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Determination of Heavy Metals in Sediments of Masinga Reservoir, Kenya.

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Abstract

In Kenya, heavy metal pollution in aquatic ecosystems due to anthropogenic activities cannot be underestimated. Therefore, an assessment of heavy metal contamination (Cu, Zn, Pb, Cr and Mn) in sediments of Masinga reservoir was carried out between January 2013 and December 2013 in five sampling sites. Heavy metal Concentrations were determined using atomic absorption spectrophotometer (AAS). The data obtained was analyzed using one way analysis of variance and significant differences accepted at $p \leq 0.05$. Post Hoc Turkeys' test was used to separate means. Mean heavy metal concentrations (mg/kg) in sediments were Cu (11.38 – 23.67), Zn (60.04 – 75.84), Pb (11.14 – 14.47), Cr (21.39-49.62) and Mn (259.12 – 642.30). There were significant differences in metal concentrations recorded for Cu, Cr, and Mn ($p < 0.05$) between the sites. The concentrations for all metals in sediments were lower than World Health Organization (WHO) set limit except for Cr at Tumutumu sampling site. The high Cr concentration is an indication of untreated or inadequately treated industrial and sewage wastes from the catchment.

Key Words: Heavy metals, Contamination, sediments, Masinga reservoir

1.0 Introduction

Reservoirs play an important role in the livelihood of human populations in Africa. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation and flood control. Additional benefits of the reservoirs are tourist attraction and opening up of new areas for development (Kitur, 2009). However, the contamination of these aquatic ecosystems with a wide range of pollutants has become a matter of concern over the past few decades (Dirilgen, 2001; Vutukuru, 2005; Yousafzai and Shakoori, 2008; Narayanan and Vinodhini, 2008). Reservoirs have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluent, agricultural run offs and bad fishing practices (Ndimele, 2008). In Kenya a number of hydroelectric power dams have been constructed along the Tana River since the late 1960's. The largest is Masinga dam which began operation in 1981(Maingi and Marsh, 2002). Masinga dam has been identified as the most effective regulator of the Tana River system because of its great size and its strategic location in the upper reaches of the system (Pacini *et al*., 1998). However, unregulated deforestation and expansion of cultivation practices onto marginal soils has resulted in significant reservoir siltation, reduced ecosystem function, and more erratic downstream flows (Jacobs *et al*., 2007). According to Bunyasi *et al.*, (2013), Masinga catchment had lost 62% forest cover (21,180.87 hectares) between the years 1976 and 2011. This has led to increased sedimentation into Masinga reservoir which is estimated at 5.45 M m^3/year (Bunyasi *et al*., 2013) and hence the reservoir has lost 10.1% of its capacity in the last 30 years.

The Contamination of sediments by heavy metals and other pollutants is one of the major threats to aquatic ecosystems and leads to serious environmental problems (Loizidou *et al*., 1992). The occurrences of enhanced concentrations of heavy metals in sediments may be an indication of human-induced perturbations rather than natural enrichment through geological weathering (Binning and Baird, 2001; Eja *et al*., 2003). Pollutants released to surface water from industrial and municipal discharges, atmospheric deposition and run off from agricultural, urban and mining areas accumulate to harmful levels in sediments (Chukwujindu *et al*., 2007). Like soils in the terrestrial system, sediments are important sinks for a range of substances including nutrients, hydrocarbons, pesticides and heavy metals (Baldwin and Howitt, 2007). Heavy metals once absorbed on the sediments are not freely available for aquatic organisms. Under changing environmental conditions (temperature, pH, redox potential, salinity) of the overlying water these toxic metals are released back to the aqueous phase (Soares *et al*., 1999).Sediments play a significant role in remobilization of contaminants in aquatic systems under favorable conditions and are used for monitoring the health of aquatic ecosystems (Singh *et al*., 1997; Abraha *et al*., 2012). They act as both carrier and sources of contaminants in aquatic environment (Shuhaimi, 2008). Sediments capture hydrophobic chemical pollutants that enter water bodies (McCready *et al*., 2006) and slowly release the contaminants back into the water column (Chapman and Chapman 1996; McCready *et al*., 2006). Heavy metal distribution and bioavailability in both sediments and the overlying water column have to be considered to obtain a better understanding of interactions between the organisms and their environment. In addition to the physical and chemical relationships between sediments and contaminants, sediments are of fundamental importance to benthic communities in terms of providing suitable habitats for essential biological processes. A good sediment quality is crucial to maintain a healthy aquatic ecosystem, which ensures good protection of human health and aquatic life. This study, therefore sought to determine the extent of heavy metal concentrations in sediments from Masinga reservoir.

2.0 Materials and Methods

2.1 Study Area

The study was carried out in Masinga reservoir which lies between latitude (0^0 45'S; 1^0 11' S) and longitude (37^0 0' E; 37^0 46'E) at an altitude of 1056.5 m above sea level. The dam has a full operation surface area of 125km^2 and extends 45km upstream along the Tana River (Figure 1). Masinga dam has a catchment area of 7,355km^2 and creates the largest storage and regulatory structure on the Tana River for regulating flows for downstream hydroelectric power dams. The reservoir is a source of livelihood to rural populations who live nearby especially from Machakos, Embu and Murang'a counties.

2.2 Sampling of Sediments

Sampling was carried out once a month for one year (January 2013 – December 2013) in five sampling sites (Figure 1 and Table1). The sediment samples were taken from the bottom surface using an Eckman grab according to method described by Osman and Kloas (2010). For each sample, three sediments grabs were randomly taken, homogenized and kept in clean polyethylene bags. The polythene bags were then labeled to indicate sampling station and date of sampling. Samples were stored in ice box for transportation to the laboratory at Kenyatta University. In the laboratory, the samples were kept in a freezer at – 20^0C until they were processed for heavy metal analysis.

Table 1: Geographical coordinates and water depth of sampling sites in Masinga Reservoir

Sampling Site	Latitude	Longitude	Depth (m)
Kathini (S1)	00^0 94 322 S	037^0 43 237 E	10.33 ± 0.99
Mathauta (S2)	00^0 92 571 S	037^0 54 548 E	22.42 ± 2.50
Manyatta (S3)	00^0 88 736 S	037^0 47 279 E	21.00 ± 6.70
Riakanau (S4)	00^0 86 476 S	037^0 38 770E	7.25 ± 1.14
Tumutumu (S5)	00^0 81 416 S	037^0 30 621E	7.58 ± 2.02

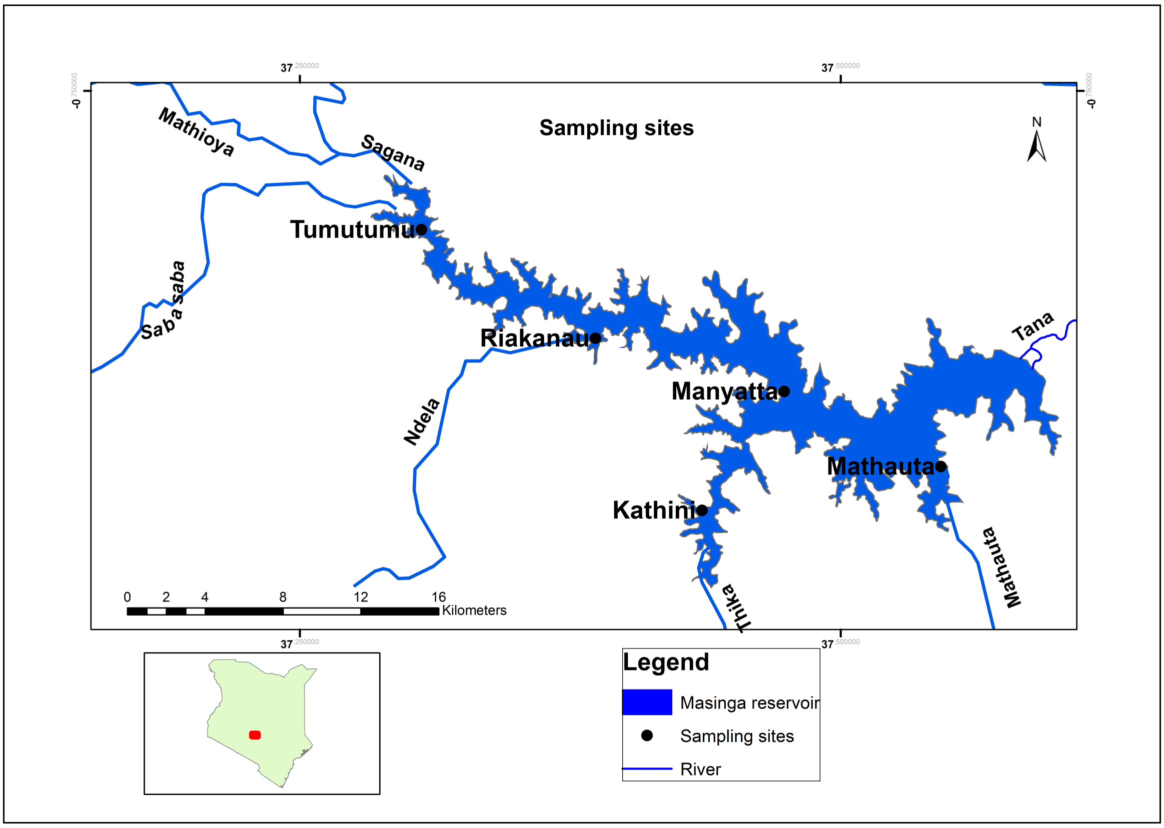

Figure 1. A map of Masinga reservoir showing the five sampling sites

2.3 Processing and Digestion of Sediments for Metal Analysis

Each sediment sample was thawed at room temperature (25^0C – 28^0C) and put into pre-acid cleaned evaporating beakers. The sediments were dried at a temperature of 50^0C in an oven until a constant weight was obtained. The dried sediment samples were ground using a porcelain mortar and pestle then sieved through a 2 mm mesh plastic sieve. For each sediment sample, 2 g was weighed using Shimadzu electronic weighing balance (Model ATX 224) into 100 ml acid cleaned beakers. To each sample, 18 ml of concentrated nitric acid (analytical grade) was added and heated at 100 ^{0}C on a hot plate in a fume hood chamber. A few drops of hydrogen peroxide (analytical grade) were added until there were no brown fumes. All the digested samples were filtered using Whatman No. 42 filter paper into a 50 ml volumetric flask and topped up to the mark with distilled water. The filtrate was analyzed for heavy metals using atomic absorption spectrophotometer (AAS). A blank solution was similarly prepared. The AAS working conditions were set as shown in Table 2.

2.4 Data Analysis

Data analysis was done using a computerized statistical programme (STATISTICA 8.0, 2007). The data were subjected to one way analysis of variance (ANOVA) and significant differences accepted at $p \leq 0.05$ (Zar, 2001). In case of significance, the mean values were separated using post-hoc Tukey's (HSD) test. Descriptive statistics for all collected data were also obtained using STATISTICA software.

Table 2: Instrument (AAS) operating conditions

Element	Cu	Zn	Pd	Cr	Mn
Lamp current (mA)	3	3	8	7	5
Fuel	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene
Support/Oxidant	Air	Air	Air	Nitrous oxide	Air
Wave length (nm)	324.7	213.9	217.0	357.9	279.5
Slit width (nm)	0.5	1.0	1.0	0.2	0.2
Detection limit (ppm)	0.003	0.002	0.02	0.005	0.003

3.0 Results and Discussions

3.1 Copper (Cu) Concentrations (mg/kg)

The mean Cu concentrations in all the sampling sites are shown in Table 3. There was significant difference ($p < 0.05$) in Cu levels between the sites. Mean Cu concentration values ranged from 11.38 ± 2.77 mg/kg (Riakanau) to 23.67 ± 6.54 mg/kg (Tumutumu). Copper gets into aquatic ecosystems from diverse sources such as Cu compounds used in fungicides, algaecides, insecticides, wood preservatives, electroplating and azo dye manufacture (Akan *et al.*, 2010). Copper compounds are also used in food additives and copper salts in water supply systems to control biological growths in reservoirs and distribution pipes (Eaton, 2005; WHO, 2004). The high Cu levels at Tumutumu could be attributed to agricultural activities in the catchment especially the use of fertilizers, fungicides and insecticides. Masinga reservoir catchment is a high potential area for agriculture, both dairy and crops. The mean Cu levels in the study area were below the WHO standard values of 25 mg/kg for the survival of aquatic organisms (WHO, 2004). Comparable Cu Concentrations in sediments have been observed in five Rift Valley Lakes (Nakuru, Naivasha, Elementaita, Bogoria and Baringo) in Kenya with a mean ranging from 1.46 – 20.95 mg/kg (Ochieng *et al.*, 2007). In Lake Kanyaboli, mean Cu concentration levels ranging from 1.80 – 30.27 mg/kg have been observed (Ochieng *et al.*, 2008). Heavy metal contamination studies done in Lake Victoria (Winam Gulf) found higher mean Cu levels (3.90 – 150.2 mg/kg) in surface sediments (Ochieng *et al.*, 2008) than those obtained in Masinga reservoir. Other studies carried out elsewhere have found lower mean Cu levels in sediments, for example Tono Irrigation Reservoir (0.25 mg/kg) in Ghana (Anim-Gyampo *et al.*, 2013) and Lake Victoria (3.31 – 3.44 mg/kg), Kenya (Oyoo-Okoth *et al.*, 2010). Saeed and Shaker (2008) obtained higher Cu levels in sediments in the Northern Delta Lakes (36.77 – 315.36 mg/kg), Egypt.

3.2 Zinc (Zn) Concentrations (mg/kg)

There was no significant variation ($p > 0.05$) in Zn concentrations between sites. The highest mean Zn concentrations were recorded at Kathini (75.84 ± 27.684 mg/kg) and the lowest values at Riakanau (60.04 ± 25.633 mg/kg). The source of Zn concentrations in reservoirs' sediments could be from a number of alloys including brass and bronze, batteries, fungicides and pigments (Akan *et al.*, 2010). Other sources could be Zn Carbonates used as pesticides (Anglin-Brown *et al.*, 1995) and textile industries' waste waters (Smith, 1988). The elevated Zn values recorded at Kathini may be attributed to Zn which is used in printing and dyeing processes in textile industries located within the Thika sub catchment. The results on Zn concentrations in all the sampling stations did not exceed the WHO recommended limit of 123 mg/kg (WHO, 2008). However, sediments have the capacity to accumulate more heavy metals with time and remobilize them back to water and the food chain (WHO, 2008), hence the need for regular monitoring. Compared to other studies, mean Zn levels in Masinga reservoir were lower than 96.2 - 229.6 mg/kg recorded in five Rift Valley lakes, Kenya (Ochieng *et al.*, 2007). The Zn levels were however, within same range as those recorded in Lake Kanyaboli (65.0 – 146 mg/kg) and 23.39 – 350.80 mg/kg at Winam gulf (Ochieng *et al.*, 2008).

Table 3: Mean ±Standard deviation and ranges for heavy metal concentrations in sediments of Masinga Reservoir. Means in same row with different superscripts are significantly different at $p < 0.05$ levels.

Element	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg/kg)	14.19 ± 6.986^{a}	19.08 ± 6.822^{ab}	18.21 ± 9.448^{ab}	11.38 ± 2.770^{a}	23.67 ± 6.543^{b}
Range	5.20 – 25.03	9.58 – 32.95	6.50 – 31.75	8.00 – 16.37	15.00 – 34.64
Zn (mg/kg)	75.84 ± 27.684^{a}	71.35 ± 29.874^{a}	65.81 ± 21.688^{a}	60.04 ± 25. 633^{a}	69.49 ± 22.434^{a}
Range	5.20 – 91.07	20.00 – 80.90	10.23 – 82.90	24.42 – 64.55	32.00 – 100.35
Pb (mg/kg)	12.03 ± 5.650^{a}	13.85 ± 9.488^{a}	11.14 ± 5.177^{a}	12.04 ± 5.652^{a}	14.47 ± 6.463^{a}
Range	4.25 – 22.63	4.68 – 32.23	3.07 – 17.83	4.15 -24.23	4.45 – 24.68
Cr (mg/kg)	31.94 ± 11.800^{b}	21.39 ± 6.540^{b}	37.40 ±21.236^{a}	24.93 ± 9.806^{b}	49. 62 ± 14.742^{a}
Range	7.50 – 43.80	15.50 – 32.30	15.50 – 77.60	11.70 – 39.58	32.90 – 77.10
Mn (mg/kg)	642.39 ± 225.346^{a}	514.91 ± 275.302^{a}	606.57 ± 276.864^{a}	259.12 ± 92.033^{b}	603.26 ± 276.399^{a}
Range	287.50 – 831.25	242.92 – 823.75	297.50 – 888.75	138.75 – 351.25	319.58 - 937.

3.3 Lead (Pb) Concentrations (mg/kg)

Pb is non essential element and excess of it in the human body can produce a damaging effect on the kidney, liver and nervous system, blood vessels and other tissues (Sharma and Pervez, 2003). The mean Pb concentration levels recorded in sediment at different sampling sites during the study showed modest variations. They ranged from 11.14 ± 5.177 mg/kg in Manyatta to 14.47 ± 6.463 mg/kg in Tumutumu. The possible sources of Pb in sediments include industrial wastes and from water pipes, lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors and plastic stabilizers (WHO 2004, Akan *et al.*, 2010). Pb concentrations observed in this study were lower than the recommended limit of 35 mg/kg for Pb in sediment (WHO, 2004). The highest mean Pb level in Masinga reservoir (14.47 mg/kg) was much lower than 38.98 mg/kg recorded in Rift Valley lakes (Ochieng *et al.,* 2007) and than what Ochieng *et al.*, (2008) found at Lake Kanyaboli (153.90 mg/kg) and Winam Gulf (66.05 mg/kg).

3.4 Chromium (Cr) Concentrations (mg/kg)

Cr in aquatic ecosystems is attributed to industrial and sewage wastes (Akan *et al.,* 2010). The mean Cr concentrations at different sites varied significantly ($p < 0.05$) and were between 21.39 ± 6.540 mg/kg (Mathauta) to 49.62 ±14.742 mg/kg (Tumutumu). The high mean Cr levels at Tumutumu could be due to industrial wastes and sewage from the towns located within the catchment. The mean Cr concentration obtained at Tumutumu was higher than the recommended limit of 37.5 mg/kg for Cr in sediments (WHO, 2008). Cr and its compounds are known to cause cancer of the lung, nasal cavity and suspected to cause cancer of the stomach and larynx (ATSDR, 2000). For Cr concentrations exceeding 25 mg/kg, a condition known as allergic dermatitis could occur (EPA, 1999). Cr mean levels in Masinga reservoir were higher than 0.42 – 1.12 mg/kg recorded in sediments of Lake Victoria, Kenya (Oyoo-Okoth *et al.,* 2010). However, they were within same range and at the same time below what (Wildi *et al.,* 2004) found (31.54 – 165.01 mg/kg) at different reservoirs in Switzerland. Other studies that have recorded higher mean Cr levels are for example off Bushehr, Persian Gulf 130.5 mg/kg(Karbassi *et al.*, 2005) and Danube river, Serbia 30.6 – 112.5 mg/kg (Milenkovic *et al.*, 2005).

3.5 Manganese (Mn) Concentrations (mg/kg)

Mn is known to be a very abundant element widely distributed in the earth's crust. It is used in manufacturing of dry cell batteries, glass, and fertilizer and in the leather and textile industries (Ziemacki *et al.*, 1989). It is also released through agricultural activities, building activities and quarry processes (Ziemacki *et al.,* 1989). Masinga reservoir catchment has several textile industries found within Thika sub basin and a lot of fertilizer is used in the agricultural sector within the catchment. In this study, the lowest mean Mn concentration was obtained at Riakanau (259.12 ± 92.033 mg/kg) while the highest was recorded at Kathini (642.39 ± 225.346 mg/kg). Kathini sampling site is within the Thika sub basin, hence the elevated Mn levels could be due to industrial and agricultural activities. Compared to other studies done elsewhere in Kenya, the Mn concentrations in this study are lower. For example, Ochieng *et al.,* (2007) while doing similar studies in sediments of five rift valley lakes found (667.7 – 3,946.8 mg/kg) and (1073 – 2,629 mg/kg) in Lake Kanyaboli. However, Osman and Kloas (2010) found slightly lower mean Mn levels (159.84 – 351.79 mg/kg) in sediments sampled along the course of River Nile, Egypt while 419.60 ± 29.99 mg/kg and 850.95 ± 63.96 mg/kg have been recorded in Lake Manzala and Lake Borollus, Egypt respectively(Saeed and Shaker (2008).

4.0 Conclusions and Recommendations

The study revealed the presence of heavy metals in the sediments of Masinga reservoir. This is a clear sign of the impacts of anthropogenic activities within the catchment to the aquatic ecosystem. The sequence of heavy metal accumulation in sediments was Mn > Zn > Cr > Cu > Pb. The heavy metal concentrations (Cu, Zn, Pb, and Mn) in sediments were below WHO set limits for survival of aquatic organisms. However, Cr levels were above the tolerable limit for sediments. Tumutumu had the highest levels of Cr concentrations in sediments while Kathini and Manyatta were slightly polluted with Cr. Therefore, it is concluded that there are industrial wastes that reach Masinga reservoir from the catchment activities and thus, regular monitoring is highly recommended.

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