

D-2-1 Studies on seasonal and spatial distribution of hazardous chemicals

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Abstract

Hazardous chemicals in the sea are liable to be accumulated in marine ecosystem, and are transported by such mechanisms as oceanic and atmospheric currents. It is important to study these mechanisms in the ocean in order to understand the nature and extent of marine pollution from hazardous chemicals.

A continuous-extraction sampling system for hazardous chemicals was developed and set up on a ferry (Kurosiwo). The extraction rate of this system, tested in a laboratory and in situ, was found to be over 90%. The detection limit in 50 L of extracted seawater was about 5 pgL⁻¹ for chlordane and 10 pgL⁻¹ for HCHs.

More than 70 samples were collected on the ferry (Kurosiwo) route from Osaka to Naha, [Japan. Hazardous chemicals in the samples were extracted by acetone and concentrated to 1 mL, then determined by the GC/MS-SIM method. Levels of organic halide chemicals such as trans-chlordane ranged from the detection limit to 30 pgL⁻¹, while α -HCH and β -HCH varied from 30 to 400 pgL⁻¹.

Key Words Hazardous Chemicals, POPs, East-Asian Seas, Spatial distribution, VOS

1. Introduction

Hazardous chemicals in the sea are liable to be accumulated in marine ecosystems, and are transported by such mechanisms as oceanic and atmospheric currents. It is important to study these mechanisms in the ocean in order to 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 observational platforms. At present, data are only collected once per year, during the same season each year, for each sampling site.

We believe that frequent spatial and seasonal observations are required in order to understand marine pollution mechanisms. For this purpose, we have been developing over the past 3 years a continuous-extraction sampling system for hazardous chemicals, using ships-of-opportunity.

2. Method

A continuous-extraction sampling system for hazardous chemicals was tested on a ferry (Kurosiwo). We evaluated 3 solid-phase extraction methods: using XAD4, polyurethane foam and Empore extraction disks. XAD4 and polyurethane foam were rinsed with acetone in a soxhlet extraction apparatus for 24 h. Empore extraction disks were rinsed with acetone on a filter holder. Acetone extraction removed all contaminant chemicals from the polyurethane foam but not enough from the XAD4. Empore disks had an insufficient flow rate and filtration volume. Therefore, a procedure using polyurethane foam for the determination of hazardous chemicals in seawater was proposed. A diagram and photograph of the continuous-extraction sampling system are shown in Figs.1 and 2, respectively. The latest system can set up 20 columns and change the columns automatically under computer control.

Hazardous chemicals were analyzed by the GC/MS-SIM method. The chemicals were extracted using acetone in a soxhlet extraction apparatus for 24 h, and condensed by nitrogen flow to about 20mL. The condensed sample was added to 500 mL of distilled water with 25 g sodium chloride in a separating funnel, mixed well, extracted by hexane twice, and further dehydrated by sodium sulfate. Final samples were concentrated to 1 mL by Kuderna-Danish evaporative concentrator and

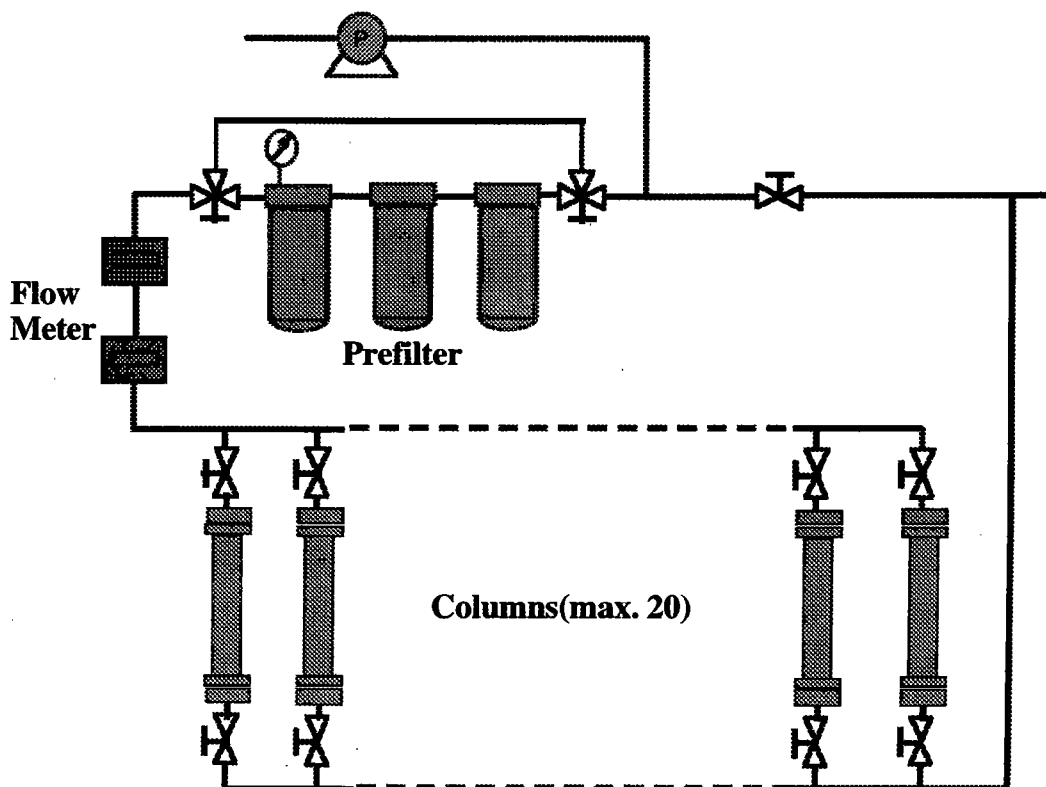


Fig.1 Schematic diagram of the continuous-extraction sampling system

HCB¹³C₆ and d₁₂-fluoranthene were added as internal standards. Samples were analyzed by GC/MS-SIM using a JEOL JMS-700 mass-spectrometer.

3. Results

We tested the recovery rate of this system in a laboratory and in situ. In the laboratory, 2 columns were connected in series, and a standard solution added to the first column. Tap water filtered with activated charcoal was then passed through the columns. The flow rate was 0.5 to 2 L/min. and total volume was 50 to 100 L. In the field, the 2 columns were again connected in series, and hazardous chemicals were sampled with a solid-phase extractor. The recovery rate in the field, calculated as the amount in the first column as a percentage of the total amount in both columns, was over 90%. The detection limit from 50[±] samples of seawater was about 5 pgL⁻¹ of chlordanes and 10 pgL⁻¹ of HCHs.

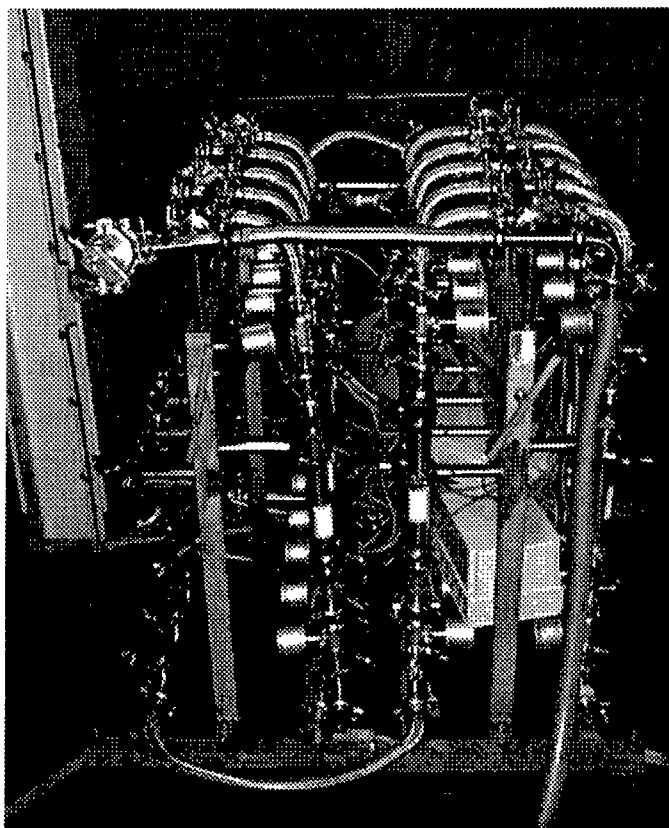


Fig.2 Photograph of the sampling system on the ferry.

More than 70 samples were collected on the ferry route from Osaka to Naha during December 5-7, 1996, and March 29-31 and September 18-25, 1997. Organic halide chemicals were detected in every sample. We made quantitative analyses of the following chemicals: chlordanes, nonachlore, HCB, HCHs and DDTs.

We found levels of trans-chlordane ranging from the detection limit to 30 pgL⁻¹, and α -HCH and β -HCH levels of 30 to 400 pgL⁻¹ in every sample using this method (Figs. 3-6).

The concentration of β -HCH was highest in the Seto Inland Sea, especially in Osaka Bay, and lower in the Pacific Ocean near Shikoku and Kyushu. Lowest values were found at the boundary of the Kuroshio Current, and concentrations became higher again near the Amami and Okinawa islands. The distribution of α -HCH was more complex. In December 1996, its concentration was lower than that of β -HCH at every station, and its spatial distribution was the same as that of β -HCH. However, in March 1997, its concentration and spatial distribution were quite different. The concentration of α -HCH was almost the same or higher than that of β -HCH, especially in the Seto Inland Sea where it was highest. In September 1997, the concentration of α -HCH was high in the Seto Inland Sea, highest near Kyusyu, and low in other areas.

Trans-chlordane levels were low and varied randomly, although in the 1997 sampling periods, the concentration of trans-chlordane was higher than in December 1996. Cis-chlordane levels were

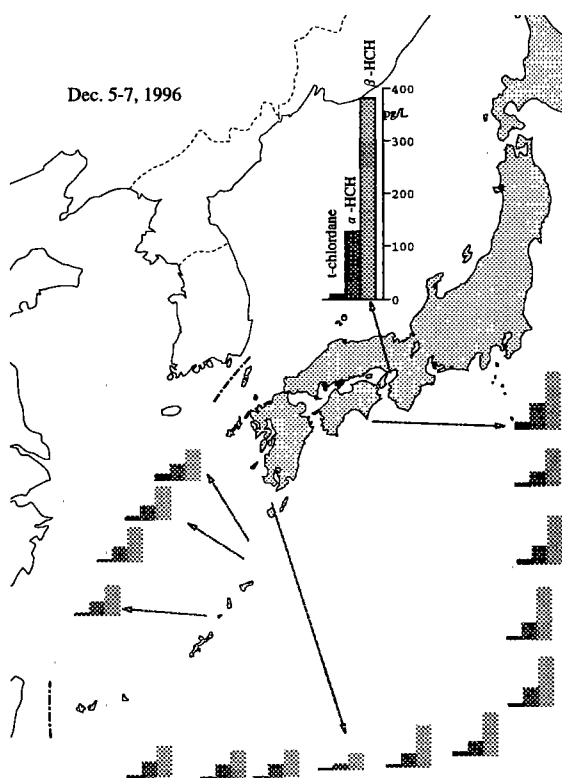


Fig.3 Concentrations of three hazardous chemicals at sampling sites on the ferry route, December 5-7, 1996.

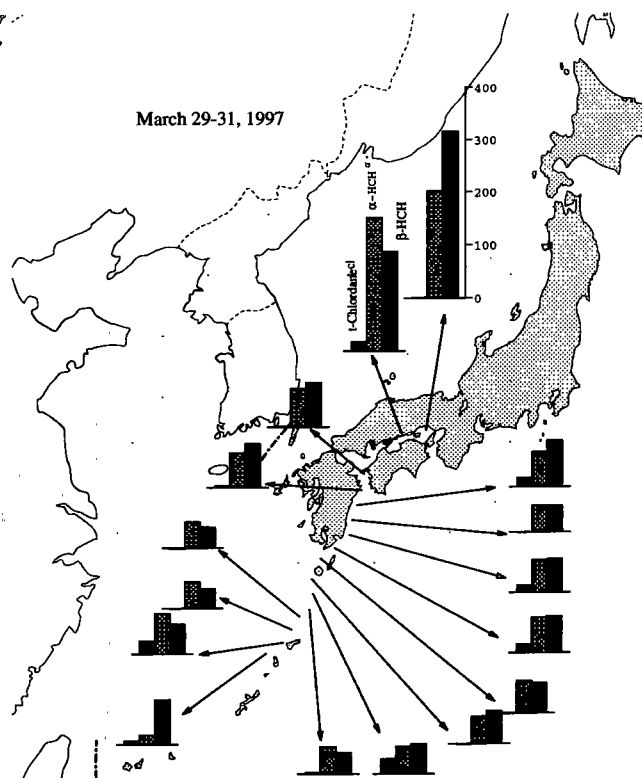


Fig.4 Concentrations of three hazardous chemicals at sampling sites on the ferry route, March 29-31, 1997.

below the detection limit in December 1996, but were detected some point in 1997.

Nonachlore species were not detected in most samples in December 1996, but trans-nonachlore, ranging from the detection limit to 25 pgL⁻¹, was found in the 1997 samples.

DDTs and HCB were not detected.

4. Discussion and conclusion

The concentration and spatial distribution of β -HCH were similar throughout the sampling period. However, the concentration of α -HCH in March 1997 was more than twice that in December 1996. Before and during the March sampling period, there was a moderate gale; a deepening low-pressure area passed through the Pacific seaboard of Japan from the East China Sea at that time. The concentration of α -HCH in September 1997 was higher near Kyushu than in the Seto Inland Sea. Immediately before the sampling, Typhoon No.19 attacked Kyushu, and there was a downpour, resulting in many suspended particles such as volcanic ash and grass being transported to the sea.

The differences in observation results may be due to differences in source and transport process. The melting points of α -HCH and β -HCH are 160°C and 315°C, respectively. Generally, the concentration of α -HCH in the atmosphere is high. However, in freshwater β -HCH levels are higher than those of other isomers. Therefore, when a moderate gale blew from China and Japan to

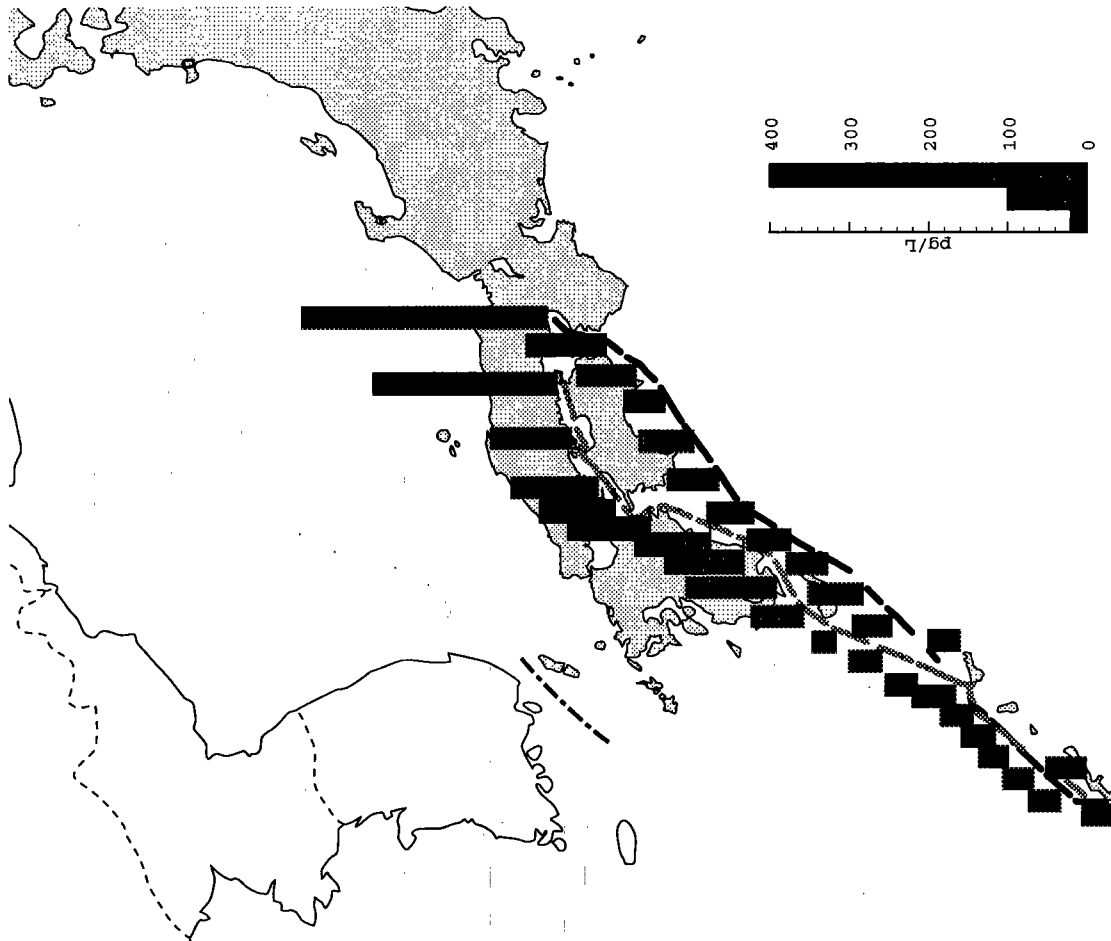


Fig. 6 Concentration of β -HCH at sampling sites on the ferry route, September 18-25, 1997.

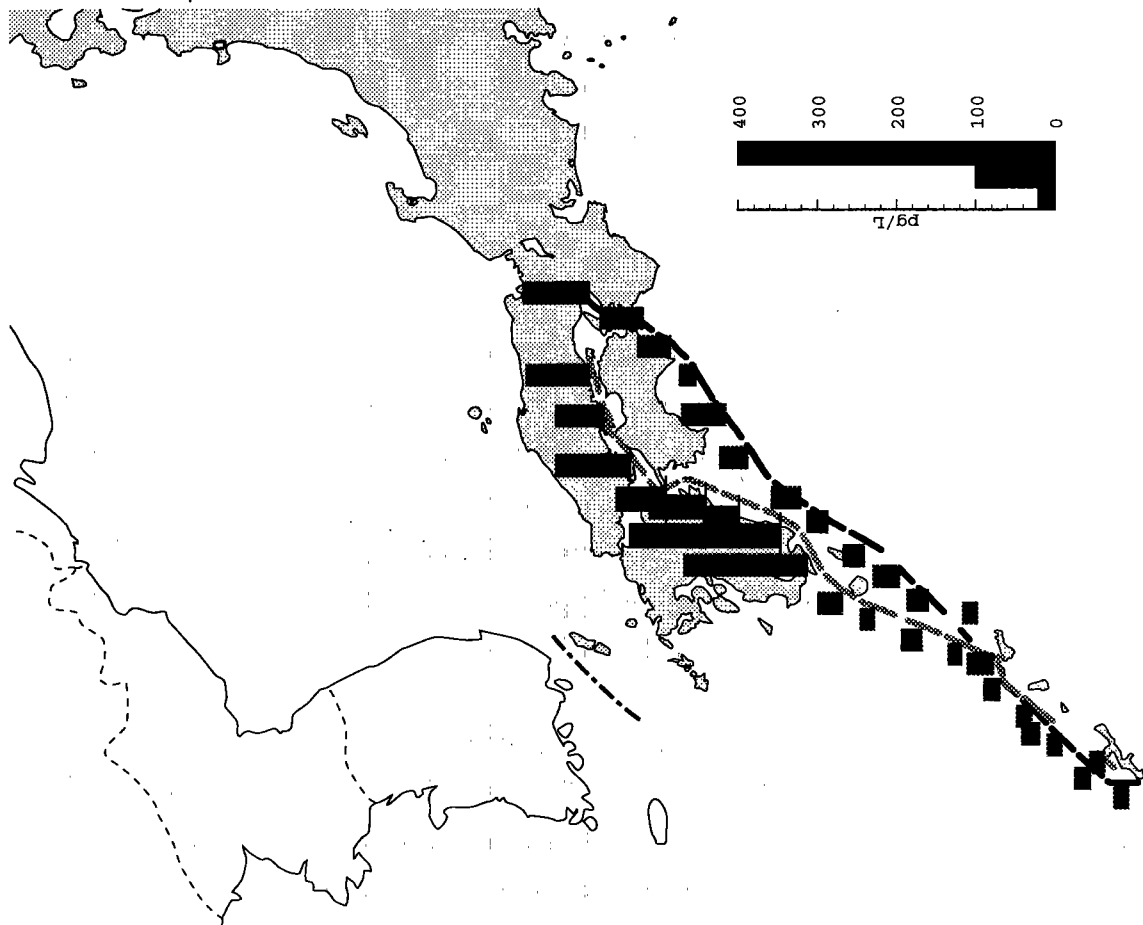


Fig.5 Concentration of α -HCH at sampling sites on the ferry route, September 18-25, 1997.

the East China Sea and Pacific seaboard of Japan in March 1997, α -HCH from the atmosphere was added to the seawater. Again in September, heavy rain washed the α -HCH from the air into the ocean.

The reason for the uniform distribution of β -HCH may be that sediments are the main sources of

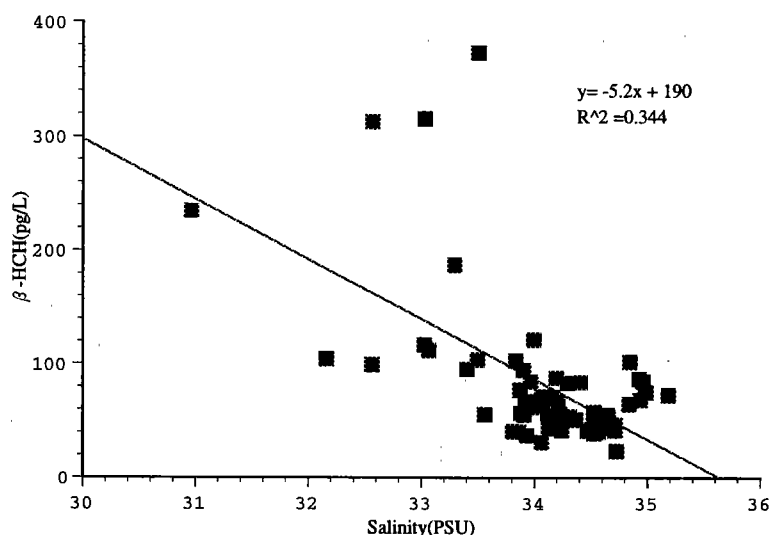


Fig. 7 Relationship between β -HCH and salinity.

β -HCH in seawater around Japan. Thus, there would not be a relationship between the concentration of β -HCH and weather conditions or with freshwater. However, the concentration of β -HCH was negatively correlated with salinity (result of subtheme D-2-4). Thus, the chemical was supplied in freshwater from Changjiang. But the coefficient of correlation was low(fig.7), and high

concentrations found in Osaka Bay were not correlated with salinity. Therefore, the β -HCH in Osaka Bay was not supplied from freshwater.

The continuous-extraction sampling system using voluntary observational ships proved very useful for analysis of movements of hazardous-chemical marine pollutants. The movements of hazardous chemicals differed according to their components, depending on weather conditions and sources.

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