FATE OF DDTs, PCBs AND CHLORDANE COMPOUNDS IN THE ANTARCTIC MARINE ECOSYSTEM

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Abstract: Bioaccumulation and environmental behavior of DDTs, PCBs and chlordane compounds in the antarctic marine ecosystem under the fast ice were studied. Many samples such as seawater, benthic invertebrates, fishes, Weddell seal *etc.*, were collected at the Tottuki Point where pollution by human activities has been most unlikely and from Syowa Station where some pollution is likely because of the research activities. In seawater samples, the concentration of PCBs (sum of several tens of individual chlorinated biphenyls) was found to be higher than that of ΣDDT (*p, p'*-DDE+ *p, p'*-DDT), but reverse in organisms. ΣChlordane (sum of several chlordane compounds and metabolites) concentrations showed the middle level between PCBs and ΣDDT in both seawater and organisms. In higher trophic level organisms, the bioconcentration factors (BCFs) increased, and variable compositions of PCBs and chlordane compounds were also found. Concentration levels of ΣDDT and PCBs in the antarctic marine ecosystem were about two orders of magnitude lower than those in the western North Pacific. The low levels are most likely attributable to the low concentration of these chemicals in seawater under the antarctic fast ice, which might be caused by the specific environmental characteristics in the Antarctic relating to its locality being far away from the intensive regions of industrial and human activities on the earth, the ice covering and the high bioproductivity during the austral summer.

1. Introduction

There are some reports on DDT and PCB residues in the antarctic biota since 1966, but they are mostly restricted to a fragmentary knowledge because of the limited collection of samples and the inadequate technique of chemical analysis (HIDAKA and TATSUKAWA, 1981). One of the present authors (HIDAKA) collected a wide range of samples during the wintering of the 22nd Japanese Antarctic Research Expedition (JARE-22, 1980–1982), for the purpose of describing a whole aspect of the environmental dynamics of chlorinated hydrocarbons (CHs) in the Antarctic (Fig. 1, HIDAKA, 1982). In this paper, we discuss the bioaccumulation and environmental behavior of DDTs, PCBs and chlordane compounds in the marine ecosystem of the Antarctic.

2. Materials and Methods

Samples used in this study were collected mainly around Syowa Station during the wintering of JARE-22 (Jan. 1981–Jan. 1982, Fig. 1). Seawater samples were

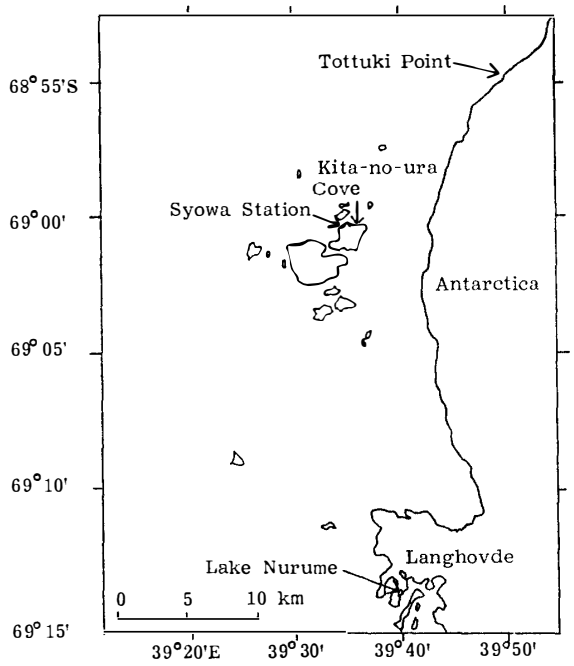

Fig. 1. Map showing the collection sites around Syowa Station (69°00'S, 39°35'E) in 1981–1982. Near Syowa Station: Air, ice (iceberg), seawater, benthic invertebrates, fish. Tottuki Point: Snow, seawater, sea ice, benthic invertebrates, fish, Weddell seal. Lake Nurume: Snow, seawater. Mizuho Station (70°42'S, 44°20'E): Snow.

pumped up by suction from under the fast ice and then passed through Amberlite XAD-2 resin columns for collecting CHs. The CHs adsorbed on the resin were eluted with ethanol and stocked in bottle at Syowa Station. Benthic invertebrate and fish samples were collected by cage trap and fishing using a fillet of endemic fish as bait. All biological samples were kept in a freezer at −18°C or lower until analysis. The Weddell seal (*Leptonychotes weddelli*) was electrocuted at the Tottuki Point and shipped to the laboratory of Ehime University in a frozen condition. After dissection, weight of each organ and tissure was measured accurately in order to obtain the burdens and concentrations of CHs on a whole body basis. Other details of sampling techniques were shown elsewhere (HIDAKA, 1982).

CHs in crude extracts from seawater were transferred to hexane, and then cleaned up by the fuming sulfuric acid and finally determined by gas chromatograph-mass spectrometer equipped with a selected-ion monitor (GC-MS-SIM). ΣDDT and PCBs in biological samples were analyzed by the alkaline alcohol digestion method of WAKIMOTO *et al.* (1971), in which DDTs were measured as a single *p,p'*-DDE peak since *p,p'*-DDT is converted into *p,p'*-DDE during the alkaline alcohol digestion. The analysis of chlordane compounds in fish and seal was carried out as follows: extraction with acetone and hexane, fat removal by acetonitrile-hexane partitioning, clean up by Florisil® column chromatography and determination by GC-ECD (electron-capture gas chromatograph) and GC-MS-SIM. The detection limits of seawater (about 500 *l*) and biological samples (about 50 g) were 0.2 pg/*l* and 0.01 ng/g

for ΣDDT, 3 pg/*l* and 0.01 ng/g for PCBs, and 0.6 pg/*l* and 0.005 ng/g for Σchlordane, respectively. The other details of chemical analysis were described previously (TANABE *et al.*, 1983 for DDTs and PCBs in seawater, SUBRAMANIAN *et al.*, 1983 and HIDAKA *et al.*, 1983 for DDTs and PCBs in fish and Weddell seal respectively, and KAWANO *et al.*, 1984 for chlordane compounds).

3. Results and Discussion

3.1. Possibility of the environmental pollution by the human activities at Syowa Station

The Antarctic, which has been intended for conducting scientific research only and not for mining and manufacturing industrial activities, is one of the most suitable regions for monitoring the global pollution by man-made pollutants. Because the human activities in scientific research there may possibly cause localized pollution by CHs, when the antarctic environmental pollution is studied, it is necessary to make a clear distinction between the pollution by the human activity in the Antarctic and the global pollution caused from outside the Antarctic. So we examined the effect of the human activities at Syowa Station concerning the environmental pollution with CHs.

When the CHs concentration in the same-aged and same-season samples of benthic fish, *Trematomus bernacchii*, is compared between two different localities, the levels of ΣDDT and PCBs were found to be about two times ($P<0.01$) and thirty times ($P<0.001$) higher near Syowa Station than at the Tottuki Point, respectively (Figs. 2A, 2B). The Tottuki Point is located about 13 km northeast on the windward of Syowa Station (Fig. 1). MORIWAKI and YOSHIDA (1982) reported that the water current under the fast ice around Syowa Station was mainly tidal (max flow rate 7.0 cm/s) and the flow from north to south (from the Tottuki Point to Syowa Station) was somewhat stronger than the opposite flow. Considering this, it can be safely concluded that the Tottuki Point is still unpolluted by the human activities at Syowa Station.

The data on snow, seawater and benthic invertebrates also suggest that Syowa Station might have been one of the sources of CHs pollution (HIDAKA and TATSUKAWA, 1983). It is assumed that PCB and DDT present in the scientific materials used for the human activities at Syowa Station, have leaked into the environment and concentrated in the benthic biota.

Therefore, the samples collected near Syowa Station are unsuitable for the environmental discussion from a global viewpoint. The following topics are dealt with, mainly on the samples from the Tottuki Point.

3.2. The chlorinated hydrocarbon concentrations in a benthic fish, Trematomus bernacchii, in correlation with body size and their seasonal variation

The Antarctic is an appropriate field for the study of bioaccumulation because of the comparatively stable and simple structure of the marine ecosystem without industrial and agricultural sources of CHs.

Body length and ΣDDT concentration in *T. bernacchii* were positively correlated, whereas no such correlation was found in the case of PCBs and Σchlordane (Fig. 2). A decrease of lower chlorinated biphenyls and an increase of higher ones with increase

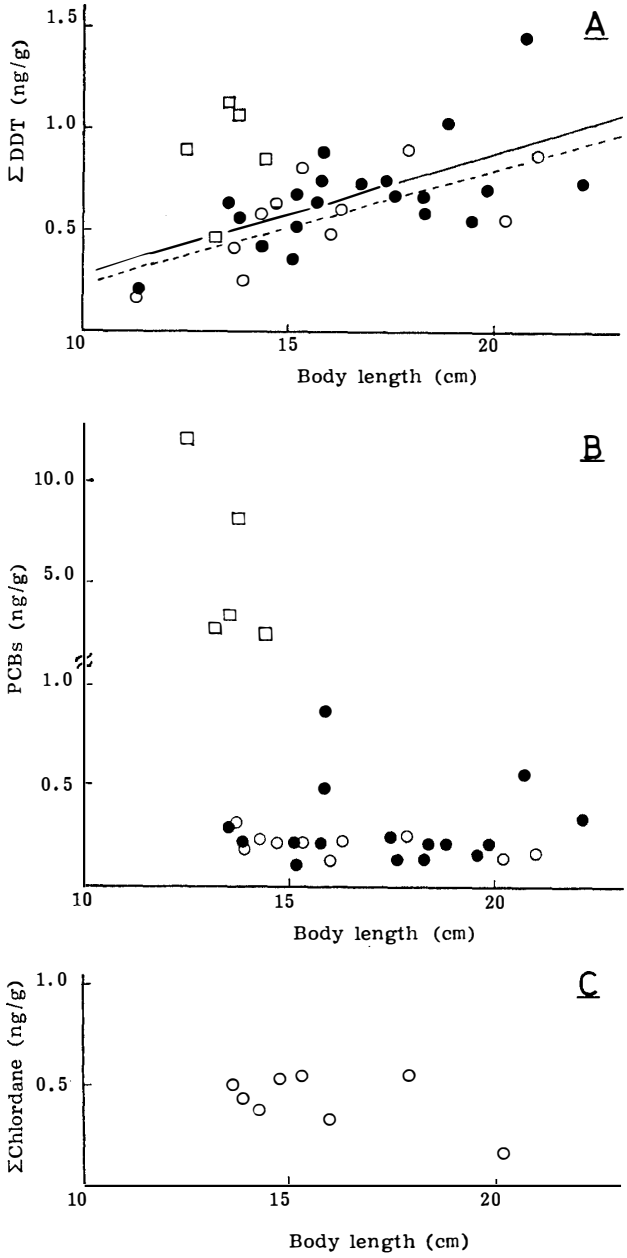

Fig. 2. Concentrations of Σ DDT (A), PCBs (B) and Σ chlordane (C) in wet whole body of the antarctic benthic fish, Trematomus bernacchii.

●—●: *Tottuki Point (July 16–September 21, 1981)*
○···○: *Tottuki Point (December 3–23, 1981)*
□: *Near Syowa Station (January 15–March 22, 1981)*
Data on Σ DDT and PCBs were cited from HIDAKA *and* TATSUKAWA *(1983), and Σ chlordane data were from* KAWANO *et al. (in preparation).*

of body size were noted in the antarctic fish, *Pagothenia borchgrevinki* (SUBRAMANIAN *et al.*, 1983). Some of the biodegradable and less lipophilic members of PCBs and chlordane compounds seem to reach the equilibrium concentration level at an earlier stage of fish growth.

Although many authors have reported the seasonal variation of CHs in fishes (ROBINSON *et al.*, 1967; HANSEN and WILSON, 1970; REINERT and BERGMAN, 1974), the residual concentrations of the CHs among the samples collected in different seasons did not differ significantly in this study (Figs. 2A, 2B). Large numbers of specimens used here were immature except for larger ones over about 18 cm in body length. According to the examination on the relationship between body length and body weight (the degree of fatness) of this fish ($n=149$), no correlation was found in the different sampling seasons and locations. The insignificant seasonal variation of CHs in the antarctic fish might be caused by the small fluctuation of the water temperature in the Antarctic Ocean.

3.3. Bioaccumulation of CHs in the Weddell seal

We have intensively studied the bioaccumulation of CHs in marine mammals using striped dolphins, *Stenella coeruleoalba* (TANABE *et al.*, 1981a, b, 1982a, 1984). Referring to this knowledge, the following observations were made on the bioaccumulation of CHs in the Weddell seal (HIDAKA *et al.*, 1983).

More than 99% of whole body burdens of ΣDDT and PCBs were retained in blubber and muscle of the Weddell seal. The transplacental transfer of these chemicals was estimated to be less than 2% of the mother's burden. The lactational transfer was estimated to be 40–50% for ΣDDT and 20–30% for PCBs from mother to newborn pup. These transfer ratios in the Weddell seal were lower than those in striped dolphin (more than 70%, TANABE *et al.*, 1981b).

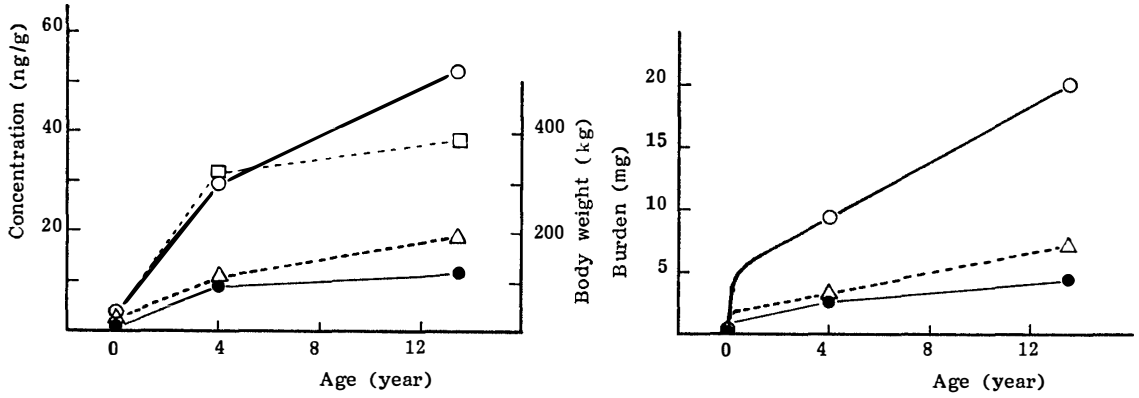

Fig. 3. Age trend of whole body concentrations (ng/g on wet weight basis) and burdens (mg) of ΣDDT, Σchlordane and PCBs in the Weddell seal.
○, ΣDDT; △, Σchlordane; ●, PCBs; □, body weight (kg).

Whole body burdens and concentrations of CHs increased with age (Fig. 3). However, these increasing rates were different according to the chemical species, that is, the slope of ΣDDT is steeper than those of PCBs and Σchlordane. This is due to the less biodegradable property of DDTs as compared with PCBs and chlordane compounds which are included in some biodegradable components of food of the Weddell seal (SUBRAMANIAN *et al.*, 1983; KAWANO *et al.*, in preparation).

3.4. *Bioaccumulation in the antarctic marine ecosystem*

Concentrations of CHs in an estimated antarctic marine food chain and possible bioconcentration factors (BCFs, concentration ratios of CHs in organisms to those in seawater) are shown in Table 1. The concentrations and BCFs of these pollutants increased in predators of higher-trophic level, where the order of BCFs was found to

Table 1. Concentrations and bioconcentration factors (BCFs) of chlorinated hydrocarbons in the marine food chain of the Antarctic Ocean.

		Σ DDT	PCBs	Σ Chlordane
Sea water	Conc. (μg/*l*)	1.0×10^{-6}	5.4×10^{-5}	5.4×10^{-6}
Krill	Conc. (ng/g)	2.6×10^{-2}	2.1×10^{-2}	6.1×10^{-2}
	BCF	2.6×10^{4}	3.9×10^{2}	1.1×10^{4}
Fish	Conc. (ng/g)	6.3×10^{-1}	2.5×10^{-1}	4.3×10^{-1}
	BCF	6.3×10^{5}	4.7×10^{3}	7.9×10^{4}
Seal	Conc. (ng/g)	5.2×10	1.2×10	1.9×10
	BCF	5.2×10^{7}	2.2×10^{5}	3.5×10^{6}

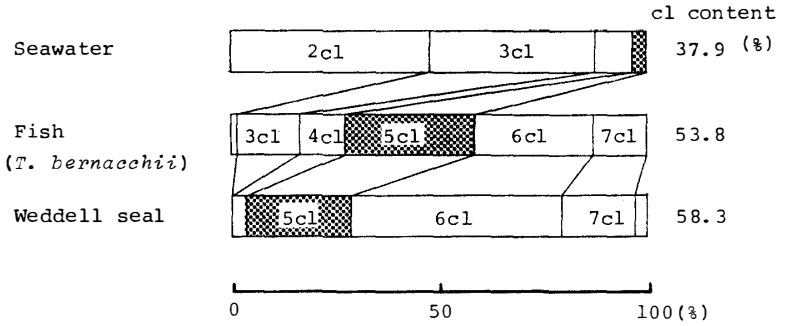

Fig. 4. Chlorobiphenyl compositions (%) of PCBs in the antarctic marine ecosystem.

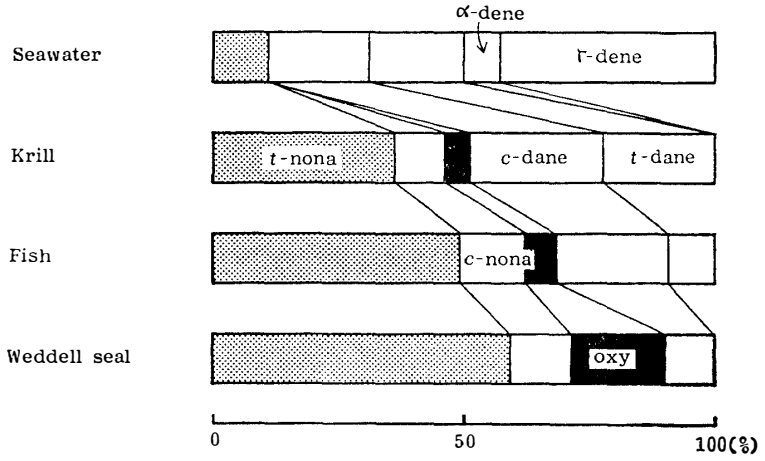

Fig. 5. Chlordane compounds compositions in the antarctic marine ecosystem. t-nona, trans-nonachlor; c-nona, cis-nonachlor; oxy, oxychlordane; c-dane, cis-chlordane; t-dane, trans-chlordane; α-dene, α-chlordene; γ-dene, γ-chlordene (KAWANO et al., in preparation).

be ΣDDT>Σchlordane>PCBs. In the PCB isomers and congeners compositions (Fig. 4), higher chlorinated biphenyls were observed more in fish than in seawater, and this trend was further marked in the Weddell seal. The variable compositions were also found in chlordane compounds, where increased proportions of nonachlor and oxychlordane were observed in higher trophic levels (Fig. 5).

The CHs examined here have a wide variety of lipophilicity, water solubility and biodegradability (METCALF, 1976; TANOUE, 1982). DDTs, higher chlorinated biphenyls, nonachlor and oxychlordane are known to be more lipophilic, less water soluble and less biodegradable than other CHs. As shown in Fig. 6, an apparent negative correlation was found in the relationship between water solubilities and BCFs of PCB isomers and congeners in the antarctic fish, but no correlation exists in the case of the Weddell seal. This strongly suggests that the bioaccumulation of CHs in the antarctic marine organisms of lower trophic levels depends primarily on physicochemical factors such as water solubility and lipophilicity of pollutants, whereas that in higher trophic levels is affected by biochemical factors such as biodegradability of pollutants and metabolic capacity of organisms. This accounts well for the fact that the Weddell seal, long life animal, tends to accumulate greater amounts of more lipophilic and less metabolizable pollutants such as DDTs, higher chlorinated biphenyls, nonachlors and oxychlordane.

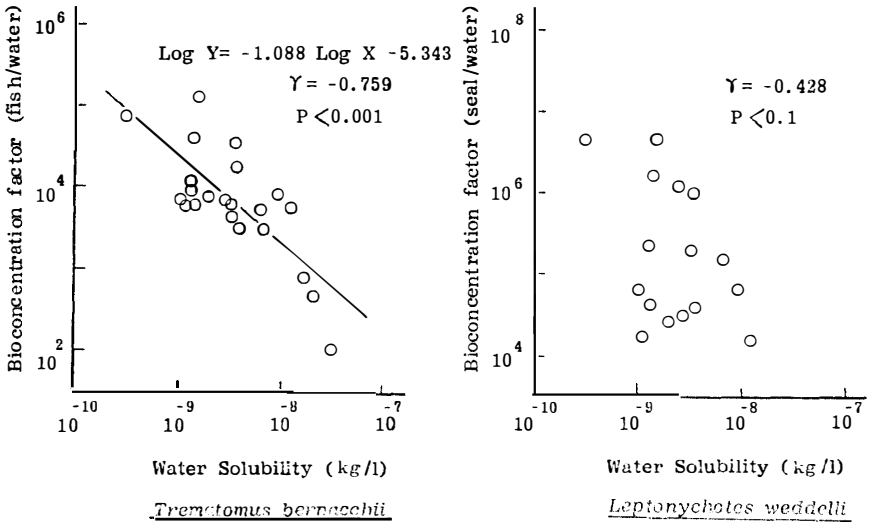

Fig. 6. Relationship between water solubility of individual chlorobiphenyls and bioconcentration factors of the antarctic fish, Trematomus bernacchii, *and the Weddell seal.*

3.5. Specific distribution profiles of CHs in the antarctic marine environment

When the concentrations of CHs in the antarctic marine ecosystem are compared, with those in the western North Pacific waters (Table 2), ΣDDT were about two orders of magnitude lower in the Antarctic than in the western North Pacific throughout seawater to marine mammals. PCBs in organisms were also about two orders of magnitude lower in the Antarctic than in the western North Pacific, but that in seawater were found to be only about one order of magnitude different between the two regions. The lower levels of CHs in the antarctic environment are mainly

Table 2. ΣDDT and PCBs concentrations (μg/l or ng/g) in the marine food chains of the Antarctic and the western North Pacific oceans.

	Antarctic			Western North Pacific	
	ΣDDT	PCBs		ΣDDT	PCBs
Seawater (under fast ice)	1.0×10^{-6}	5.4×10^{-5}	Seawater	1.4×10^{-4} (6.0×10^{-6}–4.8×10^{-4}) $n=21$	2.8×10^{-4} (4.0×10^{-5}–5.9×10^{-4}) $n=21$
Krill	2.6×10^{-2}	2.1×10^{-2}	Zooplankton	1.7	1.8
			Myctophid	4.3×10	4.8×10
Benthic fish	6.3×10^{-1}	2.5×10^{-1}	Squid	2.2×10	6.8×10
(*T. bernacchii*)	(1.6×10^{-1} –1.5) $n=31$	(1.1×10^{-1}–8.6×10^{-1}) $n=26$		(1.6×10–2.8×10) $n=6$	(3.5×10–9.5×10) $n=6$
Weddell seal	5.2×10	1.2×10	Striped dolphin	5.2×10^{3} (4.2×10^{3}–6.0×10^{3}) $n=6$	3.7×10^{3} (2.8×10^{3}–4.1×10^{3}) $n=6$

The western North Pacific data are cited from TANABE *et al.* (1984).

attributable to the fact that the locality is far away from the regions of intensive industrial and human activities.

It has been demonstrated that atmospheric transport is a major pathway of CHs from land to open ocean. TANABE *et al.* (1982b) reported that atmospheric concentrations of CHs were much lower in the Antarctic than in the western North Pacific. There is a difference between the Antarctic and the western North Pacific in relative concentrations of PCBs and DDTs in air and those in seawater and organisms. This suggests that the antarctic ambient condition and biological factors give rise to a specific distribution profile of CHs in the antarctic marine ecosystem. The transport process of CHs in the antarctic marine environment is summarized in Fig. 7.

Atmospheric DDTs and PCBs over the open ocean exist mostly in the gaseous phase. A major transport of CHs from air to water depends on the partition at the

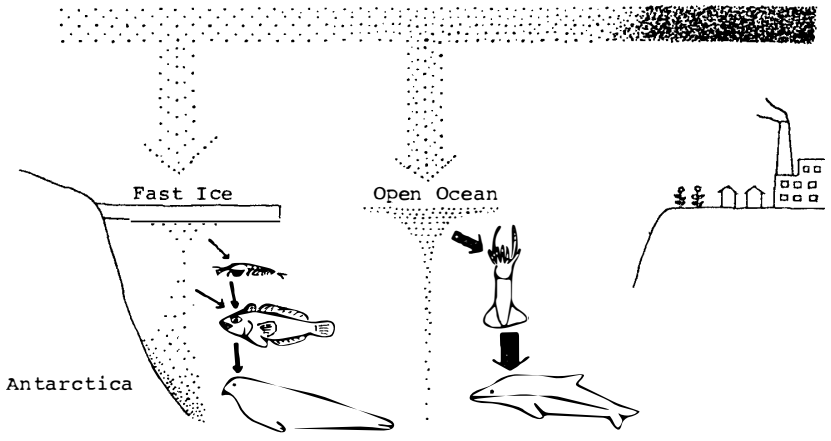

Fig. 7. Global dynamics of DDTs and PCBs.

air/water interface and the precipitation such as rainfall and snowfall. In the antarctic marine environment, which is covered with the thick fast ice except for a short summer season, the transport of CHs to seawater by gas exchange is unlikely. The major supply of CHs into the antarctic seawater is probably conducted by melting snow and ice during austral summer. This seems to be one of the reasons for the lower concentrations of CHs in the antarctic seawater and organisms.

Additionally, high primary productivity also contributes to the specific distribution profile of CHs in the antarctic marine environment. HOLM-HANSEN *et al.* (1977) reported that primary productivity of water under the fast ice is several times higher than that of the outer margin of the pack ice in the summer season. TANABE *et al.* (1983) noted that the concentrations of DDTs and higher chlorinated biphenyls were much lower in water samples under the fast ice than in those of the outer margin of the pack ice. They suggest that DDTs and higher chlorinated biphenyls are rapidly removed from the surface to deeper layers by sinking particles (which are composed mainly of dead planktonic forms) since these pollutants are extremely adsorbable on particulates in seawater. So the acitve primary productivity under the fast ice may also be a cause for the lower concentrations of CHs in the antarctic seawater and organisms.

The antarctic marine ecosystem, especially beyond south of the Antarctic Convergence, is stable and old and has a higher percentage of inherent species; thus it is simple in comparison with other ecosystems. Also, since the atmospheric mixing between north and south is very slow, the antarctic area is a comparatively closed environment. These natural barriers prevent the effects of global pollution here and probably the natural purification processes too. But, as mentioned above about the pollution from Syowa Station, since polluted from the inner area, it could not spread easily, the pollutants became localized and are being concentrated in resident organisms. When highly polluted, any closed and simple ecosystems will be easily affected and destroyed. Consequently, the antarctic marine ecosystem is basically weak to the environmental pollution from the inner area and is highly susceptible to even a little pollution within the region.

Acknowledgments

This study was performed under a project by JARE-22. The authors are grateful to Prof. Y. YOSHIDA, leader of JARE-22, National Institute of Polar Research, for his kind arrangement and encouragement in this survey. We wish to thank all of the members of JARE-22 for their cooperation. Many thanks are due to the officers and the crew of the icebreaker FUJI for their assistance on board. We are pleased to acknowledge the kind support of Profs. T. MATSUDA and T. HOSHIAI, National Institute of Polar Research, and Prof. T. TORII, Chiba Insititute of Technology, for enabling us to participate in this project. We would also like to acknowledge Dr. A. N. SUBRAMANIAN for his kind supervision of the manuscript.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Project No. 57035039).

References

HANSEN, D. J. and WILSON, A. J. (1970): Significance of DDT residues from the estuary near Pensacola, Fla. Pestic. Monit. J., **4**, 51–56.

HIDAKA, H. (1982): Ettô kansoku bumon hôkoku (Report of wintering investigation). Nihon Nankyoku Chiiki Kansokutai Dai-22-ji-tai Hôkoku (Reports of the 22nd Japanese Antarctic Research Expedition 1980–1982), Tokyo, Natl Inst. Polar Res., 170–176.

HIDAKA, H. and TATSUKAWA, R. (1981): Sôsetsu; Nankyoku ni okeru yûki enso kagôbutsu no kenkyû (Review; Environmental pollution by chlorinated hydrocarbons in the Antarctic). Nankyoku Shiryô (Antarct. Rec.), **71**, 151–164.

HIDAKA, H. and TATSUKAWA, R. (1983): Syôwa Kiti shûhen no yûki enso kagôbutsu osen (Environmental pollution of chlorinated hydrocarbons around Syowa Station). Nankyoku Shiryô (Antarct. Rec.), **80**, 14–29.

HIDAKA, H., TANABE, S. and TATSUKAWA, R. (1983): DDT compounds and PCB isomers and congeners in Weddell seals and their fate in the antarctic marine ecosystem. Agric. Biol. Chem., **47**, 2009–2017.

HOLM-HANSEN, O., EL-SAYED, S. Z., FRANCESCHINI, G. A. and CUHEL, R. L. (1977): Primary production and the factors controlling phytoplanktons growth in the Southern Oceans. Adaptations within Antarctic Ecosystems, ed. by G. A. LLANO. Washington, D. C., Smithson. Inst., 11–50.

KAWANO, M., INOUE, T., HIDAKA, H. and TATSUKAWA, R. (1984): Chlordane compounds residues in Weddell seals (*Leptonychotes weddelli*) from the Antarctic. Chemosphere, **13**, 95–100.

METCALF, R. L. (1976): Model ecosystem studies of bioconcentration and biodegradation of pesticides. Pesticides in Aquatic Environments, ed. by M. A. Q. KHAN. New York, Pleunum Press, 127–144.

MORIWAKI, K. and YOSHIDA, Y. (1982): Onguru Shôtô shûhen kaiiki ni okeru ryûkô ryûsoku sokutei (Current measurements in the waters around the Ongul Oslands). Dai-3-kai Nankyoku Chigaku Shinpojiumu Puroguramu·Kôen Yôshi (Abstr. Third Shymp. Antarct. Geosci. 1982), Tokyo, Natl Inst. Polar Res., 31.

REINERT, R. E. and BERGMAN, H. L. (1974): Residues of DDT in lake trout (*Salvelinus namaycush*) and coho samon (*Oncorhynchus kisutch*) from the Great Lakes. J. Fish. Res. Board Can., **31**, 191–199.

ROBINSON, J., RICHARDSON, A., CRABTREE, A. N., COULSON, J. C. and POTTS, G. R. (1967): Organochlorine residues in marine organisms. Nature, **214**, 1307–1311.

SUBRAMANIAN, B. R., TANABE, S., HIDAKA, H. and TATSUKAWA, R. (1983): DDTs and PCB isomers and congeners in antarctic fish. Arch. Environ. Contam. Toxicol., **12**, 621–626.

TANABE, S., TATSUKAWA, R., TANAKA, H., NARUYAMA, K., MIYAZAKI, N. and FUJIYAMA, T. (1981a): Distribution and total burdens of chlorinated hydrocarbons in bodies of striped dolphins (*Stenella coeruleoalba*). Agric. Biol. Chem., **45**, 2569–2778.

TANABE, S., TANAKA, H., MARUYAMA, K. and TATSUKAWA, R. (1981b): Elimination of chlorinated hydrocarbons from mother striped dolphins (*Stenella coeruleoalba*) through parturition and lactation. Studies on the Levels of Organochlorine Compounds and Heavy Metals in the Marine Organisms, ed. by T. FUJIYAMA. Okinawa, University of the Ryukyus, 115–121.

TANABE, S., TATSUKAWA, R., MARUYAMA, K. and MIYAZAKI, N. (1982a): Transplacental transfer of PCBs and chlorinated hydrocarbon pesticides from the pregnant striped dolphin (*Stenella coeruleoalba*) to her fetus. Agric. Biol. Chem., **46**, 1249–1254.

TANABE, S., TATSUKAWA, R., KAWANO, M. and HIDAKA, H. (1982b): Global distribution and atmospheric transport of chlorinated hydrocarbons; HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern Indian and Antarctic Oceans. J. Oceanogr. Soc. Jpn., **38**, 137–148.

TANABE, S., HIDAKA, H. and TATSUKAWA, R. (1983): PCBs and chlorinated hydrocarbon pesticides in antarctic atmosphere and hydrosphere. Chemosphere, **12**, 277–288.

TANABE, S., TANAKA, H. and TATSUKAWA, R. (1984): Biological magnification of PCBs, DDTs

and HCHs (BHCs) in the western North Pacific ecosystem including through water to marine mammals. Arch. Environ. Contam. Toxicol. (in press).

TANOUE, A. (1982): Kagaku busshitsu no bunpai keisû, mizu yôkai-do dêtashû (Partition coefficient and solubility of chemicals). Seitai Kagaku (Ecol. Chem.), **5**(3), 48–61.

WAKIMOTO, T., TATSUKAWA, R. and OGAWA, T. (1971): PCB no zanryû bunseki-hô (Analytical method of PCBs). Kôgai to Taisaku (J. Environ. Pollut. Control.), **7**, 517–522.

(Received April 1, 1984; Revised manuscript received May 10, 1984)