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Study on Soil Heavy Metal Content and Ecological Risk Assessment of Jiaozhou Bay of China

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Abstract: *Sampling and analyzing the soil of coastal public green space in Jiaozhou Bay, Qingdao, a total of 31 plots were surveyed, 242 soil samples were collected, and the types and contents of heavy metals in the soil were analyzed. The ecological risk index method and the ground accumulation index method were used to evaluate Qingdao Jiaozhou Bay. Heavy metal risk in coastal public green space. The results show that the average content of Cr, Cd, Pb, Zn, Hg, Cu and Ni in heavy metals exceeds the natural background value of soil. The content of As, Cr, Pb, Zn and Cu is lower than the value specified in the secondary standard specified in GB15618-1995 Soil Environmental Quality Standard. The content of Hg and Ni is between the values specified in the second to third grades. The content of Cd exceeds the value specified by the three-level standard. The ecological risk index and the low cumulative index evaluation show that the heavy metals with relatively high risk are Cd and Hg.*

Keywords: *soil, heavy metal, Jiaozhou bay, coastal, public green space*

1. Introduction

With regards to Qingdao's rapid economic development in recent years, industry has made a particularly outstanding contribution, but also brought serious environmental pollution, especially heavy metal pollution and affect on some cellular and molecular aspects [1-10] . Jiaozhou Bay, located in the south of Qingdao, is a typical semi closed bay. With the rapid development of the surrounding economy and society, a large amount of industrial waste water and domestic sewage are discharged into Jiaozhou Bay through rivers. Under the influence of ocean current such as economic and also energy, heavy metals in the waste water and sewage are collected to the coastal area of Jiaozhou Bay along with its sediment. Therefore, this paper samples the soil of the coastal public green space of Jiaozhou Bay, and analyzes the categories and content of heavy metals in the soil [11-29]. The potential ecological risk index and index of geoaccumulation are used to evaluate the content of heavy metals in the soil of the coastal public green space in Jiaozhou Bay.

2. Materials and methods

2.1. Collection of samples

According to the principles and methods of soil sampling in the *Technical Specifications for Soil Environmental Monitoring*, and in combination with the principle of distribution of soil points, the soil in the studied area is monitored [30, 31], with a total of 8 large soil monitoring points and 31 small soil monitoring points (Figure 1). We collect about 10 cm of soil surface samples, weighing about 1500 g, put into sample bags, and take back to the laboratory for air drying. Specific soil monitoring points information is shown in Table 1.

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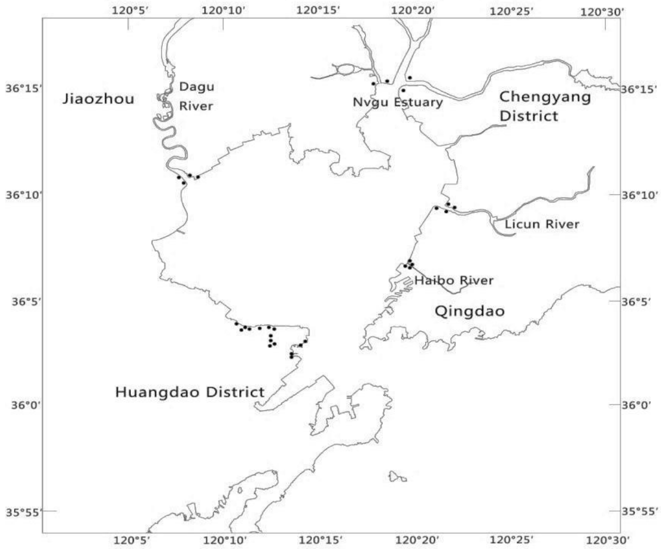

Figure 1. Location of soil sampling points

Table 1. Soil sampling points information sheet

Sr. No.	Location	Longitude and Latitude East longitude North latitude	Notes
Y1	Near Big Stone 328 provincial highway	120.176 36.061	Flat terrain, shallow water beach and wet land
Y2	Near Big Stone 328 provincial highway	120.178 36.062	Obvious slope, beside the pool, with a large amount of garbage on the slope and on the ground
Y3	Near Big Stone 328 provincial highway	120.181 36.060	Beside the pool, dry land
Y4	Near Big Stone 328 provincial highway	120.177 36.063	Obvious distinction between wet land, wet and dry land, and dry land
Y5	North of Liaohe Road Huangdao District	120.129 36.249	The east side is the oil pipeline, the site is relatively open with abundant sunshine
Y6	North of Liaohe Road Huangdao District	120.127 36.350	It is open on all sides, with part of micro terrain, ditch in the east, and with abundant sunshine
Y7	North of Liaohe Road Huangdao District	120.128 36.337	Dam in the east, serious pollution on the river beach, and serious soil salinization
Y8	Near the Huangdao petroleum explosion point	120.205 36.061	Flat ground, surrounded by a large number of herbs
Y9	Near the Huangdao petroleum explosion point	120.202 36.064	Flat terrain, rich plant communities around, close to the sea and petroleum explosion point
Y10	Near the Huangdao petroleum explosion point	120.204 36.067	Flat terrain with a lot of herbs around
Y11	Near the Huangdao petroleum explosion point	120.203 36.065	Flat terrain, rich plant communities around, close to the sea and petroleum explosion point
Y12	Estuary of Dagu River	120.129 36.177	Close to the sea on all sides
Y13	Estuary of Dagu River	120.121 36.178	Highway on the west side, with ditches in the site, with dense plants of various species
Y14	Estuary of Dagu River	120.117 36.184	Relatively flat terrain, buildings in the northwest direction, surrounded by open plant communities
Y15	Estuary of Dagu River	120.123 36.182	The horizontal distribution of plants is obvious and concentrated, and there is a path in the middle, and located at the seaside
Y16	Near the estuary of Nvgu River	120.185 36.161	Low in the west and high in the east, facing the river in the west
Y17	Near the estuary of Nvgu River	120.191 36.154	It is adjacent to the construction road in the east, and 300m in the south is the largest lake in the Nvgu River plot

Y18	Near the estuary of Nvgu River	120.188 36.162	High in the north and low in the south. The south side is adjacent to the lake. The oil pollution degree of the soil on the lake bank is relatively light
Y19	Near the estuary of Nvgu River	120.182 36.172	There are two pools at the lowest point; the soil surface around the pool is black
Y20	Estuary of Qingdao Li village	120.347 36.151	One side is close to the sea, the other side is the road, and there are few plants in the coastal area
Y21	Estuary of Qingdao Li village	120.349 36.152	It is construction waste land, overgrown with weeds
Y22	Estuary of Qingdao Li village	120.350 36.151	On one side is the road, surrounded by vast wasteland
Y23	Estuary of Qingdao Li village	120.348 36.153	One side is close to the sea, the other side is the road, and there are few plants in the coastal area
Y24	East side of estuary of Haibo River	120.322 36.111	The north side is the power plant, and the south side is the traffic land, with relatively flat terrain
Y25	East side of estuary of Haibo River	120.324 36.113	Flat terrain, with Qingdao power plant in the east and road in the west
Y26	East side of estuary of Haibo River	120.321. 36.110	Flat terrain, close to the sea, with a lot of garbage
Y27	South side of estuary of Haibo River	120.194 36.642	The north side is the estuary of Haibo River, with dams built, and the south side is the traffic land
Y28	Near the south of Liugongdao Road	120.233 36.049	The terrain is high in the west and low in the east, with ups and downs in the site
Y29	Near the south of Liugongdao Road	120.235 36.052	Man made heaps of stones and soil, uneven slope, natural growth of plant community
Y30	Near the south of Liugongdao Road	120.231 36.050	The terrain of the site has small ups and downs, with weeds and vegetable fields nearby
Y31	Near the south of Liugongdao Road	120.232 36.048	The terrain is high in the north and low in the south, with ups and downs inside, and the surrounding environment is relatively desolate

2.2. Analysis and assessment of samples

After air dried, the soil samples are filtered out of stones and other impurities, grinded by mortar, filtered by 100 mesh nylon screen, and stored in brown reagent bottle. IP900 and UV spectrophotometer are used to detect the composition and content of heavy metals in soil after air drying. Each group of soil samples by each method is measured three times in parallel, and the mean value of the three results is taken as the measurement result.

2.3. Evaluation methods of soil heavy metals

2.3.1. Potential ecological risk index (RI)

The Potential Ecological Risk Index judges the potential ecological risk of heavy metals according to the type, concentration and toxicity coefficient of heavy metals in the soil [12, 32-41]. The specific evaluation methods are as follows:

(1) The pollution coefficient of single heavy metal is: $C_f^i = C_i / C_n^i$, where C_f^i is the pollution coefficient of a certain metal, C_i is the measured value of heavy metal in soil, and C_n^i is the evaluation standard of this heavy metal.

(2) (2) The potential ecological risk coefficient of a single metal i is: $E_f^i = C_f^i / T_f^i$ where E_f^i is the potential ecological risk coefficient of a heavy metal, C_f^i is the pollution coefficient of the heavy metal, and T_f^i is the toxicity coefficient of the heavy metal.

(3) The comprehensive soil ecological risk index at a certain point is: $R_i = \sum E_f^i$.

Due to the deposition of heavy metals and the affinity of solids, there is a proportional relationship between toxicity and rarity. The potential biological toxicity of a certain metal element is inversely proportional to its richness. Therefore, the toxicity coefficient can be calculated according to the abundance value of heavy metals [42], as shown in Table 2.

Table 2. Toxicity coefficient and natural value.

Heavy Metals	As	Cr	Cd	Pb	Zn	Hg	Cu	Ni
Toxicity Coefficient	10	2	30	5	1	40	5	2
Natural Value	15	90	0.20	35	100	0.15	35	40

The Potential Ecological Risk Coefficient describes the pollution degree of a certain pollut.ant, divided into 5 levels from low to high; the Potential Ecological Risk Index (R_i) describes the comprehensive value of the potential ecological risk coefficient of multiple pollutants at a point, which is divided into 4 levels [43-46], as shown in Table 3.

Table 3. Potential ecological risk coefficient and the relationships between risk index and pollution. degree.

E_r^i with pollution degree		with pollution degree	
$E_f^i < 40$	Minor ecological risk	$R_i < 150$	Minor ecological risk
$40 \le E_f^i < 80$	Medium ecological risk	$150 \le R_i < 300$	Medium ecological risk
$80 \le E_f^i < 160$	Serious ecological risk	$300 \le R_i < 600$	Serious ecological risk
$160 \le E_f^i < 320$	Very serious ecological risk	$R_i \ge 600$	Very serious ecological risk
$E_f^i \ge 320$	Extremely serious ecological risk		

2.3.2. The Index of geoaccumulation

(1) The Index of Geoaccumulation is widely used in the evaluation of soil heavy metal pollution. The quantitative index of heavy metal pollution degree is determined by the relationship between the content of a certain heavy metal and its geochemical background value. The calculation formula is as follows: $I_{geo} = [C_s^i / (K \times C_n^i)]$ where C_s^i is the content of heavy metal element n in the soil; C_n^i is the geochemical background value of this element in the soil; the constant k is the correction index, that is to say, considering the background value change possibly caused by the rock forming movement, which is usually used to characterize the sedimentary characteristics, rock geology and other influences. In this paper, K is set as 1.5, and the classification standard of the Index of Geoaccumulation and the division of pollution degrees are shown in Table 4.

(2)

Table 4. Index of geoaccumulation and pollution degrees.

Projects	Levels	Pollution Degrees
$I_{geo} < 0$	0	No pollution
$0 < I_{geo} \le 1$	1	Minor-medium pollution
$1 < I_{geo} \le 2$	2	Medium pollution
$2 < I_{geo} \le 3$	3	Medium-heavy pollution
$3 < I_{geo} \le 4$	4	Heavy pollution
$4 < I_{geo} \le 5$	5	Heavy-extremely serious pollution

5 < I_{geo} ≤10	6	Extremely serious pollution

2.4. Data processing

Excel 2007 is used to calculate the heavy metal data, and SAS software is used to analyze the correlation of heavy metals.

3. Results and discussions

3.1. Statistics and analysis of heavy metal content in the soil

See Table 5 for the characteristics of heavy metal content in various sample sites of Jiaozhou Bay public green space in Qingdao. The average contents of As, Cr, Cd, Pb, Zn, Hg, Cu, and Ni are 6.71, 127.81, 4.27, 50.06, 188.54, 0.82, 79.64, and 52.44 mg/kg, respectively. The contents of As, Cr, Pb, Zn, and Cu are lower than those specified in the second level standard of GB15618-1995 Soil Environmental Quality Standard. The contents of Hg and Ni are between those specified in the second level and the third level, while the content of Cd is higher than that specified in the third level standard. Except from As, the average contents of Cr, Cd, Pb, Zn, Hg, Cu, and Ni are higher than the natural background values of soil [47-52].

Table 5. Soil heavy metals contents mg/kg

Heavy Metals	Contents			Standard Deviation	Coefficient of Variation	GB15618-1995 Second Level Standard
	Max.	Min.	Average			
As	318.33	0	6.71	9.74	1.45	25
Cr	14226	0	127.81	1873.33	14.66	300
Cd	95	0	4.27	5.63	1.32	0.3
Pb	1915.33	0	50.06	65.67	1.31	300
Zn	13076.67	27.67	188.54	438.1	2.32	250
Hg	30	0	0.82	1.48	1.8	0.5
Cu	6063.33	18.33	79.64	187.31	2.35	100
Ni	925.33	0	52.44	57.62	1.1	50

3.2. Evaluation of soil heavy metal pollution

3.2.1. Evaluation of ecological risk index

The single ecological risk factor value and potential ecological risk index value of each heavy metal are calculated with the soil natural background value as the reference standard, and the results are shown in Table 6. Most of the RI values of the samples of the coastal public green space in Jiaozhou Bay of Qingdao are less than 150, indicating that the potential ecological risk index is low. The potential ecological risk coefficients of samples 3, 6, 9, 11, 12, 13, 14, 15, 17, 19, 20, 21, 22, 24, 25, 26 and 29 are extremely high. The sequence of ecological risk of heavy metals in each sample site is Y20＞Y15＞Y22＞Y14＞Y9＞Y17＞Y13＞Y19＞Y21＞Y26＞Y6＞Y24＞Y12＞Y29＞Y25＞Y11＞Y3＞Y31＞Y30＞Y8＞Y28＞Y27＞Y2＞Y1＞Y18＞Y10＞Y16＞Y5＞Y4＞Y23＞Y7.It can be seen that there is still a great risk in the soil of the coastal public green space in Jiaozhou Bay.

Table 6. Ecological risk index

Sample site	Single ecological risk factor								Potential ecological risk index	Ecological risk
	As	Cr	Cd	Pb	Zn	Hg	Cu	Ni		
Y1	3.28	1.51	0	4.52	1.596	0	5.46	2.53	18.90	Low
Y2	2.53	2.46	0	4.73	1.85	0	5.48	2.99	20.04	Low
Y3	5.95	0.59	0	2.96	0.57	1021.33	2.75	1.65	1035.8	Strong
Y4	6.09	1.07	0	4.04	0.85	0	2.32	0.4	14.77	Low
Y5	0.87	2.389	0	3.624	0.78	0	5.195	2.11	14.97	Low
Y6	2	1.72	1233	3.24	0.65	0	4.204	2.89	1247.70	Strong
Y7	0.45	0.35	0	2.38	0.398	0	3.19	1.29	8.06	Low
Y8	0	5.67	0	2.78	0.97	0	9.25	14.82	33.49	Low

Y9	5.07	0	1065	4.1	0.76	693.33	5.66	2.08	1776	Strong
Y10	1.26	0.97	0	2.98	0.88	0	7	4.28	17.37	Low
Y11	2.11	1.34	1033.5	3.53	1.09	0	5.71	2.95	1050.23	Strong
Y12	6.03	0.85	1200	3.43	0.58	0	4.58	1.98	1217.45	Strong
Y13	3.5	0	1650	3.04	0.71	0	5.11	1.295	1663.66	Strong
Y14	1.81	0.84	2334	2.06	0.83	0	4.96	3.01	2347.51	Strong
Y15	5.67	1.24	1435.5	3.17	0.504	1029.33	3.003	2.23	2480.65	Strong
Y16	4.71	1.32	0	3.24	0.403	0	4.42	1.79	15.88	Low
Y17	1.25	0.84	0	2.67	0.34	1666.67	3.79	0.65	1676.21	Strong
Y18	6.45	2.61	0	3.35	0.45	0	4.31	0.97	18.14	Low
Y19	4.89	0	0	10.04	1.27	1333.33	6.47	1.07	1357.07	Strong
Y20	0.81	2.068	2650.5	10.69	1.12	0	5.27	3.48	2673.94	Strong
Y21	6	0.61	1295.25	7.601	0.99	0	4.55	2.71	1317.71	Strong
Y22	2.96	0	2400	5.97	1.24	0	4.85	1.11	2416.13	Strong
Y23	1.33	0.44	0	3.297	0.45	0	3.08	0.36	8.96	Low
Y24	4.58	1.82	1200	8.95	1.62	0	10.92	1.14	1229.03	Strong
Y25	4	1.27	0	9.52	1.83	1066.67	8.65	1.66	1093.33	Strong
Y26	0.67	1.08	1275	12.79	2.48	0	11.08	0.79	1303.89	Strong
Y27	2.11	0.43	0	9.47	1.92	0	11.04	0	24.97	Low
Y28	3.98	1.004	0	9.95	2.13	0	9.79	1.41	28.26	Low
Y29	7.57	5.68	1095	11.82	2.12	0	18.33	4.57	1145.09	Strong
Y30	2.45	43.003	0	6.96	1.78	0	18.28	9.65	82.12	Low
Y31	38.32	4.85	0	54.78	25.27	0	153.97	3.41	280.6	Medium
Average value	4.47	2.84	640.86	7.15	1.88	219.7	11.38	2.604	890.88	Strong

Among the eight heavy metals analyzed, Zn and Cr have high contents, but their toxicity coefficients are very low, 1 and 2 respectively, so the ecological risk is the lowest; Cd and Hg have low contents, but their toxicity coefficients are high, 30 and 40 respectively, so their ecological risk is relatively high compared with other heavy metals. The order of the average single ecological risk factors of eight heavy metals is Cd＞Hg＞Cu＞Pb＞As＞Cr＞Ni＞Zn.

3.2.2. Index of Geoaccumulation Evaluation

Among the eight heavy metal elements analyzed, the average index of geoaccumulation of As, Cr, Cu and Ni are all less than 0, indicating that the coastal public green space of Jiaozhou Bay is almost free from the pollution of these four heavy metals; while the average index of geoaccumulation of Cd, Pb, Zn and Hg is more than 0, 2.10 for Cd specifically, while 0-1 for other 3 heavy metals, indicating that the coastal public green space of Jiaozhou Bay is subject to the medium pollution of Cd and minor pollution of other 3 heavy metals. The order of the average index of geoaccumulation of all metal elements is Cd＞Hg＞Pb＞Zn＞Cu＞Ni＞Cr＞As.

Table 7. Soil land accumulation index

Sample site	Land accumulation index							
	As	Cr	Cd	Pb	Zn	Hg	Cu	Ni
Y1	-2.42	-0.99	0	-0.73	0.09	0	-0.46	-0.25
Y2	-2.57	-0.29	0	-0.66	0.30	0	-0.45	-0.01
Y3	-1.33	-2.36	0	-1.34	-1.40	4.09	-1.45	-0.86
Y4	-1.30	-1.48	0	-0.89	-0.82	0	-1.67	-2.91
Y5	-4.11	-0.32	0	-1.05	-0.94	0	-0.53	-0.51
Y6	-2.91	-0.80	4.78	-1.21	-1.21	0	-0.84	-0.05
Y7	-5.07	-3.09	0	-1.66	-1.91	0	-1.23	-1.21
Y8	0	0.92	0	-1.43	-0.63	0	0.30	2.30
Y9	-1.57	0	4.56	-0.87	-0.97	3.53	-0.41	-0.53
Y10	-3.57	-1.63	0	-1.33	-0.77	0	-0.10	0.51
Y11	-2.83	-1.16	4.52	-1.09	-0.46	0	-0.39	-0.02
Y12	-1.32	-1.82	4.74	-1.13	-1.38	0	-0.71	-0.60
Y13	-2.10	0	5.20	-1.30	-1.08	0	-0.55	-1.21
Y14	-3.05	-1.83	5.70	-1.87	-0.85	0	-0.60	0.01
Y15	-1.40	-1.27	5.00	-1.24	-1.57	4.10	-1.32	-0.43

Y16	-1.67	-1.19	0	-1.21	-1.90	0	-0.76	-0.75
Y17	-3.58	-1.83	0	-1.49	-2.12	4.80	-0.99	-2.21
Y18	-1.22	-0.20	0	-1.16	-1.72	0	-0.80	-1.63
Y19	-1.62	0	0	0.42	-0.24	4.47	-0.21	-1.49
Y20	-4.20	-0.54	5.88	0.51	-0.42	0	-0.51	0.21
Y21	-1.32	-2.30	4.85	0.02	-0.60	0	-0.72	-0.15
Y22	-2.34	0	5.74	-0.33	-0.27	0	-0.63	-1.44
Y23	-3.49	-2.75	0	-1.19	-1.74	0	-1.28	-3.05
Y24	-1.71	-0.72	4.74	0.26	0.11	0	0.54	-1.40
Y25	-1.91	-1.24	0	0.34	0.29	4.15	0.21	-0.85
Y26	-4.49	-1.47	4.82	0.77	0.72	0	0.56	-1.92
Y27	-2.83	-2.80	0	0.34	0.35	0	0.56	0
Y28	-1.98	-1.58	0	0.41	0.51	0	0.38	-1.09
Y29	-0.99	0.92	4.60	0.66	0.50	0	1.29	0.61
Y30	-2.62	3.84	0	-0.11	0.24	0	1.29	1.68
Y31	1.35	0.69	0	2.87	4.07	0	4.36	0.18
Average value	-1.91	-0.88	2.10	0.54	0.51	0.81	-0.23	-0.62

3.2.3. Analysis of Sources of Soil Heavy Metals

Most of the coastal public green space in Jiaozhou Bay is located at the estuary of the rivers, and some are located around the factory. The main sources of heavy metals in the soil are the heavy metals carried by the surrounding factories and the factories in the upstream of the rivers. In this paper, the content of heavy metals in the soil of the coastal public green space of Jiaozhou Bay was statistically analyzed, and it was found that the content of each index accorded with the normal distribution. On this basis, the correlation of heavy metals was analyzed, and the corresponding correlation coefficient was calculated. The results are shown in Table 8.

Table 8. Correlation analysis of heavy metals

Heavy Metals	As	Cr	Cd	Pb	Zn	Hg	Cu	Ni
As	1							
Cr	0.033	1						
Cd	0.003	-0.169	1					
Pb	0.296	0.244	0.073	1				
Zn	0.091	0.324	0.011	0.829**	1			
Hg	0.179	-0.333	-0.134	-0.096	-0.223	1		
Cu	-0.047	0.376*	-0.069	0.652**	0.844**	-0.196	1	
Ni	-0.059	0.577*	0.154	-0.002	0.231	-0.225	0.348	1

When the confidence level (both sides) is 0.01, the correlation is significant. It can be seen that the correlation among Zn, Cu, Pb is relatively large, and that between As, Cd, Hg and other metals is relatively low, with poor correlation. According to the above ecological risk index and index of geoaccumulation, the pollution degree of coastal public green space in Jiaozhou Bay is relatively low, but the pollution degree in some areas is relatively high; the heavy metals with relatively high risk are Cd and Hg, and the correlation between Cd and Hg and other heavy metals is poor, which can be considered that Cd and Hg are affected by human activities; while the other heavy metals are not affected by human activities, still in a clean state [53-62].

4. Conclusions

1) The average contents of As, Cr,Cd, Pb,Zn, Hg,Cu, Ni are 6.71, 127.81, 4.27, 50.06, 188.54, 0.82, 79.64 and 52.44mg/kg respectively. The contents of As, Cr, Pb, Zn and Cu are lower than those specified in the second level standard of GB15618-1995 Soil Environmental Quality Standard. The contents of Hg and Ni are between those specified in the second level and the third level, while the content of Cd is higher than that specified in the third level standard.

2) The single ecological risk factor value and potential ecological risk index value of each heavy metal are calculated with the soil natural background value as the reference standard. Most of the RI values of the samples of the coastal public green space in Jiaozhou Bay of Qingdao are less than 150, indicating that the potential ecological risk index is low. The potential ecological risk coefficients of samples 3, 6, 9, 11, 12, 13, 14, 15, 17, 19, 20, 21, 22, 24, 25, 26, and 29 are extremely high.The order of the average single ecological risk factors of eight heavy metals is Cd＞Hg＞Cu＞Pb＞As＞Cr＞Ni＞Zn. Among the eight heavy metal elements analyzed, the average index of geoaccumulation of As, Cr, Cu and Ni are all less than 0, indicating that the coastal public green space of Jiaozhou Bay is almost free from the pollution of these four heavy metals; while the average index of geoaccumulation of Cd, Pb, Zn, and Hg is more than 0, while 0-1 for other 3 heavy metals, indicating that the coastal public green space of Jiaozhou Bay is subject to the medium pollution of Cd and minor pollution of other 3 heavy metals. The order of the average index of geoaccumulation of all metal elements is Cd＞Hg＞Pb＞Zn＞Cu＞Ni＞Cr＞As.

3) Correlation analysis shows that Cd and Hg are affected by human activities, while other heavy metals are not affected by human activities, still in a clean state.

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