Environmental risk assessment of heavy metals in Bohai Sea, North China

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Abstract

A risk assessment method recommended by PEMSEA was introduced to assess environmental risk of heavy metals (Copper, Lead, Mercury and Cadmium) in Bohai seawater, North China. Risk quotient was calculated upon measured data of 2002 and sea water quality criteria. Monte Carlo technique was used to estimate the uncertainty of risk. The priority risk agents were Hg and Pb, the localized risk agent was Cu while risk from Cd was at acceptable level. The coastal waters near estuaries and big cities have higher potential risks; especially Bohai Bay located in the west Bohai Sea had the highest risk where the heavy metal pollution was most serious. Data of the next year verifies the uncertainty analysis result that with a confidence of more than 75% the risk quotients for Hg and Pb exceed the critical value. The sources, background concentration and biota assessment of heavy metals of Bohai Sea were discussed too.

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Keywords: Environmental risk assessment; Heavy metal; Bohai Sea

1. Introduction

Heavy metal pollution is one world-wide environmental problem. It is believed that organisms in different trophic levels are suffering from metal toxicities [1]. Accumulation of heavy metals in organisms shows different tolerant capabilities among aquatic food webs [2, 3] and human health is under threats from exposure to heavy metals through seafood intake [4, 5]. Use of leaded gasoline has caused a seven-folded increase of Pb content in ice layers in Arctic area, and Hg pollution around Brazilian Amazon is attributed to gold fossicking [6]. Stream waters or crop plants were also contaminated by heavy metals which were both edible [7, 8].

Anthropogenic activities are believed to have led a rise of heavy metals in surface sediments [9, 10] and also to the reduction of fishery yield in Bohai Sea [11], which is a semi-enclosed sea located in northern China (Fig. 1) and is
also an important receiving water body that holds the download pollutants from its surrounding Wider Bohai Sea Area (WBSA). Usually the whole sea area are divided into four cells, Liaodong Bay, Bohai Bay, Laizhou Bay and central waters, as is shown in Fig. 2. There are more than 40 rivers flowing into it, among which the Yellow River, Haihe River, Luanhe River, Shuangtaizihe River and Liaohe River are five major ones. Average discharge of all the rivers/streams was 61.8 billion m³/a [12]. A huge reduction of marine biota resources has occurred in Bohai Sea (Fig. 3) while the agricultural and industrial production got a fast rise in China at the same time. The total input for Hg, Pb and Cd was 702.5 tons [13] and the number climbed up to 1260 in 2004 tons [14]. Hg and Pb continue to be the major pollutants in Bohai Sea from 2000 on [14-16].

Fig1. Location of Bohai Sea in China

Fig2. Four cells of Bohai Sea
Studies on metal pollutions of Bohai Sea mainly focused on sediments and species sampled in scattered spots \cite{17-21} and an ecological risk index for sediments \cite{22} was the main quantitative method \cite{17, 21}. However, the risk index method introduced by Hakanson was originally designed for lakes and basins and the sedimentological toxic factor for metals was based on the toxicity tests of species in fresh water. And limited work on large-scaled environmental assessment for Bohai Sea has been carried out although regional ecological risk assessment is believed to be a useful way to identify geographic environmental stressors and priorities \cite{23-25}. The Global Environmental Facility/ United Nations Development Program/ International Maritime Organization (GEF/UNDP/IMO) set up a regional program called the Partnerships in Environmental Management for the Seas of East Asia (PEMSEA) to build up framework for eastern Asia governments in marine management. Bohai Sea was selected as demonstration site considering its unique ecological features and severe pollutions. Since risk quotient (RQ) method is widely used in identifying and quantifying risk magnitudes in an integrated assessment for different characterized chemicals \cite{26, 27}, an RQ-based technique is adopted to evaluate the environmental risks to the marine ecosystem and human beings living round the Sea. This paper is to address this assessment method as well as its application to risk assessment of heavy metals in coastal sea water of Bohai Sea.

2. RQ-based technique

The approach adopted by PEMSEA is based on the Risk Quotient (RQ) technique, which can be applied in order to determine if measured or predicted levels of environmental parameters are likely to cause harm to environmental/human targets \cite{28}. It can be accomplished by comparing their measured or predicted environmental concentrations (MECs or PECs) with appropriate threshold values or predicted no-effect concentrations (PNECs) to get Risk Quotients (RQs).

$$RQ = \frac{MEC \text{(or PEC)}}{PNEC}$$

Predicted environmental concentration is often estimated by models according to the external conditions, like CHARM \cite{29, 30}, Directive \cite{31}, Soil-Fug \cite{32}, EUSES \cite{33, 34} and Ecoman \cite{35, 36}. But for regional risk assessment, a large quantity of data is needed to cover the scenario of a large area. In that case, data from routine monitoring program can be an alternative. In this paper, measured environmental concentrations for environmental parameters are used as MEC.

A critical aspect of this method is the identification of PNEC. An assessment factor of 100 was used in the extrapolation of laboratory data to chronic sea water scenario \cite{34, 37} and unique species are selected as test objects for
marine ecosystems\cite{38}. In China, the marine ecotoxicologic study on heavy metals mostly focuses on benthos like mussels and clams\cite{19} and no acknowledged LC\textsubscript{50} or EC\textsubscript{50} was given.

It is agreeable that if the organisms in an ecosystem can be protected from adverse effects the target of a risk assessment can be identified as the ecosystem health\cite{39}. In China’s marine environmental management, sea water quality class 1 is set to protect the fishing water and endangered marine species\cite{40}. Obviously, the criteria are set as precautionary measure for ecosystem to avoid chronic toxicity of chemicals like metals or pesticides. In this paper, the Chinese Sea Water Quality Standard’s 1st class is used as the criteria.

Quantization for risk agent is based on magnitude of RQ. When RQ is less than 1, it is presumed that the likelihood of adverse effects is low, while PEC>\text{PNEC} means potential risk to ecosystem or human health, or say, possibility of adverse effect, will increase\cite{28}. In the RQ-based technique unacceptable risk refers to those with risk quotient higher than 1 and priorities of risk agents should be those with RQs greater than 1.

Uncertainty analysis is strongly recommended in an integrated environmental assessment\cite{38,41}. It presents a kind of indeterminacy in models used to estimate the risks\cite{38}, in procedures regarding to extrapolation of PNECs\cite{26}, or when limited data are used in quantifying risks\cite{42}. A quantitative uncertainty analysis is not to confuse the assessment results but to give a more transparent risk scenario to stakeholders and the public\cite{38}. Monte Carlo analysis is a mature technique in uncertainty analysis\cite{43,44}. It supposes a re-sampling happens thousands of times based on a statistical distribution generated by available data\cite{38}. In the RQ-based technique, Crystal Ball software is recommended to analyze the uncertainty\cite{28}. It is embedded in a Microsoft Excel application. Monte Carlo simulation run 5000 times according to current distribution of risk quotients. A more perspicuous image about risk distribution was presented. And estimation of probabilities like RQ > 1 was outputted by the software.

3. Materials and data source

The primary data of Copper, Lead, Mercury and Cadmium for this paper was from the routine environmental monitoring of Bohai Sea in August 2002 by North China Sea Branch of the State Oceanic Administration. There were total 52 stations shown in Fig 4.

![Fig. 4 Stations of environmental monitoring of Bohai Sea in Aug 2002](image)

Surface water samples were used in the risk assessment. These heavy metals (copper, lead, cadmium and total mercury) were sampled and analysed according to GB 17378.4-1998 Oceanographic Survey Specifications\cite{45}, see Table 1.
Table 1 Sample & analysis methods for heavy metals in Bohai Sea

<table>
<thead>
<tr>
<th>Hg</th>
<th>Pb</th>
<th>Cu</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling</td>
<td>quartz glass</td>
<td>polyethylene</td>
<td>polyethylene</td>
</tr>
<tr>
<td>Treatment</td>
<td>Guaranteed reagent grade; all water quartz suboiled and Milli-Q one time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melted by $H_2SO_4-K_2S_2O_4$</td>
<td>Acidificated by $HNO_3$ till pH1-2; stored in polyethylene bottle and sealed in polyethylene bag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS*: $HgCl_2$ dissolved in 5% (v/v) $HNO_3$ - 1.00g/L as Hg</td>
<td>SS: pure Pb (99.99%) dissolved in 50% (v/v) and then 1% (v/v) $HNO_3$ - 1.00 mg/L as Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS*: dilution with 5% (v/v) $HNO_3$ -10.0μg/L as Pb</td>
<td>WS: dilution with 1% (v/v) $HNO_3$ -1.00 μg/mL as Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis/check limit</td>
<td>Atomic fluorometry</td>
<td>CVAFS*</td>
<td>CVAFS</td>
</tr>
<tr>
<td>Recovery rate</td>
<td>---</td>
<td>39μg/L</td>
<td>7.5 μg/L</td>
</tr>
</tbody>
</table>

*ST: stock solution; WS: working solution
^ CVAFS: cold vapour atomic fluorescence spectrometry

4. Results

Risk assessment starts with calculation of average measured concentrations of Cu, Hg, Pb, and Cd for short of MEC_{aver}. A maximum scenario is also concerned and given the risk location here. P_{RQ>1} refers to probability of RQ>1.

Table 2 Risk assessment of heavy metals in sea water in Bohai sea in August 2002

<table>
<thead>
<tr>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEC_{aver} (μg/L)</td>
<td>3.35</td>
<td>0.07</td>
<td>3.29</td>
</tr>
<tr>
<td>MEC_{max} (μg/L)</td>
<td>8.02</td>
<td>0.14</td>
<td>14.10</td>
</tr>
<tr>
<td>PNEC (μg/L)</td>
<td>5.00</td>
<td>0.05</td>
<td>1.00</td>
</tr>
<tr>
<td>RQ_{aver}</td>
<td>0.67</td>
<td>1.40</td>
<td>3.29</td>
</tr>
<tr>
<td>$P_{RQ&gt;1}$</td>
<td>14%</td>
<td>75%</td>
<td>99%</td>
</tr>
<tr>
<td>RQ_{max}</td>
<td>1.60</td>
<td>2.80</td>
<td>14.10</td>
</tr>
</tbody>
</table>

According to the magnitude of RQ_{aver}, priority of risk sources should be Pb and Hg. Most of the sea was under threat of the two metals. With both average and maximum risk quotients less than 1, risk from Cadmium was acceptable. Agent with RQ_{aver} < 1 and RQ_{max} > 1 is defined as a localized risk agent [28] which means potential threat may existed in some area. So Cu was a localized risk agent. The areas that potential risks can exist in were specified in Fig 5.
In general, pollution in Bohai Bay is worse than in the other three parts. Risk from Pb has covered almost ¾ of the sea area. In some areas of Bohai Bay it exceeded more than 10 times of the threshold value.

Metal contamination near estuaries and big cities were worse than in other areas. Risk quotients of Hg and Pb were higher in sea water around Tianjin, Jinzhou, and Luanhe/Yellow River estuaries, showing evidence for metal source from river and human activities.

Monte Carlo analysis shows a confidence of more than 75% that RQ for Hg and Pb exceeded threshold value while there was little possibility for Cu and Cd to bring adverse environmental consequences. The result was confirmed by data of one year later (2003). Assessment results in August 2003 were shown in Table 3.

Obviously, risks from Hg and Pb remained at a dangerous level while Cd kept safe. Risk for Hg became worse as it gave a greater risk quotient. Cu was also an acceptable agent. The results matched the uncertainty analysis based on data of August 2002.
Table 3 Risk assessment of heavy metals in Bohai sea water in August 2003

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{E C}^{a v e r}$ (μg/L)</td>
<td>3.13</td>
<td>0.27</td>
<td>1.16</td>
<td>0.35</td>
</tr>
<tr>
<td>$M_{E C}^{m a x}$ (μg/L)</td>
<td>4.36</td>
<td>0.41</td>
<td>1.48</td>
<td>0.55</td>
</tr>
<tr>
<td>$R_{Q}^{a v e r}$</td>
<td>0.63</td>
<td>5.47</td>
<td>1.16</td>
<td>0.35</td>
</tr>
<tr>
<td>$R_{Q}^{m a x}$</td>
<td>0.87</td>
<td>8.14</td>
<td>1.48</td>
<td>0.55</td>
</tr>
</tbody>
</table>

5. Discussion

When priority agents have been identified in environmental management, policy makers usually begin to seek for risk sources. River runoff and anthropogenic activities are believed to be the main pollution sources in China seas [46]. Table 4 shows water discharge and particle heavy metals in main rivers around Bohai Sea [47].

Table 4 Water discharge and particle heavy metals in rivers around Bohai Sea

<table>
<thead>
<tr>
<th>Water discharge (billion m³/a)</th>
<th>Particle metal concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Liaohe River</td>
<td>9.4</td>
</tr>
<tr>
<td>Shuangtaizihe River</td>
<td>43.0</td>
</tr>
<tr>
<td>Luanhe River</td>
<td>48.7</td>
</tr>
<tr>
<td>Yellow River</td>
<td>44.3</td>
</tr>
</tbody>
</table>

Data source: [47]

To further illustrate the influence of anthropogenic activities to Bohai Sea, background information for heavy metals in sediments was found [48]. It is noticeable that it took more than 100 years for Pb to increase an extent of 2.43 mg/kg while to rise with extra 1.91 mg/kg just took 14 years (Table 5). A faster increase for Cd was also found with a rate about 0.01 mg/kg.a during the last 16 years, in contrast to 0.0004 mg/kg.a one century ago.

Table 5 Comparative concentrations of heavy metals in sediments of Bohai Sea

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background concentration in 1883 (mg/kg, or ×10^−6)*</td>
<td>22.10</td>
<td>——</td>
<td>13.96</td>
<td>0.088</td>
</tr>
<tr>
<td>Concentrations in 1983-1985 (mg/kg, or ×10^−6)*</td>
<td>25.75</td>
<td>——</td>
<td>16.39</td>
<td>0.123</td>
</tr>
<tr>
<td>Concentrations in 1999 (mg/kg, or ×10^−6)^</td>
<td>——</td>
<td>0.057</td>
<td>18.30</td>
<td>0.273</td>
</tr>
<tr>
<td>Input amount (ton/a)^</td>
<td>——</td>
<td>10.4</td>
<td>612.6</td>
<td>79.5</td>
</tr>
</tbody>
</table>

Data source: * [48]. Arithmetical value. [47]

Another proof comes from a comparative research about mercury in upstream sediments of Haihe River (before it passes through Tianjin city) and downstream (after traversing), which showed that industrial factories in Tianjin had contributed a lot to the mercury content increase in river sediment [49]. And total mercury in mollusc bodies sampled in Bohai Sea showed that almost all individuals were contaminated and sample taken in Huludao had the highest mercury concentration (Table 6) [50].
### Table 6 Mercury concentration scales in mollusc bodies

<table>
<thead>
<tr>
<th>Provinces</th>
<th>Coastal waters of cities</th>
<th>Gastropods (ng/g wet weight)</th>
<th>Bivalve (ng/g wet weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liaoning</td>
<td>Yingkou</td>
<td>60.5</td>
<td>15.0–43.2</td>
</tr>
<tr>
<td></td>
<td>Huludao</td>
<td>53.1–453.0</td>
<td>19.9–99.3</td>
</tr>
<tr>
<td></td>
<td>Dalian</td>
<td>39.3–109.5</td>
<td>11.1–30.9</td>
</tr>
<tr>
<td></td>
<td>Qinhuangdao</td>
<td>41.7–53.4</td>
<td>11.0–19.7</td>
</tr>
<tr>
<td>Hebei</td>
<td>Tang’gu</td>
<td>11.3–42.7</td>
<td>6.7–51.3</td>
</tr>
<tr>
<td></td>
<td>Yangkou</td>
<td>32.0–96.1</td>
<td>10.7–68.4</td>
</tr>
<tr>
<td>Shandong</td>
<td>Penglai</td>
<td>62.2–138.7</td>
<td>19.7–194.2</td>
</tr>
</tbody>
</table>

Data source: [50]

There are evidences showing that Bohai Sea has been suffered from heavy metal pollution and anthropogenic activities have greatly speeded up this environmental problem. Seafood pollution of heavy metals was becoming serious in Bohai Sea. To carry out human health risk assessment, it is suggested [28] that both seafood consumption rate and tolerable daily intake should be counted in. Tolerable daily intake is the maximum amount of chemicals that ordinary human body can take in one day. And level of concern is the quotient of tolerable daily intake divided by daily seafood consumption rate [28], which is the PNEC in human health risk assessment. Risk quotient is got by dividing measured concentration in seafood to the level of concern.

\[
RQ = \frac{MEL \text{ or } PEL}{LOC} \quad \text{or} \quad LOC = \frac{TDI}{CR}
\]

Due to lack of consumption rate and measured body level for metals, human risk assessment did not be carry out in this paper.

### 6. Conclusions

With the available information, a risk analysis approach was applied to assess environmental risk of heavy metals in Bohai sea water. The RQ-based technique takes on-site concentrations of heavy metals as MEC and the national sea water quality standard as environmentally accepted values. Risk uncertainty was analyzed based on Monte Carlo simulation. Hg and Pb were priorities in risk management. Almost ¾ of the sea area was under risk of Pb. Metal pollution near estuaries and big cities were worse than other areas. Pollution in Bohai Bay was the worst among the four parts of Bohai Sea. In some area of Bohai Bay concentration of Pb has reached 10 folds of the threshold value. An exceedance of those two metals over critical values in the next year approves the result from Monte Carlo analysis. Data cited shows sediment and biota in Bohai Sea have been contaminated by metals also. And anthropogenic activities have greatly contributed to the risk increase for heavy metals in Bohai Sea.
Acknowledgements

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References

[9]. Bing Xu, Xiaobo Yang, Zhaoyan Gu, Yanhui Zhang, Yongfu Chen, Yanwu Lv. The trend and extent of heavy metal accumulation over last one hundred years in the Liaodong Bay, China. Chemosphere 2009; 75: 442-6.


