A Contrastive Analysis of the Organotin Compound in Main Ports of Bohai Sea of China

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Abstract: Using headspace solid phase micro-extraction combined with gas chromatography and flame photometric methods, organotin compounds in surface water and bottom soil are investigated at nine sampling stations in seven harbors of the Bohai Sea of China in 2005 and 2008. The investigation result shows that the organotin pollution still exists and is serious in part of the ports. In recent years, the organotin content declines, this indicates that the product mix of the anti-fouling paints for ships has changed which shows a good trend in China and in other areas of the world as the international AFS convention is coming into force and with the retroactive application of the convention.

Keyword: *organotin, surface water, bottom water, Bohai Sea of China, TBT, AFS convention*

1. Introduction

In Year1960, the anti-fouling property of organotin (especially the TBT) was found. The use of organotin greatly extends the service life of marine construction and ships, reducing the fuel consumption and the dock repair cost and making a great economic benefit. But so far TBT is recognized as one of the most poisonous human induced chemicals in the marine environment according to recent research [1]. Organotin has a huge affect on fish, crustaceans, mollusks and marine algae. Once introduced into the environment, it interferes with the normal function of the biologic endocrine system [2].

In October 2001 in London, The international community adopted the “International Convention on the Control of Harmful Anti-fouling Systems on Ships, 2001” (AFS Convention) on the diplomatic conference held in the headquarters of IMO to deal with this important issue of marine environmental protection. The purpose of this convention is to protect the marine environment and human health from adverse effects, phase out the use of organotin compounds in anti-fouling paint and create a new mechanism to prevent the use of other hazardous substances in future anti-fouling paint. The AFS convention met the conditions of entry into force on September 17, 2007 and came into effect on September 17, 2008.

The Bohai Sea is inland sea in China and makes an important role in China’s economic development. Its ecological environment is very important. Navigable waters of the Bohai Sea is rich in resources and has a heavy shipping track. The marine self-purification ability of the Bohai Sea is very weak because it is semi-closed and there are Miaodao islands arranged in the gulf mouth, which prevents the gulf and the sea from convection. In recent years, large quantities of pollutants were discharged into the Bohai Sea, making the environmental quality of the Bohai Sea worse. The contrastive analysis of organotin compound in the surface water and bottom water of the main ports of Bohai Sea of China in recent years was carried out. The environmental factors affecting the distribution of the organotin in the Bohai Sea is analyzed in the paper, in order to get a more detailed understanding of the source of organotin, its biochemical processes after being discharged into the Bohai Sea, the pattern of organotin pollution in recent years and to provide a reliable scientific basis for future pollution control.

2. Sample collection

The samples of surface water and bottom water of seven main ports of the Bohai Sea were collected in July 2005 and May 2008 respectively. The details of sample collection are shown in Table 1.

Serial number	Latitude	Longitude
No.1 water and sediment sample	40° 18′ 12″ N	122° 03′ 38″ E
No.2 water and sediment sample	38° 54′ 38″ N	117° 54′ 04″ E
No.3 water and sediment sample	37° 33′ 75″ N	121° 23′ 43″ E
No.4 water and sediment sample	39° 54′ 24″ N	119° 36′ 26″ E
No.5 water and sediment sample	38° 35′ 58″ N	120° 09′ 47″ E
No.6 water and sediment sample	38° 56′ 27″ N	121° 39′ 02″ E
No.7 water and sediment sample	38° 56′ 10″ N	121° 39′ 11″ E

Table 1. Encoding Table of the Port Water and Sediment Samples

2.1 Sampling points

The above-mentioned sampling stations are displayed by Figure 1.

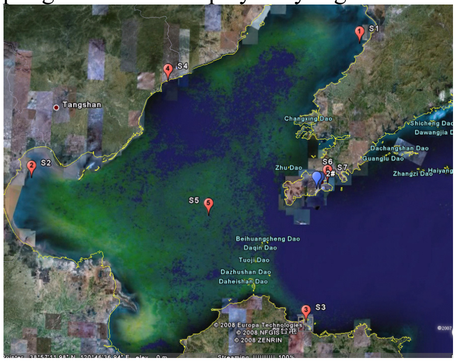

Fig. 1 Sampling Sites in Bohai Sea

2.2 Samples collection methods

2.2.1 Collection of surface water

The sample collection of surface water was carried out according to the requirement of the national standard of People’s Republic of China “Oceanographic survey norms-observation of chemical elements of sea water (GB 12763.4-91)”. The sea water samples were sealed in bottles and then carried back to the laboratory wrapped with a black plastic bag. Then the samples were preserved in darkness under 4℃ and filtered before the analysis.

2.2.2 Sediment (surface sediments) sample collection

The sample collection of surface sediments was carried out according to the requirement of the third chapter of the national standard of People’s Republic of China “Oceanographic survey norms-Marine geological and geophysical survey (GB/T 13909-92)”. In every site, the surface sediments were collected using the grabbing sediment container. The sediments were sealed up in bottles and then carried back to the laboratory wrapped with a black plastic bag. The surface area of the sediments was 10 cm2 and the thickness was 2-3cm. Then the samples were preserved in darkness and under -4℃ and filtered before the analysis.

3. Detection and analysis

The main organotin analysis methods are liquid-liquid extraction (LLE), microporous membrane liquid-liquid extraction (MMLLE), liquid extraction rods (SLMP), solid-phase extraction column (SPE), solid-phase micro-extraction Extraction (SPME), supercritical fluid extraction (SPE) and microwave extraction [3]. As the solid-phase micro-extraction (SPME) can be derived [4], extracted and enriched at the same time, so this study takes the headspace SPME method[5].

In the detection process, the organotin compounds were detected according to the analysis conjunction technology and gas chromatography and flame photometric methods, in accordance with the various steps of top SPME. Seven water samples and sediment samples were analyzed during the detection process, and the analytical instrument was SHIMADZU9A. The specific detection method is described in the following section.

3.1 Analysis of water samples

A 50ml water sample was taken and mixed with glacial acetic acid. The solution was mixed with magneton and the PH of the solution was adjusted to 3.3. The solid-phase micro-extraction fiber was exposed to the top air of the reaction bottle. 1 ml 3% sodium borohydride solution was added to the reaction bottle quickly with a syringe. Under acidic conditions, the butyltin compounds reacted violent with NaBH4 and the volatile hydride was generated. The SPME extraction fibers were directly transferred to the GC injector 15 minutes after the reaction. The butyltin hydride compounds were separated in the HP-1 capillary column under the programmed temperature control 10 minutes after being thermo-analyzed. This separation was detected by QSIL-FPD sensitively.

3.2 Sediment samples analysis methods

We took 3-5g (wet weight) sediment sample and mixed it with 1 ml 100 ng/ml tetrabutyltin methyl alcohol solution smoothly. 1-2g copper powder was added to the sediment sample for desulfurization. 10 ml HCL-THF (1:20) was added to the sample and the organotin was changed into corresponding chloride, then the mixture was ultrasonic extracted with 25 ml 0.01% tropolone-hexane for 15 minutes and 10 ml hexane for 10 minutes orderly. The combined extraction mixture was concentrated to 2-3 ml by rotary evaporation at the temperature of 25°C, and then the Green reagent was added for derivation, the mixture was ultrasonic reacted for 15 minutes under room temperature, then 5 ml 0.5 M H2SO4 solution was added to the mixture to remove the excessive green reagents, the organic phase was washed with about 40 ml deionized water and then the organic phase was transferred to the short column filled with silica gel-Florisil-anhydrous NaSO4 which was washed with 10 ml hexane for desiccation and purification, and then the column was washed with 10ml hexane. The washing liquid was concentrated to 1 ml in the flow of nitrogen, and then 1 L sample was GC-QSIL-FPD analyzed.

4. Contrastive analysis of the test results [6]

4.1 Contrastive analysis of the test results of water samples

The contrastive testing results of the organotin content in the samples analyzed in2005 and 2008 are shown in Table 2. No organotin was detected in the sites. The cause of the results were considered as the hydrodynamic action and degradation of the organotin in the surface water according to the analysis, and this can not truly reflect the organotin pollution of local waters [7]. The hydrodynamic conditions of the surface water in every port were better due to the ocean tide and the surface wind, so the exchange capacity of the sea water and the diffusion velocity of the organotin in sea water were better as a result[8]. Though the samples were collected from the surface water of the sea area in the ports, the actual water samples did not have the true representation because of the exchanging action [9]. Secondly, the organotin of the surface water was easily degradable mainly because of the ultraviolet light degradation、biodegradation and chemical degradation [10].

SITE	MBT: (ng/L) 2005/2008	DBT: 2005/2008 (ng/L)	TBT: 2005/2008 (ng/L)
1	nd/nd	nd/nd	nd/nd
2	nd/nd	nd/nd	nd/nd
3	nd/nd	nd/nd	nd/nd
4	nd/nd	nd/nd	nd/nd
5	nd/nd	nd/nd	nd/nd
6	nd/nd	nd/nd	nd/nd
7	nd/nd	nd/nd	nd/nd

Table 2. Comparative Analysis of Organotin Content of Surface Water From the Main Ports in Bohai Sea in 2005 and 2008

4.2 Contrastive analysis of the test results of sediments

The organotin pollution of sediment can reflect the organotin pollution of the sea area well according to the above research, so the emphases of the contrastive analysis of this research is focused on the changes of the organotin content of the sediment from 2005 to 2008. We got the contrastive results as shown in Table 3.

SITE	MBT: (ng/g) 2005/2008	DBT: (ng/g) 2005/2008	TBT: (ng/g) 2005/2008
1	339.13/nd	nd/nd	nd/nd
2	456.17/17.03	nd/43.89	6.30/125.36
3	644.87/nd	nd/nd	6.51/4.92
4	707.31/nd	nd/6.54	nd/6.43
5	1434.57/nd	nd/nd	36.30/8.39
6	203.2/nd	nd/5.01	26．0/3.24
7	89.6/nd	nd/4.94	11.0/3.69

Table 3. Comparative Analysis of Organotin Content of the Sediment From the Main Ports in Bohai Sea in 2005 and 2008

A. Analysis of every site

SITE 1 (Bayuquan Port): No TBT and DBT was detected twice, but the MBT content varied greatly, from 339.13 ng/g to nd. The organotin content of Bayuquan port has a downward trend as shown in this research. The Bayuquan port is developing fast in recent years and became a through port of hundred million tons in 2007, but the organotin content of this port has a downward trend and this indicates that the retroactive effect of AFS convention has already played a significantly restrictive role in organotin pollution control. It is not allowed to use organotin compounds in the anti-fouling systems of ships from January 1, 2003 according to the bulletin issued by the Ministry of Communications of China in 2003 named “Organotin compounds served as the pesticide should not been used in the anti-fouling systems of ships”.

SITE 2 (Tianjin Port): The TBT content ascends from 6.30 ng/g to 125.36 ng/g and the DBT content ascends from nd to 43.89 ng/g, but the MBT content drops from 456.17 ng/g to 17.03 ng/g. We can see that the organotin content of Tianjin port presents an upward trend, which has the biggest increase among all the sites, and the increase of the TBT content is large as the result shows. Although Tianjin port has been developing fast in recent years, the terrestrial pollution sources were the main reasons for the increase of organotin content in the surrounding sea water of Tianjin port according to our analysis and in combination with the changes of the organotin pollution caused by ships in other ports in recent years.

SITE 3 (Yantai Port): The TBT content dropped from 6.51 ng/g to 4.92 ng/g and no DBT was detected, the MBT content dropped from 644.87 ng/g to nd. The developing velocity of Yantai port is also very fast in recent years and it is close to be a hundred million ton harbor in 2007, but the overall TBT content of this port has a downward trend, the cause was the same as that of Bayuquan port.

SITE 4 (Qinhuangdao Port): The TBT content increased from nd to 6.43 ng/g and the DBT content increased from nd to 6.54 ng/g, but the MBT content dropped from 707.31 ng/g to nd. According to the analysis, the organotin pollution of the port may be associated with the use of the anti-fouling paint in the ships, because the Qinhuangdao port is the largest coal exporting port. The organotin content of Qinhuangdao port increased accompanied with the increase of the throughput in recent years.

SITE 5 (Shanhaiguan Shipyard): The TBT content drops from36.30 ng/g to 8.39 ng/g and no DBT was detected twice, the MBT content dropped from 1434.57 ng/g to nd. Shipyards are always seriously organotin polluted, but the organotin content of the Shanhaiguan Shipyard has a downward trend according to the contrastive analysis of organotin content between 2005 and 2008, which further indicates that the product structure of the anti-fouling paint used on ships has been rectified greatly and the proportion of organotin compounds in anti-foul paint decreased evidently at present in China.

SITE 6, 7 (Dalian Port): The TBT content dropped from 18.5 ng/g to 3.47 ng/g , the DBT content increased from nd to 4.98 ng/g , the MBT content dropped from 146.4 ng/g to nd. This pattern of Dalian Port is similar to that of Bayuquan Port and Yantai Port, which indicates that the organotin pollution caused by the use of anti-fouling paint on ships decreases evidently.

B. Overall analysis

Through the above-mentioned analysis of the sediment of every site, the organotin content of the main ports in Bohai Sea shows the following patterns:

(1) The overall organotin content of the ports is decreasing. This downward trend indicates that the ingredient of anti-fouling paint used on ships in China and in the world has been changed due to the constraints of the convention and the related regulations issued by the Ministry of Communications of China in 2003. This created a favorable condition for the implementation of the AFS convention.

(2) The organotin content of the ports depends not only on the sea-borne pollution, but to a great extent also on the terrestrial source pollution. Therefore, in order to protect the water environment from organotin pollution, not only the sea-borne pollution but also the related terrestrial and water environment source pollution should be limited.

(3) The organotin content of every port indicates that the emphasis on the current AFS convention of every shipping corporation is different.

5. Conclusion

According to the contrastive analysis, the organotin pollution of the Bohai Sea water environment in China can be concluded as following:

(1) The organotin content of the surface water from the main ports in Bohai Sea is lower than the detection limit. The hydrodynamic effect and degradation of the surface water have a great influence on the organotin content.

(2) The detection rate of the organotin pollutant in the sediment of the main ports in Bohai Sea reaches to 86% and the organotin content is generally higher than the detection limit and the organotin residue standards established by the developed countries, which indicates that the organotin pollution of the Bohai Sea water environment still exists and is very serious in some ports.

(3) In recent years, the overall organotin content of the ports has been decreasing. This downward trend indicates that the ingredient of anti-fouling paint used on ships in China and in the world has been changed and has created favorable condition for the retroactive application of the convention and the domestic related regulation.

(4) The organotin content of the ports depends not only on the sea-borne pollution, but to a great extent also on the terrestrial source.

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