Heavy metal pollution in intertidal sediments from Quanzhou Bay, China

YU Ruilian1,2, YUAN Xing1,*, ZHAO Yuanhui1,*, HU Gongren2, TU Xianglin3

1. Department of Environmental Science, Northeast Normal University, Changchun 130024, China. E-mail: ruiliany@hpu.edu.cn
2. Department of Environmental Science and Engineering, Huazhao University, Quanzhou 362021, China
3. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

Received 31 July 2007; revised 10 October 2007; accepted 10 December 2007

Abstract

The concentrations of eight heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, Hg, and As) in the intertidal surface sediments from Quanzhou Bay were determined to evaluate their levels and spatial distribution due to urbanization and economic development of Quanzhou region, southeast China. The ranges of the measured concentrations in the sediments are as follows: 24.8–119.7 mg/kg for Cu, 105.5–241.9 mg/kg for Zn, 34.3–100.9 mg/kg for Pb, 0.28–0.89 mg/kg for Cd, 51.1–121.7 mg/kg for Cr, 16.1–45.7 mg/kg for Ni, 0.17–0.74 mg/kg for Hg, and 17.7–30.2 mg/kg for As. The overall average concentrations of above metals exceed the primary standard criteria but meet the secondary standard criteria of the Chinese National Standard of Marine Sediment Quality. Several contents of Cu and Hg exceed the secondary standard criteria at some stations. The results of geoaccumulation index (Igeo) show that Cd causes strong pollution in most of the study area. There are no significant correlations among most of these heavy metals, indicating they have different anthropogenic and natural sources. Some locations present severe pollution by heavy metals depending on the sources, of which sewage outlets, aquatic breeding, and commercial ports are the main sources of contaminants to the area.

Key words: heavy metal; intertidal sediment; contamination; geoaccumulation index; Quanzhou Bay

Introduction

Pollution by heavy metals in natural environments has become a global problem (Irabien and Velasco, 1999). Heavy metals are of considerable environmental concern due to their toxicity, wide sources, nonbiodegradable properties, and accumulative behaviors. With the rapid industrialization and economic development in coastal region, heavy metals are continuing to be introduced to estuarine and coastal environment through rivers, runoff, and land-based point sources where metals are produced as a result of metal refining by-products. When metals enter into the marine environment, most of them will settle down and be incorporated into sediments together with organic matters, Fe/Mn oxides, sulfides, and clay (Wang and Chen, 2000). Marine sediments act as scavengers for trace metals and often provide an excellent proof of man’s impact (Guevara et al., 2005). To some extent, trace metal contents in sediment can reflect the quality of the water body. Although sediments act as one of the ultimate sinks for heavy metals input into the aquatic environment, they cannot fix metals permanently. Some of the sediment-bound metals might be released into the water body again through various processes of remobilization under variable conditions. Therefore, sediments are the main repository and source of heavy metals in the marine environment and play an important role in the transport and storage of potentially hazardous metals.

Quanzhou Bay (24°46′–24°58′N, 118°38′–118°47′E), the famous jumping-off point of the sea route of silk and porcelain road in ancient China (especially in Song and Yuan dynasty), lies in the west of Taiwan Straits and in the southeast of Fujian Province. It is a semiclosed bay with its mouth opening towards Taiwan Straits, with the largest water depth of 25 m, the mouth width of 8.9 km, the total area of 136.42 km², and the intertidal area of 89.80 km² (Yuan and Xie, 2003). The bay is adjacent to the intensely industrialized cities of Quanzhou, Jinjiang, Shishi, and Hui’an. Extensive intertidal flats in the innermost reaches of the bay have been reclaimed and converted into container and industrial complexes, and this development is a ongoing process. There are mainly two considerable rivers entering into the bay, namely Jinjiang River, the third largest river with most sand in Fujian Province, and Luoyang River, an important estuary. In addition, there is a considerable freight port nearby the mouth of Luoyang River Estuary (nearby station 8 in the study area), and a simple fishery port nearby the mouth of Jinjiang River Estuary (nearby station 7 in the study area). Another two considerable freight and fishery ports are located in the northeastern (nearby station 13 in the study area) and southeastern (nearby station 2 in the study area) part of the mouth of Quanzhou Bay, respectively. The intertidal zone is the transition belt between ocean and
land, where many halobios spawn, incubate and capture. The ecosystem of intertidal zones has been destroyed due to the rapid development of industrialization, agriculture, mining, and aquatic breeding in the regions surrounding Quanzhou Bay during the past few decades. Recently, the government of Quanzhou City has decided to restore the ecosystem of Quanzhou Bay and its adjacent areas.

Only a few studies on the pollution of Quanzhou Bay have been conducted recently, and these studies are mainly focused on seawater quality (Yuan and Xie, 2002; Yuan and Xie, 2003; Cai et al., 2005). There is almost no information available from the published literature discussing heavy metal contaminations in Quanzhou Bay sediments thus far. Therefore, how to properly assess the sediment quality is an important issue related to the regional economic development. In 2002, China enforced marine sediment quality (GB 18668-2002) to protect the marine environment (CSBTS, 2002). Therefore, marine sediment quality is used as a general measure of marine sediment contamination in China.

The objectives of this study were to investigate current heavy metal distributions and concentrations in Quanzhou Bay intertidal sediments, assess the contamination extent by heavy metals using marine sediment quality criteria and geoaccumulation index, related to the anthropogenic impact during decades of urbanization and economic development along the coastal area, and update the information for effective environmental management in the region.

1 Materials and methods

1.1 Sampling and preparation

Thirteen samples of intertidal zone surface sediments (0–5 cm) from Quanzhou Bay were collected using a Van Veen grab sampler in December 2006 (Fig.1). After sampling, sediments were carefully stored in a clean plastic vessel and kept frozen at −20°C prior to processing and analysis. In the laboratory, sediment samples were defrosted at room temperature, and air-dried in a controlled clean environment. Then, the samples were transferred to an oven and dried at 35 ± 2°C up to a constant weight. The samples were then ground with an agate pestle and mortar and sieved with a 63-μm nylon sieve. The section under the sieve (< 63 μm) was kept in a sealed plastic vessel at 4°C for future use. The fraction smaller than 63 μm was used for analyses in this study due to strong association of metals with fine-grained sediments (Horowitz and Elrick, 1987; Goh and Chou, 1997; Tam and Wong, 2000).

1.2 Analysis of heavy metals and basic physicochemical parameters

For total digestion, 0.25 g of dried sediment sample was put into a PTFE (polytetrafluoroethylene) vessel with 6 ml HNO₃, 2 ml HCl, 2 ml H₂O₂, and 1 ml HF at 180°C in a closed system for 12 h. After digestion and cooling, the completely dissolved samples were then diluted with ultrapure water with a MILLI-Q system (Millipore, Bedford, USA), to 500 ml for further analysis. For each digestion program, a blank was prepared with an equal amount of acids. All reagents were of analytical grade and contained very low concentrations of trace metals. Normal precautions for trace metals analysis were observed throughout. All the glassware and the Teflon vessels were previously soaked overnight with 20% HNO₃ and then rinsed with ultrapure water.

Sample solutions and reagent blanks were analyzed for Cu, Zn, Pb, Cd, Cr, As, and Ni using inductively coupled plasma-mass spectrometry (ICP-MS) (ELAN9000, Perkin-Elmer, USA) at a laboratory in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Hg concentration was determined with an automatic mercury analyzer RA-3 (NIC, Japan). Background correction and matrix interference were monitored throughout the analyses. All the sediment samples were analyzed in duplicates. The analytical precisions were better than 10%. To monitor the quality of chemical analysis and examine the accuracy of the data, sediment reference material, GBW07314, issued by the State Oceanographic Administration of China, were analyzed with the sediment samples during the course of analysis. The analytical results of the selected metals of interest indicate a good agreement between the reference and analytical values of the reference materials. In addition, the recovery rates for the selected metals from the standard reference material were around 96%–103%.

The basic physico-chemical parameters of the analysed sediment samples were analyzed at the same time. Total organic carbon (TOC) was determined with the HT1300-TOC equipment (Analytijkena, Germany). Grain size distribution was determined with a laser particle granularity analyzer (model Winner 2000, Shanghai, China).

2 Results and discussion

2.1 Contents of heavy metals

Heavy metal concentrations and the basic physicochemical parameters (percentages of TOC and clay) in the intertidal surface sediments (< 63 μm) from Quanzhou Bay...
Bay are shown in Table 1. The ranges of TOC and the fine fraction (clay, < 2 μm) contents of analysed sediments are 0.75%–1.83% and 3.64%–16.21%, respectively. Their average values are 1.35% and 6.30%, respectively. The results indicate that heavy metal concentrations in the surface sediments show a general consistency except for some metals in a few stations (e.g., Cu at stations 1, 2, 11, and 12; Zn and Pb at stations 5 and 11; Cd at stations 1 and 11; Cr at station 11; Ni at station 1; Hg at stations 2–6 and 13; As at stations 5 and 7). The differences could be attributed to the variations of contaminant source input. However, we do not exclude the possibility of spatial variations of metal distributions in the sediments. The concentration ranges of Cu, Zn, Pb, Cd, Cr, Ni, Hg, and As in the surface sediments of our study area were 24.8–119.7, 100.0–350.0, 130.0–164.8, 5.00–150.0, 0.34–1.50, 0.50–1.50, 0.046–270.0, and 0.17–0.74 mg/kg dw, respectively. The comparison of heavy metal concentrations in this study with that of previous studies in other regions (Table 1) shows that the concentrations of most heavy metals studied in Quanzhou Bay sediments are relatively higher than that in Xiamen Bay, China, and Pearl River Estuary, China, and significantly lower than that in other larger industrialized/urban ports in the world such as New York Harbor, USA, Bremen Harbor, Germany, and Izmir Harbor, Turkey (Table 1).

### 2.2 Assessment of heavy metal pollution

#### 2.2.1 Assessment according to marine sediment quality of China

The comparison of heavy metal concentrations from this study with that of marine sediment quality (GB 18668-2002) (Table 1) issued by China State Bureau of Quality and Technical Supervision (CSBTS, 2002) shows that the overall average concentrations of all selected heavy metals in intertidal sediments from Quanzhou Bay exceed the primary standard criteria but meet the secondary standard criteria. However, as shown in Table 1, there are significant spatial variations in the metal concentrations, of which some exceed the secondary standard criteria (e.g., Cu at stations 3 and 7; Hg at stations 2, 3, 4, 5, and 13). This may be attributed to the pollution of the aquatic breeding (stations 3, 4, and 7), sewage discharge (stations 4, 5, and 13) and ports (stations 2, 7, and 13) nearby these stations. Nevertheless, all metal concentrations meet the tertiary standard criteria at all the stations. GB 18668-2002 has three standard criteria for marine sediments. The primary sediment standard criteria, which is the most strict, is applied to protecting habitats for marine life including natural, rare, and endangered species, as well as places for human recreation and sports. The secondary standard criteria are applied to regulating general industrial use and coastal tourism and the tertiary standard criteria are for defining harbors and special use for ocean exploration.

### Table 2 Muller’s classification for the geoaccumulation index (Muller, 1981)

<table>
<thead>
<tr>
<th>$I_{geo}$ value</th>
<th>$I_{geo}$ class</th>
<th>Quality of sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\leq 0$</td>
<td>0</td>
<td>Unpolluted</td>
</tr>
<tr>
<td>0–1</td>
<td>1</td>
<td>From unpolluted to moderately polluted</td>
</tr>
<tr>
<td>1–2</td>
<td>2</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>2–3</td>
<td>3</td>
<td>From moderately to strongly polluted</td>
</tr>
<tr>
<td>3–4</td>
<td>4</td>
<td>Strongly polluted</td>
</tr>
<tr>
<td>4–5</td>
<td>5</td>
<td>From strongly to extremely polluted</td>
</tr>
<tr>
<td>$&gt; 5$</td>
<td>6</td>
<td>Extremely polluted</td>
</tr>
</tbody>
</table>
Therefore, a general conclusion can be drawn that the intertidal sediments in Quanzhou Bay have been contaminated by certain metals, and the sediment quality has been significantly impacted by heavy metal pollution, which was mostly relative to the inputs of anthropogenic sources.

### 2.2.2 Assessment according to geoaccumulation index

To understand the current environmental status and the extent of metal contamination with respect to natural environment, other approaches should be also applied.

A common criterion to evaluate the heavy metal pollution in sediments is the geoaccumulation index ($I_{ext}$), which was originally defined by Muller (1979) to determine metals contamination in sediments, by comparing current concentrations with preindustrial levels and can be calculated by the following equation:

$$I_{ext} = \log_2(C_n/(1.5B_n))$$  

where, $C_n$ is the measured concentration of the examined metal ($n$) in the sediment, $B_n$ is the geochemical background concentration of the metal ($n$), and factor 1.5 is the background matrix correction factor due to lithogenic effects. Muller (1981) has distinguished seven classes of geoaccumulation index (Table 2). The highest class (class 6) reflects 64-fold enrichment over the background values (Singh et al., 1997).

It can be more correctly evaluated if complementary information based on metal baseline values is considered using the geoaccumulation index. In this study, we did not obtain the background values of heavy metals in the sediments. Therefore, $I_{ext}$ has been calculated by using the background values of heavy metals along the coastal regions of Fujian Province (Table 1). According to the Muller scale (Muller, 1981), the calculated results of $I_{ext}$ values (Table 3) indicate that Cd can be considered as a strong pollutant at most of the study stations ($I_{ext} > 2.5$) with the exceptions of stations 1 and 11, which show moderate pollution ($I_{ext} > 2.02$–2.26). This can be considered as a moderate pollutant at all stations ($I_{ext} > 1.09$–1.86).

Cu shows unpolluted situation at station 1 ($I_{ext} = 0.12$) and less degree of pollution at station 11 ($I_{ext} = 0.32$), whereas moderate degree of pollution at other stations. Ni shows less degree of pollution at station 1 ($I_{ext} = 0.2$), whereas moderate degree of pollution at other stations. Pb and Cr can be considered as moderate pollutants at most of stations except station 11, which shows less degree of pollution ($I_{geo,Pb} = 0.01$, $I_{geo,Cr} = 0.09$). For Hg, stations 1, 7, 8, 11, and 12 show less degree of pollution ($I_{geo} < 0.02$–0.39), other stations present moderate pollution. For Zn, stations 11 and 13 show unpolluted situation ($I_{geo} < 0$), stations 1 and 5 show moderate pollution ($I_{geo} = 0.5$–1.0), and other stations show less degree of pollution ($I_{geo} < 0.45$). On the basis of the mean values of $I_{geo}$, sediments are enriched for metals in the following order: Cd > As > Cu > Ni > Hg > Pb > Cr > Zn and the pollution order for stations is 5 > 13 > 4 > 6 > 3 > 7 > 2 > 8 > 9 > 10 > 12 > 1 > 11.

The results of $I_{geo}$ values show that stations 5, 13, 4, and 6 were more seriously polluted by heavy metals than other stations. This may be attributed to a considerable sewage draining nearby each of these four stations. The moderate pollution degree of stations 2, 7, and 8 may be attributed to port transporting, and that of stations 3, 9, and 10 may be attributed to acquisitive breeding.

Stations 1 and 11 were less polluted by heavy metals than other stations because there are more sand and less TOC and clay percentages (Table 1) at these two sampling locations. It is well-established that grain size and organic matter contents are important controlling factors in the abundance of trace metals in natural sediments. Fine-grained sediments tend to have relatively high metal contents, due in part to the high specific surface of the smaller particles. This enrichment is mainly due to surface adsorption and ionic attraction (Horowitz and Elrick, 1987). Also, organic matter on particles is prevalent in fine-grained sediments, and the biofilm binds a variety of trace elements (Wangersky, 1986).

### 2.3 Sources and transport of heavy metals

Metal contaminant sources to Quanzhou Bay should include land-based point and nonpoint input, riverine/stream discharge, and atmospheric fallout. Studies on atmospheric inputs to China sea have become a new focus of biogeochemical cycle in the past few years (Gao et al., 2002). However, the information of atmospheric fallout to the

### Table 3

<table>
<thead>
<tr>
<th>Station</th>
<th>$I_{geo,Cu}$</th>
<th>$I_{geo,Pb}$</th>
<th>$I_{geo,Zn}$</th>
<th>$I_{geo,Cd}$</th>
<th>$I_{geo,Cr}$</th>
<th>$I_{geo,As}$</th>
<th>$I_{geo}$</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.12</td>
<td>0.85</td>
<td>0.72</td>
<td>2.02</td>
<td>1.19</td>
<td>0.20</td>
<td>0.02</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>0.83</td>
<td>0.37</td>
<td>0.38</td>
<td>3.07</td>
<td>0.62</td>
<td>1.18</td>
<td>1.93</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>2.15</td>
<td>0.65</td>
<td>0.01</td>
<td>2.64</td>
<td>0.55</td>
<td>1.32</td>
<td>2.08</td>
<td>1.33</td>
</tr>
<tr>
<td>4</td>
<td>1.54</td>
<td>0.86</td>
<td>0.17</td>
<td>3.40</td>
<td>0.72</td>
<td>1.37</td>
<td>1.97</td>
<td>1.24</td>
</tr>
<tr>
<td>5</td>
<td>1.74</td>
<td>1.21</td>
<td>0.84</td>
<td>3.69</td>
<td>1.34</td>
<td>1.33</td>
<td>1.81</td>
<td>1.79</td>
</tr>
<tr>
<td>6</td>
<td>1.57</td>
<td>0.88</td>
<td>0.14</td>
<td>3.05</td>
<td>1.10</td>
<td>1.71</td>
<td>1.10</td>
<td>1.43</td>
</tr>
<tr>
<td>7</td>
<td>2.04</td>
<td>0.80</td>
<td>0.14</td>
<td>2.93</td>
<td>0.85</td>
<td>1.46</td>
<td>0.39</td>
<td>1.86</td>
</tr>
<tr>
<td>8</td>
<td>1.46</td>
<td>0.83</td>
<td>0.27</td>
<td>3.46</td>
<td>0.67</td>
<td>1.28</td>
<td>0.32</td>
<td>1.27</td>
</tr>
<tr>
<td>9</td>
<td>1.54</td>
<td>0.81</td>
<td>0.45</td>
<td>2.92</td>
<td>0.43</td>
<td>1.16</td>
<td>0.79</td>
<td>1.33</td>
</tr>
<tr>
<td>10</td>
<td>1.01</td>
<td>0.72</td>
<td>0.36</td>
<td>3.30</td>
<td>0.48</td>
<td>1.11</td>
<td>0.68</td>
<td>1.41</td>
</tr>
<tr>
<td>11</td>
<td>0.32</td>
<td>0.01</td>
<td>-0.72</td>
<td>2.26</td>
<td>0.09</td>
<td>0.80</td>
<td>0.02</td>
<td>1.09</td>
</tr>
<tr>
<td>12</td>
<td>0.58</td>
<td>0.76</td>
<td>0.18</td>
<td>3.10</td>
<td>0.72</td>
<td>1.44</td>
<td>0.25</td>
<td>1.14</td>
</tr>
<tr>
<td>13</td>
<td>1.80</td>
<td>1.02</td>
<td>-0.11</td>
<td>3.61</td>
<td>0.78</td>
<td>1.46</td>
<td>2.14</td>
<td>1.34</td>
</tr>
<tr>
<td>Mean</td>
<td>1.27</td>
<td>0.75</td>
<td>0.22</td>
<td>3.04</td>
<td>0.73</td>
<td>1.22</td>
<td>1.04</td>
<td>1.37</td>
</tr>
<tr>
<td>Max.</td>
<td>2.15</td>
<td>1.21</td>
<td>0.84</td>
<td>3.69</td>
<td>1.34</td>
<td>1.71</td>
<td>2.14</td>
<td>1.86</td>
</tr>
<tr>
<td>Min.</td>
<td>-0.12</td>
<td>0.01</td>
<td>-0.72</td>
<td>2.02</td>
<td>0.09</td>
<td>0.20</td>
<td>0.02</td>
<td>1.09</td>
</tr>
</tbody>
</table>

*–** means not calculated.
study area is missing based on our literature review. As Quanzhou Bay area is within the coastal region, we expect the land-based influence should be more predominant.

In order to explore the possible associations between these variables, we performed simple statistical analysis on the measured data. Pearson’s correlation coefficient matrix among the selected heavy metals, TOC, and clay contents in surface sediments of Quanzhou Bay are presented in Table 4. Except Pb that shows statistically insignificant negative correlation with TOC, the rest of heavy metal contaminants show a considerable positive correlation with TOC. This might suggest that these metal contaminants have considerable association with organic matter, they probably have a common origin or the metals have been introduced to the system attached to organic materials. The results endorse that the sediment organic matter acts as a metal carrier and, also their complexation with organic matter plays an important role in their distribution patterns. All the selected heavy metals show a low positive correlation with clay, suggesting these metal contaminants have low association with clay content. Results of this study indicated that TOC contents were relatively more important than grain size in controlling the distribution of trace metals for the studied sediments. The above observations might suggest that the sorption mechanism of trace metals at Quanzhou Bay sediments are mainly controlled by chemical adsorption, rather than physical or deposition of metals with organic matter on top of the sediments. Metal ions can associate with the ligands through the functional COOH of the organic matters and then release the metal ions into the water column upon decomposition of organics. The organic metals seem to be stable and accumulate to a high concentration in the vicinity of the river mouths flowing into the bay. The stable organic metals decomposition rates might be far smaller than their formation rates. This leads to easy release of the metal ions in the sediments and difficult release to the water environment.

Significant correlations between the contaminations of Zn and Pb (r = 0.60), Zn and Cd (r = 0.65), Zn and Cr (r = 0.76), Pb and Cr (r = 0.70), Cd and Ni (r = 0.56), could indicate the same or similar source input. In most cases, however, there are no significant correlations among most of these heavy metals, suggesting that these metals are not associated with each other and their identical behavior during transport in estuarine environment. Furthermore, these metals might have different anthropogenic and natural sources in sediments of Quanzhou Bay. These patterns may also reflect the main anthropogenic discharges that constitute sources for several heavy metals. For instance, heavy metal contaminants in sediments of stations 2, 7, 8, and 13 may root in port transporting, that of stations 3, 9, and 10 may root in aquatic breeding, and that of stations 4, 5, and 6 may root in sewage draining.

3 Conclusions

This study shows that with the rapid industrialization and economic development in Quanzhou coastal region, the environmental impact as shown by metal contamination in Quanzhou Bay sediments is becoming a serious environmental problem. The overall average concentrations of Cu, Zn, Pb, Cd, Cr, Ni, Hg, and As in the intertidal surface sediments exceed the primary standard criteria but meet the secondary standard criteria of the Chinese National Standard of Marine Sediment Quality. In addition, several concentrations of Cu and Hg exceed the secondary standard criteria at some stations. Thus, the conclusion can be drawn that the sediment quality of Quanzhou Bay has been significantly impacted by heavy metal pollution. This phenomenon may be linked to contamination sources, distribution, river inputs, and current patterns in Quanzhou Bay. The results of Geo confirm the certain extent of metal contamination in Quanzhou Bay, particularly with regard to Cd that causes strong pollution in most of the study area. There are no significant correlations among most of these heavy metals, suggesting that these metals are not associated with each other, and these metals could have different anthropogenic and natural sources in sediments of Quanzhou Bay.

Depending on the source input, it was found that serious pollution of specific metals exist in localized sites. The results suggest that different anthropogenic source input of some specific metal contaminant(s) has caused significant sediment contamination in the local area. Although the application of national sediment quality standard criteria could be a general measurement of sediment quality, the results from this study suggest that it is not reasonable to use only this kind of criteria to evaluate the environmen-
tal status and sediment contamination. Other approaches should be considered for sediment quality assessment. With further industrialization and economic development in the region, greater attention should be paid to anthropogenic sources around the area.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (No. 40673061), the Research Program of Science and Technology of Quanzhou City Government (No. 2007Z43), and the Foundation of Key Laboratory of Nuclear Resources and Environment (East China Institute of Technology), Ministry of Education (No. 070714).

References