# Status of Trace metals’ Concentrations in Lake Baringos’ Catchment: A Review

## ABSTRACT

Lake Baringo is one of the two shallow freshwater rift valley lakes characterized by a topographically closed basin, alkaline waters, turbidity, high evaporation rates and seasonal water level changes. The lake water is an important water source, and it sustains a small fishery and high biodiversity. Located in a semi-arid area, in the floor of the rift valley and at a relatively low altitude, it is greatly influenced by materials derived from the steep gradient landscape catchment, anthropogenic activities and formations. Cadmium, lead, arsenic inorganic species, and mercury are heavy metals which are considered the most toxic to humans, animals and the environment, amongst the non-essential trace elements. Today, in the developing countries like Kenya, concerns regarding metals are increasing even in remote areas, due to increased generation of electronic wastes, uncontrolled solid waste disposal and untreated wastewater, abandoned and active mining operations, atmospheric deposits, mineral weathering processes, and leaching of terrestrially applied agrochemicals. Therefore, potential sources, occurrences and accumulation in the aquatic environmental samples are of concerns worldwide due to their known toxicities. Lake sediments and other surface waters are often important sources of trace metals exposure to fish and other organisms. Trace metals such as Cd, As, Cu, Fe, Hg, Cr, Mn, Ni, Zn, Sn, and Pb are very important contaminants known to cause severe toxicity to aquatic organisms and fish species. Through drinking water, consumption of aquatic species, humans can accumulate elevated levels, and hence the stringent regulation of toxic elements in water food and other products. Although varying and low levels of trace metals are often reported for most natural lake waters, and appreciably higher amounts in sediments, the bioavailability is what determines actual toxic effects. Therefore, being a Ramsar site, there is need to develop information and database for monitoring water quality changes and understanding anthropogenic impacts on the river and lake ecosystem. This report reviews information on the status of trace elements concentrations in the different lake compartments from previous studies, and the potential implications on water quality, ecosystem health and sustainability.

***Keywords:*** *Lake Baringo; Aquatic ecosystem; Trace elements; Metals; Sediments; Water quality;fish species*

## 1.INTRODUCTION

Lake Baringo is a freshwater lake, among the several great East African rift valley lakes, which are located in the floor of the eastern arm of the rift valley which extends northwards from Lake Natron to L. Turkana, in the southern and northern national boundaries of Kenya respectively. The lake lies at 975 meters (3,200 feet) above sea level. It is a relatively shallow and topographically closed basin which deepens towards the north. Lake Baringo in Kenya (East Africa) is a Ramsar site, famous for its high bird diversity, hippopotamus and crocodile populations. The lake once supported a substantial fishery, and it also represents a precious source of freshwater in a semi arid area (Wahlberg et al. 2003). Small-scale fisheries contribute to food security and the eradication of poverty by providing food, income and employment to millions of people (FAO 2016). The fishery of Lake Baringo is currently based on four species including *Orecochromis niloticus baringoensis, Barbus gregori, B. lineomaculatus, Clarias gariepinus*and*Protopterus aethiopicus* (Nyamweya 2011; Aloo 2006; Mageria and Kibwage

2009).

Water resources management has often focused on satisfying increasing demands for water, without adequately accounting for the need to protect water quality and preserve ecosystems and biodiversity. Today, there is increased awareness on anthropogenic impacts and pollution threats on the surface water quality of natural lakes, rivers and underground waters sources, with many national standards and guidelines on solid waste management, air pollution, wastewater and effluent discharges, as tools for sound water resources management. Certain metals and metalloids are essential for plant growth and for animal and human health. With respect to plants, these are referred to as micronutrients and include B, Cu, Fe, Zn, Mn, and Mo. In addition, As, Co, Cr, Ni, Se, Sn, and V are essential in animal nutrition. Micronutrients are also referred to as trace elements since they are required in only small quantities, unlike major nutrients such as N, P, and K. In excess, trace elements can be toxic to plants, microbes, animals, and humans. Problems also arise when there is a deficiency in essential elements. Important trace elements in the environment are As, Ag, B, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn. Trace elements in natural media are present at concentrations of less than0.1%. In biochemical and bio-medical research, trace element concentrations in plant and animal tissues are normally less than 0.01%. In food nutrition, a trace element is one that occurs at concentrations less than 0.002% (Adriano 2001).

Thirteen trace metals and metalloids are considered priority pollutants (Table 1) and they canbe derived from both natural (geogenic) and anthropogenic sources (Adriano 2005, 2001; Sparks 2005). Natural sources include parent rocks and metallic minerals (metalliferous ores). Anthropogenic sources include agriculture (fertilizers, animal manures, pesticides), metallurgy (mining, smelting, metal finishing), energy production (leaded gasoline, battery manufacture, power plants), microelectronics, and sewage sludge and scrap disposal (Adriano 2001). Atmospheric deposition is a major mechanism for metal input to plants and soils. This is particularly true in forest ecosystems, where metal contamination of soils is almost totally due to atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases (Adriano 2001; Adriano et al. 2005). In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals. These contaminants can then impact freshwater and groundwater systems. Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano 2001; Adriano et al. 2005).

Micro contaminants (essential and non-essential elements; persistent organic pollutants and microbiological contaminants) are of great concerns to the public health sector as they have known toxic effects in exposed aquatic organisms and humans, and result in a lowered water quality. In the environment, natural concentrations can be magnified through accumulation in soils, sediments and biota, leading to levels above allowed thresholds for different environmental compartments. Total mercury, methyl mercury, cadmium, lead, arsenic, PCB, DDT and metabolites, organochlorines (e.g dieldrin) and dioxins are among the most regulated industrial

**Table 1.** Inputs of trace metals from various anthropogenicsources (Adriano 2001).

| Element | Natural source or metallicmineral | Anthropogenic sources | Common forms in wastes |
|---|---|---|---|
| Ag | Freemeat (Ag)<br>chlorargyrite(AgCl)<br>acanthite($Ag_2S$),<br>copper, lead, zinc | Mining, photographic industry | Agmetal, Ag–CN complexes; Aghalides; Agthiosulfates |
| As | Metal arsenidesand arsenates, sulfide ores (arsenopyrite), arsenolite($As_2O_3$), gases,geothermal springs | Pyrometallurgical industry,spoil heaps and tailings, smelting, wood preserving, volcanic fossil fuel combustion, poultrymanure,pesticides, landfills | As oxides (oxyanions)<br>organo-metallic forms,<br>$H_2AsO_3CH_3$ (methylarsinicacid), $(CH_3)_2$-$AsO_2H$ (dimethylarsinicacid)<br>(methylarsinicacid), $(CH_3)_2$-$AsO_2H$ (dimethylarsinicacid |
| Be | Beryl (Be3Al2Si6O18),<br>phenakite(Be2SiO4) | Nuclear industry,electronic industry | Be alloys,Bemetal,<br>$Be(OH)_2$ |
| Cd | Zinccarbonate and sulfide ores, copper carbonate and sulfide | Miningand smelting, metal finishing, plastic industry, microlectronics, batterymanufacture, landfillsand refusecomplexes, disposal, phosphate fertilizer, sewagesludge metal scrapheaps | $Cd^{2+}$ions, Cd halidesand oxides,<br>Cd–CN complexes; $Cd(OH)_2$, sludge |
| Cr | Chromite($FeCr_2O_4$),<br>eskolaite($Cr_2O_3$) | Metal finishing, plasticindustry, wood treatment refineries, pyrometallurgical | Cr metal, Cr oxides (oxyanions), $Cr^{3+}$ |

| | | | |
|---|---|---|---|
| | | industry, landfills, scrapheaps | complexes with organic/inorganic ligands |
| Cu | Nativemetal (Cu),<br>chalcocite(Cu2S),<br>chalcopyrite(CuFeS2), | Miningand smelting, metal finishing, microelectronics,wood treatment, refuse disposal and landfills, pyrometallurgical industry, swinemanure,pesticides scrapheaps, mine drainage | Cu metal, Cu oxides<br>Cu humic complexes,<br>alloys, Cu ions |
| Hg | Nativemetal (Hg),<br>cinnabar(HgS),<br>degassed from Earth's crust and oceans. | Miningand smelting,electrolysisindustry, plastic industry, refusedisposal/landfills, paper/pulp industry,fungicides | Organo-Hg complexes,<br>Hghalides and oxides,<br>$Hg^{2+}$, $(Hg2)^{2+}$, $Hg^{0}$ |
| Ni | Ferromagnesian minerals,<br>ferrous sulfideores,<br>pentlandite | Iron and steel industry,miningand smelting, metal finishing, microelectronics, batterymanufacture | Ni metal, Ni2+ions,<br>Ni amines, alloys |
| Pb | Galena(PbS) | Miningand smelting, iron and steel industry, refineries, paintindustry, automobile exhaust, plumbing, battery manufacture, sewagesludge,refuse disposal/landfills, pesticides, scrapheaps | Pb metal, Pb oxides and carbonates<br>Pb-metal–oxyanioncomplexes |
| Sb | Stibnite(Sb2S3), geothermal springs. | Microelectronics, pyrometallurgical | $Sb^{3+}$ions, Sb oxides andhalides |
| Se | Free element(Se), ferroselite FeSe2), uranium deposits, black shales, chalcopyrite- | Smelting, fossil fuel combustion, irrigation waters | Seoxides (oxyanions),<br>Se-organiccomplexes |

| | | | |
|---|---|---|---|
| | pentlandite-pyrrhotite deposits | | |
| Tl | Copper, lead, silverresidues | Pyrometallurgical industry<br>microelectronics,cementindustry | Tl halides<br>Tl–CN complexes |
| Zn | Spharelite(ZnS)<br>willemite (Zn2SiO4),<br>smithsonite(ZnCO3) | microelectronics,cementindustry<br>textile, microelectronics, refusedisposal and landfills, pyrometallurgical industry, sewagesludge, pesticides, scrapheaps | Zn metal,Zn$^{2+}$ions, Zn oxides, carbonates and alloys. |

*Source: Adriano(2001);mineral nomenclature after Mandarino andBack(2004)* and environmental contaminants, with tolerance and critical limits in fish and fish products set to protect consumers (EC 2001; FDA, 1998).

Increasing amounts of chemicals may be found in predatory species as a result of biomagnification, which is the concentration of the chemicals in the higher levels of the food chain. Or, they may be there as a result of bioaccumulation, when increasing concentrations of chemicals in the body tissues accumulated over the life span of the individual (Huss et al. 2003).

There is increasing awareness and concern over the environmental and biological effects of elevated concentrations of toxic and bioavailable heavy metals and residues of persistent organic substances in most natural aquatic ecosystems. Even in relatively remote lake ecosystems located in hot and arid climates, such as L. Baringo, the inputs from two permanent rivers traversing rich upper agricultural areas and key towns, and lower steep areas under sparsely vegetation cover, with highly degraded soils are thought to contribute significant amounts of materials into the lake. In most countries, soils have been used as a repository for all types of industrial and chemical solid wastes and obsolete pesticides disposal. Also increasing use of banned and persistent organic chemicals within the lake catchment area causes increased uptake and accumulation in aquatic organisms in rivers and lakes. Such data on accumulated organic residues concentrations in sediments, biota and fauna, surface and underground waters, is still inadequate due to lack of continuous monitoring in these ecosystems. Also, concerns about factors influencing the metal aqueous concentrations, speciation and toxicity, bioavailability have not been well addressed in some natural waters. The area is known for its huge fluoride deposits and other minerals. The extent of the metals elements modification by anthropogenic activities has been explored in many studies. In volcanic formations and areas known to contain geothermal energy sources, like Lakes Baringo and Bogoria, metal sulphides can released from geothermal fluids, although such assessmentdata is only for geothermal development and consequences in adjoining aquatic ecosystems need to be prioritized. Usage of Hg in gold amalgamation and recovery techniques is also of concerns in increasing exposure hazards to artisanal gold miners, immediate ecosystems and atmospheric emissions. Anthropogenic transport and deposition are important processes in the global cycling of trace metals. Although the atmospheric flux of tracemetals is a major component of both marine and terrestrial environments, very studies report on these sources around lake ecosystems. Elsewhere and in other natural waters (Poste et al. 2015; Orata et al. 2008; Oluoch-Otiego, et al. 2016; Omwoma et al. 2015; Nnamuyomba, 2014; Orata et al. 2008; Igwegbe et al. 2014), evidence of low levels of priority metal (cadmium, mercury, Methyl Hg, lead, Arsenic) and organic residues (Dichlorodiphenyltrichloroethane and metabolites; polychlorinated biphenyls, dioxins; organochlorines; organophosphates) accumulated along aquatic food chains exists but only few data is available for L. Baringo (Campbell et al. 2003) and neighboring natural aquatic ecosystems (Mungachia et al. 1992; Muohi 2007; Jirsa et al. 2013; Bonzongo et al. 1996; Bettinetti et al. 2011; Lincer et al. 1981; Ogendi et al. 2014) and fish culture systems (Omwenga et al. 2016). Lindane was found to have the highest frequency of occurrence amongst other organochlorines studied in fish from pond culture systems (Omwenga et al. 2016) with a mean concentration of 0.723±0.011 µg/kg (muscle tissue); 0.013±0.033 µg/kg (liver tissue); 0.169±0.45 µg/kg (gonad tissue); 0.022±0.046 µg/kg (brain tissue) in Machakos county. Lesser flamingos (*Phoeniconaias minor* Geoffrey) which are associated with nearby alkaline saline rift lakes are specialized consumers of *Arthrospira fusiformis* (Voronichin) Komarek & Lund (formerly called *Spirulina platensis* (Voronichin), a cyanobacteria (Codd et al. 2003; Krienitz et al. 2003). Being the main diet of

Lesser flamingos (Owino et al. 2001) these birds tend to migrate in response to changes in Arthrospira biomass in Lakes Nakuru and Bogoria (Nasirwa 2000), and nutritional composition and quality of phytoplankton community influence their temporal and spatial abundance (Kaggwa and Gruber 2013).

Using biological indicators such as plants for monitoring both air and water pollution has also been recognized and used to a limited extent over the years. Aquatic macrophytes showed higher concentration factors of accumulated Cd, Zn, Pb, and Cu (Fayed et al., 1985) than sediments from the same site. Mosses and lichens strongly sorb metals ions from the air and water and are useful in detecting atmospheric and aquatic lead and other metal contamination (Goodman et al. 1971; MacLean and Jones 1975; Tyler 1976). Leaves and twigs of woody plants have also been used to indicate atmospheric pollution (Smith 1972). On the other hand, responses of macro-invertebrates assemblages (Kobingi et al. 2009), as bioindicators of biological integrity of effects of different land uses, especially urbanization, in inflowing rivers and streams provide valuable information on organic pollution and other impacts. Currently, urban domestic and industrial wastewater effluents are sources of concern of trace organic and inorganic residues (Kimosop et al. 2016; Chirikona et al. 2015) some of which are toxic, persistent, carcinogens, and endocrine disruptors, which are included in water quality assessments. Their discharge into the environment results from the ubiquity of use in medical, veterinary, and agricultural practices.  Some of the effects of antibiotics include development of antibiotic-resistant bacteria, making it difficult to treat diseases, variation in natural microbial communities, and enzyme activities. In the interests of safe and clean water sources, safe fish for direct human consumption and for non-food products, stringent hygiene measures have been adopted at national and international trade levels.

Therefore, the determination of metals and organic residues distribution and monitoring in lake ecosystem and other environmental samples is valuable because of the known and documented toxicity effects. Currently economically exploited fish species from L. Baringo includes:-*Clarias gariepinus, Oreochromis niloticus baringoensis, Protopterus aethiopicus, Labeocylindricus,* and *Barbus intermedius lineomaculatus* (Kembenya et al. 2014; Omondi et al. 2013). Recent studies link the reducing catches of the endemic *O. niloticus* with increasing turbidity of the lake over time, although spatially, environmental variables exhibited a small difference which was attributed to the lakes small size and shallowness, and also the daily mixing of the lake water by wind action (Omondi et al. 2014). Aquatic species serve as good indicators of metal contamination. Some of the priority pollutants that have been found in variable levels in the main compartments of Lake Baringo ecosystem includes:- Cd, Cr, Al, Fe, Mn, Pb, F, Se, Cu, and organic pesticide residues. Therefore, the primary objective of this report was to review data on distribution and any trends of heavy metals in L. Baringo ecosystem.

## 2. LOCATION AND GEOLOGICAL SETTING OF LAKE BARINGO BASIN

Lake Baringo (Fig. 1), a freshwater lake in the eastern arm of the great rift valley in Kenya, and lies in the rift floor, at an altitude of about 935 meters above sea level, between latitude (00˚30’N and 00˚45’E) and longitude (36˚00’E and 36˚10’E). The Lake is a wetland of international importance, and wasdesignated a Ramsar Wetland in 10th Jan 2002 (Ramsar Wetland).

The lake is a topographically closed basin. Recent hydrogeological evidence confirms the original assumption (Beadle 1932) that some lake water is lost by underground seepage through the fractured lake floor (Onyando et al. 2005). Dunkley et al. (1993) estimated that this outflow could exceed $10^8$ $m^3$/year. The rift geological formations have been associated with high fluoride contents in underground water sources (Olaka et al. 2016), which compromises the desired natural water quality for human consumption.

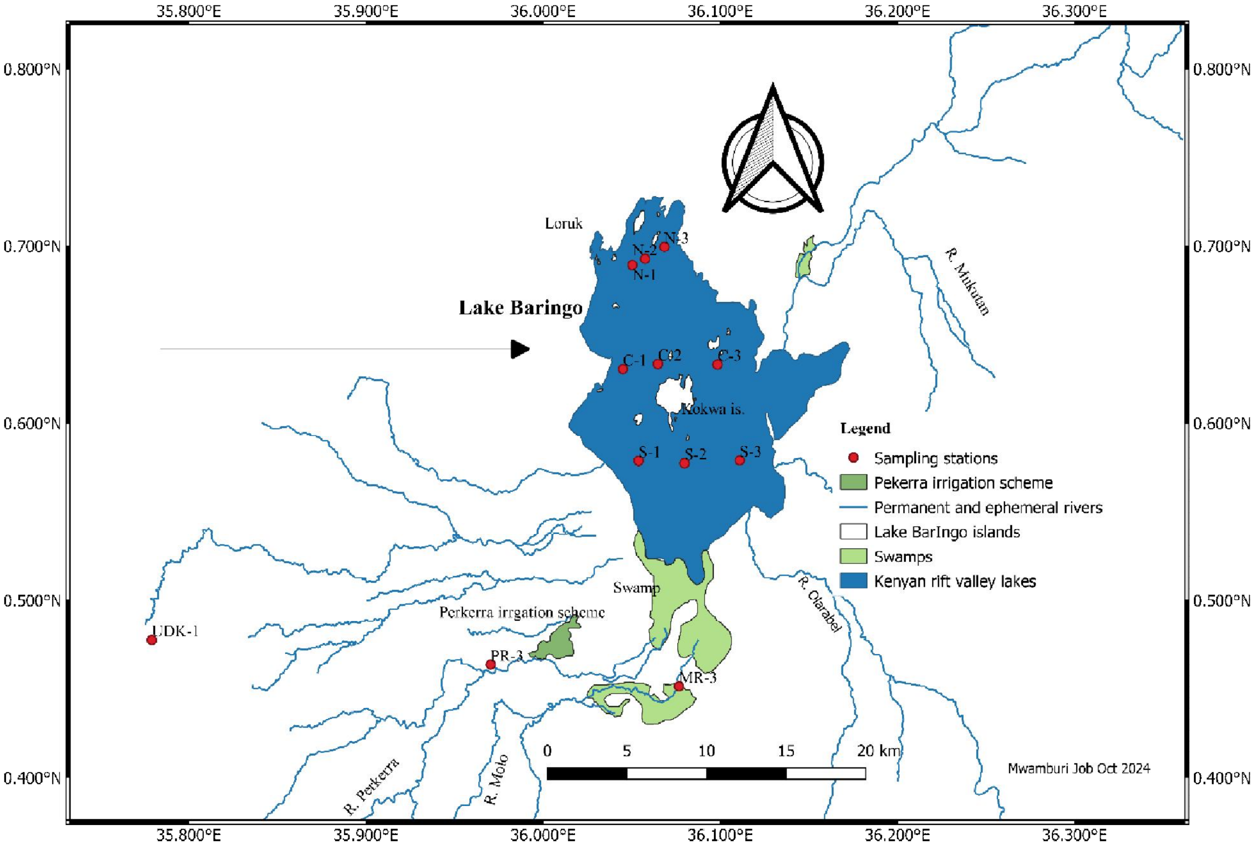

**Fig. 1**. Map of Lake Baringo showing the catchment area and the river drainage system.

The catchment area is 6820 Km2. Lake Baringo has five islands, the biggest being the Volcanic Kokwa. The Island is a remnant of a small volcanothat belongs petrogenetically to the Korosi volcano. This erupted during the Middle Pleistocene, approximately 2.6 million years ago (Cl’ement et al. 2003). On Kokwa island alkaline hot springs discharge into the lake (Beadle1932). The lake has a surface area of between 130 $Km^2$and 160 $Km^2$, with a variable waterdepth and physic-chemical characteristics, reflecting the high dry and wet seasonal influences in the semi arid climatic zone. Paleolimnological studies (Kiage and Liu 2009; Renaut et al. 2000) have also been used to generate paleogeographic information and records of the past climatic conditions and variability in Lake Baringo. the stratigraphic record from Lake Baringo reveals tow abrupt dry episodes at ca. AD 1650 and AD 1720 in East Africa led to drying up of the lake.

Soils are clay and clay loams and the risk of soil erosion is high because of the soil properties (clay fills pores or seals the surface giving low infiltration capacity). Forty-six percent of the land in the district is too steep or too dry for agriculture and pastoralism is the main source of family income (Hickley et al. 2004). High water turbidity is also cited as a major contributorto reduced water quality. 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). Late Holocene to modern sedimentation in Lake Baringo is dominated by fine grained silicicclastics (Renaut et al. 2000). Most of the lake floor is covered by detrital muds and feldspathic silts that reflect the very high soil erosion rates in the catchment (Snelder and Bryan 1995; OostwoudWijdenes and Bryan 2001; Aloo 2002). The two permanent rivers dissect the highland agricultural areas and drier valleys before entry into the lake on the southern side, north of Loboi swamp and the hypersaline L. Bogoria, with known hotsprings. In their upper reaches, these rivers drain thick series of basalts, phonolites and trachytes of Mio-pliocene age, while downstream they flow across Pleistocene trachyphonolites, pyroclastic deposits, and siliciclastic fluvial sediments. The eastern part of the Baringo watershed, drained by the rivers Mukutan and Ol Arabel , is formed by a succession of basalts and phonolites of Miocene age, several hundreds of metresthich, which form the Laikipia fault escarpment. 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).

Shallow lakes (< 5m deep) are characterized by varied environmental constraints (Talling2001). Water levels in L. Baringo fluctuates with time and responds to alternating wet and dry periods. This is reflected in changes in water characteristics (Ouma and Mwamburi 2014; Omondi et al. 2014; Oduor et al. 2003; Schagerl and Oduor 2003) as rains normally lead to increased water inflows and lake surface area, sometimes accompanied by lakeshore flooding. The most recent rise in water levels was reported in 2011. The impact of the flooding in L. Baringo has seen the area under water rise from 143,6 Km$^2$ in January 2010 to a high of 231.6Km$^2$ in September 2013, an increase of 88 Km$^2$ (61.3% increase by area). In December 2010, the lake level had risen by 28.8 Km$^2$ (Onywere et al., 2013). The mean depth of L. Baringo is reported to have been 5.6m in the 1960s (Ssentongo 1995), over 8m in the late 1970s (Meyerhoff unpubl.), decreasing to just below 3m in 1994, but reaching 4.5m again in 1998 following El Nino rains. At the time of 2003 bathymetric survey, the mean depth was 2.65 m (Hickley et al.2004). Between April 2008 and March 2013, Omondi et al. 2014 reported a mean depth of 3m with the deepest point being 7m at high water levels. The mean (±SE) lake water depth ranged from 5.31±0.13 m to 6.35±0.12 m, (Omondi et al. 2014), which is close to the maximum depth of 8m reported by Schulter (1993) and Odour (2000). The annual rainfall is between 500 mm and1000 mm in the catchment and is highly variable (Odour 2000). Lake Baringo experiences very high annual evaporation rates of 1650 to 2300 mm (Odada et al. 2006) and its survival depends on theinflows from rivers originating from the hilly basin where rainfall varies from 1100 to2700 mm. The lake is fed by several ephemeral rivers including Ol Arabel, Mukutan, Endau, andChemoron, while Molo and Perkerra are permananet rivers.

The freshwater from the lake and rivers is used for irrigation and domestic uses. Dams and irrigation infrastructure support these uses along the river drainage basin and at lower edges of the lake respectively. However, it is not well established how changes in flow impacts on the riverine ecology, especially fish species. The type of local geology, topography and meteorology (Onyando et al. 2005) coupled with anthropogenic activities; especially overgrazing and deforestation expose the Lake Baringo catchment to high erosion. According to Lwenya and Yongo (2010), livelihoods of communities around the lake are centered on livestock keeping, cultivation and charcoal burning, factors which enhance land and water degradation. Sedimentation and turbidity have been found to be significant contributors to declining population of aquatic organisms (Henley et al. 2000). The resulting sediments and suspended solids inflow influence the lakes's depth and substratum. The muddy substratum in the south of the lake is not suitable for benthopelagic potamodramous*Labeocylindricus* that prefers rocky habitats (Nyamweya et al. 2012).

## 3. MATERIALS AND METHODS USED

The review methodology used an approach for systematic literature review to search for documented information in scientific journals using the common search engines (Science direct, google scholar and scopusetc) and those used for analysis were evaluated according to table 2.

**Table 2.** A table showinghow theinternet searched and retained publication information was extracted for analysis.

| No. | Criteria | Categories | Justification |
|---|---|---|---|
| 1. | Publication year | Between 1980-2021 | Studiesbefore1980notused.Studiesbeforeand aftergazettement as aRamsarwetland |
| 2. | Name of publication | Scientific journal articles /Technical reports | Distribution ofthe work |
| 3. | Location of studyarea | Watershed/basin name | LocationofsystemwithinL.Baringo basin/watershed |
| 4. | Types of data sources | Primarydata | Field orsurveydata |
| | | Mixed or otherdata | Otherdatareadilyavailableinexternaldatasets and not verified in thefield |
| 5. | Method | Distribution | Spatial and temporal patterns |
| | | Mapping | Visualization offield data |
| | | Models | Predictive analyses |
| 6. | Scale ofstudy | Patchy | 10 - $10^2$Km$^2$ |
| | | Local | $10^2$-$10^3$Km$^2$ |
| | | Regional | $10^3$-$10^5$Km$^2$ |
| | | National | $10^6$Km$^2$ |
| | | Global | . >$10^6$Km$^2$ |
| 7. | Modeof assessment | Qualification | Reportingon the status andchanges on the environmental/chemical qualityandecological health. |
| | | Quantification | Reportingconcentration levels in each specific media/species in universallyaccepted / conventional standard |
| | | Mapping | Studies with spatial visualization offield data and futureprediction |
| | | Modelling | |
| | | Combined | Used morethan oneof the above |
| 8. | Types of ecosystem services | Cultural ecosystem services | Both tangible and intangible benefits derived from the ecosystem (recreation; aesthetics; |
| | | Provisioning ecosystem | Products obtained from ecosystem(e.gwater, wetland |
| | | Regulating ecosystem services | Silt &sediment trapping;Pollutant control; Flood control;Climatemitigation/rainfall; Hydrological recharge/discharge |

| | | | |
|---|---|---|---|
| | | Supporting ecosystem | Basicecosystem servicesthat maintain the generation ofallotherecosystem |

| | | | |
|---|---|---|---|
| | | | (nutrientcycling; soil formation buffering; pollination e.t.c) |
| 9. | Number of elements /or groupof elements assessed | Essential elements | Climatic and anthropogenic impacts; Water, air, soiland sediment qualityregulation; Waste management ;water purification; health risks |
| | | Non-essential elements | |
| | | Radioactive elements | |
| | | Major elements | |
| 10. | Expansion of sitespecific knowledge | Studies | Cleaner technologies /Environmental friendly waste treatment, material recyclingoptions at source; Siterehabilitation and future management / alternatives cost effective |
| 11. | Methodological development | To develop new methods or check | Advanced morereliableand sensitive environmentallyand userfriendly, simple, and cost effectivemeasurement |
| 12. | Purposeof publication | Management option | To recommend management options to sustain ecosystem services |
| | | Policysupport | Discussed futurepolicyissues |
| 13 | Difficulties mentioned | Methodological | Uncertainties on theresultdueto application of unclear / orless developed method.Lack of implementingrobust QC/QAmeasures; Sample |
| | | Other | Uncertainties linked withlack of conceptual clarity |
| | | Data | Primaryand secondarydata sourcequalityand scarcitythat challenges |

Thesampling andanalysismethodsusedforthedeterminationofmetalsfromdifferentstudies andenvironmentalsamplesare shownintable3.Differentanalyticalprocedures,techniquesand analysisequipmentswereemployedingeneratingtheconcentrationlevels,butinmostcases AASwas the main analytical equipment.

Resultsdiscussedinthis reportwereobtainedfromseveralsurveysconductedbetween2007and 2021inL.Baringo basin.Watersampleswerecollectedfromthesurfaceandbottomusing apre-cleaned watersampler.Bottomlakesediments were retrievedusing apre-cleanedEkmangrab sampler.

**Table 3.** Procedures used in digestion and extraction oftrace elements from differentenvironmental samples.

| **Elements** | **Equipment** | **Sources** |
|---|---|---|
| **Surfacewater** | | |
| 1.Surfacewater (Trace elements (Cr, Cd,Hg,Zn,Ni, Pb, As, Cu). | | -Yanget al. 2017. |
| 2.Filtered surfacewater,acidified, filtered;50mlevaporated to 20ml; Traceelements (Cu, Fe,Zn, Cd, Pb). | (FAAS). | Nyingi et al. 2016. |
| 3. Filtered surfacewater(0.45µm). | (AAS). | Mbuthia et al. 2014. |
| 4. Filtered surfacewater(0.2 µm filters); Major ions &traceelements (K, Ca, Mg, Na, Al,Fe, Sr, Ba-ICP-AES); (Cd, Cu, Cr, Al, Pb, Zn). | (Perkin ElmerElan 5000ICP-MS) | Tarits et al. 2006. |
| 5. Filtered surfacewater500ml(0.45µm Milliporefilters); Digestedusing5ml11.1MHNO3; 10ml 16.3MHCl.; Trace elements (Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb,Sn, Zn) | .(FAAS-Perkin Elmer) | Ochienget al. 2007. |
| 6. Surfacewater(Traceelements Cd, Cu, Hg) | | ChepkorirK. J. 2015. |
| **Surfacelakesediments** | | |
| 1. Surfacesediments Trace elements (Cr, Cd,Hg,Zn,Ni, Pb, As, Cu) | | Yanget al. 2017. |
| 2. Surfacesediments (Traceelements Cd, Cu, Hg) | | ChepkorirK. J. 2015 |
| 3. Digested with using5ml11.1MHNO$_3$;at 95Cfor1hr; centrifuged; supernatant analysedfor trace elements (Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Zn); | (FAAS-Perkin Elmer) | Ochienget al. 2007 |
| **Samples of fishtissues** | | |
| 1. Fish tissuedigested in10mlmixtureHNO andHClO$_4$, ratio 3:1v/v); Trace elements (Cu,Fe,Zn, Cd, Pb) | (FAAS) | Nyingi et al. 2016. |
| 2. Fish tissuedigested usingHNO3; HFmixture(THg, Cu, Cd,Zn); | (AAS) | Mbuthia et al. 2014 |
| 3. Fish muscle tissue; AFS&purgeprocedure; | (Total THg) | Campbell et al. 2003. |

## 4. RESULTS AND DISCUSSION

### METALS IN LAKE SEDIMENTS AND SOILS

There are few documented studies on soil metal concentrations, but with an increase in studies on the metal contents within the freshwater lakes (Lakes Baringo and Naivasha) and other rift valley saline alkaline lakes ecosystem.

### TRACE ELEMENTS IN LAKE WATER

The lake water is characterized by high pH and conductivity. The distribution of trace elements in lake water, for both dissolved and total concentrations shows wide range for most elements. Aqueous contamination represents a crucial environmental issue, especially when elements are in high concentration in the bioavailable forms. WHO health based limit guideline values for drinking water are shown in table for some of the regulated elements, and reference made on the NEMA guideline values (NEMA 2006).

Toxic inorganic elements concentrations (Hg, As, Be, Ba, Pb, Ni, Sn, Cu, Cr, Cd, Ag, Se) in water are more prioritized due to the potential long term human health hazards and when in excessive levels tend to interfere with many beneficial uses of the water, while excess concentrations of some trace metals (Al, Fe, Mn, Zn) are regulated in drinking water due to aesthetic properties (FAO). The concentration of Zn in tap water can be considerably higher than that in surface water owing to the leaching action of Zn from galvanized pipes, brass and other Zn alloys. Zinc imparts to water an undesirable astringent taste and in concentrations in excess of 5ppm. The water may appear opalescent and develop a greasy film on boiling (FAO). Macrophytes such as water hyacinth are considered good accumulators of metals, and useful in phytoremediation of wastewaters containing high levels of metals. Such information on lake macrophytes is lacking, but could also be prioritized in future studies.

### FLOURIDE ION CONCENTRATIONS IN THE LAKE BARINGO BASIN

Flouride mineral deposits occur in the Kenyan rift region, and presence of high F in rocks are often the source of high F contents in underground and surface water. Lake Baringo, being a water scarce area, the surface water of rivers, lake, together with other underground water sources are the common sources of F exposure to the surrounding communities. Fish are also exposed to F from the habitat. Although there is no much information on the fish F contents in L. Baringo and other lakes, Gikunju et al., 1992 and Gikunju 1992 reported on F levels (ranging from 1.3 mgKg$^{-1}$ to 2.0 mgKg$^{-1}$ wet weight) in fillets of tilapiine fish and *Micropterus salmoides* from Lake Naivasha. According to a study (Ganta et al., 2015), in a high fluoridated belt area, the amount of F present in the fishes is directly related to the severity of flourosis amongst fish consuming population suggesting fishes as contributing factor to flourosis depending upon dietary consumption. The mean F content of various river and sea fishes (bone, muscle and skin) ranged from 0.22 ppm to 151 ppm (river fishes) and 0.83ppm to 4.22ppm (sea water fishes). F showed more affinity towards the hard calcified tissues resulting in higher concentrations of F in the bones. In the Naivasha basin underground waters were found to contain highly variable F concentrations (0.22 mgL$^{-1}$ to 74.98 mgL$^{-1}$), an indication of geochemical F enrichment in regional groundwaters (Olaka et al., 2016). This implies that the total contribution in human F intakes can vary greatly when other sources of intake such as food are taken into account. In general, long-term use of drinking water with F significantly above 1.5 mgL$^{-1}$ can have serious effects on health. Dental and skeletal flourosis are associated with exposure to high F concentrations in drinking water (Fawell et al., 2006; Scher 2011). This observation is evident elsewhere, within the East African rift valley. In most areas of the Ethiopian rift valley, water is epidemiologically the most important source of F (75% - 90% of the daily intake) flourosis not only affects the people's health, but also has serious economic and social consequences (Tekle-Haimanot et al., 2006; Tekle-Haimanot and Haile 2014).

## TRACE METALS IN SUSPENDED AND BOTTOM SEDIMENTS

Accumulation and variations of metals in sediments shows. Most metal concentrations are below the freshwater sediment levels of potential biological impacts to aquatic organisms based on the consensus based SGQ values, although Pb, Cd and Ni exceeded the lower limit which recommends more site investigations.

Consensus based metal sediment quality guideline (SQG) values are often used to indicate probable sediment metal negative effects on the aquatic environment. Using existing SQG from other areas (Table 5), Cd, Pb, Zn and Ni levels were all above the TEC values but below the PEL, indicating that there are no signs of adverse effects to aquatic organisms.

## TRACE ELEMENTS IN FISH SPECIES

Very few studies report on trace elements levels in lake flora and fauna. The concentration levels of Cd and Hg found in fish tissues (Table 6) were below critical limits for fish and fishery products. Lead levels were above these limits (0.2 to 1.7 ppm). There is no data on MeHg concentrations in the lake compartments. Mercury is known to be transformed to other methyl forms within the aquatic environment, but only total concentrations values are available. Although the fraction of methylmercury in sediments is small, the majority of Hg that accumulates in biota is in the methylated form (Langston 1982; Bernhard and George 1986) which is also the most toxic form.

**Table 4.**Metal (±SD) concentrations in water(µg/l)
**SurfacewaterofL. Baringo**(Total &dissolved concentration)

| | | | | |
|---|---|---|---|---|
| Cd | 2.0±0.01-5.0±0.60$^{\&\&}$ | $^{k}$0.0216±0.00-0.0327±0.0242$^{k}$ | 0.01±0.001-0.19±0.003$^{y}$ | nd-0.07$^{v}$ |
| Cu | 5.0±0.11-20.2±1.20$^{\&\&}$ | 0.0157±0.00-0.0313±0.0213$^{k}$ | 0.02±0.01-0.15±0.02$^{y}$ | 3.09-5.89$^{v}$ |
| Pb | nd-65.1±5.44$^{\&\&}$ | nd-0.31±0.04$^{y}$ | 0.16-0.48$^{v}$ | |
| Zn | 45.0±4.44-105.0±8.94$^{\&\&}$ | -0.01±0.002-0.31±0.02$^{y}$ | 1.98-94.31$^{v}$ | |
| Hg | - | 0.0019±0.0011-0.0031±0.00153$^{k}$ | | |
| Cr | nd-188.0±10.2$^{\&\&}$ | 0.47-2.28$^{v}$ | | |
| Ni | nd-38.0±7$^{\&\&}$ | | | |
| Co | 5.0±0.11-25.1±0.26$^{\&\&}$ | | | |
| Ag | nd-185.0±10.1$^{\&\&}$ | | | |
| Sn | nd-301.0±16$^{\&\&}$ | | | |
| Mn | 50.0±9.64-280.0±21.2$^{\&\&}$ | | | |
| Al | 317.2 - 1,562$^{v}$ | | | |
| Fe | 112.9 - 476.1$^{v}$ | | | |

| | |
|---|---|
| Mg | 2,400 - 2,900[v] |
| Ca | 8,100 - 11,800[v] |

*Ochiengetal.2007dissolvedlevelsforfiveriftlakesNaivasha,Nakuru,Baringo,Bogoria,Elementeita=&&;Nyingietal.2016, dissolved values =y; Mbuthia et al. 2014, dissolved mean±SE values =k;Tarits, et al. 2006, dissolved =v;*

**Table 5**. Metal (±SD) concentrations in suspended and bottomsediments (values in µg/gdrywt. unless specified)

| **Surficial sediments ofL. Baringo** | | | **CBSQG** | |
|---|---|---|---|---|
| | | | TEC | PEL |
| Cd | 3.5±1.6[m] | 0.57±0.02-0.76±0.14[&&] | 0.99 | 4.98 |
| Pb | 49.9±22.9[m] | 16.57±1.44-21.83±1.08[&&] | 35.8 | 128 |
| Zn | 127±20[m] | 171.5±14.3-207.1±12.4[&&] | 121 | 459 |
| Cr | 2.17-4.87[&&] | | 43.4 | 111 |
| Ni | 25.70±2.55-39.72±13.11[&&] | | 23 | 49 |
| Co | 0.69±0.04-1.38±0.12[&&] | | - | - |
| Ag | nd-0.35±0.12[&&] | | 1.6 | 2.2 |
| Mn | 942±100-1,464±110[&&] | | 460 | 1100 |
| Cu | 15.12±1.44-20.95±1.56[&&] | | 31.6 | 149 |
| Sn | 23.39±0.84-43.41±1.34[&&] | | - | - |

| **Suspendedsediments ofL. Baringo**[v] | |
|---|---|
| Al | 102,626-132,250[v] |
| Fe | 93,086.7-102,885.3[v] |
| Mn | 1,548-1857.6[v] |
| Cr | 48,000-75,000[v] |

*Ochiengetal.2007forfiveriftlakesNaivasha,Nakuru,Baringo,Bogoria,Elementeita=&&;Mwamburi2015=m;Tarits,etal.2006,suspendedsediments=v.;CBSQG=consensusbasedSQG(MacDonaldetal.,2000;TEC=Thresholdeffectconcentration; PEL=Probable effectconcentration*

**Table 6.** Metal (±SD) concentrations infish species (µg/g wet wt.)

| **Fishspecies ofL. Baringo**(muscle tissue, wwt=wet weight or dwt = dryweight) | | |
|---|---|---|
| Cd | 0.1±0.04-1.9±0.30[y] | 3.565±0.06289[k] |
| Cu | nd-8.5±0.47[y] | 0.4728±0.12455[k] |
| Pb | 4.17±0.39-6.11±1.02[y] | nd[k] |
| Zn | 17.1±4.36-29.5±4.28[y] | 24.398±3.26165[k] |
| Fe | 53.0±2.14-125.6±55.07[y] | - |
| Hg | [r]5.3-111.3 ng/g; | nd[k] |

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*Nyingi et al. 2016, Tilapia, catfish, lungfish =y;Mbuthia et al. 2014,Oreochromis niloticus baringoensis, Clarias gariepinus, Protopterus aethiopicus=k; Campbell et al. 2003, fish species ofL.Baringo (Protopterusaethipicus, Labeocylindricus, Barbus intermedius australis, Orecohromis niloticus baringoensis, Clarias gariepinus),values ofTHgin ng/gwwt.=r*

## METAL POTENTIAL HEALTH RISKS EVALUATION

Target Hazard Quotient (THQ) was used to assess non-carcinogenic health risks of metals to consumers. Calculated risks were made using assumed parameters and reference dose for each element (USEPA 2012).

THQ = {(EFr x EDr x IRfa x C) / (RfDo x BWa x AT)}; where
EFr = exposure frequency (365 days/yr);
EDr = exposure duration;
IRfa = food item consumption per day; For fish in Kenya 5.2 kg/yr per capita;
C = metal concentration in food item mg/kg;
BWa = body weight average 60-70kg for adults;
RfDo = reference dose mg/kg bdwt/day (USEPA, 2012)
AT = average time for non-carcinogen 365 days per year.
According to THQ evaluation calculation a THQ of ≤1 indicates that there is no significant risk to health of consumer; whereas, a value greater than 1 indicates a possible health risks associated consumption of respective elements.

## CONCLUSION

The protection of water resources is one of the main challenges for most lake managers due to the different uses of lake water, fluctuating water levels and high evaporation in a closed basin area, with increasing water demands for safe and clean water, especially in a water scarce semi- arid area such as Lake Baringo. Anthropogenic activities have significant impacts on trace elements in the basin, due to the agricultural activities and natural erosion,transport and loading of external aerial and surface runoffs in to the lake. The high alkaline pH and complexation of metal ions in the lake water could probably be a significant control in availability of most metals from the aqueous environment. Occurrences of the toxic elements (As, Cd, Pb, Hg) and F ions need to be monitored more frequently (surface and underground water, soils, sediments, aerial dust, fish, water hyacinth) to improve on the database on concentrations and loadings, and develop a sediments background levels data.

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## COMPETING INTERESTS

Author has declared that NO competing interests exists.

## DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author hereby declares that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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