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Abstract

The pollution of the environment increased considerably in the past century due to industrial expansion, rapid growth of human population as well as the effects of resealed toxic compounds from domestic sewage wastewater systems. In the recent decades the levels of heavy metals in the soils, water and sediments have become critically higher as a result of sewage water and sewage sludge on agricultural fields, around industrial cities and along main roads. It is therefore necessary to periodically monitor the levels of heavy metals within cities so as to take remediation measures. Water samples from eight sites in Winam Gulf were analysed for heavy metals in order to assess the impact of anthropogenic activities on heavy metal input into the Lake. Three samples from each sampling site were mixed to form composite, digested using HNO₃ and HCl and analyzed for heavy metals using atomic absorption spectroscopy (AAS). Measurements of electrical conductivity, salinity, dissolved oxygen (DO) and total dissolved solids (TDS) were done at the sampling sites. The TDS were within the WHO permissible range except for R. Kissat which had a higher value of 799.5 mg/L. The mean values of DO were, however, lowest at R. Kissat (0.7) ppm. Other sites like Tilapia beach, Yatch and Dunga had also low DO values. The electrical conductivity values in the study area were found to be in the range of 372.3 at R. Kibos to 1239 μS/cm at R. Kissat. R. Kissat had the highest level of salinity (0.6 PSU), while R. Kibos had the lowest level (0.18 PSU). The levels of trace heavy metals in most of the samples were above WHO standard. The levels of heavy metals show that the Winam Gulf is highly polluted and there is need to come up with strategies to clean up using biosorption technique.

Keywords: Water, heavy metals, Rivers, Winam Gulf

Introduction

Heavy metals are introduced into aquatic systems as a result of agricultural and industrial processes, other processes include; weathering of soils and rocks, mining processes and volcanic eruptions. In Kenya scrap metal and metal fabrication industries which are common in most cities are good examples of
anthropogenic sources of heavy metals which discharge into aquatic sources. The agricultural sector depends on fertilizers and pesticides since several crops are cultivated within the Winam Gulf region which means that fertilizer and pesticide application is common. The water courses draining into Lake Victoria also transverse this area. The pollutants are introduced into the water system from various sources such as industrial effluents, agricultural runoff chemical spills and municipal wastes (Wandiga & Onyari, 1987). Consequently there is need to monitor water quality in Lake Victoria continuously to check on the pollution load (Karanja, 2002). This is important because it causes massive kills of fish and contamination of aquatic animals, which are eventually consumed by human beings and enter their body tissues (Bhushan et al., 1997). The presence of heavy metals in water systems is a threat to biota as they accumulate in various organisms often reaching lethal concentrations. It is therefore important that the levels of heavy metals in the water bodies be established and thereafter control pollution not only in water but also in sediment, suspended solids and organisms most of which are important in food chains with man at the top of the food chain (Turgut, 2003).

Materials and methods

Sampling and sample treatment

Water samples were collected from all the eight sites (three Rivers and five Beaches) and three samples were taken from each site and mixed to form composite samples which were then used in the analysis. Water samples were acidified with 10% HNO₃. Sampling was done on the shores of Lake Victoria (Winam Gulf) at five (5) sites that is, Yatch Club, Dunga Beach, Lwang’ni Beach Hotels, Kisumu Beach Resort and Tilapia Beach. Water was also sampled from three rivers that drain into the Lake Victoria, that is, Nyamasaria, Kibos and Kissat. The digestion method described by Lalah et al. (2008) was adopted. Representative water samples of 5 mL each were transferred into pyrex beakers containing 5 mL of conc. HNO₃. The samples were boiled slowly and then evaporated on a hot plate for 30 minutes. The beakers were
allowed to cool and another 5 mL of conc. HNO₃ acid added followed by heating on a hot plate. Some 10 mL conc. HCl was added and digestion continued until the solution remained light brown or colourless. The volume was then adjusted to 25 mL with distilled water. These solutions were then used for the elemental analysis using AAS to analyse Zn, Pb, Cd, Mn, Cu and Cr.

**Lead stock solution and working solution**

A stock solution of Pb (II) was made by dissolving 1.599 g of Pb (NO₃)₂ in nitric acid and making it to 1000 cm³. At 25 °C, the solution had a density of 1.02 g/cm³ and contained 1.000 µg/cm³ (1000 ppm) of Pb (II) ions. A stock solution of 100 ppm was prepared by pipetting 10.0 cm³ from 1000 ppm stock solution, into 100.0 cm³ volumetric flask and making it up to the mark with deionised water. Standard solutions of 2.5 ppm, 5.0 ppm, 7.5 ppm, 10.0 ppm were prepared from the stock solution. Stock solutions of Cd (II), Cu (II), Cr (II), Zn (II) and Mn(II) were prepared in a similar way.

**Results and Discussions**

Figure 1 shows the concentration of heavy metals at various sites in the Winam Gulf.
The highest levels of Cu were at Dunga beach (1.543 ± 0.03 ppm), while the other sites did not record any copper. The levels at Dunga were almost 2 times the FAO/WHO maximum acceptable limits of 1 ppm in drinking water. Mireji et al. (2008) reported values of 0.111 ppm in water of larval habitat in the Winam gulf, these values were, however, far much lower than the values obtained in this study. In another study, Matindi et al. (2014) reported mean Cu levels of 0.1603 ppm. Ongeri et al. (2009) reported values of between 1.53 ppm and 3.86 ppm in Winam gulf. The values in the three studies were all lower than the highest value in this study which implies that levels of Cu have been increasing with time and this could be due to activities going on at the beach like fishing and car washing.

The highest level of Cd was at the Tilapia beach (0.037±0.007 ppm), followed by the Yatch club which had 0.0±36 ppm. However, the lowest levels were at R. Kibos (0.013 ± 0.001 ppm). All
these values were more than ten times the WHO limits (0.003 ppm) in drinking water. A study by Muinde et al. (2013) reported Cd ranges from below detection limits to 0.02 ppm, while Ogoyi et al. (2011) did not detect any Cd in the water samples in the Winam Gulf which implies that the levels of Cd have been increasing with time. The high levels could imply that cadmium compounds from agricultural, domestic and industrial sources are released into the water bodies around Lake Victoria and are carried by run off towards the lake. This could also imply that the Lake acts as a ‘sink’ of pollution loads from both point and diffuse sources. Thus pollution in the Winam Gulf is going up year after year, which could be due to increase in activities that bring about pollution in the area.

The highest levels of Zn were at Dunga beach (3.467± 0.032 ppm) followed by Lwang’ni beach (3.06±0.015 ppm) while the lowest levels were at R. Kibos (0.3005 ppm). All the values were, however, much lower than the FAO/WHO maximum acceptable limits of 5 ppm. Muinde et al. (2005) reported Zn levels of 0.14 ppm in the same area which was still lower than the FAO/WHO limit of 5 ppm. Ogoyi et al. (2011) reported similar results, and in their study found Zn levels of between 0.36 ppm and 0.047 ppm with a mean value of 0.05 ppm. This implies that the area is still not polluted with respect to zinc and could be due to the fact that activities around the Gulf don’t release Zn into the water bodies.

The highest levels of Pb were recorded at Lwang’ni beach (1.13 ± 0.011 ppm), Tilapia beach (1.12 ± 0.031 ppm) and River Nyamasaria (1.04± 0.011 ppm), no Pb was detected at Kisumu beach Resort, Dunga beach and the Yatch club. The other sites, that is, River Kibos and River Kissat had 0.92 ± 0.008 ppm and 0.99± 0.01 ppm, respectively. The values at Lwangni, Tilapia Beach and Nyamasaria were ten times higher than the KEBS maximum acceptable limits of 0.1 ppm and more than 100 times higher than the FAO/WHO maximum acceptable limits of 0.01
ppm for drinking water. The levels at Kissat and Kibos were also more than 9 times the KEBS acceptable limits of 0.1 ppm and more than 90 times the FAO/WHO acceptable limits for drinking water. The high levels at the five sites could be due to the different activities practiced. Lwangni beach is used for car wash and Pb could be from car engines. Raw sewerage is also released into River Kissat directly by the Kisumu Municipal council and this could lead to pollution of the river by Pb from domestic and industrial sources. River Nyamasaria is also used for car wash and during the research period the area was highly eroded because the bridge was under construction. The high levels of Pb could also be due to the vehicles being washed in the area, or from the soil parent material which releases Pb into the environment as a result of erosion during the construction of the bridge. It was also found that 66% of the sites had Pb levels above the WHO prescribed limit for drinking water. A study by Ogoyi et al. (2011) reported mean Pb levels were of between 0 and 1.622 ppm, with a mean value of 0.823 ppm which was more than 80 times higher than the WHO/FAO maximum acceptable limit of 0.01 ppm. However, this value was still lower than most of the values reported in this research, which implies that the amount of Pb has been increasing with time in the Winam Gulf. Makokha et al. (2011) reported values of 0.02 ppm and 0.015 ppm at Tilapia beach and Dunga beach, respectively which were still lower than the value reported in this research.

The highest levels of Mn were at Lwang’ni beach (4.967±0.04 ppm) while the lowest was at the Yatch club (0.153±0.003 ppm), R. Kibos had also a significant amount of Mn (1.365 ± 0.021 ppm). These levels were all more than 10 times the WHO maximum permissible limit of 0.1 ppm. The results obtained indicate that 20% of the sites had manganese levels above WHO allowable range for drinking water. Mireji et al. (2008) reported values of 8.270 ppm of Mn in
water of larval habitat in the same area. This value was, however, higher than the value obtained in this study implying that the amount of Mn could be reducing. In another study by Matindi et al. (2014) the mean value of Mn in water hyacinth was reported as 16.03 ppm, which was again much higher than the mean value reported in this study. The high values could be due to the type of the rocks undergoing weathering at the sampling sites. Most of the manganese in the environment is due to burning of fossil fuels. Use of manganese bearing fertilizers also contributes to air and water pollution by this element. The industrial processes are also the major sources of manganese pollution.

The highest level of Cr was at R. Kibos (0.459 ± 0.021 ppm), but not detected at R. Nyamasaria and Lwang’ni beach. Tilapia beach had very low levels of Cr (0.033± 0.005 ppm). However, Cr levels at R. Kibos were almost 10 times the FAO/WHO maximum acceptable limit of 0.05 ppm. Other areas that had high levels were; R. Kissat (0.402± 0.02 ppm) and Kisumu beach resort (0.342 ± 0.02). The high levels of Cr at R. Kibos could be due to the river traversing the sugar belt and therefore the chromium compounds used in the catchment area in fungicides, seed protectants and wood-preservatives are released and carried by run off to the water bodies. In a study done by Ogoyi et al. (2011) reported Cr levels of between 0.183 ppm and 0.298 ppm, with a mean of 0.178 ppm, while Muinde et al. (2013) reported Cr levels of 0.06 ppm. The values in the two studies were still lower than the values obtained in this study, which implies that pollution due to Cr is increasing with time. Ogoyi et al. (2011) also found that at Winam Gulf, concentrations of metallic elements were higher in water samples than what was found in microalgae samples while the opposite was true for water and microalgae samples from the
Mwanza Gulf. All the levels of heavy metals in this study were higher than the values reported by Ogoyi et al. (2011).

Table 1 shows the values of various parameters that were investigated in this study.

Total dissolved solids (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro granular suspended form. The permissible limit of TDS of drinking water is 500 mg/L.

**Insitu measurement of water samples**

<table>
<thead>
<tr>
<th>Area/ conditions</th>
<th>DO (ppm)</th>
<th>COND. (μS/cm)</th>
<th>TDS (ppm)</th>
<th>SALINITY (psu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIBOS</td>
<td>2.52</td>
<td>372.7</td>
<td>241.8</td>
<td>0.18</td>
</tr>
<tr>
<td>R.NYAMASARIA</td>
<td>3.64</td>
<td>657</td>
<td>429</td>
<td>0.32</td>
</tr>
<tr>
<td>LWANGNI</td>
<td>2.01</td>
<td>428</td>
<td>299</td>
<td>0.22</td>
</tr>
<tr>
<td>TILAPIA BEACH</td>
<td>1.61</td>
<td>646</td>
<td>422</td>
<td>0.3</td>
</tr>
<tr>
<td>KISSAT River</td>
<td>0.7</td>
<td>1239</td>
<td>799.5</td>
<td>0.6</td>
</tr>
<tr>
<td>KISUMU BEACH RESORT</td>
<td>2.4</td>
<td>638</td>
<td>416</td>
<td>0.318</td>
</tr>
<tr>
<td>DUNGA BEACH</td>
<td>1.93</td>
<td>666</td>
<td>429</td>
<td>0.32</td>
</tr>
<tr>
<td>NEAR RIVER YATCH</td>
<td>2.17</td>
<td>673</td>
<td>436.5</td>
<td>0.32</td>
</tr>
<tr>
<td>YATCH CLUB</td>
<td>1.86</td>
<td>674</td>
<td>436.5</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The TDS were within the permissible range as prescribed by WHO except for R. Kissat with 799.5 mg/L. Other sites that recorded high values were; Yatch, Nyamasaria, Dunga, Tilapia beach and Kisumu beach Resort which had values of 436.5, 429, 429, 422 and 416 mg/L, respectively. The remaining sites had relatively low values, that is, Lwang’ni and Kibos with corresponding values of 299 ppm and 241 ppm. The high values at River Kissat could be due to the raw sewage from the municipal council that is released into the river directly. Another reason could be due to the widespread erosion around the area leading to washing of substances into the river. The other sites which recorded high levels could be as a result of food kiosks and hotels and there is a likely hood that some of the left overs are directly thrown into the water.
River Nyamasaria, Lwangni, Dunga, Kisumu beach Resort and Tilapia beach sites are also used for car washing and the high TDS could be due to oil and particulates from the cars. High TDS at Nyamasaria could be due to the bridge that was under construction and a lot of particulates could have been released into the water. Nzomo (2005) reported TDS values of 83 mg/L at Winam gulf and 113 mg/L at Kisumu bay, both of which were lower than the values reported in this study. Thus, TDS values could be increasing with time.

The mean values of DO were lowest at R. Kissat (0.7) ppm. Other sites like Tilapia beach, Yatch and Dunga had also low dissolved oxygen (DO) values of 1.61, 1.86 and 1.93 ppm, respectively. The low levels of DO could probably be due to the increase in temperature and escape of dissolved oxygen from the surface of the water. The low levels of DO may also be due to the high microbial activities in the municipal runoffs at River Kissat which is known to carry untreated effluent from the municipal treatment plant and also agricultural runoffs at the site. The high microbial activities could be due to high level of organic matter, hence, increased utilization of DO for decomposition process. The results are similar to those reported by Osumo (2001), who observed dissolved oxygen levels of 1 – 8 mg/L during the sampling period.

The values obtained in this study were between 0.7 mg/L and 3.64 mg/L, which were within the same range, implying that the Winam Gulf is getting more polluted since the amount of dissolved oxygen is reducing with time. Nzomo (2005) reported DO values of 7.3 mg/L at Winam Gulf and 5.83 mg/L at Kisumu Bay, both of which were much higher than the values obtained in this study. This implies that the amount of oxygen in water within the gulf could be reducing with time which may later not sustain higher forms of aquatic life.
Electrical conductivity signifies the amount of total dissolved salts. It is a tool that assesses the purity of water. Electrical conductivity correlates with the concentration of dissolved minerals or TDS of water samples. The electrical conductivity values in the study area were found in the range of 372.3 at R. Kibos to 1239 μS/cm at R. Kissat. High electrical conductivity values at site R. Kissat indicate the presence of high amounts of dissolved inorganic substances in ionized form. The values of electrical conductivity depend upon temperature, concentration and types of ions present. At R. Kissat raw sewage from Kisumu municipality is released and this could be the reason for the high values of electrical conductivity and TDS which are related to salinity of the water. Mdamo (2003) reported conductivity values of between 9.7 and 64.4 μS/cm in the Lake Victoria basin. The highest value was much lower than the value obtained in this study implying the conductivity values in the Winam Gulf have increased over the years, which could be due to increased human activities which release substances into the water bodies. Nzomo (2005) reported conductivity values of 167μS/cm and 176 μS/cm, at Winam Gulf and Kisumu Bay, respectively, which were, however, lower than what this study reported.

R. Kissat had the highest level of salinity (0.6 PSU), while R. Kibos had the lowest level (0.18 PSU). River Kissat had the highest salinity because of raw sewage that is released directly into the river. Nzomo (2005) reported values of 0.08 ppm and 0.06 ppm, respectively, at Kisumu bay and Winam Gulf. These values, however, were much lower than the values obtained in this study. This means that salinity has been increasing over the years, especially at R. Kissat which is loaded with wastes from Kisumu sewage plant. Municipal untreated sewage, runoff, and storm water are the main causes of increasing salinity in the area. Direct discharge of municipal
untreated effluent into rivers and the lake directly contributes to microbiological pollution which also reduces the amount of dissolved oxygen in water, which leads to degradation of river and lake-water quality for habitats and drinking use (Ntiba et al., 2001).

**Conclusions**

The present study shows that the Winam gulf is polluted with heavy metals, the detected levels of Pb, Cr, Cu, Zn, Mn and Cd in water were higher than the WHO/FAO maximum limits. Pb at Lwang’ni beach was more than 10 times the KEBS maximum acceptable limits and more than 100 times the WHO/FAO maximum acceptable limits. Mn levels at Lwang’ni beach was about 50 times the FAO/WHO maximum limits. Cr values were 10 times higher (R. Kibos), while Cd levels at Tilapia beach were more than 12 times the WHO/FAO maximum permissible limits. However, the levels of Zn were below the maximum acceptable limits. It can be concluded that the heavy metals, used in farms, for domestic activities, industries and other human activities like car washing and shipping traffic in the Winam Gulf finally end-up in water. The TDS, salinity and electrical conductivities were also high implying that the parameters were increasing with time due to pollution. On the other hand the dissolved oxygen was reported to be very low and to have reduced over the years implying that Winam gulf is getting more polluted with time.

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