

D-2.1.1 Studies on Seasonal and Spatial Distributions of Hazardous Chemicals

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Abstract

We developed a continuous-extraction system for sampling of hazardous chemicals in seawater, suitable for mounting on a merchant vessel. By mounting this system in the ferry "Sunflower Ivory", which navigated the Seto Inland Sea from December 1998 to March 2000, we observed the concentrations of hazardous chemicals in seawater a total of 11 times and confirmed the usefulness of the system. Using these observations, we analyzed the dynamics of hazardous chemical pollution in the Seto Inland Sea. In addition, from March 1999, we began to sample the levels of hazardous chemicals in the atmosphere on the Inland Sea. We detected α -HCH and β -HCH in seawater in almost all observations. In particular, β -HCH remained at a comparatively high concentration after September 1999. The spatial and seasonal fluctuations of α -HCH concentrations were greater than those of β -HCH, and the residence time of α -HCH in seawater was short. The abundance ratio of each isomer fluctuated greatly with observation point and time. We detected α -HCH and γ -HCH in the atmosphere in all samples, but β -HCH was undetected in most samples. The concentrations of chlordanes and nonachlores in seawater were under the detection limit on over half of the observations, and the concentrations fluctuated greatly in both seawater and the atmosphere.

The high concentrations of β -HCH observed after September 1999 were caused by typhoons greatly stirring the seawater and redistributing β -HCH accumulated in the sediment. The fluctuations of α -HCH, γ -HCH, chlordanes and nonachlore concentrations in seawater were correlated to the concentrations of each in the atmosphere; thus, the sea-air exchange of these chemicals seems rapid.

From these results, it is clear that frequent observations are indispensable to gain a grasp of the dynamics of marine pollution by hazardous chemicals. By observing their concentrations at various times and locations, it was possible to estimate the dominant origins of HCHs and chlordanes.

Key Words Hazardous chemicals, POPs, Spatial distribution, HCHs, VOS

1. Introduction

Hazardous chemicals in the sea are liable to accumulate in marine ecosystems, and are transported by mechanisms such as oceanic and atmospheric currents. It is important to study these transport mechanisms in the ocean in order to better understand the nature and extent of marine pollution from hazardous chemicals. There has been a lack of observational data on hazardous chemicals in seawater because of the lack of observation platforms. At present, data are only collected once per year, during the same season each year, from each sampling site.

We believe that frequent spatial and seasonal observations are required in order to fully understand the mechanisms of marine pollution. For this purpose, from research carried out through the Global Environment Research Fund between FY 1995 and FY 1997, we developed a continuous-extraction, hazardous chemical sampling system that was installed on ships-of-opportunity. From these ship-of-opportunity observations, we were able to clarify which information is useful to gain an understanding of movements of hazardous chemical marine pollution. However, to extend the area of sea under observation, it is necessary to consider various kinds of merchant vessel and to determine the optimum observation frequency.

2. Method

2.1 Automatic, continuous-extraction, hazardous chemical sampling system for installation on merchant vessels

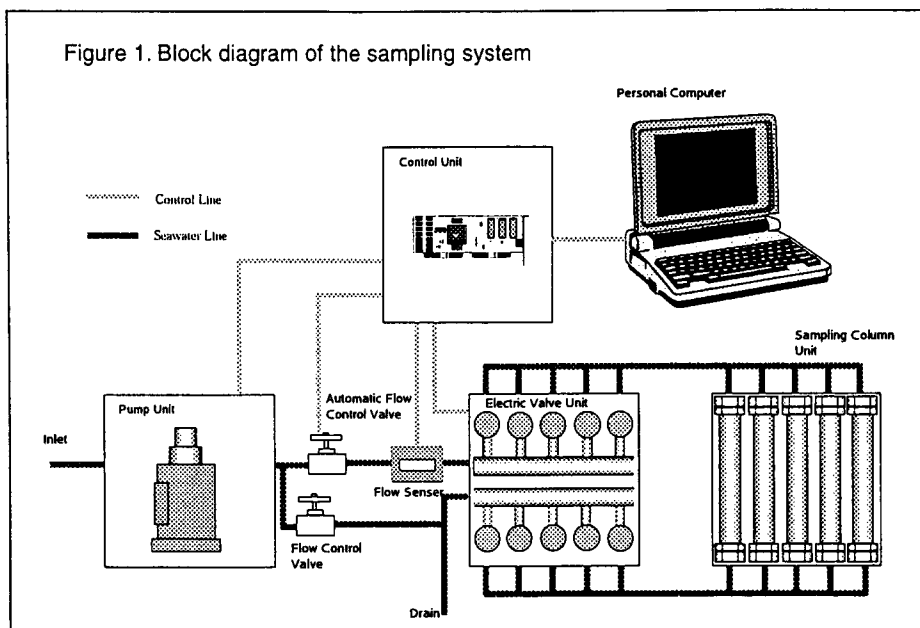
On modern merchant ships, there is limited space, and sufficient area to install conventional sampling equipment cannot be ensured. Thus, it was necessary to develop a small system that could be easily assembled and disassembled. Various factors influence the flow rate of seawater and these fluctuations can disturb an automated system. Therefore, it was also necessary to develop new flow control equipment to be included in the system.

Considering these points, we developed an automatic, continuous-extraction sampling system that was essentially identical to existing sampling systems, but which could be installed in many types of ship such as ferries, cargo boats, container ships, etc. The solid-phase extractor uses polyurethane foam in the columns, the same as that presently used in conventional systems. The basic unit of the system contains 5 columns; these column units are stackable to conserve installation space. The valve control unit and column units are separate, enabling easy installation of the system and ease of assembly and disassembly. These units combined with the pump unit and system control unit constitute the automatic, continuous-extraction sampling system (see system diagram Fig. 1 and photograph Fig. 2). An automatic flow control unit was added in FY 1999.

2.2 Measurements of hazardous chemicals in seawater using a ferry

We installed the automatic, continuous-extraction sampling system in the "Sunflower

Ivory", a ferry that navigates the Seto Inland Sea, and carried out a trial run and the first observations in December 1998. Since then, we have been carrying out observations on both legs of the Osaka Nanko-Beppu route. Observations in FY



1998 were carried out on 14-16 December 1998, and 28-30 January and 1-3 March 1999. In FY 1999, we operated during a total of 8 observation periods: 14-16 April, 26-28 May, 13-15 July, 27-29 September and 15-17 December 1999, and 27-29 January, 28 February-1 March and 27-29 March, 2000. During the observations of 15-17 December 1999, the personal computer for the control broke down, and we were only able to make observations of the atmosphere.

Collection of each water sample was conducted for 50 minutes at a time, a total of 50 L at a flow rate of about 1 L/min. For the collection of hazardous chemicals from the atmosphere, we used middle-volume polyurethane foam samplers (GPS-1, Grasby Co.) containing polyurethane foam pretreated by the EPA method (226-131, SKC Co.). We installed 2 Grasby samplers on the bridge to independently sample the air during the round trip. Using an electric timer, samples were collected for about 10 h at an airflow of about 280 L/min.

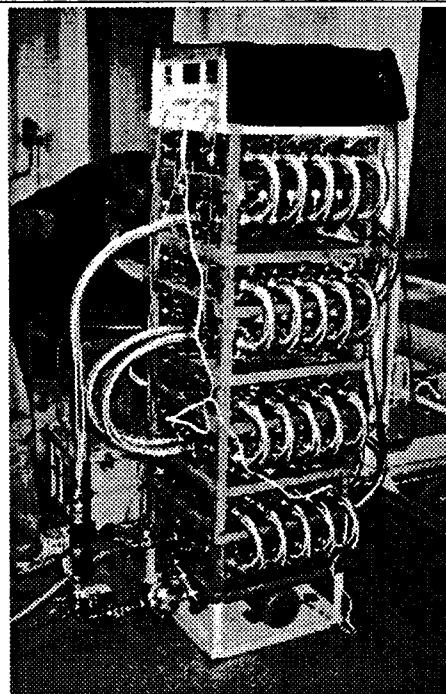


Figure 2. Photograph of the sampling system onboard the ferry "Sunflower Ivory"

3. Results and discussion

3.1 Results

3.1.1 Automatic, continuous-extraction, hazardous chemical sampling system for installation on merchant vessels

It was possible for 2 persons to install or remove the 20 columns in about 2 h. The flexible tubing and ferrules provided excellent watertightness and workability, so there was

no trouble such as water leakage. However, problems remained with flow control. The predetermined flow rate was not always achieved, and sometimes we did not reach the required total flow volume on schedule. To counter this, if the volume of water had not reached 50 L on schedule, we amended the control program en route to finish the sampling after water had passed through the sampler for 55 minutes. Insufficient flow rate caused overloading of the pump, occasionally causing it to overheat and stop in the middle of a sample.

3.1.2 Observations of hazardous chemicals in seawater and atmosphere

The seawater concentrations of α -HCH, β -HCH and γ -HCH from December 1998 to March 2000 were determined from 10 series of observations taken by the ferry "Sunflower Ivory" (Figures 3-12). As shown in these figures, both legs of the 2-day round trip follow almost the same route. Therefore, it was possible to detect short-term variations over 1-2 days. The concentrations of the HCH isomers in seawater ranged from the detection limit to 940 pg/L for α -HCH, from 44 to 1600 pg/L for β -HCH, and from the detection limit to 320 pg/L for γ -HCH. The maximum value of α -HCH was detected at the 5th sampling site (from Shiaku Islands to Hiuchinada) in April 1999; the maximum value of β -HCH was detected at the 1st sampling site (from Osaka harbor to Akashi Channel) in September 1999; and the maximum value of γ -HCH was detected at the 19th sampling site (from near Shodoshima Island to Harimanada) in March 2000. As a general trend, concentrations of HCHs were higher in Osaka Bay and tended to decline toward the west. High concentrations of β -HCH were observed throughout all observation periods after September 1999, but we did not observe the same tendency in α -HCH. The concentrations of γ -HCH were almost all as low as the detection limit, but we detected comparatively high concentrations in May and September 1999, and March 2000, at almost all sampling points. Concentrations of chlordanes and nonachlores were under the detection limits at almost all sampling points, but we occasionally detected higher levels. t-Chlordane and t-nonachlore were detected in May and September 1999 at almost all sampling points; concentrations were especially high in September. We did not detect any great short-term variability in concentrations.

From March 1999, we began observations of α -HCH, β -HCH and γ -HCH (Fig. 13), as well as t- and c-chlordane and t- and c-nonachlore (Fig. 14) in the marine atmosphere. Levels of α -HCH in the marine atmosphere ranged from 30 to 310 pg/m³; levels of β -HCH ranged from the detection limit to 65 pg/m³; and levels of γ -HCH ranged from 12 to 93 pg/m³. The fluctuation in concentrations between the legs of each round trip was small. The concentrations of HCH isomers on each trip were: $\alpha > \gamma > \beta$. The level of β -HCH was below the detection limit for all observations, except for September 1999 and March 2000. A characteristic feature of the marine atmosphere was the relatively high concentrations of chlordanes and nonachlores, which were below the detection limits in seawater. Concentrations were especially high in September 1999 where, except for c-nonachlore, concentrations were around 200 pg/m³.

Explanatory
notes for Figure
3 to 12

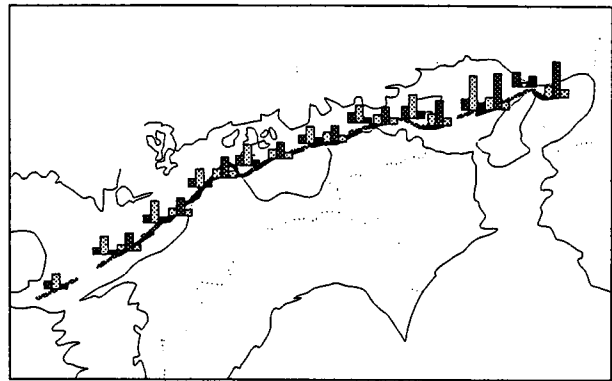
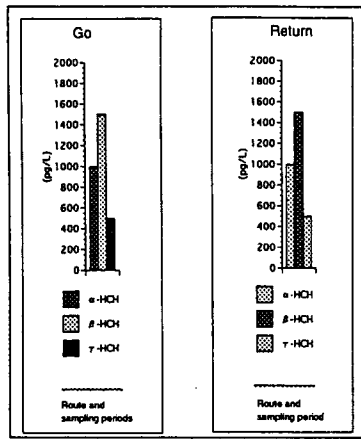


Figure 3. Concentrations of HCHs in seawater observed December 19-21, 1998

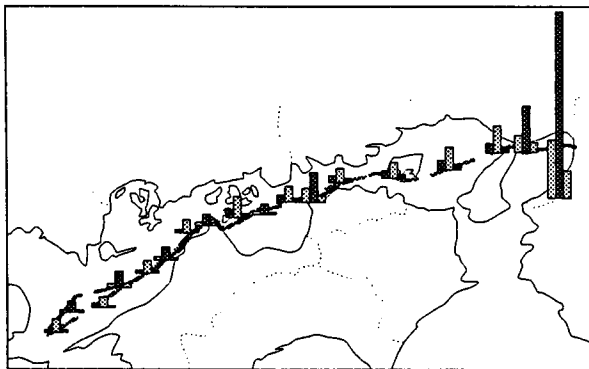


Figure 4. Concentrations of HCHs in seawater observed January 28-30, 1999

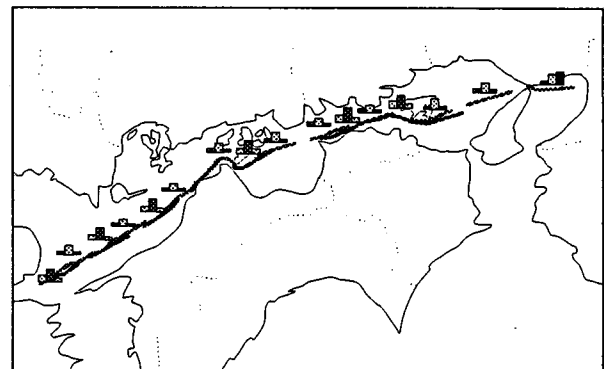


Figure 5. Concentrations of HCHs in seawater observed March 1-3, 1999

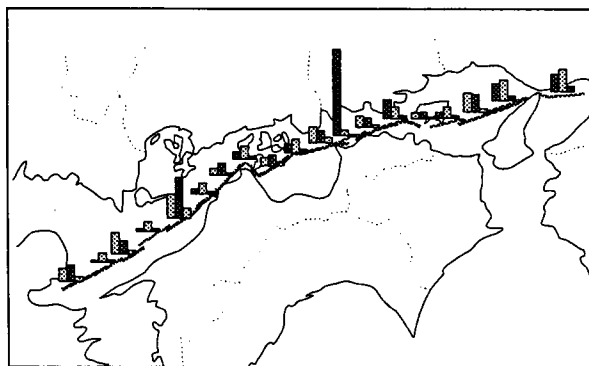


Figure 6. Concentrations of HCHs in seawater observed April 14-16, 1999

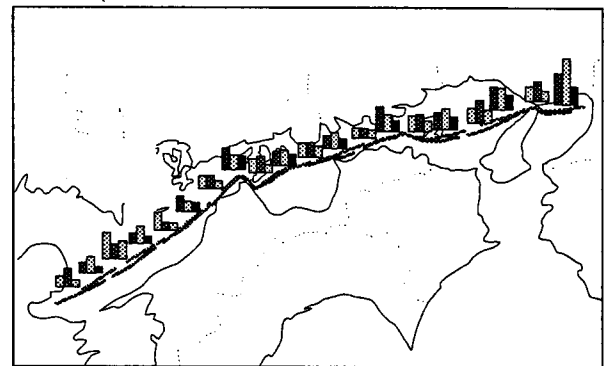


Figure 7. Concentrations of HCHs in seawater observed May 26-28, 1999

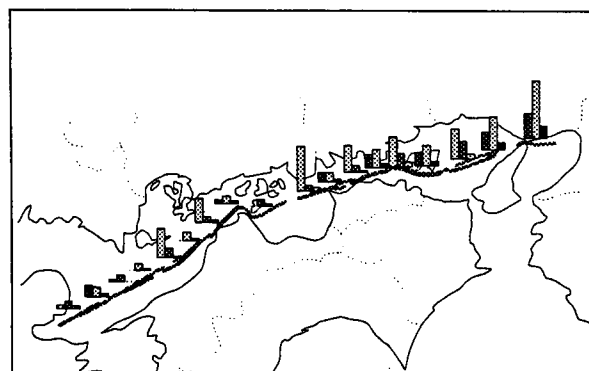


Figure 8. Concentrations of HCHs in seawater observed July 13-15, 1999

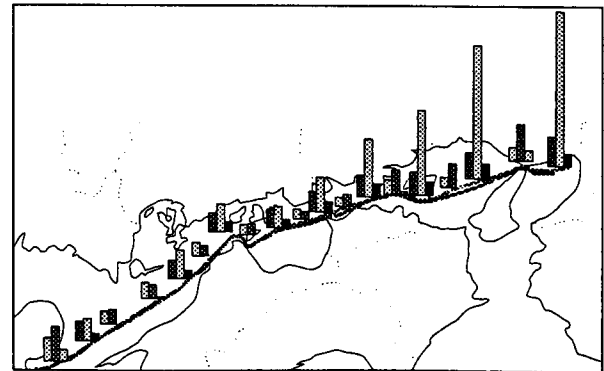


Figure 9. Concentrations of HCHs in seawater observed September 27-29, 1999

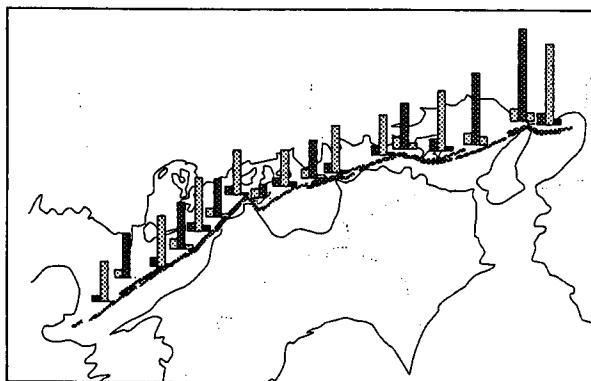


Figure 10. Concentrations of HCHs in seawater observed January 27-29, 2000

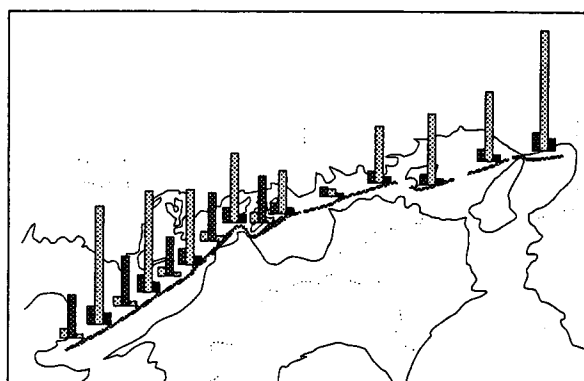


Figure 11. Concentrations of HCHs in seawater observed February 28-March 1, 2000

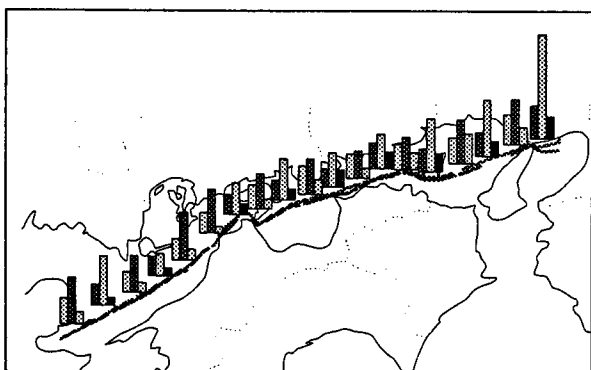


Figure 12. Concentrations of HCHs in seawater observed March 27-29, 2000

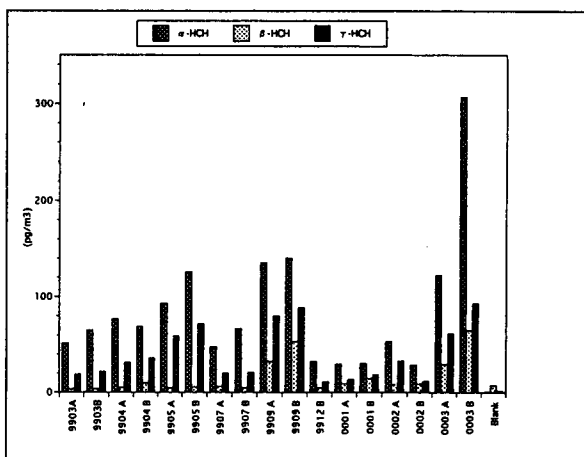


Figure 13. Concentrations of HCHs observed in the atmosphere

3.2 Discussion

3.2.1 Automatic, continuous-extraction, hazardous chemical sampling system for installation on merchant vessels

The sampling system we developed in this study worked smoothly. Nevertheless, many adjustments need to be implemented before our system can be used for general sampling of seawater in the future. The automatic flow controller we tried was usually able to adequately handle the set flow rate; however, it did not function correctly when the flow rate was extremely low due to factors

such as blockage in the columns. In these cases, there was the additional problem of the pump overheating and stopping. A countermeasure to this problem would be to install 2 pump systems and run them alternately. One of the reasons the columns did not handle the flow rate may be due to the polyurethane foam filling. Therefore, we also need to re-consider the filling methods, including the size and volume of the polyurethane foam.

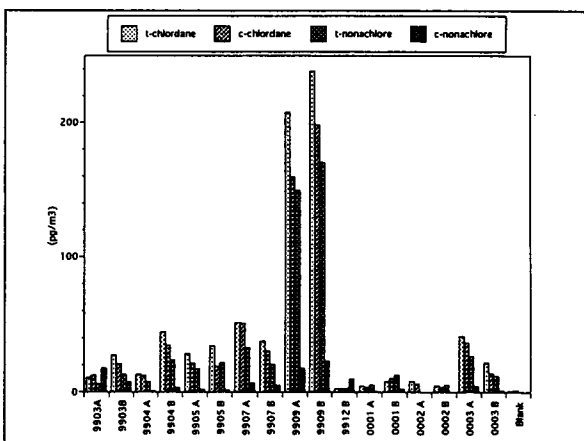


Figure 14. Concentrations of chlordanes and nonachlores observed in the atmosphere

3.2.2 Hazardous chemicals in the seawater and atmosphere

It was warm over the Seto Inland Sea during both of our observation periods in the winter of 1998/99, and there was seldom. Therefore, the variations in our winter observations were not due to temperature. Because it had rained in the Osaka district the day prior to our observations in January 1999, we think that the high concentration of β -HCH detected in Osaka Bay was due to inflow from rivers stirring up the sediment since the collection was kept by stoppage of ship right before.

There was a large difference in the seawater concentrations of β -HCH observed before and after September 1999 (Fig. 15). Each HCH isomer showed a high concentration in September 1999, from Osaka Bay through to Hiuchinada. In addition, apart from a few vacant points, β -HCH showed continuously high concentrations in January, February, and March 2000. The HCH concentration in the atmosphere was also high in September 1999 and March 2000 (Fig. 13). Many typhoons developed in FY 1999; during September, typhoons No. 16 and No. 18 directly crossed the Seto Inland Sea, and typhoon No. 17 stole past Kyushu. Our September observations were carried out right after the passage of typhoon No. 18. The typhoons seem to have had a large effect as we observed high concentrations of α -HCH, γ -HCH, chlordanes and t-nonachlore in the atmosphere (Figs. 13 and 14). Although atmospheric α -HCH levels were somewhat higher in September 1999 than in other months, they were not especially high. On the other hand, the high levels of t-chlordane and t-nonachlore in September 1999 were clearly atypical. The high concentrations of these compounds detected in the atmosphere and seawater were probably the result of the typhoons that passed over Japan in September 1999. However, despite the increased concentrations of t-chlordane and t-nonachlore in the atmosphere in March 2000, there was no clear change in the seawater concentrations. It seems that the sea-air exchange needs windy conditions or sufficient time. We also observed that, in spite of the higher concentration of α -HCH in the atmosphere on the return journey in March 2000, the concentration of α -HCH in the seawater did not fluctuate much.

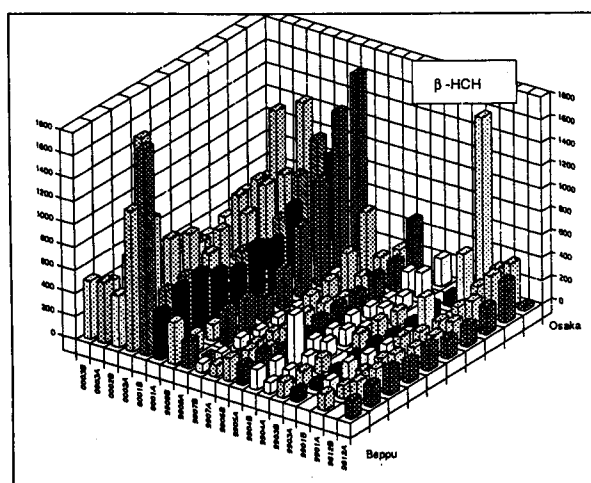


Figure 15. All concentrations of β -HCH observed in the water column

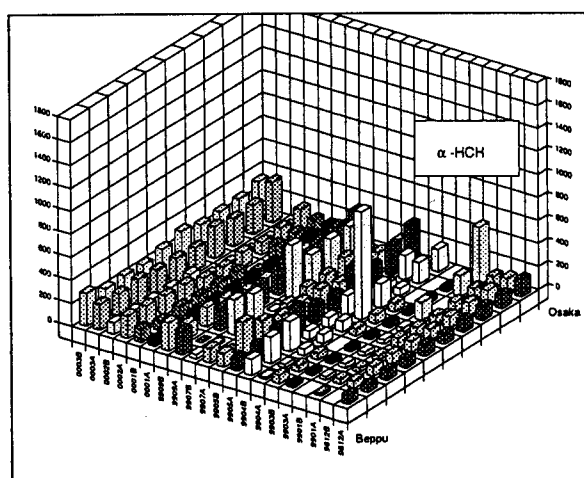


Figure 16. All concentrations of α -HCH observed in the water column

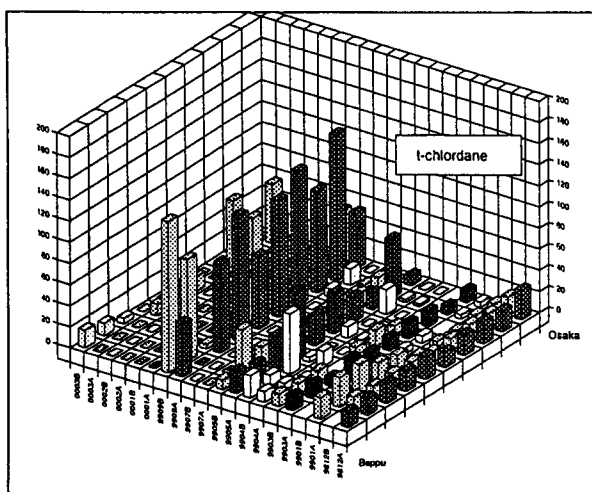


Figure 17. All concentrations of t-chlordane observed in the water column

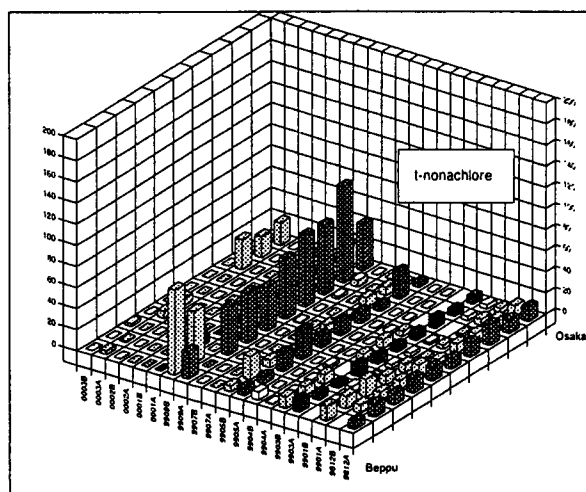


Figure 18. All concentrations of t-nonachlore observed in the water column

The concentration of α -HCH in the atmosphere appears to be correlated with the mean value of α -HCH in the seawater (correlation coefficient $r = 0.69$; Figure 19). Nevertheless, factors such as time delay should be considered in a more detailed analysis.

β -HCH was usually not detected in the atmosphere. However, we observed concentrations well over the detection limit in September 1999 and March 2000, so it must also be considered that a portion of the β -HCH in the seawater may have passed through the atmosphere from a remote source such as the continental atmosphere. In January and February 2000, the concentration of β -HCH in seawater remained high in spite of no β -HCH being observed in the atmosphere. Moreover, it seems that the high concentration in seawater continued to March 2000. The β -HCH in seawater does not appear to settle to the sediment for several months.

In March 2000, we detected high concentrations of α -HCH and γ -HCH in the atmosphere; chlordanes and nonachlores were also high. In this season, yellow sand (kosa aerosol) from continental Asia blows over western Japan and was observed in Kyushu on March 26, 2000, the day prior to the observation. The high concentrations of these compounds in the atmosphere seem to be correlated with this effect.

In summary, the main source of β -HCH in seawater was the sediment; β -HCH accumulated in the sediment returns to the seawater after the sea bottom has been greatly disturbed by typhoons, etc. Once resuspended in the water column, β -HCH remains at a high concentration for many months. Although the concentration of β -HCH in the atmosphere may rise due to the effects of typhoons and the influx of yellow sand, the concentrations of the a or g isomers were always higher.

On the other hand, the main source of α -HCH, γ -

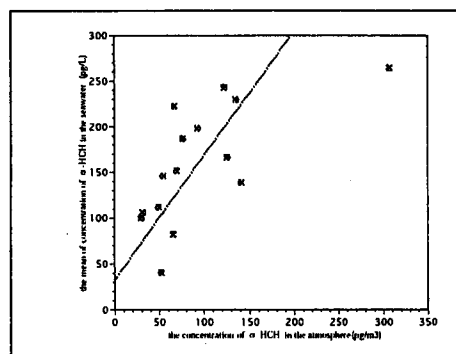


Figure 19. Correlation between α -HCH in the atmosphere and mean α -HCH in the water column

HCH, chlordanes and nonachlores in the seawater is via the atmosphere. When the atmospheric concentrations of γ -HCH, chlordanes and nonachlores were high, these were high in the seawater. However, there was a time lag between the concentration peak in the atmosphere and in the seawater. This is because it depended on sea-air exchange rate. High concentrations of α -HCH and γ -HCH were observed in the atmosphere in March 2000. It seems that the sea-air exchange needs more than 1 day to reach equilibrium, because high concentrations of these compounds were not observed in the seawater on the return leg of the journey. In September 1999, high concentrations were observed in both the atmosphere and ocean. A number of typhoons hit in September, and typhoon No. 18, which passed by right before our observations, seems to have provided sufficient sea-air exchange. The residence time in seawater of these hazardous chemicals, including α -HCH, seems to be short; even if high concentrations appear in the water column, they do not remain for long. However, the movement of α -HCH appears more complex than that of the other compounds; although we observed unusually high concentrations of α -HCH, in many cases the cause is not yet fully understood.

4. Conclusion

The automatic, continuous-extraction, hazardous chemical sampling system for installation on merchant vessels proved very useful for analyzing movements of hazardous chemical marine pollution. The origin of β -HCH in seawater is mostly the result of the resuspension of β -HCH accumulated in the sediment, and partly from rivers and via the atmosphere. The source of α -HCH, γ -HCH, chlordanes and nonachlores is mainly from the atmosphere and partly from rivers, precipitated by the rain. Therefore, by observing these 3 kinds of chemicals, including their isomers, it is possible to carry out a detailed analysis of the origins and mechanisms of marine pollution.

5. References

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Figure captions

Figure 1. Block diagram of the sampling system

Figure 2. Photograph of the sampling system onboard the ferry "Sunflower Ivory"

Figure 3. Concentrations of HCHs in seawater observed December 19-21, 1998

Figure 4. Concentrations of HCHs in seawater observed January 28-30, 1999

Figure 5. Concentrations of HCHs in seawater observed March 1-3, 1999

Figure 6. Concentrations of HCHs in seawater observed April 14-16, 1999

Figure 7. Concentrations of HCHs in seawater observed May 26-28, 1999

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Figure 15. All concentrations of β -HCH observed in the water column

Figure 16. All concentrations of α -HCH observed in the water column

Figure 17. All concentrations of t-chlordane observed in the water column

Figure 18. All concentrations of t-nonachlore observed in the water column

Figure 19. Correlation between α -HCH in the atmosphere and mean α -HCH in the water column