INVESTIGATION OF THE BEHAVIOR OF PERSISTENT ORGANIC POLLUTANTS IN JAPAN SEA

Tsurukawa M[1], Suzuki M[2], Abe S[3], Okuno T[1], Takemine S[1], Matsumura C[1], Nakano T[1], Kunugi M[4]

[1]Hyogo Prefectural Institute of Environmental Sciences, 3-1-27, Yukihira-cho, Suma-ku, Kobe, Hyogo, 654-0037, Japan , [2]Kobe University, Rokkodaicho 1-1,Nada,Kobe,Hyogo,657-8501,Japan,

[3]Hyogo Environmental Advancement Association, 3-1-31, Yukihira-cho, Suma-ku, Kobe, 654-0037 Japan,

[4]Tokyo University of Science,2641 Yamazaki,Noda-shi,Chiba 278-8510,Japan

Abstract

Although a large amount of Persistent Organic Pollutants (POPs) have been used in Asian countries such as China or Korea, the state of contamination has not been clarified in Japan Sea surrounded by these countries.

In this study, pollution levels of POPs in sea water and air over the ocean were investigated by using voluntary sampling of passenger ships. Also isomer and enantiomer analysis were conducted to estimate source and pollutant pathway of POPs. In this result, the highest concentration of Hexachlorocyclohexanes (HCHs) was in the southwest Sakhalin area. DDTs was higher in Tsushima straits than in the north of Japan Sea.

In Tsushima straits and southwest Sakhalin, enantiomer fractions (EFs) of alpha-HCH was nearly 0.5(racemic). It suggests that those areas were affected by relatively-recent pollutant source.

Introduction

According with the rapid economic development in Asian countries such as China or Korea, much POPs have been used partly at very high levels. Some of them are still produced and used especially in China. Regarding some processes such as long-range atmospheric transport from emission sources, mass transfer between air and water, oceanic water have been believed to serve as a final sink of these contaminants. However, such a role of the oceans, especially in Japan Sea surrounded by these Asian countries, is yet to be investigated in detail. Therefore it is significant to study pollution situation of ocean as transport pathways from those source areas .

The usage of hexachlorocyclohexanes (HCHs) in China is approximately 490,000,000 tons which is over 33 % of all of the world, and the production of DDTs in China began in early 1950's;by 1983,when the Chinese government banned produced this pesticide, a total of 270,000t had been produced[1,2]. These POPs were discharged to the marginal seas of the region through rivers in considerable amounts. The purpose of this study was to investigate the levels of POPs in Japan Sea and their pathway by investigating isomer patterns or enantiomeric fractions(EF). Beside the concentration of POPs, the composition of them such as isomer, metabolites and enantiomeric fractions(EF) could be used as complemental and available tools to understand the emission source areas which may affect contamination of Japan Sea.

Materials and Method

The sea water samples (approx. 50L) were taken at 50 points and air samples(approx.108m^3) were taken at 6 points by the passenger ship (NYK cruses CO.,LTD , ASKA-2) equipped with concentrating device between 24 July and 2 October in 2010.(Fig.1) Also in downstream site of Chang Jiang, water samples(approx.6L) were taken. After particle matter caught by quartz fiber filter (GC-50H, 142mm in diameter, ADVANTEC) which was changed from polypropylene cartridge filter (MCP7,ADVANTEC) because of the difficulty of extraction, dissolved component in the sea water was collected by polyurethane foams (PUF, 61mm in diameter 100mm wide,) and five activated carbon felts(ACF,disk size 61mm,Autoprep). Analysis pretreatment is as already reported[3]. Identification and quantification of POPs were performed using a gas chromatograph, (HP6890N Agilent) /high-resolution mass spectrometer(800D,JEOL Ltd.) equipped with HT-8PCB capillary column(60m*0.25mm id.Kanto Chemical) and BGB172 capillary column(30m*0.25mm id,BGB Analytik AG) for enantioselective analysis. Enantioselective degradation of a chiral compound can occur in the environment as a result of microbial activity in soil and water, leading to depletion of one enantiomer. This altered enantiomer signature can provide information on the transport and fate of POPs. It is defined as EF=(+)/((+)+(-)).

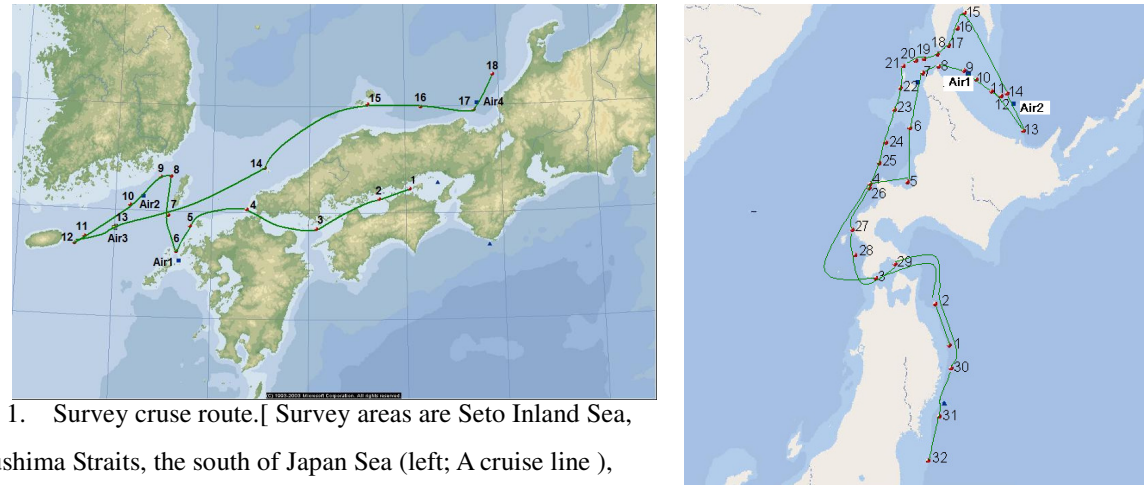

Fig 1. Survey cruse route.[Survey areas are Seto Inland Sea, Tsushima Straits, the south of Japan Sea (left; A cruise line), northeast of Japan Sea, Sanriku (right;B cruise line)]

Result and Discussion

All measured organic compounds(HCHs,HCB,DDTs,Drins,Chlordanes) are almost exclusively found in the water phase(PUF, ACF), and only a minor fraction were associated with particles in the water(almost all <5%). Therefore only water phase could be used to analyze. The concentrations of ΣHCHs in oceans were 700-880 pg/L in the southwest Sakhalin, 55-140 pg/L from Tsushima Straits to southern Japan Sea, 100-200pg/L in Seto Inland Sea. Higher concentrations were observed in down stream site of Chang Jiang , 2300±220pg/L, which was collected apart from survey cruse in order to investigate the conditions of input of contaminants to oceans . (Fig 2.) As for ΣDDTs, the concentration is 2.2±0.9pg/L around Hokkaido and Sakhalin sea area,

4.5±2.2 pg/L around Tsushima Strait, In 2009 survey, ΣDDTs was also detected relatively high ,4.4-,7.7pg/L in dumping zone of Korea in northern Tsushima Straits where a dispute has erupted over the marine pollutions of POPs and Heavy metals. On the other hand, the concentration in air is as follows.

ΣHCHs is a mean value 160pg/m^3, 32pg/m^3 and ΣDDTs is a mean value 6pg/m^3 ,1.8 pg/m^3 in north-east Hokkaido and in Tsushima Straits respectively. As for HCHs,This tendency corresponds to the contamination trend in Sea water, and these results reveal there may be some contaminant sources in Sakhalin area. The ratios (α / γ) of Sea waters were apparently different according to the areas. In general, lower α / γ ratios were observed in low-latitude region. Especially in downstream site of Chang Jiang, it was the lowest value,1.4±0.1, and 1.9±0.6 in the seas around Korea, 4.2±0.6 in southwestern Sakhalin.

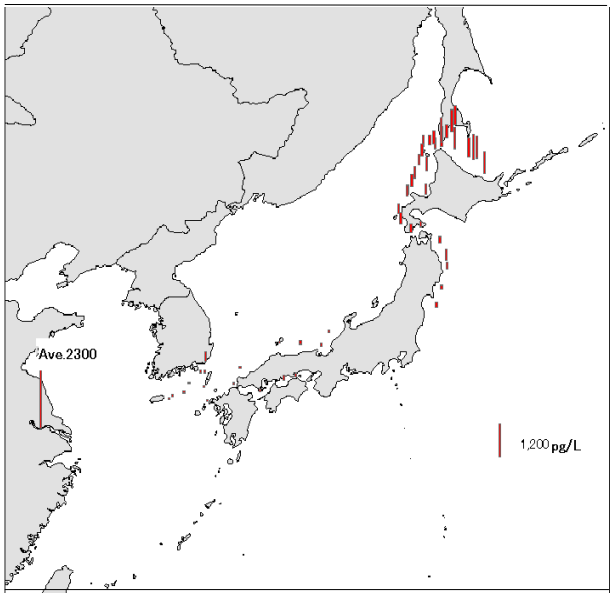

Fig 2. Distribution of HCHs concentrations in surface sea water(2010)

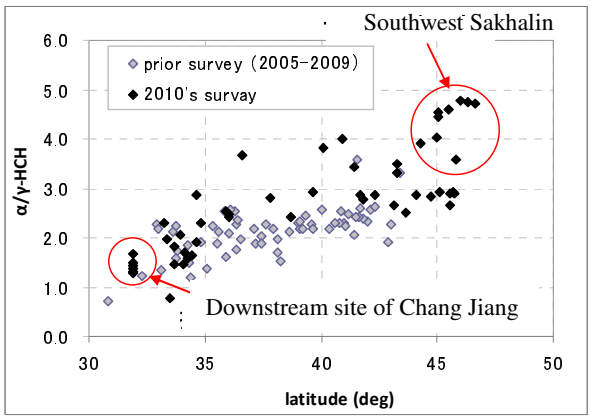

Fig 3. Relationships between α/γ-HCH ratio and the latitude of sampling points

These results seem to reflect the usage of γ -HCH (Lindane) in China and indicate that HCHs was discharged to the marginal seas of the region through rivers in considerable amounts and transported to Japan Sea via oceans. As shown in some literature, ratio of p,p'-DDT to p,p'-DDE have been often used as indicators to estimate the origin and the pathway in the long-range transport of contaminants. The higher p,p'-DDE ratios have been interpreted as a result of the long time exposure in environment because p,p'-DDT may be converted to p,p'-DDE by UV light and the metabolism by organisms during the transport. The p,p'-DDT /p,p'-DDE ratios of air samples was a mean value 0.73(primary/fresh) in Tsushima Straits, 0.41(long time exposure) in northeast Hokkaido . The currently used pesticides mirex in China was a mean value 0.14 pg/ L in A cruise line and 0.09 in B cruise line. Higher concentration was 1.3 pg/L observed in down stream site of Chang Jiang. Regarding Mirex had not registered as pesticide and no production, no import in Japan, it will be an indicator of transportation from other countries. Another currently used Chlordane (sum of trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor,heptachlor) were found at a mean value 55pg/L in A

cruise line, 36pg/L in B cuise line and 501pg/L in downstream site of Chang Jiang. Technical chlordane (a mixture of 140 compounds containing 13% trans- chlordane(TC), 11% cis- chlordane(CC) and 5% heptachlor is still being extensively used until recently in China in agriculture,gardens and building (termiticide; 500-800 ta^{-1} [4]) In general, TC is more depleted by microbial or photolytic degradation than CC and the ratio of TC/CC in technical product is usually 1.01-1.26 range. Theoretically, a lower TC/CC ratio may be expected because TC is generally more susceptible to degradation than CC. If the TC/CC ratio is less than this value, it possibly originates from past used metabolized chlordane. In this research, TC/CC ratio of 4 air samples in A cruise line(sampling point Air 1,2,3,4) was 1.1(at Air 4) -1.5(at Air 1) and that of 2 air samples in B cruise line (sampling point Air 1,2) was both 1.7. So Tsushima Strait and Hokkaido areas were considered to originate from not so metabolized chlordane. Concerning Hokkaido area, it's assumed that origin is apart from other regions as reported in other paper.[5] And model simulation illustrates the water current, from the Amur river to southern Sakhalin and northern Hokkaido through Okhotsk Sea.[6] More detailed survey is needed to clarify this, i.e, the research in the Amur river. A composition similar to the technical product (close to racemic) indicates fairly fresh release or that the compound was directly transported in air from its source, while enantioenrichment indicates that it was released some time ago and has since been subjected to recycling from water or soil. EF of α -HCH was close to racemic in southwest Sakhalin(0.5 ± 0.02) ,downstream site of Chang Jiang (0.51 ± 0.02), Tsushima Straits (0.49 ± 0.02). In Japan Sea, as latitude become higher , EF values tend to become lower. Since 2005's survey , EF values was 0.46 ± 0.05 in middle Japan Sea, 0.44 ± 0.03 in northern Japan Sea(around Hokkaido),0.46 ± 0.01(pacific sideboard of Tohoku area). These results indicate that southwest Sakhalin, downstream site of Chang Jiang and Tsushima Straits area polluted by relatively new HCHs.
From comprehensive viewpoint, contamination in Japan Sea seems to be caused by the transportation from other countries in large part and polluted area was found in around Hokkaido.

Acknowledgement

This work was supported by the Environment Research and Technology Development Fund (B-0905) of the Ministry of the Environment, Japan. We thank Prof.Hayakawa of Kanazawa University for sampling and providing direction, and ASKA-2 for cooperating with sampling.

Reference

1.Hua X, Shan Z.(1996); *Adv. Environ. Sciences* .4(2),33-45 2. Li Y F, Caik D J, Singh,A. (1999); *Adv. Environ.Res*.2,497-506 3. Suzuki M, Tsurukawa M, Abe S, MatsumuraC, Nakano T, Kunugi M. (2010); *Organohalogen Compounds*. 72,860-863 4 .PRC-POPs Research Center.(2005) ; China POPs Network. Tsinghua 5. Kobara Y, Seike N, Nishimori M, Masunaga S, Hosomi M(2010); *Environmental science.* 23(1),3-17 6. Ohshima K I, D Simizu.(2008); *Journal of Oceanography*. 64, 103-114.