

ENANTIOSELECTIVE ANALYSIS OF POPs IN THE NORTH ATLANTIC OCEAN AND THE JAPAN SEA

Abe Sachiko¹, Matsumura Chisato², Yokoya Makoto¹, Nakano Takeshi² and Kunugi Masayuki³

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

²Hyogo Prefectural Institute of Public Health and Environmental Sciences, 3-1-27, Yukihira-cho, Suma-ku, Kobe, 654-0037 Japan, ³National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, 305-8506 Japan

Abstract

The enantiomer fractions (EFs) of chiral persistent organic pollutants (POPs) in seawater have been investigated. In this study, the seawater samples were taken from the North Atlantic Ocean and the Japan Sea. The EFs of *trans*- and *cis*-chlordane ranged from about 0.4 to 0.6. Enantiomer enrichment was observed for both (+) and (-) enantiomer. The EFs of heptachlor *exo*-epoxide, the metabolite of heptachlor, showed large variability, ranging from about 0.5 to 0.7. Except for only two samples, the enrichment of first eluting enantiomer was found in all samples. The EFs of *alpha*-HCH ranged from 0.42 to 0.48. The negative correlation was found between the EFs and the *alpha*-HCH/ Σ HCH ratios. The correlation coefficients (*r*) for between the EFs and the *alpha*-HCH/ Σ HCH ratios of the North Atlantic Ocean and the Japan Sea were -0.798 and -0.749, respectively. It was observed that the transformation tendency of the samples from the Japan Sea was greater than that of the samples from the North Atlantic Ocean.

Introduction

Most of the POPs are organochlorine pesticides which have been used for agricultural purposes. Since the Stockholm Convention entered into force on May 2004, the production and use of 12 priority POPs were banned or severely restricted. Unfortunately, POPs are still detected in various environmental media because of their high persistence and capability of long-range transport.

Some POPs are chiral and present as racemates in the technical product. As they move through the environment, chiral compounds were shown to be transformed enantioselectively by microbial activity thus causing a change of the enantiomeric ratio. But physical processes such as volatilization, photolysis and absorption do not affect it. When these non-racemic residues transfer among environmental compartments such as air and water, their chiral signatures are retained and reflected in the compartment¹.

It is particularly important to identify the behavior of persistent pollutants in the environment, such as POPs. The use of enantioselective analysis may help distinguish between transport from current use regions and that from past applications. In this study, the enantiomer fractions (EFs) of the chiral POPs in seawater from the North Atlantic Ocean and from the Japan Sea were investigated.

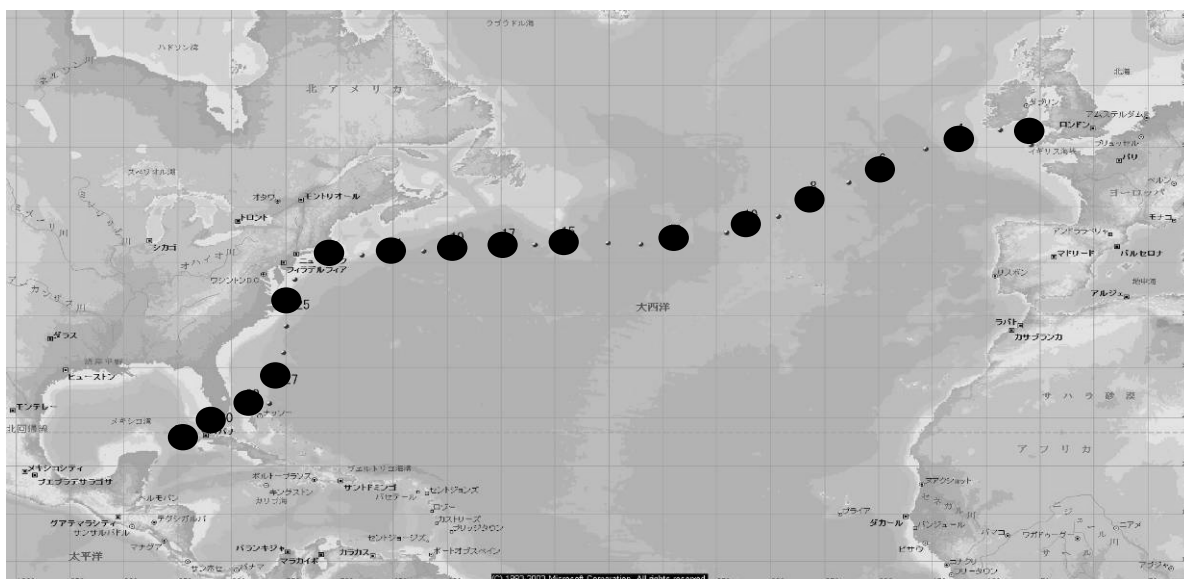


Figure 1. Sampling sites in the North Atlantic Ocean

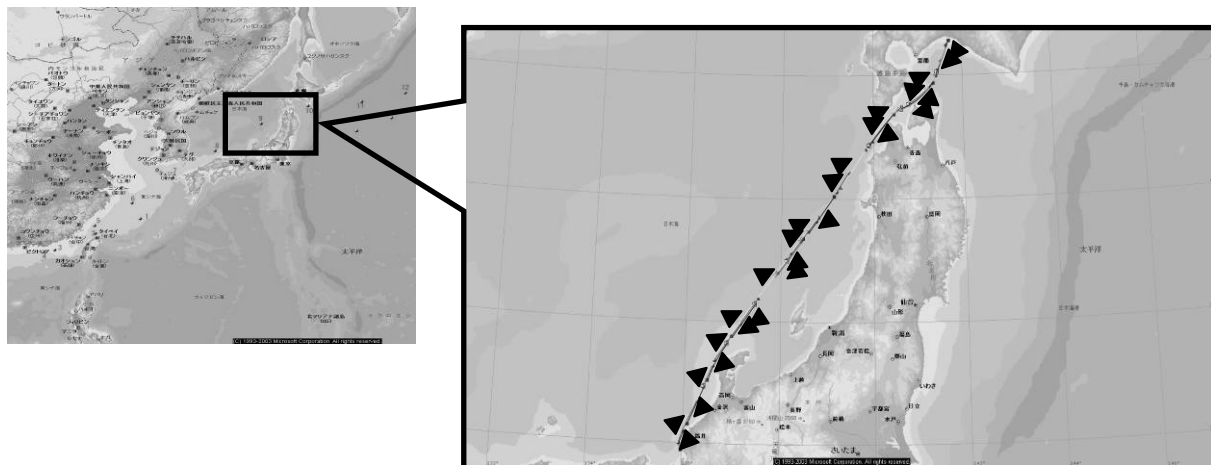


Figure 2. Sampling sites in the Japan Sea

Materials and Methods

Samples: The sampling sites are shown in Figure 1 and Figure 2. Sixteen seawater samples from the North Atlantic Ocean were taken in May and June 2007, and 26 seawater samples from the Japan Sea were taken in early November 2007, respectively. Each sample was collected using the marine pollution observation system developed by Kunugi et al.². The collection of each sample was conducted by solid phase extraction, with a column equipped with a polyurethane foam (PUF) and three sheets of active carbon fiber filters (ACF) in a glass holder. Sample volume is 100 L or 50 L.

Enantioselective Analysis: Analysis was carried out on high resolution gas chromatograph / high resolution mass spectrometry (HRGC/HRMS, JMS-800D) equipped with a BGB-172 column (30m, 0.25mm i.d., 0.25 μ m film thickness; 20% *tert*-butyldimethylsilyl- β -cyclodextrin dissolved in 15% diphenyl-polysiloxane and 85% dimethylpolysiloxane, BGB Analytik). Target analytes were *alpha*-HCH, heptachlor, heptachlor *endo*-epoxide, heptachlor *exo*-epoxide, *trans*-chlordane, *cis*-chlordane, oxychlordane, and *o,p'*-DDD. The preparation method and HRGC/HRMS conditions have been reported previously³.

Results and Discussion

The EF value was calculated as the ratio of the amount of (+) enantiomer to the total of (+) and (-) enantiomers⁴. An EF of 0.5 indicates racemic composition.

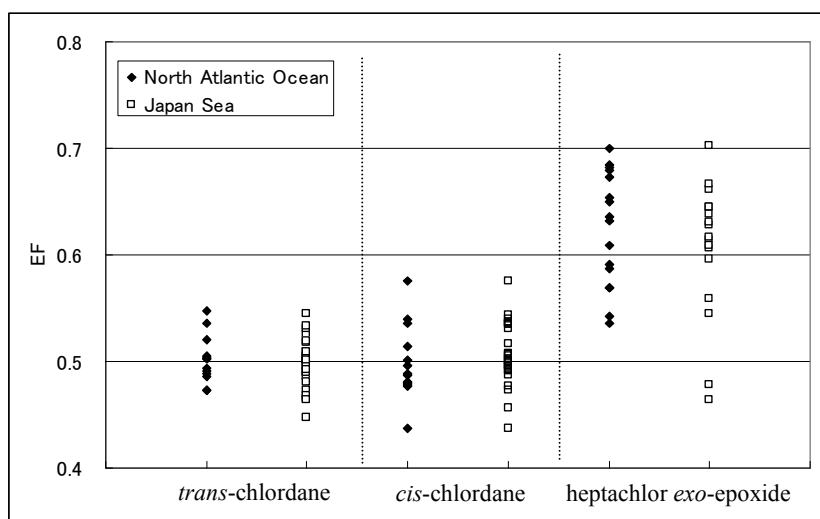


Figure 3. Variation in EFs of pesticides in ocean waters

Values of EF for heptachlor, oxychlordane and *o,p'*-DDD were not obtained because the concentrations were too low or the separation of the two enantiomers was not good.

The EF value for chlordane ranged from about 0.4 to 0.6 (Figure 3). Enantiomer enrichment was observed for both (+) and (-) enantiomers in both samples from the North Atlantic Ocean and the Japan Sea. Karlsson et al. found a gender-specific influence for chlordane in cod liver from the Barents Sea. Males preferentially accumulate (+)-*cis*-chlordane and (+)-*trans*-chlordane, while females have an excess of (-)-*cis*-chlordane and (-)-*trans*-chlordane⁵. Little is known about differences in biological effects between enantiomers of chlorinated pesticides. Further studies about global scale observations of chiral signatures are necessary to identify the environmental behavior of pollutants.

The EFs of the metabolites heptachlor *exo*-epoxide were clearly nonracemic in samples from both the North Atlantic Ocean and the Japan Sea. The average EF values were 0.63 and 0.60, respectively. The enrichment of (+)-heptachlor *exo*-epoxide was found in all samples except for only two samples (Figure 3).

The EF values for *alpha*-HCH in samples from the North Atlantic Ocean ranged from 0.42 to 0.48. And in the case of samples from the Japan Sea, it ranged 0.42 to 0.47.

Figure 4 shows the correlation between EFs and the *alpha*-HCH/ Σ HCH ratios (Σ HCH means the sum of *alpha*-, *beta*-, *gamma*- and *delta*-HCH). The correlation coefficients (*r*) of the North Atlantic Ocean and the Japan Sea are -0.798 and -0.749, respectively. We could see that a high ratio of *alpha*-HCH/ Σ HCH goes in line with a preferential transformation of the (+)-*alpha*-HCH. Besides, the slope of the Japan Sea results (-0.2631) is about three times as low as that of the North Atlantic Ocean data (-0.0782). The transformation tendency of the Japan Sea is more remarkable than that of the North Atlantic Ocean.

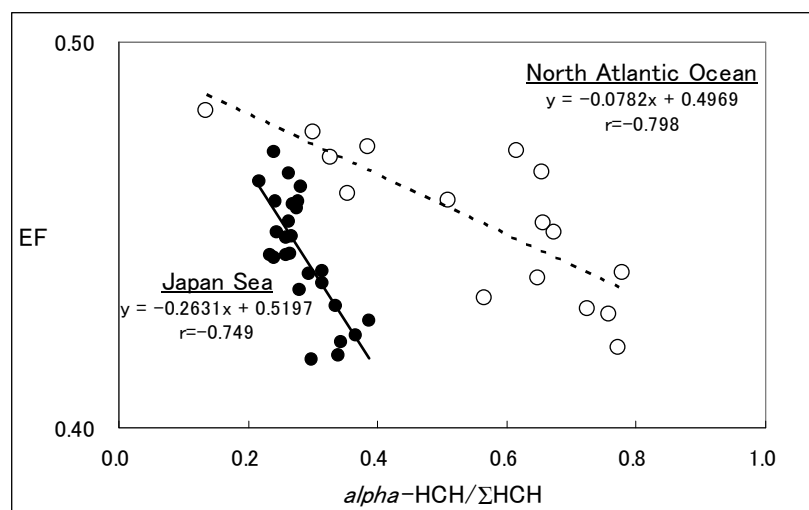


Figure 4. The correlation between EFs and *alpha*-HCH/ Σ HCH ratios

It is interesting to note the difference in HCH composition between two sea areas. Figure 5 shows the SIM mass chromatogram of HCH (average of *m/z* 218.9116 and 216.9145) and its composition in seawater from the North Atlantic Ocean and the Japan Sea. *Beta*-HCH which is the most persistent and shows the lowest volatility is the dominant isomer in the Japan Sea. In contrast, *alpha*-HCH is the dominant one in the North Atlantic Ocean. Explanations for the larger stability of the *alpha*-HCH isomer have been discussed⁶. Our results show that the enrichment of (-)-*alpha*-HCH was found in all samples though the origin of the sea area was different. On the BGB-172 column, (-)-*alpha*-HCH elutes first. Shen et al. found that (-)-*alpha*-HCH is enriched in air from eastern and Arctic Canada, which is opposite to the enantiomeric enrichment at the Pacific Coast⁷. It suggests that the trend of enantiomer fractions depends on the water body be impacted by.

Around 10 million tons of technical HCH were released into the environment between 1948 and 1997⁸. In Japan, production and usage of technical HCH had begun after WWII, and it was banned in 1971. Technical HCH contains *alpha*-: 55-80%, *beta*-: 5-14%, *gamma*-: 8-15%, *delta*-: 2-16%, and *epsilon*-: 3-5%⁸. On the other hand, in Europe the use of technical HCH has been reduced during the 1970s. Lindane (the purified *gamma*-HCH) has

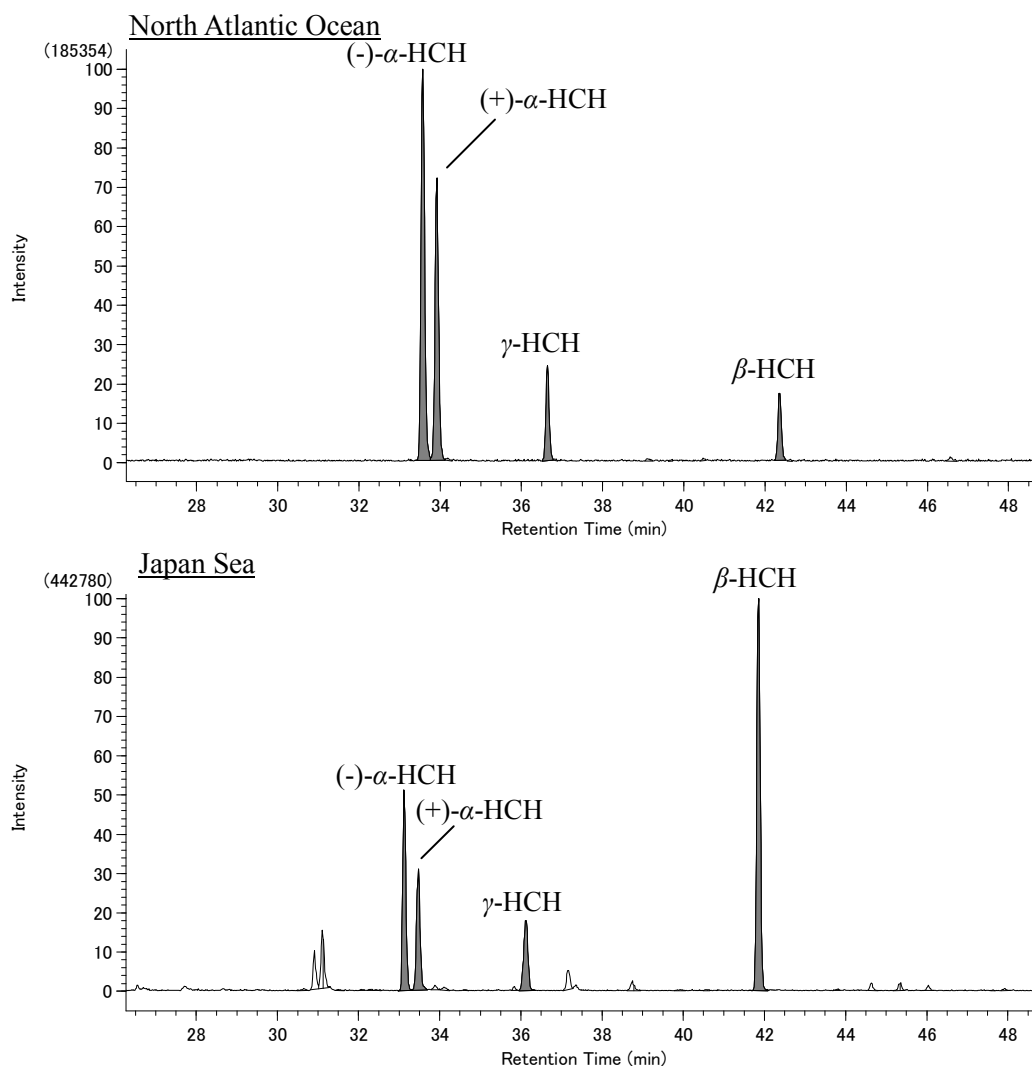


Figure 5. The SIM mass chromatogram of HCH (average of m/z 218.9116 and 216.9145) and its composition in seawater from the North Atlantic Ocean and the Japan Sea

largely replaced technical HCH. And only a small number of countries are still producing lindane⁹. It seems that the difference in transformation tendency between sea areas is reflected by the consumption, production, composition of HCH which have been used. Our result indicates that the use of enantioselective analysis may help estimate chemical sources and microbial transformation processes, and distinguish between transport from current use regions and that from past applications.

References

1. Bidleman T, Falconer R, *Environ. Sci. Technol.*, 1999; 33; 206A-209A
2. Kunugi M, Fujimori K, Nakano T, *Bunseki Kagaku*, 2006; 55; 835-845
3. Hiramoto S, Tsurukawa M, Matsumura C, Nakano T, Kunugi M, *Organohal. Compounds*, 2007; 69 279-282
4. Harner T, Wiberg K, Norstrom R, *Environ. Sci. Technol.*, 2000; 34; 218-220
5. Karlsson H, Oehme M, Skopp S, Burkow I, *Environ. Sci. Technol.*, 2000; 34; 2126-2130
6. Hühnerfuss H, Faller J, König WA, Ludwig P, *Environ. Sci. Technol.*, 1992; 26; 2127-2133
7. Shen L, Wania F, Lei Y, Teixeira C, Muir D, Bidleman T, *Environ. Sci. Technol.*, 2004; 38; 965-975
8. Li Y.F., *The Science of the Total Environment*, 1999;232;121-158
9. Vijgen J, Li Y.F., Forter M, Lal R, Weber R, *Organohal. Compounds*, 2006; 68; 899-904