Land-Based Activities as Pollution Sources on Fresh Water Resources: A Case Study of Selected Heavy Metal Contamination in River Mukurumudzi, Kwale County

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ABSTRACT
Pollution of water-body ecosystems by heavy metals through uncontrolled anthropogenic activities lead to serious ecological problems in many parts of the world. These metals continue to accumulate to high toxic levels as they are discharged into water-bodies from agricultural activities, industrial and domestic wastes, and mining operations. This study focused on assessing the concentration of selected heavy metals (Fe, Pb, Cu, Cd and As) in the waters and sediments of River Mukurumudzi in Kwale County, Kenya. Four sampling points along the course of the river were purposely chosen owing to their proximity to identified land based pollution sources, these were titanium mining sites, large scale sugarcane plantations, human settlements and a control site. Samples were collected in three different seasons (long rain, short rain, and dry season). The heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS). The results showed that the level of Fe and Cu in water was the highest during the rainy season while all the other metals were found to be below detectable limits. In sediments, Fe (0.64 mg/L, 1.97 mg/L, 0.33 mg/L and 0.21 mg/L), Cu (0.1 mg/L, 0.14 mg/L, 0.14 mg/L and 0.1 mg/L), and Pb (0.14 mg/L, 0.21 mg/L, 0.12 mg/L and 0.33 mg/L) were detected at Shimba Hills, Nguluku, Bomani and Gazi consecutively. The concentrations of metals in water were found to be within the NEMA and WHO safe limits. Though River Mukurumudzi is not contaminated with the selected heavy metals it is established that the anthropogenic activities along the river are contributing some of the heavy metals. As such, this study recommends that conservation measures be put in place to avoid contamination of the river.

Key Words: Anthropogenic activities, Heavy metals, Land-based sources, Water pollution.

INTRODUCTION
Availability of freshwater is one of the most essential factors in development. Freshwater constitutes only 3% or less of the earth’s surface water, most of which is in form of ice and snow in polar region or in underground aquifers. However, despite its importance, mismanagement of water as a resource has been observed in many parts of the world (Fakayode, 2005). Human activities have been the major causes of water pollution and this has been documented in many parts of the world (Adekunle, 2009). Many rivers, lakes, wetlands, ground waters and oceans suffer a great loss of degradation from various human activities. These activities have effects on water quality, changing both its physiochemical and biological parameters making it unsuitable not only for domestic use, but also for other purposes. Water pollution also has effects on habitats, causing species migration while exterminating others due to impacts that affect their reproducitivy.

Freshwater ecosystems are among the most critical ecosystems in Kenya. Human activities have put such ecosystems under a lot of pressure. According to the National Environmental Policy Kenya, 2014, activities such as unsustainable land use practices, poor soil and water management behaviors, and pollution lead to the degradation of natural resources in Kenya. Natural resources such as land, freshwater, marine water and biodiversity are scarce and
their degradation threatens livelihoods of a many people. Furthermore, environmental degradation in Kenya contributes to climate change impacts like the rising cost of water treatment.

Anthropogenic activities are a major cause of concern for water pollution in the world (Adekunle, 2009). Additionally, research has proven that high levels of toxic heavy metals are discharged through human activities (Gao et al., 2010; Nduka & Orisakwe 2011; Kassim et al. 2011). Pollution of ecosystems such as rivers, oceans, lakes and wetlands by heavy metals resulting from anthropogenic activities causes serious ecological problems in many parts of the world. These metals continue to accumulate to higher levels of concentration as they are discharged into water-bodies from agricultural, industrial and domestic wastes, pesticides or mining operations resulting into severe toxicological effects on humans and the aquatic ecosystem (Jung, 2001; Ezeh & Chukwu, 2011). Anthropogenic activities like mining release huge amounts of tailing waste containing heavy metals. Agrochemicals introduced as soil nutrients to improve fertility contain metals, which in most cases exceed the limits set for land application and their continuous use can exacerbate their accumulation in agricultural soils (Lim et al. 2008; Hesterberg, 1998).

The increase in the cost of water treatment as a result of pollution has led to the rise in the price of useable water. As such, protection of water sources from anthropogenic activities that are likely to compromise water quality should be encouraged. There is therefore need to evaluate the impact of land based activities on the quality of water-bodies and provide mitigating measures.

**MATERIALS AND METHODS**

The sampling was conducted in River Mukurumudzi, Kwale County, Kenya. Four sampling points (S1, S2, S3, and S4; Figure 1) were purposely chosen along the course of the river. Three sampling points were chosen owing to their proximity to anthropogenic land based activities that were suspected to be sources of heavy metals. The fourth sampling point was chosen upstream of the river to act as a pristine site free from metal contamination.

The first sampling point at Shimba hills is close to the source of the river and not much of human activities takes place at this area except that since the water is much cleaner people would come to fetch water at this site. The second site is at Nguluku area where titanium mining activities are undertaken. The third site was at Bomani area where largescale sugarcane plantations are carried out. The fourth sampling was more downstream of the river where different human activities such as small-scale agricultural activities, laundry, bathing and motorcycle washing are done.

![Fig. 1: A map of the study area showing sampling points.](image-url)
Water and sediment samples were collected in duplicate from the four sampling points. Sampling was conducted in three different seasons; short rain season (August-October 2015), dry season (January-March 2016) and during the long rains (April-July 2016).

A total of 72 samples were collected (36 water samples and 36 sediment samples). After collection the water and sediments were acidified with nitric acid of a pH of 2 and then transported to the laboratory. Heavy metals were analysed using AAS. The samples were handled carefully. The glassware was properly cleaned using chromic acid solution and distilled water. Chemicals and reagents of analytical grade were used all through the process. Instrument readings were established using blank samples.

Sediment sample of 10 to 20 g was weighed accurately in a tarred silica dish. The samples were then oven dried at 180°C. The dishes were then placed in a muffle furnace at an ambient temperature and the temperature was gradually raised to 450°C at a rate of 50°C/h. After the attainment of 450°C the samples were left there for a minimum of 8 hours. Care was taken to avoid losses by volatilization of elements. After cooling the dishes of the samples were removed from the furnace. After this, the samples were digested in 50% nitric acid on a hot plate. The samples were then filtrated using Whatman filter paper No. 44 into a 100 mL volumetric flask. The sampled was then topped to the mark using distilled water.

Water of 100 mL was taken from each sample and put in a beaker. The samples were then digested on a hot plate by 5 mL nitric acid. The samples were then filtrated to a 100 mL volumetric flask using Whatman filter paper No. 44 and then made to mark with distilled water.

The standard solution for each metal was prepared for the calibration of the AAS before analyses was performed. All samples were prepared by chemicals of analytical grade. 1 g of Cd, Cu, Pb was dissolved in HNO₃ solution; 1 g of Fe, and As were dissolved in HCL solution. All the samples were made up to 1 L in a volumetric flask using distilled water. From which the stock solution of 1000 mg/L of all elements were prepared (Cantle et al., 1983). Then 100 mL of 0.1, 0.25, 0.5, 0.75, 1.0 and 2.0 mg/L of working standards of each metal was prepared from the stocks using micropipettes in 5 mL 2N HNO₃. Reagent blank was also prepared to avoid contamination.

Atomic Absorption Spectrophotometer was set up with the flame condition and observance was optimized for the analyses. The blanks, standards, sample blanks and samples were then aspirated into the flame. Calibration curves were obtained for concentration against absorbance. The concentration of each sample was then established.

One way Analysis of Variance (ANOVA) was used to show the variations of concentration of heavy metals between different seasons and sites. The variations were graphically represented. Pearson’s product moment correlation matrix was done to identify the relation among metals to make the results obtained from multivariate analysis.

RESULTS AND DISCUSSION

The study established that the concentration of the selected heavy metals in water were within WHO and NEMA permissible limits with the exception of Fe. In sediments, all metals were found to be below detection limit (BDL). There was no significance differences between the concentration of heavy metals in sediment and water (p > 0.05).

The highest concentration of Fe in water (1.82 mg/L) was recorded during the long rainy season at Bomani sampling point while the lowest (0.07 mg/L) was recorded during the long rainy season at Nguluku sampling point. Similar observations were found by Maina (2008). He stated that the level of Fe in Mrima Hills was high and they could be influenced by the geology of the area. Okuku et al (2011) similarly found a high concentration of Fe in sea water sampled along Gazi Creek. Further analysis revealed that heavy metal content in this area was contributed by natural sources. In general, the level of Fe was higher during the long rain season across all points with the exception of the Nguluku sampling point. The sampling points of Gazi and Bomani human settlements showed an increased concentration of Fe in water. Since these points were downstream of the titanium
mining zone, it could be interpreted that there is an enrichment of Fe from the mining activities. Another attribute to the high Fe concentration along Bomani human settlements could be the use of cosmetic products. Mascara and oils are known to be rich in Fe (Kayumba, 2014). Ladies and women using the river to bathe and launder clothes might be enriching Fe from the use of these products.

The highest concentration of Cu (0.11 mg/L) was found during long rains season at Bomani sampling point. The lowest (0.08 mg/L) was detected in other sampling points during the long rain season. However, during all the other seasons the concentration of Cu was found to be below detection limit (<0.01 mg/L) at all four sampling points.

The levels of Pb in water were below the detection limit (<0.001 mg/L) across all the points during short rains (SRW), long rains (LRW) and dry season (DW). This suggests that there is minimal if any Pb contamination from the anthropogenic sources to the waters of River Muku- rumudzi. The levels of Pb in water were lower than the WHO (1993) and WAS-REB (2008) standards for domestic waters. A study done by Chege, Hashim and Merenga (2013) documented that the levels of Pb in groundwater from wells sampled within the area, ranged between BDL-1.397mg/L. The study also found out that 62.3% of the samples had a concentration above the WHO reference level of 0.01 mg/L.

In this study, the concentration of Cd and As in water was found to be (<0.01mg/l) along all the four points during all the seasons. Therefore, the results of Cd and As are not displayed in graphs. Chege et al., (2013) found the level of Cd in 42% of the sampled groundwater sources to be above 0.005mg/l. This study shows there is no Cd enrichment in surface waters as it is in groundwater.

**Fig. 2: Fe concentration in water for the three different seasons**

**Fig. 3: Cu concentration in water during the long rain season**
The level of metals in sediments was higher than in water. In general, the level of Fe in sediments was high during the long rain season (LRS) across all the four points of sampling and low during the dry season. The level of Fe in sediments along Nguluku was higher than all the other points, this could be attributed to the mining of the titanium by Base Titanium Company. Titanium is mined in ores like ilmenite (FeTiO_3) which contains iron. Mangala (1987) also showed a high concentration of Fe in the area. Another study by Maina (2008) showed a low concentration of Fe in the soils of the area. This could therefore be linked to the mining activities that are taking place in the area. The Shimba Hills area also had the second highest levels of Fe in its sediments. This could also be as a result of the mineral composition of the area (Chege et al., 2013). The sediments along Gazi and Bomani settlements had the lowest levels of Fe.

Sediments along Gazi had the highest concentration of Pb during the dry (DS) and short rain seasons (SRS) 0.54±0.0067 mg/L and 0.27±0.0033 mg/L respectively, this could be attributed to the use of agrochemicals and fertilizers that contain Pb especially in the Kwale International Sugar Company Limited (KISCOL) plantations. Sediments along the Shimba Hills area had the lowest level of Pb during the dry season (0.08±0.012) mg/L, since this is an area upstream the river where not much of land based activities are happening, these levels could be attributed to the soil mineral contents in the area. Along Nguluku, the level of Pb was 0.12±0.0088 mg/L during the dry season while along the Bomani settlements it was 0.16±0.001 mg/L. Sediments along Nguluku had the highest concentration of Pb 0.34±0.0057 mg/L during the Long rain season, this shows that there could be a possibility of pollution from anthropogenic sources through run-off and leaching of water and sediments from the surrounding.
mines. The detection of Pb in sediments and not in water strongly suggests that sediments are sinks of pollutants in aquatic environments as recorded by Horowitz, Meybeck, Idlakih and Biger (1990). There was no correlation in the levels of Pb in water and those in sediments. This could be interpreted to mean that the sources of Pb in River Mukurumudzi are anthropogenic.

The concentration of Cu in water and sediments across the different sampling points had shown no significant difference. Interrelations between metals in water and sediments provide important information on aquatic environment regarding their sources and pathways. Very strong, strong and moderate correlation indicates that, their sources of origin are similar, especially from industrial effluents, anthropogenic wastes and agricultural inputs (Schober, Boer, & Schwarte, 2018).

There was a strong positive correlation of the concentration of Fe in water across all the sampling areas (Table 1). This can be interpreted to mean that the contamination sources of Fe are the same across the different sampling points. Bomani and Ngulu-ku exhibited the strongest (r=0.800) correlation of (r=0.999). The lowest correlation was between Gazi and Bomani.
There was a negative correlation of Fe in sediments between Nguluku and other stations (Table 2). The correlation (-0.965) between Nguluku and Shimba Hills, (-1.00) between Nguluku and Bomani and (-0.96825) between Nguluku and Gazi. This is interpreted to mean that the source of Fe in Nguluku sediments is different from the sources at the other locations. All the other stations exhibited a positive correlation of Fe in sediments.

Table 2: Correlation of Fe in sediments

<table>
<thead>
<tr>
<th></th>
<th>Fe-Shimba Hills</th>
<th>Fe-Nguluku</th>
<th>Fe-Bomani</th>
<th>Fe-Gazi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Shimba Hills</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe-Nguluku</td>
<td>-0.96512</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe-Bomani</td>
<td>0.963733</td>
<td>-0.99999</td>
<td>1</td>
<td>-</td>
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<tr>
<td>Fe-Gazi</td>
<td>0.869017</td>
<td>-0.96825</td>
<td>0.969542</td>
<td>1</td>
</tr>
</tbody>
</table>

There was a positive correlation (0.990) of Pb in sediments between Shimba Hills and Nguluku (Table 3). There was also a positive correlation (0.976) of Pb in sediments between Bomani and Gazi. A negative correlation (-0.970) of Pb in sediments was observed between Shimba Hills and Bomani and (-0.893) between Shimba Hills and Gazi.

Table 3: Correlation of Pb in sediments

<table>
<thead>
<tr>
<th></th>
<th>Pb-Shimba Hills</th>
<th>Pb-Nguluku</th>
<th>Pb-Bomani</th>
<th>Pb-Gazi</th>
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</thead>
<tbody>
<tr>
<td>Pb-Shimba Hills</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-Nguluku</td>
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<td></td>
</tr>
<tr>
<td>Pb-Bomani</td>
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<td>-0.9259</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pb-Gazi</td>
<td>-0.89283</td>
<td>-0.82033</td>
<td>0.975585</td>
<td>1</td>
</tr>
</tbody>
</table>

Cu in water and sediments was strongly correlated across all the sampling points (Table 4).

Table 4: Correlation of Cu in sediments

<table>
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<th></th>
<th>Cu-Shimba Hills</th>
<th>Cu-Nguluku</th>
<th>Cu-Bomani</th>
<th>Cu-Gazi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shimba Hills</td>
<td>1</td>
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<tr>
<td>Nguluku</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bomani</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Gazi</td>
<td>1</td>
<td>1</td>
<td>1</td>
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One way ANOVA showed a significant difference (p=0.024) between the concentration of Fe in water in Nguluku and the control site along the Shimba Hills area. There was also a significant difference (p=0.050) in the concentration of Fe in sediments along Nguluku with those along the Shimba Hills area. There was no significant difference (p=0.139) in the level of Fe in water along the Bomani settlements and Shimba Hills area, there was also no significant difference (p=0.342) in the concentration of Fe in sediments along these two areas. There was no significant difference (p=0.212) in the level of Fe in sediments along Gazi and Shimba Hills area, the level of Fe in water in these two areas was also not significant (p=0.187). The difference in level of Pb in sediments along Shimba Hills and Nguluku was not significant (p=0.442). There was also no significant difference (p=0.684) in the level of Pb in sediments along Shimba Hills and Bomani settlement. There was also no significant difference (p=0.170) in the level of Pb in sediments along Shimba Hills and Gazi. This suggests that there are different sources of Pb input to the River Mukurumudzi.

CONCLUSION AND RECOMMENDATIONS

River Mukurumudzi is an important source of fresh water in Kwale County. Most of the populace use the river to get water for their domestic activities. The probable sources of contamination in the river are anthropogenic activities such as agriculture, mining and washing of clothes, motorcycles and bathing in the river. Based on this study it is concluded that the river is not contaminated by the selected heavy metals since they are all below the WHO and NEMA permissible limits. It is also concluded that there is a higher concentration of metals in sediments than waters. Conservation measures should be put in place in order to protect River Mukurumudzi from contamination. The extensive construction of dams on the river should also be controlled because it’s affecting the levels of water downstream hence, contributing to the accumulation of contaminants.

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