

ENVIRONMENTAL EVALUATION IN ARIAKE BAY, BASED ON ORGANOCHLORINE PESTICIDE RESIDUES, HCB, HCHS AND DDTs AMONG THE PERSISTENT ORGANIC POLLUTANTS (POPS)

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Introduction

Ariake Bay is one of the major inland seas with many fishery resources in Japan. The seaweed plants were damaged in the autumn of 2000 in this Bay. The other marine productivity, such as fish, shellfishes and others was also decreased in the period of the 1960s and from the 1980s to the recent years. Societal concern about this problem has become high in Japan. Choi et al., (2003)¹ reported the historical distribution of dioxins and dioxin-like PCBs in sediment cores of Tokyo Bay, Japan. This study would provide the valuable information to understand the behavior of persistent organic pollutants (POPs) caused from organochlorine pesticides, such as hexachlorobenzene (HCB), dichlorodiphenyl trichloroethane and its metabolites (DDTs) and isomers of hexachlorocyclohexane (HCHs) in the environment from the point of view of environmental pollution in Ariake Bay, Japan. The concentration and composition of PCBs and PAHs in sediment and some biota taken from Ariake Bay, Japan has been reported previously^{2,3}. In this study, HCB, HCHs and DDTs of POPs including their isomers, degradations or metabolites in sediment cores were determined to understand their historical status of contaminations.

Materials and Methods

We analyzed the POPs in order to increase precision and sensitivity for chemical analysis using high-resolution gas chromatography coupled with a high-resolution mass spectrometric detector (HRGC-HRMS). In terms of assessing the levels of contamination, recovery of POPs from environmental samples is important⁴. A sediment core, which was a cylindrical sample with a diameter of 11cm and a length of 350cm was obtained from the northern part of Ariake Bay, the Yanagawa coast (St.2; N33° 05' 477" and E130° 23' 431") on 01 November 2005. Surface sediment samples were also collected at 2 other stations, St.1 (N33° 09' 123" and E130° 21' 482") and St.3 (N33° 05' 370" and E130° 24' 735") in the Ariake Bay using an Ekman-Berge dredge. Approximately 30g of core samples were homogenized after air-dried at room temperature and extracted with 300ml acetone for 16 hrs by Soxhlet. The POPs were eluted and subsequently treated with a florisil cartridge and passed through a cartridge of active carbon. HRGC-HRMS ($R \geq 10,000$) system conditions are as follows: A sample injection separated an autosampler onto a 30m ENV-8MS column (i.d. 250 μ m, film thickness 0.25 μ m : Kanto Chemical Co., Japan). The temperature program for the column began with a 0.5min held at 120°C, followed by a 10°C/min ramp-up to 180°C, then a rate of 4°C/min to 210°C held for 12min and a rate of 10°C/min to the final

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temperature of 300°C. The sediment cores were analyzed for ^{210}Pb , ^{226}Ra and ^{137}Cs by direct gamma assay using a high purity germanium detector (Canberra; BE5025). The sedimentation rate and radiometric dates were calculated from the ^{210}Pb records based on the Constant Initial Concentration model.

Results and Discussion

The age determination with ^{210}Pb isotope revealed that the sedimentary rate in Ariake Bay (St.2) is 0.35cm per year. The maximum concentration of HCB, HCHs and DDTs was presented during the late 1960s. The results showed that the relatively high concentrations of HCB, HCHs and DDTs in the core ranged from 0.03-2.65, 0.01-2.01 and 0.01-1.16ng/g dry wt, respectively. The concentration profiles of HCB, HCHs and DDTs were similar to those of Tokyo Bay, Japan⁵. These substances' concentration began suddenly increasing in the early 1950s, showing the peak near 1970 and rising again toward upper sediment core. In this study, although the river flow on St.1 is the highest amount of inputting to the Ariake Bay, the concentration of total POPs in surface sediments collected from St. 3 was approximately 2-fold higher than the St.1. This implied that the pollution source might be emitted nearby St.3.

Hexachlorobenzene (HCB) The total concentration of HCB in sediment cores of Ariake Bay was the predominant residue among the POPs as shown in Figure1. The concentration of HCB began abruptly rising at 20cm depth, the corresponding years from 1950 to 1953. Then the maximum concentration of HCB was found from 1967 to 1970 (2.6ng/g dry wt), indicating that the large amounts of HCB discharge occurred in this period. The data observed showed that maximum concentration investigated in the cores of Ariake Bay was higher than that of Tokyo Bay, Japan, where industrial pollution is heavily progressing⁵. Emission sources of HCB in sediment cores were considered as follows; impurities in pesticides such as pentachlorophenol (PCP), pentachloronitrobenzene (PCNB), dimethyl-tetrachloroterephthalate (TCTP), incineration of HCB containing waste from tetrachloroethylene production and incineration of municipal solid waste⁶. Homologue profiles of PCP samples revealed that the most abundant impurity of dioxin was OCDD⁷. The vertical profile of the HCB is shown corresponding to that of OCDD.

Hexachlorocyclohexanes (HCHs) The HCH residues are among the most widely distributed and frequently detected organochlorine contaminants in the environment. The concentrations of HCHs in sediment cores of Ariake Bay also showed an increasing trend from the early 1950s and a peak in the late 1960s. The compositions of HCH isomers exhibited similar distribution patterns as shown in Figure 2. Interestingly, production of HCH in Japan was highest in this period and the trend of the residues level investigated in biota was dependent on its usage⁸. Concentrations and compositions of HCH isomers were found to be in order $\alpha\text{-HCH} > \beta\text{-HCH} > \gamma\text{-HCH} > \delta\text{-HCH}$ in almost all cores except surface sediment core. Decreasing concentration after early 1970s might be reflected to that prohibited the production and use of HCHs in the early 1970s in Japan. The nationwide HCHs usage in Japan was approximately 400 metric tons⁸. This is an extremely large amount when compared with DDTs and PCBs in Japan. Therefore, it can be assumed that HCHs contamination

might have occurred through the use of technical-grade HCHs until the early 1970s. The decreasing trend for composition of α isomer and the increasing trend for the β isomer after they were officially banned in the early 1970s were observed in upper sediment cores. This implies that HCHs contamination in upper cores might have originated from a relatively remote source or long-time accumulation after dispersing.

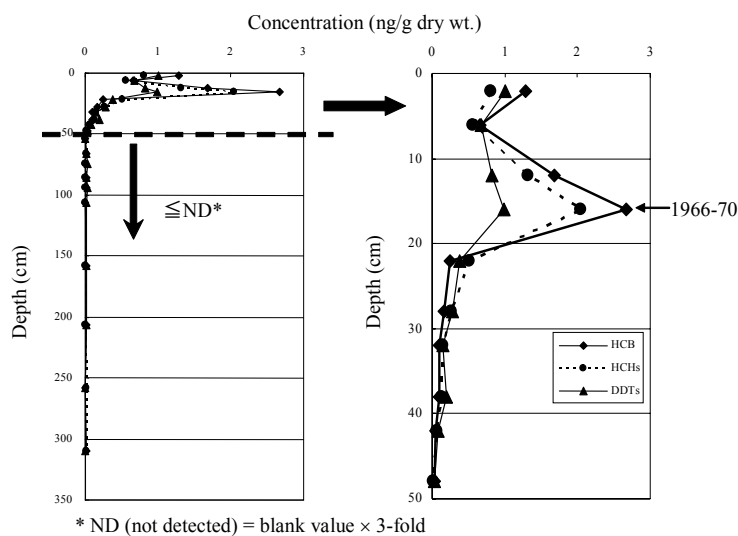


Figure 1 Vertical profiles of HCB, HCHs and DDTs in sediment cores from Ariake Bay, Japan

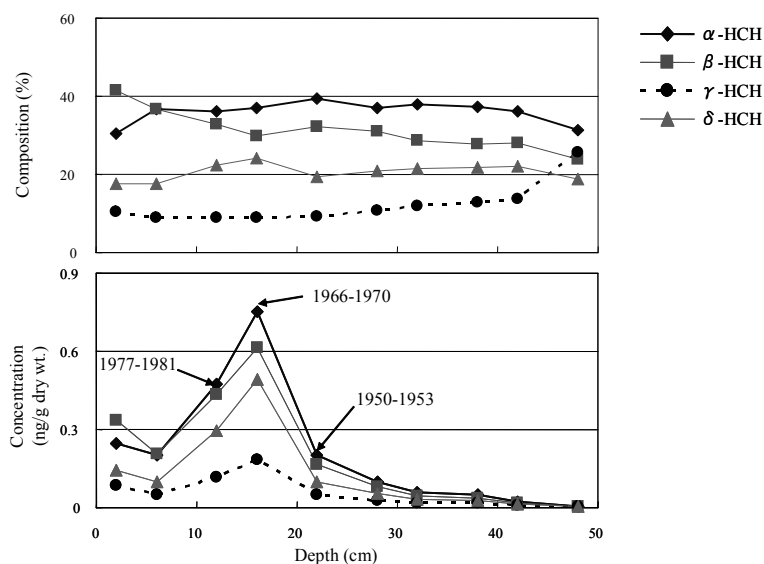


Figure 2 Concentrations and composition profiles of HCH isomers in sediment core from Ariake Bay, Japan

DDTs The vertical concentrations of DDT isomers are shown in Figure 3. Concentrations and compositions of DDT isomers were found to be in order DDE > DDD > DDT (including o,p'- and p,p'-) in almost all cores. Particularly, the concentration of p,p'-DDE dominated in most of all cores. The Ariake Bay seemed to be relatively less contaminated with DDT compounds than other areas^{5,9}. The composition of organochlorines and their metabolites can provide some information for a better understanding of the origin and transport of these

contaminants in the environment. The ratios of (DDE+DDD)/ Σ DDTs in the sediment cores ranged from 0.65 to 1.00 in Ariake Bay, Japan. The ratios were declining toward down cores (Figure 3), which it could be explained that DDT emission occurred in the past input. According to record of the Ministry of Agriculture, Forestry and Fisheries, Japan, the banned pesticides were laid under the ground, only one location in Fukuoka Prefecture. Therefore, it can be assumed as a possibility that it might be reflected by laid pesticides under the ground somewhere after banned them in 1970s. However, it should need more evidences and information about their transportation and sedimentation into sediment to confirm the possibility.

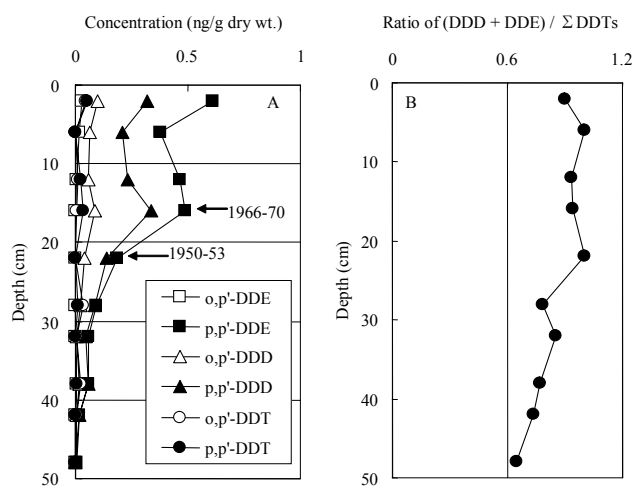


Figure 3 Vertical concentrations (A) of DDT isomers and ratio (B) of (DDD+DDE)/ Σ DDTs

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References

1. Choi, JW, Fujimaki S, Kitamura K, Hashimoto S, Ito H, Sakurai T, Suzuki N, Nagasaka H, Tanabe K, Sakai SI. *Organohalogen Comp* 2003;61:119.
2. Nakata H, Miyawaki T, Sakai Y. *J Environ Chem* 2002;12:127. (in Japanese)
3. Nakata H, Sakai Y, Miyawaki T, Takemura A. *Environ Sci Technol* 2003;37:3513.
4. Scott WC, Dean JR. *J Environ Monit* 2003;5:724.
5. Shimizu J, Yamao S, Nosaka T, Noguchi K, Mine M, Matsumoto K, Oichi K, Tsutsumi K, Miyamoto T, Ikeda Y. *Report of Hydrographic and Oceanographic Researches* 2005;41:35. (in Japanese)
6. Hirai Y, Kato T, Takatsuki H, Sakai S. *J Environ Chem* 2001;11:793. (in Japanese)
7. Masunaga S, Takasuga T, Nakanishi J. *Chemosphere* 2001;44:873.
8. Loganathan BG, Tanabe S, Goto M, Tatsukawa R. *Environ Pollut* 1989;62:237.
9. Peng X, Zhang G, Zheng L, Mai B, Zeng S. *Geochemistry: Exploration, Environment, Analysis* 2005;5:99.