



The seasonal influence on the spatial distribution of dissolved selected metals in Lake Naivasha, Kenya



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ABSTRACT

Lake Naivasha is the only freshwater Lake in Rift Valley, in Kenya. It lies in a fertile semi-arid basin. The Lake has no surface water outlet and is presumed to be under stress. Dissolved metals are directly taken up by bacteria, algae, plants, and planktonic and benthic organisms. Dissolved metals can also adsorb to particulate matter in water column and enter aquatic organisms through various routes. Cadmium, copper, lead and zinc may bioaccumulate within lower organisms, yet they do not biomagnify up the food chain as do mercury and selenium. This study reports on the levels and distribution of dissolved heavy metals and investigates the influence of physicochemical parameters on metal mobilization. The bioavailability of selected metals was investigated by relating the levels of dissolved metals to that in fish. Water abstraction for irrigation and domestic use, compounded with organic matter inflow will affect physicochemical parameters and hence influences the mobilization of heavy metals.

Dissolved Zn correlated highly with sediment pH ($r = 0.67$) indicating that dissolution increases with increase in pH. In addition, the fact that the pH also correlated positively with organic matter $r = 0.50$, Eh $r = 0.63$, temperature $r = 0.56$ and dissolved oxygen $r = 0.56$, would suggest that organic bound Zn contributed significantly to the concentration of dissolved Zn. In situ flux experiments indicated that the fringing papyrus reeds located along the shores of Lake Naivasha provided sites for metal immobilization due to their coprecipitation on redox sensitive.

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1. Introduction

Freshwater ecosystems accumulate the impacts of human activities and consequently the quality of fish habitat depends to a large extent upon the density of the human population and its activities within the basin (Zalewski and Welcomme, 2001). Water bodies and rivers bear the burden of industrialization and population explosion. The water bodies are choked with siltation, domestic and industrial pollution as well as over exploitation.

Lake Naivasha lays in a fertile semi-arid basin and is the only freshwater Rift Valley Lake in Kenya. The Lake has no surface outlet and is presumed to be under stress, reflected in the decline of fish stocks. Lake Naivasha was considered as the study site due to its importance as a natural resource supporting about 50% of the country's horticultural industry and providing a source of fish to the surrounding community. The Lakes commercial fishery is

based on three species: *Oreochromis leucostictus*, *Tilapia zillii*, *Micropogonias salmoides* (largemouth bass) and a crustacean *Procambarus clarkii* (crayfish). The average species composition of the catch between 1987 and 1998 was *O. leucostictus* 71.7%, *T. zillii* 8.8% and *M. salmoides* 19.5% (Hickley et al., 2002). Tarras-Wahlberg et al. (2002) reported that the concentrations of Fe, Zn, Cd and Ni in Lake Naivasha sediments were elevated compared to global averages.

Trace elements are found in natural water bodies at varying concentrations. The most potentially dangerous of these elements are heavy metals, viz., Pb, Cd, and Hg, and the metalloids, viz., As, Se, and Sb. Riverine suspended particulate matter is represented by a wide combination of inorganic material i.e. clay minerals and Fe and Mn oxyhydroxides and organic matter detritic or alive. These particles, due to their high surface area, and also to the carrier nature of oxides, are the main heavy metal carriers in fluvial systems (Jenne, 1968; Waren and Zimmerman, 1993). Copper and zinc are essential elements for all living organisms but elevated levels may cause adverse effects in all biological species. Cadmium and lead are presumed to be non-essential elements

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for life; more importantly, even at extremely low environmental concentrations these elements may create adverse impacts on biota. In fact molecular biology studies have demonstrated that Cd and Pb atoms may substitute for other divalent metals such as Cu and Zn within enzyme binding sites. Biochemical similarities between these atoms suggest that Cd and Pb may also compete with cell surface uptake sites or bind to sulfur and nitrogen donor atoms of various functional groups within the cell. This is more likely to occur in freshwater systems (where dissolved calcium can be low) than in saline water (Playle et al., 1993).

Dissolved metals are directly taken up by bacteria, algae, plants, and planktonic and benthic organisms. Dissolved metals can also adsorb to particulate matter in water column and enter aquatic organisms through various routes. Cadmium, copper, lead and zinc may bioaccumulate within lower organisms, yet they do not biomagnify up the food chain as do mercury and selenium (Moore and Ramamoorthy, 1984). Of all of these metals, copper is considered the most potent toxin at environmentally relevant aqueous concentrations. Copper is generally more toxic to lower aquatic organisms such as phytoplankton, copepods and ciliates than to birds or mammals because the higher animals seem capable of regulating copper concentrations in tissues (USF&W, 1998). Copper is more commonly found in herbivorous fish than carnivorous fish from the same location (USF&W, 1998). Copper is used as an aquatic herbicide to reduce algae growth in reservoirs and also applied (via antifouling paints) to boat hulls in marinas.

This study reports on the levels and distribution of dissolved heavy metals and investigates the influence of physicochemical parameters in metal mobilization. The bioavailability of selected metals was investigated by relating the levels of dissolved metals to that in fish.

1.1. Study site

Lake Naivasha is a fresh water lake, approximately 145 km² in area situated in the Eastern Rift Valley of Kenya (0°45' and 36°20'E). It lies in a closed basin at an altitude of about 1890 m above sea level. The basin is roughly circular in shape and is made up of three water bodies; the Main lake, the Crescent lake and the Ololdien lake.

About 90% of its freshwater inflow comes through River Malewa. The main catchment area is located in the Nyandarua and Kinangop Ranges (1730 km²). The remaining fresh water discharge is through rainfall, ground water seepage and ephemeral streams; main contributor being the Gilgil river which drains the Bahati highlands.

Thompson and Dodson (1963) described Lake Naivasha as a 'hydro graphic window' because water passes freely through the extremely porous volcanic rocks which form 80% of the lake basin. Water input by seepage has been shown to occur in the North-eastern and North-western sections while water loss by seepage occurs in the south and South-eastern section of the lake (Gaudet and Melack, 1981).

2. Sampling and methodology

2.1. Water column

Sampling was performed, during the dry and wet season, five sampling sites were identified, each to capture the effects of the various activities surrounding the lake as shown in Fig. 1. Crescent (SC) station has a different hydrodynamic setting it is deeper than the main lake and is isolated, has been referred to as a different lake (Gaudet and Melack, 1981). Sewage station (SS) is a shallow site averaging 2 m; it is exposed to domestic and industrial sewage

input and is located in the Northeastern section of the lake where seepage outflow is presumed to occur (Gaudet and Melack, 1981). River Malewa station (SR) is exposed to river inputs, it is a shallow site and is located in the Northeastern section of the lake where seepage outflow is presumed to occur (Gaudet and Melack, 1981). Station (SH) is located near the area with the most horticultural activities; and in the Southeastern section of the lake where water loss by seepage is presumed to occur (Gaudet and Melack, 1981). Station (SM) is located at the mid lake, it is deeper than stations SH, SS and SR and is removed from direct anthropogenic influence.

Water samples were collected 1 m above the lake bed, using a 2 l Ruttner water sampler bottle; six samples were collected per station and filtered through a cellulose nitrate membrane filter pore size 0.45 µm. The filtered samples were preserved in 2% HNO₃ acid, to await analysis for selected metals. The samples were then transported to the laboratory and stored in an air-conditioned room between 20 and 25 °C.

Water samples were analyzed by GF-AAS (Varian Spectr AA 400 plus Zeeman GTA. 96 Plus). Physicochemical parameters were taken in situ. A pH meter (Schoot Gerate model CG 817) was used to measure sediment and water pH while a WTW conductivity/temperature meter was used to measure temperature and conductivity of water samples. The sediment redox potential was obtained by using a platinum electrode and a saturated calomel reference electrode, connected to a digital multimeter model DT – 5802. Easily oxidizable organic matter was obtained by converting BOD 5 to mg of carbon equivalent per litre. It is noted that the BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C. The units are in mg/l of carbon equivalent.

2.2. Sediment

Four sediment samples were collected per station from the lake bed, at the indicated sampling sites (see Fig. 1). Only the interior portion of each sample was removed from the eckman grab into polyethylene bags. 10 g of dry sediment sample was weighed in 100 ml conical flasks, the sample was mixed with 10% HCl in a ratio of 1:3 (solid to HCl). The reaction leached out carbonates in the form of carbon dioxide gas, and was complete after about 24 h; the reaction period depended on the carbonate content in the sediment and was complete when there was no more effervescence. The remaining solution was decanted out carefully. The residue was then thoroughly washed in distilled water to remove the salts and excess acid. The rinsed residue was then dried in the oven at 105 °C for 12 h; the dried sample was then re-weighed. Loss in weight was used to determine the percent carbonate content in each sample.

2.3. Fish

Monofilament gillnets were set-up at sewage (SS) and crescent (SC) stations; where fish samples of the genus tilapia (*O. leucostictus*) were sampled. The two sites were selected due to their difference in hydrological settings and exposure to anthropogenic stress.

Once in the laboratory the fish samples were measured for their total length and sorted within the bracket 18 ± 2.5 cm. The organs were then removed and frozen to await analysis. Fish organs were thawed and dried at 80 °C for 12 h. 0.200 g of the sample was weighed in fluorocarbon microwave digestion vessels (analytical balance Precisa 310 M). The samples were digested with a mixture of 8 ml nitric acid (65%) and 2 ml hydrochloric acid (37%), in a microwave oven (Sanyo 800W Model EM-X412). The Microwave oven was programmed (15 min at 50%, 5 min at 0%, and 20 min at 85%) according to Nieuwenhuize and Poley-Vos (1989).

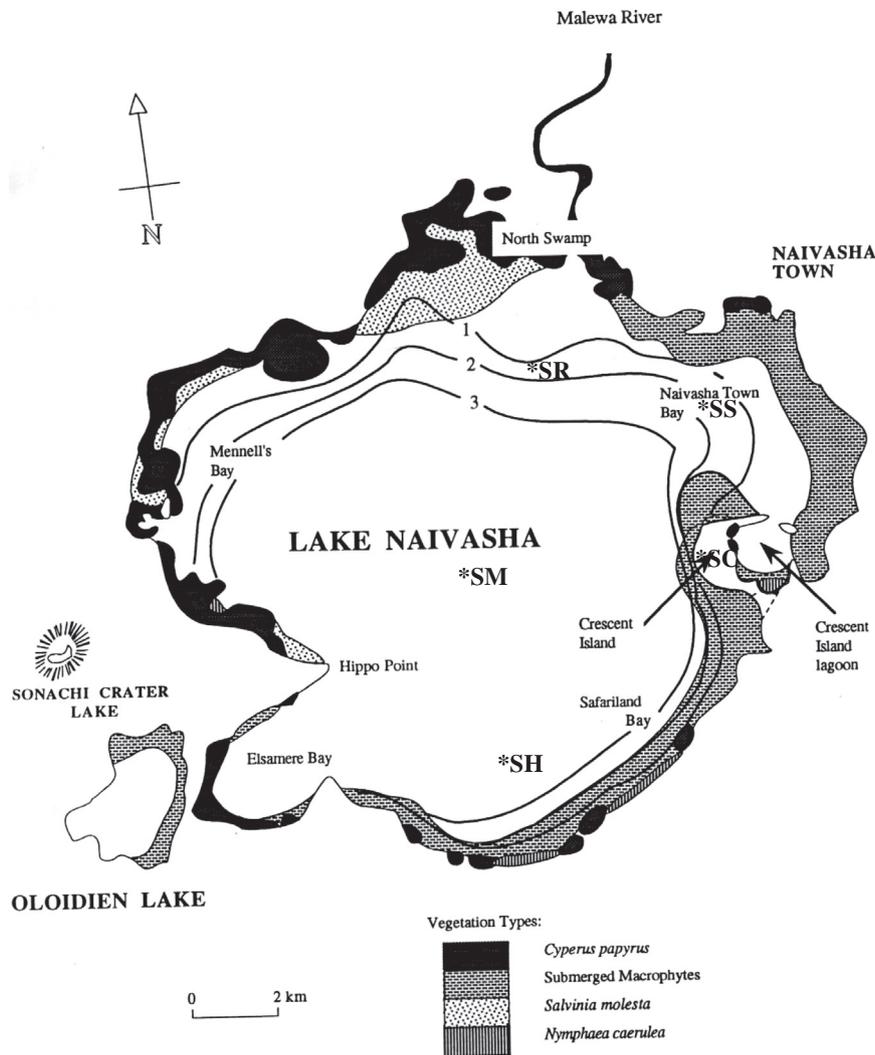


Fig. 1. Map of Lake Naivasha showing the study sites (marked *): Key: Numbers 1, 2 and 3 refer to depth contours in meters. Sampling stations are indicated as SH (next to horticulture farms), SM (mid lake), SR (next to river Malewa), SS (next to sewage input) and SC (Crescent lake).

3. Results and discussion

The values on percent sediment organic matter and sand/clay content are given in Table 1. River Malewa station (SR) had the highest seasonal variation of % clay (~60%), higher levels being during the wet season, a reflection of bad agricultural practices, deforestation and overgrazing in the catchment area. This causes high turbidity, a near extinction of submerged macrophytes and a lake bed virtually devoid of benthic fauna (Hickley et al., 2004). Sediment deposition has also resulted in the reduction of the lakes

mean depth (see bathymetry plot in Fig. 1) with repercussions on high water loss due to evaporation. Tang (1999) reported $162.00 \times 10^6 \text{ m}^3/\text{year}$ water loss by evaporation about five times higher (Fig. 2) than water abstraction for agriculture ($32.70 \times 10^6 \text{ m}^3/\text{year}$). The northern sector of the lake receives the highest sediment input mainly from river Malewa and municipal sewage; this has led to the receding of the Lake and the exposure of vast areas of riparian land during the dry season (Fig. 2). The inflow of aerated runoff water during the rainy season leads to oxidation of sulfides, amines, ammonia, etc. leading to the lowering of pH (Alvarez-Iglesias et al., 2003). Alvarez-Iglesias et al. (2003) reported that pH variations affect the metal fraction bound to carbonates (see Fig. 3).

Table 1

Percentage organic matter (OM), clay and sand content of the sediment content during wet and dry seasons ($n=4$; SD = standard deviation for $n=4$): SS = Sewage station; SM = Mid Lake station; SC = Crescent station; SH = Horticultural station; SR = River Malewa station; (-) not determined.

Station	Wet season			Dry season		
	OM ± SD	% Sand	% Clay	OM ± SD	% Sand	% Clay
SS	20.36 ± 2.05	45.2	54.8	18.85 ± 0.45	60.1	39.9
SM	24.64 ± 0.24	66.8	33.2	1.46 ± 0.96	-	-
SC	19.13 ± 0.86	43.9	56.1	19.36 ± 1.58	45.4	53.8
SH	19.54 ± 1.88	67.1	32.9	28.13 ± 0.16	51.9	43.7
SR	10.92 ± 0.54	14.2	85.8	9.46 ± 3.06	69.4	28.9

The concentration of dissolved Al at station SS was about 7000 µg/l (Fig. 4), this is quite high considering Wild (1993) report, on laboratory studies that showed the survival of brown trout fry reduced by concentrations of 250 µg/l and their growth reduced by one tenth of this concentration. One of the major sources of Al in freshwater is the discharge of alum sludge from municipal water treatment plants. Alum or aluminum sulfate is used for coagulation and flocculation of raw water supplies to remove turbidity. The high spatial variation of dissolved Al at station SS compared to the other stations (Fig. 4), point at the sewage site as a source of Al (Tables 2 and 3).

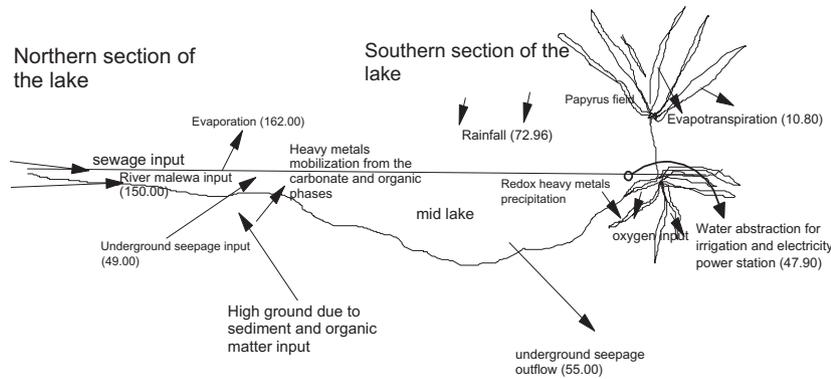


Fig. 2. Cross-section of Lake Naivasha showing heavy metals dynamics and hydrodynamics. The numbers in bracket represent water fluxes according to Tang (1999) ($\times 10^6 \text{ m}^3/\text{year}$).

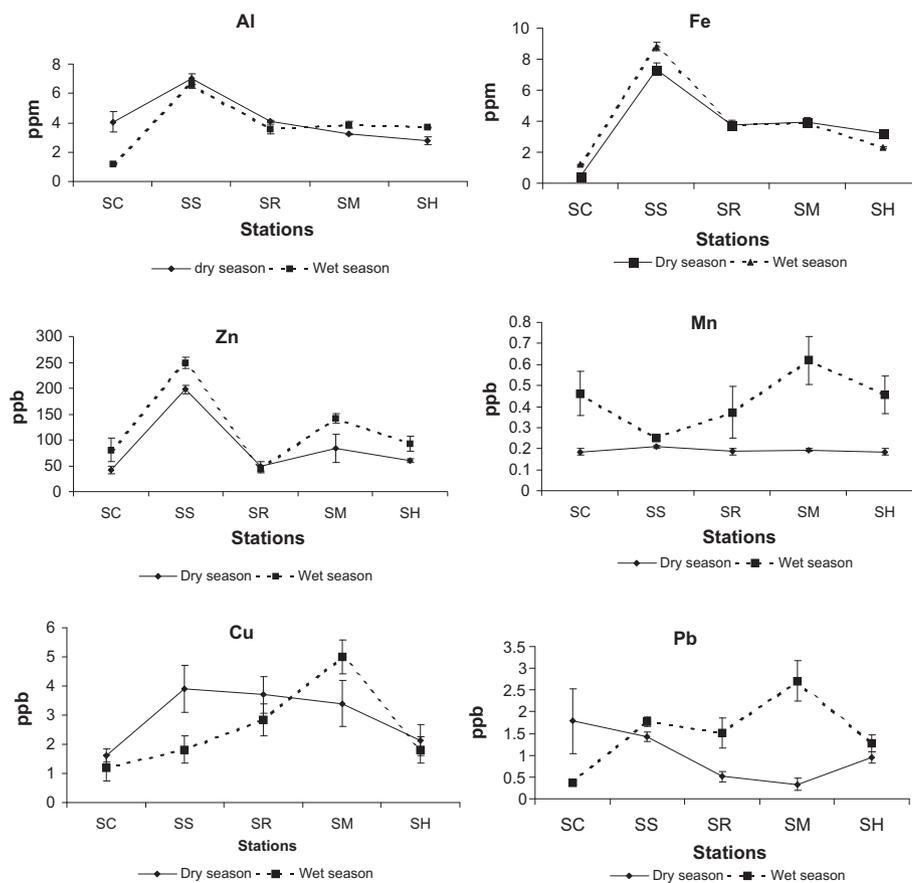


Fig. 3. The concentration of dissolved Fe was high at station SS, about seven times higher than station SC.

The effect of pH on the dissolution of Al was pronounced in the wet season, dissolved Al correlated with, sediment pH (Al-pH $r = 0.86$), Eh (Al-Eh $r = 0.70$), DO (Al-DO $r = 0.82$), water temperature (Al-water temperature $r = 0.81$) and depth (Al-depth $r = -0.73$). All the above mentioned physicochemical parameters are variables that influence organic matter breakdown, to soluble molecules and thus enhance dissolution of the organo-Al; high pH will deprotonate carboxyl groups in organic matter and will result in the negative charge repelling and thus disintegrating the intertwined organic molecule, while high dissolved oxygen concentration will result in higher organic matter decomposition, higher dissolved oxygen will result in higher Eh values, higher temperature will increase the decomposition rate, while higher

depths will have lesser oxygen thus the inverse relation. At high Eh organic matter is oxidized and is in a state where it can accept protons. Concentrations of dissolved Al are generally low in most natural waters due to the relatively low solubility of natural Al minerals under circumneutral pH values and low concentrations of complexing ligands. Stumm and Morgan (1970) reported a median value of $0.4 \mu\text{mol/l}$ for terrestrial waters. In the lithosphere, Al is largely associated with highly crystalline aluminosilicate minerals, and has low solubility (May et al., 1979) and slow dissolution kinetics (Bloom, 1983). It can therefore be assumed that the labile Al phase at station SS was mainly derived from alum sludge from municipal water treatment plants. The implication that dissolved Al was in the organic state, complexed to ligands of humic and fulvic

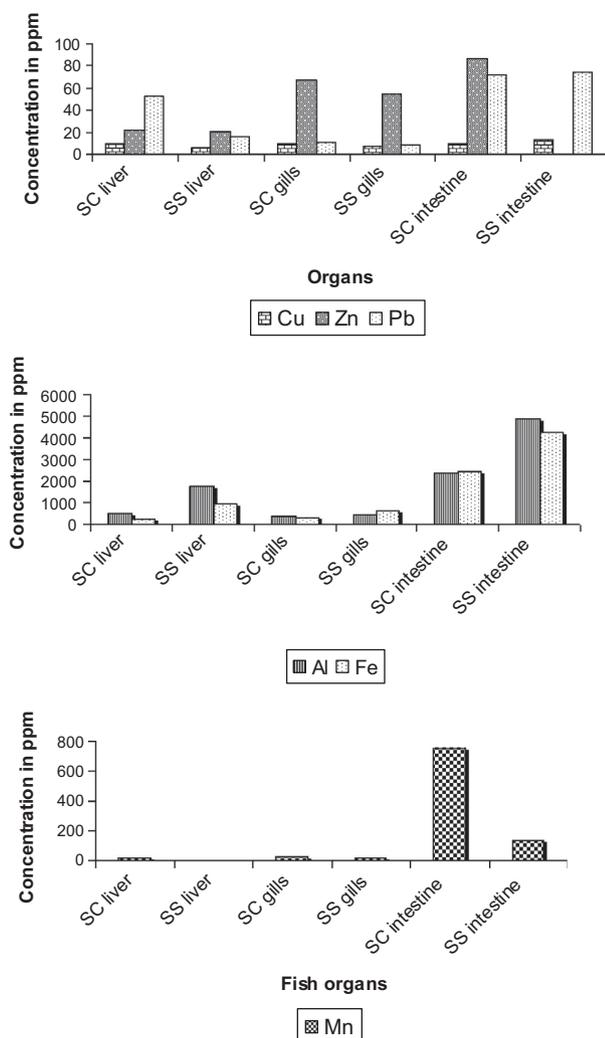


Fig. 4. Fish sampled from station SS had higher concentrations of Fe and Al in their liver and intestine; gills had more or less similar concentrations as that of the fish sampled from station SC.

acid indicates its high affinity for organic matter. Considering the high dissolved Al concentration at station SS (7000 $\mu\text{g/l}$) in comparison to that at station SC (1 $\mu\text{g/l}$), the deduction that dissolved Al was mainly in the form of organic matter would explain why there was no significant variation in the level of Al in gills of fish sampled at station SS and SC (Fig. 4). Jonasson (1977) reported on the ability of dissolved organic matter to form complexes with metal ions in wetlands, reducing their bioavailability and toxicity to living organisms. Bugenyi and Lutalo-Bosa (1990) showed that the highly alkaline organic and saline waters of the wetland-lake ecotone of lake George-Edward system in western Uganda prevented heavy metal pollution from copper coming from a dormant copper mine at Kilembe and cobalt from stockpile tailings in Kasese.

The concentration of dissolved Cu was relatively low (Fig. 4), and below the World Bank (1995) standard on ground water (300 $\mu\text{g/l}$). It was comparable to that of Honolulu Average River water 1.5 $\mu\text{g/l}$ (City and County of Honolulu 1971). Dissolved copper correlated inversely with water pH $r = -0.54$, suggesting leaching from suspended sediment. Dry season dissolved Cu related positively with easily oxidizable suspended organic carbon $r = 0.64$ and dissolved Fe $r = 0.59$; suggesting that dissolved Cu was mainly derived from the breakdown of organic matter and the fact that it also related positively with dissolved Fe is further support, since dissolved Fe was mainly in the form of humic and fluvic acids.

The concentration of dissolved Fe was high at station SS, about seven times higher than station SC (Fig. 4). Spatial distribution was similar for both seasons; wet season was higher at station SS and lower at station SH. Spatial distribution of dissolved Fe, point at station SS as a pollution input source, speciation of dissolved Fe can be assumed to have been mainly organic and ionic. Both seasons correlated positively with sediment pH ($r = 0.83$ and $r = 0.49$ wet and dry season respectively), high pH result in the deprotonation of organic matter and consequently their solubilization. The ionic species were from suspended sediments, both seasons related positively with dissolved oxygen ($r = 0.83$ and $r = 0.63$ wet and dry season respectively); high dissolved oxygen would result in the oxidation of $-\text{NH}_2$, NH_4^+ , $-\text{SH}$, FeS , S^0 , etc. and consequently the release of protons hence lowering the pH and eventual release of exchangeable or carbonate bound Fe.

Table 2

Seasonal and spatial variation of: percentage carbonate (%C), sediment- and water-pH during dry and wet season: SD = standard deviation ($n = 4$); (-) not determined; SS = Sewage station; SM = Mid-Lake station; SC = Crescent station; SH = Horticultural station; SR = River Malewa station; Sed = sediment.

Station	Dry season			Wet season		
	%C \pm SD	Sed pH	Water pH	%C \pm SD	Sed pH	Water pH
SS	10.66 \pm 1.08	7.10	9.23	8.01 \pm 1.57	7.51	8.20
SM	16.73 \pm 1.56	6.91	8.24	11.48 \pm 2.25	6.85	7.68
SC	17.80 \pm 0.86	6.80	-	9.66 \pm 1.46	6.61	7.89
SH	11.83 \pm 4.05	6.81	7.74	6.90 \pm 1.22	7.17	8.16
SR	11.29 \pm 0.94	7.21	8.92	6.54 \pm 1.71	7.19	8.00

Table 3

Performance on quality control. n = number of values; concentration in ppb, \pm is 2σ standard deviation.

	Al	Fe	Cu	Mn	Pb	Zn
Certified conc. SPS-SW2 Batch 112	250	100	100	50	25	100
This study	230 \pm 20 ($n = 3$)	96 \pm 9 ($n = 3$)	105 \pm 8 ($n = 3$)	45 \pm 5 ($n = 3$)	22 \pm 3 ($n = 3$)	107 \pm 8 ($n = 3$)

The spatial distribution of dissolved Mn was static during the dry season, it was however dynamic during the wet season. Dissolved Mn correlated inversely with water pH ($r = -0.57$) and water Eh ($r = -0.51$), implying that Mn was derived mainly from suspended sediments, low water pH would trigger the release of exchangeable Mn, while low Eh would trigger the formation of soluble Mn^{2+} .

Gills from fish sampled at station SC had slightly elevated levels of Mn in comparison to those from station SS (Fig. 4), this finding was in agreement with data on dissolved Mn (Fig. 4). The concentration of Mn in the intestine content of fish sampled at station SC was about five times higher than that of fish sample from station SS.

Seasonal variation in dissolved Pb was observed at stations SC, SR and SM, wet season being higher at stations SR and SM. River Malewa seemed to be the main input source of dissolved Pb during the wet season. There seemed to be a constant input of dissolved Pb at stations SS and SH, probably due to domestic (SS) and horticultural activities (SH). The concentration of dissolved Pb at stations SR and SM reduced markedly during the dry season, most likely lost by volatilization as tetramethyllead during the dry season. Indeed Purchase and Fergusson (1986), reported that the volatilization of tetramethyllead is an important fate process for the removal of petroleum based Pb from the water column. Interestingly the concentration of dissolved Pb at station SC was higher during the dry season this could only have been contributed by the activity at the yacht club, whose contribution was masked by the rains.

Dissolved Zn related highly with sediment pH $r = 0.67$ indicating dissolution on pH increase, the fact that it also correlated positively with organic matter $r = 0.50$, Eh $r = 0.63$, temperature $r = 0.56$ and dissolved oxygen $r = 0.56$ would suggest that organic bound Zn contributed significantly to the concentration of dissolved Zn. According to Murray (1994), at higher pH, chemisorption on oxides and aluminosilicates and complexation with human lower the solubility of Zn^{2+} markedly. Consequently Zn mobility in neutral soils is very low. If soils are slightly alkaline even though the activity of the free Zn^{2+} ion is extremely low, Zn-organic complexes can become soluble and raise mobility. In strongly alkaline soils, Zn-hydroxy anions may form to increase solubility (Murray, 1994).

Dissolved Zn concentration was highest at station SS about 250 $\mu\text{g/l}$, comparing this value to the concentration of drinking water in Rio de Janeiro, 7–350 $\mu\text{g/l}$ as reported by Azcue et al. (1988) and those reported by Ajmal et al. (1986), 2–270 $\mu\text{g/l}$ for municipal drinking water of Aligarh India, Lake Naivasha can be said to be relatively unpolluted in relation to dissolved Zn.

Fish sampled from station SS had higher concentrations of Fe and Al in their liver and intestine, however the gills had more or less similar concentrations as that of the fish sampled from station SC (Fig. 4). Highest concentration of both elements was in the intestines. Manganese was least accumulated in the liver, despite the concentration of Mn being highest in the intestines. Fish sampled from the crescent station (SC) had higher Mn concentrations in their liver, gills and intestines. The concentration of zinc was highest in fish gills sampled at station SS, and was one order of magnitude higher than Cu or Pb. Lead concentration was highest in the intestines for fish sampled from stations SS and SC, both stations had similar concentrations (Fig. 4). Fish liver sampled from station SC, had Pb concentrations twice as high as those from station SS, probably due to activities of the fishing club located there.

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