lakes and oceans after travelling long distances together with wind. With mercury contaminating rain (Levine, 2004), ground and seawater (Beldowski and Pempkowiak, 2003), no one is safe. Cloud water was collected during nine non-precipitating cloud events on Mt. Mansfield, VT in the

northeastern USA between 1 August and 31 October, 1998. The water content explained about 60% of the variability recorded in Hg concentrations (Malcolm *et al.*, 2003). There are also linkages between acidic deposition and fish mercury contamination and eutrophication of estuaries (Driscoll *et al*., 2003). Numerous factories that directly pump untreated effluents pollute groundwater. The polluted water produces acidic rain which ultimately contaminates all water bodies. Report published in a reputed Indian daily, The Hindustan Times, showed that ground water samples from six places each from Punjab, Haryana, Andhra, Pradesh, Gujarat and Kanpur analysed at the Indian Institute of Technology, Kanpur had high levels of Hg in all the samples (Balogh *et al*., 2002). Water samples from Panipat (Haryana) had the highest level of Hg at concentration 268 times that of safe limit, even the sample with least Hg value had 58 times more mercury than the upper safe limit. Algal bloom and leaf fall events can result in elevated methyl mercury (MeHg) concentrations in surface waters, potentially leading to increased MeHg accumulation in fish (Balogh *et al*., 2002).

2.7.4 Mercury Contamination of Food

2.7.4.1. Food of animal origin

The emitted mercury both natural and anthropogenic is in an inorganic form, predominantly metallic vapour, which is carried off to great distances by winds and eventually falls in water bodies. In aquatic environments, inorganic mercury is microbiologically transformed into lipophilic organic compound, Methyl mercury. This transformation makes mercury more prone to biomagnifications in food chains (Hansen and Dasher, 1997). Consequently, populations with traditionally high dietary intake of food originating from fresh or marine environment have highest dietary exposure to Hg. Extensive research done on locals across the globe have already

established this for instance polar Eskimos. Persons who routinely consume fish or a particular species of fish are at an increased risk of methyl mercury poisoning (Hansen and Dasher, 1997). Since mercury intake is expressed on a per kilogram body weight basis, exposure of children under age 14 is two to three times high because of higher food intake per kilogram body weight. After measuring total mercury in the edible portions of 244 selected fish and shellfish purchased in Canada at the retail level, the Canadian advisee to children and women of child-bearing age is to limit their consumption of fresh and frozen tuna, swordfish and shark to no more than one meal per month (Dabeka *et al.*, 2004).

When 21 fish species, cephalopods and crustaceans were analyzed for mercury accumulation the former two ranked highest (Schumacher *et al*., 1994). In Yokondelta system, bio-magnification factor of 12 was calculated for methyl mercury, out of 29% fish species, 62% contained Hg exceeding wildlife critical value for piscivorous animals. Overall 24% fish exceeded critical value for human consumption and 58% wildlife critical value (Duffy *et al*., 1998). Cattle and pigs kept in an area with contaminated river water had twice concentration of blood and hair Hg than control ones (Palhetaad and Taylor, 1995).

2.7.4.2 Food of plant origin

Emissions of mercury from the province of Guizhou in Southwestern China to the global atmosphere have been estimated to be approximately 12% of the world total anthropogenic emissions primarily due to mining, chemical discharge and electricity production. Even though the major source of mercury is inorganic, it was observed that active transformation of inorganic mercury to organic mercury species (MeHg) takes place in water, sediments and soils. It has been reported that the concentration of

mercury in rice grains can reach up to 569 g/kg of total Hg of which145g/kg is in MeHg form (Horvat *et al.,* 2003). While analyzing *in situ* aquatic and terrestrial plants in vicinity of chloralkali plants growing at Hg conc. 8.9 mg/kg it was found that Cabbage, *Bracica oleracea, B. amaranthus* and *Amaranthus oleraceous* accumulated mercury at significant levels (Lanka *et al.,* 1992). Amongst edible mushrooms representing eight species, the highest average content of mercury was found in *Boletus pinicola* at 7.37 **ppm** DW (Alonso *et al*., 2000). In Southeast Asia, the aquatic macrophyte water spinach (*Ipomoea aquatic*, Forsk) is a popular vegetable that is cultivated in freshwater courses, it was found that the vegetable accumulated various heavy metals like mercury, cadmium and lead in a nutrient deficient medium (Gothberg *et al.*,2004).

2.7.5 Mercury in Pharmaceuticals and Utility Products

Mercury has always been a popular choice for dental amalgams. Thimerosol is a mercury containing compound used as a preservative in Hepatitis B, Diphtheria, Pertusis, Acellular pertusis and Tetanus vaccines. Use of mercury in vaccines have caused furore in concerned circles owing to death of infants and speculations over long-term effects (Westphal and Hallier, 2003). Infants are exposed to phenyl mercury from treated diapers and young children ingesting mercuric chloride in teething powders have been found to develop acrodynia and Kawasaki disease (Kazantzis, 2002). Skin whitening creams and soaps from developing countries is a recognized source of chronic mercury poisoning (Harada *et al.,* 2001).

2.7.6 Mercury and Wildlife

It is well known that heavy metals in larger amounts are toxic to animals as well as plants; and mercury is no exception to this. The general signs of mercury toxicity for

sheep, cattle, pig, chicken and turkey include lack of appetite, loss of weight, muscular in-coordination, unstable gait and lameness (Nicholson *et al.,* 1983). Sea birds from mercury contaminated colony, metal dosed birds and metal dosed mice have demonstrated nephrotoxic lesions of severe type (Nicholson *et al.,* 1983). Methyl mercury was attributed for decrease in reproduction of adult fathead minnows at dietary concentrations encountered by predatory fishes in aquatic systems with contaminated food webs, implying that exposed fish populations could be adversely affected by this widespread contaminant (Hammerschmidt *et al*., 2002). Inorganic mercury disturbs a part of respiration process in shrimp larvae Pandalus borealis (St-Amand *et al.,* 1999). Embryo toxicity and teratogenecity of organic mercury compounds have been observed in fish, birds and even mammals (Leonard and Jacquet, 1983).

2.8 TOXICITY OF MERCURY

Evidence from numerous sources demonstrates that neural development extends from the embryonic period through adolescence. Different behavioural domains (e.g. sensory, motor and various cognitive functions) are sub served by different brain areas. Of critical concern is the possibility that developmental exposure to neurotoxicants may result in an acceleration of age-related functional decline. This concern is compounded by the fact that developmental neurotoxicity that results in small effects can have a profound societal impact when amortized across the entire population and across the life span of humans (Rice and Barone, 2000). The difference in sensitivity between foetus and adult organism is between 2 and 5 with foetus being more susceptible to methyl mercury toxicity (Snyder, 1971). Maternal consumption during pregnancy of methyl mercury contaminated fish in Japan and of methyl mercury contaminated bread in Iraq caused psychomotor retardation in the

offspring. Studies in Iraq suggested adverse fetal effects when maternal hair mercury concentrations were as low as 20 **ppm** (Marsh and Turner, 1995). Mothers consuming diet containing mercury pass the toxicant to foetus (Murata *et al.*, 2004) and to infants through breast milk (Grandjean *et al*., 1999). Decreased performance in areas of motor function and memory has been reported among children exposed to presumably safe mercury levels with maternal hair concentrations at 10–20 µg/g (Grandjean and Weihe, 1998). Detectable subtle effects on brain function in domains of language, memory and motor appeared at prenatal methyl mercury exposure particularly during second trimester. Neurobehavioral dysfunction was reported even if maternal hair Hg is 6 µg/g, corresponding value for blood is approximately 24 g/l (Grandjean *et al*., 1994).

Autism is a disorder that can lead to life-long disability. There is potential link between mercury toxicity and autism in children (Lee *et al*., 2003). Subtle neurological disorders in children over mercury exposure have been widely reported (Johnson, 2004). The neuropathological examination of brains of children prenatally exposed to organic mercury reveals dysplasia of cerebral and cerebellar cortexes, neuronal ectopia and several other developmental disturbances (Geelen and Dormans, 1990).

Low concentrations of some metals, including mercury can directly induce α-synuclein fibril formation which are the major constituent of intracellular protein inclusions (Lewy bodies and Lewy neurites) in dopaminergic neurons of the substantia nigra leading to Parkinson's disease (Uversky *et al*., 2001).

Moreover, low concentrations of cobalt and mercury are able to induce oxidative stress, cell cytotoxicity and increase the secretion of β-amyloid 1–40 and 1–42 which

may lead to neurodegenerative diseases, such as Alzheimer's and Parkinson's diseases (Olivieri *et al.,* 2002). Mercury binds to sulfhydryl groups of proteins and disulfide groups in amino acids resulting in inactivation of sulfur and blocks related enzymes and cofactors and hormones (Markovich and James, 1999). Besides this, it also alters permeability of cellular membrane by binding to sulfhydryl (SH) radical (Bapu *et al*., 1994). Blocked or inhibited sulfur oxidation at cellular levels has been found in many chronic neurodegenerative disorders, including Parkinson's disease, Alzheimer's disease, Rheumatoid arthritis, Autism, etc. (Wilkinson and Waring, 2002). Long-term study of low dose of mercury demonstrated hypoesthesia, ataxia, dysarthrea and impairment of hearing and visual change (Ninomiya *et al*., 1995).

In another survey of fish eating population with low hair Hg levels <10 ppm it was found that neurological symptoms particularly sensory disturbances such as glove and stocking type occurred at a very high rate. (Harada *et al.*, 1994). The adult population of Amazonian ecosystem with hair mercury below50µg/g demonstrated near visual contrast sensitivity, decreased manual dexterity, tendency for increased muscular fatigue, decreased muscular strength among women significantly in a dose dependent manner (Lebel *et al.*, 1998). Similarly disruption of attention, fine motor function and verbal memory was also found in adults of fish eating populations on exposure to low mercury levels (Yokoo *et al*., 2003). The effects of mercury exposure at levels around 0.05 mg/m^3 or lower have been of concern, include, increased complaints of tiredness, memory disturbance, subclinical finger tremor, by computerized analysis and impaired performance in neurobehavioral or neuropsychological tests (Satoh, 2000). Neuropsychological effects in mercury vapor exposed male chloralkali workers with low concentrations of urinary mercury mean U-Hg 5.9 nmol/mmol creatinine (Cr) indicated lowering of visuomotor / psychomotor speed and attention, and immediate

visual memory (Ellingsen *et al.*, 2001). Depression and impairment of short-term auditory memory was found in workers exposed to low levels of mercury (Soleo *et al*., 1990).

Kidneys accumulate highest levels of mercury compared to brain and liver (Hussein *et al*., 1998). Renal toxicity of mercuric chloride is well documented in literature. Nuclear factor $_{k}$B (NF-$_{k}$B) is a thiol- dependent transcriptional factor that promotes cell survival and protects cells from apoptotic stimuli. Mercuric ion Hg ($^{2+}$) is, one of the strongest thiol-binding agents known, impairs NF-$_{k}$B activation and DNA binding at low µM concentrations in kidney epithelial cells leading to apoptosis (Dieguez-Acuna *et al*., 2004). Renal function and immunologic markers among chloralkali workers with long-term low exposure to mercury vapor when examined indicated an effect of exposure on the kidney proximale tubule cells (Ellingsen *et al.*, 2000). Renal dysfunction increases plasma ceratinine level upon methyl mercury intoxication for 5 ppm mercury for 2 years (Yasutake *et al*., 1997). Decrease in protein (brain and liver) acid and alkaline phosphatase and glutathione S transferase was observed upon 0.5µmol/ml mercury for five consecutive days, while thiobarbituric acid reactive substances (TBARS) was found to be significantly increased in brain and liver indicating free radical stress (El-Demerdash, 2001).

Advisories to reduce consumption of contaminated fish have been issued by states since the early 1970s. Most women of child bearing age consume fish also containing mercury are linked to reproductive and developmental effects.

If concentration of methyl mercury is very high in mothers they do not conceive, if they do, the foetus is aborted or is stillborn. At even lower doses conception and live birth occurred but the child suffered from serious neurological symptoms (Harada,

1988). Women exposed to mercury vapour not exceeding the time weighted average air concentration of 0.01 mg/m^3 declared higher prevalence and incidence rates of menstrual disorders, primary sub fecundity, and adverse pregnancy outcome (De Rosis *et al.,* 1985). According to W.H.O. report 0.5 mg/kg Hg contaminated food should not be sold for human consumption. Hg accounts for sub-fertility in Hong Kong males (Dickman and Leung, 1998). Organic as well as inorganic mercury decreases the percentage of motile spermatozoa. After 30 min incubation with 20 µmol methyl mercuric chloride less than 5% of human spermatozoa were found motile (Ernstand and Lauritsen, 1991).

The immune system plays an important regulatory role in the host-defense mechanisms. Patients with certain autoimmune and allergic diseases, such as systemic lupus, multiple sclerosis, autoimmune thyroiditis or atopic eczema, often show increased lymphocyte stimulation by low doses of inorganic mercury in vitro (Prochazkova *et al*., 2004). It has been repeatedly shown that the heavy metal mercury can induce or exacerbate lupus like autoimmunity in susceptible strains of rats and mice. A hallmark of such autoimmune induction is the accompaniment of an immune shift, in which there is usually an initial skewing toward a Th2-like immune environment (Hudson *et al.*, 2003).

Exposure to methyl mercury significantly enhanced lymphocyte responsiveness in most of the exposed groups at the low concentration of 5 µg/l, with the highest proliferative response (four-fold increase) in the methyl mercury chloride group (Ortega *et al.,* 1997). Prolonged exposure to low doses of inorganic mercury, suggested an in vivo functional defect of the monocyte–macrophage system (Soleo *et al.,* 1997).

The exposure to very low levels of metallic mercury led to subtle impairment of circulating monocyte and natural killer cells (as percentages) in a particular group of workers, even though they remained clinically asymptomatic (Vimercati *et al*., 2001).

The reports for mercury genotoxicity have been coming since 1980. First report showing clear cytotoxic effects of 20 years exposure to methyl mercury on human population with a wide range of mercury exposure based on a well-known biological marker, hair mercury. A clear relation between methyl mercury contamination and cytogenetic damage in lymphocytes at levels well below 50 µg/g were found. Although their results strongly suggest that, under the conditions examined, methyl mercury is a spindle poison and a clastogen, the biological significance of these observations are as yet unknown (Amorim *et al*., 2000).

Theoretically, methyl mercury-induced chromosome damage in germ line cells could give rise to abnormal offspring. Mercuric chloride exposure in short term blood cultures lead to high sister chromosome exchanges/cell and induced C-anaphases (abnormal mitosis) (Rao *et al*., 2001).

The chromosomal genotoxicity of mercury has been attributed to its interaction with microtubule assembly mercury inhibits microtubule assembly at concentrations above 1 µM, and inhibition is complete at about 10 µM (Bonacker *et a*l., 2004). Mercury genotoxicity have been observed in animals as well as in plants. Cytogenetic analysis revealed the effects of mercury on the mitotic and meiotic chromosomes which were significantly correlated with soil-mercury levels. The bioconcentration of mercury in aerial tissues including grain was observed indicating possible contamination of the food chain (Panda *et al*., 1992). Low concentrations of inorganic mercury (Hg^{2+}) and methyl mercury chloride (CH_3HgCl) added separately or together lead to induction of

micronuclei in the binucleated erythrocytes of Prussian carp (Al-Sabti, 1994). The bioaccumulation of methyl mercuric chloride and mercuric chloride at low dose exposure was evaluated by determination of mercury levels in the larvae of *Urodele pleurodeles* Waltl. After 12 days of treatment, concentration factors (concentration in the amphibian organism/concentration in the water) of approximately 1200 and approximately 600 were found for methyl mercury and mercuric chloride, respectively (Zoll *et al*., 1988).

2.8.1 Molecular Mechanisms of Low Dose Mercury Toxicity

It is difficult to classify the molecular basis of low dose mercury toxicity to tissues and organ systems initially due to lack of data, finally because it is a complex cascade of interrelated events that may directly or indirectly translate into pathological state of a particular organ system. Its neurotoxicity to cerebellum at higher doses has been related to impairment of motor function (Marcelo *et al*., 2005) and its genotoxicity to neuronal cells in foetal state may result in abnormal offspring's or foetal deaths but its exact mode of activity at low doses, particularly at environmentally relevant concentrations which lead to subtle delays in neurodevelopment remain unexplored. Basically it blocks essential functional groups in biomolecules and also displaces essential metal ions from them. Mercuric ion is known as one of the strongest thiol-binding agents. Intracellular mercury therefore attaches itself to thiol residues of proteins particularly glutathione and cysteine resulting in inactivation of sulfur and blocks related enzymes, cofactors and hormones (Mathieson, 1995). Its molecular interactions with sulfhydryl groups in molecules of albumin, metallothionein, glutathione, and cysteine have been implicated in mechanisms involved in renal and neuronal toxicity (James *et al*., 2005). The other functional groups besides SH for which mercury has high affinity include, $CONH_2$, NH_2, COOH and PO_4 (Hayes,

1983). It also blocks immune function of Mn and Zn leading to deficiency of principal antioxidant enzyme, superoxide dismutase, CuZn–SOD and Mn–SOD (Rajanna and Hobson, 1995) which has a role in various diseases, including Alzheimer's disease, Parkinson's disease, Cancer, Downs syndrome, Dengue, etc. (Noor *et al*., 2002). Moreover, in cerebellar granule cells in culture, low concentration of mercury causes a rise in [Ca^{2+}] which may trigger a cascade of events leading to impairment of mitochondrial energy metabolism and generation of reactive oxygen species (Fonnum and Lock, 2004).

The combination of these mercury triggered events enhances free radical stress that has been cited widely in literature (Hussein *et al.*, 1998). Free radical stress has been frequently reported as key player in disease progression of as many as 50 diseases,aging and degenerative disorders (Nagy, 2001).

2.9 CADMIUM (Cd)

Cadmium is a toxic metal that is classified by the International Agency for the Research of cancer (1993), and the National Toxicology Programme as a known carcinogen (2002). The evidence for this classification is largely based on epidemiology studies in occupationally exposed workers and on animal studies (Waalkes, 2000). The main sources of human exposure to cadmium come from cigarette smoke, food and industrial pollution. Tobacco smokers are exposed to an estimated 1.7 µg cadmium per cigarette, most of which is absorbed by the body. This puts the exposure of a one pack-per day smokers at 34 µg of cadmium per day. Although am estimated 30 µg cadmium is ingested each day through food, only about 5% of this exposure is taken up by the digestive tract.

The effect of tobacco smoking on absorbed cadmium has been demonstrated by measuring tissue levels were five-ten-fold higher levels were found in the lung, liver and kidney in smokers compared to non-smokers (Lewis *et al*., 1990). Toxic responses to cadmium exposure include kidney damage, respiratory diseases, neurological disorders and lung, prostate and testicular cancers (Waalkes, 2003). Cadmium exposure can induce intracellular damage through several mechanisms. In cultured cells, cadmium produces direct and indirect genotoxic effects such as DNA stand breaks, DNA-protein cross links, oxidative DNA damage and chromosomal aberrations (Misra *et al., 1*998). Several cellular factors that respond to DNA damage to regulate proliferation also respond to cadmium exposure. Inhalation of cadmium dust in certain occupational settings may be associated with an increased incidence of lung cancer. Other symptoms include; irritation of upper respiratory tract, metallic taste in the mouth, cough and chest pain (Foulkes, 1986). Ingestion of elevated levels of cadmium has resulted in toxicity to the kidney and skeletal system and may be associated with an elevated incidence of hypertension and cardiovascular disease. Cadmium may interfere with the metallothionein's ability to regulate zinc and copper concentrations in the body. Metallothionein's is a protein that binds to copper and zinc, disrupting the homeostasis levels (Kennish, 1992). Cadmium is used in industrial manufacturer and is a by-product of the metallurgy of zinc. Cadmium is used in industrial processes and in fertilizers and is accumulating in the environment.

2.10 ARSENIC (As)

The name "arsenic" is derived from arsenikon, Greek word for potent. Medical uses of arsenic date back to Greek and Roman times (Gorby, 1988). Hippocrates (460-377 BC) and Galen (138-201 AD) prescribed a paste containing a sulphide of arsenic for the treatment of ulcers. Arsenic's resemblance to sugar and its tastelessness made it a

popular assassination poison in the middle Ages. In the 1800s, Fowler's solution, a 1% potassium arsenite solution, was used as a general tonic for treating leukemia, psoriasis and asthma. Fowler's solution was not withdrawn from the U.S market until the 1950s. Meanwhile, Erlich and Bertheim produced nearly 1000 compounds of arsenic to be used in the treatment of syphilis; the use of such compounds was not curtailed until after the advent of penicillin in 1943. The arsenic containing drug melarsorprol (Mel B) is still the drug of choice for treating African trypanosomiasis at the meningo-encephatic stage (Malachowsk, 1990). During World War 1, arsenic compounds were used as chemical warfare agents. There were gases Adamsite and Lewisite are compounds of arsenic. Lewisite (2- chlorovinylichloroarsine) causes respiratory irritation and extensive, slow-healing blisters. Its wartime use prompted the search for an antidote, resulting in the development of British anti-lewisite (BAL; 2, 3-dimercaptopropanol) (Gorby, 1988). Arsenic may occur in an inorganic or an organic form. The inorganic arsenic compounds include the arsenites, the arsenates, and elemental arsenic. The organic arsenic compounds include arsine and its organic derivatives. However, in vivo organic-to-inorganic and inorganic-to-organic conversion may occur (Wade *et al.,* 1993).

Most arsenic in the terrestrial environment is found in rocks and soils. Arsenic in surface and ground water is mostly a mixture of arsenite and arsenate. Arsenic is widely distributed in food; particularly high levels are found in seafood (Hostynek *et al.*, 1993). The major man-made sources of arsenic include the combustion of coal, nonferrous metal smelting, and the burning of agriculture wastes. Arsenic compounds have been widely used as herbicides, fungicides, wood preservatives, dessicants, cattle and sheep dips, and dyestuffs, in glass and ceramics, as a metal alloy, and in semiconductors and other electronic devices. In the past, arsenic–containing

rodenticides and ant poisons were responsible for many exposures. Suicidal and homicidal poisonings involving As continue to be reported (Fesmire, 1988).

Arsenic is primarily absorbed by ingestion, inhalation, or percutaneously. Arsenic distributes rapidly into erythrocytes and binds to the globins portion of heamoglobin. Redistribution to the liver, kidneys, spleen, lungs, and gastrointestinal tract occurs within 24 hours. Arsenic impairs cellular respiration by inhibiting mitochondrial enzymes and uncoupling oxidative phosphorylation through inhibition of sulfhydryl group-containing cellular enzymes and substitution of phosphate with arsenate in "high-energy" compounds (Tamaki *et al*., 1992). Inorganic arsenic crosses the placenta and may cause neonatal death (Lugo *et al*., 1985).

2.11 ZINC (Zn)

Zinc occurs in rocks as chalcophile and sphalarite, zinc sulphide. The presence of zinc in the environment is associated with mining and smelting which pollutes the air, water and soil with fine particles, which ultimately undergo oxidation to release Zn^{2+}. Zinc is used in a wide variety of industrial, agricultural and consumer products. It is found in all human tissue and all body fluids and is essential for growth, development and reproduction. Zinc is usually present in tap water at concentration less then 0.2 mg/l, although drinking water in galvanized pipes can contain up to 2 to 5 mg/l. Typically, concentrations are much less than 5 mg/l, which is based on the threshold for metallic taste in water (Ellingsen *et al*., 2007).

Zinc play vital roles in the functioning of the retina and is an essential for antioxidant defense mechanisms (Brewer *et al*., 2000). These mechanisms are important for the survival of the retina since this tissue is routinely exposed to high levels of oxidative stress from light and metabolic processes. Zinc levels in the retina are high compared

to other tissues and a large number of zinc binding proteins are present in retina (Ugarte and Osborne, 2001). It has many biochemical functions (catalytic, regulatory and structural). The catalytic role of zinc is understood in terms of the fact that it forms part of the specialized enzymes and proteins (Adriano, 2001). The toxicity of zinc is due to having Cadmium as an impurity. It causes phytotoxicity. Phytotoxicity may cause decreased crop yield and quality and likelihood of zinc transfer into food chain (Adriano, 2001). Zinc also affects many functions and growth. Zinc deficiencies are associated with night blindness and muscular degeneration (Newsome *et al.,* 1995).

However, low blood levels of zinc also associated with hypogensia, in which there is loss of sense of taste. Gastrointestinal distress is a common symptoms following acute oral exposure to zinc compounds (Castillo *et al.,* 2000).

2.12 COPPER

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray (Cuzzocrea *et al.*, 2003). A few examples of human activities are mining, metal production, wood production and phosphate fertilizer production (Ford 2000). Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is found near mines, industrial settings, landfills and waste disposal sites. Most copper compounds will settle and be bound to either water sediments or soils particles. Soluble copper compounds form the largest threats to human health (Gaetke *et al.*, 2003). Usually water soluble copper compounds occur in the environment after release through application in agriculture. Copper can be found in many kinds of food, in drinking water and in air. Because of these eminent quantities of copper are absorbed by

humans each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health (Cordano 1998). Although humans can handle proportionally large concentrations of copper, too much copper still cause eminent health problems. Copper concentrations in air are usually quite low, so that exposure to copper through breathing is negligible. However, people that live near smelters that process copper ore into metals do experience this kind of exposure. People that live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking water through corrosion of pipes (Fewtrell *et al*., 2001). Occupational exposure to copper often occurs. In the workplace environment, copper contagion can lead to a flu-like condition known as metal. This condition will pass after two days and is caused by over sensitivity. Copper can exist in either the Cu^{+} or Cu^{2+} state and can therefore act as an important co-factor in a number of fundamental redox reactions (Donley *et al.*, 2002). However, due to this powerful redox activity, excess copper can lead to the production of the highly damaging hydroxyl radical; nonetheless, copper-requiring proteins are widespread and are involved in a number of biological processes including oxidative phosphorylation, cellular anti oxidant status and oxidation of iron (Davis *et al.,* 2001).

Long term exposure to copper can cause irritation of the nose, mouth, eyes and it causes headaches, stomach aches, dizziness, vomiting and diarrhea (Fuentealba *et al.*, 2000). High updates of copper may cause liver and kidney damage and even death. There are scientific articles that indicate a link between long term exposure to high concentrations of copper are decline in intelligence with young adolescents (Gotteland *et al.*,2001). Industrial exposure to copper fumes, dusts or mists may results in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper

poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage, demyelination, renal disease and copper deposition in cornea. Human disorders of copper metabolism, Menkes disease, and Wilson's disease, results in retinal degeneration (Waggonet *et al.*, 1999), possibly from the loss of copper transporting proteins in the retinal pigments epithelium (Krajacic *e al.*, 2006). The presence of copper (II) ions, cause serious toxicological concerns, it is usually known to deposit in brain, skin, liver, pancreas and myocardium. (Davies *et al.*, 2000).

2.13 METHODS OF REMOVING HEAVY METALS FROM WATER

2.13.1 Adsorption and Biosorption Processes

Adsorption is the ability of the adsorbate to adhere or attach to the adsorbent. It is a well established separation technique to remove dilute pollutants as well as to recover valuable products from aqueous streams. In the conventional adsorption process, the particle size of the adsorbent is restricted because of hydrodynamic phenomena such as pressure drop (Chia-Chang and Hwai-Shen, 2000). Adsorption is divided into two; one is due to forces of physical nature called van der Waals force. This adsorption is relatively weak and plays an unimportant part in connection with surface reactions, since they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is considerably stronger. The adsorbed molecules are held to the surface by valence force of the same type as those occurring between bound atoms in molecules. This is known as chemisorptions and the heat evolved is of the order 10 to 100 kcal per mole, compared to physisorption which has less than 5 kcal per mole Adsorptive removal of heavy metals from aqueous effluents which have received much attention in recent years is usually achieved by using activated carbon or activated alumina (Igwe *et al.*, 2005a). Activated carbon is a porous material with an extremely large surface area and intrinsic adsorption to many chemicals. Polymer

resins that can form complexes with the heavy metal ions are the best adsorbents. These are called conventional adsorbents and many others have been reported such as silica gel, active alumina, zeolite, metal oxides and so on. These conventional adsorbents are employed in many processes for the removal of heavy metals from wastewater such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, reverse osmosis, ion exchange and membrane technologies (Preetha and Viruthagiri 2005). These processes may be ineffective or expensive especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/L .Activated carbon is only able to remove 30-40 mg/g of Cd, Zn, and Cr in water and is non-regenerable, which is quite costly to wastewater treatment (Gang and Wiexing, 1998).

A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique, but it is not economically appealing because of high operational cost. As a result of these, biological methods such as biosorption /bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. Biosorption or bioremediations consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants. This process is characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic, materials to treatment sites (Gavrilescu, 2004). Biosorbents are prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and very cost-effective source of the raw material, biosorption is a progression towards a perspective method. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further

research. Biosorbents of plant origin are mainly agricultural by-products such as, maize cob and husk , sunflower stalk, *Medicago sativa* (Alfalfa) , cassava waste , wild cocoyam, sphagnum peat moss , sawdust , Sago waste , peanut skins , Shea butter seed husks , banana pith ,coconut fiber ,sugar-beet pulp, wheat bran , sugarcane bagasse and so on. Many other biosorbents of algal, fungal and bacteria biomass have been utilized. These includes among others; bacterial strains (*Pseudomonas ambigua, Desulfovibrio vulgaris, Enterobacter cloacae* Ho-1, *Alcaligenes eutrophus, Dinococcus radiodurans* R1) (Ioannis and Zouboulis, 2004). Bacteria are widespread, abundant, geochemically reactive components of aquatic environments. Fungal biomass has also been used. Most studies of biosorption for metal removal have involved the use of either laboratory-grown microorganism or biomass generated by the pharmacology and food processing industries or wastewater treatment unit. Therefore, this promotes environment eco-friendliness. The mechanisms by which microorganisms remove metals from solutions are: (i) extracellular accumulation / precipitation; (ii) cell-surface sorption or complexation; and (iii) intracellular accumulation. Among these mechanisms, extracellular accumulation/precipitation may be facilitated by using viable microorganisms, cell-surface sorption or complexation can occur with alive or dead microorganisms, while intracellular accumulation requires microbial activity. Although living and dead cells are capable of metal accumulation, there are differences in the mechanisms involved, depending on the extent of metabolic dependence. The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth and the environmental conditions during the biosorption process (such as pH, temperature, and the presence of certain co-ions) are important parameters that affect the performance of a living biosorbent. The efficiency of metal concentration on the

biosorbent is also influenced by metal solution chemical features. For agricultural by-products, the mode of sorption can be attributed to two main terms; intrinsic adsorption and coulombic interaction (Gang and Weixing, 1998). The coulombic term results from the electrostatic energy of interactions between the adsorbents and adsorbates. The charges on both substrates as well as softness or hardness of charge on both sides are mostly responsible for the intensity of the interaction. Coulombic interaction can be observed from the adsorption of cationic species versus anionic species on adsorbents (Gang and Weixing, 1998). The intrinsic adsorption of the materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbent on adsorption capacity.

Most biosorbents contain micropores and adsorption process is affected by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of micropores determines the accessibility of adsorbate molecules to the adsorption surface. Therefore, the pore size distribution of micropore is an important property for characterizing adsorptivity of adsorbents. Also, the existence of macropores, which serve as diffusion paths of adsorbate molecules from outside the granule to the micropores in fine powders and crystals can be used to classify adsorbents. These properties or attributes are possessed both by conventional and non-conventional adsorbents. This explains why they are capable of removing heavy metals from solution. In addition, non-conventional adsorbents contain cellulose which is made up of repeating units of β-D-glucose as a major component of cell walls. The polar hydroxyl groups on the cellulose could be involved in chemical reaction and hence bind heavy metals from solutions. The surface properties of these

functional groups on cellulose could be modified by incorporation of other functional groups, and this also affects the adsorption capacity (Igwe *et al.*, 2005b).

Chitosan is synthesized from chitin (2-acetamido-2- deoxy-b-D-glucose–(N-acetylglucan), which is the main structural component of mollusks, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps. Chitosan (2-acetamido-2-deoxy-b-Dglucose-(N-acetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution. The structure also looks very much like that of glucose.

2.14 SEDIMENT

Pollutants in the aquatic ecosystems will precipitate on the sediment surface and form as deposited pollutants. Sediments naturally consist of a complex mixture of organic and inorganic components like clays, silicate, carbonate, sulphide, minerals and bacteria. Sediments are well known as important sink and source for metal contaminants (Li and Thornton, 2001).

Pollutants like heavy metals are spread in sediment components and react through ion exchange, absorption and precipitation (Yuan *et al.*, 2004) there are three major mechanisms in heavy metals intake by sediments, which are physico-chemical absorption from water, biological intakes and accumulation of metals that are enriched with particles (Hart, 1982).

The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for absorption caused by the variation in grain size distribution (Davies *et*

al., 1991). Digenetic process in the sediments can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilized through sedimentation (Hanson *et al*., 1983). According to (Biney *et al*., 1991), microbial and redox processes may change the properties of sediments and affect the composition of interstitial water, while reworking of the sediments by the organisms will also bring sediments to the surface, where a significant fraction of heavy metals will be released.

In the sediment, metals accumulate through complex mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds. Several physico-chemical properties such as oxidation reductive potential, dissolved oxygen, organic and inorganic carbon content and the presence of some anions and cations influence (Fatma *et al*., 2009).

Sediments can play a useful role in the assessment of metal contamination because in unperturbed environment, metals are preferentially transferred from the dissolved to the particulate phase and as a result metal concentration in sediments are generally higher than in the overlying water and can reflect contamination load over long period of time (Forstner and Wittmann, 1981).

Heavy metals contamination in sediment can affect the water quality and the bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007).

Consequently, sediments enriched by heavy metals constitute a threat to the health of aquatic organisms (U.S Environmental Protection Agency, 2003).

2.15 WATER POLLUTION

Water Pollution is an undesirable change in the state of water, contaminated with harmful substances. It is the second most important environmental issue next to air pollution. Any change in the physical, chemical and biological properties of water that has a harmful effect on living things is water pollution. Water pollution affects all the major water bodies of the world such as lakes, rivers, oceans and groundwater. Polluted water is unfit for drinking and for other consumption processes. It is also not suitable for agricultural and industrial use. The effects of water pollution are harmful to human beings, plants, animals, fish and birds. Polluted water also contains viruses, bacteria, intestinal parasites and other harmful microorganisms, which can cause waterborne diseases such as diarrhea, dysentery, and typhoid. Due to water pollution, the entire ecosystem gets disturbed. It has been suggested that it is the leading worldwide cause of deaths and diseases (Pink, 2006) and that it accounts for the deaths of more than 14,000 people daily.

2.16 NEUTRON ACTIVATION ANALYSIS (NAA)

Neutron activation analysis (NAA) was discovered in 1936, when Heresy and Levi found that samples containing rare earth elements become highly radioactive after exposure to source of neutrons. From this observation, they quickly recognized the potential of employing nuclear reactions on samples followed by measurement of the induced radioactivity to facilitate both qualitative and quantitative identification of elements present in samples. NAA measures the total amount of an element in a material without regard to its chemical or physical form and has the following advantages;

(1) Samples for NAA can be liquids, solids or powders.

(2) NAA is non-destructive and since no pre-chemistry is required, reagent introduced contaminant are completely avoided.

(3) NAA is multi-elemental analytical technique in that many elements can readily be determined simultaneously.

(4) NAA has high sensitivity to identification of trace elements (Landsberger *et al*., 1994).

(5) NAA is totally unaffected by the presence of organic material in the sample. Organic material is a significant matrix problem in many types of conventional chemical methods.

Instrumental neutron activation analysis (INAA) procedure involves irradiating samples and appropriate standard reference material (SRM) with neutrons in a nuclear reactor to produce unstable radioactive nuclides. Many of these radionuclides emit gamma rays with characteristic energies that can be measured utilizing high resolution semiconductor detectors. Sample as small as 1mg can be quantitavely analyzed by INAA. Detection limits are in the parts per million to parts per billion range depending on the element. (Nyarko *et al*., 2003).

CHAPTER THREE

MATERIALS AND METHODS

3.1 THE STUDY AREA

Lake Tadee is situated at Ashanti Mampong in the Ashanti region of Ghana. Ashanti Mampong is situated at an altitude of about 475.5m above sea level and lies between latitudes 6.55 degrees and 7.30 degrees north and longitudes 0.05 degrees and 1.30 degrees west covering total land area of 2346 km^2 (Meteorological Services Department, 1988). The vegetation is a transitional zone which lies between the front of the south and Guinea Savanna of the north of Ghana. The area experiences 2 peaks of rainfalls. The major rainfall season is between March and July with short day spells in August and the minor season from September to October. The average humidity is about 90% during the wet season and 57% in the dry season. The mean daily temperature and monthly rainfall are 30.5 ^oC and 912 mm respectively (Meteorological Services Department, 2003). The soil is Savanna Ochrosol which is derived from the Voltain Sandstone within the Bediase Series which occurs in the upper slopes of the catena. The soil is well drained, friable, permeable and hard moderate water holding capacity (Soil Research Institute, 1989).

There are vegetable farmers that cultivate carrots, cabbage, green pepper, etc. around the catchment area of the lake as well as the washing of cars within the vicinity of the lake.

Figure 3.1: Map of Ashanti Mampong showing the study area.

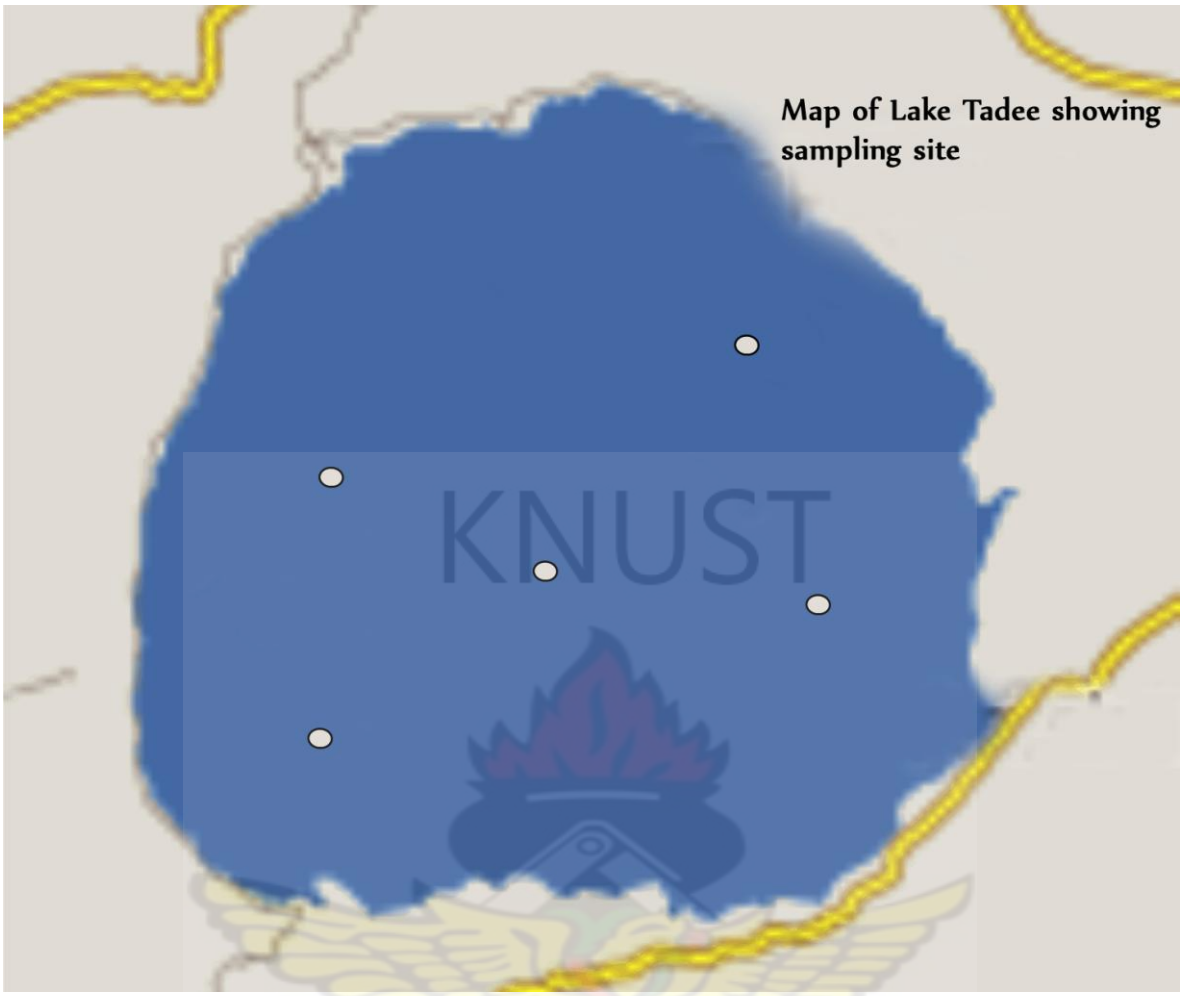

Figure 3.2: Map of Lake Tadee.

3.2 SAMPLE COLLECTION AND PREPARATION

Samples of water and sediments were collected from 5 sampling points from October 2010 to February, 2011. Samples were collected once every month from all the designated five sampling points.

3.2.1 Water Sampling and preparation

Polyethylene bottles for water collection were soaked in 10% nitric acid over night after they had been washed with soap. They were then washed with tap water and rinsed with doubled distilled water and dried before use. Water samples were taken from five (5) sampling points (from two inlets into the lake, one outlet and from two other points). The samples were collected to cover the sampling points of both littorals and limnetic zones of the lake. The water samples were collected at a depth of 20 cm using a pre-cleaned polyethylene 1litre sampling bottles. The samples were preserved by adding 2 ml of nitric acid to every 1L according to the method of Serfor-Armah *et al.,* (2006). The samples were then labeled and stored in ice in an ice chest and transported to Ghana Atomic Energy Laboratory and kept in a refrigerator until they were analyzed. Samples of water were filtered to remove solid particles in it. Water samples were prepared by weighing 500 mg of the sample into a smaller polyethylene capsule of diameter 1.2 cm and height 2.5 cm and heat sealed. The liquid samples were in turn put into bigger polyethylene capsule of diameter 1.6 cm and height 5.5 cm (Rabbit Capsule) that is double encapsulation. The standards for the controlled elements were equally prepared in the same way as the test samples.

3.2.2 Sediment Sampling and Preparation

Sediments were collected from all the five sampling points where water samples were collected. Sediment samples at a depth of about 10 – 20 cm were collected with pre-

cleaned plastic shovel. The plastic shovel was used to scoop the sediment. The sediment samples were transferred into pre-cleaned polyethylene bags and transported to the laboratory. The sediment samples were air dried at room temperature for three days. Using the polyethylene gloves, organic debris and other unwanted large particles were hand picked from each sample. They were pulverized to 80 mm mesh and were homogenized. Six replicate samples, 100 mg of each of the sediments was weighed into clean polyethylene foils, wrapped and heat sealed. The sub samples were packed into a 7ml polyethylene capsule and heat sealed.

3.2.3 Water and Sediment sampling of Kyiremfa river (Control).

Water and sediment samples were also collected from the river Kyiremfa as control which had little or no pollution as a result of less or no activities taking place at its catchment area. However, this water serves as the main source of drinking water for the community.

3.2.4 Preparation of Standards

The three standards 2 ppm, 5 ppm, and 10 ppm were prepared from the stock concentration of 1000ppm. The standards for various elements of interest were prepared. Copper standards (2 ppm and 5 ppm), mercury standards (0.04 ppm and 0.1 ppm) and cadmium standards (0.5 ppm and 1.0 ppm). The working standard solutions were prepared from the stock solution of 1000ppm (Fluka Analytical) using the formula:

$$\textit{Initial concentration} \times \textit{initial volume} = \textit{final concentration} \times \textit{final volume}$$

3.3 QUALITY CONTROL

The standard reference materials were obtained from the International Atomic Energy Agency (IAEA) - Soil 7 and sediment standard were used as quality control for the Instrumental Neutron Activation Analyzer (INAA) analysis. Six replicate samples were prepared for the reference materials in the same manner as the samples.

3.4 SAMPLES IRRADIATION AND COUNTING

All prepared samples and standards were irradiated using the Ghana Research Reactor-(GHARR-1) facility at Natural Nuclear Research Institute Laboratory of Ghana Atomic Energy commission (GAEC). The reactor was operated at a half full power of 15 kw and at thermal neutron flux of $5x10^{11}ncm^{-2}s^{-1}$. The capsules were sent into the inner irradiation sites of the reactor by means of a pneumatic transfer system operating at a pressure of 0.25 atms. The irradiation times, decay time and counting time were chosen according to the half-lives of the elements of interest. For water, irradiation times were two minutes, one hour and four hours and two weeks. For soil, irradiation times were ten seconds, one hour and two hours with corresponding cooling times of two minutes twenty four hours and two weeks according to the method of Dampare *et al.*, (2005). The irradiated samples were placed on top of the detector and counts time to obtain the spectra intensities.

3.5 QUALITATIVE AND QUANTITATIVE ANALYSIS

The qualitative and quantitative measurements of elements in samples were performed using PC-based gamma ray spectroscopy consisting of n-type high purity germanium (HPGe) detector model GR 2518 (Canberra industries Inc.), HV power supply model 3103, amplifier model 2020, an 8K ortec multi-channel buffer (MCB) emulation software card and a Pentium II computer for spectrum and data evaluation

and analysis. The detector had a relative efficiency of 25% to NaI detector and operated on a bias voltage of (-ve) 3000V with a resolution of 1.8KeV for ^{60}Co gamma-ray energy of 1332KeV. The multi-channel buffer (MCB) card was used to obtain the spectra intensities of the samples. The qualitative analysis involves the identification of the photopeaks of the elements of interest and quantitative analysis involves the conversion of the area under the photopeak of the identified element into concentrations. A Microsoft window based software MAESTRO was used for the analysis. The nuclear data which was used for the determination of the various elements in this study have been summarized in table 3.1

Table 3.1: Nuclear data of the elements used in NAA analysis

Element Counting	Isotope Produced	Gamma ray	Half-life	Decay time	Irradiation time		Counting Time (Tc)
					Sediment	Water	
Cu	Cu^{66}	1115.6	5.1min	5min	10 sec	2 min	10 min
Zn	Zn^{65}	1039.4	64 days	2-4 weeks	2hrs	4hrs	3600 sec
Cd	Cd^{115m}	336.3	53.3hrs	1-2 days	1hr	1hr	600 sec
Hg	Hg^{197}	77.4	64.1hrs	1-2 days	1hr	1hr	600 sec
As	As^{76}	559.1	26.3hrs	1-2 days	1hr	1hr	3600 sec

3.6 VALIDATION OF ANALYTICAL METHOD

The accuracy of the analytical method was evaluated using IAEA-1646a (trace elements and methylmercury in estuarine sediment) as certified reference material. The analytical values of the reference material obtained from this study were compared with the certified values (in ppm).

3.7 STATISTICAL ANALYSIS

The effects of water and sediment media on metal concentrations were determined by Mann Whitney rank-sum test. This test was chosen because the data was non-parametric. The analysis was made between the water and sediments with respect to the individual metal and to all the metals. The analysis was conducted with Genstat 15 software at a significance level of 5%.

CHAPTER FOUR

RESULTS

4.1 QUALITY CONTROL FOR ELEMENTAL ANALYSIS

The analytical results obtained at GHARR-1 laboratory for soil 7 and reference material IAEA-1646a compared with certified values are shown in table 4.1. The values compare favourably well with the recommended values for copper, zinc, cadmium, mercury and arsenic with bias less than 6%. The precision was calculated as a percentage relative standard deviation (%RSD) of six replicate samples of the prepared standard, and was found to be less than 5%.

Table 4.1: Analytical results (in ppm) of standard reference material IAEA-1646a (estuarine sediment), showing local laboratory values and recommended values

Analyte	This Work	Certified Value	Bias
% RSD			
Cu	10.00±0.366	10.01	-0.01
3.66			
Zn	51.28±1.780	48.90	2.38
3.47			
Cd	0.14±0.006	0.148	0.008
4.29			
Hg	0.03±0.001	0.04	-0.01
3.33			
As	6.12±0.166	6.23	-0.11
2.71			

4.2 Concentatration of Heavy Metals in Surface Water of Lake Tadee and Kyiremfa River

Table 4.2 provides results of the mean concentrations of heavy metals in the surface water of Lake Tadee and water quality guidelines of the World Health Organisation and the United State Environmental Agency. The mean concentration of zinc in the surface water in Lake and its control (Kyiremfa) river, were found to be 0.0932 and 0.026 mg/l respectively during the study period. Mean concentration of copper in the Lake Tadee and Kyiremfa River were also 0.017 mg/l and 0.0038 mg/l respectively. Cadmium, mercury and arsenic concentrations in both the surface water of the lake Tadee and the Kyiremfa River were below 0.001 mg/l.

Maximum concentrations of zinc and copper in the lake Tadee and Kyiremfa River were, however, recorded in different months. Whilst the maximum concentration of zinc in Lake Tadee was in October, Kyiremfa River recorded its highest concentration in December. The minimum concentrations of zinc in the Lake Tadee and Kyiremfa River were also recorded in January and October respectively (Table 4.2).

Maximum and Minimum concentrations of copper also followed similar monthly variations for Zinc. There were significant differences ($p<0.05$) recorded for the following metals (Zinc, Copper, Cadmium and Arsenic) in the surface water of Lake Tadee and Kyerimfa River.

There were also significant differences ($P<0.05$) observed for these metals (Zinc, Copper and Cadmium) in the surface water of the Lake Tadee and surface water of Kyerimfa River (control) except arsenic and mercury which showed insignificant differences ($P>0.05$). There were no significant differences ($P<0.05$) noticed between

the total metals in the surface water of the Lake Tadee and the surface water of Kyerimfa River.

Table 4.2: Mean Heavy Metals Concentration (mg/l) in Surface Water of Lake Tadee and United State Environmental Protection Agency and World Health Organization Guidelines.

Month	Heavy Metals (mean concentration)				
	Zinc	Copper	Cadmium	Mercury	Arsenic
October	0.174 (0.021)	0.020 (<0.001)	<0.001 (<0.001)	<0.001(<0.001)	<0.001(<0.001)
November	0.078 (0.022)	0.017 (<0.001)	<0.001 (<0.001)	<0.001(<0.001)	<0.001(<0.001)
December	0.079 (0.036)	0.019 (<0.001)	<0.001 (<0.001)	<0.001(<0.001)	<0.001(<0.001)
January	0.066 (0.024)	0.014 (<0.001)	<0.001 (<0.001)	<0.001(<0.001)	<0.001(<0.001)
February	0.069 (0.027)	0.015 (0.015)	<0.001 (<0.001)	<0.001(<0.001)	<0.001(<0.001)
Overall mean	0.093 (0.026)	0.017 (0.004)	<0.001 (<0.001)	<0.001(<0.001)	<0.001 (<0.001)
min	0.066 (0.021)	0.015 (0.001	<0.001 (<0.001)	<0.001(<0.001)	<0.001 (<0.001)
max	0.174 (0.036)	0.020 (0.015)	- -	--	- -
*USEPA	5.0	1.0	0.001	0.01	0.01
*WHO	3.0	2.0	0.001	0.01	0.01

Means in parenthesis are control values from Kyiremfa river

4.3 Mean Concentrations of Heavy Metals in Two Water Bodies With Reference to Water Quality Guidelines

The mean concentrations of study metals of the two water bodies and the United States Environmental Protection Agency (USEPA, 1997) and World Health

Organization (WHO, 1996). Generally, concentrations of all the study metals were different from the recommended concentrations of USEPA and WHO (table 4.2).

4.4 Concentrations of Heavy Metals in the Sediment of Lake Tadee and Kyiremfa River

In general, mean concentrations of zinc, copper and arsenic in the sediment of Lake Tadee and Kyiremfa River varied significantly during the period of study. There was, however, no difference in the concentrations of mercury in the two water bodies (Table 4.3). Mean zinc concentrations in the lake Tadee and in Kyiremfa River were respectively 9.0456 mg/kg and 7.408 mg/kg. The maximum zinc concentration in the Lake Tadee and in Kyiremfa River was recorded in October and December.

Results of the mean, maximum and minimum concentrations of copper and arsenic followed the trend recorded for the zinc in the sediments of the two water bodies. Relatively higher concentrations of cadmium were recorded in the lake Tadee than that of Kyiremfa River. Interestingly, all the cadmium concentrations in sediments of Kyiremfa River recorded during the study period was less than 0.001 mg/kg. A significantly higher differences ($P<0.05$) were noticed for the following metals: zinc, arsenic, and cadmium, in the bottom sediments of Lake Tadee and bottom sediment of Kyerimfa River except concentrations for copper. Also, significantly differences ($P<0.05$) were also recorded for the overall total metals concentrations in the Lake Tadee and Kyerimfa River.

Table 4.3: Mean Heavy Metals Concentration (mg/kg) in Sediment from Lake *Tadee*

Month	Heavy Metals									
	Zinc		Copper		Cadmium		Mercury		Arsenic	
October	8.683	(3.946)	10.072	(3.532)	0.096	(<0.001)	<0.001	(<0.001)	0.653	(0.286)
November	8.801	(5.135)	9.213	(4.001)	0.044	(<0.001)	<0.001	(<0.001)	0.619	(0.192)
December	10.041	(9.936)	9.687	(11.997)	0.043	(<0.001)	<0.001	(<0.001)	0.658	(0.394)
January	8.854	(9.004)	8.560	(10.899)	0.037	(<0.001)	<0.001	(<0.001)	0.553	(0.347)
February	8.849	(9.019)	8.561	(10.901)	0.036	(<0.001)	<0.001	(<0.001)	0.583	(0.311)
Overall mean	9.046	(7.408)	9.219	(8.266)	0.051	(<0.001)	<0.001	(<0.001)	0.613	(0.306)
min -	8.683	(3.946)	8.560	(3.532)	0.036	(<0.001)	<0.001	(<0.001)	0.553	(0.192)
max	10.041	(9.936)	10.072	(11.997)	0.096	(<0.001)	<0.001	(<0.001)	0.658	(0.394)

Means in parenthesis are control values from Kyiremfa river

CHAPTER FIVE

DISCUSSION

5.1 Concentration of Heavy Metals in Lake Tadee

The bottom sediment contains higher concentrations of the heavy metals investigated than that of overlying water. Results of this study revealed that, there were significant differences ($P< 0.05$) in the concentration of heavy metals in the bottom sediment compared to the surface water of the lake. The higher concentrations of heavy metals in the sediment of the lake may be due to the washing of cars around the lake, farming and dumping of waste. Surface runoff water through the gutters constructed into the lake may have also contributed to higher levels of heavy metals in the lake sediments. As heavy metals flow into the lake they adsorb to particulate matter and become heavier, settling at the bottom of the lake. This may have contributed to higher levels of heavy metals in the sediments than the surface water of the lake. The results were consistent with earlier research carried out by Depinto and Martin (1980) and Adomako *et al* (2008). According to Adomako *et al* (2008), concentrations of the heavy metals in sediments are higher than that of water and this might be due to the fact that metals can be either transported with the water or suspended sediment stored within lakebed bottom sediment. Again, suspended sediments and other solids are stored in lakebed sediment after they aggregated to form larger denser particles that settle at the bottom of the water.

Fostener and Wittmann (1981), believes that, sediments can play a useful role in the assessment of metal contamination because in stable environments, metals are preferentially transferred from the dissolved to the particulate phase. Consequently, metal concentration in sediments may be generally higher than the overlying water. This assertion may probably, account for the higher contamination load or

concentration recorded in sediments during the study. Other factors such as changes in temperature, pH and redox condition as well as effluent from domestic, municipal and agricultural waste including pesticides might have contributed to the higher level of heavy metals in the bottom sediments (Okweye *et. al.*, 2009). The higher concentration of heavy metals in the lake Tadee sediment is worrying as this may result in reduction in the benthic biodiversity. However, heavy metals were low at the surface water as a result of adsorption of the metals onto the particulate matter which becomes heavier and consequently settled at the bottom of the lake.

Mercury (Hg) concentration in both the Lake Sediment and Lake Water were below the detection limits. This could be attributed to the fact that, people living close to the catchment area as well as the vegetable farmers farming around the Lake have not been using mercury products.

Higher concentrations of zinc, cadmium, copper and arsenic in sediments might be due to the nature of the catchment area, municipal or domestic wastes, urban storm-water runoffs such as car batteries and other electrical wastes, agricultural wastes (fertilizers), leaching of metals from garbage and solid waste dump and geological weathering of parent rocks and atmospheric sources. Zinc is used in a wide variety of industrial, agricultural, and consumer products.

5.2 Concentration of Heavy Metals in Lake Tadee and Kyiremfa River

The concentrations of heavy metals in Lake Tadee and the Kyiremfa River (control stream) showed significant differences ($P < 0.05$) (Appendix viii). The increased concentrations of heavy metals in the Lake Tadee could be attributed to the current land use practices around the lake. Extensive use of pesticides in vegetable cultivation

such as carrot, lettuce, green pepper and garden eggs around the vicinity of the lake could be responsible for the increased contamination by heavy metals of the lake.
Car washing activities and dumping of domestic waste could be other factors responsible for the increased concentration of heavy metals in the lake.

As a river, Kyiremfa has the potential of reducing the build up of heavy metals as it moves along. Some of the pollutants in the stream adsorbed to other particles and its ability to disperse pollutants.

Concentrations of the other four metals (Cd, Zn, Cu and As) showed significant variations in sediments the two water bodies as a result of anthropogenic inputs, both point and non- point sources. These heavy metals may have entered the lake as a result of wet deposition through rain.

5.3 Comparisons of Heavy Mean Metal Concentrations and Recommended Guidelines

Comparing the results obtained in this study with the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) permissible levels of heavy metals in drinking water its clear that, the concentrations of Zn, Cu, Cd, As and Hg in the Lake Tadee and Kyiremfa River were below WHO and USEPA Levels (Table 4.2). This suggests that, although the two water bodies had witnessed some level of contamination, currently, they are within acceptable limits of USEPA (1997) and WHO (1996) recommended guidelines. Considering, however, the two water bodies, the current activities around the lake Tadee could pollute it faster than that of the Kyiremfa River. Sources of pollutants include direct disposal of domestic

waste, surface run off, agricultural waste including spraying of vegetables and car washing.

The Kyiremfa River being the main source of water supply for the Mampong Municipality was found to be less contaminated as a result of being controlled by Ghana Water Company. People have also been banned from farming around the river. This may have contributed to the stream being less contaminated than the Lake Tadee. In general, Lake Tadee and Kyiremfa River were not contaminated with heavy metals and is not injurious to aquatic organisms and health of people who use the water for their domestic activities and irrigation of crops.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The results of this study showed that, concentrations of heavy metals in the surface water and bottom sediments of Lake Tadee were significantly higher than that of the Kyerimfa River which could be an indication of heavy metal pollution. However, the heavy metal concentrations in Lake Tadee were below the USEPA and WHO recommended levels for heavy metals in drinking water. Therefore using water from Lake Tadee for domestic and agricultural purposes would not pose any heavy metallic related threats to the health of the people who use water from the Lake.

6.2 Recommendations

From the results of this study, it is recommended that;

- Further study should be conducted to assess pollution of the Lake Tadee by other heavy metals not considered in this study.
- There should be educational campaign by organizations such as the Ghana Water Company, EPA and the Public Health Divisions of the Ghana Health Service to create awareness of the consequences of heavy metals accumulation in the lake.
- The traditional leaders and district assemblies should institute bye-laws to prevent people from discharging wastes, washing of cars and farming near or around the lake.
- There should be redirection of the gutters that have been constructed into the lake to prevent run off water which transport both liquid and solid waste into the lake.

- Fines and imprisonment should meted to people who dump waste, wash cars and also perform unhygienic activities that can result in heavy metal concentration in the lake.
- Afforestation should be undertaken around the lake.

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APPENDIX I IN

CONCENTRATION OF WATER SAMPLES (mg /l)

OCTOBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	0.234±0.011	0.051+0.002	<0.001	<0.001	<0.001
B	0.022±0.001	<0.001	<0.001	<0.001	<0.001
C	0.052±0.001	<0.001	<0.001	<0.001	<0.001
D	0.032±0.001	<0.001	<0.001	<0.001	<0.001
E	0.033±0.001	<0.001	<0.001	<0.001	<0.001
contol	0.021±0.001	<0.001	<0.001	<0.001	<0.001

CONCENTRATION OF SEDIMENT SAMPLES (mg/kg)

OCTOBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	13.093±1.623	13.973±0.962	0.173±0.011	<0.001	0.700±0.007
B	5.093±0599	7.027±0.899	0.013±0.011	<0.001	0.413±0.044
C	4.947±0.565	5.533±0.652	<0.001	<0.001	0.704±0.066
D	12.787±1.561	16.467±1.067	0.173±0.002	<0.001	0.588±0.057
E	7.493±0.935	7.360±0.103	0.120±0.001	<0.001	0.814±0.062
Control	3.946±0.564	3.532±0.372	<0.001	<0.001	0.601±0.056

APPENDIX II

CONCENTRATION OF WATER SAMPLES (mg/l)

NOVEMBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	0.244±0.011	0.044+0.001	<0.001	<0.001	<0.001
B	0.018±0.001	<0.001	<0.001	<0.001	<0.001
C	0.055±0.001	<0.001	<0.001	<0.001	<0.001
D	0.041±0.001	0.038±0.001	<0.001	<0.001	<0.001
E	0.031±0.001	<0.001	<0.001	<0.001	<0.001
Control	0.022±0.001	<0.001	<0.001	<0.001	<0.001

CONCENTRATION OF SEDIMENT SAMPLES (mg/kg)

NOVEMBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	14.073±1.891	13.7633±0.962	0.073±0.001	<0.001	0.685±0.055
B	5.769±0.663	6.007±0.757	0.011±0.001	<0.001	0.311±0.032
C	5.144±0.510	4.642±0.542	<0.001	<0.001	0.701±0.076
D	11.932±1.788	13.670±1.009	0.113±0.002	<0.001	0.611±0.062
E	7.089±0.788	7.984±0.793	0.022±0.001	<0.001	0.789±0.071
Control	5.135±0.421	4.001±0.321	<0.001	<0.001	0.192±0.013

APPENDIX III

CONCENTRATION OF WATER SAMPLES (mg/l)

DECEMBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	0.246±0.011	0.049+0.001	<0.001	<0.001	<0.001
B	0.021±0.001	<0.001	<0.001	<0.001	<0.001
C	0.052±0.001	<0.001	<0.001	<0.001	<0.001
D	0.049±0.001	0.041±0.001	<0.001	<0.001	<0.001
E	0.027±0.001	<0.001	<0.001	<0.001	<0.001
Control	0.036±0.001	<0.001	<0.001	<0.001	<0.001

CONCENTRATION OF SEDIMENT SAMPLES (mg/kg)

DECEMBER '10

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	13.928±1.407	14.315±1.526	0.069±0.001	<0.001	0.773±0.052
B	6.691±0.616	7.211±0.699	0.017±0.001	<0.001	0.324±0.029
C	6.114±0.602	4.894±0.312	<0.001	<0.001	0.792±0.068
D	12.482±1.810	13.702±1.121	0.092±0.001	<0.001	0.599±0.049
E	10.992±1.094	8.916±0.701	0.036±0.001	<0.001	0.080±0.079
Control	9.936±1.002	11.997±1.079	<0.001	<0.001	0.394±0.027

APPENDIX IV

CONCENTRATION OF WATER SAMPLES (mg/l)

JANUARY '11

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	0.187±0.011	0.037+0.001	<0.001	<0.001	<0.001
B	0.017±0.001	<0.001	<0.001	<0.001	<0.001
C	0.051±0.001	<0.001	<0.001	<0.001	<0.001
D	0.041±0.001	0.031±0.001	<0.001	<0.001	<0.001
E	0.032±0.001	<0.001	<0.001	<0.001	<0.001
Control	0.024±0.001	<0.001	<0.001	<0.001	<0.001

CONCENTRATION OF SEDIMENT SAMPLES (mg/kg)

JANUARY '11

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	12.076±1.411	13.299±1.399	0.061±0.04	<0.001	0.642±0.049
B	4.99±0.611	6.412±0.731	0.016±0.01	<0.001	0.219±0.017
C	4.314±0.603	3.912±0.441	<0.001	<0.001	0.701±0.068
D	11.817±1.311	11.291±1.312	0.079±0.001	<0.001	0.489±0.061
E	11.073±1.101	7.888±0.798	0.028±0.001	<0.001	0.717±0.077
Control	9.004±1.004	10.899±1.067	<0.001	<0.001	0.347±0.029

APPENDIX V

CONCENTRATION OF WATER SAMPLES (mg/l)

FEBRUARY '11

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	0.201±0.009	0.039+0.001	<0.001	<0.001	<0.001
B	0.019±0.001	<0.001	<0.001	<0.001	<0.001
C	0.052±0.001	<0.001	<0.001	<0.001	<0.001
D	0.050±0.001	0.033±0.001	<0.001	<0.001	<0.001
E	0.030±0.001	<0.001	<0.001	<0.001	<0.001
Control	0.027±0.001	0.015±0.002	<0.001	<0.001	<0.001

CONCENTRATION OF SEDIMENT SAMPLES (mg/kg)

FEBRUARY '11

WATER SAMPLE ID	ZINC	COPPER	CADMIUM	MERCURY	ARSENIC
A	12.012±1.402	13.319±1.413	0.059±0.001	<0.001	0.661±0.059
B	5.007±0.701	6.555±0.699	0.019±0.001	<0.001	0.211±0.017
C	4.431±0.607	3.814±0.497	<0.001	<0.001	0.812±0.072
D	11.779±1.291	11.112±1.296	0.071±0.001	<0.001	0.511±0.060
E	11.015±1.101	8.007±0.799	0.031±0.001	<0.001	0.723±0.079
Control	9.019±1.005	10.901±1.061	<0.001	<0.001	0.311±0.005

APPENDIX VI

```
GenStat Release 11.1 ( PC/Windows) 26 April 2011 20:39:10
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Registered to: TEAM TBE 2008-06-19

                    ____________________________________________

                    GenStat Eleventh Edition
                    GenStat Procedure Library Release PL19.1
                    ____________________________________________

 1  %CD 'C:/Users/paddykay/Documents'
 2  "Data taken from unsaved spreadsheet: New Data;1"
 3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
 4  READ [PRINT=*; SETNVALUES=yes] _stitle_
 7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 26-Apr-2011 20:39:25

 8  DELETE [REDEFINE=yes] ZONE,METAL,MONTH,CONC_Hg
 9  UNITS [NVALUES=*]
10  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Sediment','Water')\
11  ; REFERENCE=1] ZONE
12  READ ZONE; FREPRESENTATION=ordinal

            Identifier      Values     Missing      Levels
                  ZONE          50           0           2

15  TEXT [NVALUES=50] METAL
16  READ METAL

            Identifier     Minimum        Mean     Maximum      Values     Missing
                 METAL                                             50           0

21  TEXT [NVALUES=50] MONTH
22  READ MONTH

            Identifier     Minimum        Mean     Maximum      Values     Missing
                 MONTH                                             50           0

31  VARIATE [NVALUES=50] CONC_Hg
32  READ CONC_Hg

            Identifier     Minimum        Mean     Maximum      Values     Missing
               CONC_Hg    0.001000      0.3073      0.8140          50           0

38
39  MANNWHITNEY  [PRINT=test; METHOD=twosided; GROUPS=ZONE] CONC_Hg

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONC_As
Group factor: ZONE

Value of U: 0.0 (first sample has higher rank sum).
```

Exact probability < 0.001
(under null hypothesis that group Sediment is equal to group Water).

Sample sizes: 25, 25.

GenStat Release 11.1 (PC/Windows) 26 April 2011 20:27:16

Registered to: TEAM TBE 2008-06-19

GenStat Eleventh Edition
GenStat Procedure Library Release PL19.1

```
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 2  "Data taken from unsaved spreadsheet: New Data;1"
 3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
 4  READ [PRINT=*; SETNVALUES=yes] _stitle_
 7  PRINT [IPRINT=*] _stitle_; JUST=left
```

Data imported from Clipboard
on: 26-Apr-2011 20:27:28

```
 8  DELETE [REDEFINE=yes] ZONE,METAL,MONTH,CONC_Cd
 9  UNITS [NVALUES=*]
10  FACTOR [MODIFY=yes; NVALUES=53; LEVELS=2; LABELS=!t('Sediment','Water')\
11  ; REFERENCE=1] ZONE
12  READ ZONE; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
ZONE	53	0	2

```
15  TEXT [NVALUES=53] METAL
16  READ METAL
```

Identifier	Minimum	Mean	Maximum	Values	Missing
METAL				53	0

```
21  TEXT [NVALUES=53] MONTH
22  READ MONTH
```

Identifier	Minimum	Mean	Maximum	Values	Missing
MONTH				53	0

```
31  VARIATE [NVALUES=53] CONC_Cd
32  READ CONC_Cd
```

Identifier	Minimum	Mean	Maximum	Values	Missing	
CONC_Cd	0.001000	0.02612	0.1730	53	3	Skew

```
38
39  MANNWHITNEY  [PRINT=test; METHOD=twosided; GROUPS=ZONE] CONC_Cd
```

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONC_Cd
Group factor: ZONE

Value of U: 62.5 (first sample has higher rank sum).

Exact probability (adjusted for ties) < 0.001
(under null hypothesis that group Sediment is equal to group Water).

Sample sizes: 25, 25.

Message: missing values have been ignored.

```
 40  MANNWHITNEY  [PRINT=test; METHOD=twosided; GROUPS=ZONE] CONC_Cu
```

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONC_Cu
Group factor: ZONE

Value of U: 0.0 (first sample has higher rank sum).

Exact probability < 0.001
(under null hypothesis that group Sediment is equal to group Water).

Sample sizes: 25, 25.

GenStat Release 11.1 (PC/Windows) 26 April 2011 20:35:53
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  1  %CD 'C:/Users/paddykay/Documents'
  2  "Data taken from unsaved spreadsheet: New Data;1"
  3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
  4  READ [PRINT=*; SETNVALUES=yes] _stitle_
  7  PRINT [IPRINT=*] _stitle_; JUST=left
```

Data imported from Clipboard
on: 26-Apr-2011 20:36:05

```
  8  DELETE [REDEFINE=yes] ZONE,METAL,MONTH,CONC_Hg
  9  UNITS [NVALUES=*]
 10  FACTOR [MODIFY=yes; NVALUES=52; LEVELS=2; LABELS=!t('Sediment','Water')\
 11  ; REFERENCE=1] ZONE
 12  READ ZONE; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
ZONE	52	0	2

```
 15  TEXT [NVALUES=52] METAL
 16  READ METAL

      Identifier     Minimum        Mean     Maximum      Values     Missing
           METAL                                             52           0

 21  TEXT [NVALUES=52] MONTH
 22  READ MONTH

      Identifier     Minimum        Mean     Maximum      Values     Missing
           MONTH                                             52           0

 31  VARIATE [NVALUES=52] CONC_Hg
 32  READ CONC_Hg

      Identifier     Minimum        Mean     Maximum      Values     Missing
          CONC_Hg    0.001000    0.001000    0.001000          52           0

 38
 39  MANNWHITNEY  [PRINT=test; METHOD=twosided; GROUPS=ZONE] CONC_Hg

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONC_Hg
Group factor: ZONE
Message: all values are tied.

Value of U: 338.0 (second sample has higher rank sum).

Exact probability (adjusted for ties): 1.000
(under null hypothesis that group Sediment is equal to group Water).

Sample sizes: 26, 26.
```

APPENDIX VII

```
GenStat Release 11.1 ( PC/Windows) 26 April 2011 17:09:35
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                    ____________________________________________

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                    GenStat Procedure Library Release PL19.1
                    ____________________________________________

  1  %CD 'C:/Users/paddykay/Documents'
  2  "Data taken from unsaved spreadsheet: New Data;1"
  3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
  4  READ [PRINT=*; SETNVALUES=yes] _stitle_
  7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 26-Apr-2011 17:09:48
```

```
 8  DELETE [REDEFINE=yes] ZONE,METAL,MONTH,CONC_Zn
 9  UNITS [NVALUES=*]
10  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Sediment','Water')\
11  ; REFERENCE=1] ZONE
12  READ ZONE; FREPRESENTATION=ordinal

    Identifier      Values     Missing      Levels
          ZONE          50           0           2

15  TEXT [NVALUES=50] METAL
16  READ METAL

    Identifier     Minimum        Mean     Maximum      Values     Missing
         METAL                                             50           0

21  TEXT [NVALUES=50] MONTH
22  READ MONTH

    Identifier     Minimum        Mean     Maximum      Values     Missing
         MONTH                                             50           0

31  VARIATE [NVALUES=50] CONC_Zn
32  READ CONC_Zn

    Identifier     Minimum        Mean     Maximum      Values     Missing
       CONC_Zn     0.01100       4.569       14.07          50           0

38
39  MANNWHITNEY  [PRINT=test; METHOD=twosided; GROUPS=ZONE] CONC_Zn

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONC_Zn
Group factor: ZONE

Value of U: 0.0 (first sample has higher rank sum).

Exact probability < 0.001
(under null hypothesis that group Sediment is equal to group Water).

Sample sizes: 25, 25.
```

APPENDIX VIII

```
Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: WATER_BODY

Value of U: 27398.0 (first sample has higher rank sum).

Normal approximation: 2.38 (p=0.017)
Adjusted for ties:    2.60 (p=0.009)
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 250, 250.
```

Ranks for individual variables

group Lake												
359.0	358.0	334.0	312.5	374.0	360.0	277.0	336.0	326.0	310.0	361.0	281.5	334.0
329.5	301.0	349.0	275.5	332.0	326.0	312.5	355.0	271.5	334.0	331.0	308.0	337.0
135.5	135.5	322.5	135.5	328.0	135.5	135.5	322.5	135.5	329.5	135.5	135.5	326.0
135.5	321.0	135.5	135.5	310.0	135.5	324.0	135.5	135.5	314.0	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	490.0	424.0	421.0	489.0	442.0
498.0	432.0	430.0	479.0	439.0	496.0	437.0	434.0	488.0	472.0	487.0	422.0	417.0
478.0	474.0	486.0	423.0	418.0	477.0	473.0	497.0	438.0	431.0	500.0	441.0	495.0
433.0	419.0	494.0	444.0	499.0	440.0	420.0	491.0	446.0	492.0	435.0	407.0	476.0
443.0	493.0	436.0	406.0	475.0	445.0	347.5	273.0	135.5	347.5	346.0	342.0	271.5
135.5	345.0	287.5	340.0	275.5	135.5	344.0	317.5	339.0	274.0	135.5	343.0	307.0
338.0	278.0	135.5	341.0	310.0	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	394.0	380.0	391.0	383.0	400.0	388.0	369.5	389.5	385.0
396.0	395.0	373.0	397.0	384.0	398.0	386.0	357.0	389.5	381.0	392.0	387.0	356.0
399.0	382.0	393.0										
group Stream												
281.5	281.5	281.5	281.5	281.5	287.5	287.5	287.5	287.5	287.5	317.5	317.5	317.5
317.5	317.5	293.0	293.0	293.0	293.0	293.0	301.0	301.0	301.0	301.0	301.0	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	410.0	410.0	410.0	410.0	410.0
427.0	427.0	427.0	427.0	427.0	459.0	459.0	459.0	459.0	459.0	449.0	449.0	449.0
449.0	449.0	454.0	454.0	454.0	454.0	454.0	403.0	403.0	403.0	403.0	403.0	414.5
414.5	414.5	414.5	482.5	482.5	482.5	482.5	482.5	482.5	464.0	464.0	464.0	464.0
464.0	469.0	469.0	469.0	469.0	469.0	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5
135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5	135.5

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: WATER_BODY

Value of U: 6885.0 (first sample has higher rank sum).

Normal approximation: 1.62 (p=0.105)
Adjusted for ties: 2.17 (p=0.030)
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 125, 125.

Ranks for individual variables

group Lake

247.0	246.0	240.0	219.5	250.0	248.0	193.0	242.0	232.0	217.5	249.0	196.5	240.0
235.5	212.5	244.0	192.0	238.0	232.0	219.5	245.0	191.0	240.0	237.0	216.0	243.0
95.5	95.5	228.5	95.5	234.0	95.5	95.5	228.5	95.5	235.5	95.5	95.5	232.0
95.5	227.0	95.5	95.5	217.5	95.5	230.0	95.5	95.5	221.0	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5					

group Stream

196.5	196.5	196.5	196.5	196.5	202.0	202.0	202.0	202.0	202.0	224.0	224.0	224.0
224.0	224.0	207.0	207.0	207.0	207.0	207.0	212.5	212.5	212.5	212.5	212.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5					

APPENDIX IX

Kruskal-Wallis one-way analysis of variance

Variate: CONCENTRATION
Group factor: METAL
Value of H = 97.30
Adjusted for ties = 109.4

Sample	Size	Mean rank
Group As	50	124.01
Group Cd	50	95.34
Group Cu	50	160.26
Group Hg	50	60.50
Group Zn	50	187.39

Degrees of freedom = 4
Chi-square probability < 0.001

Message: missing values have been ignored.

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: WATER_BODY

Value of U: 6675.5 (first sample has higher rank sum).

Normal approximation: 1.99 (p=0.047)
Adjusted for ties: 2.02 (p=0.043)
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 125, 125.

Ranks for individual variables

group Lake

240.0	174.0	171.0	239.0	192.0	248.0	182.0	180.0	229.0	189.0	246.0	187.0	184.0
238.0	222.0	237.0	172.0	167.0	228.0	224.0	236.0	173.0	168.0	227.0	223.0	247.0
188.0	181.0	250.0	191.0	245.0	183.0	169.0	244.0	194.0	249.0	190.0	170.0	241.0
196.0	242.0	185.0	157.0	226.0	193.0	243.0	186.0	156.0	225.0	195.0	104.5	82.0
40.5	104.5	103.0	99.0	81.0	40.5	102.0	86.0	97.0	84.0	40.5	101.0	94.0
96.0	83.0	40.5	100.0	92.0	95.0	85.0	40.5	98.0	93.0	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	144.0	130.0	141.0	133.0
150.0	138.0	120.5	139.5	135.0	146.0	145.0	124.0	147.0	134.0	148.0	136.0	112.0
139.5	131.0	142.0	137.0	111.0	149.0	132.0	143.0					

group Stream

160.0	160.0	160.0	160.0	160.0	177.0	177.0	177.0	177.0	177.0	209.0	209.0	209.0
209.0	209.0	199.0	199.0	199.0	199.0	199.0	204.0	204.0	204.0	204.0	204.0	153.0
153.0	153.0	153.0	153.0	164.5	164.5	164.5	164.5	232.5	232.5	232.5	232.5	232.5
232.5	214.0	214.0	214.0	214.0	214.0	219.0	219.0	219.0	219.0	219.0	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	115.0	115.0	115.0	115.0
115.0	108.0	108.0	108.0	108.0	108.0	89.0	89.0	89.0	89.0	89.0	127.0	127.0
127.0	127.0	127.0	120.5	120.5	120.5	120.5	120.5					

APPENDIX

30 MANNWHITNEY [PRINT=test,ranks; METHOD=twosided; GROUPS=Zone] Concentration

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: Concentration
Group factor: Zone

Value of U: 42.5 (first sample has higher rank sum).

Exact probability (adjusted for ties) < 0.001
(under null hypothesis that group Lake sediment is equal to group Stream sediment).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake sediment

44.0	30.0	41.0	33.0	50.0	38.0	20.5	39.5	35.0	46.0	45.0	24.0	47.0
34.0	48.0	36.0	12.0	39.5	31.0	42.0	37.0	11.0	49.0	32.0	43.0	

group Stream sediment

15.0	15.0	15.0	15.0	15.0	8.0	8.0	8.0	8.0	8.0	3.0	3.0	3.0
3.0	3.0	27.0	27.0	27.0	27.0	27.0	20.5	20.5	20.5	20.5	20.5	

```
  1  %CD 'C:/Users/paddykay/Documents'
  2  "Data taken from unsaved spreadsheet: New Data;1"
  3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
  4  READ [PRINT=*; SETNVALUES=yes] _stitle_
  7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 5-May-2011 17:54:39

  8  DELETE [REDEFINE=yes] Zone,C2,Concentration
  9  UNITS [NVALUES=*]
 10  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Lake water',\
 11  'Stream water'); REFERENCE=1] Zone
 12  READ Zone; FREPRESENTATION=ordinal

          Identifier          Values         Missing          Levels
                Zone              50               0               2

 15  TEXT [NVALUES=50] C2
 16  READ C2

          Identifier         Minimum            Mean         Maximum          Values         Missing
                  C2                                                            50               0

 21  VARIATE [NVALUES=50] Concentration
 22  READ Concentration

          Identifier         Minimum            Mean         Maximum          Values         Missing
       Concentration        0.001000        0.001000        0.001000              50               0

 28
 29  WSTATISTIC [PRINT=test] Concentration

Shapiro-Wilk test for Normality

Data variate:                Concentration
Test statistic W:             1.0000
Probability:                  1.000

 40  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=Zone] Concentration

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: Concentration
Group factor: Zone
Message: all values are tied.

Value of U: 312.5 (second sample has higher rank sum).

Exact probability (adjusted for ties): 1.000
(under null hypothesis that group Lake water is equal to group Stream water).

Sample sizes: 25, 25.

Ranks for individual variables
```

group Lake water
25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5
25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5
group Stream water
25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5
25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5 25.5

APPENDIX XI

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```
 1  %CD 'C:/Users/paddykay/Documents'
 2  "Data taken from unsaved spreadsheet: New Data;1"
 3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
 4  READ [PRINT=*; SETNVALUES=yes] _stitle_
 7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 5-May-2011 17:51:46

 8  DELETE [REDEFINE=yes] Water_body,Zone,C3,Concentration
 9  UNITS [NVALUES=*]
10  FACTOR [MODIFY=yes; NVALUES=100; LEVELS=2; LABELS=!t('Lake','Stream')\
11  ; REFERENCE=1] Water_body
12  READ Water_body; FREPRESENTATION=ordinal

      Identifier        Values       Missing        Levels
      Water_body           100             0             2

16  TEXT [NVALUES=100] Zone
17  READ Zone

      Identifier       Minimum          Mean       Maximum        Values       Missing
            Zone                                                    100             0

41  TEXT [NVALUES=100] C3
42  READ C3

      Identifier       Minimum          Mean       Maximum        Values       Missing
              C3                                                    100             0

50  VARIATE [NVALUES=100] Concentration
51  READ Concentration

      Identifier       Minimum          Mean       Maximum        Values       Missing
   Concentration      0.001000        0.2121        0.8140           100             0
```

61
62 MANNWHITNEY [PRINT=test,ranks; METHOD=twosided; GROUPS=Water_body]
Concentration

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: Concentration
Group factor: Water_body

Value of U: 980.0 (first sample has higher rank sum).

Exact probability (adjusted for ties): 0.046
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 50, 50.

Ranks for individual variables

group Lake

25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5
25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	94.0
80.0	91.0	83.0	100.0	88.0	70.5	89.5	85.0	96.0	95.0	74.0	97.0	84.0
98.0	86.0	62.0	89.5	81.0	92.0	87.0	61.0	99.0	82.0	93.0		

group Stream

25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5
25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	65.0
65.0	65.0	65.0	65.0	58.0	58.0	58.0	58.0	58.0	53.0	53.0	53.0	53.0
53.0	77.0	77.0	77.0	77.0	77.0	70.5	70.5	70.5	70.5	70.5		

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1 %CD 'C:/Users/paddykay/Documents'
70 MANNWHITNEY [PRINT=test,ranks; METHOD=twosided; GROUPS=Water_body]
Concetration

Mann-Whitney U (Wilcoxon rank-sum) test
Variate: Concetration
Group factor: Water_body

Value of U: 750.0 (first sample has higher rank sum).

Exact probability (adjusted for ties) < 0.001
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 50, 50.

Ranks for individual variables

group Lake

40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	99.5
82.0	40.5	99.5	98.0	94.0	81.0	40.5	97.0	86.0	92.0	84.0	40.5	96.0
89.0	91.0	83.0	40.5	95.0	87.0	90.0	85.0	40.5	93.0	88.0		

group Stream

40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5
40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5		

APPENDIX XII

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```
 1  %CD 'C:/Users/paddykay/Documents'
40  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=Zone] Concentration
```

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: Concentration
Group factor: Zone

Value of U: 62.5 (first sample has higher rank sum).

Exact probability (adjusted for ties) < 0.001
(under null hypothesis that group Lake Sediment is equal to group Stream Sediment).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake Sediment

49.5	32.0	15.5	49.5	48.0	44.0	31.0	15.5	47.0	36.0	42.0	34.0	15.5
46.0	39.0	41.0	33.0	15.5	45.0	37.0	40.0	35.0	15.5	43.0	38.0	

group Stream Sediment

15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5
15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	

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```
  1  %CD 'C:/Users/paddykay/Documents'
 30  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=ZONE]
CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: ZONE

Value of U: 260.0 (first sample has higher rank sum).

Exact probability: 0.316
(under null hypothesis that group Lake Sediment is equal to group Stream
Sediment).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake Sediment
    48.0    18.0    14.0    50.0    20.0    47.0    15.0    12.0    46.0    22.0    49.0    19.0    13.0
    43.0    24.0    44.0    16.0     7.0    36.0    21.0    45.0    17.0     6.0    35.0    23.0
group Stream Sediment
     3.0     3.0     3.0     3.0     3.0     9.5     9.5     9.5     9.5    39.5    39.5    39.5    39.5
    39.5    39.5    27.0    27.0    27.0    27.0    27.0    32.0    32.0    32.0    32.0    32.0


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                    ____________________________________

  1  %CD 'C:/Users/paddykay/Documents'
 53  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=WATER_BODY]
CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: WATER_BODY

Value of U: 1110.0 (first sample has higher rank sum).

Exact probability (adjusted for ties): 0.326
(under null hypothesis that group Lake is equal to group Stream).

Sample sizes: 50, 50.

Ranks for individual variables

group Lake
    50.0    18.0    18.0    44.5    18.0    48.0    18.0    18.0    44.5    18.0    49.0    18.0    18.0
    47.0    18.0    43.0    18.0    18.0    41.0    18.0    46.0    18.0    18.0    42.0    18.0    98.0
    68.0    64.0   100.0    70.0    97.0    65.0    62.0    96.0    72.0    99.0    69.0    63.0    93.0
    74.0    94.0    66.0    57.0    86.0    71.0    95.0    67.0    56.0    85.0    73.0
```

group Stream

18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
18.0	18.0	18.0	18.0	18.0	18.0	18.0	38.0	38.0	38.0	38.0	38.0	53.0
53.0	53.0	53.0	53.0	59.5	59.5	59.5	59.5	89.5	89.5	89.5	89.5	89.5
89.5	77.0	77.0	77.0	77.0	77.0	82.0	82.0	82.0	82.0	82.0		

APPENDIX XIII

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```
 1  %CD 'C:/Users/paddykay/Documents'
 2  "Data taken from unsaved spreadsheet: New Data;1"
 3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
 4  READ [PRINT=*; SETNVALUES=yes] _stitle_
 7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 5-May-2011 18:13:58

 8  DELETE [REDEFINE=yes] WATER_BODY,ZONE,METAL,CONCENTRATION
 9  UNITS [NVALUES=*]
10  TEXT [NVALUES=50] WATER_BODY
11  READ WATER_BODY

            Identifier      Minimum         Mean      Maximum       Values      Missing
  WATER_BODY                                                            50            0

18  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Lake water',\
19  'Stream water'); REFERENCE=1] ZONE
20  READ ZONE; FREPRESENTATION=ordinal

            Identifier      Values     Missing      Levels
                  ZONE          50           0           2

23  TEXT [NVALUES=50] METAL
24  READ METAL

            Identifier      Minimum         Mean      Maximum       Values      Missing
                 METAL                                                  50            0

29  VARIATE [NVALUES=50] CONCENTRATION
30  READ CONCENTRATION

            Identifier      Minimum         Mean      Maximum       Values      Missing
CONCENTRATION              0.001000      0.01034      0.05700           50            0   Skew
```

```
 36
 37  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=ZONE]
CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: ZONE

Value of U: 225.0 (first sample has higher rank sum).

Exact probability (adjusted for ties): 0.038
(under null hypothesis that group Lake water is equal to group Stream water).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake water
     50.0    18.0    18.0    44.5    18.0    48.0    18.0    18.0    44.5    18.0    49.0    18.0    18.0
     47.0    18.0    43.0    18.0    18.0    41.0    18.0    46.0    18.0    18.0    42.0    18.0
group Stream water
     18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0    18.0
     18.0    18.0    18.0    18.0    18.0    18.0    18.0    38.0    38.0    38.0    38.0    38.0



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                                  ____________________________________

  1  %CD 'C:/Users/paddykay/Documents'
  2  "Data taken from unsaved spreadsheet: New Data;1"
  3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
  4  READ [PRINT=*; SETNVALUES=yes] _stitle_
  7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 5-May-2011 12:21:46

  8  DELETE [REDEFINE=yes] ZONE,METAL,CONCENTRATION
  9  UNITS [NVALUES=*]
 10  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Lake sediment',\
 11  'Stream sediment'); REFERENCE=1] ZONE
 12  READ ZONE; FREPRESENTATION=ordinal

            Identifier          Values         Missing          Levels
                  ZONE              50               0               2

 15  TEXT [NVALUES=50] METAL
 16  READ METAL

            Identifier         Minimum            Mean         Maximum          Values         Missing
                 METAL                                                            50               0
```

```
 21  VARIATE [NVALUES=50] CONCENTRATION
 22  READ CONCENTRATION

            Identifier      Minimum         Mean      Maximum       Values      Missing
CONCENTRATION                 3.946        8.227        14.07           50            0

 28
 29  WSTATISTIC [PRINT=test] CONCENTRATION

Shapiro-Wilk test for Normality

Data variate:               CONCENTRATION
Test statistic W:            0.9188
Probability:                 0.002

 30  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=ZONE]
CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: ZONE

Value of U: 210.0 (first sample has higher rank sum).

Exact probability: 0.047
(under null hypothesis that group Lake sediment is equal to group Stream
sediment).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake sediment
    48.0    11.0     8.0    47.0    22.0    50.0    18.0    17.0    43.0    21.0    49.0    20.0    19.0
    46.0    38.0    45.0     9.0     6.0    42.0    40.0    44.0    10.0     7.0    41.0    39.0
group Stream sediment
     3.0     3.0     3.0     3.0     3.0    14.0    14.0    14.0    14.0    14.0    35.0    35.0    35.0
    35.0    35.0    25.0    25.0    25.0    25.0    25.0    30.0    30.0    30.0    30.0    30.0
```

APPENDIX XIV

```
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```

```
  1  %CD 'C:/Users/paddykay/Documents'
  2  "Data taken from unsaved spreadsheet: New Data;1"
  3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
  4  READ [PRINT=*; SETNVALUES=yes] _stitle_
  7  PRINT [IPRINT=*] _stitle_; JUST=left

Data imported from Clipboard
 on: 5-May-2011 12:15:57

  8  DELETE [REDEFINE=yes] WATER_BODY,ZONE,METAL,CONCENTRATION
  9  UNITS [NVALUES=*]
 10  FACTOR [MODIFY=yes; NVALUES=100; LEVELS=2; LABELS=!t('Lake','Stream')\
 11  ; REFERENCE=1] WATER_BODY
 12  READ WATER_BODY; FREPRESENTATION=ordinal

          Identifier         Values        Missing         Levels
 WATER_BODY                    100              0              2

 16  FACTOR [MODIFY=yes; NVALUES=100; LEVELS=2; LABELS=!t('Sediment','Water')\
 17  ; REFERENCE=1] ZONE
 18  READ ZONE; FREPRESENTATION=ordinal

          Identifier         Values        Missing         Levels
                ZONE            100              0              2

 22  TEXT [NVALUES=100] METAL
 23  READ METAL

          Identifier        Minimum           Mean        Maximum         Values        Missing
               METAL                                                        100              0

 31  VARIATE [NVALUES=100] CONCENTRATION
 32  READ CONCENTRATION

          Identifier        Minimum           Mean        Maximum         Values        Missing
CONCENTRATION            0.01100          4.143          14.07            100              0

 42
 43  WSTATISTIC [PRINT=test] CONCENTRATION

Shapiro-Wilk test for Normality

Data variate:               CONCENTRATION
Test statistic W:            0.8052
Probability:                 <0.001

 47  MANNWHITNEY  [PRINT=test,ranks; METHOD=twosided; GROUPS=WATER_BODY]
CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: WATER_BODY

Value of U: 960.0 (first sample has higher rank sum).

Exact probability (adjusted for ties): 0.045
(under null hypothesis that group Lake is equal to group Stream).
```

Sample sizes: 50, 50.

Ranks for individual variables

group Lake

47.0	46.0	41.0	28.5	50.0	48.0	3.0	43.0	35.5	27.0	49.0	6.5	41.0
37.0	22.5	44.0	2.0	39.0	35.5	28.5	45.0	1.0	41.0	38.0	26.0	98.0
61.0	58.0	97.0	72.0	100.0	68.0	67.0	93.0	71.0	99.0	70.0	69.0	96.0
88.0	95.0	59.0	56.0	92.0	90.0	94.0	60.0	57.0	91.0	89.0		

group Stream

6.5	6.5	6.5	6.5	6.5	12.0	12.0	12.0	12.0	12.0	32.0	32.0	32.0
32.0	32.0	17.0	17.0	17.0	17.0	17.0	22.5	22.5	22.5	22.5	22.5	53.0
53.0	53.0	53.0	53.0	64.0	64.0	64.0	64.0	64.0	85.0	85.0	85.0	85.0
85.0	75.0	75.0	75.0	75.0	75.0	80.0	80.0	80.0	80.0	80.0		

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```
 1  %CD 'C:/Users/paddykay/Documents'
 2  "Data taken from unsaved spreadsheet: New Data;1"
 3  DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
 4  READ [PRINT=*; SETNVALUES=yes] _stitle_
 7  PRINT [IPRINT=*] _stitle_; JUST=left
```

Data imported from Clipboard
on: 5-May-2011 12:24:45

```
 8  DELETE [REDEFINE=yes] ZONE,METAL,CONCENTRATION
 9  UNITS [NVALUES=*]
10  FACTOR [MODIFY=yes; NVALUES=50; LEVELS=2; LABELS=!t('Lake Water',\
11  'Stream water'); REFERENCE=1] ZONE
12  READ ZONE; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
ZONE	50	0	2

```
15  TEXT [NVALUES=50] METAL
16  READ METAL
```

Identifier	Minimum	Mean	Maximum	Values	Missing
METAL				50	0

```
21  VARIATE [NVALUES=50] CONCENTRATION
22  READ CONCENTRATION
```

Identifier	Minimum	Mean	Maximum	Values	Missing	
CONCENTRATION	0.01100	0.05948	0.3300	50	0	Skew

```
27
28  WSTATISTIC [PRINT=test] CONCENTRATION
```

Shapiro-Wilk test for Normality

Data variate: CONCENTRATION
Test statistic W: 0.5622
Probability: <0.001

29 MANNWHITNEY [PRINT=test,ranks; METHOD=twosided; GROUPS=ZONE] CONCENTRATION

Mann-Whitney U (Wilcoxon rank-sum) test

Variate: CONCENTRATION
Group factor: ZONE

Value of U: 125.0 (first sample has higher rank sum).

Exact probability (adjusted for ties) < 0.001
(under null hypothesis that group Lake Water is equal to group Stream water).

Sample sizes: 25, 25.

Ranks for individual variables

group Lake Water

47.0	46.0	41.0	28.5	50.0	48.0	3.0	43.0	35.5	27.0	49.0	6.5	41.0
37.0	22.5	44.0	2.0	39.0	35.5	28.5	45.0	1.0	41.0	38.0	26.0	

group Stream water

6.5	6.5	6.5	6.5	6.5	12.0	12.0	12.0	12.0	12.0	32.0	32.0	32.0
32.0	32.0	17.0	17.0	17.0	17.0	17.0	22.5	22.5	22.5	22.5	22.5	