

DEVELOPMENT OF OBSERVATION TECHNOLOGY FOR GLOBAL-SCALE MARINE POLLUTION WITH HAZARDOUS CHEMICALS DEPLOYED ON VOLUNTARY OBSERVATION SHIPS

Kunugi M¹, Fujimori K², Nakano T²

¹Environmental Chemistry Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Japan; ²Environmental Safety Division, Hyogo Prefectural Institute of Public Health and Environmental Science, 3-1-27, Yukihirocho, Suma-ku, Kobe, Japan

Introduction

Hazardous chemicals in the sea are liable to accumulate in marine ecosystems, and are transported by mechanisms such as oceanic and atmospheric currents¹⁻³). 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. On May 2001, Persistent Organic Pollutants (POPs) Convention was adopted in Stockholm, and taken effect on May 2004. We believe that frequent spatial and seasonal observations are required in order to fully understand the mechanisms of marine pollution with hazardous chemicals such as POPs. For this purpose, we developed a continuous-extraction, hazardous chemical sampling system that was installed on merchant vessels⁴⁻⁶).

Method

To know the occurrence and behavior of POPs and endocrine disrupting chemicals in marine environment, 3 types of automated sampling systems were developed and installed in the very large crude carrier transporting from the Persian Gulf to Japan, the bulk carrier from Australia to Japan, the container ship between Japan and USA, and the cruising vessel around the world. A photo of the one of automatic sampling systems is shown in Fig. 1.

Collection of each water sample was conducted for 200 minutes at a time, a total of 100 L at a flow rate of about 0.5 L/min, by solid phase extraction method. Solid phase extraction columns were containing a poly-urethane foam (PUF) and active carbon fiber filters(ACF). And we spiked ¹³C stable-isotope standard mixture sample into a sampling line when sample collection was started at all sampling periods. Collection samples were conserved in the freezer

at -20°C. Hazardous chemicals were extracted by the Soxhlet extraction with acetone (24hr) and dichloromethane (24hr) from these columns. POPs were determined by high resolution gas chromatograph/high resolution mass spectrometry (HRGC/HRMS, JMS-700).

Water temperature, pH, chlorophyll-A and conductivity were also monitored. We have been observing hazardous chemicals in sea water around the world from 2001 using these systems. Typical



Figure 1 Photograph of marine pollution observation system on board the bulk carrier.

Sample preparation and analysis

sampling positions were shown in Fig. 2.

Results and Discussion

Recovery rates were tested as follow; two PUF and ACF columns connected in series and spiked ^{13}C stable-isotope standard mixture sample on the PUF of 1st column, then 100L of tap water passed through at a flow rate of about 0.5l/min. Recoveries are shown Table 1. The recoveries from the 1st column were approximately 100% and those from the 2nd column were almost zero. Recoveries of surrogate compounds labeled with ^{13}C tested using real seawater in the field are shown in Table 2. The recoveries from the 1st column were 30 to 80% and those from 2nd column were 0%. Since this seems to be due to the incomplete extraction from the ACF, a further extraction from the ACF with dichloromethane by Soxhlet extraction was conducted. Even by this extraction the recoveries did not reach 100%, but fairly good improvement was observed, and this extraction was adopted. Washing twice the PUF with acetone and the ACF with dichloromethane by Soxhlet extraction for each 24hr before use was very effective to decrease the blank.

One hundred liters of seawater was passed through PUF and ACF columns and was analyzed by HRGC/HRMS (SIM). We detected hexachlorocyclohexanes (HCHs) from almost samples. And we detected chlordanes and nonachlors from many samples. Concentrations of HCHs were very different in sea area. In general, HCHs in the Southern Hemisphere were low in the Northern Hemisphere. Between Japan and Australia the concentration of β -HCH gradually

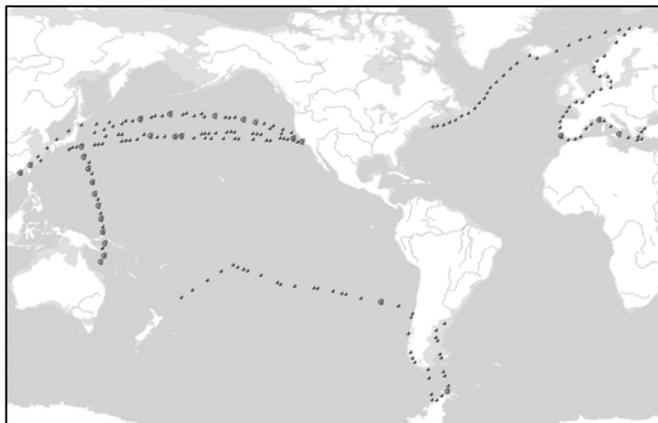


Figure 2 Sampling positions at Dec. 2003 by the bulk carrier, March and Sep. 2005 by the container ships, and Feb. to March, 2004 and May to June, 2005 by the cruising vessels.

Table 1 Recovery tests of HCHs, aldrin, dieldrin, chlordane, nonachlor PUF and ACF column for solid-phase extractor (%)

Column	1 st	2 nd
α -HCH	110	2
β -HCH	115	0
γ -HCH	111	0
aldrine	128	0
dieldrine	104	0
t-chlordane	113	29
t-nonachlor	121	30
c-nonachlor	101	35

Table 2 Recovery tests of surrogate compounds labeled with ^{13}C of PUF and ACF column for solid-phase extractor in situ (%)

Sample No.	No.3		No.19	
	1 st	2 nd	1 st	2 nd
α -HCH	34	0	28	0
β -HCH	79	0	73	0
γ -HCH	42	0	46	0
t-chlordane	56	0	34	0
t-nonachlor	68	0	47	0
c-nonachlor	69	0	64	0

Sample preparation and analysis

decreased from Japan to the equator and was constantly low at pg/l level from the equator to the Australia. The emission source of β -HCH is suspected to be Asian countries. In the South Pacific, the concentration of β -HCH gradually increased from New Zealand to Tahiti Islands, but those of α -HCH and γ -HCH decreased. β -HCH was detected near Tahiti Islands and central part of the South Pacific, nevertheless α -HCH and γ -HCH were not detected or detected only at very low concentration. From east part of the South Pacific to the offing of Chile, α -HCH and γ -HCH were detected, but β -HCH could not be detected. From the Patagonia fjord to the Antarctic Ocean, α , β , γ -HCH were detected. Then, from the Atlantic Ocean side of the Drake Channel to the offing of Argentina, α -HCH gradually decreased from south to north. We think that these distributions of HCHs depend on the temperature of seawater and distance of the emission source and sink of hazardous chemicals.

Conclusion

We developed a marine pollution observation system, suitable for mounting on a merchant vessel. By mounting these systems in bulk carriers, a container ship and a cruising vessel, navigated around the world. We observed the concentration of hazardous chemicals such as persistent organic pollutants, endocrine disrupting chemicals, organotin compounds, poly-aromatic hydrocarbons, and heavy metals in seawater a total of 10 tomes and confirmed the usefulness of the system. We detected α -HCH, β -HCH, γ -HCH, TBT, nonylphenol, parental PAHs in seawater in almost all observations.

From these results, it is clear that global scale observations are indispensable to gain a grasp of the dynamics of marine pollution by hazardous chemicals.

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