The analysis of impact factor on temporal and spatial distribution characteristics of petroleum pollution in surface sediments of Laizhou Bay

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Abstract. According to the monitoring data of five cruises in Laizhou Bay from 2013 to 2018, the content, pollution status and spatial distribution characteristics of petroleum hydrocarbons in the surface sediments were analyzed. The results showed that the content range of petroleum hydrocarbons in the sediments was from 0.00~377.00 mg/kg, with an average of 63.34 mg/kg, which indicated that the pollution extent was light. The obtained monitoring data were analyzed through DPS18.10 software and PRIMER 7 software. The analysis results showed that the spatial dispersion extent of inter-annual petroleum hydrocarbon content at the monitoring stations was high, the difference was not significant, the clustering similarity was low, and the grouping was not obvious. The results showed that the spatial distribution trend of petroleum hydrocarbon contents in the sediments was uniform, and there were high value areas in some areas. The spatial distribution of petroleum hydrocarbons in Laizhou Bay was dominated by the distribution of ports and the input of human activities. The inter-annual variation of petroleum hydrocarbon contents in the sediments was not obvious. The area where the decrease or increase of petroleum hydrocarbon content in each monitoring station was obvious, was in the SW-NE direction.

1. Introduction

Oil pollution has become one of the prominent problems of the global Marine ecological environment, which is easy to become the focus of social attention [1]. Marine ecological environment pollution may be caused by all links of offshore oil exploration, exploitation, transportation and use [2, 3]. Petroleum hydrocarbons are homogeneous mixtures composed of alkanes, olefin, aromatics, heterocyclic aromatics and other complex molecular structures with multiple components. Once the offshore oil spill occurs, it will not only affect the photosynthesis of phytoplankton, but also reduce the primary productivity of the waters [4]. Moreover, it will reduce the Marine biodiversity index, cause the decline of Marine biological resources and weaken the Marine ecosystem. Furthermore, it affects human health through biological enrichment and food chain transmission [5, 6]. Petroleum hydrocarbons in seawater may partially enter the sediments through physical processes and pollute the Marine sedimentary environment, which may do harm to benthic organisms [7].
Laizhou Bay, one of the three major bays of the Bohai Sea, is a semi-closed shallow sea with weak water exchange capacity and poor self-purification ability to pollutants. It is an important spawning and feeding ground for the three major Marine organisms of the Yellow Sea and the Bohai Sea, as well as a famous fishing ground in China [7-9]. The shipping industry of Laizhou Bay is well-developed. Laizhou Port, Longkou Port, Weifang Port and many other ports are distributed along the coast. And there are rich submarine oil and gas resources. With the rapid development of regional society and economy and the increasing intensity of human activities, the pressure of Marine ecological environment protection has become increasingly prominent. At present, ecological environment studies of Laizhou Bay mainly involve benthic fauna community, ecological environment quality, nutrient content, persistent pollutants and seawater intrusion [10-14]. However, there are few reports on petroleum hydrocarbons in the surface sediments of Laizhou Bay. The content and distribution of petroleum hydrocarbons in sediments can not only reflect the pollution status of the bay, but also have great significance for the study of the influence of petroleum hydrocarbons on benthic organisms [8,9,15-17]. In this paper, the content and spatial distribution of petroleum hydrocarbons in surface sediments were analyzed based on the monitoring data of five voyages in Laizhou Bay from 2013 to 2018. The single factor index method and coefficient of variation method were used to analyze and evaluate the pollution status of petroleum hydrocarbons, in order to provide scientific support for the control of petroleum hydrocarbon pollution, the analysis of pollution sources and the management of ecological environment protection in the surface sediments of Laizhou Bay.

2. Materials and methods

2.1. Sample source and analysis

In this study, data came from the national Marine sediment quality monitoring work organized and implemented by the former State Oceanic Administration from 2013 to 2018 and a total of 20 surface sediment monitoring stations in Laizhou Bay were selected (Figure 1). The monitoring factor was petroleum hydrocarbon, and the sampling depth was 0~10cm. Sample collection and analysis was carried out in accordance with Marine Monitoring Specifications (GB17378-2007) of China, Marine Monitoring Technical Specification Part 2: Sediments (HY/T147.2-2013) and "Basic Technical Requirements for Annual Marine Ecological Environment Monitoring" of China, and the quality
control was carried out in accordance with "Annual National Marine Ecological Environment Monitoring Quality Assurance Work Plan" of China.

2.2. Data evaluation and analysis methods

2.2.1. Evaluation method. In order to evaluate the environmental quality of the monitoring station in the simplest and most intuitive way, the single factor index method is used to obtain the results of the oil hydrocarbon content in the monitoring station, such as the rate of reaching the standard or exceeding the standard, and the multiple of exceeding the standard. The single factor index method is used to evaluate each pollution factor separately. By comparing the measured value of the evaluation factor with the standard reference value, the result of reaching the standard rate or exceeding the standard rate and exceeding the standard multiple can be obtained through statistics. The mathematical expression of single-factor index calculation is as follows [9,18]:

\[ I_i = \frac{C_i}{S_i} \] (1)

Where \( I_i \) is the pollution index of the i factor, \( C_i \) is the measured value of the i factor and \( S_i \) is the standard reference value of the i factor. When \( I_i > 1 \), it shows that the evaluation factor in sediment has exceeded the standard and the environment has been polluted. The greater the \( I_i \) value, the higher the pollution level. And when \( I_i \leq 1 \), the evaluation factor in sediment has not exceeded the standard and the environment has not been polluted.

Meanwhile, in order to quantitatively reflect the difference of the fluctuation degree of petroleum hydrocarbon at the spatial scale among the monitoring stations and inter-year, and objectively evaluate the important influence degree of the evaluation factors, this paper used the coefficient of variation method to evaluate the variation degree of petroleum hydrocarbon content at each station and inter-year. The mathematical expression of coefficient of variation is as follows [15]:

\[ CV = \frac{SD}{\bar{X}} \] (2)

Where \( CV \) is the coefficient of variation, and \( SD \), \( \bar{X} \) is the standard deviation and average value of the evaluation factors of each monitoring station.

2.2.2. Data analysis. ArcGIS10.5 software was used to map the spatial distribution of petroleum hydrocarbons in sediments, in which the inverse distance weight method was used for data interpolation. DPS18.10 software was used to carry out mathematical statistical calculation on the monitoring data, and Kruskal-Wallis non-parametric test method was used to analyze the significance of the differences of petroleum hydrocarbons between different monitoring stations and between different years. And then the statistical results were compared. When \( P \geq 0.01 \), the difference was not significant.

PRIMER 7 software was used for Cluster Analysis and Multi-Dimensional Scaling. The results are tested by Stress. When Stress\(<0.20\), the analysis results have certain credibility; when Stress\(<0.10\), the order of the analysis results is better; when Stress\(<0.05\), the analysis results are very representative.

3. Results and discussion

3.1. The contents and changes of petroleum hydrocarbons in the surface sediments

The survey and monitoring data between 2013 and 2018 in Laizhou Bay were statistically analyzed, and the results were as shown in Table 1. The petroleum hydrocarbon content in the surface sediments of Laizhou Bay from 2013 to 2018 ranged from 0.00 mg/kg to 377.00 mg/kg, with a mean of 63.34 mg/kg. According to the Quality of Marine Sediments (GB18668-2002) of China, the petroleum hydrocarbon content during 2013-2018 conformed to the Class I standard for Marine sediments (500 mg/kg or less). The order of the average content of petroleum hydrocarbons was:

2015 > 2013 > 2017 > 2018 > 2016. Due to the petroleum hydrocarbon contents fluctuated little between 2013-2018, showing a slight downward trend overall (Figure 2). The flow of rivers around Laizhou Bay arrived a peak in 2015, thus the average value of petroleum hydrocarbons contents in 2015 was
the highest in the five years. The results further illustrated that the rivers were the main sources of petroleum hydrocarbons pollution. The average concentration per unit water mass of Laizhou Bay was 0.0118 ~ 0.0585 mg/L between 2013-2018, which met the national class I (class II) seawater standard of China. From Table 2, the $I_q$ values of minimum, maximum and average petroleum hydrocarbon contents were all less than 1, indicating that the pollution degree of petroleum hydrocarbon in the surface sediments of Laizhou Bay was slight. Between 2013-2018, the coefficient order of annual variation of petroleum hydrocarbons contents was: 2018 > 2016 > 2013 > 2017 > 2015. The mean value was 1.12 and the variation level was high, indicating that the petroleum hydrocarbon content of each monitoring station and each year fluctuated greatly on the spatial scale, the spatial dispersion degree was high, the spatial distribution of petroleum hydrocarbon content was not uniform, and there might be some abnormal values in the local areas, which was basically consistent with the performance in Figure 2.

**Table 1.** The statistical characteristic values of petroleum hydrocarbons in the surface sediments of Laizhou Bay from 2013 to 2018.

| Year | Content range (mg/kg) | The average (mg/kg) | The median (mg/kg) | The standard deviation (mg/kg) |
|------|-----------------------|---------------------|--------------------|-------------------------------|
| 2013 | 0.00~366.00           | 68.93               | 48.25              | 82.13                         |
| 2015 | 7.11~199.00           | 72.63               | 49.28              | 57.71                         |
| 2016 | 3.14~250.10           | 50.13               | 12.60              | 64.35                         |
| 2017 | 6.95~268.00           | 65.03               | 40.10              | 60.54                         |
| 2018 | 5.30~377.00           | 59.99               | 32.90              | 85.71                         |

**Figure 2.** The content change of petroleum hydrocarbon in the surface sediments of Laizhou Bay from 2013 to 2018.
**Table 2.** The single factor index and coefficient of variation of petroleum hydrocarbon in the surface sediments of Laizhou Bay from 2013 to 2018.

| Year | Single factor index \((I_i)\) | Coefficient of variation \((CV)\) |
|------|-------------------------------|---------------------------------|
|      | minimum value | maximal value | average value |      |
| 2013 | 0.00            | 0.73             | 0.14           | 1.19 |
| 2015 | 0.01            | 0.40             | 0.15           | 0.79 |
| 2016 | 0.01            | 0.50             | 0.10           | 1.28 |
| 2017 | 0.01            | 0.54             | 0.13           | 0.93 |
| 2018 | 0.01            | 0.75             | 0.12           | 1.43 |

3.2. *The differences and cluster analysis of petroleum hydrocarbons in the surface sediments*

The difference of petroleum hydrocarbon content in the surface sediments of 20 monitoring stations from 2013 to 2018 was analyzed. The significance test of approximate chi-square distribution showed that the \(P\) value is approximately equal to 0.19, and the \(P\) value of Monte Carlo sampling probability analysis was also approximately equal to 0.19. Two kinds of inspection results values were higher than 0.01, indicating that the difference of petroleum hydrocarbon content between years was not obvious [19, 20]. This was consistent with the analysis conclusion in Section 2.1 that petroleum hydrocarbon content fluctuated little between 2013 and 2018.

The results of cluster analysis showed that the overall clustering similarity of petroleum hydrocarbon content among monitoring stations and inter-years was low, and the grouping was not obvious (Figure 3). In order to further verify the cluster analysis results, the Bray-Curtis similarity index was used to calculate MDS graph (Figure 4). The stress coefficient value in the Figure was 0.03, indicating that the Figures in the results was representative. Figure 4 showed that the distribution of petroleum hydrocarbon content in the surface sediments of 20 monitoring stations in the five voyages from 2013 to 2018 was relatively uniform on the whole, and the overall grouping was not obvious, which further indicated that it was consistent with the results of cluster analysis.

**Figure 3.** The cluster analysis of petroleum hydrocarbon in the surface sediments of Laizhou Bay: (a) the stations cluster analysis results; (b) the annual cluster analysis results.
3.3. The spatial distribution of petroleum hydrocarbons in the surface sediments

The spatial distribution trend of petroleum hydrocarbon content in surface sediments of five voyages from 2013 to 2018 was generally consistent (Figure 5), which showed a uniform spatial distribution. The level of spatial difference and variation was basically the same, but there were differences in local areas, mainly manifested as certain abnormal values in local areas. There were two high values of petroleum hydrocarbon content in sediments in the evaluation area, one was station No. 4 of 2013 and 2018 (366 mg/kg and 377 mg/kg, respectively) and the other was station No. 20 of 2016 (250.10 mg/kg). In general, the two areas of high petroleum hydrocarbon content were basically distributed with the monitoring station as the graph of the center of the circle, with the highest value near the center of the circle and the outer edge gradually decreasing. The spatial distribution of petroleum hydrocarbon content in surface sediments of the monitoring station was consistent with the distribution of ports in Laizhou Bay. Weifang Port was near the high value area of the monitoring station No. 4, and Longkou Port was near the high value area of the monitoring station No. 20. Therefore, the results of the paper were consistent with the research results that petroleum hydrocarbon pollutants were mainly derived from human activity input.

The annual variation chart (2013-2018) in Figure 5 indicated that the inter-annual variation of petroleum hydrocarbon content in surface sediments in the study area was generally small. The variations range were from -151.12mg/kg to 141.84mg/kg, and the vast range of the evaluation area varied from -50 mg/kg to 0mg/kg. The areas with large changes in the reduction amount were mainly in the coastal waters of Weifang Port and the waters around the No. 4 monitoring station, while the areas with large changes in the increase amount were mainly in the waters around the No. 5 and No. 10 monitoring stations. The areas with obvious changes in the reduction amount or increase amount at each monitoring station were all in the SW-NE direction.
Figure 5. The spatial distribution of contents and annual variation of petroleum hydrocarbon in the surface sediments of Laizhou Bay: (a-e) the spatial distribution of petroleum hydrocarbon in the surface sediments of Laizhou Bay; (f) the annual variation of petroleum hydrocarbon contents in the surface sediments of Laizhou Bay.

4. Conclusion
The petroleum hydrocarbon content in the surface sediments of Laizhou Bay from 2013 to 2018 ranged from 0.00 mg/kg to 377.00mg/kg, with an average value of 63.34mg/kg. The pollution degree was slight, and the spatial dispersion degree of petroleum hydrocarbon content among monitoring stations and inter-years was high.

There was no significant difference in petroleum hydrocarbon content between different years. The overall clustering similarity of petroleum hydrocarbon content was low and the grouping was not obvious. The results of MDS analysis were consistent with those of cluster analysis.

The spatial distribution trend of petroleum hydrocarbon content in sediments was generally consistent, showing a uniform spatial distribution, and there were high content areas in some areas. The inter-annual variation of petroleum hydrocarbon content in sediments from 2013 to 2018 was generally small, and the areas with obvious changes of decreasing or increasing amount at each monitoring station were all in the SW-NE direction.

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