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The content and pollution evaluation of heavy metals in surface seawater in Dalian Bay

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Qinbang Sun [1], Fan Gao, Zhaolin Chen, Yang Wang and Depeng Li

National Marine Environmental Monitoring Center, Dalian 116023, China

[1] Email:qbsun@nmemc.org.cn

Abstract. Surface seawater samples at 23 sites in the offshore area of Dalian Bay were collected in November 2014 and May 2015, to investigate the concentration and pollution characteristics of the six heavy metals (Cu, Pb, Zn, Cd, Hg and As) in that area. The heavy metals pollution condition was evaluated using single factor pollution index evaluation method and comprehensive pollution evaluation method, the variation coefficient method was used to analyze the dispersion degree of pollutants on the spatial scale between the stations, and the correlation analysis and PCA method was used to study the main resources of heavy metals pollutants. The results showed that the average value of Cu, Pb, Zn, Cd, Hg and As met the I water quality requirements of the seawater water quality standard. The single factor pollution index values of the six heavy metals in the two seasons were in the following order: Cu＞Pb＞Zn＞Hg＞Cd＞As. The evaluation result of the comprehensive pollution index method showed the average value was less than 1, so the study area was clean. The result of the variation coefficient showed that the heavy metal content in the water body between the stations was small in the investigation area, and the pollution degree of the heavy metal pollution factors in the sea area was basically the same. The results of correlation analysis and principal component analysis indicated the correlation coefficient of Cu, Pb, Zn, Cd, Hg and As was small and the positive load of heavy metals was low. Therefoere, there were no similar pollution level or common source of pollution between six metals, that is, the probability of common sources was lower among the elements.

1. Introduction

Heavy metals in water are one of the main pollutants in the marine environment, and heavy metals pollution is one of the most serious world environmental problems today [1-2]. Heavy metals in water are enriched in sediments and organisms through various ways, which will cause unavoidable harm to the organism. In the assessment system of water environmental pollution, heavy metals have already become the important factor of the marine environmental quality evaluation [3-6]. Dalian Bay is a semi-closed natural harbor in the southern end of Liaodong peninsula, which is rich in port resources and along which there are a large number of chemical plants and sewage outfalls [7-8]. In recent years, the large-scale reclamation and the development of port industries have brought great pressure to the marine environment in the region.

At present, the most commonly used water quality evaluation methods are single factor pollution index evaluation method, comprehensive pollution evaluation method, grey theory analysis method, fuzzy comprehensive evaluation method, artificial neural network method and so on [9-12]. This paper chose the widely used single factor pollution index evaluation method and comprehensive pollution evaluation method to assess and analyze the pollution condition of the study sea area, and chose variation coefficient method to analyze the dispersion degree of pollutants on the spatial scale between the stations, and chose correlation analysis and PCA method to study the main resources of heavy metals pollutants. Through the aforementioned study, this paper would provide a scientific basis for the marine environment protection.

2. Materials and methods

2.1. Samples collection and analysis

In September 2014 and May 2015, 23 survey stations were set up in Dalian Bay (Figure 1) to collect the surface sea water samples of 6 heavy metal parameters Cu, Pb, Zn, Cd, Hg and As. The investigation was carried out according to <Marine Survey Specification> (GB/T 12763.4-2007). The analysis was carried out according to <Marine Monitoring Specification> (GB 17378.4-2007). The surface sea water samples were collected with plastic containers, and the sample bottles were soaked in nitric acid solution for 24h before use. The water samples were repeatedly rinse 3 times with the super pure water and stored in a sealed plastic bag after drying. The samples were filtered by 0.45μm microporous filter membrane. After filtration, pH was adjusted to less than 2 by adding concentrated nitric acid. It was sealed in a clean environment and frozen at low temperature. After returning to the laboratory, it was immediately analyzed under the clean conditions of the 1000 level. The contents of Cu, Pb, Zn and Cd were measured by atomic absorption spectrometry, and the content of Hg and As was determined by atomic fluorescence spectrometry. The quality control method was based on parallel double sample test, parallel sample preparation and synchronous analysis under the same conditions.

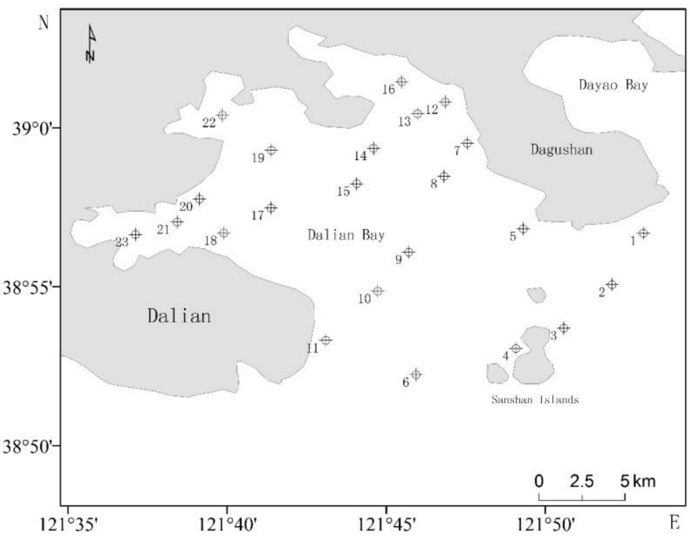

Figure 1. Distribution of sampling stations.

2.2. Single-factor pollution index method

The single-factor pollution index method is the simplest method of evaluating the environmental quality index. There is no dimension, and each pollution factor is evaluated separately, and the results of the standard-reaching rate/exceeding standard rate, exceeding standard multiplier, statistical multiplier and statistical representative value are obtained by the statistical analysis [13-14].

The mathematical calculation expression of the single-factor pollution index is:

$$I_i = C_i / S_i \quad (1)$$

In the expression, I_i is the pollution index of factor i, and C_i is the measuring content of factor i, and S_i is the assessment standard value of factor i.

2.3. Comprehensive pollution index method

The comprehensive pollution index method is an important method for water quality environmental assessment. It can comprehensively evaluate the water pollution status. The mathematical expression is [15]:

$$C_f^i = C^i / C_n^i \tag{2}$$

$$WQI = \frac{1}{n}\sum_{i=1}^{n} C_f^i \tag{3}$$

Among them, WQI is the comprehensive pollution index of heavy metals in seawater. C_f^i, $C^i$and $C_n^i$are the single index, the measured content and the evaluation standard value of single metal element i, respectively. n is the number of metal elements involved in the evaluation. The relationship of the WQI value of the surface seawater and the degree of seawater pollution is listed in table 1.

Table 1. Relationships between combined pollution index and pollution level of heavy metals in surface seawater.

Pollution Degree	Clean	Mild Pollution	Moderate Pollution	Serious Pollution
Comprehensive Pollution Index(WQI)	$WQI \le 1$	$1 < WQI \le 2$	$2 < WQI \le 3$	$WQI > 3$

2.4. Variation coefficient method

The variation coefficient can quantitatively reflect the difference in the magnitude of the fluctuation of the pollutants on the spatial scale, and the index weight of each evaluation factor is determined by the coefficient of variation, which can objectively reflect the relative importance of the evaluation index and weaken the influence of the extremum index on the evaluation results. The mathematical expression is [16]:

$$CV = SD/\bar{X} \tag{4}$$

In the expression, *CV* is the variation coefficient, *SD* is the standard deviation of each station's investigation factor, and $\bar{X}$ is the mean of each station's investigation factor.

2.5. Principal component analysis method

The Principal Component Analysis (PCA) is a statistical analysis method of mastering the main contradiction. It can reflect the most of the original information of multiple variables by simplifying the data (that is, using less comprehensive indicators instead of a large number of indicators that have a certain correlation). Many studies have proved that the principal component analysis method can be used to analyze the source of the elements and the main affecting factors on the enrichment of the elements in the sediments［17］.

3. Results and discussion

3.1. The content analysis of heavy metals elements

Table 2. The contents of heavy metals in surface seawater(mg·L^{-1}).

Metals Elements	2014.9		2015.5		The seawater water quality standard(GB3097-1997)/mg·L^{-1}			
	Content range	Average value	Content range	Average value	I	II	III	IV
Cu	0.0008~0.0041	0.0015	0.0009~0.0023	0.0018	≤0.005	≤0.010	≤0.050	
Pb	0.0002~0.0007	0.0003	0.0002~0.0003	0.0003	≤0.001	≤0.005	≤0.010	≤0.050
Zn	0.0032~0.0067	0.0043	0.0033~0.0067	0.0044	≤0.020	≤0.050	≤0.10	≤0.50
Cd	0.0001~0.0002	0.0002	0.0001~0.0003	0.0002	≤0.001	≤0.005	≤0.010	
Hg	0~0.000018	0.000009	0~0.000020	0.000011	≤0.00005	≤0.0002	≤0.0005	
As	0.0002~0.0034	0.0006	0~0.0008	0.0005	≤0.020	≤0.030	≤0.050	

According to Table 2, the average content of heavy metals (Cu, Pb, Zn, Cd, Hg and As) in the surface seawater of Dalian Bay in September 2014 and May 2015 were all satisfied with the requirement of I class water quality of <the seawater water quality standard>[18]. Therefore, according to the requirement of I class water quality of the seawater water quality standard, and all the exceeding standard rates of heavy metals (Cu, Pb, Zn, Cd, Hg and As) in the surface seawater of Dalian Bay in September 2014 and May 2015 were zero, that is, there was no survey station of exceeding the standard.

3.2. The risk index assessment of heavy metals pollution in surface seawater

3.2.1. The assessment of single-factor pollution index With I class water quality requirement of the seawater water quality standard as a reference standard, the contents of heavy metals in the surface seawater of Dalian Bay were evaluated through Single factor index method. According to Eq.1, the single factor index of heavy metals in the surface seawater of Dalian Bay was calculated (Table 3).

According to Table 3, all the average contents of heavy metals (Cu, Pb, Zn, Cd, Hg and As) met the requirement of I class water quality of the seawater water quality standard. The order of 6 heavy metals average contents of two seasons were Cu＞Pb＞Zn＞Hg＞Cd＞As.

Table 3. Single factor pollution index evaluation of heavy metals in surface seawater.

Metals Elements	Single Factor Index	
	2014.9	2015.5
Cu	0.30	0.37
Pb	0.25	0.24
Zn	0.22	0.22
Cd	0.16	0.17
Hg	0.18	0.21
As	0.03	0.03

3.2.2. The assessment of comprehensive pollution index The comprehensive pollution index of heavy metals in surface seawater (Table 4) was studied by Eq. (2) and Eq. (3). From table 4, the average value of the comprehensive pollution index of heavy metals Cu, Pb, Zn, Cd, Hg and As in the surface seawater in September 2014 and May 2015 was less than 1. From Table 1, the study area is a clean sea area. The main reason is that the pollution sources are well prevented and controlled by the various measures.

According to figure 2, the pollution index spatial distribution of heavy metals in the surface seawater in September 2014 and May 2015 is overall the same and appeared the characteristic of “the value of shore in the bay was high and the central value was low”. The pollution index of the sea area was overall small, and the quality of the sea water environment was better.

Table 4. The combined pollution index of heavy metals in surface seawater.

Pollution Condition	2014.9			2015.5		
	Min.	Max.	Average	Min.	Max.	Average
Comprehensive Pollution Index(WQI)	0.10	0.44	0.19	0.11	0.31	0.21

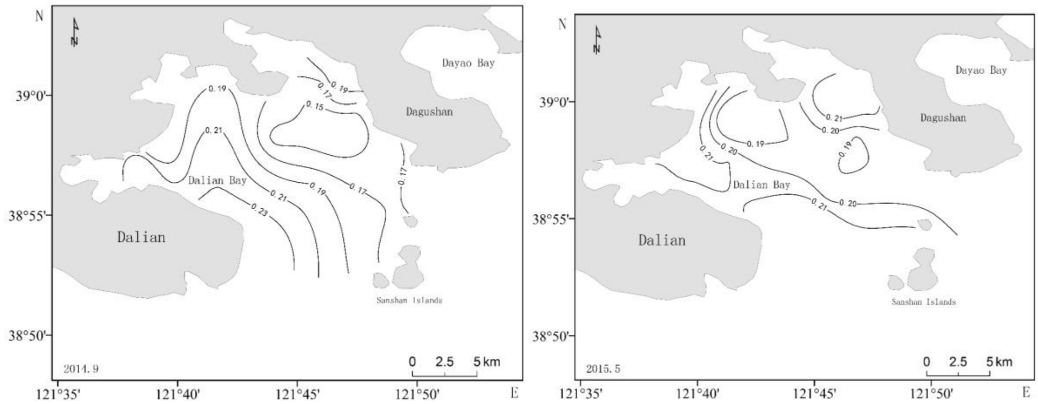

Figure 2. Spatial distribution of heavy metals in surface seawater.

3.2.3. The variation coefficient of heavy metals in the surface seawater. In this study, the variation coefficient was used to quantify the difference in the magnitude of the fluctuation of heavy metals between stations. This study used DPS17.0 software to analyze the survey data. The results were calculated by Eq. (4), and the variation coefficient of the average value of heavy metals contents in the surface seawater was calculated in May and November 2015. The results were shown in Table 5.

From Table 5, it could be seen that the variation coefficient of each factor was relatively small, indicating that the concentration of heavy metals in the surface seawater between the stations was small in the investigation area. Therefore, it could be found that the pollution degree of each heavy metal pollution factor in the sea area was basically the same.

Table 5. The statistical feature values of heavy metals in surface seawater.

Metals Elements	2014.9			2015.5		
	Average	Standard deviation	Variation coefficient	Average	Variation coefficient	Variation coefficient
Cu	0.0015	0.00073	0.50	0.0018	0.00039	0.21
Pb	0.0003	0.00011	0.41	0.0003	0.00004	0.15
Zn	0.0043	0.00100	0.23	0.0044	0.00108	0.24
Cd	0.0002	0.00003	0.17	0.0002	0.00004	0.22
Hg	0.000009	0.0000055	0.61	0.000011	0.0000048	0.45
As	0.0006	0.00068	1.07	0.0005	0.00019	0.38

3.2.4. The correlation analysis of heavy metals Heavy metals in water are not persistent, and they are susceptible to migrate and transform under the effect of water dynamics and environment. Therefore, the sources of heavy metals in water bodies appear to be more complex. It appears higher significance between heavy metals, which indicates that the pollution level of heavy metals is same or the pollutants come from the same source. Hence, the homology of heavy metals can be determined by the correlation analysis of heavy metals [19-20].

Table 6. Correlation coefficients among heavy metals in surface seawater.

Factors	C_{Cu}	C_{Pb}	C_{Zn}	C_{Cd}	C_{Hg}	C_{As}
C_{Cu}	1					
C_{Pb}	-0.098	1				
C_{Zn}	-0.033	0.188	1			
C_{Cd}	0.150	-0.086	0.291*	1		
C_{Hg}	0.087	0.223	0.088	-0.117	1	
C_{As}	-0.133	-0.143	-0.147	-0.027	-0.288	1

Note: * Two-sided test p＜0.05

In this study, the content of 6 heavy metals in the surface seawater in September 2014 and May 2015 was analysed by Pearson correlation. It was seen from Table 6 that only Zn and Cd in the surface seawater were related under less than 0.05 of significant probability in the two-side test analysis, but the correlation coefficient was smaller and the correlation between Zn and Cd was weaker. Therefore, there was no stronger correlation between the heavy metal elements (Cu, Pb, Zn, Cd, Hg and As) in seawater, that is, they had no similar pollution levels or common sources of pollution.

3.2.5. The source analysis of heavy metal pollutants based on PCA method. By the principal component analysis (as shown in Table 7), the eigenvalues of the first 3 principal component factors were 1.556, 1.304, and 1.135, respectively, and the contribution rates were 25.936%, 21.736% and 18.922%, respectively, and the cumulative contribution rate of the first 3 main components was 66.593%, that is, the first 3 principal components only account for 2/3 of all the data. As shown in Table 7, the characteristic of the first principal component was that there was a higher positive load on the factor variables of Pb, Zn and Hg. The second principal component factor variable had higher positive load on the Cd, and the third principal component factor variable had no high positive load. According to the correlation coefficient matrix analysis of heavy metals in surface seawater, the correlation between Zn and Cd was small, and Zn and Cd had a weak correlation. It further indicated that the probability of the common sources of heavy metals such as Cu, Pb, Zn, Cd, Hg and As in the surface water was lower, which was in agreement with the conclusion of the correlation analysis of 2.2.4 section.

Table 7. The main calculated results of principal component analysis (PCA).

Items	The first principal component	The second principal component	The third principal component
Eigenvalue	1.556	1.304	1.135
Contribution rate(%)	25.936	21.736	18.922
Cumulative contribution rate(%)	25.936	47.671	66.593
Cu	0.167	0.372	-0.753
Pb	0.572	-0.327	0.403
Zn	0.534	0.467	0.484
Cd	0.129	0.852	0.111
Hg	0.663	-0.340	-0.256
As	-0.678	0.013	0.307

4. Conclusions

Through the analysis of the contents of heavy metal elements, Cu, Pb, Zn, Cd, Hg and As in the surface water of Dalian Bay in September 2014 and May 2015, the main results obtained were as follows:

(1) the average value of Cu, Pb, Zn, Cd, Hg and As content in the surface water of Dalian Bay met the I water quality requirements of the seawater water quality standard. In September 2014 and May 2015, the contents of Cu, Pb, Zn, Cd, Hg and As were zero, that is, there was no investigation station of exceeding the standard.

(2) the average content of heavy metals Cu, Pb, Zn, Cd, Hg and As in the surface seawater was evaluated with the single factor pollution index method. The average pollution degree of the average content of 6 heavy metals was generally ranked as: Cu > Pb > Zn > Hg > Cd >. The average value of the comprehensive pollution index of metals (Cu, Pb, Zn, Cd, Cr, Hg and As) was less than 1. The study area belonged to the clean sea area. The result of the variation coefficient showed that the heavy metal content in the water body between the stations was small in the investigation area, and the pollution degree of the heavy metal pollution factors in the sea area was basically the same.

(3) the correlation analysis of heavy metals in surface seawater: the correlation coefficient between heavy metals in the surface seawater was small and there was no stronger correlation between each other, that is, they had no similar pollution level or common source of pollution. The first 3 main components only accounted for 2/3 of all the data by the principal component analysis. And the positive load of heavy metals was low, which indicated that the probability of common sources of heavy metals in the surface seawater was low.

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