Pollution Characteristics and Risk Assessment of Heavy Metals in Sediment from Shenzhen-Zhongshan Channel

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Abstract: In order to study the pollution status of heavy metals in sediments of Shenzhen, the concentrations of heavy metals Cu, Pb, Zn, Cd, Cr, Hg and As in sediments were measured at 15 locations in the western man-made island. The results shows that, on average, Zn was the highest, 108.61 mg.kg⁻¹, followed by Cr, the smallest average of Cd was only 0.22 mg.kg⁻¹. Except Cd, the coefficient of variation of the remaining 6 heavy metals is relatively small. The coefficient of variation between is 12% to 36%, which is moderately mutated. The coefficient of variation of Cd is 55.73%. In the investigated surface sediments, the levels of 7 heavy metals were low. According to the potential ecological risk assessment, the ecological environment of the sediments in the study area is excellent, and the potential ecological hazard of each heavy metal is low.

1. Introduction
Heavy metals have high ecological risks due to their high toxicity, non-degradability and easy enrichment [1-3]. The heavy metals entering into the sea water are mostly adsorbed by particulates to settle into the sediment. Under certain environmental conditions (pH decreases, organic matter degradation, etc.), these heavy metals are re-released into the water body, which forms secondary pollution, disturbing and even destroying ecological balance [4-6]. At present, many international organizations/convention as Marine sediments, heavy metal pollution evaluation index, and evaluation method of environmental risk of heavy metals in sediment is established, mainly according to the amount of single heavy metal and the ratio of background value evaluation, such as enrichment factor (EF), and the cumulative index method (Igeo). Sediment quality criteria (SQGs) is derived according to the biological toxicity of heavy metals at baseline [critical effect concentration (TEL) may effect concentrations (the PEL)] evaluate the potential adverse effects of heavy metals on the benthic. However, as a permanent construction project, cross-sea passage and artificial island construction, there are few studies and reports on the influence of heavy metals on Marine sediments at home and abroad [7-8]. In this paper, the sediments of the artificial island of the cross-sea passage project from Shenzhen to Zhongshan were taken as the research object to test the heavy metals in the sediments and quantify the ecological and environmental risks.

Cross-sea passage, as a major infrastructure in the region, can eliminate regional traffic barriers and make it convenient for the external traffic of the city. The construction of the west artificial island, the main channel project, started in December 2016. The artificial island west of research work as the research object, collecting surface sediment as the object, through the test of heavy metal elements in sediments, analysis of the spatial distribution characteristics of the cumulative impact analysis and evaluation method for the ecological risk assessment index of heavy metal elements, reveal the west island influence on Marine ecosystems and potential ecological risk assessment.
2. Study area and Methodology

2.1. Study area
The bridge from Shenzhen to Zhongshan is about 30km away from human bridge in the north and 38km away from Hong kong-Zhuhai-Macao Bridge in the south. The project is connected to expressway in the east, crosses the Pearl River estuarine in the west, lands at man-made island in Zhongshan, and connects with the planned Zhongkai and eastern outer ring expressway, and lands in Shenzhen, Zhongshan through connecting lines. The total length of the project is about 24km, among which the cross-sea section is about 22.4km.

Fig 1. Shenzhen-Zhongshan channel in study area

2.2. Sample collection and Laboratory analysis
For sample collection, representative sampling points were selected and sections with relatively slow flow rate were selected. Grab dredger was used to collect surface sediment samples. A total of 15 sampling points were set. At each sampling point, 3 points were random selected, and 0.5~1kg mixed sediment samples were taken from the bottom 0~5cm with the grab bottom sampler. After all samples are kept in incubator Riga ice, and shipped to the lab on the same day, in front of the analysis are kept at 4 ℃ condition⁹¹². The samples were air-dried, ground and passed through a 100-mesh sieve at room temperature and placed in a brown glass bottle for testing. This project data sampling time on December 29, 2016, on the basis of the evaluation gauge ocean dumping material area "(GB 30980-2014), Marine sediment indicators of heavy metals of Cu, Pb, zinc, Cd, Cr, Hg, As, testing methods based on the Marine monitoring standard part 5: sediment analysis test (GB 17378.5 2007)¹³¹⁴.

Table 1. Location of sample station.

|   | Lon  | Lat  | Depth(m) |
|---|------|------|----------|
| 1 | 113.760483 | 22.5731805 | 11.5     |
| 2 | 113.754358  | 22.5704527 | 12.0     |
| 3 | 113.757750  | 22.5603722 | 12.5     |
| 4 | 113.768916  | 22.5694777 | 12.5     |
| 5 | 113.768113  | 22.5680916 | 13.5     |
| 6 | 113.767480  | 22.5677500 | 13.5     |
| 7 | 113.765383  | 22.5661166 | 12.0     |
| 8 | 113.761291  | 22.5637694 | 12.5     |
| 9 | 113.762125  | 22.5630388 | 11.5     |
|10 | 113.759069  | 22.5634111 | 12.0     |
|11 | 113.757380  | 22.5658361 | 12.5     |
|12 | 113.759730  | 22.5702833 | 13.5     |
|13 | 113.762833  | 22.5715166 | 12.5     |
|14 | 113.765336  | 22.570611  | 14.5     |
|15 | 113.764352  | 22.5669916 | 12.0     |

2.3. Methodology
SQGs is a method for evaluating the potential ecological harm of heavy metals in sediments based on critical effect concentration (TEL) and possible effect concentration (PEL). When the content of a
certain heavy metal in the sediment is less than TEL, the adverse biological toxicity effect rarely occurs, but greater than PEL, the adverse biological toxicity effect will occur frequently, and in between, the adverse biological toxicity effect occasionally occurs [15-18].

Table 2. TEL, PEL of sediment (mg.kg⁻¹).

|   | Cu    | Pb    | Zn    | Cd | Cr  | Hg | As |
|---|-------|-------|-------|----|-----|----|----|
| TEL | 18.7  | 30.2  | 124   | 0.68 | 52.3 | 0.13 | 7.24 |
| PEL | 108   | 112   | 271   | 4.21 | 160  | 0.70 | 41.6 |

Geo-accumulation Index is a quantitative index for evaluating heavy metal pollution of water sediments. It is widely used for evaluating heavy metal pollution of modern sediments. Its calculation formula is:

\[ I_{\text{geo}} = \log_2 \frac{C_n}{(k \times B_n)} \]

Where, \( I_{\text{geo}} \) is the ground accumulation index; the measured content of \( C_n \) microelement n in sediments; \( B_n \) is the geochemical background value of element n in sediments. \( k \) is the coefficient (generally 1.5) set to take into account the change of background value possibly caused by diagnosis. According to the \( I_{\text{geo}} \) value, the heavy metal pollution degree of sediments can be divided into 7 levels [19-22].

Table 3. The \( I_{\text{geo}} \) and contamination grades of heavy metals.

| Class | None | Mild | Partial | Moderate | Partial sever | Severe | Serious |
|-------|------|------|---------|----------|---------------|--------|---------|
| \( I_{\text{geo}} \) | 0    | 1    | 2       | 3        | 4             | 5      | 6       |

3. Result and Discussion

3.1. Heavy metal concentration analysis

The results of heavy metal content determination in sediment were compared with relevant standards and background values, as shown in the table.

(1) Descriptive statistical characteristics of heavy metals in sediments

Table 4. Statistical analysis of heavy metals in sediments in the study area.

| Heavy metal | Range (mg.kg⁻¹) | Mean± standard deviation (mg.kg⁻¹) | Cv (%) | Background (mg.kg⁻¹) |
|-------------|-----------------|-----------------------------------|--------|----------------------|
| Cu          | 12.7~49.6       | 27.79±10.25                      | 36.88  | 35                   |
| Pb          | 24.4~54.2       | 34.88±7.13                       | 20.44  | 60                   |
| Zn          | 67.7~179.2      | 108.61±27.76                     | 25.55  | 150                  |
| Cd          | 0.07~0.22       | 0.22±0.12                        | 55.73  | 0.5                  |
| Cr          | 44.5~70.3       | 61.73±7.70                       | 12.48  | 80                   |
| Hg          | 0.08~0.17       | 0.09±0.03                        | 36.25  | 0.2                  |
| As          | 7.2~17.6        | 13.66±4.03                       | 29.62  | 2.0                  |

The results of heavy metal content determination in sediment were compared with relevant standards and background values, as shown in the table.

The Cu content ranged from 12.7 to 49.6mg. Kg⁻¹, with an average content of 27.79mg. Kg⁻¹, Pb content ranging from 24.4 to 54.2mg. Kg⁻¹, with an average content of 34.88mg. Kg⁻¹, Zn content ranging from 67.7 to 179.2mg. Kg⁻¹, with an average content of 108.61mg.Kg⁻¹. The content of Hg ranged from 0.08 to 0.17mg. Kg⁻¹, with an average of 0.09mg. Kg⁻¹, and the content of As ranged from 7.2 to 17.6mg. Kg⁻¹, with an average of 13.66mg. Kg⁻¹. Except for Cd, the variation coefficient of the other 6 heavy metals ranged from 12.48% to 36.88% with small variation. The contents of Cu, Pb, Zn, Cd, Cr, Hg and As7 heavy metals are all higher than the PEL value of the benchmark, which means that no negative biological effects will occur. The contents of Cd were all lower than the baseline TEL value, indicating that negative biological effects would not occur [27-28].
3.2. Correlations analysis

Table 5. Spearman’s correlations between heavy metals in sediment.

|       | Silt | Clay | Sulphide | TOC  | Cu   | Pb   | Zn   | Cd   | Cr   | Hg   | As   | Petroleum |
|-------|------|------|----------|------|------|------|------|------|------|------|------|-----------|
| Silt  |      | -0.995** | 1       |      |      |      |      |      |      |      |      |           |
| Clay  | 0.227| -0.243 | 1       | -0.375| 0.374| 0.348| 1    |      |      |      |      |           |
| Sulphide |      |      | 0.227   | -0.375| 0.374| 0.348| 1    |      |      |      |      |           |
| TOC   | -0.436| 0.459 | 0.372   | 0.700**| 1    |      |      |      |      |      |      |           |
| Cu    | -0.399| 0.414 | 0.294   | 0.696 | 0.964**| 1    |      |      |      |      |      |           |
| Pb    | -0.380| 0.402 | 0.312   | 0.664 | 0.985**| 0.990**| 1    |      |      |      |      |           |
| Zn    | -0.246| 0.251 | 0.331   | 0.569**| 0.888**| 0.953**| 0.949**| 1    |      |      |      |           |
| Cd    | -0.401| 0.441 | 0.393   | 0.678**| 0.987**| 0.954**| 0.973**| 0.897**| 0.251|      |      |           |
| Cr    |      |      | 0.201   | 0.294 | 0.047 | 0.247 | 0.201 | 0.243 | 0.279|      |      |           |
| Hg    |      |      |      |      |      |      |      |      |      |      |      | 0.673**  |
| As    | 0.320| 0.321 | 0.531*  | 0.580*| 0.834**| 0.809**| 0.834**| 0.859**| 0.366| 0.886*| 0.491|           |
| Petroleum| 0.320| 0.321 | 0.531*  | 0.580*| 0.834**| 0.809**| 0.834**| 0.859**| 0.366| 0.886*| 0.491|           |

*indicates a significant correlation at the 0.05 level, ** indicates a significant correlation at the 0.01 level.

The correlation analysis shows (Table 5) that the heavy metal correlation in the sediments of the western artificial island of the deep and middle channels is relatively complex, among which the heavy metal Cu-Pb-Zn and Hg-As are highly correlated. The correlation coefficients of heavy metal combination Cu-Pb, Pb-Zn, Hg-As and Zn-Cu at the level of $P < 0.01$ were 0.964, 0.990, 0.693 and 0.983 respectively, which were extremely significant. Heavy metals. The correlation coefficients of heavy metal combination Hg-Zn and Zn-Cd at $P < 0.01$ were 0.973 and 0.949, respectively. The correlation coefficient of heavy metal combination hg-as at the level of $P < 0.01$ was 0.673, and that of heavy metal combination as-cu at the level of $P < 0.01$ was 0.716, indicating an extremely significant positive correlation.

Principal component analysis (PCA) is an effective method to identify the sources of heavy metals in the environment. The results of PCA show that 7 heavy metal elements can identify 2 principal components, accounting for 38.63% and 27.31% of the total factors, respectively. The contents of Cd, Hg and As in the first principal component were all lower than the background value, and the correlation between the elements was strong. The correlation between Cu and Pb in the first principal component was strong. The content of Zn in the second principal component is relatively high, but also lower than the background value.

3.3. Spatial analysis

The representative method of accurate interpolation is IDW interpolation, which uses the distance between the interpolation point and the sample point as the weight to carry out the weighted average. The closer the interpolation point is, the greater the weight will be given to the sample point. The predicted value at the sample point will be equal to the measured value, and the range of maximum and minimum values of the original data will not be changed. The spatial distribution of heavy metal content in the sediments in the study area showed significant heterogeneity, especially for Cu, Hg and Zn, all of which had obvious high value area. Except Cr, other heavy metal elements are high in the southwest and low in the northeast. The southwest region is adjacent to the LingDingYang bay sea area, but the high value area is lower than the background value, which is the same as the results of sediment heavy metal risk assessment.
The calculation results of geo-accumulation index show that the geo-accumulation index of Cu, Pb, Zn, Cd, Cr, Hg and As7 heavy metals is less than 0, which is non-pollution.

| Heavy metal | $I_{geo}$ | $I_{geo}$ Range |
|-------------|-----------|-----------------|
| Cu          | -2.18     | -12.19~0.49     |
| Pb          | -0.75     | -1.37~0.53      |
| Zn          | -1.08     | -3.04~0.58      |
| Cd          | -0.71     | -3.10~0.29      |
| Cr          | -1.06     | -1.29~0.69      |
| Hg          | -0.62     | -1.19~0.38      |
| As          | -0.95     | -1.52~0.49      |

The single potential ecological hazard coefficient and comprehensive potential ecological hazard index in the sediments of western artificial island are shown in the table.

| Heavy metal | $E_i$ | $E_i$ | $RI$ |
|-------------|-------|-------|------|
| Cu          | 7.08  | 1.81  | 3.97 |
| Pb          | 4.51  | 2.03  | 2.91 |
| Zn          | 1.19  | 0.54  | 0.72 |
| Cd          | 4.20  | 36.00 | 13.44|
| Cr          | 1.11  | 1.76  | 1.54 |
| Hg          | 11.60 | 33.60 | 18.68|
| As          | 3.60  | 7.45  | 6.83 |
| $RI$        | 23.64 | 92.25 | 48.09|

The potential ecological risk coefficient ($E_i$) of all heavy metal elements is less than 40, and the degree of potential hazard is low. The potential ecological hazard impact of heavy metal elements in sediments is successively Hg > Cd > As > Cu > Pb > Cr > Zn, indicating that the risk parameter of Hg is high and the Zn is the lowest. Judging from the average value of the comprehensive potential ecological hazard index, the average value of $RI$ in the sediments of the entire west artificial island is 48.09, and the maximum value is only 92.25, which is less than 150.

4. Conclusion
(1) For the same heavy metal elements in the surface sediments, the distribution of their contents in the sediments of the western artificial island is not significantly different. The Cu content is 12.7~49.6mg·Kg$^{-1}$, Pb content is 24.4~54.2mg·Kg$^{-1}$, Zn content is 67.7~179.2mg·Kg$^{-1}$, average content is 108.61mg·Kg$^{-1}$, Cd content is 0.07~0.22mg·Kg$^{-1}$, Cr content is 44.5~70.3mg·Kg$^{-1}$, Hg content is 0.08~0.17mg·Kg$^{-1}$, As content is 7.2~17.6mg·Kg$^{-1}$. The variation coefficient of the other 6 heavy metals ranged from 12.48% to 36.88%.
(2) according to the evaluation results of the cumulative index method, the results show that the geo-accumulation indexes of Cu, Pb, Zn, Cd, Cr, Hg and As heavy metals are all less than 0, which is pollution-free.

(3) The potential ecological risk coefficient ($E_i^r$) of all heavy metal elements is less than 40, and the degree of potential hazard is low. The potential ecological hazard impact of heavy metal elements in sediments is successively Hg > Cd > As > Cu > Pb > Cr > Zn, indicating that the risk parameter of Hg is high and the Zn is the lowest. Judging from the average value of the comprehensive potential ecological hazard index, the average value of RI in the sediments of the entire west artificial island is 48.09, and the maximum value is only 92.25, which is less than 150.

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