

# Assessment of Heavy Metal Contamination in Surface Water of Masinga Reservoir, Kenya

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## Abstract

An assessment of heavy metal contamination (Cu, Zn, Pb, Cr, Mn and Cd) in surface water of Masinga reservoir was carried out between January 2013 and December 2013. The 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 Tukeys' test was used to separate means. The mean metal concentrations ( $\text{mg L}^{-1}$ ) were; Cu (0.003 - 0.019), Zn (0.092 - 0.132), Pb (0.004 - 0.009), Cr (0.003 - 0.006) and Mn (0.006 - 0.146). No significant differences were observed in heavy metal concentrations in surface water among the different sites. The concentrations for all metals in surface water did not exceed the WHO recommended limit for drinking water.

**Key Words:** Water Quality, Heavy Metals, Contamination, Masinga Reservoir

## 1. Introduction

Aquatic ecosystems such as rivers, dams and lakes provide livelihood for rural populations in many developing countries in Africa. However, in the recent past, they 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). Increasing pollution in water bodies is directly or indirectly related to increasing urbanization and indiscriminate disposal of agrochemical and industrial effluents (Dua and Gupta, 2005, Bakare *et al.*, 2003). As a result, many water resources have been rendered polluted and hazardous to man and other living systems. Heavy metals in water can originate both from natural sources, industrial, agricultural and domestic activities in the drainage basin of a water system. As the metal levels in many aquatic ecosystems increase due to anthropogenic activities, they raise the concern on metal bioaccumulation through the food chain and related human health hazards (Wright and Welbourn, 2002; Indrajith *et al.*, 2008; Agah *et al.*, 2009). Consumption of biota from contaminated aquatic bodies is an important route of exposure to pollutant compounds. However, water quality criteria for aquatic biota have not received the attention that they deserve. All too often, water has been considered quite adequate for fish as long as there is no obvious mortality ascribed to known pollutants. Trace metal analysis in freshwater is very important because these ecosystems provide drinking water as well as habitat for flora and fauna. Heavy metal contaminations in inland waters can be monitored by using the metal levels in water; sediments and resident biota especially fish (Senarathne and Pathiratne, 2007). The heavy metals of most environmental concern in water are lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu) and zinc (Zn) (Martin and Coughtrey, 1982). Contamination by these heavy metals can be expressed by their high concentrations in water, as well as in sediments and aquatic organisms (Pham *et al.*, 2007). Cadmium, copper, lead and zinc salts are usually found in agricultural and industrial liquid wastes (Qiao *et al.*, 2007) which are discharged into water resources.

Over the years, numerous factors have contributed to the degradation of water resources within the upper Tana River catchment. The Tana River is the longest river system in Kenya (approximately 1, 200 km) with a catchment area of about 120, 000  $\text{km}^2$  and an average annual discharge of  $4 \times 10^9 \text{m}^3$  (Kitheka *et al.*, 2005). The upper Tana catchment area is characterized by high population densities, rapid urbanization and high agricultural activities. The key environmental issues include catchment degradation due to pollution from agro-based industries, agro-chemicals, urban effluent, car washing, soil erosion (siltation), river bank encroachment and industrial discharge (UN – WATER, 2006). All these human activities within the catchment lead to anthropogenic pollutants being transported in the streams, rivers and other municipal drainage water systems; either dissolved in the water or attached to suspended matter and eventually gets into the Tana River dams (Nzeve *et al.*, 2014). The catchment comprises of three river subsystems, namely Tana River (91%), Thiba River (2.8%) and Thika River (4.2%). The Tana River and Thika River sub basins drain into Masinga reservoir (UN-WATER, 2006). According to UNEP (2000), economic activities in the catchments would affect the status of aquatic ecosystems. This means that impacts caused by human activities in the catchment are transmitted to

receiving waters of Masinga reservoir. This study therefore, sought to assess the extent of heavy metal levels in surface water of Masinga reservoir.

## **2. Materials and Methods**

### **2.1 Study Area**

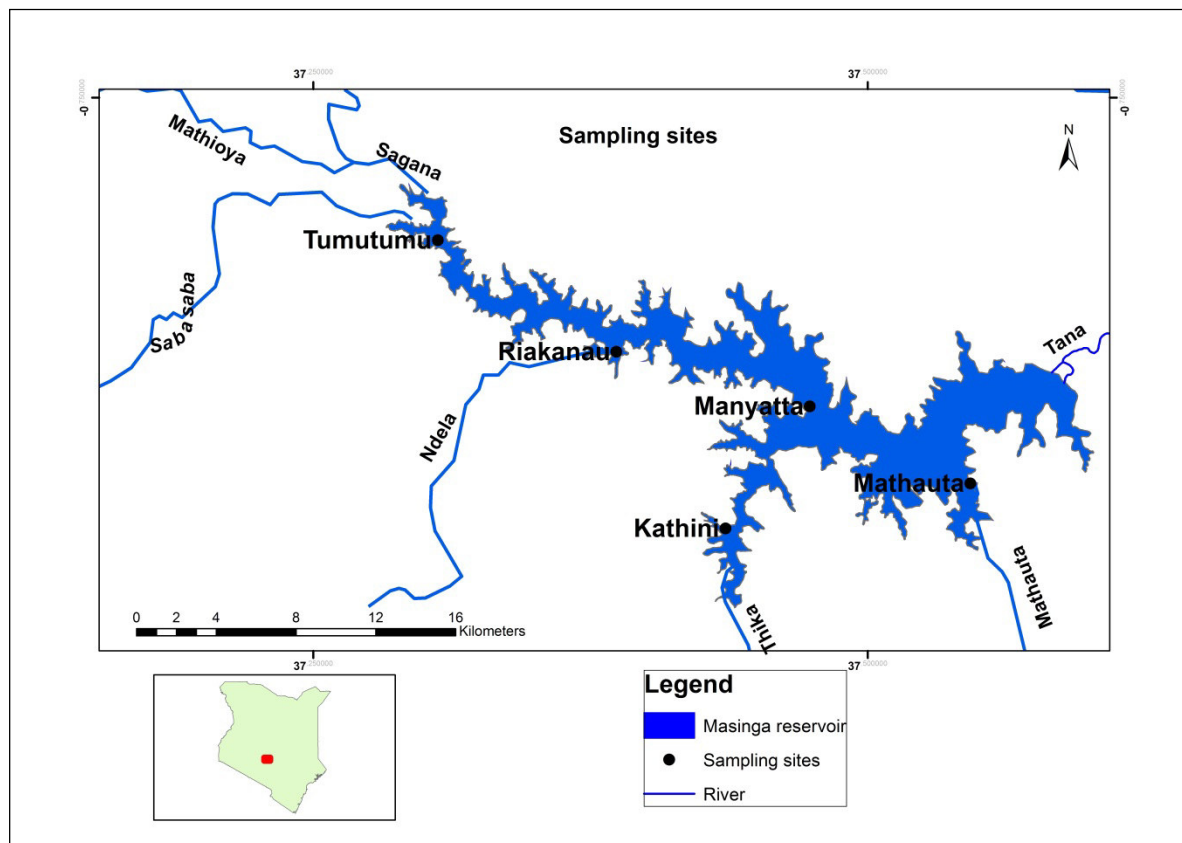
The study was carried out in Masinga reservoir which is located 100km North East of Nairobi City, Kenya. It lies between latitude ( $0^{\circ} 45' S$ ;  $1^{\circ} 11' S$ ) and longitude ( $37^{\circ} 0' E$ ;  $37^{\circ} 46' E$ ) with an altitude of 1056.5 m above sea level. It is the upper most cascade dam of the seven forks development scheme on the Tana River. The dam was constructed between 1976 and 1980 as a storage reservoir to regulate water flows to the lower dams whose water levels fluctuated drastically during the dry season. It is a multi-branched type with a large number of shallow bays and high shore line surface area ratio. The dam has a full operation surface area of  $125\text{km}^2$  and extends 45km upstream along the Tana River (Figure 1). The mean depth is 13.8 m while the maximum depth at the dam wall is 48 m (Jumbe, 2003). The dam provides hydro-electricity power (40mw), irrigation water for agriculture and commercial fishing.

### **2.2 Sampling and Frequency**

During a field reconnaissance, five sampling stations were selected from the Masinga reservoir (Figure 1). The dam was divided into three regions; the upper, middle and lower regions. The upper and middle regions had two stations each (Tumutumu, Riakanau, Manyatta and Kathini respectively), while the lower region had one station (Mathauta). The five sampling sites were chosen to represent different sub basins that drain into the reservoir in order to understand the influence of natural and human activities on the reservoir. The geographical location of each selected sampling site within the reservoir is shown in Table 1. Sampling was carried out once a month for one year (January 2013 – December 2013) in all the sampling sites.

### **2.3 Sampling of Water and Storage**

Water sampling was done according to the procedure described by Ndimele and Kumolu-Johnson (2012). Water samples from all five (5) sampling sites were collected at a depth of about 0.3m below water surface into 500 ml plastic bottles. Prior to sampling, the bottles were cleaned with 10% nitric acid and rinsed with distilled water. The bottles were rinsed three times with the dam water at the time of sampling. Samples were then collected by direct immersion of the sampling bottle into the dam. Immediately after sample collection, 2 ml nitric acid (AR grade) was added to the water samples to reduce adsorption of metals onto the walls of the plastic bottles. Sample bottles were then labeled to indicate date of sampling and the sampling site. Samples were transported in an ice-box to the laboratory at Kenyatta University and stored at  $4^{\circ}\text{C}$  awaiting analysis.



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

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

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

#### 2.4 Digestion of Water samples for Metal Analysis

Digestion of the water samples were done in triplicates using concentrated nitric acid (Analytical Grade) according to method described by Zhang (2007). Concentrated acid (5 ml) was added to 50 ml of sample water in a 100 ml beaker, and then heated on a hot plate (100°C) to boil until its volume reduced to 20 ml. Another 5 ml of concentrated HNO<sub>3</sub> was added and then heated for 10 minutes and allowed to cool. About 5 ml of nitric acid was used to rinse the sides of the beaker and the solution filtered using Whatman 0.42µm filter paper into a 50 ml volumetric flask and topped up to the mark with distilled water. A blank solution was similarly prepared. Heavy metal analysis was done using Varian Atomic Absorption Spectrometer (model Spectra AA-10) at Mines and Geological department, Nairobi - Kenya. The blanks were aspirated along with the analytical samples in order to collect background adsorption. The operating conditions of the instrument (AAS) were set according to manufacturer's specifications (Table 2).

**Table 2:** Instrument (AAS) operating conditions

Element	Cu	Zn	Cd	Pd	Cr	Mn
Lamp current (mA)	3	3	5	8	7	5
Fuel	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene
Support/Oxidant	Air	Air	Air	Air	Nitrous oxide	Air
Wave length (nm)	324.7	213.9	228.8	217.0	357.9	279.5
Slit width (nm)	0.5	1.0	0.5	1.0	0.2	0.2
Detection limit (ppm)	0.003	0.002	0.006	0.02	0.005	0.003

## 2.5 Statistical 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). Where significant differences were found, the mean values were separated using post-hoc Tukey's (HSD) test. Descriptive statistics for all collected data were also obtained using STATISTICA software.

## 3 Results and Discussions

### 3.1 Copper (Cu) concentration ( $\text{mg L}^{-1}$ )

Copper is a natural element which is widely distributed in soils, rocks and in rivers. It is released into water as a result of natural weathering of soil and discharges from industries and sewage treatment plants (Romo-Kroger *et al.*, 1994 and Hutchinson, 2002). The mean concentrations of Cu ( $\text{mg L}^{-1}$ ) in surface water from all sampling sites are shown in Table 3. There was no significant variation ( $p > 0.05$ ) in Cu concentrations levels between the different sampling sites. The mean Cu concentrations recorded were  $0.003 \pm 0.002 \text{ mg L}^{-1}$  (Riakanau),  $0.006 \pm 0.003 \text{ mg L}^{-1}$  (Kathini),  $0.008 \pm 0.003 \text{ mg L}^{-1}$  (Tumutumu),  $0.018 \pm 0.007 \text{ mg L}^{-1}$  (Manyatta) and  $0.019 \pm 0.003 \text{ mg L}^{-1}$  (Mathauta). Cu in surface water is from extensive use of pesticides sprays which contain Cu compounds for agricultural purposes (Al-Weher, 2008). In the dissolved form, Cu is potentially very toxic to aquatic animals and plants, especially to young life-stages such as fish larvae. However, the toxicity is greatly reduced when Cu is bound to particulate matter in the river water and when the water is hard (Damodharan, 2013).

The mean Cu levels obtained in this study were lower compared to  $0.69 - 0.94 \text{ mg L}^{-1}$  observed in surface waters of Lake Victoria, Kenya (Oyoo-Okoth *et al.*, 2010). However, they were within same range  $0.005 - 0.01 \text{ mg L}^{-1}$  of mean Cu levels recorded in five Rift Valley lakes in Kenya (Ochieng *et al.*, 2007). Studies by Ochieng *et al.*, (2008) found higher mean Cu levels  $0.012 - 0.043 \text{ mg L}^{-1}$  in surface water of Lake Kanyaboli, Kenya. The mean Cu levels obtained in Masinga reservoir did not exceed the WHO limits of  $1.00 \text{ mg L}^{-1}$  of Cu concentration in water for drinking (WHO, 2004).

### 3.2 Zinc (Zn) concentration ( $\text{mg L}^{-1}$ )

Zn is introduced into water bodies through artificial pathways such as by-products of steel production or coal-fired power stations and burning of waste materials (Damodharan, 2013). It is also through leaching from fertilizers, effluents of commercial industries during mining and smelting (metal processing) activities. Other sources of Zn into aquatic ecosystems include urban runoff and municipal sewages (Damodharan, 2013). In this study the mean Zn concentration levels in surface water for all the sampling sites are presented in Table 3. The results indicated no significant difference in mean Zn concentration levels ( $p > 0.05$ ) among the different sampling stations. The mean Zn levels recorded ranged from  $0.092 \pm 0.013 \text{ mg L}^{-1}$  (Kathini),  $0.108 \pm 0.018 \text{ mg L}^{-1}$  (Riakanau),  $0.109 \pm 0.018 \text{ mg L}^{-1}$  (Mathauta),  $0.111 \pm 0.019 \text{ mg L}^{-1}$  (Tumutumu) and  $0.132 \pm 0.019 \text{ mg L}^{-1}$  (Manyatta). Zn is an essential nutrient for body growth and development; however drinking water containing high levels of zinc can lead to stomach cramps, nausea and vomiting. The concentration of Zn in surface water recorded in this study did not exceed the recommended limit of  $3 \text{ mg L}^{-1}$  for Zn levels in drinking water (WHO, 2008).

Similar studies done in Lake Victoria, Kenya have recorded Zn concentration levels as high as 0.220 mg L<sup>-1</sup> (Lalah *et al.*, 2008 and Mwamburi, 2009). Also, Muiruri *et al.*, (2013) observed higher mean Zn levels (0.055 – 0.695 mg L<sup>-1</sup>) in Athi River tributaries. Ochieng *et al.*, (2007) observed mean Zn levels ranging 0.029 – 0.235 mg L<sup>-1</sup> in five rift valley lakes (Nakuru, Naivasha, Baringo, Elementaita and Bogoria). At Lake Kanyaboli mean Zn levels in surface water ranging from 0.015 – 0.056 mg L<sup>-1</sup> have been recorded (Ochieng *et al.*, 2008). Olatunji and Osibanjo (2012) obtained higher mean Zn levels (1.98 – 4.03 mg L<sup>-1</sup>) in River Niger, North Central Nigeria compared to those observed in Masinga reservoir. Fahmy and Fathi (2011) obtained higher Zn levels in Wetland Lake, Al-Asfar, Saudi Arabia.

### 3.3 Lead (Pb) concentration (mg L<sup>-1</sup>)

Mean Pb concentration levels in surface water are shown in Table 3 and revealed no significant difference ( $p > 0.05$ ) among the sampling sites. The lowest mean Pb levels were recorded in Manyatta  $0.004 \pm 0.001$  mg L<sup>-1</sup> and Riakanau  $0.004 \pm 0.002$  mg L<sup>-1</sup> while the highest mean Pb level was observed at Kathini  $0.009 \pm 0.005$  mg L<sup>-1</sup>. Mathauta and Tumutumu had similar mean Pb levels of  $0.005 \pm 0.002$  mg L<sup>-1</sup>. Pb concentration in natural water increases mainly through anthropogenic activities (Geol, 1997). Hence, likely source of Pb in water bodies is from soil erosion, municipal and industrial wastes and run off (DWAF, 1996). Soil erosion within Masinga reservoir catchment coupled with municipal waste discharges could be the source of Pb levels observed in this study. Kathini sampling station had slightly higher Pb levels than other sites and this could be attributed to industrial effluents discharged into Thika River from industries within the Thika Sub basin. The Pb levels observed in all the sampling stations were lower than the recommended limit of 0.01mg L<sup>-1</sup> in drinking water (WHO, 2008). This means that the water in Masinga reservoir is not polluted by Pb.

Studies done elsewhere in Kenya indicate higher Pb concentration levels. For example Oyoo-Okoth *et al.*, (2010) found mean Pb levels ranging from 0.26 – 0.99 mg L<sup>-1</sup> in Lake Victoria. Also, Muiruri *et al.*, (2013) recorded lower and higher mean Pb levels at different sites ( $nd - 0.047$  mg L<sup>-1</sup>) in surface water of Athi River tributaries. Other studies in Kenya that have recorded higher mean Pb levels include open waters of Winam gulf (0.2 mg L<sup>-1</sup>), River Nyando (0.19 mg L<sup>-1</sup>), and 0.015 mg L<sup>-1</sup> in River Sondu Miriu (Tole and Shitsama, 2003). Ochieng *et al.*, (2007) obtained higher mean Pb levels ranging 0.025 – 0.563 mg L<sup>-1</sup> in surface water of five Rift valley Lakes. Ochieng *et al.*, (2008) recorded Pb concentration levels of 0.006 – 0.048 mg L<sup>-1</sup> in Lake Kanyaboli, Kenya. Studies carried out by Olatunji and Osibanjo (2012) also recorded higher mean Pb levels (0.02 – 0.04 mg L<sup>-1</sup>) in surface water of River Niger, Nigeria.

**Table 3:** Mean  $\pm$  Standard deviation and range for heavy metal concentrations in surface water during the study period. Means in same row with different superscripts are significantly different at  $p < 0.05$  levels. Nd – Below detectable limit

Element/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg L <sup>-1</sup> )	$0.006 \pm 0.003^a$	$0.019 \pm 0.009^a$	$0.018 \pm 0.007^a$	$0.003 \pm 0.002^a$	$0.008 \pm 0.003^a$
Range	Nd – 0.026	Nd – 0.057	Nd – 0.073	Nd -0.020	Nd – 0.024
Zn (mg L <sup>-1</sup> )	$0.092 \pm 0.013^a$	$0.109 \pm 0.018^a$	$0.132 \pm 0.019^a$	$0.108 \pm 0.018^a$	$0.111 \pm 0.019^a$
Range	0.046 – 0.184	0.056 – 0.282	0.062 – 0.255	0.060 – 0.262	0.071 – 0.291
Pb (mg L <sup>-1</sup> )	$0.009 \pm 0.005^a$	$0.005 \pm 0.002^a$	$0.004 \pm 0.001^a$	$0.004 \pm 0.002^a$	$0.005 \pm 0.002^a$
Range	Nd -0.063	Nd – 0.023	Nd – 0.015	Nd – 0.023	Nd – 0.021
Cr (mg L <sup>-1</sup> )	$0.003 \pm 0.002^a$	$0.005 \pm 0.005^a$	$0.003 \pm 0.001^a$	$0.006 \pm 0.004^a$	$0.006 \pm 0.003^a$
Range	Nd – 0.028	Nd – 0.058	Nd – 0.013	Nd – 0.042	Nd – 0.039
Mn (mg L <sup>-1</sup> )	$0.085 \pm 0.084^a$	$0.006 \pm 0.005^a$	$0.038 \pm 0.037^a$	$0.012 \pm 0.006^a$	$0.146 \pm 0.046^a$
Range	Nd – 0.504	Nd – 0.033	Nd – 0.221	Nd – 0.031	0.003 – 0.348
Cd (mg L <sup>-1</sup> )	Nd	Nd	Nd	Nd	Nd

### 3.4 Chromium (Cr) concentration (mg L<sup>-1</sup>)

The mean Cr concentration levels recorded at different sampling stations during the study period ranged from  $0.003 \pm 0.001$  mg L<sup>-1</sup> (Manyatta) to  $0.006 \pm 0.004$  mg L<sup>-1</sup> (Riakanau). Mean Cr level at Tumutumu was  $0.006 \pm 0.003$  mg L<sup>-1</sup>, Mathauta  $0.005 \pm 0.005$  mg L<sup>-1</sup> and  $0.003 \pm 0.002$  mg L<sup>-1</sup> (Kathini). The Cr levels showed no significant variations ( $p > 0.05$ ) at different sites. The main sources of Cr are industrial wastes such as Cr pigment, tannery wastes, leather manufacturing wastes and municipal sewage sludge (Rahman *et al.*, 2012). In



this study, the elevated Cr levels at Tumutumumu and Riakanau could be attributed to municipal and tannery wastes from the towns located in the upper Masinga reservoir catchment. However, the mean Cr levels obtained in this study did not exceed the recommended limit of  $0.05 \text{ mg L}^{-1}$  for Cr in drinking water (WHO, 2008).

Compared to other studies, the mean Cr levels in surface water of Masinga reservoir were lower than  $0.23 - 0.79 \text{ mg L}^{-1}$  recorded in Lake Victoria (Oyoo-Okoth *et al.*, 2010),  $0.025 - 0.188 \text{ mg L}^{-1}$  in five rift valley lakes (Ochieng *et al.*, 2007) and  $0.068 \text{ mg L}^{-1}$  in Athi River tributaries (Muiruri *et al.*, 2013). Ochieng *et al.*, (2008) found mean Cr levels of  $0.005 - 0.061 \text{ mg L}^{-1}$  at different sites in Lake Kanyaboli while Olatunji and Osibanjo (2012) recorded a much higher mean Cr levels of  $1.19 - 3.16 \text{ mg L}^{-1}$  in River Niger, Nigeria compared to Cr levels in Masinga reservoir. A higher mean Cr level of  $0.049 \pm 0.02 \text{ mg L}^{-1}$  has been recorded in Owen multi-purpose dam water, Nigeria (Oyhakilome *et al.*, 2012). However, mean Cr levels observed at Masinga reservoir were within the range of  $0.003 - 0.088 \text{ mg L}^{-1}$  recorded in River Nile, Egypt (Osman and Kloas, 2010).

### 3.5 Manganese (Mn) concentration ( $\text{mg L}^{-1}$ )

There was no significant difference ( $p > 0.05$ ) in Mn levels in surface water at the different sampling sites. The mean Mn concentration ranged from  $0.006 \pm 0.005 \text{ mg L}^{-1}$  (Mathauta) to  $0.146 \pm 0.046 \text{ mg L}^{-1}$  (Tumutumumu). Kathini had the second highest mean Mn level ( $0.085 \text{ mg L}^{-1}$ ) in surface water while Manyatta and Riakanau had  $0.038 \text{ mg L}^{-1}$  and  $0.012 \text{ mg L}^{-1}$  respectively. In all the sampling sites the mean Mn concentration levels in surface water was found to be lower than recommended limit of  $0.40 \text{ mg L}^{-1}$  for Mn in drinking water (WHO, 2008). Mn is an abundant metal in earth's crust and usually occurs with iron. It is used in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient in various products (WHO 2011). It gets into the aquatic ecosystems from industries manufacturing dry-cell batteries, glass, and fertilizer and in leather and textile (Ziemacki *et al.*, 1989). The high levels observed at Kathini could be due to industrial activities in the Thika sub catchment while at Tumutumumu the Mn levels recorded may be due to high use of agricultural fertilizers, soil erosion and quarry activities within the catchment.

Comparable studies carried out in Kenya have recorded higher mean Mn values than observed in Masinga reservoir. These studies include those done by Lalah *et al.*, (2008) in Winam Gulf, Lake Victoria ( $0.05 - 3.276 \text{ mg L}^{-1}$ ) and Ochieng *et al.*, (2008) in Lake Kanyaboli, Kenya ( $0.185 - 0.376 \text{ mg L}^{-1}$ ). Also, Ochieng *et al.*, (2007) obtained higher mean levels of Mn in five rift valley lakes ( $0.050 - 0.282 \text{ mg L}^{-1}$ ). Akoto *et al.*, (2008) recorded similar mean Mn values ranging from  $0.099 - 0.140 \text{ mg L}^{-1}$  in Owabi reservoir, Ghana while Mahadev and Gholami (2010) in KRS reservoir, India observed ( $0.0001 - 0.107 \text{ mg L}^{-1}$ ) and Osman and Kloas (2010) in River Nile, Egypt ( $0.033 - 0.099 \text{ mg L}^{-1}$ ). Oyhakilome *et al.*, (2012) recorded higher Mn Values ( $0.346 \pm 0.391 \text{ mg L}^{-1}$ ) in Owen multi-purpose dam water, Nigeria.

## 4.0 Conclusion and recommendation

The results revealed the presence of heavy metals in Masinga reservoir. The metal concentrations were in the sequence  $\text{Zn} > \text{Mn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Cd}$ . All the heavy metals studied (Cu, Zn, Pb, Cr, Cd and Mn) had lower levels than WHO recommended limit for drinking water. However, since the local communities around Masinga reservoir use the water for irrigation and watering their livestock, there is need for regular monitoring of the heavy metals in the reservoir.

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