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Pollution and Potential Ecological Risk Evaluation of Heavy Metals in the Sediments around Dongjiang Harbor, Tianjin

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Abstract

Distribution, enrichment characteristics of heavy metals (such as lead, cadmium, copper, zinc, mercury and arsenic) in the sediments around Dongjiang Harbor, Tianjin, were measured and analyzed in March, 2009. The potential harmful effects of these heavy metals were evaluated by Sediment Enrichment Factor Method (SEF) and Potential Ecological Risk Index Method (PERI) based on considering the specialty of the area and the applicability of evaluation methods, which could quantify the potential ecological risk levels of heavy metals. The results showed that the sediment enrichment factors of heavy metals were: As >Zn> Cu >Hg >Pb >Cd. Pb and Cd in the sediments around Dongjiang Harbor, Tianjin, were natural and did not originate from human activities. The pollution of Cu was low and from nature, which was affected by human activities slightly. Hg was polluted by human and exceeded standard much in many monitoring stations. As and Zn were affected seriously by human activities. In a word, the ecological risk levels of heavy metals in the sediments from this area were low. Potential Ecological Risk Indices (E_f^i) for heavy metals were: Hg >Cd >As >Cu >Pb >Zn. Hg had moderate potential ecological risk to the ecological environment and contributed most to potential toxicity response indices for various heavy metals (RI) in the sediments around Dongjiang Harbor, Tianjin.

Keywords: Sediments, Heavy metals, Sediment Enrichment Factor Method (SEF), Potential Ecological Risk Index (PERI), Mercury, Dongjiang Harbor, Tianjin;

1. Introduction

A large number of heavy metals and suspended particulate matter are brought into the sea by terrestrial runoff, atmospheric deposition, sewage discharge and others. Heavy metal pollutants in receiving water were poorly soluble, which had been mostly absorbed by suspended particulate. After a series of process, heavy metals deposited along with colloid and were accumulated from the water into the sediments, so the sediments became the main repository

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of heavy metals and other chemicals [1]. Thus many researchers believed that the sediments were indicator for water pollution and the distribution of heavy metals in the sediments could reflect the water pollution level [2,3].

However, once the pollution of sedimentary environment was serious and exceeded the limit of bearing capacity, or other external factors changed (such as climate, hydrodynamic conditions, pH, salinity, Eh, temperature and other environmental factors changed, or a large number of organic and inorganic pollutants discharged) could caused the heavy metals re-released from the sediments which were long-term accumulated, and could led to the deterioration of ecological environment, even posed a threat to the organism through the food chain [4].

In recent years, with the development of the coastal zone economy, sea water was polluted seriously and ecological environment in Bohai Bay was more severe than ever before [5]. Chaobai New River, Beiyun River and Jiyun River, etc. flow into Yongding New River and discharge into Bohai Bay. Large amount of heavy metals and suspended particles were brought into the sea by these rivers. So it's of great significance to study the situation of marine pollution. The distribution and enrichment characters of heavy metals were studied, such as lead, cadmium, copper, zinc, mercury and arsenic in the sediments from this area. And the potential ecological risk levels of heavy metals were evaluated by Potential Ecological Risk Index Method [6] for analyzing the pollution and ecological risk of heavy metals in the sediments from Bohai Bay.

2. Sample collection, treatment and analysis

2.1. Sample collection

11 monitoring stations around Dongjiang Harbor, Tianjin (Fig. 1) were positioned with Global Positioning Satellite System (GPS) in March, 2009. And the surface sediments samples were collected by Grab Borrow device and preserved in the polyethylene bags which were washed with nitric acid and distilled water, then brought to the laboratory. The samples were air-dried at room temperature and then grinded and sifted through 80-mesh nylon sieve, stored in brown glasses at 4℃after tagged [7].

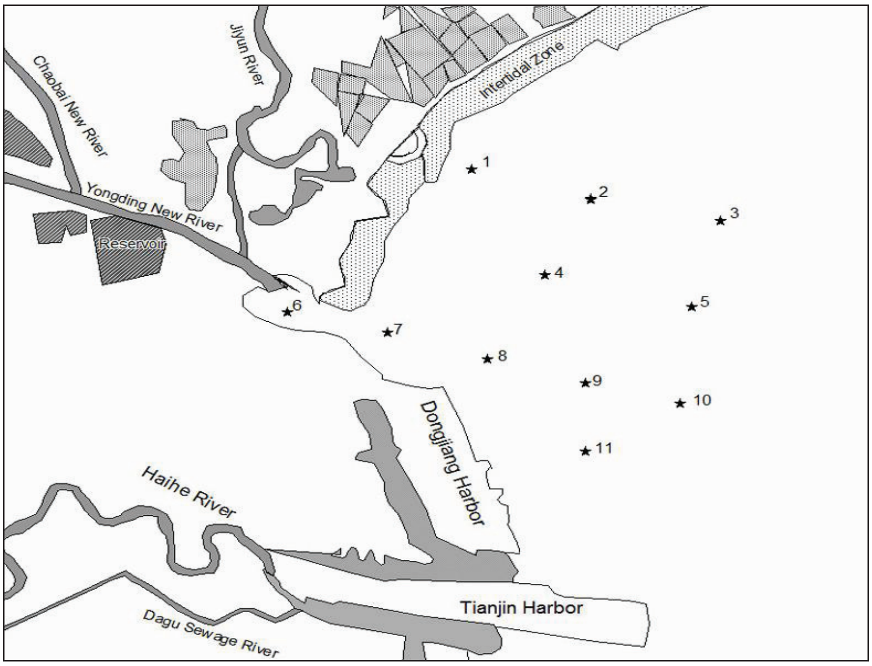

Fig. 1. Monitoring stations around Dongjiang Harbor, Tianjin.

2.2. Sample treatment

Weigh 0.12 - 0.13 g sediment samples respectively, place in 30 mL polytetra-fluoroethylene (PTFE) beaker, and add a little water for wetting samples. Then add 5 mL hydrochloric acid, cover the lid and place in temperature-controlled heating board and heat about 30 mins, then add 2.5 mL nitric acid, heat to boiling until nitric acid totally break down. Add 7 mL hydrofluoric acid, 0.5 mL perchlorate, cover it and heat until the solution become clarification, heat at 140 ℃ so that perchlorate completely volatilize. Cool it and add 1.7 mL hydrochloric acid and a small amount of water, heat to dissolve, transfer them to 25 mL colorimetric tube three times, fix volume, prepare to measured the content of heavy metals. The reagents for analysis and determination were analytically pure, water was secondary deionized water [8].

2.3. Sample analysis

The analysis methods and the lowest detection limits were showed in Table 1.

Table 1. The analysis methods and detection limits

Items	Pb	Cd	Cu	Zn	Hg	As
Methods	Flameless atomic absorption spectroscopy			Flame atomic absorption spectroscopy	Atomic fluorescence spectrophotometer	Hydride generation atomic absorption spectroscopy
Lowest detection limits	1×10^{-6}	0.045×10^{-6}	2×10^{-6}	6×10^{-6}	2×10^{-9}	3×10^{-6}
Instruments	Beijing Rayleigh analysis instrument company WFX-130 disc-type atomic absorption spectrophotometer				Wi-314720 atomic fluorescence spectrophotometer	

3. Evaluation methods

There are a number of evaluation methods of heavy metals in the sediments internationally, such as Geo-accumulation Index Method, Sediment Enrichment Factor (SEF), Potential Ecological Risk Index Method (PERI), Excessive Regression Analysis Method and Face Graph Method [9,10,11], etc. Different evaluation methods have different merits. The specialty of the area and the applicability of evaluation methods should be first considered in order to evaluate potential ecological risk of heavy metals in the sediments more reliably.

Pollution condition of heavy metals could be known generally by SEF which was used to evaluate according to the content of heavy metals, but it hardly distinguish their source. Also the evaluation results cannot show chemical activity and biological availability of heavy metals. So SEF cannot be evaluated migration features and potential ecological risk of heavy metals effectively.

As an international method to study the heavy metals in sediments, Potential Ecological Risk Index Method is simple, relative shortcut and precise [6,7,8], not only reflects the single impact of heavy metals to ecological environment but also takes into accounts the different background values of the geography [12] and combines environmental chemistry with biological toxicology and ecology.

According to above consideration, SEF and PERI are used to evaluate heavy metals pollution in the sediments around Dongjiang Harbor, Tianjin.

3.1. Sediment Enrichment Factor (SEF)

Sediment Enrichment Factor was proposed by Kemp in 1979, the formula was [13]:

$$K_{SEF} = (E_s/Al_s - E_a/Al_a)/(E_a/Al_a) \tag{1}$$

Where K_{SEF} was the enrichment factor for heavy metals in sediments, E_s was the content of heavy metals in sediments, Al_s was the content of Al in sediments, Ea was the content of heavy metals in unpolluted sediments, Ala was the content of Al in unpolluted sediments. Because Al is inert in the migration process, it was selected as the reference element. The greater the enrichment factor of heavy metals in sediments, the higher the level of sediments contaminated by heavy metals.

3.2. Potential Ecological Risk Index Method (PERI)

Potential Ecological Risk Index Method (PERI) was proposed by Swedish scientist Hakanson in 1980, had been applied to evaluate the harm of heavy metals in the sediments. The method was used widely and had great influence in international. The method was described as follow [8]:

3.2.1. Pollution index (C_f^i for short)

Pollution index is used to evaluate the pollution of heavy metals in the sediments, C_f^i is used to reflect the pollution of single heavy metal in the sediments, the formula for pollution index of the single heavy metal is:

$$C_f^i = C_{surface}^i / C_{reference}^i \tag{2}$$

Where C_f^i is pollution coefficient for a certain heavy metal, which can reflect the pollution character of the investigated region but can not reveal the ecological effects and hazards. $C_{surface}^i$ is the measured values of heavy metals in surface sediments. $C_{reference}^i$ is the parameters for calculation. The background values upper limits of heavy metals in the sediments from Bohai were based on previous research [14,15] and were used as reference values to evaluate the pollution in the paper (Table 2).

Table 2. Environmental background values of heavy metals in the sediments from Bohai Bay

Element	Cu	Zn	Pb	Cd	As	Hg
Upper limits of background values /$mg{\cdot}kg^{-1}$	25.86	75	16.63	0.136	13	0.05

3.2.2. Potential ecological risk index for the single heavy metal pollution (E_f^i for short):

The formula for potential ecological risk index for the single heavy metal pollution:

$$E_f^i = C_f^i \times T_f^i \tag{3}$$

Where T_f^i is the response coefficient for the toxicity of the single heavy metal. The formula reveals the hazards of heavy metals on the human and aquatic ecosystem and reflects the level of heavy metal toxicity and ecological sensitivity to the heavy metal pollution. The standardized response coefficient for the toxicity of heavy metals, which was made by Hakanson [6], was adopted to be evaluation criterion. Respectively, the corresponding coefficients based on its toxicity were: Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, Zn=1 [16].

3.2.3. Potential toxicity response index for various heavy metals in the sediments (RI for short)

The formula for potential toxicity response index for various heavy metals**:**

$$RI = \sum E_f^i \tag{4}$$

The grading standards of potential ecological risk of heavy metals were in Table 3.

Table 3. Relationship among RI, E_f^i and pollution levels

Scope of potential ecological risk index (E_f^i)	Ecological risk level of single-factor pollution	Scope of potential toxicity index (RI)	General level of potential ecological risk
$E_f^i < 40$	low	$\mathrm{RI} < 150$	low-grade
$40 \le E_f^i < 80$	moderate	$150 \le \mathrm{RI} < 300$	moderate
$80 \le E_f^i < 160$	higher	$300 \le \mathrm{RI} < 600$	severe
$160 \le E_f^i < 320$	high	$600 \le \mathrm{RI}$	serious
$320 \le E_f^i$	serious		

4. Results and discussion

4.1. Evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin by SEF

The contents and the enrichment factors of heavy metals in the sediments from different monitoring stations around Dongjiang Harbor, Tianjin, were showed in Table 4.

Table 4. Contents and enrichment factors of heavy metals in the sediments from different monitoring stations

Station number	Pb		Cd		Cu		Zn		Hg		As	
	C	K_{SEF}	C	K_{SEF}	C	K_{SEF}	C	K_{SEF}	C	K_{SEF}	C	K_{SEF}
1	2.48	0.10	0.05	0.10	13.49	0.45	87.63	1.10	0.10	0.40	13.41	0.89
2	5.56	0.22	0.08	0.16	16.13	0.54	87.36	1.09	0.27	1.08	19.26	1.28
3	0.62	0.02	0.02	0.04	16.56	0.55	77.10	0.96	0.01	0.04	12.04	0.80
4	4.43	0.18	0.05	0.10	21.96	0.73	94.91	1.19	0.02	0.08	17.33	1.16
5	4.25	0.17	0.07	0.14	22.79	0.76	89.69	1.12	0.06	0.24	17.33	1.16
6	3.37	0.13	0.05	0.10	13.00	0.43	55.62	0.70	0.11	0.44	10.43	0.70
7	6.02	0.24	0.09	0.18	18.91	0.63	93.42	1.17	0.06	0.24	23.88	1.59
8	3.42	0.14	0.06	0.12	22.16	0.74	93.60	1.17	0.05	0.20	20.77	1.38
9	5.39	0.22	0.09	0.18	26.82	0.89	101.26	1.27	0.04	0.16	18.05	1.20
10	6.39	0.26	0.06	0.12	20.92	0.70	95.47	1.19	0.05	0.20	19.72	1.31
11	5.82	0.23	0.09	0.18	20.20	0.67	96.33	1.20	0.04	0.16	16.18	1.08
Max.	6.39	0.26	0.09	0.18	26.82	0.89	101.26	1.27	0.27	1.08	23.88	1.59
Min.	0.62	0.02	0.02	0.04	13.00	0.43	55.62	0.70	0.01	0.04	10.43	0.70
Average	4.34	0.17	0.06	0.13	19.36	0.64	88.40	1.11	0.07	0.29	17.13	1.14

Annotation: In Table 4, C stands for the content of heavy metal ($mg\cdot kg^{-1}$) and K_{SEF} stands for the enrichment factor of heavy metal in the sediments, is the ratio of the actual measured heavy metal content and the highest background value of the heavy metal in the reference value table [17]. (Table 5)

Table 5. The reference value and toxicity coefficient of heavy metals

Element	Pb	Cd	Cu	Zn	Hg	As
C_n^i / $mg\cdot kg^{-1}$	25.00	0.50	30.00	80.00	0.25	15.00
T_n^i	5	30	5	1	40	10

In Table 4, the enrichment factors of heavy metals in the sediments around Dongjiang Harbor, Tianjin were: As >Zn> Cu >Hg >Pb >Cd. The enrichment degree of As was the highest, its average value of K_{SEF} was 1.14, the max was 1.59. The enrichment degree of Zn was lower than As, its average K_{SEF} was 1.11. The enrichment degree of Cd is the lowest and its average K_{SEF} was 0.13.

Distributing in a line from stations 6 to10 is perpendicular to the coastline. Station 6 is the nearest to the estuary of Yongding New River. Comparing with K_{SEF} of heavy metals in these monitoring stations, we can conclude, the enrichment factors of heavy metals except Hg in station 6 were the lowest, K_{SEF} in station 7 increased significantly and others farther from the estuary decreased slowly. The reason is that station 7 is near the estuary of Yongding New River, where the river brought some pollutant into the sea. Then the environmental medium changed in salinity and pH due to salt and fresh water intersected in the estuary, where heavy metals will be hydrolyzed and cohered first, and completed the course of enrichment after exchanged, adsorbed by colloidal materials. But further from the estuary, less heavy metal enriched.

4.2. Single pollution index analysis of heavy metals in the sediments around Dongjiang Harbor, Tianjin

According to the calculation results (Table 4 and 6), the content of Pb was the lowest, its maximum value was 6.39 mg·kg^{-1} with an average of 4.34 mg·kg^{-1} which didn't exceed the background value 16.63 mg·kg^{-1}. The content of Cd was low too, its maximum was 0.09 mg·kg^{-1}, the average was 0.06 mg·kg^{-1} which didn't exceed the reference value 0.136 mg·kg^{-1}. The content of Cu was not great, but station 9 was 26.82 mg·kg^{-1} which exceeded standard 4 times, the other 10 stations didn't exceed the background value. The content Hg, As and Zn exceeded their background values. The content of Zn in station 6 was 55.62 mg·kg^{-1} which didn't exceed the standard, the other stations exceeded the standard. The content of As in station 3 and 6 didn't exceed the standard, but the others exceeded the standard. The content of Hg in station 1, 2, 5, 6 and 7 exceeded the standard, and station 2 exceeded the background value 4.40 times, the other stations didn't exceed the standard.

Table 6. Potential Ecological Risk Index for the single heavy metal in the sediments from different monitoring stations

Station number	Potential ecological risk index for the single heavy metal (C_f^i)					
	Pb	Cd	Cu	Zn	Hg	As
1	0.15	0.37	0.52	1.17	2.00	1.03
2	0.33	0.59	0.62	1.16	5.40	1.48
3	0.04	0.15	0.64	1.03	0.20	0.93
4	0.27	0.37	0.85	1.27	0.40	1.33
5	0.26	0.51	0.88	1.20	1.20	1.33
6	0.20	0.37	0.50	0.74	2.20	0.80
7	0.36	0.66	0.73	1.25	1.20	1.84
8	0.21	0.44	0.86	1.25	1.00	1.60
9	0.32	0.66	1.04	1.35	0.80	1.39
10	0.38	0.44	0.81	1.27	1.00	1.52
11	0.35	0.66	0.78	1.28	0.80	1.24
average	0.26	0.47	0.75	1.18	1.47	1.32
over-limit ratio/%	0.00	0.00	9.10	90.90	45.45	81.82

From above, Pb and Cd in the sediments around Dongjiang Harbor, Tianjin, were natural and did not originate from human activities The exceeded standard ratios of Cu, Hg, As, Zn were 9.10%, 45.45%, 81.82%, 90.90% respectively. So the pollution of Cu was low and from nature which was affected slightly by human activities. Hg was polluted by human sources and some monitoring stations exceeded the background value much. The pollution of As and Zn were from human too and affected seriously by human activities.

4.3. Potential ecological risk indices and potential toxicity response indices of heavy metals

Potential ecological risk indices and potential toxicity response indices of heavy metals in the sediments around Dongjiang Harbor, Tianjin were listed as follow (Table 7).

Table 7. Potential Ecological Risk Indices and Potential Toxicity Response Indices of heavy metals

Station number	Potential ecological risk indices for single heavy metal (E_f^i)						Potential toxicity response indices for heavy metals (RI)
	Pb	Cd	Cu	Zn	Hg	As	
1	0.75	11.1	2.60	1.17	80	10.3	105.92
2	1.65	17.7	3.10	1.16	216	14.8	254.41
3	0.20	4.50	3.20	1.03	8	9.3	26.23
4	1.35	11.1	4.25	1.27	16	13.3	47.27
5	1.30	15.3	4.40	1.20	48	13.3	83.50
6	1.00	11.1	2.50	0.74	88	8.0	111.34
7	1.80	19.8	3.65	1.25	48	18.4	92.90
8	1.05	13.2	4.30	1.25	40	16.0	75.80
9	1.60	19.8	5.20	1.35	32	13.9	73.85
10	1.90	13.2	4.05	1.27	40	15.2	75.62
11	1.75	19.8	3.90	1.28	32	12.4	71.13
average	1.30	14.24	3.74	1.18	58.91	13.17	92.54

In table 7, the potential ecological risk indices of Pb, Cd, Cu, Zn, As in 11 stations were lower than 40, which indicated slight potential ecological risk of all five metals in 11 stations. The main element causing ecological hazards was Hg, and its average E_f^i was 58.91. There were 4 stations with light ecological hazards and 4 stations with moderate ecological hazards. E_f^i in station 2 was 216, which had serious risk. Station 1, 2, 3 are far from the estuary, and the pollution of Hg was serious especially in station2, which had serious ecological risk. And the monitoring results could only reflect the enrichment of heavy metals in recent years because station 6 to 11 located in the channel, Dongjiang Harbor, Tianjin, where the sediment had been dredged a few years ago.

The maximum RI of 11 stations was 254.41 in station 2, and the RI of 11 stations was 26.23 in station 3. The average RI of 11 stations was 92.54. And from station 6 to 11, the further into the sea from the estuary, the lower RI was. According to the evaluating standard, station 2 had moderate ecological risk level ($150 \leq RI < 300$) and the other ten stations had low potential ecological risk levels with $RI < 150$ (Table 6).

5. Conclusions

The sediment enrichment factors of heavy metals around Dongjiang Harbor, Tianjin were: As >Zn> Cu >Hg >Pb >Cd. The enrichment degree of As was the highest, while Cd was the lowest.

Pb and Cd in the sediments around Dongjiang Harbor, Tianjin were natural and did not originate from human activities. The pollution of Cu was low and from nature, which was affected by human activities slightly. Hg was polluted by human and exceeded standard much in many monitoring stations. As and Zn were affected seriously by human activities.

The potential ecological risk indices (E_f^i) of heavy metals in the sediments around Dongjiang Harbor, Tianjin were: Hg >Cd >As >Cu >Pb >Zn. The main heavy metals pollution was Hg, which had low content (average 0.07mg·kg^{-1}) but moderate potential ecological risk (average E_f^i =58.91) and contributed most to RI. All in all, the ecological risk level of heavy metals in the sediments around Dongjiang Harbor, Tianjin was slight.

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