An appraisal of pollution level in the sediments of forthcoming Vizhinjam port zone, Southwest coast of India

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A pilot study on the granulometry and geochemical distribution of major and trace elements were carried out in the surface sediments of the port zone. Granulometric studies inferred the dominance of sand fractions in this high energy regime. Heavy metal concentrations in the area are below the threshold levels associated with the toxicological effects and the regulatory limits and this confirms the lithogenic origin of metals. Metal enrichments observed at Kovalam, an international tourist destination specifies the anthropogenic influence. Present study reveals that as of now there is no distinctiveness either in the distribution of sediments or the heavy metals signifying an immaculate coastal environment.

[Keywords: Vizhinjam port, Granulometry, Geochemistry, Pollution.]

Introduction
Pollution by heavy metals in natural environments has become a global problem1. The concentration of heavy metals in the aquatic environment needs considerable ecological concern due to their toxicity, non biodegradable properties and accumulative behaviours. Several studies on heavy metal contamination were conducted on port zones of different parts of the world and majority of them recorded toxicity of heavy metals in and around the zone2, 3, 4, and 5. With the rapid industrialization and economic development in coastal region, heavy metals are introduced to the estuarine and coastal environment where metals are produced as by-products6. Since the operating activities of the port terminals/harbours are recognized to be extremely harmful to the coastal environment an Environmental Impact Assessment (EIA) is inevitable. As the maximum transportation of the state is through sea, it is inevitable for the state to develop a container terminal to crater traded goods. To sustain an international seaport at Vizhinjam a serious assessment on environmental pollution should be taken before the development of the seaports. Hence the present study proposes to investigate the heavy metal contamination in and around the upcoming Vizhinjam port zone. The study area extending from Adimalathura to Kovalam (6km) has earthy/rocky cliffs fronted by narrow sandy beaches (Figure 1). The coastal stretch of Adimalathura which is at the south of the proposed port is a sandy beach whereas the Vizhinjam to Kovalam coastal stretch possesses rocky headlands. The cenozoic sedimentary formations of Kerala unconformably overlie the Precambrian crystalline rocks7, comprising mainly of charnockite and khondalite group of rocks and these structures have played a significant role in graben subsidence and in the formation of sedimentary basins in the west coast8.

Materials and Methods
The nearshore surface samples were collected from 3 transects T1 (Adimalathura), T2 (Mullur) and T3 (Kovalam) at a depth of 3m, 5m, 10m, 15m and 20m (Figure 1). A total of 14 surficial sediment samples were collected using van Veen grab and were subjected to pre-treatment. Textural studies on the sediments were performed for sand, silt and clay distributions9. Organic carbon (OC) was determined by wet oxidation method10. Analysis of major and trace elements was done using XRF facility which consists of a Bruker Model S4 Pioneer sequential wave length dispersive X-ray fluorescence and sample preparation units. Major and trace metal
contamination and its relation with organic carbon in the samples were studied using contamination factor (CF)\textsuperscript{11}, Pollution load index (PLI)\textsuperscript{12} and Geoaccumulation index (I_{geo})\textsuperscript{11}.

**Results**

The sand, silt and clay proportions are given in table 1 and majority of the sediments exhibit sandy nature. Percentage of sand ranges from 99.3% to 99.7% at Adimalathura, 89.9% to 99.6% at Mullur and 97.4% to 99.5% at Kovalam respectively. Mean values indicated a predominant distribution of fine to very fine sand in the area. Sediments are moderately well sorted to very well sorted and are symmetrical to coarse skewed. Percentage of organic carbon varies from 0.10 to 0.82% (Table 2) and the low value signifies the predominance of sand. Low organic carbon content in the study area can be attributed to the coarse nature of the sediments and high tidal and wave activity.

Natural concentrations of major and trace elements are strongly influenced by the nature of the inorganic matter that results from physical and chemical weathering. The concentrations and the averages of all the measured metals in the Vizhinjam nearshore surface sediments are depicted in table 2. Percentage of Na content at Adimalathura, Mullur and Kovalam varies from 1.10 to 1.39%, while the concentration of K is of 0.02 to 0.59% indicating detrital origin. Sodium and potassium mainly comes into sediments as a weathering product of minerals like feldspars, feldspathoids, amphiboles and pyroxenes from the source rock. Maximum concentrations of Ca and Mg are observed at Adimalathura and Mullur which is due to the leaching of dead shelled organisms. Fe in the study area can be attributed to detrital mineral composition in particular to heavy minerals. The distribution of Fe and Ti shows maximum percentage at Kovalam where heavy mineral assemblages dominate. Heavy minerals are highly enriched in the

### Table 1 — Percentage of sand, silt and clay of nearshore sediments of Vizhinjam Port area

<table>
<thead>
<tr>
<th>Locations</th>
<th>Sand %</th>
<th>Silt %</th>
<th>Clay %</th>
<th>Sediment type</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (3m)</td>
<td>99.63</td>
<td>0.69</td>
<td>0.02</td>
<td>Sand</td>
</tr>
<tr>
<td>T1 (5m)</td>
<td>99.30</td>
<td>0.97</td>
<td>0.05</td>
<td>Sand</td>
</tr>
<tr>
<td>T1 (10m)</td>
<td>99.40</td>
<td>1.24</td>
<td>0.75</td>
<td>Sand</td>
</tr>
<tr>
<td>T1 (15m)</td>
<td>99.73</td>
<td>0.83</td>
<td>0.07</td>
<td>Sand</td>
</tr>
<tr>
<td>T2 (3m)</td>
<td>99.33</td>
<td>1.18</td>
<td>0.03</td>
<td>Sand</td>
</tr>
<tr>
<td>T2 (5m)</td>
<td>99.67</td>
<td>0.88</td>
<td>0.02</td>
<td>Sand</td>
</tr>
<tr>
<td>T2 (10m)</td>
<td>89.99</td>
<td>8.62</td>
<td>1.39</td>
<td>silty Sand</td>
</tr>
<tr>
<td>T2 (15m)</td>
<td>90.92</td>
<td>7.69</td>
<td>1.39</td>
<td>silty Sand</td>
</tr>
<tr>
<td>T2 (20m)</td>
<td>97.43</td>
<td>1.92</td>
<td>0.65</td>
<td>Sand</td>
</tr>
<tr>
<td>T3 (3m)</td>
<td>98.72</td>
<td>1.34</td>
<td>0.04</td>
<td>Sand</td>
</tr>
<tr>
<td>T3 (5m)</td>
<td>99.51</td>
<td>1.06</td>
<td>0.13</td>
<td>Sand</td>
</tr>
<tr>
<td>T3 (10m)</td>
<td>97.99</td>
<td>1.34</td>
<td>0.67</td>
<td>Sand</td>
</tr>
<tr>
<td>T3 (15m)</td>
<td>98.11</td>
<td>0.95</td>
<td>0.94</td>
<td>Sand</td>
</tr>
<tr>
<td>T3 (20m)</td>
<td>99.32</td>
<td>0.45</td>
<td>0.24</td>
<td>Sand</td>
</tr>
</tbody>
</table>

### Table 2 — Concentration of C-org and major elements (%) in the nearshore sediments of Vizhinjam Port area

<table>
<thead>
<tr>
<th>Locations C-org Na K Ca Mg Fe Mn Ti Si Al P</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (3m)</td>
</tr>
<tr>
<td>T1 (5m)</td>
</tr>
<tr>
<td>T1 (10m)</td>
</tr>
<tr>
<td>T1 (15m)</td>
</tr>
<tr>
<td>T2 (3m)</td>
</tr>
<tr>
<td>T2 (5m)</td>
</tr>
<tr>
<td>T2 (10m)</td>
</tr>
<tr>
<td>T2 (15m)</td>
</tr>
<tr>
<td>T2 (20m)</td>
</tr>
<tr>
<td>T3 (3m)</td>
</tr>
<tr>
<td>T3 (5m)</td>
</tr>
<tr>
<td>T3 (10m)</td>
</tr>
<tr>
<td>T3 (15m)</td>
</tr>
<tr>
<td>T3 (20m)</td>
</tr>
</tbody>
</table>
beach sand along the west coast of India. From Adimalathura to Kovalam the average concentration of Si is 38.72% and it can be attributed to the higher sand content in the study area. The phosphorus content in the study area also reflects the supply of detrital minerals and the biogenic materials found in the form of shell fragments.

Average concentrations of trace elements in the nearshore sediments of Vizhinjam port zone are provided in the table 3.

The maximum concentration of Cu is observed at Adimalathura where intense fishing activities are going on. Boating activities in particular, paint chips or flakes resulting from the annual cleaning or scraping of automobiles may increase the concentration of Cu in sediments. Even though the values of Ni are of low concentration in the present study, they show a maximum range in Kovalam suggesting the anthropogenic contribution due to tourism. The concentration of Cu and Ni does not show much variation in the study area designating the source of these metals either from detrital minerals or fishing activities. Lower concentrations of Pb and Zn in the study area reflect the supply of detrital minerals and the biogenic materials found in the form of shell fragments.

Most of the trace metals analysed show positive correlation with mud than organic carbon (Table 4) which indicates that finer particles are the main carriers of elements. Al and Fe are positively correlated with majority of the elements studied. Hydrous oxides of Al and Fe readily sorbs and co precipitate elements when they sink to the bottom of water. This association may be due to the large surface area, extensive cation exchange and wide availability of the elements. In the present study trace elements show positive correlation with Fe than Mn. Correlation of Cr with clay indicates that illite traps Cr in a reducing environment. Cu enrichment is generally found associated with clay as well as the high organic content and this proves the negative correlation of these elements in the area. Correlation of Ni with Cr and mud indicates that these elements are either absorbed/adsorbed by mud rather than organic carbon.

Contamination Factor (CF) is used to evaluate the extent of metal contamination and also anthropogenic inputs (Table 5). The values of CF for almost all the trace elements except Zr in the study area are less than one indicating low contamination. Zr shows highest value due to the presence of zircon in the heavy minerals of Kovalam. Concentration of heavy mineral assemblages in Kovalam is the result of strong winnowing action of waves rather than selective transport by longshore currents. Moreover, the rocky headlands is the another source for these minerals. The pollution load index values (PLI) (<1) also supports the CF values indicating no pollution in the Vizhinjam seaport area (Figure 2). The obtained Igeo value for the trace elements shows that the Vizhinjam port area is not at all polluted (Table 6). Also from the result, it is inferred that Kovalam is

| Table 3 — Concentration of trace elements (ppm) in the nearshore sediments of Vizhinjam Port area |
| Locations | Cu | Ni | Pb | Zn | Zr | Cr |
| T1 (3m)   | 38 | 12 | 3  | 8  | 251| 50 |
| T1 (5m)   | 57 | 28 | 8  | 14 | 122| 29 |
| T1 (10m)  | 26 | 38 | 13 | 37 | 2897|88 |
| T1 (15m)  | 29 | 33 | 16 | 31 | 111|15 |
| T2 (3m)   | 12 | 16 | 7  | 21 | 974| 60 |
| T2 (5m)   | 37 | 23 | 4  | 29 | 477|38 |
| T2 (10m)  | 29 | 45 | 16 | 61 | 2467|97 |
| T2 (15m)  | 27 | 42 | 12 | 53 | 3643|93 |
| T2 (20m)  | 40 | 22 | 9  | 51 | 1786|48 |
| T3 (3m)   | 17 | 31 | 11 | 24 | 1597|62 |
| T3 (5m)   | 9  | 46 | 15 | 53 | 2509|92 |
| T3 (10m)  | 25 | 62 | 18 | 74 | 8550|136 |
| T3 (15m)  | 31 | 51 | 23 | 66 | 4518|86 |
| T3 (20m)  | 37 | 30 | 14 | 48 | 697|56 |
| Average   | 30 | 34 | 12 | 40 | 2096|66 |

| Table 4 — Inter-elemental correlation matrix of minor elements in the nearshore sediments of Vizhinjam port area |
| C- Sand | Silt | Clay | Cu | Ni | Pb | Zn | Zr | Cr |
| org | % | % | % | % | % | % | % | % |
| C-org | 1.00 |
| Sand | 0.68 | 1.00 |
| Silt | 0.60 | 0.99 | 1.00 |
| Clay | -0.75 | -0.86 | 0.80 | 1.00 |
| Cu | 0.29 | 0.04 | -0.08 | -0.03 | 1.00 |
| Ni | -0.78 | -0.36 | 0.30 | 0.58 | -0.28 | 1.00 |
| Pb | -0.69 | -0.24 | 0.16 | 0.51 | -0.27 | 0.86 | 1.00 |
| Zn | -0.76 | -0.47 | 0.38 | 0.71 | -0.24 | 0.84 | 0.79 | 1.00 |
| Zr | -0.71 | -0.28 | 0.20 | 0.56 | -0.30 | 0.84 | 0.62 | 0.79 | 1.00 |
| Cr | -0.72 | -0.44 | 0.39 | 0.62 | -0.47 | 0.77 | 0.53 | 0.74 | 0.89 | 1.00 |
under moderately polluted condition compared to other stations and this is due to the anthropogenic influence owing to tourism activities.

### Discussions

The wave energy regime along the Kerala coast exhibits distinct patterns, with highest energy observed off Thiruvananthapuram region\(^4\). Winnowing action of the waves aided by the steep bathymetry may be a reason for the high concentration of sand in the region\(^5\). Southern Kerala coast (Paravur and Veli) recorded low organic carbon with high percentage of sand\(^6\) and the low organic carbon values might be related with the poor absorbability of organics by sand dominant regions and constant flushing activity by tides along with the input of waves\(^7\). Carbonate materials have a coarse texture and as a result the Ca contents are very high in coarse sediments\(^8\). The Ca is abundant in the southern side of Tuticorin, East coast of India where the shelf is widest and shell debris is main constituent\(^9\). Another source of Ca is the plagioclase mineral\(^10\). Mg concentrations reveal a higher average in the surface sediments of Gulf of Mannar (Mg: 1.12-8.32%) than for other coastal regions along the southeast coast of India due to the abundance of skeletal components\(^11\). Abundance of heavy mineral assemblages in Kovalam reveals that the morphodynamics of the coast and the hydrodynamics of the region are the major factors that determine the distribution patterns of these minerals in the area\(^12\). Atomic minerals directorate for exploration and research (2001) reported an average total heavy mineral concentration of 21.33% at Vizhinjam-Kovalam stretch. Higher percentage of sand implies that Si is related to terrestrial input of quartz\(^13\).

The concentration of Cu (48.8µg/g) and Ni (71.1µg/g) at the nearshore sediments of Ennore, south east coast of India may be due to the industrial and petroleum related activities\(^14\). Cu and Ni enrichment are commonly observed in a region where harbour and petroleum-related activities are intense\(^15\). Presence of Pb and Zn can be due to the heavy input of industrial effluents from the industrial regions\(^16\) and also from the vehicle emissions, municipal refuse and automobiles\(^17, 25, 26, 27\). Trace metals do not seem to constitute a threat to the marine environment of central south west coast of India\(^18\) and this supports the results of our study. Chromium is an essential nutrient for plants and animal metabolism and it indicate the anthropogenic influence in the marine

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**Table 5 — Contamination factor (CF) and pollution load index (PLI) of minor elements of nearshore sediments in Vizhinjam port area**

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Zr</th>
<th>Cr</th>
<th>PLI</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (3m)</td>
<td>0.84</td>
<td>0.24</td>
<td>0.15</td>
<td>0.08</td>
<td>1.57</td>
<td>0.56</td>
<td>0.35</td>
</tr>
<tr>
<td>T1 (5m)</td>
<td>1.27</td>
<td>0.56</td>
<td>0.40</td>
<td>0.15</td>
<td>0.76</td>
<td>0.32</td>
<td>0.46</td>
</tr>
<tr>
<td>T1 (10m)</td>
<td>0.58</td>
<td>0.76</td>
<td>0.65</td>
<td>0.39</td>
<td>18.11</td>
<td>0.98</td>
<td>1.12</td>
</tr>
<tr>
<td>T1 (15m)</td>
<td>0.64</td>
<td>0.66</td>
<td>0.80</td>
<td>0.33</td>
<td>0.69</td>
<td>0.17</td>
<td>0.48</td>
</tr>
<tr>
<td>T2 (3m)</td>
<td>0.27</td>
<td>0.32</td>
<td>0.35</td>
<td>0.22</td>
<td>6.09</td>
<td>0.67</td>
<td>0.55</td>
</tr>
<tr>
<td>T2 (5m)</td>
<td>0.82</td>
<td>0.46</td>
<td>0.20</td>
<td>0.31</td>
<td>2.98</td>
<td>0.42</td>
<td>0.55</td>
</tr>
<tr>
<td>T2 (10m)</td>
<td>0.64</td>
<td>0.90</td>
<td>0.80</td>
<td>0.64</td>
<td>15.42</td>
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<td>1.31</td>
</tr>
<tr>
<td>T2 (15m)</td>
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<td>0.84</td>
<td>0.60</td>
<td>0.56</td>
<td>22.77</td>
<td>1.03</td>
<td>1.26</td>
</tr>
<tr>
<td>T2 (20m)</td>
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<td>0.44</td>
<td>0.45</td>
<td>0.54</td>
<td>11.16</td>
<td>0.53</td>
<td>0.91</td>
</tr>
<tr>
<td>T3 (3m)</td>
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<td>0.62</td>
<td>0.55</td>
<td>0.25</td>
<td>9.98</td>
<td>0.69</td>
<td>0.78</td>
</tr>
<tr>
<td>T3 (5m)</td>
<td>0.20</td>
<td>0.92</td>
<td>0.75</td>
<td>0.56</td>
<td>15.68</td>
<td>1.02</td>
<td>1.04</td>
</tr>
<tr>
<td>T3 (10m)</td>
<td>0.56</td>
<td>1.24</td>
<td>0.90</td>
<td>0.78</td>
<td>53.44</td>
<td>1.51</td>
<td>1.84</td>
</tr>
<tr>
<td>T3 (15m)</td>
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<td>1.02</td>
<td>1.15</td>
<td>0.69</td>
<td>28.24</td>
<td>0.96</td>
<td>1.57</td>
</tr>
<tr>
<td>T3 (20m)</td>
<td>0.82</td>
<td>0.60</td>
<td>0.70</td>
<td>0.51</td>
<td>4.36</td>
<td>0.62</td>
<td>0.88</td>
</tr>
</tbody>
</table>

**Table 6 — Geo accumulation index of minor elements of nearshore sediments in Vizhinjam port area**

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu (I_{geo})</th>
<th>Ni (I_{geo})</th>
<th>Pb (I_{geo})</th>
<th>Zn (I_{geo})</th>
<th>Zr (I_{geo})</th>
<th>Cr (I_{geo})</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (3m)</td>
<td>0.17</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
<td>0.31</td>
<td>0.11</td>
</tr>
<tr>
<td>T1 (5m)</td>
<td>0.25</td>
<td>0.11</td>
<td>0.08</td>
<td>0.03</td>
<td>0.15</td>
<td>0.06</td>
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<tr>
<td>T1 (10m)</td>
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<td>0.08</td>
<td>3.63</td>
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<tr>
<td>T1 (15m)</td>
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<td>0.13</td>
<td>0.16</td>
<td>0.07</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>T2 (3m)</td>
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<td>0.06</td>
<td>0.07</td>
<td>0.04</td>
<td>1.22</td>
<td>0.13</td>
</tr>
<tr>
<td>T2 (5m)</td>
<td>0.17</td>
<td>0.09</td>
<td>0.04</td>
<td>0.06</td>
<td>0.60</td>
<td>0.08</td>
</tr>
<tr>
<td>T2 (10m)</td>
<td>0.13</td>
<td>0.18</td>
<td>0.16</td>
<td>0.13</td>
<td>3.09</td>
<td>0.22</td>
</tr>
<tr>
<td>T2 (15m)</td>
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<td>0.12</td>
<td>0.11</td>
<td>4.57</td>
<td>0.21</td>
</tr>
<tr>
<td>T2 (20m)</td>
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<td>0.09</td>
<td>0.09</td>
<td>0.11</td>
<td>2.24</td>
<td>0.11</td>
</tr>
<tr>
<td>T3 (3m)</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
<td>0.05</td>
<td>2.00</td>
<td>0.14</td>
</tr>
<tr>
<td>T3 (5m)</td>
<td>0.04</td>
<td>0.18</td>
<td>0.15</td>
<td>0.11</td>
<td>3.15</td>
<td>0.21</td>
</tr>
<tr>
<td>T3 (10m)</td>
<td>0.11</td>
<td>0.25</td>
<td>0.18</td>
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<td>10.72</td>
<td>0.30</td>
</tr>
<tr>
<td>T3 (15m)</td>
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<td>0.20</td>
<td>0.23</td>
<td>0.14</td>
<td>5.67</td>
<td>0.19</td>
</tr>
<tr>
<td>T3 (20m)</td>
<td>0.17</td>
<td>0.12</td>
<td>0.14</td>
<td>0.10</td>
<td>0.87</td>
<td>0.12</td>
</tr>
</tbody>
</table>

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Fig. 2 — Spatial distribution of PLI in the Vizhinjam port area
sediments due to the occupational exposure of numerous processes 29.

The correlation of Fe/Mn hydroxides with trace element was also reported in Cochin estuary 30. Significant correlation between Cu and Zn is primarily due to uptake of these elements by micro organisms as these elements are the micronutrients for plankton growth 31, 32. Lack of correlation of Cu with other elements and finer particles is due to desorption capacity of the element when they get in contact with seawater 33. The Cu concentration in ocean water depends on the nutrient content, chemical composition of plankton and water depth 34. These trace metals like Cu, Ni, Pb, Cr and Zn form a major factor in the marine contamination studies for evaluating the anthropogenic activities 35.

Conclusion

The occurrence of major and minor elements in the study area is mainly of detrital origin and is lower than the world average shale values. A slight variation is noticed in Kovalam and it may due to the anthropogenic activity which is mainly due to tourism. There is no uniqueness either in the distribution of sediments or heavy metals which is indicative of pristine coastal environment. The present study reveals that, of now, the area is neither under stress nor environmentally degraded. Most of the seaports in the world as well as in India face considerable heavy metal pollution which can be correlated with the urbanization or industrialization in the area. This is a major environmental issue and the remediation of this problem is often problematic due to the persistent and non biodegradable properties of the contaminants in the environment.

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