Assessment of Heavy Metals Allocation and Contamination Indicator in the Sediments of Coastal Areas of Karachi, Sindh, Pakistan

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Abstract: Coastal areas of Karachi, Sindh, Pakistan were selected with the intention of study the accessibility of heavy metals and their concentrations in the surficial sediments (<60 μm). These top soil samples were analyzed for Fe (Iron), Mn (Manganese), Cr (Chromium), Pb (Lead), Zn (Zinc), Cu (Copper), Co (Cobalt) and As (Arsenic) to scrutinize metals concentrations in sediments. Evaluation of anthropogenic pollution in sediments contamination indicator by Single-factor index analysis. Basic concentration of Mn is maximum in coastal sediments followed by Fe, Zn, Pb and As that is Mn > Fe > Zn > Pb > Co > Cu > As. This study exposed that confined geology has not revealed a few noteworthy influence on coastal sediments of the study area. The consequences of this study showed that Fe, Cr and As are the mainly severe pollutants in creek / beach sediments especially at Port Qasim industrial area and Ketti Bunder.

Key words: Heavy Metals • Contamination • Sediments • Coastal Area • Pollutants

INTRODUCTION

Soil is not only a medium for plants to grow or a pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface, ground and coastal water. So the accumulated pollutants in surface soils ultimately transported to different environmental components of coastal aquifers. Soil analysis offers advantages over water analysis for the control and detection of metal pollution in estuaries [1], although metal concentrations may also fluctuate over time [2].

Heavy elements found in soils/sediments are immobilized in water and thus could be involved in absorption, co-precipitation and complex formation [3]. Sometimes they are co-adsorbed with other elements as oxides, hydroxides of Fe, Mn, or may occur in particulate form [4]. Their concentrations in stream and coastal sediment compartments can be used to reveal the history and intensity of local and regional pollution [5].

Anthropogenic activities have greatly altered the geochemical cycle of heavy metals, resulting in widespread environmental contamination [6]. The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon mineralogical composition and depositional environment of the sediments [7].

The coastal areas of Sindh present to the northern part of the Arabian Sea and specially the beaches of Karachi are among the best beaches in the world. The beaches of Karachi are almost bounded by the Hub River in the west and the Indus River in the east. The coast of Karachi can be divided into two parts; lying on the west of the navigation channel of Karachi harbor, starting from Manora Island extending up to Cape Monze and ultimately to Makran coast beginning from Gadani beaches. The other part of the coastline is on the eastern side on navigation channel, which comprises of Clifton, Gizri and Ibrahim Haidari beaches. Discharge of toxic chemicals, over pumping of aquifer and contamination of water bodies with substance that promote algae growth are some of the today’s major cause for water quality degradation.

It has been observed worldwide that the impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to the study areas [8] as the coastal area receives significant amount
Table 1: Sampling sites and soil analysis results of coastal sediments from different locations of Karachi, Sindh.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name of Locations</th>
<th>X</th>
<th>Y</th>
<th>Cr (ppm)</th>
<th>Cu(ppm)</th>
<th>Fe(ppm)</th>
<th>Mn(ppm)</th>
<th>Pb(ppm)</th>
<th>Co(ppm)</th>
<th>Zn(ppm)</th>
<th>As(ppm)</th>
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<tbody>
<tr>
<td>1</td>
<td>Qazi Muhammad, Runn of Kutch</td>
<td>68°47'4.26&quot;E</td>
<td>24°21'0.15&quot;N</td>
<td>0</td>
<td>0</td>
<td>9.2</td>
<td>84</td>
<td>5</td>
<td>0</td>
<td>48</td>
<td>0.002</td>
</tr>
<tr>
<td>2</td>
<td>Qazi Muhammad, Runn of Kutch</td>
<td>67°11'5.43&quot;E</td>
<td>24°55'2.46&quot;N</td>
<td>0</td>
<td>0</td>
<td>11.7</td>
<td>77</td>
<td>8</td>
<td>0</td>
<td>51</td>
<td>0.001</td>
</tr>
<tr>
<td>3</td>
<td>Main keti Bandar (East)</td>
<td>67°27'9.47&quot;E</td>
<td>24°5'20.63&quot;N</td>
<td>0.3</td>
<td>0.9</td>
<td>56</td>
<td>57</td>
<td>2</td>
<td>4.5</td>
<td>24</td>
<td>4.7</td>
</tr>
<tr>
<td>4</td>
<td>Keti bandar 1</td>
<td>67°27'9.59&quot;E</td>
<td>24°8'0.43&quot;N</td>
<td>1</td>
<td>1.1</td>
<td>38</td>
<td>48</td>
<td>2</td>
<td>4.3</td>
<td>18</td>
<td>6.1</td>
</tr>
<tr>
<td>5</td>
<td>Keti bandar 2</td>
<td>67°27'6.97&quot;E</td>
<td>24°7.78&quot;N</td>
<td>0.7</td>
<td>0</td>
<td>43</td>
<td>52</td>
<td>0</td>
<td>4.2</td>
<td>22</td>
<td>4.3</td>
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<td>6</td>
<td>Port Qasim JT</td>
<td>67°34'8.22&quot;E</td>
<td>24°77.58&quot;N</td>
<td>34</td>
<td>3</td>
<td>1130</td>
<td>433</td>
<td>37</td>
<td>6.9</td>
<td>213</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>Steel mill, Bin Qasim</td>
<td>67°33'9.03&quot;E</td>
<td>24°78'7.37&quot;N</td>
<td>28</td>
<td>2.6</td>
<td>1078</td>
<td>321</td>
<td>36</td>
<td>7.7</td>
<td>161</td>
<td>1.7</td>
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<tr>
<td>8</td>
<td>Mazar Russian Beach, Back side of Steel Mill, Bin Qasim</td>
<td>67°33'9.11&quot;E</td>
<td>24°78'7.63&quot;N</td>
<td>24</td>
<td>2.1</td>
<td>876</td>
<td>378</td>
<td>28</td>
<td>5.8</td>
<td>195</td>
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<td>9</td>
<td>Ibraheem Hyderi Korangi</td>
<td>67°14'0.41&quot;E</td>
<td>24°78'4.84&quot;N</td>
<td>35</td>
<td>3.6</td>
<td>374</td>
<td>912</td>
<td>29</td>
<td>8.5</td>
<td>151</td>
<td>0.04</td>
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<td>10</td>
<td>Sea View, Hyper Star Building, Clifton</td>
<td>67°02'7.72&quot;E</td>
<td>24°80'3.22&quot;N</td>
<td>0.7</td>
<td>0.6</td>
<td>37</td>
<td>718</td>
<td>11</td>
<td>11.1</td>
<td>81</td>
<td>0.035</td>
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<tr>
<td>11</td>
<td>Sea View, Floating Ship, Clifton</td>
<td>67°04'4.47&quot;E</td>
<td>24°78'9.71&quot;N</td>
<td>0.9</td>
<td>0.7</td>
<td>34</td>
<td>688</td>
<td>13</td>
<td>12.4</td>
<td>76</td>
<td>0.055</td>
</tr>
<tr>
<td>12</td>
<td>Main Manora</td>
<td>66°58'11.15&quot;E</td>
<td>24°48'13.99&quot;N</td>
<td>26</td>
<td>2.3</td>
<td>24</td>
<td>349</td>
<td>18</td>
<td>12.7</td>
<td>587</td>
<td>0.06</td>
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<td>13</td>
<td>Manora beach 1</td>
<td>66°58'17.29&quot;E</td>
<td>24°47'48.93&quot;N</td>
<td>28</td>
<td>2.8</td>
<td>27.7</td>
<td>356</td>
<td>22</td>
<td>13.7</td>
<td>543</td>
<td>0.05</td>
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<tr>
<td>14</td>
<td>Manora beach 2</td>
<td>66°56'41.81&quot;E</td>
<td>24°48'56.98&quot;N</td>
<td>25</td>
<td>2.5</td>
<td>26.1</td>
<td>330</td>
<td>19</td>
<td>12.9</td>
<td>564</td>
<td>0.02</td>
</tr>
<tr>
<td>15</td>
<td>Native Jeti Bridge, Left Side, Kemari</td>
<td>66°98'3.42&quot;E</td>
<td>24°8'3.36&quot;N</td>
<td>16</td>
<td>2.7</td>
<td>28</td>
<td>366</td>
<td>26</td>
<td>17.9</td>
<td>596</td>
<td>0.07</td>
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<tr>
<td>16</td>
<td>Main Sandspit</td>
<td>66°55'23.30&quot;E</td>
<td>24°49'57.74&quot;N</td>
<td>8</td>
<td>2.7</td>
<td>19.8</td>
<td>418</td>
<td>14</td>
<td>14.2</td>
<td>56</td>
<td>0.004</td>
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<td>17</td>
<td>Main Hawks bay</td>
<td>66°52'26.79&quot;E</td>
<td>24°51'22.07&quot;N</td>
<td>6</td>
<td>5</td>
<td>33</td>
<td>385</td>
<td>16</td>
<td>14.8</td>
<td>53</td>
<td>0.012</td>
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<td>18</td>
<td>Hawks Bay 1</td>
<td>66°50'54.48&quot;E</td>
<td>24°51'40.73&quot;N</td>
<td>4</td>
<td>2.8</td>
<td>34</td>
<td>417</td>
<td>17</td>
<td>15.8</td>
<td>65</td>
<td>0.003</td>
</tr>
<tr>
<td>19</td>
<td>Hawks Bay 2</td>
<td>66°56'57.76&quot;E</td>
<td>24°48'5.01&quot;N</td>
<td>7</td>
<td>2.5</td>
<td>32</td>
<td>410</td>
<td>18</td>
<td>16.6</td>
<td>61</td>
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<tr>
<td>20</td>
<td>Paradise Point 1</td>
<td>66°77'5.79&quot;E</td>
<td>24°48'5.51&quot;N</td>
<td>5</td>
<td>2.9</td>
<td>42</td>
<td>389</td>
<td>16</td>
<td>12.4</td>
<td>54</td>
<td>0.43</td>
</tr>
<tr>
<td>21</td>
<td>Paradise Point 2</td>
<td>66°80'9.69&quot;E</td>
<td>24°48'5.73&quot;N</td>
<td>4</td>
<td>2.4</td>
<td>47</td>
<td>475</td>
<td>15</td>
<td>12.8</td>
<td>49</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The collection of soil samples for trace metals in the study area has been done to serve a basis for the planning of control strategies to achieve better environmental quality and will as a key for an effective management of soil quality; similar extensive investigations of coastal soils have been carried out recently in many countries [10]. These soil samples were analyzed for Fe, Mn, Cr, Pb, Zn, Cu, Co and As to examine metal concentrations in sediment. Therefore, the study will attempt to evaluate the extent of heavy metal contamination from the surface to the bottom sediments and the degree to which heavy metals are influenced. The special distribution and the transportation procession of trace element in surficial sediments were studied to illustrate distinct pattern of the functional area and were plotted by Golden Software’s SURFER program. The q-q plot made by SPSS, the single-factor model.

MATERIAL AND METHODS

A total twenty one samples of coastal sediments from different locations of Karachi, Sindh were collected during 2012-2013 (Figure 1) (Table 1). The inference of the entire metals concentration, from sediments was determined according to [16]. Sediment samples were taken at a depth of 0-20 cm which was promptly crammed in air fixed plastic bottles. Sub-samples of the material were oven dried at 500°C for 48 hours and ground using
RESULT AND DISCUSSION

Allocation of Heavy Metals Concentration: In this study area, heavy metals allocation in the coastal sediments exhibits three trends. Highest values were detected in the deepest area near to Ketti Bundar, in the background of port Bin Qasim and in the axial areas. Most important elements (Fe, Mn, Cr, Cu, Pb, Zn and As) best imitate these trends (Fig. 2a - e, g & h). Iron and Manganese concentrations have a peak at station no. 8 and 5 in the transect between Ketti Bundar and port Bin Qasim (Fig. 2a & b). In contrast, the allocation model of the majority of the heavy elements follows only one or two of these trends. For instance Chromium and Zinc showed highest values towards south east and south west part of the study area (Fig. 2 c & g). Copper, Lead and Cobalt are circulated in different way (Fig. 2 d, e & f) with the omission that allocation pattern of Copper showing ordinary pattern with both Lead and Cobalt. While Manganese and Arsenic have shown fairly similar allocation pattern (Fig.2 b & h) as both of these element are concentrated in the south east region of the study area at station no. 7, 8 and 9.

The Iron content showed a very elevated value in the internal part of the port Bin Qasim (1130, 1078 and 876 ppm), but, excluding these value, mean values are approximately 190 ppm (see Fig.2a). While the Manganese maximum concentrations (912, 718 and 688 ppm) are placed at coastal belt of Karachi (i.e., Ibrahim Hyderi, Hyper star building and Floating ship) corresponding to sandy areas (see Fig. 2b). It is predictable that in the

Fig 2: (a, b, c & d): Allocation pattern of Fe, Mn, Cr & Cu in soil sediments of coastal aquifers.
Fig 2: (e, f, g & h): Allocation pattern of Pb, Co, Zn & As in soil sediments of coastal aquifers.

study area the presence of Manganese surrounded by the calcite in the sediments indicates the gathering of these sediments under toxic conditions. The allocation pattern of Manganese discovered that the coastal area of Karachi has highly elevated in Manganese concentration (Fig. 2b). So, the elevated concentration of Manganese is found in Karachi due to origin of the marine environment.

The contour pattern of Chromium showed high values at Ibrahim Hyderi (35ppm) (Fig.2c). However, at only some locations samples have a little noticeable value. The irregular allocation of Chromium is recognized to its incidence due to release of industrial waste water release into stream and coastal sediments.

Copper has similar allocation pattern (Fig. 2d) as of Cobalt and Lead. The incidence of Lead content showed a high value in the inner part of the port Bin Qasim (37 and 36 ppm), but, not including these value, mean values are approximately 17.6 ppm (Fig. 2e). This might be attributed to release of Lead adsorption by marine sediments. The elevated content of this metal in sediments have been sourced from either Lead released from death and decay of marine organisms and / or through precipitation. There is slight proof that Lead is readily missing from soil profiles by leaching. The majority of heavy metals, including Lead, remain in an insoluble or stable form in surface layers of sediments after application of sewage sludge. So it can be assume that in the study area the source would be geogenic from the run of sediments.

By distinction, Cobalt content (Fig.2 f) shows high values (17.9 ppm) in Kemari (Native Jetty) with a minimum at Ketti Bunder (4.2 ppm). In the study area, Cobalt tends to be co-precipitated with Iron oxides and particularly with Manganese oxides.

Allocation pattern of Zinc also showed the high trends in stations located in south west site of coastal area i.e., Kemari and Manora harbor (598 and 587 ppm) (Fig. 2 g), but, apart from these value, mean values are approximately 174 ppm. These stations were most likely exaggerated by industrial dissipate.

Arsenic showed high value at Ketti Bunder (6.1 ppm) (Fig.2h). In numerous locations concentration of this element has below 0.001 ppm. This element has very low measurable values in all samples. In the study area the occurrence of Arsenic is associated with sedimentary rocks of marine origin, fossil fuels, industrial wastes, agricultural use and irrigation practices.

High concentrations of heavy metals are found in stations located in south eastern part or in the central region of the study area. This result may be due to decrease water current in these parts that causes reduce chemical interactions between metals and sediment such as: suspended solid absorption, surface sediment sorption and rate of re-deposition which is dependable an augment metals concentration.

Number of researchers reported that silt and clay in sediment play significant role in deposition and entrapment of pollutants during adsorption process [11]. Zn and Cr also showed the high trends in stations located in south east site of coastal area; these stations were probably affected by industrial waste which is loaded from the industrial outlets that were located along coastline. The content of As, Zn and Pb decreased from mangrove line to coastlines. The concentration of As, Zn and Pb peaked at Ketti Bunder, Kemari and port Bin Qasim because these stations are influenced both the mangrove sedimentation and industrial waste which is loading from coastline. Several researchers suggested that
silt and clay that increase metals adsorption Zn > Pb > Co > Cu > As. The sediments from industrial discharge sites have the highest concentrations of Fe, Mn and Zn. Mean Pb concentration is highest in port Bin Qasim and Steel Mill wastewater discharge point. This study also revealed that local geology has not shown any significant influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of unconfined aquifers occurs; there is no effect of geology in the chemical composition of coastal aquifers of the study area. Furthermore the hydrological pathways of these aquifers also demonstrate that the coastal aquifers of the study area are not influenced by the local geology.

Heavy Metals Contamination: The most important reason of sediment quality guidelines (SQGs) are to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants and is a useful tool for evaluating potential for contaminants within sediment to persuade biological effects.

Single-factor Index Analysis: The pollution indexes of the heavy metals in each region are calculated and shown in Table 3, respectively. The single factor index evaluation method is engaged to get actual quantitative information of key contamination elements and excessive multiples, which is one of the most existing methods used in evaluation of the degree of heavy contamination in soil. Heavy metal contaminants Fe, Mn, Cr, Cu, Pb, Co, Zn and As are numbered as 1 to 8, respectively.

According to the value of \( P_i \), this can be determinate which kind of pollutants exceeds and the excessive multiple in different area in the coastal belt of the province and additional determine what are the most serious pollutants and most serious regions of the pollution. According to the related information, the grading standard of single-factor is shown in Table 3.
The results of this study showed that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Bin Qasim industrial area and Ketti Bunder, where the pollution index of these metals are relatively high as the usual value (Table 3). The observable fact indicates that there are many factories in the industrial areas of Port Bin Qasim and Landi. The results of the study further demonstrates that heavy metal pollution index, showing a state of potential contamination with respect to chromium where municipal and industrial waste received from Korangi and Landi industrial areas are discharging their waste at fishing harbor. While the samples collected from beach at Paradise point, Hawksbay and Ketti Bunder (close to creek) have not shown any noteworthy impact with respect to other heavy metals excluding Arsenic which is due to accumulation of vertebrate animal in sea sediment.

CONCLUSION

Except Cu, Co, As and Mn, most of the metals showed different pattern. High concentrations of heavy metals are found in stations located in south eastern part or in the central region of the study area. This result may be due to decrease water current in these parts that causes reduce chemical interactions between metals and sediment. This study also revealed that local geology has not shown any major influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of unconfined aquifers occurs; there is no effect of geology in chemical composition of coastal aquifers of the study area. Samples collected from Paradise point, Hawksbay and Ketti Bunder (close to creek) have not shown any significant impact with respect to other heavy metals except for Arsenic. The results of this study showed that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Bin Qasim industrial area and Ketti Bunder where the pollution index of these metals are relatively high as the normal value.

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REFERENCES


