Speciation of Trace Metals Pb, Zn, Cu and Cd in Surficial Sediment from Makupa Creek Mombasa, Coastal Kenya

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Abstract

Trace metals (Zn, Pb, Cu, Cd) speciation of surface sediments from Makupa creek, coastal Kenya were determined by sequential extraction procedure. The procedure was used to extract the trace metals in sediments geochemical phases (exchangeable, carbonates, Fe-Mn oxides, organic matter/sulphide, and residual). Trace metals analysis was done using ICP/MS. The trace metal speciation results indicated that Pb, Zn, and Cd were mainly associated with the exchangeable, carbonates and Fe-Mn oxides in most of the sampling sites. The highest concentration of the trace metals were associated with Fe-Mn oxides with Zn concentration at 362.5 µg/g, Pb, 31.5 µg/g. Copper was mostly associated with the organic matter/sulphide and carbonate at concentration of 117.5 µg/g and 69.9 µg/g respectively. Generally, trace metals in sediment from Makupa creek were mainly associated with the bioavailable fractions (BAF) and their ranges were: Pb (60% - 98%), Zn (90% - 99%), Cu (70% - 91%). It was found therefore, that there was trace metals enrichment in sediments from Makupa from anthropogenic sources and bioavailable to biota.

Keywords

Speciation, Sequence Extraction Procedure, Bioavailability, Trace Metals, Sediment

Subject Areas: Environmental Sciences

1. Introduction

Trace metals are of concerns as contaminants of water bodies because of their persistence and high toxicity to many aquatic organisms. Trace metals occurrence in most rivers binds to suspended solid and a small fraction is in the soluble form. These suspended solids sink and settle as sediments. Nature sediments are complex mixtures
of various phases such as residues of weathering and erosion such as clays and other aluminosilicates and iron and aluminum oxyhydroxides and sulphides, substances produced by biological activities, both organic (microorganisms, humic substances, biological detritus) and inorganic (carbonates, phosphates, silica) [1]. Trace metals in sediments associate with specific phases of natural sediments by way of sorption. Therefore sediments are solids phases in aquatic environment that controls dissolved level of metals by mechanism of sorption-desorption. Surface sediments are “natural sponge” that absorb all kinds of pollutants from water and accumulate all sorts of harmful substances [2] [3]. Therefore sediments act as sinks and sources of trace metals to overlying water [4].

Monitoring of sediments contaminant is critical to tract regional trends, understand potential toxic impacts to marine resources and make management decisions [5]. The sediments provide both short and long term memory of contaminant loading to the marine environment. Sediments not only provide an indication of the current quality of coastal waters but also provide important information on the transportation and fate of pollutants [6]. The source of trace metals into marine environment includes river discharge, agricultural activities, urban runoff, industrial and domestic sewerage and oil spills and natural sources such as rock weathering [7].

Trace metals can be highly toxic to various living organism while others are essential but can be toxic at high doses. Most of their toxicity depends on their particular form in which the trace metal is present in the system [8]. The different forms of particular trace metals or compounds are referred to as “species”. Speciation of trace metals is defined as distribution of trace metals among defined chemical species in a system [9]. It is the available forms (species) of trace metals in aquatic systems which is causing toxicity in organisms not the total concentration in the matrices. The distribution of trace metals in the sediment Phases is a better way in understanding of the metal available to biota.

The speciation of dissolved metals is relatively well understood. But there is a considerable uncertainty about the nature of the bioavailable forms of trace metals in sediments. Determination of specific chemical species in sediments is difficult and sometimes impossible [10]. The composition of sediments is very complex and variable and it’s extremely difficult to determine the bioavailability of sediment bound metals. Geochemical methods for determining the concentrations of metal binding on to sediments components and assessing the potential bioavailability of metals in the field as a consequence are based mainly on empirical and chemical extraction technique [11].

This technique was first developed by Tessier in 1979 [14]. It is based on the fact that trace metals in sediments are present in a wide variety of physico-chemical form or (species). The speciation of metals has a profound influence on its transport, fate and effects in the aquatic environment. The extraction procedures or fractionation of metals according to sediments phases, such as exchangeable, Bounds to carbonates, Bound to iron and magnesium oxides, Bond to organic matter and residual can be done by method of Sequential Extraction.

The Sequence extraction procedures method has been widely accepted and has been used in determining metal speciation in solid matrix [10] [12] [13]. It has been established from the procedures that pretreatment of samples affects metal speciation. Therefore samples should be analyzed fresh within 24 hours in order to minimize effects of samples pretreatment [11].

Makupa creek is generally shallow and is sheltered from high tidal currents. The creek has been used as a domestic and industrial dumping site for the last forty years [15]. The wastes from harbor activities at Fort Reitz creek which includes waste from petroleum and other pollutants mainly end up at Makupa creek which acts as their sink because of its enclosed nature and low flushing rate of its waters during tidal cycles.

Trace metals studies on surface sediments from the creek shows a significant increase of total trace metals concentration [16] [17]. But these studies on trace metals at Makupa creek are only limited to total metal concentrations in sediments. Total trace metal content in sediments provide a simple means of expressing a measure of pollution, it has been pointed out by numerous report that this measures are deficient in predicting the toxicity of these pollutants [6]. Therefore the aim of this study is to determine the concentrations of trace metals (Cu, Zn, Pb and Cd) in Makupa creek sediments phases. It is hypothesize that trace metals in Makupa creek sediments are not available to biota.

2. Material and Methods

2.1. Study Area

The study area is located within Mombasa county in Kenya and its specific location is defined by latitude 39°38'E, and longitude 4°02'S (Figure 3). The area has a tropical climate with two seasons, dry in January/February and wet in April/May. The total annual precipitations is 1072.7 mm. The yearly average temperature is
26.30°C. To the north of the creek is Makupa causeway which occurs between it and Tudor Creek blocking their waters from mixing. To the south of the study area is Port Reitz where Kilindini harbor is situated and is separated by Kipevu Bridge channel. At high tide water from Port Reitz flows over to Makupa Creek and at low tide the water flows back to the sea. To the western side of the creek its borders Kiparani Dump site. Because of its enclose nature of the creek there is less flushing water by sea waves. Therefore the creek act as a sink of pollutants from the town rain water runoff, shipping activities at Kilindini harbor at port Reitz creek as well leachate and discharge from the Kibarani dumping site.

2.2. Sampling

Surface sediment samples were collected in duplicate using 32 mm diameter corer. Two samples were collected from each of the seven identified sample sites (Figure 1) between April and Oct 2013. Sampling was done during low tides in order to access the sediment easily. At each of the sampling sites the top 1 - 5 cm sediment were extruded using corer piston on to a polyethylene sheet. Using plastic spoon, large stones and debris were re-
moved and the samples wet sieved through <63 µm polyethylene sieves to obtained homogeneous sample. After
sieving the samples were transferred into a labeled plastic bag and place in an ice box at 4°C for transporting
them the laboratory. At the laboratory the sample were divided into three sub samples. The subsamples were
used for determination of moisture content, total metal extraction by acid digestion, and sequential extraction
procedures. The samples for sequential extraction procedures were done on wet sediments immediately on ar-
riving at the laboratory. Samples for total metal concentration were air dried and digested with aqua regia acid.

2.3. Moisture Content Determination

The moisture contents of the samples were determined by weighing approximately1g of the samples and placing
them in an oven at 100°C over nite. This was used to calculate the equivalent dry weight of each samples.

2.3.1. Total Metals Extraction Procedures

All reagent used for extraction and analysis were analytical grade.

For total metal extraction, air dried 1 g aliquots were weighed into Teflon beakers to which 6ml of nitric was
added and shaken gently for 2 minute and finally 3 ml of hydrochloric acid were added. The beakers were trans-
ferred on to a hot plate at 86°C and heated for 3 hours until no brown fumes evolved and occasionally adding
drop of nitric acids in order not to allow the beakers to dry. On cooling the solution were filtered with Whiteman
45 um filter paper and made to 20 ml in a volumetric flask. The samples were kept cool at 4°C until analysis.

2.3.2. Sequential Extraction Procedure

An equivalent of 1g dry weigh of sediment were weighed into plastic centrifuge tubes for the extraction. The
Sequential extraction procedure is summarised in Table 1.

2.4. Sample Analysis

Trace metal analysis was done using an inductively coupled plasma-mass spectrometry (ICP/MS) model ELAN
900 Perkin Elmer, equipped with Perkin Elmer AS91 auto sampler. ICP/MS analysis was done using external
calibration. The calibration standard solution was prepared from 1000 ug/g stock solution. The results for the
calibration are shown in Table 2.

Table 1. Five fractions Sequence extraction procedure.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Geochemical phases</th>
<th>Extraction Reagent/Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Exchangeable</td>
<td>8 ml, IM MgCl2, adjust pH with Acetic acid to pH 7, shake for 1 hr, room temp.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Mechanical shaker Julabo sw-20c was used)</td>
</tr>
<tr>
<td>F2</td>
<td>Bound to carbonate</td>
<td>8 ml, 1 M sodium acetate, added drops of Acetic acid for PH adjustment to PH 5,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>shaken for 5 hrs at room temp (Mechanical shaker Julabo sw-20c was used)</td>
</tr>
<tr>
<td>F3</td>
<td>Bound to iron and manganese oxide</td>
<td>20 ml, 1 M Hydroxylamine hydrochloride + 25% V/V acetic acid, PH2, 96°C,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shaken for 3hrs (Mechanical shaker Julabo sw-20c was used)</td>
</tr>
<tr>
<td>F4</td>
<td>Bound to organic matter and sulphides</td>
<td>5 ml, 30% hydrogen peroxide Add added drop wise allowing initial reaction to subsidies</td>
</tr>
<tr>
<td></td>
<td></td>
<td>then add 3 ml, 0.02M nitric acid, pH 2, heat for 5 hrs at 80°C, occasionally shaking</td>
</tr>
<tr>
<td>F5</td>
<td>Residual</td>
<td>Digested with 20 ml 1:3 HCL acid:Nitric acid (aqua regia) for 3hrs in Teflon beakers</td>
</tr>
</tbody>
</table>

*Note: For every fraction extracted the extracts were centrifuge at 3000 rpm for 20 min and the supernatants decanted into a 20 ml volumetric flask
and made to the mark with extraction reagent. The residue water rinsed with 8 ml of deionized water and the decanted before adding the extraction
reagent of the next step. The 20 ml extract was kept at 4°C until analysis.

Table 2. Standard Calibration results (ng/ml).

<table>
<thead>
<tr>
<th>Calibration standard (ng/ml)</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>10</td>
<td>50.914</td>
<td>100.113</td>
<td>202.038</td>
<td>498.658</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>48.914</td>
<td>93.605</td>
<td>196.051</td>
<td>498.790</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
<td>50.893</td>
<td>98.404</td>
<td>203.210</td>
<td>499.146</td>
</tr>
<tr>
<td>Cd</td>
<td>10</td>
<td>50.120</td>
<td>99.280</td>
<td>201.541</td>
<td>499.515</td>
</tr>
</tbody>
</table>
Quality Control Analysis
For all the sampling sites, the total metals concentration of each metal obtained by acid digestion is compared with total metal obtained by sequence extraction procedures in order to evaluate the accuracy of the methodology. The results of the sum of concentration of each metal in sediment phases (fraction) in sequential extraction agreed to within with ±20% the independently determined total metal concentrations by acid digestion, supporting the overall accuracy of extraction procedure (Table 3).

3. Results and Discussion
The geochemical phases/fraction are Exchangeable (F1), Carbonates (F2), Fe-Mn oxides (F3), organic matter/sulphide (F4), residual (F5). Figures 2-5 shows graphs of distribution of the trace metals among the geochemical phases by each site. The percentage of the Bioavailable fraction (BAF) and Non Bioavialale fraction (NBAF) of the trace metals Pb, Zn, Cu, and Cd, by site are presented in Figures 6-9. The BAF the sum of Exchangeable, Carbonates, Reducible (Fe-Mn oxides ) and NBAF sum of organic matter/sulphide and residual was determine by method by Young [5] [18].

3.1. Lead Pb
The results for lead distribution in the geochemical phases per site is presented in Figure 2. Lead appears to be well
Figure 4. Percentage distribution of Cu in each geochemical fraction by site.

Figure 5. Percentage distribution of Cd in geochemical fractions by site.

Figure 6. Distribution of Pb in BAF and NBAF by site.
Figure 7. Percentage distribution of Zn in BAF and NBAF by site.

Table 3. Percentage recoveries of acid digestion and Sequential extraction methods by site.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Pb Acid dig. ng/ml</th>
<th>Sequent Extr. ng/ml</th>
<th>% Reco.</th>
<th>AcidDig. ng/ml</th>
<th>Seque. Extr. ng/ml</th>
<th>% Recoveries</th>
<th>Acid Diges. ng/ml</th>
<th>Seque. Extraction</th>
<th>% Recoveries</th>
<th>Acid Diges. ng/ml</th>
<th>Seque. Extracting/ml</th>
<th>% Recoveries</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MS</td>
<td>1621.5</td>
<td>1580.53</td>
<td>97.5</td>
<td>4284.0</td>
<td>4422.0</td>
<td>103</td>
<td>1612.0</td>
<td>4694.4</td>
<td>91.1</td>
<td>1612.0</td>
<td>1469.4</td>
<td>103</td>
</tr>
<tr>
<td>2 ms</td>
<td>769.3</td>
<td>816.7</td>
<td>106</td>
<td>2910.2</td>
<td>2435.3</td>
<td>83.7</td>
<td>631.6</td>
<td>857.7</td>
<td>135</td>
<td>631.6</td>
<td>857.7</td>
<td>135</td>
</tr>
<tr>
<td>3 ms</td>
<td>1219.4</td>
<td>1048.2</td>
<td>85.9</td>
<td>6917.2</td>
<td>6096.5</td>
<td>77.0</td>
<td>1175.1</td>
<td>1044.4</td>
<td>88.8</td>
<td>1175.1</td>
<td>1044.4</td>
<td>88.8</td>
</tr>
<tr>
<td>4 ms</td>
<td>2441.4</td>
<td>2567.3</td>
<td>105.0</td>
<td>10244.8</td>
<td>3741.5</td>
<td>36.5</td>
<td>16240.8</td>
<td>1586</td>
<td>9.76</td>
<td>16240.8</td>
<td>1586</td>
<td>9.76</td>
</tr>
<tr>
<td>5 ms</td>
<td>1233.9</td>
<td>1685.19</td>
<td>136</td>
<td>4997.3</td>
<td>5297</td>
<td>105</td>
<td>1171.3</td>
<td>1288.8</td>
<td>109.8</td>
<td>1171.3</td>
<td>1288.8</td>
<td>109.8</td>
</tr>
<tr>
<td>6 ms</td>
<td>953.9</td>
<td>941.7</td>
<td>98.7</td>
<td>9690</td>
<td>7699.7</td>
<td>79.5</td>
<td>8775</td>
<td>6829</td>
<td>77.8</td>
<td>8775</td>
<td>6829</td>
<td>77.8</td>
</tr>
<tr>
<td>7 ms</td>
<td>341.9</td>
<td>364.4</td>
<td>93.8</td>
<td>1631</td>
<td>20108</td>
<td>123</td>
<td>487.2</td>
<td>521.3</td>
<td>106.9</td>
<td>487.2</td>
<td>521.3</td>
<td>106.9</td>
</tr>
</tbody>
</table>

Figure 8. Percentage distribution of Pb in BAF and NBAF by site.
distributed among the seven sites. The concentrations of lead in high in exchangeable and reducible fractions among the sites with the residual being the lowest. The highest concentration of Pb was at site 1 in Fe-Mn oxides phase (31.5 µg/g). This is consistence with the results obtained by other authors [19]-[21]. This could be due to formation of stable complexes with Fe and Mn oxides. The metal in this fraction may be release into the reducable phase if the sediment is subjected to more reducing conditions [22] [23]. A major source of lead input into the creek at the sites 1 could be deposition of waste from Mombasa harbor and traffic crossing Kibevu bridge. At site where there are death mangroves is the Kibarani dump sites which discharges leachate into the creek at site 4 hence increase lead concentrations. The percentage of the bioavailable Fraction (BAF) and Non bioavailable fraction (NBAF) of lead in sediment at each site is presented in Figure 6. At site1, 2, 6 and 7 the bioavailable and non bioavailable fractions of lead were over 90% respectively. The high percentage of Pb lead in the bioavalable fraction means that the sources of lead in Makupa creek sediments is from anthropogenic sources.

### 3.2. Zinc Zn

The distribution of Zn in geochemical phase by site is presented in Figure 3. Zinc appears is well distributed in Makupa creek. It is mainly associated with Fe-Mn oxides, exchangeable, and carbonates fractions in most of the sites. The highest concentration of Zn was in site 7 bounded on Fe-Mn oxides fraction (F3) 362.5 µg/g followed by site 5 and 4, with 288.2 µg/g (F1) and 234.6 µg/g (F3) respectively. The high concentration of Zn was found to associate with Fe-Mn-oxides fraction in the Makupa creek. This is not unusually because Zn adsorbed on these oxides has high stability constants than carbonate [18]. High percentage of Zn has been found to associate with Fe-Mn oxides in other studies of polluted sediments [22] [23].

The presence high concentration of Zn in the first four fractions (F1, F2, F3) at site 4 and 5 could be due to leaching from Kibarani Dumpsite situated at the shore of the creek. At the dumpsite, sewage and solid waste are deposed and during raining seasons, runoff and leachate from it enters Makupa creek at the two sites. At site 7 the concentration of Zn is high in F3 this could be attributed to urban effluent discharge observed at the site from areas around Maritini urban. The percentage distribution of Zn among the geochemical phases at each site is shown in Figure 7. The chemical partitioning of Zn is mainly hosted by the BAF in most of the sites except in site 5 which indicate high percentage of Zn in the NBAF. Therefore the high percentage of Zn in BAF could be due to anthropogenic sources into the creek.

### 3.3. Copper Cu

At site 6, is an entry of urban runoff from Maritini into the creek. These runoff might be containing high organic content. Copper in Figure 4 is mainly bound in organic/sulphide fraction (F3). This is due to its stable organic-copper complexes [14] [25] [26]. Several studies have also reported high concentration of Cu bounded with organic matter in sediments [25] [27]. Copper bioavailability in makupa creek is less than for Pb and Zn although the percentage of copper in the bioavailable fraction BAF and those in NBAF are almost in equal ratios.
3.4. Cadmium Cd

Cadmium appeared to be below detection limit in most of the sites. This trend was also observed by Muohi, on total metal concentration studies in makupa sediments [16]. The concentration of Cd in all the geochemical phases is below the detection limit as shown in Figure 5, except in carbonate fraction F3 in site 4. The Cd at this site is bioavailable since the carbonate represent the portion of the metal that can be easily mobilized by changes in pH and salinity. At site 4 the leaching from the dumpsite is discharged to the creek. Therefore the presence of Cd at this site is possibly due to the waste deposited in the creek.

4. Conclusions

The trace metal speciation results showed that Pb, Zn, and Cd were mainly associated with the exchangeable, carbonates and Fe-Mn oxides in most of the sampling sites in the study area. Copper was mostly associated with the organic matter/sulphide at only site 6 but on other sites it followed the same pattern like the other metals. This feature for copper may be due to large flux of organic matter from the urban runoff. It has been found that Pb, Zn, and Cu are the major contaminant in the sediments confirming earlier report by Muohi et al. during the studies of total metal concentration in sediments from Makupa creek [16]. The presence of high concentration of metals in the Bioavailable fractions at site 4 and 5 indicate that the Kibarani dumpsite is the major contributor of pollutant to Makupa creek. Therefore, it can be concluded that metals speciation studies have identified the potential pollution sources in this creek which could have been missed in total metals studies.

The trace metals in sediment of Makupa creek were mainly associated with the bioavailable fractions BAF at ranges of Pb (60% - 98%), Zn (90% - 99%), Cu (70% - 91%). This confirms that there is high risk of metals poisoning to biota in the creek. Fishing is done by the local communities living around the creek hence exposing themselves to metal toxicity. Further studies is necessary to determine viable mitigation measures against the risks posed by high levels of trace metals in the sediment and the levels of the metals in aquatic organism living the area.

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References


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