THE SEA WATER CONCENTRATION AND ENANTIOMERIC FRACTION OF HCHs IN THE SEAS AROUND JAPAN

Suzuki M[1], Tsurukawa M[1], Abe S[2], Matsumura C[1], Nakano T[1], Kunugi M[3]
[1]Hyogo Prefectural Institute of Environmental Sciences, Yukihira-cho 3-1-27, Suma-ku, Kobe, Hyogo 654-0037, Japan, [2]Hyogo Environmental Advancement Association, Yukihira-cho 3-1-31, Suma-ku, Kobe, Hyogo 654-0037, Japan, [3]Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan

Abstract

Hexachlorocyclohexanes (HCHs) designated as new POPs have long–range transport potential, and are transported by ocean currents. A large amount of HCHs have been used in China and other Asian countries. Though the Japan Sea is surrounded by these countries, there is a few measured data of HCHs.

In this study, HCHs pollution levels around the Japan Sea were investigated by voluntary sampling of passenger ships in 2009. HCHs were detected 71-440 ng L^{-1} in the sea water at sampling points. In southern Japan Sea, relatively highly HCHs polluted points were found, and correspond to the area around the ocean dumping zone of Korea. Another pollution pathway is suspected to exist in the northern area of Japan Sea because high concentrations of HCHs were also detected there. It was verified the ratios of alpha/gamma-HCH become low and enantiomeric fractions (EF) for alpha-HCH become high as latitude becomes low. These trends were similar to the ones of survey conducted since 2005.

Introduction

Technical HCHs mainly contained α-HCH (55-80%), β-HCH (5-14%) and γ-HCH (8-15%) has been used for insecticide all over the world. The Global usage of technical HCH was dominated by more than dozens of countries including China, Former Soviet Union, India and Japan. Especially in China, the usage of HCHs is appoximately 49 million tons witch is over 33 percent of that of all of the world[1]. HCHs pollutions were even observed in the Arctic Ocean where HCHs have never been used. Alpha-HCH and γ-HCH were detected 350-1630 pg L^{-1} and 120-400 pg L^{-1} in the Eastern Arctic Ocean in 1996, respectively[2]. And several thousand tones of HCHs were estimated to be contained within the surface layer in the Arctic Ocean more than a decade ago[3]. In China, Korea, Russia and Japan, relatively high environmental contaminations of HCHs were deduced and observed in 1990[4]. The Japan Sea is surrounded by these countries, and has water input of 2.5 million t s^{-1} by northward-flowing Tsushima Current from southern part of Japan. Therefore it is concern that HCHs and other POPs are transported with Tsushima Current to the Japan Sea from high polluted area. However the investigation of POPs pollution in the Japan Sea is very few, and inquired by Northwest Pacific Action Plan (NOWPAP). We have investigated HCHs pollution in the area of South China Sea, the Pacific and the Atlantic Ocean by voluntary sampling of passenger ships since 2005[5]. In this study, it is intended that to reveal the HCHs and other POPs pollution levels and their pollution pathway in the Japan Sea by analyzing the sea water concentration, isomer patterns and enantiomeric fractions (EF) for three years. In this paper, it was reported the knowledge of HCHs from the survey in 2009.

Materials and Methods

The sea water samples (50-113 L) were taken at 19 points by the passenger ship (*ASKA-2*) equipped with concentrating sampling device between 24 September and 5 October 2009 (Fig.1). After particle matter caught by polypropylene cartridge filter (MCP7, Advantic), dissolved matter in the sea water was collected by polyurethane foams (PUF, 100mm wide, 61mm in diameter) and five activated carbon felts (ACF, disk size 61mm, Autoprep) and extracted by acetone and dichloromethane with Accelerated Solvent Extractor (ASE) respectively. The extracts were cleaned up by silica-cartridge column (LC-Silica, 500mg, Supelco) after solvent was changed to Hexane. Identification and quantification of HCHs were performed using a gas chromatograph (HP6890N, Agilent) / high-resolution mass spectrometer (800D, JEOL Ltd.) equipped with HT-8PCB capillary column (60 m*0.25 mm id, Kanto Chemical). Enantioselective analysis was performed using HRGC/HRMS equipped with BGB-172 capillary column (30 m*0.25 mm id, 0.25 µm film thickness, BGB Analytik AG).

Results and Discussion

The sea water concentration of HCHs at each sampling point was shown in Fig.2. The relatively higher concentrations of HCHs were detected at the points of No.1, No.2 and No.3 in the Inland Sea in which there are some metropolises. On the other hand, the concentrations of HCHs at some points in the Japan Sea were even higher. Especially, the highest one was detected 435ng L^{-1} at No.19 of all the points and the relatively higher one was detected 259 ng L^{-1} at No.18 in northern area of Japan Sea. According to quick bulletin of ocean condition by Japan Coast Guard, the sea water temperature at No.18 and No.19 were approximately 20 degree and lower than point No.17 by a degree. Though the sea water temperature at No.11 was lower than that of No.17 by approximately 3 degree, HCHs concentrations were almost same except No.13. Therefore, it was suspected that the elevation of HCHs was influenced not by volatilization significantly but by a pollution pathway in the northern area of the Japan Sea. On the other hand, in the southern parts of Japan Sea, relatively higher concentrations of HCHs were detected at No.9 and No.10. In addition, DDTs and DDDs were also detected there at high concentrations compared with those in others. These points corresponded with the area around the ocean dumping zone of Korea where a dispute has erupted over the marine pollutions of POPs and Heavy metals.

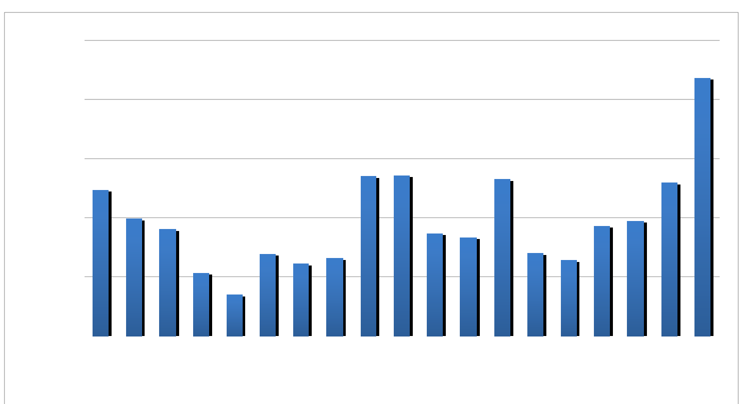

Fig.2 The sea water concentration of HCHs at each sampling point.

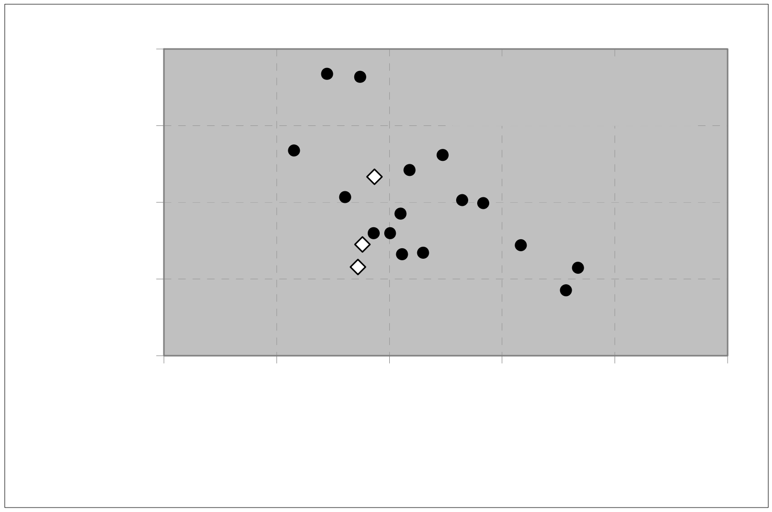

Fig.4 Relationship between the latitude of sampling points and the enantiomeric fractions (EF) for alpha-HCH. Black points indicate sampling points at No.4-19 (r^2 = 0.42, p = 0.0067), White points indicate that at No.1-3.

Acknowledgements

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 thank *ASKA-2* for cooperating with this investigation.

References

1. Hua X, Shan Z. (1996); *Adv. Environ. Sciences* 4(2): 33-45
2. Harner T, Kylin H, Bidleman T, Strachan W. (1999); *Environ. Sci. Technol.* 33; 1157-1164
3. Macdonald Y, Jantunen M, Harner T, Bidleman T, Strachan W. (2000); *Sci. Total Environ.* 254; 93-234
4. Li Y. (1999); *Sci. Total Environ.* 232; 121-158
5. Abe S, Matsumura C, Yokoya M, Nakano T, Kunugi M. (2008); *Organohalogen Compounds* 70; 341-344
6. Yunyun Y, Deliang L, Dehai M. (2008); *Atmos. Env.* 42; 677-687
7. Liua M, Chenga S, Oua D, Yangb Y, Liua H, Houc L, Gaoa L, Xua S. (2008); *Environ. Pllut*. 156; 168-173
8. Buser R, Muller D. (1998); *Environ. Sci. Technol.* 32(5); 626-633
9. Jantunen L, Kylin H, Bidleman T. (2004); Deep-Sea Research 2 51; 2661-2672