

Evaluation model of major heavy metals pollution factors in coastal waters and sediments

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ABSTRACT

It has great a subjective influence on the evaluation of major heavy metal pollution factors in coastal waters and sediments by using the traditional Nemerow exponential method, without considering the harmful differences of different heavy metals, and resulting in a low accuracy of the evaluation results. In this paper, a new model to evaluate the major heavy metal pollution factors in coastal waters and sediments is established, to calculate the single pollution index and potential ecological risk index of heavy metals. On this basis, the fuzzy comprehensive evaluation method is used to construct the main heavy metal pollution factor model of coastal waters and sediments. The heavy metal pollution factor is reasonably evaluated and the risk grade of heavy metal pollution factor in coastal waters and sediments is obtained. The results of sampling analysis show that the evaluation results obtained by the model are as follows: the pollution index of heavy metals in the coastal water with the order of $Pb > Cu > Hg > As > Cd > Zn$; the potential ecological risk index of heavy metals in sediments is $Pb > Cu > As > Zn > Hg > Cd$. The pollution degree of area C is the highest, area A is the second, and area B is the smallest. The results show that the model can accurately evaluate the main heavy metal pollution factors in coastal waters and sediments.

Keywords: Coastal waters; Water bodies; Sediments; Single pollution index; Fuzzy comprehensive evaluation; Heavy metals; Pollution factors

1. Introduction

Heavy metals, as a kind of persistent toxic pollutants, can enter the sea water body through atmospheric deposition, waste water discharge, leaching and so on, and then settle down to the mud bottom through complex physical, chemical, biological and sedimentary processes and gradually enrich. Sediments are considered to be the main destination of these metal elements. Based on a study, sediments are indicators of water pollution, and their pollution status directly reflects the environmental quality of the water body [1]. With the expansion of industrial production scale, the discharge of industrial sewage is increasing. According to research, many

coastal waters are seriously polluted by heavy metals. It is very important to make an accurate evaluation of the main heavy metal pollution factors [2]. At present, the commonly used methods for evaluating heavy metal pollution factors are Nemerow index method, potential ecological hazard index method, fuzzy comprehensive evaluation method, etc. [3].

The subjective nature of traditional Nemerow index method has a great influence on the evaluation results, without considering the hazard differences of different heavy metals. When abnormal values appear, the results will cause greater interference [4]. Study showed potential ecological hazard index method is disturbed by the weighting of heavy metal toxicity, and the evaluation results were inaccurate [5].

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Fuzzy comprehensive evaluation method fully takes into account the complexity of heavy metal pollution, with less human influence, and the evaluation results tend to the actual situation. In groundwater, soil heavy metal pollution, air quality evaluation, and environmental safety evaluation of industrial sewage, fuzzy comprehensive evaluation method has a high application value.

In order to obtain accurate evaluation results of major heavy metal pollution factors in coastal waters and sediments, based on the calculation of single pollution index and potential ecological risk index of heavy metals, a fuzzy comprehensive evaluation method is used to construct a model of major heavy metal pollution factors in coastal waters and sediments, to obtain the risk grade of heavy metal pollution factors in coastal waters and sediments, and evaluate heavy metal pollution to water and sediments [6].

2. Methods

2.1. Calculation of single pollution index and single potential ecological risk index of heavy metals

According to a study, the limits of class I seawater quality in the “Seawater Quality Standard” and the class I sediment standard in the “Marine Sediment Standard” are used as the evaluation criteria [7]. The single pollution index C_f^i is used to evaluate the risk of heavy metal pollution in seawater quality and sediments. When $C_f^i \leq 1$, the heavy metals meet the criteria, and when $C_f^i > 1$, the content of heavy metals exceeded the criteria.

The single pollution index can be calculated by Eq. (1) as follows:

$$C_f^i = \frac{C_s^i}{C_n^i} \tag{1}$$

In the equation, C_s^i is the measured value of heavy metal content at the i th station; C_n^i is the standard limit value of the first type of heavy metal content.

The potential ecological risk index E_r^i for single heavy metals is calculated by Eq. (2) [8]:

$$E_r^i = T_f^i \times C_f^i \tag{2}$$

Here T_f^i is the toxicity response coefficient of heavy metals, which reflects the toxicity level of heavy metals and the sensitivity of organisms to their pollution [9].

On the basis of calculating the single pollution index and the single potential ecological risk index of heavy metals, a fuzzy comprehensive evaluation method is used to construct the model of major heavy metals pollution factors in coastal waters and sediments. The heavy metal pollution factors are evaluated and the risk level of heavy metal pollution factor in coastal waters and sediments is obtained.

2.2. Fuzzy comprehensive evaluation method

2.2.1. Membership function

Based on a study, the membership of the fuzzy comprehensive evaluation method is calculated by the reduced

half trapezoid function, and the sectional limit value is the standard value of corresponding environmental quality [10]. The membership function of a heavy metal for grade I heavy metal pollution is:

$$u_1(x_i) = \begin{cases} 1 & (x_i \leq a_1) \\ \frac{a_2 - x_i}{a_2 - a_1} & (a_1 < x_i < a_2) \\ 0 & (x_i \geq a_2) \end{cases} \tag{3}$$

The membership function of a heavy metal for the grade II, III and IV of heavy metal pollution is:

$$u_j(x_i) = \begin{cases} 1 - \frac{a_j - x_i}{a_j - a_{j-1}} & (a_{j-1} \leq x_i \leq a_j) \\ \frac{a_{j+1} - x_i}{a_{j+1} - a_j} & (a_j < x_i < a_{j+1}) \\ 0 & (x_i \leq a_{j-1}, x_i \geq a_{j+1}) \end{cases} \tag{4}$$

The membership function of a heavy metal for grade V of heavy metal pollution is:

$$u_s(x_i) = \begin{cases} 0 & (x_i \leq a_4) \\ \frac{x_i - a_4}{a_5 - a_4} & (a_4 < x_i < a_5) \\ 1 & (x_i \geq a_5) \end{cases} \tag{5}$$

In Eqs. (3)–(5): x_i is the measured value of heavy metals; a_i is the standard value of heavy metal pollution status of the corresponding level of heavy metals. Through the membership function of each index, the membership of each single index to the pollution status of heavy metals in different levels of sea area is obtained, to composed of the fuzzy function, called the relation fuzzy function R , then there is [11]:

$$R = f(u_1(x_i), u_j(x_i), u_s(x_i)), u_1(x_i), u_j(x_i), u_s(x_i)) \in [0, 1] \tag{6}$$

2.2.2. Calculation of evaluation factor weight

Due to the differences in the contribution of each single index to the environmental complex, there should be a different weight [12]. Considering the effect of external toxic substances, the weight calculation equation is as follows:

$$a_i = \frac{(x_i + e_i) / (s_i + e_i)}{\sum_{i=1}^n [(x_i + e_i) / (s_i + e_i)]} \tag{7}$$

Here a_i is the weight of the i th factor; x_i is the measured value of the index; $S_i = \frac{1}{5} \sum_{i=1}^5 d_i$, d_i is the standard value of a

certain heavy metal to the *i*th level; e_i is the corresponding heavy metal influence constant.

2.2.3. Calculation of evaluation results

The weighted average model is used to calculate the membership of the overall pollution factor B , $B = (b_1, b_2, \dots, b_m)$, and the calculation method of b_i is as follows:

$$b_i = R \sum_{j=1}^m a_j R_{ij}, (i = 1, 2, \dots, m) \tag{8}$$

Here b_i is the membership of the *i*th grade; a_i is the corresponding weight. The corresponding score of each grade is determined by the weight formed by the component of the evaluation vector, and then the weighted average of the score of each grade is carried out to get the evaluation score. The final comprehensive evaluation model is:

$$z_i = \frac{cb_i^k}{\sum_{i=1}^m b_i^k} \tag{9}$$

$$c = \sum_{i=1}^m z_i p_i \tag{10}$$

Here p_i is the score for the *i*th level of environmental quality; b_i^k is the value of the *i*th level of environmental quality p_i ; k is the selected real number, here it is 2.0. Among them, the set scores are: grade I 5.0, grade II 4.0, grade III 3.0, grade IV 2.0, grade V 1.0. The lower the evaluation results, the stronger the pollution.

The process explained in this paper describes the use of risk evaluation model of heavy metal pollution to evaluate the main heavy metal pollution factors in coastal waters and sediments and obtain the risk level of heavy metal pollution factors in coastal waters and sediments.

2.3. Sampling analysis

Taking the coastal waters of a certain area as an example, the main heavy metal pollution factors in the water and sediments are analyzed by using the proposed evaluation model of heavy metal pollution factors. The sampling time of this survey is November 2017. In a certain offshore sea area, three research areas of A, B, C are random set, and there is a total of 12 stations to collect surface seawater and sediment, the 12 stations are: A1, A2, A3, B1, B2, B3, B4, B5, C1, C2, C3, C4.

2.5 dm³ plexiglass water sampler is used to collect surface seawater. All samples are collected, stored and pre-treated according to the requirements of "Ocean Monitoring Standards". Surface sediment is collected by grab-type dredger, and the undisturbed surface sediment in the center is collected by plastic spoon in polyethylene bag. Cu, Pb, Zn, Cd and As samples are dried in an oven at 105°C ± 1°C, grinded by the agate mortar and all passed through 160 mesh sieves. After mixing, the samples are collected for standby [13]. Hg samples are dried by natural air, grinded and passed

through 80 mesh sieves. After mixing enough, the samples are collected for standby [14].

The determination of heavy metals in coastal waters and sediment samples is carried out in accordance with the requirements of the "Marine Monitoring Standards". The contents of Cu, Pb, Zn and Cd are determined by atomic absorption spectrometry, and the contents of Hg and As are determined by atomic fluorescence spectrometry [15–19]. According to the measured contents of different heavy metal factors, the proposed model is used to calculate the corresponding parameters to evaluate the main heavy metal pollution factors in coastal waters and sediments [20–23].

3. Results

3.1. Analysis of heavy metal pollution in coastal waters

The single heavy metal pollution index of different stations is calculated, and the single heavy metal pollution index of three study areas is taken as the average value of each station [24]. The results are shown in Fig. 1. Based on the results, the heavy metal pollution in the surface seawater of the monitoring area is evaluated.

Analysis of Fig. 1 shows that the pollution index of Hg, Pb, Cu and As in the area A is larger than 1, and the pollution is more obvious. The content of rest of Cd and Zn in this area is not higher than the first-class national standard limit of seawater quality; the pollution index of heavy metals in the area B is less than 1, which conforms to the standard; similar to the area A, the pollution index of Hg, Pb, Cu, A in the area C is larger than 1, and the pollution is more obvious [25,26]. The pollution index of S was higher than 1, and the content of Cd and Zn was less than the national first-class standard limit. The content of rest of Cd and Zn in this area is not higher than the first-class national standard limit of seawater quality

3.2. Heavy metal pollution in surface sediments of coastal waters

The potential ecological risk index of heavy metals in sediments of different stations is calculated. The potential

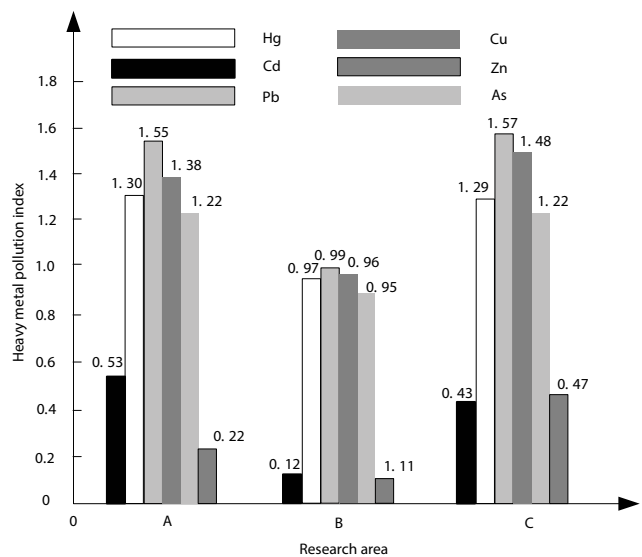


Fig. 1. Main pollution index of heavy metals in each study area.

ecological risk index of heavy metals in the three study areas takes the mean values of each station [27]. The results are shown in Fig. 2. Based on the results, the pollution of heavy metals in surface sediments of the sea area is evaluated.

The potential ecological risk indexes of Pb, Cu and As in area A are 52, 44 and 43, respectively, which are higher than 40; the ecological risk indexes of heavy metals in area B are lower than 40; the potential ecological risk indexes of Pb, Cu and As in area C are 49, 47 and 43, respectively, which are higher than 40.

3.3. Fuzzy comprehensive evaluation analysis

3.3.1. Weight calculation of different heavy metals

The weights of the major heavy metal pollution factors at the sampling sites in the coastal waters of a certain area are calculated by using the model constructed in this paper, as shown in Table 1.

The weight of major heavy metal pollution factors in different sampling points can be seen in Table 1.

3.3.2. Fuzzy comprehensive evaluation results

According to the weight of heavy metal pollution factors at each sampling point, the fuzzy comprehensive evaluation results of heavy metal pollution in surface sediments of each sampling point are obtained, as shown in Table 2.

From Table 2, it can be seen that the fuzzy comprehensive evaluation scores of the three sampling points in area A are 1.1–1.2, and the pollution levels are all of grade V, that is, it is the severe pollution; the fuzzy comprehensive evaluation scores of the five sampling points in area B are 2.1–4.0, and the surface sediments in this sea area are not polluted seriously, and the pollution levels are between grade II and grade IV [27]. In area C, the scores of fuzzy comprehensive evaluations of three sampling points is 1, and the pollution level is all grade V, that is, severe pollution.

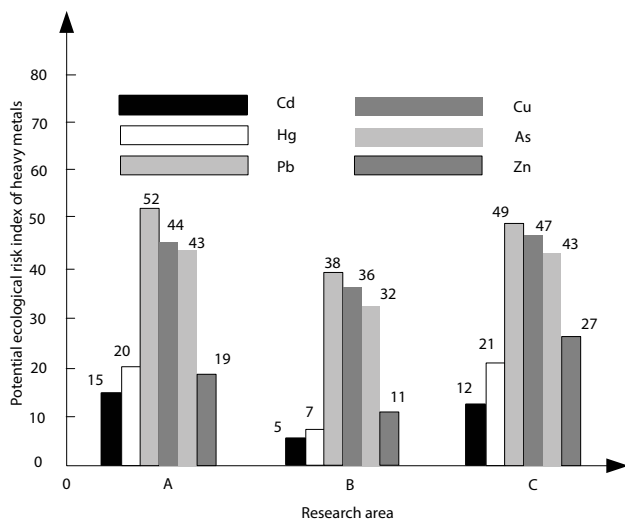


Fig. 2. Potential ecological risk index of major heavy metals in each study area.

Table 1 Weight of heavy metals at each sampling point

Research area	Sampling point	Hg	Cd	As	Pb	Cu	Zn
A	A1	0.06	0.57	0.03	0.04	0.08	0.15
	A2	0.06	0.43	0.04	0.05	0.05	0.30
	A3	0.05	0.53	0.03	0.05	0.08	0.20
B	B1	0.13	0.20	0.10	0.04	0.10	0.33
	B2	0.10	0.20	0.08	0.03	0.14	0.30
	B3	0.10	0.11	0.07	0.03	0.17	0.38
	B4	0.11	0.16	0.06	0.03	0.15	0.37
	B5	0.20	0.09	0.03	0.01	0.21	0.29
C	C1	0.01	0.72	0.01	0.03	0.03	0.19
	C2	0.01	0.72	0.01	0.02	0.03	0.20
	C3	0.01	0.72	0.01	0.02	0.03	0.20
	C4	0.01	0.69	0.01	0.02	0.03	0.23

4. Discussion

4.1. Discussion on heavy metal pollution in coastal waters

The results show that the pollution of Hg, Pb, Cu and As is more obvious in area A and C, while the content of Cd and Zn is not higher than the first-class national standard limit of seawater quality; the pollution of heavy metals in area B is relatively weak. Comprehensive analysis shows that the heavy metal pollution index in the waters of this area is ranked as Pb > Cu > Hg > As > Cd > Zn. The main reason is that the coastal area has a long exchange period with the sea water, the self-purification ability of the sea water is poor, and the coast is mostly plain coast, and the beach is wider [28,29]. The bottom of the beach is mainly sandy and muddy, accounting for more than 70% of the total area of the beach. The adhesion to pollutants is greater, which is not conducive to the diffusion of pollutants to the deep sea, thus the water quality of the coastal waters is affected. In addition, industrial production and the discharge of social life sewage cause a certain degree of pollution to the sea area. The high content of heavy metals in industrial wastewater is the direct cause of heavy metal pollution in research area A and C.

Because this model uses single pollution index C_f^i to evaluate the risk of heavy metal pollution in coastal waters and sediments, when $C_f^i \leq 1$, it indicates that the heavy metal conforms to the standard; when $C_f^i > 1$, it indicates that the content of heavy metal exceeds the standard. Through this equation, the pollution index of single heavy metal can be calculated, and the pollution index of different heavy metals can be compared, to obtain accurate evaluation results of heavy metal pollution factors in coastal waters.

4.2. Discussion on heavy metal pollution in surface sediments of coastal waters

The potential ecological risk indexes of Pb, Cu and As in area A and C are all higher than 40, indicating that the potential ecological risk indexes of Pb, Cu and As in these two study areas exceeded the standard, and the ecological risk

Table 2
Fuzzy comprehensive evaluation results of major heavy metals

Research area	Sampling point	Level I affiliation	Level II affiliation	Level III affiliation	Level IV affiliation	Level V affiliation	Overall evaluation score	Level of comprehensive evaluation
A	A1	0.029	0.084	0.170	0.048	0.67	1.2	V
	A2	0.059	0.170	0.041	0.000	0.730	1.2	V
	A3	0.063	0.023	0.170	0.018	0.73	1.1	V
B	B1	0.210	0.380	0.240	0.170	0.00	4.0	II
	B2	0.180	0.450	0.260	0.120	0.00	4.1	II
	B3	0.074	0.310	0.240	0.000	0.38	2.7	IV
	B4	0.250	0.270	0.120	0.230	0.13	3.7	III
	B5	0.040	0.069	0.100	0.480	0.31	2.1	IV
C	C1	0.001	0.009	0.009	0.009	0.98	1.0	V
	C2	0.001	0.009	0.011	0.000	0.98	1.0	V
	C3	0.006	0.006	0.007	0.001	0.98	1.0	V
	C4	0.002	0.010	0.010	0.000	0.98	1.0	V

is higher; the ecological risk indexes of heavy metals in area B are all lower than 40, and the risk of ecological environment is relatively small. The reason for this risk is consistent with the description of Section 4.1. Comprehensive analysis shows that the potential ecological risk index of heavy metals in the surface sediments of the coastal area is ordered as $Pb > Cu > As > Zn > Hg > Cd$. Because this model uses a single potential ecological risk index to evaluate the risk of heavy metal pollution in coastal waters and sediments, the value is more than 40, which belongs to severe pollution. Using a single potential ecological risk index calculation equation can obtain accurate potential ecological risk index of heavy metals, to accurate evaluation of major heavy metal pollution factors in coastal waters and sediments.

4.3. Discussion on the results of fuzzy comprehensive evaluation

According to the results of fuzzy comprehensive evaluation, the pollution degree of heavy metals in area A is higher. The main reasons are as follows: the study area is the main residential area, the distribution of factories is less, and the metal compounds in garden soil, fertilizers and pesticides enter area A through surface runoff and enrich by sedimentation and adsorption. In the sediment, the direct discharge of domestic sewage from residential areas and the dumping of domestic garbage lead to the high content of heavy metals in the sediments of offshore waters; the sewage produced by marine operations can also cause heavy metal pollution; the dry and wet deposition of atmospheric pollutants can lead to the increase of heavy metals in the sediments of offshore waters, but the degree of pollution is relatively weak.

Surface sediments in area B are not polluted much, mainly because the study area is far away from the shore compared with the other two study areas and is less polluted by domestic sewage and industrial water. The heavy metal pollution in area C is relatively high, that is, severe pollution, mainly due to the influence of industrial wastewater and domestic sewage discharged from the surrounding factories. The industrial parks near the study area are dense

and the discharge of sewage is huge, which leads to the high content of heavy metals in the sediments of the study area and the serious pollution of heavy metals. Comprehensive analysis shows that the pollution level of area C is the highest, followed by area A, and area B is the smallest.

In this paper, the membership function of environmental quality of heavy metals in sediments of different grades is given. On this basis, the weight of pollution factors is calculated, and the fuzzy comprehensive evaluation results of heavy metal pollution factors are obtained. According to the weight of different pollution factors, the pollution degree is sorted, which ensures the scientific and reliability of the results, and realizes the accurate evaluation of the main heavy metal pollution factors in the coastal waters and sediments.

5. Conclusions

- On the basis of calculating single heavy metal pollution index and single potential ecological risk index, this paper uses fuzzy comprehensive evaluation method to construct the evaluation model of main heavy metal pollution factors in coastal waters and sediments, which can accurately calculate the pollution index and potential ecological risk index of different heavy metal factors, so as to evaluate pollution level of the region.
- The model uses single heavy metal pollution index to analyze the heavy metal pollution in the three study areas. The ranks of heavy metal pollution index in the sea area is as $Pb > Cu > Hg > As > Cd > Zn$. The potential ecological risk index is used to analyze the heavy metal pollution risk in the three study areas. The order of ecological risk index is as $Pb > Cu > As > Zn > Hg > Cd$. The pollution degree of three areas was analyzed by fuzzy comprehensive evaluation method. The pollution degree of area C is the highest, area A is the second, and area B is the least. Sampling analysis results show that the model can accurately obtain the evaluation results of the main heavy metal pollution factors in the water and sediments

of offshore waters and provide an effective means for the evaluation of the degree of environmental pollution and the risk evaluation of water pollution.

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