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Levels of Toxic Metals in Multisectoral Samples from Winam Gulf of Lake Victoria

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Abstract In this study, the distribution and sources of inputs of trace metals including Cd, Cu, Zn and Pb from various sources as well as Fe which is widely used in the construction industry, into Winam Gulf of Lake Victoria were investigated. The sampling sites were located up streams and down streams of four rivers (Sio, Nyamasaria, Nyando and Sondu-Miriu), in four beaches along the lake (Port Victoria, Kisumu Car Wash, Dunga and Hippo point beaches) and in three estates (Nyamasaria, Migosi and Nyawita) in Kisumu city, covering potential agrochemical and industrial sources and drinking water points, respectively. The concentrations (in µg/L) of trace metals analysed in the lake and river waters ranged from <1.79 (Cd), <3.83 (Pb), <1.53–3.86 (Cu), 4.37–11.6 (Zn), 11.8–2,440 (Fe). The sediment concentrations (in µg/kg × 10^3) ranged from 0.19 to 1.91 (Cd), 6.86–138 (Pb), 18–100 (Cu), 36.2–443 (Zn) and 960–73,200 (Fe), with highest concentrations of all metals being recorded at Kisumu Car Wash area. The study confirmed that the concentrations of the metals accumulate downstream in the rivers both in water and sediment and these rivers are major sources of the heavy metal load into Winam Gulf of Lake Victoria.

Keywords Heavy metals · Multisectoral sources · WINAM Gulf

Sediment is a major sink for trace metals in aquatic systems where metals can be accumulated to several orders of magnitude greater than the overlying water (Luoma et al. 1989). Heavy metals are frequently detected in the environment including both bed sediments and water columns and have gradually become a major worldwide concern due to lots of wastes discharged into water bodies (Pardo et al. 1990; Boughriet et al. 1992; Warran and Zimmerman 1993). The exposure of aquatic organisms to heavy metals has the potential of deleterious effects on this population (Carbonell and Tarazona 1993) and metal bioaccumulation leads to possible health hazards for the human consumer of these organisms (Vos and Hovens 1986).

Past studies show that samples of water, sediment and biota from Lake Victoria have high levels of heavy metals (Ochieng 1987; Onyari and Wandiga 1989; Mpendazoe et al. 1993; Harnza 1996; Mwamburi and Oloo 1997). Because of the large size of the lake, diverse anthropogenic activities and geochemical processes could cause major variations in heavy metal levels in its various parts. The current state of affairs regarding heavy metal concentration levels in Winam Gulf is not known 18 years down the line. This situation applies to piped, rain and well water sources, which are widely used by the local population surrounding the Winam Gulf and this, necessitated an up-to-date data to be generated in this respect. This paper presents data that highlights on some of the important water sources in the Winam Gulf beaches and rivers discharging into the lake as well as in drinking water.

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Materials and Methods

The rivers selected were Sio, Nyamasaria, Nyando and Sondu-Miriu. Both the upstream and down streams of rivers were sampled. The landing beaches considered included Port Victoria, Dunga, Hippopoint and Kisumu car wash. Sioport and Kisumu port were also selected for sampling; however, Sioport is next to the mouth of river Sio while Kisumu port is next to Kisumu Car Wash. Three estates namely Nyamasaria, Migosi and Nyawita were selected to supply piped, well, rain and private treatment plant water samples. The choice of the sampling points was based on the availability of perennial rivers, ports, landing beaches, car washing beaches and proximity of industrial/commercial towns to the Winam Gulf of Lake Victoria shore. The samples were taken in May 2006.

A sediment sample measuring l00 g weas taken from a hole which measures 5 cm deep with the aid of a plastic tube of size 5 cm in diameter and 72 cm in length. Five replicate samples of each type were taken. Solid and liquid samples were stored at −20°C and 4°C respectively to wait processing. Each water sample measuring 500 mL was treated with 1 mL concentrated nitric acid before storage to minimize metal adsorption onto the plastic container surface. Water samples were taken by immersing pre-cleaned plastic containers at a depth of about 1 metre in the water. To determine the dry weight of the sediment samples, one gram of semi-dry sediment samples was sieved through 45 μm nylon sieve was weighed out and dried at 100°C for 24 h and the dry mass recorded. Estate water and rainwater samples were taken from the various sources using pre-cleaned plastic bottles.

For sample preparation, a mass of 1 g of dried sediment sieved through 45 μm nylon sieve was weighed into a Pyrex digestion tube and 10 mL mixture of concentrated nitric and hydrochloric acid (4:1) added. The contents were placed in a digester for 3 h at 50°C, followed by filtration through a 0.45 μm polyethersulfon filter membrane into a 50 mL volumetric flask. This was made up to volume with de-ionized water. The extract was analyzed for Cd, Cu, Zn, Fe and Pb using induced couple plasma mass spectrophotometer, ICP-MS at 228.8, 324.8, 213.8, 243.3 and 283.3 nm respectively. A water sample measuring 100 mL was filtered through a 0.45 μm polyethersulfon filter membrane. This was acidified to 1% with nitric acid (AR), placed in a digester at 60°C and allowed to evaporate to 15 mL. The sample was transferred into 25 mL volumetric flask and made up to volume with double distilled and de-ionized water. The concentrations of Cd, Cu, Fe, Pb and Zn were measured using an ICP-MS. The water filters were also digested in a microwave oven before determination of the total metal content in the water sample. Recovery studies for the metals in water and sediment were done using fortified samples of soil and water free from the residues.

Results and Discussion

The results obtained are summarized in the following tables. The wet weight (ww)/dry weight (dw) ratio for sediment obtained in this study was 1.264 (Tables 1–6). The concentration of the metals given in Table 4 is based on dry weight of sediment. Otherwise the ww/dw ratio will be of importance when there is need of knowing the concentration of the metal on wet weight basis.

The highest concentration (Table 4) of cadmium (1,910 μg/kg) recorded at Kisumu Car Wash area had significant difference ($p < 0.05$). This was attributed to the intense car washing activity at the shores of the lake at this site. The lowest concentration of cadmium (192 μg/kg) was recorded at the mouth of River Sio. The significant low concentration observed in the upper stream of river Nyamasaria and the down stream of river Sio can be attributed to the intense sand mining activities at these two sites. These activities lead to dispersion/desorption of the metals into water from sediment. The high and low concentrations of cadmium and lead; 138,000 μg/kg and 6,860 μg/kg respectively observed at Kisumu Car Wash area and Sio River Mouth showed significant difference ($p < 0.05$). The high concentration of copper, 100,000 μg/kg observed at Kisumu Car Wash and the low concentration 18,100 μg/kg noted at Sondu-Miriu River Mouth showed significant difference ($p < 0.05$). The high concentration of zinc 443,000 and 241,000 μg/kg noted at Kisumu Car Wash and Sondu-Miriu River Mouth, respectively, showed significant difference at $p < 0.05$. Similarly, the low concentration of zinc, 36,200 and 45,100 μg/kg noted at Sio River Mouth, Sio River Upstream, and Port Victoria, respectively, had significant difference ($p < 0.05$).

The high concentrations 73.2×10^6, 69.8×10^6, 68.0×10^6 and 64.7×10^6 μg/kg noted for iron at Kisumu Car Wash area, Nyando River Mouth, Nyando River

Table 1 Dry weight for sediment

Site	Wet weight (ww) (g)	Dry weight (dw) (g)	ww/dw
Kisumu car wash	1	0.7751	1.2901
Sio river upstream	1	0.9519	1.0505
Sio river mouth	1	0.9166	1.0910
Sondu-Miriu river upstream	1	0.7678	1.3024
Sondu-Miriu river mouth	1	0.8891	1.1247
Nyando river upstream	1	0.6430	1.5552
Nyando river mouth	1	0.6977	1.4333

Average ww/dw = 1.264

Upstream and Sondu-Miriu River Mouth respectively showed significant difference at $p < 0.05$. Similarly, the low concentrations 9.6×10^5 and 28.3×10^6 µg/kg of iron observed in Kisumu Dunga beach and Sio River Mouth respectively were significant at $p < 0.05$. Sediment from Kisumu Car Wash was the most polluted while that from Sio River Mouth was least. This can generally be attributed to car washing and sand mining activities respectively at the two sampling sites. Kisumu City car wash area is centre of car-washing activities, accidental oil spills and industrial effluent from River Kisat which flows through the Kisumu City industrial area and discharges in to the lake. The trend of these metal concentration in sediment is Fe > Zn > Cu > Pb > Cd in all the sampling sites except that at the Kisumu Car Wash and Sondu-Miriu River Mouth the Pb > Cu and this nearly proves that the car washing business highly contribute to sediment contamination with the trace metals. These activities help in dispersion of the element lead, which is least soluble in water, and hence the change in trend observed in Kisumu car wash and Sondu-Miriu river mouth. In a study carried out by Onyari and Wandiga (1989) in this same area, the ranges in concentrations of the metals figures are reasonably lower than in the current study. This shows that there is some significant increase (Table 4) in the present study 18 years down the line.

For the estate water samples, there was no much variation in the concentration levels of cadmium and lead metals among the sampling sites (Table 2). All the Cd and Pb concentrations were <1.78 and <3.83 µg/L respectively. In a study carried out in 100 largest US cities by NAS (1977) to determine lead levels in water after passing through water treatment plants, the median concentration was 3.7 µg/L with a maximum concentration of 62 µg/L. This is an indication that in the present study, estate water supplies are comparably clean. Only the ground water had a high copper concentration of 6.41 µg/L that showed a significant difference at $p < 0.05$. This relatively high concentration can be attributed to the ground source that contains the element Cu in the earth's crust and this enhances chances of leaching into the ground water due to the low altitude of the estates. The very high concentration, 2,880 µg/L of Zn for rain water showed significant difference at $p < 0.05$ and this was most probably due to contamination in the storage tank for rain water. For the rest of the Zn concentrations in this study, the results are much less than the concentrations that were observed in a past study of Boston tap water in the USA where levels of Zn were found to be up to 1,600 µg/L with a mean of 200 µg/L (NAS 1977). This is an indication that in the present study, the estate water samples have a low Zn content or its concentration is relatively safe. The concentration of iron, 17.3 µg/L in the water sampled at Nyamasaria Private Water Treatment Plant had significant difference at $p < 0.05$. However, this figure for Fe is very safe since it is way below the maximum allowed concentration of 300 µg/L in drinking water (Table 5).

For the lake and river water samples (Table 3), the cadmium and lead metals showed no concentration variation among the sites sampled. In the Kisumu Car Wash area, the concentration values <1.79 and <3.84 µg/L for Cd and Pb respectively were minimally higher than for all the other sites. Since the concentration observed in sediment (Table 4) is significantly high, it would be expected that the concentration of Pb be also high in water which was not the case in this study. This would probably be due to the low solubility of the compounds of Pb, which therefore directs the metal to settle on the sediment and hence the high concentration observed in sediment (Table 4). Dunga and Sio River sites seemed to be contaminated with copper and hence their copper concentrations of 3.15 and 3.86 µg/L respectively showed significant difference at $p < 0.05$ (Tables 3, 5).

The high zinc concentrations of 11.6 and 16.6 µg/L observed in Kisumu Dunga site and Nyando River Mouth respectively showed significant difference at $p < 0.05$. The

Table 2 Mean concentration of the metals (µg/L) in estate water samples

Site	Cd	Pb	Cu	Zn	Fe
Rain water	<1.78	<3.83	<1.50	1,084	6.6
Kajulu municipal supply	<1.78	<3.83	<1.50	10.2	12.3
Nyamasaria private treatment plant	<1.78	<3.83	<1.51	48.1	17.3
Nyamasaria municipal supply	<1.78	<3.83	2.59	244	2.37
Nyawita well	<1.78	<3.83	6.41	15.4	2.80
Nyamasaria well	<1.77	<3.83	2.24	28.3	<1.62

Table 3 Mean concentrations of the metals in Lake Victoria and river water samples (µg/L)

Site	Cd	Pb	Cu	Zn	Fe
Kisumu Dunga	<1.79	<3.83	3.25	11.66	2,440
Kisumu car wash	<1.79	<3.84	1.62	6.37	289
Port Victoria	<1.77	<3.83	<1.53	4.37	11.8
Sio river mouth	<1.77	<3.83	3.86	12.5	2,030
Sio river upstream	<1.77	<3.83	3.09	8.90	972
Sondu-Miriu river mouth	<1.77	<3.83	2.06	9.56	1,140
Sondu-Miriu river upstream	<1.77	<3.83	2.00	8.76	670
Nyamasaria river mouth	<1.78	<3.83	<1.58	7.90	1,012
Nyamasaria river upstream	<1.78	<3.83	<1.52	4.87	489
Nyando river mouth	<1.77	<3.83	1.59	16.6	20.2
Nyando river upstream	<1.77	<3.83	1.57	2.50	12.0

Table 4 Mean concentration in sediment on dry weight basis (μg/kg × 10^3)

Site	Cd	Pb	Cu	Zn	Fe
Kisumu Dunga beach	0.725	31.1	22.8	175	28,300
Kisumu car wash	1.91	138	100	443	73,200
Nyamasaria river mouth	0.723	18.4	28.3	126	41,700
Nyamasaria river upstream	0.591	15.9	21.8	104	34,400
Nyando river mouth	1.22	12.9	52.8	162	69,800
Nyando river upstream	01.2	14.4	63.6	163	68,000
Sio river mouth	0.192	6.86	18.1	36.2	960
Sio river upstream	1.678	10.1	20.1	53.9	38,100
Sondu-Miriu river mouth	1.29	18.8	18	241	64,200
Sondu-Miriu river upstream	1.11	18.7	26.8	174	53,500
Port Victoria	0.758	9.5	21.3	45.1	35,400

Table 5 Maximum international allowable concentration of selected water quality values for different uses (μg/mL)

Element	KEBS	WHO	EU	Canada	USA	Russia
Drinking water						
Cd	–	3	5	5	5	3
Cu	100	1	0–3.0	1.0	1.0	2.0
Fe	300	300	200	300	300	300
Pb	50	10	10	50	15	100
Zn	5,000	3,000	100–5,000	5,000	5,000	5,000
Fisheries and aquatic life						
Cd			–	0.2–1.8		5
Cu			0.005–0.112	0.002–0.004		1
Fe			–	300		100
Pb			–	1–7		100
Zn			30–2,000	30		10

WHO (1996), Neubauer and Wolf (2004), KEBS (1996)

upstream of River Nyando had low Zn concentration of 2.50 μg/L, which is significant at $p < 0.05$. The variation for this river concentration of Zn between the upstream and river mouth could be attributed to the wetland between the two sites that could probably be absorbing and adsorbing much of this metal. It was generally noted that the upstream sites of the rivers had lower concentration compared to the downstream sites. This showed accumulation of the trace metals as the river progresses towards the lake. The highest concentration of iron, 2,440 μg/L noted in Kisumu Dunga site had significant difference at $p < 0.05$ while the lowest concentration, 11.8 μg/L (Table 3) observed at Port Victoria had significant difference at $p < 0.05$. This metal showed highest concentration in all sites compared to other metals. This probably could be due to its highest concentration in the sediment that can be desorbed into water when the concentration in water decreases. This is also related to the extensive use of Fe in the steel industry. River Nyamasaria flows through the estate effluent carrying domestic and industrial effluent in to the lake. The concentration levels of heavy metals in this river indicate heavy metal input from municipal waste waters into Winam Gulf. While River Kisat was identified in previous studies (Ochieng 1987) to be a main source of heavy metal loads from the city industrial activities in to the car wash area, River Nyamasaria indicates a source of heavy metals from domestic/municipal waste waters and industrial discharges in to the lake in Dunga Beach area. Sio River passes through a less intensively cultivated and developed area as it flows into the lake and therefore weathering as a result of soil erosion and flooding could be the main contributor to the higher concentrations of metals downstream compared with upstream. Rivers Sondu Miriu and Nyando are both influenced by agricultural residues as well as frequent flooding. In a study carried out by Ochieng (1987) in the car wash area, the concentrations of Pb, Cu and Zn noted then were higher than what was observed in the present study (Table 6). This could probably be due to better management of industrial wastes as well as reduction in the number of industries as a result of closures e.g. the textile mill and the breweries, which were in operation at that time but have now been out of operation for more than 10 years. There has also been a waterweed known as water

Table 6 Comparison of the heavy metal concentration ranges in various samples in the present and past studies

Samples analysed	Cd	Pb	Cu	Zn	Fe
Estate water (μg/L)[a]	<1.78	<3.83	<1.50–6.41	10.2–2,880	<1.62–17.3
Lake and river water (μg/L)[a]	<1.79	<3.84	<1.52–3.86	2.50–12.5	11.8–2,440
Sediment (μg/kg dw) × 10^3[a]	0.192–1.91	6.86–138	18–100	45.1–443	(0.096–7.32) × 10^4
Winam Gulf water (μg/L)[b]	nr	7–93.6	5–57.6	25–125	nr
Sediment (μg/kg dw) × 10^3[c]	nr	nd–100	1–79	3–265	1.18 × 10^3–522 × 10^4

[a] Present study

[b] Ochieng (1987)

[c] Onyari (1985), Onyari and Wandiga (1989), Mwamburi and Oloo (1997)

nr, not reported; nd, below detection limit hyacinth that is threatening to fill up the Winam Gulf surface. This weed is prevalent in the car wash area and could be bio-concentrating the heavy metals from the lake water and reducing their concentrations in the water. This is an issue that deserves some urgent investigation.

There was no much difference in concentration of Cd and Pb between the Lake and Estate water samples. The Cu concentration in the Estate water was relatively lower as expected than that of the Winam Gulf except for the water from the wells. This was attributed to the earth's crust contribution to the Cu concentration in the wells. Zinc concentration range in the Lake water samples was relatively much lower than that of the Estate water samples (Tables 2, 3). Since some of these water samples were municipality supplied tap water which has its source as the Winam Gulf, this indicates a possible contamination of this municipality supplied water by the steel pipes. However, this is also an issue that deserves some investigation to ascertain the source of this extra load of Zn in the municipal water supplies. The concentration of all the heavy metals in sediment showed positive correlations. The correlations of Zn:Cd, Zn:Pb, Fe:Cd showed significant positive relations at $p < 0.01$ while Fe:Cu and Fe:Zn showed positive relations at $p < 0.05$. These good correlations of these metals indicate that they most likely have one or more common major sources. The metals Cu, Zn and Fe in the Estate water had negative correlations, however, that between Fe and Cu was significantly higher. There were positive significant correlations in the Zn:Cu and Fe:Cu at $p < 0.01$ for the Lake water samples. Similarly the Fe:Zn showed significant positive relationship at $p < 0.05$.

The high concentration of the metals Cu, Zn and Fe in water noted at the Sio River Mouth Table 3 can also be attributed to the sand mining activities at this site which increases the dispersion of these metals into the lake water hence the high figures observed relative to the other river mouths where sand mining is minimal or not done at all. In all the four rivers, it was observed that accumulation occurs down stream. This is an indication that these rivers increase the metal load in Lake Victoria and these metals have their major sources upstream. These sources are most likely agricultural activities upstream as well as industrial and car washing activities downstream (Table 7).

All the estate water samples conformed to the international standards of drinking water requirements for these heavy metals set out by the World Health Organization (WHO) and even for other countries like the European Union (EU), Canada, United States of America (USA) and Russia (Tables 2, 5) (WHO 1996). The concentration of all the metals except iron in the lake water samples analyzed, conformed to the WHO, EU, Canada, USA and Russia standards set out for these metals in drinking water. All the lake and river water samples exceeded the international standards for iron in drinking water except samples from Nyando River and Port Victoria (Tables 3, 5). The amount of iron in these lake samples is beyond the maximum allowed in fisheries and aquatic life for the EU, Canada and Russia (Table 5) (WHO 1996). Some fish species in Winam Gulf are becoming either extinct or their production is getting very low. The excess iron in the lake water could be one of the major contributing factors to the low tonnage of the fish in the lake. This is a critical issue because some human communities with no access to clean water use this lake water for drinking and other domestic purposes and hence end up endangering their lives from the negative effects of such metals.

Table 7 Correlation matrices of the concentrations of the heavy metals in various samples

	Cd	Pb	Cu	Zn	Fe
Sediment					
Cd	1.000				
Pb	0.517	1.000			
Cu	0.490	0.371	1.000		
Zn	0.783**	0.916**	0.399	1.000	
Fe	0.890**	0.392	0.648*	0.651*	1.000
Estate water					
Cd	[a]				
Pb	[a]	[a]			
Cu	[a]	[a]	1.000		
Zn	[a]	[a]	−0.116	1.000	
Fe	[a]	[a]	−0.580	−0.086	1.000
Lake and river water					
Cd	1.000				
Pb	0.524	1.000			
Cu	−0.058	0.000	1.000		
Zn	−0.122	−0.200	0.745**	1.000	
Fe	0.254	−0.200	0.773**	0.618*	1.000

* Correlation is significant at the 0.05 level (2-level)

** Correlation is significant at the 0.01 level (2-tailed)

[a] Cannot be computed because at least one of the variables is constant

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