

EVALUATION OF HEAVYMETAL POLLUTION AND PETROLEUM OF SEAWATER OF YANGSHAN PORT

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Abstract: *Analysis of samples which were taken at Yangshan port in China in 2011, 2012 to assess the level of heavy metal pollution of heavy metals and petroleum hydrocarbon with two main purposes; the first is to evaluate the main pollutants and their pollution level; the second is to evaluate the impact of operations on the port to environmental quality. The application of Grey clustering model to assess heavy metals and petroleum hydrocarbons shows that the heavy metals and petroleum hydrocarbons in sea water at Yangshan port was at grade I.*

Keywords: *Heavy metal pollution, sea water pollution, petroleum pollution.*

1. Introduction

The development of a port is particularly important to each country's economic development. However, the activities of ships on the sea and other commercial ones on the seaport such as oil and fuel supply, ship repairing, shipbuilding are major causes of marine pollution. As a matter of fact, to achieve sustainable development, the environmental quality should be a primary concern. Therefore, it is necessary to have a database on the background status and trends in environmental quality as well as the main cause of pollution in order to maintain the port operation in the future. Among the numerous pollution factors, the heavy metals and petroleum hydrocarbons are two of the most dangerous agents. They directly affect human health and organisms. The accumulation of heavy metals can cause severe damage to human health such as cancer or cell destruction. Heavy metals go into food chain and accumulate in their bodies. Until the end of 2011, there has been no in-depth study on heavy metal pollution at Duong Son port. This will be the first on-going research to help environmental managers help the operation of Duong Son port to ensure sustainable development. From the reason, research on "Evaluation of heavy metals and petroleum hydrocarbon contamination in the sea water of Yangshan port in Shanghai, China" was conducted.

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2. Materials and method

2.1. Sampling

Concentration of 8 elements: Cu, Pb, Zn, Hg, As, Cr, Cd were checked in the samples. The samples in 17 stations were collected from 09/2011 to 12/2012 with three kinds of samples: a, b and c. For samples a and b, 6 samples were taken every month. For samples c, 05 samples were taken for twice a month. Samples were taken on the surface of water and put in plastic bottles.

2.2. The samples treatment and measurement method

2.2.1. Preservation method for the analysis of Hg, As, Cr

By using the fiber filter 0.45 μ cellulose acetate membranes, the samples were filtered. They were preserved in the glasses bottle, then put H₂SO₄ into the bottles and shake the bottles.

2.2.2. Preservation method for the analysis of Cu, Pb, Cd, Zn

By using the filter paper 0.45 μ cellulose acetate membranes, the samples were filtered. They were preserved in the plastic bottles, then HNO₃ into the bottles and to shake bottles.

2.2.3. Preservation method for the analysis of petroleum hydrocarbons

The samples were analyzed immediately after they were taken from the sea. Samples procedure and analytical method of samples used the Specification for Marine Monitoring of China (GB 17378.4-2007) [1]. The concentration of petroleum hydrocarbons was determined by the optical resolution fluorescence method by using the fluorescence spectrophotometer (F-4600).

2.2.4. Analytical method

Samples procedure and analytical method we used were based on the Specification for Marine Monitoring of China (GB 17378.4-2007).

The concentration of As and Hg were determined by atomic fluorescence method by using the atomic fluorescence spectrometer (AFS-9130). Cu, Pb, Cd and Cr content were determined by atomic absorption spectrophotometer method without flame using the TAS-990 machine (Atomic Absorption Spectrophotometer). Zn content was determined by flame atomic absorption method with the GBC-932 machine.

2.3. Data analysis

Concentration of the samples were determined by

$$P_i = C_i/S_i$$

Where: P_i is concentration of each heavy metals and petroleum hydrocarbons; C_i is the actual concentration of heavy metals and petroleum hydrocarbons I ($I=1; 2; 3; \dots; 8$); S_i is the value of standard concentration of each index i .

$$WQI = \sum P_i / S_i$$

Where: WQI is the standard value; $\sum P_i$ is total of P_i ; S_i is the value of standard concentration of each index i .

Gray clustering method was established in this experiment with 8 clustering objects, (Cu, Pb, Cd, Cr, Hg, As, Zn, petroleum) and 4 grey matter values.

3. Result and discussion

3.1. Concentration of heavy metals of seawater

The result from Figure 1 shows that the grade of heavy metals concentrations and petroleum hydrocarbons in Yangshan port were following this order Zn > petroleum hydrocarbons > Cu > Pb > As > Cr > Cd > Hg.

The concentration of heavy metals was changed with the same rules. From January to June, the concentration of heavy metals was high and the concentration of heavy metals began to decline from July to December. The concentration of Cu (45.69 μ g/L) and the concentration of Pb (34.9 μ g/L) was maximum value in March. The concentration of Cd and concentration of Zn (144), As (5.12), Hg (0.772) had highest value in January. There was the same situation with all of heavy metals and petroleum hydrocarbons that all of the concentration of heavy metal concentration and concentration of petroleum hydrocarbons in surface seawater were minimum value in December. The change of heavy metal concentration is explained by the cause of the change of sea level seasonly.

Table 1. The average value of heavy metals and petroleum hydrocarbons concentration of Yangshan port

(μ g/L)	Cu	Pb	Cd	Zn	As	Hg	Cr	Petro
Highest	45.69	34.9	2.1	118.74	5.12	0.772	4.57	119.3
Lowest	1.91	0.49	0.1	42.81	0.49	0.136	0.69	12.78
Average	16.19	12.5	0.71	87.4	2.64	0.37	2.45	63.94

The annual average concentration of the substance is as follows: the concentration of Cu, Hg, Zn were higher than secondary standard but the value of difference was negligible. Concentrations of Cd, As, Cr were high. Concentration of Cd, As, and Cr were lower than the standard at grade I; concentration of petroleum hydrocarbons was higher than primary standards, but the value of difference was negligible with the difference in concentration compared to the standard level I was 13.94 μ g/L. According to the actual results of the analysis, it is necessary to pay attention to the concentration of Pb (12.5 μ g/L). It was higher than grade III.

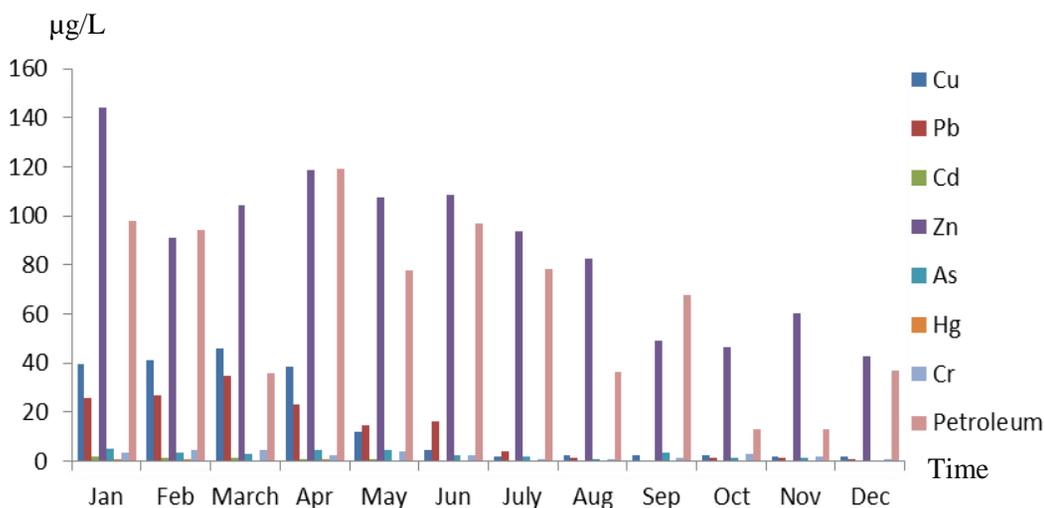


Figure 1. The concentration of heavy metals and petroleum hydrocarbons in 2012

Table 2 showed that the concentration of Cu, Pb, Zn, As, Cr in Yangshan was many times higher than other seas, especially the concentration of Cu and Zn.

Table 2. Comparison of heavy metals of surface water in some sea areas

Area	Cu	Pb	Cd	Zn	As	Hg	Cr
Yangshan port [this study]	16.19	12.5	0.71	87.4	2.64	0.37	2.45
Luoyan Bay [3]	0.27	0.83	0.31	15.3	2.5	/	/
Jinzhou Bay [4]	3.06	0.61	0.92	11.87	0.030	2.190	/
Tianjin Bohai Bay[5]	2.54	7.18	0.12	26.9	1.26	0.04	0.40
Lianyungang [6]	1.93	0.206	0.131	12.9	/	/	/
Liaodong Bay [7]	5.01	4.91	1.04	34.06	/	/	/

/: no data

All of concentration of heavy metals in Yangshan was higher than concentration of heavy metals in other areas. It's because of Yangshan is the very huge port. Yangshan is primarily industrial development and service area, like port services: import and export, export processing, bonded logistics, purchasing and distribution, and market transportation [8].

3.2. Evaluation of degree contamination of heavy metals and petroleum hydrocarbons of seawater

According to the Grey clustering method, the result from August to December 2011 (Table 3) showed that the water quality at Yangshan port was quite good. Result indicated that the water quality was good.

Table 3. Clustering coefficient of heavy metal and petroleum hydrocarbons in 2011

Month	Grade				Result
	I	II	III	IV	
September	0.52	0.22	0.00	0.49	I
October	0.54	0.00	0.00	0.58	IV
November	0.54	0.13	0.21	0.04	I
December	0.67		0.09	0.12	I

Table 4 also showed that the measured result in 2012 followed a gradual increase from January (0.62) and the highest value was in December (0.89). The data in 2011 year and 2012 year showed that water quality in Yangshan at all of 17 sampling stations belong to I grade. This result indicated that the surface water quality in Yangshan port was good in a whole, and the water was not polluted.

Table 4. Clustering coefficient of heavy metal and petroleum hydrocarbons in 2012

Month	Grade				Result
	I	II	III	IV	
January	0.62	0.10	0.23	0.20	I
February	0.65	0.08	0.23	0.18	I
March	0.68	0.01	0.24	0.22	I
April	0.65	0.08	0.23	0.17	I
May	0.67	0.10	0.12	0.13	I
June	0.77	0.15	0.14	0.03	I
July	0.79	0.20	0.08	0.00	I
August	0.83	0.15	0.07	0.00	I
September	0.86	0.18	0.00	0.00	I
October	0.84	0.18	0.03	0.00	I
November	0.83	0.07	0.16	0.00	I
December	0.89	0.14	0.00	0.00	I

These analyse showed that most of the values in the location a and b were higher than c positions. This may be due to different sampling locations. At a and b positions are close the anchorage area of the large ships to transport cargo handling to the place (Fig 1).

Table 5. Clustering coefficient heavy metals and petroleum hydrocarbons according to the spatial distribution in 2011

Grade					
Position of samples	I	II	III	IV	Result
S1a	0.54	0.05	0.27	0.31	I
S2a	0.54	0.15	0.20	0.30	I
S3a	0.54	0.19	0.15	0.32	I
S4a	0.54	0.02	0.03	0.41	I
S5a	0.54	0.03	0.16	0.38	I
S1c	0.69	0.16	0.09	0.01	I
S2c	0.69	0.11	0.13	0.01	I
S3c	0.65	0.07	0.05	0.13	I
S4c	0.69	0.02	0.19	0.03	I
S5c	0.69	0.00	0.05	0.13	I
S1b	0.56	0.22	0.11	0.24	I
S2b	0.54	0.18	0.16	0.29	I
S3b	0.54	0.04	0.15	0.41	I
S4b	0.54	0.22	0.15	0.31	I
S5b	0.54	0.02	0.16	0.42	I
b	0.54	0.17	0.20	0.38	I
a	0.54	0.10	0.25	0.38	I

Table 6. Clustering coefficient of heavy metals and petroleum hydrocarbons according to the spatial distribution in 2012

Grade					
Position of samples	I	II	III	IV	Result
S1a	0.67	0.28	0.11	0.00	I
S2a	0.67	0.17	0.22	0.00	I
S3a	0.71	0.19	0.13	0.01	I
S4a	0.67	0.24	0.12	0.00	I
S5a	0.67	0.24	0.13	0.01	I
S1c	0.68	0.23	0.12	0.02	I
S2c	0.72	0.26	0.09	0.00	I
S3c	0.67	0.2	0.15	0.07	I

S4c	0.67	0.22	0.14	0.05	I
S5c	0.68	0.2	0.15	0.01	I
S1b	0.68	0.22	0.15	0.00	I
S2b	0.68	0.19	0.17	0.00	I
S3b	0.68	0.07	0.16	0.1	I
S4b	0.68	0.12	0.24	0.04	I
S5b	0.67	0.14	0.25	0.04	I
b	0.67	0.06	0.2	0.12	I
a	0.67	0.08	0.19	0.13	I

4. Conclusion

(1) The order of heavy metals concentration and petroleum hydrocarbons concentrations was $Zn > oil > Cu > Pb > As > Cr > Cd > Hg$. The concentration of Cu, Hg, Zn was higher than grade II standard but the value of difference was negligible. Concentrations of Cd, As, Cr were good. They were smaller than the primary standard; the concentration of petroleum hydrocarbons was higher than primary standard, but the higher value was negligible. It was necessary to pay attention to the concentration of Pb. It was higher than grade III of standard.

(2) All of heavy metals had the same situation. All of heavy metals concentration at b positions was higher than positions a and positions c. For petroleum hydrocarbons, the concentration at positions a was higher than positions b and positions c.

(3) The application of Grey clustering model to assess of heavy metals and petroleum hydrocarbons in Yangshan port from August of 2011 year to 2012 year shows that the heavy metals and petroleum hydrocarbons in sea water at Yangshan port in 2011 and 2012 was at grade I. There was only the result in October 2011 was at IV grade. This means that the water quality at heavy metals and oil factor at the Yangshan port until 2012 year was quite good in a whole.

5. Recommendation and suggestion

5.1. Recommendation

In order to protect and improve the environmental quality of seaport operations, in the coming time, management agencies and port operators should set up the implementation of many solutions. Specifically, it is necessary to promote propaganda, dissemination and guidance to port owners, factories to build, repair, maintain and dismantle ships to strictly comply with regulations on environmental protection; organize the close inspection and supervision of activities of seaport enterprises and vessels when operating in seaport waters; To inspect the maritime safety of vehicles engaged in operation in the management area so as

to detect and promptly warn in order to eliminate potential dangers that may cause environmental pollution.

Besides, it is necessary to coordinate with other agencies and organizations to mobilize people and appropriate means to handle environmental incidents caused by the operation of sea-going ships. At the same time, it is necessary to regularly monitor the compliance of diary logs, the ability to ensure the operation and technical condition of installed equipment, tanks, valves, throat outlet. The potential or related factors to ensure the safety of environmental pollution or avoid environmental pollution from ships, special-use ships carrying petrol and oil, floating petroleum storage depots.

5.2. Suggestions

This research subject can be applied at Nghi Son port, Thanh Hoa province. However, due to natural conditions and climate different from Duong Son port in China, it is necessary to study the integration of criteria for water quality assessment according to Vietnamese standards which should include temperature, turbidity, N,P, K, heavy metals, biological indicators (DO, BOD, microorganism).

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