Sources and ecological assessment of heavy metal contamination in the surface sediment in Honghai Bay

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Abstract. The sources and ecological environment of heavy metal contamination in the surface sediment of the Honghai Bay were studied, and the contents of seven heavy metals in sediment samples from 20 sampling stations were analysed. Principal Component Analysis (PCA) showed that the contribution rates of the first and second principal component was 60.41% and 16.48%, respectively. The study showed that the major sources of heavy metal contamination were industrial wastewater and municipal wastewater. Combined with the results of correlation analysis between heavy metals and TOC, it was found that Cu, Pb, Zn, Cr and As had a certain degree of homology. The contribution rate of each pollutant variable calculated by PCA method was used to determine the marine sediment pollution index (MSPI) to evaluate the contamination level of heavy metal, and the potential adverse effects of heavy metal contamination on the ecological environment were evaluated by the mean sediment guideline quotient (SQG-Q). The results showed that the sediment conditions were average (MSPI: 40.30-57.92), and the potential adverse biological effects had reached a moderate level (SQG-Q: 0.10-0.21). Heavy metal contamination level of the study area was moderate.

1. Introduction
Heavy metal contamination has become an important part of marine environmental pollution assessment, sediment contamination is one of the most serious environmental problems in water ecosystem [1]. Sediments play an important role in the migration and transformation of heavy metals, and are the major enrichment sites of heavy metals in water environment. The sediment that is both a “sink” of heavy metals in water and an important “source”[2-3]. Heavy metals, as non-biodegradable pollutants, found in natural environment have high potential ecological risks [4], which can further affect human health through bioaccumulation and food chain enlargement [5-6]. Heavy metal contamination has become an important part of water environmental pollution because of its non-destructive and biological toxicity in the environment [7]. Heavy metals of the sediments reflect the pollution, therefore can easily be collected, maintained and analyzed, representing the regional marine environmental quality levels and trends [8]. This diagnostic mediait is very important for ecological environment monitoring and ecological health assessment to correctly evaluate heavy metal contamination in sediments.

At present, the contamination level of heavy metal in the coastal waters has been studied[9-15]. Li et al. (2012) used the comprehensive index method to evaluate the contamination level of heavy metal in the surface waters in Honghai Bay [16], Peng et al. (2014) used the single factor pollution index method to evaluate the level of heavy metals in seafood and the risk of human exposure in Honghai Bay [17], Sun et al. (2018) used the potential ecological hazard index method to study the pollution level of heavy metals in the surface sediment in Honghai Bay [18]. The conclusions of heavy metal...
contamination and ecological risk analysis and evaluation are diverse for different methods [19], and the evaluation of sediment environmental quality is more complex and uncertain than that of water environment. Each evaluation method has its advantages and limitations [20]. In this study, the source of heavy metal in sediments is analyzed by principal component analysis, and the results are applied to evaluate the contamination level and potential biological effects of heavy metal in marine sediments, such as the marine sediment pollution index and the mean sediment guideline quotient.

2. Materials and methods

2.1. Sampling and analysis

In May 2015, 20 sediment sites (Figure 1) were set up in the Honghai Bay Area to sample surface sediments at depths of 0-10 cm. The survey parameters mainly included Cu, Pb, Zn, Cd, Cr, Hg, As and TOC. The sediment samples were collected by the 0.025m3 grab dredge, and the samples were collected in situ and stored in the clean polyethylene bags. Samples to analyse Hg and TOC were stored in sealed wide-mouth grinding bottles. After freeze-drying, grinding and sieving, the sediments were digested in the laboratory. The contents of Cu, Pb, Zn, Cd and Cr in each sampling station were determined by the atomic absorption spectrophotometry. The contents of Hg and As were determined by atomic fluorescence spectrometry. The content of TOC was determined with the potassium dichromate redox capacity method.

\[ MSPI = \left( \sum q_i \cdot w_i \right)^2 / 100 \]  

In this expression, \( q_i \) is the sediment quality rating of the \( i \) contaminant; \( w_i \) the weight attributed to the \( i \) variable(proportion of eigenvalues obtained from the results of PCA). For each variable the sediment quality is rated(\( q_i \)) five guidelines from 0 to 100 according to the pollutant concentration to describe the sediment quality levels, and shown Table 1.
Table 1. Sediment quality rating guidelines.

| Quality guidelines (%) | Cu | Pb | Zn | Cd | Cr | Hg | As |
|------------------------|----|----|----|----|----|----|----|
| 0-20 (excellent)       | 3.0| 3.3| 15.4| 0.6| 2.0| 0.06| 7.0|
| 21-40 (good)           | 6.0| 5.0| 34.0| 1.0| 5.0| 0.07| 8.0|
| 41-60 (average)        | 12.0| 8.0| 57.0| 1.5| 9.2| 0.08| 10.2|
| 61-80 (poor)           | 30.6| 18.2| 101| 2.9| 19.6| 0.2| 21.0|
| 81-100 (bad)           | 191.0| 69.0| 507| 8.0| 63.0| 0.7| 58.0|

2.4. Mean sediment quality guideline quotient \( (SQG-Q) \)

\( SQG-Q \) is a method of ecological risk index that can evaluate the toxicity of pollutants in sediments and the potential adverse biological effects of sediment toxicity, and its predictive ability present some limitation [23]. But \( SQG-Q \) can be used as a reference method for evaluation. The mathematical expression is as follows:

\[
SQG - Q = \left( \frac{\sum PEL - Q_i}{n} \right)
\]  
(2)

In this expression, \( PEL - Q_i \) is the probable effect level quotient; \( PEL \) then probable effect level for each contaminant [24], is shown in Table 2. Sediment locations are then scored according to their impact level[25]: \( SQG - Q \leq 0.1 \): unimpecked, lowest potential for observing adverse biological effects; \( 0.1 < SQG - Q < 1 \) : moderate impact potential for observing adverse biological effects; \( SQG - Q \geq 1 \) : highly impact potential for observing adverse biological effects.

Table 2. PEL values for the contaminant.

| Heavy metals | Cu | Pb | Zn | Cd | Cr | Hg | As |
|--------------|----|----|----|----|----|----|----|
| PEL (mg/kg)  | 108| 112| 271| 4.21| 160| 0.7| 41.6|

3. Results and discussion

3.1. Contents and distribution of heavy metals

From Table 3, it could be seen that the average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As were 6.29, 25.44, 57.87, 0.03, 15.32, 0.07 and 7.97 mg·kg\(^{-1}\), respectively. Compared with the background value of the coastal zone of China, the average concentrations of Cu, Zn, Cd, Cr and Hg are lower than the background values, and the average contents of Pb are slightly higher than the background values. Among them, the maximum concentration of Cu, Cd and Cr is lower than the background value; the average concentration of Pb is 1.02 times of the background value, and the area higher than the background value is mainly located in the coastal waters, with the highest value at station No.5(38.00 mg·kg\(^{-1}\)); and the concentration of Zn is 1.01 times higher than the background value at station No.5(81.10 mg·kg\(^{-1}\)). The concentration of Hg was 2.50 times higher than the background value at station No.19 (0.50 mg·kg\(^{-1}\)), and the concentration of As was 1.02 times higher than the background value at station No.6 (10.20 mg·kg\(^{-1}\)) and station No.7 (10.20 mg·kg\(^{-1}\)), with the background value of the coastal zone of China, the contamination level of heavy metals in the sediments of Honghai Bay was relatively light, and the main pollution factor was Pb, and the exceeding standard rate was 50%.

From Figure 2, it can be seen that the distribution characteristics of Cu, Pb and Zn are similar in plane, shown high near-shore content and low bay mouth content; Cd content shows NE-SW direction distribution, low NE direction content and high SW direction content; Cr content shows symmetrical distribution characteristics, high near-shore content and low bay mouth content; Hg content shows NE-SW direction symmetrical distribution, relatively high in the middle part; the planar distribution of As content is similar to that of Cd, and NE content is high, SW content is low, and TOC content is high near shore and low at bay mouth.
Figure 2. Spatial distribution of the contaminants indices.
3.2. The source analysis of heavy metal contamination

Pearson correlation analysis of heavy metals and TOC contents in seven surface sediments in the study area was carried out. The results were shown in Table 4. The variation of TOC content and composition was one of the important factors determining the distribution of heavy metals in the surface sediment, the source and homology of pollutants are preliminarily determined by correlation analysis between heavy metals and TOC content. From Table 4, it could be seen that there was a positive correlation between heavy metals such as Cu, Pb, Zn, Cr and As, which indicated that they had a certain degree of homology, which was basically consistent with the research results of Gan et al. in Honghai Bay [26]. At the same time, the content of TOC was positively correlated with the contents of heavy metals such as Cu, Pb, Zn, Cr and As, which indicated that heavy metals in seawater may easily chelate with TOC through surface adsorption, and the metal-organic complexes formed by the reaction were removed from the water body and adsorbed in the particles of surface sediments.

Table 3. Contents of heavy metals in the surface sediment (mg·kg⁻¹).

| Heavy metal | Content range | Average value | The background value of the coastal zone of China |
|-------------|---------------|---------------|---------------------------------------------|
| Cu          | 2.60~13.30    | 6.29          | 30                                          |
| Pb          | 16.70~38.00   | 25.44         | 25                                          |
| Zn          | 45.20~81.10   | 57.87         | 80                                          |
| Cd          | 0.00~0.11     | 0.03          | 0.5                                         |
| Cr          | 10.40~23.10   | 15.32         | 60                                          |
| Hg          | 0.03~0.50     | 0.07          | 0.2                                         |
| As          | 6.42~10.20    | 7.97          | 10                                          |

Table 4. Correlation coefficients among heavy metals and TOC in sediments.

| Elements | $C_{Cu}$ | $C_{Pb}$ | $C_{Zn}$ | $C_{Cd}$ | $C_{Cr}$ | $C_{Hg}$ | $C_{As}$ | $C_{TOC}$ |
|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| $C_{Cu}$ | 1        |          |          |          |          |          |          |           |
| $C_{Pb}$ | 0.878**  | 1        |          |          |          |          |          |           |
| $C_{Zn}$ | 0.927**  | 0.839**  | 1        |          |          |          |          |           |
| $C_{Cd}$ | -0.097   | -0.153   | -0.100   | 1        |          |          |          |           |
| $C_{Cr}$ | 0.833**  | 0.627**  | 0.752**  | 0.182    | 1        |          |          |           |
| $C_{Hg}$ | 0.006    | -0.117   | -0.018   | 0.153    | 0.176    | 1        |          |           |
| $C_{As}$ | 0.587**  | 0.729**  | 0.634**  | -0.198   | 0.477*   | -0.086   | 1        |           |
| $C_{TOC}$| 0.839**  | 0.860**  | 0.889**  | -0.039   | 0.701**  | -0.001   | 0.823**  | 1         |

Note: * Correlation is significant at the 0.05 level (two-tailed).
** Correlation is significant at the 0.01 level (two-tailed).

According to the above analysis, there was a strong correlation between heavy metal elements in the surface sediment of the study area. By principal component analysis (Table 5), the total information of seven pollutants could be reflected by two principal components (eigenvalues: 4.83 + 1.32 = 6.15 variables), meaning that the first 2 principal components had been able to reflect the most of the data.

The contribution rate of the first principal component was 60.41%, which showed that the factor had high positive load on the concentration of Cu, Pb, Zn, Cr and As, and the load of the first principal component on TOC is 0.952, and the high load on TOC showed the importance of organic matter as metal ion binding compound(Table 5). Five heavy metals (Cu, Pb, Zn, Cr and As) had a significantly positive correlation with TOC. It could be concluded that the release of metal ions accompanied by the degradation of organic matter was one of the sources of heavy metals in sediments, and it could be an
attributed also to a grain-size effect-colloidal organic matter particulate could act as a carrier for heavy metals. The first principal component mainly showed the contribution of organic matter to the source of heavy metals in sediments, which was consistent with the conclusion of the correlation analysis between heavy metals and TOC in this paper. Through literature reviewed, the sedimentary environment of the Honghai Bay was affected by river sewage near Shanwei, and there were signs of pollution of Cu, Pb and Zn in the sediments of Shanwei coastal waters. The contribution of heavy metals such as Cu, Pb and Zn to the first principal component could be used to understand the actual significance of the first principal component, which reflected the pollution effects of industrial wastewater and urban sewage. According to the correlation analysis of various pollutants, there was a strong correlation between Cu, Pb, Zn, Cr and As. The correlation coefficients ranged from 0.587 (Cu-As) to 0.927 (Cu-Zn). It could be seen that the first principal component dominated the sources of heavy metals such as Cu and Zn in sediments, and partially dominated the sources of heavy metals such as Pb, Cr and As. Table 5 showed the load of the second principal component on Cd and Hg concentration, of which Cd was the highest (0.760). The correlation between Cd and Hg was relatively little with TOC, it could be concluded that Cd and Hg were less likely to exist in sediments as organic matter conjugates, and the distribution of Cd and Hg elements was less affected by industrial wastewater and urban sewage in the region.

| Component | First principal component | Second principal component |
|-----------|---------------------------|----------------------------|
| Total     | 4.83                      | 1.32                       |
| % of Variance | 60.41                    | 16.48                      |
| Cumulative | 60.41                    | 76.89                      |
| Cu        | 0.947                     | 0.062                      |
| Pb        | 0.924                     | -0.144                     |
| Zn        | 0.944                     | 0.016                      |
| Cd        | -0.098                    | 0.760                      |
| Cr        | 0.809                     | 0.402                      |
| Hg        | -0.016                    | 0.706                      |
| As        | 0.787                     | -0.234                     |
| TOC       | 0.952                     | 0.004                      |

Table 5. The main calculated results of PCA.

Table 6. Calculated weight for PCA in the surface sediment.

| Component | Eigenvalues | Relative eigenvalues | Variables | Loads | Relative loads | Weight |
|-----------|-------------|---------------------|-----------|-------|----------------|--------|
| 1         | 4.83        | 0.785               | Cu        | 0.947 | 0.215          | 0.169  |
|           |             |                     | Pb        | 0.924 | 0.209          | 0.164  |
|           |             |                     | Zn        | 0.944 | 0.214          | 0.168  |
|           |             |                     | Cr        | 0.809 | 0.183          | 0.144  |
|           |             |                     | As        | 0.787 | 0.178          | 0.140  |
| 2         | 1.32        | 0.215               | Cd        | 0.760 | 0.518          | 0.111  |
|           |             |                     | Hg        | 0.706 | 0.482          | 0.104  |

3.3. Heavy metal contamination and ecological risk assessment

Section 2.2 showed that the contribution rate of pollutant change was based on the product of the relative eigenvalue and the relative load of the principal component calculation. The weight of heavy metals in the surface sediments of the study area could be calculated according to Table 5(shown in Table 6). Combined with Table 1, the marine sediment pollution index (MSPI) of each survey station
could be calculated by formula (1). The value of MSPI ranged from 40.30 to 57.92. The contamination level was moderate, and the sediment conditions were average. The spatial distribution (seen from Figure 3a) of marine sediment pollution index showed a gradual upward trend from the outer sea to the inner bay, and the northeast and southwest coasts of the bay were relatively high, and the overall MSPI values were different.

The mean sediment quality guideline quotient \((SQG-Q)\) values of heavy metals ranged from 0.10 to 0.21, indicating that the potential adverse effects on the ecological environment had reached a medium level. Figure 3b showed that the spatial distribution of the mean sediment quality guideline quotient of heavy metals were basically consistent with the spatial distribution of marine sediment pollution index, and the overall \(SQG-Q\) value was not so much different.

![Figure 3a. Spatial distribution of MSPI.](image)

![Figure 3b. Spatial distribution of SQG-Q.](image)

4. Conclusions

In this paper, the sources of heavy metal in the surface sediment of the coastal waters of the Honghai Bay were studied by principal component analysis (PCA), the contribution rate of each pollutant variable calculated by the principal component analysis method was used to determine the marine sediment pollution index (MSPI) to evaluate the contamination level of heavy metals, and the potential adverse effects of heavy metals contamination on the ecological environment were evaluated by the mean sediment guideline quotient (\(SQG-Q\)). The study showed that the contribution rates of the first 2 principal components were 60.41% and 16.48%, respectively. The major sources of heavy metals were industrial wastewater and municipal wastewater. The results of MSPI and \(SQG-Q\) showed that the sediment conditions were average (MSPI: 40.30-57.92), and the potential adverse biological effects had reached a moderate level (\(SQG-Q\): 0.10-0.21). The contamination level of heavy metal in the surface sediment of the study area was moderate.

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