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# Selected heavy metal levels in water and fish from winam gulf in Lake Victoria near Kisumu city, Kenya

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## Abstract

Lake Victoria is the largest freshwater and fishery lake in Africa. Kisumu City, located at the shore of Winam Gulf has industrial activities discharging effluents into the lake with potential of contaminating the lake water with heavy metals. The contribution of these activities to heavy metal loads of lake water and fish from the gulf is not fully quantified. The assessment of the influence of the surrounding anthropogenic activities and seasons on the metal levels in aquatic samples (water and fish) from Winam Gulf is reported. Water was sampled in triplicates from sites at Molasses Plant, Coca-Cola Plant, Rivers Kisat and Kisian discharge points at intervals of 50 m from the shoreline into the lake in the wet and dry seasons. Fish samples were also collected in triplicates from the lake near Kisumu City. The samples were analyzed for heavy metals (Cd, Cr, Cu, Fe, Mn, Pb and Zn) using a calibrated AAS (6200 Shimadzu Model) following standard methods. There were variations at ($p \leq 0.05$) in the heavy metal levels with sites but not with seasons in both water and fish samples. The range of levels (µg/L) of all analyzed metals in lake water were: 0.20 (Cd) – 334 (Mn). The levels of all analyzed metals in the edible fish tissues (µg/g, *dw*) ranged from 0.40 (Pb) to 90.85 (Mn). The metal levels in lake water and fish were above WHO limits. The relatively high metal levels in water and fish were attributed to intense anthropogenic activities near the lake. Therefore, consumption of water and fish from Winam Gulf may pose health risks to the residents. There is need for regular environmental assessment of heavy metal levels in water and fish from the lake near Kisumu City.

**Keywords:** industrial activities, heavy metals, water, fish, winam gulf

## Introduction

Heavy metal pollution of aquatic ecosystems is a global problem (Mwita *et al.*, 2011; Orlu and Gabriel, 2011) [21, 29]. As human population increases, urbanization and industrial developments concurrently increase. This may lead to increase in heavy metals discharge into aquatic ecosystems causing water quality deterioration (Kishe, 2004; Deheyn and Latz, 2006; Franca *et al.*, 2005; Ochieng *et al.*, 2008; Lalah *et al.*,2009; Sarma, 2011; Orlu and Gabriel, 2011) [14, 4, 9, 16, 17, 30, 29]. There are increased concerns about possible accumulation of heavy metals in water and aquatic biota ultimately threatening human life (Gibbs and Miskiewicz, 1995) [10]. Some aquatic environments close to anthropogenic activities could rapidly become sources of ill health of aquatic species if the heavy metals discharged into aquatic environment are not controlled (Beyersmann and Hartwig, 2008; Earthwatch, 2009) [2, 5].

Freshwater bodies in developing countries were considered to be least polluted (Ochieng *et al.*, 2008) [16]. But the scenario could be changing rapidly due to increased anthropogenic activities that include mining, urbanization, agricultural and industrial developments in these countries (Ukonmaanaho *et al.*, 1998; Lwanga *et al.*, 2003; Kishe, 2004; Franca *et al.*, 2005; Deheyn and Latz, 2006; Ochieng *et al.*, 2008; Lalah *et al.*, 2009; Sarma, 2011; Orlu and Gabriel, 2011; La Kenya and Edwards, 2011; Mwita *et al.*, 2011) [36, 18, 14, 9, 4, 16, 17, 30]. Incidences of pollution of freshwater surfaces by heavy metals have reached an alarming rate in some surface freshwater (Mwita *et al.*, 2011) [21]. In freshwater bodies heavy metals can be bioaccumulated by aquatic organisms such as fish species until they reach toxic levels (Jain, 2004) [12]. The heavy metal contamination of freshwater bodies is less visible, but the effects on the ecosystem and humans could be intensive and extensive (Edem *et al.*, 2008) [6] compared to other pollutants. It is therefore necessary to determine heavy metal levels in surface waters in areas with high anthropogenic activities and evaluate if the predominant fish species in such waters are polluted with high heavy metals loads.

Lake Victoria is the largest freshwater lake in Africa with an area of 68,800 km$^2$ (Van Densen and Witte, 1995) [37]. The lake is shared by Kenya, Uganda and Tanzania. The shoreline of the lake is surrounded by many towns with different anthropogenic activities and regions with different geochemical processes. These activities and geochemical processes could cause variations in heavy metal levels in water in its various parts (Lalah *et al.*, 2009) [17]. The maintenance of a healthy Lake Victoria ecosystem is therefore a challenge to concerned agencies. In the 1980s, heavy metal pollution was not detected in the lake (Onyari, 1985; Ochieng, 1987; Onyari and Wandiga, 1989). However, recently, sediments, water and biota have shown a general increasing trend in heavy metal levels (Ochieng *et al.*, 2008; Ongeri, 2008; Lalah *et al.*, 2009; Mwita *et al.*, 2011) [16, 26]. Water quality from the Winam Gulf of Lake Victoria has also declined with time (Ochieng 1987; Ongeri, 2008) [26]. The trend was attributed to increase in urbanization, agricultural activities, pharmaceutical discharges, domestic discharges, industrial processes and municipal waste discharges (Ochieng 1987; Ongeri, 2008; Ochieng *et al.*, 2008; Lalah *et al.*, 2009; Mwita *et al.*, 2011) [24, 26, 16, 21].

Generally, levels of metallic pollutants in aquatic samples are greatest near towns, indicating their urban industrial origins (Tole and Shitsama, 2001). Traces of heavy metals find their ways into aquatic environment through surface runoffs, inflowing rivers and direct waste discharges into the lake from surrounding anthropogenic activities. Kisumu City, on the shoreline of Winam Gulf is characterized by several anthropogenic activities including several industries such as the Coca-Cola Plant, Kisumu International Airport, Molasses Plant, Kenya Pipeline Depot, Kenya Marine and Fisheries Research Institute (KMFRI), Kenya Medical Research Institute (KEMRI), Port Florence Hospital, Kisumu-Busia Highway and Kisumu-Butere railway line that runs parallel to the lakeshore, Bandani and Obunga slums among others. These activities discharge their effluents, either poorly treated or untreated directly or indirectly into the lake (Kishe and Machiwa, 2001). These industrial activities and processes have caused increase of heavy metal concentrations (Lwanga *et al.*, 2003; Chaparro *et al.*, 2004; Lalah *et al.*, 2009; Sekabira *et al.*, 2010) [18, 3, 17, 31] in water and fish. Previous studies determined heavy metal levels in water without considering the locational sources. Thus, the effects of proximity of the anthropogenic activities on heavy metal levels in water samples in the Winam Gulf of Lake Victoria near Kisumu City have not been evaluated. This study evaluated the effects of locational anthropogenic activities within the area on the heavy metal levels in lake water and selected fish species (*Lates niloticus*, *Synodontis victoriae*, *Oreochromis niloticus* and *Clarias batrachus*).

## Materials and Methods

### Study Area

The study was carried out within latitudes 00˚ 05’46. 00’’ to 00° 05’ 08.13’’ S and longitudes 34˚ 41’15. 96’’ to 34° 45’ 01.76’’ E (Kisumu County, Western Kenya), between two streams namely; Rivers Kisat and Kisian, which drain into Winam Gulf near Kisumu City (Figure 1). River Kisat drains an area with dense industrial activities while River Kisian drains an area with minimum anthropogenic activities.

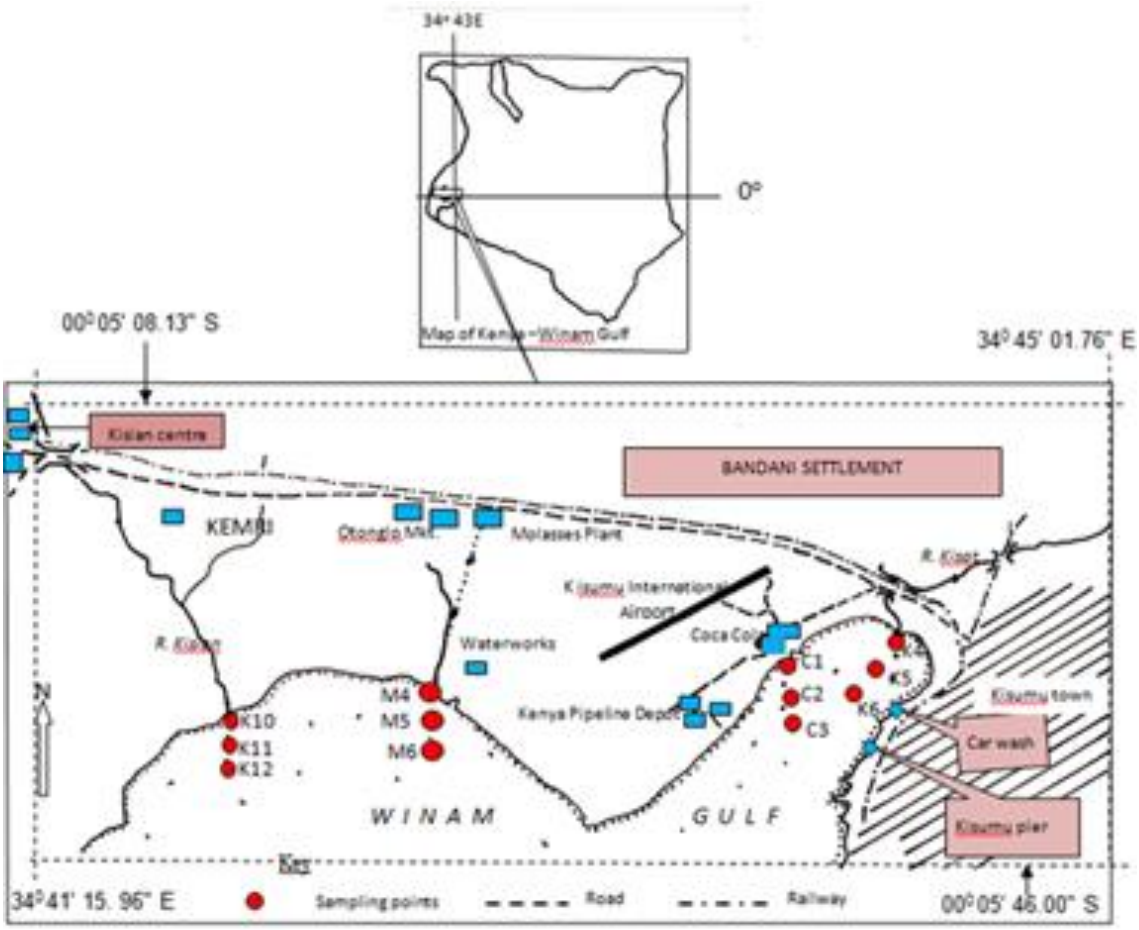

**Fig 1:** Sketch map of Winam Gulf showing sampling sites in Lake Victoria near Kisumu City

### Sampling

Twelve sampling sites in the Winam Gulf shoreline near Kisumu City were selected at four different discharge points into the lake. The sampling discharge points were based on the activities within the adjacent land. These were River Kisat, Coca Cola Plant, Molasses Plant and River Kisian discharge points. At each discharge point, three sampling sites at intervals of 50 m from the shore into the lake were identified (Figure 1). Water samples were taken in triplicates. Six sites $K_4$, $K_5$, $K_6$ and $C_1$, $C_2$ and $C_3$ were selected within the lake shoreline stretch receiving discharges from the Kisumu Industrial Area (Discharge points of River Kisat and Coca Cola Plant respectively). Sites $M_4$, $M_5$ and $M_6$ were within the lake at the discharge point of Molasses Plant and sites $K_{10}$, $K_{11}$ and $K_{12}$ were in the lake at the discharge point of River Kisian.

Sampling was conducted during the wet season (April 2013) and the dry season (January 2014). Water samples, 500 mL were taken by immersing plastic bottles, pretreated with conc. $HNO_3$) to a depth of one metre and lifting up then mixing with 2 mL of concentrated $HNO_3$ (for preservation). The samples were stored in a refrigerator at $4^oC$ awaiting processing and analysis. Different fish species (*Lates niloticus*, *Synodontis victoriae, Oreochromis niloticus* and *Clarias batrachus*) were netted in the lake area under study using appropriate gill nets. The sampled fish species were stored in an ice box at $0^oC$ for transportation to the laboratory where were rinsed with de-ionized water and stored in a deep freezer awaiting digestion and analysis.

## Sample preparation

Water samples of exactly 100 mL each were pre-concentrated to 20 mL and digested at 100°C for three hours using a mixture of HCL and $HNO_3$ concentrated acids. The digests were cooled, then filtered using 0.45 µm polyethersulfoon filter membrane into a 50 mL volumetric flask and diluted to the mark with de-ionized water ready for metal analysis using calibrated Atomic Absorption Spectrophotometer (AAS 6200 Shimadzu Model) for metals Cd, Cr, Cu, Fe, Mn, Pb and Zn. The lower limit of detection of the instrument was 0.001µg/g.

The edible tissue muscles of the different fish species were dried to constant weight in an automated oven (Mermet model) at $105^oC$. One gram of the sub-sample of each fish species was homogenized and digested using concentrated acids ($HNO_3/H_2SO_4$ mixture 1:1). The digest was cooled, then filtered using 0.45 µm polyethersulfoon filter membrane into a 50 mL volumetric flask and diluted to the mark with de-ionized water ready for the same heavy metals analysis as in water samples using the calibrated AAS 6200 spectrophotometer.

## Results and Discussion

### Effects of distance from the shore into the lake on heavy metal levels in lake water

The levels (µg/L) of the seven analyzed heavy metals in water samples from the lake areas adjacent to the discharge points of River Kisat, Coca Cola Plant, Molasses Plant and River Kisian are presented in Table 1.

### Kisat discharge point

Except for Fe, the heavy metal levels in water at River Kisat discharge point decreased ($p \leq 0.05$) with the increase in distance from the shore into the lake. Levels of Pb, Mn, Cr, Cu, Zn and Cd were in the same pattern but higher than those in previous studies within Winam Gulf (Tole and Shitsama, 2001; Ongeri, 2008; Lalah *et al.*, 2009; Mwita *et al.*, 2011) [26, 21] (Table 2). The results confirm that the surrounding anthropogenic activities are continuously increasing heavy metal loading into the lake. The constant levels of Fe with distance from shore suggest the Fe levels might not have been arising from the activities within the adjoining Kisumu City area. The Cr levels in water were above the recommended allowable threshold limit for aquatic life tolerance by WHO (2004) [26] and European Union or Canada (Neubauer and Wolf, 2004) [23] (Table 2). The anthropogenic activities in the lake and/or adjoining environment were therefore causing Cr pollution of the Winam Gulf water. It is therefore necessary to establish the point sources of Cr to enable deployment of appropriate mitigation measures. The decrease ($p \leq 0.05$) in heavy metal levels in water with distance from the shore into the lake was due to dilution and dispersion effects caused by water currents and waves in the lake. Other activities possibly contributing to heavy metal loads into the lake include direct industrial discharges, pharmaceutical discharges, surface urban runoffs from the *Jua Kali* battery and scrap metal entrepreneurs, municipal, domestic wastewater, Kisumu-Busia Highway oil spillages and fuel exhausts from the automobiles in the city, motorised boats in the lake area, car washing activities directly opposite the site at approximately a kilometre away and close proximity of Bandani and Obunga settlements slums. The heavy metal levels in water from River Kisat discharge point did not show significant seasonal variations. These results were at variance with previous results from Winam Gulf water (Ongeri, 2008) [26] where seasonal variations were recorded. The results indicate that the activities around and within the area could be uniform and continuous during the two seasons. This suggests possible direct discharges of the pollutants caused by non-seasonal events as the major cause of heavy metal pollution in the lake area.

### Coca-Cola discharge point

In the lake around the discharge point of the Coca-Cola Plant, the heavy metal levels decreased ($p \leq 0.05$) with distance from the shore into the lake with an exception of Zn (Table 1). There were similar patterns as in previous related studies (Tole and Shitsama, 2001; Lalah *et al.*, 2009; Mwita *et al.*, 2011) [17, 21]. The decreased metal concentrations with increased distance into the lake indicated dilution effects. The Pb levels in the lake water from this site were low compared to levels recorded in previous related studies in Winam Gulf (Tole and Shitsama, 2001, Tole and Shitsama, 2003) (Table 2). This implies that there could be decrease in Pb related activities or improvement in Pb waste management practices within the area. The results were however, higher than those observed in water samples from the Kisumu car wash in the lake near Kisumu City (Lalah *et al.*, 2009) [17].

The Zn levels were lower than those measured in Mwanza Gulf of Lake Victoria, Tanzania (Kisamo, 2003) [13], but higher than those recorded in water samples from the Kisumu car wash in the Winam Gulf (Lalah *et al.*, 2009) [17] (Table 2). The Zn levels increased within and/or around the site suggesting increase in releasing activities. The activities may include *Jua Kali* car maintenance activities, motorised boating, urbanization, automobiles and food processing industries. This observation may also be attributed to discharges emanating from the Kisat Wastewater Treatment Plant as was demonstrated as a point source in recently concluded study (Shikuku *et al.*, 2017) [32]. The Cd levels were low compared to those recorded earlier in Winam Gulf water (Tole and Shitsama, 2001). All the heavy metals in water samples were below the recommended permissible limits for aquatic life and human use purposes (WHO, 2004). (Table 2).

There were no significant seasonal variations in levels of heavy metals in water from this site except for Fe (Table 1). Possibly, the activities emitting heavy metals into the lake water from this point did not vary with seasons for the studied heavy metals except Fe. These results were at variance with previous study (Ongeri, 2008) [26] in the Winam Gulf where heavy metal concentrations increased during the wet season. Thus, the heavy metal levels in the Winam Gulf seem to be dependent on locations.

**Molasses discharge point**

The heavy metal levels in water from the Molasses Plant discharge point decreased ($P \leq 0.05$) with the increased distance into the lake from the shore (Tables 1). The levels were generally lower than those obtained in previous related studies in various parts of Lake Victoria (Tole and Shitsama, 2001; Tole and Shitsama, 2003; Kisamo, 2003; Ongeri, 2008; Mwita *et al.*, 2011) [13, 26, 21] (Table 2) or Lake Kanyaboli in Kenya (Lalah *et al.*, 2008) The range of Pb in the water was low compared to ranges in previous studies (Tole and Shitsama, 2001, Tole and Shitsama, 2003) (Table 2) from the Winam Gulf. The Zn levels were lower than those obtained previously in the Winam Gulf (Mwita *et al*., 2011), but higher than the levels in water from Kisumu Car Wash area (Lalah *et al.*, 2009) [17]. The Cr levels in lake water were lower than those obtained in a past study from the same lake area (Mwita *et al*., 2011) [21]. It seems either there was reduction of Cr emitting activities or an improvement in the management of Cr containing wastewaters. Levels of Cd in lake water were lower than those observed in water samples in previous studies in the Winam Gulf (Tole and Shitsama, 2001; Tole and Shitsama, 2003; Lalah *et al.*, 2009) [26, 34] (Table 2).

**Table 1:** Variations in levels of selected heavy metals in lake water from different discharge points into Lake Victoria near Kisumu City with distance and seasons

| Site | Distance | Pb | Cr | Cu | Zn | Fe | Mn | Cd |
|---|---|---|---|---|---|---|---|---|
| Kisat | 0m | 15.50 | 62.50 | 35.00 | 32.00 | 289.00 | 388.50 | 2.24 |
| | 50m | 9.00 | 56.00 | 26.50 | 17.00 | 218.00 | 318.00 | 1.13 |
| | 100m | 6.00 | 46.50 | 14.00 | 13.50 | 168.50 | 300.00 | 0.65 |
| C.V. (%) | | 10.79 | 6.10 | 3.41 | 20.55 | 2.21 | 5.13 | 8.00 |
| LSD ($p \leq 0.05$) | | 2.50 | 11.50 | 2.00 | 18.50 | NS | 42.50 | 0.27 |
| Mean (season) | Wet | 10.50 | 55.00 | 26.00 | 23.00 | 235.50 | 341.50 | 1.44 |
| | Dry | 9.50 | 52.50 | 24.00 | 19.00 | 215.00 | 324.50 | 1.26 |
| LSD ($p \leq 0.05$) | | NS | NS | NS | NS | NS | NS | NS |
| Coca-Cola | 0m | 8.50 | 43.00 | 33.50 | 16.50 | 192.00 | 252.50 | 1.25 |
| | 50m | 7.00 | 37.50 | 27.50 | 16.00 | 166.50 | 175.00 | 1.09 |
| | 100m | 5.00 | 36.50 | 13.00 | 15.50 | 153.50 | 144.00 | 0.91 |
| C.V. (%) | | 4.23 | 5.57 | 4.23 | 6.27 | 2.40 | 16.09 | 7.38 |
| LSD ($p \leq 0.05$) | | 0.50 | 5.50 | 2.50 | NS | 10.00 | 76.00 | 0.20 |
| Mean (season) | Wet | 7.50 | 41.00 | 26.00 | 16.50 | 184.00 | 194.50 | 1.16 |
| | Dry | 6.50 | 37.00 | 23.50 | 15.50 | 157.00 | 186.50 | 1.01 |
| LSD ($p \leq 0.05$) | | NS | NS | NS | NS | 0.05 | NS | NS |
| Molasses | 0m | 7.00 | 35.50 | 17.50 | 19.50 | 163.50 | 92.50 | 0.29 |
| | 50m | 6.50 | 32.00 | 11.50 | 12.50 | 122.00 | 74.50 | 0.21 |
| | 100m | 7.00 | 27.50 | 6.50 | 11.50 | 52.00 | 61.50 | 0.11 |
| C.V. (%) | | 9.51 | 4.26 | 3.91 | 14.41 | 4.93 | 13.18 | 22.51 |
| LSD ($p \leq 0.05$) | | 1.50 | 3.50 | 1.00 | 5.00 | 15.50 | 25.00 | 0.11 |
| Mean (season) | Wet | 6.00 | 35.00 | 12.50 | 15.50 | 135.50 | 78.50 | 0.20 |
| | Dry | 5.50 | 29.00 | 11.00 | 13.50 | 119.50 | 74.00 | 0.21 |
| LSD ($p \leq 0.05$) | | NS | NS | NS | NS | NS | NS | NS |
| Kisian | 0m | 7.00 | 30.00 | 15.50 | 10.00 | 225.50 | 102.00 | 0.30 |
| | 50m | 4.50 | 21.50 | 6.00 | 9.00 | 190.00 | 87.00 | 0.22 |
| | 100m | 3.50 | 10.50 | 4.00 | 7.50 | 134.50 | 79.00 | 0.15 |
| C.V. (%) | | 6.98 | 7.28 | 12.14 | 25.61 | 9.98 | 15.66 | 21.21 |
| LSD ($p \leq 0.05$) | | 1.00 | 3.50 | 2.50 | NS | 45.50 | NS | 0.12 |
| Mean (season) | Wet | 5.50 | 23.00 | 9.8 | 9.50 | 189.00 | 92.50 | 0.23 |
| | Dry | 5.00 | 18.50 | 8.50 | 8.00 | 177.50 | 86.00 | 0.22 |
| LSD ($p \leq 0.05$) | | NS | NS | NS | NS | NS | NS | NS |
| Overall mean (season) for all 4 sites | Dry | 7.50 | 39.00 | 19.50 | 16.50 | 185.00 | 177.00 | 0.75 |
| | Wet | 6.50 | 34.50 | 16.50 | 14.00 | 168.00 | 167.50 | 0.67 |
| C.V.% | | 9.52 | 5.69 | 9.09 | 15.43 | 6.54 | 11.03 | 9.28 |
| LSD ($p \leq 0.05$) | | NS | 7.00 | NS | NS | NS | NS | NS |
| Overall mean (distance) for all 4 sites | 0m | 9.50 | 43.00 | 25.00 | 19.50 | 217.50 | 209.00 | 1.02 |
| | 50m | 6.50 | 37.00 | 20.00 | 13.50 | 174.00 | 163.50 | 0.66 |
| | 100m | 5.00 | 30.50 | 9.00 | 12.50 | 138.50 | 144.50 | 0.45 |
| C.V% | | 9.52 | 5.69 | 9.09 | 15.43 | 6.54 | 11.03 | 9.28 |
| LSD ($p \leq 0.05$) | | 1.00 | 7.00 | 2.00 | 3.00 | NS | 23.50 | NS |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Overall mean (site) for all 4 sites | Kisat | 10.00 | 55.00 | 25.00 | 21.00 | 225.00 | 334.00 | 1.34 |
| | Coca-Cola | 7.00 | 39.00 | 24.50 | 16.00 | 170.50 | 190.50 | 1.08 |
| | Molasses | 6.00 | 32.00 | 12.00 | 14.50 | 127.50 | 76.00 | 0.20 |
| | Kisian | 5.00 | 21.00 | 8.00 | 9.00 | 183.50 | 89.00 | 0.22 |
| C.V.% | | 9.52 | 5.69 | 9.09 | 15.43 | 6.54 | 11.03 | 9.28 |
| LSD ($p \leq 0.05$) | | 0.50 | 6.00 | 2.00 | 2.50 | NS | 20.50 | 0.07 |
| Interactions ($p \leq 0.05$) | | S x D =1.00 | S x D = 3.00 | SxD=2.00, SxS1=2.50, DxS1=2.50, | S x D = 3.50 | S x D = 16.00 | S x D = 27.00 | SxD=0.09, SxS1=0.10 |

NS = Not significant; S = Site; S1 = Season; D = Distance

**Table 2:** Comparing levels (µg/L) of heavy metals in lake water with past studies and maximum international allowable limits for aquatic life and other uses

| Reference/ Study limit | | Water use | Cu | Pb | Mn | Zn | Cd | Cr | Fe |
|---|---|---|---|---|---|---|---|---|---|
| Tole and Shitsama, 2001(Winam Gulf) (µg/L) | | | - | 120.00-450.00 | - | - | 10.00 | 160.00-1820.00 | - |
| Kisamo, 2003 [13] (µg/L) L. Victoria, Tanzania | | | - | 350.00-630.00 | - | 40.00-80.00 | - | - | 10.00-5620.00 |
| Tole and Shitsama, 2003 (µg/L) (Winam Gulf) | | | - | 190.00-200.00 | - | - | 10.00 | - | - |
| Muwanga and Barifaijo, 2006 (Lake Victoria, Uganda) (µg/L) | | | 60.00 | 1440.00 | 1170.00 | 10.00 | 1.00 | 20.00 | - |
| Lalah *et al.*, 2009a (µg/L) (Kisumu car wash) | | | 1.62 | >3.84 | - | 6.37 | >1.79 | - | 2440.00 |
| Lalah *et al.*, 2009a. (R. Nyamasaria) (µg/L) | | | 3.83 | 3.83 | - | 7.90 | 1.78 | - | 1012.00 |
| Mwita *et al.*, 2011 [21] (Lake area near River Kisat) (µg/L) | | | - | - | - | 36.00 | - | 157.00 | - |
| Kisian discharge point (µg/L)$^a$ | | | 8.00 | 5.00 | 89.50 | 9.00 | 0.22 | 21.00 | 183.50 |
| Molasses discharge point (µg/L)$^a$ | | | 12.00 | 6.00 | 76.00 | 14.50 | 0.20 | 32.00 | 127.50 |
| Coca-Cola discharge point (µg/L)$^a$ | | | 24.50 | 7.00 | 190.50 | 16.00 | 1.08 | 39.00 | 170.50 |
| Kisat discharge point (µg/L)$^a$ | | | 25.00 | 10.00 | 334.00 | 21.00 | 1.34 | 55.00 | 225.00 |
| TC$^b$ | (µg/L) | Aquatic Life | 2.00 - 104.00 | 100.00 | - | 100.00 | 10.00 | 50.00 | - |
| EU$^b$ | | | 5-112 | - | - | 30.00-2000.00 | - | - | - |
| Canada$^b$ | | | 2.00 - 4.00 | 1.00 - 7.00 | - | 30.00 | 0.20-1.80 | - | 300.00 |
| Canada$^b$ | | Drinking water | 1000.00 | 50.00 | - | 5000.00 | 5.00 | - | 300.00 |
| WHO (2004) (µg/L) | | Standards | 1000.00 | 10.00 | 400.00 | 5000.00 | 3.00 | 50.00 | 300.00 |

***Source:*** International data of standards obtained from Lalah *et al.*, 2009a

nd: not detected, TC: threshold concentration for aquatic life tolerance (for most fishes), Neubauer and Wolf (2004) [23].

$^a$ Present study, 2018 Kenya.

$^b$ Neubauer and Wolf (2004)

There was reduction in Cd levels over time an indication that there could be improved management of waste discharges and/or reduction in activities related to Cd pollution into the environment. The observed low levels of Cd can be associated to lesser Cd producing anthropogenic activities which may be found around. However, the Cu levels were higher than those in water from the Kisumu car wash area (Lalah *et al.*, 2009).

These observations demonstrated that there were varied anthropogenic activities that were responsible for the levels of the studied metals at the discharge point. The heavy metal concentrations recorded at the Molasses Plant discharge point were below the international (WHO, 2004) set limits for drinking and fisheries water (Neubauer and Wolf, 2004) [23] (Table 2). The results showed that water from the site was safe for domestic use and aquatic life. There were no seasonal variations ($p \leq 0.05$) in the studied heavy metal levels in water in the Molasses Plant discharge point. These results contradict the observations made in water samples from Winam Gulf where the metal levels in water were significantly ($p \leq 0.05$) higher in the wet season than in the dry season (Ongeri, 2008) [26]. Therefore, these results suggested that the anthropogenic activities within the lake area and on the adjoining land were not exhibiting seasonal differences in the discharge of the heavy metals.

## Kisian discharge point

The levels of Pb, Fe, Cr, Cd and Cu (Table 1) in water samples from Kisian discharge point decreased ($p \leq 0.05$) with increased distance into the lake from the shore. Pb, Cu, and Zn levels were higher than the levels obtained in a study in Winam Gulf at the Kisumu Car Wash (Lalah *et al.*, 2009) (Table 2). However, Pb, Zn, Fe, Cd and Cr levels were lower than those obtained in water samples from different sites of Lake Victoria in Tanzania (Kisamo, 2003) [13] and Kenya (Tole and Shitsama, 2001; Mwita *et al.*, 2011) [21] (Table 2). Range of Pb levels in water samples in the current study was comparable to those from Kisumu car wash (Lalah *et al.*, 2009a) (Table 2). However, the levels were much lower compared to those from Mwanza Gulf (350.00-630.00 µg/L) in Tanzania (Kisamo, 2003) [13] and in Uganda (Muwanga and Barifaijo, 2006) (Table 2). The data demonstrated that the anthropogenic activities in these different areas may be different or the intensity of the activities found in each area may be different. However, the differences in metal levels in the areas indicated either few activities or lack of activities emitting the metals into the water system. The Zn (9.00 - 21.00 µg/L) levels were higher compared to levels (6.37 µg/L) in water samples from the Kisumu car wash (Lalah *et al.*, 2009a) an indication that there was an unknown source of the metal in the lake around

River Kisian discharge point which caused the pollution. There is therefore need to determine and monitor the source of this metal to enable appropriate mitigation measures. However, these levels were lower than those obtained in water samples from Mwanza Gulf (Kisamo, 2003) [13] and in water samples from Lake Victoria in Uganda (Muwanga and Barifaijo, 2006) (Table 2). Levels of Cd and Fe in water samples from this site were 0.20 and 183.50 µg/L respectively and were lower compared to levels obtained in water samples from the Kisumu car wash area which had >1.78 and 2440.00 µg/L, respectively (Lalah *et al.,* 2009) (Table 2). Thus, the activities within and around the lake area at Kisian discharge point were contributing insignificant heavy metals loads into the lake water. All the studied heavy metal levels in the lake water in this site were within the international allowable levels for drinking water and aquatic life (WHO, 2004; Neubauer and Wolf 2004) [23] (Table 2). Therefore water from this site was safe for fisheries and domestic use. The levels of studied heavy metals showed no seasonal variation ($p \leq 0.05$) (Tables 1) although wet season recorded higher levels for all studied metals showing a general trend. These results were in variance with the observed results in water samples from the Winam Gulf where heavy metal levels varied with seasons (Ongeri, 2008) [26]. The lack of seasonal variations ($p \leq 0.05$) in heavy metal levels in lake water was similar to those observed in water samples from Kisat, Coca-Cola Plant and Molasses Plant discharge points in this study. Thus, heavy metal loads in lake water from this site may partly be attributed to anthropogenic activities and geochemical sources.

### Comparison of heavy metal levels in lake water from different studied sites

Overall, levels of Pb, Cr, Cu, Mn and Zn in the lake water for all the four sites decreased ($p \leq 0.05$) with the increase in distances into the lake from the shore with an exception of Fe and Cd metals (Table 1). These results were in agreement with the observations made for water samples from the Winam Gulf at the river deltas of Rivers Nyamasaria, Sondu-Miriu, Kuja, Awach,Yala, Sio, Nyando and Nzoia (Ochieng *et al.,* 2008; Ongeri, 2008; Lalah *et al*., 2009b) [16, 26] where dilution effects were observed as the distance increased into the lake. The metal levels in water samples from the four sites did not exhibit seasonal variations ($p \leq 0.05$) (Table 1). The results obtained were in variance with previous data (Ongeri, 2008) [16] on lake water which showed seasonal variations. These observations implied that seasonal runoffs from the area did not influence the heavy metal pollution of the studied metals into the lake water despite a general effect of season seen for all studied metals during the wet season though insignificant. The results demonstrated that the non-seasonal events within the sites were the major sources of heavy metal pollution into the lake.

The levels of all analyzed heavy metals in water varied significantly ($p \leq 0.05$) among the sites, except for the levels of Fe (Table 1). Results of the current study were in agreement with those obtained in various parts of Lake Victoria in Kenya (Tole and Shitsama, 2001; Tole and Shitsama, 2003; Lalah *et al.*, 2009a; Mwita *et al*., 2011) [34, 21] and Tanzania (Kisamo, 2003) [13] (Table 2). The significant site variations ($p \leq 0.05$) observed in all the sites for the analyzed metals reflected the differences in the anthropogenic activities responsible for the heavy metal pollution at the sites. There were significant interactions ($p \leq 0.05$) effects between site and distance in all analyzed heavy metals. Thus, the trend of change in heavy metal concentrations in water due to variations of site activities and variations in distances of the discharge sources to sampling points of water samples were not uniform. This was due to the variations in anthropogenic activities along the channels draining water to the different sites. The levels of Cd and Cu in water samples showed significant interactions ($p \leq 0.05$) effects between sites and seasons at all sites. Thus, the patterns of seasonal changes in the Cd and Cu levels at locations and seasons variations were not the same. The observed results may be attributed to variations in sources of heavy metals into the ecosystem at the different sites and in different seasons. Cu in water samples showed significant interaction ($p \leq 0.05$) effects between season and distance in all sites. These observations indicated that the trends of change in Cu levels due to variations in seasons and the different distances of the activities emitting the metal to the sampling points of the water samples was not uniform.

### Evaluation of heavy metals in fish

The dry weight (µg/g) levels of metals (Pb, Cd, Cu, Zn, Mn, Cr and Fe) in muscle tissues of the four selected fish species (*Lates niloticus, Synodontis victoriae, Oreochromis niloticus and Clarias batrachus)* are presented in (Table 3). Fe and Cd levels in all the four fish species were not significantly different. Levels of Fe in *Lates niloticus* and *Oreochromis niloticus* of 33.70 and 36.90 µg/g, respectively, were close to 45.70 and 48.00 µg/g obtained in a previous study (Ongeri, 2008) [26] on the same fish species from Winam Gulf (Table 4). However, the Fe levels in *Lates niloticus* and *Oreochromis niloticus* were higher than levels obtained in a related study (Achionye-Nzeh *et al*., 2011) in Nigeria (Table 4). The levels of Cd in *Lates niloticus* and *Oreochromis niloticus* were within the range obtained (Tole and Shitsama, 2003) in the same fish species from Lake Victoria (Table 4). The levels of Fe in the tissues of all analyzed fish species were within the acceptable levels for human consumption (Wyse *et al*., 2003) [39] (Table 5). The Cd levels in tissues of all analyzed fish species were above the international recommended levels 0.05 µg/g (FAO/WHO, 2004) (Table 5). Fe levels in the fish were therefore safe for human consumption. However, consumption of fish from the lake shall have health risks due to Cd. Thus there is need for the concerned policy makers to put in place measures to mitigate the Cd metal pollution into the lake.

**Table 3:** Seasonal heavy metal variations in concentrations (µg/g in dry weight) in selected fish species obtained from Winam Gulf of Lake Victoria

| Metal | Season | L. niloticus | S. victoriae | O. niloticus | C. batrachus | Mean Seasons |
|---|---|---|---|---|---|---|
| Fe | Wet | 35.15 | 36.35 | 35.35 | 37.75 | 36.15 |
| | Dry | 32.25 | 36.85 | 38.50 | 35.10 | 35.65 |
| Mean species | | 33.70 | 36.60 | 36.90 | 36.40 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| C.V. (%) | | 19.80 | | | | |
| LSD (p ≤ 0.05) | | NS | | | | NS |
| Zn | Wet | 42.30 | 38.60 | 40.85 | 32.00 | 38.45 |
| | Dry | 40.05 | 36.95 | 38.55 | 30.65 | 36.55 |
| Mean species | | 41.20 | 37.80 | 39.70 | 31.30 | |
| C.V. (%) | | 12.62 | | | | |
| LSD (p ≤ 0.05) | | 8.70 | | | | NS |
| Pb | Wet | 0.65 | 0.35 | 0.60 | 0.55 | 0.55 |
| | Dry | 0.60 | 0.40 | 0.60 | 0.50 | 0.50 |
| Mean species | | 0.65 | 0.40 | 0.60 | 0.50 | |
| C.V. (%) | | 15.10 | | | | |
| LSD (p ≤ 0.05) | | 0.15 | | | | NS |
| Cr | Wet | 0.90 | 0.70 | 0.80 | 0.60 | 0.75 |
| | Dry | 0.75 | 0.60 | 0.80 | 0.55 | 0.70 |
| Mean species | | 0.80 | 0.65 | 0.80 | 0.55 | |
| C.V. (%) | | 15.36 | | | | |
| LSD (p ≤ 0.05) | | 0.20 | | | | NS |
| Cu | Wet | 3.75 | 3.45 | 3.60 | 2.85 | 3.40 |
| | Dry | 3.55 | 3.25 | 3.40 | 2.85 | 3.25 |
| Mean species | | 3.65 | 3.35 | 3.50 | 2.85 | |
| C.V. (%) | | 12.75 | | | | |
| LSD (p ≤ 0.05) | | 0.80 | | | | NS |
| Cd | Wet | 0.70 | 0.70 | 0.70 | 0.55 | 0.65 |
| | Dry | 0.70 | 0.65 | 0.65 | 0.65 | 0.65 |
| Mean species | | 0.70 | 0.65 | 0.65 | 0.60 | |
| C.V. (%) | | 14.77 | | | | |
| LSD (p ≤ 0.05) | | NS | | | | NS |
| Mn | Wet | 76.15 | 80.55 | 92.65 | 85.00 | 83.60 |
| | Dry | 73.20 | 79.10 | 89.10 | 81.30 | 80.70 |
| Mean species | | 74.70 | 79.85 | 90.85 | 83.15 | |
| C.V. (%) | | 5.24 | | | | |
| LSD (p ≤ 0.05) | | 7.90 | | | | NS |

NS = Not significant

Zn levels in tissues from *Lates niloticus*, *Synodontis victoriae and Oreochromis niloticus* fish species were not different (p≤0.05) (Table 3). The Zn levels in tissues of *Clarias batrachus* were lower (p≤0.05) than the levels noted in the *Lates niloticus* (Table 3). These levels were close to results obtained in a study (Ongeri, 2008) [26] on Zn levels in *Oreochromis niloticus* and *Lates niloticus* tissues from Winam Gulf in Lake Victoria (Table 3). However, the Zn levels in *Lates niloticus* tissues in the current study were higher than levels obtained in previous related studies (Machiwa, 2003; Ongeri, 2008) [19, 26] on the same fish species from Lake Victoria and freshwater fish bought from the market in Nigeria (Achionye-Nzeh *et al*., 2011) (Table 3). The Zn metal concentrations in the tissues of the studied fish species were above the WHO recommended acceptable levels in human diet (FAO/WHO, 2004) (Table 5). Consumption of fish from the lake may therefore cause Zn related health problems such as fatigue, dizziness and netropenia (Hess and Schmid, 2002) [11].

**Table 4:** Comparison of levels of heavy metals (µg/g in dry weight) in the fish species (*Oreochromis niloticus and Lates niloticus)* with data from previous similar studies

| | **Fish species** | **Pb** | **Cd** | **Cu** | **Zn** | **Fe** | **Mn** |
|---|---|---|---|---|---|---|---|
| Onyari, 1985 [27] | *L. niloticus* | 0.40-33.70 | 0.04-3.10 | - | - | - | - |
| Tole and Shitsama, 2003 [34] | *O. niloticus* | 3.60-20.30 | 0.30-1.40 | - | - | - | - |
| | *L. niloticus* | 13.80-15.80 | 0.60-0.90 | - | - | - | - |
| Machiwa, 2003 [19] | *L. L. niloticus* | 0.13 | 0.00 | 0.70 | 8.80 | - | - |
| Ongeri, 2008 [26] | *O. niloticus* | 0.61 | 0.21 | 2.70 | 35.90 | 48.00 | - |
| | *L. niloticus* | 0.87 | 0.21 | 3.40 | 36.40 | 45.70 | - |
| Achionye-Nzeh *et al*., 2011 [1] | *L. niloticus* | - | - | 0.30-0.40 | 0.70-0.90 | 5.70-5.90 | 0.9-8.0 |
| | *O. niloticus* | - | - | 0.1-0.2 | 0.4-0.6 | 5-6.0 | 6.4-12.6 |
| Current study | *O. niloticus* | 0.60 | 0.65 | 3.50 | 39.70 | 36.90 | 90.85 |
| | *L. niloticus* | 0.65 | 0.70 | 3.65 | 41.20 | 33.70 | 74.70 |
| Ekeanyanwu *et al*., 2010 [7] | *O. niloticus* | < 0.01 | 0.62 | - | - | - | 1.97 |

**Table 5:** Comparison of heavy metal levels (µg/g in dry weight) in tissues of selected fish species with international permissible limits

| | Lates niloticus | Synodontis victoriae | Oreochromis niloticus | Clarias batrachus | Wyse et al., 2003 [39] (IAEA-407) (µg/g) | FAO/WHO 2004 (ug/g) |
|---|---|---|---|---|---|---|
| Fe | 33.70 | 36.60 | 36.90 | 36.4 | 146.00 | nl |
| Zn | 41.20 | 37.80 | 39.70 | 31.30 | nl | 0.30-10 |
| Pb | 0.65 | 0.40 | 0.60 | 0.50 | 0.12 | 0.20 |
| Cr | 0.80 | 0.65 | 0.80 | 0.55 | 0.73 | 0.15 |
| Cu | 3.65 | 3.35 | 3.50 | 2.85 | 3.28 | nl |
| Cd | 0.70 | 0.65 | 0.65 | 0.60 | 0.18 | 0.05 |
| Mn | 74.70 | 79.85 | 90.85 | 83.15 | 11.00 | nl |

Nl = not in literature

In this study, levels of Pb (0.65 µg/g) in tissues of *Lates niloticus* were significantly ($p \leq 0.05$) different from those observed in tissues of *Synodontis victoriae* (0.40 µg/g) and *Clarias batrachus* (0.50 µg/g) fish even though they were not significantly ($p \leq 0.05$) different from the levels noted in *Oreochromis niloticus* tissues (0.60 µg/g) (Table 3). The levels of Pb in *Lates niloticus* and *Oreochromis niloticus* fish tissues were lower than the levels obtained in a previous study (Tole and Shitsama, 2003) [34] on the same fish species from Lake Victoria (Table 4). However, Pb levels in *Lates niloticus* and *Oreochromis niloticus* tissues were close to the levels obtained in a previous related study (Ongeri, 2008) [26] on the same fish species (Table 4). This observation indicated possible reduction in Pb levels in these two fish species since 2008. The data suggested that there has been reduction in Pb related activities or an improvement in the management of Pb related waste which caused the metal contamination in the fish. However, the levels of Pb in *Oreochromis niloticus* tissues were higher than the levels obtained for the same fish species in a study done in Nigeria (Ekeanyanwu *et al*., 2010) [7] (Table 5).

The concentrations of Cr of 0.80 µg/g in tissues of *Lates niloticus* and *Oreochromis niloticus* each, were significantly ($p \leq 0.05$) different from the levels observed in tissues of *Clarias batrachus* in the current study (Table 3). Generally, Cr levels in the tissues of S*ynodontis victoriae, Lates niloticus* and *Oreochromis niloticus* were the same ($p \leq 0.05$) (Table 3). However, the Cr levels in the tissues of all fish species were higher than in *Oreochromis niloticus* (0.06 µg/g) from Delta State, Nigeria (Ekeanyanwu *et al*., 2010) [7] (Table 5). The Cu levels in *Lates niloticus* tissues were significantly ($p \leq 0.05$) different from the levels recorded in *Clarias batrachus* tissues although were not different from the levels in *Synodontis victoriae* and *Oreochromis niloticus* (Table 3). The Cu levels of 3.35 µg/g in S*ynodontis victoriae* tissues were not significantly ($p \leq 0.05$) different from 3.50 µg/g of those recorded in *Oreochromis niloticus* (Table 3). The Cu levels obtained in tissues of *Lates niloticus* in this study were higher compared to levels in a study (Machiwa, 2003; Ongeri, 2008) [19, 26] on heavy metals in the same fish species in Lake Victoria and freshwater fish from Nigeria (Achionye Nzeh *et al.,* 2010) (Table 4). Therefore, Cu levels in *Lates niloticus* showed an increase. Mn levels in *Lates niloticus* tissues differed significantly ($p \leq 0.05$) from the levels in *Oreochromis niloticus* and *Clarias batrachus* tissues, while there was no significant ($p \leq 0.05$) difference between *Synodontis victoriae* (Table 3). The concentration range of Mn of 74.70-90.85 µg/g in the tissues of the studied fish species was narrow compared to a wide range of 81.50-132.70 µg/g in *Oreochromis niloticus* from Athi-Galana-Sabaki tributaries, Kenya (Nawiri *et al*., 2013) [22].

The heavy metal concentrations in fish tissues varied significantly ($p \leq 0.05$) among the fish species for all the analyzed metals except Fe and Cd (Table 3). The differences in metal concentrations in the different fish tissues may be attributed to the different fish species and their feeding behavior among other characteristics (Tuzen, 2003). Abiotic ecological factors such as season, place of development, nutrient availability, temperature and pH of the water may also contribute to the inconsistency of heavy metal concentrations observed in the fish tissues (Clearwater *et al*., 2002; Tuzen, 2003).

The levels of all analyzed heavy metals in the fish species did not show seasonal variations ($p \leq 0.05$) (Table 3). These results contradict earlier results (Ongeri, 2008) [26] in fish from Winam Gulf where heavy metal levels in fish showed seasonal variations. This observation implied that non-seasonal activities were constantly and continuously polluting the aquatic ecosystem with heavy metals. Generally, the levels of most analyzed metals in all fish species were above the international set levels acceptable for human consumption by FAO/WHO, (2004) and IAEA-407 (Wyse *et al.,* 2003) [39] (Table 5). Therefore, consumption of the fish from the lake may pose health risks. Data obtained in this study confirmed that the anthropogenic activities around and within the lake were causing heavy metal pollution to the analyzed fish. The results therefore calls for an improvement of the existing policies by putting in place appropriate mitigation measures by the relevant agencies to curb further heavy metal pollution of the lake and advice on consumption of fish from the Winam Gulf.

## Conclusions

The general trend in decrease of all analyzed heavy metals in water samples from all sites as the distance increased from the shore into the lake was due to dilution. Seasons were generally not influencing change in the heavy metal loads into the lake water and the studied fish species obtained from the Winam Gulf near Kisumu City. Therefore, locational anthropogenic activities were the major contributors of heavy metals into the lake. The heavy metal levels of Zn, Pb, Cr and Cd in the studied fish were above the WHO (2004) [8] recommended acceptable levels for human consumption. Therefore, consumption of the studied fish from Winam Gulf may pose health risks.

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