PHYSICOCHEMICAL PARAMETERS, HEAVY METAL RESIDUE LEVELS AND THEIR SPECIATION STUDIES IN LAKE VICTORIA BASIN

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ABSTRACT

The occurrence of heavy metal contaminants in excess of natural loads is a problem of increasing concern in aquatic ecosystems. This has been caused by anthropogenic, industrial and urban wastes as well as natural geochemical activities. Winam Gulf of Lake Victoria is no exception to these contamination processes even though it is an important resource for food, drinking water and communication to the local community and an important habitat for fish and other aquatic organisms of great biodiversity. This therefore, necessitated the study of the physical and chemical properties which influence water quality and ecosystem balance, the speciation and distribution of trace metals of environmental concern, which include Cd, Cu, Zn and Pb in addition to Fe, which is widely used in the construction industry. The study had a randomized complete block design and the sampling sites were located upstreams and river mouths of rivers Sio, Nyamasaria, Nyando and Sondu-Miriu, and in Port Victoria, Kisumu Car Wash, Dunga and Hippo Point beaches along the lake, as well as Nyamasaria, Migosi and Nyawita Estates in Kisumu City. The samples were taken during the wet months of May and October, 2006 and the dry months of January and February, 2007. The samples were extracted in quadruplets for total and bioavailable metal concentration for solid samples and total metal concentration for water samples. The samples were then analysed using atomic absorption spectrophotometer, AAS (Shimadzu Corporation AA-6300 model) and the results confirmed by inductively coupled plasma mass spectrophotometer, X series 2 ICP-MS model.

Physicochemical properties of water were determined. The pH ranged from 7.2-7.8 for estate waters and 6.5-8.8 for lake and upstream waters. Total Alkalinity, Conductivity, Dissolved oxygen, Turbidity, Acidity and Temperature for estate water samples averaged 47.0 mg/L, 333 μS/cm, 5.4 mg/L, 1.0 NTU, ND and 26.3°C respectively while those of lake and upstream water samples averaged 47.1 mg/L, 140.5 µS/cm, 4.9 mg/L, 270.4 NTU, ND and 27.5°C respectively. The Cd, Pb, Cu, Zn and Fe metal concentrations in µg/L in estate water samples averaged ND, 9.1, 44.6, 232.7 and 242.4 while those of lake and upstream river water samples averaged ND, 12.7, 53.0, 232.3 and 2,588, respectively. All the water samples analysed conformed to the set international standards for drinking water for the metals investigated except lead and iron in lake water samples. The amount of Fe in lake water samples was beyond the maximum allowable limits in fisheries and aquatic life internationally. The concentrations of the metals increased downstream for both water and sediment signifying that these rivers are among the major sources of the heavy metal load in Winam Gulf. The average total heavy metal concentrations in µg/g for Cd, Pb, Cu, Zn and Fe in sediments on dry weight basis were 1.2, 32.5, 36.7, 163.3 and 45,990 respectively. The % average bioavailable Cd, Pb, Cu, Zn and Fe metal concentrations in the sediments on dry weight basis were 55.8, 66.9, 57.1, 73.3 and 65.6 respectively. Statistical analysis showed significant variation ($p < 0.05$) between the sample sites, seasons and their interactions. These significant variations were attributed to the wide range of activities taking place in the vicinity of each sampling site in addition to the effects of each season especially on the rivers feeding the lake.

Total heavy metal concentrations were also determined in the three most abundant fish species in the Winam Gulf (*Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea*). The fish samples were obtained from Dunga, Port Victoria, Sio Port and Hippo Point beaches. The average total metal concentrations determined on dry weight basis were 0.21 µg/g Cd, 0.87 µg/g Pb, 3.4 µg/g Cu, 36.4 µg/g Zn and 45.7 µg/g Fe for *Lates niloticus*, 0.21 µg/g Cd, 0.61 µg/g Pb, 2.7 µg/g Cu, 35.9 µg/g Zn and 48.0 µg/g Fe for *Oreochromis niloticus* and

0.26 µg/g Cd, 1.2 µg/g Pb, 6.5 µg/g Cu, 250.1 µg/g Zn and 139.1 µg/g Fe for *Rastrineobola argentea*. The % average bioavailable Cd, Pb, Cu, Zn and Fe metal concentrations in the three species were 67.1, 27.5, 46.3, 79.4 and 29.8 respectively for *Lates niloticus*, 66.7, 40.9, 41.7, 71.0 and 37.3 respectively for *Oreochromis niloticus* and 59.1, 47.4, 65.7, 76.2 and 44.5 respectively for *Rastrineobola argentea*. Statistical analysis showed significant variation ($p < 0.05$) between the fish species, sample sites, seasons and their interactions. This situation was attributed to the complex mobility trends of fish. The abundance trend of the metals in *Lates niloticus* and *Oreochromis niloticus* was Fe > Zn > Cu > Pb > Cd while that of *Rastrineobola argentea* species was Zn > Fe > Cu > Pb > Cd. The difference in the trends was attributed to the fact that *Rastrineobola argentea* was analysed whole while only muscle of *Lates niloticus* was determined after removing the internal organs. These parts were selected for analysis because they represent edible parts of the fish species by man. The fish samples of the three species conformed to the limits set out by the international standards organisations, however, the concentration of Zn on wet weight basis for *Rastrineobola argentea* species went beyond the set out international upper limits during the wet season and this was attributed to it being consumed with its internal organs in place.

The wet season generally registered higher metal concentrations in all types of samples analysed in this study.

Sediments accumulated metals many more times compared to fish and water. The order of accumulation was found to be Sediment > Fish > Water. Metals in sediments are more bioavailable compared to the metals in fish and therefore could be desorped into the water much more readily than from fish.

CHAPTER 1

1 INTRODUCTION

Lake Victoria is the second largest fresh water lake in the world covering an area of 68,800 km^2 (Van Densen and Witte, 1995). It traverses the three East African States: Kenya, Uganda and Tanzania (Van Densen and Witte, 1995; Philip, 2001).The main urban centres in Winam Gulf include Kisumu City, Homa Bay, Migori, Siaya, Bondo, Agwasi and Busia towns. Activities of Winam Gulf include fishing, farming, transportation, tourism and mining of sand. Seven major rivers including Nyando, Nzoia, Yala, Sondu-Miriu, Kuja, Kibos and Sio within the Kenyan side flow into Winam Gulf of Lake Victoria. These rivers and their tributaries emanate from Kisii, Kericho, Mt Elgon and Nandi-Hills where there are major agricultural activities such as coffee-, tea- and tobacco-farming. These activities use a lot of copper-based pesticides for crop protection against various diseases.

Copper compounds are used in pesticides, especially in antifouling paints, algicides, fungicides, and insecticides. Some Cu compounds are used as paint pigments and in ceramics (Piscator, 1977; Stokinger, 1981). Copper-based compounds have both bactericidal and fungicidal properties (Piscator, 1977, Stokinger, 1981) by virtue of which the copper formulations are the most widely and frequently used in Kenya to combat the major diseases in coffee farming since the year 1920 (French and MacCleland, 1932; Griffith, 1971; Kairu *et al.*, 1985). Some of the copper based pesticides used in Kenya are Nordox (Copper (I) Oxide), Cobox (Copper Chloride), Kocide 101 (Copper hydroxide) and Bordeaux mixture (Calcium hydroxide + Copper II Sulphate). Tea and coffee farming utilizes copper-Zinc sprays. Copper chloride is sprayed on tobacco. All these formulations have their active ingredients as copper ions. Apart from controlling diseases, copper sprays have also been used for leaf retention, and as a general growth stimulant (Hollies, 1967). GopalaKrishnan and Ananth (1960) in a preliminary study on transpiration in coffee plants observed that Bordeaux mixture, when sprayed on leaves influenced transpiration more effectively. In Tanzania, Tapley (1965) controlled excessive leaf fall in coffee plants by a routine copper spray programme. Furtado (1970) observed increased coffee yield, leaf retention and production of dark foliage, an effect referred to as 'tonic' by coffee farmers in Kenya, when copper sprays are applied. Furtado (1970) noted that these copper 'tonic' effects are not dependent on the disease that is being controlled.

Spraying of copper fungicides in coffee plantations in Kenya is done just before the onset of rains. The long rain's season starts in March and continues up to end of May while the short rain's season is from October to December. The October to December season leads to early crop yields while March to May season gives late crop yields (Coffee Research Foundation (CRF), 2004).

It has been reported that most pesticide residues reach the soil either through direct application or indirectly through transport by wind and rainfall (McEwen and Stephenson, 1979). Residues are also transported from the point of application to other locations by leaching in soil and by surface runoff and often eventually enter the aquatic environments where they can have adverse effects on aquatic organisms as well as humans who depend on these organisms as a source of food (Ongeri *et al.*, 2000). It is estimated that up to 50% of all pesticides applied to crop foliage reach the soil as spray drift or runoff (Vorley and Keeney, 1998; Bey-Dyke *et al.*, 1990). Similarly under field conditions, the rain or irrigation water usually weathers large amounts of copper from coffee leaf surfaces 48 hours after spraying (Park and Buderkin, 1964). Pesticide residues, as well as copper are known to settle on the soil after drifting or missing the target during spraying. The residues enter watercourses through leaching of the deposited residues on soil by water or through run-off as well as wash off by water used to process coffee. The effluent from the processing of coffee often ends up in rivers (Ongeri *et al.*, 2000).

The other important trace metal pollutants of considerable importance that are transported and distributed into rivers that discharge into Winam Gulf of Lake Victoria include iron (Fe), zinc (Zn), lead (Pb) and cadmium (Cd). Iron and zinc with lead and cadmium as impurities are applied together with fertilizers as micronutrients to coffee trees (Njeru, 1994). All these metallic nutrients are not used up completely by the trees therefore some of the residues end up being leached or swept away into the rivers by irrigation water and during heavy rainfall. Steel wool is a widely used commodity in modern households in Kenya today. It is used for scrapping stains from cooking pots often made of aluminium and iron. Rusting iron sheets or scrap metals made out of steel are present in large quantities in the city of Kisumu and major towns at the shores of Lake Victoria. The rust or pot scrapings could be ending up in the lake. In a study carried out in the Netherlands, it was found that in the inner city area corrosion of metals in use, e.g. sewage pipes (Pb), roofs and pipes (Cu, Pb), stainless steel (Cr, Ni), painted surface (Pb, Cr, As, Cd, Zn) and rust preventative coating on steel (Cd, Zn) are significant sources of trace pollutants among the inner city sources (Wenchuan and Kelderman, 2001). Silver (1993) reported that the most commercially important form of iron for industrial exploitation is steel. All forms of steel are composed mainly of iron with less than 2% carbon and other elements such as manganese, nickel, chromium, tungsten and vanadium. Rusting of iron (Evans and Leigh, 1991) occurs due to the formation of a hydrated oxide of iron [$Fe(OH)_3$] or $FeO(OH)$. In moist air, iron rusts rapidly. The hydrous oxide gives no protection as it flakes off exposing fresh metal surfaces leading to extensive corrosion. One of the most frequently used metals is zinc whose major uses include coating to protect iron and steel (Taylor *et al.*, 1982). Zinc and Cd are released during steel production, while incinerators are also responsible for emitting Pb and Zn. Cadmium is mainly produced entirely from zinc ores and is present in phosphate based fertilizers and is also used increasingly in batteries. Decomposition of phosphate fertilizers, pigments and paints, plastics, fuels, alloys and solders, batteries and other electricals increase the metal load of Cd, Fe, Zn, Pb and Cu in the environment. Cadmium is mostly an impurity in most of the preceding applications (Biney *et al.*, 1994; Deighton and Goodman, 1995). In a study carried out in China, it was reported that anthropogenic inputs, such as atmospheric deposition and street dust are the main sources of Cu, Zn, Pb and Cr in Nanjing urban soils (Lu, 2000).

Most lead (Pb) is used as a metal and its sulphate salt is used in storage batteries, in the formation of inorganic pigments and as solder (Stokinger, 1981). The uses of Pb contribute to environmental Pb accumulation, for example if old storage Pb batteries, formulations of pigment and solder are improperly disposed of. Similarly, lead from leaded-fuel used in cars may remain as particulates in the atmosphere. These particulates could drift directly into the lake or could be swept during the rains into Lake Victoria. Car washing is itself a common activity at the shores of the lake. This is common to all the towns at the shores of the lake such as Kisumu City and Homa Bay Town. Car washing could therefore be another major source of lead in the lake as most of the cars use leaded fuel, which may be spilling, into the water. With current phasing out of leaded fuel from the market, this source will no longer be a major worry to the environmentalists. Shipping or rowing vessels in the lake transport leaded fuel and therefore increase chances of spillage during accidents. Earlier studies on sediment, water and biota from Lake Victoria (Alala, 1981; Onyari, 1985; Ochieng, 1987) have shown no significant heavy metal pollution. But more recent studies in the same area reveal increased lead levels largely due to increased shipping traffic and other associated problems, car washing and discharges from local industries (Wandiga and Onyari, 1987; Onyari and Wandiga, 1989). However, use of leaded fuel in cars has been on its declining trend, especially in the developed countries particularly in the northern hemisphere and this marked a drop in the overall atmospheric lead levels as was witnessed from measurement of marine aerosols (Stokinger, 1981; Kersten *et al.*, 1994). Kenya has also stopped processing leaded fuel as from December 2005 and is instead processing unleaded fuel.

There are also many possible sources that contribute to trace metal inputs into the aquatic environment. These include industrial, domestic wastewaters and runoff from grassland agriculture soils (Nriagu and Pacyna, 1988). Indeed copper salts are liberally included in swine feed as additives because they promote th~~ei~~r immune system function and growth (Omole, 1980; O'Dell, 1998). Unfortunately, the unabsorbed copper in swine feed is lost from the body and the practice of slurry applications on farming soils because they are nutrient rich, contain trace minerals including in particular copper and this significantly increases copper concentrations in soils (Godin, 1983; Arzul and Maguer, 1990; Nicholson *et al.*, 1999; De la Torre *et al.*, 2000; Price *et al.*, 2001). Copper stored in soil can pass in solution during rain events and thus join the hydrological system. Consequently rivers that are characterised by agricultural catchments are then susceptible to receive substantial quantities of copper (Monbet, 2004). However, sediment represent an important sink for trace metals in aquatic systems, and metal concentrations in sediment can be several orders of magnitude greater than in overlying water (Luoma *et al.*, 1989). Sediment associated metals pose a direct risk to detrital and deposit feeding benthic organisms, and may also represent a longterm-source of contamination to higher trophic levels (Luoma, 1983; Smock, 1983). A major difficulty in establishing the effects of contaminants on benthic animals is in the context of distinguishing between those impacts mediated by sediment pore water (Reynoldson, 1987).

1.1 **Statement of the problem**

The levels of physical and chemical parameters of lake and upstream river waters keep on changing and these properties can determine the fate of the metals in the aquatic environment. Toxicity of a heavy metal is dependent on its bioavailable fraction and therefore speciation of the metal in the environment is very crucial in understanding its toxic potential. A lot has been done on speciation of heavy metals in the western world which experiences a temperate climate while speciation data for the heavy metals is very limited or lacking in this lake basin with tropical conditions and this study was geared towards availing this data for future applications.

1.2 Justification of the study

Agricultural runoff and industrial effluent carry heavy metals into Winam Gulf and this can be shown by variation in concentration upstream and downstream before entry into the lake. The rivers sampled Sio, Sondu-Miriu, Nyando and Nyamasaria carry agricultural runoff loads into the gulf as they flow down into the lake. The variation in concentration levels upstream and downstream can show this impact.

River Nyamasaria carries industrial effluent as well as municipal effluent which are sources of heavy metals into Winam Gulf.

Accumulation of metals in three fishes namely *Lates niloticus* (Plate 1), *Oreochromis niloticus* (Plate 2) and *Rastrineobola argentea* (Plate 3) analysed could be precarious as they do not stay in one locality and therefore the fish can be endangered. Variations in concentration in the three fish species could be expected due to their differences in feeding modes. Analysis of the edible parts of the fish could show the potential exposure to human.

Plate 1. Photograph of *Lates niloticus* species

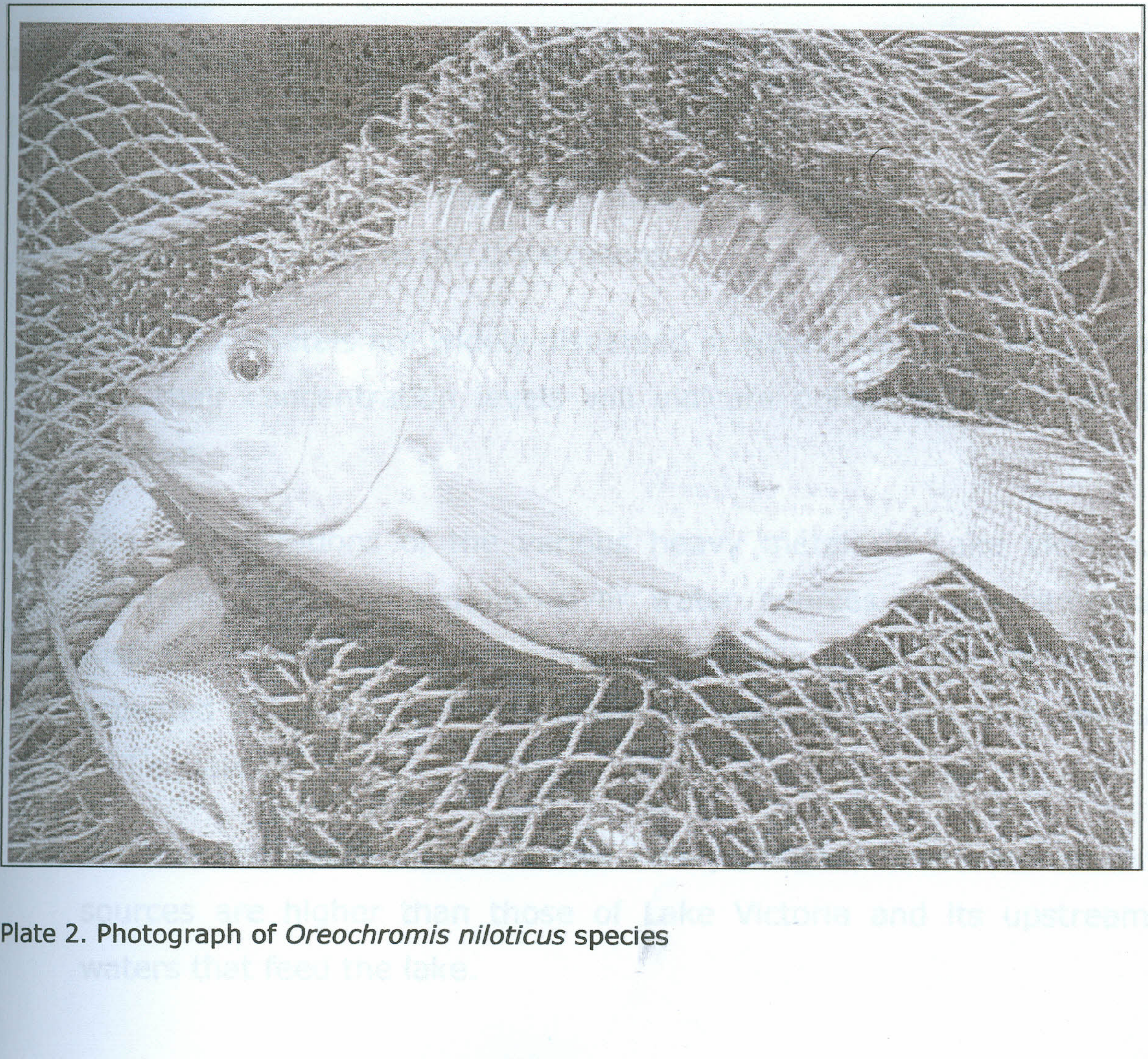

Plate 2. Photograph of *Oreochromis niloticus* species

Plate 3. Photograph of *Rastrineobola argentea* species

1.3 Hypotheses

It was hypothesised that:

1. The concentrations of the heavy metals are highest during the wet seasons compared to the dry seasons.
2. The heavy metals are widely dispersed in water, sediment and biota and their concentration levels will indicate pollution from various sources.
3. The concentrations of the various heavy metals in Lake Victoria, upstream of rivers and non-river water sources in the sampled Kisumu estates are above the nationally and internationally accepted standards for drinking water and water quality for fisheries and aquatic life.
4. The concentrations of the various heavy metals in non-river water sources are higher than those of Lake Victoria and its upstream waters that feed the lake.

1.4 Objectives

Objectives of this study were to:

1. Establish the distribution of copper, iron, zinc, cadmium and lead in the water, fish, and lake sediment from Lake Victoria and its upstream waters.
2. Determine the concentration profile trend of the heavy metals during the rainy and dry seasons.
3. Establish the extent of dispersion of the heavy metals in the lake water.
4. Determine the concentration levels of these heavy metals in the non-river water sources within Kisumu municipality.
5. Determine the bioavailable fraction of these heavy metals and hence the speciation of cadmium, lead, copper, zinc and iron, in sediment and fish samples from the lake.
6. Determine the current levels of the physical and chemical parameters; turbidity, alkalinity, pH, dissolved oxygen, temperature and acidity.

CHAPTER 2

2 LITERATURE REVIEW

2.1 The Area under investigation

This project covered Lake Victoria shoreline of Busia and Kisumu districts as well as non-river sources of water within Kisumu municipality. The study area lies between latitudes 0°50′ south and 0°45′north and longitudes 33°20′ and 35°20′ east (see Figures 1 and 2). This implies that the area generally experiences an equatorial type of climate. The annual temperatures range from 14°C to 35°C. Most of the rain is received during the long rainy season which is from March to late May. The short rains season is from August to December (DDP, 1994; DDP, 2002; CRF, 2004).

Surface water especially Lake Victoria is the area's second most important source of livelihood after farming of crops and livestock. The lake provides abundant supply of fish, which is important to the economic and social development of the region. Some of the most important species of fish found in the lake in terms of mass landed are the *Lates niloticus* (Nile Perch) (55%), *Oreochromis niloticus* (Tilapia) (5.5%) and *Rastrineobola argentea* (Silver Cyprinid) (36%) (DDP, 1994). The output of *Lates niloticus* significantly declined from 55% in the year 1994 to 24% in the year 2006 while that of *Rastrineobola argentea* increased from 36% to 54% during the same period (DDP, 1994; LVFO, 2008) (Appendix II: Table 36, pg 142). Several rivers like Nyando, Nzoia, Kuja, Sio, Yala, Sondu-Miriu and other small ones drain into Lake Victoria through this basin of the lake. During the rains, some of these rivers like Nyando and Nzoia flood and thereby carrying with them the chemicals, applied on the agricultural lands, into the lake. Flooding in Budalangi area traversed by River Nzoia is a common phenomenon in western Kenya.

The area investigated has a number of ports including Kisumu port, Sio Port, Port Bunyula and Port Victoria (DDP, 2002). These areas are concentrated with human and commercial activities that can contribute to seasonal pollution load including heavy metals and other chemical residues and therefore deserve to be investigated to ascertain their status.

Some survey of water usage from various water points in Kisumu district in Kenya has been carried out and the data evaluated (DDP, 1994 and DDP, 1997). The following are the water points by type and seasonal reliability:

Table 1. Water points in Kisumu district.

Type of water point	Wet season proportion Of consumers out of total of 102 sampled	Dry season proportion Of consumers out of total of 115 sampled
Dams	0	2
Borehole	2	6
Ground Catchments	13	4
Lake Victoria	3	32
Rivers	25	1
Roof Catchments	3	11
Springs	11	3
Water holes	4	22
Wells	23	20
Piped supplies	18	14

Source: DDP, 1994 and DDP, 1997

It is clear from the table that during the wet season more than 65% of consumers get water from rivers, wells and piped supplies while during the dry season this figure plummets to 34%. During the dry season more than 64% of consumers get water from Lake Victoria, water holes and water wells while during the wet season this % plummets to 26. In both seasons wells play a crucial role as a major water point with an average of 20% of consumers drawing water from them. It is the only water supply system that is well balanced in both seasons. However, it must be pointed out that a number of consumers do get water from more than one water point. This could be attributed to water quality, water availability, cost and convenience (DDP, 1994 and DDP, 1997). Water quality status from all these water resources in terms of heavy metal contamination has not been ascertained and reported. The understanding of heavy metal speciation in these fresh water resources is important in understanding the health status and potential effects as a result of climatic and geological changes in the surrounding areas. The current study covered only a fraction of the above water resources namely Lake Victoria, rivers feeding Lake Victoria, piped supplies, roof catchments and wells. The fraction of the water resources selected in the present study covers 71% and 77% of the water supplies during the wet and dry seasons respectively.

2.2 Heavy metal environmental accumulation and impact on human health

Rapid growth of human population in some urban areas has outpaced the ability of some governments to develop and maintain existing sewage treatment facilities implying that raw sewage is released into the water masses and therefore, increasing the heavy metal load (FWR, 2004). This situation also applies to Kisumu City. Heavy metal contamination in aquatic environments is of critical concern, due to the toxicity of metals and their accumulation in aquatic habitats. Heavy metals, in contrast to most pollutants, are not biodegradable, and they undergo an ecological cycle in which natural waters are the pathways (Tam and Wong, 1995). Sediment is a major sink for trace metals in aquatic systems and metals can be accumulated to several orders of magnitude greater than the overlying water (Luoma *et al.*, 1989). Heavy metals are therefore frequently detected in the environment at elevated levels including both bed sediments and water columns and have gradually become a major worldwide concern due to lots of wastes discharged into water bodies (Pardo *et al.*, 1990; Boughriet *et al.*, 1992; Warran and Zimmerman, 1993). The exposure of aquatic organisms to heavy metals has the potential of deleterious effects on their populations (Carbonell and Tarazona, 1993) and metal bioaccumulation leads to possible health hazards to the human consumer of these organisms (Vos and Hovens, 1986). Bioconcentration and bioaccumulation of toxic metal residues in the food chain can put terrestrial consumers including humans and birds at risk. Contaminated food webs can also have health and economic disadvantages for people as contaminated commercial, sport and sustenance fisheries become restricted or closed due to high metal burdens in fish (Ongley, 1996; Driscoll *et al.*, 1994; Gough and Herring, 1993; Wang, 1987).

2.2.1 Copper (Cu)

There is no literature, which has been documented showing the human health risks associated with copper residues in Lake Victoria. However, general literature on its importance as a trace essential element and its toxicity at high levels is available and covering reports from other regions outside Kenya. Copper is generally known to be an essential trace element to man and in fact to all vertebrates. The human adult Recommended Daily Allowable (RDA) copper intake is 2-3 mg, however, some studies indicate that levels between 1 and 2 mg, can maintain a positive copper balance (NAS, 1980). It is a component of most vital enzymes; including tyrosinase, cytochrome oxidase, and amine oxidases (Piscator, 1977; USEPA, 1980). Copper is largely combined with serum albumin and alpha-globulin ceruloplasmin, which serve to transport and regulate copper in the body (Stokinger, 1981). The metabolism of copper involves a turn over of the copper-containing enzymes. Menke's disease, a copper deficiency disease, is a disorder in the metabolism whereby there exists an inability to absorb copper (USEPA, 1980). Copper is especially essential in the electron transfer processes which also involve iron in haemoglobin, photosynthesis in plants and the terminal step of mitochondrial respiration and hence Cu influences life support functions like production of red blood cells and carbohydrate synthesis (Malmstrom, 1979).

Copper, together with iron, is the dominating prosthetic metal ion in the electron-carrier proteins participating in the biological oxidation of organic substrates by dioxygen (Keevil and Mason, 1978). As a transition element, copper has a particular chemical suitability of having a functional role in electron transfer and oxygen transport proteins as it has two common valence states; Cu(I) and Cu(II). Furthermore, the oxidation-reduction potential governing the relative predominance of these two valence states is sensitive to the nature and steric arrangement of the surrounding ligand potentials (Reinhammar, 1979). In addition, it has been found that Cu^+, like the low-valence forms of many other transition metals, in certain complexes can bind O_2 and CO reversibly (Lontie and Vanquickenborne, 1974) despite the fact that O_2 is a neutral symmetric molecule.

However, at high doses, copper is one of the common metallic elements toxic to humans found in polluted environments (Purves, 1977). A condition known as Wilson's disease is due to inability to utilize copper and is a hereditary metabolic disorder whereby there is accumulation of copper in some organs of the body, the most sensitive being the brain and liver (USEPA, 1980; Prasad and Oberleas, 1976). Acute copper poisoning also causes hemolytic anaemia (Finelli *et al.,* 1981).

Copper is actively absorbed in the stomach and duodenum. Typically, about half of the ingested dose is absorbed, but this can be decreased by competition with zinc and binding by ascorbic acid and other compounds. However, except for a few occupational exposures, daily intakes of airborne copper, even near copper smelters are negligible compared to oral ingestion. Similarly, dermal absorption is negligible through intact skin. However, copper can also be excreted and the major excretion route for the absorbed copper is the bile. Minor routes of excretion of Cu include sweat, urine, and saliva (USEPA, 1980, Stokinger, 1981).

2.2.2 Lead (Pb)

The classic studies by Kehoe *et al.* (1933) indicate that under normal circumstances, 300 μg of Pb are ingested daily by an adult. He noted that ingestion of 600 μg of Pb daily could result in Pb intoxication. Other than its deposition in bone and toxic reactions, lead has minimal involvement with metabolism (Tsuchiya, 1977; Stokinger, 1981).

Food and Agricultural Organisation (FAO) and World Health Organization (WHO) have recommended a provisional tolerable intake for Pb by adults, as 3 mg/wk i.e. the daily Pb intake should not exceed 5 μg/kg (body weight)$^{-1}$. They also recommend that no more than 50% of a population's blood lead values should exceed 0.2 ppm.

According to Snyder *et al.* (1975), the Pb balance for a 70 kg reference man requires an intake of 0.44 mg/day from food and fluids and 0.01mg/day from air; loses 0.045 mg/day through urine, 0.3 mg/day through faeces and 0.1 mg/day through other routes for instance sweating. The total body burden has been estimated to range between 100 to 400 mg and thus increases with age (Tsuchiya, 1977). Snyder *et al.* (1975) reported a value of 120 mg to be the total body burden with 11 mg in soft tissues.

"Lead arthralgia" (joint pains) has long been described. Some evidence implies that this is actually lead-induced gout caused by lead's interference with uric acid excretion through the kidney. Lead inhibition of guanine aminohydrolase could also be involved in this (Cullen *et al.*, 1983). Nephrotoxicity is most commonly seen in childhood lead toxicities. Lead causes tubular dysfunction, with ultra structural changes in the mitochondria, which result in aminoaciduria, glysuria, and phosphaturia, as well as gout. Despite earlier reports, there is no apparent increase in hypertension related to Pb intoxication (Tsuchiya, 1977; Stokinger, 1981; Cullen *et al.*, 1983). Lead is also associated with depression of endocrine functions, particularly the thyroid and adrenal, but details are not clear (Tsuchiya, 1977; Cullen *et al.*, 1983). There is limited, but graphic, evidence that lead is associated with a high incidence of premature deliveries and spontaneous abortions in humans. Lead also suppresses testicular function, even to sterility, in men (Cullen *et al.,* 1983).

Most of the Pb exposure that occurs among non-industrial populations' results from the food and drink consumed. Normal adults will absorb about 10% of an oral dose of Pb compounds, the remainder excreted via faeces and urine (Snyder *et al.*, 1975). This increases in children (up to 50%), if taken on empty stomach, and with some unusual diets. Most excretion occurs in the urine. Some occurs in gastrointestinal secretion, hair, sweat and faeces (Lauwerys, 1983; Snyder *et al.*, 1975).

2.2.3 Iron (Fe)

Iron is an essential mineral and therefore a component of several cofactors, including haemoglobin and cytochromes. The recommended daily allowance is 10 mg for men and 18 mg for women (NAS, 1980; Stokinger, 1981). Iron is a major control element and many enzymes require iron for their activity and in some cases it is weakly bound, for example, with aconitase (Beinert and Kennedy, 1989). Da Silva and Williams (1991) had reviewed the importance of Fe as a major control element and noted that many enzymes involved in secondary metabolism in the body require iron for their activity. Since some of these are enzymes, including hormones, Da Silva and Williams concluded that, at least in prokaryotes, there is a relationship between the levels of free Fe^{2+} and the whole of the cell activity up to the point of initiation of cell division.

Iron is found in virtually every food, with higher concentrations in animal tissues than in plant tissues (Hammond and Beliles, 1980). In the United States of America (USA) and Europe, men consume 16 mg/day and women, 12 mg/day. Some drinking waters are high in Fe. About 140 µg Fe/day comes from average United States drinking waters (Snyder *et al.,* 1975). The total body burden is estimated to range from 4.2 to 4.5 g (Stockinger, 1981; Snyder *et al.*, 1975). According to Snyder *et al*

(1975), the iron balance for a 70-kg reference man, is intake from food and fluids 16 mg/day and airborne intake of 0.03 mg/day, including losses via urine of 0.25 mg/day, faeces 15 mg/day, and through other routes 0.51 mg/day. For a 50-kg reference woman, the values are 12 mg/day and 0.03 mg/day, respectively, for intake and 0.20 mg/day, 11 mg/day and 1.2 mg/day for losses (0.6 mg/day as menstrual loss).

Intestinal absorption of iron, especially Fe(II), is a complicated active process. The rate of uptake is inversely related to the state of the body's iron stores (Hammond and Beliles, 1980). In adults iron absorption has been reported to be 30% (Snyder *et al.*, 1975). Toxic signs are caused by free iron in human body. The signs appear after the carrier has been saturated with iron (Stokinger, 1981). Serious acute poisoning in children can occur following ingestion in excess of 1 g of iron (Forbes, 1947). The normal iron intake for children is 10-20 mg/kg body weight. It had also been reported that workers with iron pneumoconiosis had an average 160 µg Fe/100 g serum compared to 127 µg Fe/100 g in unexposed workers (Stockinger, 1981).

2.2.4 Zinc (Zn)

Zinc is ubiquitous in mammalian tissues and is involved in the activity of many enzymes. Thus, zinc participates in many metabolic processes (USEPA, 1980). Zinc is essential in enzyme and enzymatic functions, such as DNA, RNA, and protein synthesis; carbohydrate metabolism; utilization of nitrogen and sulphur; and cell division and growth. It is essential for spermatogenesis, ova formation, and foetal nutrition. It is also involved in pituitary and adrenal gland metabolism. Absolute amounts required range from 1.1 mg/day in infancy, 2.2 mg/day in child hood and adult hood, 2.8 mg/day at puberty, 2.55-3.0 mg/day in pregnancy, and 5.45 mg/kg body weight during lactation (Taylor *et al*, 1982).

Zinc is present in the erythrocytes as the zinc metalloenzyme carbonic anhydrase; in the leucocytes, in several zinc metalloenzymes; in the plasma, bound mainly to albumin and in the serum, bound to αmacroglobulin and to amino acids. Zinc is also essential for the activity of the following enzymes; alcohol dehydrogenase, carboxypeptidase, leucine amino peptidase, alkaline phosphatase, carbonic anhydrase, RNA-polymerase, and DNA-polymerase. Thymidinekinase is also zinc dependent (USEPA, 1980).

In the United States of America, The National Research Council (National Academy of Sciences (NAS), 1974) published Recommended Daily Allowances (RDAs) of 15, 20, and 25 mg Zn/day for adults, pregnant women and lactating women respectively. Surveys of adults of different ages and physiological states including pregnancy and lactating found that normal daily zinc intakes range between 8.6-1.4 mg/day or 46-67% of the RDAs (Solomons, 1982). A daily intake via food for the United States of America adult population was noted to be 10-20 mg Zn/day (USEPA, 1980). A mean value of 0.6 mg Zn/L in United States drinking water would contribute 0.5 to 1 mg Zn/day (Snyder *et al.* 1975). Zinc biovailabilty from food ranges from 10 to 40% (Solomons, 1982) while Snyder *et al.* (1975) considered 35% zinc absorption from food to be the optimum value. However, excessive zinc intake has been associated with copper–deficiency anaemia. Apparently, zinc interferes with copper and iron metabolism (USEPA, 1980).

2.2.5 Cadmium (Cd)

Cadmium has been found to be toxic to consumers. Excessive Cd in river Jintsu in Japan led to the Itai-Itai disease (Summary Report, 1992). Cadmium is carcinogenic, mutagenic and teratogenic, although some workers suggest that it is an essential element for human neonates (Michalke and Schramel, 1992). It has been shown that cadmium is strongly absorbed by ferritin in the intestinal mucosa where metallothioneins are not induced (Heubers *et al.*, 1987). Interestingly, in iron-deficiency (where ferritin biosythesis is depressed) cadmium uptake in the gut is substantially increased (Flanagan *et al.*, 1978).

2.3 Effects of excess heavy metals in the environment

Heavy metals like Cu, Zn and Pb are pollutants of great concern in aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains and, at high levels, can have adverse effects on biota (El Nabawi *et al.*, 1987; Mwamburi and Oloo, 1997). Due to their strong affinity for particles (Luoma, 1990), metals tend to be accumulated by suspended matter or trapped immediately by bottom sediments to high concentration levels (Dauvalter, 1998). The accumulation of metals in sediments has significant environmental implications for local communities, as well as for water quality. For instance, many freshwater invertebrates process sediments as a food source and can be susceptible to bioaccumulation of toxic metals. This bioaccumulation can potentially threaten the health of many species at the top of the food chain, especially birds, fish and humans (Wright and Mason, 1999). Trace metals can be harmful to aquatic organisms. The effects include decreased growth rates, impaired reproduction and sometimes death. Acute or chronic toxicity will influence the species numbers and diversity, altering community structure and function (Ongley, 1996; Driscoll *et al.*, 1994; Gough and Herring, 1993; Wang, 1987).

Fish communities can be used to indicate congestion or wider effects of changes on the aquatic environment because many fish species are relatively long-lived and mobile. They tend to integrate effects of lower trophic levels, thereby providing a measure of integrated environmental health. In this respect, fish are important for assessing contaminants in an ecosystem since they generally represent the top of the food chain and are susceptible to bioaccumulation and biomagnification of heavy metals (Barbour *et al.*, 1999).

2.3.1 Copper (Cu)

In Kenya, little has been done to study the distribution of copper in water or air surrounding those farms sprayed with copper based pesticides which are believed to be a major source of Cu. Part of the sprayed copper ends up in air and water surrounding these farms and do get transported to long distances. This copper ends up polluting Lake Victoria water that is used for domestic purposes. The lake water is also used for irrigation, is a habitat for fish and other aquatic biota, drinking and a variety of other domestic purposes like bathing, cooking and washing utensils. The accumulation of copper residues in the water can therefore interfere with these activities.

The Kenya Bureau of Standards (KEBS) (1996) reported that safe drinking water should not contain more than 0.1 ppm of copper. The World Health Organization (WHO) (1971) requires that copper in drinking water should not exceed 1 ppm. Consumers have complained of stained laundry and sanitary ware if they use water containing at least 1 ppm of copper (WHO, 1998). Allowable maximum limits for copper in drinking water in the United Kingdom (UK), European Union (EU) and United States of America (USA) are 3 ppm, 1 ppm and 1 ppm, respectively (Neubauer and Wolf, 2004).

Copper in water has been noted to be exceedingly toxic to aquatic biota in contrast to its low toxicity to mammalian consumers of water. Whereas concentrations as low as 0.005 to 0.025 ppm are lethal to some invertebrate and fish species within 4 days, the recommended standard for public water supplies based on palatability is 1 ppm (USEPA, 1980). Undesirable taste and odour have been linked to aqueous concentrations greater than 1 ppm (USEPA, 1980). The greater sensitivity of most aquatic biota could be as a result of high surface to volume ratios of algae and, highly permeable gill to surface area in various fish species, which facilitates rapid uptake of large amounts of copper. Consequently, sensitivity of aquatic biota to water borne metals is analogous to mammalian sensitivity to airborne metals as a result of rapid respiratory uptake. The maximum allowable concentrations of copper in fisheries and aquatic life are 0.005-0.112 ppm, 0.002-0.004 ppm and ≤0.001 ppm in the EU, Canada and Russia respectively (Neubauer and Wolf, 2004). These allowable concentration ranges are chosen based on hardness of water and on the dissolved metal (WHO, 1998).

Although copper is an essential element for all life, at high concentrations it is potentially toxic to soil microorganisms, soil fauna, and higher plants (Vulkan *et al.,* 2000). Several studies have reported adverse effects of heavy metals on soil microbial biomass, populations of individual species, microbial biodiversity and microbial mediated processes (Vulkan *et al.*, 2000; Baath, 1989; McGrath *et al.*, 1995; Giller *et al.*, 1998). In most studies involving soil microorganisms or plants growing in soils, toxicity has been expressed in terms of total soil concentrations or in terms of some operationally defined extractable fractions (Sauve *et al.*, 1998). Existing legislation and guidelines in the United Kingdom (UK) on heavy metals in soil toxicities of copper are also based on total concentrations (McGrath *et al.*, 1992). However, it is well established that total metal concentrations in soils do not reflect bioavailability, and the relationships between bioavailability and operationally defined fractions of metals are often influenced by other soil properties (Peijnenburg *et al.*, 1997; Sauve *et al.*, 1998). Free metal activity is the main factor controlling metal toxicity to aquatic organisms and the same free metal ion activity in soil pore water is one of the key factors controlling metal bioavailability to soil microorganisms and plants (Sunda and Lewis, 1978; Anderson and Morel, 1978; Peterson, 1982; Minnich *et al.*, 1987; McGrath *et al.*, 1992; Parker *et al.*, 1995; Sauve *et al.*, 1996; Peijnenburg *et al.*, 1997; Sauve *et al.*, 1998; McGrath *et al.*, 1999). Also, soil microorganisms and soil microbial processes appear to be more sensitive to Cu toxicity than higher plants (Sauve *et al.*, 1998).

Copper is a micronutrient required in very small amounts and its common concentration range in plant tissues has been reported as 3-50 ppm (Frank, 1952). Copper plays a significant role both as a micronutrient and as a constituent of copper protein enzyme essential in plant redox processes. However, higher concentration levels can easily interfere with the growth of aquatic plants and hence with the Lake Victoria ecosystem. Baker (1974) reported toxicity of copper to various types of plants when the amount added over a period of time exceeded 150-400 ppm in soil.

2.3.2 Lead (Pb)

The Kenya Bureau of Standards (KEBS) (1996) reported that lead content in drinking water should not exceed 0.05 ppm. In the United States of America, the national primary drinking water standard for maximum content of lead was put at 0.05 ppm (USEPA, 1979; NRC, 1979). A safe guideline value of 0.01 ppm of lead in drinking water has been given by WHO (1998). Allowable maximum limits for lead in drinking water in the UK, EU and USA are 0.05 ppm, 0.01 ppm and 0.015 ppm respectively (Neubauer and Wolf, 2004). Similarly, the maximum allowable concentrations of Pb in fisheries and other aquatic life are 0.001-0.007 ppm and 0.1 ppm in Canada and Russia respectively (WHO, 1998). These various standards indicate the concern expressed worldwide on Pb toxicity in human.

Most inorganic salts of lead have poor to negligible solubility in water except for the acetate, nitrate, and chloride. Therefore water-borne lead is minimal, because it forms essentially insoluble sulphates and carbonates (Stokinger, 1981). An exception is lead-lined tanks and lead pipes in water distribution systems, which produce toxic concentrations, both in acid and soft waters (Tsuchiya, 1977, USEPA 1980).

Several studies have been carried out (NAS, 1977) in the United States of America to determine the level of Pb in water after treatment (finished water), and when the same water reaches the tap. In a study of finished-water in 100 largest USA cities, the median Pb level was 0.0037 ppm with a maximum concentration of 0.062 ppm. In another similar study, Pb was found in 18.1% of finished waters with a mean level of 0.0339 ppm (NAS, 1977). A study of 969 USA water systems found an average Pb concentration at the tap of 0.0131 ppm with 1.4% of the samples exceeding the drinking water standard of 0.05 ppm. Similarly, 95% of tap-water samples in Seattle exceeded 0.05 ppm; in Boston, 65% exceeded the limit. Lead levels at the tap may be higher than in the finished water at the treatment plant; a study of cities with wide usage of Pb pipes found mean tap concentrations of Pb to be 0.03 ppm with 26.7% exceeding 0.05 ppm standard for drinking water (NAS, 1977).

The effects of heavy metals including Pb on natural immunity and /or physiological changes have received much attention with regard to enzymatic changes. Similar studies have been reported on infection of *Hymenolepis nana* linked to Pb treatment in mice (Agrawal *et al*., 1989). A single intracardiac injection of lead acetate caused abnormal DNA and RNA synthesis in mouse kidney (Fairchild, 1978). A high degree of abnormalities was found in tissue nucleic acids of rats treated with Pb (Chakraborty *et al*., 1988). Studies have also been carried out by several workers on tissue response to *Ancytlostoma caninum* larvae and on toxic effect of Pb on immunophysiology in mice (Griggs, 1964; Brown, 1980; Vardhani, 1986; Latha and Vardhani, 2002). Alteration of phosphate levels was observed in liver diseases, tumours, and other abnormalities of cardiovascular system in these studies.

2.3.3 Iron (Fe)

The Kenya Bureau of Standards (KEBS) (1996) reported that safe drinking water should not exceed 0.3 ppm of iron. It was reported by WHO (1998) that in drinking water, Fe levels of at least 0.3 ppm stain laundry and sanitary ware. Allowable limits for Fe in drinking water in the UK, EU and USA are 0.2 ppm, 0.2 ppm and 0.3 ppm, respectively (Neubauer and Wolf, 2004). However, the maximum allowable concentrations of Fe in fisheries and aquatic life are 0.3 ppm, 0.1 ppm in Canada and Russia, respectively (WHO, 1998).

2.3.4 Zinc (Zn)

The Kenya Bureau of Standards (KEBS) (1996) reported that safe drinking water should not exceed 5 ppm of zinc. A safe level of 3 ppm of zinc in drinking water has been reported to make consumers complain about the appearance and taste of the water (WHO, 1998). The United States Environmental Protection Agency (USEPA) (1980) and World Health Organization (1998) standard for zinc in drinking water is 5 ppm based on the bitter taste zinc imparts to water at that level. Allowable maximum limits for Zn in drinking water in the UK and USA is 5 ppm (Neubauer and Wolf, 2004).

Zinc is present in drinking water usually at concentrations much less than 5 ppm although soft waters could have such concentrations from materials used in the distribution systems and house hold plumbing (USEPA, 1980). From a study of Boston tap water in the United States of America, levels of zinc were found up to 1.6 ppm with a mean of 0.2 ppm. There was an increase in zinc levels at the tap over finished water levels indicating zinc pickup from the pipe; this was attributed to the soft acid nature of Boston's water (NAS, 1977). In the more acidic water of Seattle, zinc levels in tap water were higher than in the finished water 95% of the time 10 % exceeding the 5 ppm drinking water standard. The highest reported level was 5.5 ppm (NAS, 1977).

The taste threshold for zinc in water is 15 ppm. Levels of as high as 675-2,280 ppm in water have been reported to be emetic (Stockinger, 1981). In laboratory animals, inorganic zinc salts are highly toxic by parental transfer routes, but are relatively non-toxic when taken by mouth, with rat oral LD_{50}'s in the 1,000 to 3,000 mg/kg body weight range. The organic salts apparently have similar toxicities. The maximum allowable concentrations of Zn in fisheries and aquatic life are in the range of 0.03-2.0 ppm, 0.030 ppm and 0.01 ppm in the EU, Canada and Russia, respectively (WHO, 1998).

2.3.5 Cadmium (Cd)

Cadmium ranks among the most toxic metals in the aquatic systems and it is a particular problem because it is highly toxic with a long biological half-life, and its toxicity is also cumulative at least in invertebrates and fish (Larson *et al.,* 1985; Heath, 1987). Several negative effects of exposure to sub lethal concentration of copper and cadmium have been reported in fish. These include decreased survival, growth and reproduction (Buckley *et al.*, 1982; Hilmy *et al.*, 1985). High levels of cadmium leads to Necrosis of epithelium of secondary lamellae of gills and this can also affect the liver, heart and brain of the fish (Bilinski and Jonas, 1973). Impairment of carbohydrate metabolism in *Clarius batrachus* and *Tilapia mossambicus*, anaemia and hyperglycaemia attributed to the biochemical effects of cadmium in teleosts have also been reported (Larson, 1977).

Evidence has been adduced that the survival period of fish in low concentrations of Cd is reduced at lethal concentrations of Cu and zinc. In the South ESK River, Tasmania (Thorp and Lake, 1974), which was heavily polluted by mining wastes and contained about 40 ppb Cd, 150 ppb Zn and 30 ppb Cu; Crustacea, molluscs and larvae of Odonata and Plecoptera were eliminated, and mayflies, beetles and caddfly were severely affected. Further downstream where the concentrations were 20-30 % lower, all the taxa were present.

The acute toxicity of Cd to fish is increased by increase in temperature, water hardness and by reduction in dissolved oxygen (Department of Environment, UK., 1972). Salinity only shows effect at levels isotonic with the blood in the fish. Toxicity is not apparently affected by the presence of suspended solids (turbidity) at concentrations below 25 mg/L (Department of Environment, UK., 1972).

Cadmium interferes with the photosynthesis of terrestrial plants, partly by reducing the total concentration of chlorophyll pigments and altering their ratios thereby reducing growth rates and crop yields (Haghiri, 1973). A concentration of 300 ppb of Cd in water kills green algae *Selenastrum capricornutum*, and 50 ppb of Cd inhibits its growth (Bartlet *et al.*, 1974).

2.4 Speciation and environmental monitoring studies

Speciation of an element refers to the process of identifying and quantifying the different oxidation states of the element in a concerned system or it can be defined as the determination of the bioavailable amount of the element in a sample compared to the total amount of the element. There is no generally accepted definition of speciation and the meaning of the term is extracted from the problem at hand (Ure *et al.*, 1993a, b; Ure and Davidson, 1995). In natural aquatic systems, metal ions are rarely present as free hydrated ions (Buffle, 1988). Natural organic matter (NOM) provides binding sites for metal ions influencing their bioavailability, toxicity and general transport behaviour (Hodel *et al.*, 1995; Christensen *et al.*, 1996). Metal binding of NOM increases with increasing pH value (Christensen, J.B. and Christensen, T.H., 2000). It has been found that trivalent ions are generally bound more strongly to NOM than divalent ions (Cacheris and Choppin, 1987; Rao *et al.*, 1994).

The interaction of metals with naturally occurring dissolved organic matter (DOM) plays an important role in determining the fate of those metals in soils and water. Not only does association with DOM influence the bioavailability of metals through the soil system (Fox, 1995; Sauve' *et al.*, 2000), it also affects their bioavailability and toxicity (Lores *et al.*, 1999; Simpson *et al.*, 1997; Tam and McColl, 1990). The 'free' metals usually consist of hydrated metal cations and soluble inorganic metal complexes and are usually considered to represent the bioavailable metal fraction during extraction (Jansen *et al.*, 2001). Knowledge of the distribution of metals between bioavailable and residual fractions ascertains the bioavailability and toxicity of the metals. The metal fraction introduced by man's activities in the environment is adsorptive and exchangeable and bound to carbonates and is therefore considered to be weakly bound and may equilibrate with aqueous phase thus becoming rapidly bioavailable (Gibbs, 1977). The metal fraction present in the residual fraction is detrital and lattice in origin and is therefore taken as a measure of contribution by natural sources (Salomons and Forstner, 1980).

The rates of uptake of zinc and cadmium from solution by decapod crustacean P*alaemon elegans* increase with dissolved metal concentrations (White and Rainbow, 1984, White and Rainbow, 1986; Rainbow and White, 1989). In this crustacean the zinc uptake rate appears to be determined by physicochemical control of the decapod since it correlates with the concentration of the (hydrated) free metal ion in the exposure medium (Rainbow, 1995). Thus the zinc uptake rate of *P. elegans* is reduced by the addition of the hydrophilic chelating agent ethylenediamminetetraacetic acid (EDTA) (Nugegoda and Rainbow, 1988; O'Brien *et al.*, 1990) and is increased by a decrease in salinity (due to reduced chloride complexation of the free zinc ion) independently of changes in osmolality that might cause physiological responses (Nugegoda and Rainbow, 1989a, b). Although such studies have not been done for other metals, their uptake and bioavailability would be controlled by similar binding and solubility controls.

Heavy metal contamination in urban soils can be harmful to the biota and human beings, and extensive investigations have been carried out in some countries and regions (Culbard *et al.*, 1988; Thornton, 1991; Weiss *et al.*, 1994; Chon *et al.*, 1995; Markus and McBrantney, 1996; Chen *et al.*, 1997; Kasimov and Lychagin, 1998; Lavado *et al.*, 1998; Stroganova *et al.*, 1998; Wilcke *et al.*, 1998, 1999). Total metal content analysis may give information concerning possible enrichment of the soil with heavy metals, but it is generally recognised that it is the chemical form of a metal in the soil that determines its mobilization capacity in the environment (Lu *et al.*, 2003) and therefore the need for speciation analysis.

The elements Cu, Fe, Pb and Zn exhibit various oxidation states. Copper forms two common oxidation states; Cu^{+} and Cu^{2+}. Both oxidation states are involved in many stable compounds and complexes such as $Cu(NH_3)Cl_2$ (Stokinger, 1981). Copper salts may hydrolyse at ambient pH values and can be precipitated as $CuCO_3$ (NAS, 1977). Lead and iron form two common oxidation states. Lead forms $Pb^{2+}$and Pb^{4+} while iron forms Fe^{2+} (reducing and unstable) and Fe^{3+} (most stable). There is also an unstable oxidation state of +6 for iron that is powerfully oxidizing. Most inorganic salts of lead are in the +2 oxidation state; some are +4 and their water solubility ranges from poor to negligible, except for the acetate, nitrate, and chloride. Zinc forms one common oxidation state; Zn^{2+} (Stokinger, 1981).

2.4.1 Temperature influence on aquatic life

Low temperatures are not favourable to fish and they normally lead to fish kill (Alabaster and Lloyd, 1984). Bottom fauna in five European lakes that provide water for cooling systems of two power stations; revealed a marked decrease in abundance of chironomids in the most heated lake while oligochaetes flourished (Alabaster and Lloyd, 1984). Excessive heat and cold diminish the value of the bottom sediments as feeding grounds for fish and therefore are not favourable to fish production. Though fishes prefer a narrow range of temperatures to accomplish reproduction successfully, hatching rates are boosted at elevated temperatures (Embody, 1934). Monitoring temperature fluctuation is therefore an important water quality check as it influences both flora and fauna in the aquatic environment.

2.4.2 Turbidity influence on aquatic life

Turbidity is an expression of the optical property of a sample that causes light to be scattered and absorbed rather than be transmitted in straight lines through a sample. Turbidity is caused by the presence of suspended matter in a liquid (Willard *et al.*, 1992). This could be an important factor in determining the speciation studies. This is because the metal ions get adsorbed to the solid particulates in water depending on the adsorption strengths of the particulates and therefore determines the proportions of free ions in water (Florence and Batley, 1980; Newman *et al.*, 1994). A maximum turbidity measuring 5 NTU (Nephelometric Turbidity Units) in drinking water is recommended by KEBS (1996) and WHO (1998).

Turbidity measuring less than 25 mgL^{-1} suspended solids has no harmful effects on fisheries while that between 25-80 mgL^{-1} suspended solids maintains good to moderate fisheries. Values ranging from 80-400 mgL^{-1} suspended solids are likely to maintain well freshwater fisheries while a figure of more than 400 mgL^{-1} suspended solids shows poor fisheries maintenance (Alabaster and Lloyd, 1984). Fish resistance to disease is reduced at a concentration of 100-200 mgL^{-1} suspended solids. The fish suffer from fin-rot. Nests and spawning grounds are covered with eroded silt as a blanket and this kills bottom fauna while the eggs of fish suffocate in the nests. High mortalities due to this phenomenon have been observed in rainbow trout (*Salmo gairdneri*) and silver salmon (*Oncorhynchus kisutch*) (Alabaster and Lloyd, 1984).

Good fisheries are dependent on unlimited supply of food for fish in freshwaters. The food supply ultimately depends upon the growth of green plants (algae and higher aquatic plants). Such plants are restricted by high turbidity which can cause severe abrasive leaf damage to aquatic plants. It is therefore not surprising for green algae to disappear at the shores of water masses due to the high turbidity and lack of enough sunshine during heavy rains or winter periods. Benthic organisms are also at risk from suspended solids and the particulates which settle at the bottom. It has been noted in Lake Erie that high levels of turbidity cause a greater proportion of zooplankton to grow near the water surface instead of the bottom than at times of less turbidity (Kenneth, 1942).

2.4.3 Alkalinity and pH influence on aquatic life

Majority of fish population live in a pH range of 6.3-9.0, as most of the water systems have the pH range of 6.7-8.6. At pH > 5.0, a balance exists between the influx and efflux of Na^+ ions, while below that the latter effect is enhanced, increasing the permeability of cell membranes due to lack of Ca^{2+} ions. Fish weakened by acid pH values can be susceptible to diseases. Nees (1949) stated that below pH 5, Carp fish develops a hypersensitivity to bacteria. The structure and composition of zooplankton populations also change with increasing acidity. *Daphnia* drops out as the pH falls to 6.0 and below, leaving the hardy species like *Bosmina* to flourish in such waters (Gerald, 1979).

Slight alkaline conditions have proved favourable for fish life. In Belgium, ponds maintained at pH of 7.0-7.5 are more productive than those at pH of 5.0-5.6 (Alabaster and Lloyd, 1984). However, the pH values arising from pollution affect the nutrient circulation by reducing the rate of decomposition of organic matter and inhibiting nitrogen fixation.

2.4.4 Dissolved Oxygen (DO) influence on aquatic life

High mortalities have been noted in Young salmonids when they are exposed to sudden reduction of DO to the level of 2-3 mgL^{-1} at the time of hatching (Alabaster and Lloyd, 1984). Sudden exposure to moderately high concentrations of CO_2 causes a normally tolerable low DO to be rapidly fatal, but the effect is not considered to be due to a pH decrease. However, increase in temperature, CO_2, and H^+ ion concentration; either independently or collectively, leads to low affinity for oxygen in the blood of rainbow trout (Eddy, 1971). Various researchers have evidently pointed out a close relationship between low DO and parasitic and bacterial diseases of fishes. A serious epidemic in fish *Leucichthys artedi*, occurred in certain Wisconsin lakes, America, resulting in large numbers of dead fish onshore (Welch, 1952).

2.5 Previous studies done in the study area (in Kenya)

Some work has been done on total heavy metals in samples from Lake Victoria. Speciation studies on heavy metals are a rather new phenomenon in heavy metal studies in which very little data is available especially on Lake Victoria. Some work has been done on total heavy metal concentrations on Lake Victoria as a whole concerning some species of fish, sediment and water (Biney *et al.*, 1994). Research carried out on heavy metal concentrations in freshwater of Lake Victoria on Kenyan side by Ochieng (1987) indicated 0.002-0.008 ppm Cd, 0.007-0.0936 ppm Pb, 0.005-0.0579 ppm Cu, 0.025-0.125 ppm Zn and 0.127-2.29 ppm Fe. Analysis of sediment for total heavy metal concentrations on dry weight basis gave 0.19-1.3 µg/g Cd, ND-100 µg/g Pb, 1-79 µg/g Cu, 3-334 µg/g Zn and 1.18×10^3-9.22×10^4 µg/g Fe (Onyari, 1985; Ochieng, 1987; Onyari and Wandiga, 1989; Mwamburi and Oloo, 1997). Studies have also been carried out in Tanzanian basin indicating that the sediment, water and biota in Lake Victoria contain alarming levels of heavy metals (Mpendazoe *et al.*, 1993; Hamza, 1996; Mohammed, 2000).

In some study carried out by Kishe and Machiwa (2001) on *Oreochromis niloticus* (Tilapia) sampled from Mwanza Gulf, it was noted that copper and zinc concentrations in the muscle of the fish were 1.9 ppm and 29.8 ppm respectively based on dry weight while the maximum allowable concentrations are 10.0 ppm (wet weight) and 60 ppm (wet weight), respectively (Morelli, 1990). Ochieng (1987) observed concentration ranges of trace metals in muscle of Nile perch sampled from Kisumu town zone as 0.2-0.5 ppm Cu and 1.0-6.4 ppm Fe on dry weight basis. It was also noted that the limnological features of Lake Victoria and other Kenyan lakes and rivers met the international standards relating to these living environments with the exception of the Rift Valley Lakes Bogoria, Nakuru and Elmentaita and River Kisati. River Kisati was highly polluted as reported by Ochieng (1987). This river feeds Kisumu City Car Wash area of Winam Gulf with industrial and sewage effluents from Kisumu City.

Studies carried out on some rivers traversing coffee farms and processing factories registered processing effluents from overflowing drainage pits (Mburu and Mwaura, 1998). The processing effluents are of crops such as coffee, tea and tobacco that use heavy metal based farm chemicals. An investigation into the environmental pollution situation, of Ruiru and Komothai rivers (in Kiambu District in Kenya) with 18 and 12 coffee factories along them respectively, observed that pulping, washing and grading use a lot of water but without any proper control (Mburu and Mwaura, 1998). On wastewater treatment, the stabilization ponds were poorly maintained. Coffee processing facilities were not well protected from run-off water. Discharges into rivers due to overflow of pits were rampant during rainy periods. Eroded pits acted as discharge points. Blocked wastewater draining channels diverted the effluent to rivers instead of it disposing into the seepage pits (Mburu and Mwaura, 1998). These two rivers join River Tana, which drain into the Indian Ocean. This is an indication that analysis of rivers going through agricultural farms can be a good indicator of agrochemical sources of heavy metals since the farms use fungicides and fertilizers (DDP, 1994).

CHAPTER 3

3 MATERIALS AND METHODS

3.1 Choice and description of the study area

The rivers selected were Sio, Nyamasaria, Nyando and Sondu-Miriu. Both the upstream and downstream of these rivers were sampled. The landing beaches considered were Port Victoria, Dunga, Hippo Point, Sio Port and Kisumu Car Wash. Sio Port and Kisumu Port were also selected for sampling. Sio Port is next to the mouth of river Sio while Kisumu Port is next to Kisumu Car Wash. Three estates namely Nyamasaria, Migosi and Nyawita were selected to supply piped, well, rain and private treatment plant water samples for drinking water for quality assessment. The choice of the study area was based on the availability of perennial rivers, ports, landing beaches, car washing beaches, sources of drinking water and proximity of industrial/commercial towns to the Winam Gulf of Lake Victoria shore and sources of drinking water.

Nyando and Nyamasaria rivers drain from the rich agricultural areas such as Nandi hills and they are heavily polluted with insecticides, herbicides, fungicides and fertilizers coming from farms and factories from their catchments (DDP, 1994). Sondu-Miriu and Nyando rivers provide water for rice growing through irrigation (DDP, 2002). Nandi hills and Nyando plateau provide a good environment for dairy farming and it is here that coffee growing that uses a lot of fertilizers and pesticides is practised (DDP, 2002). River Sio goes through Funyula and Nambale divisions which are rich in agricultural activities. There is local mineral exploitation for iron and fluorspar. The local population always involved itself in making traditional ornaments like simple weapons and farm implements. The rocks of this area are associated with availability of gold, copper pyrite, molybdenite, manganese and rod metal (DDP, 1994). Kisumu Port handles Ships carrying petroleum products to various destinations (DDP, 2002). Sio Port and Port Victoria handle motorised boats which use diesel for their operations ((DDP, 2002). There are also a lot of sand mining activities at the mouth of river Sio and this could be contributing to spread of heavy metals into Lake Victoria. Dunga, Car Wash, Sio Port, Port Victoria and Hippo Point beaches are served by some motorised boats that use diesel while river Nyamasaria carrying all industrial effluents from Kisumu city and agricultural effluents enters the lake at Hippo Point. The sampling area is shown in Figures 1 and 2.

3.2 Sampling sites

There were four sampling sites for each district. Two of the sites were along the beaches on Lake Victoria and were two kilometres apart. One site was three kilometres upstream on each perennial river chosen for study. This was to confirm the source of the heavy metals. The fourth site was two kilometres offshore from Sio Port pier and offshore of Hippo Point. In Kisumu the car washing beach and the Kisumu Port pier area were the other sampling areas. The Sio Port and Port Victoria in Busia district were part of the sampling sites. The sampling sites in Winam Gulf and the estates sampled in Kisumu City are shown in Figures 1 and 2 respectively.

1	Sio Port Beach	9	Nyamasaria River Upstream
2	Kisumu Port	10	Nyando River Mouth
3	Kisumu Car Wash	11	Nyando River Upstream
4	Port Victoria	12	Sondu-Miriu River Mouth
5	Kisumu Dunga	13	Sondu-Miriu River Upstream
6	Sio River Mouth	14	Hippo Point
7	Sio River Upstream	15	Sio Port Offshore
8	Nyamasaria River Mouth	16	Hippo Point Offshore

Figure 1. Map of Winam Gulf showing sampling sites

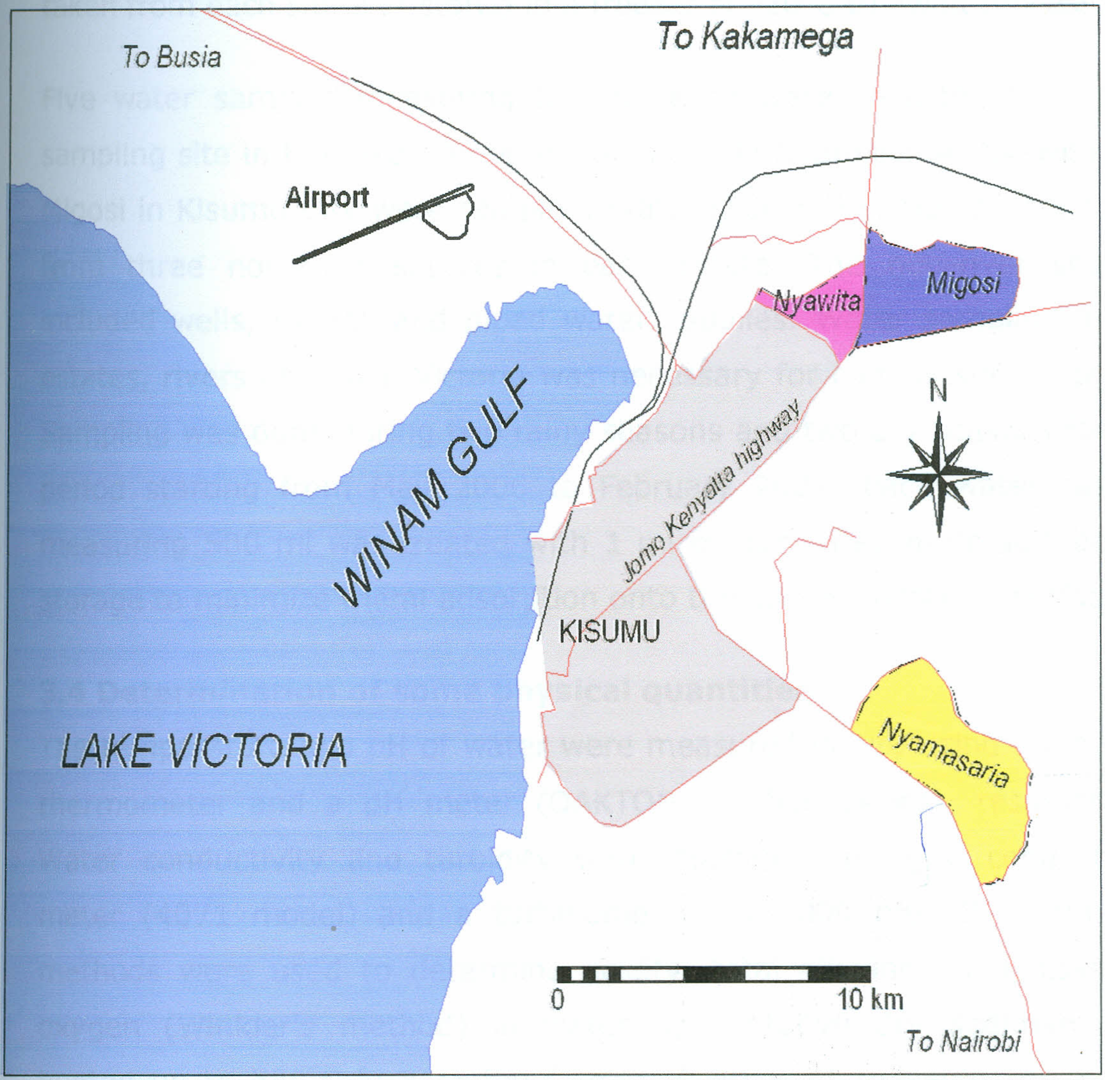

Figure 2. Map of Kisumu City showing the location of estates from which water was sampled

3.3 Sampling methodology

A Sediment sample weighing l00 g was taken from a hole which measures 5 cm deep with the aid of a plastic tube of size 5 cm in diameter and 72 cm in length (Angelidis and Aluopi, 1995). Five samples of each type were taken. Fish samples were collected as the boats landed on the beaches. *Lates niloticus* locally known as Mbuta and commonly known as Nile perch measured between 15 cm to 20 cm in length. *Oreochromis niloticus* which is locally known as Ngege and commonly known as Tilapia samples were similarly taken. Samples measuring 100 g of *Rastrineobola argentea* locally known as Dagga or Omena and commonly known as Silver cyprinid were collected in polyethylene bags. Five samples of each species were taken from each site and stored in a freezer at -20^{0}C to await processing.

Five water samples measuring 500 ml each were collected from each sampling site in the lake. Three estates namely Nyamasaria, Nyawita and Migosi in Kisumu City were sampled. Water (500 ml) samples were taken from three non-river sources in each estate. The non-river sources included wells, rainfall and piped water supplies. Water sampling in the estates, rivers and Lake Victoria was necessary for comparison purposes. Sampling was done during two rainy seasons and two dry seasons for the period starting from May 2006 to February 2007. Each water sample measuring 500 ml was treated with 1 ml concentrated nitric acid before storage to minimize metal adsorption onto the plastic container surface.

3.4 Determination of some physical quantities

The temperature and pH of water were measured *in situ* using a mercury thermometer and a pH meter (OAKTON ion 510 series), respectively. Water conductivity and turbidity were measured using a conductivity meter (4071 model) and a turbidometer (Al 1000 model). Titrimetric methods were used to determine acidity, total alkalinity and dissolved oxygen (Winkler's method) in water. Quantitative dry sediment was heated up to 550°C in a muffle furnace (Carbolite) to determine the % organic matter by mass loss. Percentage fat (oil) content in dry fish was determined by Sohxlet extracting Muscle and whole fish tissues for the two niloticus and *Rastrineobola argentea* species respectively for 8 hours and rotary evaporating to give mass % fat residues. All the data in these determinations were recorded.

3.5 Sample handling before extraction

Once collected, the samples were transported in an icebox at 0°C to the laboratory for storage and processing. All solid samples were stored in a freezer at –20°C according to Kishe and Machiwa (2001) while liquid samples were stored according to Nichole and Mason (2001) and Rivaro *et* *al.*, (2005) at 4^0C to preserve them while waiting for extraction and analysis.

3.6 Determination of dry weight of solid samples

Dry weight was determined for fish according to the procedure followed by Bolton *et al*. (2003). In this procedure, some fish muscle measuring 1 g was dissected out of *Lates niloticus* after removing scales and placed in a pre-weighed acid cleaned Petri dish. This was oven dried to a constant mass at 60^0C for a period of 72 hours after which the dry weight was recorded. The dry weight of *Oreochromis niloticus* was similarly determined. The dry weight of *Rastrineobola argentea* was similarly determined except that whole fish was used the way it is consumed by human beings. One gram of sediment sample sieved through 45 μm nylon sieve was weighed out and dried according to Tack and Verloo (1999) at 100°C for 24 hours and the dry mass recorded.

3.7 Determination of heavy metals and their speciation

3.7.1 Determination of heavy metals in sediment

3.7.1.1 Total metal determination

Sediment samples were dry sieved through 45 μm nylon sieves. Metal concentrations were determined in this fraction (< 45 μm) of the samples, which is considered the most important carrier of metals in the marine environment (Forstner and Wittmann, 1983). Total sediment extraction was carried out according to the procedure of Tack and Verloo (1999) with some minor modifications. A mass of 1 g of dried sediment sieved through 45 μm nylon sieve was weighed into a Pyrex digestion tube and 10 ml mixture of concentrated nitric and hydrochloric acid (4:1) added. The contents were placed in a digester for 3 hours at 100^0C, followed by filtration through a 0.45 μm cellulose acetate filter into a 25 ml volumetric flask. This was made to volume with double-distilled and deionised water. The extract was analyzed for Cd, Cu, Zn, Fe and Pb using atomic absorption spectroscopy (AAS) and the results confirmed by inductively coupled plasma-mass spectrophotometer (X series 2 ICP-MS model). The ICP-MS analysis was carried out in Germany.

3.7.1.2 Bioavailable metal determination

One gram of a sieved dry sediment sample was treated with 10 ml of 0.5 N HCl overnight in a Pyrex digestion tube at room temperature to extract the most available fraction of the metals in the sediment (Agemian and Chau, 1976; Angelidis and Aluopi, 1995). The metal fraction, which is extracted with mild acid, represents the most biologically available part of the metals (Luoma and Bryan, 1981) and can be used as an indicator of the anthropogenic contamination of sediments (Chester and Voutsinou, 1981). The extract was filtered through 0.45 µm cellulose acetate filter and analysed for Cd, Cu, Fe, Zn and Pb by using atomic absorption spectrophotometer (AAS) according to Angelidis and Aluopi (1995).

3.7.2 Digestion of fish

3.7.2.1 Total metal determination

The procedure for total tissue determination by Tack and Verloo (1999) was followed with minor modifications. Muscle and whole fish tissues for the two niloticus species and *Rastrineobola argentea* species respectively were used for extraction. One gram of oven dried fish tissue ground to fine powder with a grinder was soaked in a digestion tube with 10 ml of concentrated nitric acid for 24 hours. The acid solution was then heated to 120^{0}C for 3 hours and the extract filtered through 0.45 µm cellulose acetate filter. The filtrate was placed in a 25 ml volumetric flask and made to volume with distilled water. The concentration of the metals, Cd, Cu, Zn, Fe and Pb were then determined according to Berman (1986) using atomic absorption spectrophotometer (AAS) at 228.8 nm, 324.8 nm, 213.8 nm, 243.3 nm and 283.3 nm respectively and confirmed with ICP-MS.

3.7.2.2 Bioavailable metal determination

One gram of oven dried fish tissue was treated with 10 ml of 0.5 N HCl overnight in a digestion tube at room temperature to extract according to Agemian and Chau (1976) the most available fraction of the metals in the tissues. The extract was then filtered through a 0.45 µm cellulose acetate filter. The filtrate was placed in a 25 ml volumetric flask and made to volume with distilled water and the concentration of the metals; Cd, Cu, Zn, Fe and Pb were then determined according to Berman (1986) using atomic absorption spectrophotometer (AAS) at 228.8 nm, 324.8 nm, 213.8 nm, 243.3 nm and 283.3 nm respectively.

3.7.3 Determination of heavy metals in water

The procedure adopted by Mzimela *et al* (2003) for total metal extraction was followed with minor modifications. A water sample measuring 100 ml was filtered through a 0.45 µm cellulose acetate filter. This was acidified to 1% with nitric acid (AR), placed in a digester at 60^0C and allowed to evaporate to 15 ml. The sample was transferred into a 25 ml volumetric flask and made up to volume with double distilled and deionised water. The concentrations of Cd, Cu, Fe, Pb and Zn were measured using atomic absorption spectroscopy (AAS) and confirmed by an ICP-MS. The water filters were also digested for 30 minutes in a microwave using concentrated nitric and hydrochloric acid (4:1) to determine the total metal content in the water sample.

3.7.4 Recovery studies

Recovery studies were done for each metal to ascertain the quality of the extraction procedures used. Analytical reagents of cadmium nitrate, lead nitrate, copper sulphate, zinc nitrate and iron nitrate were used to make 10,000 ppm stock solution for spiking samples for recovery studies. Three 100 ml water samples in triplicates were each spiked with 10 µl of stock solution to give 1 ppm of each spiked metal in the water. The water samples with their respective blanks were concentrated in a digester and quantitatively taken and stored for analysis. Similarly three 1 g sediment and three 1 g fish samples of each type were each spiked with 10 µl of the stock solution. The spiked samples were digested together with some blanks of the respective samples and solvents used in the extraction process and the digests were stored for analysis by AAS. Various concentrations of the analytical reagent of each metal were analysed by the AAS and a calibration curve for each standard metal was drawn. Each of the digested samples was then analysed for each metal by the AAS with the aid of the respective calibration curve.

3.8 Statistical Analysis

The means and ranges of the data collected were determined in this study. Confidence limits of 5% and 1% were applied to test the significance of the analytical results that is to prove the hypotheses right or wrong. Analysis of variance (ANOVA) ($p < 0.05$) and Student's T-test ($p < 0.05$ and $p < 0.01$) were used to check the variations. Pearson correlation coefficients (Bivariate correlations) were used to determine significant metal interrelationships within and across samples. Statistical analyses were performed with SPSS and MSTATC software packages. Statistically significant differences were expressed at $p < 0.05$ and $p < 0.01$.

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 Assessment of the total metal levels in sediment

The mean wet weight (ww)/dry weight (dw) ratio for sediment obtained in this study was 1.264 (Table 2). The dry weights of river Sio sediment collected from upstream was lowly significant ($p < 0.05$) while that of river Nyando upstream was highly significant ($p < 0.05$). This variation was attributed to the highly sandy and highly loamy sediment texture of the two sites, respectively. It was noted in the research laboratory that the sediment sample from river Nyando upstream could easily go through a 45 μm sieve after grinding while that of river Sio upstream had difficulties. Clearly loam soil has high moisture content than sand soils under similar conditions. The ww/dw ratio could be of importance in this study when there was need of using it to evaluate the concentration of the metals on wet weight basis.

Table 2. Wet weight/Dry weight ratios for sediment from different sampling sites

Site	Dry weight (dw) in g	ww/dw ratio	Average ww/dw ratio
3	0.7751	1.2901	
6	0.9166	1.0910	1.264 ± 0.187
7	0.9519	1.0505	
10	0.6977	1.4333	
11	0.6430	1.5552	
12	0.8891	1.1247	
13	0.7678	1.3024	

ww-Wet weight of sediment = 1g, dw-Dry weight of sediment.
Sites 1 and 6 are less than a kilometre apart, 2 and 3 are also less than a kilometre apart and therefore one site was sampled for sediment in each case for dry weight determination. Some sites were for specific samples to achieve specific objectives and this is why therefore they do not appear in the table.
Sites: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu Rivers Mouth and 13 - Sondu-Miriu Rivers Upstream

The % organic matter in sediments ranged from 1.20-14.97 with a mean of 7.58 (Table 3). The results for % organic matter in sediments are in agreement with those of Mwamburi (2003) in a study of sediments of some major rivers that feed Lake Victoria but the results are relatively higher than those obtained by Jain (2004) in a study of bed sediments of River Yamuna in India (Table 4). This shows that Winam Gulf sediments are rich in organic matter with an average of 7.70 (Table 4).

Table 3. Variation of mean % organic matter in sediment samples on dry weight basis

Site	% Organic matter
Lake Victoria (Winam Gulf)	
3	10.52
4	2.07
5	4.35
6	1.20
8	9.35
10	11.44
12	14.97
Average	7.70
Upstream river	
7	2.10
9	7.14
11	12.62
13	7.60
Average	7.37
Mean % organic matter	7.58

Least Significant Difference (LSD) = 1.96 at $p < 0.05$.
Site: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

Table 4. Comparison of % organic matter ranges in sediments with other previous studies and regions on dry weight basis.

	Lake and Upstream[a]	Major rivers feeding Lake Victoria[b]	Yamuna River[c]
% range	1.20-14.97	3.5-9.6	1.04-6.87
% mean	7.58	6.7	2.3

[a]present study 2006/7 Kenya, [b]Mwamburi (2003) Kenya, [c]Jain (2004) India.

The AAS analysis gave mean % recovery values for the extraction of the spiked sediment samples for Cd, Pb, Cu, Zn and Fe as 92, 87, 89, 93 and 97 respectively. The total concentrations of the metals in sediment samples analysed by the AAS and confirmed with ICP-MS gave results that were comparatively close for the two analytical instruments with detection limits (Shimadzu Corporation, 1992; Shimadzu Corporation, 1993) of Cd, Pb, Cu and Zn of 0.001 ng/ml, 0.001 ng/ml, 0.003 ng/ml and 0.001 ng/ml respectively. The results are presented in Tables 5 to 9 based on the dry weight of sediment. The average Cd concentrations in sediments at the sites ranged from 0.257-2.402 µg/g with an average of 1.239 µg/g (Table 5).

Table 5. Seasonal variation of mean concentration of total Cadmium Cd (µg/g on dry weight basis) in sediment in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
3	3.300	1.862	2.434	2.012	2.402	1.910
4	1.144	0.931	1.032	0.906	1.003	0.758
5	1.110	0.900	0.977	0.850	0.959	0.725
6	0.290	0.239	0.265	0.235	0.257	0.192
8	1.142	0.905	0.938	0.929	0.977	0.723
10	2.100	1.563	1.430	1.575	1.667	1.220
12	1.950	1.425	1.774	1.475	1.656	1.290
Seasonal average	1.347		1.202		1.274	0.974
Upstream						
7	1.066	0.862	0.880	0.813	0.905	0.678
9	0.931	0.755	0.807	0.668	0.790	0.591
11	1.920	1.488	1.430	1.350	1.547	1.200
13	1.757	1.325	1.389	1.362	1.458	1.110
Seasonal average	1.263		1.087		1.175	0.895
Lake and Upstream seasonal average	1.317		1.161		1.239	0.945

Trips A – May 2006, Trip B - October 2006, Trip C - January 2007 and Trip D - February 2007.

At $p < 0.05$: LSD = 0.122 for sites, LSD = 0.295 for seasons, LSD = 0.172 for interactions between sites and seasons.

Sites: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

These Cd values compare well with those reported in the studies of Ochieng (1987), Onyari and Wandiga (1989) and those recorded by Saeki *et al.* (1993). Considering the past studies in Lake Victoria region, there has been considerable accumulation of Cd in the sediments (Table 10).

The high mean sediment concentrations of 2.402 µg/g Cd, 1.667 µg/g Cd and 1.656 µg/g Cd recorded at Car Wash, Nyando River Mouth and Sio River Mouth, respectively (Table 5), showed significant difference ($p < 0.05$) from the sample mean of the study area. The high concentration of all metals noted at Car Wash area was attributed to the intense car washing activities (Appendix I: Plate 4, pg 135), oil spills from the nearby Kisumu Port and the petroleum depot and river Kisati which are close by. River Kisati had in past studies been reported to be highly polluted with sewerage, industrial, agricultural and organic effluents as well as Kisumu City wastes by Ochieng (1987). The high concentrations at the mouths of Rivers Nyando and Sondu-Miriu were attributed to the Ahero town and Sondu market centre wastes respectively and due to the use of the water of these two rivers in irrigating agricultural crops like rice and flooding of the rivers; carrying with them some of the chemical residues used in agricultural production. The lowest concentration of 0.257 µg/g Cd recorded at the mouth of River Sio showed significant difference ($p < 0.05$) with the mean of the study area. The significant low concentration observed at Sio River Mouth was attributed to the intense sand mining activities at the site (Appendix I: Plates 5 and 6, pg 136). These activities take away the bed sediments that hold the already settled heavy metal residues and thereby decreasing the concentration of the metal at the river mouth. However, the upstream of River Sio showed a relatively higher concentration of 0.905 µg/g Cd compared to that of the downstream. The high concentration on the upstream could be due to the agricultural activities, oil wastes and spillage from the water pumping engines installed along the river (Appendix I: Plate 7, pg 137). The Cd seasonal concentration which was generally high during the rainy seasons decreased during the dry seasons although during the sampling period the dry seasons of Trips C and D (early January 2007 and late February 2007 respectively) experienced relatively high rainfall in the 2007 sampling period while it had been dry in the other years. Floods were witnessed in various parts of Kenya in the months of December 2006 and this situation continued into mid February 2007. Rivers Sondu-Miriu and

Nyando broke their banks during this period of December 2006 to February 2007 causing devastating effects on the agricultural farms along the river banks; a situation that is only witnessed during the rainy season of March to late May every year.

The average site Pb concentration in sediment ranged from 8.1-152.2 µg/g with a mean of 32.5 µg/g (Table 6).

Table 6. Seasonal variation of mean concentration of total Lead Pb (µg/g on dry weight basis) in sediment in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
3	210	96.4	127.5	174.9	152.2	138
4	15.3	12.3	12.7	10.8	12.8	9.5
5	45.0	34.8	41.5	30.3	37.9	31.1
6	10.5	8.6	7.8	5.6	8.1	6.86
8	29.6	23.3	26.3	21.5	25.1	18.4
10	20.1	15.6	18.0	14.3	17.0	12.9
12	30.4	21.0	26.0	23.1	25.1	18.8
Seasonal average	40.9		38.6		39.7	33.7
Upstream						
7	17.3	10.2	13.3	13.3	13.5	10.1
9	25.0	19.6	22.1	19.5	21.5	15.9
11	23.5	15.6	20.0	16.8	19.0	14.4
13	31.4	22.7	24.1	22.5	25.2	18.7
Seasonal average	20.7		19.0		19.8	14.8
Lake and Upstream seasonal average	33.6		31.5		32.5	26.8

At $p < 0.05$: LSD = 1.97 for sites, LSD = 4.79 for seasons, LSD = 0.84 for interactions between sites and seasons.
Sites: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

The high concentration recorded of 152.2 µg/g Pb at Kisumu Car Wash showed significant difference ($p < 0.05$) with the mean of the study area. This was mainly attributed to petroleum spill residues from car washing activities, oil depot nearby and ships. The concentration of Pb was found to be higher during the wet season. This was attributed to metal residues eroded by rain water from the agricultural lands, municipal and domestic wastes which finally settle to the surface sediments of Lake Victoria and the rivers that feed the lake. The high concentration levels of the metal Pb is in agreement to Ochieng (1987) and Onyari (1985) who had previously found high levels of the metal in River Kisati whose mouth is less than a kilometre away from Car Wash area.

The average site concentration of Cu in sediment ranged from 18.5-93.1 µg/g with a mean of 36.7 µg/g (Table 7). The mean of copper concentration compares well with that recorded by Soltan *et al*. (2005) in their study at Lake Nasser in Egypt. The high average concentrations of 93.1 µg/g Cu, 66.6 µg/g Cu and 56.3 µg/g Cu recorded at Kisumu Car Wash, Nyando River Upstream and Nyando River Mouth, respectively, had significant differences ($p < 0.05$) with the mean of the study area. This was attributed to the high metal loads that these sites experience. River Nyando is well known to flood agricultural farms with devastating consequences and in such circumstances it carries with it agricultural effluents which thereby increase the Cu load in its sediment. The effects of the floods were supported by the huge turbidity values recorded both in the upstream and downstream waters of River Nyando (Table 27). However, the upstream mean Cu concentration was relatively higher than that of the downstream and this was attributed to the adsorption of Cu by sediment within the large wetland between the two sites and this effectively could be reducing the concentration at the river mouth. The high value of mean Cu concentration recorded agrees well with Ochieng (1987) who had similarly recorded high Cu concentrations in River Nyando sediment. The low average concentration of 18.5 µg/g Cu recorded at Sio River Mouth showed significant difference ($p < 0.05$) from the rest and this was attributed to the sand mining activities at the site (Appendix I: Plates 5 and 6, pg 136). Seasonal variation in concentration of Cu in sediment (Table 7) showed a similar trend to that of Cd and Pb above.

Table 7. Seasonal variation of mean concentration of total Copper Cu (μg/g on dry weight basis) in sediment in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
3	132	78.5	77.9	83.9	93.1	100
4	26.9	21.2	23.3	20.3	22.9	21.3
5	27.7	22.6	25.3	20.1	23.9	22.8
6	22.5	17.3	18.8	15.5	18.5	18.1
8	35.0	26.1	27.2	24.8	28.3	28.3
10	64.3	51.2	57.3	52.3	56.3	52.8
12	23.5	19.1	22.4	18.5	20.9	18.0
Seasonal average	40.6		34.8		37.7	37.3
Upstream						
7	26.6	20.2	19.8	21.7	22.1	20.1
9	26.5	21.4	22.2	19.6	22.4	21.8
11	77.2	63.4	64.0	61.6	66.6	63.6
13	33.2	26.6	30.9	24.6	28.8	26.8
Seasonal average	36.9		33.1		35.0	33.1
Lake and Upstream seasonal average	39.2		34.2		36.7	35.8

At $p < 0.05$: LSD = 1.70 for sites, LSD = 4.14 seasons, LSD = 2.41 for interactions between sites and seasons.

Sites: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

The site concentration of Zn in sediment ranged from 37.7-441.6 μg/g with a mean of 163.3 μg/g (Table 8). The mean of Zn compares well with that recorded by Abdel-Moati and El-Sammak (1996) in their study of the sediments of Lake Mariut in Egypt. The range is in agreement with the results of Onyari and Wandiga (1989). The mean of 182.2 recorded for the lake in the current study (Table 8) concurs with the range in a study taken by Ochieng (1987) in Lake Victoria (Table 10). The concentrations of 441.6 μg/g Zn and 258.4 μg/g Zn for Kisumu Car Wash and Sondu-Miriu River Mouth respectively were highly significant ($p < 0.05$) and this was attributed to the high metal Zn load from the flooding of agricultural farms by River Sondu-Miriu and use of its water in irrigating agricultural activities. The low concentrations of 48.5 μg/g Zn, 37.7 μg/g Zn and 56.3 μg/g Zn for Port Victoria, Sio River Mouth and Sio River Upstream respectively showed significant differences ($p < 0.05$) with the mean of the study area.

Table 8. Seasonal variation of mean concentration of total Zinc Zn (µg/g on dry weight basis) in sediment in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
3	529.2	389.8	438.4	409.0	441.6	443
4	55.6	44.3	49.7	44.6	48.5	45.1
5	214.1	184.3	182.8	160.1	185.3	175
6	44.9	32.0	39.7	34.3	37.7	36.2
8	152.9	125.3	138.6	110.5	131.8	126
10	198.0	159.4	175.0	156.3	172.2	162
12	294.0	236.2	264.8	238.7	258.4	241
Seasonal average	190.0		174.5		182.2	175.5
Upstream						
7	66.5	50.6	54.8	53.5	56.4	53.9
9	123.6	98.2	112.6	109.5	111.0	104
11	198.5	158.2	176.1	162.3	173.8	163
13	207.7	172.4	187.4	151.4	179.7	174
Seasonal average	134.5		126.0		130.2	123.7
Lake and Upstream seasonal average	169.8		156.8		163.3	157.0

At $p < 0.05$: LSD = 3.60 for sites, LSD = 8.74 for seasons, LSD = 5.08 for interactions between sites and seasons.

Sites: 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

While all the other sampling sites had physically cloudy/muddy waters throughout the sampling period; having a lot of suspended solids (Appendix I: Plate 8, pg 138), that of Port Victoria was surprisingly clear (Appendix I: Plate 9, pg 138). This was a clear indication of little sedimentation going on at Port Victoria sampling site. This was supported by the low turbidity of 2.0 NTU recorded at Port Victoria (Table 27). The area is surrounded by rocky hills with little agricultural potential and River Nzoia that feeds this part of the lake is at least three kilometres away from the site. Therefore minimal agricultural activities could be noticed that could reasonably contribute to the Zn load of the sampling site of Port Victoria and hence the low Zn concentration level recorded. Sio River

Mouth site showed low Zn concentration in sediment due to the sand mining activities while Sio River Upstream's low concentration could be attributed to the low organic matter content (Table 3) of this sediment and hence low capability of adsorption of Zn metal.

The average site concentrations of Fe in sediment ranged from 960.0-70,619.3 µg/g with a mean of 45,990 µg/g (Table 9). The mean of the upstream samples was higher than that of lake samples confirming that the rivers feeding Winam Gulf could be among the major anthropogenic sources of this metal in Lake Victoria (Table 9). The mean concentration of Fe recorded in this study is comparable to that recorded in a study of bed sediments of Lake Teganuma in Japan taken by Saeki *et al*. (1993). The range and mean recorded in this study signifies some accumulation of the metal Fe in Winam Gulf when compared to the ranges reported by Ochieng (1987) as well as Wandiga and Onyari (1989) in the studies of Lake Victoria sediments. The average Value of 44,520 µg/g Fe recorded in sediments of Winam Gulf of Lake Victoria (Table 9) is much higher compared to the mean of 8,700 µg/g Fe recorded at Lake Bentshoe by Coquery and Welbourn (1995). The high concentrations of 706.2 x 10^2 µg/g Fe, 685.6 x 10^2 µg/g Fe, 685.7 x 10^2 µg/g Fe and 651.4 x 10^2 µg/g Fe recorded at Car Wash area, Nyando River Mouth, Nyando River Upstream and Sondu-Miriu River Mouth respectively showed significant difference at $p < 0.05$. Similarly, the low concentrations of 9.6 x 10^2 µg/g Fe and 284.6 x 10^2 µg/g Fe recorded in Kisumu Dunga and Sio River Mouth, respectively, were significant at $p < 0.05$. These differences are mainly due to source inputs and the activities such as sand mining for Sio River Mouth.

Table 9. Seasonal variation of mean concentration of total Iron Fe (µg/g on dry weight basis) x 10^2 in sediment in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
3	780.2	646.5	734.8	663.3	706.2	732
4	385.4	352.0	377.2	329.0	360.9	354
5	299.5	290.2	306.9	241.9	284.6	283
6	10.4	9.5	9.6	8.9	9.6	9.6
8	456.8	372.0	423.3	421.0	418.3	417
10	737.1	635.0	713.4	657.0	685.6	698
12	684.6	645.0	663.2	613.0	651.4	642
Seasonal average	450.3		440.2		445.2	447.9
Upstream						
7	393.8	362.5	369.0	358.0	370.8	381
9	381.2	328.0	365.9	367.0	360.5	344
11	725.6	678.0	660.1	679.0	685.7	680
13	574.4	533.0	513.5	482.0	525.7	535
Seasonal average	497.1		474.3		485.7	485
Lake and Upstream seasonal average	467.3		452.6		459.9	461

At $p < 0.05$: LSD = 6.16 for sites, LSD = 14.97 for seasons, LSD = 8.71 for interactions between sites and seasons.

Sites: 3 - Kisumu Car Wash , 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth and 13 - Sondu-Miriu River Upstream

Sediment from Kisumu Car Wash was the most polluted with metal residues while that from Sio River Mouth was least polluted. This could generally be attributed to the car washing and sand mining activities respectively at the two sampling sites. The trend of these metal concentrations in sediment was Fe > Zn > Cu > Pb > Cd in all the sampling sites and this is in agreement with the trend observed in the sediments of San Diego Bay in California, USA, by Deheyn and Latz (2006), however, at the Car Wash, Dunga and Sondu-Miriu River Mouth the concentration of Pb > Cu and this nearly proves that the car washing business and petroleum spills highly contribute to sediment contamination with the trace metals at the deviating sites. A number of motorised boats that transport charcoal from Uganda and those carrying fish enter Kisumu Dunga landing bay. These activities help in dispersion of the metal Pb, which is least soluble in water, and hence the change in trend observed in these three sites. In a study carried out by Onyari and Wandiga (1989) in Winam Gulf of this lake, the ranges in concentrations of the metal figures were relatively lower than in the current study. This shows that there is some significant increase in metal concentration levels (Table 10) in the present study 18 years down the line.

Table 10. Comparison of some total metal concentration ranges/means in sediments of different lakes (National and international) in µg/g on dry weight basis.

	Lake					
Metal	Victoria[a]	Victoria[b]	Victoria[c]	Nasser[d]	Mariut[e]	Teganuma[f]
Cd	0.257-2.402 (1.3)	0.188-1.345	0.55-1.02	0.08	10.8	1.2
Pb	8.1-152.2 (39.7)	22.5-192.0	6.02-69.4	4.77	114.0	43.9
Cu	18.5-93.1 (37.7)	20.4-57.3	0.96-78.6	29.3	574.0	87.9
Zn	37.7- 441.6 (182.2)	171.1-334.3	2.54-265	357.5	229.0	413.2
Fe	960.0-70,619.3 (44,520)	3,775-45,800	1,180-52,900	32,828	31,900	44,600

ng-Not given, ()-mean concentrations.
[a]Present study 2006/7 Kenya, [b]Ochieng (1987) Kenya, [c]Onyari and Wandiga (1989) Kenya, [d]Soltan *et al.*(2005) Egypt, [e]Abdel-Moati and El-Sammak (1996) Egypt, [f]Saeki *et al.* (1993) Japan.

The metal concentrations in sediments generally increased downstream in the rivers covered in this study and this is basically in agreement with Saiz-Salinas *et al.* (1996). The increased concentration downstream is a clear indication of entry of agricultural, domestic and industrial metal residues into the rivers which end up accumulating in this direction.

Statistical analysis of the concentrations of all the heavy metals analysed in sediment showed positive correlations among themselves (Table 35). The correlations of Cu:Cd, Cu:Pb, Zn:Cd, Zn:Pb, Zn:Cu and Fe:Cd showed significant positive correlations at $p < 0.01$ while Pb:Cd, Fe:Cu and Fe:Zn showed significant positive correlations at $p < 0.05$. The good positive correlations of these metals indicate that they most likely have one or more common major sources.

4.2 Bioavailable distributions of the metals analysed in sediment

The bioavailable % averages of the metals in sediments of Winam Gulf and upstream river sites on dry weight basis are presented in Appendix

II: Table 37, pg 146 The bioavailable % of Cd in sediments ranged from 28.6-79.7 with a mean of 55.8 (Figure 3). The results are comparatively lower than those obtained by Jain (2004) in a study of bed sediments of River Yamuna in India and in a study of Naples City Port by Adamo *et al.* (2005) (Table 11). This could be due to difference in texture of the sediments and % organic matter content which lead to difference in adsorption capabilities.

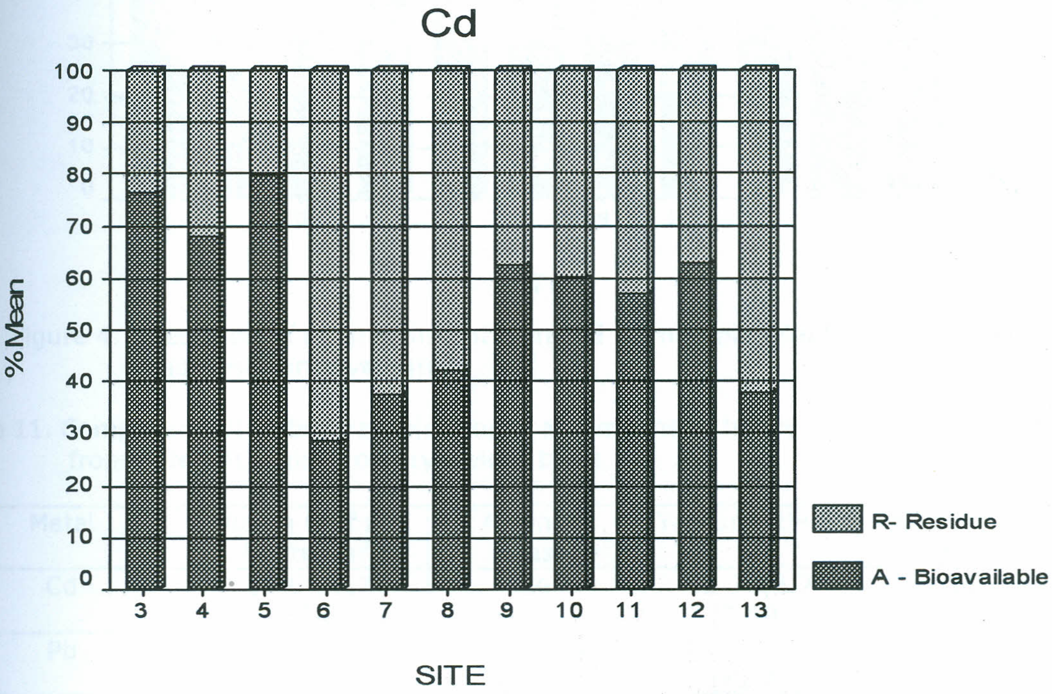

Figure 3. Speciation of Cd in sediment sampled from Winam Gulf of Lake Victoria and upstream river sites

The bioavailable % averages of Pb in sediment ranged from 46.6-94.6 with a mean of 66.9 (Figure 4). The results in this study are in agreement with those of Jain (2004) in which a % bioavailable mean of 62.4 was recorded, however, the figures are relatively higher compared to those of Rivaro *et al.* (2005) who reported a bioavailable range of 6.6-77.7% in Albania coastal sediments (Table 11). According to Rubio *et al.* (1991), metals with an anthropogenic origin are mainly associated to the 1st phase in sequential extraction procedure and this is the most labile and bioavailable fraction that is most important in determining the metal toxicity of a sediment. The high bioavailable % average obtained in the present study therefore signifies anthropogenic sources for the metal Pb.

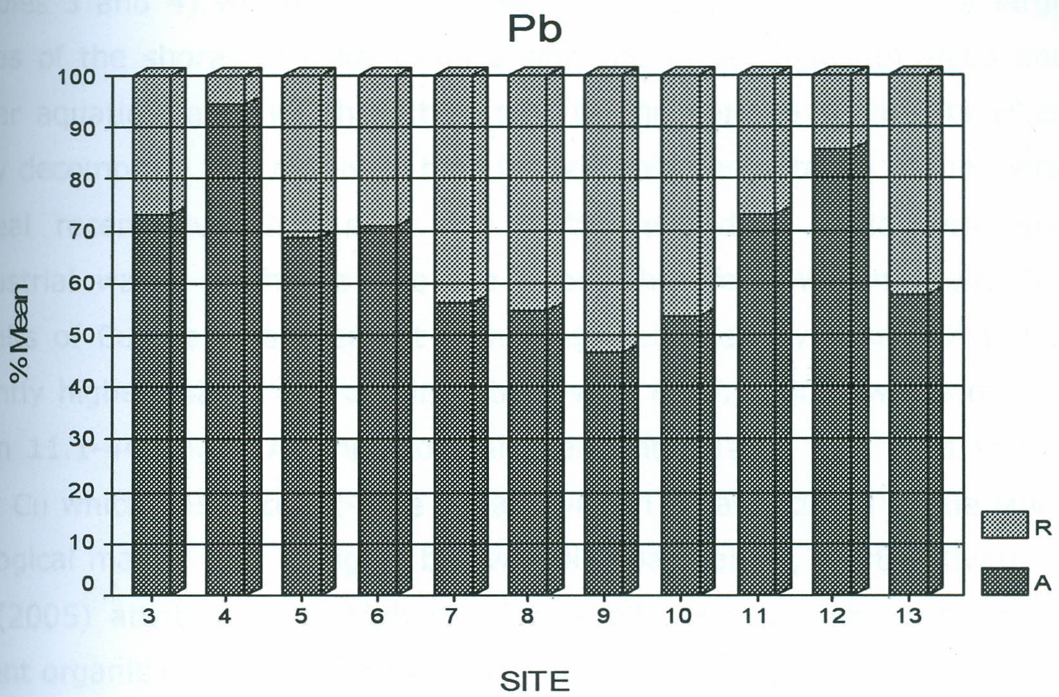

Figure 4. Speciation of Pb in sediment sampled from Winam Gulf of Lake Victoria and upstream river sites

Table 11. Comparison of % bioavailable ranges and means of heavy metals in sediments from different regions on dry weight basis.

Metal	Winam Gulf and Upstream[a]	Albanian coast[b]	Yamuna River[c]	Naples City Port[d]
Cd	28.6-79.7 (55.8)	ng	62.7-83.7 (77.9)	91
Pb	46.6-94.6 (66.9)	6.7-77.7 (34.1)	56.5-71.7 (62.4)	19
Cu	26.3-80.7 (57.1)	11.1-44.4 (33.4)	29.2-72.9 (64.8)	62
Zn	41.5-93.8 (73.3)	ng	37.5-66.7 (56.0)	69
Fe	45.7-84.3 (65.6)	ng	ng	ng
Mean % organic matter	7.58	ng	2.3	ng

ng - Not given, () - Average % of range.
[a]Present study 2006/7 Kenya, [b]Rivaro *et al*. [2005] Albania, [c]Jain [2004] India, [d]Adamo *et al*. (2005).

Copper in sediment showed a bioavailable % concentration range of 26.3-80.7 with a mean of 57.1 (Figure 5). The high values recorded in the Winam Gulf and upstream river sites in this study again points to the anthropogenic nature of this metal load in the sediments and therefore the metal is susceptible to higher bioavailability %. This is also supported by the fact that the gulf sediments showed high % of organic matter

(Tables 3 and 4) which is no surprise considering the covering of large areas of the shores of Lake Victoria with the Water hyacinth weed and other aquatic plants which settle down to the surface sediments when they decompose. The relatively high bioavailable percentages of the metal reveal recent river inputs of this metal related to agricultural and industrial waste discharge into the rivers that feed Winam Gulf. The results of Cu are in agreement with those recorded by Jain (2004) but slightly higher than those obtained by Rivaro *et al.* (2005) which ranged from 11.1-44.4% in Albania Coastal sediments (Table 11). It is known that Cu which has nutrient-type behaviour can be associated to the labile biological matter that is highly bioavailable (Baffi *et al.*, 1998). Rivaro *et al.* (2005) attributed the high % of bioavailable Cu to the richness of recent organic matter in Drin Bay sediments.

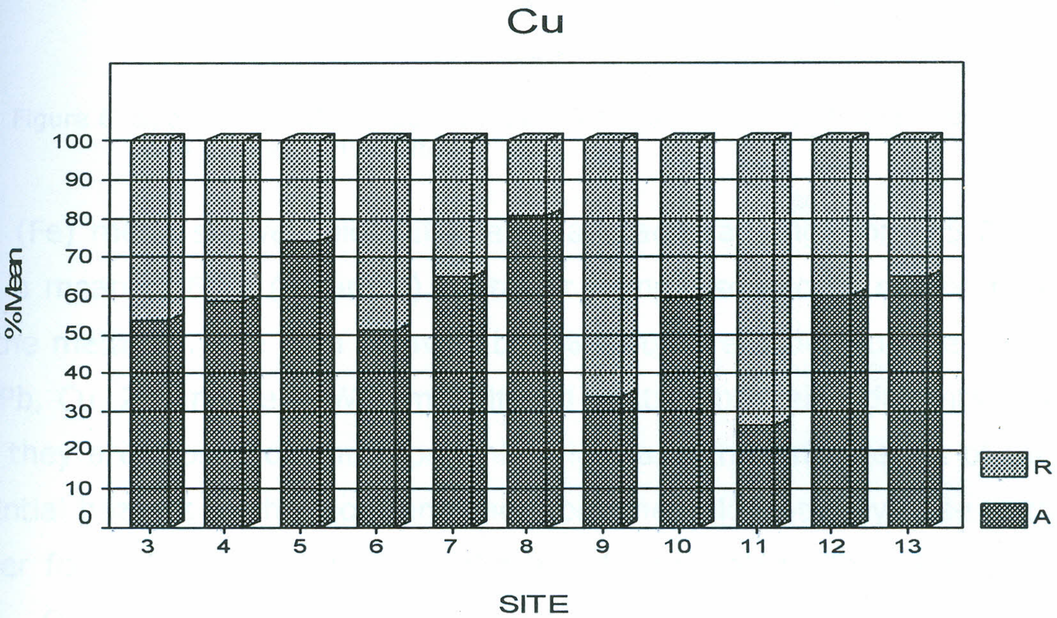

Figure 5. Speciation of Cu in sediment sampled from Winam Gulf of Lake Victoria and upstream river sites

The average bioavailable % of Zn in sediment ranged from 41.5-93.8 with a mean of 73.3 (Figure 6). The high bioavailable values recorded were attributed to the anthropogenic sources of Zn in Winam Gulf which render the metal to be highly bioavalable. The results in this study are slightly higher than those recorded by Jain (2004) in a study of bed sediments of River Yamuna, India (Table 11). The difference in the two studies could be due to the lower % organic matter content of the bed sediments of River Yamuna, India compared to that of Winam Gulf as noted in Table 4.

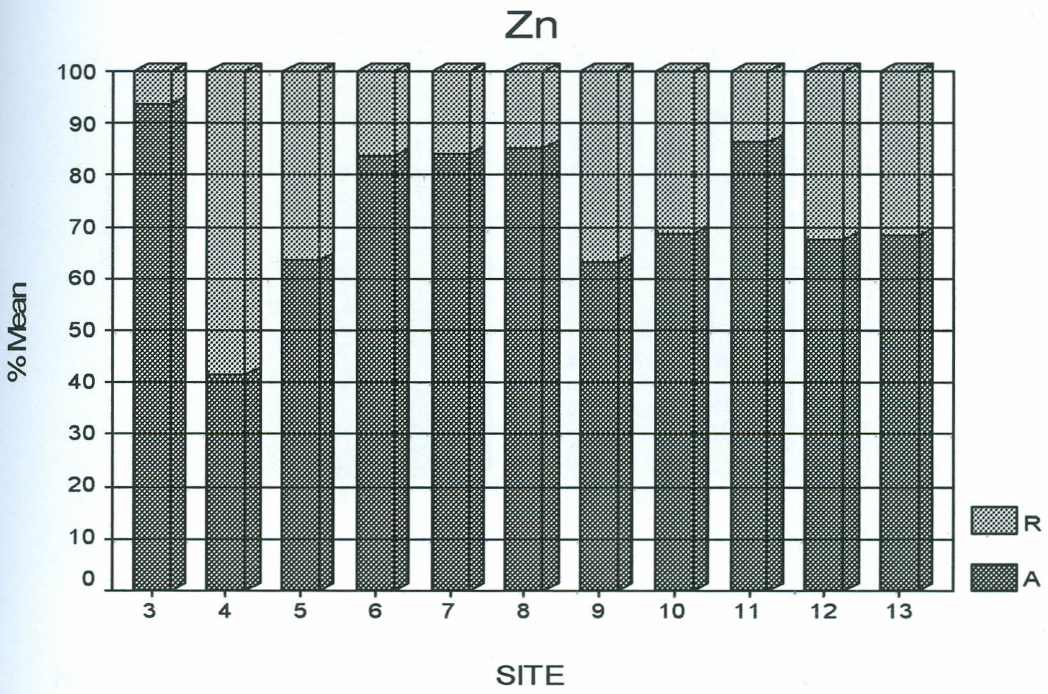

Figure 6. Speciation of Zn in sediment sampled from Winam Gulf of Lake Victoria and upstream river sites

Iron (Fe) metal showed bioavailable % average ranging from 45.7-84.3 with a mean of 65.6 (Figure 7). Data for comparison could not be found for the metal Fe. The high bioavailable % values recorded for the metals Cd, Pb, Cu, Zn and Fe in Winam Gulf and upstream river sediments show that they are mostly of anthropogenic origin and thus suggestive of their potential hazards to the biota and therefore the risk that they pose to the higher food chain dependants of the aquatic organisms for survival like man. Ochieng (1987) observed that generally most of the total exchangeable metal cations in river sediments ranged from 2-20% of the total trace metal contents of the sediments, while those of dilute Kenyan lakes' sediments ranged from 1-30% of the total. The exchangeable % values of Ochieng (1987) do not reflect all the fraction of the bioavailable metal in sediment but rather some proportion of it and hence the low values in his study.

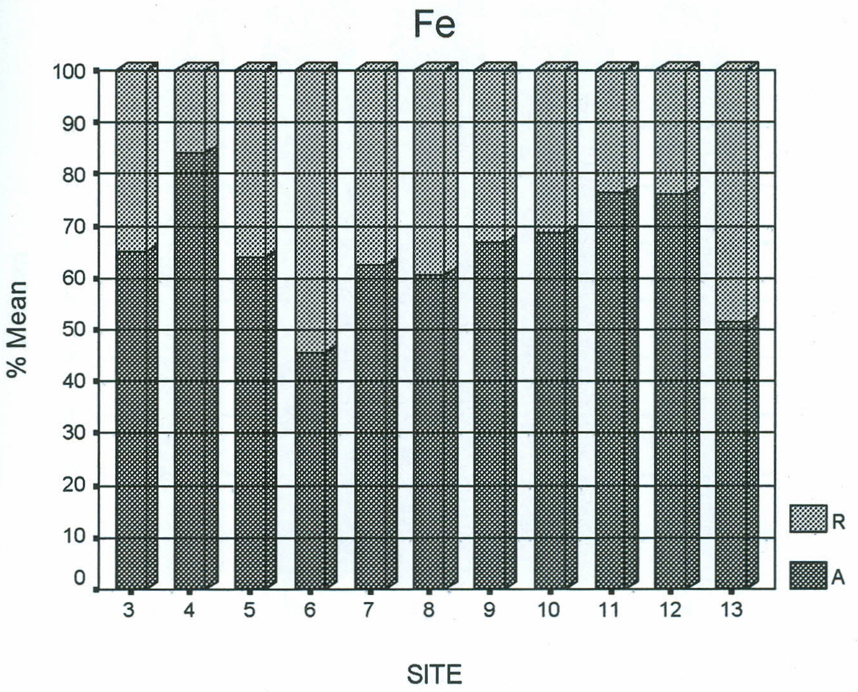

Figure 7. Speciation of Fe in sediment sampled from Winam Gulf of Lake Victoria and upstream river sites

Zinc was found to be the most bioavailable of the analysed metals while Cu was the least (Figure 8). The trend of bioavailability for the five metals in Winam Gulf sediments was Zn > Pb > Fe > Cd > Cu. The difference in bioavailability trend recorded could probably be attributed to the ligand binding strength of each metal.

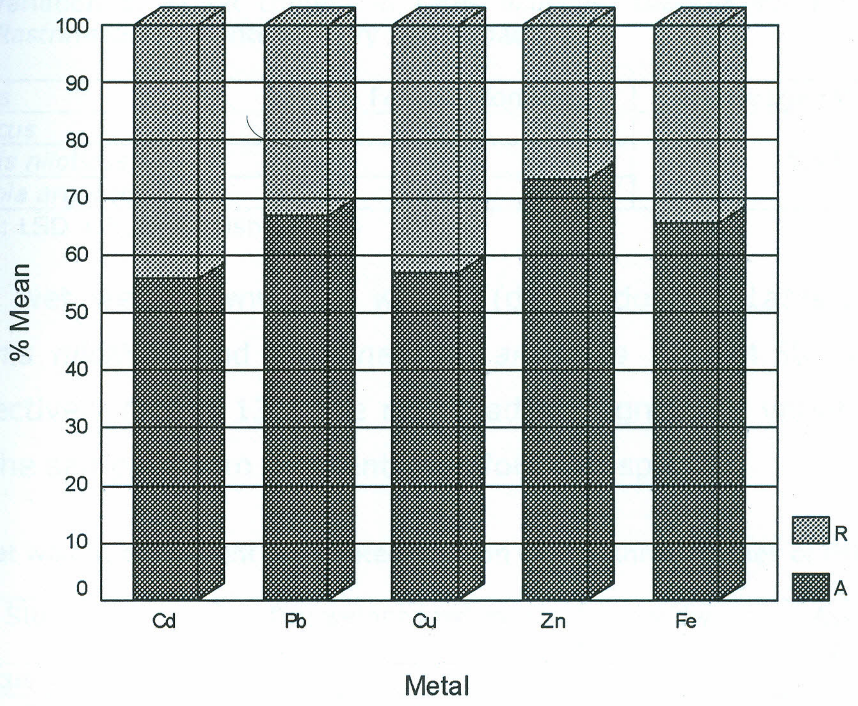

Figure 8. Comparison of % means of bioavailable metal concentrations in sediments

4.3 Total metal concentration levels in three species of fish: *Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea*

The three fish species were analysed for percentage fat content on dry weight basis and the data collected is presented in Table 12. *Rastrineobola argentea* recorded significantly high % fat content of 11.44 at $p < 0.05$ compared to the other two species while there was little variation between that of *Lates niloticus* and *Oreochromis niloticus* which recorded 2.12 and 2.77 respectively. The high % fat content in *Rastrineobola argentea* was attributed to the fact that the fish was analysed whole; with all its internal organs intact while in the other two species, the internal organs were dissected out. The internal organs of animals are associated with lots of fat content compared to the rest of the body.

Table 12. Variation of % fat content in *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* on dry weight basis

Fish Species	% Fat (oil) content	% Average fat content
Lates niloticus	2.12	5.44
Oreochromis niloticus	2.77	
Rastrineobola argentea	11.44	

A t $p < 0.05$: LSD = 2.24 for fish species

The mean wet weight (ww)/Dry weight (dw) ratios for *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* were 4.58, 4.70 and 5.05 respectively (Table 13). The ratio had no significant variation ($p < 0.05$) for the samples from different sites for each species.

Table 13. Wet weight/dry weight ratio determination for the three species of fish

Site	Dry weight (dw) in g	ww/dw	Average ww/dw
Lates niloticus			
1	0.2107	4.745	4.58
4	0.2342	4.270	
5	0.2198	4.550	
14	0.2103	4.755	
Oreochromis niloticus			
1	0.2134	4.687	4.70
4	0.2144	4.664	
5	0.2112	4.735	
14	0.2121	4.714	
Rastrineobola argentea			
1	0.2100	4.762	5.05
4	0.1984	5.041	
5	0.1870	5.347	
14	0.1976	5.060	

ww - Wet weight = 1 g, dw – Dry weight.

Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

The variation in the ratios was attributed to difference in % fat content among the three fish species (Table 12). Since fat has lower density compared to muscle, decrease in weight during drying is likely to follow the trend *Rastrineobola argentea* > *Oreochromis niloticus* > *Lates niloticus.* The ww/dw ratio was necessary in case there was convenience of expressing the concentration of the metals based on fresh weight. The ww/dw ratios obtained here of 4.58, 4.70 and 5.05 compare well with a ratio of 4.5 which had been quoted by Darmno and Denton (1990) and were therefore applied in the this study to calculate the concentrations of the trace metals in the three fish species on wet weight basis (Table 20).

The AAS analysis gave mean % recovery values for the extraction of the spiked fish samples for Cd, Pb, Cu, Zn and Fe as 88, 103, 93 90 and 91 respectively. The average site concentrations of Cd, Pb, Cu, Zn and Fe expressed in µg/g on dry weight basis are presented in Tables 14 to 18. Analysis of variance (ANOVA) recorded significant variation ($p < 0.05$) in the average site concentrations of all the five metals analysed for all the sampling sites for the three fish species, sampling sites, seasons and interactions of the three factors (Appendix III, pg 158-167). This could be attributed to the complex mobility of the fish species and their different feeding habits in the aquatic environment. The Cd concentrations recorded on dry weight basis for the three fish species of 0.21 µg/g, 0.21 µg/g and 0.26 µg/g for *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea,* respectively, are in agreement with the Cd concentration levels recorded in Lake Nasser in Egypt in a study taken by Soltan *et al*. (2005) for *Tilapia galilea* and *Tilapia nilotica*. The concentration levels of Cd also compare well with that recorded in *Oreochomis niloticus* in Mwanza Gulf of Lake Victoria in a study taken by Kishe and Machiwa (2001) (Table 19). On wet weight basis the Cd concentration levels of 4.59×10^{-2} µg/g, 4.47×10^{-2} µg/g and 5.15×10^{-2} µg/g based on the wet weight/dry weight ratios for *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea*, respectively, are within the ranges recorded in studies taken by Wandiga and Onyari (1987) in Lake Victoria, Kenya (Table 20). The concentrations are also in good agreement with Greichus *et al*. (1978a) in a study of Lake Nakuru in Kenya and with another study of Nozha Hydrodome in Egypt taken by Saad (1987) of fish samples from River Nile (Table 20).

Table 14. Seasonal variation of mean concentration of total Cadmium Cd (µg/g on dry weight basis) in fish in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lates niloticus						
1	0.202	0.160	0.193	0.151	0.176	0.133
4	0.244	0.196	0.232	0.185	0.214	0.157
5	0.346	0.209	0.296	0.128	0.245	0.159
14	0.241	0.184	0.228	0.179	0.208	0.158
Seasonal average	0.223		0.199		0.211	0.152
Oreochromis niloticus						
1	0.254	0.164	0.199	0.155	0.193	na
4	0.447	0.210	0.123	0.198	0.245	na
5	0.317	0.178	0.204	0.154	0.213	na
14	0.228	0.184	0.209	0.185	0.201	na
Seasonal average	0.248		0.179		0.213	na
Rastrineobola argentea						
1	0.247	0.274	0.347	0.168	0.259	0.161
4	0.263	0.224	0.116	0.329	0.233	0.167
5	0.550	0.246	0.192	0.210	0.299	0.167
14	0.358	0.182	0.276	0.208	0.256	0.168
Seasonal average	0.294		0.231		0.262	0.166
Seasonal average (LN, ON, AG)	0.255		0.203		0.229	nc

LN - *Lates niloticus,* ON - *Oreochromis niloticus,* AG - *Rastrineobola argentea,* na – Not analysed, nc – Not calculated.

At $p < 0.05$: LSD = 0.021 for fish species, LSD = 0.018 for sites, LSD = 0.023 for interactions between fish species and sites, LSD = 0.050 for seasons, LSD = 0.025 for interactions between sites and seasons, LSD = 0.034 for interactions between fish species, sites and seasons.

Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

The average Pb concentration levels on dry weight basis of 0.87 µg/g Pb, 0.61 µg/g Pb and 1.2 µg/g Pb were recorded for *Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea,* respectively (Table 15). The Pb concentration levels recorded in the two *niloticus* species compare well with that recorded in *Tilapia nilotica* in a study of Lake Nasser in Egypt by Soltan *et al.* (2005) (Table 19). The fish species showed concentrations of 1.90 × 10^{-1} µg/g Pb, 1.29 × 10^{-1} µg/g Pb and 2.43 × 10^{-1} µg/g Pb on wet weight basis respectively (Table 20). These concentration levels are comparable to that of 1.70 × 10^{-1} µg/g Pb reported in a study of Lake Nakuru by Greichus *et al.* (1978a) while they fall much below the range of 1.22-6.48 µg/g Pb reported in a study of marine finfish from Indian Ocean by Wandiga and Onyari (1987) in Kenya and that of 4.0×10^{-1}-1.100 µg/g Pb in fish from Lake Victoria. The concentrations of this metal in the three species are within the permissible levels of FAO (1983), European Communities (2001) and Nauen (1983).

Table 15. Seasonal variation of mean concentration of total Lead Pb (µg/g on dry weight basis) in fish in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lates niloticus						
1	0.961	0.740	0.703	1.096	0.875	0.562
4	0.711	0.698	0.906	0.823	0.785	0.461
5	1.270	1.040	1.309	1.444	1.266	0.759
14	0.536	0.404	0.644	0.590	0.544	0.349
Seasonal average	0.796		0.940		0.867	0.533
Oreochromis niloticus						
1	0.913	0.607	0.964	0.882	0.842	na
4	ND	ND	ND	ND	ND	na
5	0.798	0.575	0.756	0.918	0.762	na
14	0.655	0.861	0.922	0.864	0.826	na
Seasonal average	0.553		0.664		0.608	na
Rastrineobola argentea						
1	3.370	1.340	2.466	2.592	2.442	1.560
4	0.780	0.705	0.569	0.914	0.742	0.519
5	0.702	0.684	0.770	0.814	0.993	0.454
14	1.281	0.360	0.342	0.936	0.730	0.850
Seasonal average	1.278		1.176		1.227	0.846
Seasonal average (LN, ON, AG)	0.876		0.927		0.901	nc

na – Not analysed, nc – not calculated.
At $p < 0.05$: LSD = 0.153 for fish species, LSD = 0.131 for sites, LSD = 0.175 for interactions between fish species and sites, LSD = 0.370 for seasons.
Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

The site concentrations of Cu in the three fish species on dry weight basis are recorded in Table 16. *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* recorded average concentration levels of 3.4 µg/g Cu, 2.7 µg/g Cu and 6.5 µg/g Cu, respectively. These results are much higher than the range of 0.2-0.5 µg/g Cu and a mean concentration of 1.9 µg/g Cu recorded in studies of fish from Lake Victoria taken by Ochieng (1987) and Kishe and Machiwa (2001), respectively, which suggest some substantial bioaccumulation of the metal in the three species especially *Rastrineobola argentea*.

Table 16. Seasonal variation of mean concentration of total Copper Cu (µg/g on dry weight basis) in fish in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lates niloticus						
1	3.420	2.480	2.882	3.258	3.01	2.79
4	3.852	5.240	2.277	1.982	3.338	3.16
5	5.808	2.550	7.040	4.160	4.89	4.72
14	3.024	2.097	2.574	2.260	2.489	2.41
Seasonal average	3.559		3.304		3.432	3.27
Oreochromis niloticus						
1	2.141	2.200	2.948	2.137	2.356	na
4	3.216	1.398	3.028	2.470	2.528	na
5	2.932	2.850	2.618	2.781	2.795	na
14	3.505	3.610	2.848	2.490	3.113	na
Seasonal average	2.732		2.665		2.698	na
Rastrineobola argentea						
1	9.720	7.750	7.984	6.600	8.013	7.87
4	7.080	3.820	5.292	6.640	5.708	5.83
5	8.412	5.920	6.743	6.375	6.863	6.89
14	7.968	4.860	5.027	4.010	5.466	6.58
Seasonal average	6.942		6.084		6.513	6.79
Seasonal average (LN, ON, AG)	4.411		4.018		4.214	nc

na - Not analysed, nc - Not calculated.

At $p < 0.05$: LSD = 0.533 for fish species, LSD = 0.455 for sites, LSD = 0.606 for interactions between fish species and sites, LSD = 1.283 for seasons, LSD = 0.753 for interactions between fish species and seasons, LSD = 0.643 at for interactions between sites and seasons, LSD = 0.857 at interactions between fish species, sites and seasons.

Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

The results of the concentrations of Cu in the two *niloticus* species are relatively lower while that of *Rastrineobola argentea* compares well with the concentrations of Cu recorded in *Tilapia galilea* and *Tilapia nilotica* in a study of Lake Nasser in Egypt by Soltan *et al*. (2005). On wet weight basis, the Cu concentrations were 7.49×10^{-1} µg/g, 5.74×10^{-1} µg/g and 1.287 µg/g for the three species respectively (Table 20). The results are in good agreement with the range recorded in a study carried out in Kenya while they are above the range recorded in a study of Lake Victoria by Wandiga and Onyari (1987) which suggests substantial bioaccumulation of Cu metal in the Lake Victoria fish and water. The concentrations of the *niloticus* species are comparable to the Cu concentration level recorded in a study of Niger Delta by Kakulu *et al.* (1987). The concentrations are much below the permissible concentration limits of Cu on fresh weight basis by European Communities (2001), FAO (1983) and Nauen (1983) (Table 20).

The average Zn site concentrations for *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* ranged from 31.0-40.0 µg/g, 32.2-38.0 µg/g and 226.4-317.3 µg/g with averages of 36.4 µg/g, 35.9 µg/g and 250.1 µg/g on dry weight basis for the three species, respectively (Table 17). The average concentration of *Rastrineobola argentea* is much higher than those of the *niloticus* species but it is in agreement with the concentration of 273.1 µg/g Zn in *Tilapia nilotica* recorded by Soltan *et al.* (2005) while that of *Oreochromis niloticus* which is of the same family is much below. This is a probable positive indication on how safe the *Lates niloticus* and *Oreochromis niloticus* species are in terms of food in comparison to finfish produced in some areas of Africa (Table 19).

Table 17. Seasonal variation of mean concentration of total Zinc Zn (µg/g on dry weight basis) in fish in the studied area during 2006-2007.

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lates niloticus						
1	48.5	36.2	40.8	34.6	40.0	38.7
4	42.1	34.2	38.0	30.6	36.2	34.6
5	44.7	34.6	39.7	33.7	38.2	36.8
14	37.7	28.7	32.0	25.7	31.0	30.1
Seasonal average	38.3		34.4		36.4	35.1
Oreochromis niloticus						
1	37.7	30.6	32.1	28.6	32.2	na
4	45.8	39.2	29.8	35.5	37.6	na
5	40.8	29.7	37.2	32.4	35.8	na
14	50.9	43.1	33.8	26.2	38.0	na
Seasonal average	39.4		32.5		35.9	na
Rastrineobola argentea						
1	286.8	190.6	197.8	230.6	226.4	237.0
4	453.6	365.0	230.5	220.0	317.3	372.0
5	296.4	204.8	218.9	195.2	228.8	241.0
14	284.4	194.3	243.3	188.5	227.6	223.0
Seasonal average	284.5		215.6		250.1	268.0
Seasonal average (LN, ON, AG)	120.7		94.2		107.5	nc

na - Not analysed, nc - Not calculated.

At $p < 0.05$: LSD = 6.747 for fish species, LSD = 5.761 for sites, LSD = 7.674 for interactions between fish species and sites, LSD = 16.267 for seasons, LSD = 9.541 for interactions between species and seasons, LSD = 8.147 for interactions between sites and seasons, LSD = 10.852 interactions between fish, sites and seasons.

Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

The results of the two *niloticus* species compare well with a mean concentration of 29.8 µg/g Zn recorded in a study of Mwanza Gulf in Tanzania by Kishe and Machiwa (2001). The average concentrations of the three species on wet weight basis were 7.948 µg/g, 7.638 µg/g and 49.525 µg/g respectively (Table 20). The results for the two *niloticus* species are in good agreement with the mean and range of concentrations of Zn recorded in the studies taken by Wandiga and Onyari (1987) and El-Nabawi *et al.* (1987). The mean result of *Rastrineobola argentea* is comparatively higher than the upper limit recorded by Wandiga and Onyari (1987) in their study of Lake Victoria. The concentration of 49.525

µg/g Zn for *Rastrineobola argentea* is above the limit set by Median International Standards (MIS) and nearly goes beyond the upper limit of 50 µg/g Zn set by the European communities (2001) (Table 20). In fact considering the concentration for the *Rastrineobola argentea* species during the heavy rain season of May (Trip A) the concentration is above the 50 µg/g Zn limit.

The average Fe site concentrations for *Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea* ranged from 34.4-65.5 µg/g, 43.4-54.1 µg/g and 93.1-207.7 µg/g with averages of 45.7 µg/g, 48.0 µg/g and 139.1 µg/g on dry weight basis for the three species, respectively (Table 18). Iron concentration levels in the three species are much higher than those recorded in a study of Winam Gulf by Ochieng (1987) (Table 19) and this implies a significant bioaccumulation of the metal Fe by fish. While the mean Fe concentration level is high in *Rastrineobola argentea* species, the results for the two *niloticus* species are relatively lower than the concentration levels of 69.9 µg/g Fe and 89.8 µg/g Fe recorded in *Tilapia galilea* and *Tilapia nilotica,* respectively, in a study of Lake Nasser by Soltan *et al.* (2005). The average Fe concentration levels in the three (*Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea*) species of fish on wet weight basis were 9.978 µg/g, 10.213 µg/g and 27.545 µg/g, respectively. The results of the fish metal concentrations are comparatively higher than the concentration range recorded for fish in a study of Lake Victoria by Wandiga and Onyari (1987) and also in a study of the Niger Delta by Kakulu *et al.* (1987). Although the mean Fe concentration recorded in *Rastrineobola argentea* is much greater, the Fe concentrations in the two *niloticus* species compare well with Fe concentrations of 11.200 µg/g and 12.600 µg/g recorded in studies in Egypt of Lakes Mariut and Nozha Hydrodome by Saad *et al.* (1981a) and Saad (1987), respectively, while *Rastrineobola argentea* in the present study shows more than double these concentrations. Although recent Fe concentrations data for comparison with these results are scarce, the metal concentrations in this study portray some substantial bioaccumulation in the fish tissues of Winam Gulf of Lake Victoria.

Table 18. Seasonal variation of mean concentration of total Iron Fe (μg/g on dry weight basis) in fish in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lates niloticus						
1	80.3	66.2	59.4	56.1	65.5	66.2
4	39.7	35.0	34.6	28.2	34.4	32.4
5	54.1	47.5	34.5	45.8	44.7	44.5
14	48.5	39.9	32.8	31.1	38.1	37.5
Seasonal average	51.4		39.95		45.7	45.2
Oreochromis niloticus						
1	57.2	46.5	45.5	41.4	47.7	na
4	55.0	51.6	40.7	37.6	46.7	na
5	65.4	53.6	46.8	50.6	54.1	na
14	50.6	44.5	37.7	40.7	43.4	na
Seasonal average	53.1		42.9		48.0	na
Rastrineobola argentea						
1	130.6	101.8	76.8	63.2	93.1	127.0
4	127.0	147.2	55.8	150.2	120.0	122.0
5	205.0	211.2	212.9	201.6	207.7	207.0
14	180.3	132.6	113.7	116.3	135.7	173.0
Seasonal average	154.5		123.8		139.1	157.3
Seasonal average (LN, ON, AG)	86.3		68.9		77.6	nc

na – Not analysed, nc – Not calculated.

At $p < 0.05$: LSD = 4.650 for fish species, LSD = 3.971 for sites, LSD = 5.289 for fish species and sites, LSD = 11.211 for seasons, LSD = 6.576 for interactions between fish species and seasons, LSD = 5.616 for interactions between sites and seasons, LSD = 7.480 for interactions between fish, sites and seasons.

Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

Table 19. Comparison of total metal concentration levels (µg/g on dry weight basis) in finfish as consumed by man

		Metal				
	species	Cd	Pb	Cu	Zn	Fe
Winam Gulf[a]	*Lates niloticus*	0.21	0.87	3.4	36.4	45.7
	Oreochromis niloticus	0.21	0.81	2.7	35.9	48.0
	Rastrineobola argentea	0.26	1.2	6.5	250.1	139.1
Winam Gulf[b]	*Lates niloticus*	ng	ng	0.2-0.5	ng	1.0-6.4
Lake Nasser[c]	*Tilapia galilea*	0.25	0.69	5.7	139.1	69.9
	Tilapia nilotica	0.25	0.48	5.7	273.1	89.8
Mwanza Gulf[d]	*Oreochromis niloticus*	0.3	ng	1.9	29.8	ng
Manchar Lake[e]	*Oreochromis mossambicus*	1.39	2.4	2.3	188.9	1517
Manly Lagoon Catchment[f]	*Gambusiah holbrooki*	<0.05	<0.05	2-20	50-400	50-200

ng - Not given.
[a]Present study 2006/7 Kenya, [b]Ochieng (1987) Kenya, [c]Soltan *et al*. (2005) Egypt, [d]Kishe and Machiwa (2001) Tanzania, [e]Arain *et al*. (2007) Pakistan, [f]Van *et al*. (2002) Australia.

Table 20. Comparison of the levels of the metals in the three species of fish in this study, other past studies and some of the internationally allowed limits on finfish in µg/g × 10^{-3} on fresh weight basis.

		Metal				
	species	Cd	Pb	Cu	Zn	Fe
Winam Gulf[a]	*Lates niloticus*	45.9	190	749	7,948	9,978
	Oreochromis niloticus	44.7	129	574	7,638	10,213
	Rastrineobola argentea	51.5	243	1,287	49,525	27,545
Kenya[b]	ng	40-380	1,220-6,480	360-2,040	4,670-40,800	ng
Lake Victoria[b]	ng	40-120	400-1,100	150-530	2210-7,020	530-4650
Lake Nakuru[c]	ng	50	170	2,000	22,000	ng
Lakes Idku, Mariut[d]	ng	4	670	1,770	7,400	ng
Niger Delta[e]	ng	30	480	700	4,800	5400
MIS[f]	ng	300	2,000	20,000	45,000	ng
EC[g]	ng	100	400	10,000	50,000	ng
FAO[h]	ng	ng	500	30,000	ng	ng

ng - Not given.
[a]Present study 2006/7 Kenya, [b]Wandiga and Onyari (1987) Kenya, [c]Greichus *et al*. (1978a) Kenya, [d]El-Nabawi *et al*. (1987) Egypt, [e]Kakulu *et al*. (1987a) Nigeria, [f]Nauen (1983) MIS permissible limits, [g]European Communities (2001) permissible limits, [h]FAO (1983) permissible limits.

Iron recorded the highest concentrations in all the three species of fish except that in *Rastrineobola argentea* Zn was found to be the most abundant while cadmium had the lowest concentrations in the three species. The trend in the metal concentrations noted was Fe > Zn > Cu > Pb > Cd for *Lates niloticus* and *Oreochromis niloticus*. A comparable trend of Fe > Zn > Cu > Pb had been observed by Mzimela *et al.* (2003) in whole fish sampled in Mhlathuze Estuary in South Africa. The trend in the current study could be attributed to the fact that Fe is the most abundant in the lake water and sediment while cadmium is the least of the five metals analysed (Table 35). Therefore, Fe has a chance of being bioaccumulated most by the fish.

The mean of concentrations of the metals in *Rastrineobola argentea* were much higher than the corresponding concentrations observed in the two *niloticus* species (Tables 14-18). This could be attributed to the fact that *Rastrineobola argentea* was analysed whole without removing the internal organs while for *Lates niloticus* and *Oreochromis niloticus,* the internal organs were removed before analysis in order to determine the potential exposure of human to the metals. This means that some of the organs in *Rastrineobola argentea* could be accumulating the metals especially Cu, Zn and Fe to much higher levels leading to overall higher mean metal concentrations in *Rastrineobola argentea* than in the other two species. This is supported by Soltan.*et al.* (2005), Kishe and Machiwa (2001) who found that gills, liver, intestines and stomach are among the most biaccumulator organs in fish. The mean concentrations of Fe in *Lates niloticus* and *Oreochromis niloticus* were more than that of Zn, however, this trend was reversed in *Rastrineobola argentea*. This implies that some organ(s) in *Rastrineobola argentea* could be accumulating Zn to higher levels than Fe and hence reversing the trend observed in the other two species. Therefore, the abundance trend of these metals observed in the current study *Rastrineobola argentea* was Zn > Fe > Cu > Pb > Cd. This probably explains why the mean concentrations of Zn and Fe for *Rastrineobola argentea* were much higher than those recorded in the past studies in East Africa and Northern Africa for other finfish consumed after removal of their internal organs (Biney *et al.,* 1994). Topping (1973) similarly found that the metal zinc was the most abundant compared with the other heavy metals copper, cadmium and lead when four species of fish namely herring (*Clupea harengus*), cod (*Gadus morrhua*), plaice (*Pleuronectes platessa*) and haddock (*Melanogrammus aeglefinus*) sampled from the Scottish waters were studied. Even in this study, Zn concentration in *Rastrineobola argentea* was highest compared with Fe, Cu, Pb and Cd while in the other two species (*niloticus*) Fe concentration was higher than those of Zn, Cu, Pb and Cd in that order.

Pearson correlation analysis was done on the trace metal concentrations on the three species of fish and their correlation matrices are presented in Table 34. There was a significant positive correlation between Cu and Pb in *Lates niloticus* ($p < 0.05$). There was also a very positive correlation ($r = 0.921$, $p < 0.05$) between Cu and Pb in *Rastrineobola argentea* while the correlation between Cu and Pb in *Oreochromis niloticus* had a low negative value. There was a highly negative correlation between Pb and Cd in *Oreochromis niloticus* and a very small correlation between Pb and Cd in *Rastrineobola argentea* while these two metals had a relatively positive correlation in *Lates niloticus*. These differences in correlations were attributed to difference in feeding habits of the three species of fish. There was a reasonably negative relationship between Fe and Zn in *Rastrineobola argentea.* This signifies that the element Fe probably had different bioaccumulation factor values from Zn in the two major internal organs of fish namely the liver and the gills and hence the difference in the concentration of the two metals in the three fish species. This probably means that Zn has a higher factor in gills while Fe has a higher factor in liver. However, this is something that can be investigated.

The concentrations of heavy metals in *Oreochromis niloticus* collected from Lake Victoria (Mwanza Gulf) showed that fish organ and tissues (gills, muscle and scales) analysed for cadmium, copper and zinc content had highest heavy metal concentrations in gills and scales and the lowest concentrations in muscles (Kishe and Machiwa, 2001; Ochieng, 1987). The livers in fish have been considered suitable as bioindicator organs for contaminants. This is possibly attributed to the tendency of the liver to accumulate pollutants of various kinds at higher levels from their environment (Galindo *et al.*, 1986).

The three fish species analysed in this study had concentrations of Cd, Pb, Cu and Zn that conform to the international residue limit requirements on wet weight basis except for the element Zn in *Rastrineobola argentea*. *Rastrineobola argentea* had an average concentration of 49,525 µg/Kg of Zn, which is beyond or nearly going overboard the maximum allowed concentration on wet weight basis (Table 20) (Nauen, 1983; European Communities, 2001).

It is clear from the present study that *Rastrineobola argentea* is a significant source of heavy metals to humans compared to *Lates niloticus* and *Oreochromis niloticus* and probably other finfish, which are consumed after removing their internal organs just like these two finfish species. Since gills are among the best heavy metal bioaccumulating organs, consuming the *Rastrineobola argentea* after head detaching could probably alleviate the high zinc concentrations in this fish species.

4.4 Speciation of the metals in the three species of fish

The average bioavailable percentages of the metals for the three species sampled from different sites are presented in Table 21. Tables representing bioavailale concentrations are presented in Appendix II: pg 143-147).

Table 21. Percentage means of bioavailable and residual metal concentrations in *Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea* on dry weight basis.

Site	Cd A %	Cd R %	Pb A %	Pb R %	Cu A %	Cu R %	Zn A %	Zn R %	Fe A %	Fe R %
Lates niloticus										
1	61.7	38.3	32.3	67.7	70.6	29.4	75.1	24.9	11.9	88.1
4	78.2	21.8	20.4	79.6	12.5	87.5	73.5	26.5	32.7	67.3
5	72.8	27.2	28.4	71.6	45.1	54.9	86.9	13.1	31.3	68.7
14	55.6	44.4	28.7	71.3	57.1	42.9	81.9	18.1	43.2	56.8
Average	67.1	32.9	27.5	72.5	46.3	53.7	79.4	20.6	29.8	70.2
Oreochromis niloticus										
1	64.9	35.1	64.8	35.2	36.1	63.9	61.6	38.4	43.2	56.8
4	61.4	38.6	ND	ND	36.6	63.4	77.1	22.9	37.7	62.3
5	73.0	27.0	43.2	56.8	57.4	42.6	63.7	36.3	20.6	79.4
14	67.3	32.7	52.8	47.2	36.7	63.3	81.7	18.3	47.6	52.4
Average	66.7	33.3	40.9	59.1	41.7	58.3	71.0	29.0	37.3	62.7
Rastrineobola argentea										
1	60.4	39.6	51.5	48.5	59.6	40.4	85.9	14.1	62.2	37.8
4	58.0	42.0	50.2	49.8	55.5	44.5	70.3	29.7	21.9	78.1
5	64.2	35.8	44.8	55.2	56.6	43.4	69.6	30.4	24.7	75.3
14	53.8	46.2	43.2	56.8	91.2	8.8	78.8	21.2	69.3	30.7
Average	59.1	40.9	47.4	52.6	65.7	34.3	76.2	23.8	44.5	55.5
Mean(LN, ON, AG)	64.3	35.7	38.6	61.3	51.2	48.8	75.5	24.5	37.2	62.8

A - Bioavailable percentage , R - Residual percentage, LN - *Lates niloticus,* ON - *Oreochromis niloticus,* AG - *Rastrineobola argentea,* R%=100-A%
Sites: 1 - Sio Port Beach, 4 - Port Victoria, 5 - Kisumu Dunga and 14 - Hippo Point

Lates niloticus showed % bioavailable averages of the metals Cd, Pb, Cu, Zn and Fe at the sites sampled; Sio Port, Port Victoria, Hippo Point and Dunga that ranged from 55.6-78.2, 20.4-32.3, 12.5-70.6, 73.5-86.9 and 11.9-43.2 with means of 67.1, 27.5, 46.3, 79.4 and 29.8, respectively. *Oreochromis niloticus* recorded average bioavailable % average for the metals Cd, Pb, Cu, Zn and Fe at the sites sampled that ranged from 61.4-73.0, ND-64.8, 36.1-57.4, 61.6-81.7 and 20.6-47.6 with means of 66.7, 40.9, 41.7, 71.0 and 37.3, respectively. The average bioavailable % at the sites for the metals Cd, Pb, Cu, Zn and Fe in *Rastrineobola argentea* ranged from 55.6-78.2, 43.2-51.5, 55.56-91.2, 69.6-85.9 and 21.9-69.3 with means of 59.1, 47.4, 65.7, 76.2 and 44.5, respectively.

The average bioavailable % of the metals in the three species are presented in Figures 9-23. The Cd metal registered highest bioavailable percentages in *Lates niloticus, Oreochromis niloticus* and *Rastrineobola* *argentea* sampled from Port Victoria, Dunga and Dunga, respectively. The Pb metal similarly recorded highest bioavailable percentages in *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* sampled from Port Victoria, Sio Port and Hippo Point, respectively. The element Cu recorded highest bioavailable percentages in *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* sampled from Sio Port, Dunga and Hippo Point. The element Zn recorded highest bioavailable percentages in *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* sampled from Dunga, Hippo Point and Sio Port. The Fe metal recorded highest bioavailable percentages in *Lates niloticus*, *Oreochromis niloticus* and *Rastrineobola argentea* all sampled from Hippo Point. There was no clear highest % bioavailability trend for a specific metal for a certain species.

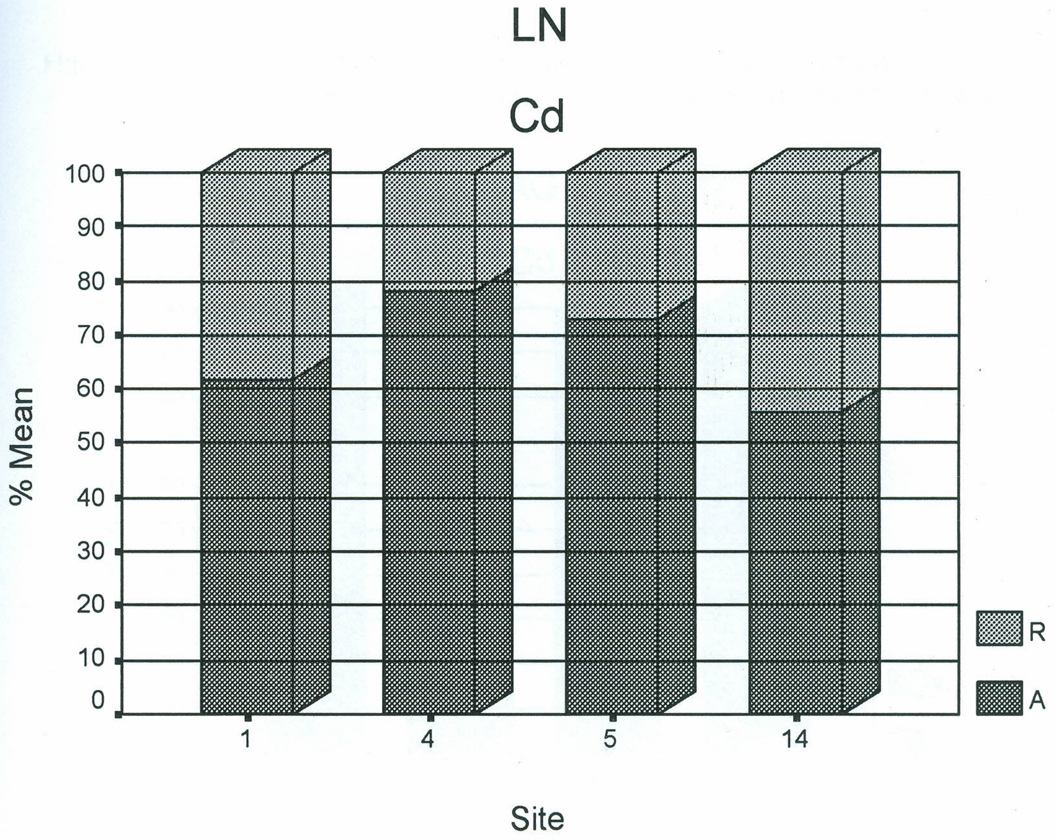

Figure 9. Speciation of mean % bioavailable concentration for Cd in *Lates niloticus* sampled from Winam Gulf of Lake Victoria

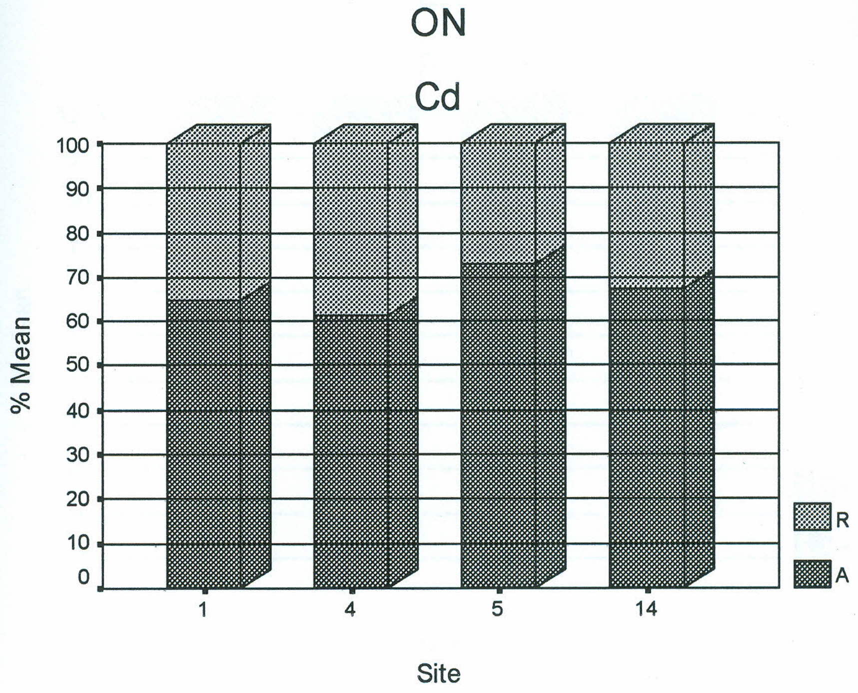

Figure 10. Speciation of mean % bioavailable concentration for Cd in *Oreochromis niloticus* sampled from Winam Gulf of Lake Victoria

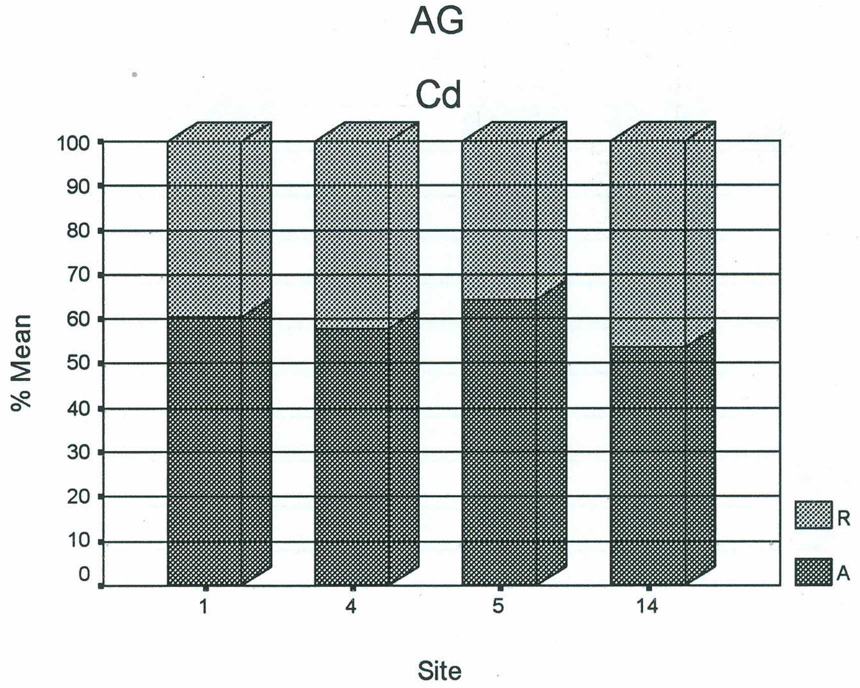

Figure 11. Speciation of mean % bioavailable concentration for Cd in *Rastrineobola argentea* sampled from Winam Gulf of Lake Victoria

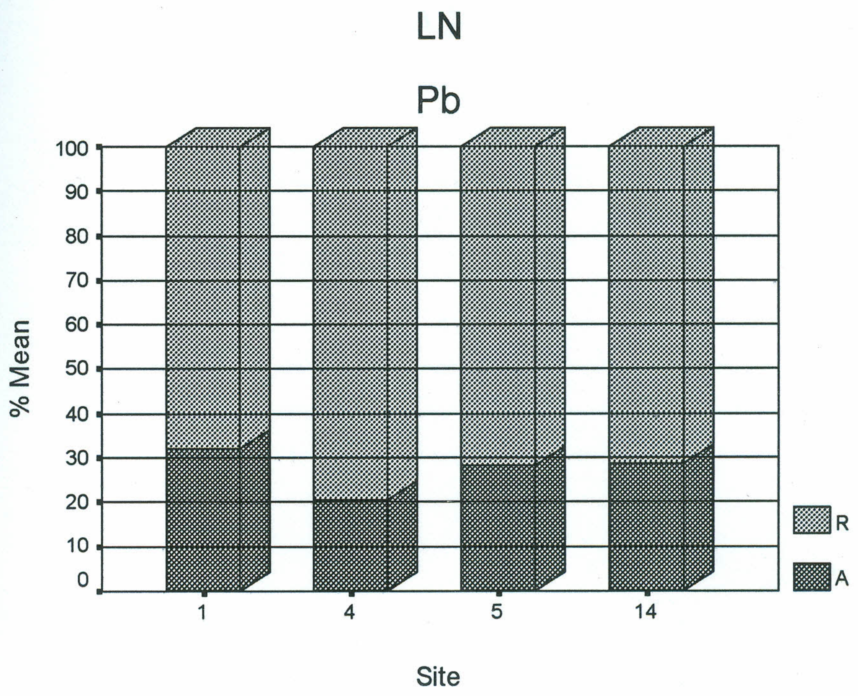

Figure 12. Speciation of mean % bioavailable concentration for Pb in *Lates niloticus* sampled from Winam Gulf of Lake Victoria

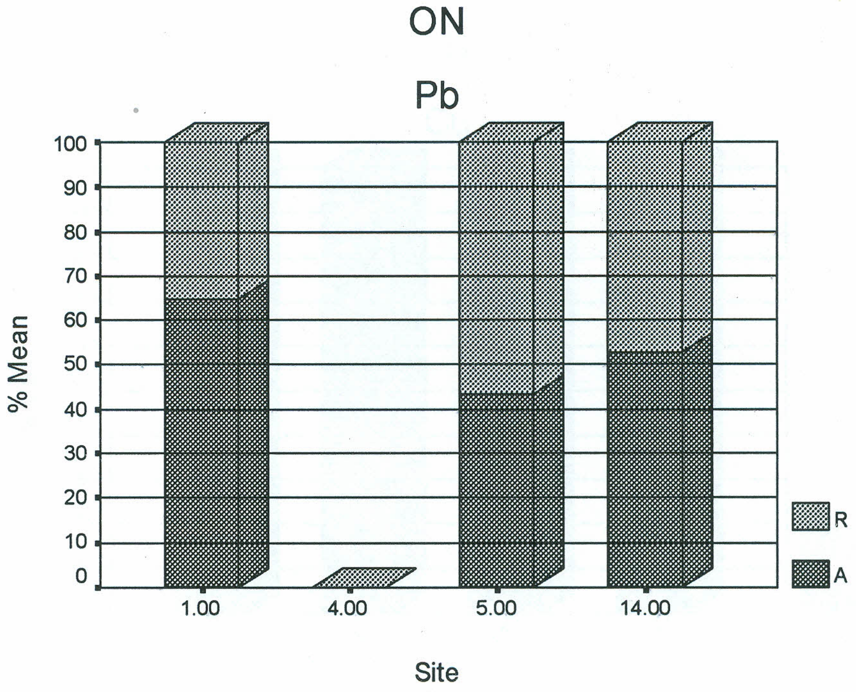

Figure 13. Speciation of mean % bioavailable concentration for Pb in *Oreochromis niloticus* sampled from Winam Gulf of Lake Victoria

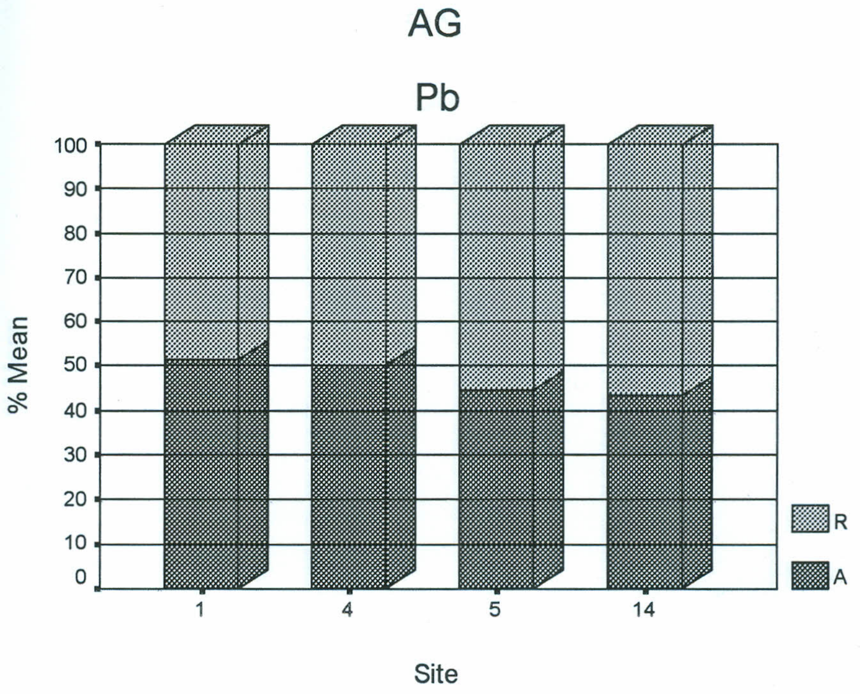

Figure 14. Speciation of mean % bioavailable concentration for Pb in *Rastrineobola argentea* sampled from Winam Gulf of Lake Victoria

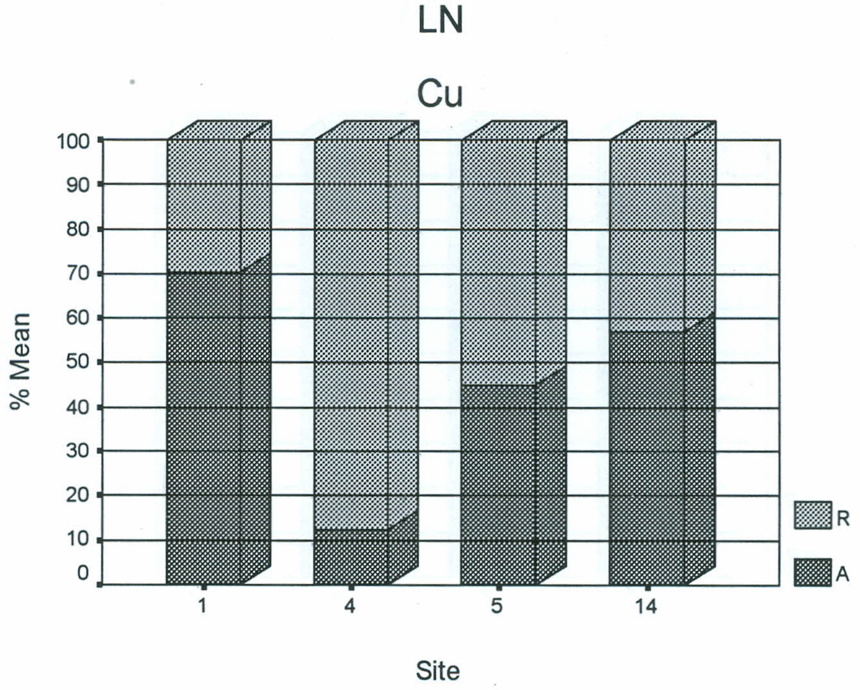

Figure 15. Speciation of mean % bioavailable concentration for Cu in *Lates niloticus* sampled from Winam Gulf of Lake Victoria.

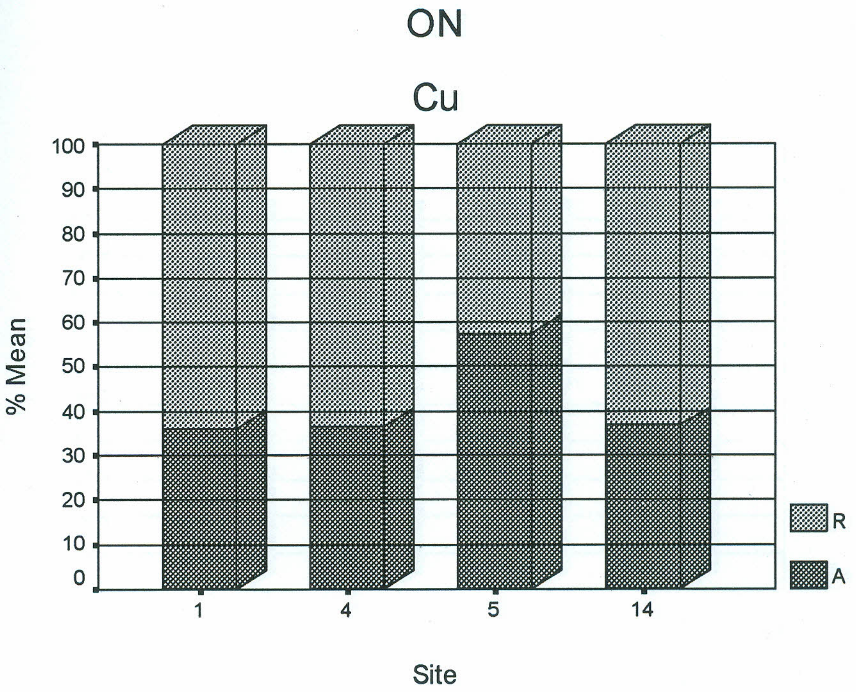

Figure 16. Speciation of mean % bioavailable concentration for Cu in *Oreochromis niloticus* sampled from Winam Gulf of Lake Victoria

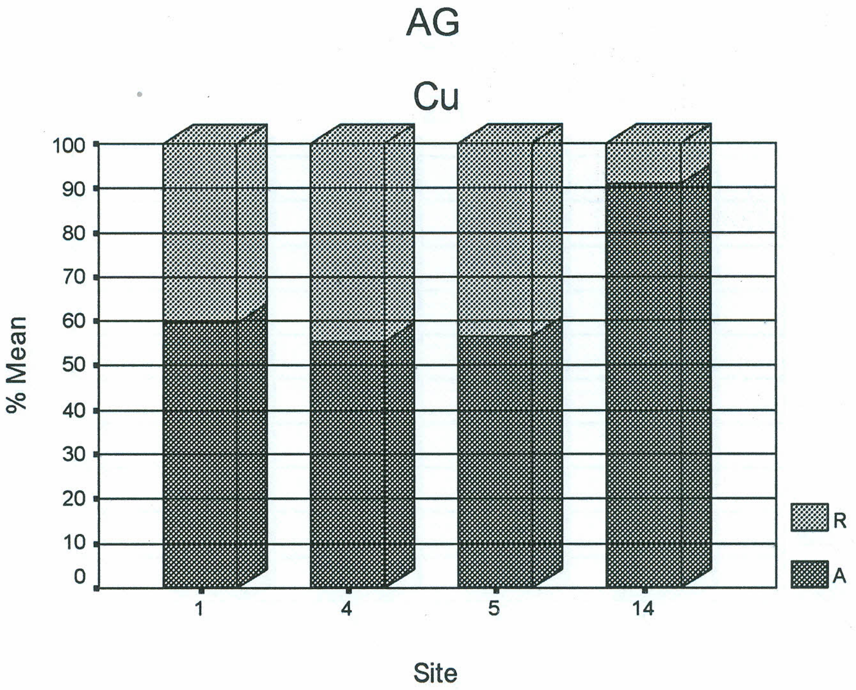

Figure 17. Speciation of mean % bioavailable concentration for Cu in *Rastrineobola argentea* sampled from Winam Gulf of Lake Victoria

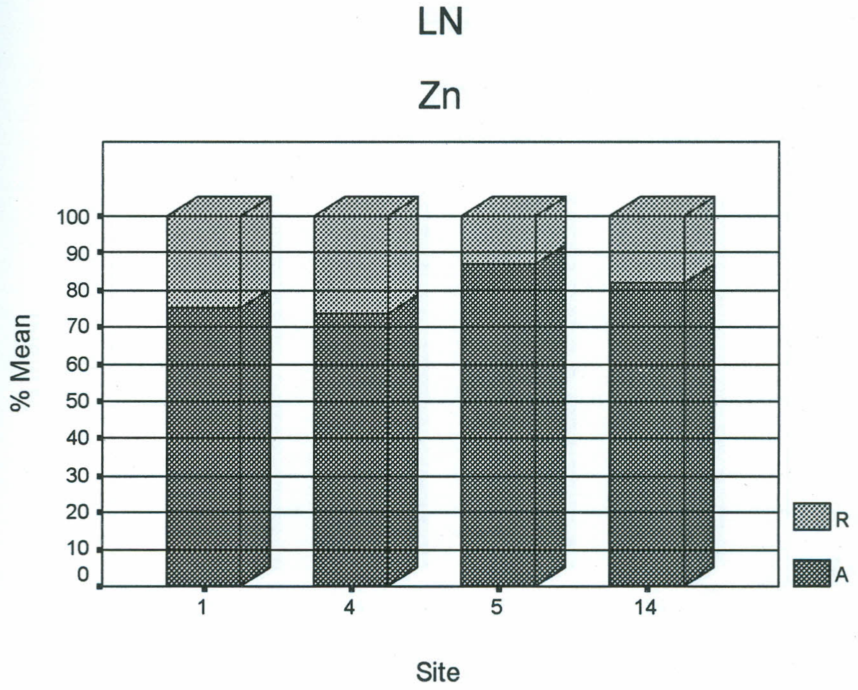

Figure 18. Speciation of mean % bioavailable concentration for Zn in *Lates niloticus* sampled from Winam Gulf of Lake Victoria

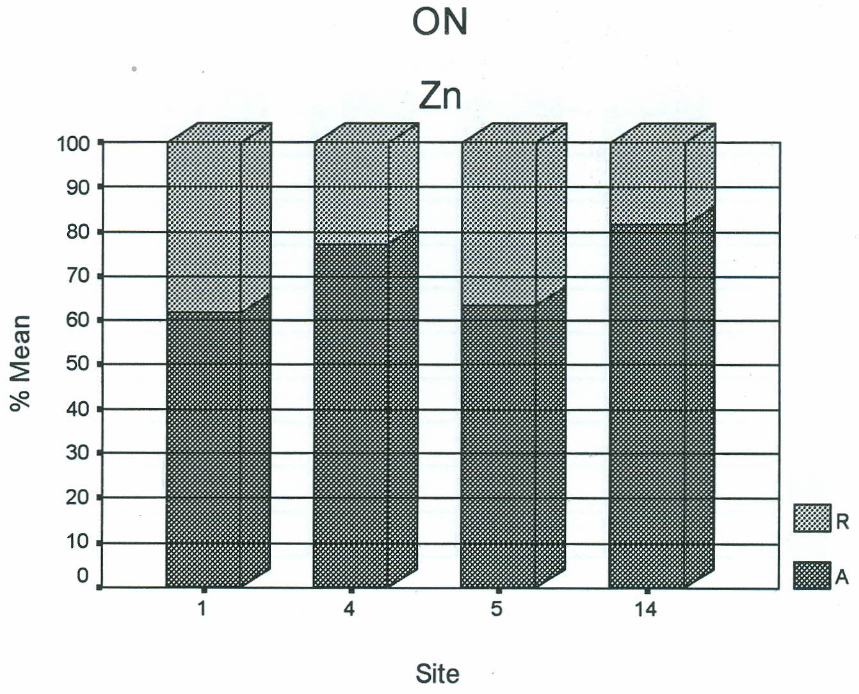

Figure 19. Speciation of mean % bioavailable concentration for Zn in *Oreochromis niloticus* sampled from Winam Gulf of Lake Victoria

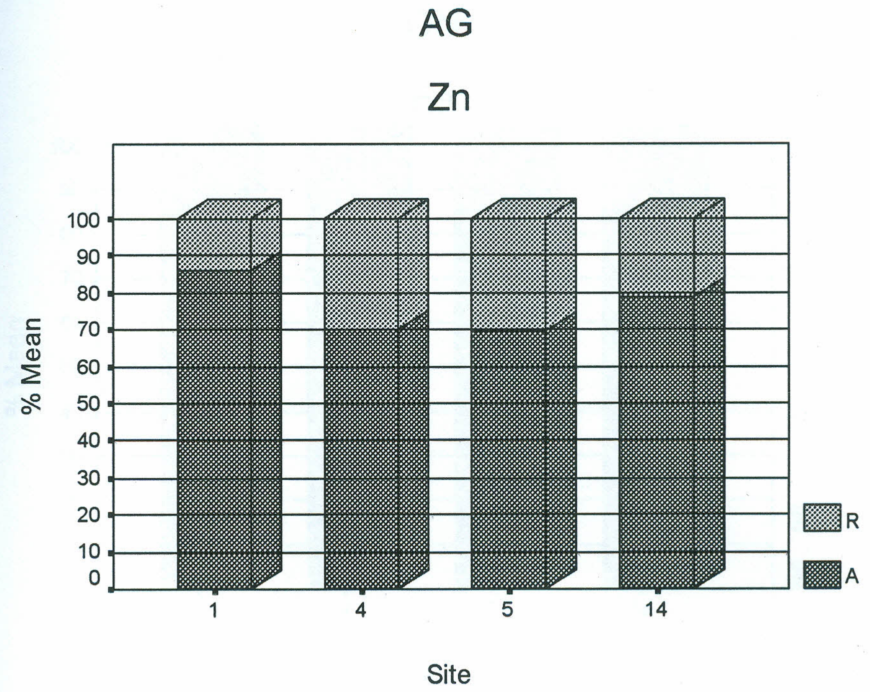

Figure 20. Speciation of mean % bioavailable concentration for Zn in *Rastrineobola argentea* sampled from Winam Gulf of Lake Victoria

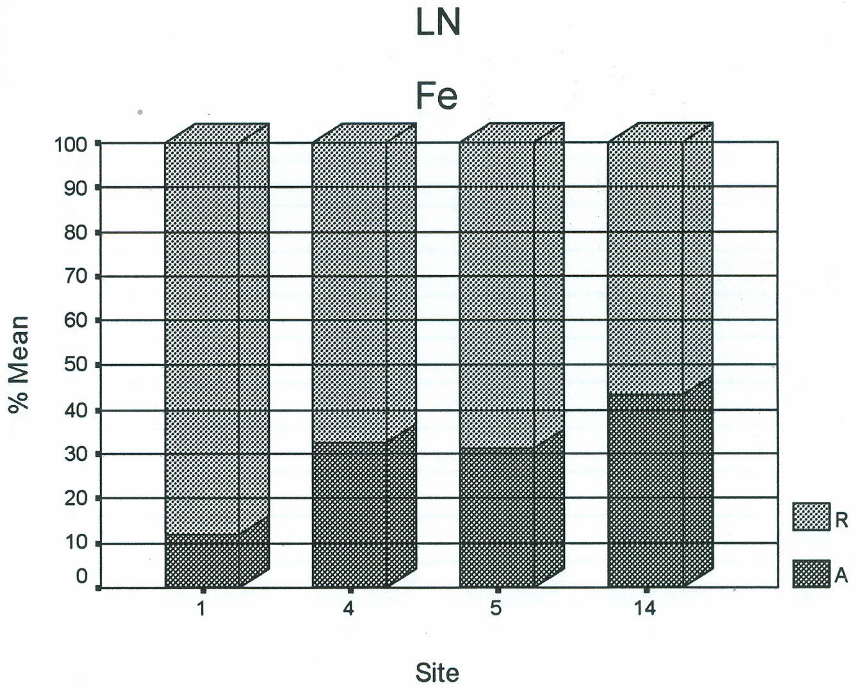

Figure 21. Speciation of mean % bioavailable concentration for Fe in *Lates niloticus* sampled from Winam Gulf of Lake Victoria

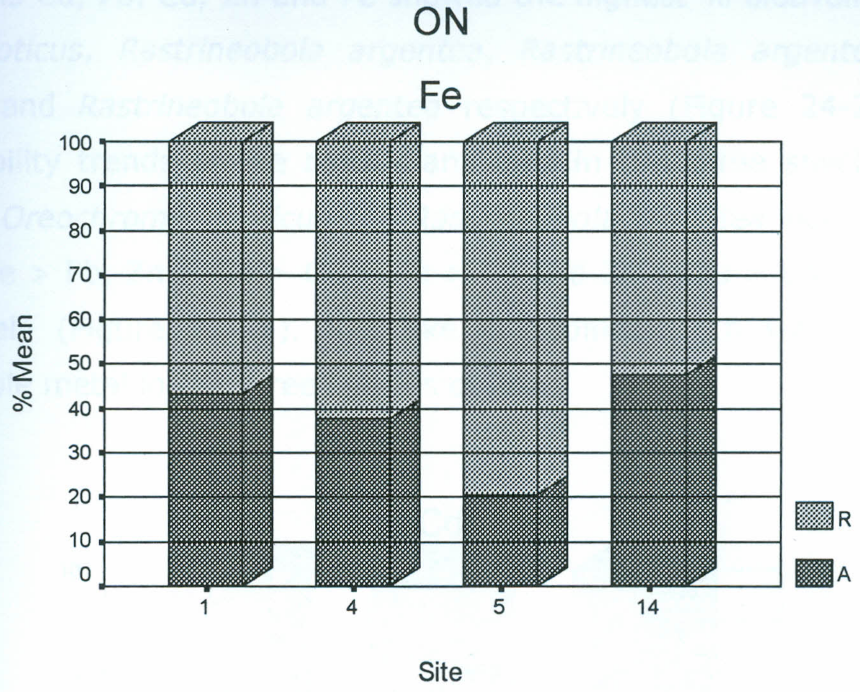

Figure 22. Speciation of mean % bioavailable concentration for Fe in *Oreochromis niloticus* sampled from Winam Gulf of Lake Victoria

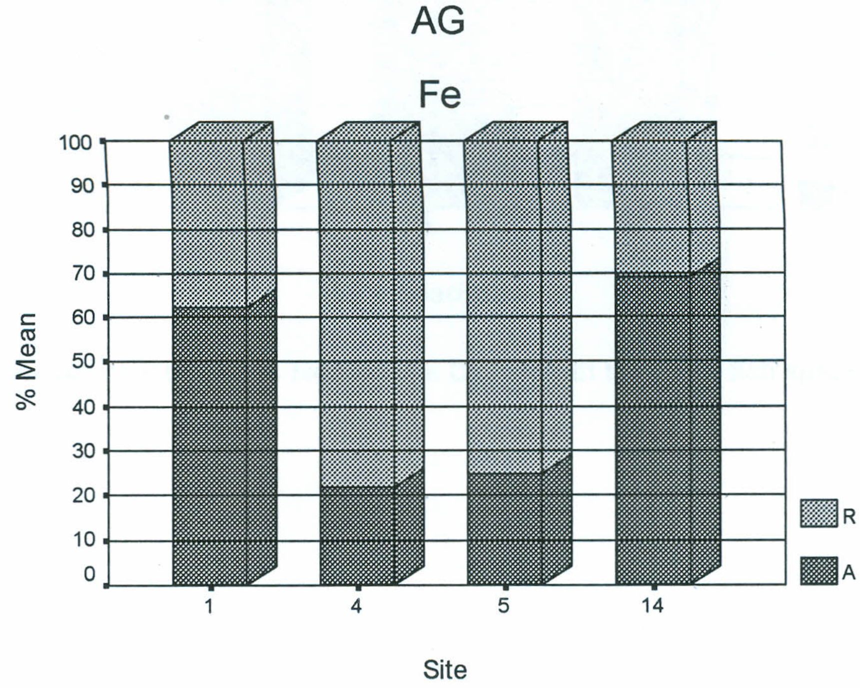

Figure 23. Speciation of mean % bioavailable concentration for Fe in *Rastrineobola argentea* sampled from Winam Gulf of Lake Victoria

The metals Cd, Pb, Cu, Zn and Fe showed the highest % bioavailability in *Lates niloticus*, *Rastrineobola argentea*, *Rastrineobola argentea Lates niloticus* and *Rastrineobola argentea* respectively (Figure 24-28). The bioavailability trends of the metals analysed in the three species *Lates niloticus, Oreochromis niloticus* and *Rastrineobola argentea* were Zn > Cd > Cu > Fe > Pb, Zn > Cd > Cu > Pb > Fe and Zn > Cu > Cd > Pb > Fe respectively (Figure 24-28). Just like in sediment, Zn was the most bioavailable metal in the three species of fish.

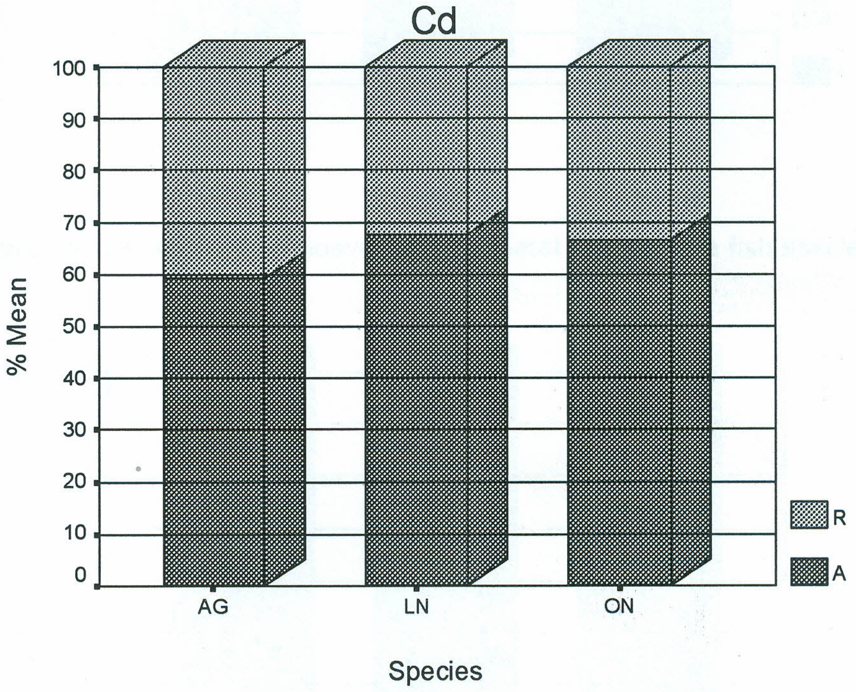

Figure 24. Variation of % bioavailable Cd metal in the three fish species

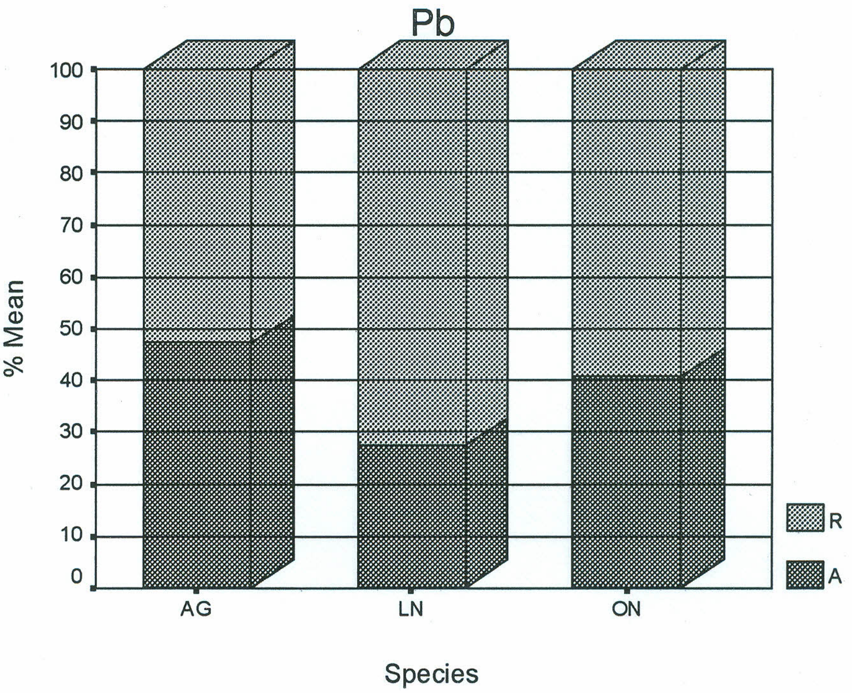

Figure 25. Variation of % bioavailable Pb metal in the three fish species

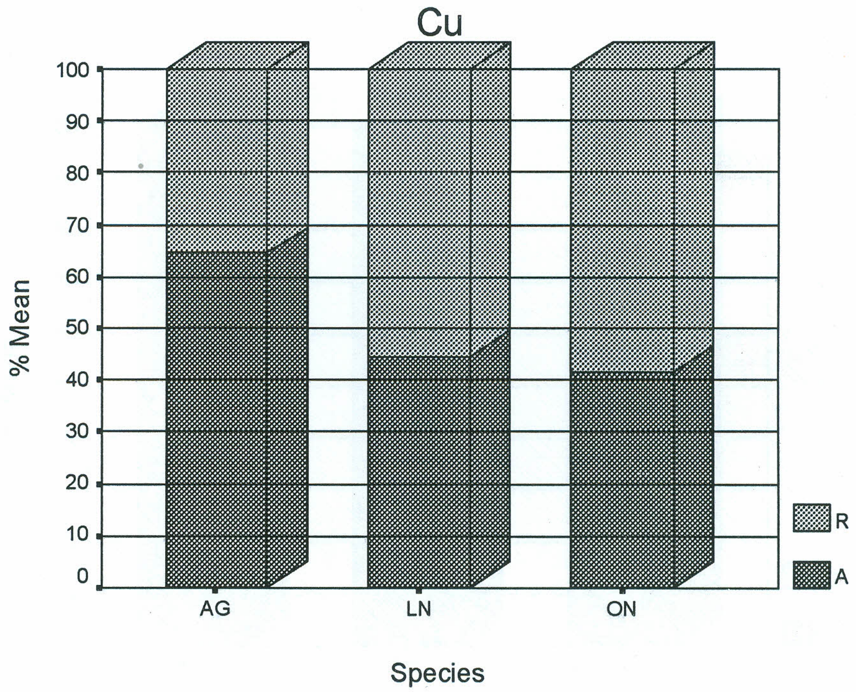

Figure 26. Variation of % bioavailable Cu metal in the three fish species

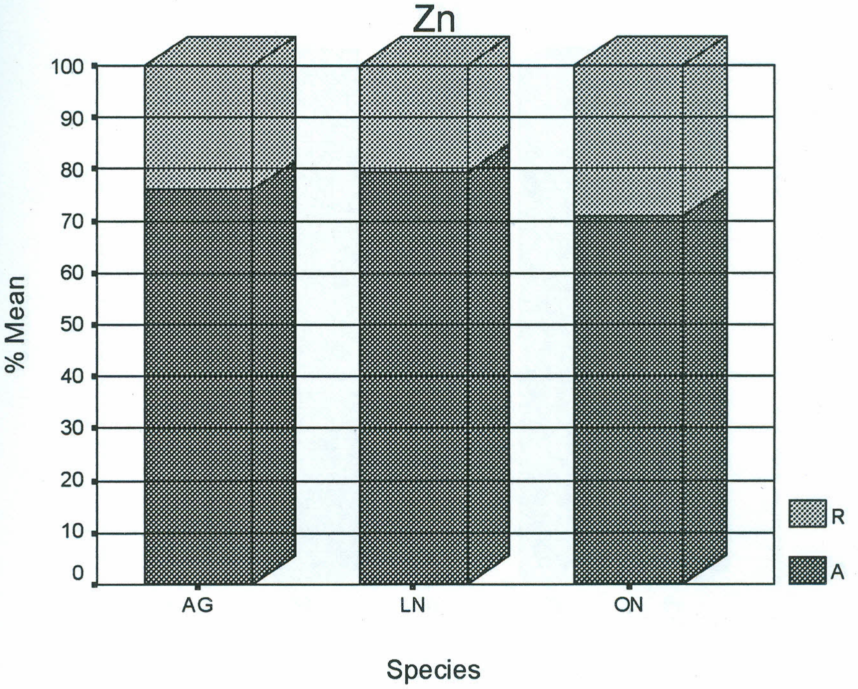

Figure 27. Variation of % bioavailable Zn metal in the three fish species

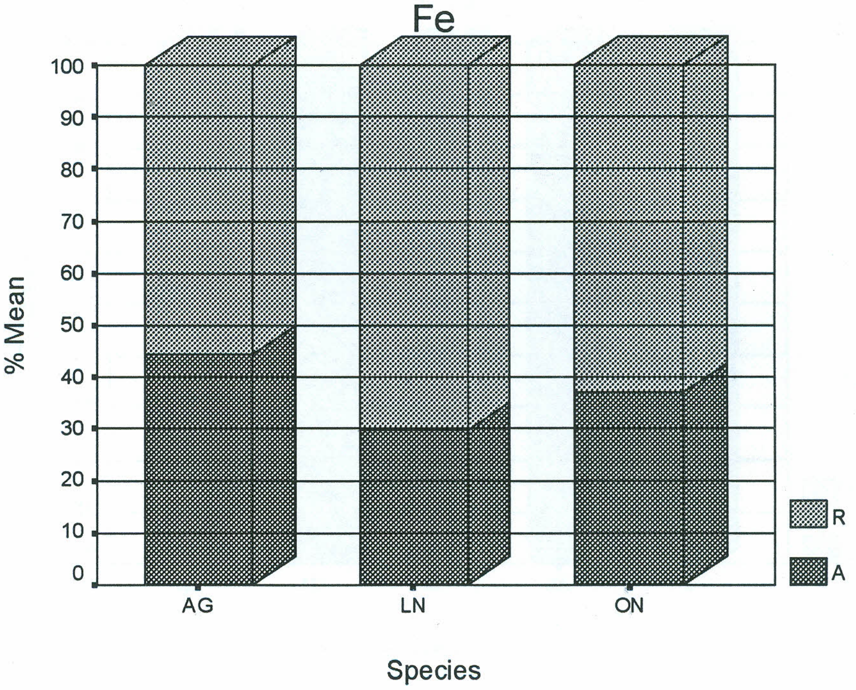

Figure 28. Variation of % bioavailable Fe metal in the three fish species

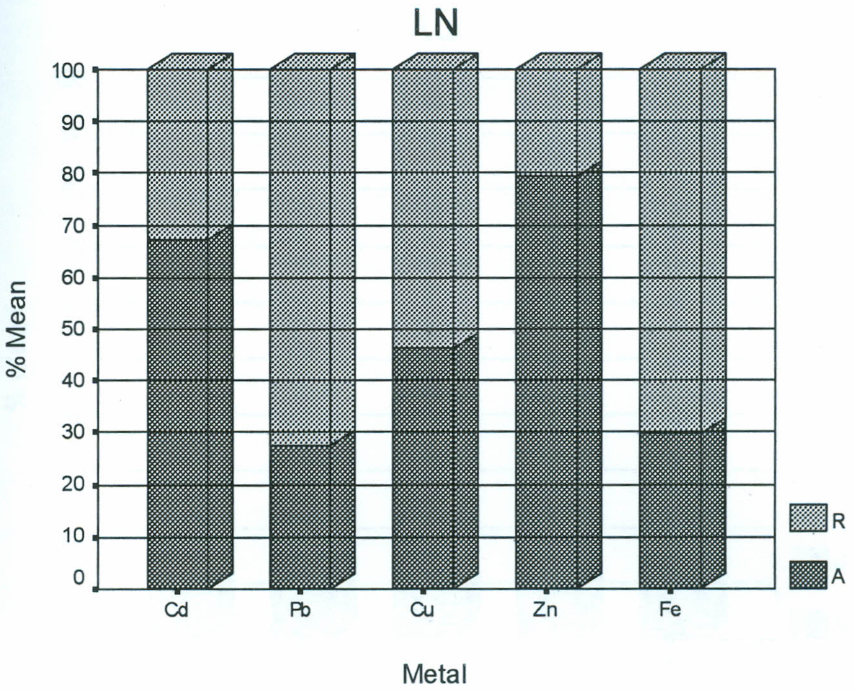

Figure 29. Variation of % bioavailability of the metals in LN

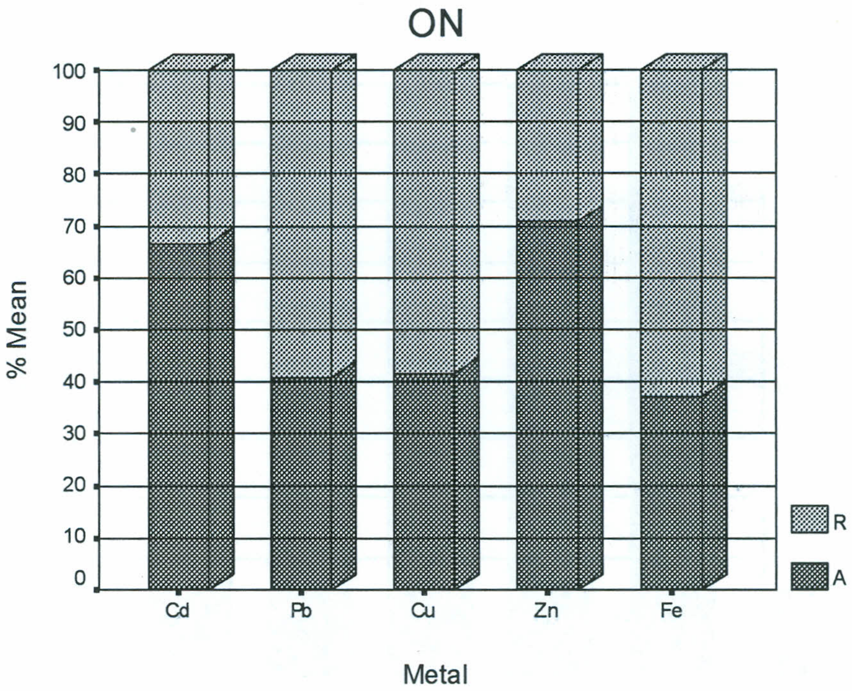

Figure 30. Variation of % bioavailability of the metals in ON

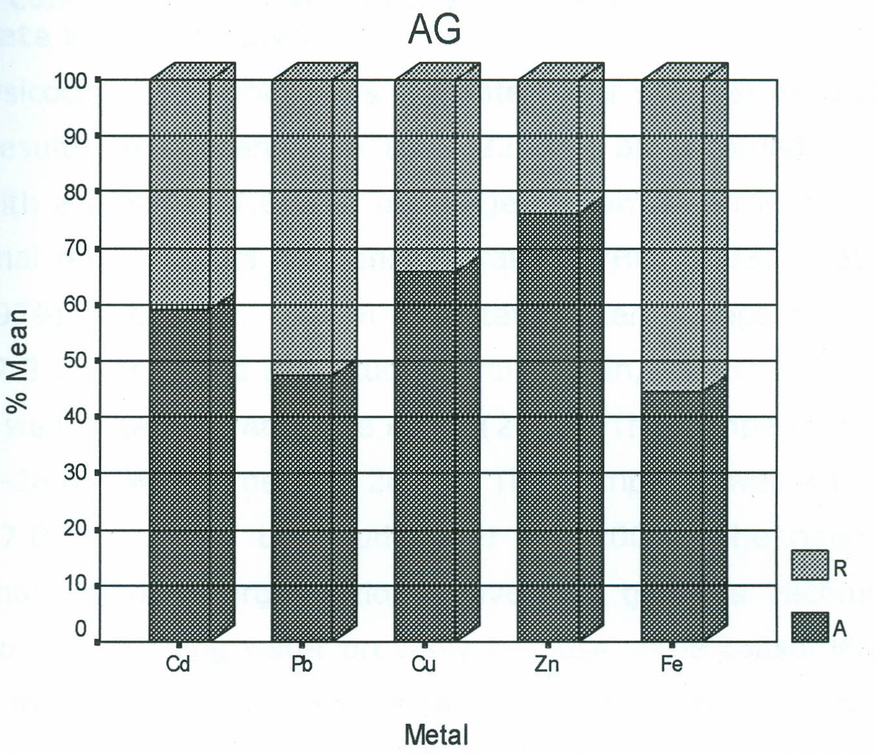

Figure 31. Variation of % bioavailability of the metals in AG

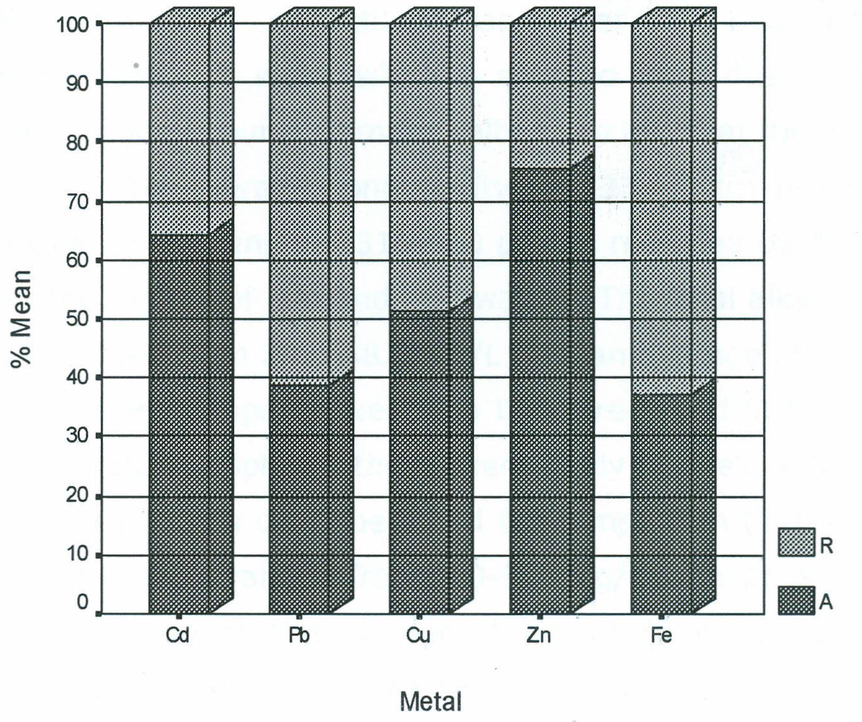

Figure 32. Percentage (%) bioavailable means of each metal in the three species LN, ON and AG

4.5 Total concentration levels of the metals in water

4.5.1 Estate water samples

Some physicochemical parameters of estate water samples were analysed and the results are presented in Table 22. The pH recorded a range of 7.2-7.8 with a mean of 7.6. The pH range conforms to the national and international requirements for drinking water (WHO, 1993; KEBS, 1996; USEPA, 1979) (Table 28). The pH for estate waters compare well with a range of 7.3-7.6 recorded in a study of rain (plain, Asbestos roof and Zn roof) and well waters by Abudude *et al*. (2007). The temperature ranged from 24.5-28.0^{0}C with a mean of 26.3^{0}C. This compared well with a range of 24.3-27.0^{0}C recorded by Abudude *et al*. (2007). The national and international standard organizations have not given a recommended temperature for drinking water probably because some consumers prefer hot water to cold water and vice versa and therefore this depends on an individual and the environmental conditions at the specific moment.

The conductivity ranged from 112-988 µS/cm with an average of 333 µS/cm. This average for conductivity was rather high due to the high value recorded from well water which is sourced from deep the ground and is probably a good source of many salts of metals that therefore raise its conductivity. The average conductivity of 333 µS/cm in the estate waters agrees with the range of 310-420 µS/cm recorded by Abudude *et al*. (2007) in their study of rain and well waters. The total alkalinity in the current study ranged from 20.0-88.0 mg/L with an average of 47.0 mg/L. The alkalinity values compared well with those recorded in the lake and upstream river water samples in the present study (Table27). No national or international standards could be found for comparison (Table 28). The dissolved oxygen levels ranged from 5.0-5.7 mg/L with an average 5.4 mg/L which conforms with the average of 5 mg/L (minimum of 4 mg/L) recommended by USEPA(1979), however the average in the current study is much smaller than 10 mg/L recommended by Egyptian Chemical Standards (1994) (Table 28). The values of dissolved oxygen in the present study are comparatively much lower than the range of 7.4-15.2

mg/L recorded by Abudude *et al.* (2007) in a study of rain and well waters. Turbidity in all estate water sources measured 1.0 NTU which conforms to the maximum value of 5 NTU recommended for drinking water by KEBS (1996). Turbidity in estate water samples was much below the average value of 270.4 NTU recorded in lake and upstream water samples in this study (Table 27). The acidity parameter was found to be below detection level.

Table 22. Some physical parameters of estate water samples from various sources

Water source	pH	Temperature °C	Conductivity (μS/cm)	Total Alkalinity (mg/L) $CaCO_3$	Dissolved Oxygen (mg/L)	Turbidity (NTU)
K	7.2	24.5	114	20.0	5.7	1.0
L	7.5	25.5	988	88.0	5.0	1.0
M	7.7	27.0	116	38.0	5.3	1.0
N	7.8	28.0	112	42.0	5.4	1.0
Average	7.6	26.3	333	47.0	5.4	1.0

ND-Not detectable.
At $p < 0.05$: LSD = 0.39 for pH, LSD = 1.48 for Temperature, LSD = 44.36 for Conductivity, LSD = 5.55 for Total Alkalinity, LSD = 0.42 for Dissolved Oxygen.
Source: K-Rain, L-Well, M-Municipality supplies, N-Private treatment plant supply.

The AAS analysis gave mean % recovery values for the spiked water samples for Cd, Pb, Cu, Zn and Fe as 94, 95, 94, 97 and 90 respectively. The Cd metal was in the undetectable range in the estate water samples just like in the lake and upstream water samples. The average Cd concentrations of the estate water sources for drinking water were within the international permissible limits presented in Table 33.

Cadmium was found to be below detection level in estate water samples and this agrees with the range of ND-100 μg/L Cd recorded by Abudude *et al.* (2007) in a study of rain water (different roofs) and well water. The Pb concentrations in the present study ranged from ND-20.8 μg/L recording a mean of 9.7 μg/L (Table 23). The Pb values in this study are much lower than a range of 100-200 μg/L Pb recorded by Abudude *et al.* (2007) in a study of rain (plain, Asbestos roof and Zn roof) and well waters. The large difference between the present study and this could be due to the type of roof and soils in the study areas which could be having different amounts of Pb as a contaminant. The high average concentration of 20.8 µg/L Pb recorded in Municipal water in the current study showed significant difference ($p < 0.05$) from the mean of the sources of water studied in the estates.

Table 23. Seasonal variation of mean concentration of Lead Pb (µg/L) in water in the studied area during 2006-2007

	AAS Analysis				
	Wet season		Dry season		Average site concentration
Source	Trip A	Trip B	Trip C	Trip D	
K	ND	ND	ND	ND	ND
L	16.9	13.7	12.8	15.0	14.6
M	22.3	15.6	20.0	25.5	20.8
N	4.5	2.5	3.0	3.5	3.4
Seasonal average	9.4		10.0		9.7

ND-Not detectable.

At $p < 0.05$: LSD = 1.11 for source of water, LSD = 3.13 for seasons, LSD = 1.57 for interactions between source of water and seasons.

Source: K-Rain, L-Well, M-Municipality supplies, N-Private treatment plant supply.

The Municipal water is pumped from Winam Gulf where the mean Pb concentration in water was 12.7 µg/L (Table 29) indicating a possible Pb contamination in the water supply system in Kisumu City. Water can also be contaminated with Pb during piping after the water treatment processes. In a study carried out in 100 largest United States of America cities by NAS (1977) to determine lead levels in water after passing through water treatment plants, the median concentration recorded was 3.7 µg/L with a maximum concentration measuring 62 µg/L. This is an indication that in the present study, estate water supplies in Kisumu City are comparatively cleaner though there is a possibility of Pb contamination in the handling processes. The average Pb concentrations of the estate water sources for drinking water were within the national permissible limit of 50 µg/L (KEBS, 1996) and the international limits of 50 µg/L for Canada and Russia (Neubauer Wolf, 2004) while the Pb concentrations of well and Municipal waters were above the permissible limits of 10 µg/L for some international organizations such as EU and WHO (Table 33). However, the mean Pb concentration of 9.7 µg/L in drinking water for the estates meets most of the international standards

(Table 23 and 33). Since a large percentage of Kisumu City residents could be using piped water supplies, this is then an issue that deserves some urgent attention since the municipal supplies have a high concentration that exceeds the permissible international limits as set out by the EU and WHO (Table 33).

The low average Pb concentration of 3.4 µg/L recorded in water samples from Private Treatment Plant showed significant difference ($p < 0.05$) with the mean of the estate water sources. This was probably because the Treatment Plant does not pump the water to consumers' homes but consumers just pick it from the plant as noted during the sampling period. Therefore the treated water is not exposed to possible recontamination through the piping systems. The Pb concentration in rain water was below the detection limit. This could probably be due to the cleaner atmosphere and cleaner handling containers for the rain water.

The Cu concentration in the estate water samples ranged from 37.8-47.9 µg/L with a mean of 44.6 µg/L Cu (Table 24). The average Cu concentration in municipal water supply was more than double the concentration level of 17.1 µg/L reported by Ochieng (1987), however, the concentration level of 44.6 µg/L is far much below the national and international permissible limits (Table 33). There was significant variation in Cu concentration among the different water sources.

Table 24. Seasonal variation of mean concentration of Copper Cu (µg/L) in water in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Source	Trip A	Trip B	Trip C	Trip D		Trip A
K	52.5	45.3	43.8	50.3	47.9	4.30
L	47.2	48.6	48.2	47.9	47.9	4.33
M	49.6	49.1	41.5	38.4	44.7	2.05
N	43.0	40.8	29.0	38.5	37.8	<1.51
Seasonal average	47.0		42.2		44.6	3.56

At $p < 0.05$: LSD = 1.34 for source of water, LSD = 3.79 for seasons, LSD = 1.90 for interactions between source of water and seasons.
Source: K-Rain, L-Well, M-Municipality supplies, N-Private treatment plant supply.

The Zn concentration ranged from 213.5-267.9 µg/L with a mean of 232.7 µg/L (Table 25). There was significant variation in Zn concentration among the different water sources in the sampled estates ($p < 0.05$). The mean of Zn concentrations in this study compared well to that of a past study of Boston tap water in the USA in which a maximum level of 1, 600 µg/L was reported with a mean of 200 µg/L (NAS, 1977). The Zn concentration recorded in the present study was much higher than the undetectable concentration recorded by Abudude *et al.* (2007) in a study of rain and well waters.

Table 25. Seasonal variation of mean concentration of Zinc Zn (µg/L) in water in the studied area during 2006–2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Source	Trip A	Trip B	Trip C	Trip D		Trip A
K	265.0	253.8	215.0	180.0	228.5	288
L	171.2	206.0	227.4	249.4	213.5	21.9
M	285.5	285.2	253.2	247.7	267.9	127.1
N	298.8	97.3	253.7	234.0	221.0	48.1
Seasonal average	232.9		232.6		232.7	121.3

At $p < 0.05$: LSD = 39.34 for source of water, LSD = 55.64 for interactions between source of water and seasons.
Source: K-Rain, L-Well, M-Municipality supplies, N-Private treatment plant supply.

The concentration of iron in the estate water samples ranged from 98-523 µg/L with a mean of 242.4 µg/L Fe (Table 26). The high concentration of 523 µg/L Fe recorded in Municipal water showed significant difference (p

< 0.05) from the mean of the water sources sampled from the study area. This was attributed to the high concentration of Fe in the water sourced from Lake Victoria which had a much higher average Fe concentration of 2,588 µg/L (Table 32) and the possibility of reducing the high Fe concentration level during treatment to very low values exhibited by other estate water sources (Table 26) could therefore be minimal. While all the average concentrations of Fe in the estate water sources satisfied the international maximum concentration levels for drinking water the municipal supplied water exceeded the permissible maximum concentration of 300 µg/L for this metal in drinking water (WHO, 1998; Neubauer and Wolf, 2004; KEBS, 1996) (Table 33). The concentration range in the current study is much lower compared to that of 3,500-5,400 µg/L Fe recorded by Abudude *et al.* (2007) in a study of rain and well waters.

Table 26. Seasonal variation of mean concentration of Iron Fe (µg/L) in water in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Source	Trip A	Trip B	Trip C	Trip D		Trip A
K	248.0	158.0	204.0	256.0	216.5	6.60
L	77.0	81.0	121.3	250.8	132.5	2.21
M	444.5	906.0	359.5	380.5	522.6	7.34
N	146.0	90.0	35.0	121.0	98.0	17.30
Seasonal average	268.9		216.0		242.4	8.36

At $p < 0.05$: LSD = 1.83 for source of water, LSD = 5.17 for seasons, LSD = 2.59 for interactions between source of water and seasons.
Source: K-Rain, L-Well, M-Municipality supplies, N-Private treatment plant supply.

The metals Pb, Cu, Zn and Fe in the Estate water samples showed positive correlations among themselves (Table 34). The positive correlation between Fe:Zn showed a significant difference ($p < 0.05$). This signifies a common source for the two metals in this estate water sources.

4.5.2 Lake and upstream river water samples

4.5.2.1 Some physical and chemical parameters of water

The data collected for some physical parameters in water are presented in Table 27. The pH recorded a range of 6.5-8.8 with a mean of 7.67. The pH values are within the recommended national and international standards (WHO, 1993; KEBS, 1996; USEPA, 1979). The pH range recorded compared well with what had been reported by Ochieng (1987) and Hydrobiology (1969) in Lake Victoria (Table 28) even though this study indicated some slight widening range. The pH showed an average positive correlation ($r = -0.541$, $p < 0.05$) with dissolved oxygen. The sites at Kisumu Port and Car Wash showed slightly acidic characteristics while the rest of the sites had neutral or alkaline characteristics. Temperature recorded a range of 26.0-29.0°C with a mean of 27.5°C. There was little variation in average temperatures recorded among different sampling sites. Temperature showed an average negative correlation ($r = -0.513$, $p < 0.05$) with turbidity.

Conductivity ranged from 69-230 µS/cm with a site mean of 140.5 µS/cm. There was a general increase of conductivity downstream in all the rivers sampled. The sites of River Nyando registered the highest values of conductivity which implies substantial loading of the lake with salts from upstream areas of the rivers. Conductivity registered a near perfect positive correlation with total alkalinity with significant difference ($r < 0.951$, $p < 0.01$) while it also showed a positive correlation with turbidity with significant difference ($r = 0.667$, $p < 0.05$). The average conductivity of 140.5 µS/cm in this study is in agreement with the range of 122-236 µS/cm reported in a study of the Manly Lagoon by Van *et al.* (2002). The average conductivity of 145.3 µS/cm recorded in Winam Gulf shows continual accumulation from the average values of 129.8 µS/cm and 95 µS/cm recorded by Ochieng (1987) and Hydrobiology (1969) respectively. Awadallah and Moalla (1996) noted that increase in conductivity can be ascribed to the hydrolysis and re-dissolution of insoluble salts and desorption of these salts into the water. The average conductivity value recorded in the present study is comparatively lower than 178 µS/cm recorded in a study of Lake Nasser by Soltan *et al.* (2005) (Table 28).

Table 27. Some Physical Parameters analysed for lake and upstream water samples

Site	pH	Temperature °C	Conductivity (µS/cm)	Total Alkalinity (mg/L) $CaCO_3$	Dissolved Oxygen (mg/L)	Turbidity (NTU)
Lake						
2	6.5	28.5	167	66.0	4.00	53.0
3	6.8	28.5	185	56.0	5.10	131
4	8.2	26.0	110	33.0	5.60	2.0
5	8.8	27.5	156	46.0	5.85	80.0
6	8.5	28.0	76	28.0	5.85	33.0
8	7.3	28.0	143	44.0	5.05	202.0
10	7.5	26.0	230	88.0	4.20	980.0
12	7.6	28.0	170	50.0	4.65	410
15	8.7	28.5	102	32.0	4.70	3.0
16	8.2	29.0	114	35.0	4.60	10.0
Average	7.8	27.8	145.3	47.8	4.96	190.4
Upstream						
7	7.3	26.5	69	26.0	5.50	101.0
9	7.1	26.5	77	34.0	4.45	350.0
11	7.4	27.0	203	74.0	4.10	880.0
13	7.5	27.5	165	47.0	4.30	550.0
Average	7.3	26.9	128.5	45.3	4.59	470.3
Lake and Upstream Average	7.67	27.5	140.5	47.1	4.85	270.4

Acidity parameter was below detection limit

At $p < 0.05$: LSD = 0.34 for pH, LSD = 1.31 for Temperature, LSD = 6.79 for Conductivity, LSD = 5.79 for Total Alkalinity, LSD = 0.35 for Dissolved Oxygen.

Sites: 2 - Kisumu Port, 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth, 13 - Sondu-Miriu Rivers Upstream, 15 - Sio Port Offshore and 16 - Hippo Point Offshore.

Table 28. Comparison of physicochemical properties of Winam Gulf of Lake Victoria, with past studies and some National and International standards.

	Physicochemical Properties				
	pH	Alkalinity (mg/L)	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Turbidity (NTU)
Winam Gulf[a]	6.5-8.8 (7.8)	47.8	145.3	4.96	2-980 (190.4)
Lake Victoria[b]	7.05-8.05 (7.7)	61.8	129.8	7.48	10-37
Lake Victoria[c]	8.0-8.6 (7.5)	45.8	95	ng	ng
Manly Lagoon catchment[d]	6.4-7.1	ng	122-236	ng	ng
WHO[e] standard	6.5-8.5	ng	ng	ng	ng
KEBS[f] standard	6.5-8.5	ng	ng	ng	5
Egyptian[g] Standard	6-9	ng	ng	10	ng
USEPA[h]	6-9.5	ng	ng	5 average 4 minimum	ng

ng-Not given, () Average of range.
[a]Present study 2006/7 Kenya, [b]Ochieng (1987) Kenya, [c]Hydrobiology (1969), [d]Van *et al.* (2002, [e]WHO (1993) maximum permissible limits, [f]KEBS (1996) Maximum permissible limits, [g]ECS (Egyptian Chemical standards) (1994) permissible limits, [h]USEPA (1979) permissible limits.

Total alkalinity ranged from 26.0-88.0 mg/L with a site mean of 47.1 mg/L. Alkalinity showed an increasing trend downstream. Generally, sites of the rivers had higher alkalinity compared to those of the lake which implies that the rivers could be contributing to an increase in the alkalinity in the lake. Total alkalinity showed a significant positive correlation with turbidity ($r = 0.781$, $p < 0.01$) while it had a negative correlation with DO ($r = -0.641$, $p < 0.05$). The average alkalinity recorded in Winam Gulf agrees with that of 45.8 mg/L recorded by Hydrobiology (1969) but is relatively lower than 61.8 mg/L recorded by Ochieng (1987). Dissolved oxygen (DO) ranged from 4.00-5.85 mg/L with a site mean of 4.85 mg/L. There was a slight increment in dissolved oxygen downstream in all the river waters analysed. There was minimal variation in dissolved oxygen concentration in the water of all sites. The average concentration level of DO in this study is comparatively lower than 7.48 mg/L reported by Ochieng (1987) and a range of 7.7-9.4 mg/L reported by Soltan *et al.* (2005)) indicating a decline in water quality since Ochieng's time. The much lower value of DO recorded in this study was attributed to increased pollution in the lake with organic matter which eventually consumes the oxygen during decomposition by biological organisms (Gindy, 2001). Fawzy (2000) noted that there is production of CO_2 at the bottom of water masses during decomposition of organic matter. This is supported by the average negative correlation recorded between DO and turbidity ($r = -0.564$, $p < 0.05$). Turbidity ranged from 2.0-980 NTU with a site mean of 270.4 NTU. The mean turbidity of 470.3 NTU noted in upstream water samples was much higher compared to the mean of 190.4 NTU recorded at the lake sites and therefore this study confirms that most of the turbidity in Winam Gulf originates from the rivers that feed the lake (Table 27). The range in this study was much higher than what had been reported by Ochieng (1987). The high figure of 980 NTU recorded in this study at the Mouth of River Nyando is not unusual since Ochieng (1987) had reported a value of 1000 NTU in a study of other rivers and lakes in Kenya twenty years down the line. Though there are no clear national or international guidelines on turbidity levels, high turbidity levels affect fish feeding and growth; the ability of salmonids to find and capture food is impaired at turbidities from 25-70 NTU. Gill functioning in some fish can also be impaired after 5-10 days of exposure to a turbidity level of 25 NTU (Barnes, 1998). It has also been observed that water measuring <10 NTU is very clear, > 50 NTU is cloudy and > 500 NTU is downright muddy. In the present study, acidity was below the detection limit in the water samples.

4.5.2.2 Concentration of metals in lake and upstream water samples

The Cd metal was below the detection limit in the present study by both the AAS and ICP-MS analytical instruments. The concentration of Cd in water samples in this study was lower at the undetectable range compared to the range recorded by Ochieng (1987). This shows some unprecedented decrease of this metal in water. However, there has been closure of some industries including a textile factory and a brewery which could therefore explain the lower Cd levels. The undectable levels in water could also be attributed probably to low Cd solubility in water. Similarly the average site concentrations for Pb ranged from 3.1-45.7 µg/L with a mean of 12.7 µg/L (Table 29).

Table 29. Seasonal variation of mean concentration of Lead Pb (µg/L) in water in the studied area during 2006-2007

	AAS Analysis				
	Wet season		Dry season		Average site concentration
Site	Trip A	Trip B	Trip C	Trip D	
Lake					
2	25.0	22.0	122.3	13.5	45.7
3	12.0	9.5	7.5	4.8	8.4
4	3.3	4.5	3.5	1.3	3.1
5	18.8	11.5	24.5	17.0	17.9
6	9.8	8.0	4.5	6.3	7.1
8	6.0	4.8	4.5	3.0	4.6
10	14.8	12.3	5.3	25.5	14.4
12	21.5	18.0	13.5	20.8	18.4
15	7.5	8.5	1.50	2.5	5.0
16	18.8	15.5	16.0	17.5	16.9
Seasonal average	12.6		15.8		14.2
Upstream					
7	12.5	6.5	7.5	9.0	8.9
9	4.0	2.5	3.5	2.5	3.1
11	9.5	6.0	3.8	12.0	7.8
13	14.8	16.0	13.0	18.8	15.6
Seasonal average	9.0		8.8		8.9
Lake and Upstream average	11.6		13.8		12.7

At $p < 0.05$: LSD = 0.84 for sites, LSD = 1.88 for seasons, LSD = 1.20 for interactions between sites and seasons.
Sites: 2 - Kisumu Port, 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth, 13 - Sondu-Miriu Rivers Upstream, 15 - Sio Port Offshore and 16 - Hippo Point Offshore.

The Pb concentration range recorded in this study was slightly lower than that reported by some study carried out by Ochieng (1987) where the range of concentrations of Pb registered was higher than that recorded in the present study 20 years later (Table 33). This could probably be due to the awareness of the public about the dangers of leaving these heavy metals to accumulate in the lake water and therefore better management of waste materials. There has also been a waterweed known as water hyacinth that is threatening to fill up the Winam Gulf water surface

(Appendix I: Plate 10, pg 140). There has also been closure of textiles and breweries industries since the study carried out by Ochieng (1987).

Kisumu Port had a significant high average site concentration of 45.7 µg/L Pb ($p < 0.05$) compared to the mean of the study area (Table 29). This high average concentration was probably caused by an oil spill at the port because on the third sampling Trip C, the concentration of Pb was quite high at 122.3 µg/L while for the rest of the other three trips the Pb concentrations were comparable with those of the other sites. Port Victoria, Nyamasaria River Mouth, Nyamasaria River Upstream and Offshore of Sio Port registered low average concentrations of 3.1 µg/L Pb, 4.6 µg/L Pb, 3.1 µg/L Pb and 5.0 µg/L Pb respectively that had significant difference ($p < 0.05$) compared to the mean of the study area (Table 29). Seasonal variation for Pb in the lake and upstream river waters showed lower concentration during wet season compared to the dry season and this was attributed to the probable oil spillage at the Kisumu Port sampling site which made the seasonal average on the third Trip C to record the highest average concentration (Table 29).

The sites sampled showed little variation of the average concentrations of Cu in water which ranged from 44.9 µg/L to 68.5 µg/L with an average of 53.0 µg/L (Table 30). The high concentrations of 68.5 µg/L Cu, 57.5 µg/L Cu and 59.3 µg/L Cu recorded at Kisumu Port, Nyando River Mouth and Nyando River Upstream respectively showed significant difference ($p < 0.05$) compared to the mean of the study area. Kisumu Port water samples for Trip C recorded a very high mean concentration of 116.0 µg/L Cu which points to a possible oil spillage at this port site.

Table 30. Seasonal variation of mean concentration of Copper Cu (μg/L) in water in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
2	63.0	38.0	116.0	57.0	68.5	na
3	61.5	55.8	54.5	46.5	54.6	1.62
4	56.0	40.8	54.5	58.8	52.5	<1.53
5	58.5	59.3	32.8	44.5	48.8	3.15
6	58.0	56.8	51.3	54.5	55.1	3.86
8	56.9	53.0	55.8	44.0	52.4	<1.58
10	66.8	64.5	45.0	53.8	57.5	1.59
12	57.8	55.3	40.0	35.0	47.0	2.06
15	54.8	56.3	38.3	53.0	50.6	na
16	52.5	42.5	56.8	45.3	49.3	na
Seasonal average	55.4		51.9		53.6	nc
Upstream						
7	55.0	55.3	52.8	60.3	55.8	3.09
9	52.5	48.8	45.8	37.0	46.0	<1.52
11	61.3	63.5	56.8	55.5	59.3	1.57
13	48.0	45.5	42.8	43.5	44.9	2.00
Seasonal average	53.7		49.3		51.5	nc
Lake and Upstream average	54.9		51.1		53.0	nc

At $p < 0.05$: LSD = 1.42 for sites, LSD = 3.16 for seasons, LSD = 2.01 for interactions between sites and seasons.
Sites: 2 - Kisumu Port, 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth, 13 - Sondu-Miriu Rivers Upstream, 15 - Sio Port Offshore and 16 - Hippo Point Offshore.

The high concentrations of Cu recorded at the sites of River Nyando were attributed to the agricultural and industrial effluents carried downstream by the river due to its flooding. The relatively low concentrations of 48.8 μg/L, 46.0 μg/L, 47.0 μg/L, 44.9 μg/L and 49.3 μg/L for Dunga, Nyamasaria River Mouth, Sondu-Miriu River Mouth, Sondu-Miriu River Upstream and Hippo Point Offshore, respectively, showed significant difference at $p < 0.05$ in relation to the mean of the study area. The concentrations of these sites have been rendered significant due to an immediate possible contamination at the Kisumu Port and thereby increasing the mean for the average site concentrations. There was a higher seasonal average concentration during the rainy season which decreased during the dry season. There was significant seasonal variation among the four sampling trips ($p < 0.05$).

The site average concentrations of Zn ranged from 202.6-269.5 µg/L with a mean of 232.3 µg/L (Table 31).

Table 31. Seasonal variation of mean concentration of Zinc Zn (µg/L) in water in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
2	267.0	138.3	245.0	217.6	217.0	na
3	257.0	254.0	252.1	239.0	250.5	6.37
4	253.0	248.0	242.0	250.0	248.3	4.37
5	276.0	162.0	285.0	152.4	218.9	11.66
6	280.0	261.0	267.0	270.0	269.5	12.5
8	265.0	256.6	216.0	274.5	253.1	7.90
10	269.0	131.4	272.6	256.2	232.3	16.6
12	258.0	134.3	256.9	251.4	225.2	9.56
15	225.0	211.8	192.8	245.9	218.9	na
16	278.3	171.4	259.6	185.1	223.6	na
Seasonal average	229.9		241.6		235.7	nc
Upstream						
7	267.0	253.6	262.7	231.3	253.7	8.90
9	186.0	111.9	263.2	273.2	208.6	4.87
11	247.0	126.2	200.6	236.4	202.6	2.50
13	260.0	145.0	256.6	255.4	229.3	8.76
Seasonal average	199.6		247.4		223.6	6.26
Lake and Upstream average	221.2		243.4		232.3	nc

na-Not analysed, nc – Not calculated.
At $p < 0.05$: LSD = 8.49 for sites, LSD = 18.88 for seasons, LSD = 12.01 for interactions between sites and seasons.
Sites: 2 - Kisumu Port, 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth, 13 - Sondu-Miriu Rivers Upstream, 15 - Sio Port Offshore and 16 - Hippo Point Offshore.

The high concentrations of 250.5 µg/L Zn, 248.3 µg/L Zn, 269.5 µg/L Zn, 253.2 µg/L Zn and 253.2 µg/L Zn for Car Wash, Port Victoria, Sio River Mouth, Sio River Upstream and Nyamasaria River Mouth, respectively, showed significant difference at $p<0.01$ compared to the mean of the study area. The upstream of the rivers Nyamasaria and Nyando had lower Zn concentrations of 208.6 µg/L and 202.6 µg/L, respectively which showed significant difference at $p < 0.01$ compared to the mean of the study area. The variation of the Zn concentrations between the upstream and river mouth for these rivers could be attributed to the accumulation of the metal Zn as the rivers flood taking with them agricultural, domestic and industrial effluents which increase the metal load in them.

The site average concentrations in the lake and upstream water for Fe ranged from 649-4,340 µg/L with a mean of 2,588 µg/L (Table 32). The high water concentrations of 4,340 µg/L Fe and 3,368 µg/L Fe for Kisumu Port and Dunga showed significant difference ($p < 0.01$) from the mean. The concentration of Fe concentration in water for Trip C at Kisumu Port was more than double the second highest concentration among the other sampling sites and this high metal load was attributed to a possible oil spillage within the port area just before this trip which may have contributed to the higher average recorded at this site. The high concentration of Fe recorded at Dunga area was attributed to the oil spills from motorised boats which are common at this site. The low concentrations of 1,810 µg/L Fe, 1,799 µg/L Fe and 649 µg/L Fe for Port Victoria, Nyamasaria River Upstream and Offshore of Sio Port showed significant difference at $p < 0.01$ compared to the mean of the study area. The upstream of this Nyamasaria River is a mining zone (Appendix I: Plate 11, pg 139) for sand that is used for construction and this mining activity could be disturbing the already settled metal in the sand which is desorbed into the water and it is consequently swept downstream and this reduces the amount hence the low concentration recorded at this site.

Table 32. Seasonal variation of mean concentration of Iron Fe (µg/L) in water in the studied area during 2006-2007

	AAS Analysis					ICP-MS Analysis
	Wet season		Dry season		Average site concentration	
Site	Trip A	Trip B	Trip C	Trip D		Trip A
Lake						
2	4,596	3,276	7,120	2,366	4,340	na
3	3,420	3,270	3,169	2,971	3,208	289
4	1,890	1,730	2,178	1,440	1,810	11.8
5	3,860	3,005	3,012	3,595	3,368	2,440
6	3,372	3,126	3,017	2,929	3,111	2,030
8	3,853	1,306	3,039	3,998	3,049	1,012
10	3,620	3,093	3,166	1,462	2,835	20.2
12	2,845	2,116	2,319	1,998	2,320	1,140
15	895	756	87	857	649	na
16	2,153	3,271	2,774	4,153	3,088	na
Seasonal average	2,773		2,783		2,778	nc
Upstream						
7	2,277	2,170	2,193	1,982	2,156	972
9	1,865	1,263	1,951	2,117	1,799	489
11	3,406	3,576	1,544	734	2,315	12.0
13	2,571	2,035	2,126	2,018	2,188	670
Seasonal average	2,395		1,833		2,115	536
Lake and Upstream average	2,665		2,512		2,588	nc

na-Not analysed, nc – Not calculated.

At $p < 0.05$: LSD = 2114.97 for sites, LSD = 4702.31 for seasons, LSD = 2991.03 for interactions between sites and seasons.

Sites: 2 - Kisumu Port, 3 - Kisumu Car Wash, 4 - Port Victoria, 5 - Kisumu Dunga, 6 - Sio River Mouth, 7 - Sio River Upstream, 8 - Nyamasaria River Mouth, 9 - Nyamasaria River Upstream, 10 - Nyando River Mouth, 11 - Nyando River Upstream, 12 - Sondu-Miriu River Mouth, 13 - Sondu-Miriu Rivers Upstream, 15 - Sio Port Offshore and 16 - Hippo Point Offshore.

The seasonal average concentration variation of Fe during the rainy season was higher in relation to that of the dry season. This metal showed highest concentration in all sites compared to the other metals analysed. This probably could be due to its highest concentration in the sediment and probable desorption into water when the concentration in water goes down. This could also be related to the extensive use of Fe in the steel industry in Kisumu City and its environs and this activity increases its proportionate amounts entering the environment of the aquatic lake.

It was generally noted that the wet season on average recorded higher metal concentrations compared to the dry season. These results are in agreement with the assertion by Bugenyi (1979) and Wright (1982) that metal concentration levels vary seasonally since as observed by Mance (1987) during the rainy season more metals are washed out from the soils and from flooded grounds. The current results also are in agreement with Okonkwo and Mothiba (2005) who observed that the metal concentrations in river water for the wet season are generally higher than that of the dry season and they attributed this to runoff from land into rivers during the wet season consequently increasing the suspended particulate loads in the rivers. Okonkwo and Mothiba (2005) had also noted that Cd and Pb occur in fertilizers as impurities and this increase their chance of getting into water during runoff. The present study recorded lower metal concentrations at the upstream sites of the rivers compared to the downstream sites. This was attributed to accumulation of the trace metals as the river progresses towards the lake. This is in agreement with Greichus *et al.*, (1977), Bugenyi (1979) and Saad (1981) who observed that high metal levels are associated to river mouths where metals bound to particles settle especially if the river drains a contaminated area.

There was no much difference in concentration of Pb between the Lake and upstream water and Estate water samples (Table 33). The average metal concentrations for various metals in the estate water samples were lower than those of lake and upstream water samples, however, Fe showed a large difference in concentration with the lake and upstream samples recording an average of 2,588 µg/L (Table 33).

Table 33. Comparison of metal concentrations (µg/L) in water of different water sources with past studies and maximum international allowable concentrations for water quality for different uses

		Metal				
	Type of water	Cd	Pb	Cu	Zn	Fe
Lake Victoria Basin water sources[a]	Rain	ND	ND	47.9	228.5	216.5
	Well	ND	13.8	48.0	213.5	132.5
	Municipal water	ND	20.8	44.7	267.9	522.6
	Private Treatment	ND	3.4	37.8	221.0	98.0
	Lake (Winam Gulf)	ND	14.2	53.6	237	2,778
	Upstream	ND	8.9	51.5	224	2,115
Lake Victoria water[b]	Municipal supply	0.25	67	17.1	532	ng
	Raw water	ND	67	16.9	48.4	ng
Lake Nasser[c]	Raw water	1.5	3.2	2.9	147.6	106.1
KEBS[d]	Drinking water standards	5	50	100	5,000	300
WHO[e]		3	10	1,000	5,000	300
NRC[f]		ng	50	ng	ng	ng
USEPA[g]		5	50	1,000	5,000	300
UK[h]		ng	50	3,000	5,000	200
EU[h]		5	10	1,000	100-5,000	200
Canada[h]		5	50	1,000	5,000	300
USA[h]		5	15	1,000	5,000	300
Russia[h]		3	100	2,000	5,000	300
EU[h]	Fisheries and aquatic life	ng	ng	5-112	30-2,000	ng
Canada[h]		0.2-1.8	1-7	2-4	30	300
Russia[h]		5	100	1	10	100

ND-Not detectable, ng -Not given.

[a]Present study 2006/7 Kenya, [b]Ochieng (1987) Kenya, [c]Soltan *et al.* (2005) Egypt, [d]KEBS (1996), [e]WHO (1998), [f]NRC (1979), [g]USEPA (1979, 1980) USA, [h]Neubauer and Wolf (2004).

There were positive significant correlations in the Fe:Pb and Fe:Cu at $p < 0.05$ for the Lake and upstream river water samples (Table 34). Similarly the Cu:Pb showed reasonable positive correlations. These correlations point to a common source for these three metals in the water and this probably explains why the three metals showed a very high concentration during Trip C at Kisumu Port while the concentration of Zn was little affected during Trip C in comparison to the other trips. Indeed the Zn:Pb ratio showed a negative correlation ($r = -0.301$, $p < 0.05$) which points that these two metals have little in common in terms of their sources in the water analysed.

Table 34. Correlation matrices of the total heavy metals in sediment, fish and water samples

Sediment					
	Cd	Pb	Cu	Zn	Fe
Cd	1.000				
Pb	0.701*	1.000			
Cu	0.803**	0.745**	1.000		
Zn	0.884**	0.872**	0.741**	1.000	
Fe	0.920**	0.413	0.691*	0.696*	1.000
Lates niloticus					
Cd	1.000				
Pb	0.550	1.000			
Cu	0.763	0.957*	1.000		
Zn	-0.153	0.712	0.511	1.000	
Fe	-0.626	0.254	0.035	0.696	1.000
Oreochromis niloticus					
Cd	1.000				
Pb	-0.972	1.000			
Cu	-0.148	-0.279	1.000		
Zn	0.570	-0.317	0.705	1.000	
Fe	0.069	-0.825	-0.224	-0.323	1.000
Rastrineobola argentea					
Cd	1.000				
Pb	0.068	1.000			
Cu	0.394	0.921	1.000		
Zn	-0.683	-0.410	-0.460	1.000	
Fe	0.808	-0.507	0.152	-0.239	1.000
Estate water samples					
Cd	a				
Pb	a	1.000			
Cu	a	0.741	1.000		
Zn	a	0.722	0.008	1.000	
Fe	a	0.845	0.194	0.980*	1.000
Lake and upstream river water					
Cd	a				
Pb	a	1.000			
Cu	a	0.515	1.000		
Zn	a	-0.301	0.028	1.000	
Fe	a	0.663*	0.563*	0.168	1.000

a-Cannot be computed because at least one of the variables is constant, *.Correlation is significant at the 0.05 level (2-level), **.Correlation is significant at the 0.01level (2-tailed).

In all the four rivers, it was observed that accumulation occurs downstream. This is an indication that these rivers increase the metal load in Lake Victoria and these metals have their major sources upstream. These sources are most likely agricultural, industrial, domestic effluents and car washing activities upstream.

The average concentrations of Cd, Cu and Zn conformed to the KEBS, WHO, EU, Canada, USA and Russia permissible concentration limits set out for these metals in drinking water. While the average concentration of Fe in lake and upstream river waters exceeded all the allowable limits of drinking water, that of Pb conformed with the National limit of 50 µg/L but was above the WHO and EU guidelines for drinking water (Table 33). The metal Cd conformed with the fisheries and aquatic limits of Canada and Russia while that of Pb could conform only to the requirements of Russia. The concentrations of the metals Cu, Zn and Fe exceeded the permissible concentration limits of fisheries and aquatic life water for Canada, EU and Russia by big margins (WHO, 1998) (Table 33). Some fish species in Winam Gulf are getting extinct and their reproduction output is getting low. The excess heavy metals in the lake water could be one of the major contributing factors to the low tonnage of fish in the lake. This is a critical issue because some human communities with no access to clean water use this lake water for drinking, cooking, washing utensils and other domestic chores (Appendix I: Plate 12, pg 140) and hence end up endangering their lives as well as that of aquatic life resulting from the negative effects of excess levels of such metals.

4.5.3 Comparison of the metal concentration levels in sediment, fish and water

Comparison of the average metal concentrations of the three types of samples analysed showed that sediment concentrates the heavy metals highest followed by fish and last is water (Table 35). This was attributed to the fact that the metals are swept into the lake adsorbed to the sediments and organic particulates and most of these particulates could be settling onto the sediment without desorption of the metals. Fish are second in bioaccumulation since they acquire the metals from the water and from their food at the surface of sediments. The foods of fish analysed in this study include plants that grow on the surface of the already contaminated sediments and therefore fish have higher chances of bioaccumulating high levels of the metals.

Table 35. Comparison of the average metal concentrations in ppm across the types of samples on fresh weight basis

	Metal				
Sample type	Cd	Pb	Cu	Zn	Fe
Sediment					
Lake	1.01	31.4	29.8	144.2	35,224
Upstream	0.930	15.7	27.7	103.0	38,424
Fish					
Lates niloticus	0.046	0.190	0.749	7.948	9.978
Oreochromis niloticus	0.045	0.129	0.574	7.638	10.213
Rastrineobola argentea	0.052	0.243	1.290	49.525	27.545
Water					
Estate	ND	0.0097	0.0446	0.233	0.242
Lake	ND	0.0142	0.0536	0.237	2.778
Upstream	ND	0.0089	0.0515	0.224	2.115

4.5.4 Statistical analysis of properties across the samples

Most of the correlations between the metals in water and sediment had small negative correlations. This was attributed to the settling of suspended particulates from water to the surface of sediment or slight desorption of the metals from sediment into water when the concentrations in water got low.

Copper concentration in both *Lates niloticus* and *Rastrineobola argentea* showed little negative correlation with Cu concentration level in water while *Oreochromis niloticus* Cu concentration showed a more negative correlation with Cu concentration in water. Lead concentration in *Lates niloticus* showed little negative correlation with Pb concentration level in water while the concentration in *Oreochromis niloticus* had a sizeable negative correlation with Pb in water, however, *Rastrineobola argentea* showed less than average negative correlation with Pb concentration in water. Zinc showed little negative correlation with Zn in water while the correlation with *Oreochromis niloticus* had an average positive correlation with Zn in water. Zinc in *Rastrineobola argentea* and Zn in water had a near perfect positive correlation ($p < 0.05$). The metal Cd in *Lates niloticus* exhibited good positive correlations ($r = 0.611$ and $r = 0.848$, $p < 0.05$) with Pb and Fe in water, respectively. This is supported by the known ability of $Fe(OH)_3$ for Cd adsorption (Moalla *et al*. 1998). The Cd in *Oreochromis niloticus* also showed a near perfect positive correlation ($r = 0.915$, $p < 0.05$) with Zn in water while it showed a more than average positive correlation ($r = 0.671$, $p < 0.05$) with Cu in water. The Cd in *Rastrineobola argentea* had a good positive correlation ($r = 0.730$, $p < 0.05$) with the element Pb in water while it exhibited negative correlations ($r =-0.838$ and $r =-0.747$, $p < 0.05$) with the metals Cu and Zn respectively in water. The metal Pb in *Oreochromis niloticus* showed a good positive correlation ($r = 0.833$, $p < 0.05$) with the Cu in water while the same metal showed substantial negative correlations ($r = -0.706$ and $r = -0.723$, $p < 0.05$) with the metals Pb and Fe respectively in water. The metal Pb in *Rastrineobola argentea* showed a sizable negative correlation ($r = -0.783$, $p < 0.05$) with the element Fe in water. The metal Cu in *Oreochromis niloticus* showed good positive correlations ($r = 0.848$ and $r = 0.869$, $p < 0.05$) with the elements Pb and Fe, respectively, in water while there was a more than average negative correlation ($r = -0.632$, $p < 0.05$) with Cu in water. The Cu in *Rastrineobola argentea* exhibited slightly more than average negative correlations ($r = -0.569$ and $r = -0.576$, $p < 0.05$) with the Zn and Fe in water respectively.

The metal Zn in *Lates niloticus* exhibited a negative average correlation ($r = -0.566$, $p < 0.05$) with the Fe in water. The Zn in *Oreochromis niloticus* exhibited more than average positive correlations ($r = 0.524$ and $r = 0.687$, $p < 0.05$) with the metals Zn and Fe in water respectively. The metal Zn in *Rastrineobola argentea* species exhibited a significant positive correlation ($r = 0.989$, $p < 0.05$) with Zn in water and also a good positive correlation ($r = 0.880$, $p < 0.05$) with the metal Cu in water while there was a more than average negative correlation ($r = -0.639$, $p < 0.05$) with the metal Pb in water. The metal Fe in *Lates niloticus* exhibited more than average negative correlations ($r = -0.621$ and $r = -0.654$, $p < 0.05$) with the metals Zn and Fe in water respectively. The metal Fe in AG showed good positive correlations with the metals Pb and Fe in water respectively while there was a more than average negative correlation ($r = -0.637$, $p < 0.05$) with Cu in water. There was little correlation between the metal Fe in *Oreochromis niloticus* and the metals in water.

The pH of water showed slightly more than negative average correlation with Cu levels in water ($r = -0.541$, $p < 0.05$). Total alkalinity showed positive correlation with Cu concentration in water with significant difference ($r = 0.576$, $p < 0.05$). Dissolved oxygen registered a positive correlation with Zn concentration level in water with significant difference ($r = 0.678$, $p < 0.05$).

4.6 Analysis of the Hypotheses

The hypothesis that 'the concentrations of the heavy metals are highest during the wet seasons compared to the dry seasons' holds according to the results realised for water, sediment and fish. However, the metal Pb contrasts with this conclusion in water as well as in *Lates niloticus* and *Oreochromis niloticus* samples analysed.

The second hypothesis that the metals are widely dispersed in water, sediment and fish holds since wide variations in concentration were noted from the point of entry.

The third hypothesis that 'the concentrations of the various heavy metals in Lake Victoria, upstream and non-river water sources in the sampled Kisumu estates are above the nationally and internationally accepted standards for drinking water and water quality for fisheries and aquatic life' holds for Fe and Pb while it does not for Cd, Cu and Zn.

The fourth hypothesis that 'the concentrations of the various heavy metals in non-river water sources are higher than those of Lake Victoria' does not hold considering the mean values of estate, lake and upstream waters presented on Table 35. However, considering the individual estate water sources, the hypothesis holds for Pb in well and municipal waters as well as Zn in municipal water (Table 33).

CONCLUSION

Sediments accumulate metals many more times compared to fish and water. The order of accumulation is Sediment > Fish > Water.

Metals in sediments are more bioavailable compared to the metals in fish and therefore can be desorped into the water much more readily than from fish. *Lates niloticus* and *Oreochromis niloticus* fished out from Winam Gulf of Lake Victoria are safe to consume, however, *Rastrineobola argentea* need to be consumed after detaching its head to get rid of the gills and therefore reduce the levels of the bioaccumulated metals. It was noted that the metal Zn goes beyond the international concentration levels recommended, however, the speciation studies have proved that it is only 76.2% of the Zn concentration in *Rastrineobola argentea* that can be bioavailable to the consumer's body. Since the international standards are worked out using the total concentration level it implies that consumption of this species of fish without detaching its head is still very safe. The speciation study of the heavy metals in the three species of fish sampled from Winam Gulf is a reassurance to the consumers on the safety of fish consumption in this area.

Water sampled from Winam Gulf of Lake Victoria contains exceedingly high concentration levels of the metal Fe and is therefore unsafe to drink this water without undergoing the recommended clean up processes. The water has also Pb levels that are above the limits of some countries/international organizations. This is therefore an urgent call to the concerned authorities to put in place remedial measures before this heavy metal pollution problem goes out of hand. The concentration of the heavy metals reduces as one moves away from the water inlets as well as from the shores of the lake. It is the strong tidal waves especially in the evening that could mainly be accounting for the wide dispersion of the heavy metals from their major entry points into the offshore of the lake.

RECOMMENDATIONS

- Consumers could detach the head hence the gills before cooking *Rastrineobola argentea* to alleviate the levels of the heavy metals in the species since as noted by soltan.*et al.* (2005) and Kishe and Machiwa (2001), gills, liver and stomach are among the most biaccumulator organs in fish
- The concerned parties should sensitize the public on the dangers of using the river and lake waters of Lake Victoria basin in cooking and other domestic chores that aid the heavy metals to be ingested.
- Well equipped wells should be sunk to alleviate the clean water shortage problem. The public should be encouraged to trap rain water and use it specifically for cooking and drinking as it is relatively safe.
- If river or lake water has to be used for washing utensils then the items should be thoroughly rinsed with clean water.
- The public should be informed that treating the river water with recommended chemicals only kills bacteria; however, the heavy metals will always remain intact till proper adsorption methods are employed to trap these metals and therefore reduce their levels to the safe concentrations.
- Since Pb and Fe concentrations in Lake Victoria water exceeds drinking water requirements even after water treatment, the treatment process should be revised as a priority by the concerned authorities. This is because a large population of Kisumu City residents could be dependant on the municipality piped water supplies and therefore could be at great risk.
- This study has only tried to concentrate on areas which are thought to be polluted. To get a clearer picture of what could be happening it is recommended that a study be carried out that will incorporate the

centre of the lake. It could be that 5 to 10 Km away from the shores of Winam Gulf of Lake Victoria, water and sediment have negligible amounts of the heavy metals and therefore most of the aquatic biota is very safe. However, the water that is pumped out of the lake for municipal water supplies is collected from the lake shores and therefore the human population is still at risk and hence remedial measures need to be taken.

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