Sediment Grain size and heavy metal pollution characteristics in the mud deposit area offshore the Shandong Peninsula before 5000 years

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Abstract. In this paper, we analyzed the characteristics of grain size, distribution of seven heavy metals and pollution characteristics of sediments from mud deposit area offshore the Shandong Peninsula before 5000 years, and quantitatively evaluate the ecological risk by the potential ecological risk index method. From 5000 to 8500a, the sediment types in the muddy area offshore Shandong Peninsula are very simple, all of which were silt. The average contents of seven heavy metals were 84.03, 78.78, 30.12, 24.71, 7.39, 0.10 and 0.01 μg/g, respectively. The results of single factor pollution evaluation showed that only the content of Cr in the sediment exceeded the standard slightly 5000 years ago, with the maximum exceeding ration of 5%. The RI values of heavy metals in the sediments ranged from 71.28 to 180.79, and the sediments were at low potential ecological risk and had little biological toxicity except for individual layers.

1. Introduction
The mud deposit area offshore the Shandong Peninsula are distributed along the north coast of Shandong Peninsula from Bohai Strait to the east side of Shandong Peninsula, showing "Ω" shape. The sedimentary thickness gradually decreases from shore to sea and from north to south (Wang et al., 2019), and the deposition rate is about 2~4mm/yr (Qiao et al., 2017). A large number of nature reserves and fishery areas are distributed along the coast of Shandong Peninsula. Good marine environment is the basis for the development of marine reserves and the fundamental guarantee for the development of coastal agriculture and fishery.

Since the 1980s, with the rapid development of coastal economy, the pollution of heavy metals in the North Yellow Sea has become more and more serious. Therefore, the pollution assessment of heavy metals in sediments is more important. However, the background values of heavy metals in sediments are relatively few, and most of them refer to the contents of heavy metals in source sediments (Lan et al., 2018). When the sediment is composed of multiple source materials, we must determine the source composition of sediment firstly, which would undoubtedly increase the workload and increase the error in the evaluation process. As a result, the selection of background value is very important. In this paper, we chose the sediments before 5000 years as research object, and analyzed the contents of seven heavy metals in them. We quantitatively evaluate the ecological risk by the potential ecological risk index method, so as to provide background reference values for the sediment in the mud deposit area offshore the Shandong Peninsula.
2. Materials and methods

2.1. Sample collection
The sediment samples were collected by the Ocean University of China in December 2019 in the water northeast to Shandong Peninsula. The samples were separated at intervals of 2 ~ 4cm and placed in clean sample bags for test. We chose 60 samples for experimental testing by the interval of 10 ~ 25cm.

2.2. Methods

2.2.1. Grain size analyses
Grain size measurements were performed using a laser diffraction particle size analyzer (LS 13 320) over a range of 0.017–2000 μm and a resolution of 0.1Φ. The relative error of repeated measurements was <1%. The sediments were classified following Folk's classification system (Folk and Ward, 1957; Figure 2). The grain size parameters were calculated using the moment method (McManus et al., 1999). The sample preparation and measurements were completed at the Ocean University of China in the Key Laboratory of Submarine Geosciences and Prospecting Technology.

2.2.2. Heavy metals analyses
Element concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS; Cu, Zn, Pb, Cd, Cr). The relative error was <2%. The analyses were completed at Qingdao Institute of Marine Geology, China Geological Survey. The content of As and Hg were analyzed by the method of atomic fluorescence, and the detection limits were $1 \times 10^{-6}$ and $0.005 \times 10^{-6}$, respectively. The analyses were completed at the Ocean University of China in the Key Laboratory of Submarine Geosciences and Prospecting Technology.

2.2.3. AMS$^{14}$C analyses
A proper amount of wet sample were placed in the clean beaker, dried at 50 °C, and then soak. After the sample is completely dispersed, it is transferred to a stainless steel sieve (63 μm) for washing. The washed sample is transferred to a beaker and dried at 50 °C. Under the microscope, about 8mg of planktonic foraminiferal shell with clean and uniform size is selected and collected into a small centrifugal tube for testing. The analyses were completed at Beta Lab in USA. The results show that the ages of the surface and bottom sediments are 5000a and 8500a respectively.

3. Results

3.1. Sediment grain size characteristics
From 5000 to 8500a, the sediment types in the muddy area offshore Shandong Peninsula are very simple,
all of them were silt. The sediment was mainly composed of silt, accounting for 71.58~93.68%, with an average of 85.06%. The mean sediment grain size (Mz) varied between 6.13~7.24Φ, with an average of 6.68Φ. The average value of sorting coefficient (δ) is 1.77, skewness (Sk) is -1.93, the average kurtosis (Ku) is 1.49. The single sediment type show that the sedimentary environment is stable, which is conducive to the study of the background value of heavy metals in sediments.

Table 1. Statistics of grain size parameters of sediments

| Grain size parameters | Clay | Silt | Sand | Mz/Φ | δ   | Sk  | Ku |
|----------------------|------|------|------|------|------|-----|-----|
| Max                  | 28.42| 93.68| 9.44 | 7.24 | 3.62 | -0.66| 2.08|
| Min                  | 6.32 | 71.58| 0.00 | 6.13 | 1.36 | -4.01| 1.17|
| Avg                  | 14.39| 85.06| 0.55 | 6.68 | 1.77 | -1.93| 1.49|
| CV                   | 0.32 | 0.05 | 3.34 | 0.03 | 0.21 | -0.26| 0.19|

3.2. The content and distribution of heavy metals

On the whole, the average contents of seven heavy metals in the sediments showed that Zn > Cr > Cu > Pb > As > Cd > Hg, and the average contents were 84.03, 78.78, 30.12, 24.71, 7.39, 0.10 and 0.01 μg/g, respectively. From the changing trend of heavy metal content, the content of Hg fluctuated most fiercely, the coefficient of variation reached 0.52, and the fluctuation of the content of Cd was the weakest, the coefficient of variation was only 0.15. The contents of Cu, Pb, Zn, Cd and Cr showed similar changing trend, and the contents decreased from bottom to top. But the change of the content of Hg was just opposite to this changing trend, showing an overall increasing trend. The change of the content of As showed a phased trend, and the overall performance showed a trend of decreasing first and then increasing.

Table 2. Statistics of heavy metals in sediments

| Elements | Al | As | Hg | Cr | Cu | Zn | Pb | Cd |
|----------|----|----|----|----|----|----|----|----|
|          | %  | 10^-6 | %  | 10^-6 | %  | 10^-6 | %  | 10^-6 |
| Max      | 7.21 | 11.99 | 0.05 | 84.38 | 34.22 | 92.22 | 29.50 | 0.13 |
| Min      | 5.97 | 2.22 | 0.01 | 66.11 | 20.74 | 65.74 | 18.75 | 0.06 |
| Avg      | 6.78 | 7.39 | 0.01 | 78.78 | 30.12 | 84.03 | 24.71 | 0.10 |
| CV       | 0.03 | 0.25 | 0.52 | 0.05 | 0.09 | 0.06 | 0.08 | 0.15 |

Figure 3. Distribution of the content of heavy metals in sediments

4. Discussion

4.1. Single factor pollution evaluation

According to Marine Sediment Quality Guidelines (GB18668-2002), the quality of marine sediments can be divided into three levels. The evaluation standards (level 1) are shown in Table 3.

Table 3. Marine sediment quality guidelines (GB18668-2002)

| Indexes | Cu | Pb | Zn | Cd | Hg | Cr | As |
|---------|----|----|----|----|----|----|----|
| Max     | 7.21| 11.99| 0.05| 84.38| 34.22| 92.22| 29.50| 0.13|
| Min     | 5.97| 2.22| 0.01| 66.11| 20.74 | 65.74| 18.75| 0.06|
| Avg     | 6.78| 7.39| 0.01| 78.78| 30.12 | 84.03| 24.71| 0.10|
| CV      | 0.03| 0.25| 0.52| 0.05 | 0.09 | 0.06 | 0.08 | 0.15|
The single pollution evaluation model is as follows:

\[ \text{II} = \frac{C_i}{S_i} \]  

Where \( \text{II} \) is the pollution index of pollutant \( i \); \( C_i \) is the measured concentration of pollutant \( i \); \( S_i \) is the evaluation standards of pollutant \( i \). \( \text{II} \) is a dimensionless quantity, and its value describes the quality of the sample. The value of 1.0 is the basic limit of the evaluation factor. When the evaluation factor is greater than 1.0, it indicates that the pollution factor has exceeded the evaluation standard and the sea area is polluted by the evaluation factor. Considering that there was no industrial activity before 5000 years ago, we selected the first level to evaluate the contents of seven heavy metals in sediments (Table 4). The single factor pollution index ranges of As, Hg, Cu, Zn, Pb and Cd in the sediments are as follows 0.11~0.60, 0.03~0.25, 0. 59~0.98, 0.44~0.61, 0.12~0.60, and the average values are 0.37, 0.06, 0.56, 0.41, 0.20, respectively. These values are all less than 1, indicating that the six elements are not polluted. Only Cr exceed the standard level, the highest standard exceeding ration is 5%, which belongs to light pollution. It can be seen from Figure 4 that the high value area of \( \text{ICr} \) and \( \text{ICu} \) are both between -16m and -9m, indicating that the two metals were homologous.

![Table 4. Single pollution indices of heavy metals in sediments from the core WH05](image)

| Parameter | \( \text{II} \) |
|-----------|----------------|
| Heavy metals | As | Hg | Cr | Cu | Zn | Pb | Cd |
| Max       | 0.60 | 0.25 | 1.05 | 0.98 | 0.61 | 0.49 | 0.60 |
| Min       | 0.11 | 0.03 | 0.83 | 0.59 | 0.44 | 0.31 | 0.12 |
| Avg       | 0.37 | 0.06 | 0.98 | 0.86 | 0.56 | 0.41 | 0.20 |

4.2. Potential ecological risk evaluation

The potential ecological risk (PER) index method of heavy metals in sediments proposed by Hankanson can reflect not only the impact of pollutants in a specific environment, but also the comprehensive impact of various pollutants. The evaluation model is as follows (Hakanson, 1980):

\[ C_i^f = \frac{C_i^f}{C_n^f} \]  
\[ E_i^f = T_i^f * C_i^f \]  
\[ RI = \sum E_i^f = \sum T_i^f * C_i^f = \sum T_i^f * \frac{C_i^f}{C_n^f} \]

Where: \( RI \) is the potential ecological risk index of multi metals; \( C_i^f \) is the pollution index of a specified metal; \( C_i^f \) is the measured content of heavy metals in the environment; \( C_n^f \) is the required background reference value; \( E_i^f \) is a potential ecological risk parameter for a specified heavy metal; \( T_i^f \) is the toxicity response coefficient of a single pollutant, which reflects the toxicity level of heavy metals.
and the sensitivity of water to heavy metal pollution. In this paper, we chose the highest background values of heavy metals before industrialization as the background reference values of Cr, Cu, Zn, Cd, Pb, As and Hg, which are 61, 15, 65, 0.065, 20, 7.7 and 0.025, respectively (Zhao and Yan., 2007). The toxicity response coefficients of Cr, Cu, Zn, Cd, Pb, As and Hg were 2, 5, 1, 30, 5, 10, 40, respectively (Xu et al., 2008).

The RI values of heavy metals in the sediments ranged from 71.28 to 180.79, which were in the low to medium ecological risk level as a whole (Table 6). However, except for individual layers, the sediments were at low potential ecological risk and had little biological toxicity (Figure 5). According to the potential ecological risk parameters of individual metals, only Cd is in the low to medium ecological risk level, and its contribution to the overall ecological risk index is as high as 48.68%.

Table 5. The potential ecological risk index of heavy metals

| Indices | E<sub>1</sub> | PER classification of single pollutant | RI | Total PER indices |
|---------|-------------|---------------------------------------|----|------------------|
| <40     | low         | low                                  | <150 | low             |
| 40–80   | medium      | 150–300                               | medium |
| 80–160  | high        | 300–600                               | high |
| 160–320 | very high   | >600                                  | very high |
| ≥320    | extremely high | extremely high | extremely high |

Table 6. Potential ecological risk indices of heavy metals in the sediments from the core WH-05

| Indices | E<sub>1</sub> | RI |
|---------|-------------|----|
| As      | 15.58      | 78.7          |
| Hg      | 7.27       | 2.77          |
| Cr      | 11.41      | 1.42          |
| Cu      | 1.29       | 10.04         |
| Zn      | 1.42       | 7.38          |
| Pb      | 4.69       | 138.57        |
| Cd      | 28.37      | 180.79        |

5. Conclusions
(1) From 5000 to 8500a, the sediment types in the muddy area offshore Shandong Peninsula are very simple, all of which were silt. The average mean sediment grain size was 6.68Φ.

(2) On the whole, the average contents of seven heavy metals in the sediments showed that Zn > Cr > Cu > Pb > As > Cd > Hg, and the average contents were 84.03, 78.78, 30.12, 24.71, 7.39, 0.10 and 0.01μg/g, respectively. The content of Hg fluctuated most fiercely, and the fluctuation of the content of Cd was the weakest.

(3) The results of single factor pollution evaluation showed that only the content of Cr in the sediment exceeded the standard slightly 5000 years ago, with the maximum exceeding ration of 5%. The RI values of heavy metals in the sediments ranged from 71.28 to 180.79, and the sediments were at low potential ecological risk and had little biological toxicity except for individual layers.

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