

Full Length Research Paper

Comparative evaluation of the concentrations of lead, cadmium and zinc in surficial sediments from two shallow tectonic freshwater lake basins, Kenya

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Sources of metals in the environment are widespread and data on typical concentrations in the various media and environmental settings exists worldwide. Distribution and comparative concentrations of some selected metals in surface sediments of two shallow tectonic freshwater basins were assessed, as useful indicators of the level or magnitude of anthropogenic influences, as well as other aquatic processes, considering the increasing challenges in management of waste disposal. Concentrations of Pb, Cd and Zn in the sediments were detectable in all sites, albeit there were relatively lower levels reported in the column of alkaline waters. In dry weight basis, and in increasing order, the levels were Cd<Pb<Zn in both basins. Cd, Pb and Zn elements are all chalcophiles. However, using a student t-test, the concentrations of Cd and Pb in the sediments showed significant differences ($p<0.05$) between the two basins. Using freshwater sediment quality guidelines (ISQG) values, all the three metal mean contents in L. Baringo were above these values. Average levels of Zn and Cd were also above the ISQG values. However, all the mean concentrations of Zn, Cd and Pb in surficial sediments were found to be below the probable effect level, and above normal concentrations ranges found in sedimentary and igneous formations. Concentrations of Pb and Zn found are comparable to other relatively large basins, with extensive drainage basins and urban influences. Cadmium sediment levels are a concern, as the evaluation shows increasing accumulation in sediments, with possible future exposure risks to aquatic organisms. Surface runoff, waste discharges and particulate deposition is thought to be significant in these basins, and to understand overall impacts from anthropogenic deposition, it is important that background metal levels are determined together with supporting chemical partitioning to reveal more information on available metal contents.

Key words: Tectonic lake basins, surface sediments, concentrations, lead, zinc, cadmium.

INTRODUCTION

Sediments receive both autochthonous and allochthonous inputs in a lake ecosystem and contain records of contaminants over time. Urban storm waters, eroded

soils and runoff waters, floodwaters, untreated domestic wastewaters and leachates from uncontrolled solid waste dumpsites and landfills, mining operations, and use

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of petroleum products are activities which accelerate the loading of various inorganic and organic contaminant substances in surface water and sediments of lakes and rivers.

Lead (Pb) and cadmium (Cd) and their compounds together with zinc (Zn) compounds are characterized as hazardous constituents under the international list of hazardous substances or OECD Environment Directorate and UNEP international register of potentially toxic chemicals (Suzanne, 1993). However, Zn, Cu, Fe, Mo, Co and Mn are essential elements and form important metalloenzymes. Differences in chemical properties of elements and their transformations within the aquatic environment determine their retention, bioavailability and toxicity. At low natural levels, metals are easily immobilized in natural environments and eliminated from tissues of organisms, depending on the influence of other regulating factors. The water compartment contains heterogenous polyligands (fluvic, humic and tannic acids, amorphous metaloxyhydroxides of Mn, Al and Fe, clay, bacterial surfaces and associated exocopolymers, suspended particles and macro molecules (polysaccharides, proteins, etc) (Tesseir et al., 1979; Luoma and Bryan, 1981; Greenland and Hayes, 1978), which can demobilize the dissolved metal fraction. In sediments, inherent sediment and overlying water characteristics such as redox conditions, pH, temperature, organic matter, sediment composition and degree of hydrolysis, adsorption, complexation, and precipitation processes may in combination determine exposure concentrations and availability of metals for uptake. The ability to distinguish background and anthropogenic influences on metal concentrations can also be attained through use of selective extractants for the various geochemically defined phases or fractions, with the aim of simulating various environmental conditions to which the sediments can be subjected to. Kamau et al. (2008, 2007), Mutia et al. (2012), Ochieng et al. (2007), Dharani et al. (2010, 2007), Tarits et al. (2006), Campbell et al. (2003), Hakan Tarras-Wahlberg et al. (2002), Bonzongo et al. (1996) and Njenga et al. (2009), provided very useful information on detectable levels of several metals in the rift valley lakes water, sediment and aquatic organisms, and soils of surrounding areas. Increased cobalt, nickel and copper concentrations in sediments of the remote Lake Baringo were among the first few documented results on heavy metals in the rift valley lake sediments (Ochieng et al., 2007). High levels of Cd and Zn in soils and *Acacia xanthophloea* Berth., were also reported in polluted sites around L. Nakuru, another closed basin saline rift valley lake (Dharani et al., 2010, 2007). Therefore, both surficial and core sediments provide better understanding of water related risks of accumulated potential toxicants among water users and managers, also will encourage a better sustainable management of water resources and maintenance of

ecosystem integrity. Information on metal concentrations in bottom sediments of L. Baringo is lacking, yet catchment degradation, increasing lake water turbidity and changing lake water levels are environmental threats of concern in this area. Recently, temporal and spatial changes in the physical and temporal conditions showed that a general variation of physical and chemical parameters observed in the south-north transect was due to the effect of the affluent rivers and streams (Omondi et al., 2014). This study presents total concentrations of some of the priority metals, which were monitored in surficial sediments of two shallow freshwater lake basins to understand possible associated anthropogenic influences and processes.

MATERIALS AND METHODS

Study areas

Lakes Baringo and Naivasha (Figures 1 and 2) are both shallow freshwater lakes located in Kenya, within the Eastern arm of the Great Rift Valley (Figure 3). They are internationally recognized as Ramsar sites and the surrounding communities depend on them for relatively small-scale fishery. Lake Naivasha (Figure 2) is important for flower production (export), geothermal electricity generation, tourism and conservation (Harper et al., 1990). Lake Baringo is important for agriculture, with water diverted from the lake for irrigation (Hickley et al., 2004). A feature of both lakes are fluctuating water levels, resulting from periods of low rainfall, with this accentuated in recent years by the increased agricultural use of water (Harper and Mavuti, 2004).

Lakes Naivasha and Baringo are important water bodies with a thriving commercial fishery based on introduced species (Muchiri and Hickley, 1991; Hickley et al., 2008; Ojuok et al., 2007), with the common carp *Cyprinus carpio* L. and the marbled lungfish *Protopterus aethiopicus* (Heckel, 1851) dominating the catches respectively. Whilst the role of habitat degradation in impeding stock recovery remains unclear, it is apparent the species now dominating catches in Naivasha (*C. carpio*) and Baringo (*P. aethiopicus*) both have wide environmental tolerances when compared with the other exploited species (Britton et al., 2005). Persistence of the water hyacinth in lake Naivasha has added another challenge to the water resource managers and other stakeholders relying on the lakes water sources and livelihood. Effects of the water hyacinth on lake water quality and ecology (Mironga et al., 2012) and impacts of environmental degradation (Onywere et al. 2012) are signs of the threats from a wide range of human activities.

Lake Baringo basin

Lake Baringo is located between longitude 036° 00' and 036° 10'E and latitude 00° 30' and 00 34'N, at 975 m. a. s. l (Figure 1), in a semi-arid area north of Lake Naivasha within the same arm of the valley, and they both lie at relatively lower ground of the rift floor. The relatively shallow lake basins are therefore receptors of eroded materials from relatively high gradient catchment areas. Perkerra and Molo rivers flow into the lake from the southern edge. The lake and Perkerra catchment areas are about 6820 and 1207 km², respectively. Most of the surrounding lower zones are semi-arid grasslands with sparse vegetation, providing grazing lands.

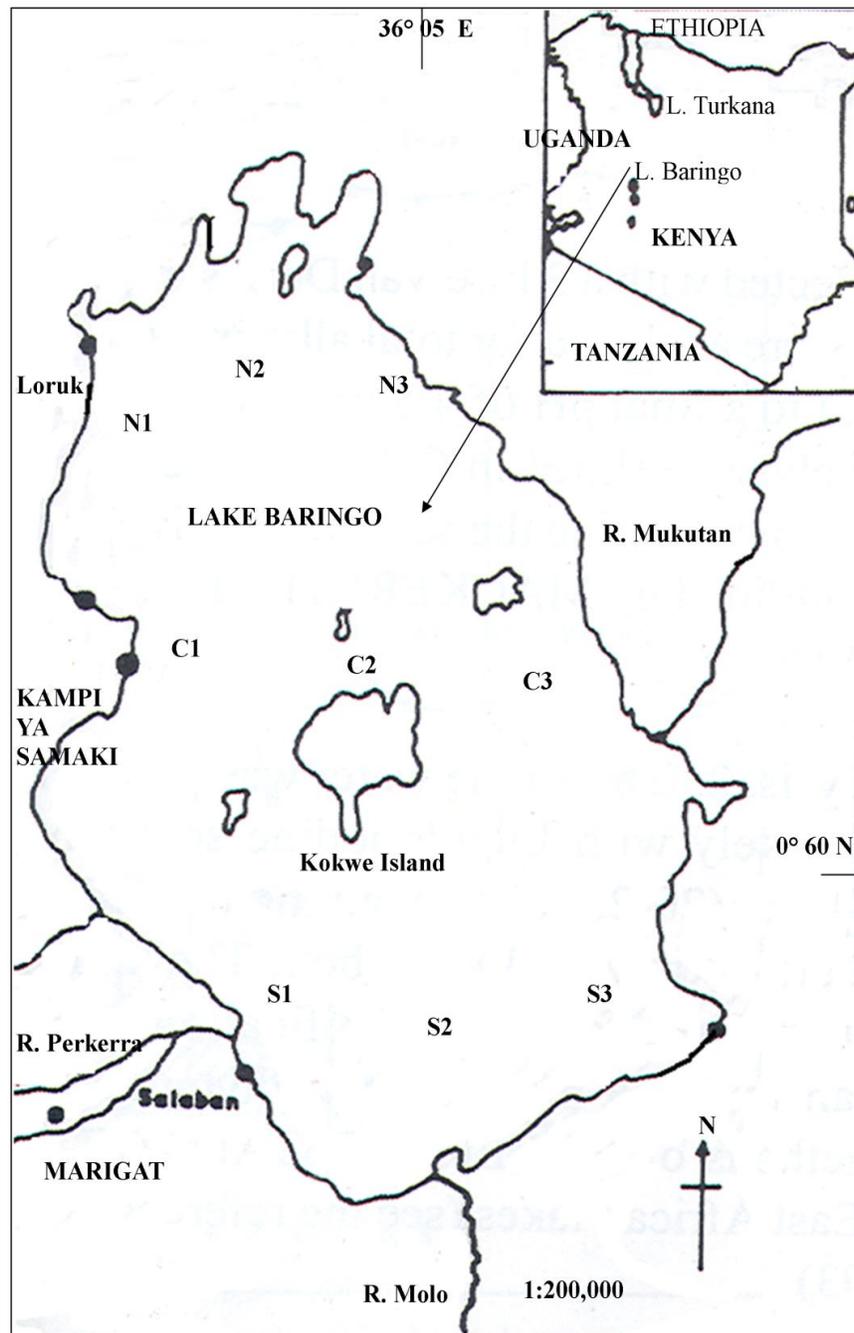


Figure 1. Map of Lake Baringo showing sampling sites.

However, in the upland corresponding to the high altitude river source areas, important farming and settlement areas develop.

The general geology and soils of Lake Baringo basin

Late Holocene to modern sedimentation in Lake Baringo is dominated by fine grained siliciclastics (Renaut et al., 2000). Most of the lake floor is covered by detrital muds and felspathic silts which reflect the very high soil erosion rates in the catchment (Aloo,

2002; Snelder and Bryan, 1995; Oostwoud and Brayan, 2001). In their upper reaches, the rivers mainly drain thick series of basalts, phonolites and trachytes of Mio-Pliocene age, while downstream they flow across Pleistocene trachphonolites, pyroclastic deposits and siliciclastic fluvial and alluvial sediments. The eastern part of Baringo watershed, drained by the rivers Mukutan and Orabel, is formed by a succession of basalts and phonolites of Miocene age, several hundred meters thick, which form the Laikipia fault escarpment. The geology of the area is mainly undifferentiated volcanic rocks, while the soils are of clay type (Odada et al., 2006).

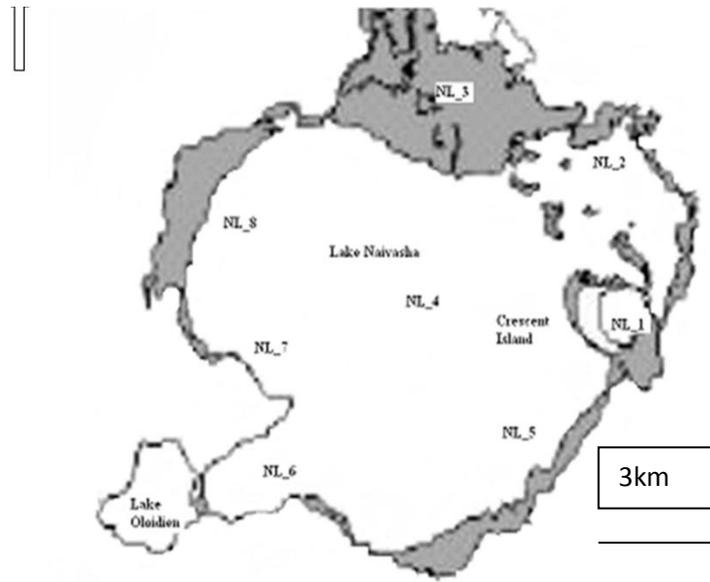


Figure 2. Map of Lake Naivasha showing the sampling sites.



Figure 3. Hydrographic map showing lakes of the Kenyan Rift Valley (adopted from Gichuki et al., 2005).

Although detrital sediment is washed into the lake throughout the year, the maximum influx occurs in August following the heavy rains. Winds then mix the loose sediments on the shallow lake floor, generating very high turbidity (Oduor et al., 2003). A gradual increase in salinity and pH have been reported (Barton et al., 1987; Aloo, 2002; Oduor et al., 2003), coincident with shrinking of the lake.

The lake depth reduced from 8 m in 1972 to 2.5 m in 2003 due to siltation resulting from high erosion rates in the catchment (Onyando et al., 2005). The lake lies in a highly faulted rift and geothermally active area, with hot springs, north of the saline Lake Bogoria. The steep gradient and loose soil makes the area highly vulnerable to surface erosion during heavy precipitation. Using a universal soil loss equation (USLE) (Wischmeier and Smith 1978), with geographic information system (GIS) and integrated land and water information system (ILWIS), the estimated potential soil erosion from the catchment was 1.73 million tons per year (Onyando et al., 2005). Other assessments have provided information on environmental threats that lake's biodiversity and livelihoods are facing (Odada et al., 2006). Therefore, changing hydrological regime and siltation in such a shallow closed basin coupled by evaporative concentration effects are factors thought to influence the aquatic environment and may undermine its ecological health. This is reflected in the lake waters which are characterized by low water transparency and a relatively lower fishery production.

Lake Naivasha basin

Lake Naivasha has a surface area of between 120 to 150 km² and a mean depth of 4 – 6 m without a physical outlet. Lake Naivasha is mainly recharged by perennial rivers and ephemeral streams during the rainy season, and an underground outflow from the lake has been proposed (Darling et al., 1990; Bretch et al., 2005). Its freshness is mainly maintained by the inflows, biogeochemical sedimentation and the underground seepage (Gaudet and Melack, 1981). Transects made along a south-western direction also traces the gentle sloping of the Lake Naivasha basin (Gaudet and Melack 1981), excluding the deep sheltered waters at Crescent Island basin lake.

The general geology and soils of Lake Naivasha basin

Lake Naivasha basin is formed of volcanic rocks (Thompson and Dodson, 1963; Noble and Ojiambo, 1976) consisting of tephrites, basalts, trachytes, phonolites, ashes, tuffs, agglomerates and acid lavas (rhyolite, comendite and obsidian). Craters, fumaroles, hot springs and steam vents are found in several places in the south-eastern and south-western regions. The lake beds are mainly composed of reworked volcanic material or subaqueously deposited pyroclastics and organic matter produced locally. The distribution of the soil types and the underlying rocks in and around L. Naivasha is complex as a consequence of past influences: intensive variation in climatic condition, volcanic activities (Sombroek et al., 1980). Ongweny (1973) described the soils occupying the floor of the rift valley from L. Naivasha to L. Baringo as light grey or brown to pinkish non-calcareous soils. In the high areas of the catchment, there are non-calcareous black or grey soils overlying yellow brown compact subsoils with iron concretions.

The lake was found to support a diversity of activities such as intensive agriculture under irrigation. This is one of the main foreign exchange earners and employs more than 300,000 people (Mageria et al., 2006). The lake catchments are situated in fertile and productive Western Aberdare's ranges and Kinangop plateau. The high human population density and forest clearing from

settlement has resulted in extensive catchments degradation and changes in land use. Paleoclimatic studies have revealed historical fluctuations from a deep lake discharging to the south through Njorowa gorge to a complete desiccated lake (Richardson and Richardson, 1972; Washbourne, 1967). Water levels in the Lake fluctuate due to rainfall, high surface evaporation rate, underground drainage and water use.

Most of the lake edges are lined with littoral macrophytes, which are dominated by *Cyperus papyrus* L., and occasionally extended by attached floating water hyacinth mats, providing suitable fish breeding and nursery areas.

Crescent Island basin is a deeper and sheltered part of the main lake with a maximum depth of 14 m. Ololdien is a smaller saline crater lake, with a depth of 5 m, separated from the main freshwater lake at the southwestern edge, a home for flamingos and hippos and hence an important touristic feature. Rivers Malewa and Gilgil are the main permanent inflowing rivers, forming the main sources of water input into the lake, besides direct precipitation and other seasonal inflows from smaller ephemeral streams and surface runoff. The rivers thus form major transport channels of particulate matter into the lake.

Sampling

Representative sampling sites were selected and marked using GPS global positioning system, and covering areas with high potential of external influences. Sampling was conducted during the wet season in April 2007.

The physical and chemical parameters were determined *in situ*, using appropriate meters. The water pH, water temperature, dissolved oxygen (D.O), turbidity, conductivity, were determined using a multi-parameter water quality meter (YSI-610DM) environmental monitoring system. Other field analyses of the bottom and surface water were characterized according to recommended standard methods of analysis (APHA, 1985). Water transparency was determined using a standard 25 cm diameter disk. A Van Dorn water sampler was used to collect sub-surface water samples for total alkalinity and hardness, and total dissolved solids and total suspended solids, according to standard methods (APHA, 1985)

In L. Baringo, a total of 9 sampling sites were sampled in the southern (S1, S2, S3), central (C1, C2, C3) and northern zones (N1, N2, N3) of the lake. The sites were marked from left to right side of the lake water surface. The southern zone represents the permanent river mouth areas and is also close to the Perkerra irrigation scheme and Marigat town area. The central zone consists of the main islands, and the northern end has more rocky bays and shores with lesser littoral vegetation. Surrounding areas from the central to the northern zone are surrounded by eroded rocky grounds with scattered vegetation.

In L. Naivasha, 8 sampling stations were selected to represent the different land influenced zones of the shallow lake, including: the deeper crescent Island (station 1), the area receiving town waste discharges (station 2) and an area off the R. Malewa mouth (station 3). Station 4 is a mid-area of the main lake, with the rest of the sites located near shore clockwise from off Sher agencies (station 5), off Oserian bay (station 6), off Hippo point (station 7) and off Korongo area (station 8).

Sample digestion and analysis

The bottom sediments were collected using a pre-cleaned stainless steel Ekman grab sampler at each sampling site. The inner most portion of sediment not in contact with equipment was scooped with a stainless steel spoon and transferred into pre-cleaned PET

containers and stored under refrigeration in the field. In the laboratory, samples were dried in an oven at 105°C, crushed into powder and sieved (to less than 0.063 mm grain size), before digestion using high purity analytical grade acids (AR) and reagents.

The sediments were characterized by determination of the percentage of water, organic matter and carbonate contents. The water content was determined by oven drying about 5.0 g of the wet sediment at 105°C for 6 h and to a constant weight. About 1.0 g of the dry sediment was used to determine the carbonate and organic matter contents, using excess acid titration reaction of Walkey and Black (Nelson and Sommers 1982). The percentage loss on ignition (%L.O.I) was also determined by heating about 1.0 g of the dry sediment at 550°C (Hakanson et al., 1983), in a furnace and determining the weight loss.

About 1.0 g of the dry sediment samples were digested using 3:1 v/v Aqua regia, a concentrated mixture of hydrochloric acid (35.4% w/w A.R) and nitric acid (70% w/w A.R), using a digestion block. Digest of the sediment samples were cooled and filtered (using Whatman filter papers no. 542), and solutions made to volume in a volumetric flask. The solutions were then analyzed for Cd, Pb and Zn using an atomic absorption spectrophotometer equipment (Varia Techtron AA-10, AAS, Varian Techtron PTY Ltd. Varian Associates Inc.) according to the instrument operating procedures. Samples were analyzed in triplicates, using appropriate metal calibration standards and acid blank digests, ensuring no external contamination of samples occurred during the whole analytical process. All reagents used were of analytical grade to check for possible contamination.

Where appropriate, data analysis and statistical parameters were determined using SPSS and excel packages.

RESULTS AND DISCUSSION

The physico-chemical characteristics

The water physical and chemical measurements were made between 09.00 and 15.00 h. Lakes Naivasha and Baringo, are of shallow, with a relatively low transparency. The sampled lake water depths were similar and ranged from 2 to 4 and 2.5 to 4 m in L. Naivasha and L. Baringo, respectively. The commonly known deep zone in L. Naivasha recorded a total depth of 14 m.

Water temperatures of waters of L. Naivasha ranged from 21.4 to 24.8°C (surface) and 20.5 to 24.4°C (bottom water). Relatively higher surface water temperatures were found in L. Baringo (26.2 to 28.3°C). Lower bottom water temperatures recorded for both basins were lower than the surface waters. A narrow pH range was recorded between surface and bottom waters in both lakes. In lake Naivasha, the water was relatively less alkaline with pH ranging from 7.2 to 7.7 (surface waters) and 7.3 to 7.7 (bottom waters) as compared to L. Baringo (pH 7.9 to 8.5). Overall turbidity was low in L. Naivasha (2.0 N.T.U. to 14.0 N.T.U.) as compared to the more turbid waters of L. Baringo (510 to 561 N.T.U.). More turbid waters were found at site 2 and the clear waters were at the deeper Crescent area, where a deep underwater light transparency of 130 cm was recorded,

with a mean lake water transparency of 56 ±11.4 cm. In L. Baringo, most parameters showed little variations spatially, although values is distinctly different from measurements from L. Naivasha. The water transparency in L. Baringo remained low (8 ±0.7 to 9 ±1.4 cm), but the conductivity was higher and ranged from 662 to 808 μScm^{-1} as compared to values for L. Naivasha water (236 to 322 μScm^{-1}). Riverine and overland surface erosion cause influx of high volumes of suspended particles in surface lake waters which contributes to the reduced under-water light penetration. Winds mix the loose sediments on the shallow lake floor, generating very high turbidity (Oduor et al., 2003).

The water characteristics of Lake Baringo are shown in Figure 4a-c. The lake was sampled during a relatively low water level and the water depth was less than 4.0 m. Lake waters are weakly alkaline and the total alkalinity and hardness of the waters ranged from 58±0.0 to 101±61 $\text{mg CaCO}_3\text{l}^{-1}$ to 50±0.0 to 57±10 $\text{mg CaCO}_3\text{l}^{-1}$. In L. Naivasha, more uniform values for total alkalinity were recorded (22 mg to 36 $\text{mg CaCO}_3\text{l}^{-1}$) with a mean value of 29±1.4 $\text{mg CaCO}_3\text{l}^{-1}$. Relatively low D.O levels were recorded in both lakes with 4.2 to 6.9 mg l^{-1} in surface and 2.0 to 4.7 mg l^{-1} in bottom waters of L. Naivasha. In the deeper site of Crescent island, surface water D.O. was the highest (7.2 mg l^{-1}) as compared to a low level at the bottom (2.0 to 2.7 mg l^{-1}); the Mean D.O. concentrations varied from 5.0±1.5 to 5.9±2.1 mg l^{-1} , in surface water and 2.8±1.1 to 3.7±1.5 mg l^{-1} in bottom water of L. Baringo.

Influences of river water and high evaporation on water solute composition in these basins has been described by several authors. Among the standing waters in the Naivasha basin, Na and HCO_3^- predominate (Gaudet and Melack, 1981). Lake Baringo waters are described as of a Na-Ca- HCO_3^- composition, with variable and relatively high TDS. Oduor et al. (2003) reported threefold increases in Na^+ and Cl^- and a fourfold increase in SO_4^{2-} between 1965 and 2000. The southern area of the lake is weakly influenced by evaporation and is characterized by low TDS, whereas in the central and northern parts of the lake, evaporation increases the salinity up to 8 times that of the dilute flow (Tarits et al., 2006). The Ol Kokwe thermal springs (TDS > 2800 mg/l) are also enriched in SiO_2 , HCO_3^- , F, Na and poor in Cl, Ca and SO_4^{2-} . Similar high and less variable water conductivity values were reported in lake waters and this may reflect the different time period of sampling.

Sediment metal concentrations

Sediment mean carbonate ($\text{CaCO}_3\%$) ranged from 2.3±0.9 to 8.9±0.4 in L. Baringo, whereas the contents in L. Naivasha ranged from 2.1±1.5 to 6.7±0.6, with a relatively high and less variable organic matter content. This may be a reflection of the similar volcanic lithology of these shallow basins, a relatively small surface area and

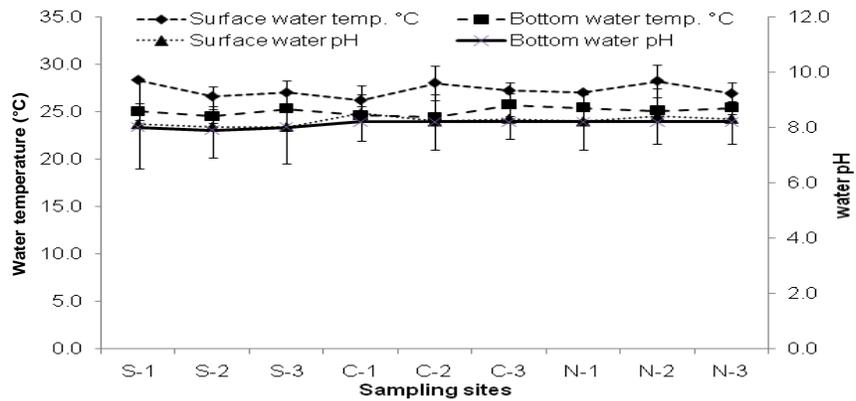


Figure 4a. Mean (\pm SD) pH and temperature of surface and bottom water of Lake Baringo.

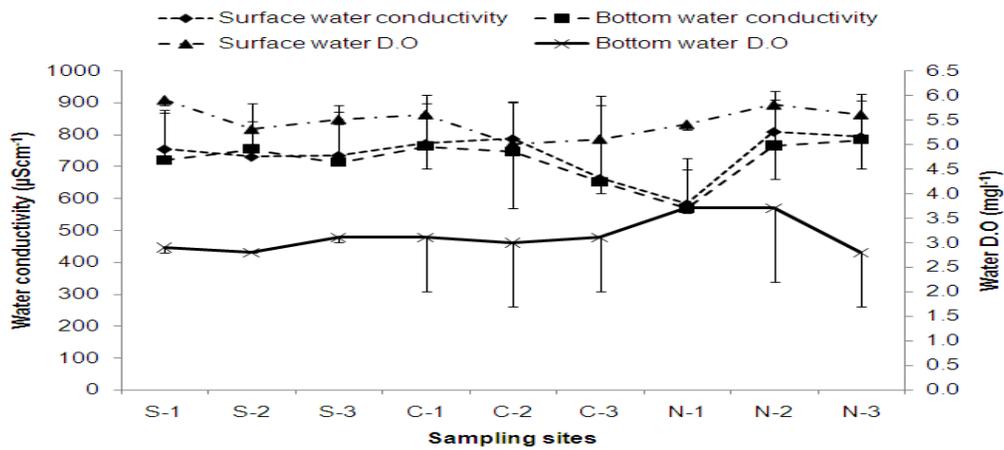


Figure 4b. Mean (\pm SD) conductivity and dissolved oxygen in surface and bottom water of L. Baringo.

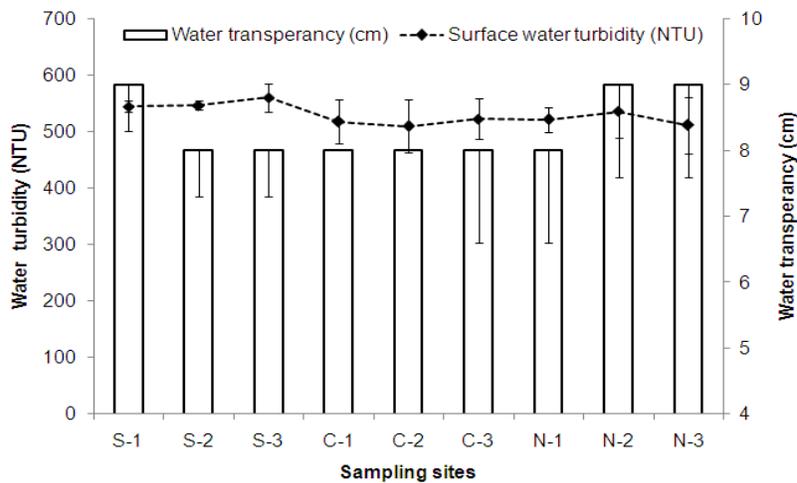


Figure 4c. Mean (\pm SD) turbidity and water transparency in Lake Baringo.

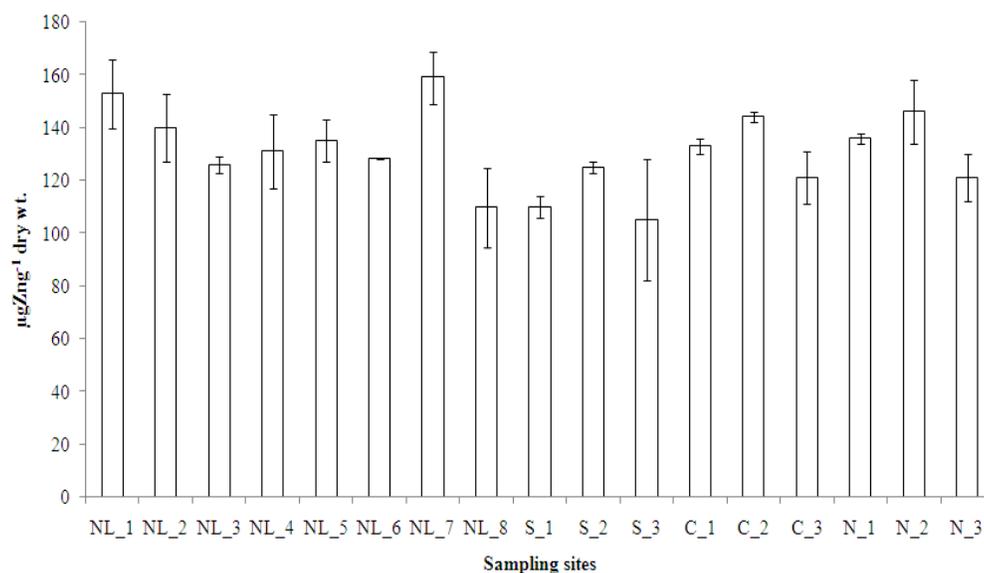


Figure 5. Mean (\pm s.d) zinc concentration (μgZng^{-1}) in lake sediments of both lakes.

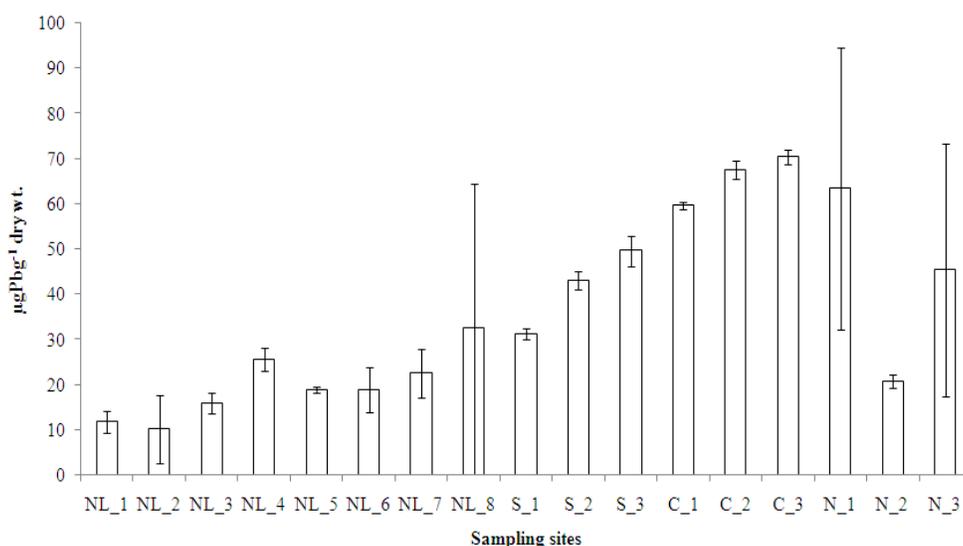


Figure 6. Mean (\pm s.d) lead concentration (μgPbg^{-1}) in lake sediments of both lakes.

arid climate, with the river mouth areas as the only sites which show a distinctly different sediment texture (more sandy).

The mean concentrations of metals in the surface lake sediments ($n=27$ for L. Baringo and $n=24$ for L. Naivasha) are shown in Figures 5, 6 and 7. The results reveal highly variable concentrations of Pb and Cd. Zinc concentrations are high in both lakes but show a small range of variation as compared to the other two metals. The highest and minimum single concentrations of Zn were 168 and 93 μgZng^{-1} in L. Naivasha and 168 to 59

μgZng^{-1} in L. Baringo, respectively. Most of the mean (\pm s.d) concentrations in each site were above 100 μgZng^{-1} . Single lead concentrations ranged from 4.6 to 67.1 μgPbg^{-1} and 15.1 to 101.1 μgPbg^{-1} in L. Naivasha and Baringo, respectively. The highest and minimum single concentrations of Cd were 1.0 and 3.0 μgCd^{-1} in L. Naivasha and 1.5 to 6.5 μgCd^{-1} in L. Baringo, respectively. In most cases, Cd concentrations are lower than the Zn and Pb concentrations and the trend in metal concentrations were as follows: $\text{Zn} > \text{Pb} > \text{Cd}$. Sampling sites which showed the highest mean Zn, Pb and Cd

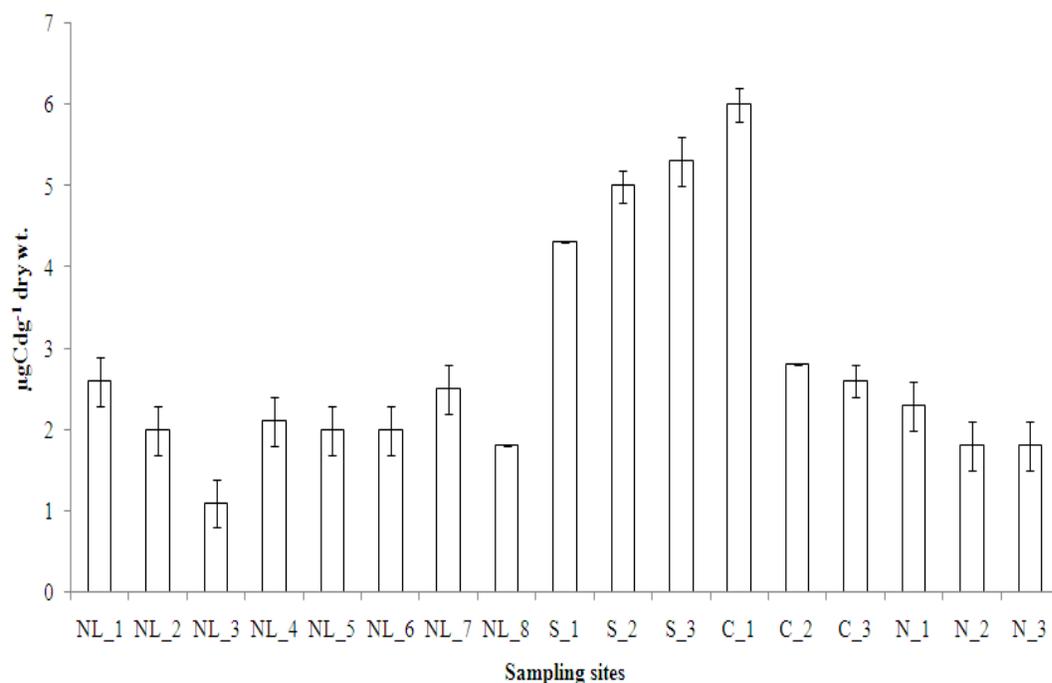


Figure 7. Mean (\pm s.d) cadmium concentration ($\mu\text{gCd g}^{-1}$) in lake sediments of both lakes.

concentrations in L. Baringo were C_2, N_1, N_2 (Zn), C_2, C_3, N_1 (Pb), and S_1, S_2, S_3, C_1 (Cd). In L. Naivasha, the highest mean concentrations of the Zn, Pb, and Cd were in sites NL_7, NL_1, NL_2, NL_5 (Zn), NL_4, NL_7, NL_8 (Pb) and NL_1, NL_7, NL_4 (Cd).

Cadmium and Pb are some of the toxic non-essential metals normally found in trace concentrations in the lake waters. Much lower concentrations are encountered in uncontaminated waters, representing natural concentrations. However, detectable dissolved and total concentrations reported in waters of the rift valley lakes (Ochieng et al., 2007; Mutia et al., 2012; Tarits et al., 2006) are signs of increasing concentrations. In the five rift valley lakes (two freshwater lakes L. Baringo and Naivasha and three saline lakes Nakuru, Elementaita and Bogoria), dissolved Pb, Zn and Cd ranged from 7- 93.6, 25 - 219.5 $\mu\text{g l}^{-1}$ and nd - 8 $\mu\text{g l}^{-1}$ respectively. Weathering of volcanic rock minerals, leaching from soils and related ore bodies, waste discharges, fuel emissions and diverse aerial sources are potentially important contributors of these metals into the lake ecosystems. Vehicle emissions are sources of accumulated lead from gasoline additives, where leaded fuel was previously used. The relative contribution of dry and wet depositions to overall lead removal varies from one location to another and depends on local climatic conditions and the type of terrain (UNEP, 2008). External sources are therefore continuously modifying natural background concentrations, and increasing the secondary sources from sediments, with

potential pore water - sediment exchange, bioaccumulation and retention in tissues of aquatic organisms. Cadmium is produced mainly as a by-product of mining, smelting and refining of zinc and, to a lesser degree, as a by-product of lead and copper production (UNEP, 2010). Measurements of cadmium concentration in ice cores, freshwater sediments and peat bogs demonstrate an essential increase of airborne cadmium depositions as compared to the pre-industrial period (UNEP, 2010). Table 1 shows average contents of Pb, Cd and Zn in lake sediments, water, fish and soils. Average (range values) contents of Pb, Zn and Cd in soils are 20 (2-200) $\mu\text{g g}^{-1}$, 50 (10-400) $\mu\text{g g}^{-1}$ and 1 $\mu\text{g g}^{-1}$ (Taylor, 1964, 1966). Hazardous waste disposal sites are a large source of Cd concentrations found in soil (about 4 ng g^{-1}) and in water (about 5 ng g^{-1}) (ATSDR, 1993). Soil formation around another saline Kenyan rift lake were found to contain significant amounts of Cd, Pb and Zn (Dharani et al., 2007, 2010), with significant correlations between soil Cd and Zn with terrestrial plant. Soil Zn, Pb and Cd concentrations in $\mu\text{g g}^{-1}$ ranged from 157 \pm 5.0 to 178 \pm 11.4 (Zn), 16.0 \pm 1.3 to 43.4 \pm 4.2 (Pb) and 9.6 \pm 1.0 to 12.2 \pm 2.2 (Cd) (Dharani et al., 2007, 2010). Similarly, soils outside the rift show relatively high levels of Cd, Pb and Zn of 14.0 \pm 1.1 to 14.8 \pm 0.1¹, 7.4 \pm 2.1 to 38.5 \pm 3.4 and 42.7 \pm 4.1 to 78.9 \pm 16.6 $\mu\text{g g}^{-1}$ (Florence et al., 2011), respectively. Increased sediment losses into rift basins are alarming especially from the arid areas of the L. Baringo catchment (Odada et al., 2006; Onyanda et al.,

Table 1. Mean \pm (s.d) range concentrations of Pb, Zn and Cd concentrations recorded in water, sediments, soils and fish species.

Metal	Water ($\mu\text{g l}^{-1}$)	Sediments (mg kg^{-1}) (dwt.)	Fish (mg kg^{-1}) (wwt.)	Soils (mg kg^{-1}) (wwt.)
Pb	16.56 \pm (9.55) ^{&}	32.71 \pm (16.49) ^{&}	1.7 \pm 0.91 ^{&}	25.69 \pm (10.62) ^{&}
	nd [§]	1.67-16.7 [§]	nd [§]	-
	25.0-563.0 ^{&&}	10.92-38.98 ^{&&}	-	-
	<100.00-179.83 ^{##}	17.11-53.07 ^{##}	5.12-58.11 ^{##}	-
	-	84.0-134.71 [#]	-	-
	-	<0.3-7 [*]	-	-
		19.2 (\pm 12.1)-49.9(\pm 22.9)	-	-
Cd	12.69 \pm (9.54) ^{&}	1.65 \pm (0.96) ^{&}	0.33 \pm (0.3) ^{&}	2.56 \pm (1.40) ^{&}
	nd [§]	nd-9.3 [§]	0.28-1.6 [§]	-
	2.0-43.0 ^{&&}	0.05-1.18 ^{&&}	-	-
	<10.00-10.06 ^{##}	1.18-5.58 ^{##}	1.06-1.73 ^{##} -<0.17-7 [*]	-
	-	<0.17-7 [*]	-	-
	-	19.2(\pm 12.1)-49.9(\pm 22.9)	-	-
Zn	1340 \pm (480) ^{&}	42.39 \pm (17.95) ^{&}	0.33 \pm (0.3) ^{&}	53.28 \pm (19.41) ^{&}
	770 \pm (50)-1570 \pm (200) [§]	9-54 [§]	2.1-2.22 [§]	-
	29.0-235.0 ^{&&}	96.2-229.6 ^{&&}	-	-
	-	205.4-287.1 [#]	-	-
	-	127(\pm 20)-135(\pm 18)	-	-

= Mutia et al. (2012); # = Kamau et al. (2007); * = Hakan Tarras-Wahlberg et al. (2002); & = Njogu et al. (2011); § = dissolved values, LNRP (2002); && = dissolved mean range values for rift lakes Naivasha, Nakuru, Baringo, Bogoria and Elementeita, Ochieng et al. (2007); nd = not detected; dwt. and wwt.= dry and wet weight.

2003). Estimated sediment yield for Lake Baringo basin extrapolated from erosion studies of Perkerra catchment is 10.38 million tonnes/year (Onyando, 2003; Onyando et al., 2005). Therefore, as an impurity of phosphate fertilizers, accumulated soil Cd may also be an important source during erosion of agricultural soils into lake basins. Wind induced mixing of the shallow lake surficial sediments could expose them to different redox conditions and cause increased remobilization of sediment bound metals into the water column. In L. Naivasha, significant levels of metals were found associated with river sediments (Hakan et al., 2002). This source could become more important in L. Baringo as compared to L. Naivasha, and may be a reflection of the much higher contents in those sediments. Cd and Pb are elements found in several industrial products, where they may become sources to the whole environment after disposal.

Total metal contents in sediments are normally much higher than dissolved or particulate forms in the water column. However, total Cd contents, bioavailability and mobility within aquatic systems are highly influenced by speciation or physico-chemical forms (Laxen, 1984). As shown above, the lake waters are neutral to alkaline. At neutral to alkaline pH in oxidizing environments, metals often adsorb onto surfaces of insoluble iron hydroxides

and Mn oxides particles, especially when phosphate is present to act as bridging ion (Levinson, 1974). Adsorption onto natural substrates (e.g. hydroxides of Fe and Mn, clays) provide one mechanism whereby the speciation can be significantly altered. Although, Cd and Zn are geochemically associated in most occurrences (Levinson, 1974), Zn mobility may be reduced in alkaline conditions and precipitated in conditions of high abundance of carbonate and phosphates in water. In hydrothermal zones, Cd may become enriched relative to Zn in secondary environments. Cadmium mobility in aquatic environments is enhanced by low pH, low hardness, low suspended matter levels, high redox potential and low salinity (Government of Canada, 1994). The complexation of cadmium with chloride in seawater has been shown to greatly influence its bioavailability and hence toxicity to marine organisms. It is most probable that chloride complexation is responsible for the reduced cadmium accumulation and toxicity in a variety of organisms observed with increasing salinities (IPCS, 1992). In natural water bioavailability of cadmium is reduced through sorption on suspended particles so that biological responses occur at higher cadmium levels (ECB, 2005). Variable concentrations of Cd are found in alkaline lake waters (Table 1), and therefore most of the

high sediment Cd may provide considerable secondary sources, and the contents may pose a high risk if it is bound to the bottom sediments in the more bioavailable fractions.

The water hardness, pH and salinity is known to influence lead speciation and toxicity (UNEP, 2008). Adsorption decreases with water hardness (SRC, 1999). Lake waters are weakly alkaline with relatively low hardness and alkalinity. Increasing alkalinity and salinity due to high evaporation in these lakes may mean more complexed forms of these metals and increased particulate amounts into bottom sediments. Lead sorption to suspended or bed sediments or suspended organic matter typically increases with increasing pH, increasing amounts of iron or manganese; and with the polarity of particulate matter (e.g., clays) (UNEP, 2008). At higher pH, lead precipitates as $Pb(OH)^+$ and $PbHCO_3^+$ into bed sediments (Weber, 1993). According to Tarits et al. (2006), authigenic clay minerals and calcite may be precipitating from the more concentrated fluids in the northern zone of L. Baringo. Changes in water chemistry (e.g., reduced pH or ionic composition) can cause sediment lead to become re-mobilized and potentially bioavailable to aquatic organisms (Weber, 1993). Methylation may result in re-mobilization and reintroduction of lead into the aqueous environment compartment and its subsequent release into the atmosphere (SRC, 1999).

Increasing anthropogenic influence on surficial contaminants is a concern as some of these elements may become geochemically available. Zn and Cd were significantly correlated ($p < 0.05$) with a person correlation coefficient of 0.679 in L. Naivasha sediments. Relatively high organic matter, clay (Kamau et al., 2007) and carbonates were reported in sediments, which promote metal accumulation in lake sediments, although low and insignificant (at $p = 0.01$ significance level) correlations between metals and sediment water content, organic matter and carbonate contents were also observed in L. Baringo. Using a student T-test, the sediment with only Cd and Pb contents in L. Naivasha showed a significant difference ($p < 0.05$) between the two basin sediments. There could be differences in extent of some of the above geochemical barriers mentioned and particulate sources.

Influence of urban areas on metal contents was reported in urban wetland areas soil as compared to rural control sites. Analysis of heavy metals by atomic absorption spectrophotometry (AAS) yielded higher mean total Cd, Pb and Zn concentrations in urban wetland soil than rural arable control sites where values ranged from 1.452 ± 0.415 , 47.54 ± 6.08 and 151.54 ± 9.22 (urban wetland soil) to 0.741 ± 0.447 , 12.47 ± 3.66 , 7.50 ± 1.62 $mgkg^{-1}$, respectively, indicative of relative heavy metal pollution in the suburban drainage (Mbabazi et al., 2010). All the cocoyam and sugarcane samples drawn from the urban wetland drainage system in this study were relatively polluted with cadmium and lead, although the

two crops were found to differ in their abilities of uptake and accumulation of the heavy metal pollutants. Other wetland sediments (Henry and Semili, 2005) along L. Victoria (Mwanza region) recorded similar high Cd contents (0.2 to 3.33 $mgkg^{-1}$).

In this study the overall mean (\pm s.d) contents of Zn, Pb and Cd were 135 ± 18 , 19.2 ± 12.1 , 2.0 ± 0.5 and 127 ± 20 , 49.9 ± 22.9 , 3.5 ± 1.6 $\mu g g^{-1}$ in L. Naivasha and Baringo, respectively. Similar high Cd contents ($1.18 - 5.58$ $\mu g g^{-1}$) were reported by Mutia et al. (2012) in L. Naivasha sediments. The concentration of Pb and Zn fall within the range of values reported for the 5 rift valley lakes (Ochieng et al., 2007) except Cd levels which are above the reported range of nd to 1.78 $\mu g g^{-1}$. In L. Naivasha, similar high Pb and Zn contents were found by Kamau et al. (2007). Cadmium in volcanic and sedimentary rocks ranges from 0.1 to < 1 $\mu g g^{-1}$ (Taylor, 1964, 1966) with a mean value of 0.2 $\mu g g^{-1}$. The ranges of Pb and Zn in the same rock formations are 5 to 20 and 25 – 1000 $\mu g g^{-1}$ (Taylor, 1964, 1966), respectively.

In addition to sediment metal concentrations, several approaches such as sediment bioassays using sensitive organisms and ratio of metal binding by acid volatile sulphides to simultaneously extracted metals (especially Cd, Zn and Pb) in anaerobic conditions, are used to evaluate potential sediment toxicity. According to the interpretive protocol of DiToro et al. (1990) and Allen et al. (1993), a surplus of AVS on a molar basis relative to SEM extracted divalent ions is predictive of metals sulfur binding, corresponding metals insolubility and a lack of toxicity in sediment. However, the converse, a surplus of SEM relative to AVS, cannot be inferred to be unbound and bioavailable and is not necessarily predictive of toxicity (DiToro et al., 1992; Ankley et al., 1993; Fu et al., 1992; Zhuang et al., 1994). Such information is lacking in this study but could provide more insight on bioavailability of these metals where strongly reducing conditions in sediment pore waters prevail.

MOE (1993) and Persuad et al. (1993) provided a set of numerical guidelines for protection of aquatic biota (the no-effect level, NEL, the lowest effect level, LEL and severe effect level, SEL) in marine and freshwater sediments. The NEL indicates a concentration of a chemical in the sediment that does not affect fish or sediment-dwelling organisms. At this level, negligible transfer of chemicals through the food chain and no effect on water quality is expected. Sediment meeting the NEL are considered clean. The lowest effect level (LEL) indicates a level of contamination that can be tolerated by the majority of sediment-dwelling organisms. Sediments meeting the LEL are considered clean to marginally polluted. The severe effect level (SEL) indicates a level of contamination that is expected to be detrimental to the majority of sediment-dwelling organisms. Sediments exceeding the SEL are considered heavily contaminated. When the provincial sediment quality guidelines (PSQGs)

are exceeded, additional biological assessments, such as sediment toxicity tests and other biological effects (e.g. benthic community and biomagnification potential), are evaluated.

When compared with sediment quality standards for freshwaters (MOE, 1993; Persuad et al., 1993), the three elements appear elevated. Traditionally, sediment contamination was determined by assessing the bulk chemical concentrations of individual compounds and often comparing them with background or reference values (Burton, 2002). Although some SQGs have been found to be relatively good predictors of significant site contamination, they also have several limitations (Burton, 2002). Some of these guidelines have been adopted by various regulatory agencies in several countries and are being used as cleanup goals in remediation activities and to identify priority polluted sites (Burton, 2002). Similarly, to identify potential concern of toxic metals in the lake sediments, the results were compared with sediment quality guidelines established by the MacDonald and Ingersoll (2000). These guidelines provide concentrations of metals that have no effect on the majority of sediment-dwelling organisms, designated as "threshold effect concentration" (TEC), and concentrations that indicate polluted sediment and are likely to affect organism health, designated as "probable effect concentration" (PEC). The midpoint effect concentration (MEC) is a concentration midway between the TEC and PEC concentrations. Above sediment metal contents were all below PEC guideline values.

Conclusions

The sediments deposited in the two lakes are undergoing contamination from diverse sources, as indicated by the relatively high Cd, Zn and Pb levels. The sediment Cd and Pb concentrations showed significant differences between the two basins. Using freshwater sediments interim sediment quality guidelines (ISQG) values, all the three metal mean contents in L. Baringo were above these values. Average levels of Zn and Cd were also above the ISQG values. However, all the mean concentrations of Zn, Cd and Pb in surficial sediments were found to be below the probable effect level, and above normal concentrations ranges found in sedimentary and igneous formations. Concentrations of Pb and Zn found are comparable to other relatively large basins, with extensive drainage basins and urban influences. Cadmium sediment levels are a concern, as the evaluation shows increasing accumulation in sediments, with possible future exposure risks to aquatic organisms. Surface runoff, waste discharges and particulate deposition is thought to be significant in these basins, and to understand overall impacts from anthropogenic deposition, it is important that background metal levels

are determined together with supporting chemical partitioning to reveal more information on available metal contents.

Scarce blue water resources (lakes, rivers and groundwater aquifers) are sometimes at the centre of conflicting demands and are impacted mostly by increasing demands for agricultural production, industrial developments and lack of suitable waste management technologies, besides the natural influences in the long-term. To ensure its protection and safe use, to maintain ecosystems, biodiversity fisheries and livelihoods, we must continue to monitor the more vulnerable freshwaters using all suitable indicators.

Conflict of interest

The author(s) did not declare any conflict of interest.

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