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Effects of Near Shore Dumping of Solid Waste on Fe(Ii) /Fe(Iii) Redox Processes And Nutrients Release At The Kibarani Dumpsite, Mombasa, Kenya

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Abstract: *Kibarani used to be a dumping site of solid waste of Mombasa on the shore of Makupa Creek. This work was aimed at evaluating the impact of this practice on the shores of the creek. Sediment samples were analysed for Fe(II)/ Fe(III), ammonium, phosphates using the UV-Visible Spectrophotometer. The levels of porosity, total organic matter content and redox potential values were determined. Results showed that lowest redox potential values were present in Station 3 which was the most impacted area. This showed that the area was highly anaerobic and the stable form of iron was Fe(II). Fe(III) levels ranged from 0-6% of the total HCl extractable iron content found in the sediment and was not detected at a depth of 6-12 cm in the highly polluted areas. The levels of phosphates increased with increase in contamination from 2.39± 0.25 µg/g in least contaminated to 16.43±0.67 µg/g in most contaminated site. While the levels of ammonium were highest ranging from 301.42±7.50 µg/g to 402.21±0.01µg/g in the most contaminated area and the levels were lowest ranging from 183.83±9.19 µg/g to 216.24±2.72 µg/g) in the area that is rooted and animal burrowing was high. Therefore, this study showed that solid waste disposal at the shores alters the geochemical properties of an environment and as a result left negative effects on the shoreline's flora and fauna.*

Key Words: *solid waste, Kibarani, Fe(II) /Fe(III), redox, nutrients*

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I. Introduction

Poor waste management causes an increase in health problems and poverty in many developing countries through high cost of health and loss of workforce productivity. The water resources are under a lot of pressure as a result of continuous population growth, urbanization, industrialization and food production. This presents a threat to the marine ecosystem and human health and wellbeing. It is estimated that 900 million people worldwide do not have access to safe water and over 2.6 billion people do not have access to adequate sanitation (Crocoran *et al*., 2010; Boblme, 2011). There is an increase of pollution in aquatic ecosystem due to the large amounts of solid waste and effluent load from domestic waste, industrial and agricultural activities. This has become a threat to life in the aquatic environment and humans. Solid wastes in many countries are discharged in uncontrolled dumpsites without any concern with the disposition technique or environmental implications. This can generate public health problems and degradation of the environment, due to contamination of the natural resources (Mara, 2004, UNEP/GPA, 2006; Okuku *et al*., 2011).

The major sources of pollution of the marine environment in Mombasa are solid waste and wastewater from industries, domestic sewage and storm water runoff. The Mombasa Local Authority used to dispose approximately 50% of domestic solid waste at an uncontrolled dumpsite known as Kibarani. This practice has lead to destruction of the mangrove ecosystem at the shore and has had detrimental effects on organisms at the shore (Mwaguni and Munga, 1997; Okuku *et al*., 2011; Matoka *et al*., 2014; Swaleh *et al*,. 2016).

To assess the impact of this activity on the marine ecosystem, scientific research is required to link the causes and effects of such activities. This study aimed to examine the effects of near shore dumping of solid wastes on the sediment biogeochemical processes. This was achieved by determining the levels of nutrients released at the dumpsite and redox processes of iron in the biodegradation of organic matter.

II. Methodology

Study site

The Kibarani dumpsite is located on the west of Mombasa mainland next the shores of the Makupa Creek. Mombasa is the largest town in the coast of Kenya. It is the largest urban center in the coastal region of

Kenya, with a population of approximately 939, 370 people (Kenya National Bureau of Statistics, 2009). Fig 1 shows Map of Mombasa and Kibarani dumpsite.

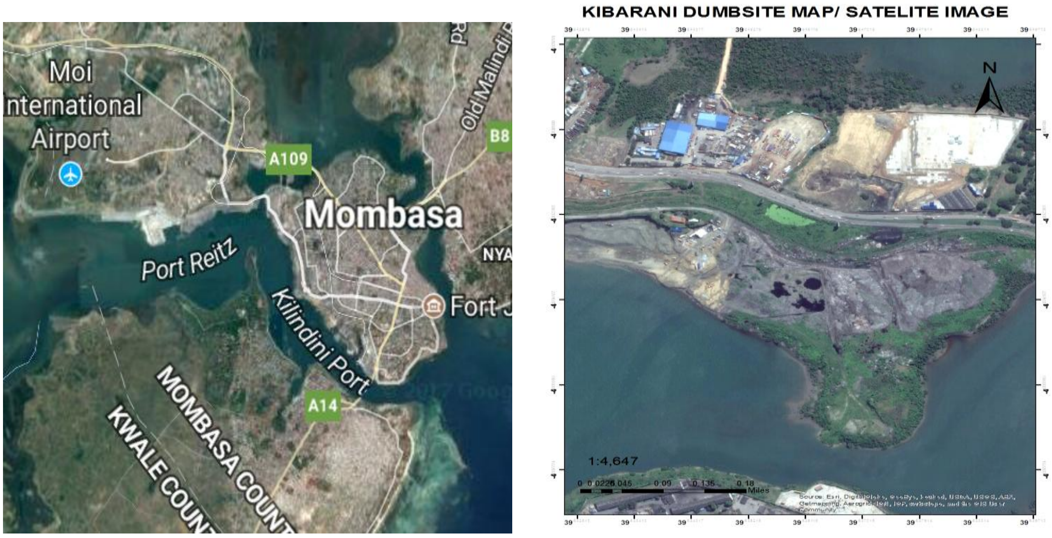

Figure 1: Map of Mombasa and Kibarani dumpsite

Source: Google maps and https://kiharagabrielmapping.wordpree.com/gallery/kibarani-dumpsite/

Sampling

Sampling was done during low tide. Three sites were selected from a least impacted area to the most impacted area. Where station 1 is the least impacted area, Station 2 is the moderately impacted area and Station 3 is most impacted area (Figure 2).

Figure 2: Station 1, least impacted; 2, moderately impacted; 3 most impacted area by the dumping on the shore.

Sediment was sampled using plastic sediment cores (4 cm internal diameter and 30 cm deep). Coring was done four times in each station on the sampling day. Redox potential was measured *in situ*. The readings were taken for each selected depth, 0-2, 4-6, 6-8 and 10-12 cm. Then sectioning of the selected depths was done at the sampling site after each redox potential reading. The four slices from each depth interval and station were pooled and mixed thoroughly. The homogeneous sediment mixture was put in air tight plastic bags for storage.

Once in the lab, porosity and organic matter content was determined. Porosity was determined by drying the sample in an oven at 25 ^{O}C for 24 hours and calculated as volume of water in the sample divided by total volume of sample. Then the dry sample was ashed at 450^{O}C for 6 hours in order to determine organic matter content.

Chemical analysis

Determination of iron reduction rates

The particulate iron pools were determined by the Ferrozine Method (Stookey, 1970). Of the sediment sample, 0.2 g was weighed and put in centrifuge bottles. This was followed by adding 0.5 M HCl to the sample for extraction of dissolved iron. The bottles were tightly closed and placed on a shaking table for 30 minutes. The samples were then centrifuged at 3000 rpm for 5 minutes.

For Fe(II) determination, 0.5 ml of extracted sample was pipetted into a scintillation vial then 2 ml of 0.02% Ferrozine was added. Absorbance for Fe(II) was measured against Ferrozine. Determination of Fe(III) was done by adding 0.2 ml of hydroxylamine to 0.5 ml of extracted sample in a scintillation vial. This was followed by 2 ml of 0.02% Ferrozine. Total Fe(II) was measured against ferrozine and the concentration of Fe(II) determined from the calibration graphs of the standards.

Nutrients extraction and analysis

To 10 g of sample in a plastic bottle, 40 ml of 1 M KCl was added. Then the samples were placed on a shaking table for a period of two hours. The samples were then put in a centrifuge for a period 10 minutes at 2000 rpm. The supernatant solution obtained was used for nutrient analysis according to Parsons *et al.* (1984).

Phosphates were determined using a mixed reagent containing 100 ml of ammonium molybdate, 250 ml sulphuric acid, 100 ml ascorbic acid and 50 ml potassium antimonyl-tartrate solution. To 20ml of the sample, 1ml of reagent was added. Absorbance was measured using a UV-spectrophotometer.

Ammonium was determined using two reagents. Reagent 1 was made of phenol solution and sodium nitroprusside solution and reagent 2 which was the oxidizing solution was made of sodium citrate solution and sodium hypochlorite solution. To 35 ml of the sample 2 ml of reagent 1 and 2 ml of reagent 2 were added consequently. Absorbance was measured using a UV- visible spectrophotometer.

III. Results And Discussion

Sediment properties at the site

There was a gradual change of the sediment from the least impacted area to the most impacted, from organic-poor silt to organic rich silt. Only the first 2 cm of station 1 and 2 was void of roots. There were no visible plant roots at station 3, which had a few dead mangrove trees and showed no sign of burrowing animals. Station 1 and 2 had a large number of burrowing animals. The sediment at Station 3 was a brown oxidized surface layer overlying grey-black subsurface sediment smelling of hydrogen sulphide (H_2S). The grey-black colour was due to reduction of ferric oxide (a normal constituent of beaches) to sulphide; this was caused by the anaerobic conditions at this area (Southward, 1965). Sediment in Station 2 was also grey-black in colour with green algae formed on the surface sediment. Station 1 sediment was grey-brown in colour, and this site was the least impacted by solid waste deposits. This soil colour was not unusual.

Porosity and organic matter content

Porosity was highest near the surface at all stations, but decreased from about 0.57 to 0.47 down the depth as shown in Table 1. These results were mainly attributed to the muddy type of soil present at the site. These soils retain water by capillary action between the soil particles when the tide falls (Southward, 1965). The organic matter content increased along the transect. The levels of organic matter increased with depth for all stations except for Station 3 where the first 8 cm showed no significant difference.

Table 1: Profiles of porosity given as mean ± S.D. (n = 3)

Depth cm	Station 1 Porosity	Station 2 Porosity	Station 3 Porosity
0-2	0.55±0.03	0.57±0.09	0.55±0.05
4-6	0.53±0.04	0.53±0.06	0.53±0.03
6-8	0.48±0.02	0.51±0.06	0.50±0.03
10-12	0.48±0.05	0.47±0.04	0.47±0.04

The organic matter content ranged from 0.78 g to 2.61 g with Station 2 and 3 having the highest levels of organic matter content as seen in Table 2. The high organic matter in station 2 could be because of organic input mostly in the form of mangrove litter on surface sediments and in the deeper sediments because of root matter. In Station 3 it could be due to the dead plants and plant roots and also this station was the most impacted by solid waste deposits. The organic matter content reduced the circulation of interstitial water and encourages the growth of bacteria thus depriving the deeper layers of oxygen.

Table 2: Total organic matter (T.O.M.) given as mean± S.D. (n= 3)

Depth cm	Station 1 T.O.M. (g)	Station 2 T.O.M. (g)	Station 3 T.O.M. (g)
0-2	0.78±0.12	1.16±0.19	1.70±0.13
4-6	0.95±0.28	1.23±0.23	1.70±0.21
6-8	1.04±0.34	1.35±0.32	1.69±0.78
10-12	0.93±0.05	1.13±0.04	2.61±0.23

Iron (Fe(II) and Fe(III))

High levels of Fe(II) appear in anaerobic environment via decomposition of organic matter and reduction of Fe(III) by microbial action. Fe(III) is an electron acceptor and it acts as an intermediate oxidant for microbial activities. The highest Fe(II) content were observed in Station 3 which was the most contaminated area, while Station 1 and Station 2 reflected low levels of iron compared to Station 3 as seen in Table 3. The levels of Fe(II) ranged from 8.20 to 12.25 µg/g in Station 3 which was the most impacted station and that of Fe(III) was from 0.00 to 0.55 µg/g. Station 2 which was highly vegetated had Fe(II) ranging from 6.74 to 9.58 µg/g and Fe(III) ranged from 0.00 to 1.27 µg/g.

At low tide, animal burrows and cracks especially in vegetated areas increased the area of air-sediment interface that was seen mostly in Station 2 and a little in Station 1. Root excretion of oxygen and downward transport of oxygen via burrows by sea animals increased the redox and thus the Fe(III) content in deeper sediment layers. The contribution of Fe(III) respiration, was not significant in Station 3. Fe(III) was only found in the upper sediment layer, and this could be because of lack of respiration pathways for Fe(III) due to plant roots and burrowing by animals. The organic matter content also encouraged the growth of bacteria thus depriving the deeper layers of oxygen. Station 3 had no Fe(III) in the deeper sediments as seen in Table. 3.

Table 3: Profiles of iron (Fe(II) and Fe(III)) given as mean± S.D. (n = 3)

Depth cm	Station 1		Station 2		Station 3	
	Fe(II) (µg/g)	**Fe(III) (µg/g)**	**Fe(II) (µg/g)**	**Fe(III) (µg/g)**	**Fe(II) (µg/g)**	**Fe(III) (µg/g)**
0 - 2	6.72±0.47	0.77±0.18	6.74±0.08	0.80±0.20	8.20±0.13	0.55±0.04
4 -6	7.58±0.42	0.64±0.24	7.60±0.12	1.27±0.38	9.12±0.08	0.12±0.01
6 - 8	8.02±0.20	0.63±0.12	7.46±0.63	1.12±0.06	11.26±0.18	0.00±0.00
10 - 12	7.78±0.05	0.57±0.10	9.58±0.73	0.00±0.00	12.25±0.15	0.00±0.00

Variation of Fe(II) and Fe(III) at the different stations

The level of Fe(III) decreased with depth increase and was found absent in Stations 2 and 3 at depth 10 – 12 (figure 2d). At a depth of 6-8 cm (2d) Fe III was found absent in Station 3. At a depth of 4-6 cm (2b) Fe III was found absent at station 3. This showed that its role as an intermediate oxidant diminished with depth. Fe(III) accounted for 0-6% of the total HCl extractable iron content in the upper 8 cm of the most contaminated area (Station 3) (figure 2a,b). Below this depth, Fe(III) decreased to trace amounts less than 1% of the total. At the rooted and bioturbated stations, Station 1 and 2 Fe(III) reached 7-14% (figure 2a, b) of the total HCl extractable iron content in the upper 8 cm of the sediment and deeper down decreased to less than 6% (Figure 2d).

Station 3 had organic rich sediments and was the most impacted thus highly anaerobic. The organic matter encouraged the growth of bacteria thus depriving the deeper layers of oxygen, as seen in Table. 2.

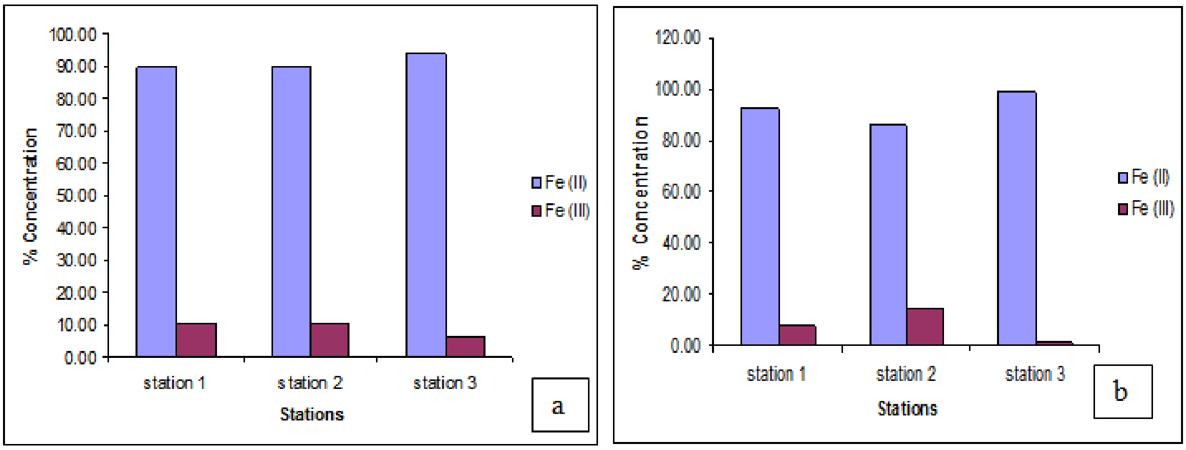

Figure 2: Variation of Fe(II) and Fe(III) concentration with depth

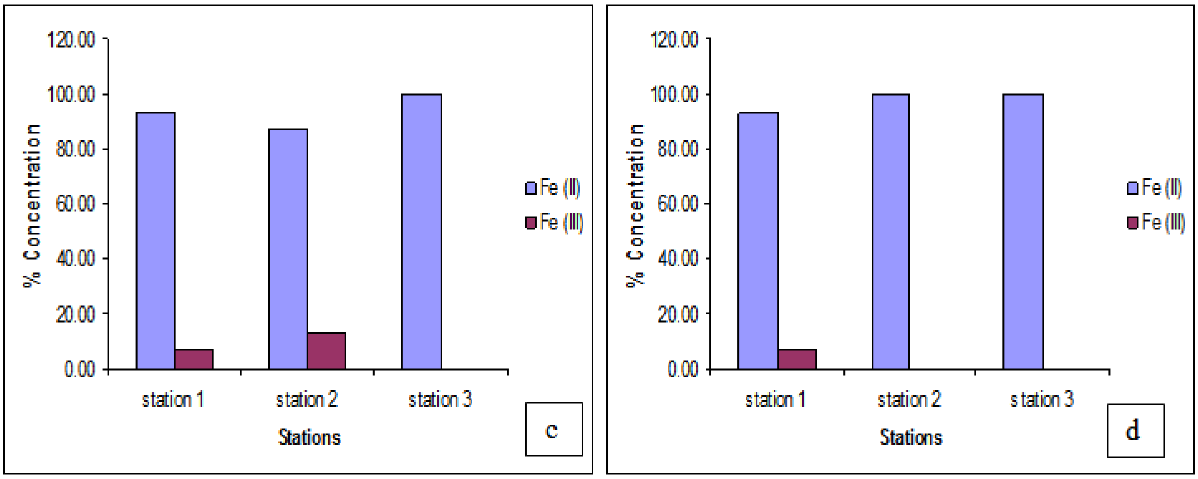

Figure 2 (a): Variation of Fe(II) and Fe(III) concentration at depth 0 – 2 cm; **Figure 2 (b):** Variation of Fe(II) and Fe(III) concentration at depth 4-6 cm; **Figure 2 (c):** Variation of Fe(II) and Fe(III) concentration at depth 6 – 8 cm ; **Figure 2 (d):** Variation of Fe(II) and Fe(III) concentration at depth 10 – 12 cm

Comparison of vertical distribution of Fe(III) and redox potential values

Lowest redox potential values showed lowest Fe(III) levels at Station 3 which was the most impacted area as per Table 4. This showed that the area was highly anaerobic and the stable form of iron was Fe(II). Highest redox potential value showed highest Fe(III) levels were at Station 2 which was highly vegetated. The plant roots and burrowing by animals increased air sediment interface thus partially anaerobic.

Table 4: Comparison of vertical profile of Fe(III) and Redox potential

Depth cm	**Station 1**		**Station 2**		**Station 3**	
	Fe(III) (µg/g)	**mV**	**Fe(III) (µg/g)**	**mV**	**Fe(III) (µg/g)**	**mV**
0-2	0.77	136.8	0.80	163.60	0.55	95.40
4-6	0.64	192.35	1.27	215.85	0.12	-104.75
6-8	0.63	207.55	1.12	179.45	0.00	17.00
10-12	0.57	62.3	0.00	72.05	0.00	-85.95

Nutrients

Ammonium

The levels of Ammonia were highest in Station 3 and lowest in Station 2. In table 5 it was seen that ammonium in Station 3 increased with increase in depth. The increase of ammonium with depth could have been attributed to the ammonification process where ammonia was introduced into the ecosystem by either decay of dead living organisms or by the reduction of nitrates (Rivera-Monroy et al., 1995). Station 3 was the most contaminated area of the three sites; the high levels of ammonium at this station could be attributed to the decay of dead plants and animals and other protein containing products of the decayed deposited waste. In the deeper sediment, the conditions were anaerobic.

While the levels of ammonium at Station 2 decreased with increase in depth but was lowest on the surface. The decrease in levels of ammonium in Station 2 could have been due to uptake by rooted plants like mangrove trees and the algae on the surface sediments. Station 1 had ammonium levels increasing with increase in depth. The levels of ammonium from Table 5, ranged from 183 to 402 µg/g. The decrease in levels of ammonium could also be because of oxidation of ammonia via bacterial action to nitrite then nitrates.

Table 5: Profiles of ammonia given as mean ± S.D. (n=3)

Depth	**Station 1** **NH_4^+(µg/g)**	**Station 2** **NH_4^+ (µg/g)**	**Station 3** **NH_4^+ (µg/g)**
0-2	241.02±5.30	183.83±9.19	301.42±7.50
4-6	356.06±6.77	216.24±2.72	389.64±5.79
6-8	375.08±5.86	207.77±5.17	397.70±0.01
10-12	387.79±1.89	187.73±4.78	402.21±0.01

Phosphates

The levels of phosphates increased from Station 1 to Station 3 (Table 6). Station 3 had the highest concentrations of phosphates which could have been due to the high levels of solid waste deposited in this area and lack of plants to take up these nutrients. The decrease of phosphates levels in Station 2 could be ascribed to the up take of the nutrient by the mangrove trees in the area. In Station 1, phosphates levels increased with increase in depth. The range of phosphates for all stations was from 2.39 to 16.4 µg/g (Table. 6).

Table 6: Profiles of phosphates given as mean ± S.D. (n = 3)

Depth	**Station 1** **PO_4^{3-}(µg/g)**	**Station 2** **PO_4^{3-}(µg/g)**	**Station 3** **PO_4^{3-}(µg/g)**
0-2	2.39 ± 0.25	8.44 ± 0.45	9.84 ± 0.41
4-6	2.45 ± 0.17	8.15 ± 0.43	8.73 ± 0.79
6-8	4.12 ± 0.24	6.73 ± 0.57	14.69 ± 1.70
10-12	4.86 ± 0.42	8.51 ± 0.76	16.43 ± 0.67

IV. Conclusion

From the findings of this study, it can be concluded that nutrients release is highly affected by the waste disposal process. The levels of ammonium were highest in the area that was most impacted by the dumping and lowest in the moderately impacted area with high vegetation and animals. Ammonium increased with depth in the most impacted area and decreased with depth in moderately impacted area with high vegetation. The levels of phosphates increased from the least impacted area to the most impacted area and increased with depth in the most impacted area and decreased with depth in the area with high vegetation. The redox processes of iron are affected by the dumping, giving more Fe(II) in the most impacted area and less in the area with high vegetation and animals. Redox potential levels were highest in area with highest Fe(III) values and lowest in areas with low Fe(III) levels.

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