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DEPARTMENT OF CIVIL ENGINEERING

Impacts of alum residues from Morton Jaffray water works on water quality and fish, Harare, Zimbabwe.

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Integrated Water Resources Management of the University of Zimbabwe.

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DECLARATION

I, **Norah Muisa**, declare that this research report is my own work. It is being submitted for the degree of Master of Science in Integrated Water Resources Management (IWRM) in the University of Zimbabwe. It has not been submitted before for any degree in any other University.

Signature: _____

Date: _____

The findings, interpretations and conclusions expressed in this study do neither reflect the views of the University of Zimbabwe, Department of Civil Engineering nor of the individual members of the MSc Examination Committee, nor of their respective employers.

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LIST OF SYMBOLS AND ABBBREVIATIONS

AAS	Atomic Absorption Spectrophotometry
Al	Aluminium
ANOVA	Analysis of Variance
APHA	American Public Health Association
AU	African Union
BcF	Bioconcentration factor
CEQG	Canadian Environmental Quality Guidelines
CSO	Central Statistics Office
DO	Dissolved Oxygen
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
IAEA	International Atomic Energy Agency
ICMP	Integrated Catchment Management Plan
MAV	Minimum Allowable Values
MDL	Method Detection Limit
MJ	Morton Jaffray
n.a	Not available
PBC	Province of British Columbia
SPSS	Statistical package for the Social Sciences
TaL	Total aluminium
TDS	Total Dissolved Solids
TS	Total Solids
TWQR	Target Water Quality Range
UMRB	Upper Manyame River Basin
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
ZINWA	Zimbabwe National Water Authority
ZNPWMA	Zimbabwe National Parks and Wildlife Management Authority

DEDICATION

This study is dedicated to my beautiful daughter, Sibonginkosi Zikhali, and the other ones still to come. You are truly the reason why I wake up everyday. Everything I do, I do for you.

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ABSTRACT

Metal pollution of freshwater resources due to human activities is a major problem confronting most urban centres in developing countries. A study was carried out on the impacts of aluminium (Al) sulphate (alum) residues from Morton Jaffray Waterworks on Al concentrations in fish, sediment and water in the Manyame River and Lake Manyame. Morton Jaffray Waterworks and Lake Manyame are located southwest of Harare, the capital city of Zimbabwe in the Upper Manyame Catchment. Lake Manyame is the third largest commercial fishery in Zimbabwe and the second-largest raw water supplier to Morton Jaffray. Morton Jaffray supplies drinking water to Harare and its satellite towns. Alum is the sole coagulant used at Morton Jaffray such that aluminium hydroxide dominates the resulting residues. Alum doses and frequency of discharge of residues have been increasing since mid-90s than is optimal. These residues are discharged directly into Manyame River immediately upstream of Lake Manyame at a total rate of approximately, 108 800 m^3/day which is about 80 and 90 % of the 60 to 70 tonnes of alum used each day. However, most studies in literature on metal water pollution and toxicity to aquatic life have mainly focused on all other sources of pollution other than water treatment plants. Residues from Morton Jaffray Waterworks have been linked to fish kills in Lake Manyame. Bioaccumulation of aluminium in fish and the subsequent toxic effects have been reported in literature. Therefore, the study investigated the extent to which the waterworks' residues affected the water and sediment quality of the river and lake and fish in the lake, particularly, Nile tilapia (*Oreochromis niloticus*), in respect of Al concentrations. Total aluminium concentrations in the water, sediments, residues and fish were determined. In addition, other parameters were measured namely; total solids, total dissolved solids, conductivity, pH, dissolved oxygen, temperature, and sediment texture. Eight depth integrated water samples, and sediment grab samples and six adult fish were collected between January and March, 2010, from Manyame River and Lake Manyame at six selected sites. Three grab residue samples were collected before discharge. Variations in all the parameters among the sites, and fish tissues were significantly different (ANOVA; $p < 0.05$). Aluminium levels surpassed permissible maximum levels and other levels in documented studies for all the sites during both sampling campaigns. This indicated the presence of other sources of aluminium though their magnitude was less compared to Morton Jaffray. Total aluminium levels were generally in the order of; sediments > fish > water while in fish, the general order was; liver > kidney > gill > muscle. The residues are greatly increasing aluminium concentrations in the affected water bodies and fish. There is need for interventions in water treatment practices for the protection of aquatic life as well as human life which is highly dependent on the aquatic life and water. These interventions include: treatment of the residues before discharge; strict monitoring of the quality of the residues before discharge; local standards for quality of residues discharged into waterways from waterworks; re-use of the residues as well as reduction of alum used for water processing or use of other effective but harmless coagulants.

1. INTROD UCTION

The levels of heavy metals in aquatic ecosystems are now among the highest reported in the world and they are reaching unprecedented levels (Adham, 2001; Akan *et al*., 2009). Consumption of food containing these contaminants by aquatic organisms may not only affect their productivity and reproduction but it will also affect the health of human beings that depend on these organisms as a source of protein (Davies *et al*., 2006). Several heavy metals have been studied worldwide and they include; mercury, lead, cadmium, zinc, aluminium, copper, among many others (Esmail *et al*., 2009). Findings from these metal pollution studies suggest that these metals are persistent in nature and tend to bioaccumulate and biomagnify in living organisms (Retief *et al*., 2009). Mostly, the top carnivores that include fish will have higher concentrations of the toxic metals much greater than the ambient water concentrations (Sarkar *et al*., 2008). Metals that include aluminium, arsenic, cadmium, chromium, lead, mercury, and silver are reported to have human health effects (McGee, 1991). The overall consequences of trace metal contamination in aquatic ecosystems are a reduction in biological species richness and diversity and a change in species composition (Javed, 2005).

Aluminium is one of the important factors in the toxicity of acidified waters to freshwater fish species because low pH and high concentrations of Al have been of particular concern in affected waters (Sharma, 2003). Aluminium is also one of the toxic constituents of water that seldom occur in high concentrations in unimpacted sites (DWAF, 1996). Although aluminium is naturally present in nature where it constitutes about 8 % of the earth's crust (Azzaoui *et al*., 2008), aluminium is generally found in only trace concentrations of less than 1.0 mg/l in natural waters (PBC, 1998). Aluminium may be present in residues from waterworks as a residual from the alum coagulation process and Al is practically present in almost all surface waters (Bartram and Balance, 1996). The concentrations of aluminum in waters with pH near neutral will rarely exceed a few tenths of a milligram per litre. Median concentration in rivers has been reported to be 0.24 mg/l with a range of 0.01 to 2.5 mg/l (Bartram and Balance, 1996). Aluminium can become present at elevated levels in water bodies due to anthropogenic sources (Coetzee *et al*., 2002; Sharma, 2003). In addition, Al is rapidly adsorbed onto sediments and precipitated from solution (PBC, 1998). Aluminium is rarely found in humans and animal organisms but avoiding it in the environment is difficult as it is abundant in the environment (Uyanik *et al*., 2008). Aluminium in drinking water is of more concern than in food in relation to human health effects (Ghori and Yaqub, 1999).

1.1 Background

Elliott *et al*. (1990) reported that water treatment sludges do not pose any heavy metal hazard particularly in land application and subsequently, aquatic ecosystems. Tebutt (1998) went further to say that, in the United Kingdom, the sludges from water works are actually landfilled or even sprayed in moorlands and forests. However, the study by Elliott *et al*. (1990) was

looking at those metals that are regularly monitored even in sewage effluents that include; copper, cadmium, zinc, lead, chromium and nickel and not the aluminium that is dominant (according to the same authors) in the wastes coming from the water treatment plants that were being studied. This study by Elliott *et al*. (1990) was, however, motivated by the fact that data on heavy metals' content in water treatment sludges was very limited even though these sludges or residues are most likely to contain considerable amounts as with sewage wastes. In short, Elliott *et al*. (1990) was concerned with the less focus being awarded to sludges from waterworks in relation to metal water pollution.

A study on sediments and water was undertaken by Abdullah *et al*. (1995) in Malaysia on the Linggi River exposed to water works sludge' dumping and it was shown that aluminium accumulates in sediments and it was concluded that the aluminium may be potentially toxic to aquatic life. It was later confirmed for some other sources of pollution other than water treatment that aluminium bioaccumulates and biomagnifies in aquatic organisms, including fish, (Coetzee *et al*., 2002; Sharma, 2003). Effects of Al toxicity in fish include increased mortality, changes in feeding habits, genetics, growth and physiology, malfunctioning gills (Kegley *et al*., 2009). Aluminium is toxic to fish at concentrations above 0.2 mg/l (Giller and Malmquist, 1998) or even at 0.1 mg/l (PBC, 1998). Canadian Water Quality Guidelines for Protection of Aquatic Organisms (CEQG, 2003) use 100 µg/l Al for freshwater whereas the United States Environmental Protection Agency (EPA) guideline for continuous exposure to Al by aquatic life is 87 µg/l (EPA-AU, 2006). Aluminium toxicity has also been shown in humans where it causes neurological disorders such as dialysis encephalopathy and onset of Alzheimer's disease (Prolo *et al*., 2007). This is particularly so for patients on haemodialysis being administered with oral aluminium hydroxide as a phosphate binder (Ghori and Yaqub, 1999). High aluminium intake in normal humans causes renal excretion that is elevated many-fold in renal failure patients because they are unable to excrete the excess Al from their bodies (Ghori and Yaqub, 1999).

Alum ($Al_2(SO_4)_3.14H_2O$) is commonly used in water treatment processes as a coagulant (Degrémont, 1991). The principle behind the use of aluminium sulphate is that it contains positively charged trivalent aluminium particles that will react with the alkalinity in the raw water to give aluminium hydroxide flocs, $Al(OH)_3$, which are denser than the original individual suspended solid particles and can settle easily (Degrémont, 1991). The doses usually required of coagulants are 30-70 mg/l (Tebutt, 1998). Water treatment works generally produce residues that comprise the sludge from the sedimentation tanks or clarifiers following chemical coagulation, or precipitation and softening, and the backwash waters from the backwashing of the sand filters after the filtration process (Viessman and Hammer, 1998). The mixture of sludge and backwash water is termed residues, a term that is adopted in this study (Viessman and Hammer, 1998). Morton Jaffray also generates these residues (Nhapi, 2007). Aluminium hydroxide, $Al(OH)_3$, flocs are dominant in these waste products (hence, the name alum residues or sludge), as well as silt, clay, sand and humic particles removed from the raw water and any other chemicals used during the process (Elliott *et al*., 1990; Viessman and Hammer, 1998). The backwash water from any water treatment plant should be discharged into a lagoon first where it

settles for some time after which the clear supernatant would then be directed into a river every 24 to 72 hours (Tebutt, 1998). As a matter of fact, Wanielista *et al*. (1984) had reported that runs of backwashing of filters can vary from 20 to 140 hours with 30 to 40 hours between washings being considered optimum. The supernatant can also be recycled to the plant influent (Viessman and Hammer, 1998). Alum sludge or waterworks sludge should be directed to sludge drying beds where it is dewatered, dried and disposed of in landfills and/or incinerated (Tebutt, 1998). Water quality regulations now require processing of these wastes before discharge (Viessman and Hammer, 1998).

Lake Manyame is situated downstream of the discharge point of the residues from Morton Jaffray waterworks. Lake Chivero and Lake Manyame supply approximately, 416 000 and 84 000 m^3 raw water per day, respectively, to Morton Jaffray Waterworks (MJ) according to a JICA Report (1996). In turn, Morton Jaffray supplies drinking water to Harare and its satellite towns of Chitungwiza, Epworth, Ruwa and Norton (Nhapi, 2007). These urban areas constitute a population of approximately 2.6 million of the 12 million population of Zimbabwe. Morton Jaffray Waterworks (MJ) uses aluminium sulphate (alum) as the sole coagulant (Makado, 2007) and aluminium hydroxide is dominant in the residues according to Wanielista *et al*. (1984); Tebutt (1998); Viessman and Hammer (1998). Alum doses have been increasing (40 mg/l to 100 mg/l) from 1982 and 1995, respectively, due to deterioration of raw water quality (Makado, 2007; Moyo, 1997). Approximately, 60 to 70 tonnes of alum are used per day at Morton Jaffray to treat about 544 000 m^3 raw water per day. About 20 % of the treated water is wasted away as residues per day which is approximately 108 800 m^3/day, according to key personnel in the City of Harare water quality assurance section. This 20 % loss in water treatment is also higher than 5 to 10 % which is experienced elsewhere (Uwimana *et al*., 2007). Thus, the residues emanating from Morton Jaffray waterworks are concentrated with Al and are also in huge quantities such that the lagoons can no longer contain the huge quantities of wash waters while the sludge drying beds are not yet in use. This is because sludge drying beds are not yet in use at Morton Jaffray while lagoons have become too small to use for the sludge or the wash waters. Therefore, there is direct disposal of Al-laden residues into Manyame River upstream of Lake Manyame every 4 to 6 hours without prior treatment (Makado, 2007).

1.2 Problem statement

There are limited studies concerning aluminium pollution from waterworks' residues. However, the residues discharged by Morton Jaffray water treatment plant have been linked to fish kills in Lake Manyame though these are still assertions (Moyo, 1997; Magadza, 2003). No study has been carried out in the country concerning the residues from Morton Jaffray and their effect on fish as well as quality of the receiving water bodies. It has been shown elsewhere, however, that Al accumulates in sediments and water and that Al bioaccumulates in fish and its toxic effects in fish have been reported in literature (Abdullah *et al*., 1995; Giller and Malmquist, 1998; PBC, 1998; Coetzee *et al*., 2002; Sharma, 2003; Kegley *et al*., 2009) as well as in humans (Prolo *et al*., 2007).

1.3 Justification

Lake Manyame is the third largest commercial fishery in Zimbabwe providing a source of livelihood for the fisherpersons and a major source of protein for the residents of Harare and its satellite towns (ZPWMA, 2005). The Lake is also a prime fishing destination attracting local, regional and international fishing enthusiasts (ZPWMA, 2005). *Oreochromis niloticus* is an important and common fish in the lake and one of the most common in the market where it is marketed fresh, dried or canned (ZPWMA, 2005). Pollution of Lake Manyame with aluminium may have a negative effect on fish existence in the lake. Monitoring of fish in this study will have an added advantage of giving an evaluation of water quality which can be easily understood by stakeholders who are non-specialists. This helps to ensure their participation towards safeguarding the ecological integrity of water resources.

Residents of Harare and its satellite towns are also dependent on the water supplied by Morton Jaffray. Aluminium in drinking water has been linked to occurrences of Alzheimer disease and other neurological disorders (Ghori and Yaqub, 1999; Prolo *et al.*, 2007). Nhapi (2007) recommended increased raw water abstractions from Lake Manyame. This recommendation was motivated by the fact that the levels in Lake Chivero decline rapidly in the dry season and also, abstraction from Lake Chivero has reached the abstraction limit. This recommendation might not be appropriate in light of a potential risk of excessive amounts of Al in the raw water from Lake Manyame. Also, Gumbo (1997) recommended an Integrated Catchment Management Plan (ICMP) for the Upper Manyame River Basin (UMRB). In order to produce this ICMP for the UMRB, Gumbo (1997) saw it as necessary that there be the implementation of surveys of water, sediments and groundwater of the UMRB to determine the dynamics of pollution, and the magnitude of the sources of pollution, among other strategies. Maintenance of the health of these water resources would thus ensure availability of an adequate water supply, in both quantity and quality, which is crucial for economic development and sustenance of ecosystems.

Overall, this study will continue to contribute to the scientific body of knowledge on impacts of wastes from water treatment works on aquatic resources. Specifically, findings from this study will not only help to understand the impacts of Morton Jaffray on the health of fish and the water quality in Lake Manyame; these results will directly inform the Integrated Catchment Management Plan, other programmes and organizations in the formulation of pollution prevention strategies. This study is also a move towards achieving some of the Millenium Development Goals to which Zimbabwe is a signatory, particularly, Millenium Development Goal Number 7 of ensuring environmental sustainability. This study is also in line with the Integrated Water Resources Management (IWRM) principle on ensuring ecological integrity of the environment.

1.4 Objectives

1.4.1 Main objective

To investigate the impacts of residues from Morton Jaffray Waterworks on the concentration of aluminium in water, sediments and fish in Lake Manyame.

1.4.2 Specific Objectives

1. To determine the quality of residues discharged into Manyame River and compare with effluent standards for discharge in surface waters according to ZINWA (2000).

2. To determine the level of total aluminium in the water, sediments and fish tissues (gills, skeleton, kidney and muscle) in Manyame River, Lake Manyame, Lake Chivero and Cleveland dam and compare with previous studies and water quality guidelines suggested by EPB 356 (2006) and EPA-AU (2006).

3. To determine the levels of other physico-chemical parameters that affect solubility and bioavailability of Al to organisms that include; pH, dissolved oxygen (DO), temperature, total dissolved solids (TSS), total solids, electrical conductivity, sediment texture and adsorbed water content and compare with literature and permissible levels as suggested by DWAF (1996); EPB 356 (2006) EPA-AU (2006).

2. LITERATURE REVIEW

2.1 Waste generation, characterization and disposal at water treatment plants

Basic processes involved in water treatment include: coagulation and flocculation; sedimentation; filtration and disinfection (Tebutt, 1998). Clark *et al*. (1977) also had additional processes particularly for water from a lake or reservoir or for hard, turbid surface waters that include lime softening and use of activated carbon to control taste and odour. Coagulation is a process which uses coagulants to neutralize the negative surface charge around the colloids so that they can bind together to form flocs that are denser and able to settle (Degrémont, 1991; Metcalf and Eddy Inc, 1995). The higher the valence of the coagulant, the more effective the coagulation action will be hence the wide use of Al and other ions such as iron, besides other reasons such as cost and "perceived" harmlessness (Degrémont, 1991; Viessman and Hammer, 1998). Schultz-Hardy theory says that "a trivalent ion is ten times more effective than a divalent ion" (Degrémont, 1991). Morton Jaffray water treatment plant is currently using aluminium sulphate as the sole coagulant (Makado, 2007; Moyo, 1997). The principle behind the use of aluminium sulphate is that it contains positively charged trivalent aluminium ions which react with the alkalinity in the raw water to give aluminium hydroxide floc $Al(OH)_3$ which precipitates together with the bound colloidal and other suspended particles (Tebutt, 1998). This action also applies to other coagulants. Flocculation is a mechanical process that proceeds after coagulation to induce collisions between the bound particles and result in agglomeration and formation of even denser particles or flocs which can easily settle to the bottom of the flocculation tanks (Metcalf and Eddy Inc, 1995; Tebutt, 1998). Sedimentation follows where the supernatant from the flocculation tank is directed for further clarification of the water. Sedimentation removes the settleable solids and then concentrates these solids into a smaller volume of sludge (Metcalf and Eddy Inc, 1995; Tebutt, 1998). The filtration process further clarifies the supernatant from the sedimentation tanks and is the process that results in the production of liquid wastes or the backwash waters (Viessman and Hammer, 1998). Sludge and backwash waters are thus the wastes generated by water treatment plants (Clark *et al*. 1977). Together, the two types of waste products are termed residues (Viessman and Hammer, 1998). This is the term and definition adopted for use in this study. Lastly, disinfection is undertaken to further eliminate the living organisms that may still be present in the water before the final water is directed into the distribution system (Metcalf and Eddy Inc, 1995; Tebutt, 1998). What is obtaining from this paragraph is that wastes from a water treatment are dominated by the coagulant elements, for example, alum wastes are dominated by $Al(OH)_3$ flocs.

The composition of the residues varies widely depending on the character of the source of raw water and chemicals added to it during water treatment (Clark *et al*. 1977). Possible raw water sources for any community include; rainwater, surface water (lakes, rivers, reservoir

impoundments) and ground water (Wanielista *et al*. 1984). According to Clark *et al*. (1977), the characteristics of the sludge from a water treatment plant using the above-mentioned treatment processes will typically include the following: silt and detritus from the pre-sedimentation deposit; a mixture of inerts, organics and chemical precipitates, including metal oxides from settling tanks sludge; flocs of coagulated colloids and unspent coagulant hydroxides dominating the filter backwash water. Driscoll and Letterman (1988) showed that total Al concentration in water increased fivefold from 10 ± 9 µg/l in raw water to 49 ± 9 µg/l in filtered water after treatment with alum. In the same study, Al in raw water was in the form of particulate Al (3 ± 6 µg/l) or non-labile (organic) monomeric form (7 ± 6 µg/l) while concentrations of the toxic labile (inorganic) monomeric form was insignificant. In addition, 11 % of the incoming Al (Al in raw water plus Al from alum use) was not removed during water treatment and was carried over in the final potable water. Of the remaining Al, 71 % was the inorganic Al [comprised of 52 % alumino-hydroxy (21.8 ± 10 µg/l) and 19 % alumino-fluoride (8 ± 4 µg/l) complexes] with organic Al constituting 29 % (12 ± 8 µg/l) of the remaining total Al. Thus, the higher the concentration of the incoming Al, the higher the residual Al in the distribution system and the Al that becomes part of the waste products. These findings might also be taken to mean that 89 % of the Al in incoming water may have been "lost" probably as wastes in sludge and backwash waters, in addition to natural sources as they were unaccounted for in the above breakdown. Also, the proportion of the dissolved, toxic, inorganic forms of Al in raw water is usually insignificant, especially in a water body with a neutral –alkaline pH range.

The desired disposal of these wastes will range between pressure filtration, centrifugation, drying in drying beds and drying lagoons, all of which should be followed by landfilling or incineration (Clark *et al*. 1977; Viessman and Hammer, 1998). The same authors also reported another option of discharging to a municipal sewer or to produce soil conditioners for use in agricultural lands if beneficial to soil. Another use for the sludge is chemical recovery particularly, alum recovery, and recalcination of lime precipitates (Clark *et al*. 1977). However, Clark *et al*. 1977 pointed out that alum recovery is not widely practiced because the chemical that is usually produced is of poor quality for further use and the recovery process will still lead to production of more solid and liquid wastes that would need further handling. According to Viessman and Hammer (1998), water supply processes should also include management of the catchment. However, it is pointed out by the same author that, in contrast, the main focus of most water treatment plants is on the provision of potable water fit for its expected uses. In addition, the choice of the processes and chemicals used is dependent on the effectiveness to achieve the desired reactions and also, cost-effectiveness. It seems therefore that the attention towards catchment protection in water supply systems is overcome by the need to supply water at the least cost possible and as effective as possible with minimal regards to the environment. However, what is clear from the current trends in waterworks' waste disposal is that the discharge of chemical residues direct into surface waters is a historical practice which is against the current trends in water quality regulations which now require processing of these wastes to minimal environmental degradation.

2.2 Sources of heavy metals in aquatic systems

According to Rashed (2001), heavy metals may enter and contaminate the aquatic environment through such sources as; geological weathering (the source of natural /background levels), industrial metal processing, leachates from waste dumps such as mine dumps, landfills. Additional sources of heavy metals identified worldwide also include; afforestation, power generation, air depositions of dust and aerosols, tsunamis, deliberate or accidental oil spills, sewage effluents, pest or disease control agents applied to plants (Javed, 2005; Etesin and Benson, 2007). In Zimbabwe, metal pollution has been attributed to sewage irrigation, mining wastes, sewage and industrial effluent and agricultural runoff (Gumbo, 1997; Mathuthu *et al*., 1997; Moyo, 1997; Nyamangara *et al*., 2008). Aluminium also enters the aquatic environment via, soil erosion, leaching of minerals and soils, contamination from atmospheric dust and precipitation or acid rain (Rosseland *et al*., 1990; Neal *et al*., 2004).

The above sources of metal pollution are the widely published in literature so far. There is less attention or published studies done concerning water treatment plants as water pollution sources. However, Abdullah *et al*. (1995) showed that waterworks sludge dumping in Malaysia resulted in Al accumulation in sediments and water. However, Tebutt, (1998) reported that in the United Kingdom, waterworks' sludge (also called alum sludge) is viewed as relatively inert which poses little problems compared to sewage or wastewater works' sludge. The alum sludge is thus, either sprayed in moorlands or in forested plantations. Also, it is reported by Villella (2007) that, historically, many water treatment plants in the United States of America discharged sludge directly into streams and lakes because there appeared to be little environmental significance to the practice. In Zimbabwe, sludge generated from Morton Jaffray is discharged into Manyame River through a retention tank or pumped to farmlands for irrigation uses though there used to be a lagoon which became small with increased population growth, water consumption and production and thus increased production of the wastes (Nhapi, 2007).

Therefore, the studies above concerning sources of heavy metals have indicated that the geology of an area also influences Al concentrations in water besides pH and other diffuse and point sources such that these metals are already present in the environment at optimum levels that are not adverse to the environment. It is rather the human actions that either alter water quality conditions in such a way as to cause the naturally harmless elements to become available in harmful forms and concentrations or directly add these metals to the water systems. Also noticeable is that wastes from waterworks are less focused on and handled. It also shows that residues from waterworks are unperceived modes of possibly significant pollution to water bodies probably because there has been less focus on them as one of the major sources of surface water pollution.

2.3 Occurrence of aluminium in the environment

Aluminium is the third most abundant element (about 8 % of the earth's crust) in nature after oxygen and silicon occuring in minerals, rocks, air, food and water (Azzaoui *et al*., 2008).

Aluminium is amphoteric, soluble in extremely acidic (pH<6) and alkaline (pH>8.5) conditions and insoluble as Al hydroxide precipitates between pH 6.5 to 8.5 (Srinivasan *et al*., 1999; CEQG, 2003). Aluminium exists as a trivalent cation, Al^{3+}, and because also of its small ionic radius (0.51), it is too reactive to be found free in nature (Srinivasan *et al*., 1999). Total Al comprises suspended Al, colloidal Al and monomeric Al of which the first two form the particulate fraction of Al (Prolo *et al*., 2007). Monomeric Al occurs as the non-labile or water-insoluble (organic) Al that is associated with dissolved organic carbon and as the labile or water soluble inorganic Al (Prolo *et al*., 2007). The water- soluble monomeric Al is comprised of hydroxyl, fluoride, silicate, carbonate and sulphate complexes as well as the aquo-Al (Prolo *et al*., 2007). It is this labile inorganic monomeric Al that has been implicated in toxicity studies concerning Al and aquatic biota, including fish (Giller and Malmquist, 1998; Bittl *et al*., 2001), particularly the hydroxyl complexes; Al^{3+}, $Al(OH)_2^+$ and $Al(OH)^{2+}$, (Sharma, 2003).
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Generally, there is a strong correlation between pH and heavy metals such as copper, zinc, lead *etcetera*, in water bodies (Nyamangara *et al*., 2008). This strong correlation has also been confirmed for Al in water bodies and for soils as well (Srinivasan *et al*., 1999; Sharma, 2003; Neal *et al*., 2004). Davies and Day (1996) and Sharma (2003) agree that aluminum becomes most soluble and bioavailable in acidic waters with a pH of 5 or less. Chapman (1996) also reported this fact but went on further to generalize it to all the other metals, including copper (Cu), iron (Fe), manganese (Mn) with a few exceptions. However, Tebutt (1998) maintained that even at any pH outside the range of 5 and 8.5 pH units; aluminium hydroxide becomes bioavailable as the soluble and toxic aquo-aluminium ion, Al^{3+} which is in more agreement with findings by Srinivasan *et al*. (1999). The findings between pH and Al thus have got a common view that Al becomes most soluble below a pH of 5 but contrast each other concerning the other side of the pH scale, *i.e*., the alkaline side. However, considering that Al is amphoteric, it may also be true that Al becomes most soluble at a pH that is extremely alkaline*, i.e.*, above 8.5 which is the rationale or concept adopted in this study.

A study carried out in the United States of America (US) revealed that Al in groundwater is very negligible (0.2 to 100 µg/l) when compared with surface water concentrations (Sorenson *et al*., 1974). This is most likely considering that surface waters are most directly affected by anthropogenic sources of pollution besides the geology which, according to Rashed (2001), is the main source of natural levels of any metal. Sorenson *et al*. (1974) also found out that the levels of Al in natural surface waters were in the range of 10 to 2000 µg/l (or 0.01 to 2 mg/l). This agrees more/less with PBC (1998) and Bartram and Ballance (1996) which reported that Al is present in trace concentrations of at most 1 mg/l or 2.5 mg/l, respectively, in natural waters. The same study also showed that, in surface waters that are acidic (pH 4 to 5), Al levels were in excess of 40 000 µg/l or 40 mg/l which is way above the finding of Giller and Malmquist (1998) of 2 mg/l, in the same country, which caused toxicity effects to fish though the species of Al in the latter study was not mentioned.

From these paragraphs, it can be summarized that Al occurs everywhere in nature, it is amphoteric in water and highly reactive such that Al will almost always occur bound to other substances. This means that Al is less likely to be found in huge quantities as the toxic ionic forms in water unless in extremely acidic or alkaline conditions. Naturally, Al quantities will not exceed at most 5 mg/l while in acidic surface waters it can increase to 40 mg/l. Al solubility is thus impacted mostly by pH conditions in a water body. Aluminium in groundwater is negligible compared to surface waters.

2.4 Accumulation of metals in sediments

High levels of heavy metal concentration in sediments and water is one major example of environmental pollution (Rapin *et al*., 1983). Accumulation of heavy metals in streams and lakes is more effectively monitored by analyzing the sediments rather than the water because metals tend to accumulate more in sediments and aquatic biota than water (Nyamangara *et al*., 2008). Most metals are insoluble at neutral to alkaline pH ranges, which is the pH range of most natural freshwater bodies, which means that metals will therefore precipitate and attach to river sediments in most water resources (Nyamangara *et al*., 2008). Aluminium is one of the metals that forms insoluble precipitates in this pH range such that sediments will most likely contain significant amounts of this metal in surface waters. Abdullah *et al*. (1995) and Coetzee *et al*. (2002) observed that the concentrations of total Al significantly increased in the sediments compared to the water media. This basically shows the remarkable efficiency of the settling, adsorbing, scavenging and assimilating particles. These settling particles include; phytoplankton and biological debris, calcium carbonate, iron (III) (hydr) oxides, manganese (III, IV) and aluminium silicates, which are the clays and oxides (Stumm and Morgan, 1996). Kamau *et al*. (2008) also established that most trace metals are found adsorbed on suspended particulate matter which is transported to the bottom through flocculation and sedimentation processes to form the metal-rich sediments. The Fe and Mn oxides have very strong affinity for heavy metals, especially Fe (III) oxides even in small proportions, while calcium carbonates have a relatively low affinity for metals. Surfaces of organisms also have a strong affinity for heavy metals (surface complex formation) such as Cu, lead (Pb), Zn, *etcetera*. Metals can be absorbed mistakenly with nutrients in the assimilation process by plants and it is important to note that, especially in eutrophic lakes, photosynthetic production and sedimentation of the dead metal-rich photosynthesizing organisms are actually dominant processes (Stumm and Morgan, 1996).

2.5 Mobilization or immobilization of heavy metals in sediments

Metals become bioavailable when they are mobilized from the sediments where they were bound into the water column. There are processes which affect the metal fluxes from the bottom to top or vice versa in a water body such as a lake which include; bioturbation, water turbulence, concentration gradients between the top and the bottom (Bentivegna *et al*., 2004). These processes will effect movement of metals, usually from the bottom, and mixing of sediments and overlying water (Petersen *et al*., 1991). Mineralization processes can also affect the mobility of metals when metal-containing particles are mineralized thereby releasing the bound metals

(Ciceri *et al*., 1992). Organic materials can be mineralized by microorganisms under oxic conditions, or the Fe and Mn oxides can be reduced during anoxic conditions at the bottom of lakes thereby releasing the bound metals (Stumm and Morgan, 1996). Factors or processes that influence mobility also influence the bioavailability and toxicity of the metals to the aquatic biota (Bentivegna *et al*., 2004). Contaminant bioavailability is the degree to which contaminants can be taken up by plants or animals (Hansen and Berry, 1996).

There are also varieties of factors that influence the solubility and mobility of sediment-bound contaminants. These factors include; i) the season, ii) decomposing trace metal – containing organic matter content, iii) lowering of pH, iv) changing redox conditions, v) increased salt conditions (Stumm and Morgan, 1996). Concentration of metals in sediments is dependent on the season to some extent according to a study by Ronagh *et al*. (2009). The authors showed that the differences in sediment-metal concentrations among different seasons were not significant ($p > 0.05$) though the variations showed higher concentration in the summer season than other seasons. These variations were explained as being due to differences in the sources of contamination and due to physical-chemical conditions in the sediment-water interface. These findings may be further explained by that sediments are almost static in a location over considerable time periods as they are non-flowing, unless when they are re-suspended by rains and re-located. In lakes for example, during the dry season when water level reduces due to high evaporation and water abstractions, reduced sediments become exposed to the atmosphere and they get oxidized (Kocharyan *et al*., 2003). However, during the wet periods when the water levels start to increase, the previously exposed surfaces at the bottom become covered with water creating anoxic conditions and the sediments start releasing protons which also results in the mobilization of bound metals which were harmless to aquatic organisms in the bound form (Kocharyan *et al*., 2003). Anoxic conditions also reduce metal oxides, *i.e*., Fe and Mn, and they then release the bound metals. Decomposing organic material results in reduced dissolved oxygen at the sediment surface, the decomposing bacteria also tend to use up the iron and manganese oxides and the oxidized forms of nitrate creating reducing conditions which result in the mobilization of the once immobilized metals (Stumm and Morgan, 1996; Billon *et al*., 2002). Metals become soluble and mobile in the overlying water column.

Bentivegna *et al*. (2004) added sediment grain size and oxides and sulphides of iron (Fe) and manganese (Mn) to the factors affecting solubility and mobility of metals bound to sediments. Sediments comprised of small grain-sized particles with a larger specific surface area and high organic material for adsorption will mostly be associated with reduced heavy metal bioavailability (IAEA, 2003; Kamau *et al*., 2008). This is because most of the metals will be bound thus immobilized and unavailable to organisms and will not pose any harmful effects to organisms. The metals are removed from solution either through precipitation during oxide formation or they are adsorbed to already formed oxides (Dong *et al*., 2000). Sulphides tend to react with Fe under anaerobic conditions to form a solid precipitate called iron sulphide. Other metals such as copper (Cu), zinc (Zn), nickel (Ni) *etcetera*, have been reported as displacing Fe

from its sulphides and becoming bound to the sulphide themselves hence becoming insoluble and less bioavailable (Bentivegna *et al.*, 2004).

It is concluded from the above two sections (2.4 and 2.5) that concentrations of metals in sediments show the status of pollution over time and that the sediments are usually containing the largest share of these substances in any water body. Contaminants from the sediments can become detached from the sediments and become harmful to aquatic life. Plants, among many other particles, are also likely to take up these metals during nutrient uptake and then when the plants die off they will sink and settle to the bottom adding to the pool of metals in the sediments. Mathuthu and Ndapadzwa (1997) also did a study on water hyacinth in Zimbabwe and also established that these plants do take up metals such as copper, *etcetera*. Thus, sediments are basically the sources and sinks of the metals in any water body as metals bound to sediments can be released from these storage sites and be available to the overlying water and also to organisms, including plants, therein, with possible effects if conditions change with time. Therefore, heavy metal concentrations in water, sediments or fish or any other media are affected by a myriad of factors, besides direct anthropogenic factors. It is thus important to carry out measurements of metal accumulation in the sediments so as to be able to assess the potential dangers of toxic or even naturally less toxic metals in any water body.

2.6 Bioaccumulation of heavy metals

2.6.1 Accumulation and effects in aquatic organisms

Bioaccumulation is the process by which a compound is taken up and accumulates in an organism, from elements of its environment, such as water, food, and sediments (Refief *et al.*, 2009). The analysis of biological tissues which accumulate toxic residues over life spans of many years, especially tissues of fish and mammals, is one method for providing a very long-term integration of environmental conditions particularly the presence of these toxic residues (Kudirat, 2008). Metals are non-biodegradable and are considered as major environmental pollutants causing cytotoxic, mutagenic and carcinogenic effects in animals (More *et al.*, 2003).

Small increases in the concentrations of heavy or trace metals in the aquatic environment can result in reduction in species diversity and ultimately, loss of nutrient cycling in streams and lakes (Rauf *et al.*, 2009). Bittl *et al.* (2001) explained this for Al as being due to Al affecting the metabolism of phosphorous (P) probably due to P immobilization in river basins resulting in limited quantities of P in lakes or disturbance of in-lake P cycling. The mechanism through which Al exerts its effects in aquatic organisms, particularly fish, seems to be interference with the ionic and osmotic balance as well as respiration resulting from coagulation of mucus on the gills (DWAF, 1996; Phippen and Horvath 1998; Bjerknes *et al.*, 2003; Sharma, 2003). Binding of Al to the gill epithelium and intracellularly within lamellar epithelial cells is a prerequisite to acute toxicity (Phippen and Horvath 1998). This will cause osmoregulatory failure, respiratory failure and then death (Rosseland and Staurnes, 1994). Sharma (2003) also reported that the

number of fish and amphibians, in the lakes studied, was declining due to fish deaths as a result of reactions of Al ions with proteins in the gills of fish, and embryos of frogs.

High mortality of the Atlantic salmon also occurred from fjord-based fish farms in western Norway and this was often related to snowmelt and heavy rainfall during the winter (Bjerknes *et al.*, 2003). Mount *et al.* (1990) and Gunn and Noakes (1987) explained that heavy rains and snowmelt cause excessive leaching of Al from the catchment soils and that these short term changes can have severe negative effects on aquatic life. In a study carried out by Giller and Malmquist (1998), toxicity of Al to fish occurred at Al concentrations above 0.2 mg/l though there was no mention of the species of Al measured. High concentration of Al in water (between 50 and 200 µg/l) has strong correlation with Al accumulation in fish organs such as the kidney, skeleton and gills whereas liver and muscles accumulate relatively low concentrations of less than 50 µg/l (Rodushkin *et al.*, 1995). Such an accumulation in different organs may have some negative effects depending on total Al concentrations unlike direct toxic effects of ionic Al forms (Rodushkin *et al.*, 1995). However, the toxicity of total aluminium (TaL) is strongly influenced by pH and dissolved organic matter (CEQG, 2003). Dissolved organic carbon generally acts to decrease the toxicity of Al in fish while low or high (<5 or >8.5, respectively) pH increases toxicity (CEQG, 2003). Under acidic conditions (pH<5), dissolution of Al occurs in lakes which causes asphyxiation in fish due to Al oxide deposition out of solution on the gill filaments as the oxide precipitates (Chapman, 1996).

It is concluded from this section that bioaccumulation occurs in fish, as well other aquatic organisms, and that environmental conditions play an important role in enhancing the bioavailability of these metals to the organisms. Dissolved organic carbon, pH, among others, particularly influence Al bioaccumulation and increase the toxicity of Al. The main mode of Al toxicity is through the gills where they can cause clogging of the gills which are used for respiration in fish causing even death in extreme cases. The inorganic, ionic forms of Al are particularly toxic though the amount of total Al will determine the amount of the ionic forms present at any particular time. Aluminium toxicity is also elevated when the Al levels are high, regardless of species of Al. It is thus becoming increasingly difficult to ignore the urgent need for a thorough assessment of the environment to which the fish are exposed to daily, that is, the sediments and water, as well as the fish itself in Lake Manyame, as far as pollution with Al is concerned.

2.6.2 Accumulation of metals in different organs

Kotze *et al.* (1999) showed that bioaccumulation of metals in the fish studied occurred in the following order of decreasing intensity: liver>gills>skin>muscle. Further studies have confirmed these findings but in different fish such as *Oreochromis niloticus, Cyprinus carpio* and *Labeo umbratus, Tilapia nilotica, Tilapia zilli, Clarias anguillaris, Protoptenus, Eutropius niloticus and Synodentis budgetti* (Rashed, 2001; Coetzee *et al.*, 2002; Vinodhini and Narayanan, 2008; Akan, 2009; Rauf *et al.*, 2009). Rauf *et al.* (2009) also obtained the same results as Kotze

et al. (1999) and established that the metal concentrations in the liver and gills were significantly different (p<0.01) and the minimum concentrations in the liver (4.26±1.57 and 6.23±1.14 µg/g) were higher than for gills (1.10±0.53 and 1.46±0.52 µg/g) for cadmium and chromium, respectively. These authors concluded that the main target organs for metal accumulation in fish are the liver, gills and vertebral column though this varied with the different fish species. The muscles had the least metal concentrations in all these studies. However, Adham (2001) showed that the kidney of *O. niloticus* is the principal store organ for most of the metals that were studied. The gills, skeleton, kidneys, liver and muscles are the main target organs for Al toxicity in fish while the first three are the most susceptible organs to Al bioaccumulation in fish (Sharma, 2003). In contrast, Coetzee *et al*. (2002) had shown that Al is accumulated mostly in the gill and liver tissue, followed by the muscle and skin tissues and that this uptake occurred primarily through the gills just as with any other heavy metal. These studies on Al accumulation agree that the gills are among the most susceptible to Al accumulation while the muscle accumulates the least but disagree in terms of the liver as Sharma reported that the liver and the muscle are the least susceptible. No conclusive trend can be drawn from these results though, only that the gills are quite important in metal accumulation as well as for *O. niloticus*, the species used in this study. From all these studies done so far, it seems that different metals are more susceptible to different fish organs than others and that this susceptibility differs with fish species. Hence, this study will also serve to add to the scientific knowledge base the actual organ in *O. niloticus* that accumulates the most aluminium.

For fish, the gills, skin and digestive tract are potential sites of absorption of water-borne chemicals. The muscle and skin, as well as the skeleton, are the edible parts of a fish. The skin and gill tissues are characterized by a mucus layer on the outer surface (Coetzee *et al*., 2002). Varanasi and Markey (1978) explained that the presence of this layer indicates that these tissues act as excretion routes involving sloughing off of mucus from their surfaces. However, the gills are in direct contact with water and thus provide a high surface area for absorption or ion entry/exit and also, the gills can act as a depot tissue where the uptake of metals significantly exceeds the elimination (Coetzee *et al*., 2002; Rauf *et al*., 2009). Absorbed chemicals can be transported by the blood to either a storage point such as the bone, or to the liver for transportation.

Metals transported to the liver, may be stored there, excreted in the bile, or passed back into the blood for possible excretion by the kidney or gills or stored in extra hepatic tissues such as fat (McNicol and Scherer, 1991). It is important to note that for some species of the family of *Oreochromis*, for example, *O. mossambicus* of the same feeding habit as *O. niloticus*, the pH in its stomach decreases significantly (from about 6 to as low as 2.9) after feeding commences (Deacon, 1998). The author reported that this reduction in pH could make the metals more bioavailable from the food sources and silt in the stomach. The metals could then be taken up via the intestines to other parts of the body and bioaccumulate. The liver acts as the main detoxifying organ in all the animals in which it is present (Coetzee *et al*., 2002). Kotze *et al*.

(1999) elaborated on this as that under unpolluted conditions; the liver will act as a storage organ for metals through binding with metallothioniens and under normal conditions, the liver will thus contain higher metal levels than any other tissue. In polluted conditions however, the liver will strive to detoxify the fish body of the excess metals. By so doing, it is possible that the liver can over-compensate and find that the liver in fish in polluted areas will have lower levels of the metals than fish in unpolluted areas. Detoxification is the removal of toxins, or poisons which is part of homeostasis and helps to maintain the composition of blood in a steady state (Taylor *et al*., 1984). Therefore, the concentration of metals in gills reflects their concentration in water where the fish lives, whereas the concentrations in liver represent storage of metals in the water (Romeo *et al*., 1999). The kidney is the passageway of metals unabsorbed by the metabolic system or detoxified by the body (Vinodhini and Narayanan, 2008). It is thus clear that the most impacted upon tissues in fish are the gills and liver whilst for aluminium; the gills, liver, kidneys and the skeleton are the most affected though this may vary from one fish species to another. The liver tissue concentrations can thus help show the pollution status in a water body.

2.6.3 Bioaccumulation of metals over time

Temporal or seasonal variations in bioaccumulation of heavy metals have been shown in various studies in different aquatic biota (Kotze *et al*., 1999; Coetzee *et al*., 2002; Rauf, 2009). Examples of biota studied by these authors include: fish- *Oreochromis mossambicus* and *Clarias gariepinus*; bivalve mollusks-*Anodontites trapesialis*; tapeworms - *Bothriocephalus acheilognathi*, respectively. These variations indicated an increased level of bioaccumulation under high flows for mobile, top surface dwellers, which include *O. mossambicus* and *O. niloticus*. Retief *et al*. (2009) found out that metal bioaccumulation in benthic dwellers increased under low flows. This was generally attributed to the influence of variations in metal concentrations in the surrounding environment. Metal-laden sediments are re-suspended in the wet season to increase contact with fish at the surface while in the dry season, sediments are undisturbed and in contact with the bottom dwellers during low flows. Also, gills are known to get clogged with fine sediment particles, a situation which can even lead to suffocation of the fish when flows increase (Buerman *et al*., 1995). When fish are stressed like this, especially, during periods of higher flows and increased turbidity, respiratory and metabolic processes tend to increase leading to increased uptake of contaminants from water hence higher metals in the fish during higher flows than low flows. Another reason could be increased contaminants from diffuse and point sources during times of high flows (Kotze *et al*., 1999). However, Seymore (1994) had different observations whereby there were reduced metal concentrations in the top surface dwellers in higher flows than low flows and this was explained by the author as being due to dilution effects which reduce the metal concentrations in the water environment. Another reason for seasonal variations in bioaccumulation is the variation in animal physiology (Retief *et al*., 2009). Retief *et al*., 2009 also reported the type of sex, changes in reproductive cycles and stress due to manipulations and adaptations to new environmental conditions as contributing factors to changes in uptake, storage and excretion by organisms of metals.

Conclusion from the above studies is therefore that, bioaccumulation occurs differently in different types of aquatic biota under different seasonal conditions due to dilution effects, changes in physiology, habitat and mobilization of metal-bound sediments. These changes in metal levels in the organisms may be amplified by changes in the physiology of the organisms themselves to either reduce or increase the impact of the metals on the organisms. Sediments are thus a huge sink and source of metal pollution to biota such that present pollution may have future impacts as the pollutants will be stored in the sediment bank. Determination of metal accumulation should be done in both the dry and the wet periods to get a comprehensive true picture of bioaccumulation of Al.

2.7 General water quality parameters: Occurrences and effects

Sources and sinks of DO include surface re-aeration, sediment oxygen demand, photosynthesis and respiration (Metcalf and Eddy Inc, 1995) but mainly oxygen from the atmosphere and oxygen generated from photosynthesis (Abowei, 2010; Hunt and Christiansen, 2000). The growth of algae and weeds constitute a source of oxygen during daylight due to photosynthesis and a continuous oxygen sink due to respiration during the night. Dissolved oxygen is important for respiration (DWAF, 1996). Standard DO results at temperature ranges between 23 and 29 °C are 8.38 and 7.64 mg/l, respectively (Colt, 1984; DWAF, 1996). Metcalf and Eddy Inc (1995) and Egborge (1971) reported that DO is usually higher in the wet season due to increased water flows and subsequent re-aeration contrary to other findings which had lower results in the wet season (McNeely *et al*., 1979; Davies *et al*., 2006; Abowei, 2010). These lowered DO results in the wet season were attributed to increased runoff and turbidity from the surrounding catchment, decomposing organic and inorganic wastes as well as reduced photoperiod and photosynthetic activity. Hunt and Christiansen (2000) also support the findings that DO is less when there is overcast weather, *i.e*., in wet periods, which reduces photosynthesis and hence oxygen production, which becomes lower than oxygen consumption through plant respiration. Hunt and Christiansen (2000) added that floating vegetation mats (macrophytes) can result in very low DO levels as they completely smother water surfaces. In contrast, they reported that submerged plants generally produce about six times more oxygen through photosynthesis than is consumed in respiration. Floating plants reduce DO levels through the following ways; they block oxygen transfer from the atmosphere, prevent light penetration for photosynthesis by submerged plants, floating plants also do not add to oxygen in the water but are involved with oxygen exchange with the atmosphere, and their root systems provide a constant supply of organic matter which, accompanied by their death and decay, exert an oxygen demand to the water. Sensitivity of fish to depleted oxygen usually depends on the species, age and behavourial patterns whereby juvenile fish are more sensitive than adults (Abowei, 2010; DWAF, 1996). Dissolved oxygen is an important parameter for aquatic life because detrimental effects can occur if DO levels drop below 4 to 5 mg/l, depending on aquatic species (Metcalf and Eddy Inc, 1995; Dallas and Day, 1993). Low levels of DO also present stressful conditions to fish which then increases their respiratory and metabolic rates resulting in increased uptake of dissolved toxic constituents from the water environment and their effects (Tebutt, 1998). Oxygen concentration above saturation

is indicative of eutrophic conditions and may cause gas bubble disease in fish and also favour growth of blue-green algae which may be a problem to other water uses (DWAF, 1996). Depletion of oxygen can cause fish deaths due to impaired respiration, depressed feeding or embryonic development and hatching success (Clark, 1996).

Typical range of pH in surface waters is 4 to 11 while in well buffered fresh waters it may be between 6 and 8 (DWAF, 1996). The livable pH range for most fish is from 5.5 to 10 (Moyle, 1993). Just like DO, pH also varies diurnally and seasonally. Photosynthesis is a major factor affecting pH particularly in productive systems due to removal of carbonate ions from solution hence creating alkaline conditions in the water. Temperature and the concentrations of inorganic and organic constituents also affect pH besides biological activity. An increase in temperature by 20 ℃ may result in a drop in pH by 0.1 of a unit. Lowered pH affects the solubility of toxic trace metals and thus their toxicity to aquatic life forms. Very low pH can result in death and more subtle effects while a pH less than 6 has got effects on fish oogenesis, egg fertility, growth of fry, egg hatchability or growth (Matthews, 1998). Changes in pH also cause changes in ionic and osmotic balance in aquatic organisms which may lead to reduced growth and fecundity, and also changes to community structures. A strong correlation between pH and most heavy metals is also apparent in most heavy metal studies as highlighted in Section 2.3. Also, pH determines desorption / adsorption capacity of sediments of contaminants (IAEA, 2003). Generally, pH less than 5 results in the solubilization of such metals as iron (Fe), manganese (Mn), Al and many others except for, for example, lead (Chapman, 1996).

Temperature of natural inland surface waters generally varies between 25 ℃ and 35 ℃ (Alabaster and Lloyd, 1980). In a study conducted by Abowei (2010), significant correlation was observed between temperature and other parameters such as conductivity and pH. Temperature showed significant seasonal variations and values were higher in the dry than wet season. This trend has also been reported in other earlier studies (Mathuthu *et al*., 1997; Braide *et al*., 2004). Higher temperature in the dry period is expected as heat transfer from the sunlight into the water body will warm up the water surface. The toxicity of most substances and the vulnerability of organisms to these substances are increased as temperature increases (DWAF, 1996). Temperature also has an impact on DO content of freshwaters whereby an increase in temperature will result in reduced DO of water (Colt, 1984; Hunt and Christiansen, 2000). Lydersen *et al*. (1990) also established that temperature affects Al speciation and solubility in water whereby at a low temperature of 2 ^{o}C at a higher pH, the most toxic species of Al would be prevalent than at a higher temperature of 20 ^{o}C.

An increase in total solids also has a direct bearing on the total dissolved solids content or conductivity of any water (Metcalf and Eddy Inc, 1995). The dissolved solids content of water will affect the water balance in the cells of aquatic organisms through osmotic imbalances (Davies and Day, 1998). According to Davies and Day (1998), if solids outside the body are lower than inside the body then there will be a net movement of water into the organism's body and vice-versa. This can be taken to imply that in an environment with increased dissolved

solids content, water and the associated dissolved constituents that include dissolved metals will find their way easily into the body of the organisms. This phenomenon should also explain the impacts of increased or decreased conductivity in water considering that conductivity and dissolved solids content are positively and directly related (Metcalf and Eddy Inc, 1995; Dallas and Day, 2004). The solids content of water is influenced by the degree of weathering, chemical composition of rocks, evaporation and rainfall from the catchment (EPA-AU, 2006).

3. STUDY AREA

3.1 Location

The study area includes the Upper Manyame River Basin (UMRB) or Catchment and mainly, Lake Manyame and the Manyame River (Fig. 3.1). The UMRB extends upstream from Lake Manyame and it is where Harare and its satellite towns, Chitungwiza, Norton, Ruwa and Epworth are located and is also the major source of raw water that supplies drinking water to these urban areas (Gumbo, 1997). The UMRB consists of the Manyame River and its tributaries, the Mukuvisi and Marimba River (Nhapi, 2007). Manyame River discharges water into man-made lakes, Chivero and Manyame, each situated 29 km and 33 km, respectively, south-west of Harare, the capital city of Zimbabwe (Chikwenhere, 2001) as shown in Fig. 3.1. Manyame River as well as the Sanyati, Gwayi and Shangani rivers, all feed into the Middle Zambezi river system (Bell-Cross and Minshul, 1988). The Zambezi (together with its tributaries) is the most shared river basin and third in size in Africa after the Congo and the Nile (Granit, 2000). Cleveland dam is located east of Harare further upstream the city of Harare and the Mukuvisi River, a tributary of Manyame River, and less impacted by the pollution sources from Harare as compared to Lake Chivero and Lake Manyame (formerly, Darwendale Dam) due to its upstream location (Fig. 3.1). It is located 2 km below the headwaters of Mukuvisi River, a tributary of the Manyame River (Machena, 1997). The major water bodies in the catchment include Lake Chivero, Lake Manyame, Prince Edward Dam and Manyame River. Morton Jaffray Water Treatment Works is the main water supply source for the city of Harare and its satellite towns and is located south-west of Harare along the Harare-Bulawayo Road (Fig. 3.1).

3.2 Morphology of water bodies under study

Lake Manyame has a full capacity surface area of 81 km^2 with a maximum water depth of 22.6 m compared to 27 m for Lake Chivero (ZPWMA, 2005). Lake Manyame has a drainage area of 3792 km^2 (Nhapi, 2007). According to records of the government parastatal for water resources development and management, the Zimbabwe National Water Authority (ZINWA), the lake is almost double the size or gross capacity (490 Mm^3) of Lake Chivero of about 250 Mm^3. Lake Chivero has a full capacity surface area of 26.5 km^2 (Nhapi, 2007). Lake Chivero drains an area of 2230 km^2 and the bulk of this water comes from the Manyame River system (80 %) followed by the Marimba and Mukuvisi rivers (Hillman, 1995).
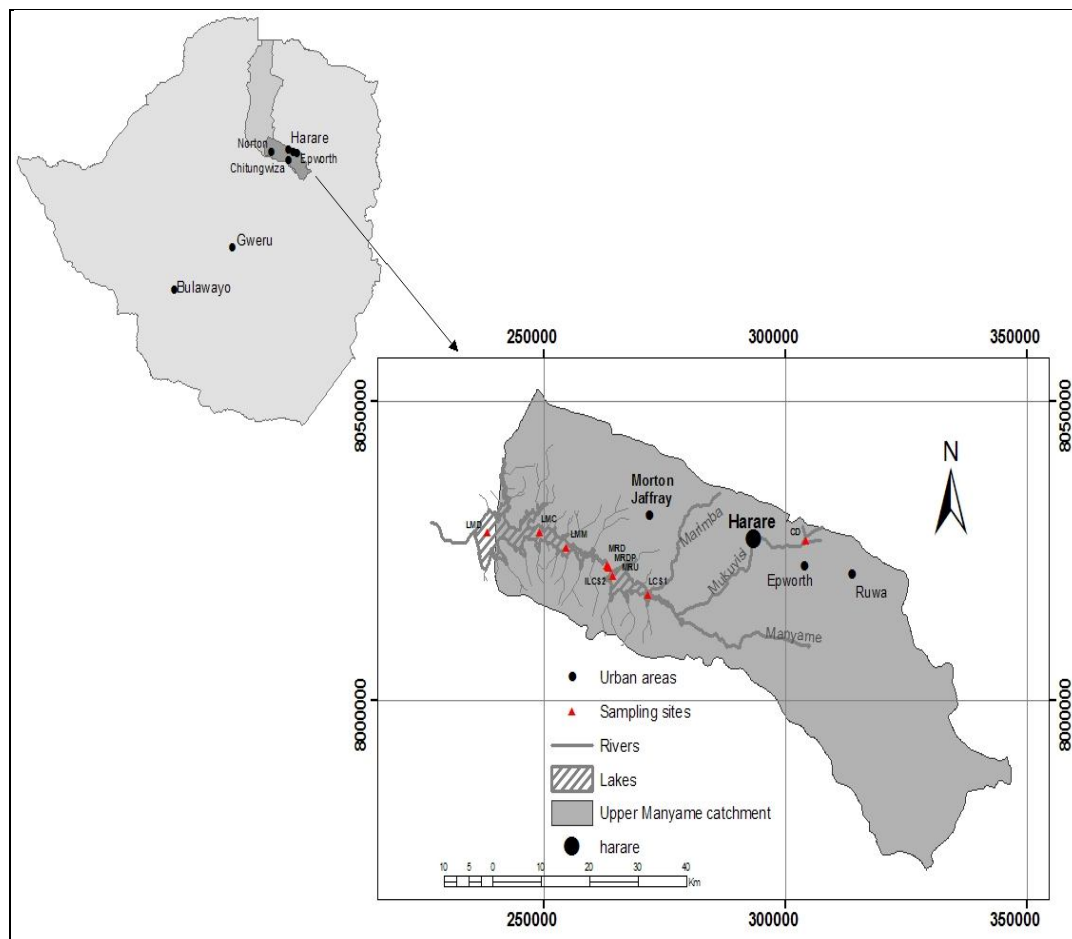
Figure 3.1: Study area map showing the location of Morton Jaffray water works and the sampling sites.

3.3 Fish assemblages

In Lake Manyame, the fish populations have been generally increasing due to eutrophication. The common species in the dam are *Oreochromis macrochir, Oreochromis niloticus*, *O. mossambicus Tilapia rendalli, Labeo altivelis, Clarias gariepinus* and *Hydrocynus vitattus.* The common species in the commercial fishery are *O. macrochir, T. rendalli* and *L. altivelis* (ZPWMA, 2005). The Manyame River is part of the middle of the Zambezi river system from which 58 indigenous fish species have been recorded, *Clarias gariepinus* being more abundant in the Manyame River and Lake Manyame than in Lake Chivero (ZPWMA, 2005). There are 27 reported fish species in Lake Chivero. The common ones include *Oreochromis niloticus, O. macrochir, O. mossambicus, Tilapia rendalli, Labeo altivelis, Clarias gariepinus* and *Hydrocynus vitattus* (ZPWMA, 2005). Cleveland dam is not used as a commercial fishery and there is no monitoring of its fish populations as compared to the other four major fisheries found in Zimbabwe that are Lake Kariba, Lake Chivero, Lake Mutirikwi and Lake Manyame.

3.4 Climate

The annual rainfall of Zimbabwe is 675 mm/annum while that of the UMRB is 830 mm/annum (Nhapi, 2007) which is higher than the national average. However, this rainfall varies in time and space over the catchment. The climate of the Upper Manyame catchment can be divided into three main seasons in a year (Thornton and Nduku, 1982), namely:

1. The rainy season is termed summer and falls between November and April. This summer season is characterized by wet weather and high temperatures 20±6 °C.
2. The winter season occurs from May to August and is characterized by cold and dry weather with temperatures averaging 14±7 °C.
3. Spring which is a hot and dry season that occurs between September and November. This season is characterized by average daily temperatures of approximately 22±6 °C. Intense rainfall is unlikely to occur although light falls may be expected.

3.5 Topography and geology

The UMRB is generally a gentle, undulating, featureless plateau which lies between 1300 and 1500 m above sea level with the largest portion of the catchment lying between 1400 and 1500 m (Thornton and Nduku, 1982). Lake Chivero was constructed downstream of the city of Harare at an elevation some 200 m lower than the city (Fig. 3.1). Lake Manyame is further downstream from Lake Chivero (Fig. 3.1). This location for the downstream reservoirs means that wastewater from the urban complex easily drains into them hence they are more prone to pollution as compared to the upstream Cleveland dam. Cleveland dam was built about 2 km from the source of the Mukuvisi River, a tributary of Manyame River. The Cleveland Dam catchment area is protected and the dam is situated upstream of Harare such that the water in the dam is considered unpolluted (Jarawaza, 1997).

The UMRB is almost entirely on a coarse-grained granitic rock except for some larger part of the northern chunk and a part of the north-western boundary (Munzwa, 1982; Baldock *et al.*, 1991). The major constituents of granite constituting more than 10 % of the granite include; microcline, albite, quartz (Klein and Hurlbut, 1977). Of these constituents, microcline consists of 18.4 % Al_2O_3, the content of which is not specified in the other constituents but just that the three constituents are dominated SiO_2. In addition, the catchment of the Manyame River is generally constituted by granitic, sandy soils (Magadza, 2003).

3.6 Population

The Manyame catchment is the most urbanized in the country. It contains one city, Harare, and three small towns, Ruwa, Chitungwiza and Norton. In addition, there is now another urban area called Epworth. Of these urban centers, Harare, Chitungwiza and Ruwa are located upstream Lake Chivero hence, impacts more directly on Lake Chivero (Zanamwe, 1997). Marshall (1997) noted that the most important ecological factor of Lake Chivero and Lake Manyame is their eutrophication status. The author attributed this phenomenon to frequent sewage overflows and

increased amounts of sewage effluents due to increased population in the above mentioned urban areas. The increase in population dating from 1969 to the latest population census of 2002 is shown in Table 3.1. Growth rate for the whole population of Zimbabwe is 1.1 % per annum though the rate for all the other provinces and individual districts is not available as it could not be computed due to changes in the geographical areas of the provinces between 1992 and 2002 (CSO, 2002).

Table 3.1: Population of the major urban areas of the Manyame Catchment, 1969-2002.

Urban area	1969[a]	1982[a]	1992[a]	2002[b]
Harare	386 000	658 000	1 189 103	1 903 510
Chitungwiza	15 000	172 000	274 912	321 782
Norton	3 400	12 400	20 405	44 054
Ruwa			1447	22 038
Epworth	n.a.	n.a.	n.a.	113 884
Total Population	389 400	842 400	1 485 867	2 405 268
% of national population/area	7.60	11.20	14.29	20.67[c]

Source: [a]Zanamwe (1997), [b]CSO (2002), [c] Total national population used to derive this percentage is 11 634 663 according to CSO (2002), n.a means not available

However, using this background information and mere proportions generalizing this growth rate to all the areas, it can be envisaged that the current population (*i.e.*, 2010) would be 2 643 390. The major urban areas of the Upper Manyame catchment currently contains approximately 21 % of the national population of which Harare (currently contributing 16.36 % to the national population) is the largest urban area in the catchment in terms of population size as well as the surface area of the city (Table 3.1). The population of these major urban areas as a whole was estimated to reach an estimated 3.8 million people by 2010 (Gumbo, 1997).

3.7 Water and land use

Lake Chivero and Lake Manyame were built in 1952 and 1976, respectively, for the main purpose of water supply for the city of Harare as well as irrigation water supply for Lake Chivero (ZINWA files). Other uses include support for aquatic life and recreation (Nhapi and Tirivarombo, 2004). Cleveland dam used to provide drinking water source for the city of Harare until it became too small to supply increased demands of a growing population. Lake Chivero catchment area encompasses the following rivers: Mukuvisi, Manyame, and Marimba rivers, all of which flow through heavily industrialized and densely-populated areas on their way to the lake (Jarawaza, 1997). The Manyame River is fed by Ruwa and Nyatsime rivers which drain the

towns of Ruwa and Chitungwiza, respectively. Mukuvisi and Marimba rivers receive runoff and wastewater from the city of Harare and this effluent is increased by effluent from Crowborough and Firle sewage treatment works, which are the major sewage treatment plants in Harare

Lake Manyame is situated in an intensive agricultural farming area where use of fertilizers and pesticides is high. The UMRB is however 90 % rural and 10 % urban (Nhapi, 2007). Munzwa (1982) established eleven (11) major land use categories, which are currently expanding, in the Upper Manyame catchment which are: lakes and dams; sewage farms; hospitals; industrial areas; Central Business District (CBD) and avenues; residential areas; cultivation and rural subsistence farming; cultivation and commercial farming; grassland and vlei; shrubland and woodland (including plantations). This land use pattern has a direct bearing on water pollution. Morton Jaffray abstracts its raw water from Lake Chivero and Lake Manyame. As of 1996, eight treatment chemicals have been used at the plant due to deteriorating quality of raw water (Moyo, 1997). These include; aluminium sulphate (coagulant), activated carbon (removal of taste, odour and toxic organic materials), sodium silicate (coagulant aid), hydrated lime (pH correction agent), chlorine (disinfectant), algae kill (copper sulphate), ammonia and sulphuric acid.

4. MATERIALS AND METHODS

4.1 Study design

4.1.1 Selection of sampling sites

Table 4.1 gives the names and locations of the sites that were chosen in this study. These sites are also shown in Fig. 4.1. Three sites were located in Manyame River of which one was upstream and two others were downstream of the discharge point (Figure 4.1; Table 4.1).
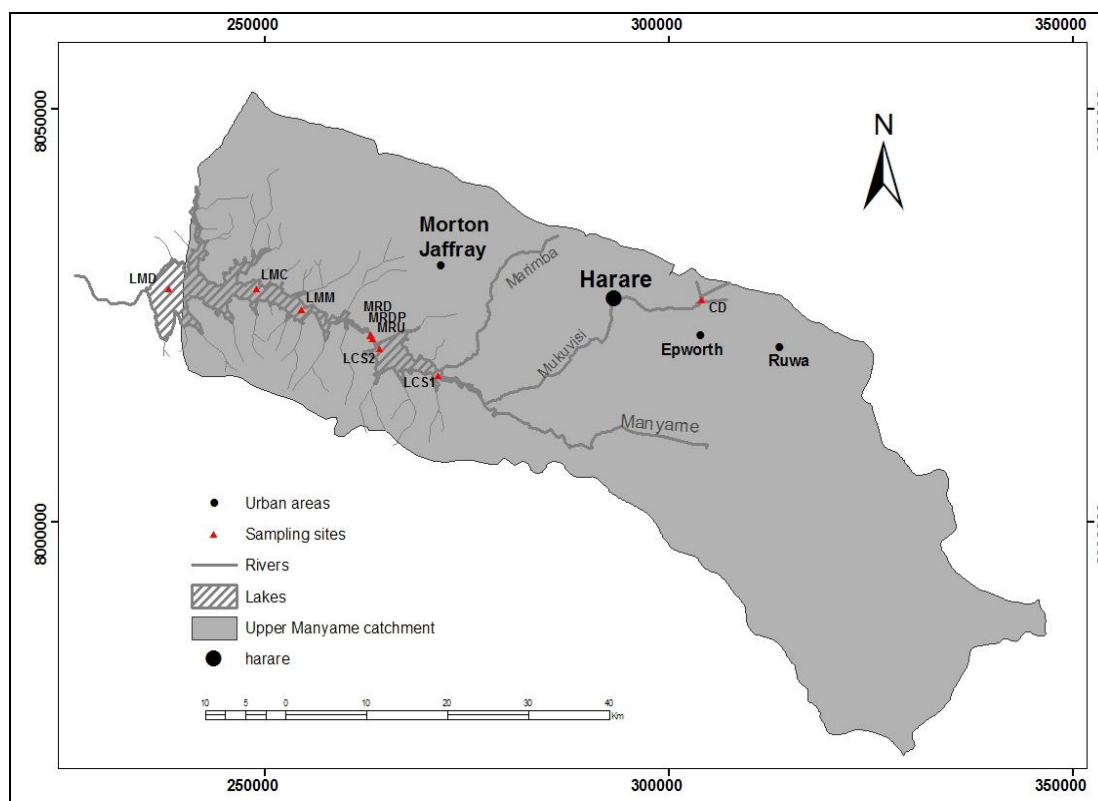
Figure 4.1: The sampling sites

These three sites are close together hence, they could not be separated in the diagram above and appears as if there is a single site. These sites were chosen to investigate the variations between the aluminium levels upstream and downstream of the point of discharge of the residues from Morton Jaffray. The sites are detailed as follows:

- **MRU -** This was located approximately 200 m upstream of Morton Jaffray discharge point. This site was the control site that was used to show the conditions in the river before pollution by the residues for comparison with the polluted sites downstream.
  MRDP - This site was immediately downstream (approximately 5 m) of the waste discharge point to determine the immediate impacts of the wastes on the concentrations of Al in the water, fish and sediments. This distance was also chosen due to accessibility reasons and also it is the only part just after the discharge point with an open body of water, otherwise, thereafter, the water is covered by weeds.

Table 4.1: Location of the sampling

Name of site	Abbreviation	Geographic position/Location
Cleveland Dam	CD	17˚ 50'12.19''S, 031˚ 09'07.64''E
Lake Chivero Station 1	LCS1	17˚ 54'57.54''S,030˚ 50'32.16''E
Lake Chivero Station 2	LCS2	17˚ 55'04.40''S, 030˚ 50'11.20''E
Manyame River Upstream	MRU	17˚ 52'29.07'' S, 030˚ 46'01.41''E
Manyame River Discharged Point	MRDP	17˚ 52'20.75''S, 030˚ 45'55.87''E
Residues	WW	Morton Jaffray outlet
Manyame River Downstream	MRD	17˚ 52'16.60''S, 030˚ 45'53.10''E
Lake Manyame Mouth	LMM	17˚ 50'45.22''S, 030˚41'01.45''E
Lake Manyame Centre	LMC	17˚ 50'32.94''S, 030˚ 37'57.26''E
Lake Manyame Dam wall	LMD	17˚ 49'05.49''S, 030˚ 31'49.14''E

- **MRD -** This site was approximately 100 m from the discharge point but separated from MRDP by weeds that are present after the discharge point. This site served to show the role, if any, being played by the weeds in terms of uptake of the metals and recovery in water quality.
- **LMM, LMC and LMD -** These three sites were located in Lake Manyame, one at the mouth of the lake (LMM), LMC in the centre at approximately 8 km from LMM and another site at the dam wall or exit of the lake (LMD) at about 12 km from LMC. These sites were chosen to allow for investigation on the spread of Al. These sites also served to study the decay and retention processes that might have been occurring. Observations obtained from this lake were compared with those from the supposedly un-impacted sites in Cleveland dam and Lake Chivero.
- **Residues -** This site was located in Morton Jaffray water works where the residues were collected before they were discharged into Manyame River. These residues were to be used to determine the quality of the residues being discharged into Manyame River.

- **CD** - Cleveland dam is on average 1 km long and it acted as a reference site for comparison with sites in Lake Manyame as well as in Lake Chivero. The site served to show background Al levels and also to indicate Al pollution and the level of the pollution. Cleveland dam receives minimal pollution as it is located upstream of the pollution sources of Harare and its satellite towns and is further upstream of MJ in the same catchment (Jarawaza, 1997; Moyo, 1997) as shown in Fig. 3 1.

- **LCS1 and LCS2** - These sites were located in Lake Chivero, a highly polluted and hyper-eutrophic lake, at the entry of (LCS1) and exit into (LCS2) Manyame River. The sites were about 6 km apart. These sites were used also to indicate and confirm Al pollution by Morton Jaffray, determine the level of pollution emanating from Morton Jaffray and be able to categorize the pollution levels in the three reservoirs; Lake Manyame, Cleveland dam and Lake Chivero.

4.1.2 Selection of sampling parameters

- *Total Aluminium*

Dissolved, monomeric, labile forms of Al, mainly, the hydroxyl- Al and the aquo-Al, are of particular concern in toxicity studies (Sharma, 2003; Prolo *et al*., 2007). However, Lake Manyame was considered unlikely to be acidic such that it may be difficult to detect dissolved aluminium hence the choice of total Al in the water samples. Also, in this pH range, studies have shown that dissolved toxic forms would generally be insignificant (Driscoll and Letterman, 1988; Srinivasan *et al*., 1999). Total metal is the metal in both the dissolved and suspended portions of the sample (Adams, 1990). The study was mainly concerned with the magnitudes of aluminium coming from Morton Jaffray and not its speciation *per se*.

- *Sediment texture and adsorbed water/moisture content*

The specific surface area of soil or sediments is a key particle property which controls the adsorption capacity and it is inversely proportional to particle size (Chapman, 1996). Sediments with a high percentage of small grains, such as silt and clay, with high organic contents, have high surface-to-volume ratios and can adsorb more heavy metals than sediments composed of large grains, such as sand which reduce metal bioavailability and toxicity. The moisture in sediments is also associated with contaminants such that the higher the moisture content would imply a higher content of contaminants (IAEA, 2003).

- *pH*

The pH of water is a measure of the concentration of hydrogen ions. One of the main ways in which pH affects aquatic ecosystems is by determining the chemical species, and thus the availability and the potential toxicity of many heavy metals and other substances (Dallas and Day, 2004). A strong correlation was confirmed between Al and pH in water bodies (Sharma, 2003; Neal *et al*., 2004; Kamau *et al*., 2008). It was thus imperative to measure pH of the water.

- *Dissolved oxygen (DO) and temperature*

These two parameters are also very important as far as fish and organisms, in general, are concerned whereby an increase in temperature increases metabolic rate and reduces the level at which a toxic material is toxic (Tebutt, 1998). Changes in temperature can have lethal effects on sensitive plants or animals as temperature influences all biological and chemical reactions. Also, variations in temperature affect the density and hence, the transport of water (Thomann and Mueller, 1987). Under natural conditions the concentration of dissolved oxygen fluctuates diurnally, depending on the relative rates of photosynthesis and respiration. It is usually lowest near dawn, increasing during the day, peaking in the afternoon, and decreasing at night (Dallas and Day, 2004).

- *Total dissolved solids, total solids and conductivity*

Total solids comprise all the solids in a water body, dissolved, or suspended (Adams, 1990). The total amount of materials dissolved in a water sample is commonly measured as total dissolved solids (TDS), as conductivity or as salinity. TDS represents the total quantity of dissolved material, organic and inorganic, ionised and un-ionised, in a sample of water. Conductivity is a measure of the ability of a sample of water to conduct an electrical current, and is therefore a measure of the number of ions (charged particles) in solution (Metcalfe and Eddy Inc, 1995). In natural aquatic ecosystems, TDS is determined by the degree of weathering and the chemical composition of rocks, and by the relative influences of evaporation and rainfall in the catchment. TDS and conductivity are usually closely correlated for a particular type of water (Dallas and Day, 2004). Dissolved solids content will affect the osmotic balances in aquatic organisms as mentioned in section 2.7. This has a direct bearing on the uptake of the metals dissolved in water.

- *Use of fish media*

Fish are widely used as biomonitors as they are at the top of the food chain in aquatic ecosystems and hence tend to bioaccumulate high concentrations of toxins from the environment through the process of biomagnification (Ronagh *et al*., 2009). Biomonitors are organisms that generally accumulate heavy metals to concentrations that are relatively easy to measure since they concentrate the metals over several orders of magnitude above ambient water levels (Sarkar *et al*., 2008). Fish are also often used as a human food source such that results of pollution studies have a bearing on human health. According to Sarkar *et al*. (2008) and Refief *et al*. (2006), biomonitors are characterized by: their capacity to accumulate pollutants without being killed by the encountered levels; mobility in order to be representative of the habitat; abundant in the area of study; sufficiently long-lived and of a reasonable size to be able to provide enough tissue for analysis. Analysis of fish consumed by humans may provide a rough idea of possible human health impacts as well as complete the possible pathway of these non-biodegradable metals from the environment. Analysis of fish tissue will also help determine whether pollution has been occurring over a long or a short period of time.

4.1.3 Sampling frequency and timing

- *Sediments and water*

Sampling was undertaken to cater for seasonal (temporal) and spatial variations. Sampling was carried out in January and March, during the dry spell when flows were reduced and the peak of the rainy season, respectively. Sampling in different weather conditions helps to show the influence of the different water flows and volumes on the variations in metal concentrations in the water column and sediments at the sites (Chapman 1996). This also brings out a true reflection of the conditions in which fish are subjected to during their life span. Sampling of fish under different seasonal conditions also allows for inference to be made on the potential toxicity to which fish may be exposed to at different times and environmental conditions. The dry period was also particularly chosen for this one-off first sampling campaign that consisted of sites in Lake Chivero and Cleveland dam because the period of low flows constitutes a larger portion of the life span of aquatic organisms that spend all of their lives in water compared to a rainy period which is usually three to four months or even less in a year. Sampling was carried out at the same time of the day in each of the sampling campaigns.

4.2 Determination of quality of the residues discharged by Morton Jaffray Waterworks

4.2.1 Sampling of residues

Two replicate time integrated samples were collected at the discharge point before entry of the wastes into the river. The backwash waters from the filtration units and the sludge from the sedimentation tanks are combined into one waste component before being discharged at the waterworks hence, they were not sampled separately. Sampling followed the daytime discharge frequency of the residues which occurs every 4-6 hours, so as to capture the peak concentrations or loads getting into the river. The samples were preserved immediately with 50 % v/v nitric acid, placed in a cooler box and transported to the laboratory for further analyses.

4.2.2 Laboratory analyses of residues

Accurately weighed 100 ml of the residues was transferred into a beaker and 5 ml of concentrated HNO_3 was added. The beaker with the contents was placed on a hot plate and evaporated down to about 20 ml. The contents were allowed to cool down and another 5 ml concentrated HNO_3 added again, the beaker was covered with a watch glass and returned on the hot plate. The heating was continued and more acid added until the solution appeared light coloured and clear. The beaker and watch glass were washed with distilled water into the heated sample and then sample was filtered using Whatman glass fibre filter papers. The volume was adjusted to 100 ml with double distilled water (Ademoroti, 1996). Determination of total aluminium (TaL) in the residues samples was done using a Varian AA Spec 55B flame Atomic Absorption Spectrophotometer with nitrous-acetylene gas (APHA, 1989). The method detection limit (MDL) was 0.01 mg/l. Standards of known concentrations and blanks were used as quality control measures. Actual concentrations incorporated the dilution volume of 100 ml.

4.3 Determination of Total aluminium (TaL) in the water, sediments and fish

4.3.1   Water samples

4.3.1.1 Field Sampling

Eight depth integrated samples of water per site were collected into polythene bottles using a Ruttner depth sampler. A grab sample was taken at the bottom, middle and the top 1 m of the water column and mixed in one container to form an integrated depth sample. The samples were placed in an ice box for transportation and later stored in a refrigerator at 4 ºC following standard procedures (APHA, 1989; Chapman, 1996).

4.3.1.2 Laboratory analysis

The unfiltered water samples were immediately preserved with 50 % v/v nitric acid (HNO_3) solution by adding enough acid (approximately 1.5 ml) to reduce the pH of the sample to less than pH of 2 (Adams, 1990; APHA, 1989). 100 ml aliquot preserved samples were filtered using glass fiber filter papers which are acid resistant and placed in acid-washed polythene bottles in preparation for analysis. Total aluminium (TaL) was determined using a flame atomic absorption spectrophotometer. Standards of known concentrations and blanks were used as quality control measures. No dilutions were made for water samples.

4.3.2   Sediment samples

4.3.2.1 Field Sampling

Eight grab samples were collected at random points at each site where water and fish samples had been collected using a mud grab sampler (IAEA, 2003). Sediment samples were collected into polythene papers, placed in an ice box for transportation (IAEA, 2003).

4.3.2.2 Laboratory analysis

The laboratory glass apparatus were washed with concentrated soap and rinsed with tap water then distilled water, then acid–washed in 1 M Hydrochloric acid (HCl) for 24 hours and then rinsed in distilled water to ensure that all traces of cleaning reagent were removed prior to use. Finally, they were oven-dried and stored in a clean place. The sediment samples were oven-dried overnight at 105 ^{o}C and ground to fine powder using pestle and mortar to homogenize the samples (IAEA, 2003). The sediment samples were digested for total metal extraction using the aqua regia acid (Hydrochloric acid, HCL: Nitric acid, HNO_3 =1:3 volume/volume (v/v)) digestion technique (APHA, 1989; Adams, 1990). Accurately measured 2 g samples of dried sediments were weighed in crucibles and placed into digestion tubes and digested using 15 ml aqua-regia solution for 2 hrs at 120 ^{o}C (Praveena *et al*., 2008). Radojevic and Bashkin (1999) stated that the aqua regia digestion technique is safer and adequate for total heavy metals extraction. The digested samples were diluted with double distilled water to make up 100 ml

samples. Total aluminium concentration was measured using the Varian AA Spectr 55B flame atomic absorption spectrophotometer method with nitrous oxide-acetylene flame at a specific wavelength of 309.3 nm and MDL of 0.01 mg/l. Standards of known concentrations and blanks were used as quality control measures. The actual concentration of the sediments was determined incorporated the dilution factor (*i.e*., factor of 10) for those samples that exceeded the standards and the weight of the dried sediments used (*i.e*., 2 g).

4.3.3 Fish samples

4.3.3.1 Field sampling

Freshwater fish species (*Oreochromis niloticus*) were collected in January 2010 and March 2010 at stations in Lake Chivero (January only), Manyame River and Lake Manyame (January and March) by means of gillnets (150 mm stretched mesh size) and beach seine nets in the river. The fish were caught and placed in polythene papers, transported in cooler boxes with ice to the laboratory where they were stored in a refrigerator at 4 °C for analysis within two weeks of collection. Six adult fish were caught at each site. However, due to the weed "carpet", zero flows and unfavorable conditions, fish could not be found at the site upstream (MRU). Fish could not be caught at site downstream (MRD) of the discharge point due also to accessibility reasons mainly. Fish were also not caught in Cleveland dam.

4.3.3.2 Laboratory analysis

The laboratory apparatus were washed with concentrated soap and rinsed with tap water then distilled water, then acid–washed in 1 M Hydrochloric acid (HCl) for 24 hours and then rinsed in distilled water to ensure that all traces of cleaning reagent were removed prior to use. The gills, liver, muscle and kidneys were removed on a dissection board using stainless dissecting equipment which had been swabbed in 70 % alcohol to prevent any possible contamination of the samples. The samples were placed in acid-washed crucibles and oven-dried to constant weight at 120 °C. Equal dry weights of each of the same tissues were placed in digestion flasks where 15 ml aqua regia was added and heated for 2 hrs at 120 °C as for the sediments. The digested samples were made up to 100 ml with distilled water in preparation for analysis. The Al concentrations in the tissue samples were determined using nitrous oxide-acetylene flame atomic absorption spectrophotometry (AAS) as explained in APHA (1989). Standards of known concentrations and blanks were also used as quality control measures. Blanks and standards were re-analyzed before analysis of fish from a different site to avoid contamination. The actual concentration in mg/g dry was then obtained by multiplying the AAS reading with the volume used and dividing by the weight of dried tissue sample used. The volume used for all the samples was 100 ml and no further dilutions were made for all fish tissues.

4.4 Determination of general physico-chemical parameters

4.4.1   Water samples

4.4.1.1 Field analyses

Table 4.2 shows the parameters that were determined in the field and the instruments that were used for measurement. Determinations were made before preservation with nitric acid.

4.4.1.2 Laboratory analyses

Total solids were measured on composite water and wastewater samples as duplicates to ensure representativeness of results. Weight of each empty 150 ml Pyrex beaker was determined and 50 ml unfiltered sample was placed in each of the weighed beaker. The samples were evaporated to constant weight overnight using a 103 ^{o}C oven. The samples were cooled in a desicator and weighed to determine the total solids.

Table 4.2: Instrumentation for field measurements

Parameter	Units	Instrumentation	Model
pH	pH units	pH meter	HACH
Dissolved Oxygen, DO	mg/l	Oxygen meter	HACH HQ10 Oxi3301 set
Dissolved Oxygen saturation	%	Oxygen meter	HACH HQ10 Oxi3301 set
Electrical Conductivity, EC	µS/cm	Conductivity meter	HACH WTW LF330
Temperature	$^{\circ}$C	pH meter	HACH
Total dissolved solids, TDS	mg/l	Conductivity meter	HACH WTW LF330
Geographic coordinates	-	GPS	Garmin GPSMAP 76C

GPS-Global Positioning System

The total solids content was calculated using Equation 1 according to APHA (1989) and Adams (1990):

Total Solids calculation: mg Solids/l $= \dfrac{(A-B-C)*1000}{\text{volume of sample,l}}$…………………………**Equation 1**

Where: A= Final weight = beaker +sample after evaporation

   B = Initial weight = beaker weight

   C = Blank correction = (final weight of blank) - (initial weight of blank) where the difference between the weight of blank is zero.

4.4.2   Sediment samples

4.4.2.1 Laboratory analyses

Adsorbed water content was determined as the weight loss after drying 10 g of sediments at 105 ^{o}C overnight and weighing the dry weight and subtracting to get the adsorbed water content (IAEA, 2003). The heated sediments were cooled in a desicator. The weight loss is interpreted as the adsorbed water.   Particle size determination was carried out in the laboratory on composited wet sediments through wet sieving using different mesh sizes (IAEA, 2003). The sediments (approximately, 50 g) were mixed with 10 % sodium hexametaphosphate (calgon) solution for dispersal of the different grain sizes and shaken in a ro-tap shaker overnight. Wet sieving was carried out on the dispersed sediments through the following mesh sizes: 125 µm, 58 µm, and 38 µm as these were the sieve sizes available. These sieve sizes account for the sand and silt fraction such that the clay part would be obtained by subtracting from the total. Duplicate samples were determined for each site.   Equation 2 was used to calculate the individual particle size fractions and is as follows according to Okalebo *et al*. (1993):

$$\textbf{Particle size fraction}\ (\%) = \frac{(\textbf{Weight of beaker+dried sediments}-\textbf{Weight of empty beaker})}{\textbf{Initial total weight of sediments}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\textbf{Equation 2}$$

4.5 Data analysis

- ✓ The Statistical Package for Social Sciences (SPSS), SPSS 16.0 for Windows, was used to carry out analysis of the data:
- One-way ANOVA was used to check for variations among sites, between the sampling campaigns for water, sediments and among the fish tissues.

- Homogeneity of variances test was used to check on equality of variances which would help in choosing the most suitable Post-Hoc range test to use.

- The Least Squares Differences was used to check for multiple comparisons across sites. Post-Hoc range tests are further tests used to check on which particular points or sites may be causing the variations, if any, and also which ones are particularly different from each other.

- Pearson correlation analysis was used to check if there are any relationships between the metal concentrations in fish tissues and concentrations in water or sediments, and also between aluminium concentrations in the water and each of the parameters.

- Hierarchical cluster analysis for fish data was used to show similarities, if any, in the Al concentrations from the different tissues in fish from the different sites. Hierarchical cluster analysis is the most common procedure of clustering that attempts to identify relatively homogeneous groups of variables based on selected characteristics or

observations for example, Al concentrations in fish tissues from different sites as in this study (Praus, 2007). The procedure uses an algorithm that starts with each variable in a separate cluster, compares it to the rest of the data set and combines clusters until only one is left to form a dendrogram or a tree diagram (Praus, 2007; Shrestha and Kazama, 2007). Distance or similarity measures are generated by a Proximities procedure and the Euclidean distance is usually generated which gives the similarity between two samples and separates the variables into clusters (Otto, 1998). Variables in the same cluster are similar or have high internal homogeneity whilst those in different clusters have high external heterogeneity and are thus, dissimilar (Praus, 2007).

✓ Bioconcentration factors (BcF) were generated (Adham, 2001). This factor is a measure of how much of the metal present in the water or sediments will be available to the organism (Adham, 2001). The formula for its calculation is given in Equation 3 according to Adham (2001):

$$\text{BcF} = \frac{C_{org}}{C_{water/sediments}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{Equation 3}$$

Where: C_{org} is the mean concentration of the metal in the organism's tissue (dry weight) due to uptake from the water or sediments and $C_{water/sediments}$ is the corresponding mean concentration of the metal in the water or sediments. The generated BcFs were then analyses to compare significance of any variations.

5. RESULTS AND DISCUSSION

5.1 Quality of residues discharged into Manyame River

Table 5.1 shows the results on the quality of the residues being discharged into Manyame River. The dosage of alum during the first campaign was 65 mg/l while that in the second campaign was 80 mg/l. The pH was outside the range stipulated by the Government of Zimbabwe S.I 274 of 2000 standards for effluent discharge into waterways though most parameters were as recommended by the standards (Table 5.1).

Table 5.1: The quality of the residues (mean±standard deviation) in sampling campaign 1 and 2.

Parameter	Units	Sampling campaign		ZINWA (2000) Standards
		1	2	
TaL	mg /l	777±149	1819±141	n.a
Temperature	∘C	22.8±0.09	23. 9±0.14	≤35
pH	pH units	4.15±0.01	4.13±0.01	6.5-8.5
DO	mg /l	6.6±0.01	6.2±0.00	-
DO Saturation	%	90.4±0.03	86.7±0.06	60
EC	μS/cm	580±0.09	625±0.01	1000
TDS	mg /l	492±0.44	582±0.58	500
TS	mg /l	534±0.03	600±0.02	n.a

n.a. means not available, TaL means total aluminium

The pH obtained in this study was also much acidic (Table 5.1) than the pH obtained by Uwimana *et al*. (2007) for sludges from Kadahokwa water treatment plant in Uganda of 6.5 to 7.45, though this pH was from the solid sludge from the sedimentation tanks before blending with the backwash waters from the filters as is the case at Morton Jaffray. The pH range obtained in this study should render the Al in the residues mobile and toxic and also available for plant and animal uptake in an aquatic environment. This is coming from the fact that pH affects the solubility, bioavailability and toxicity of Al, particularly pH below 5 (Chapman, 1996; Davies and Day, 1998; Srinivasan *et al*., 1999; CEQG, 2003; Sharma, 2003). This finding on pH contrasts with Elliott *et al*. (1990) who suggested that most metals in water treatment sludges are in a predominantly weakly mobile and non-bioavailable form to reduce plant growth. Actually, there is no plant growth in the area immediately around MRDP but further downstream (see photograph on cover page). The pH obtained in this study is also much acidic in comparison to

other types of wastewater such as sewage effluents. For instance, in a study by Mathuthu *et al*. (1997) on Crowborough sewage treatment works effluent in Harare, the pH for the effluent was 7.54±0.24. The low pH of the residues can cause the pH of the receiving waters to be lower than usual unless if the surface water body is well-buffered (Dallas and Day, 1993). Sulphuric acid is used in the treatment of the raw water for pH correction and also, the process of coagulation lowers pH hence the alum residues will have a low pH.

There was an increase in TaL, EC, TDS and TS in sampling campaign 2 with a decrease in DO and pH. These increases suggest that the increase in dosages resulted in increased levels of Al in the residues and a depression in pH. The second sampling campaign was characterized by increases in water flows due to the high rainfall activity at the time. Rainfall activity results in increased runoff from the catchment resulting in increased solids content of the raw water in the lakes and re-suspension of sediments from the bottom waters in the lakes from which the raw water is abstracted. In addition, increased runoff is more so in these water bodies due to their downstream location in relation to the urban areas as mentioned in Section 3.5. Also, approximately 60 % of the abstracted water treated at Morton Jaffray comes from Lake Chivero which, as mentioned in Section 3.5 and 3.6, directly and easily receives most of the pollution from the heavily industrialized city of Harare. This implies that there is high inorganic and organic pollution content in the raw water treated at Morton Jaffray which increases in the rainy period. Increased solids content in the abstracted raw water means that there will also be increased use of alum for binding the suspended and colloidal material and with this, there is an increase in suspended and dissolved solids and coagulant particles in the residues as the processes of coagulation and sedimentation are basically to remove these problems from the raw water. As the quality of treated water at Morton Jaffray has been deterioration since early 90s, the number of chemicals used to treat the water has also been increasing as mentioned earlier on in Section 3.7 such that even the dosages of alum used have also been increasing (see Section 1.1). The decrease in DO also indicates presence of some oxygen-demanding substances, both biological and chemical. However, DO was within the standards and guidelines compared to results for sewage effluent (5.4±1.2 mg/l) in the same study by Mathuthu *et al*. (1997), which implies that these oxygen demanding substances are much less as compared to those found in sewage effluents. It also indicates that these oxygen-demanding substances must be of a physical and chemical rather than biological nature. However, results obtained in the residues were comparable to what was obtained in wastewater from sewage works and industries by Akan *et al*. (2009).

The Al levels obtained in this study were however four-fold higher than those that were obtained by Uwimana *et al*. (2007) of 280 mg/l, though this figure was for sludges from the sedimentation tanks alone before blending. Results by Uwimana *et al*. (2007) were obtained from a water works that uses alum dosages in the range of 12 to 20 mg/l compared to those used at Morton Jaffray of 60 to 80 mg/l. The sludge was also digested using nitric acid and Al content determined using AAS technique as in this study. Re-use of Al in the sludges produced at Kadahokwa water works was recommended by Uwimana *et al*. (2007). This is more so for

Morton Jaffray residues which are much richer in Al than those from Kadahokwa. It also shows that the higher the alum used the higher the Al remaining in the residues and possibly in the final water for distribution to consumers.

5.2 Total aluminium in the fish tissues, water and sediments

5.2.1 Bioaccumulation of Aluminium in fish tissues and their Bioconcentration factors

The Al concentrations in the tissues were generally higher in sampling campaign 1 than sampling campaign 2 (Fig. 5.1).
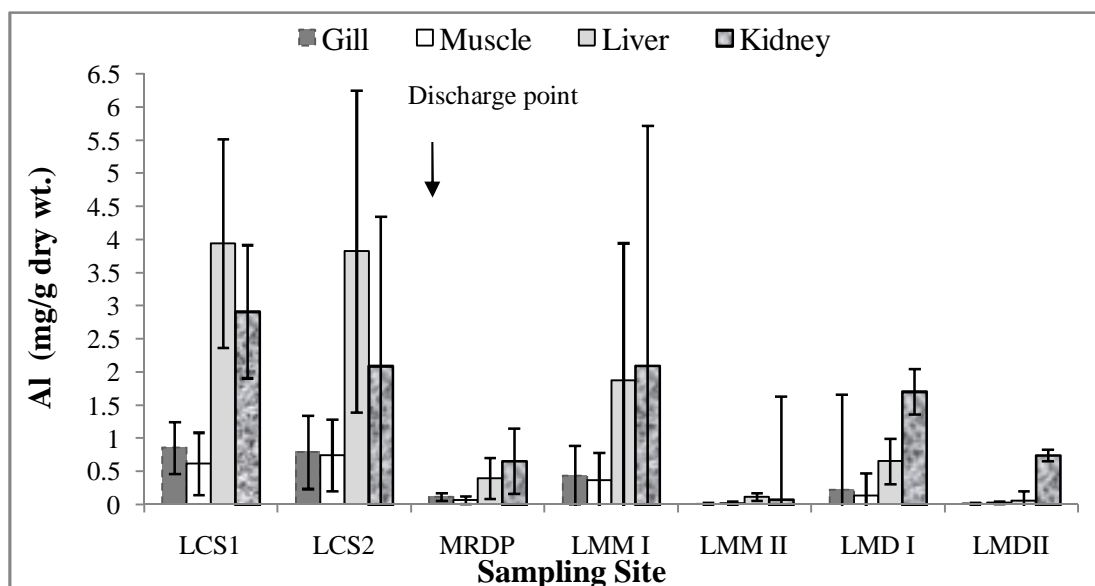
Figure 5.1: Bioaccumulation of Al in fish tissues in different sites and sampling campaigns. LMMII and LMDII represent LMM and LMD in sampling campaign 2, respectively.

The bioaccumulation of Al in the different tissues was significantly varying but with a consistent pattern across the sites in both sampling campaigns (ANOVA: $p < 0.05$) as shown in Fig. 5.1. In sampling campaign 1, sites in Lake Chivero registered the highest Al tissue concentrations followed by sites in Lake Manyame then MRDP (Fig 5.1). In the same campaign, the highest bioaccumulation tissue was the liver, *i.e.*, 3.94±1.57 mg/l and 3.82±2.43 mg/l, while the lowest was the muscle 0.62±0.47 mg/l and 0.75±0.54 mg/l for LCS1 and LCS2, respectively (Fig. 5.1; Appendix A). The mean TaL concentration in the kidney was higher than in the liver 60 % in space and 67 % in time though the liver was higher 100 % in space in Lake Chivero and thus carried the higher total tissue average (Fig. 5.1; Appendix A). Therefore, the general degree of bioaccumulation of Al in sampling campaign 1 in decreasing order was: liver > kidney > gills > muscle. For sampling campaign 2, the highest bioaccumulation levels were evident in the kidney (0.75±1.56, LMM) and liver (0.12±0.15, LMD) which is consistent with sampling campaign 1 in

the same lake, *i.e*., Lake Manyame, whereby the fish accumulated the most Al in the kidney for both sites (Fig. 5.1; Appendix A). The kidney also had the highest mean tissue total of 0.83 mg/l and it is concluded that the order of bioaccumulation in sampling campaign 2 was: kidney > liver > muscle > gills, though for Lake Manyame, the trend was: kidney>liver>gill>muscle (Fig. 5.1). The lowest bioaccumulation tissues in the study were the muscle and gills with mean tissue total of 0.03 mg/l and 0.06 mg/l for gills and muscle, respectively (Fig. 5.1; Appendix A). This was also confirmed by the pattern depicted by the cluster analysis of Al concentrations of the fish tissues from the sites were fish were sampled (Fig. 5.2). As is shown in Fig. 5.2; LMMK, LC1K, LC2L and LC1L formed their own cluster which is obviously due their high concentrations, followed by another cluster with LC2K, LMDK and LMML. This clustering mainly showed that the liver and the kidneys were in the same level of pollution whilst the gills and muscles fell in their own separate cluster. This finding has already been indicated in Fig. 5.1. However, the standard deviations in all the sampling campaigns are indicative of the degree of variation which occurred between individuals in a sample.
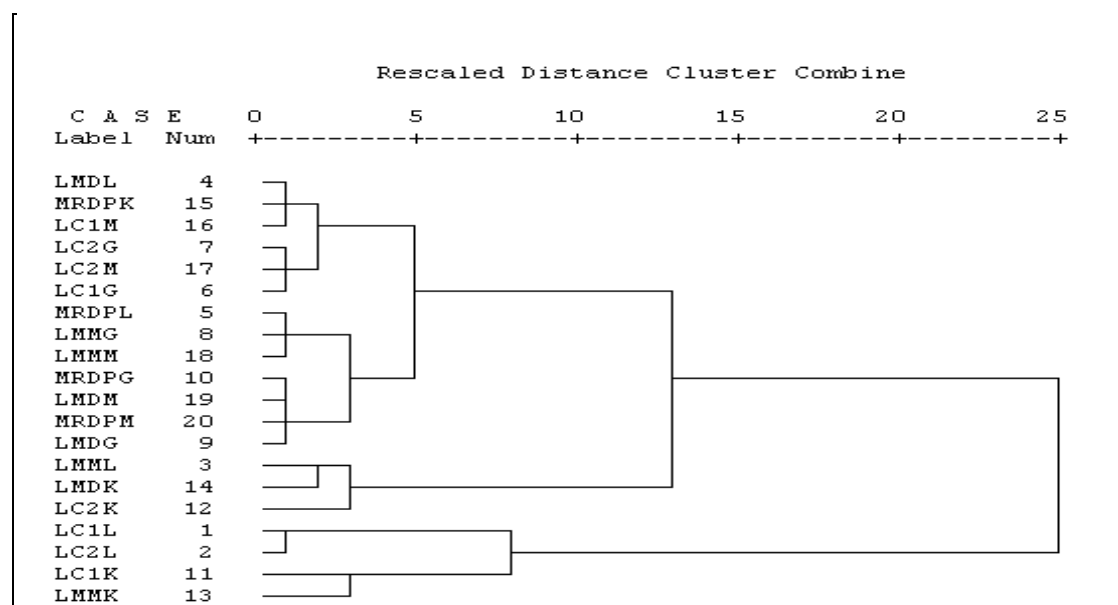
Figure 5.2: Hierarchical cluster analysis of Al concentrations in different fish tissues from the sites. LMD, MRDP, LC1 and LC2 (LCS1 and LCS2, respectively), LMM are the sites; L-liver, K-kidney, M- muscle and G-gill and Num is the number of the cluster.

Aluminium bioconcentration factor (BcF) values between tissues and water (BcF$_w$) were generally much higher than those of sediments (BcF$_s$) for all the sites where fish were sampled and in both sampling campaigns (Table 5.2). Bioconcentration factors show the metal quantities that will be bioavailable from the water and sediments. The variations among sites were significant (ANOVA: $p<0.05$). For sampling campaign 1, the BcF$_w$ ranged from 0.00 for the gills (MRDP) and muscle (MRDP and LMD) to 1.67 for the liver in LCS1 (Table 5.2). In sampling campaign 2, the range was between 0.00 (gills and liver – LMM; gills, liver and muscle

- LMD) and 0.07 for the kidney at LMM. For the BcF_s, the range was between 0.00 for gills and muscle at MRDP and 0.14 for the liver at LCS1 in sampling campaign 1. In sampling campaign 2, the range was from 0.00 for the muscle, to 0.05 for the liver at LMD (Table 5.2).

Table 5.2: Bioconcentration factors in water (BcF_w) and in sediments (BcF_s).

	Sampling site	Statistic	Gills	Muscle	Liver	Kidney
Sampling campaign1	LCS1	BcF_w	0.36	0.26	1.67	1.23
		BcF_s	0.03	0.02	0.14	0.11
	LCS2	BcF_w	0.24	0.22	1.14	0.62
		BcF_s	0.03	0.02	0.12	0.07
	MRDP	BcF_w	0.00	0.01	0.01	0.02
		BcF_s	0.02	0.02	0.09	0.15
	LMM	BcF_w	0.01	0.01	0.04	0.07
		BcF_s	0.02	0.01	0.04	0.07
	LMD	BcF_w	0.02	0.00	0.04	0.11
		BcF_s	0.09	0.05	0.26	0.69
Sampling campaign 2	LMM	BcF_w	0.00	0.00	0.01	0.07
		BcF_s	0.00	0.00	0.00	0.01
	LMD	BcF_w	0.00	0.00	0.00	0.01
		BcF_s	0.01	0.01	0.05	0.03

The pH at sites in Lake Chivero, LMM and LMD was higher than 8.5, a condition that can render Al soluble and bioavailable to organisms (Tebutt, 1998; Srinivasan *et al.*, 1999; CEQG, 2003). However, there was DO stress in Lake Chivero at both sites which may have increased uptake of substances from the environment (Fig. 5.6). There is also much more proliferation of phytoplankton, food for the fish under study, in Lake Chivero than Lake Manyame, which also take up the metals along with nutrients during photosynthesis. Lake Chivero is hypereutrophic whilst lake Manyame is eutrophic (Magadza, 2003; Nhapi, 2007). These reasons may explain higher Al concentrations in the tissues in fish from LCS1 and LCS2 compared to those from LMM, MRDP or LMD. Strong correlations have been established in one study between high concentrations of aluminium in water and accumulation in such organs as the kidneys, gills and skeleton while the liver and muscles have been shown to accumulate low concentrations (Rodushkin *et al.*, 1995). In contrast to Rodushkin *et al.* (1995), there was no relationship between concentrations of Al in water and those in the different tissues (Appendix C; Table 8.4). This means that the levels of Al in the water did not have much impact on bioaccumulation of Al in the fish organs and so did the levels in the sediments (Appendix C; Table 8.5). Probably, the conditions highlighted above, as well as the diet, may have elevated the bioavailability of the metal over time. For example, it can be seen in Fig. 5.3 and Table 5.2 that LCS1 and LCS2 had

Al$_{water}$ significantly lower than at LMM but their BCF$_{w/s}$ and accumulation in tissues was generally higher than for LMM. Also, fish are migratory such that the concentrations at one site in the water may not be indicative of the levels in the fish caught at that site at the particular time of capture.

In a study by Coetzee *et al*. (2002), the liver and gills were shown as the major recipients of Al followed by the muscle and skin. The following authors also obtained the same results as Coetzee *et al*. (2002) though for different fish and metals: Kotze *et al*. (1999); Rashed (2001); Vinodhini and Narayanan (2008); Akan (2009); Rauf *et al*. (2009), particularly for mobile top surface dwellers such as *O. niloticus* fish species. Earlier on, Rodushkin *et al*. (1995) had established that Al is accumulated the most in such organs as the kidneys, gills and skeleton while Adham (2001) showed that the kidney of *O. niloticus* is the principal store organ for most of the metals that were studied. This study came out with results that depicted the liver and the kidney as accumulating the most Al while the muscle accumulated low quantities of Al in agreement with all of the above studies. In contrast to these findings however, was that the gills accumulated low concentrations because of low concentrations in the water.

The gills were expected to have high concentrations of Al if there was high Al levels in the water or if Al might have been re-introduced into the water due to water quality conditions or if there was excretion via the gills according to Kotze *et al*. (1999). The gills are in direct contact with the water hence have got a larger surface area for absorption of metals from the water (Coetzee *et al*., 2002; Rauf *et al*., 2009). However, the water had low Al explaining the presence of low concentrations in the gills. Lake Chivero had high Al gill concentrations than all the other sites because of the poor water quality conditions characterized by low DO ranging between 2 and 3.5 mg/l and high pH (pH>8.5). Besides, the BcF results show that more Al in the tissues was coming from the water than sediments. The muscles also constituted the lowest concentrations in this study in agreement to previous studies on metal bioaccumulation in fish though the levels were also higher in fish from LCS1 and LCS2 than all the other sites. The pH of water has been shown as having a major impact on Al solubility, bioavailability and toxicity (Wilson *et al.* 1994; Buckler *et al.* 1995; Rodushkin *et al*., 1995; Chapman, 1996; Tebutt, 1998; Srinivasan *et al*., 1999; CEQG, 2003; Sharma, 2003). Such parameters as DO and temperature have an impact on general metal availability and uptake in aquatic organisms (Dallas and Day, 1993; Tebutt, 1998). The muscles were very important in this study as they are the edible part of the fish such that the results obtained in this study for muscles suggest that there is minimal impact on human health from consuming these fish, more so, fish from Lake Manyame. The residues have an impact on Al uptake by fish though this bioavailability is greatly affected by the water quality conditions in the water body.

Heavy metals enter fish in three routes; absorption through their body surfaces such as the gills and digestive tracts, through food, and through polluted water and sediments (Javed, 2005). A possible explanation for the high accumulation in the liver could be due to the fact that *O.*

niloticus generally feeds on algae, phytoplankton and other aquatic macroinvertebrates like other species in the family of *Oreochromis* (Coetzee *et al*., 2002). Aquatic macroinvertebrates and phytoplanktons are an important food source of many fish and have been shown to accumulate Al, among many other metals, providing a route of entry of Al into the wider food chains (Zaranyika and Ndapwadzwa, 1995; Elangovan, 1999). Phytoplankton, which are abundant in Lake Chivero, obtain all their nutrients from the water (Machena, 1997) and plants tend to co-absorb nutrients with the metals (Stumm and Morgan, 1996). According to Hodson (1988), the liver receives its blood supply from the intestinal portal system while all the other tissues in a fish receive their blood supply from the gills. As such, most of the metals contained in the diet of the fish will directly and firstly pass through the liver before being transported to the other parts of the fish. Considering also that the water had low amounts of Al in this study, the route of entry via food source may have provided a larger contributory source to the concentrations found in the fish. However, phytoplankton were not included in this study due to limited resources. Another explanation for high concentrations in the liver could be that the liver is the main detoxifying organ in the fish, and accompanied by the favourable conditions for Al bioavailability and uptake, particularly in Lake Chivero, the liver will act as the main destination for foreign toxic elements introduced into the fish body from the environment and/or the diet. Kotze *et al*. (1999) explained that under unpolluted conditions; the liver will act as a storage organ for metals through binding with metallothioniens and under normal conditions, the liver will thus contain higher metal levels than any other tissue. In polluted conditions however, the liver will strive to detoxify the fish body of the excess metals as part of homeostasis. By so doing, it is possible that the liver can over-compensate and we find that the liver in fish in polluted areas will have lower levels of the metals than fish in unpolluted areas. This could have been the situation considering that Lake Chivero was less polluted in terms of Al than Lake Manyame such that the fish in Lake Manyame ended up having less Al in the liver than in Lake Chivero (Fig. 5.2; Fig. 5.3). This situation indicates the impact of the residues discharged by Morton Jaffray. The detoxified pollutants will be excreted via the kidneys hence also the high levels in the kidneys especially for fish in Lake Manyame. Levels in all the tissues were high in sampling campaign 1 and greatly reduced in sampling campaign 2 (Fig. 5.1; Appendix A). This was probably due to the weather conditions (clear skies, sunny) which permitted increased evaporation and less dilution of the metal concentrations in the water bodies.

The observed concentrations in the fish tissues were generally higher than in the water for all the sites where fish were sampled (Table 5.2 and Fig. 5.2). Ellis (1989) and Robinson and Avenant-Oldewage (1997) also had the same results. This is because fish get their Al from several sources and there is accumulation in their bodies over time as the fish used were adult fish. The BcF_w was higher than BcF_s as was also obtained in another study by Robinson and Avenant-Oldewage (1997) and Coetzee *et al*. (2002). Higher BcF_w than BcF_s should be a normal result considering that Al bound to sediments cannot be bioavailable to fish particularly in sampling campaign 1. This is because, in sampling campaign 1, the sediments are less disturbed, oxic conditions are prevailing at the bottom sediments when water levels are reduced which exposes

these sediments such that bound particles are still tightly bound. In sampling campaign 2, there is increased flow and volume of water which results in the re-suspension of sediments, creation of anoxic conditions which reduce such complexing agents as Fe and Mn resulting in desorption of bound particles. More important also is the dilution effect with increased flow of water in the wet period which reduces concentrations in water and thus explains the more or less equal BcF values in water or sediments in sampling campaign 2 as well as lower BcF_w in sampling campaign 2 than sampling campaign 1. Lake Manyame maybe such a big lake (refer to Section 3.2) that it is not greatly impacted upon by diffuse sources as was reasoned by some authors (Kotze *et al.*, 1999; Coetzee *et al.*, 2002; Rauf, 2009). Also, being a large water body, dilution effects may play a bigger role than re-suspension from bottom sediments. Another important reason for lower Al concentrations in fish in sampling campaign 2 may be that with time fish grow up to a time when the fish body starts to shed off some of the metals as well stop taking in substances from the environment.

5.2.2 Accumulation in water

In sampling campaign 1, TaL concentrations ranged from 1.22±11.46 mg/l (CD) to 68.93±61.74 mg/l (MRD) as shown in Fig. 5.3 and in Appendix B. The mean TaL at MRD was significantly different from all the other sites (ANOVA: p=0.000<0.05) while all those other sites were not significantly different from each other (ANOVA: p>0.05). In sampling campaign 2, the range was between 2.23±1.16 mg/l (LMC) to 38.18±21.54 mg/l (MRD) with the same pattern of variation (Fig. 5.3). However, the standard deviations show that there were great variations among the samples at a site. Levels of Al in sampling campaign 2 for MRU and MRDP were higher than those in sampling campaign 1 while there was a decrease for MRD and LMM in sampling campaign 2 compared to sampling campaign 1 and very slight decreases for LMC (Fig. 5.3). There was a gradient in accumulation of Al in water whereby levels peaked at MRD and decreased sharply at LMM up to LMD.

The levels of TaL in water obtained in this study for all the sites and sampling campaigns were much higher than the permissible limits of 0.05 to 0.1 mg/l (EPB 356, 2006) or 0.087 mg/l to 0.75 mg/l required by EPA-AU (2006) to prevent chronic and acute effects in fish in freshwaters, respectively (Appendix C). This was more so for the sites immediately downstream of the discharge point, MRDP, MRD and LMM. Srinivasan *et al.* (1999) and Uwimana *et al.* (2007) observed that residual Al in treated water increases after treatment with alum. This implies that the levels obtained in the raw water used for supply of drinking water to the city of Harare will result in a further increase in the levels in drinking water for distribution to levels higher than the maximum acceptable World Health Organization (WHO) safety guidelines of 0.2 mg/l stated by House and Reed (2004).
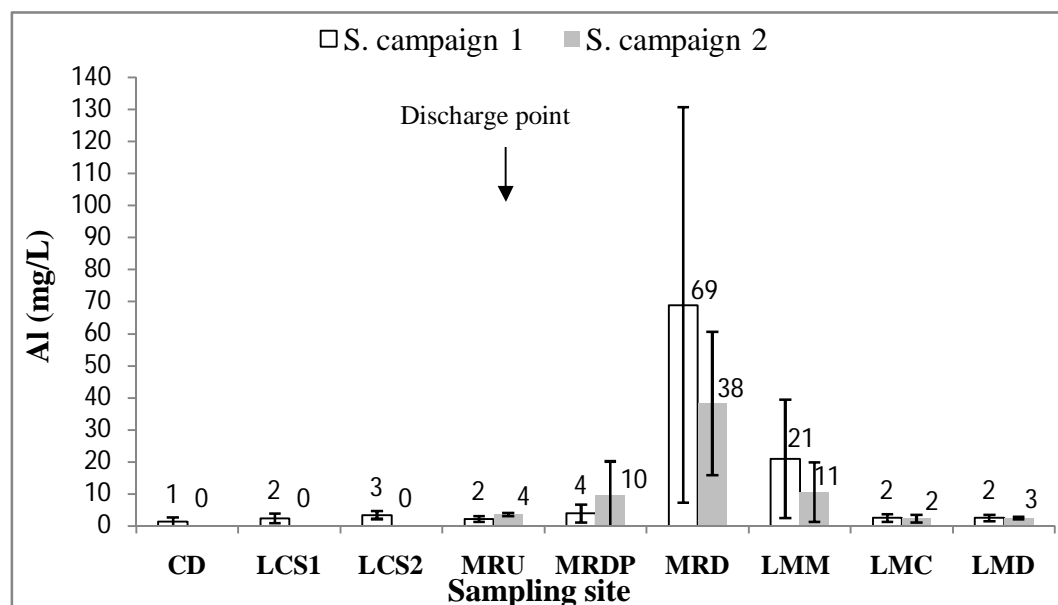
Figure 5.3: Mean TaL concentrations (mg/L) in water from all the sites.

The levels obtained in this study for water are also comparable to those that were obtained for acidic waters in the United States of America by Sorenson *et al*. (1974). The difference between obtaining these levels in the water systems under this study and obtaining them in those acidic waters are the conditions that will render Al bioavailable and toxic to the fish. Very low (< 5.0) or high pH (>8.5) levels will render the bioavailability and toxicity of the metal. The impact of the residues is shown by the increase from 2.19 ± 0.9 (MRU) to 3.86 ± 2.83 (MRDP) and then a sharp increase at MRD to 68.93 ± 61.74 mg/l in campaign 1 and sharp decreases from LMC to LMD (Fig. 5.3). However, the concentrations greatly reduced from those in the residues due to dilution with the river water, sedimentation processes, uptake by plants and transportation further downstream. This pattern of increases at MRD and decreases from LMM onwards was also the same in sampling campaign 2 though the magnitudes were less in the latter campaign for all the sites. This decrease in magnitudes was probably due to dilution effects as flows in a river increase in a wet period. The peak was always at MRD and not MRDP probably due to river transport downstream. Water sampling generally shows the pollution status at that particular time of sampling (Chapman, 1996). Thus, these results indicate that the residues from Morton Jaffray have got a great impact on Al concentrations in the receiving water bodies at any particular moment in time. The results obtained in this study are also comparable to those that were obtained by Abdullah *et al*. (1995) in that downstream sites had higher levels than upstream sites of a waterworks discharge point though it is not clear as to the distance of the downstream site away from the discharge point. However, the downstream site in the study by Abdullah is much less impacted (TaL level of 1.14 mg/l) compared to levels of 68.93 ± 61.74 mg/l or 38.18 ± 21.54 mg/l for MRD. The studies by Sorenson *et al*. (1974) and Abdullah *et al*. (1995) serve to highlight the magnitude of pollution emanating from Morton Jaffray waterworks. As

the levels of TaL increase, the levels of the labile, toxic forms of Al also increase (Abdullah *et al*., 1995).

The impact of residues from Morton Jaffray is shown to be limited in space downstream and then dissipates probably due to several reasons. One reason could be dilution effects as water volume increases in the lake from that in the river; uptake by the dense network of aquatic vegetation from MRDP to LMM or sedimentation processes as water moves from a greater speed in a river to a lower speed in a lake. Also, the pH observed in this study, according to Srinivasan *et al*. (1999), is such that most of the Al will most likely become insoluble and form precipitates that can settle to the bottom (Fig 5.5). In addition, the water from MRD to further downstream is dominated by clay (Table 5.4) which, according to Kamau *et al*. (2008) and Stumm and Morgan (1996), has got a high surface area for adsorption of dissolved particles such as metals that include Al, and other complexing agents that can adsorb Al from the water. Clay particles are most likely associated with high organic matter which also tends to bind with metals reducing the concentrations in the water and thus, bioavailability and toxicity of these metals in water (CEQG, 2003). This might also explain the low Al in water at LCS, LCS2 and CD.

The presence of Al in upstream sites suggests that there are other sources of Al to Manyame River but that the sources are minimal as compared to that emanating from Morton Jaffray, in terms of Al content as the levels in those sites were much lower than those from sites immediately downstream the discharge point. Relatively unimpacted CD had a mean concentration of 1.22 ± 1.46 which implies that this may be the natural background level obtainable in the catchment probably from the geology and soils (Rashed, 2001). Sorenson *et al*. (1974) also found out that the levels of Al in natural surface waters were in the range of 0.001 to 2 mg/l while PBC (1998) reported the levels to be at most 1 mg/l. These studies were carried out in countries of different weather conditions but the reported levels are more/less the same hence, these levels can be taken as a general guide to possible levels of naturally occurring Al. However, further downstream in the same catchment and downstream to anthropogenic sources of pollution, LCS1 and LCS2 had higher Al concentrations than CD though not significant (Fig. 5.3). This increase might be due to additional quantities from industrial and municipal waste effluents that find their way into the lake. There was an increase in Al levels at MRU in sampling campaign 2 probably due to additional sources from Lake Chivero that had started spilling as the rains peaked. A decrease at MRD and LMM in sampling campaign 2 may be an indication of dilution effects with increased flow of water characteristic of wet periods. Therefore, pollution at any given time is greater for sites downstream of the discharge point followed by sites in Lake Chivero and then CD. Therefore, the impact of industries and sewage effluents, among others, which pollute Lake Chivero have got less impact on al concentrations at any given time compared to pollution from the residues.

5.2.3 Accumulation in sediments

The range of Al accumulated in sediments in the first sampling campaign was from 10.29±6.94 mg/l (MRU) to 103.79±55.96 mg/l at MRD while in the second campaign it was from 4.47±0.31 mg/l (MRU) to 131.84±16.48 mg/l for MRD (Fig. 5.4; Appendix B). MRD had the highest levels, followed by LMM, while MRU had the lowest followed by LMD, in both sampling campaigns.
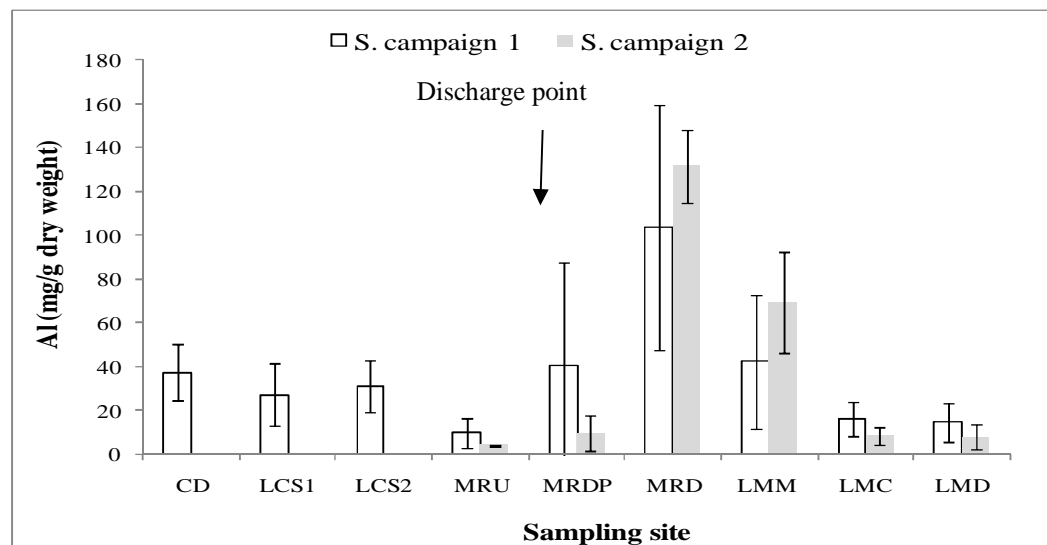
Figure 5.4: Mean TaL concentrations in sediments from all the sites and sampling campaigns.

Noticeable, was the high concentration of Al in sediments from CD even comparable to downstream sites and sites in Lake Chivero (Fig. 5.4). Aluminium concentrations from MRD and LMM were significantly different from all the other sites and from each other in sampling campaign 2 (p<0.05). In sampling campaign 1, only MRD was significantly different from all the other sites with those other sites not being markedly different from each other except for MRU and LMM (ANOVA: p>0.05). The levels in the other sites, excluding MRD and LMM, ranged between 4.47±0.31 mg/l (MRU, Sampling campaign 2) to 40.69±47.20 mg/l (MRDP, Sampling campaign 1) as detailed in Appendix B. Levels of Al in sampling campaign 1 were generally higher (approximately, 67 % of the time) than those in sampling campaign 2 (Fig. 5.4). The trend of accumulation between sediments and water in sampling campaign 2 showed some antagonistic effects whereby levels in water increased while in the sediments they decreased though for MRD and LMM, levels in the water decreased whereas in the sediments they increased. However, there was no significant correlation between the Al in the water and in the sediments (Pearson correlation, R = -0.033; p=0.944) though relationship was negative. The same gradient as observed for water was apparent for sediments with a peak at MRD and sharp decreases at LMM lowering up to LMD.

The impact of the residues on the receiving water bodies is also highlighted with the pattern of accumulation of Al in the sediments (Fig. 5.4). MRD was the only site with a concentration quite high and also significantly different from the other ones whilst the levels in the rest of the sites were not significantly different from each other. Also, Al in sediments was highest at MRD followed by LMM in both sampling campaigns further illustrating the impact of the residues and its spread or coverage. These high levels in sediments registered at MRD and LMM is an indication of environmental pollution, according to Rapin *et al.* (1983). LMD had the lowest Al levels in sampling campaign 2 demonstrating that the distance covered by the pollution load from Morton Jaffray is limited to approximately 10 km of the discharge point due to several factors as highlighted above. The distance from MRD to LMM is approximately 8 km hence the specification of 10 km in the above sentence and there is sharp decrease from LMM to LMC which means that the spread of the pollution becomes minimal. In addition, sediments are less mobile particularly, in a lake which is almost stagnant and so, pollutants attached to sediments are less likely to move greater distances as compared to those carried in water. The high amounts of Al at CD could have been due to the geology of the catchment (refer to Section 3.5) which has constituents that consists of Al and are also dominated by silicon oxides. Silicon oxides have been shown as being remarkably efficient in settling, and having high affinity for, metals such as Al (Stumm and Morgan, 1996). As such, the sediments will thus contain much of the metals in any water body. In addition, CD is located at the head waters of a river, the Mukuvisi River, such that the sediments in the dam may not be disturbed by any incoming water as the water at the beginning of a river will probably be of low speed and flow. Therefore, accumulation over time may be increased. Also the high levels in the sediments at CD may be so considering that sampling was carried out in a dry period which may result in insignificant re-suspension to see the reduction in metal levels in the sediments.

Re-suspension of sediments may explain the general reduction in the concentrations of Al in sediments in sampling campaign 2. Retief *et al.* (2009) obtained the same results as in this study in terms of high levels in the dry period and less concentrations in sediments in the wet period. The authors explained that heavy rains and strong wind action increase flows and movement in the river and lake which disturbs the water and the bottom sediments. Also, heavy rainfall activity and strong winds cause concentration gradients between the top and the bottom waters resulting in movement of contaminants from the bottom to the top in the wet period or re-suspension of the sediments. Re-suspension may also be the major explanation for the increased levels of Al in water followed by decreases in sediments for all the other sites except MRD and LMM. Also, as volume of water increases anoxic conditions are created at the bottom creating reducing conditions for the naturally-occurring complexing agents such as Fe and Mn oxides which then release the bound particles. Thus, Al levels in the sediments decreased for MRU, MRDP, LMC and LMD and increased in the overlying water. LMM is characterized by a dense network of submerged plants which continually add oxygen to the water creating oxic conditions in the water. However, the increase in concentrations of Al in the water in upstream sites accompanied by the neutral to alkaline pH range for the sites, enhance precipitation of Al which

are fast transported by the increased water flow allowing for faster settling in the downstream sites as also explained by Nyamangara *et al*. (2008).

What can be concluded from the above sections on Al is that the sediment medium had the largest store of Al compared to water or fish or the residues in both sampling campaigns in all the sites as also obtained by Abdullah (1995) and Nyamangara *et al* (2008) between sediments and water. Accumulation in sediments shows accumulation over time as was concluded from information obtaining in sections 2.4 and 2.5. Thus, this sink for the metal may present possible future toxicity to fish and other aquatic life if conditions permit for desorption, bioavailability and toxicity of the metal to the aquatic life. Actually, contaminants from the sediments can become detached from the sediments and become harmful to aquatic life (Praveena *et al*., 2008). Also, there was generally reduced Al in Lake Manyame towards the dam wall which is also the area where raw water is abstracted for treatment and supply as potable water to greater Harare. It may be concluded that the water abstracted at the intake tower at LMD has minimal residual Al levels comparing to the other upstream sites in the river downstream the discharge point. This would imply that the water is less likely to significantly impact on the drinking water and health of the residents of greater Harare. This would also apply for water abstracted at LCS1, which is the area for the intake tower in Lake Chivero. LCS1 had a mean lower than that of LMD but the two were not significantly different ($p>0.05$). However, it should be pointed out that the concentrations obtained in the raw water at either LMD or LCS1 are still high compared to what was obtained elsewhere. For example, in a study reported in Srinivasan *et al*. (1999), TaL levels obtained in the raw water for further treatment was 0.01 ± 0.009 mg/l which would then increase to 0.49 ± 0.009 mg/l after treatment with alum. It can be inferred from this study that the possible range of Al in filtered water after treatment with alum would be between approximately 116.3 ± 1.51 mg/l (raw water from LCS1) to 122.5 ± 0.36 mg/l for raw water from LMD. This range is far much higher than the Al recommended by WHO drinking water safety guidelines (House and Reed, 2004) of 0.2 mg/l. It can also be concluded that Al is naturally present in the catchment at levels below 5 mg/l for water and below 50 mg/l for sediments. Levels for the sites immediately downstream the discharge point of the residues was quite elevated while Al was also higher than the standards in the other unimpacted sites. Therefore, the residues from Morton Jaffray have an impact on accumulation of Al in water, sediments and fish in Lake Manyame while there are other sources of Al with a magnitude that is quite less compared to that fro Morton Jaffray water works.

5.3 Physico-chemical parameters

5.3.1 pH and temperature

The variations in pH among the sites were significant (ANOVA: $p<0.05$). The pH in the sites in Lake Chivero was not significantly different between the two sites and from that of MRU, LMC and LMD but from sites immediately downstream of the discharge point (MRDP, MRD and LMM) and at CD. The pH observed in Lake Chivero and Lake Manyame (in both sampling

campaigns) was greater than 8.5 while in the sites immediately below the discharge point (MRDP and MRD), the pH had lowered (*e.g.* 6.89±0.49, MRDP, Sampling campaign 1) from that observed at MRU (8.78±0.49, Sampling campaign 1) as shown in Fig. 5.5. However, there was recovery from MRD onwards in terms of increased pH in both sampling campaigns (Fig. 5.5). The sites immediately downstream of the discharge point, MRDP, MRD and LMM, were not significantly different from each other though pH increased from MRDP up to LMM (ANOVA: $p>0.05$). The pH of LMM was however, significantly different from LMC and LMD in both sampling campaigns (ANOVA: $p<0.05$). There was a significant general decrease in pH in sampling campaign 2 whereby the pH averaged 8.36±1.07 in sampling campaign 1 whilst the average in sampling campaign 2 was 7.49±0.60.

Temperatures recorded in this study fell within the range of 24.31±0.17 ℃ (LMD, Sampling campaign 2) and 28.11±0.24 ℃ (CD, Sampling campaign 1) as shown in Fig. 5.5. Temperature was generally higher in sampling campaign 1 than 2 with an average of 26.58±0.80 ℃ compared to 25.00±0.89 ℃ in sampling campaign 2. The variations among the sites were significant (ANOVA: $p<0.05$). In sampling campaign 2, MRU was significantly different from all the other sites except LMM and registered increased temperature. These two sites are the only sites that recorded temperatures greater than 25 ℃ in this campaign. Temperature showed no marked variations from MRDP, MRD up to LMM but showed a decreasing pattern. However, LMM was significantly different from LMC whilst LMC was not different from LMD.
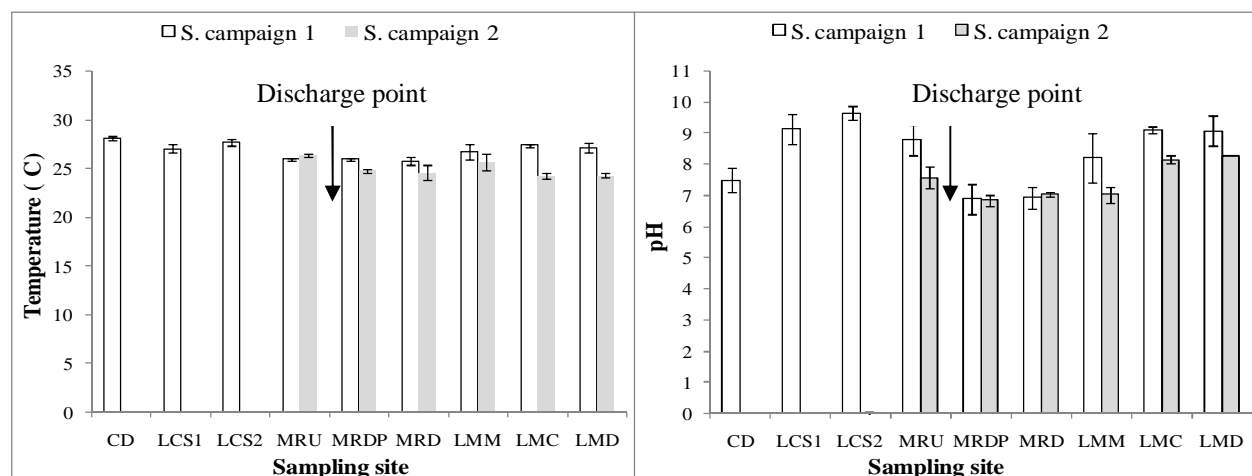
Figure 5.5: Variations in temperature and pH (mean and standard deviations) along the sites.

The pH range (5.5-10 or 6-9), has got varied effects on Al solubility, availability and toxicity according to: Chapman (1996); Davies and Day (1996); Tebutt (1998); Srinivasan *et al.* (1999); CEQG (2003); Sharma (2003) as explained in Section 2.3. The pH observed in Lake Chivero and Lake Manyame (LMC and LMD), in both sampling campaigns, was greater than 8.5 and can

render Al bioavailable to fish and increase toxicity to fish. This high pH in the two lakes was attributed to high levels of photosynthetic activity. Photosynthesis removes carbon dioxide (CO_2) from the water resulting in free hydroxyl ions which elevate the pH in the water during daytime. The higher the removal rate of CO_2 the higher the pH or the less the acidity of the water (Billings, 1984). Sampling in this study at all sites was conducted during the day from mid-morning to afternoon when photosynthesis would possibly be at its maximum due to presence of sunlight hence also the high pH in the highly productive lakes. LMM is impacted most probably by the residues from Morton Jaffray hence the lowered pH compared to LMC and LMD. Cleveland Dam is characterized by submerged plants but its pH is maintained in an almost neutral range which probably shows that it is well buffered.

The pH values for all the sites in this study fell within the recommended ranges of between 6 and 8 or 9 (Appendix C). The European Union also set pH protection limits of 6.0 to 9.0 for fisheries and aquatic life (Chapman, 1996). According to Kaiff (2002), the largest varieties of aquatic animals prefer a range of 6.5-8.0 such that pH outside this range reduces diversity in streams. This is particularly so because pH outside this range stresses the physiological systems of most organisms and can also reduce reproduction. However, as specified by Moyle (1993), a pH range of 5.5 and 10 is capable of maintaining fish life. Therefore, the residues from Morton Jaffray waterworks impacted on pH of the receiving waters by decreasing the pH of the sites immediately downstream the discharge point in both sampling campaigns.

The pH of the residues is acidic which explains the generally lowered pH at MRDP and MRD spreading to LMM downstream the discharge point as shown in Table 5.1 and Figure 5.5. Nevertheless, the pH at these sites showed some measure of recovery which indicates the presence of an efficient buffering capacity of the river water which serves to neutralize the acidity received from the residues. A significant weak negative correlation ($r = -0.33$; $p<0.05$) was obtained between Al and pH (Table 5.3). This means that as pH increased (becoming more alkaline), there was a decrease in the concentrations of TaL in water which may be true as indicated by the patterns in Fig. 5.3 and Fig. 5.5. The differences in pH between sampling campaigns 1 and 2 are an indication of expected seasonal variations in pH. During dry periods, as in campaign 1, there are high water temperatures which increase photosynthetic activity in the water hence higher pH values in campaign 1 than campaign 2. Sampling was also carried out during daytime when photosynthetic activity would be at its maximum as well. The pH at MRU decreased in sampling campaign 2 which might have been due to possible leaching of organic acids from the catchment as it is surrounded by trees on both sides.

Temperature of natural inland surface waters generally varies between 25 °C and 35 °C according to Alabaster and Lloyd (1980) while in neighbouring country, South Africa, the general range is from 5 °C to 30 °C (DWAF, 1996). Temperatures recorded in this study also fell within these natural ranges for all the sites in both the sampling campaigns (Fig. 5.5). This indicates that the temperature in the water bodies is optimal for support of aquatic life as well all other possible

uses that include drinking water source. The reason for variations between sites could have been due to the different times of the day when the samples were collected and measured and different surrounding environments.

Temperature generally affects conductivity and dissolved oxygen content in a water body. Increased temperatures can result in increased respiratory and metabolic activity in aquatic organisms resulting in increased oxygen demand leading to a decrease in oxygen content of the water (DWAF, 1996). High temperatures also reduce the solubility of oxygen resulting in dissolved oxygen depletion. At the temperature range of 23.8 ^{o}C to 28.5 ^{o}C, as observed in this study, DO should range between 7.81 and 8.73 mg/l at zero salinity. As salinity increases, for example at salinity of 25 000 mg/l for the same temperature range, DO would be expected to range between 6.79 and 7.94 mg/l (Metcalf and Eddy Inc, 1995). Salinity was however, not measured in this study. Thus, as the dissolved oxygen content between molecules in water decrease, the amounts of dissolved solids will increase. An increase in the solids content indicates an increase in all the dissolved solids, including Al. However, this negative relationship was also observed in this study and it was strong for DO concentration and temperature (Appendix C; Table 8.5). As metabolic rate increases, absorption of water and the nutrients therein is supposed to be increased as well. This means that Al and other dissolved particles should increase in organisms' bodies as temperature increases according to Tebutt (1998). There was however, no significant correlation between temperature and Al content of water (Appendix C). However, sites in the lakes had high temperatures and also the Al content in the fish was also high.

Sites in the river had lower temperatures than sites in the lakes and dam possibly due to the vegetation cover in the surrounding catchment which provided shade to the sites hence reducing the amount of solar radiation reaching the water. The increase in temperature in the second sampling campaign at MRU might have been due to release of water from the upstream reservoir, Lake Chivero, which registered high temperatures in sampling campaign 1. As the rains peaked in March there was increased volume of water in the lake which resulted in spillage of the water from the lake into the downstream river stretch. Lake Chivero is an open body of water exposed to maximum sunlight such that the water coming from it is warm. This also indicates that pollution coming from Lake Chivero is another source of pollution or deterioration in water quality at MRU and possibly, even for the other sites downstream. However, if this was so for the other downstream sites then an increased temperature should have been observed at MRDP and further but it can be seen that there is a decrease at MRDP which decreases further at MRD corresponding to the residues of low temperature (Fig. 5.5; Table 5.1). Also, it seems also that pH of MRDP and MRD is affected more so by the residues as there was a decrease at MRDP instead of a recovery as happened at LMM onwards (Fig. 5.5). This observation accompanied by the gradient from MRDP up to LMD highlighted the impact of residues from Morton Jaffray waterworks on the temperature status of immediate downstream sites, a trend which was also observed with variations in pH (Fig. 5.5). Temperatures in the sites in Lake

Manyame in sampling campaign 2 were on the lower side because of the cloudy conditions during that particular time of sampling.

5.3.2 Dissolved oxygen (DO)

Variations among the sites for DO concentration and percent DO saturation were significant (ANOVA: $p<0.05$). Dissolved oxygen (DO) levels were quite high for LMM and CD (8.60 ± 2.16 at 126.75 % saturation and 9.00 ± 2.31 mg/l at 136.84 % saturation in campaign 1, respectively) as shown in Fig. 5.6. However, DO was very low for Lake Chivero and Manyame River where DO concentration was less than 5 mg/l at DO saturation ranging from 5.23 ± 3.67 % (LCS1, campaign 1) to 84.55 ± 17.16 (MRD, campaign 2) also illustrated in Fig. 5.6. There was a general decrease in DO content in Lake Manyame in the wet period from sampling campaign 1. In both sampling campaigns, there was improvement in the DO content further downstream towards LMD (Fig. 5.6).

In the supposedly polluted sites in Lake Chivero and Manyame River, generally, DO saturation was correspondingly, below the DWAF (1996) guidelines of between 80 and 120 %. This is an indication of the level of pollution in the water systems. The concentration was also below the acceptable levels in literature of 4 to 5 mg/l required to prevent detrimental effects to fish though it depends on species (Metcalf and Eddy Inc, 1995).
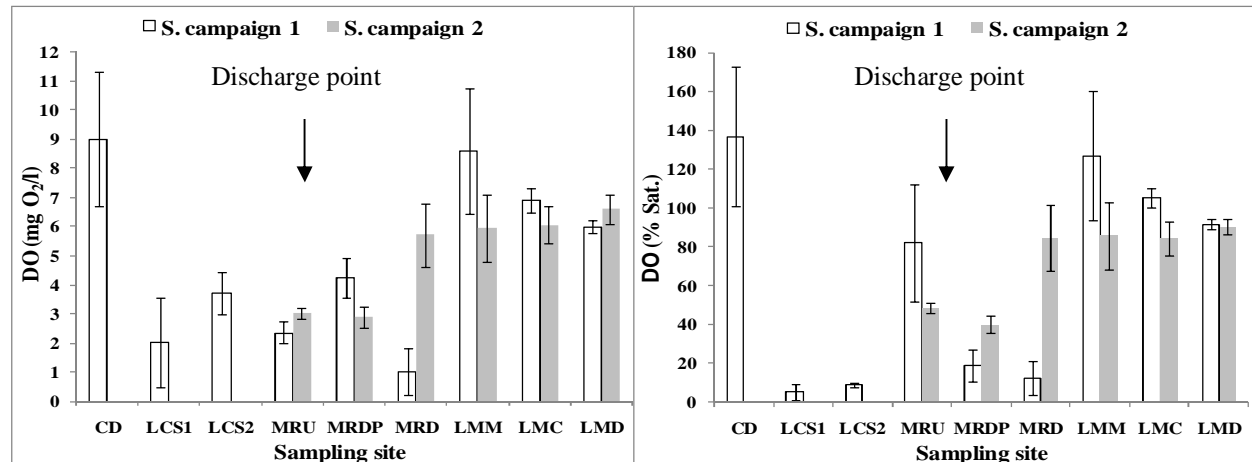
Figure 5.6:   Variations in DO concentration and percent saturation (mean and standard deviations) along the sites.

In a study by Moyo on Lake Chivero (1997) the levels of DO on 29 March 1996 between 12 mid-day and 16 00 hours in the afternoon was 1.8 and 2.0 mg/l, respectively. However, the values for Lake Chivero were obtained in January when there was less rainfall activity. Nevertheless, there seems to be less improvement in the quality of the lake from 1996 to now. Lake Chivero is highly polluted with sewage effluent irrigation runoff and seepage, raw sewage or sewage effluent from sewage treatment plants that discharge their raw sewage or untreated

effluent into rivers discharging into Lake Chivero (Marimba River- Nhapi and Tirivarombo, 2004; Mathuthu *et al.*, 1997, Mukuvisi River- Kamudyariwa, 2000; Zaranyika, 1997). Thus, although the lake is eutrophic with high photosynthetic activity, the incoming wastes exert an oxygen demand on the water which results in the depletion of oxygen hence the low results (Metcalf and Eddy Inc, 1995; Tebutt, 1998; Abowei, 2010). The DO saturation percentages for LCS1, LCS2, MRU and MRDP were in the sub-lethal to lethal range according to South African Water Quality Guidelines (DWAF, 1996) as given in Appendix D.

High photosynthetic activity can increase oxygen levels in the water but this reduces in the wet period due to cloud cover that reduces photosynthesis (McNeely *et al.*, 1979; Davies *et al.*, 2008; Abowei, 2010). This may explain the reduced oxygen concentrations for Lake Manyame sites in sampling campaign 2. During the dry season when Lake Chivero is not spilling, MRU would be recording zero flows at the gauging station (C17) such that the water is almost non-flowing under the weeds covering the water surface at the site; there is thus no turbulence or surface re-aeration. Also, the weeds naturally undergo a cycle of rapid growth, senescence and death which results in decomposition by microbial action which uses up the oxygen in the water for respiration hence contributing to very low results at the site particularly during the "no flow" period (Metcalf and Eddy Inc, 1995; Tebutt, 1998). Metcalf and Eddy Inc (1995) reported that in a water body with no open space of water the major processes controlling the amount of dissolved oxygen would be photosynthesis and respiration.

Standard DO results at temperature ranges between 23 ºC and 29 ºC, which was the range in this study, are 8.38 mg/l and 7.64 mg/l, respectively (DWAF, 1996). This was not confirmed in this study except for Cleveland dam though there is a trend of increases in temperature accompanied by decreases in DO content for sites in Lake Manyame. This highlights that these standards are characteristic of unimpacted freshwaters such as CD. Cleveland dam and LMM (sampling campaign 1) are supersaturated as can be seen by the DO percentages greater than 120 %. This shows that there is free oxygen due to net photosynthesis exceeding oxygen consumption in respiration. This also shows that there is less or no organic pollution which can exert an oxygen demand that lowers DO in water bodies as in Lake Chivero according to Abowei (2010). Cleveland dam is characterized by submerged plants which is also the case at LMM but even worse for the latter. Submerged plants release oxygen direct into the water column. These high values occurred in the first sampling campaign as there was minimal runoff of material from the catchment which could bring with it oxygen demanding materials which act to lower the DO levels. In addition, sampling campaign 1 was a dry period with relatively high amounts of sunlight which facilitate increased photosynthetic activity. The high levels of DO may have been more so considering also that sampling was carried out during the day when there is maximum sunlight.

The impact of different sampling periods with differing flow regimes was varied for the different sites in this study. Oxygen content at MRU increased in sampling campaign 2 probably due to increased water flow. There was, however, no clear trend between the two sampling campaigns

to be able to conclude on which season has got what impact on DO concentrations. Fish existence at MRU is threatened more so for dry periods because of very low DO and poor re-aeration capabilities. Lack of surface re-aeration or turbulence could explain the very low DO at MRD in sampling campaign 1 where the water was gentle to almost stagnant probably due to the weeds that disturb the normal flow of water in the upstream and downstream areas and no-flow situation in the river during dry periods. There was improvement in DO levels at MRDP as compared to MRU in sampling campaign 1 probably due to water turbulence as the residues are discharged from under the water surface. Sampling at the site was carried out either during or just after the discharge periods when the water had been disturbed such that oxygen from the atmosphere could have escaped into the water. MRDP and MRD are areas characterized by an open body of water which agrees with the report by Metcalf and Eddy Inc (1995) that turbulence and/or re-aeration would be playing a major role in an open body of water in terms of the dissolved oxygen content of the water. A decrease in DO content of the residues might also have been the cause of reduced oxygen content at MRDP. There was a general improvement in DO further downstream up to LMD which might probably been due to the possibly present self-purification system in the water system. Water from Lake Chivero has got limited impact, in terms of distance or space, on sites further downstream, *i.e.* MRDP and others thereafter. Residues from the water works also have limited impact on sites further downstream from the discharge point in terms of DO concentrations.

5.3.3 Electrical conductivity (EC), Total dissolved solids (TDS), Total solids (TS)

The trends observed for Electrical conductivity (EC), Total dissolved solids (TDS) and Total solids (TS) for all the sites and both campaigns were the same (Fig. 5.7). Noticeable is the trend in the levels of the three parameters of an increase from MRDP to MRD and a decrease thereafter from LMM up to LMD, in both sampling campaigns (Fig. 5.7).

The differences among the sites were significant (ANOVA: $p<0.05$). The levels of these parameters between the sites in Lake Chivero were not significantly different from each other but from all the other sites though LCS1 was not different from MRDP and MRD. MRU was not significantly different from LMM while sites in Lake Manyame were also not different from each other (ANOVA: $p>0.05$). In sampling campaign 2, however, sites in Lake Manyame were significantly different from each other while MRU was no longer significantly different from MRDP. EC, TDS and TS were higher 67 %, 100 % and 83 % in space in the wet period, respectively. Levels of these three parameters were higher in the river sites than the lake sites, particularly, Lake Manyame. The levels of these three parameters were higher at LCS1 and LCS2 than in all the sites in Lake Manyame. It can be seen from Fig. 5.7 that total solids were much greater than TDS for all the sites and sampling campaigns as is expected. Total solids ranged from 216±50.91 mg/l (LMD) to 1081±3.53 mg/l (MRD) and 713.5±28.28 mg/l (LMD) to 1311±80.61 mg/l (MRD) in sampling campaign 1 and 2, respectively, while TDS ranged from115±10.74 mg/l (CD) to 338±12.63 mg/l (MRD) in sampling campaign 1 and 330±0.76 mg/l (LMC) and 387±9.41 mg/l (MRDP) in sampling campaign 2.
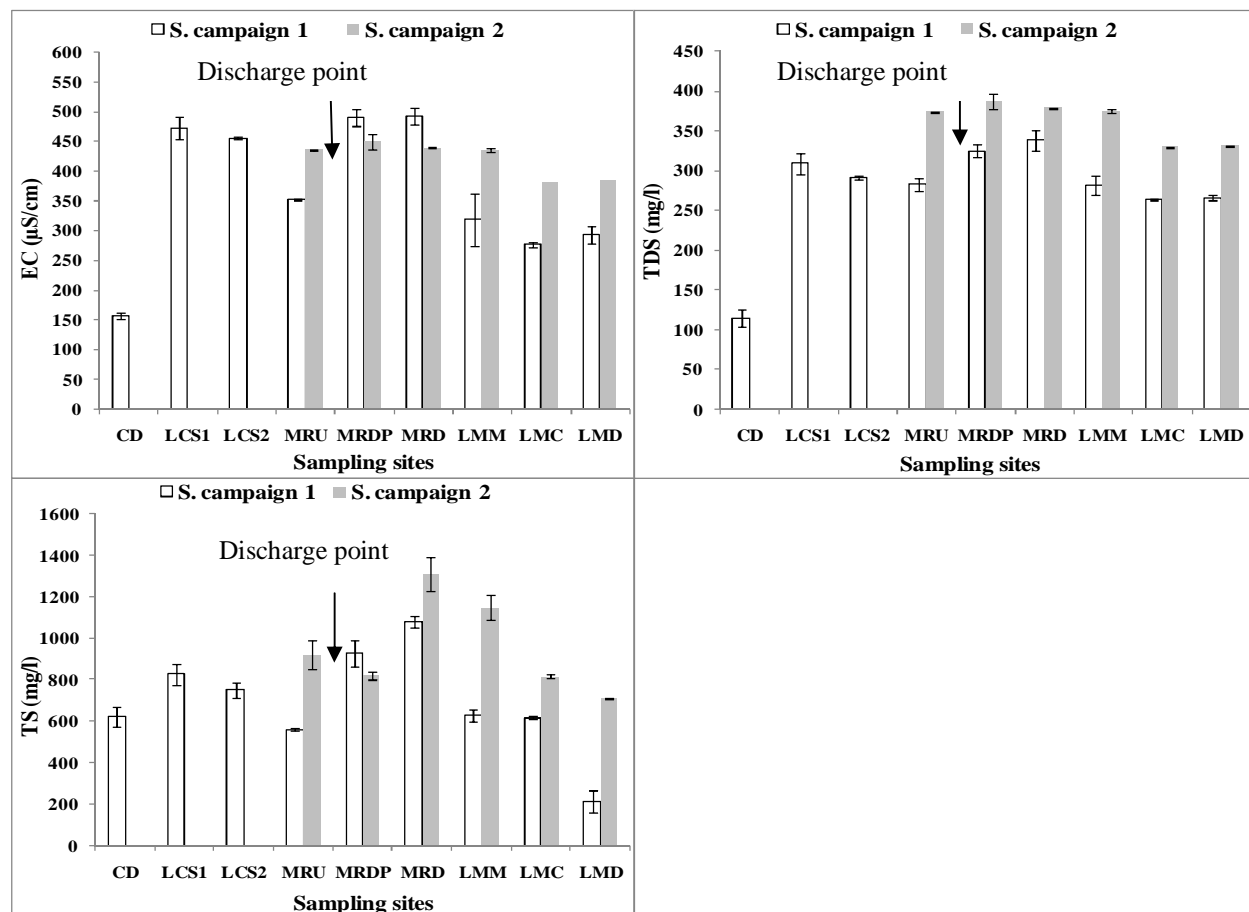
Figure 5.7: Variations in EC, TDS and TS levels (mean and standard deviations) along the sites. (The arrow shows position of the discharge point).

The increase in EC, TDS and TS immediately after the discharge point indicated the impact of the residues from the treatment works on the receiving waters. EC is a measure of inorganic constituents whilst TDS is a measure of all dissolved substances both inorganic and organic and there was thus a significant correlation (Appendix C). The acceptable limit for EC for surface water used for domestic water supply in South Africa is 70 µS/cm and this was exceeded in all the sites in this study. However, higher conductivities were observed upstream (LCS1, LCS2 and MRU) and downstream of the discharge point in the dry and wet periods suggesting that there could be other point sources of inorganic pollution entering into the receiving water bodies resulting in the high values. CD is further upstream of the major sources of pollution coming from Harare and other satellite towns hence the low levels of EC and TDS. TDS for all the sites was above the limit of 120 mg/l as suggested by DWAF (1996) though CD met the EPA-AU (2006) guideline of 250 mg/l required for the protection of human health for consumption of water and organisms. CD had high TS though, which highlights dominancy of suspended particles probably due to wind and wave action, at time of sampling, which can re-suspend

settled particles. The gradual decrease in all the parameters by site LMD may be due to sedimentation processes that occur when water loses its speed upon entering a bigger water body such as a lake resulting in settling of the particles in the river water (Chapman, 1996). This decreasing gradient towards LMD was also observed for Al in water which indicates that there is a relationship between the presence of high or low solids content with increased or decreased Al content. A strong, positive relationship was confirmed between Al in water and TDS and EC content and was stronger with TDS ($p=0.016$) which also implies that the Al species in this study was also in dissolved states but probably non- ionic states which are less toxic than the toxic forms of Al.

These three parameters were higher in sampling campaign 2 than 1 which might have been due to additions from rainwater, weathered and eroded particles from the catchment as well as sediment re-suspension as water levels increase. Levels of TS were higher than levels of TDS which is expected because basically TS is a measure of both dissolved and suspended solids hence its results are generally higher than for TDS. There was thus a significant ($p<0.05$) strong positive correlation between TDS and TS ($r=0.928$) and also between TDS and EC ($r=0.980$) as shown in Appendix C. The results obtained in this study were much lower than what was obtained elsewhere in sites impacted mainly by wastewater from sewage effluents and industries (Akan *et al*., 2009; Esmail *et al*., 2009) but similar to results obtained elsewhere on other sources of pollution that include sewage effluents (Igbinosa and Okoh, 2009; Fatoki *et al*., 2003). The high solids content in water bodies that are used also as sources of drinking water is problematic and a cause of concern. Increased solids content can have a visual impact on fish which use their sight in feeding and also it can result in increased turbidity which makes treatment of the raw water expensive as is the case at Morton Jaffray currently according to personnel from City of Harare. Residues from Morton Jaffray have got a great impact on conductivity and solid content of the receiving water though the impact is limited in space. There are also other sources of inorganic pollution in the catchment.

5.4.4 Sediment texture and moisture content

The texture obtaining in the different sites is as shown in Table 5.3. All the sites were dominated by clay fraction followed by sand then silt.

Moisture content followed the same trend as for Al in sediments (Fig.5.8; Fig. 5.4). According to Kralik (1999), it is assumed that water and dissolved metals will occupy the same position in the sediments meaning that the level of adsorbed water will correspond to the amount of contaminants. It is concluded that all the sites have got potential for adsorption and accumulation of pollutants and the levels of Al corresponds with the moisture content of the sediments.

Table 5.3: Sediment texture for the different sites.

Site	Percentage (%) Fraction			Total
	Clay	Silt	Sand	100
CD	64.79	12.21	23.00	100
LCS1	75.21	13.45	11.34	100
LCS2	63.47	9.12	27.41	100
MRU	55.16	11.84	33.00	100
MRDP	47.24	13.32	39.44	100
MRD	55.16	11.84	33.00	100
LMM	98.08	1.76	0.16	100
LMC	72.10	5.22	22.68	100
LMD	47.24	13.32	39.44	100
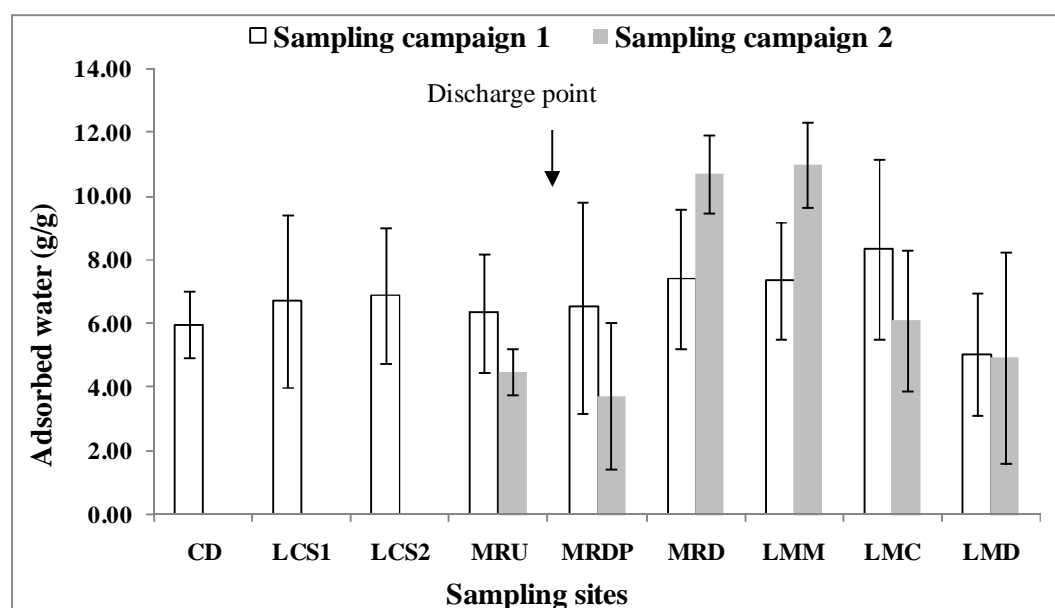
Figure 5.8: Variations in adsorbed water content of sediments (mean and standard deviations) along the sites.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions were made from this study:

1. The residues complied with ZINWA (2000) standards for physico-chemical parameters for discharge of effluent in surface waters except for pH which was acidic and total aluminium concentrations which were four - to five - fold higher than is reported in literature.

2. The residues from Morton Jaffray waterworks are impacting (*i.e.*, increasing) on the Al concentrations in the water, sediments and fish of downstream receiving water bodies.

3. The sediments contained the largest chunk of the Al in the water systems. The general order of Al accumulation in fish tissues in decreasing order was: kidney>liver>gill>muscle with fish from Lake Chivero having the higher Al levels than fish from Lake Manyame. Fish are at great risk of Al toxicity.

4. There was general deterioration in the water quality after Morton Jaffray with recovery further downstream and the pollution emanating from Morton Jaffray is limited to a short distance downstream.

6.2 Recommendations

1. There is need for pretreatment of the residues for pH re-adjustment and residual Al reduction before disposal as well as use of other effective but less harmful coagulants (Al-free) other than aluminium sulphate.

2. If reduction of residual Al is difficult or impossible, then research is needed to develop ways of re-using the Al in the residues for example, in sewage works and agriculture, as a way of disposal.

3. Further studies recommended:
    3.1 Fish capture was problematic in some sites resulting in some sites not having fish samples and also fish are migratory such that for the same river stretch, it would be tricky to isolate fish from one site to another. Therefore another long-term study is required that will look at the same variables as used in this study but using other less mobile organisms such as macroinvertebrates.

3.2 Investigation on the other sources of Al in the catchment which include mainly, industries and sewage treatment works, to explain the high levels of Al in fish in Lake Chivero, and also to explain the high levels in the sediments in Cleveland Dam.

3.3 Investigations on possible sources of high Al in sediments in Cleveland Dam.

7. REFERENCES

Abdullah, M. P, Baba, I, Sarmani, S, Erdawati., 1995. Distribution of aluminium from alum sludge in water and sediments. Marine and Freshwater Research, 46 (1), 159-165.

Abowei, J.F.N., 2010.   Salinity, Dissolved Oxygen, pH and Surface Water Temperature Conditions in Nkoro River, Niger Delta, Nigeria.   Advance Journal of Food Science and Technology 2 (1), 36-40.

Adams, V.D., 1990.   Water and Wastewater Examination Manual.   Lewis Publishers Inc., Michigan, USA.

Ademoroti, C.M.A., 1996.   Environmental Chemistry and Toxicology.   Foludex Press Ltd, Ibadan, Nigeria.

Adham, K.G., 2001.   Metallic Micro-pollutants in the Harvest of *Oreochromis niloticus* (Linnaeus, 1757) from Polluted Waters: Wildlife and Human Concerns, Pakistan Journal of Biological Sciences, 4 (12), 1550-1558.

Akan, J. C, Abdulrahman F. I, Sodipo, O. A, Akandu, P. I., 2009. Bioaccumulation of Some Heavy Metals of Six Fresh Water Fishes Caught from Lake Chad in Doron Buhari, Maiduguri, Borno State, Nigeria. European Journal of Scientific Research, 23 (1), 122-133.

Alabaster, J. S., Lloyd, R., 1980.   Water quality criteria for freshwater fish. Butterworth's, London, U.K.

American Public Health Association., 1989. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Water Environment Foundation and American Water Works Association, Washington, DC.

Azzaoui, F.Z, Ahami, O.T, Khadhamaui, A., 2008. Impact of Aluminium Sub-Chronic Toxicity on Body Weight and Recognition Memory of Vistar Rat. Pakistan Journal of Biological Sciences, 11 (14), 1830-1834.

Baldock, J.W, Styles, M.T., Kalbskop, S, Muchemwa, E., 1991. The Geology of the Harare Greenstone Belt and Surrounding Granitic Terrain. Zimbabwe Geological Survey, Bulletin No. 94

Bartram, J, Balance, R (eds)., 1996. Water Quality Monitoring: A practical guide to the design and implementation of freshwater quality studies and monitoring programmes. 1st Ed. E & FN Spon, an Imprint of Chapman and Hall, London, UK.

Bell-Cross, G, Minshul, J., 1988. The Fishes of Zimbabwe. Trustees of the National Museum and Monuments of Zimbabwe. Harare, Zimbabwe.

Bentivegna, C.S, Alfano, J-E, Bugel, S.M, Czechowicz, K., 2004. Influence of Characteristics on Heavy Metal in an Urban Marsh. Urban Habitats, 2 (1), 91-103.

Bjerknes, V., Fyllingen, I., Holtet, L., Teien, H.C., Rosseland, B.O., Kroglund, F., 2003. Aluminium in acidic river water causes mortality of farmed Atlantic salmon (*Salmo salar* L.) in Norwegian fjords. Marine Chemistry 83 (3-4), 169-174. In: Sharma, C.M., 2003. Effects of Exposure to Aluminium on Fish in Acidic Waters, Department of Ecology and Natural *http://www.geocities.com/chhatra_sharma/publications.html* (Accessed: 3 July 2009).

Billings, W.D, Golley, F, Lange, O.L, Olson, J.S, Remmerth., 1984. Ecological Studies, Analysis and Syntheis. Spinger-Verlag Inc., New York, USA.

Bittl, T, Vrba, J, Nedoma, J, KopaAclek, J., 2001. Impact of ionic aluminium on extracellular phosphatases in acidified lakes. Environmental Microbiology, 3 (9), 578-587.

Braide, S.A., Izonfuo, W.A.L., Adiukwu, P.U., A.C., Chindah, Obunwo, C.C., 2004. Water Quality of Miniweja stream, A Swamp forest stream receiving non-point source waste discharges in Eastern Niger Delta, Nigeria. Scientia. Afr., 3 (1): 1-8. In: Abowei, J.F.N., 2010. Salinity, Dissolved Oxygen, pH and Surface Water Temperature Conditions in Nkoro River, Niger Delta, Nigeria. Advance Journal of Food Science and Technology 2 (1), 36-40.

Buerman, Y, Du Preez, H.H, Steyn, G.J, Harmse, J.T, Deacon, A., 1995. Suspended silt concentrations in the lower Olifants River (Mpumalanga) and the impact of silt releases from the Phalaborwa Barrage on the water quality and fish survival. Koedoe, 38 (2), 11-434.

Canadian Environmental Quality Guidelines (CEQG), Canadian Council of Ministers of the Environment., 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Aluminium.

Central Statistical Office (CSO). (2002) Census 2002: Zimbabwe. Preliminary Report, Central Census Office, Government of Zimbabwe, Harare, Zimbabwe.

Chapman, D, (ed), 1996. Water Quality Assessments: A guide to the Use of biota, sediments and water in Environmental Monitoring. 2nd Ed. E & FN Spon, an imprint of Chapman & Hall, United Kingdom.

Chikwenhere, G.P., 2001. Current strategies for the Management of Water Hyacinth in the Manyame River System in Zimbabwe. Biological and Integrated Control of Water Hyacinth, Eichhornia crassipes. ACIAR Proceedings 102: 105-108.

Ciceri, G., Maran, S., Martinotti, W., Quierazza, G., 1992. Geochemical cycling of heavy metals in a marine coastal area: benthic flux determination from pore water profiles and in situ measurements using benthic chamber. Hydrobiologia 235/236, 501–17. In: Kamau, J. N, Gachanja, A, Ngila, C, Kazungu, J.M, Zhai, M., 2008. Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. Lake & Reservoirs: Research and Management, 13, 145-154.

Clark, J.W, Viessman, W (Jr), Hammer, M.J., 1977. Water Supply and Pollution Control. 3rd Ed. Thomas Y. Crowelll Company, Inc., USA.

Clark, J.R., 1996. Coastal zone management handbook. London: Lewis Publishers.

Coetzee, L, du Preez, H.H, van Vuren, J.H, J., 2002. Metal concentrations in *Clarias gariepinus* and *Labeo umbratus* from the Olifants River and Klein Olifants River, Mpumalanga, south Africa: Zinc, copper, manganese, lead, chromium, nickel, aluminium and iron. Water SA, 28 (4), 432-438.

Colt, J., 1984. Computation of dissolved gas concentrations in water as functions of temperature, salinity & pressure. American Fisheries Society Special Publication, 14.

Dallas, H.F, Day, J.A., 2004. The effects of water quality variables on aquatic ecosystems: a review. (2nd ed. of Dallas & Day 1993). Water Research Commission Technical Report No. TT 224/04. Pretoria.

Dallas, H.F, Day, J.A., 1993. The effect of water quality variables on riverine ecosystems: A review. Fresh Water Unit. University of Cape Town. Rondebosch, South Africa.

Davies, B., Day, J., 1998. Vanishing Waters. University of Cape Town. UCT Press, Rondebosch, Cape Town, South Africa.

Davies, O.A, Allison, M.E, Uyi, H.S., 2006. Bioaccumulation of heavy metals in water, sediment and periwinkle (*Tympanotonus fuscatus var radula*) from the Elechi Creek, Niger Delta. African Journal of Biotechnology, 5 (10), 968-973.

Deacon, A.R., 1988. Die voiding sekologie en voedings fisiologie van die kurpers, *Tilapia rendalli* (Bloulenger) en *Oreochromis mossambicus* (Peters) in 'n warm rioolverrykte habitat. PhD thesis (Unpublished), RAV, Johannesburg, South Africa. In: Kotze, P, du Preez, H.H, van Vuren, J.H.J., 1999. Bioaccumulation of Cu and Zn in *Oreochromis mossambicus* and *Clarius gariepinus*, from the Olifants River, Mpumalanga, South Africa. Water SA, 25 (1), 99-110.

Degrémont., 1991. Water Treatment Handbook. 6th Ed, Volume 2. Lavoisier Publishing, Rueil-Malmaison Cedex, France.

Department of Water Affairs and Forestry (DWAF), 1996. South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems. Holmes, S (ed). CSIR Environmental Services, Pretoria 0001, Republic of South Africa.

Dong, D, Nelson, Y.M, Lion, L.W, Shuler, M.L, Ghiorse, W.C., 2000. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: New evidence for the importance of Mn and Fe oxides. Water Research, 34 (2), 427–436. In: Bentivegna, C.S, Alfano, J-E, Bugel, S.M, Czechowicz, K., 2004. Influence of Characteristics on Heavy Metal in an Urban Marsh. Urban Habitats, 2 (1), 91-103.

Driscoll, C.T, Letterman, R.D., 1988. Chemistry and fate of Al III in treated drinking water. J. Environ. Eng. Div., ACSE. 11 (1), 21-37. In: Srinivasan, P.T, Viraraghavan, T, Subramanian, 1999. Aluminium in drinking water: An overview. Water SA, 25 (1), 47-55.

Egborge, A.B.M., 1971. The chemical hydrology of River Oshun, Western State, Nigeria. Freshwater Biol., 1, 257-271. In: Abowei, J.F.N., 2010. Salinity, Dissolved Oxygen, pH and Surface Water Temperature Conditions in Nkoro River, Niger Delta, Nigeria. Advance Journal of Food Science and Technology 2 (1), 36-40.

Elangovan, R., Ballance, S., White, K.N., McCrohan, C.R., Powell, J.J., 1999. Accumulation of aluminium by the freshwater crustacean *Asellus aquaticus* in neutral water. Environmental Pollution, 106 (3), 257-263. In: Sharma, C.M., 2003. Effects of Exposure to Aluminium on Fish in Acidic Waters, Department of Ecology and Natural *http://www.geocities.com/chhatra_sharma/publications.html* (Accessed: 3 July 2009).

Elliott, H.A, Dempsey, B.A, Maille, P.J., 1990. Content and Fractionation of Heavy Metals in Water Treatment Sludges. J. Environ. Qual., 19, 330-334.

Ellis, K.V., 1989. Surface water Pollution and its Control. MacMillan Press Ltd., London, England.

Environmental Protection Agency-African Union (EPA-AU)., 2006. Monitoring and Assessing Water Quality. United States Environmental Protection Agency. *http://www.epa.sa.gov.au/water_what.html.* (Accessed: 23 April 2010).

EPB 356., 2006. Interim Edition. Surface Water Quality Objetives. Saskastchewan Environment.

Esmail, A.S, Abdul, R.S, Wan Zuhairi, W.Y.A, Fadhl, A.N., 2009. Assessment of Groundwater and Surface water Pollution at Mitm Area, Ibb City, Yemen American Journal of Applied Sciences, 6 (4), 772-783.

Etesin, M.U, Benson, N.U., 2007. Cadmium, Copper, Lead and Zinc Tissue Levels in Banga Shad (*Ethmalosa fimbriata*) and Tilapia (*Tilapia guineensis*) Caught from Iman River, Nigeria. American Journal of Food Technology, 2 (1), 48-54.

Fatoki, S. O., Gogwana, P., Ogunfowokan, A. O., 2003. Pollution assessment in the Keiskamma River and in the impoundment downstream. Water SA, 29 (3). 183-187.

Giller, P.S, Malmquist, B., 1998. The Biology of Streams and Rivers. Oxford University Press Inc., New York, United States of America.

Ghori, M. I, Yaqub, M., 1999. Aluminium (Al^{3+}) Levels in Renal Failure Patients. Pakistan Journal of Biological Sciences, 2 (4), 1569-1571.

Granit, J., 2000. Management of Shared Water Resources in Southern Africa and the Role of External Assistance, 1st WARFSA/WaterNet Symposium: Sustainable Use of Water Resources; Maputo, 1-2 November 2000, Swedish International Development Cooperation Agency Sida/Asdi.

Greenfield, R, Van Vuren, J.H.J, Wepener, V., 2007. Determination of sediment quality in the Nyl River system, Limpopo Province, South Africa, WaterSA, 33 (5), 693-700.

Gumbo, B., 1997. Integrated water management in Harare. Water and Sanitation for All: Partnerships and Innovations. 23rd WEDC Conference, Durban, South Africa.

Gunn, J.M., Noakes, D.L.G., 1987. Latent effects of pulse exposure to aluminum and low pH on size, ionic composition, and feeding efficiency of lake trout (*Salvelinus fontinalis*) alevins. Can. J. Fish. Aquat. Sci., 44. 1418-1424. In: Canadian Environmental Quality Guidelines (CEQG), Canadian Council of Ministers of the Environment., 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Aluminium.

Hansen, D.J, Berry, W.J, Mahony, J.D, Boothman, W.S. Di Toro, D.M, Robson, D.L, Ankley, G.T, Ma, D, Yan, Q, Pesch, C.E., 1996. Predicting the toxicity of metal-contaminated field sediments using interstitial concentration of metals and acid-volatile sulfide normalizations. Environmental Toxicology and Chemistry, 15 (12), 2080–2094. In: Bentivegna, C.S, Alfano, J-E, Bugel, S.M, Czechowicz, K., 2004. Influence of Characteristics on Heavy Metal in an Urban Marsh. Urban Habitats, 2 (1), 91-103.

Hillman, C., 1995. Heavy Metals and Organochlorine Pesticides in Lake Chivero. MSc thesis (Unpublished). Department of Biological Sciences, University of Zimbabwe.

House, S.J, Reed, R. A., 2004. Emergency Water Sources: Guidelines for Selection and Treatment. (3rd Ed). Water Engineering and Development Centre (WEDC), Loughborough.

Hunt, R.J, Christianssen, I.H., Dissolved Oxygen Information Kit. A CRC Sugar Technical Publication, November 2000. CRC for Sustainable Sugar Production, Townsville.

IAEA (International Atomic Energy Agency), 2003. Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements, IAEA-TECDOC-1360, Vienna, Austria.

Igbinosa, E.O, Okoh, A, I., 2009. Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community. Int. J. Environ. Sci. Tech., 6 (2). 175-182.

Jarawaza, M., 1997. Water Quality Monitoring in Harare. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 27-34.

Javed, M., 2005. Heavy Metal Contamination of Freshwater Fish and Bed Sediments in the River Ravi Stretch and Related Tributaries. Pakistan Journal of Biological Sciences, 8 (10), 1337-1341.

JICA Report., (1996). The Study of Water Pollution Control in Upper Manyame River Basin in the Republic of Zimbabwe. Nippon Jogeduido Sekkei Co. Ltd., Nippon Koei Co. Ltd., Ministry of Local Government and Public Construction, Zimbabwe. In: Nhapi, I., 2007. Inventory of water management practices in Harare, Zimbabwe. Water and Environmental Journal, 22, 54-63.

Kaiff J., 2002. Limnology; Inland Water Ecosystems. Prentice –Hall, U.S.A.

Kamau, J. N, Gachanja, A, Ngila, C, Kazungu, J.M, Zhai, M., 2008. Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. Lakes & Reservoirs: Research and Management, 13, 145-154.

Kamudyariwa, C., 2000. Seasonal variation of water quality with Respect to Anthropogenic Activities along Mukuvisi River, Harare, Zimbabwe. MSc thesis (Unpublished). IHE Delft, the Netherlands.

Kegley, S.E., Hill, B.R., Orme S., Choi A.H., 2009. *PAN* Pesticide Database*, Pesticide Action Network, North America, San Francisco, CA. *http:www.pesticideinfo.org* (Accessed: 22 October 2009).

Klein, C, Hurlbut, Jr, C.S., 1977. Manual of Mineralogy. 20th Ed. John Wiley and Sons, Inc, New York,, United states of America.

Kocharyan, A. G, Venitsianov, E. V, Safronova, N. S, Seren'kaya, E. P., 2003. Seasonal variation in the forms of heavy metal occurrence in the Kuibyshev reservoir waters and bottom

deposits. Water Res., 30, 404–12. In: Kamau, J. N, Gachanja, A, Ngila, C, Kazungu, J.M, Zhai, M., 2008. Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. Lakes & Reservoirs: Research and Management, 13, 145-154.

Kotze, P, du Preez, H.H, van Vuren, J.H.J., 1999. Bioaccumulation of Cu and Zn in *Oreochromis mossambicus* and *Clarius gariepinus*, from the Olifants River, Mpumalanga, South Africa. Water SA, 25 (1), 99-110.

Kralik, M., 1999. A rapid procedure for environmental sampling and evaluation of polluted sediments. Applied Geochemistry, 14, 807–816. In: IAEA (International Atomic Energy Agency), 2003. Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements, IAEA-TECDOC-1360, Vienna, Austria.

Kudirat, A. O., 2008. Bioconcentration of Lead in the Tissues of Feral and laboratory Exposed *Clarias gariepinus*. J. Med. Sci., 8 (3), 281-286.

Lydersen, E, Salbu, B, Poleo, A.B.S, Muniz, I.P., 1990. The influences of temperature on aqueous aluminium chemistry. Wat. Air Soil Pollut., 51. 203-215. In: Canadian Environmental Quality Guidelines (CEQG), Canadian Council of Ministers of the Environment., 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Aluminium.

Machena, C., 1997. The Pollution and Self-purification Capacity of the Mukuvisi River. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 75-91.

Makado, P., 2007. Optimization of algal control processes at Morton Jaffray water works, Harare. MSc thesis (Unpublished), Department of Civil Engineering, University of Zimbabwe

Magadza C.H.D, 2003. Lake Chivero: A management case study. Lakes & Reservoirs: Research and Management, 8 (2), 69-81.

Marshall, B.E., 1997. Lake Chivero After Forty Years: The Impact Of Eutrophication. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 1-12.

Mathuthu, A.S, Mwanga, K, Simoro, A., 1997. Impact assessment for industrial and sewage effluents on water quality of the receiving Marimba River in Harare. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 43-52.

Matthews, W., 1998. Patterns in Freshwater Fish Ecology. Kluwer Academic Publishers, New York.

McGee, T.J., 1991. Water Supply and Sewerage Engineering. 6th Ed. McGraw-Hill Book Co., Singapore.

McNeely, R.N., Neimanis, V.P, Dwyer, L., 1979. Water quality sources book – A guide to water quality parameters. pp 112. In: Abowei, J.F.N., 2010. Salinity, Dissolved Oxygen, pH and Surface Water Temperature Conditions in Nkoro River, Niger Delta, Nigeria. Advance Journal of Food Science and Technology 2 (1), 36-40.

McNicol, R.E, Scherer, E., 1991. Behavioral responses of lake whitefish (*Coregonus clupeaformis*) to cadmium during preference- avoidance testing. Environmental Toxicology and Chemical. 10: 225-234. In: Adham, K.G., 2001. Metallic Micro-pollutants in the Harvest of *Oreochromis niloticus* (Linnaeus, 1757) from Polluted Waters: Wildlife and Human Concerns, Pakistan Journal of Biological Sciences, 4 (12), 1550-1558.

Metcalf & Eddy, Inc., 1995. Wastewater Engineering: Treatment, Disposal and Re-use. 3rd Ed. Tata McGrawHill Co Ltd, New York, USA.

More, T. G., Rajput, R. A, Bandela, N. N., 2003. Impact of heavy metals on DNA content in the whole body of freshwater bivalve, *Lamelleiden marginalis*. Environ. Sci. Pollut. Res., 22. 605-616.

Mount, D.R, Swanson, M.J, Breck, J.E, Farag, A.M, Bergman, H.L., 1990. Responses of brook trout (*Salvelinus fontinalis*) fry to fluctuating acid, aluminum, and low calcium exposure. Can. J.Fish. Aquat. Sci., 47. 1623-1630. In: Canadian Environmental Quality Guidelines (CEQG), Canadian Council of Ministers of the Environment., 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Aluminium.

Moyle, P., 1993. Fish; An Enthusiast's Guide. University of California Press, Berkley, United States of America.

Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe.

Munzwa, K., 1982. Land use survey of the Upper Hunyani catchment. In: Thornton, J.A, Nduku, W.K., (eds), 1982. Lake Mcllwaine: The Eutrophication and Recovery of a Tropical African Man-made Lake, Dr W Junk Publishers, The Hague-Boston-London. pp 11-23.

Neal, C, Reynolds, B, Neal, M, Wickham, H, Hill, L, Williams, B., 2004. The water quality of streams draining a plantation forest on gley soils: the Nant Tanllwyth, Plylimon mid-Wales. Hydrology and Earth System Sciences, 8 (3), 485-502.

Nhapi, I, Tirivarombo, S., 2004. Sewage discharges and nutrient levels in Marimba River, Zimbabwe. Water SA, 30 (1), 107-113.

Nhapi, I., 2007. Inventory of water management practices in Harare, Zimbabwe. Water and Environmental Journal, 22, 54-63.

Nyamangara, J, Bangira, C, Taruvinga, T, Masona, C, Nyemba, A, Ndlovu, D., 2008. Effects of sewage and industrial effluent on the concentration of Zn, Cu, Pb and Cd in water and sediments along waterfalls stream and lower Mukuvisi River in Harare, Zimbabwe. Physics and Chemistry of the Earth, 33, 709-711.

Okalebo, R.J, Woomer, P.L., 1993. Laboratory Methods of Soil and Plant Analysis: A Working Manual. Tropical Soil Biology and Fertility Programme. Soil Science Society of East Africa, Technical Publication No. 1, Kenya. pp 13-15.

Otto, M., 1998. Multivariate methods. In: Kellner, R, Mermet, J. M, Otto, M, Widmer, H. M. (Eds.), Analytical Chemistry. WileyeVCH, Weinheim. In: Shrestha, S, Kazama, F., 2007. Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. Environmental Modelling & Software, 22, 464-475.

Petersen, W, Willer, E, Willamowski, C., 1997. Remobilization of trace elements from polluted anoxic sediments after re-suspension in oxic water. Water Air Soil Pollut., 99, 515–22. In: Kamau, J. N, Gachanja, A, Ngila, C, Kazungu, J.M, Zhai, M., 2008. Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. Lakes & Reservoirs: Research and Management, 13, 145-154.

Phippen, B, Horvath, C., 1998. Review of literature pertaining to aquatic toxicity of aluminum. BWP Consulting. 1.   In: Canadian Environmental Quality Guidelines (CEQG), Canadian Council of Ministers of the Environment., 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Aluminium.

Praus, P., 2007. Urban water quality evaluation using multivariate analysis. Acta Montanistica Slovaca 12 (2), 150-158.

Praveena, S.M, Radojevic, M, Abdullah, M.H, Ari, A.Z., 2008. Application of sediment quality guidelines in the assessment of mangrove surface sediment in mengkabong lagoon, Sabah, Malaysia. Iran. J. Environ. Health. Sci. Eng., 5 (1), 35-42.

Prolo, P, Chiappelli, F, Crasso, E, Rosso, M.G, Neagos, N, Dovio, A, Sartori, M.L, Perotti, P, Fanto, F, Civita, M, Fioruca, A, Villanueva, P, Angeli, A., 2007. Aluminium blunts the proliferative response and increases apoptosis of cultured human cells: Putative relationship to Alzheimer's disease. Bioinformation, 2 (1), 24-27.

Province of British Columbia (PBC)., 1998. Guidelines for Interpreting Water Quality Data. Resources **I**nventory **C**ommittee. *http://imbwww.gov.bc.ca/risc/pubs/aquatic/interp-01.htm* (Accessed: 14 October 2009)

Radojevic, M, Bashkin, V.N., 1999. Practical Environmental Analysis. The Royal Society Of Chemistry, Cambridge, United Kingdom.

Rapin, F, Nembrini, G.P, Forstner, U, Garcia, J.L., 1983. Heavy metals in marine sediment phases determined by sequential chemical extraction and their interaction with interstitial water. Environ. Technol. Lett. 4, 387-396. In: Kamau, J. N, Gachanja, A, Ngila, C, Kazungu, J.M, Zhai, M., 2008. Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. Lakes & Reservoirs: Research and Management, 13, 145-154.

Rashed, M.N., 2001. Cadmium and Lead levels in fish (*Tilapia nilotica*) tissues as biological indicator for lake water pollution. Environmental Monitoring and Assessment, 68, 75–89.

Rauf, A, Javed, M, and Ubaidullah, M., 2009. Heavy metal levels in the major carps (*Catla catla*, *Labeo rohita* and *Cirrhina mrigala*) from the River Ravi, Pakistan. Pakistan Vet. J., 29 (1), 24-26.

Retief, N. R, Avent-Oldewage, A, du Preez, H., 2009. The use of cestode parasites from the largemouth yellowfish *Labeobarbus kimberleyensis* (Gilchrist and Thompson, 1913) in the Vaal Dam, South Africa, as indicators of heavy metal bioaccumulation. Physics and Chemistry of the Earth, 31, 840-847.

Robinson, J, Avenant-Oldewage, A., 1997. Chromium, copper, iron and manganese bioaccumulation in some organs and tissues of *O. mossambicus* from the Olifants River, inside the Kruger National Park. WaterSA, 23 (4), 388-404.

Rodushkin, I., Moiseenko, T., Kudravsjeva, L., 1995. Aluminium in the surface waters of the Kola Peninsula, Russia. The Science of the Total Environment. 163 (1-3), 55-59. In: Sharma, C.M., 2003. Effects of Exposure to Aluminium on Fish in Acidic Waters, Department of Ecology and Natural *http://www.geocities.com/chhatra_sharma/publications.html* (Accessed: 3 July 2009).

Romeo, M, Siau, Y, Sidoumou, Z, Gnassia-Barelli, M., 1999. Heavy metal distribution in different fish species from the Mauritania coast. Sci. Total Environ., 232, 169-175. In: Etesin, M.U, Benson, N.U., 2007. Cadmium, Copper, Lead and Zinc Tissue Levels in Banga Shad (*Ethmalosa fimbriata*) and Tilapia (*Tilapia guineensis*) Caught from Iman River, Nigeria. American Journal of Food Technology, 2 (1), 48-54.

Ronagh, M.T, Savarii, A, Papahn, Heesni, M.A., 2009. Bioaccumulatiion of heavy metals in Euryglossa orientalis from the Hendijan Seaport (Coastal of Persian Gulf), Iran. Journal of

Biological Sciences, 9 (3), 272-275.

Rosseland, B.O, Eldhuset, T.D, Staurnes, M., 1990. Environmental effects of aluminium. Environmental Geochemistry and Health 12(1-2), 17-27. In: Sharma, C.M., 2003. Effects of Exposure to Aluminium on Fish in Acidic Waters, Department of Ecology and Natural Resource Management (INA), Agricultural University of Norway(NHL), Norway : *http://www.geocities.com/chhatra_sharma/publications.html* (Accessed: 3 July 2009).

Rosseland, B.O, Staurnes, M., 1994. Physiological Mechanisms for Toxic Effects and Resistance to Acidic Water: an Ecophysiological and Ecotoxicological Approach. In: C.E.W. Steinberg, C.E.W, Wright, R.F., (eds.). Acidification of Freshwater Ecosystems: Implications for the Future. John Wiley & Sons Ltd. pp 227-246.

Seymore, T., 1994. Bioaccumulation of Metals in *Barbus morequensis* from the Olifants River, Kruger national Park and Lethal Levels of Manganese to Juvenile *Oreochromis mossambicus*. MSc thesis (Unpublished), Rand African University, South Africa.

Sharma, C.M., 2003. Effects of Exposure to Aluminium on Fish in Acidic Waters, Department of Ecology and Natural *http://www.geocities.com/chhatra_sharma/publications.html* (Accessed: 3 July 2009).

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

Sorenson, J, Campbell, I, Tepper, L, Lingg, R., 1974. Aluminium in the environment and human health. Environ. Health Persp., 8, 3-95. In: Srinivasan, P.T, Viraraghavan, T, Subramanian, 1999. Aluminium in drinking water: An overview. Water SA, 25 (1), 47-55.

Srinivasan, P.T, Viraraghavan, T, Subramanian, 1999. Aluminium in drinking water: An overview. Water SA, 25 (1), 47-55.

Stumm, W, Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 3rd Ed. John Wiley and Sons, Inc, New York, United States of America.

Taylor, D.J, Green, N.P.O, Stat, G.W., 1984. Biological Science. 3rd Ed. Cambridge University Press, Cambridge, United Kingdom.

Tebutt, T.H.Y., 1998. Principles of Water Quality Control. 5th Ed. Butterworth-Heinemann, Oxford, United Kingdom.

Thirumalini, S, Joseph, K., 2009. Correlation between Electrical Conductivity and Total Dissolved Solids in Natural Waters. Malaysian Journal of Science, 28 (1), 55-61.

Thomann, R.V, Mueller, J.A., 1987. Principles of Surface Water Quality Modelling and Control. HarperCollins Publishers Inc., New York, United States of America.

Thornton, J.A, Nduku, W.K., (eds), 1982. Lake Mcllwaine: The Eutrophication and Recovery of a Tropical African Man-made Lake, Dr W Junk Publishers, The Hague-Boston-London.

Uwimana, A, Nhapi, I, Wali, U.G, Hoko, Z, Kashaigili, J., 2007. Sludge Characterization at Kadahokwa Water Treatment Plant, Rwanda. Conference paper presented at the 7th WaterNet Symposium, Zambia.

Uyanik, F, Meryem, E, Guclu, B, K, Atasever, A, Yoku, B., 2008. Effects of Aluminium Toxication on Performance, Egg Quality, Serum Chemistry and Organs of Japanese Quail and Efficacy of Phosphorous Supplementation on Aluminium Induced Alterations. Journal of Animal and Veterinary Advances, 7 (5), 557-563.

Varanasi, U, Markey, Y.D., 1978. Uptake and release of lead and cadmium in skin and mucus of coho salmon (*Onccorhynchus kisutch*). Comp. Biochem. Physiol., 60C, 187-191. In: Coetzee, L, du Preez, H.H, van Vuren, J.H, J., 2002. Metal concentrations in *Clarias gariepinus* and *Labeo umbratus* from the Olifants River and Klein Olifants River, Mpumalanga, south Africa: Zinc, copper, manganese, lead, chromium, nickel, aluminium and iron. Water SA, 28 (4), 432-438.

Viessman, W (Jr), Hammer, M.J., 1998. Water Supply and Pollution Control. 6th Ed. Addison-Wesley: An imprint of Addison Wesley Longman, Inc., California, USA.

Villella, R., 2007. Impact of aluminum-laden sediment discharge on viability of native freshwater mussels in the Potomac River. US Department of the Interior, US Geological Survey, Kearnysville, USA. *http://www.lsc.usgs.gov/SPN.asp?StudyPlanNum=02098* (Accessed: 22 Mrach 2010).

Vinodhini, R, Narayanan, M., 2008. Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). Int. J. Environ. Sci. Tech., 5 (2), 179-182.

Wanielista, M.P, Yausef, Y.A, Taylor, J.S, Cooper, C.D., 2004. Engineering and the Environment. Wadsmouth, Inc., Belmont, California, USA.

Zanamwe, L., 1997. Population Growth and Land Use in the Manyame Catchment Area. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 113-123.

Zaranyika, M.F, Ndapadzwa, T., 1995. Uptake of Ni, Zn, Fe, Co, Cr, Pb, Cu and Cd by Water Hyacinth (*Eichhornia crassipes*) in Mukuvisi and Manyame Rivers, Zimbabwe. J. Environ. Sci. Health, A30 (1), 157-169.

Zaranyika, M.F., 1997. Sources and levels of pollution along Mukuvisi River: A Review. In: Moyo, N.A.G (ed), 1997. Lake Chivero: A Polluted Lake, University of Zimbabwe Publications, Harare, Zimbabwe. pp 35-42.

Zimbabwe Parks and Wildlife Management Authority (ZPWMA). 2005. *http://www.fao.org/fi/oldsite/FCP/en/ZWE/body.htm* (Accessed: 27 August 2010).

Zimbabwe National Water Authority (ZINWA) Files. Pax House, 48 Kwame Nkrumah Road, Harare, Zimbabwe.

Zimbabwe National Water Authority (ZINWA)., 2000. Government of Zimbabwe, Water (Waste and Effluent Disposal) Regulations, Statutory Instrument 274 of 2000.

8. APPENDICES

Appendix A: Bioaccumulation of Al in fish tissues from the sites and sampling campaigns.

	Sampling site	Statistics	Liver	Kidney	Gills	Muscle
Sampling campaign 1	LCS1	Mean	3.94	2.92	0.86	0.62
		Standard deviation	1.57	1.00	0.39	0.47
		Minimum	1.40	1.33	0.23	0.01
		Maximum	5.42	3.78	1.26	1.12
	LCS2	Mean	3.82	2.52	0.80	0.75
		Standard deviation	2.43	2.23	0.55	0.54
		Minimum	0.61	0.02	0.01	0.01
		Maximum	0.61	0.02	0.16	0.10
	MRDP	Mean	0.41	0.66	0.12	0.08
		Standard deviation	0.31	0.49	0.06	0.05
		Minimum	0.01	0.01	0.07	0.01
		Maximum	0.86	1.39	0.18	0.16
	LMM	Mean	1.94	3.23	0.44	0.37
		Standard deviation	2.01	3.59	0.46	0.42
		Minimum	0.09	0.08	0.00	0.00
		Maximum	4.55	7.81	1.09	0.89
	LMD	Mean	0.66	1.71	0.23	0.14
		Standard deviation	0.34	0.34	1.44	0.34
		Minimum	0.52	0.90	0.13	0.12
		Maximum	0.84	4.44	0.31	0.17
		Tissue Mean Total	10.71	9.49	2.44	1.95
Sampling campaign 2						
	LMM	Mean	0.06	0.75	0.02	0.03
		Standard deviation	0.06	1.56	0.02	0.03
		Minimum	0.00	0.00	0.00	0.00
		Maximum	0.16	4.26	0.03	0.08
	LMD	Mean	0.12	0.08	0.01	0.02
		Standard deviation	0.15	0.08	0.01	0.02
		Minimum	0.00	0.00	0.00	0.01
		Maximum	0.38	0.19	0.03	0.05
		Tissue Mean Total	0.18	0.83	0.03	0.06

Appendix B: Aluminium concentrations in water and sediments

Table 8.1: Concentrations of Al in water from the sites and for sampling campaign 1 (dry period) and 2 (wet period).

	Statistics	Sampling Sites								
		CD	LCS1	LCS2	MRU	MRDP	MRD	LMM	LMC	LMD
Sampling campaign 1	Mean	1.22	2.37	3.37	2.19	3.86	68.93	20.94	2.49	2.49
	SD	1.46	1.51	1.23	0.90	2.83	61.74	18.50	1.20	1.01
	Minimum	0.27	0.80	1.59	0.70	0.48	10.15	3.02	0.40	0.98
	Maximum	4.78	5.48	5.59	3.07	7.20	163.99	53.54	4.32	3.65
Sampling campaign 2										
	Mean				3.58	9.66	38.18	10.80	2.23	2.50
	SD				0.47	10.47	21.54	9.04	1.16	0.36
	Minimum				3.20	4.80	6.80	2.00	1.70	2.10
	Maximum				4.60	35.30	90.90	24.60	5.10	3.20

Table 8.2: Concentrations of Al in sediments from the sites and for sampling campaign 1 (dry period) and 2 (wet period).

	Statistics	Sampling Sites								
		CD	LCS1	LCS2	MRU	MRDP	MRD	LMM	LMC	LMD
Sampling campaign1	**Mean**	37.77	27.50	31.31	10.29	40.69	103.79	42.62	16.53	15.02
	SD	12.82	14.16	11.73	6.94	47.20	55.96	30.26	7.86	8.85
	Minimum	10.24	1.80	11.11	2.81	3.00	6.92	10.02	7.86	2.96
	Maximum	46.65	43.81	45.09	19.03	111.74	167.17	96.93	26.42	34.67
Sampling campaign 2	**Mean**				4.47	10.29	131.84	70.06	2.23	2.50
	SD				0.31	8.18	16.48	23.23	1.16	0.36
	Minimum				3.90	4.35	119.30	49.60	1.70	2.10
	Maximum				4.80	29.95	140.60	92.30	5.10	3.20

Appendix C: Correlation Tables

Table 8.3: Bivariate correlations between aluminium concentrations in water (Al_{water}) with aluminium in the fish tissues and among the tissues.

		Liver	Gill	Kidney	Muscle	Al_{water}
Liver	Pearson Correlation	1	.794[*]	.761[*]	.988[**]	-.084
	Sig. (2-tailed)		.033	.047	.000	.858
Gill	Pearson Correlation		1	.444	.767[*]	-.266
	Sig. (2-tailed)			.318	.044	.564
Kidney	Pearson Correlation			1	.751	.417
	Sig. (2-tailed)				.052	.352
Muscle	Pearson Correlation				1	-.038
	Sig. (2-tailed)					.936
Al_{water}	Pearson Correlation					1
	Sig. (2-tailed)					

* Correlation is significant at the 0.05 level (2-tailed), ****** Correlation is significant at the 0.05 level (2-tailed), N=7

Table 8.4: Bivariate correlations between aluminium concentrations in sediments ($Al_{sediments}$)
with aluminium in the fish tissues and among the tissues.

		Liver	Gill	Kidney	Muscle	$Al_{sediment}$
Liver	Pearson Correlation	1	.794[*]	.761[*]	.988[**]	-.108
	Sig. (2-tailed)		.033	.047	.000	.817
Gill	Pearson Correlation		1	.444	.767[*]	.397
	Sig. (2-tailed)			.318	.044	.377
Kidney	Pearson Correlation			1	.751	-.255
	Sig. (2-tailed)				.052	.581
Muscle	Pearson Correlation				1	-.115
	Sig. (2-tailed)					.806
$Al_{sediment}$	Pearson Correlation					1
	Sig. (2-tailed)					

* Correlation is significant at the 0.05 level (2-tailed), ****** Correlation is significant at the 0.05 level (2-tailed), N=7

Table 8.5: Correlations between Al and the other physico-chemical parameters.

		Al	Temp.	pH	DO_{sat}	DO_{conc}	TDS	EC	TS
Al	Pearson Correlation	1	-.111	-.333[*]	.184	.126	.348[*]	.321[*]	.126
	Sig. (2-tailed)		.454	.021	.210	.393	.016	.026	.697
Temp.	Pearson Correlation		1	-.252	-.270	-.354[*]	.449[**]	.474[**]	.367
	Sig. (2-tailed)			.084	.064	.013	.001	.001	.241
pH	Pearson Correlation			1	.413[**]	.451[**]	-.908[**]	-.880[**]	-.819[**]
	Sig. (2-tailed)				.004	.001	.000	.000	.001
DO_{sat}	Pearson Correlation				1	.983[**]	-.546[**]	-.541[**]	-.753[**]
	Sig. (2-tailed)					.000	.000	.000	.005
DO_{conc}	Pearson Correlation					1	-.610[**]	-.610[**]	-.787[**]
	Sig. (2-tailed)						.000	.000	.002
TDS	Pearson Correlation						1	.980[**]	.928[**]
	Sig. (2-tailed)							.000	.000
EC	Pearson Correlation							1	.923[**]
	Sig. (2-tailed)								.000
TS	Pearson Correlation								1
	Sig. (2-tailed)								

Correlations are significant at the 0.05 level (*) and 0.01 level (**) (2-tailed), n=48 except for TS where n=12.

Appendix D: Water quality guidelines for physico-chemical parameters in freshwaters.

Parameter	Units	DWAF (1996)				EPB 356 (2006)	EPA-AU (2006)	
TaL	mg/l	n.a.[a]				0.05-0.1[c]	Acute effects	Chronic effects
							0.75[e]	0.087[e]
DO	mg/l	TWAR[f]	MAV[f]			5.5-9.5[d]	n.a.	
			Sub-lethal	Lethal				
	% saturation	80-120	>60	>40		n.a.	n.a.	
pH	pH units	No specific values 6-8[b]				n.a	6-9	
Temperature	^{o}C	Not specified				n.a.	n.a.-species dependent	
EC	µS/cm	2500 (effluent)				n.a	n.a	
TDS	mg/l	120				n.a	250	
TS	mg/l	n.a				n.a	n.a	

[a] n.a. stands for not available.

[b] This pH range is for well-buffered freshwater systems in South Africa.

[c] Aluminum Objective: 0.05 mg/l is for pH <6.5, Ca <4 mg/l and DOC <2 mg/l; 0.1 mg/l is for pH $\geq$ 6.5, Ca $\geq$ 4 mg/l and DOC $\geq$ 2mg/l.

[d] DO should be 6.0 mg/L for warm-water biota in early life stages; 5.5 mg/L for warm-water biota in other life stages.

[e] This TaL concentrations is for a pH range of 6.5 to 9. This value was obtained from a toxicity test with the striped bass at a ph between 6.0 and 6.6 and hardness <10 mg/l.

[f] TWAR stands for Target Water Quality Range while MAV stands for Maximum Allowable Values.