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Influence of particle size and total organic carbon on heavy metal concentrations in sediments of Lake Baringo, Kenya

Koskey J. C.[1]*, Ogendi G. M.[1], M' Erimba C. M.[2] and Tamba C. L.[3]

[1]Department of Environmental Science, Egerton University, P. O. Box 536-20115, Egerton, Kenya.
[2]Department of Biological Sciences, Egerton University, P. O. Box 536-20115, Egerton, Kenya.
[3]Department of Mathematics, Egerton University, P. O. Box 536-20115, Egerton, Kenya.

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Heavy metals impair water and sediment quality and thus, can cause adverse impacts on aquatic organisms especially when they exceed the recommended threshold levels. Heavy metal concentrations in water and sediments are a reflection of the anthropogenic activities on the watershed as well as the geology of the area. Metal concentrations and subsequently their bioavailability are influenced by the sediment characteristics including particle size and total organic carbon among others. This study determined the concentration of heavy metals - cadmium (Cd), copper (Cu) mercury (Hg) and lead (Pb) in the sediments in relation to grain size and total organic carbon in Lake Baringo. Samples were collected from five sites using a grab sampler and analyzed for total heavy metals using AAS. Particle size classification was done using the sieve method, while organic carbon (OC) was estimated using the Loss on Ignition (L.O.I) method. One way ANOVA revealed significant difference in mean Cu concentrations amongst the sampling sites at $P<0.05$ ($F (4, 14) =6.945$ $p=0.01$). However, there was no significant differences in the levels of Cd and Hg, that is, $F (4, 14) =0.03$, $p= 1.0$ and $F (4, 14) = 0.36$ $p=0.83$ respectively. However, there was no significant difference in the levels of Cd and Hg. Sites with higher percentages of silt and clay recorded a higher concentration of Cd and Cu as well as percentage of TOC. The results indicated the pollution of the lake by heavy metals presented an ecological and a human health concern requiring monitoring.

Key words: Sediment quality, heavy metals, particle size, total organic carbon.

INTRODUCTION

Aquatic systems are important ecosystem services such as hydrological cycling climate regulation, and habitat for aquatic organisms (Xu et al., 2014). The intensity of anthropogenic activities in the recent past has affected the existing balance of the nature. Water pollution is one of the serious environmental problems that have been

*Corresponding author. E-mail: judithkoskeyc@gmail.com. Tel: +254719440054.

caused by the increase in human activities (Petrosyan et al., 2019). Sediment is considered as the largest pool of heavy metals in the aquatic environment and they are considered to be the ultimate sink for a variety of toxicants (Xu et al., 2017; Soares et al., 1999). In the hydrologic systems, sediments reflect the pollution status and concentrations of heavy metals in the sediment are usually four or five times higher than that found in the overlying water (Hu et al., 2013).

Heavy metals enter the aquatic ecosystems naturally for example through rock weathering or atmospheric deposition. They can also enter through anthropogenic activities such as industrial wastewater discharge and agricultural fertilizer leaching (Xu et al., 2018). Heavy metals are of major concern to human health workers, tourist entrepreneurs, wildlife, fisheries managers, and conservationists due to their long residual time, strong concealment and toxicity among other characteristics. Heavy metals in the surrounding and/or underlying environments enter into water bodies and have been shown to affect aquatic life depending on their chemical speciation, toxicity, bioavailability, the rate of uptake and metabolic regulation by specific organisms (Karadede-Akin and Unlü, 2007).

Xu et al. (2017) and Soares et al. (1999) reported that sediments have the capacity to accumulate and integrate low concentrations of trace elements in water over time. This allows the possibility for metal determination even when levels in overlying waters are extremely low and undetectable. Increased metal loads in lake water and sediments are of human health concern due to biomagnification of metals along the aquatic and terrestrial food chains (Ogendi et al., 2007). Human health risks are primarily due to the elevated concentrations of heavy metals in water and fisheries that are part of the local people's diet.

The physical and chemical properties of sediments (grain size, surface to volume ratio, heavy metal contents of the main geochemistry phase), are the main factors that influence heavy metals content in sediments, of which grain size is the primary controling parameter (Zhu et al., 2006; Jernström et al., 2010; Maslennikova et al., 2012). It is believed that coarse sediments contain a lower concentration of heavy metals than finer sediments partly due to the low clay content and higher surface-to-volume ratio (Yao et al., 2015). However, some studies have indicated that coarser particles show similar or even higher heavy metal concentrations than finer ones and the residence time of coarser particles are possibly responsible for the higher metal content (Zhu et al., 2006; Jernström et al., 2010; Maslennikova et al., 2012). Sediment grain size is also associated with the availability of contaminants. Fine grain sediments tend to be higher in clay content and they contain higher levels of organic carbon, which is an indication of organic pollution.

Organic matter controls the distribution of trace elements such as mercury in soil as well as, suspended and bottom aquatic sediments. This makes the measurement of the total organic carbon present in the sediments an important parameter (Hedges and Keil, 1995; Goodarzi and Sanei, 2006). The capacity of organic matter to concentrate traces elements; however, varies with the amount and type of organic matter. Various factors that affect the ability of organic matter to concentrate elements include chemical and physical factors such as large surface area, high cation - exchange capacity and high negative ability (Baran et al., 2019). The chemical relationship between organic matter and trace elements at the molecular level has been described and focuses primarily on the role of organic complex materials, such as humic substances in concentrating trace elements during geochemical processes in sediments (Gomez et al., 2007). The organic matter present in the form of surface coatings provides a larger surface area since it is able to concentrate on the small sediment size fractions leading to the accumulation of toxicants including heavy metals (Goodarzi and Sanei, 2006).

Anthropogenic activities such as farming, livestock rearing and charcoal burning on the shores as well as in the drainage basin of Lake Baringo are responsible for the degradation of the lake and the land-water ecotone (Johansson and Svensson, 2002). The lake basin is shallow and has no known surface outlet. The waters are believed to seep through lake sediments into the faulted volcanic bedrock. Studies on basic physicochemical characteristics carried out in various rivers and lakes in Kenya have focused on the water quality parameters with little or no consideration given to the sediment characteristics. Recently, sediment studies have gained importance and are carried out to evaluate the quality of a water body as well as the overall ecosystem health (Petrosyan et al., 2019; Nnaji et al., 2010). This is because the sediments have the ability to absorb heavy metals, the so-called hidden pollution which in under external conditions could turn into real pollution (Petrosyan et al., 2019). The goal of this study therefore was to assess the influence of sediment particle size and organic carbon on the concentration of heavy metals and distribution in Lake Baringo.

MATERIALS AND METHODS

Sampling sites and sample collection

An ecological survey research design was used and based on the research objective, five sampling sites were selected viz: Kampi Samaki (S1), Salabani (S2), Molo River mouth (S3) and Endao River mouth (S4) (Figure 1). These sites are impacted by human activities such as rapid over water movement, solid and liquid waste disposal, tree removal and constructions near the shorelines, pastures, and cropland near the shorelines and the river banks. Communities that live around Lake Baringo, Kampi Samaki, Salabani, Molo River and Endao River are pastoralists who graze large numbers of livestock around the lake, causing soil

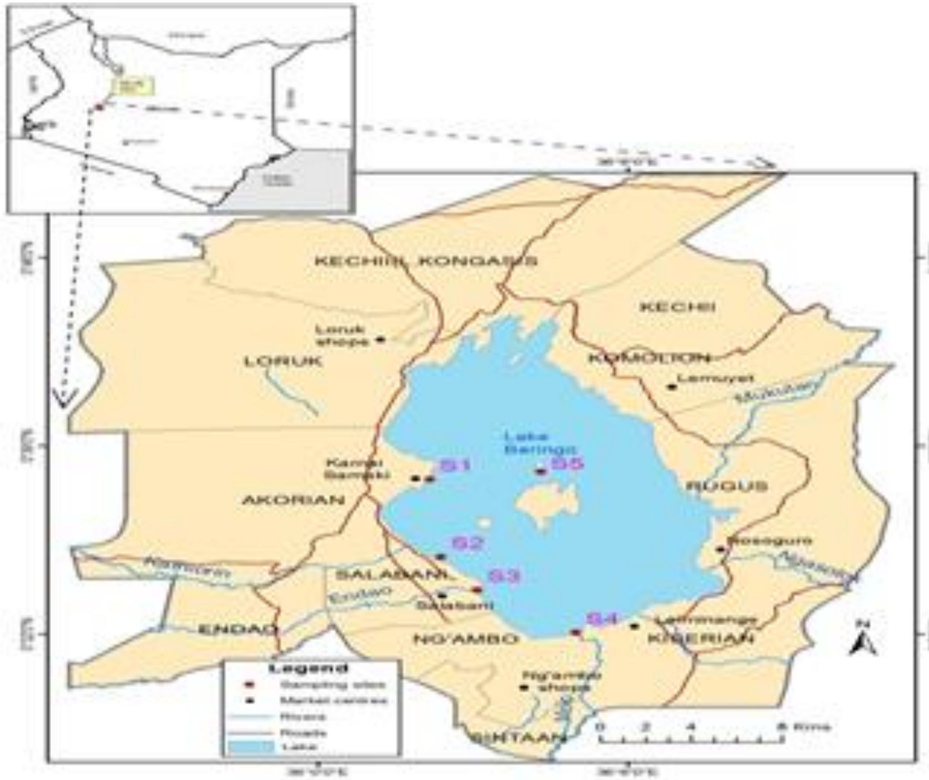

Figure 1. Map showing water sampling sites: S1-Kampi yaSamaki, S2- Salabani, S3- Endao River mouth, S4-Molo River mouth and S5- OlKokwa Island.

degradation resulting in soil erosion. They also fell trees to clear land for cultivation or to harvest wood for fuel, leaving the land bare and exposed to soil erosion. During the rains around the lake, there are flush-floods from inflowing rivers due to poor farming practices carrying along pesticides and fertilizers some which contain heavy metals which end up in the lake. These rivers also carry enormous amounts of soils into the lake (Aloo, 2002).

Endao River, one of the main rivers draining into Lake Baringo has been dammed to create the Chemeron dam whose water is being used for irrigating the surrounding farmlands where maize, onions, tomatoes and bananas are being grown. The Molo River has been diverted for agricultural purposes around Marigat and Bogoria areas (Aloo, 2002). River Ol Arabel River has also been diverted for agricultural purposes has been seasonal and has dried since the last heavy El Nino due to damming. OlKokwa sampling point, (S5) was used as the control due to its low population and fewer human activities. Global Positioning System (GPS) (Garmin 2 model) was used to mark the sampling sites.

Sediment sample collection and analysis

Two replicate sediment samples were collected from each of the five sampling sites during each sampling period) using a grab sampler. The samples were then placed and wrapped in polythene bags and kept in ice boxes before being transported to the laboratory for analysis. Thus, a total of 40 samples of sediments (5 sites, 2 replicates and 4 sampling periods) were collected by the end of the study. This sampling strategy captured the spatial variation of heavy metal concentrations in sediments.

The samples for heavy metal determination were digested using the multi-acid digestion method as described by Briggs and Meier (1999). The heavy metals (Pb, Cd, Cu, and Hg) were analyzed using Perkin Elmer Atomic Absorption Mass Spectrophotometer (AAS) Analyst 800 according to APHA (2005). Sediment organic carbon (OC) was determined, using the Loss on Ignition method as described by Ball (1964). Sediment particle size classification was done by standard sieve method following Dishman (2000). The heavy metal data was tested for normality and homogeneity of variance using Kolmogorov-Smirnov Normality Test and Levene's Test for equal variances respectively (Minitab Ver. 14). Using data that satisfy the assumptions of normality, heavy metal concentrations in sediment samples were compared using one-way analysis of variance (ANOVA) to test for significant differences ($P < 0.05$) among sites.

RESULTS AND DISCUSSION

Heavy metal concentration in sediments

The means obtained for the concentrations of heavy metal in the sediments (pooled data) from all the sampling sites are presented in Table 1. They were as follows in mg/kg, Cu = 12.97±1.0, Cd = 1.15±0.4, Hg = 0.25±0.1; while Pb concentrations were below limits of detection by the machine type that used. The study showed variations in heavy metal contents among the

Table 1. Heavy metal concentrations (Mean±SE) in sediments (Mg/Kg).

Site	Cu	Cd	Hg	Pb
S1	6.95±2.32	1.20±0.98	0.18±0.10	ND
S2	17.01±1.25	1.34±0.98	0.19±0.10	ND
S3	13.17±0.18	1.03±0.84	0.39±0.14	ND
S4	13.09±0.53	1.98±0.96	0.25±0.14	ND
S5	14.61±1.64	1.14±0.93	0.26±0.05	ND
P value	0.01**	1.0	0.83	

Significance levels *=0.05 and **=0.01. df =4 and n=14.WHO limits for sediment: Cd = 0.6 mg/kg; Cu = 16 mg/kg; Pb = 31 mg/kg (Ozturk et al., 2009): ND: Not Detected.

sites. Cu was the most predominant heavy metal in the lake sediments. One-way ANOVA revealed a significant difference ($P<0.05$) in Cu between the sampling sites. S1 was significantly lower compared to the other sampling sites (Table 1). Cu concentrations in S2 was 17.01 mg/kg, which exceeded the WHO limits for sediments (that is 16 mg/kg); thus, likely to adversely impact aquatic organisms particularly the diversities of benthic communities (Ali and Fishar, 2005; Ogendi et al., 2007). Rivers Molo and Endao are considered to be a major source of heavy metals into this lake as they drain through agricultural areas where there is a high usage of pesticides and animal wastes. The mean Cu value from all the sites in this study was 12.97 mg/kg, which was relatively lower than 20.95 mg/kg as recorded by Ochieng et al. (2007) in Lake Baringo.

There was no significant differences ($P<0.05$) in Cd mean concentrations. Cadmium is highly toxic to both plant and animal species. Main anthropogenic sources relate to metallurgical industries, mine wastes, sewage sludge, and municipal effluents (Khan et al., 2017). The trend in Cd concentrations was similar to the Cu concentrations, where the sediment samples from S2 recorded the highest values. On the other hand, S1 and S2 recorded slightly lower values of Hg concentrations. Site 3 had the highest concentration though not significant. The concentrations of Cd in sediments collected from the five sampling sites exceeded the WHO recommended guidelines for sediments (0.6 mg/kg). Such elevated metal concentrations in sediments can be attributed to several factors including municipal runoff, atmospheric deposition, domestic and industrial effluents and agricultural activities in the catchment areas. It is, therefore, likely that sediment-dwelling organisms at these sites will be adversely impacted in terms of their growth, survival, and reproduction (Karadede-Akin and Ünlü, 2007). There was no significant difference in the mean Hg concentrations. Levels of Hg in Lake Baringo were low compared to the other Cu and Cd. However, the existence of Hg in aquatic ecosystems is of concern. This is because compounds of Hg can be microbially transformed into methylmercury (MeHg) in water and sediments. Methylmercury can biomagnify in the food web resulting in high Total mercury (THg) even in remote areas from industrial sources (Campbell et al., 2003). Presence of Hg in Lake Baringo can be attributed to biomass burnings. Plants assimilate Hg from the soil and when burnt they release stored Hg to the atmosphere (Campbell et al., 2003). Most of the precipitation to Lake Baringo is derived from the lake catchment which frequently experiences agricultural burning. Biomass burnings are a highly significant potential source of THg to African lakes (Campbell, 2001). Soil erosion aggravated by human activities in the catchment is another potentially important Hg source to Lake Baringo, as sequestered Hg in soil oxyhydroxide particles can be released rapidly upon reduction in water quantity (Roulet et al., 1998).

Sediment characteristics (Grain size and TOC)

There was a significant difference ($P<0.05$) in the percentage of sand amongst sediment samples collected from all the sites. Similarly, percentage silt and clay also showed significant difference amongst the sampling sites as shown in Table 2. The amount of sand contained in the sediment samples collected ranged from 38.9 to 71.6% and the highest value was recorded at S1. The lowest value for clay was also recorded in this site 28.3%. Post-Hoc test (LSD) showed that at the level of 0.05, the mean differences of sand, silt and clay in S1 varied significantly. S3 had the lowest amount of sand but recorded the highest values for silt and clay. Site 4 and S5 almost had the same amounts of silt and clay.

The highest percentage of sand with low silt and clay particles was recorded at S1. However, it recorded low amounts of Cu and relatively low amounts of Hg. This can be attributed to the low water levels as the sampling site was near the bank and that the coarser particles were easily transported and deposited there and due to the strong hydrodynamical disturbance at low lake level the finer particles were washed away easily (Chen et al., 2004) resulting in larger sediment particle sizes deposition. The other sampling sites had low percentages of silt and clay as the locations were far from the banks

Table 2. TOC and grain size distribution of sediments (means ±SE) in Lake Baringo.

Variable	Sites					
	S1	**S2**	**S3**	**S4**	**S5**	**P value**
Coarse particles (Sand) (%)	71.6	47.2	38.9	44.0	46.9	0.03
Fine particles(silt and clay)	28.3	52.8	61.2	56.0	53.1	0.02
TOC	12.3	11.8	9.41	10.1	11.2	0.02

and the depth was relatively deeper. Hence, the coarser particles have little chance of drifting to this site due to the weak hydrodynamical forces that instead facilitate sedimentation of finer particles (Svetlana et al., 2012). The other sites had a higher percentage of fine particles allowing the heavy metals to accumulate in them due to their high surface-to-volume ratio (Zhu et al., 2006; Jernström et al., 2010; Maslennikova et al., 2012; Svetlana et al., 2012). Results showed that municipal and domestic discharges to the lake through the populated urban area contained high concentrations of heavy metals.

The highest concentrations of Cu were recorded at S2 and S5 sampling sites and S3 had a high concentration of Hg. The sites recorded 52 and 53% respectively. The sediments from these sites consisted of fine grain particles which act as effective collectors and carriers of dissolved metals from the water column to the sediments and thus elevated concentrations of heavy metals in sediments. The abundance of fine particles is assumed to be due to the anthropogenic input associated with erosion of upstream agricultural areas and settling out of the sediments in the lake due to low water currents. Similar findings were observed by Chouba et al. (2007) where absence of strong water currents led to accumulation of fine sediments with high metal concentrations.

The mean TOC values in the five sediment samples collected ranged from 9.4 to 12.3% and showed variations for the different sampling sites. TOC was significantly difference ($P \leq 0.05$). The relatively lower TOC levels in the S3 and S4 indicated a higher contribution of autochthonous organic matter to the sediments. In S2 and S5 sites, the autochthonous organic matter probably contributed to an increasing amount of organic matter in the sediments. The variations of the levels of TOC in the lake sediments were possibly ascribed to the mixed contribution of autochthonous and allochthonous organic matter (Kritzberg et al., 2004).

The TOC levels in S1 was the highest since the region was a major nutrient enriched area, fed by the large amount of industrial, domestic sewage and agricultural wastewater loading with relative high TOC from the catchment. Sites S2 and S5 recorded the highest readings of copper and relatively high TOC. Areas that are rich in organic matter are also richer in heavy metals due to the fact that organic matter has the ability to form complexes with heavy metals (Marchand et al., 2011). Mercury tends to bond strongly to particulate matter in freshwater, largely in inorganic mercuric form. The behavior of Cu in aquatic ecosystems often is influenced by its strong affinity for organic matter (Ogendi et al., 2007) and clay and organic carbon can substantially influence metal binding and extraction from sediments.

CONCLUSION AND RECOMMENDATIONS

The concentrations of heavy metals in Lake Baringo followed the order of Cu>Cd>Hg and Pb was below the limit detection. Cu was the major polluting heavy metal since its mean concentration was much higher than the recommended limits. The concentrations of Cd also exceeded WHO levels for lake sediments and the levels of Hg were below the recommended levels. The heavy metals mostly originated from the lake's catchment area, the most important sources being agricultural, horticultural and the waste disposal activities.

The metal content of the lake sediments could also be influenced by textural characteristics (silt and clay-sized grains which provided a larger surface area that retained high amounts of heavy metals. Percent silt and clay were high in all sampling sites apart from Kampi Samaki which had a high percentage of coarse particles also recorded high amounts of TOC. The TOC levels were high in the lake sediments was predominantly allochthonous. The study presents an overall pollution status of heavy metals in the surface sediments; thus providing the government and researchers working on management and restoration of the lake with some useful information for drafting remediation measures because of the bioaccumulative and biomagnifying nature of heavy metals. In spite of the low observed sediment metal concentrations, continuous monitoring is recommended to protect human and environmental health.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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