Global Distribution, Dynamics and Fate of Semivolatile Persistent Organochlorines

（中揮発性有機塩素化合物の地球規模での分布・動態・ゆくえ）

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Global Distribution, Dynamics and Fate
of Semivolatile Persistent Organochlorines

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Summary

Global chemical pollution has been a matter of great concern with the increase in public awareness towards such serious problems. Among a large number of anthropogenic chemicals, greater attention has been focused on semivolatile persistent organochlorines due to the facts that these compounds were subjected to long-range atmospheric transport contaminating our environment on a global scale. Toxic impacts of organochlorines such as, polychlorinated biphenyls (PCBs) and DDT to the ecosystems are strongly apprehended because of their high bio-accumulation potential and harmful biological effects. It has been suspected that mass mortalities of seals and dolphins occurred in the North Sea, Lake Baikal and Meditterranean Sea were triggered by the marine pollution of these compounds, although the direct cause of these animal deaths were due to morbillivirus infection. These chemicals are now being used mainly in the tropical third world and the former socialist countries. Nevertheless, only a few informations are available on their production and usage, and the current status on worldwide pollution are therefore still not clear. In addition, the transport pathways and ultimate fate of organochlorines released from these sources are also disputable. In order to elucidate the geographical distributions and comprehensive dynamics of these compounds, global monitoring studies including not only the sources but also remote areas are necessary. However, most attempts have been limited to temporal

and spatial terms. In the present study, geographical distributions of organochlorines such as hexachlorocyclohexanes (HCHs), DDTs, chlordane compounds (CHLs) and PCBs were determined and their dynamics and fate were discussed on a global viewpoint.

Field researches were carried out in tropical Asia (India, Thailand, Vietnam, Malaysia, Indonesia) and Oceania (Papua New Guinea and Solomon Islands) during 1989 to 1991. Concurrently, environmental compartments in Japan, Taiwan, Australia and Russia belonging to temperate to cold areas were also monitored. Air, river (lake) water and sediment samples were collected for this survey. Furthermore, organochlorines in oceanic air and surface seawater collected from the Chukchi Sea, Bering Sea, Gulf of Alaska, North Pacific, East China Sea, South China Sea, North Atlantic, Mediterranean Sea, Arabian Sea, Bay of Bengal, eastern Indian and Southern Oceans were also investigated. Analytical method for the organochlorines was as reported previously.

Atmospheric and hydrospheric concentrations of HCHs and DDTs in the tropics were apparently higher than those observed in the temperate areas. CHLs and PCBs were also occasionally observed at higher levels in the tropics. These results indicate that their usage areas are expanding (have already shifted) southward. On the other hand, distribution patterns of organochlorines in sediments showed smaller spatial variations on global terms, implying that the chemicals released in the tropical environment are dispersed rapidly through air, latitudinally redistributed from lower latitudes according to climatic features like temperature and therefore retained less in tropical sediments. The most apparent distribution tendency was observed for HCHs, which were favorably transported to remote areas through terrestrial air. This study provides an example to elicit multi-matrices monitoring for assessing the magnitude and fate of the organochlorine contaminations on a global scale.

In the ocean study, the atmospheric concentrations were found to be still higher in the northern hemisphere than in the southern ones, although the distribution pattern supported again the shift or expansion of their major sources from mid- to low-latitudes during the last decade. As for surface seawater, organochlorines revealed contaminant-specific pattern of distributions. HCH residues showed a considerable contamination over 40°N latitude in the North Pacific, whereas higher DDT residues were observed in the seas nearby tropical Asia. The distributions of CHLs and PCBs were rather uniform in both the hemispheres. A combination of Henry's law constant (HLC) and HLC/octanol-water partition coefficient (H/K_{OW}) of these compounds was found to influence the global organochlorine distributions. Ambient temperatures and a proportion of water (oceanic) and lipophilic (terrestrial) surface areas in the environment were also the factors controlling pollutant dynamics. For example, while HCHs are relatively more dissolved in the water phase because of their moderately lower HLCs, the compounds with higher H/K_{OW} values are predicted to be less adsorptive on the lipophilic solid phase such as soils and aerosols. This can reasonably explain the lower contaminations of HCHs in the tropical solid phase and their significant condensation in the cold surface water. These assumptions were also supported by estimating fluxes for gas exchange process across the air-water interface.

Considering these results, global dynamics of organochlorines released from sources to the atmosphere can be generally explicable by their inherent physico-chemical properties and geographical features. It means that the ultimate global distributions are controlled by the HLC and H/K_{OW} values, and colder regions tend to latitudinally serve as a more efficient sink for them.

It has been generally believed that the earth mixes and dilutes anthropogenic chemicals and leads them to a homogenous state. However, it requires a premise that molecular diffusion of these compounds can be well facilitated under any conditions on the globe. Persistent organochlorines dealt in this study do not entirely fulfill the premise. In conclusion, it is considered that these organochlorines with low to intermediate HLC and H/K_{OW} values are redistributed to their specifically designated regions (and/or compartments) on the heterogeneous world with latitudinal gradient temperatures.

1 Geographical Distributions in the Tropics and Implications for Global Redistribution from Lower Latitudes

Abstract

Semivolatile persistent organochlorines in air, river water and sediment samples were analysed from eastern and southern Asia (India, Thailand, Vietnam, Malaysia, Indonesia) and Oceania (Papua New Guinea and Solomon Islands) to elucidate their geographical distribution in tropical environment. The concentrations of organochlorines in these abiotic samples collected from Taiwan, Japan and Australia were also monitored for comparison. Atmospheric and hydrospheric concentrations of HCHs (hexachlorocyclohexanes) and DDTs (DDT and its metabolites) in the tropical developing countries were apparently higher than those observed in the developed nations, suggesting extensive usage of these chemicals in the lower latitudes. CHLs (chlordane compounds) and PCBs (polychlorinated biphenyls) were also occasionally observed at higher levels in the tropics, implying that their usage area is also expanding southward. Distribution patterns of organochlorines in sediments showed smaller spatial variations on global terms, indicating that the chemicals released in tropical environment are dispersed rapidly through air and water and retained less in sediments. The ratios of organochlorine concentrations in sediment and water phases were positively correlated with the latitude of sampling, suggesting that persistent and semivolatile

compounds discharged in the tropics tend to be redistributed on a global scale.

Introduction

Global chemical pollution has been a matter of great concern with the increase in public awareness towards environmental problems. Among a large number of man-made chemicals, greater attention has been focused on semivolatile and persistent organochlorines such as DDT and polychlorinated biphenyls (PCBs) because of their high bioaccumulation potential and harmful biological effects. These compounds have been found in a wide range of environmental compartments throughout the world since their first report in 1960s (Risebrough *et al.*, 1968; Bidleman and Olney, 1974; Tanabe and Tatsukawa, 1980; Atlas and Giam, 1981).

A recent report showed the transport of organic contaminants through atmosphere to the Arctic from Russia, Europe, and North America (Barrie *et al.*, 1989). Consequently, considerable levels of organochlorine compounds have been detected in air, water, soil, plant and wildlife from the Arctic in recent years (Oehme and Stray, 1982; Hargrave *et al.*, 1988; Muir *et al.*, 1988; Norstrom *et al.*, 1988; Patton *et al.*, 1989; Calamari *et al.*, 1991). In this context, a recent study has demonstrated that the Arctic water bodies are likely to serve as a sink of persistent and semivolatile contaminants (see Chapter 3). In fact, HCH residues in Arctic waters showed considerably high levels. As no prominent source of these toxic contaminants is likely to be present in the polar regions, investigations are necessary to understand the source and mechanism of transport of such compounds. Although the production and usage of many organochlorine pesticides have already been banned or restricted in developed nations, considerable quantities of PCBs are still in use in older electrical equipments and deposited as landfills in these countries. It has also been pointed out that about 15% of the total world stock of PCBs are held in the developing countries (Cummins, 1988). In addition, organochlorine pesticides are being used increasingly in tropical agroecosystems and in public health programs to control pests and vector borne diseases (Forget, 1991). Goldberg (1975) pointed out this phenomenon as "southward tilt" of DDT usage. Similar to tropical Asian countries, the usage of organochlorine compounds is increasing in southern Pacific Islands (Mowbray, 1986) and the demand is estimated to rise in future. It is predicted that environmental fate of organochlorines in tropical ecosystems may be different from that in temperate and cold ones, because of the prevailing high temperature and heavy rainfall. However, only few monitoring surveys are available on the organochlorine contaminations in air, water and sediments of tropical countries and therefore recent sources and spatial distribution of such toxic contaminants on global terms are still unclear.

In the present study, urban and estuarine areas of tropical countries such as India, Thailand, Vietnam, Malaysia, Indonesia, Papua New Guinea and Solomon Islands in the eastern and southern Asia and Oceania were investigated, and air, water and sediment samples were collected. In order to compare the recent contamination levels of organochlorines between low- and mid-latitude countries, surveys were also carried out in Japan, Taiwan, and Australia.

Residue levels of organochlorines in air, river water and sediments were determined. Based on the results, factors controlling their geographical distributions and partitioning between these abiotic compartments in the tropics were discussed, and furthermore the significance of tropical area as organochlorine sources was evaluated.

Materials and Methods

Sampling location and sample collection

A total of 21 air, 56 water and 63 sediment samples were collected from several cities in eastern and southern Asia and Oceania, to represent low- to mid-latitude areas. Sampling locations for air, river and estuarine water and sediments are shown in Fig. 1-1. All the samples were collected between August, 1989 and October, 1991. Details of sampling location, date and volume for air, water and sediments are summarized in Tables 1-2, 1-2 and 1-3, respectively.

Polyurethane foam plugs (PUF: Model HA, Achilles Co. Ltd, Japan, diameter 31 mm, length 50 mm) were used as adsorbents of

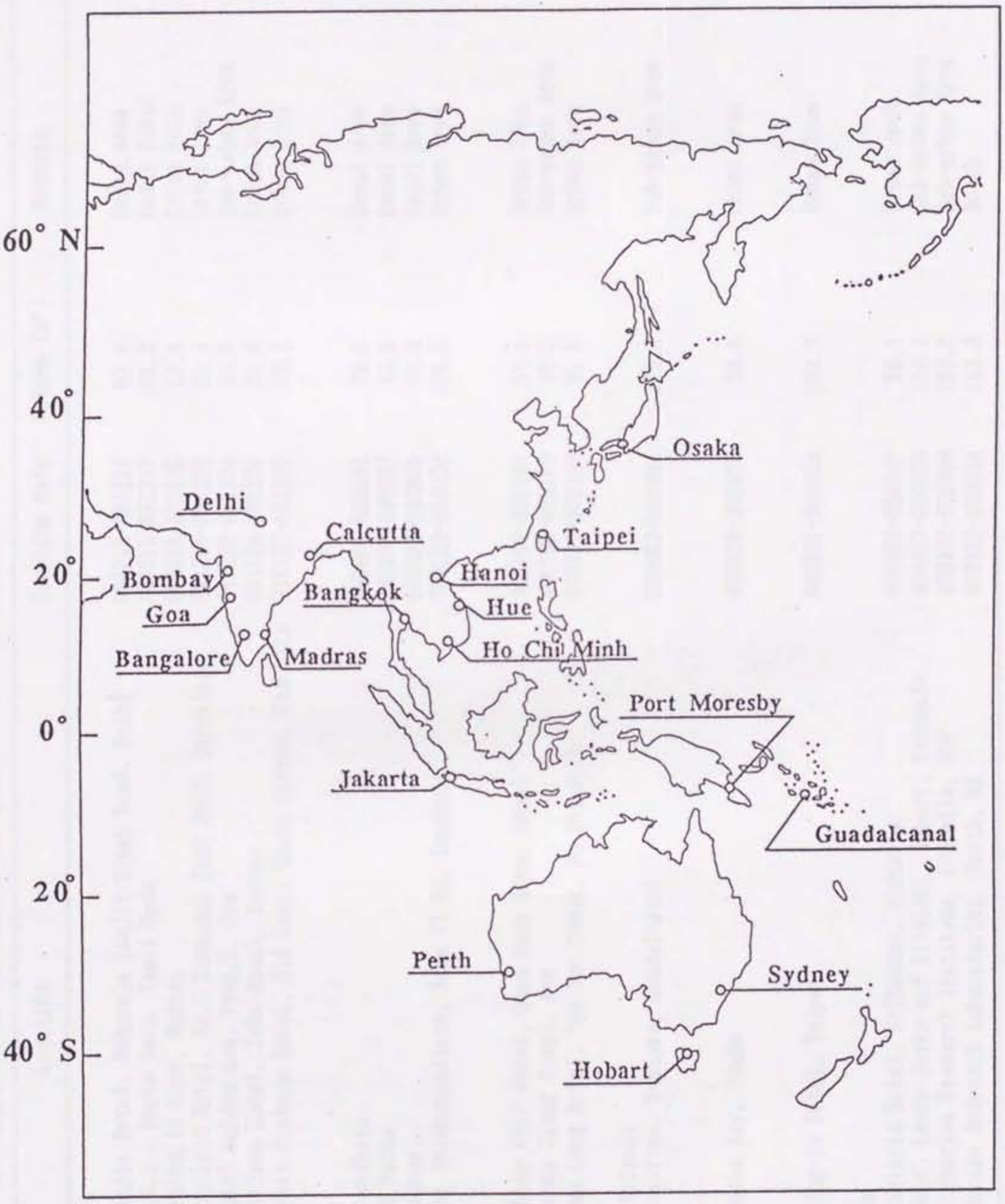

Fig. 1-1. Map showing sampling location for air, water and sediment samples.

Table 1-1. List of air samples from the eastern and southern Asia and Oceania.

Sample No.	Location	Sampling Date	Volume (m^3)	Remarks
	India			
IND-1A	Ranjit Hotel, Maharaja Ranjit Singh Road, Delhi	891212-891214	69.4	Urban Area
IND-2A	C.A.S., Porto Novo, Tamil Nadu	891215-891217	103.2	Paddy Field
IND-3A	Habibulla Road, Madras	891218-891220	59.4	Urban Area
IND-4A	Woodland Hotel, No.5 Sampangi Tank Road, Bangalore	891220-891222	81.4	Urban Area
IND-5A	Hotel Golden Goa, Panaji, Goa	891222-891224	51.7	Sub-urban Area
IND-6A	Citizen Hotel, Juhu Beach, Bombay	891224-891226	63.8	Urban Area
IND-7A	Great Eastern Hotel, Old Court House Street, Calcutta	891227-891230	93.4	Urban Area
	Thailand			
THA-1A	Ayutthaya	890801-890803	79.2	Rural Area
THA-2A	Si Racha	890806-890807	45.0	Rural Area
THA-3A	Minburi	890803-890805	75.6	Rural Area
THA-4A	Soi Phiboonwattana, Rama VI Rd, Bangkok	900122-900124	106.6	Urban Area
	Vietnam			
VIE-1A	Thong Nhat Hotel, Quan Hoan Kiem, Hanoi	900103-900104	57.1	Urban Area
VIE-2A	Huong Giang Hotel, Hue	900105-900106	28.2	Sub-urban Area
VIE-3A	Cuu Long Hotel, Ton Duc Thang, Ho Chi Minh	900107-900109	91.8	Urban Area
	Solomon Islands			
SOL-1A	Panatina, Honiara, Guadalcanal	900902-900904	115.2	Sub-urban Area
	Japan			
JPN-1A	Osaka Bay, Osaka	900526-900527	39.4	Urban Area
	Taiwan			
TAW-1A	Ming-fu Hotel, Taipei	900821-900825	102.7	Urban Area
	Australia			
AUS-1A	Victoria Hotel, Melbourne, Victoria	900826-900827	26.1	Urban Area
AUS-2A	Dept. Lands Parks and Wildlife, Hobart, Tasmania	900827-900829	110.1	Sub-urban Area
AUS-3A	Fisheries Research Institute, Cronulla, NSW	900908-900910	102.0	Sub-urban Area
AUS-4A	Marine Research Laboratories, Perth, WA	900912-900914	113.2	Beach

Table 1-2. List of water samples from the eastern and southern Asia and Oceania.

Sample No.	Location	Sampling Date	Volume (l)	Remarks
	India			
IND-1W	Yamuna River, Nizamudin Bridge, Delhi	891213	20	Urban Area
IND-2W	Vellar River, Porto Novo, Tamil Nadu	891216	20	Paddy Field
IND-3W	Cooum River, South Beach Road Bridge, Madras	891219	20	Urban Area
IND-4W	Ulsoor Lake, Bangalore	891221	5	Urban Area
IND-5W	Mandovi River Tributary, Panaji, Goa	891223	20	Sub-urban Area
IND-6W	Mahim Creek, Mahim Bridge, Bombay	891225	20	Urban Area
IND-7W	Circular Canal, R.G. Kar Road Bridge, Calcutta	891228	20	Urban Area (Municipal Sewage)
IND-8W	Hooghly River, Babu Ghat, Calcutta	891229	20	Urban Area
	Thailand			
THA-1W	Chao Phraya River, Ayutthaya	900101	20	Paddy Field
THA-2W	Klong Sam-rong Canal, Bangkok	900102	20	Industrial Area
THA-3W	Chao Phraya River, Chao Sa-ming Prai Pier, Bangkok	900102	20	Urban Area
THA-4W	Chao Phraya River Estuary, Bangkok	900102	20	Urban Area
THA-5W	Krung Kasem Pumping Station, Bangkok	900102	20	Urban Area (Municipal Sewage)
	Vietnam			
VIE-1W	Song Hong, Hanoi	900104	20	Urban Area
VIE-2W	Phuloc Lake, Phu Da, Thua Thien	900105	20	Paddy Field
VIE-3W	Song Huong, Hue	900105	20	Sub-urban Area
VIE-4W	Song Nha Be, Ferry Pier, Ho Chi Minh	900108	20	Paddy Field & Mangroves
VIE-5W	Canal Gua, My Hung Village, Cu Chi	900110	12	Paddy Field
VIE-6W	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	20	Paddy Field & Mangroves
VIE-7W	Rach Thi Nghe Canal, Ho Chi Minh	900112	20	Urban (Municipal Sewage)
	Malaysia			
MAL-1W	Pantai Jeram, Selangor	911029	18	Rural Area
	Indonesia			
INS-1W	Ciliwung River, Jl.Gunung Sahari, Jakarta	911029	18	Urban Area
INS-2W	Ciliwung River, Ancol, Jakarta	911029	19	Urban Area
INS-3W	Ciliwung River, Bogor	911103	20	Rural Area
	Solomon Islands			
SOL-1W	Nggurambusu River, Komundi, Paripao, Guadalcanal	900903	25	Rural Area
SOL-2W	Mbalisuna River, Karoururu, Tadhimboko, Guadalcanal	900903	25	Agricultural Farm Area
SOL-3W	Ngalimbiu River, Mbaravuli, Ghaombata, Guadalcanal	900903	25	Agricultural Farm Area
SOL-4W	Lungga River, Lungga, Ghaombata, Guadalcanal	900904	25	Rural Area
SOL-5W	Lio Beach, Honiara, Guadalcanal	900904	25	Urban Area (Seawater)
SOL-6W	Mataniko River, Honiara, Guadalcanal	900904	25	Urban Area
	Japan			
JPN-1W	Osaka Bay, Osaka	900527	20	Urban Area (Seawater)
JPN-2W	Osaka Bay, Osaka	900527	20	Urban Area (Seawater)
JPN-3W	Osaka Bay, Osaka	900527	20	Urban Area (Seawater)
	Taiwan			
TAW-1W	Hekihyou-bridge, Tan-shui Ho, Taipei	900823	20	Sub-urban Area
TAW-2W	Yung-shan Water Pumping Station, Keelong River, Taipei	900824	20	Urban Area
TAW-3W	9th Water Gate, Tan-shui Ho, Taipei	900824	40	Urban Area
	Australia			
AUS-1W	Harbour Bridge, Parramata River, Sydney, NSW	900909	30	Urban Area
AUS-2W	Five Dock Bay, Parramata River, Chiswick, NSW	900909	30	Sub-urban Area
AUS-3W	Ryde Bridge, Parramata River, Meadowbank, NSW	900909	30	Sub-urban Area
AUS-4W	Salt Pan Creek, Lawson Drive, Riverwood, NSW	900909	30	Sub-urban Area
AUS-5W	Cooks River at Sydney Airport, NSW	900909	30	Sub-urban Area
AUS-6W	Captain Cook Bridge, Georges River, Rocky Pt., NSW	900909	30	Sub-urban Area
AUS-7W	Port Hacking, Hungry Pt., Cronulla, NSW	900910	13	Sub-urban Area
AUS-8W	Fremantle Bridge, Swan River, Fremantle, WA	900912	25	Sub-urban Area
AUS-9W	Canning Bridge, Canning River, Melville, WA	900912	25	Urban Area
AUS-10W	Narrows Bridge, Swan River, Perth, WA	900912	25	Urban Area
AUS-11W	Garret Road Bridge, Swan River, Bassendean, WA	900912	25	Sub-urban Area
AUS-12W	Reg Bond Park, Swan River, Swan, WA	900912	25	Rural Area
AUS-13W	Mandurah Bridge, Peel Inlet, Mandurah, WA	900913	25	Residential Area
AUS-14W	Harvey Estuary, Dawensville, WA	900913	25	Rural Area
AUS-15W	Murray River, Pinjarra, WA	900913	25	Rural Area
AUS-16W	Marine Reserch Laboratories, Waterman, Perth, WA	900914	75	Beach (Seawater)
AUS-17W	Norfolk Bridge, Derwent River, Hobart, Tasmania	900828	27	Rural Area
AUS-18W	Boyer Paper Mill, Derwent River, Hobart, Tasmania	900828	16	Rural Area (Paper Mill Drain)
AUS-19W	Prince of Wales Bay, Derwent River, Hobart, Tasmania	900828	28	Urban Area
AUS-20W	Macquarie Point, Derwent River, Hobart, Tasmania	900828	28	Urban Area

Table 1-3. List of sediment samples from the eastern and southern Asia and Oceania.

Sample No.	Location	Sampling Date	Remarks
India			
IND-1S	Cooum River, Madras	891219	Urban Area
IND-2S	Adayar River, Madras	891219	Urban Area
IND-3S	Mandovi River Estuary, Panaji, Goa	891223	Sub-urban Area
IND-4S	Mandovi River Tributary, Panaji, Goa	891223	Sub-urban Area
IND-5S	Mahim Creek, Mahim Bridge, Bombay	891225	Urban Area (Municipal Sewage)
IND-6S	Circular Canal, Calcutta	891228	Urban Area (Municipal Sewage)
Thailand			
THA-1S	Klong Sam-rong Canal, Bangkok	900102	Industrial Area (Upper Stream)
THA-2S	Klong Sam-rong Canal, Bangkok	900102	Industrial Area (Lower Stream)
THA-3S	Chao Phraya River Estuary, Bangkok	900102	Urban Area
THA-4S	Krung Kasem Pumping Station, Bangkok	900102	Urban Area (Municipal Sewage)
Vietnam			
VIE-1S	Phu Da, Thua Thien	900105	Paddy Field
VIE-2S	Ta Bat, A Loui, Binh Tri Thien	900106	Urban Area (Municipal Sewage)
VIE-3S	Long Giang Canal, Duyen Hai	900108	Paddy Field & Mangroves
VIE-4S	Lo Giang River, Duyen Hai	900108	Paddy Field & Mangroves
VIE-5S	Don Canal, Duyen Hai	900108	Paddy Field & Mangroves
VIE-6S	La Canal, Duyen Hai	900108	Paddy Field & Mangroves
VIE-7S	Rach Ben Nghe Canal, Ho Chi Minh	900108	Urban Area (Municipal Sewage)
VIE-8S	Tan Binh Village, Tan Bien, Tay Ninh	900109	Paddy Field
VIE-9S	Gua Canal, My Hung Village, Cu Chi	900110	Paddy Field
VIE-10S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Paddy Field & Mangroves
VIE-11S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Paddy Field & Mangroves
VIE-12S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Paddy Field & Mangroves
VIE-13S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Paddy Field & Mangroves
VIE-14S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Paddy Field & Mangroves
VIE-15S	Song Long Tau, Duyen Hai, Ho Chi Minh	900111	Cannal (near Ferry Pier)
VIE-16S	Rach Thi Nghe Canal, Ho Chi Minh	900112	Urban Area (Municipal Sewage: Lower Stream)
VIE-17S	Rach Thi Nghe Canal, Ho Chi Minh	900112	Urban Area (Municipal Sewage: Middle Stream)
VIE-18S	Rach Thi Nghe Canal, Ho Chi Minh	900112	Urban Area (Municipal Sewage: Upper Stream)
Malaysia			
MAL-1S	Pantai Jeram, Selangor	911029	Rural Area
Indonesia			
INS-1S	Ciliwung River, Jl. Gunung Sahari, Jakarta	911102	Urban Area
INS-2S	Ciliwung River, Ancol, Jakarta	911102	Urban Area
INS-3S	Ciliwung River, Bogor	911103	Residential Area (Muddy)
INS-4S	Ciliwung River, Bogor	911103	Residential Area (Sandy)
Papua New Guinea			
PNG-1S	Poreporena Villages, Kaevaga, Port Moresby	900901	Residential Area
PNG-2S	Baruni, Port Moresby	900901	Mangrove
PNG-3S	Abahua Head, Port Moresby	900901	Mangrove
Solomon Islands			
SOL-1S	Mbokokimbo River, Komlonga, Reko, Guadalcanal	900903	Rural Area
SOL-2S	Mataniko River, Honiara, Guadalcanal	900904	Urban Area
Japan			
JPN-1S	Osaka Bay, Osaka	900527	Urban Area (Estuary)
JPN-2S	Osaka Bay, Osaka	900527	Urban Area (Estuary)
JPN-3S	Osaka Bay, Osaka	900527	Urban Area (Estuary)
Taiwan			
TAW-1S	Hekihyou-bridge, Tan-Shui Ho, Taipei	900823	Sub-urban Area
TAW-2S	Yung-shan Water Pumping Stn., Keelong River	900824	Urban Area
TAW-3S	9th Water Gate, Tan-shui Ho, Taipei	900824	Urban Area
Australia			
AUS-1S	Harbour Bridge, Parramata River, Sydney, NSW	900909	Urban Area
AUS-2S	Five Dock Bay, Parramata River, Chiswick, NSW	900909	Sub-urban Area
AUS-3S	Ryde Bridge, Parramata River, Meadowbank, NSW	900909	Sub-urban Area
AUS-4S	Salt Pan Creek, Lawson Drive, Riverwood, NSW	900909	Sub-urban Area
AUS-5S	Cooks River at Sydney Airport, NSW	900909	Sub-urban Area
AUS-6S	Captain Cook Bridge, Georges River, Rocky Pt., NSW	900909	Sub-urban Area
AUS-7S	Fremantle Bridge, Swan River, Fremantle, WA	900912	Sub-urban Area
AUS-8S	Canning Bridge, Canning River, Melville, WA	900912	Urban Area
AUS-9S	Garret Road Bridge, Swan River, Bassendean, WA	900912	Sub-urban Area
AUS-10S	Reg Bond Park, Swan River, Swan, WA	900912	Rural Area
AUS-11S	Mandurah Bridge, Peel Inlet, Mandurah, WA	900913	Residential Area
AUS-12S	Harvey Estuary, Dawensville, WA	900913	Rural Area
AUS-13S	Murray River, Pinjarra, WA	900913	Rural Area
AUS-14S	Boyer Paper Mill, Derwent River, Hobart, Tasmania	900828	Rural Area (Paper Mill Drain)
AUS-15S	Bridge Water, Derwent River, Hobart, Tasmania	900828	Rural Area
AUS-16S	Austins Ferry Sawmill, Derwent River, Hobart, Tasmania	900828	Urban Area
AUS-17S	Prince of Wales Bay, Derwent River, Hobart, Tasmania	900828	Urban Area
AUS-18S	Pasminco Ez Zinc Works Wharf, Derwent River, Hobart, Tasmania	900828	Urban Area
AUS-19S	Newtown Bay, Derwent River, Hobart, Tasmania	900828	Urban Area

organochlorines for air sampling. Details of the preparation methods of PUF columns are reported elsewhere (see Chapter 3). Six precleaned PUF plugs were packed in a glass column (i.d. 27 mm, length 390 mm) with polyethylene caps at both the ends and sealed in polyethylene bags until sampling. Air sampling was carried out using the prepared glass column connected with a low volume air pump (Model AP-240Z, IWAKI Co. LTD, Japan). About 26 to 115 m^3 of air (flow rate 35 to 38 l/min.) was collected for from several hours to two days. The flow rate was monitored using a flow meter (Model RK1400, KOFLOC, KOJIMA Co. LTD, Japan) at the beginning and end of sample collection.

For water sampling, precleaned Amberlite XAD-2 (styrene-divinylbenzene copolymer macroreticular) resin packed in a glass column (i.d. 18 mm, length 50 mm) was used as adsorbent. The XAD-2 columns were also prepared in the same way as reported previously (see Chapter 3). Five to 75 L of river and estuarine water were collected in polyethylene containers, which were washed previously with acetone, and immediately passed through the XAD-2 resin column by siphonage at a flow rate of less than 0.3 L/min. After the adsorption of organochlorines in the column, several ml of formalin was added to the column to avoid biological degradation of these compounds.

Surface sediment samples (0-5 cm) were collected using a stainless steel grab sampler. Sediments were well mixed in a precleaned aluminium plate and preserved in a polyethylene bag with several ml of formalin.

The air, water and sediment samples were transported to the laboratory and stored at -20°C until analysis.

Chemical analysis

Organochlorines adsorbed on PUF were Soxhlet extracted using 300 ml of acetone and 100 ml of hexane for three hours. The extracts were concentrated using a Kuderna-Danish (KD) concentrator and by passing a stream of nitrogen gas until several hundred µl. Five ml of acetone was added to the extract and hexane was removed during this step. The acetone extract was transferred to 10 ml of hexane in a separatory funnel.

In the case of water samples, organochlorines trapped on XAD-2 resin were eluted with 300 ml of ethanol and transferred to 100 ml of hexane in a separatory funnel. The extract was then concentrated in a KD concentrator upto 5 ml.

Sediment samples were air-dried and mixed thoroughly before analysis. About 10-20 g of sediment was transferred into a 250 ml glass stoppered Erlenmeyer flask and allowed to soak with hexane-washed water for 30 min. Organochlorines were extracted with 200 ml of acetone by shaking for 2 hours. If necessary, sediment particles in the extracts were removed using a filter paper (Toyo Roshi Kaisha, LTD., Japan) and the lipophilic pollutants were transferred to 100 ml of hexane in a separatory funnel. The hexane layer was concentrated using a KD concentrator until 5 ml. Meanwhile, several grams of sediment taken in a glass cup was dried at 105°C for three hours to obtain dry weight data. Carbon contents in sediment samples were also measured using gas chromatograph (Shimadzu GC-8A: Shimadzu Co. LTD., Japan) equipped with a thermal conductivity detector, after the sediment was dried and meshed thoroughly. Detector and oven temperatures of GC-TCD were 100° and 70°C, respectively. The electric current was kept at 150 mA. Helium (80 ml/min) was used as a carrier gas. Oxygen flow was set at 300 ml/min.

Hexane extracts of air and water samples were cleaned up with 5 % of fuming sulfuric acid in concentrated sulfuric acid. After washing the extract with hexane-washed water, it was microconcentrated under a gentle stream of nitrogen to 100 µl and then subjected to high performance liquid chromatography (HPLC) for further clean-up and fractionation. HPLC procedures employed in this study were identical to those reported previously (see Chapter 3). Hexane extract of sediment was subjected to Florisil column chromatography activated at a 130°C for 12 hours and fractioned with 100% hexane as first fraction and 20% dichloromethane in hexane as second fraction. The first fraction contained PCBs, *p,p'*-DDE and a part of *trans*-nonachlor, and in the second fraction chlordane-related compounds (*trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and *cis*-nonachlor), other DDT compounds (*o,p'*-DDT, *p,p'*-DDD and *p,p'*-DDT) and HCH isomers are present. Both extracts were cleaned up with 5% fuming sulfuric acid and then treated with copper chips to remove sulphur from the extracts.

The identification and quantification of organochlorines was made on a high resolution gas chromatograph equipped with a ^{63}Ni electron capture detector (HRGC-ECD: Hewlett Packard 5890) and a moving needle type injection system (splitless and solvent cut mode, Shimadzu Co. Ltd, Japan) for identification and quantification of the chemicals. GC columns (fused silica capillary, i.d. 0.25 mm, length 30 m) consisted of DB-1701 (J & W Scientific Co. Ltd, USA: 14 % cyanopropyl phenyl polysiloxane, 0.25 µm bonded phase) for organochlorine pesticides and DB-1 (J & W Scientific Co. Ltd, USA: 100 % dimethylpolysiloxane, 0.25 µm bonded phase) for PCBs. The column oven temperature was programmed at a rate of 2°C/min from an initial temperature of 160°C (10 min hold) to a final temperature of 250°C (30-60 min hold). Helium and nitrogen were used as carrier (20-30 cm/sec) and make-up gases (60ml/min), respectively. The injector temperature was kept at 250°C and the detector was maintained at 300°C. The methods of quantification and peak identification of organochlorines were followed as described previously (Tanabe *et al.*, 1987).

The detection limits for organochlorine pesticides in most cases ranged from 1.0-10 pg/m^3 for air, 0.2-7.0 pg/l for water and 0.003-0.10 ng/g (dry weight) for sediments, and those of total PCBs were 10 pg/m^3, 50 pg/l and 0.1 ng/g (dry weight), respectively.

Results and Discussion

Distribution in air, water and sediments

The distribution of persistent organochlorines in air from eastern and southern Asia and Oceania is illustrated in Fig. 1-2. HCHs (sum of α-, β- and γ-isomers) and DDTs (sum of *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT) levels were apparently higher in the lower latitudes than in the higher ones. As for CHLs (sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor and *trans*-nonachlor) and PCBs (sum of isomers and congeners), the latitudinal variations in atmospheric concentrations were less prominent compared to HCHs and DDTs.

The levels of HCHs in air varied by a factor of six among the sampling locations in tropical regions, whereas atmospheric concentrations in the mid-latitude nations showed a less variation (Table 1-4). Significantly higher levels of HCH residues were detected in Calcutta, India (11,000 ng/m^3) and in Hue, Vietnam (12,000 ng/m^3). Kaushik *et al.* (1987) reported the presence of 43 to 22,000 ng/m^3 of HCHs (average 930 ng/m^3) in air from Delhi, India and attributed the higher concentrations during August-December to the extensive use in mosquito control programs. The high residue levels found in Calcutta, Delhi and Hue suggest the prevalence of mosquito control programes in urban areas in tropics.

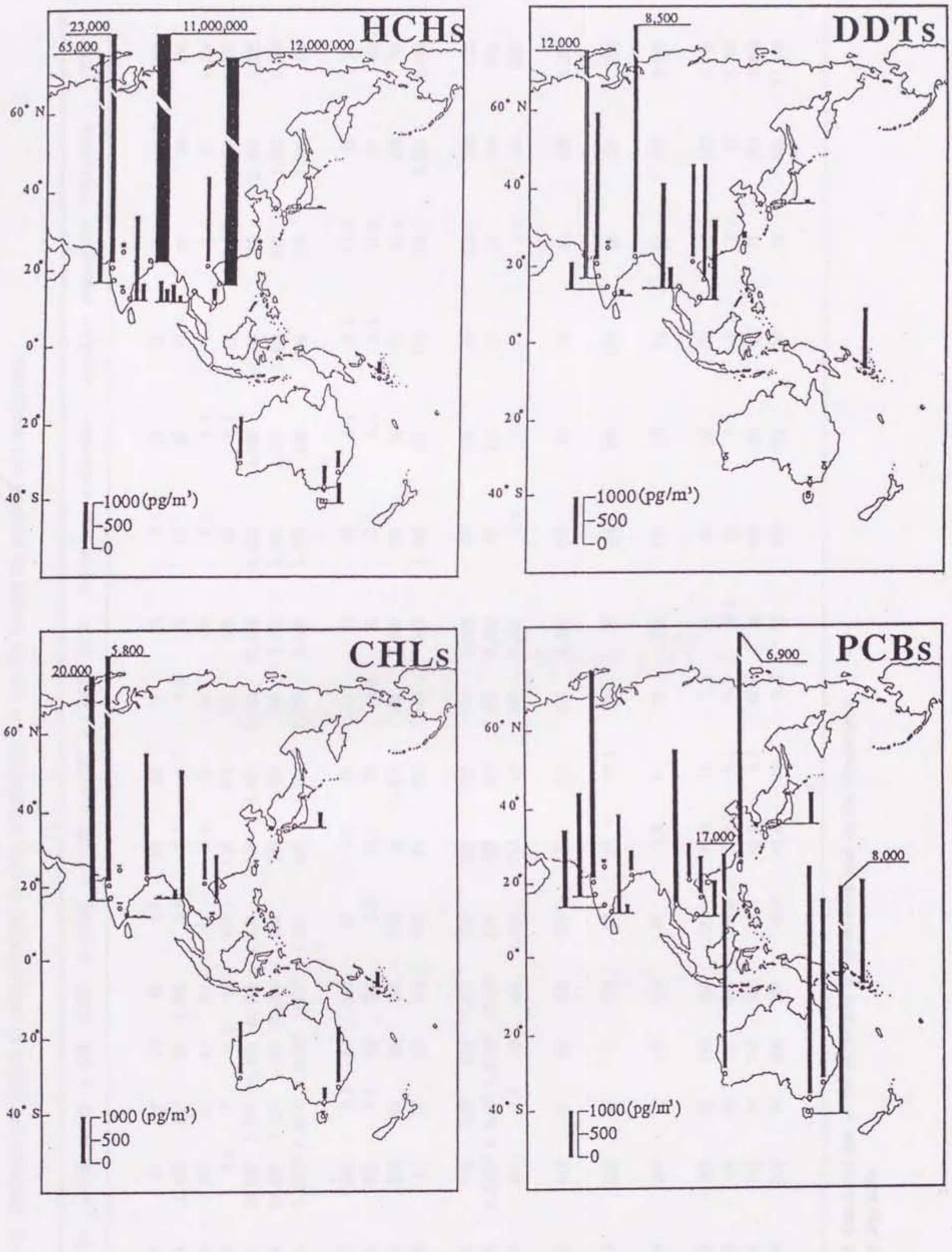

Fig. 1-2. **Distributions of persistent organochlorines in river and estuarine air from the eastern and southern Asia and Oceania.**

Table 1-4. Concentrations (pg/m³) of organochlorines in river and estuarine air from the eastern and southern Asia and Oceania.

Sample No.	α-HCH	β-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	*o,p'*-DDT	ΣDDT	*t*-chlordane	*c*-chlordane	*t*-nonachlor	*c*-nonachlor	Σchlordane	PCBs
IND-1A	41	IF	48	89	1.5	24	20	IF	46	5.7	IF	IF	IF	5.7	74
IND-2A	1,000	220	54	1,800	3.2	6.8	8.0	3.8	22	16	10	<3.0	IF	26	190
IND-3A	280	32	27	340	40	7.5	52	20	120	4.3	2.0	5.6	3.3	15	2,200
IND-4A	7.5	IF	5.5	13	190	<10	270	120	580	10	5.2	IF	4.6	20	1,700
IND-5A	28,000	2,100	35,000	65,000	2,400	300	7,400	1,700	12,000	12,000	4,800	2,400	780	20,000	2,300
IND-6A	17,000	1,100	5,000	23,000	590	220	1,700	650	3,200	2,500	2,000	1,100	230	5,800	4,600
IND-7A	$7.0 \mathrm{x} 10^6$	$1.3 \mathrm{x} 10^5$	$4.0 \mathrm{x} 10^6$	$11 \mathrm{x} 10^6$	1,500	670	4,100	2,200	8,500	1,800	440	290	170	2,700	420
THA-1A	340	3.3	44	390	12	1.8	20	11	45	36	5.3	3.3	<1.0	45	NA
THA-2A	230	5.0	46	280	6.8	<1.0	20	8.3	35	13	5.5	8.1	<1.0	27	NA
THA-3A	240	13	86	340	250	74	2,200	120	2,600	130	34	25	<5.0	190	NA
THA-4A	82	IF	37	120	150	67	460	170	800	1,300	760	310	130	2,500	3,500
VIE-1A	640	530	650	1,800	740	150	710	330	1,900	54	<50	12	<50	66	710
VIE-2A	$8.2 \mathrm{x} 10^6$	$0.3 \mathrm{x} 10^6$	$3.9 \mathrm{x} 10^6$	$12 \mathrm{x} 10^6$	690	470	880	380	2,400	IF	310	28	IF	340	800
VIE-3A	180	7.7	28	220	1,300	<10	IF	390	1,700	5.9	4.3	19	1.7	31	830
SOL-1A	140	31	90	260	200	13	920	210	1,300	120	69	53	11	250	2,300
JPN-1A	120	IF	71	190	29	27	<2.0	19	75	100	100	100	28	330	700
TAW-1A	280	52	140	470	68	1.9	81	78	230	110	79	63	13	270	6,900
AUS-1A	180	62	140	380	<10	<1.0	13	7.8	21	66	36	30	<1.0	130	8,000
AUS-2A	76	19	350	450	<2.0	<1.0	5.5	3.3	8.8	12	7.5	6.7	3.3	30	4,700
AUS-3A	120	20	210	350	8.9	<1.0	5.0	<2.0	14	220	93	68	11	390	3,900
AUS-4A	510	36	350	900	<6.0	<1.0	14	7.8	22	290	190	150	23	650	17,000

IF: not quantified due to the occurrence of interfering peak on the chromatogram.
NA: not available.

The concentrations of DDTs in some cities in India, Thailand, Vietnam and Solomon Islands were found to be two to three orders of magnitude higher than those in Japan, Australia (this study), USA (Foreman and Bidleman, 1990) and in some European countries such as Sweden, former West Germany and France (Bidleman *et al.*, 1987; Wittlinger and Ballschmiter, 1987; Chevreuil *et al.*, 1989). However, DDT levels were comparable to those in Brazzaville, Congo, Africa (Ngabe and Bidleman, 1992) and other reports from India (Kaushik *et al.*, 1987; Ramesh *et al.*, 1989).

Atmospheric concentrations of CHLs also varied among cities in tropical areas. Considerably high concentrations of CHL residues were detected in several urban areas in the tropics such as Goa (20,000 pg/m^3), Bombay (5,800 pg/m^3) and Calcutta (2,700 pg/m^3), and Bangkok (2,500 pg/m^3), while other areas showed similar or lower levels than Japan and Australia. A recent study (see Chapter 3) noted the presence of 2.8-21 pg/m^3 of CHLs in the open ocean atmosphere from tropical Asia. The occurrence of CHL residues in the tropical urban atmosphere with much higher concentrations than those in the open ocean strongly suggests the significant usage of this compound. The purpose of CHLs usage and the production amount in the tropics are still unclear.

The distribution pattern of PCBs in air implied the presence of sporadic emission sources in the tropics, as evidenced by a wide range of the concentrations (74-4,600 pg/m^3). The atmospheric levels of PCBs in the tropics were comparable to those reported in European and North American urban air (Foreman and Bidleman, 1990; Bruckman *et al.*, 1988; Hermanson and Hites, 1989; Chevreuil *et al.*, 1989; Larsson and Okla, 1989; Holsen *et al.*, 1991), while these concentrations were much higher than those in the open ocean which is far away from the source areas (see Chapter 3).

Similar to the atmospheric distributions of HCHs and DDTs, water samples also recorded higher levels for these organochlorines in the lower latitudes (Fig. 1-3). Besides the atmospheric and hydrospheric distributions of HCHs and DDTs, biological samples such as human breast milk (Jensen, 1983; Tanabe *et al.*, 1990) and birds (Ramesh *et al.*, 1992) revealed a similar spatial pattern of contamination, with higher levels in tropical regions and lower levels in mid-latitude countries. All these results for air, water and terrestrial biota support the presence of major emission sources of HCHs and DDTs in tropical countries. Indian pesticide manufacturing firms have been producing large quantities of HCHs in Delhi, Bombay, Madras and Calcutta (Gupta, 1986), where higher residues of HCHs were detected in this study. Similar to the southward tilt of DDT usage predicted by Goldberg (1975), it can be possibly mentioned that consumption of HCHs has also been shifted from the northern mid-latitude countries to the southern tropical ones. The compositions of HCH isomers in the samples of this study showed specific

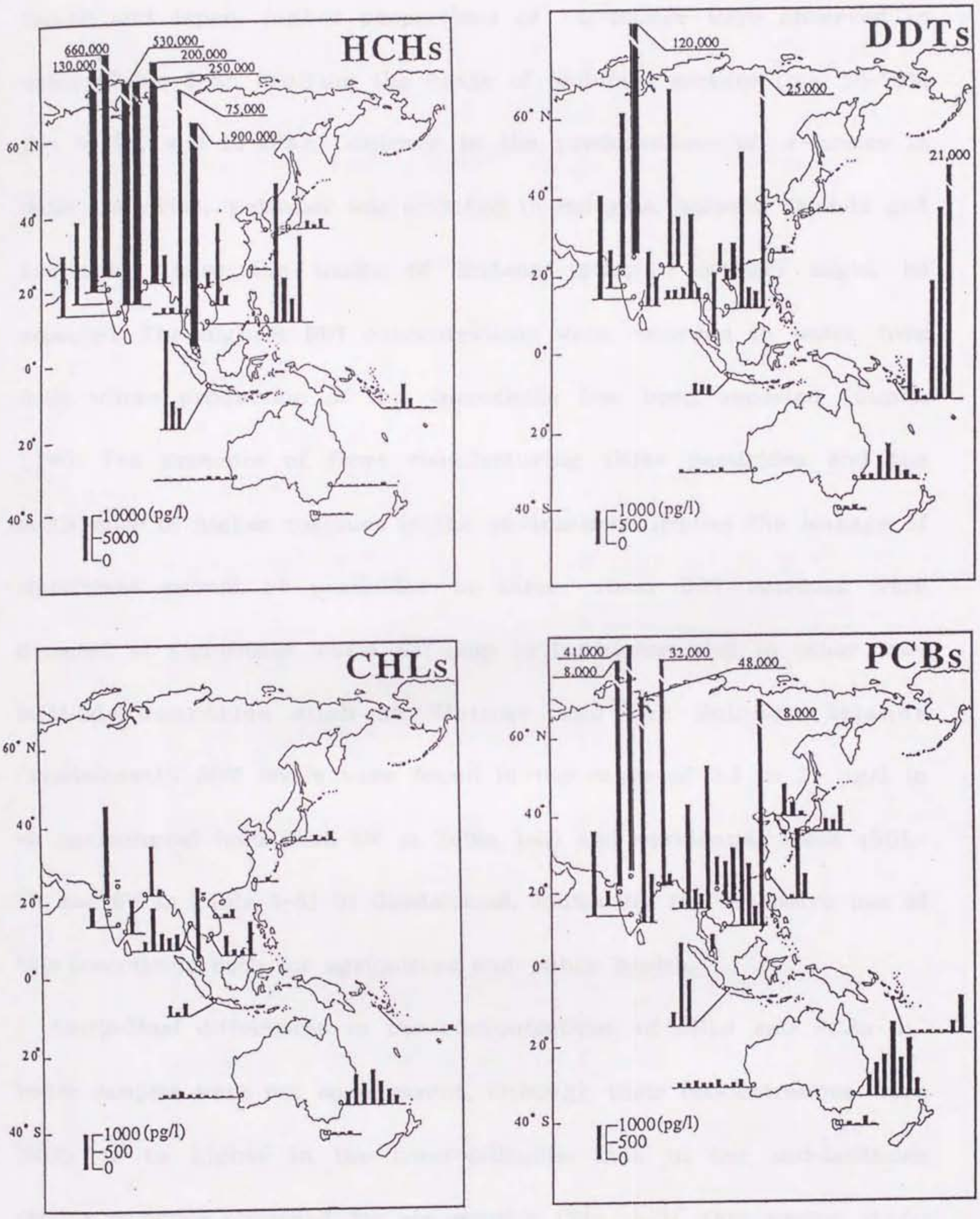

Fig. 1-3. Distributions of persistent organochlorines in river and estuarine water from the eastern and southern Asia and Oceania.

patterns among the locations. In India, Thailand, Vietnam, Indonesia, Taiwan and Japan, higher proportions of α-isomer were observed in water (Table 1-5), implying the usage of technical mixture (α-: 55-70%, β-: 5-14%, γ-: 10-18%). Contrary to the predominance of α-isomer in those countries, γ-isomer was enriched in Malaysia, Solomon Islands and Australia, where the usage of lindane (pure γ-isomer) might be expected. The highest DDT concentrations were recorded in water from Delhi where production of this insecticide has been reported (Gupta, 1986). The presence of firms manufacturing these pesticides and the occurrence of higher residues in the environment implies the leakage of significant amount of pesticides in these cities. DDT residues were detected at significant levels not only in India, but also in other low-latitude countries such as Vietnam and the Solomon Islands (Guadalcanal). DDT levels were found in the range of 3.5 to 21 ng/l in an agricultural field (SOL-3W in Table 1-5) and residential areas (SOL-5W and 6W in Table 1-5) in Guadalcanal, indicating the extensive use of this insecticide both for agriculture and public health.

Latitudinal differences in the concentrations of CHLs and PCBs in water samples were not so apparent, although their concentrations were likely to be higher in the lower-latitudes than in the mid-latitudes similar to those observed for air samples (Fig. 1-3). Our recent study (see Chapter 3) also showed that the distributions of CHLs and PCBs in the oceanic air and surface seawater were rather uniform irrespective of

Table 1-5. Concentrations (pg/litre) of organochlorines in river and estuarine waters from the eastern and southern Asia and Oceania.

	α-HCH	β-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	*o,p'*-DDT	ΣDDT	*t*-chlordane	*c*-chlordane	*t*-nonachlor	*c*-nonachlor	Σchlordane	PCBs
IND-1W	470,000	80,000	110,000	660,000	500	89,000	25,000	9,500	120,000	<2.0	<2.0	<2.0	<2.0	<8.0	41,000
IND-2W	250,000	88,000	190,000	530,000	88	530	220	29	870	<2.0	<2.0	<2.0	<2.0	<8.0	1,500
IND-3W	210,000	12,000	29,000	250,000	530	630	140	270	1,600	530	380	130	IF	1,000	48,000
IND-4W	1,600	11,000	680	13,000	680	1,300	600	480	3,100	200	200	140	IF	540	2,600
IND-5W	12,000	3.500	2,100	18,000	83	870	44	32	1,100	18	<2.0	17	IF	35	450
IND-6W	88,000	31,000	13,000	130,000	850	2,700	1,000	180	4,700	1,100	820	660	170	2,800	8,000
IND-7W	140,000	31,000	23,000	200,000	1,800	3,000	2,000	600	7,400	480	380	370	270	1,500	32,000
IND-8W	3,900	1,600	740	6,200	170	470	570	310	1,500	130	IF	49	IF	180	340
THA-1W	54,000	3,400	18,000	75,000	100	120	92	33	340	84	74	50	<2.0	210	<240
THA-2W	330	290	490	1,100	38	930	1,200	360	2,500	620	380	230	110	1,300	3,200
THA-3W	NA	NA	NA	NA	150	NA	130	27	310	170	130	140	NA	440	580
THA-4W	100	35	44	180	150	42	28	6.4	230	70	49	61	IF	180	450
THA-5W	470	360	210	1,000	47	150	31	3.8	230	180	140	79	27	430	4,400
VIE-1W	2,000	680	480	3,200	44	420	140	71	680	20	18	6.7	IF	45	840
VIE-2W	14,000	1.300	3,100	18,000	15	230	31	16	290	130	59	19	<2.0	210	1,200
VIE-3W	1,200	340	360	1,900	140	540	300	150	1,100	50	14	6.0	<2.0	70	1,600
VIE-4W	23,000	2,200	5,300	31,000	200	4,100	280	88	4,700	220	100	230	IF	550	2,700
VIE-5W	6,600	910	2,000	9,500	69	350	110	71	600	89	50	16	IF	160	1,900
VIE-6W	3,700	790	670	5,200	37	400	86	23	550	81	40	10	IF	130	570
VIE-7W	4,100	2,800	12,000	19,000	3,200	11,000	9,000	2,000	25,000	330	360	240	93	1,000	8,000
MAL-1W	69,000	64,000	1,800,000	1,900,000	250	1,200	210	IF	1,700	180	980	750	230	2,100	450
INS-1W	1,700	530	840	3,100	94	64	87	20	270	25	23	17	6.3	71	380
INS-2W	3,200	780	1,200	5,200	120	87	16	IF	220	90	100	50	22	260	2,100
INS-3W	14,000	4,200	3,700	22,000	73	38	71	12	190	77	85	57	21	240	1,300
SOL-1W	50	34	100	180	20	140	1,000	72	1,200	7.2	4.7	2.1	<1.0	14	<50
SOL-2W	31	28	63	120	20	21	220	25	290	4.9	3.1	2.7	1.1	12	<50
SOL-3W	63	39	5,200	5,300	40	71	2,800	590	3,500	6.4	5.3	5.2	<0.3	17	<50
SOL-4W	30	26	170	230	9.1	3.9	39	10	62	8.7	8.6	6.0	<0.2	23	<50
SOL-5W	360	170	1,500	2,000	460	1,100	3,700	430	5,700	<0.5	<0.5	<0.5	<0.3	<1.8	330
SOL-6W	160	99	76	340	2,000	91	16,000	2,700	21,000	47	36	30	22	140	1,100
JPN-1W	290	1,100	150	1,500	5.5	NA	3.1	IF	8.6	58	49	33	13	150	350
JPN-2W	240	550	76	870	3.9	NA	1.5	1.1	6.5	15	19	14	15	63	320
JPN-3W	420	1,200	190	1,800	8.8	NA	4.6	2.7	16	110	61	40	17	230	740
TAW-1W	170	47	36	250	6.6	1.9	<0.2	0.7	9.5	4.9	4.2	1.8	0.6	12	85
TAW-2W	64	130	47	240	130	37	13	12	190	39	38	27	10	110	2,100
TAW-3W	30	22	30	82	53	2.1	1.0	IF	56	2.0	6.6	3.5	3.5	16	750

Table 1-5. To be continued.

AUS-1W	97	59	510	670	17	<14	75	33	130	150	110	47	19	330	620
AUS-2W	110	73	310	490	36	58	83	28	210	620	280	160	80	1,100	950
AUS-3W	120	110	270	500	82	550	54	14	700	430	250	120	39	840	1,200
AUS-4W	95	160	310	570	170	750	130	35	1,100	620	330	200	63	1,200	2,200
AUS-5W	97	74	490	660	30	220	120	38	410	490	270	150	41	950	1,100
AUS-6W	59	66	120	250	52	160	80	30	320	210	120	77	<9.0	410	1,700
AUS-7W	170	110	590	870	16	35	60	28	140	81	63	37	21	200	470
AUS-8W	55	34	58	150	8.3	<7.0	33	14	55	22	19	10	<4.0	51	140
AUS-9W	81	49	99	230	14	<7.0	<1.0	<1.0	14	31	31	9.8	<4.0	72	150
AUS-10W	67	30	82	180	34	<6.0	22	12	68	71	42	26	8.3	150	180
AUS-11W	41	33	70	140	16	<7.0	<2.0	<2.0	16	37	11	7.1	<4.0	55	120
AUS-12W	57	15	68	140	14	<7.0	9.4	6.8	30	30	20	3.7	<4.0	54	120
AUS-13W	68	31	46	150	8.2	16	67	22	110	14	7.1	7.2	<4.0	28	210
AUS-14W	330	300	190	820	2.1	<5.0	<5.0	<5.0	2.1	12	6.9	6.4	<3.0	25	<50
AUS-15W	420	IF	180	600	5.0	<3.0	5.5	<3.0	11	16	8.6	7.2	<1.5	32	140
AUS-16W	150	100	57	310	1.3	<1.0	<1.0	<1.0	1.3	10	4.6	3.5	<0.5	18	220
AUS-17W	44	IF	41	85	7.5	<3.0	8.2	3.4	19	17	14	15	<2.0	46	93
AUS-18W	40	IF	74	110	30	<6.0	3.6	3.5	37	9.9	7.5	15	<3.0	33	<50
AUS-19W	14	17	48	79	69	11	19	11	110	27	20	21	<1.0	68	240
AUS-20W	8.1	19	84	110	1.6	<2.0	<2.0	<2.0	1.6	<1.5	<1.5	<1.5	<1.5	<6.0	<50

IF: not quantified due to the occurrence of interfering peak on the chromatogram.
NA: not available.

the latitudinal degree. Since PCBs are mainly used for industrial purposes, the industrialized countries such as the USA, Europe and Japan have been significant point sources of this toxic contaminant. A technical mixture of CHLs has also been considered as a chemical which was primarily used as an insecticide in the northern countries in the mid-latitudes such as the USA, and Japan (Dearth and Hites, 1991; Kawano, 1991), although its use has been stopped in both the countries in recent years. There was a highly contaminated belt of PCBs and organochlorine pesticides in the mid-latitude of the northern hemisphere until the beginning of 1980s (Tanabe *et al.*, 1982). However, it could be concluded from the geographical distributions for CHLs and PCBs that the uniform pattern might be due to increased exportation of such chemicals to the low-latitude nations from the mid-latitude ones, as is called as "southward expansion". In fact, some developing countries in the tropics have imported transformers and capacitors from industrialized nations. For example, Richardson and Waid (1982) pointed out that some electrical goods containing PCBs had been exported to countries such as Vietnam. The imported electrical equipments containing PCBs would be subsequently disposed or dumped in landfills, resulting in contamination of the tropical air and water phases. Noticeable evidence could be provided from the water samples in Ho Chi Minh, Vietnam. The water sample collected from municipal sewage contained 3-

14 times higher concentrations of PCBs (VIE-7w: 8.0 ng/l), compared with those from other sites in Vietnam (0.57-2.7 ng/l)(Table 1-5). As for CHLs, no information on trade for this chemical was followed. High residues of CHLs in air and water in tropical areas may be due to their application as termiticides as was used in the USA and Japan, although further studies are needed to trace the source of this chemical in these countries.

Regarding with the distribution patterns in sediments, the organochlorine residues showed smaller geographical variations (Fig. 1-4). Although HCH and DDT concentrations in air and water samples were clearly found to be higher in the tropical regions than in Japan and Australia, the levels in sediments were rather comparable in all the regions surveyed (Table 1-6). Such a trend has also been observed in marine organisms. HCH residue levels in fish samples from the Indian coast showed a small difference with those collected from northern countries, where HCH usage has been prohibited since the 1970s (Ramesh *et al.*, 1992). Furthermore, a prominent geographical variation was also noted in open ocean water, showing that HCH residues from the northern Indian Ocean were lower than those in colder waters such as the northern North Pacific and the Bering Sea (see Chapter 3). The uniform distribution of organochlorines in sediment samples may be explained by their rapid evaporation from water phase to atmosphere in the tropics because of the prevailing high temperature in the lower

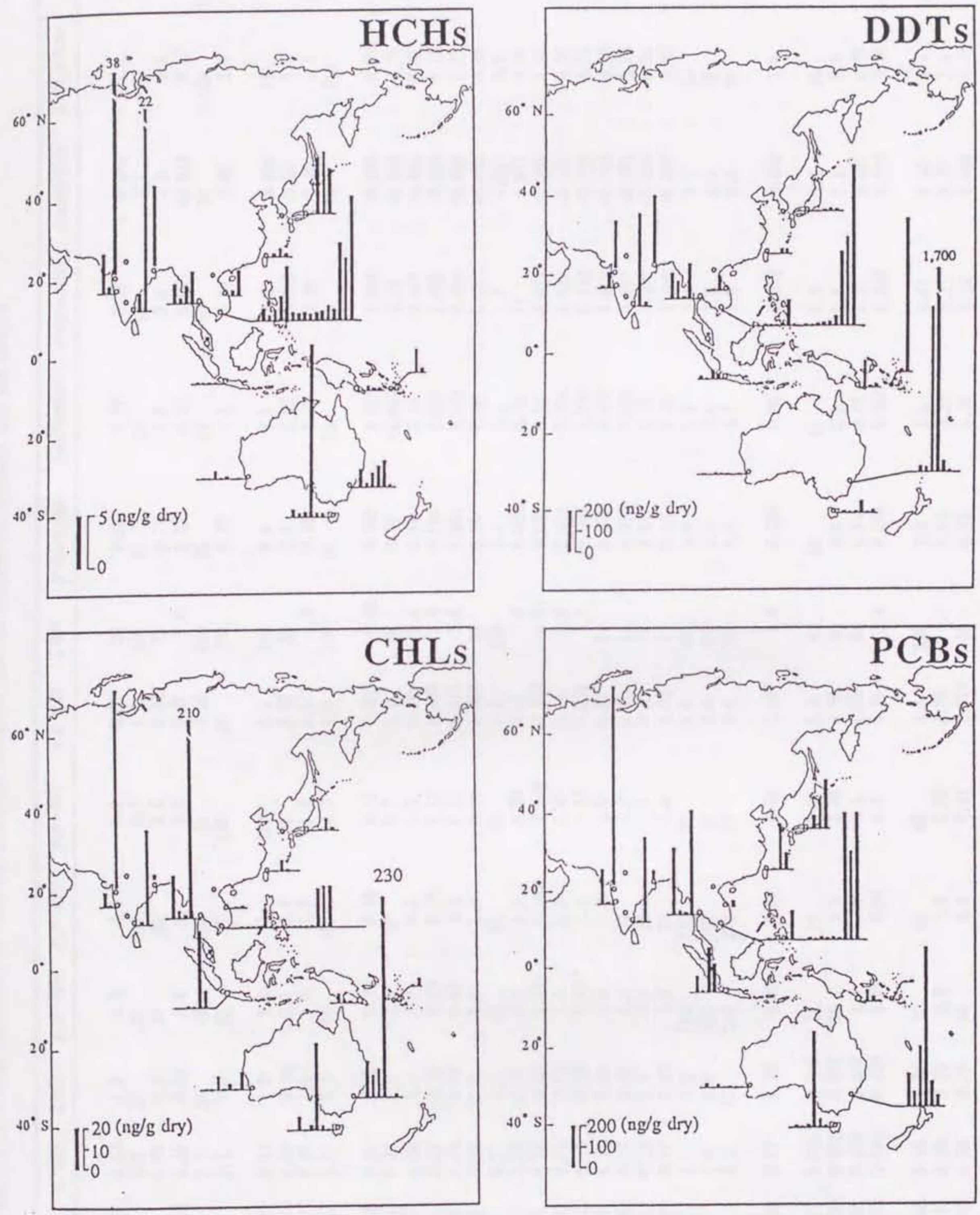

Fig. 1-4. Distributions of persistent organochlorines in river and estuarine sediments from the eastern and southern Asia and Oceania.

Table 1-6. Concentrations (ng/g dry) of organochlorines in river and estuarine sediments from the eastern and southern Asia and Oceania.

	α-HCH	β-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	*o,p'*-DDT	ΣDDT	*t*-chlordane	*c*-chlordane	*t*-nonachlor	*c*-nonachlor	Σchlordane	PCBs
IND-1S	0.80	0.27	0.50	1.6	3.8	9.4	6.2	0.21	20	0.84	0.27	0.24	0.044	1.4	4.8
IND-2S	4.6	14	3.8	22	100	340	8.7	1.1	450	24	10	10	3.1	47	420
IND-3S	1.6	1.6	0.63	3.8	40	29	2.9	0.92	73	0.79	1.9	2.4	1.3	6.4	170
IND-4S	0.32	0.078	0.18	0.58	1.9	3.0	2.8	0.27	8.0	0.27	0.13	0.071	<0.010	0.47	6.8
IND-5S	13	23	1.7	38	73	120	35	0.10	230	60	33	28	10	130	1,000
IND-6S	2.9	3.8	1.1	7.8	32	87	190	13	320	0.16	1.3	0.30	0.62	2.4	30
THA-1S	0.84	0.57	0.47	1.9	9.0	11	100	1.1	120	8.9	8.5	3.3	0.092	21	330
THA-2S	0.28	<0.10	0.20	0.48	2.1	4.4	76	0.82	83	2.0	0.92	0.069	0.29	3.3	17
THA-3S	1.2	0.19	0.20	1.6	1.8	1.7	1.2	0.071	4.8	0.36	0.43	0.38	0.18	1.4	11
THA-4S	1.0	0.42	1.7	3.1	59	100	4.3	1.8	170	94	56	47	15	210	520
VIE-1S	0.26	0.056	0.11	0.43	0.21	0.18	0.11	0.015	0.52	0.030	0.024	0.018	<0.003	0.072	0.65
VIE-2S	1.1	0.79	0.47	2.4	1.4	56	9.2	1.1	68	0.56	<0.010	0.23	<0.010	0.79	0.18
VIE-3S	0.56	0.15	0.38	1.1	1.0	5.2	1.3	0.54	8.0	0.19	0.15	0.077	<0.003	0.42	3.7
VIE-4S	0.21	0.11	0.13	0.45	0.43	0.46	0.12	0.009	1.0	0.066	0.050	0.033	<0.003	0.15	2.2
VIE-5S	0.47	0.24	0.23	0.94	0.41	2.8	0.11	0.011	3.3	0.084	0.079	0.049	<0.003	0.21	2.1
VIE-6S	1.4	0.22	0.66	2.3	1.5	7.9	0.79	0.060	10	0.25	0.20	0.13	<0.003	0.58	9.7
VIE-7S	2.0	1.0	2.2	5.2	48	51	18	1.2	120	3.4	3.2	1.7	0.54	8.8	140
VIE-8S	0.50	IF	0.20	0.70	5.7	1.5	0.29	0.31	7.8	0.082	0.16	IF	0.071	0.31	NA
VIE-9S	0.25	0.25	0.13	0.63	0.22	0.082	0.049	0.022	0.37	0.089	0.13	0.017	<0.003	0.24	0.22
VIE-10S	0.40	0.10	0.15	0.65	1.4	5.5	0.97	0.14	8.0	0.064	0.056	0.047	<0.003	0.17	5.1
VIE-11S	0.26	0.13	0.11	0.50	0.71	1.2	0.13	0.031	2.1	0.069	0.038	0.032	<0.003	0.14	2.3
VIE-12S	0.38	0.13	0.15	0.66	1.5	7.0	1.8	0.22	11	0.078	0.070	0.067	<0.003	0.22	8.9
VIE-13S	0.46	0.20	0.18	0.84	2.3	10	1.2	0.15	14	0.099	0.094	0.057	<0.003	0.25	4.8
VIE-14S	0.87	0.16	0.26	1.3	3.1	14	1.4	0.85	19	0.12	0.12	0.096	<0.003	0.34	8.6
VIE-15S	0.66	0.14	0.17	0.97	1.8	37	7.4	0.52	47	0.18	0.20	0.079	<0.003	0.46	7.6
VIE-16S	3.5	2.3	1.7	7.5	160	130	63	5.8	360	5.9	5.9	5.4	1.7	19	630
VIE-17S	2.5	1.7	1.8	6.0	200	190	42	2.9	430	6.5	7.5	3.6	2.0	20	440
VIE-18S	2.4	IF	9.3	12	540	210	37	2.8	790	9.0	4.7	3.0	2.9	20	630
MAL-1S	<0.005	0.066	0.11	0.18	0.22	0.89	0.63	0.097	1.8	0.088	0.85	0.053	0.025	1.0	<5.0
INS-1S	0.002	0.018	0.015	0.035	21	15	3.2	2.9	42	13	12	8.9	3.7	38	220
INS-2S	<0.002	0.020	0.051	0.071	19	5.5	0.86	0.25	26	2.9	2.0	1.6	1.5	8.0	140
INS-3S	<0.002	0.040	0.059	0.099	4.1	3.6	4.4	0.69	13	0.14	0.15	0.11	0.087	0.49	79
INS-4S	<0.003	0.013	0.045	0.058	0.95	0.94	1.3	0.21	3.4	0.061	0.053	0.046	0.003	0.16	5.9
PNG-1S	0.19	<0.040	0.15	0.34	11	25	89	3.6	130	1.8	1.4	0.41	0.53	4.1	54
PNG-2S	0.010	0.043	0.19	0.24	1.9	1.6	0.95	0.22	4.7	0.44	0.33	0.17	0.19	1.1	24
PNG-3S	0.022	<0.040	0.15	0.17	11	4.4	0.44	0.077	16	0.33	0.19	0.15	0.084	0.75	3.3
SOL-1S	1.4	<0.040	0.79	2.2	0.37	4.5	3.8	0.59	9.3	0.24	0.21	0.068	0.007	0.53	1.1
SOL-2S	<0.19	IF	<0.14	<0.33	140	130	450	27	750	2.3	0.65	0.58	0.38	3.9	5.0

Table 1-6. To be continued.

JPN-1S	4.5	0.36	0.69	5.6	1.3	0.9	0.27	NA	2.5	0.30	0.31	0.22	0.30	1.1	63
JPN-2S	5.1	0.42	0.70	6.2	1.4	9.8	0.65	NA	12	0.075	0.14	0.13	0.31	0.66	140
JPN-3S	0.75	3.5	0.29	4.5	2.6	2.0	0.2	NA	4.8	0.42	0.56	0.48	0.68	2.1	240
TAW-1S	0.12	0.12	0.049	0.29	0.16	0.072	0.12	0.035	0.39	0.040	0.059	0.010	0.030	0.14	2.3
TAW-2S	0.38	0.34	0.066	0.79	5.0	3.6	1.1	0.30	10	1.6	2.0	0.60	1.4	5.6	230
TAW-3S	0.12	0.12	0.049	0.29	5.2	3.9	1.2	0.28	11	0.35	0.40	0.17	0.31	1.2	80
AUS-1S	0.54	0.63	0.49	1.7	7.7	15	3.6	<1.0	26	8.2	3.3	4.5	1.9	18	160
AUS-2S	0.049	0.16	0.15	0.36	6.9	10	3.6	0.36	21	5.3	2.2	1.8	1.2	11	69
AUS-3S	0.19	0.98	0.11	1.3	320	310	150	30	810	6.4	3.3	2.9	1.4	14	300
AUS-4S	0.45	1.0	0.57	2.0	400	1,300	12	<10	1,700	140	61	26	6.0	230	790
AUS-5S	0.65	1.4	0.43	2.5	5.6	18	16	11	51	15	5.6	5.5	4.1	30	120
AUS-6S	0.041	0.15	0.032	0.22	1.9	2.5	1.9	<0.10	6.3	0.64	0.27	0.42	0.16	1.5	52
AUS-7S	0.018	0.010	0.018	0.046	1.3	1.4	0.72	0.015	3.4	0.088	0.047	0.057	0.11	0.30	18
AUS-8S	0.010	0.003	0.005	0.018	0.050	0.061	0.093	0.017	0.22	0.029	0.018	0.026	0.10	0.17	0.49
AUS-9S	0.40	0.054	0.27	0.72	4.9	2.0	0.52	<0.10	7.4	3.4	1.2	1.1	0.73	6.4	13
AUS-10S	0.011	0.020	0.026	0.057	0.98	0.14	0.083	0.017	1.2	0.19	0.076	0.065	0.020	0.35	0.68
AUS-11S	0.14	0.026	0.023	0.19	0.19	0.57	0.69	<0.010	1.5	2.4	0.093	0.060	0.11	2.7	5.0
AUS-12S	IF	IF	IF	IF	0.041	0.018	0.019	<0.010	0.078	0.17	0.082	0.038	0.020	0.31	0.69
AUS-13S	0.009	0.019	0.017	0.045	0.17	0.20	0.40	<0.010	0.77	6.9	1.0	0.13	0.46	8.5	0.85
AUS-14S	0.19	0.37	0.15	0.71	3.0	1.8	0.65	0.23	5.7	4.2	1.5	0.63	0.10	6.4	8.1
AUS-15S	0.12	0.11	0.084	0.31	0.23	0.70	0.099	<0.010	1.0	0.18	0.061	0.041	0.010	0.29	2.4
AUS-16S	0.028	0.011	0.42	0.46	2.2	2.0	0.39	0.063	4.7	0.60	0.59	0.41	1.1	2.7	11
AUS-17S	9.9	5.8	1.1	17	24	22	12	<1.0	58	17	6.0	15	4.6	43	470
AUS-18S	0.16	0.060	0.15	0.37	1.2	0.78	0.14	<0.10	2.1	0.26	1.5	0.14	0.54	2.4	35
AUS-19S	0.18	0.010	0.097	0.29	4.1	6.7	1.8	<1.0	13	0.45	0.18	0.10	0.015	0.75	7.3

IF: not quantified due to the occurrence of interfering peak on the chromatogram.
NA: not available.

latitude. As a result, shorter residence times in the water phase preserve sediments from severe contamination. Alternative explanation is that variation in organic carbon content of sediments between mid- and low-latitude areas may also influence the geographical distribution of organochlorines, since sediments with higher organic carbon levels are likely to adsorb lipophilic organochlorines than those with lower organic carbon levels such as sandy or clayish bottoms. If the sediments from the tropics are less enriched with organic carbon, then the tropical sediments would retain low residues according to the degree of organic carbon contents. However, no significant difference in organic carbon content was geographically found between mid- and low-latitude areas (Table 1-7). This denies the latter assumption (less residues in tropical sediments are due to the lower organic carbon contents) and supports that the persistent chemicals used in tropical areas are rapidly dissipated during their initial transport through inland air and water. This conclusion for shorter residence time of organochlorines in river and estuarine waters leading to their lower residues in sediments, coastal biota and open ocean water in the tropical areas is also supported by several studies carried out in southern India (Ramesh *et al.*, 1990; Takeoka *et al.*, 1991; Tanabe *et al.*, 1991). Using hydrokinetic parameters of a river and the data on HCH residue levels in air and water, the HCHs flux in estuarine and coastal areas was

Table 1-7. Organic carbon contents (OCC) of sediment samples (dry wt basis).

Sample No.	OCC (%)	Sample No.	OCC (%)
IND-1S	5.9	JPN-1S	1.3
IND-2S	11	JPN-2S	3.9
IND-3S	3.5	JPN-3S	3.2
IND-4S	1.9		
IND-5S	13	TAW-1S	0.74
IND-6S	5.1	TAW-2S	2.6
		TAW-3S	2.1
THA-1S	3.1		
THA-2S	2.1	AUS-1S	6.0
THA-3S	1.7	AUS-2S	2.6
THA-4S	6.4	AUS-3S	3.0
		AUS-4S	3.3
VIE-1S	0.98	AUS-5S	1.5
VIE-2S	2.1	AUS-6S	0.88
VIE-3S	2.6	AUS-7S	2.9
VIE-4S	2.1	AUS-8S	0.46
VIE-5S	3.2	AUS-9S	5.2
VIE-6S	2.9	AUS-10S	1.0
VIE-7S	3.1	AUS-11S	5.9
VIE-8S	7.7	AUS-12S	1.2
VIE-9S	9.1	AUS-13S	0.75
VIE-10S	2.5	AUS-14S	27
VIE-11S	2.3	AUS-15S	1.8
VIE-12S	2.3	AUS-16S	17
VIE-13S	2.4	AUS-17S	8.5
VIE-14S	2.9	AUS-18S	2.9
VIE-15S	3.1	AUS-19S	6.2
VIE-16S	7.7		
VIE-17S	9.1		
VIE-18S	7.1		
MAL-1S	1.8		
INS-1S	7.3		
INS-2S	4.3		
INS-3S	3.7		
INS-4S	0.57		
PNG-1S	2.1		
PNG-2S	5.5		
PNG-3S	5.2		
SOL-1S	1.0		
SOL-2S	4.8		

calculated (Takeoka *et al.*, 1991). Consequently, it was estimated that about 99.6% of the applied HCHs in agricultural areas escaped to the air and only 0.4% drained to coastal estuaries, of which 75% was further transferred to air. The result obtained in southern India seems to be an extreme case. However, the geographical pattern in the sediment in this study may indicate that the rapid volatilization of organochlorines is rather common in the tropical ecosystem and impose a global concern on their long-range atmospheric transport.

Redistribution on a global scale

It has been hypothesized in general that inputs of semivolatile organochlorines to the aquatic environment decrease with increasing distance from the point source. When the mobility of these chemicals is considered on a small scale, the result would be in consistent with this hypothesis. An example could be observed in the distributions of organochlorines in sediments collected from a southern Vietnamese estuary (Fig. 1-5). All organochlorines studied showed higher residue levels in Ho Chi Minh that can be regarded as an organochlorine sources and an apparent decreasing trend from the upper to lower stream of the estuary. On the contrary, in sediments from various parts of eastern and southern Asia and Oceania, a consistent and uniform distributions of organochlorines suggest a different implication as shown in Fig. 1-4. Thus, it is noticeable that the dynamics of organochlorines in large scale should take into account for geographical features such as temperature.

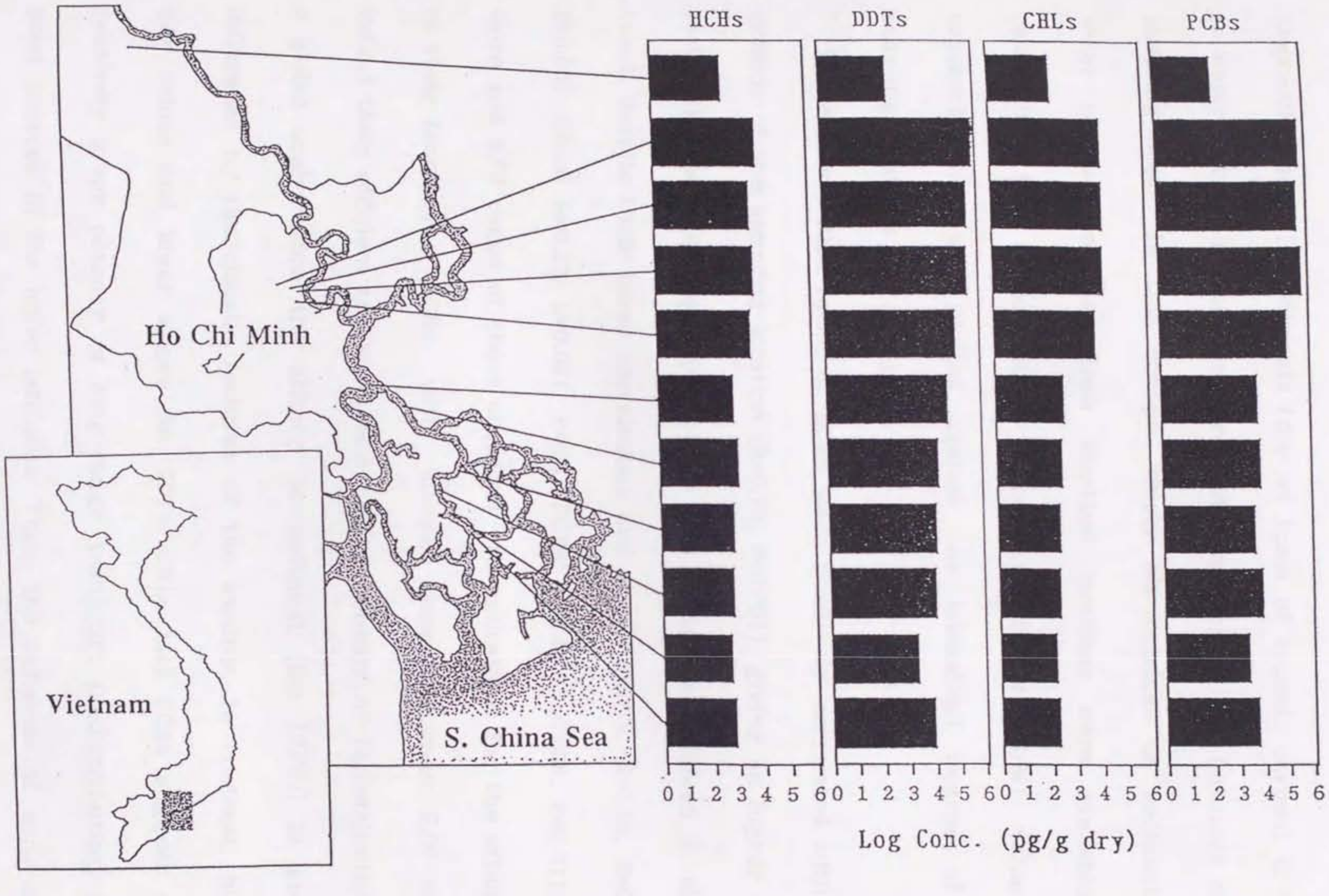

Fig. 1-5. Distributions of organochlorines in sediments from the southern Vietnamese estuary.

In order to clarify this, the concentration ratios (S/W) of organochlorines in sediments (dry wt basis of organic carbon) to those in water were calculated and ordered according to the latitudes of the sampling areas. In this context, thirty six pairings of sediment and water samples collected from identical locations were available for calculating the concentration ratios. Logarithmic (S/W) value for organochlorines was plotted against the latitudinal degree of the sampling locations (Fig. 1-6).

The concentration ratios of HCHs were positively correlated with the latitude of the sampling location (R=0.72, P<0.001), giving an higher slope (S=0.078). The ratios of DDTs, CHLs and PCBs also showed a similar trend, despite their lower correlations and slopes (DDTs: R=0.50, S=0.031, P<0.005, CHLs: R=0.32, S=0.021, P<0.1, PCBs: R=0.45, S=0.036, P<0.01). The slope and S/W ratios of these chemicals are indications for the efficiency of their transport. HCHs with steeper slope and lower S/W values reflect their efficient transport and higher potency of redistribution on a global scale, since the affinity to sediment [log (S/W)] is greatly influenced by the climatic features of the locality. In contrast, higher S/W values and lower slopes for DDTs, CHLs and PCBs suggest their relatively lower potency of long-range transport (redistribution) from point sources in the lower latitudes. Thus, the behavior of semivolatile persistent chemicals released in the tropics might be controlled by the

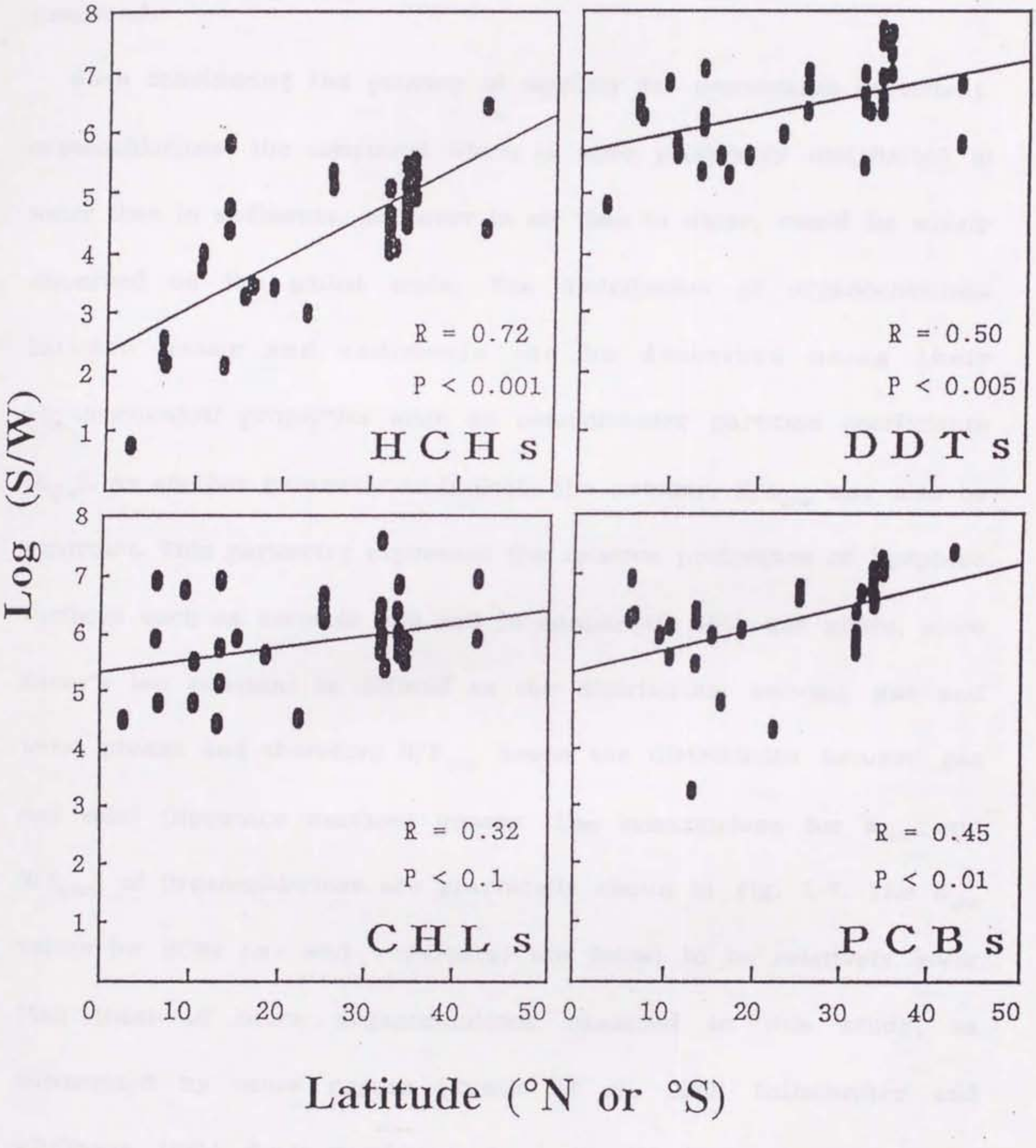

Fig. 1-6. Relationships between the concentration ratios (*S/W*) of organochlorines in sediment (*S*) to those in water (*W*) and the latitudes of sampling locations.

latitudinal meteorological gradients such as temperature, although the extent for redistribution is considered to vary depending on the compound.

When considering the potency of mobility for semivolatile persistent organochlorines, the compound which is more preferably distributed in water than in sediments, moreover in air than in water, would be widely dispersed on the global scale. The distribution of organochlorines between water and sediments can be described using their physicochemical properties such as octanol-water partition coefficients (K_{OW}). As another parameter to indicate the mobility, H/K_{OW} may also be important. This parameter expresses the relative preference of lipophilic surfaces such as aerosols and soil in comparison with gas phase, since Henry's law constant is defined as the distribution between gas and water phases and therefore H/K_{OW} means the distribution between gas and solid (lipophilic surface) phases. The relationships for K_{OW} and H/K_{OW} of organochlorines are graphically shown in Fig. 1-7. The K_{OW} values for HCHs (α- and γ-isomers) are found to be relatively lower than those of other organochlorines examined in this study, as summarized by other papers (Suntio *et al.*, 1988; Ballschmiter and Wittlinger, 1991). Since persistent chemicals with lower K_{OW} values are considered to be relatively distributed in the water phase than those with higher K_{OW}, such compounds are likely to be transported and to be redistributed by the circulation of water and subsequently by gas

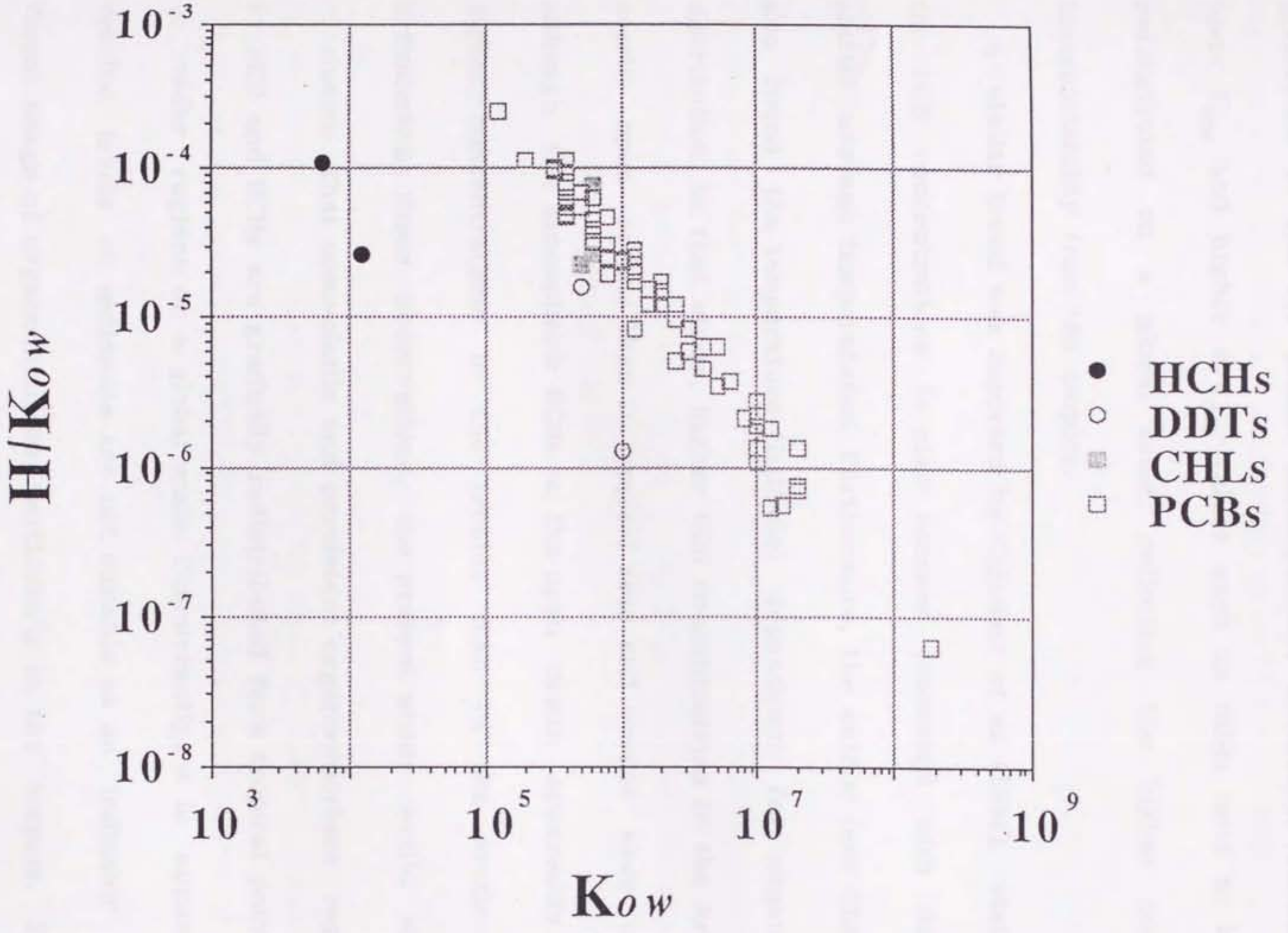

Fig. 1-7. Relationship between K*ow* and H/K*ow* of organochlorines.

Data are cited from Mackay *et al.* (1986), Shiu and Mackay (1986), Suntio *et al.* (1988), Kawano (1991), Kucklick *et al.* (1991) and Dunnivant *et al.* (1992).

exchange processes between air and water. On the other hand, H/K_{OW} values for HCHs are found to be larger, indicating their relative preference in the air phase. Consequently, persistent chemicals with lower K_{OW} and higher H/K_{OW} values such as HCHs tend to be widely redistributed on a global scale, reflecting the higher potency of transportability from the tropics.

A similar trend was reported by Calamari *et al.* (1991), stating that the HCB concentrations in plant biomass increased with decreasing annual average temperatures. Furthermore, the author (see Chapter 3) also found the temperature (latitude) dependence for organochlorine distribution. In that study, higher HCH concentrations in the Arctic and nearby open oceans than in tropical seas and oceans were observed, although the atmospheric HCHs in the open ocean apparently showed higher concentrations in the tropics than in the Arctic regions. Considering these observations, the present study would allow the conclusion that semivolatile and persistent organochlorines represented by HCB and HCHs are gradually redistributed from tropical point sources to colder regions on a global scale. Concurrently, it is apparent that residue levels in sediments are not suitable as an indicator for the recent usage of organochlorines, particularly in the tropics. Therefore, multi-compartment monitoring is essential to elucidate their behavior and fate and to assess the current status of these contaminations.

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2 Behavior in the Cold Environment: A Case Study in the Lake Baikal Region, Russia

Abstract

Contamination of semivolatile organochlorines such as hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), DDTs, chlordanes and PCBs was assessed in air, water, sediments and soils from the Lake Baikal region, Russia. Comparison of the residue levels in the lake with those in other regions suggested the presence of local sources of DDTs and PCBs, although the residues were considered to be lower than those in the low-latitude areas in the eastern Asia and Oceania. Larger proportion of *p,p'*-DDT to total DDTs and similarities of PCB congener compositions to a Russian technical PCB formation were found in the samples analyzed, implying their usages nearby the Lake. The estimated fluxes of organochlorines by gas exchange across air-water interface applying the two film model indicated that the lake water plays a role as a sink for HCB, HCHs and DDTs, and also serves as a source for PCBs. The magnitude for PCB volatilization in this lake was found to be smaller than those in the Great Lakes for which the values have been previously reported. This study provides an example to elicit the availability of multi-matrices monitoring for assessing the magnitude and fate of the organochlorine contaminations on global terms.

Introduction

During the last decade, it was reported that the Arctic and its adjacent areas were certainly exposed to the persistent organochlorines released elsewhere (Barrie *et al.*, 1992), as evidenced by their detection in air, surface seawater (Tanabe and Tatsukawa, 1980; Oehme and Stray, 1982; Hargrave *et al.*, 1988), snow (Gregor and Gummer, 1989), surface sediments (see Chapter 4) and wildlife (Norstrom *et al.*, 1989; Muir *et al.*, 1988; Hargrave *et al.*, 1992) in significant quantities. In this context, long-range atmospheric transport of organochlorines is considered with much concern to the sources of contamination in the Arctic ecosystem. It has been predicted that some of organochlories transported through atmosphere are accumulated in the terra and ocean by the cold trap effect. Calamari *et al.* (1991) indicated using foliage samples that the global distribution of hexachlorobenzene (HCB) was strongly dependent on the temperature and the highly contaminated samples were found in cold areas. The prominent contamination by hexachlorocyclohexanes (HCHs) was also noted in the Arctic and its adjacent oceanic waters, nevertheless the aerial concentrations were lower than those in the tropical regions (see Chapter 3).

In contrast to several evidences indicating the elevated organochlorine contaminations in the Arctic, their sources and pathways still remain obscure. This is partly due to the existence of unsurveyed areas of organochlorine pollution. While the reports on recent status of

OC contaminations are increasing in tropical Asia, Oceania (Kaushik *et al.*, 1987; Ramesh *et al.*, 1989; Ramesh *et al.*, 1990; see Chapters 1 and 3), Africa (Bacci *et al.*, 1988; Ngabe *et al.*, 1992), North America (Rapaport and Eisenreich, 1988; Hermanson and Hites, 1989; Bidleman *et al.*, 1992) and Europe (Wittlinger and Ballschmiter, 1987; Larsson and Okla, 1989; Jones *et al.*, 1992), little information is available for those in the north-eastern areas such as Siberia. As suggested in our previous study, the multi-matrices monitoring is an useful tool to identify the presence and the significance of pollution sources on a global scale (see Chapter 1). For example, the OC concentrations in sediment samples from tropical eastern Asia and Oceania were found to be less, while air and river water showed high residue levels. This indicates that the distribution and partitioning of OCs among matrices depend on temperatures. However, such an approach has never been attempted in cold regions and hence this placed it in an impasse to understand a complete aspect of global contamination by organochlorines. Based on these backgrounds, the present study deals with the organochlorine contaminations in the Lake Baikal region, eastern Siberia, Russia. During the period of 1987 to 1988, several thousands of seals inhabiting in this lake had died. While the immediate cause of mass mortality of Baikal seals was attributed to morbillivirus infection (Grachev *et al.*, 1989), the triggering mechanisms behind infection are still unclear. However, it is partly suspected that hazardous persistent organochlorines affect the immune systems of seals.

In this investigation, air, lake water, sediments and soil samples were collected and their contamination levels of HCB, HCHs, DDTs, chlordane compounds and polychlorinated biphenyls (PCBs) were determined. These data were compared with those of lower latitude countries in the eastern Asia and Oceania previously reported (see Chapter 1). Furthermore, in order to understand their volatilization, deposition and transport processes in the eastern cold region, fluxes for organochlorines across the air-water interface were estimated by simultaneous measurements of atmospheric and hydrospheric concentrations of organochlorines, and the role of large lake waterbody in the terrestrial area was discussed in comparison with those in the other lakes and oceans.

Geographical features of the Lake Baikal region

The Lake Baikal located in the eastern Siberia (52-56°N, 104-110°E) is the deepest (max. 1637m) and the most ancient (20-30 million years) fresh water lake in the world (Fig. 2-1). It retains a fifth of the world's fresh water. The Baikal is inhabited by about 2,000 species of freshwater organisms, two-third of which are endemic. The lake water is mainly exchanged through one outflowing and two inflowing rivers. The Upper Angara river originating from northern Siberian forests flows into northern part of the Lake Baikal, and the other inflowing one, Selenga river, forms a vast delta in the lower reaches through the Mongolian

Fig. 2-1. Map showing survey cruise route in the Lake Baikal from May 14 to June 1, 1992.

People's Republic and Ulan Ude. The Angara river flows out from south-western part of the lake and the waters rendezvousing with the Yenisey's waters in the midstream are ultimately swept down to the Kara Sea. The Lake Baikal is annually covered by ice between November and mid-April and then the ice begins to thaw and break apart until the end of May.

Irkutsk, situated along the Angara river at about 60km north-west away from the Lake, is known for the giant hydro-power plants, pulp-and-paper and aluminum plants. In Baikalsk and Slyudyanka, located in the southern lakeshore, a cellulose-paper and a coal-fired power plant are still operating, respectively.

Experimental Section

Sample Collection

Samples of air (n=6), surface lake water (n=16) and sediments (n=6) were collected from the research vessel "Balkhash" during May 14 - June 1 in 1992. The cruise route covered south to middle parts of the Lake Baikal (Fig. 2-1). Although the surface was mostly covered by ice at the beginning of the cruise, high southern wind on 15 May immediately thawed out ice upto the middle part of lake.

Glass columns packed with polyurethane foam plugs (i.d. 27mm, length 390mm) and Amberlite XAD-2 resin (i.d. 15mm, length 200mm) were used as adsorbents for organochlorines in air and water samples, respectively. Methods of the glass column preparation and sample collection for air and water are given elsewhere in detail (see Chapters 1 and 3). About 100m^3 of air was sampled using a low-volume air pump (flow rate: 38 L/min.) on the upper deck of the vessel during the cruise. Twenty litres of surface water was collected using a stainless bucket. The water samples were concurrently taken during the operation for air sampling. The collected water was immediately passed through the XAD-2 resin column at a flow rate of less than 0.3 L/min. Surface sediment samples were collected using a stainless steel grab sampler. Besides these collection on board, surface soil samples (n=4) were also taken from agricultural fields around Irkutsk. Each sample of the sediment and soil was well mixed in a precleaned aluminum plate and preserved in a polyethylene bag with several ml of formalin. All samples were carried to the laboratory and stored below -20°C until analysis. Details of air, water and sediments are summarized in Table 2-1.

Sample Analysis

Prior to analysis, samples were thawed at room temperature. Organochlorines in PUF plugs were extracted in a Soxhlet apparatus with 400 ml of acetone for 3 hrs. The acetone extracts were concentrated up to 5 ml in a Kuderna-Danish (KD) concentrator and then transferred to 10 ml of hexane in a separatory funnel containing 70 ml of hexane-washed water. Organic contaminants trapped on XAD-2 resin were eluted with 300 ml of ethanol and transferred to 100 ml of hexane in 1.8 L of

Table 2-1. List of air, water and sediments samples collected from the Lake Baikal in 1992.

Sample No.	Latitude & Longitude	Collection Date	Volume	Covered Area	Remarks
air			(m³)		
A-1	51° 42'-51° 47'N, 105° 09'-105° 38'E	15-17 May	109	south	
A-2	51° 56'-52° 25'N, 105° 28'-106° 20'E	17-19 May	64.8	south to central	
A-3	52° 25'-52° 55'N, 106° 20'-107° 23'E	19-21 May	109	central	
A-4	52° 54'-52° 56'N, 107° 28'-107° 37'E	21-23 May	109	central	
A-5	53° 45'-53° 54'N, 107° 52'-108° 36'E	25-27 May	109	central	
A-6	51° 31'-52° 33'N, 103° 44'-107° 07'E	30-31 May	76.1	central to south	
water			(L)		water temp.(° C)
W-1	51° 42'N, 105° 09'E	15 May	20	south	0^{a}
W-2	52° 16'N, 105° 58'E	18 May	20	south	0^{a}
W-3	51° 42'N, 105° 09'E	18 May	20	south	0^{a}
W-4	51° 42'N, 105° 09'E	18 May	20	south	0^{a}
W-5	51° 57'N, 105° 28'E	18 May	20	south	2.0
W-6	52° 30'N, 106° 41'E	19 May	20	central	2.4
W-7	52° 55'N, 107° 37'E	21 May	20	central	2.2
W-8	53° 53'N, 108° 36'E	25 May	20	central	1.9
W-9	52° 26'N, 106° 42'E	30 May	20	Selenga delta	8.8
W-10	52° 24'N, 106° 30'E	30 May	20	Selenga delta	13.4
W-11	52° 22'N, 106° 20'E	30 May	20	Selenga delta	11.1
W-12	52° 17'N, 106° 14'E	30 May	20	Selenga delta	17.1
W-13	52° 13'N, 106° 13'E	30 May	20	Selenga delta	9.7
W-14	51° 31'N, 104° 09'E	31 May	20	off Baikalsk	3.6
W-15	51° 39'N, 103° 44'E	31 May	20	off Slyudyanka	3.5
W-16	51° 40'N, 104° 05'E	31 May	20	south	3.2
sediments					
S-1	52° 26'N, 106° 42'E	30 May		Selenga delta	at the same site as W-9
S-2	52° 24'N, 106° 30'E	30 May		Selenga delta	at the same site as W-10
S-3	52° 22'N, 106° 20'E	30 May		Selenga delta	at the same site as W-11
S-4	52° 17'N, 106° 14'E	30 May		Selenga delta	at the same site as W-12
S-5	52° 13'N, 106° 13'E	30 May		Selenga delta	at the same site as W-13
S-6	51° 39'N, 103° 44'E	31 May		off Slyudyanka	at the same site as W-15

a: The value was estimated, since the surface of lake was covered by ice.

hexane-washed water. The hexane extract was also concentrated up to 5 ml in a KD concentrator. Approximately 10-20 g of sediment and soil samples were placed in 250 ml glass-stoppered Erlenmeyer flasks. Soils were allowed to soak with hexane-washed water for 30 min. Sediment and soil samples were shaken with 200 ml of acetone for two hrs and then organochlorines were transferred to 100 ml of hexane in 1.5 L of hexane-washed water. The hexane layer taken was also concentrated up to 5 ml in the same manner as the cases for air and water samples. The extracts were treated with copper chips to remove sulfur. Concurrently, several grams of sediment and soil samples were taken in a glass cup and dried at 105°C for three hrs to obtain the dry weight.

Hexane extracts of all the samples were cleaned up with 5 % of fuming sulfuric acid in concentrated sulfuric acid. After washing the hexane extract with hexane-washed water, it was microconcentrated up to 100 µl under a gentle stream of nitrogen and injected into a high performance liquid chromatography (HPLC) for further cleanup and fractionation. The HPLC conditions and eluates in each fraction were identical to those reported previously (see Chapter 3).

Eluates from the HPLC were subjected for identification and quantification of organochlorines in a high resolution gas chromatograph equipped with ^{63}Ni electron capture detector (HRGC-ECD: Hewlett Packard 5890 Series II), installed with a moving needle type injection system (splitless and solvent cut mode, Shimadzu Co. Ltd., Japan). HCB, HCH isomers, DDT and its metabolites, and chlordane compounds were analysed on a 30 m x 0.25 mm i.d. 14 % cyanopropyl phenyl polysiloxane fused silica capillary column with a 0.25 µm film thickness (DB-1701, J&W Scientific Co. Ltd., U.S.A.). In some cases, a 100 % dimethylpolysiloxane capillary column (DB-1, J&W Scientific) with the same size and film thickness as DB-1701 was also used for further confirmation of the peaks. PCB isomers and congeners were separated on the DB-1 column. A sample volume injected on HRGC-ECD ranged 5-20 µl. The GC oven temperature was programmed at a rate of 20 °C /min from an initial temperature of 60 °C (1 min hold) to 160 °C (10 min hold) and then to 250 °C at a rate of 2 °C/min (30-60 min hold). Helium as a carrier gas was purged at 15 psi and nitrogen as a make-up gas was kept at 60 ml/min. The injector and detector temperatures were 250 and 300 °C, respectively. Data on the chromatogram were calibrated as peak areas using an integrator (Hewlett Packard 3396A). Concentrations of organochlorines were quantified in comparison with the corresponding external standard. Kanechlors 300, 400, 500 and 600 equivalent mixture was used as an external standard for PCBs quantification. Peak identification was followed by Tanabe *et al.* (1987).

Total organic carbon contents in sediment and soil samples were also measured by a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (GC-TCD) and a high sensitivity N.C.-

analyser (Sumigraph NC-80: Sumitomo Chemical Industry Co. Ltd., Japan), after these samples were dried and meshed homogeneously. The conditions for GC-TCD and N.C.-analyser have been already described elsewhere (see Chapter 4).

Blank samples for air and water consisted of cleaned PUF and XAD-2 resin columns transported to the field and returned to the laboratory were also analysed in the same manner as samples. Procedural blanks for sediments and soil were simultaneously treated and quantified with those samples through the whole analytical procedure. The blank values for individual organochlorine pesticides and total PCBs ranged as follows, respectively; air: 0.5-1.0 and 5 pg/m^3, water: 1-2 and 15 pg/l, sediments and soils: 1.0-10 and 40 pg/g dry wt. The detection limits for OCs in samples were twice that of the blank values.

Quantification error for organochlorines through analytical procedures was checked three times by spiking about 5 ng of pesticides and 50 ng of total PCBs onto cleaned PUF and XAD-2 columns. In the case of sediments and soils, about 100 ng of pesticides and 1 µg of PCBs were spiked in a less contaminated paddy sediments and the recoveries were calculated. The errors were less than 10% in these matrices for all the chemicals analysed in this study.

Results and Discussion

Organochlorine concentrations

Aerial concentrations for organochlorines over the Lake Baikal showed a small spatial variations in the area covered (Fig. 2-2). HCHs (α- and γ- isomers) and HCB concentrations were relatively higher than those of DDTs (*p,p'*-DDE and *p,p'*-DDT), CHLs (*trans*-, *cis*-chlordanes and *trans*-nonachlor) and PCBs (sum of individual isomers and congeners) as shown in Table 2-2. However, the concentrations for HCB and HCHs were very close to the lowest (base-line) levels (less than hundreds pg/m^3) found in the northern hemisphere. CHLs and PCBs concentrations were also comparable to those (CHLs; a few pg/m^3, PCBs; less than one hundred pg/m^3) in the Arctic, which is regarded as a "remote site" from the source. On the contrary, DDT concentrations recorded in this study, appeared to be one order of magnitude higher than those of the Arctic levels, ranged in a few pg/m^3 (Hargrave *et al.*, 1988; Patton *et al.*, 1989; Hinckley *et al.*, 1991; see Chapter 3).

Regarding the organochlorines in surface water, the distribution patterns seemed to be different among the organochlorines examined (Fig. 2-3). HCB concentrations were relatively homogeneous. HCHs and PCBs concentrations were found to be higher in the lower reaches of Selenga river and the southern basin of the lake. This indicates the inflow of HCHs and PCBs through the Selenga river and the southern tributaries. Particulary, PCBs showed a wide range of concentrations (18-590 pg/L). This might be due to the variation in the particulate

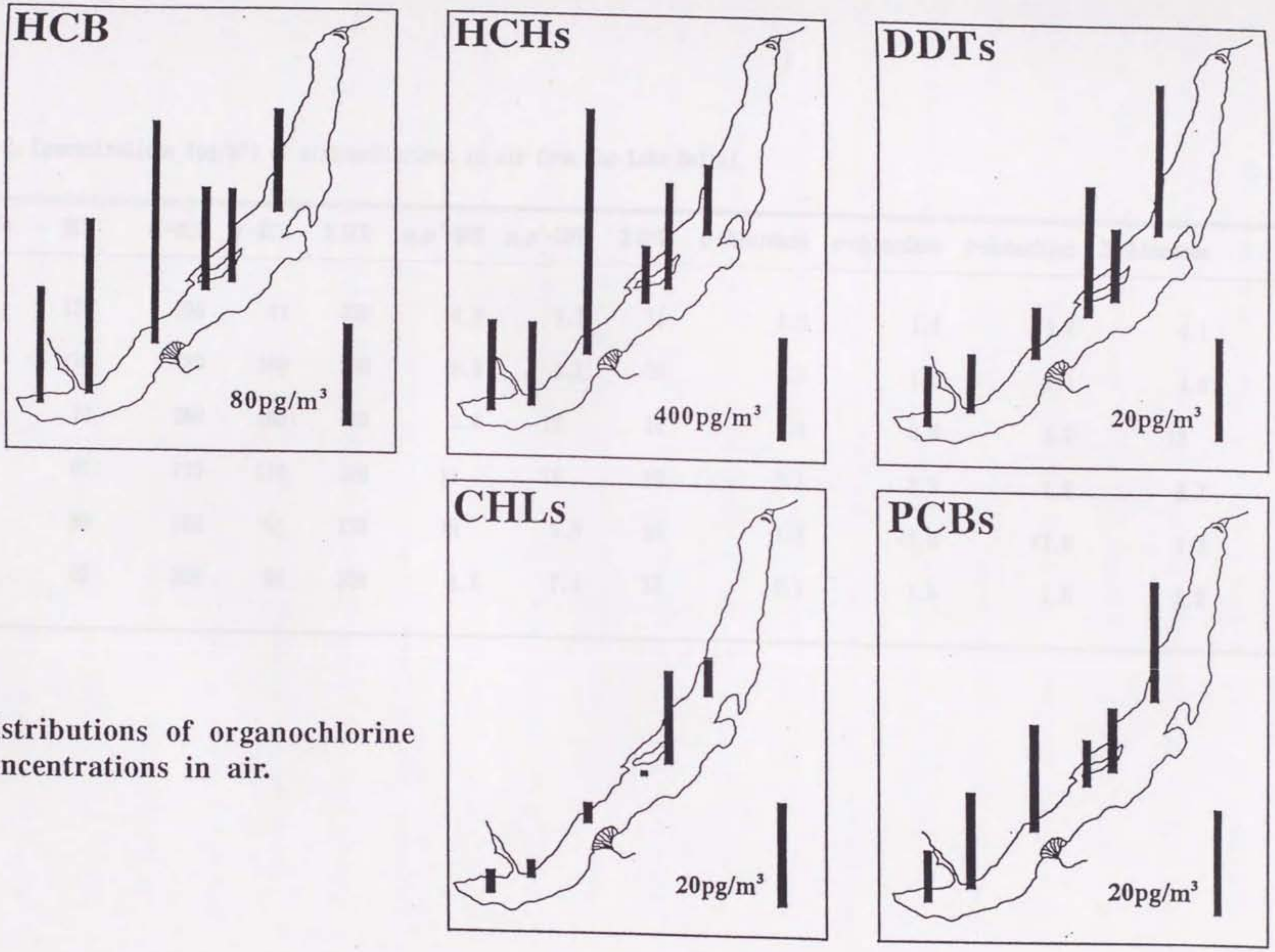

Fig. 2-2. Distributions of organochlorine concentrations in air.

Table 2-2. Concentrations (pg/m^3) of organochlorines in air from the Lake Baikal.

Sample No.	HCB	α-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDT	ΣDDT	*t*-chlordane	*c*-chlordane	*t*-nonachlor	Σchlordane	PCBs
A-1	130	290	44	330	4.0	7.3	11	1.3	1.4	1.4	4.1	18
A-2	170	780	180	960	8.9	1.3	10	1.7	1.2	1.1	4.0	20
A-3	70	260	160	420	3.0	12	15	7.4	5.8	5.2	18	13
A-4	81	170	110	280	11	18	29	3.1	3.3	1.8	8.2	23
A-5	80	180	51	230	18	6.8	25	1.3	<1.0	<1.0	1.3	8.7
A-6	92	260	94	350	4.1	7.4	12	2.1	1.5	1.6	5.2	9.4

fractions with which PCBs associate (Achman *et al.*, 1993), as the estuarine water is considered to contain larger mass of suspended materials. PCB residue levels in the Selenga river estuary of the Lake Baikal (Table 2-3) were one order of magnitude higher than that observed for the Arctic ocean (Hargrave *et al.*, 1988; see Chapter 3). Comparison of PCB residues in the lake water with those in the cold ocean clearly demonstrates the significant riverine inputs into the lake. Considering the observation of background levels in the atmosphere over the lake as mentioned above, the atmospheric input to lake water seems to be smaller than the hydrospheric one. In addition to PCBs, DDTs also occasionally revealed higher concentrations in the lake water than in the Arctic. However, in the case of DDTs, the higher residue levels in water were consistent with those from the aerial concentrations, suggesting the possibility of significant atmospheric input for DDTs. CHL concentrations were almost close to the detection limit and recorded levels were comparable with those in the open ocean.

Apart from air and water, PCB and DDT residues in sediments surpassed HCHs (Table 2-4). This is due to the greater lipophilic properties of PCBs and DDTs than HCHs, which are represented as octanol-water partition coefficients (K_{OW}). The coefficients for PCBs (Shiu and Mackay, 1986) and DDTs (Suntio *et al.*, 1988) are known to be one to three orders of magnitude higher than those for HCHs (Suntio *et al.*, 1988). Furthermore, prominent concentrations of PCBs, DDTs and HCB

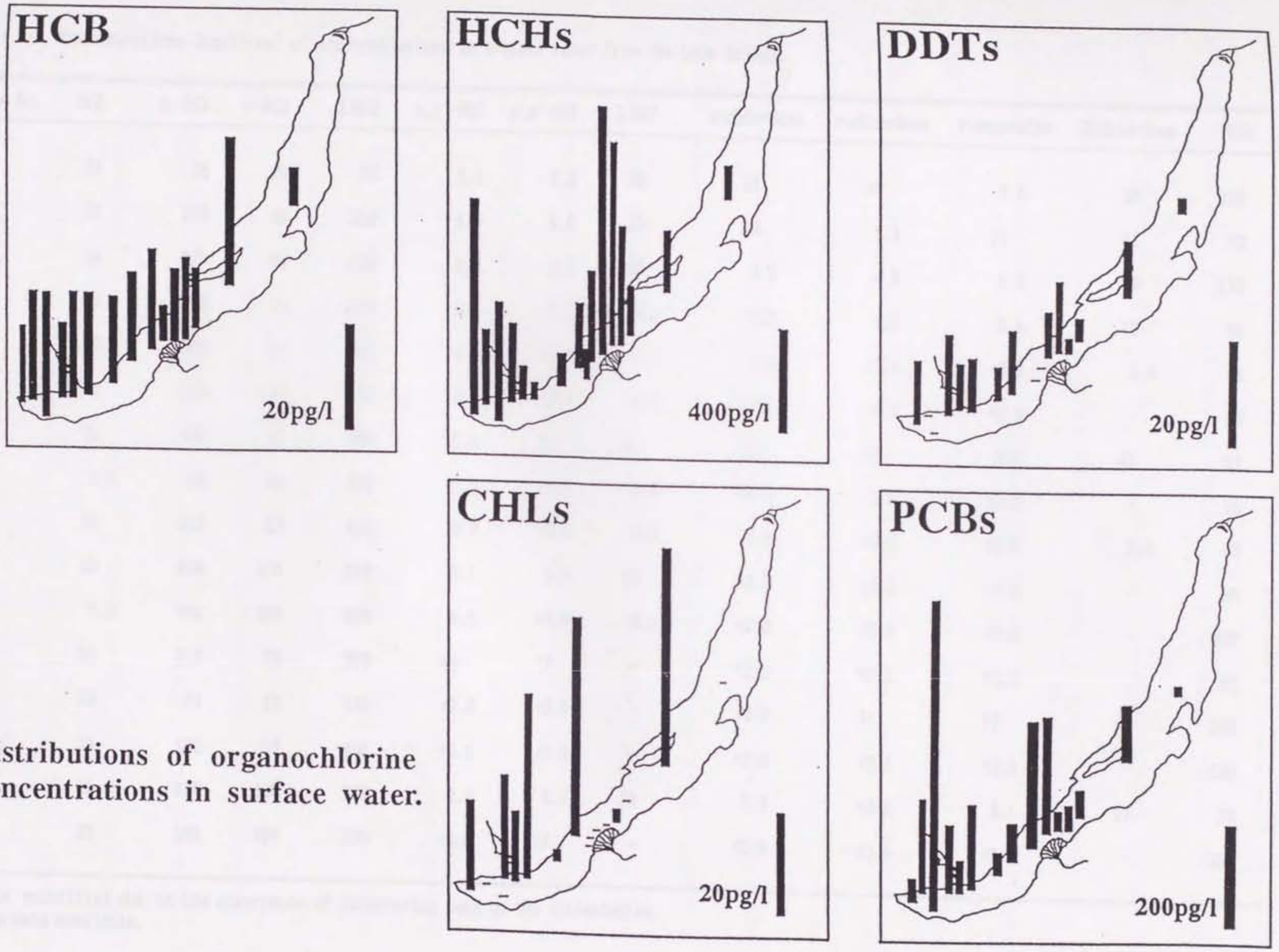

Fig. 2-3. Distributions of organochlorine concentrations in surface water.

Table 2-3. Concentrations (pg/litre) of organochlorines in surface water from the Lake Baikal.

Sample No.	HCB	α-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDT	ΣDDT	*t*-chlordane	*c*-chlordane	*t*-nonachlor	Σchlordane	PCBs
W-1	19	36	20	56	3.4	6.8	10	18	10	7.0	35	160
W-2	17	200	49	250	5.5	6.6	12	19	7.4	15	41	73
W-3	14	220	65	290	5.6	9.1	15	9.2	4.1	6.8	20	130
W-4	20	100	18	120	3.6	5.1	8.7	5.2	4.7	3.0	13	60
W-5	16	100	31	130	6.1	<2.0	6.1	2.0	<3.5	<2.0	2.0	43
W-6	10	140	33	170	4.9	<2.0	4.9	<2.0	<3.5	<2.0	-	48
W-7	28	190	43	230	<2.0	11	11	19	13	9.0	41	97
W-8	7.0	82	35	120	3.0	<2.0	3.0	<2.0	<3.5	<2.0	-	18
W-9	16	340	92	430	2.7	<2.0	2.7	3.4	<3.5	<2.0	3.4	43
W-10	13	640	130	770	7.7	5.8	14	<2.0	<3.5	<2.0	-	36
W-11	7.0	760	200	960	8.5	<2.0	8.5	<2.0	<3.5	<2.0	-	220
W-12	NA	310	78	390	NA	IF	-	<2.0	<3.5	<2.0	-	NA
W-13	19	94	29	120	<2.0	<2.0	-	<2.0	IF	IF	-	240
W-14	23	360	92	450	<2.0	<2.0	-	<2.0	<3.5	<2.0	-	590
W-15	15	630	180	810	2.6	9.1	12	9.0	<3.5	8.1	17	37
W-16	20	190	100	290	<2.0	IF	-	<2.0	<3.5	<2.0	-	180

IF: not quantified due to the occurrence of interfering peak on the chromatogram.
NA: no data available.

were found in the southern basin (Sample No. Se-6). This site is likely to be influenced by discharges from the coal-fired power plant in Slyudyanka and revealed higher content of organic carbon (3.4%) in sediments (Table 2-4). Interestingly, organochlorine concentrations normalized to organic carbon content (pg/g org C) showed an uniform spatial distributions. This result implies that the geographical variations of organochlorine concentrations are determined by their partitioning between water and sediments depending on the sediment organic carbon contents rather than the direct discharge of organochlorines from the pollution source. The lake sediments are apparently more contaminated by PCBs and DDTs in comparison with those of the Chukchi Sea and Bering Sea sediments (see Chapter 4). In contrast, the residue levels of HCB and HCHs were found to be relatively invariant between the Russian lake and oceanic sediments, indicating the efficient transport of these compounds. CHL concentrations were close to their detection limit, suggesting little usage of this compounds.

Organochlorine residues in soil samples are summarized in Table 2-5. One soil sample collected from a potato field (Sample No. So-1) was highly contaminated by HCHs and DDTs. Although the concentrations of HCHs and DDTs are one to two orders of magnitude lower than paddy, cotton and tea field soils in South India, which is still using these insecticides (Kawano *et al.*, 1992), the present results of soil samples

Table 2-4. Concentrations (ng/g dry wt.) of organochlorines and organic carbon contents (%) in sediments from the Lake Baikal.

Sample No.	HCB	α-HCH	β-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	ΣDDT	*trans*-chlordane	*cis*-chlordane	*trans*-nonachlor	Σchlordane	PCBs	OCC (%)
Se-1	0.008	0.006	0.010	0.003	0.019	0.007	IF	0.007	0.014	<0.001	0.002	0.001	0.003	0.080	0.2
Se-2	0.044	0.015	0.011	0.005	0.031	0.067	0.011	0.007	0.085	<0.001	<0.001	<0.001	-	0.51	1.3
Se-3	0.005	0.010	0.016	0.004	0.030	0.010	0.009	0.040	0.059	<0.001	IF	<0.001	-	0.13	0.1
Se-4	0.043	0.029	0.018	0.013	0.060	0.063	0.025	0.023	0.11	<0.001	<0.001	<0.001	-	0.59	1.4
Se-5	0.021	0.054	0.042	0.017	0.11	0.048	0.043	0.062	0.14	<0.001	0.001	0.002	0.003	0.28	0.6
Se-6	0.16	0.053	0.056	0.009	0.12	1.3	0.60	0.83	2.7	<0.001	<0.001	<0.001	-	6.1	3.4

IF: not quantified due to the occurrence of interfering peak on the chromatogram.
OCC: organic carbon content.

Table 2-5. Concentrations (ng/g dry wt.) of organochlorines and organic carbon contents (%) in soils collected from agricultural fields around Irkutsk.

Sample No.	HCB	α-HCH	β-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	ΣDDT	*trans*-chlordane	*cis*-chlordane	*trans*-nonachlor	Σchlordane	PCBs	OCC (%)
So-1	0.083	3.7	11	2.4	16	10	2.0	16	28	<0.001	<0.001	<0.001	-	1.4	2.4
So-2	1.6	0.012	0.024	0.007	0.043	0.61	0.022	0.096	0.73	0.004	0.004	0.001	0.009	2.9	1.6
So-3	1.2	0.054	0.042	0.018	0.11	0.049	0.040	0.25	0.34	<0.001	0.002	IF	0.002	2.5	1.7
So-4	0.050	0.065	0.056	0.034	0.16	0.77	0.052	0.34	1.2	<0.001	<0.001	<0.001	-	92	1.4

So-1, 2 and 3: potato field. So-4: red beet field.
IF: not quantified due to the occurrence of interfering peak on the chromatogram.
OCC: organic carbon content.

suggest the possible usage of these chemicals around the Lake Baikal at present or in the past. The other potato (Sample Nos. So-2 and 3) and red beet field (Sample No. So-4) soils contained PCBs and HCB at higher concentrations, respectively. Recently, Ivanov and Sandell (1992) presented two technical PCB formulations in the former USSR that has been synthesized as Sovol and Trichlorodiphenyl (TCD). Sovol has been used in capacitors, transformers, hydraulic equipments, sealing paste additives, plasticizers, paints, plastics and for improvement of wire insulation properties. TCD was mainly used as dielectric liquids. In addition, three different mixtures of Sovol and trichlorobenzenes were also produced under the trade name "Sovtol". Taking into account for these production and usage of PCBs, it is possible to consider that the agricultural soil was contaminated by this technical mixture. Similarly, the possible pollution source of HCB might be the Sovtol, as this chemical is formed as a by-product in the production of chlorinated compounds such as trichlorobenzene.

Organochlorine compositions

Compositions of organochlorine compounds including isomers and metabolites are considered as a useful tool for understanding their formulation types, origin and transport pathways etc.

HCHs have been produced commercially as a technical mixture and lindane. The technical mixture contains 60-70% α-, 5-12% β-, 10-15% γ-isomers and the other minor isomers (Demozay and Marechal, 1972), and lindane is composed of the purified γ-isomer. Hence, the ratios of α-isomer to γ-isomer (α/γ ratio) would be between 4-7 (60/15-70/10) for the technical mixture and nearly zero for lindane. The α/γ ratios found in the Baikal region ranged in 1.5-6.6 for air, 1.5-5.6 for surface water, 2.0-5.9 for sediments and 1.5-3.0 for soil samples (Tables 2-2, 2-3, 2-4 and 2-5), indicating the sources of HCHs are arising out of both the formulations. These values can be enough to predict the usage of 90% lindane formulation (Hinckley *et al.*, 1991) or the technical mixture used in the former USSR. In the Bering Sea, located on the similar latitude as the Lake Baikal, the atmospheric α/γ ratios (8.3±3.3, n=5) in 1990 (11) were found to be higher than the values observed in this study. The author (see Chapter 3) suggested a possible increasing of α/γ ratio in HCH residues during their transport through oceanic air. The lower values in the Lake Baikal region imply the relative proximity of HCH sources, as also suggested by the higher residue levels of soil samples.

DDT composition ratios (*p,p'*-DDE/*p,p'*-DDT: DDE/DDT) showed larger variations in all matrices (air: 0.25-6.8, surface water: <0.2->4.3, sediments: 0.25-9.6, soil: 0.2-6.4). A similar variation was also observed in other studies (Ramesh *et al.*, 1989; Patton *et al.*, 1989; Hoff *et al.*, 1992; see Chapters 1 and 3). The DDE/DDT ratio can be used to know whether DDTs input occurs recently or in the past. Since *p,p'*-DDE is a metabolite of *p,p'*-DDT and is not included in the technical DDT, lower and higher values of this ratio mean the recent and past usage of the technical DDT, respectively. Higher ratio of DDE/DDT may also be led during the process of long-range atmospheric transport, because of higher transportability of *p,p'*-DDE than *p,p'*-DDT, due to their different physicochemical properties (Atlas and Giam, 1988; see Chapter 3). The lower DDE/DDT values as well as the higher DDT concentrations in the Baikal region also indicate the present sporadic usage of DDT around the Lake Baikal, as was suggested from the DDT compositions in the high-latitude oceanic air (see Chapter 3).

Consideration on CHL compositions in the Baikal region was possible only for air samples because of the comparable values or less than detection limit of CHL concentrations for other samples. The ratios of *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor (TC:CC:TN) in the Baikal air were 1.2±0.24:1.0:0.89±0.20 (n=5), differing from the ratio (TC:CC:TN = 1.26:1.0:0.37) in the technical mixture (Sovocool *et al.*, 1977). The compositions of CHL compounds in this study were quite close to those found in Gulf of Alaska sediments with elevated ratios of *trans*-nonachlor (see Chapter 4). On the other hand, in Canadian Arctic air, the average ratios were 0.56:1.0:0.37 in June 1984 (Hoff and Chan, 1986), 0.39:1.0:0.54 in August 1986 and 0.58:1.0:0.93 in June 1987 (Patton *et al.*, 1989) and presented the depletion of *trans*-chlordane with the relative abundance of *trans*-nonachlor. Norwegian air in August/September 1991 was also reported to show similar ratios (0.53±0.12:1.0:0.72±0.10) as

Canadian Arctic air (Buser and Müller, 1993). Considering the presence of major CHL sources in lower latitudes (see Chapter 1), the transportability and/or persistency of each CHL component is in the order of *trans*-nonachlor > *cis*-chlordane > *trans*-chlordane. The higher vapour pressure (Kawano, 1991) and Henry's law constant (see Chapter 3) of *trans*-nonachlor in comparison with those of *cis*- and *trans*-chlordanes would be explicable for the relative abundance of *trans*-nonachlor in samples collected from the non-point source areas like the Lake Baikal. However, such physicochemical properties would not allow *cis*-chlordane to be more abundant than *trans*-chlordane, because of their similar natures between *cis*- and *trans*-chlordane. Hence, biodegradation and photochemical processes for *trans*-chlordane could be taken into account for explaining the ratio in remote air.

Representative congener patterns of PCBs in air, water, sediments and soil samples are presented in Fig. 2-4. In general, tetra- to hexachlorinated biphenyls prevailed in most of the samples, although an exception could be seen in water samples collected from the central part of the lake, where lower chlorinated congeners were abundant (W-7). As oceanic air and surface seawater in higher latitudes are reported to contain mostly lower (di- to tetra-) chlorinated congeners (Tatsukawa and Tanabe, 1984; see Chapter 3), these congener patterns, as well as higher contamination levels in the Lake Baikal samples, again suggest

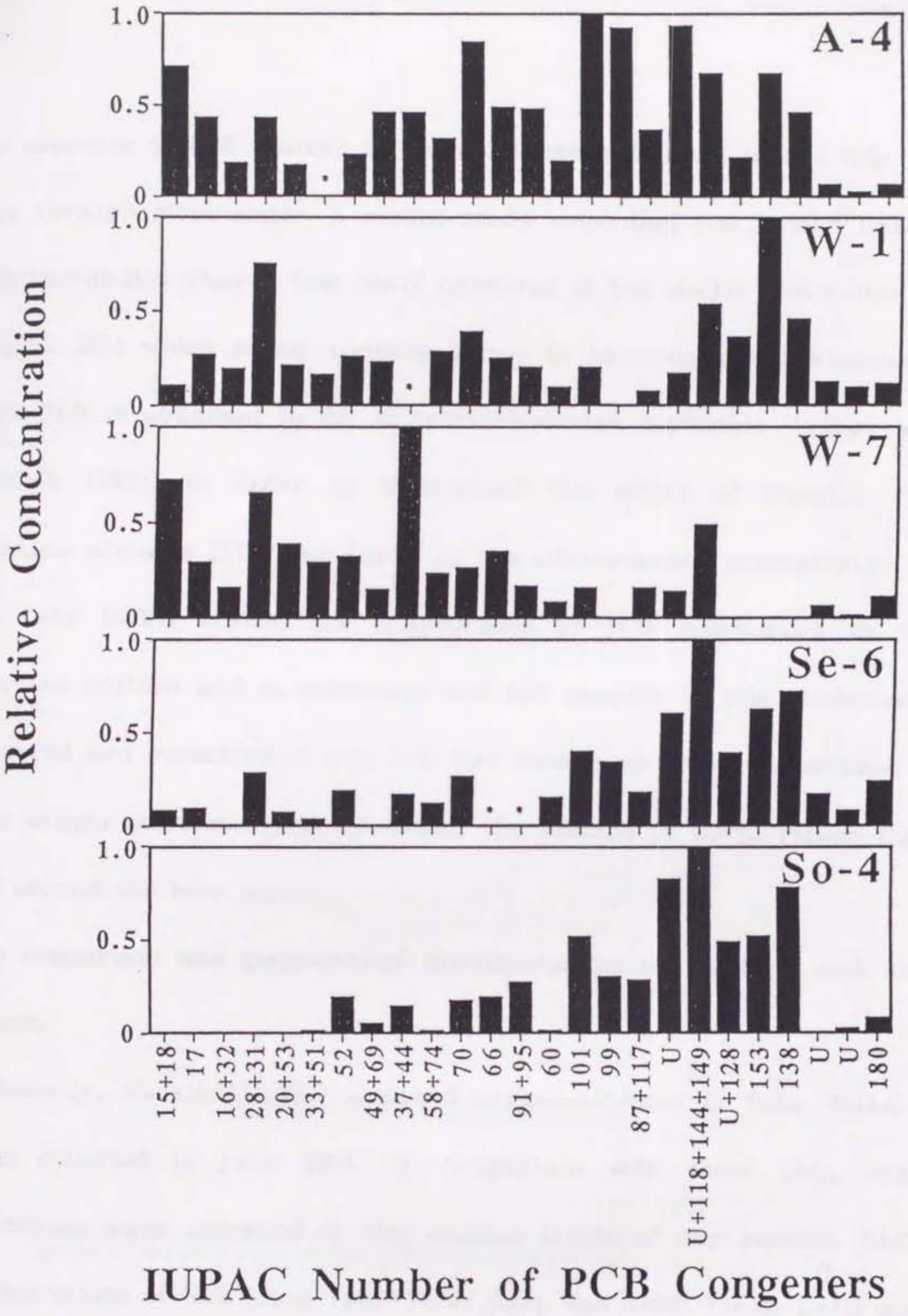

Fig. 2-4. Profiles of PCB isomer and congener concentrations in air (A-4), surface water (W-1 & W-7), sediments (Se-6) and soil (So-4) samples from the Lake Baikal region.

The highest peak concentration was regarded as 1.0.

* denotes the congener that was not quantified due to the occurrence of interfering peak on the chromatogram.

U means the PCB peaks with no IUPAC number.

the presence of PCB sources in the watershed and their inputs into the lake through river water. A recent study regarding the former USSR's PCB formulation showed that Sovol consisted of the similar composites as Aroclor 1254 which mainly contains tetra- to hexachlorinated congeners, while TCD is abundant in di- to tetrachlorinated biphenyls (Ivanov and Sandell, 1992). In order to understand the effect of Russian PCB technical mixtures (TCD and Sovol) on the environmental contamination in the Lake Baikal region, the compositions of PCB homologues in the technical mixture and in sediments and soil samples in this study were compared and presented in Fig. 2-5. Our results on PCB compositions in such sample matrices evidently reflect the leakage of Sovol rather than TCD around the lake region.

Data comparison and geographical distribution in the eastern Asia and Oceania

Recently, Kucklick (1992) analysed organochlorines in Lake Baikal water collected in June 1991. In comparison with those data, some differences were observed in the residue levels of our results. While concentrations of HCB (June 1991: 16-27 pg/l, May 1992: 7.0-28 pg/l) and CHLs (*trans*-chlordane, *cis*-chlordane and *trans*-nonachlor; June 1991: 32-74 pg/l, May 1992: <7.5-41 pg/l) reported in both studies were almost comparable, the other organochlorine concentrations such as HCHs (α- and γ-isomers; June 1991: 1,200-1,400 pg/l, May 1992: 56-960 pg/l), DDTs (*p,p'*-DDE and *p,p'*-DDT; June 1991: 22-77 pg/l, May 1992: <4.0-15 pg/l),

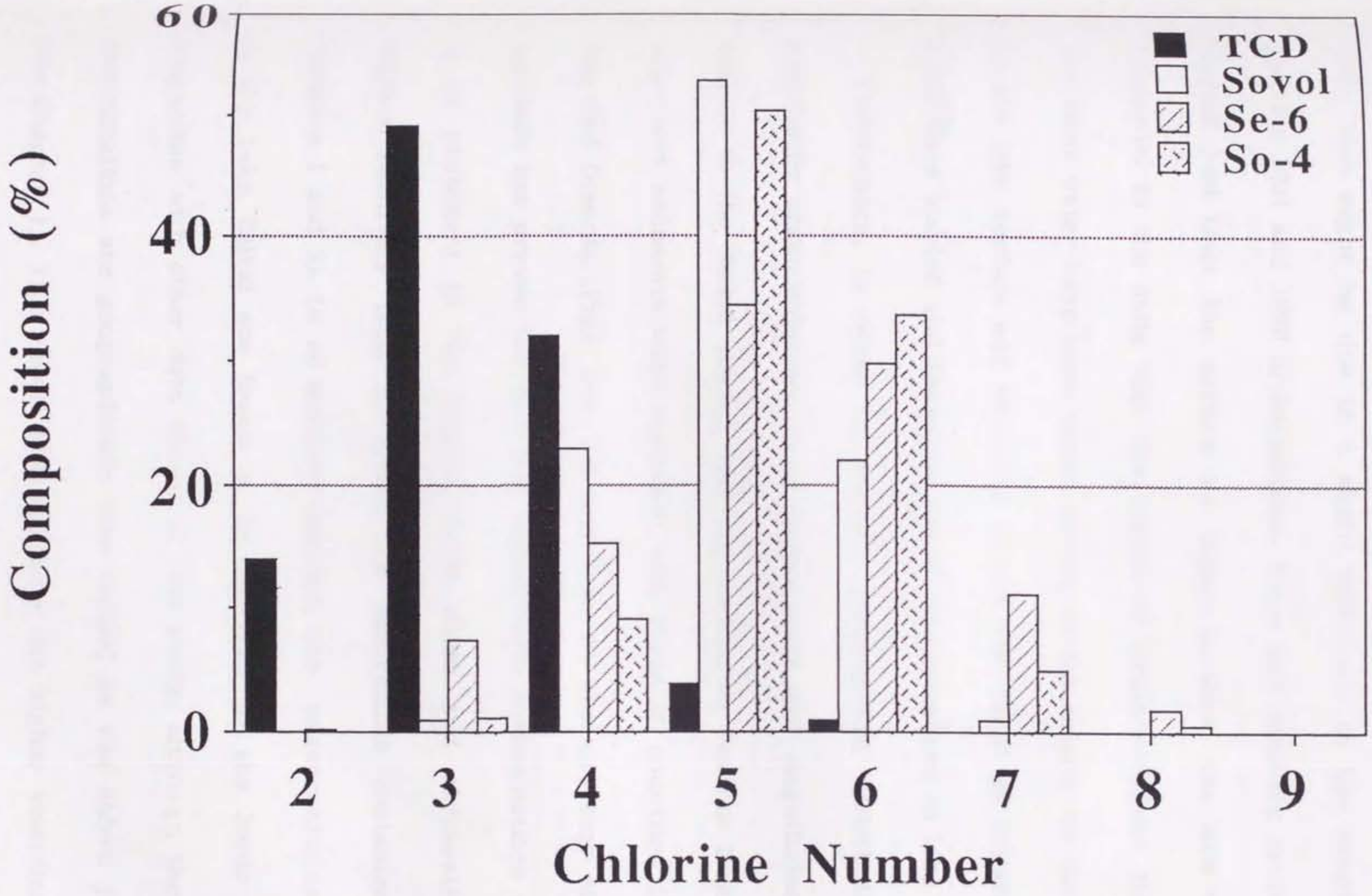

Fig. 2-5. Concentrations of PCB homologues in Russian technical PCB mixtures (Trichlorodiphenyl and Sovol), sediments and soil samples from the Lake Baikal region.

Data for Trichlorodiphenyl and Sovol were cited from Ivanov and Sandell (1992).

and PCBs (June 1991: 300-1,500 pg/l, May 1992: 18-590 pg/l) appeared to be different, showing the higher concentrations in 1991 than those in 1992. This might be due to a slight difference in the sampling terms between 1991 and 1992 investigations. Since our sampling cruise in 1992 started just after the surface ice began to thaw, the lake water was preserved in the state that the inputs of organochlorines through air and river water have been closed during winter season. As the ice melts on the lake surface and inflowing rivers, the input of organochlorines might have started and therefore raised concentrations in lake water.

Furthermore, in order to evaluate geographical distributions of semivolatile organochlorines on a global scale and magnitudes of their sources in the Baikal region, the organochlorine residue levels in air, water and sediments were compared with those of countries in eastern Asia and Oceania (Figs. 2-6, 2-7 and 2-8). In the previous study, this approach has proven the fact that atmospheric contaminations are likely to be prominent in the tropics, while water and sediments in cold regions relatively tend to retain the semivolatile contaminants (see Chapters 1 and 3). In all matrices sampled, the organochlorine residues in the Lake Baikal are found to be affiliated to the lower levels in comparison with other data shown in this study, although the sediment contaminations are geographically less variant as was shown previously (see Chapter 1). This result also supports the higher volatilization rate

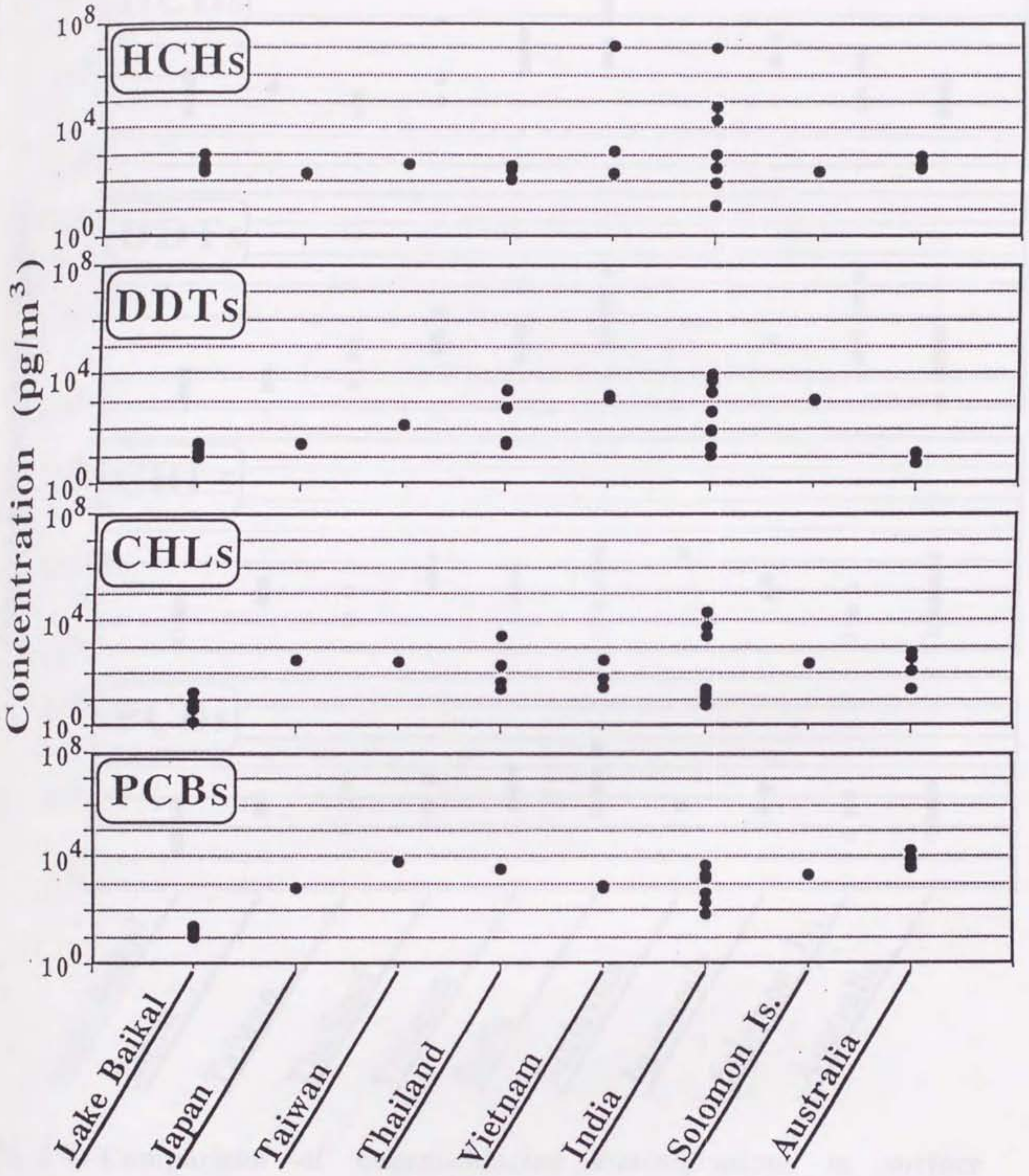

Fig. 2-6. **Comparison of organochlorine concentrations in air from the Lake Baikal with those in the eastern Asia and Oceania. HCHs: α- and γ-isomers. DDTs: *p,p'* -DDE and *p,p'* -DDT. CHLs: *trans* -chlordane, *cis* -chlordane and *trans* -nonachlor.**

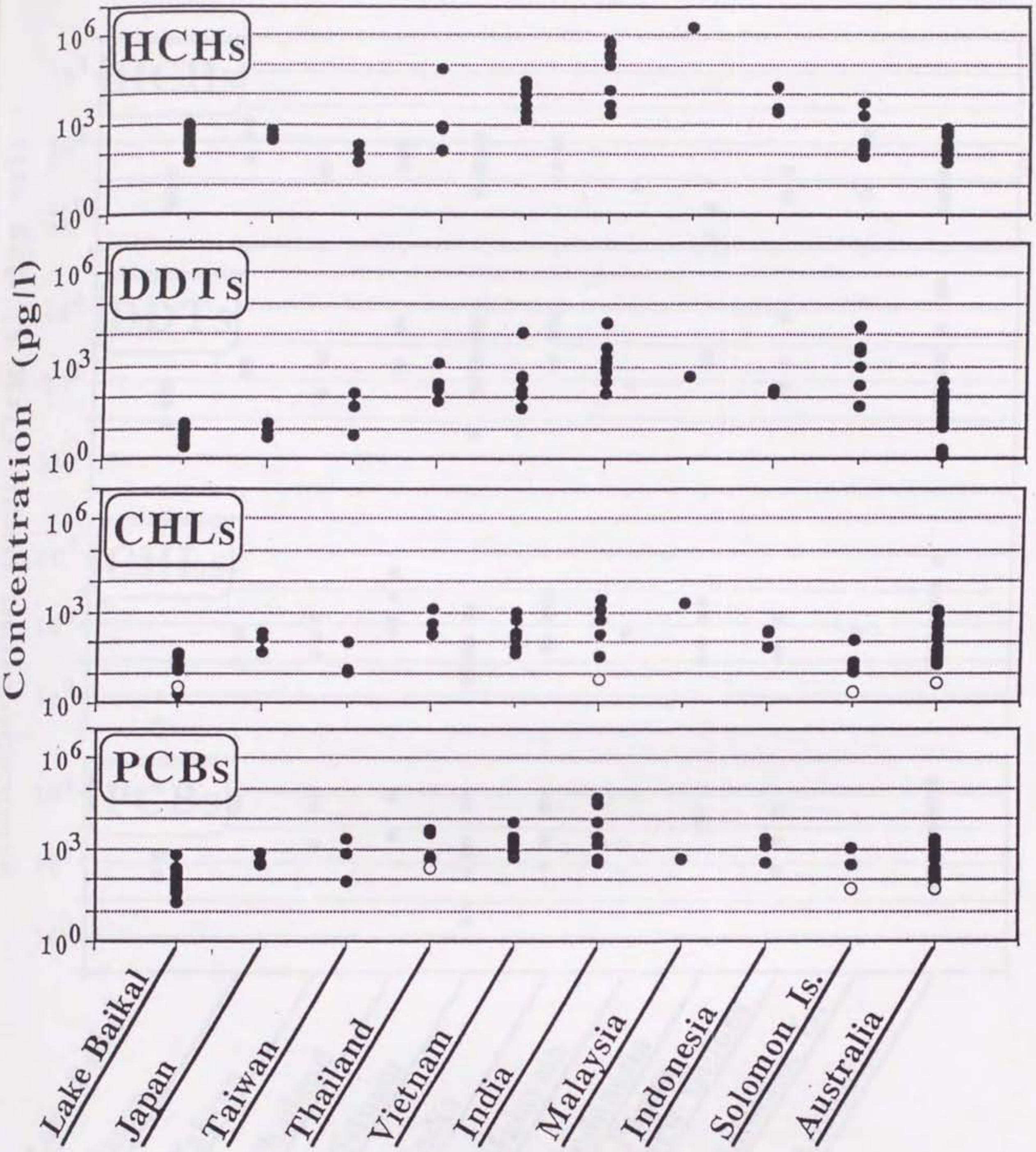

Fig. 2-7. Comparison of organochlorine concentrations in surface water from the Lake Baikal with those in the eastern Asia and Oceania.
Open circles mean lower concentrations than the plotted values.
HCHs : α- and γ-isomers. DDTs: *p,p'*-DDE and *p,p'*-DDT.
CHLs : *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor.

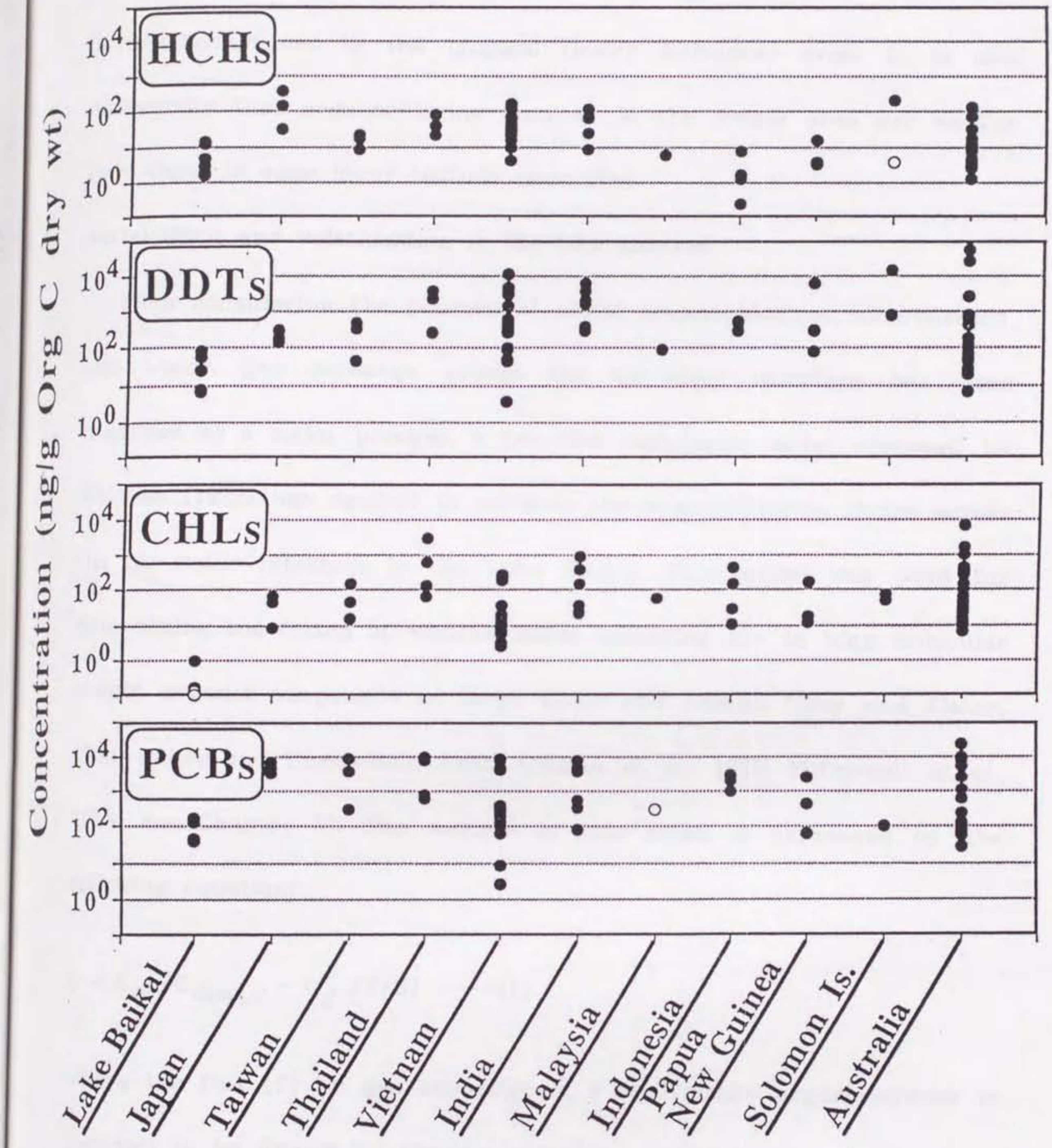

Fig. 2-8. Comparison of organochlorine concentrations in sediments from the Lake Baikal with those in the eastern Asia and Oceania.
Open circles mean lower concentrations than the plotted values.
HCHs : α- and γ-isomers. DDTs: *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT. CHLs : *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor.

of organochlorines in the tropical (lower latitudes) area. It is also noteworthy that organochlorine sources in the Baikal area are smaller than those in some lower latitude countries.

Aerial input and volatilization in the lake surface

When considering the process of aerial organochlorines incorporated into water, gas exchange across the air-water interface has been regarded as a major process. A two-film resistance model proposed by Whitman (1923) was applied to estimate the organochlorine fluxes across the air-water interface in the Lake Baikal. This model was used for determining the fluxes of various gases including low to high molecular weight organic compounds in large lakes and oceans (Liss and Slater, 1974; Baker and Eisenreich, 1990; Achman *et al.*, 1993; McConnell *et al.*, 1993; see Chapter 3). The concept of this model is expressed by the following equation:

$$F = K_{ol} (C_{diss,w} - C_g RT/H) \quad ---(1)$$

where the flux (F) by gas exchange of a semivolatile organochlorine is assumed to be driven by the concentration gradient between air (C_g : pg/m^3) and surface water ($C_{diss,w}$: pg/m^3) converted in terms of Henry's law constant (HLC: Pa m^3 mol^{-1}). Magnitude of flux by gas exchange across the air-water interface is quantified by the product of the concentration gradient and a gas exchange constant (K_{ol} : m/s), and the flux direction is determined by the inclination of concentrations between air and water phases. Volatilization and deposition occur in the case of $C_{diss,w} > C_g RT/H$ and $C_g RT/H > C_{diss,w}$, respectively. R is the universal gas constant (Pa m^3 mol^{-1} K^{-1}) and T is the absolute temperature (K). Total resistance (R_t) is the reciprocal of K_{ol}, which consists of the sum of residences in liquid (r_l) and gas (r_g):

$$R_t = r_l + r_g \quad ---(2)$$

The equation (2) can also be expressed as

$$1/K_{ol} = 1/k_l + RT/Hk_g \quad ---(3)$$

k_l and k_g are defined as the liquid- and gas-phase mass transfer coefficients (m/s), respectively. Mackay and Yeun (1983) experimentally related both the parameters with wind speed at 10 m altitude (U10; m/s) and Schmidt numbers for liquid (S_{cl}) and gas (S_{cg}).

$$k_l = 1.0\text{x}10^{-6} + 3.41\text{x}10^{-5}(6.1 + 0.63U_{10})^{0.5}U_{10}(S_{cl})^{-0.5} \quad ---(4)$$

$$k_g = 1.0\text{x}10^{-3} + 4.62\text{x}10^{-4}(6.1 + 0.63U_{10})^{0.5}U_{10}(S_{cg})^{-0.67} \quad ---(5)$$

In this study, measured water temperatures (0 - 2.4°C) at each sampling site were available to substitute T value. In the case of wind speed, 0, 5 and 10 m/s were assumed for the flux estimation, as it is variable during the sampling period. The S_{cl} and S_{cg} were treated to be 2.0 and 1,000, respectively, since they are known to range from 800 to 1,200 for

S_{cl} and from 1.8 to 2.2 for S_{cg} in organic solutes (Strachan and Eisenreich, 1988). HLCs for organochlorines used in this study as well as the reference values are listed in Table 2-6. As these HLCs (HLC_k) cited were determined under the condition of 20-25°C (T_k), HLC_k depending on temperature were corrected into those (HLC_x) at the actual field water temperature (T_x), using the following equations.

$$\ln HLC_k = m/T_k + b \quad \text{---(6)}$$

$$\ln HLC_x = m/T_x + b \quad \text{---(7)}$$

Hence, these two equations can be converted as follows:

$$\ln (HLC_k/HLC_x) = m(1/T_x - 1/T_k) \quad \text{---(8)}$$

The slope (m) for HCB was determined by a regression analysis ($\ln HLC = -5734/T + 23.1$, $R^2 = 0.98$) originating from HLCs measured at various temperatures (14.8 - 50.5°C) by Hulscher *et al.* (1992). As for HCHs, the slopes for α-HCH (m= -2810) and γ-HCH (m= -2382) reported recently (Kucklick *et al.*, 1991) were used in this study. The relationship between HLC and temperature for PCBs has been already reported (Tateya *et al.*, 1988) and the slope (m= -7868) was used to obtain the HLC at lower temperature. Regarding DDTs and CHLs, as no attempts have been made to determine the HLC-temperature relationships, the slope for PCBs was substituted for these organochlorines. As an example, K_{ol} values under

Table 2-6. Selected and temperature corrected Henry's law constants (HLC: Pa m^3 /mol), and K_{ol} (m/day) estimated under various wind speed for organochlorines.

Organochlorines	HLC		K_{ol} (2.0° C)		
	selected (° C)	corrected (2.0° C)	0m/s	5m/s	10m/s
HCB	30.0 (20)^{a}	8.28	0.0677	0.796	1.72
HCHs					
α-HCH	0.677 (23)^{b}	0.328	0.0108	0.0642	0.134
γ-HCH	0.339 (23)^{b}	0.183	0.00641	0.0366	0.0760
DDTs					
p,p'-DDE	7.95 (20)^{c}	1.37	0.0324	0.236	0.496
p,p'-DDT	1.31 (25)^{d}	0.144	0.00512	0.0289	0.0600
CHLs					
t-chlordane	16.5 (25)^{e}	1.81	0.0382	0.297	0.626
c-chlordane	11.2 (25)^{e}	1.23	0.0303	0.216	0.453
t-nonachlor	49.5 (25)^{e}	5.44	0.0608	0.640	1.37
PCB isomers and congeners					
15,18	27.6 (25)^{fg}	3.03	0.0492	0.439	0.930
17	37.8 (25)^{f}	4.16	0.0557	0.543	1.16
16,32	32.6 (25)^{fg}	3.58	0.0527	0.493	1.05
28,31	28.4 (25)^{fg}	3.12	0.0498	0.448	0.949
20,53	32.8 (25)^{fg}	3.61	0.0529	0.495	1.05
33,51	38.0 (25)^{fg}	4.18	0.0558	0.545	1.16
52	32.3 (25)^{f}	3.55	0.0526	0.490	1.04
49,69	43.6 (25)^{fg}	4.78	0.0585	0.593	1.27
37,44	19.4 (25)^{fg}	2.13	0.0416	0.338	0.712
58,74	23.6 (25)^{fg}	2.59	0.0459	0.392	0.828
70	20.5 (25)^{f}	2.25	0.0429	0.353	0.744
66	20.5 (25)^{f}	2.26	0.0429	0.353	0.746
91,95	32.8 (25)^{fg}	3.60	0.0528	0.494	1.05
60	15.5 (25)^{f}	1.70	0.0369	0.283	0.549
101	24.9 (25)^{f}	2.73	0.0470	0.408	0.862
99	25.3 (25)^{f}	2.78	0.0474	0.412	0.873
87,117	21.5 (25)^{fg}	2.36	0.0439	0.366	0.773
118,144,149	17.1 (25)^{fg}	1.88	0.0389	0.306	0.644
128	10.5 (25)^{f}	1.16	0.0290	0.204	0.428
153	16.7 (25)^{f}	1.84	0.0385	0.300	0.632
138	13.2 (25)^{f}	1.45	0.0335	0.247	0.519
180	10.9 (25)^{f}	1.20	0.0297	0.210	0.441

a: after Hulscher *et al.* (1992), b: after Kucklick *et al.* (1991), c: after Suntio *et al.* (1988), d: after Mackay *et al.* (1986), e: calculated from the subcooled liquid vapor pressure and the water solubility after Kawano (1991), f: after Dunnivant *et al.* (1992), g: averaged with the HLCs for congeners concerned.

the conditions of $T = 2.0^{\circ}C$ and $U_{10} = 0$, 5 and 10 m/s are also shown in Table 2-6. The K_{ol} estimated for organochlorines under the conditions showed lower values for HCHs and *p,p'*-DDT, and higher ones for HCB, PCBs and CHLs. According to the eq. 3-5, the magnitude of K_{ol} is mainly influenced by that of U_{10}, T and H. As the T values (0 - 2.4°C) recorded in this study were invariant (H which is a function of T also showed invariant values), K_{ol} values at a given wind speed (U_{10}) also showed to be almost constant. The K_{ol} values at 5 m/s of U_{10} for HCB and *p,p'*-DDT, as examples, only varied by factors of 1.1 and 1.3, respectively, under the measured range of T values. In contrast to the invariance of K_{ol} related with T, K_{ol} at a given temperature (T) greatly varies within the range of U_{10} assumed (0 - 10 m/s). The K_{ol} values at 0°C for HCB and *p,p'*-DDT enhanced by factors of 24 and 12, respectively, with an increase of U_{10} from 0 to 10 m/s.

Gas exchange process of organochlorines across the air-water interface are derived by the gradients between actual gaseous concentrations in air and dissolved ones in water. However, no filteration in the sampling of air and water was conducted to distinguish the organochlorines in gaseous or dissolved phases and those in solid phase. In the case of air samples, the major fraction of semivolatile organochlorines dealt in this study are known to be present in gas phase even in the cold region such as the Arctic (Oehme and Stray, 1982; Hargrave *et al.*, 1988; Patton *et al.*, 1989), although one of the factors controlling the distribution between gas and particulate phases is atmospheric temperature. Moreover, even in the mid-latitude air containing high density of aerosols, that is also a factor influencing the distribution, it has been reported by several authors that organochlorines were not detected on the filter (Baker and Eisenreich, 1990; Bidleman *et al.*, 1987; Nakano *et al.*, 1990). Therefore, the organochlorines retained on PUFs from the Lake Baikal can regard to be in the gaseous phase. While in water, a portion of organochlorines in water is reported to be associated with particles, particularly in water containing large amount of suspended materials (Achman *et al.*, 1993). On the other hand, the estimation of truly dissolved organochlorines in water sample by any conventional filteration would be impossible, as organochlorines on smaller size of nonsettling solid material (called colloid) can not be operationally separated from those in the dissolved phase (Gschwend and Wu, 1985). As a result, organochlorine concentrations trapped on XAD-2 might be overestimated as a dissolved state including a portion in the nonsettling and settling particulate phases. However, according to an estimation of the dissolved fraction in the Arctic Ocean using a equilibrium partitioning model in dissolved, settling and nonsettling particulate phases (Cotham and Bidleman, 1991), the particulate (settling and nonsettling particle) fraction of α-HCH, γ-HCH, chlordane and *p,p'*-DDT was found to be quite small (0 - 21%).

Baker and Eisenreich (1990) reported the small contribution of colloidal binding fraction of PCBs in the Lake Superior. Considering the low productivity of Lake Baikal which is strongly oligotrophic approaching typical open-ocean values (Weiss *et al.*, 1991), the contribution of particulate phase in lake water while calculating fluxes of organochlorines was regarded to be negligible in this study. Hence, the estimations in the Lake Baikal may indicate the minimum deposition or maximum volatilization fluxes for organochlorines under given conditions. In Table 2-7, sample pairings for air and water used for flux calculations and water temperatures are listed.

The estimated fluxes by gas exchange of organochlorines across the air-water interface are also summarized in Table 2-7. Air to water fluxes in most cases were predicted for HCB, HCHs and DDTs. On the contrary, volatilization was indicated for PCBs, suggesting the role of lake water as a source of this compounds. CHL fluxes seemed to be comparatively close to the equilibrium state due to the existence of positive to negative range of fluxes. The magnitude of fluxes were generally larger for HCHs and smaller for DDTs and CHLs, relating with higher concentration gradients for HCHs rather than the magnitude of K_{ol} values.

As uniform water temperature was recorded at each sampling site for the flux calculation, the wind speed for the magnitude of

Table 2-7. Estimated fluxes (ng/m^2/day) of organochlorines by gas exchange across the air-water interface under various wind speeds in the Lake Baikal on May, 1992.

Sample Pairing <air x water>	Wind Speed (m/s)	HCB	α-HCH	γ-HCH	ΣHCH	*p,p'*-DDE	*p,p'*-DDT	ΣDDT	*trans*-chlordane	*cis*-chlordane	*trans*-nonachlor	Σchlordane	PCBs
A-1 x W-1 (0° C)	0	-1.5	-22	-26	-48	-0.14	-0.57	-0.71	0.54	0.18	0.36	1.1	5.1
	5	-17	-130	-150	-280	-0.95	-3.2	-4.1	4.0	1.2	3.6	8.8	42
	10	-36	-270	-310	-580	-2.0	-6.6	-8.6	8.5	2.6	7.6	19	88
A-2 x W-2,3,4,5 (2.0° C)	0	-2.0	-57	-77	-130	-0.31	-0.07	-0.38	0.26	0.10	0.47	0.83	2.9
	5	-24	-340	-440	-780	-2.3	-0.40	-2.7	2.0	0.69	5.0	7.7	25
	10	-52	-710	-910	-1600	-4.8	-0.82	-5.6	4.2	1.4	11	16	54
A-3 x W-6 (2.4° C)	0	-0.60	-18	-33	-51	<0.01	-0.97	-0.97	-0.35	-0.32	-0.13	-0.80	0.73
	5	-7.1	-110	-190	-300	0.02	-5.5	-5.5	-2.8	-2.3	-1.4	-6.4	6.9
	10	-15	-220	-390	-620	0.05	-11	-11	-5.8	-4.8	-2.9	-14	15
A-4 x W-7 (2.2° C)	0	0.42	-11	-22	-33	-0.59	-1.4	-2.0	0.59	0.21	0.51	1.3	3.2
	5	5.0	-64	-130	-190	-4.3	-7.9	-12	4.6	1.5	5.3	11	29
	10	11	-130	-260	-390	-9.1	-16	-26	9.6	3.2	11	24	61
A-5 x W-8 (1.9° C)	0	-1.1	-14	-19	-33	-0.95	-0.60	-1.5	-0.07	-	-	-0.07	0.47
	5	-13	-81	-110	-190	-6.9	-3.4	-10	-0.52	-	-	-0.52	4.3
	10	-29	-170	-230	-400	-15	-7.0	-22	-1.1	-	-	-1.1	9.1

Numbers in parentheses are the water temperatures at each collection site for water samples.
Plus and minus values of fluxes mean the transfer of organochlorines from water to air and vice versa, respectively.
-: not estimated due to less than detection limit of the organochlorine concentrations in air and water samples.

organochlorine fluxes would be the most influential factor. Therefore, the fluxes vary in parallel with the K_{ol}, which is a function of U_{10}. The influence of wind speed was different among organochlorines studied. HCB was most dependent on wind speed, raising the magnitude more than twenty times at each station with an increase of wind speed from 0 to 10 m/s. Even the most insensitive compound (*p,p'*-DDT) raised the flux by a factor of 12 within the same range of wind speed. Watson *et al.* (1991) experimentally demonstrated the rapid enhancement of gas exchange rate for carbon dioxide between air and water at high wind speed using a dual tracer technique. These estimates indicate that the episodic high winds such as storm conditions suddenly affect the dynamics of OCs in air-water environment.

Referring to isomers of HCHs, deposition fluxes of γ-HCH exceeded that of α-HCH at all sites. As for PCB congeners, the lower chlorinated biphenyls predominated the large portion of total volatilization except for the flux consisting of the pairing for A-1 and W-1, where considerable concentrations of higher chlorinated congeners in the lake water contributed to their significant fluxes. These differences among isomers and congeners might be due to the lower HLCs for γ-HCH and higher chlorinated biphenyls which mean the more preferential distribution of water phase. The author (see Chapter 3) pointed out that the selective deposition of compounds with lower HLCs to water phase via atmospheric transport would alter the composition ratios in isomer group in atmosphere. The divergence for ratios of α-isomer to γ-isomer and compositions of PCB congeners found in air over lake may support the compound-specific behavior for organochlorines with different physicochemical properties between air and water.

In Table 2-8, our flux estimates in the Lake Baikal were compared with those in the Great Lakes (Achman *et al.*, 1993; Baker and Eisenreich, 1990; McConnell *et al.*, 1993), the northern North Pacific, Gulf of Alaska, Bering Sea and the Chukchi Sea (see Chapter 3) which were also estimated by the two-film model using the similar approach of simultaneous sampling for air and water.

Deposition fluxes of HCHs (α-HCH: 64-340 ng/m^2/day, γ-HCH: 110-440 ng/m^2/day) at wind speed of 5 m/s estimated in the Lake Baikal were somewhat higher than those (α-HCH: 70 ng/m^2/day, γ-HCH: 45 ng/m^2/day) in the Green Bay, USA in June, 1989. The difference for deposition rate between two lakes might be due to the lower concentrations in water phase and lower water temperatures in the Lake Baikal, as the air concentrations and wind speed used for these estimations were similar. Lower water temperatures reduce the HLC values, thus raises the capacity to retain these compounds up to their saturation in water phase. McConnell *et al.* (1993) estimated the volatilization flux of HCHs in the Great Lakes in August, 1990, attributing to the higher water temperatures and the stratification of

Table 2-8. Comparison of organochlorine fluxes (ng/m^2/day) by gas exchange across the air-water interface among various areas.

Location	Applied Temp. (° C)	Wind Speed (m/s)	ΣHCH[a]	ΣDDT[b]	Σchlordane[c]	PCBs	Reference
Lake Baikal	0 ～ 2.4	5	-780～-190	-12 ～2.7	-6.4～11	4.3～42	This study
Lake Superior	15	5				141	Baker and Eisenreich (1990)
Green Bay	6.0 ～15.3	4 ～ 6.5				40～1300	Achman *et al.* (1993)
Green Bay	8.5	4.9	-115				McConnell *et al.* (1993)
Lake Michigan	18.9	6.4	30[d]				McConnell *et al.* (1993)
Lake Huron	18.5	8.9	41				McConnell *et al.* (1993)
Lake Erie	22.3	4.5	29				McConnell *et al.* (1993)
Lake Ontario	22.3	4.4	-11				McConnell *et al.* (1993)
Chukchi Sea	0	7	-62～-50	-4.2～-2.2	-8.3～-4.9	-50～-25	see Chapter 3
Bering Sea	0 ～10	5 ～ 7	-150～1.1	-3.4～0.73	-12～-0.57	-120～1.3	see Chapter 3
Gulf of Alaska	10	5	-73～-16	-1.2～-0.10	-6.8～-1.9	-49～2.7	see Chapter 3
N. North Pacific	10 ～20	5	-370～23	-14～1.1	-13～5.2	-100～8.5	see Chapter 3

Plus and minus values of fluxes mean the transfer of organochlorines from water to air and vice versa, respectively.
a: Sum of α and γ isomers. b: Sum of *p,p'*-DDE and *p,p'*-DDT. c: Sum of *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor.
d: Values estimated from a figure in the reference.

lake water. Increase of water temperature in the Lake Baikal also may change the direction of flux from deposition to volatilization in the following summer season. The fluxes by deposition of HCHs in the ocean seemed to be comparable with those in the Lake Baikal, although the estimates in the ocean were mostly available in summer season.

Comparison of DDT fluxes by gas exchange in the Lake Baikal with those for the ocean showed that the direction of fluxes in both areas were downward (from air to water). Moreover, flux values were found to be similar.

The comparison of volatilization rates (4.3-42 ng/m^2/day) of PCBs in this study with those in the Green Bay (50-1,300 ng/m^2/day) and Lake Superior (141 ng/m^2/day) at similar wind speed clearly indicated the smaller source of PCBs in Lake Baikal water than the Great Lakes. The lower PCB volatilization in the Lake Baikal can also attribute to the lower concentrations and lower temperatures in this Lake water, as well as in the case of HCHs. On the contrary, the flux direction in high latitude oceans indicated to be mainly from air to water. The average magnitude of PCB depositions during the period of summer in the northern North Pacific (10 ng/m^2/day), Gulf of Alaska (17 ng/m^2/day), Bering Sea (53 ng/m^2/day) and the Chukchi Sea (37 ng/m^2/day) is likely to compensate enough for the volatilization from the Lake Baikal. These estimates of directions of mass transfer in both marine and lakes suggest that the oceanic water bodies serve as absorbents of PCBs for their release from the Lake Baikal and others, while HCHs and DDTs in atmosphere can be retained in both ocean and lake water.

It would be difficult to depict the accurate feature of organochlorine behavior across the air-water interface in this study, since the monitoring term does not cover the whole season and include all of conditions such as wind speed and water temperature which may affect the direction and magnitude of gas exchange. During the winter season, surface of the lake is covered by ice. Therefore, the interference of gas exchange of organochlorines would occur and may change their mass flow. Seasonal variation in flux magnitude and transfer direction for organochlorines in this lake is necessary to estimate the net flux in a longer time scale and to evaluate the accurate role of lake water on the comprehensive dynamics of organochlorines.

Conclusions

It can be concluded that DDT concentrations in Baikal air and water were one order of magnitude higher than those in the Arctic that has been regarded as a "remote area" from the contamination sources. As for PCBs, estuarine area in the lake water showed notable contaminations in comparison with the Arctic residue levels, indicating the significant riverine inputs into the lake. Reflecting the contaminations of DDTs and PCBs in air and water samples, higher residues of DDTs and PCBs in sediments and soils from the Lake Baikal were also detected than those from the Arctic. Lower p,p'-DDE/p,p'-DDT ratios and predominance of higher chlorinated PCB congeners in such samples also support the present usage of these organochlorines, as well as the notable concentrations. On the contrary, concentrations of HCB and HCHs in air and water were rather comparable with those in the Arctic and nearby seas, although their significant contaminations were found in agricultural soils. This indicates that HCB and HCHs are efficiently transported even in the cold environment. Residue levels of CHLs were low in all sample matrices, suggesting little usage of this compounds.

Data in the Lake Baikal were compared with those from various regions in the eastern hemisphere to evaluate the geographical distributions and magnitude of their sources in this lake. As a conclusion, it was suggested that organochlorine sources in the lake region were smaller than those in lower-latitude (tropical) countries.

According to the estimation of organochlorines mass transfer by gas exchange between air and water, deposition fluxes for HCB, HCHs and DDTs, and volatilization for PCB congeners were shown. CHL fluxes seemed to be relatively close to the equilibrium state, since deposition and volatilization were within the small range of flux magnitudes. Almost an uniform water temperature at each sampling site made the flux magnitudes of organochlorines dependent on wind speed. Comparison of the deposition fluxes of HCHs in the Lake Baikal with those in the Green

Bay, USA, indicated that the former lake has an higher capacity to retain this compounds than the latter. Volatilization of PCBs in this study suggested the smaller sources of PCBs in this lake than the Great Lakes. The differences between the Lake Baikal and the North American lakes can attribute to the lower contaminations and temperatures in the former lake water. Further studies are necessary to estimate the annual cycle of organochlorines across the air-water interface. Determination of temperature-dependent HLCs for DDTs and CHLs, in particular, at lower temperatures would lead to more profound consideration on their behaviour in this lake.

This study gives a conspicuous proof of semivolatile organochlorine contaminations in the Lake Baikal and verifies the availability of multi-matrices monitoring for assessing the magnitude and fate of such contaminants on a global scale.

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3 Role of Ocean on the Global Transport

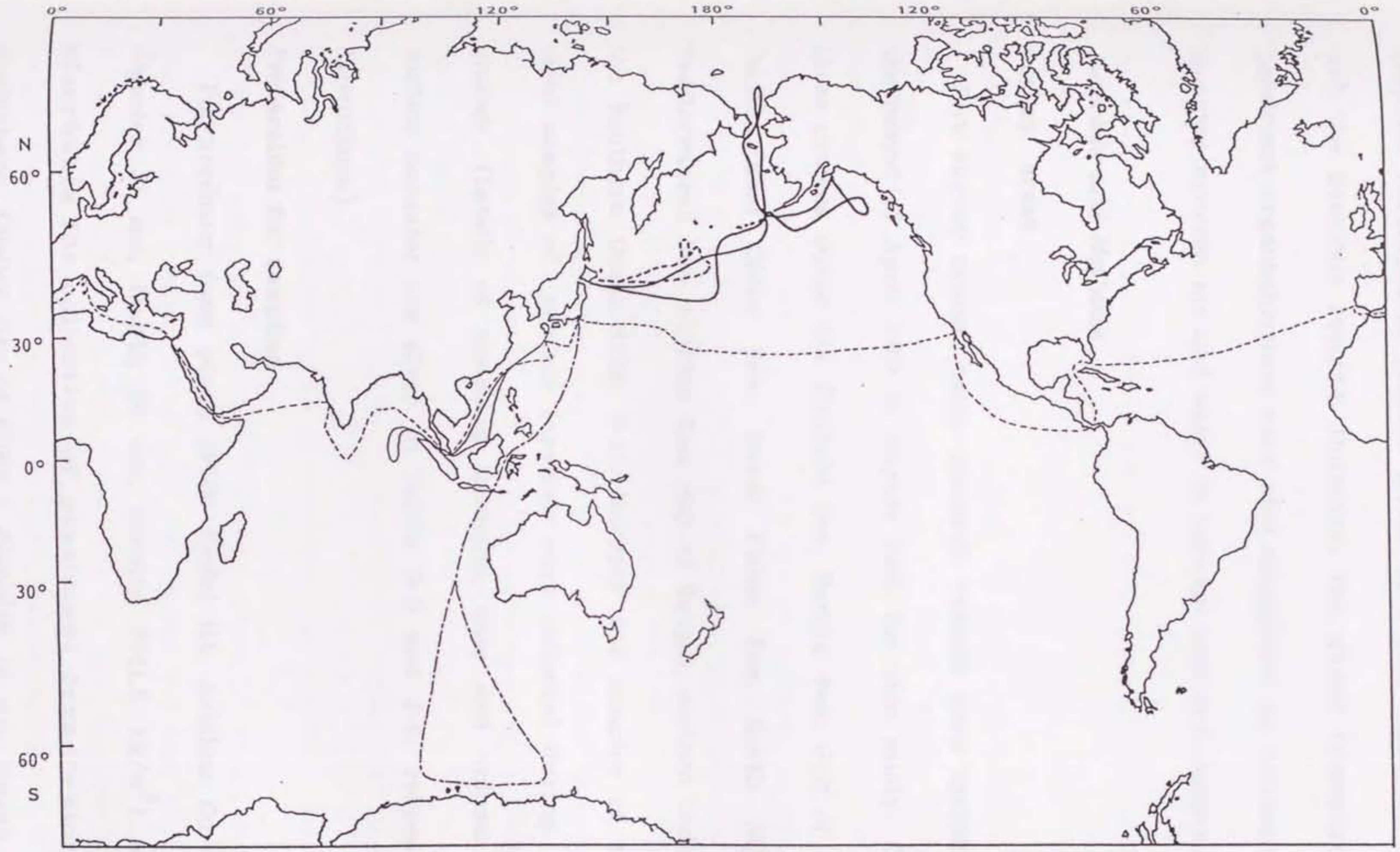
Abstract

Concentrations of organochlorines such as HCHs, DDTs, chlordanes and PCBs were determined in the air and surface water from various oceans in 1989-1990, for understanding their recent distribution and the role of ocean in the long-range atmospheric transport and fate on global terms. The atmospheric concentrations were found to be still higher in the northern hemisphere than in the southern ones, although the distribution pattern suggested the shift or expansion of their major sources from the mid- to low-latitudes during the last decade. In surface water, HCHs showed a considerable contamination over 40° N, whereas DDTs were higher nearby tropical Asia. Chlordanes and PCBs exhibited rather uniform distributions in both the hemispheres. Estimations of fluxes by gas exchange across the air-water interface give insight into the dispersal of organochlorines through oceanic atmosphere depending on their Henry's law constants and the tendency of more transportable ones to deposit into the cold waters as an ultimate sink.

Introduction

During the last decade, many investigations have been conducted to make clear the global distribution of persistent organochlorines such as polychlorinated biphenyls (PCBs) and DDT, and documented that these contaminants are transportable widely through atmosphere and eventually contaminated all over the world including polar regions (Bidelman and Olney, 1974; Goldberg, 1975; Risebrough *et al.*, 1976; Tanabe and Tatsukawa, 1980; Atlas and Giam, 1981; Tanabe *et al.*, 1982; Tanabe *et al.*, 1983; Hargrave *et al.*, 1988). The concern of these organochlorines has also extended to the ecotoxicological context of which their residues pose a toxic threat to humans and wildlifes, particularly marine mammals (Cummins, 1988; Tanabe, 1988). Among these findings and views, recent studies are highlighting concern to the Arctic region where unexpectedly higher contamination by organochlorines were observed in air, seawater (Hargrave *et al.*, 1988; Patton *et al.*, 1989), precipitation (Gregor and Gummer, 1989), plankton (Bidleman *et al.*, 1989) and wild animals (Norstrom *et al.*, 1988; Muir *et al.*, 1988). These facts suggest the significant atmospheric transport of persistent organochlorines to the Arctic from lower latitudes. In spite of regulation or prohibition on the chemicals imposed in most developed nations since the 1970s, their usage and disposal are still continuing or increasing in developing countries nearby tropical regions (Mowbray, 1986; Forget, 1991). Although such a geographical transition in chemical usage is expected to affect the current status of global contamination, worldwide survey in the ocean environment has not been made in recent years.

Regarding the global transport and ultimate fate of persistent organochlorines, oceanic water bodies have been believed to serve as a final sink of these toxic contaminants after undergoing some processes such as long-range atmospheric transport from emission sources, mass transfer between air and water and scavenging to deep sea layers with particles (Goldberg, 1975; Knap *et al.*, 1986; Tanabe and Tatsukawa, 1983). However, such a role of oceans are yet to be understood in detail because the monitoring studies of organochlorines in open ocean air and water have been limited in the temporal and spatial terms. Particularly, the air-water exchange of organochlorines has been discussed using the data from smaller number of surveys in limited areas (Cotham and Bidleman, 1991), which still make it disputable the role of oceans on global transport and fate of persistent organochlorines. In order to elucidate the mass transfer of contaminants by gas exchange across the air-seawater interface, simultaneous sampling of air and surface seawater is necessary, because their diffusive fluxes are variable according to the meteorological, geographical and temporal conditions (Baker and Eisenreich, 1990). The present study collected air and surface seawater simultaneously from a wide range of oceans during the period of 1989-1990 and determined the concentrations of persistent organochlorines such as hexachlorocyclohexanes (HCHs), DDT and its metabolites (DDTs), chlordane compounds (CHLs) and PCBs. Based on these data, their global



——— Kagoshima-Maru (April - June, 1989)
·········· Shin-Riasu-Maru (June - July, 1989)
— · — · — · Daisan-Nissin-Maru (Nov., 1989 - March, 1990)
- - - - - - - - - - Hakuho-Maru (Nov., 1989 - March, 1990)
——— Osyoro-Maru (June - August, 1990)

Fig. 3-1. Survey cruise route.

distribution in the atmosphere and hydrosphere were described and temporal variations of residue levels were also discussed by comparing with the previous reports. Moreover, the global transport and fate of persistent organochlorines were also considered by estimating their mass transfer between air and water in various seas and oceans.

Materials and Methods

Survey areas

Five survey cruises using research vessels were carried out during the period of April 1989 to August 1990 for this study. The routes of these cruises cover the Chukchi Sea, Bering Sea, Gulf of Alaska, North Pacific, East China Sea, South China Sea, North Atlantic Ocean, Mediterranean Sea, Arabian Sea, Bay of Bengal, eastern Indian Ocean and the Southern Ocean (Fig. 3-1). Seventy one samples of air and sixty eight samples of surface seawater were collected during these survey cruises. (Details of sampling locations, date and volume for air and surface seawater are given in Tables 3-5 and 3-6, respectively in the Appendixes.)

Preparation for sampling

Polyurethane foam plugs (PUF: Model HA, Achilles Co. Ltd, Japan, diameter 31 mm, length 50 mm, density 20±1.6 kg/m^3) were used as adsorbents for collection of persistent organochlorines in the atmosphere. Smaller size of PUFs (diameter 18 mm, length 50mm) were used only in Kagoshima-Maru cruise (Fig. 3-1). PUF plugs were precleaned by squeezing with detergent and then with analytical grade acetone. These plugs were further cleaned with acetone in a Soxhlet extractor (2,000 ml) for more than 7 days. During the Soxhlet cleaning, the acetone was changed four times. About 1,500ml of acetone in the fourth PUF cleaning was concentrated to 5 ml and used to check the contamination and interferring substances using high resolution gas chromatograph ^{63}Ni electron capture detector (HRGC-ECD). The cleaned PUF plugs were immidiately dried in a heated vaccum desiccator. If the PUF plugs were found to contain organochlorine residues or interferring substances, they were further cleaned to remove these residues. Six plugs of the dried PUF were packed in a glass column (i.d. 27 mm, length 390 mm) with polyethylene caps at the both ends and sealed in polyethylene bags until sampling. In the case of sampling by Kagoshima-Maru cruise, three small PUFs were packed in a small glass column (i.d. 15 mm, length 200mm).

Amberlite XAD-2 (stylene-divinylbenzene copolymer macroreticular) resin as adsorbents of organochlorines in seawater was employed to enable the sampling of several hundred liters of water. Prior to use, it was throughly washed by shaking with water and then with ethanol. The further clean up of the resin using ethanol was the same as that of PUF plugs. The residue-free XAD-2 resin was dried on a hot plate and packed in a glass column (i.d. 22 mm, length 300 mm) with glass caps.

The columns were preserved in the same manner as for air until sampling.

Sample collection

Air sampling was performed on the upper deck of research vessel. An air pump (Model AP-240Z, IWAKI Co. Ltd, Japan) and a PUF column were set into the stainless steel shelter to prevent it from sea splash and rain, which was fixed using acrylic resin rope. Atmospheric collection was continued for two days per sample. About 100 m^3 of air (flow rate 32 to 37 l/min.) was passed through the PUF column. At the beginning and end of the sampling, the flow rate was checked using a flow meter (Model RK1400, KOFLOC, KOJIMA Co. Ltd, Japan). The collection efficiency in the present method using larger column was preliminarily examined three times during summer season in Japan (temperature 21.8-34.1°C) to check the breakthrough of organochlorines. Five hundred ng of individual organochlorine pesticides and five µg of PCBs were spiked on the PUF and were extracted by the same method used for samples, after 100 m^3 of air were collected. Average adsorption efficiencies for 100m^3 of air were more than 90 % for all the organochlorines examined. However, HCHs (α- and γ-isomers) showed less efficiency of adsorption in the case of smaller size of PUF and hence the data collected during Kagoshima-Maru cruise were omitted from the following consideration.

About 150 L to 400 L of surface seawater was taken by pumping from a seawater foucet of each vessel. In some cases, a metal bucket was used for the water collection during cruise in the northern North Pacific. However, results from both the sampling methods showed no significant differences. The collected water was immediately passed through the XAD-2 resin column at a flow rate of less than 0.3 L/min.

After the sampling, PUF and XAD-2 resin columns were capped in both ends and packed in polyethylene bags again. These samples were shipped to laboratory and stored below -20°C until analysis.

Chemical analysis

Organochlorines adsorbed on PUF were Soxhlet extracted using mixed solvents of 300 ml acetone and 100 ml hexane for three hours. The extracts were microconcentrated using a Kuderna-Danish (KD) concentrator and by passing a stream of nitrogen. Five ml of acetone was added to the extract and the hexane was removed during this step. The acetone extract was then transferred to 10 ml of hexane in a separatory funnel.

In the case of water samples, organochlorines trapped on XAD-2 resin were eluted with 300 ml of ethanol and transferred to 100 ml of hexane in a separatory funnel. The extract was then concentrated in a KD concentrator upto 5 ml.

Hexane extracts of air and water samples were cleaned up with 5 % of fuming sulfuric acid in concentrated sulfuric acid. After washing the extract with hexane-washed water, it was microconcentrated under a gentle stream of nitrogen gas to 100 µl and then subjected to further clean up and fractionation by high performance liquid chromatography (HPLC: LC-6A series, Shimadzu Co. Ltd, Japan). A silica gel column packed with Simpack-SIL (i.d. 4.6 mm, length 250mm, Shimadzu Co. Ltd, Japan) was used in HPLC. Flow rate of carrier solvents (hexane and dichloromethane) was adjusted at a rate of 0.5 ml/min and column oven temperature was programmed at 35°C isothermal. The absolute amounts of 100% hexane, 20% dichloromethane in hexane and 100% dichloromethane used in the HPLC clean up of samples are 4.5ml, 4.5ml and 2.5ml, respectively. Eluates from the HPLC column were separated into four fractions. Hexachlorobenzene was eluted in the first fraction (1ml) but not quantified in this work. The second fraction (3.5ml) included PCB isomers and congeners and *p,p'*-DDE. *o,p'*-DDT, *p,p'*-DDT and *trans*-nonachlor were contained in the third fraction (3.5ml) and other pesticides examined were eluted in the fourth fraction (3.5ml). The second, third and fourth fractions obtained from the HPLC analysis were injected into HRGC-ECD (Hewlett Packard 5890) with a moving needle type injection system (splitless and solvent cut mode, Shimadzu Co. Ltd, Japan) for identification and quantification of organochlorines. GC columns (fused silica capillary, 0.25 mm id x 30 m length) consisted of DB-1701 (J & W Scientific Co. Ltd, U.S.A : 14 % cyanopropyl phenyl polysiloxane, 0.25 µm bonded phase) for organochlorine pesticides and

DB-1 (J & W Scientific Co. Ltd, U.S.A : 100 % dimethylpolysiloxane, 0.25 μm bonded phase) for PCBs. The column oven temperature was programmed at a rate of 2°C/min from a initial temperature of 160°C (10 min. hold) to a final temperature of 250°C (30-60 min. hold). Helium and nitrogen were used as carrier (20-30 cm/sec) and make-up gas (60ml/min.), respectively. Injector temperature was kept at 200°C or 250°C and detector was maintained at 300°C. Data on the chromatogram from HRGC-ECD were collected with a integrator (Hewlett Packard 3396A). Concentrations of individual organochlorines were quantified from the peak height on sample chromatograms to that of the corresponding external standard. A mixture of equal quantities of Kanechlors 300, 400, 500 and 600 was used as the external standard for PCBs quantification. Total PCB concentrations in the samples were calculated by adding the concentrations of the individually resolved peaks of different PCB isomers and congeners. Peak identification of PCB isomers and congeners was followed as described previously (Tanabe *et al.*, 1987).

Seven blanks for air samples and six for seawater samples were also analyzed. Procedural blank including adsorbent extraction were ranged from 0.05-1 pg/m^3 (or pg/l in case of water) for organochlorine pesticides and 0.01-0.1 pg/m^3 (or pg/l) for individual PCB congeners. The detection limits of contaminants in samples were designated to be twice the values of procedural blanks.

Concentrations of organochlorines in the samples were not corrected based on the spiking experiment, because of the high collection efficiencies (more than 90% for all organochlorines studied). Additionally, loss of organochlorines through analytical procedure has been also checked by spiking about 5ng of pesticides and 50ng of total PCBs onto PUFs. The loss was less than 10% for all chemicals.

Results and Discussion

Residue levels and features of distribution

Mean and range of organochlorine concentrations in air and surface seawaters were given in Tables 3-1 and 3-2, respectively.

Among the organochlorines examined, HCH levels were found to be the highest both in air and seawater in most locations. Two isomers of HCHs (α- and γ-isomers) were detected all over the oceans surveyed, but residue levels were varied according to the seas and oceans (Fig. 3-2). The noticeable distribution of HCH residues was recognized in their interhemispheric pattern which showed much higher levels in the northern hemisphere than in the southern one. In the atmospheric samples, considerably higher concentrations over 10ng/m^3 were observed in the Bay of Bengal and Arabian Sea. Interestingly, significant residue levels were also recorded in the seas and oceans of southeast Asia such as the South (1,300 pg/m^3) and East China (640 pg/m^3) Seas and the northern North Pacific (28-1,300 pg/m^3). It should also be noted that the HCH contamination extends over the Atlantic Ocean, Mediterranean Sea

Table 3-1. Range and mean concentrations of persistent organochlorines (pg/m³) in air from various seas and oceans.

Sampling Location		α-HCH	γ-HCH	Σ HCHs	*t*-Chlor.	*c*-Chlor.	*t*-Nona.	Σ CHLs	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT	Σ DDTs	Σ PCBs
Chukchi Sea (n=2)													
	mean	270	28	300	4.9	5.8	5.1	16	0.5	0.9	4.5	5.8	85
	range	240-300	26-29	270-330	3.6-6.1	4.9-6.6	4.2-6.0	13-19	0.3-0.7	<0.3-1.7	3.2-5.9	3.4-8.3	60-110
Bering Sea (n=5)													
	mean	300	42	340	4.5	5.8	3.9	14	0.8	0.3	2.5	3.6	93
	range	230-390	21-67	250-420	2.9-8.5	3.8-10	1.0-7.8	9.1-26	0.5-1.8	<0.3-1.3	0.7-3.9	1.1-5.6	18-260
Gulf of Alaska (n=4)													
	mean	360	57	420	10	9.4	2.7	22	0.8	0.9	2.2	3.9	130
	range	310-450	41-82	350-530	6-18	6.8-12	0.9-4.1	14-34	0.3-1.3	<0.3-1.9	0.3-4.7	1.0-7.5	11-340
N.N. Pacific (n=14)													
	mean	520	76	600	8.9	8.3	3.6	21	3.8	4.8	5.7	12	83
	range	22-1300	6.3-160	28-1300	1.5-32	2.6-17	0.5-14	5.5-55	0.4-12	<0.3-14	0.4-27	1.3-41	15-580
N. Pacific (n=9)													
	mean	170	42	210	6.9	5.9	3.2	16	2.0	5.1	4.7	12	130
	range	25-510	8.4-100	38-620	<0.5-22	<0.3-19	<0.2-8.7	<1.0-49	0.3-6.0	0.9-17	0.8-16	2.0-39	12-390
Caribbean Sea (n=1)													
		96	27	120	1.4	0.3	0.2	1.9	6.4	2.1	4.6	13	320
Gulf of Mexico (n=1)													
		61	16	78	<0.5	<0.3	<0.2	<1.0	9.1	17	22	48	160
N. Atlantic (n=4)													
	mean	200	66	260	8.5	6.1	5.3	20	3.4	1.8	3.9	8.7	290
	range	87-320	14-120	100-430	<0.5-18	<0.3-12	<0.2-18	<1.0-43	1.3-6.3	0.9-3.1	1.1-9.6	4.1-17	72-600
Mediterranean (n=2)													
	mean	150	75	230	9.0	5.7	2.5	18	10	3.7	4.1	18	330
	range	100-200	42-110	210-240	<0.5-18	<0.3-11	<0.2-4.9	<1.0-35	8.4-12	3.0-4.4	2.9-5.3	14-22	170-490

Table 3-1. To be continued.

Red Sea (n=1)													
		61	24	86	0.6	<0.3	<0.2	0.6	5.8	3.5	6.8	16	250
East China Sea (n=1 for HCHs, n=3 for others)													
	mean	520	120	640	13	12	9.2	35	3.7	8.3	6.9	19	140
	range				3.2-27	3.1-24	1.6-19	7.9-70	0.1-8.0	1.3-20	1.5-15	2.9-43	62-250
South China Sea (n=1 for HCHs, n=5 for others)													
	mean	810	500	1300	24	15	7.8	46	17	20	20	54	140
	range				3.2-90	3.3-48	1.6-25	8.1-160	3.4-51	8.6-39	3.7-46	7.8-140	17-480
Str. of Malacca (n=1)													
		N.D.	N.D.	N.D.	7.3	8.5	4.0	20	180	180	220	580	30
Celebes Sea (n=1)													
		95	23	120	3.3	2.8	1.8	7.9	0.7	13	23	37	22
Java Sea (n=1)													
		56	19	75	1.2	1.3	1.4	3.9	1.5	14	23	39	36
Bay of Bengal and Arabian Sea (n=5 for HCHs, n=7 for others)													
	mean	8600	1100	9600	15	9.3	5.2	30	19	100	140	250	270
	range	570-29000	120-3500	690-32000	<0.5-38	<0.3-22	<0.2-9.8	<1.0-69	2.0-41	18-420	19-590	42-1000	19-710
E. Indian Ocean (n=5)													
	mean	32	19	50	1.9	1.0	0.8	3.7	2.1	1.3	1.7	4.8	33
	range	11-84	9.4-35	27-120	0.1-8.0	0.2-3.5	<0.1-2.7	0.3-14	0.2-5.8	0.5-2.0	0.8-3.9	2.5-8.1	3.3-110
Southern Ocean (n=5)													
	mean	26	12	38	1.1	0.6	0.9	2.6	0.3	0.9	1.2	2.4	28
	range	6.6-40	7.6-16	14-55	<0.2-2.3	<0.2-1.6	<0.1-2.0	<0.5-5.9	0.2-0.4	0.7-1.2	0.9-1.5	2.1-2.7	3.7-54

t-Chlor.: *trans*-chlordane   *c*-Chlor.: *cis*-chlordane   *t*-Nona.: *trans*-nonachlor

Values below detection limit are calculated as zero for arithmetic means.

N.D. Not determined

Table 3-2. Range and mean concentrations of persistent organochlorines (pg/l) in surface seawater from various seas and oceans.

Sampling Location	α-HCH	γ-HCH	Σ HCHs	*t*-Chlor.	*c*-Chlor.	*t*-Nona.	Σ CHLs	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT	Σ DDTs	Σ PCBs
Chukchi Sea (n=3)												
mean	1400	180	1600	0.9	2.6	0.6	4.0	0.2	0.1	0.1	0.3	8.4
range	1300-1600	150-220	1500-1800	0.5-1.3	2.4-2.8	0.5-0.6	3.6-4.7	0.2	0.1	<0.1-0.1	0.2-0.4	6.6-9.3
Bering Sea (n=4)												
mean	1500	190	1700	1.5	1.9	0.5	3.9	0.9	<0.1	0.1	1.0	12
range	1200-1900	160-230	1400-2100	1.1-1.8	1.3-2.5	0.5-0.6	2.9-4.6	0.2-2.7	<0.1-0.1	<0.1-0.2	0.2-2.9	11-12
Gulf of Alaska (n=3)												
mean	1600	260	1900	1.9	2.8	0.6	5.3	0.2	0.1	0.9	1.2	12
range	1500-1800	200-310	1700-2100	1.7-2.1	1.7-4.9	0.4-0.8	3.8-7.5	0.1-0.2	0.1-0.2	0.5-1.3	0.9-1.6	8.8-17
N.N. Pacific (n=12)												
mean	870	170	1000	2.9	3.9	1.3	8.3	1.0	0.3	1.4	2.5	14
range	200-1400	43-320	240-1600	1.5-8.5	1.7-7.6	0.2-3.5	4.3-17	0.2-2.8	<0.1-1.5	0.3-2.5	0.6-5.5	7.4-24
N. Pacific (n=8)												
mean	200	47	250	3.4	3.0	1.3	7.6	0.5	0.3	0.5	1.2	24
range	65-460	9.5-90	75-550	<0.5-9.2	0.9-5.6	0.6-2.5	3.8-14	0.2-1.2	0.2-0.5	0.1-1.3	0.3-2.8	9.1-63
Caribbean Sea (n=1)												
	180	36	220	2.8	2.1	1.1	6.0	0.5	0.8	2.6	3.9	18
Gulf of Mexico (n=1)												
	44	14	58	5.6	2.6	1.0	9.2	0.3	0.6	1.4	2.2	16
N. Atlantic (n=4)												
mean	120	21	140	2.7	1.8	1.0	5.5	0.5	0.1	0.2	0.8	26
range	70-140	10-27	80-170	1.8-4.5	1.4-2.5	0.8-1.3	4.1-8.3	0.4-0.6	0.1	0.2	0.7-0.9	21-29
Mediterranean (n=2)												
mean	180	150	330	2.1	1.6	1.1	4.7	1.2	0.4	0.9	2.5	27
range	170-190	150-150	320-340	1.9-2.2	1.9-1.2	1.3-0.8	5.4-4.0	1.0-1.4	0.3-0.5	0.8-0.9	2.1-2.8	24-30

Table 3-2. To be continued.

Red Sea (n=1)												
	89	19	110	3.2	1.7	0.6	5.4	0.3	0.2	0.1	0.6	9.3
East China Sea (n=3)												
mean	480	78	580	4.8	5.7	2.3	13	3.0	5.8	7.5	16	17
range	100-1100	11-150	110-1300	1.7-8.2	1.3-9.4	0.9-4.8	3.9-22	0.5-7.9	0.3-14	0.7-19	1.5-41	14-19
South China Sea (n=6)												
mean	380	97	480	4.0	5.3	2.4	12	1.0	2.7	3.3	6.9	17
range	62-740	11-170	73-910	0.6-8.4	0.5-8.1	0.8-4.1	1.9-21	0.5-1.8	0.5-5.1	1.3-7.4	3.5-12	9.6-33
Str. of Malacca (n=1)												
	360	120	480	2.6	5.0	1.8	9.4	0.9	2.6	2.9	6.4	20
Celebes Sea (n=1)												
	240	43	280	1.0	2.5	1.6	5.1	1.0	0.5	1.1	2.6	20
Java Sea (n=1)												
	46	12	58	< 0.5	1.5	1.3	2.8	0.9	1.3	3.4	5.6	22
Bay of Bengal and Arabian Sea (n=7)												
mean	610	110	720	4.1	3.8	1.5	9.5	1.4	3.1	5.7	10	21
range	100-1200	27-190	130-1300	1.5-9.1	1.3-8.3	0.6-3.2	3.4-17	0.4-5.4	0.3-8.5	0.9-10	1.6-24	13-46
E. Indian Ocean (n=5)												
mean	74	20	94	3.9	2.2	1.2	7.5	0.8	0.5	0.7	2.1	21
range	40-130	14-39	54-170	<0.5-11	1.2-2.7	0.9-1.9	2.4-15	0.7-0.9	0.3-1.0	<0.1-2.4	1.3-4.3	9.7-42
Southern Ocean (n=5)												
mean	28	8.2	36	1.8	1.6	0.8	4.2	0.5	0.2	0.3	1.0	8.3
range	18-43	4.9-11	23-54	0.8-3.1	1.0-2.0	0.6-1.1	2.4-5.6	0.3-0.8	0.1-0.2	0.1-0.5	0.6-1.5	4.6-10

t-Chlor.: *trans*-chlordane *c*-Chlor.: *cis*-chlordane *t*-Nona.: *trans*-nonachlor

Values below detection limit are calculated as zero for arithmetric means.

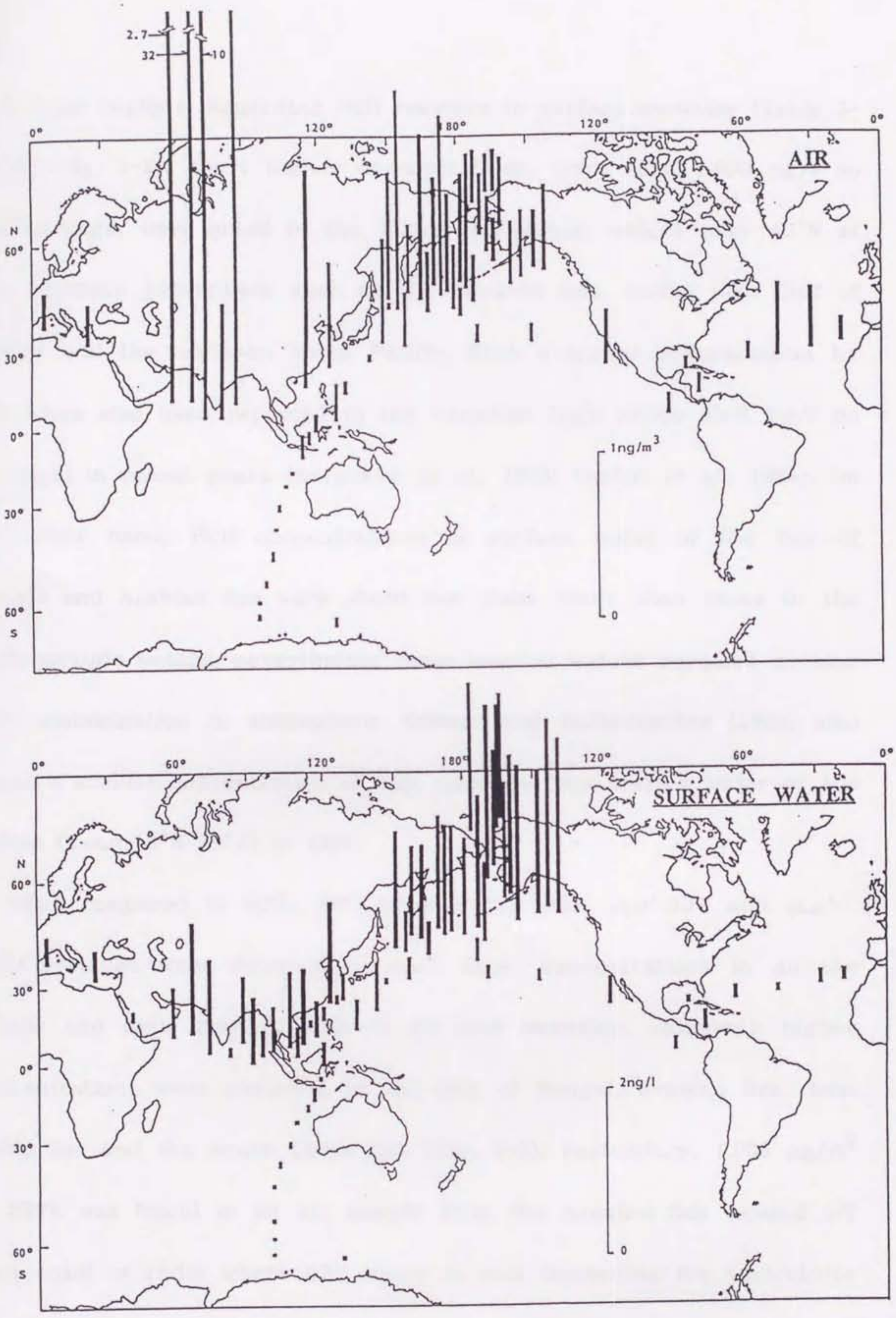


Fig. 3-2. Distribution of HCH (α - and γ -isomers) concentrations in air and surface seawater (1989-1990).

and polar regions. Regarding HCH residues in surface seawater (Table 3-2 and Fig. 3-2), much higher concentrations, more than 1,000 pg/l on the average, were noted in the higher latitudinal waters over 40°N of the northern hemisphere such as the Chukchi Sea, Bering Sea, Gulf of Alaska and the northern North Pacific. Such a higher contamination by HCHs has also been reported in the Canadian high Arctic (5-8 ng/l on average) in recent years (Hargrave *et al.*, 1988; Patton *et al.*, 1989). On the other hand, HCH concentrations in surface water of the Bay of Bengal and Arabian Sea were about two times lower than those in the high latitude waters, nevertheless these tropical waters revealed greater HCH contamination in atmosphere. Krämer and Ballschmitter (1988) also found a simillar concentration of HCH residues from surface water of the Indian Ocean (5°N 73°E) in 1985.

When compared to HCHs, DDT (sum of *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT) residues were detected in much lower concentrations in all the oceans and seas studied. Both in air and seawater, relatively higher concentrations were observed in the Bay of Bengal, Arabian Sea, East China Sea and the South China Sea (Fig. 3-3). Particulary, 1,000 pg/m^3 of DDTs was found in an air sample from the Arabian Sea located off west coast of India where DDT usage is still continuing for agriculture and vector control (Ray *et al.*, 1985). It was apparent that DDT concentrations drastically decreased with distance from the point source

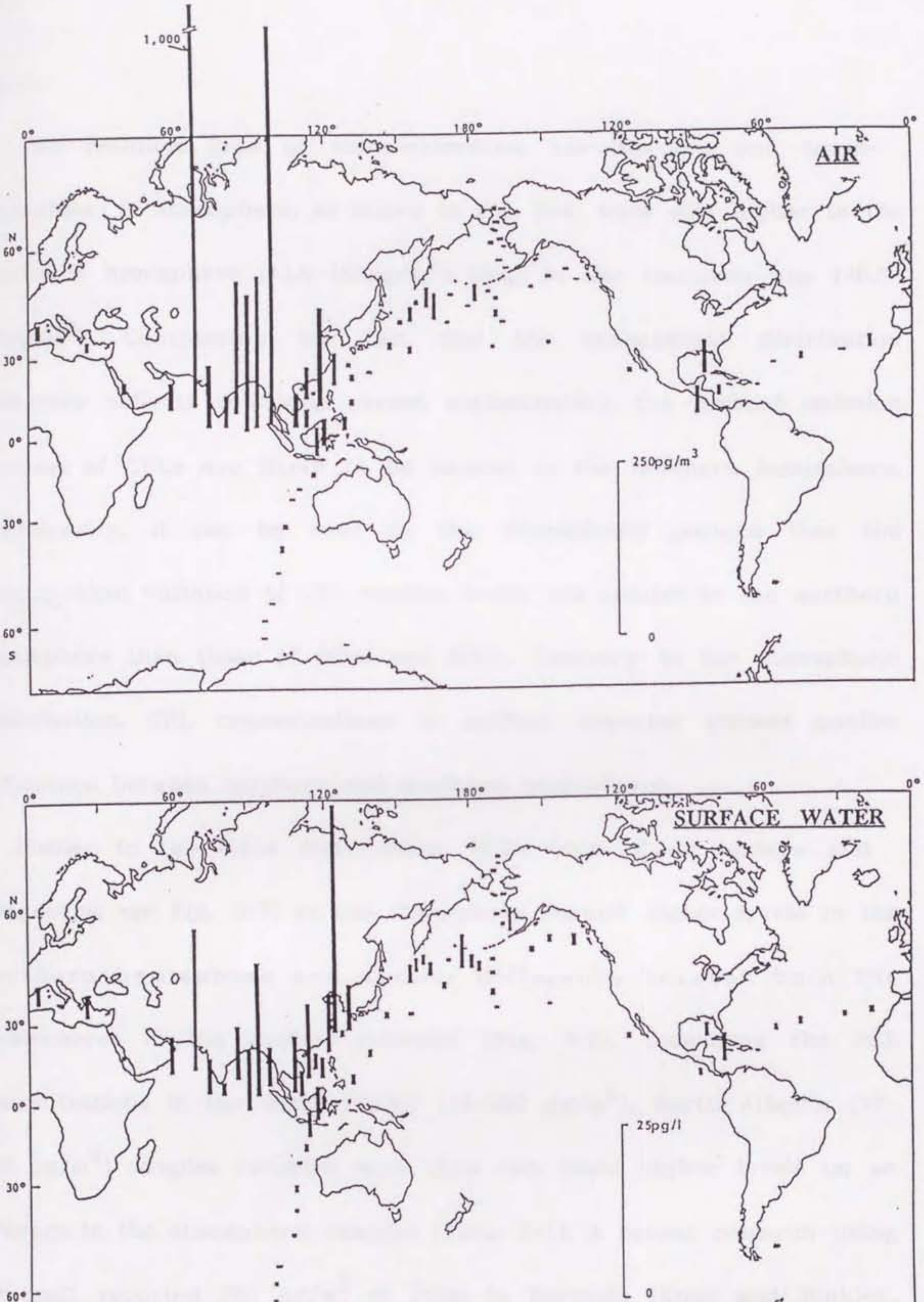


Fig. 3-3. Distribution of DDT (*p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT) concentrations in air and surface water (1989-1990).

areas.

CHL residues (sum of *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor) in atmosphere, as shown in Fig. 3-4, were also higher in the northern hemisphere (<1.0-160pg/m^3) than in the southern one (<0.5-14pg/m^3). Considering the fact that the atmospheric distribution generally reflects relatively recent contamination, the present emission sources of CHLs are likely to be located in the northern hemisphere. Additionally, it can be seen in the atmospheric pattern that the geographical variation of CHL residue levels was smaller in the northern hemisphere than those of HCHs and DDTs. Contrary to the atmospheric distribution, CHL concentrations in surface seawater showed smaller difference between northern and southern hemispheres.

Similar to the CHLs distribution, PCBs (sum of 40 isomers and congeners; see Fig. 3-7) in the atmosphere showed higher levels in the northern hemisphere and smaller difference between both the hemispheres in the surface seawater (Fig. 3-5). Comparing the PCB concentrations in the North Pacific (12-390 pg/m^3), North Atlantic (72-600 pg/m^3) samples revealed more than two times higher levels on an average in the atmospheric samples (Table 3-1). A recent research using air-craft reported 265 pg/m^3 of PCBs in Bermuda (Knap and Binkley, 1991) which is comparable to our data. There has also been reported about recent PCB contaminations in open ocean water samples. For example, 7 pg/l of mean PCB residues (quantified as Arochlor 1254) was

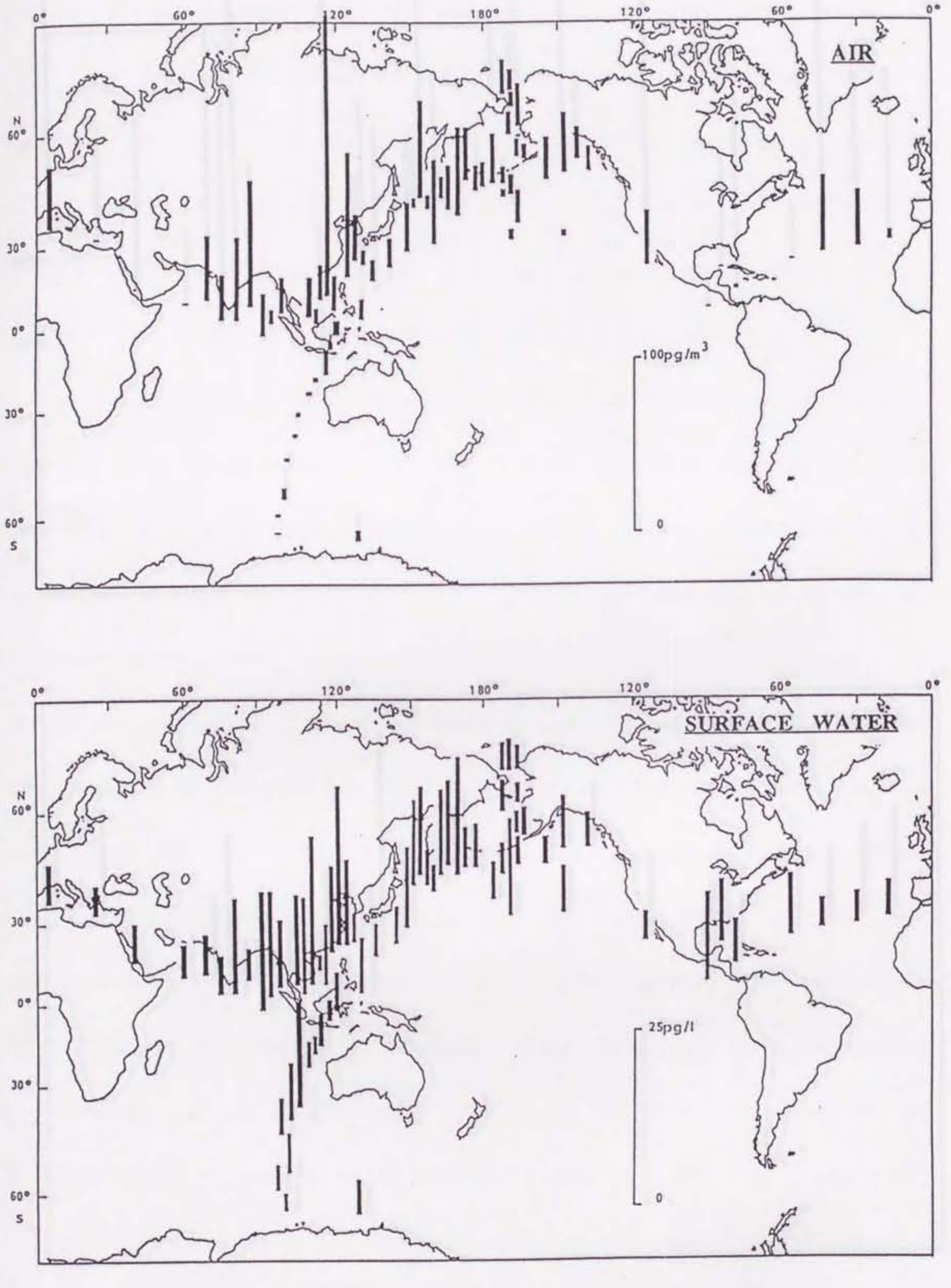


Fig. 3-4. Distribution of CHL (*trans*-chlordane, *cis*-chlordane and *trans*-nonachlor) concentrations in air and surface water (1989-1990).

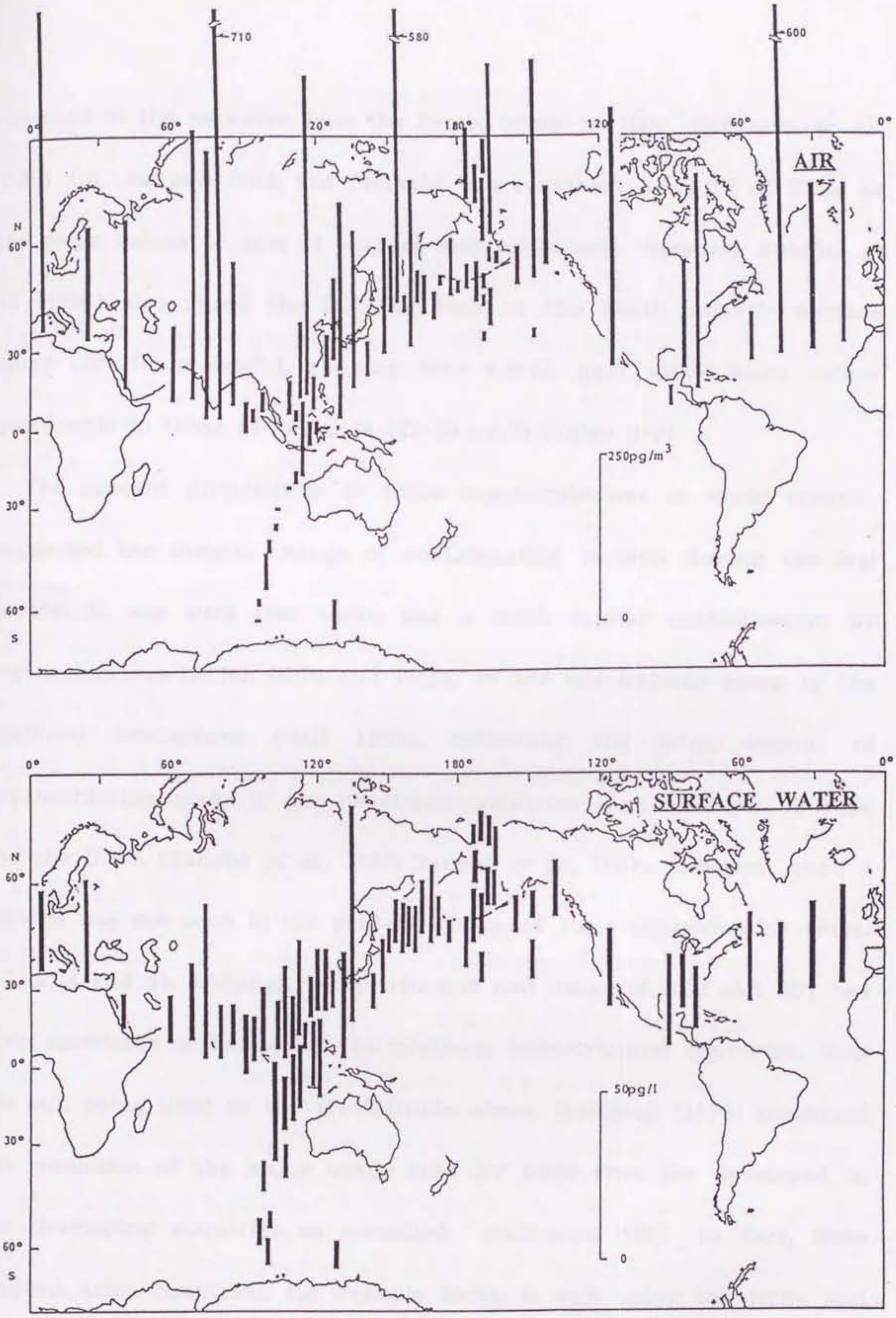


Fig. 3-5. Distribution of PCB concentrations in air and surface seawater (1989-1990).

detected in the seawater from the Arctic Ocean in 1986 (Hargrave *et al.*, 1988). Our samples from the Chukchi Sea contained 8.4 pg/l of PCBs as the mean values of sum of isomers and congeners. Moreover Schultz *et al.* (1988) also found the PCB residues in the North Atlantic surface water (10-250 m depth), ranging from 6.6-21 pg/l which were rather comparable to those of our data (21-29 pg/l) (Table 3-2).

The present distribution of these organochlorines in world oceans suggested the drastic change of contamination pattern during the last decade. It was sure that there was a much higher contamination by organochlorines (HCHs, DDTs and PCBs) in the mid-latitude ocean of the northern hemisphere until 1980s, reflecting the large amount of organochlorine usage in the developed countries such as Japan, Europe and the U.S.A (Tanabe *et al.*, 1982; Tanabe *et al.*, 1983). However, such a pattern was not seen in the present status of their contamination (Figs. 3-2, 3, 4 and 5). Although the production and usage of HCH and DDT has been restricted or banned in the northern industrialized countries, they are still being used in the low-latitude areas. Goldberg (1975) predicted the transition of the major usage area for DDTs from the developed to the developing countries as so-called "southward tilt". In fact, some tropical Asian countries, for example India, is still using the HCHs and DDTs in large quantities as insecticides for mosquito control and against crop pests (Kaushik *et al.*, 1987; Ramesh *et al.*, 1989). The amount of annual usage in this country was estimated to be about 47,000 tons for HCHs and 20,000 tons for DDTs (Ray *et al.*, 1985). Much higher concentrations, more than 100ng/m^3 of HCHs and DDTs have been reported in urban air from New Dehli (Kaushik *et al.*, 1987) and rural air from South India (Ramesh *et al.*, 1989). Moreover, Wolfe *et al.* (1984) reported extensive usage of HCHs and DDTs in China, even though this country had officially ceased the production of these contaminants from March 1983. According to a study over the Arabian Sea in 1976-77 (Bidleman and Leonard, 1982), HCH residue levels in air exceeded more than 1ng/m^3 and *p,p'*-DDT concentrations ranged from 4.7 to 580 pg/m^3. These values are quite close to the present residue levels in the Bay of Bengal and Arabian Sea (640-32,000 pg/m^3 for HCHs and 19-590 pg/m^3 for *p,p'*-DDT), implying that the usage of HCH and DDT are still continuing in some countries nearby northern Indian Ocean since 1970s. On the contrary, the levels of DDTs in air over the eastern Indian Ocean and the Southern Ocean are much lower than found by Tanabe *et al.* (1982) in the early 1980s. This strongly means that the usage of DDTs in some countries of the southern hemisphere has decreased over the last decade. Latitudinal distribution of atmospheric HCHs and DDTs in this study suggest that the major contamination source in global terms has clearly shifted from mid to low latitudes during the last decade. The present distribution implies that the tropical Asia is a significant emission source of persistent organochlorines on the global contamination.

Besides HCHs and DDTs, CHLs has been produced more than 70,000 tons in U.S.A. between 1960 and 1988 (Dearth and Hites, 1991) and used to control termites and other pests, and as a wood preservative in freight containers (Kawano *et al.*, 1988). A significant quantity of this pesticide has been exported to Japan and other nations. Nevertheless its use has been stopped in the U.S.A. and Japan in recent years, continuous consumption in some other countries is suspected (Dearth and Hites, 1991). Similar to other organochlorines, CHLs are also known as worldwide contaminants, as evidenced by their detection in the Arctic and Antarctic samples (Kawano *et al.*, 1988; Kawano, 1991). However, little is known on their distribution in the tropical marine environment. In the present atmospheric distribution of CHL concentrations (Fig. 3-4), smaller geographical variation in the northern hemisphere may suggest the expansion of their point source areas of contamination including the tropical developing countries. The fact that CHL concentrations in the Bay of Bengal and Arabian Sea in the present study (ranging from <1.0 to 69 pg/m^3) were found to be several times higher than those in 1976 to 1977 (Bidleman and Leonard, 1982) is likely to support the southward expansion of CHLs usage on global basis.

It has been demonstrated in a previous study that higher concentrations of PCBs in the open ocean surface seawater were seen in the mid-latitude of the northern hemisphere (Tanabe *et al.*, 1983). However, such a pattern was rather unified during the last decade, which was evidenced with a smaller variation of PCB residue levels all over the oceans surveyed (Fig. 3-5). The significant and indiscriminate usage and disposal of PCBs in tropical countries might contribute to such a uniform pattern of PCB distribution in the open ocean. Cummins (1988) reported that the developing countries hold about 15 % of the total world stock of PCBs. The observed pattern of PCB distribution is likely to indicate the reduction of highly contaminated areas in developed nations and the expansion of PCBs usage to the tropics during recent decade.

Regarding the previous survey of atmospheric PCBs, Bidleman *et al.* (1981) reported the mean concentrations of 115 and 57 pg/m^3 of PCBs as Arochlor 1254 over Barbados and Bermuda in 1977 to 78, respectively. It is noteworthy that these values are rather comparable or somewhat lower than those over the North Atlantic in the present study (290 pg/m^3 on an average). Moreover, in the North Pacific, mean PCB levels in atmosphere were found to be 540 pg/m^3 in 1979 (Atlas and Giam, 1981), 250 pg/m^3 in 1980-81 (Tanabe *et al.*, 1982) and 130 pg/m^3 in 1989 (present study). Despite the small number of samples, it is apparant that atmospheric PCB concentrations over the ocean are not decreasing rapidly since the 1980s.

Composition of residues

Besides the residue concentrations, the composition of organochlorines and their related compounds such as isomers and metabolites could be used as complemental and available tool to understand the emission source areas of global contamination. As shown in some literatures (Oehme and Ottar, 1984; Oehme and Stray, 1982; Oehme and Manø, 1984; Pacyna and Oehme, 1988; Atlas and Giam, 1988), ratios of α-HCH to γ-HCH and *p,p'*-DDT to *p,p'*-DDE have been used as indicators to estimate the origin and pathway of air mass in the long-range atmospheric transport of contaminants.

In the present study, the most noticeable variation was recognized in HCH isomer compositions in air regarding their latitudinal distribution. Although concentrations of α-HCH were found to be higher than γ-HCH in almost all the air samples (Table 3-1), the ratios (α/γ) were apparently different according to the seas and oceans (Table 3-3). In general, lower α/γ ratios were observed in the South China Sea, Mediterranean Sea, North Altantic and in the southern hemisphere. The observed lower ratio may indicate the presence of possible sporadic emission source of lindane nearby these seas and oceans. According to the earlier survey conducted in 1980, Tanabe *et al.* (1983) suggested the usage of lindane in Australia based on the data of dominant residues of γ-HCH in the urban and remote air. However, the present proportions of γ-HCH in air samples from the southern hemisphere were relatively less

Table 3-3. Concentration ratios of HCHs (α/γ: α-HCH/γ-HCH) and CHLs (N/C: *trans*-nonachlor /*trans*-chlordane) in the atmospheric samples from various seas and oceans.

Sampling Location	α/γ	N/C	Sampling Location	α/γ	N/C
Chukchi Sea			Mediterranean		
n	2	2	n	2	1
mean	9.6	1.1	mean	2.9	0.27
range	9.2-10	1.2-0.99	range	0.93-4.8	-
sd	-	-	sd	-	-
Bering Sea			East China Sea		
n	5	5	n	1	3
mean	8.3	0.84	mean	4.3	0.65
range	4.8-12	0.29-1.2	range	-	0.5-0.75
sd	3.3	0.38	sd	-	0.13
Gulf of Alaska			South China Sea		
n	4	4	n	1	5
mean	6.5	0.26	mean	1.6	0.44
range	5.5-7.6	0.16-0.40	range	-	0.28-0.54
sd	0.87	0.11	sd	-	0.12
N.N. Pacific			Bay of Bengal and Arabian Sea		
n	14	14	n	5	6
mean	8.1	0.46	mean	6.9	0.39
range	3.5-40	0.13-0.78	range	4.8-9.6	0.22-0.54
sd	9.5	0.22	sd	2.1	0.14
N. Pacific (coastal)			E. Indian Ocean		
n	7	6	n	5	3
mean	3.8	0.47	mean	1.5	0.79
range	1.4-7.1	0.29-0.83	range	0.65-2.4	0.34-1.3
sd	2.1	0.19	sd	0.68	0.46
N. Pacific (central)			Southern Ocean		
n	2	2	n	5	3
mean	8.9	1.5	mean	1.9	0.86
range	7.7-10	1.2-1.8	range	0.87-2.9	0.75-0.95
sd	-	-	sd	0.94	0.10
N. Atlantic					
n	4	3			
mean	3.6	0.60			
range	2.0-6.2	0.15-1.2			
sd	1.9	0.54			

n: Number of samples
mean: Sum of ratios for individual samples divided by number of samples.
sd: Standard deviation

significant than the previous survey. The downward trend of γ-HCH proportion in the southern hemisphere may imply the decreasing usage of lindane in Australia since 1980. On the other hand, higher α/γ ratios were seen in the northern atmospheric samples and the values tended to decrease southward. The higher ratios more than 10 were observed in northern regions such as the Chukchi Sea, Bering Sea, northern and central part of North Pacific (Table 3-3), similar to those reported from summer to fall over the Canadian Arctic atmosphere (Patton *et al.*, 1989). Extraordinarily high α/γ ratio was also found in the northern North Pacific (α/γ=40). The same phenomena has also been recorded in the Norwegian Arctic air during summer season (Oehme and Ottar, 1984; Oehme and Stray, 1982; Oehme and Manø, 1984; Pacyna and Oehme, 1988). Such a high ratio more than 10 can not be explained by the effect arising out of the usage of technical formulation which consists of 55-70% α-, 5-14% β-, 10-18% γ-HCH and other minor isomers (Demozay and Marechal, 1972). Hence, the photochemical transformation of γ- to α-isomer in the atmosphere has been given as one of the plausible explanations (Oehme and Manø, 1984; Pacyna and Oehme, 1988). Significant isomerization of the solid γ-isomer into the α-isomer has been experimentally demonstrated under conditions of the presence of ferrous salts and sunlight (Malaiyandi and Shah, 1984). If γ-HCH significantly isomerize into α-HCH under natural conditions, specific higher proportion of α-isomer must be found even in the emission sites and nearby oceans. However, higher values were only detected in some areas far away from emission sources like India and China. This phenomena is not specific only in Arctic and nearby northern oceans because higher ratio was also observed in the central North Pacific (Table 3-3). The geographical variation of α/γ ratios may impose an insight into the different deposition rates of HCH isomers to surface seawater during the atmospheric transport and deal less of the photoisomerization.

Regarding DDT compound compositions, the higher ratios of *p,p'*-DDT to *p,p'*-DDE (T/E) in the air sample were especially observed around the seas and oceans nearby India and southeast Asian countries (Fig. 3-6). This result also indicates the presence of significant source of DDT in tropical Asia still now, as only a small amount of *p,p'*-DDE is contained in the commercial products. In contrast, low ratios of T/E could be seen in the North Pacific and North Atlantic basins which are rather remote areas from the contamination sources like tropical regions. The higher *p,p'*-DDE ratios have been interpreted as a result of the long time exposure in environment because *p,p'*-DDT may be converted to *p,p'*-DDE by U.V.-light and the metabolism by organisms during the atmospheric transport (Atlas and Giam, 1988). As another possibility, this might be also explicable by the relatively higher transportability of *p,p'*-DDE than *p,p'*-DDT in the atmosphere, which is based on their physico-chemical

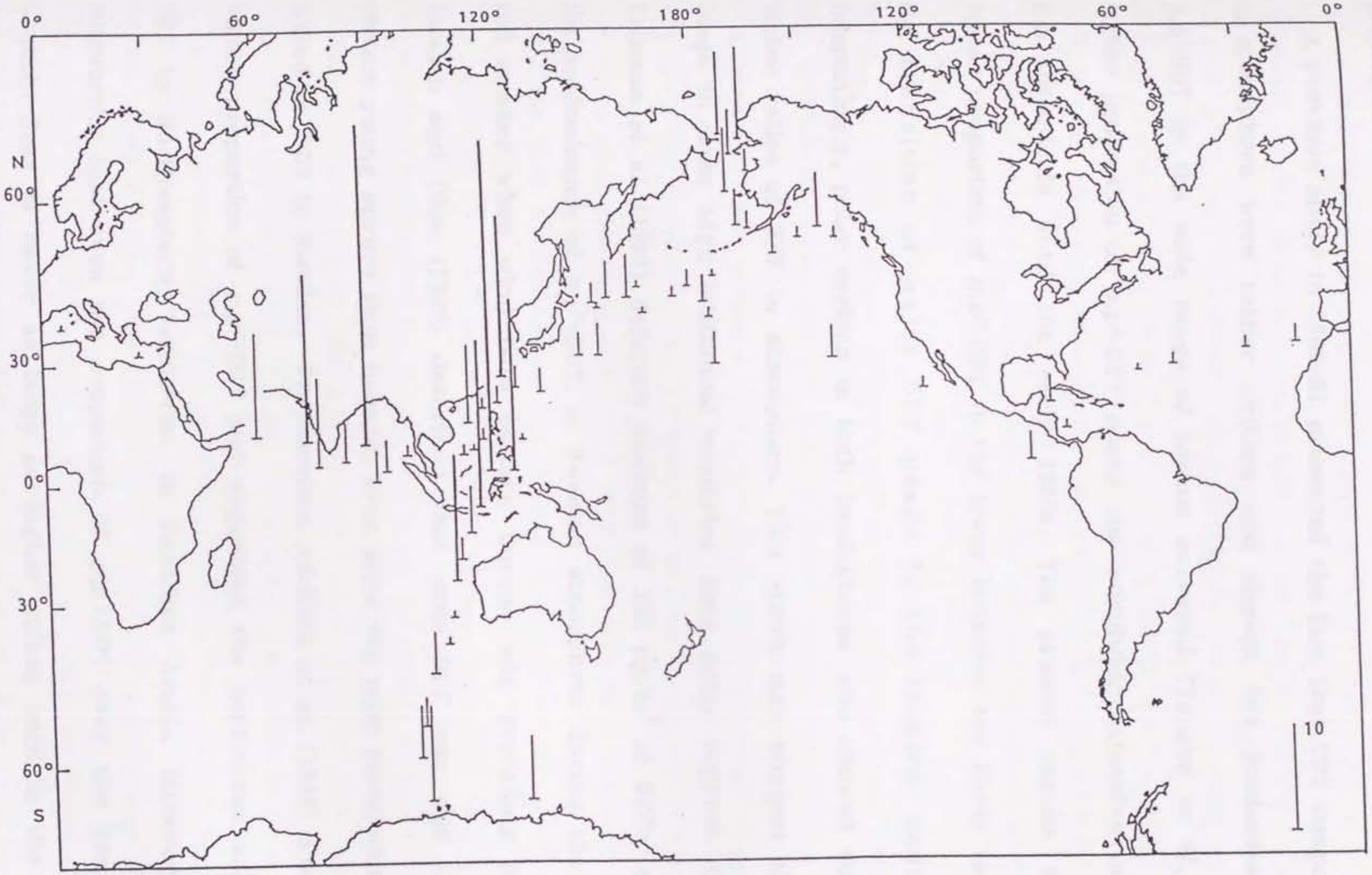


Fig. 3-6. Distribution of the concentration ratios of *p,p*'-DDT/*p,p*'-DDE in air (1989-1990).

properties.

A previous study in 1980-81 presented the fact that DDT compositions in atmosphere were rather uniform and showed the predominance of *p,p'*-DDT in the wide range of oceans surveyed (Tanabe *et al.*, 1982). Higher proportion of *p,p'*-DDT means the worldwide extensive usage of this insecticide until the early 1980s. The present results showing higher proportion of *p,p'*-DDT in the lower latitudes are likely to depict the transition of major DDT usage to the tropical countries. Interestingly, polar regions in both hemispheres also showed somewhat higher ratios of T/E in atmosphere. This result may suggest the DDT usage in some high latitudinal countries near polar regions. In fact, Bidleman *et al.* (1987) detected maximum of 140 pg/m^3 of DDTs, showing the predominance of *p,p'*-DDT, in Swedish atmosphere during the spring and summer when wind from eastern Europe was prevailing in 1984. Larsson and Okla (1989) described that some DDT was still used to protect young spruce from insects, even after the main restrictions were placed on DDT in Sweden. Furthermore, Addison *et al.* (1986) also noted higher proportion of *p,p'*-DDT and suggested the continuous supply of DDT to Northwestern Territories in Canadian Arctic. However, it is noteworthy that even the proportion of *p,p'*-DDT over the Bering and Chukchi Seas is never as large as higher values seen in the Bay of Bengal, Arabian Sea and other tropical Asian seas. This result as well as the atmospheric distribution of DDTs also implies that the source of this pesticide in the higher latitudes is not stronger than that in the lower latitudes. In the southern hemisphere, recent report suggests that DDT is still being used for limited agricultural purposes in some Australian states (Corrigan and Seneviratna, 1990). Moreover, *p,p'*-DDT was detected as the most abundant component in the atmosphere of the South Atlantic and Southern Oceans, even at low concentrations (Weber and Montone, 1990).

As suggested from the distribution of CHL concentrations (Fig. 3-4), the southward expansion of this chemical usage might be further evidenced by the compound composition like *trans*-nonachlor/*trans*-chlordane (N/C) ratio in the air samples. Technical chlordane consists of a mixture of *trans*-chlordane [24±2 wt%], *cis*-chlordane [19±3 %], *trans*-nonachlor [7±3 %] and other compounds (Sovocool *et al.*, 1977). Under the situation of continuous usage of CHLs, the N/C ratio in the environment is likely to be nearly 0.15-0.45. As shown in Table 3-3, such values are obtained in the wide regions such as the Gulf of Alaska [0.16-0.40], northern North Pacific [0.13-0.78], coastal sides of N. Pacific [0.29-0.83], Mediterranean Sea [0.27], South China Sea [0.28-0.54], Bay of Bengal and Arabian Sea [0.22-0.54], suggesting numerous emission sources of CHLs from southern tropical countries, Japan, U.S.A. and Europe. As contrasted with these seas and oceans, higher N/C ratios can be seen in the Chukchi Sea [0.99-1.2], Bering Sea [0.29-1.2], central part of Pacific [1.2-1.8] and the Southern Ocean [0.75-0.95] which are rather far from above possible sources. Some authors also pointed out the higher ratios of N/C in remote area like the Canadian Arctic (Patton *et al.*, 1989; Hoff and Chan, 1986). Alhough they believed that the higher N/C ratios were related to the preferential depletion of *trans*-chlordane, the plausible explanation is yet to be made.

PCB isomer and congener compositions have been used as chemical tracers to clarify the biological and ecological parameters of the marine mammal populations (Subramanian *et al.*, 1988; Subramanian *et al.*, 1988). At the same time, these isomer and congener patterns are also useful tracers to elucidate the geochemical phenomena yet to be solved, because of their persistency and wide range of physico-chemical properties. According to the isomer specific analysis of PCBs in atmosphere, high latitude oceans such as the Bering Sea and Southern Ocean revealed relatively larger proportion of less chlorinated members when comparing to those in mid and low latitude waters such as the North Pacific and eastern Indian Ocean (Fig. 3-7). PCB compositions in the open ocean atmosphere have been determined by some authors and are rather common to contain largely the less chlorinated members (Atlas and Giam, 1981; Tanabe and Tatsukawa, 1986). However, to our knowledge, this is a first report to note that PCB compositions in oceanic atmosphere are different between high and low latitude. These

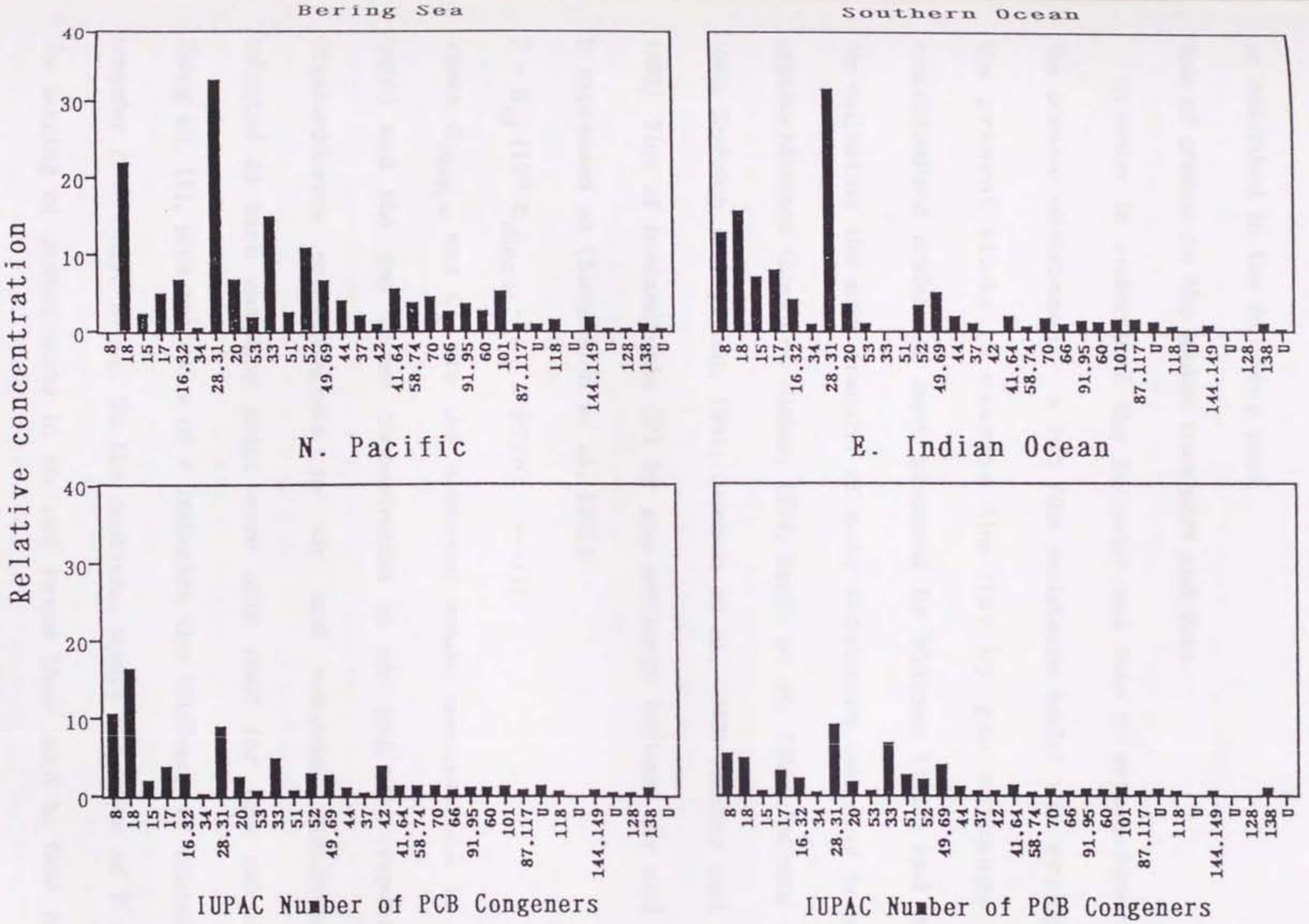


Fig. 3-7. Relative concentrations of PCB isomers and congeners in open ocean atmosphere. Concentration of IUPAC no. 138 was defined as 1.0.
Upper and lower figures represent higher and lower latitude areas, respectively.
U means the PCB peaks with no IUPAC number.

variations might arise from the isomer specific behavior between air and water phases through long-range atmospheric transport over the ocean, as described in the following part.

Role of oceans on the global transport and fate

In order to understand the behavior and fate of organochlorines in the oceanic environment, a two film resistance model was employed in the present study to examine the flux by gas exchange. This conceptualized model has been proposed by Whitman (1923) and applied for estimating the mass transfer of many substances including persistent organochlorines (Liss and Slater, 1974; Smith *et al.*, 1980; Zafiriou *et al.*, 1980; Rudolph and Ehhalt, 1981; Gammon *et al.*, 1982; Mackay and Yeun, 1983). Flux of contaminants (F) by gas exchange between air and water is expressed as (Eisenreich *et al.*, 1981):

$$F = K_{ol}\,(10^3\,C_{diss,w} - C_g \times RT/H) \quad ---(1)$$

where $C_{diss,w}$ and C_g are the dissolved solute concentration in water (pg/l) and the gas phase concentration in air (pg/m^3), respectively. Organochlorine concentrations in air and seawater simultaneously collected at each sampling point were only used for this calculation. Using eq. (1), plus (+) value of F indicates the tendency of contaminant transfer from water to air. On the contrary, minus (-) value of F means the leaning of contaminants in air and hence they tend to flow toward water phase from atmosphere. T is the absolute temperature (K) at the air-water interface, R is the universal gas constant (Pa m^3 mol^{-1} K^{-1})

and K_{ol} is the overall mass transfer coefficient (m/s). H is the Henry's law constant (HLC; Pa m^3 mol^{-1}) which is the ratio of solute partial pressure in the air to the equilibrium water concentration.

Moreover, K_{ol} can be estimated using the following equation (Mackay and Yeun, 1983).

$$1/K_{ol} = 1/k_l + RT/H \times 1/k_g \quad \text{---(2)}$$

$$k_g = 1.0\times10^{-3} + 4.62\times10^{-4}(6.1+0.63\times U_{10})^{0.5}\times U_{10}\times(S_{cg})^{-0.67} \quad \text{---(3)}$$

$$k_l = 1.0\times10^{-6} + 3.41\times10^{-5}(6.1+0.63\times U_{10})^{0.5}\times U_{10}\times(S_{cl})^{-0.5} \quad \text{---(4)}$$

where k_l and k_g are the liquid-phase and gas-phase mass transfer coefficients (m/s), respectively. Both parameters are controlled by the wind speed at 10 m altitude (U_{10}: m/s) and the Schmidt number (S_{cg} and S_{cl}) which are the dimensionless ratios of viscosity / (density x diffusivity), ranging from 1.8-2.2 for S_{cg} and 800-1,200 for S_{cl} in organic solutes (Strachan and Eisenreich, 1988). In this study, 2.0 for S_{cg} and 1,000 for S_{cl} were used for all organochlorines examined. Wind speed was approximated to 7 m/s (> 60° latitude), 5 m/s (20°-60° lat.) and 3 m/s (0°-20° lat.) at each latitude of the sampling site, referring the wind velocity data during the cruises of Kagoshima-Maru and Osyoro-Maru (see Fig. 3-1). As the oceans provide the atmosphere with heat, temperature at surface water rather than at the bulk air temperature was considered to be closer to that at air-water interface. The water temperature (T) was determined to be 0°C (>60° lat.), 10°C

(40°-60° lat.), 20°C (20°-40° lat.) and 30°C (0°-20° lat.) in each sampling site, which is based on the seasonal average water temperature in the Pacific Ocean from Barkley (1968). Table 3-4 presents the comparison of HLCs of organochlorines which have been already reported in other papers. These HLCs were mainly based on the review by Suntio *et al.* (1988), a combination of reported solubilities and vapor pressures (Mackay *et al.*, 1986; Murphy *et al.*, 1987; Tateya *et al.*, 1988), direct measurements (Atlas *et al.*, 1982; Fendinger *et al.*, 1989; Brunner *et al.*, 1990; Kucklick *et al.*, 1991) such as bubble stripping and wetted-wall column techniques, and the quantitative structure-property relationship models (Dunnivant *et al.*, 1992). The HLCs for HCHs (at 20-25°C) were within 2-3 factors among these presented values. Kucklick *et al.* (1991) recently determined the HLCs for HCHs as a function of temperature in artificial seawater and distilled water using the gas stripping method. In this study, their directly measured values were selected. The HLCs for *p,p'*-DDE yielded by two independent approaches (Suntio *et al.*, 1988; Atlas *et al.*, 1982) exhibit large differences. The lower value was employed here, as the influence of using the larger value is discussed in the latter part of this paper. Two representative HLCs for *p,p'*-DDT (Mackay *et al.*, 1986; Fendinger *et al.*, 1989) were virtually similar, although the estimated values are obtained by different methods. To unify the data source between *p,p'*-DDE and *p,p'*-DDT, the HLC (1.31) by Mackay's group was selected. Recent study (Kawano, 1991) which offered the vapor pressures and the water solubilities for CHLs allowed to calculate their HLCs. The HLCs seem to be considerably close to the estimations and measurements by other authors, except for those by Atlas *et al.* (1982). For the HLC of *trans*-nonachlor, only our estimated value was available. Hence, the HLCs for other CHL compounds from the same data source were also employed. The HLCs for PCB isomers and congeners showed small variations approximately within a factor of 3 among reported values. Furthermore, all reported HLCs tend to decrease with the increasing of the number of chlorine substitutes. In this study, most recent data by Dunnivant *et al.* (1992) were used. The constants of all the organochlorines at diverse temperatures were obtained using the slope (m) of the following equation (5).

$\ln H = m/T + b$ ---(5)

As for HCHs, the slopes determined by a recent study (Kucklick *et al.*, 1991) were applied ($m = -2969$ for α-HCH and $m = -2703$ for γ-HCH). The slope ($m = -7868$) obtained for PCBs earlier (Tateya *et al.*, 1988) was substituted for that of other organochlorines except for HCHs. K_{ol} was also calculated by using the parameters determined in each latitude. As a representative, K_{ol} s under conditions of $T = 20°C$ and $U_{10} = 5m/s$ are summarized in Table 3-4.

The fluxes were estimated in the different seas and oceans. In this process, particle binding fraction of organochlorines was taken into

Table 3-4. Henry's law constants (HLC: Pa m^3 /mol) and K_{ol} (m/day) for organochlorines.

Organochlorines	HLC										K_{ol}^{g}
HCHs											
α-HCH	2.4	(23℃)$^{1)}$	1.1	(23℃)$^{1)a}$	0.87	(20℃)$^{2)}$	0.677	(23℃)$^{3)}$	0.710	(23℃)$^{3)af}$	0.110
γ-HCH	0.158	(25℃)$^{4)}$	0.13	(20℃)$^{2)}$	0.20	(23℃)$^{5)}$	0.339	(23℃)$^{3)}$	0.363	(23℃)$^{3)af}$	0.0590
DDTs											
p,p'-DDE	120	(23℃)$^{1)}$	370	(23℃)$^{1)a}$	7.95	(20℃)$^{2)f}$					0.745
p,p'-DDT	1.31	(25℃)$^{4)f}$	0.86	(23℃)$^{5)}$							0.141
CHLs											
t-chlordane	140	(23℃)$^{1)}$	570	(23℃)$^{1)a}$	9.64	(25℃)$^{4)b}$	9.02	(20℃)$^{2)b}$	16.5	(25℃)$^{6)f}$	0.849
c-chlordane	89	(23℃)$^{1)}$	420	(23℃)$^{1)a}$	9.64	(25℃)$^{4)b}$	9.02	(20℃)$^{2)b}$	11.2	(25℃)$^{6)f}$	0.705
t-nonachlor	49.5	(25℃)$^{6)f}$									1.20
PCB isomers and congeners											
8	28.4	(20℃)$^{7)}$	45.5	(20℃)$^{8)a}$	23.3	(25℃)$^{9)e}$	30.7	(25℃)$^{10)f}$			1.07
18	30.3	(20℃)$^{7)}$	33.5	(20℃)$^{8)a}$	25.3	(25℃)$^{9)}$	32.4	(25℃)$^{10)f}$			1.09
15	N.A.	(20℃)$^{7)}$	29.0	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	22.7	(25℃)$^{10)f}$			0.976
17	33.0	(20℃)$^{7)}$	N.A.	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	37.8	(25℃)$^{10)f}$			1.13
16,32	24.1	(20℃)$^{7)c}$	27.6	(20℃)$^{8)a}$	20.3	(25℃)$^{9)}$	31.6	(25℃)$^{10)df}$			1.08
34	N.A.	(20℃)$^{7)}$	N.A.	(20℃)$^{8)a}$	20.3	(25℃)$^{9)e}$	42.7	(25℃)$^{10)f}$			1.17
28,31	26.7	(20℃)$^{7)}$	36.0	(20℃)$^{8)a}$	19.8	(25℃)$^{9)d}$	28.4	(25℃)$^{10)df}$			1.05
20	N.A.	(20℃)$^{7)}$	21.8	(20℃)$^{8)a}$	16.2	(25℃)$^{9)e}$	22.0	(25℃)$^{10)f}$			0.965
53	28.7	(20℃)$^{7)}$	24.7	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	43.6	(25℃)$^{10)f}$			1.17
33	22.7	(20℃)$^{7)}$	17.0	(20℃)$^{8)a}$	16.2	(25℃)$^{9)e}$	24.3	(25℃)$^{10)f}$			0.999
51	N.A.	(20℃)$^{7)}$	19.3	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	51.7	(25℃)$^{10)f}$			1.21
52	24.1	(20℃)$^{7)}$	32.0	(20℃)$^{8)a}$	20.3	(25℃)$^{9)}$	32.3	(25℃)$^{10)f}$			1.09
49,69	28.0	(20℃)$^{7)c}$	34.2	(20℃)$^{8)a}$	21.3	(25℃)$^{9)}$	42.8	(25℃)$^{10)df}$			1.17
44	19.2	(20℃)$^{7)}$	N.A.	(20℃)$^{8)a}$	14.2	(25℃)$^{9)e}$	23.3	(25℃)$^{10)f}$			0.985
37	15.4	(20℃)$^{7)}$	N.A.	(20℃)$^{8)a}$	10.1	(25℃)$^{9)}$	15.4	(25℃)$^{10)f}$			0.836
42	N.A.	(20℃)$^{7)}$	24.0	(20℃)$^{8)a}$	14.2	(25℃)$^{9)e}$	25.9	(25℃)$^{10)f}$			1.02
41,64	18.8	(20℃)$^{7)d}$	22.5	(20℃)$^{8)a}$	14.2	(25℃)$^{9)}$	26.1	(25℃)$^{10)df}$			1.02
58,74	21.2	(20℃)$^{7)c}$	N.A.	(20℃)$^{8)a}$	10.1	(25℃)$^{9)c}$	23.5	(25℃)$^{10)df}$			0.987
70	19.0	(20℃)$^{7)}$	22.6	(20℃)$^{8)a}$	10.1	(25℃)$^{9)}$	20.5	(25℃)$^{10)f}$			0.940
66	20.4	(20℃)$^{7)}$	23.4	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	20.5	(25℃)$^{10)f}$			0.941
91,95	23.8	(20℃)$^{7)d}$	26.2	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	32.6	(25℃)$^{10)df}$			1.09
60	16.4	(20℃)$^{7)}$	17.7	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	15.5	(25℃)$^{10)f}$			0.838
101	18.1	(20℃)$^{7)}$	31.5	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	24.9	(25℃)$^{10)f}$			1.01
87,117	12.9	(20℃)$^{7)c}$	22.1	(20℃)$^{8)a}$	7.5	(25℃)$^{9)c}$	21.3	(25℃)$^{10)df}$			0.954
118	8.6	(20℃)$^{7)}$	21.4	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	12.7	(25℃)$^{10)f}$			0.765
144,149	14.6	(20℃)$^{7)d}$	N.A.	(20℃)$^{8)a}$	N.A.	(25℃)$^{9)}$	26.8	(25℃)$^{10)df}$			1.03
128	5.8	(20℃)$^{7)}$	14.2	(20℃)$^{8)a}$	1.3	(25℃)$^{9)}$	10.5	(25℃)$^{10)f}$			0.693
138	7.6	(20℃)$^{7)}$	41.7	(20℃)$^{8)a}$	2.1	(25℃)$^{9)}$	13.2	(25℃)$^{10)f}$			0.778

N.A.: not available.

1)after Atlas *et al.*, (1982). 2)after Suntio *et al.*, (1988). 3)after Kucklick *et al.*, (1991). 4)after Mackay *et al.*, (1986). 5)after Fendinger *et al.*, (1989). 6)calculated from the subcooled liquid vapor pressure and the water solubility after Kawano, (1991). 7)after Murphy *et al.*, (1987). 8)after Tateya *et al.*, (1988). 9)after Brunner *et al.*, (1990). 10)after Dunnivant *et al.*, (1992).

a)measurement using seawater. b)isomer not specified. c)represented with the HLC for one congeners.
d)averaged with the HLC for two congeners. e)including the HLC for other congener.
f)selected for flux estimation. g)estimated under the conditions of T = 20℃ and U_{10} = 5m/s.

consideration. Generally, atmospheric persistent organochlorines are distributed both in gas and aerosol phases, depending on the air temperature (Yamasaki *et al.*, 1982). Some attempts have been made to understand the distribution rate of organochlorines in air. The major fractions of organochlorines have been recorded in the gas phase even in the urban air of mid-latitude containing the high density airborne particles (Baker and Eisenreich, 1990; Bidleman *et al.*, 1987; Nakano *et al.*, 1990). Moreover, even under the condition of low temperature in the Arctic region, organochlorines in aerosol phase could not be detected (Patton *et al.*, 1989). Taking into account of these facts, it is likely to mention that persistent organochlorines in the aerosol binding fraction are negligible when calculating their fluxes by gas exchange between air and water phases. While in water samples, it has been pointed out in some studies that significant quantities of persistent organochlorines are retained in particulate (macroparticle) and colloidal (nonsettling microparticle) fractions (Tanabe and Tatsukawa, 1983; Gschwendwend and Wu, 1985; Baker *et al.*, 1986). However, the filteration of water samples was not carried out in the present study, because of the methodological difficulties to separate the dissolved and colloidal phases by conventional filteration and centrifugation (Baker and Eisenreich, 1990; Gschwend and Wu, 1985; Baker *et al.*, 1986). Hence, the obtained values of organochlorine concentrations using XAD-2 resin were regarded either as dissolved fraction (case 1; $C_{diss,w}$ = detected value in eqn. (1)) or adsorbed (case 2; $C_{diss,w} = 0$ in eqn. (1)). Cases 1 and 2 mean no binding and 100% binding to particles of organochlorines in water, respectively. The arithmetic mean of fluxes in both cases and their ranges in seas and oceans surveyed are graphically presented in Figs. 3-8, 3-9, 3-10 and 3-11. (These values are available in Table 3-7 as the Appendix.)

As a result, HCHs (α- and γ-isomers) revealed minus (-) values of the fluxes in most seas and oceans surveyed, indicating the tendency to transfer these contaminants from air to water (Fig. 3-8). This implies that the marine water bodies principally play a role as a sink for HCHs. Particularly, higher minus values were obtained in the tropical waters such as the Arabian Sea, Bay of Bengal (case 1 avg.; -2,500ng/m^2/day, case 2 avg.; -2,600ng/m^2/day), East China (-260ng/m^2/day, -270ng/m^2/day) and South China (-350ng/m^2/day, -360ng/m^2/day) Seas, where active transfer of HCHs into water was predicted. Such a transfer is due to the geographical proximity of these seas to tropical countries which are still using this insecticide. The considerable flux was also identified in the northern high latitude waters such as the Chukchi Sea (-56ng/m^2/day, -190ng/m^2/day), Bering Sea (-73ng/m^2/day, -220ng/m^2/day), Gulf of Alaska (-43ng/m^2/day, -190ng/m^2/day) and the northern North Pacific (-150ng/m^2/day, -240ng/m^2/day).

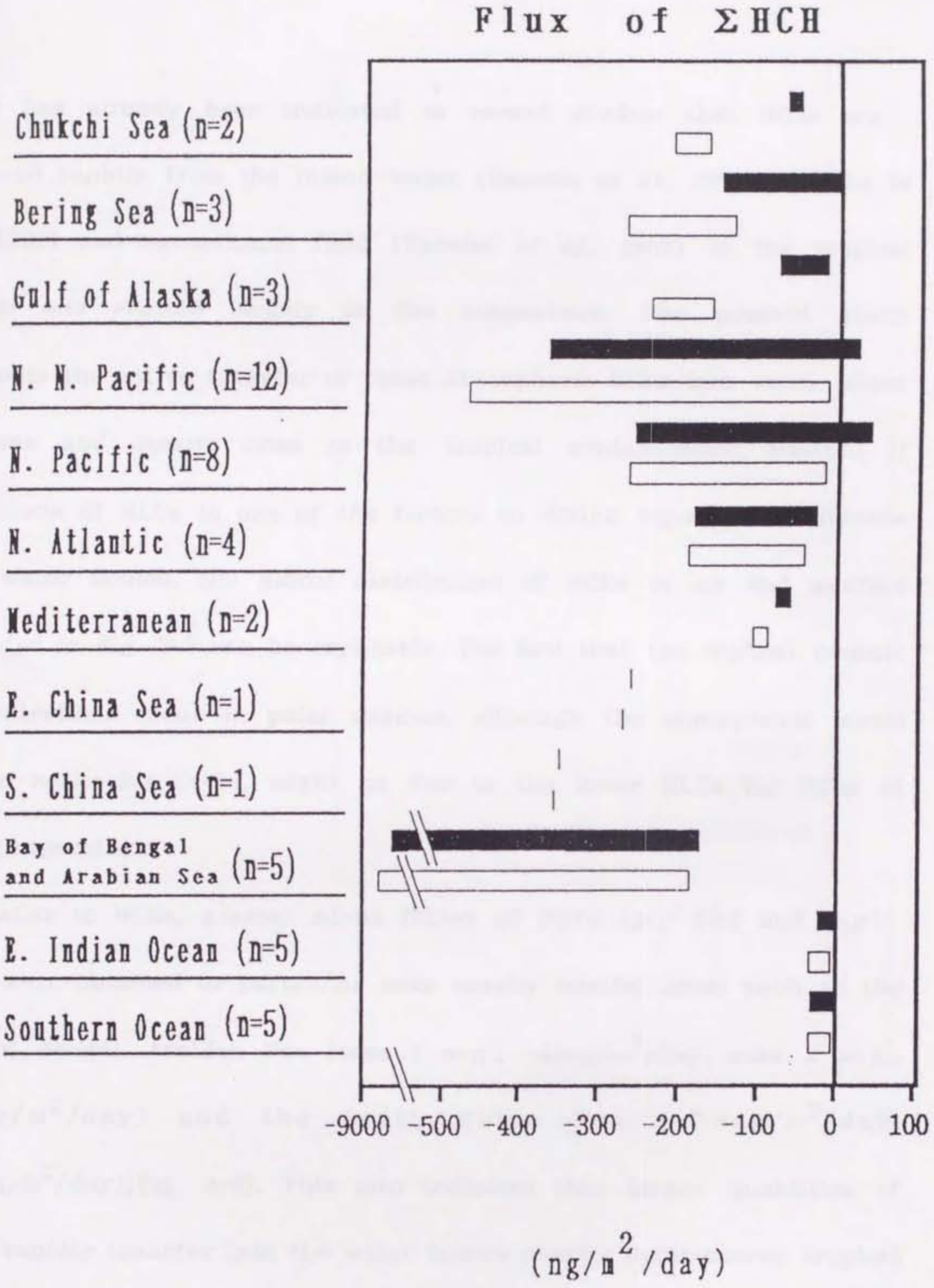


Fig. 3-8. Fluxes by gas exchange of HCHs (α - and γ -isomers) across the air-water interface in various seas and oceans.
Figures in parentheses are the number of pairings for air and surface water samples.
Length of a bar shows the range of flux.
Solid and open bars represent the flux for case 1 and 2 (see text), respectively.

It has already been indicated in recent studies that HCHs are removed rapidly from the inland water (Ramesh *et al.*, 1990; Takeoka *et al.*, 1991) and agricultural field (Tanabe *et al.*, 1982) in the tropical region and emitted largely to the atmosphere. The present study suggests the active transfer of these atmospheric HCHs into water phase of seas and oceans close to the tropical contamination source. If magnitude of HLCs is one of the factors to define input of substances into water bodies, the global distribution of HCHs in air and surface seawater in Fig. 3-2 can be explicable. The fact that the highest oceanic concentrations occur in polar regions, although the atmospheric levels are so noticeable there, might be due to the lower HLCs for HCHs at cold temperature.

Similar to HCHs, greater minus fluxes of DDTs (*p,p'*-DDT and *p,p'*-DDE) were obtained in particular seas nearby coastal areas such as the Bay of Bengal, Arabian Sea (case 1 avg.; -33ng/m^2/day, case 2 avg.; -33ng/m^2/day) and the South China Sea (-7.8ng/m^2/day, -9.1ng/m^2/day)(Fig. 3-9). This also indicates that larger quantities of DDTs rapidly transfer into the water bodies nearby point-source tropical countries during the earlier process of atmospheric transport because of their lower HLCs. Consequently, it may be concluded that DDTs are relatively less dispersible through air on a wide geographical scale. Taking into account for the direction of the flux estimation for DDTs, it will be noted that the concentration of DDTs as well as HCHs in surface

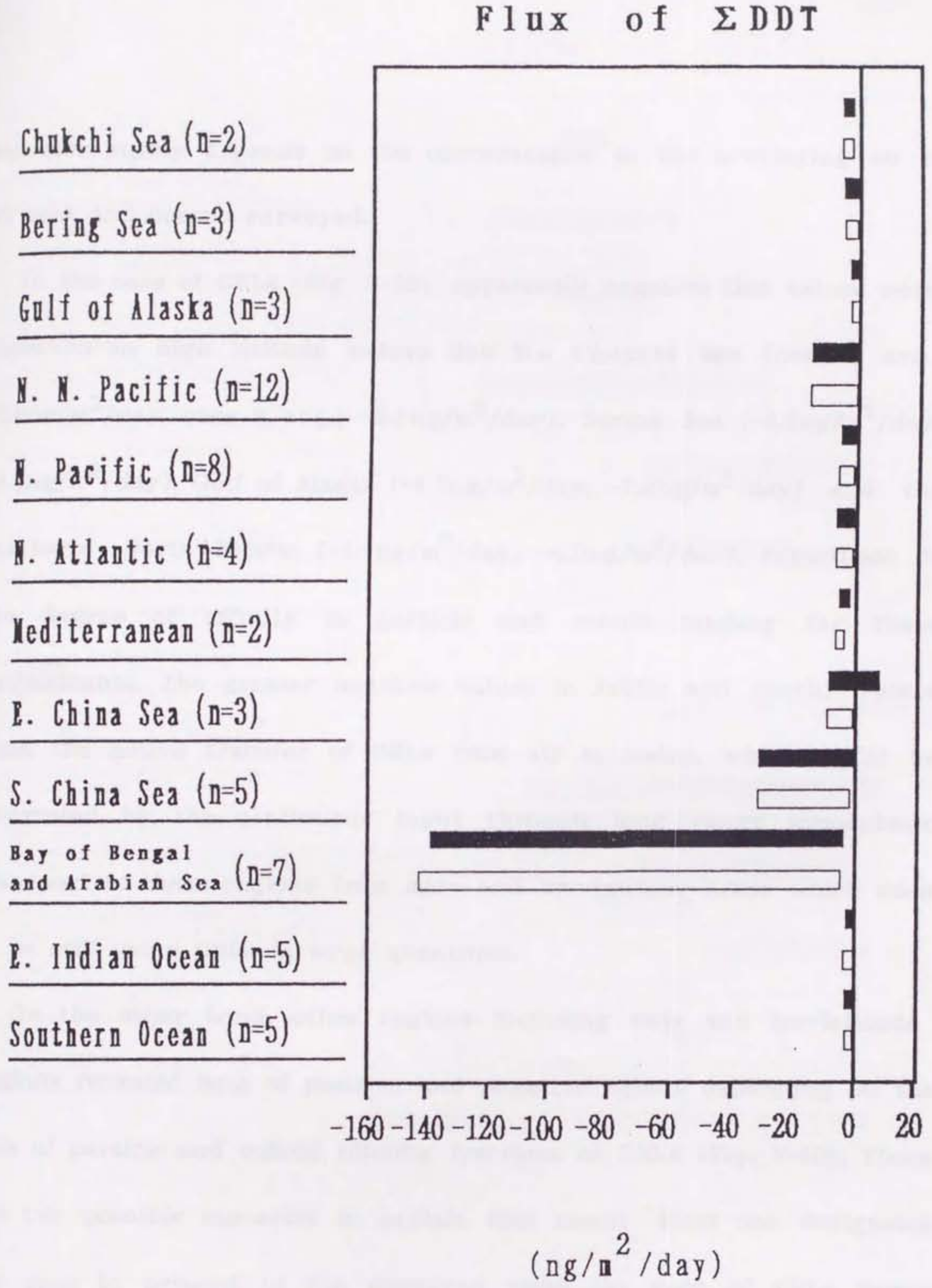


Fig. 3-9. Fluxes by gas exchange of DDTs (*p,p'*-DDE and *p,p'*-DDT) across the air-water interface in various seas and oceans.
Figures in parentheses are the number of pairings for air and surface water samples.
Length of a bar shows the range of flux.
Solid and open bars represent the flux for case 1 and 2 (see text), respectively.

seawater surely depends on the concentration in the overlaying air in all seas and oceans surveyed.

In the case of CHLs (Fig. 3-10), apparently negative flux values were observed in high latitude waters like the Chukchi Sea (case 1 avg.; -6.6ng/m^2/day, case 2 avg.; -8.1ng/m^2/day), Bering Sea (-6.2ng/m^2/day, -8.0ng/m^2/day), Gulf of Alaska (-4.7ng/m^2/day, -7.4ng/m^2/day) and the northern North Pacific (-1.4ng/m^2/day, -6.0ng/m^2/day), regardless of the degree of affinity to particle and colloid binding for these contaminants. The greater negative values in Arctic and nearby waters mean the active transfer of CHLs from air to water, which might be suggested by the continuous input through long range atmospheric transport to these regions from mid- and low-latitude areas which seem to be still using CHLs in large quantities.

On the other hand, other regions including mid- and low-latitude regions revealed both of positive and negative values depending on the rate of particle and colloid binding fractions of CHLs (Fig. 3-10). There are two possible scenarios to explain this result. First one designates the case to present in the dissolved state for most of CHLs means volatilization of the organochlorines from the surface waters, which is graphically shown as case 1 in Fig. 3-10. As mentioned earlier, the increasing or continuous usage of CHLs is suggested in tropical and temperate countries. In this case, net fluxes between air and water

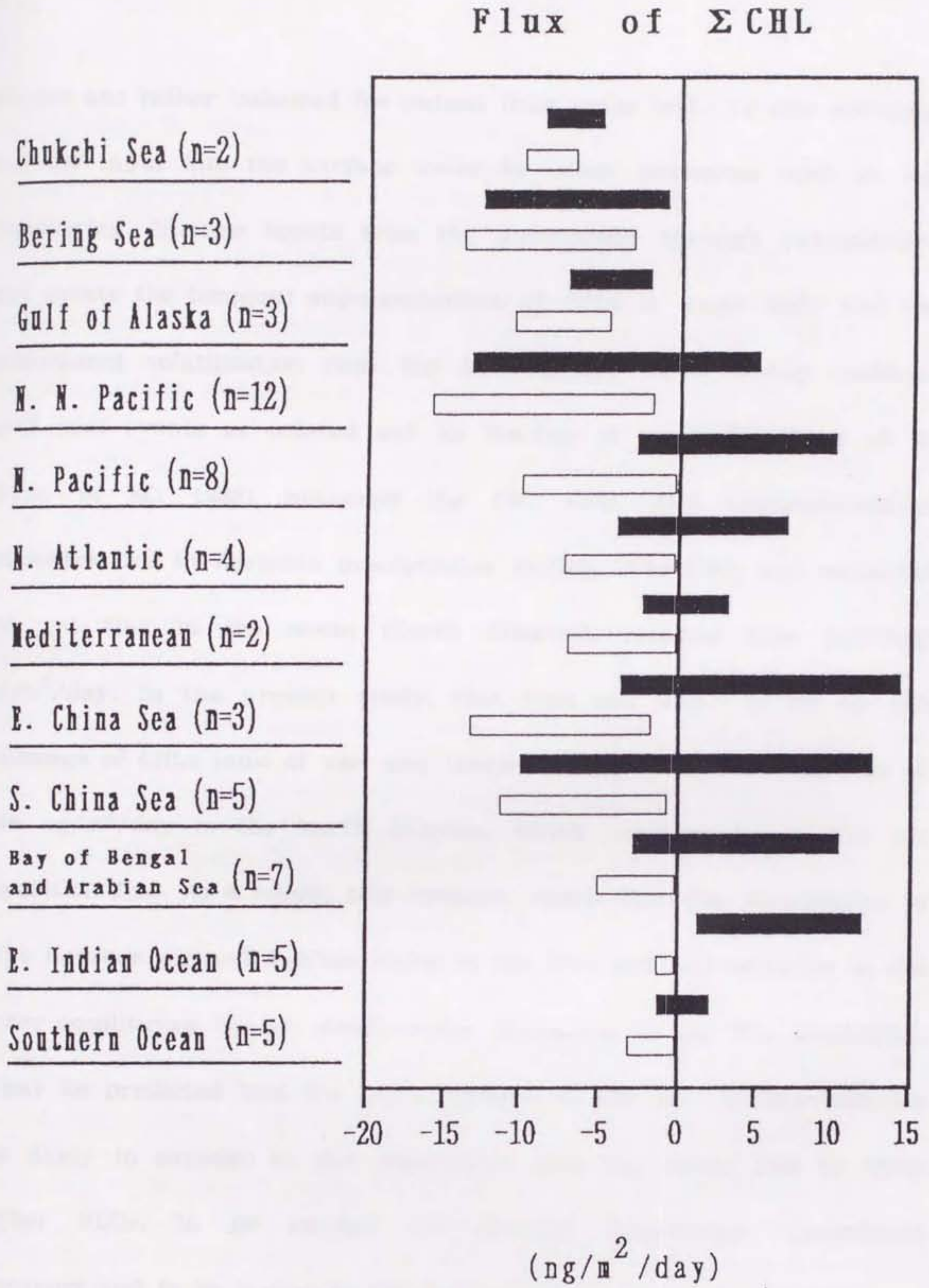


Fig. **3-10. Fluxes by gas exchange of CHLs (*trans*-chlordane, *cis*-chlordane and *trans*-nonachlor) across the air-water interface in various seas and oceans.**
Figures in parentheses are the number of pairings for air and surface water samples.
Length of a bar shows the range of flux.
Solid and open bars represent the flux for case 1 and 2 (see text), respectively.

phases are rather balanced for output from water body by gas exchange and for input into the surface water by other processes such as wet scavenging. Intense inputs from the atmosphere through precipitation may create the temporal supersaturation of CHLs in water body and the subsequent volatilization from the hydrosphere would slowly continue until next events as pointed out by Mackay *et al.* (1986). Knap *et al.* (Knap *et al.*, 1988) measured the CHL (*cis*- and *trans*-chlordane) concentrations in Bermuda precipitation during 1983-1984, and estimated the wet flux in the ocean (North Atlantic), ranging from 0.21-0.32 ng/m^2/day. In the present study, flux from sea water to air by gas exchange of CHLs (sum of *cis*- and *trans*-chlordane) was estimated to be 0.46 ng/m^2/day in the North Atlantic, which corresponds to the wet deposition flux. As a result, this scenario means that the distribution of CHLs between air and surface water in the low- and mid-latitudes is not under equilibrium but in steady-state. According to the flux estimation, it may be predicted that the CHLs released in the low- to mid-latitudes are likely to present in the atmosphere over the ocean due to their higher HLCs, to be carried out through long-range atmospheric transport and to be loaded to the Arctic.

Another scenario derives from the case that a significant mass of the contaminants are present on particles in water bodies (case 2). To some extent, this case may be realized in the Southern Ocean which is characterized by high primary production. It means that the oceanic environment is close to the equilibrium state of the gas exchange process. However, even if the results of laboratory experiment (Gschwend and Wu, 1985) on the adsorption effect of aqueous hydrophobic organochlorines to microparticle are considered, the contribution of microparticle to retain the organochlorines in ocean water seems to be quite small. Cotham and Bidleman (1991) estimated the truly dissolved fraction of organochlorines in the Arctic Ocean using the three-phase (dissolved, macroparticle and microparticle phases) equilibrium partitioning model (Gschwend and Wu, 1985; Baker *et al.*, 1986). The estimated dissolved fraction for α-HCH, γ-HCH, chlordane (not specified) and *p,p'*-DDT were 1.0, 1.0, 0.88 and 0.79, respectively. These results from other authors may imply that the contribution of colloidal and macroparticle phases associated with organochlorines is considerably negligible, as far as it is predicted by using the above model. If the estimation on the partitioning model is realistic, the distribution status for CHLs substantially results in case 1. An ambiguity of the partitioning among those three phases in the natural water is still disputable, if whole ocean surface waters are assumed to be a sink rather than a source of atmospheric organochlorines.

As for PCBs (sum of 36 isomers and congeners), the positive to negative range of fluxes as well as those for CHLs can be seen in lower latitudes and negative ones in higher latitudes (Fig. 3-11). This result

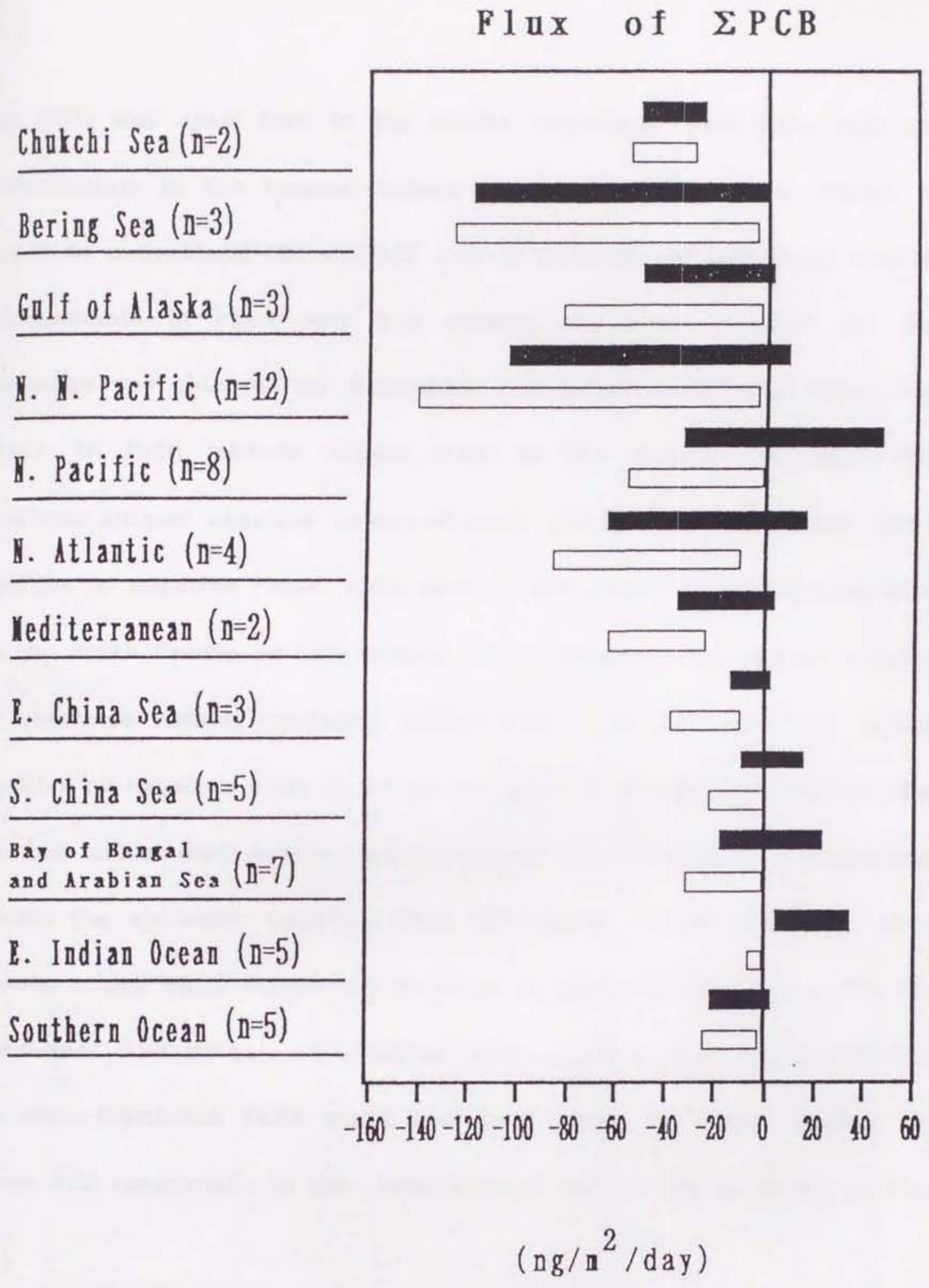


Fig. 3-11. **Fluxes by gas exchange of PCBs across the air-water interface in various seas and oceans.**
Figures in parentheses are the number of pairings for air and surface water samples.
Length of a bar shows the range of flux.
Solid and open bars represent the flux for case 1 and 2 (see text), respectively.

for PCBs may again lead to the similar conclusion with CHLs that the volatilization in the tropical waters and the loading to the Arctic. In order to understand the general rule of behavior of persistent organic contaminants in open seas and oceans, the mass transfer by gas exchange was obtained for individual PCB isomers and congeners (Fig. 3-12). In high latitude oceans such as the Bering Sea, most PCB members showed negative values of mass transfer. On the other hand, positive to negative fluxes were seen in the lower latitude oceans such as the North Pacific. In this regard, PCB congeners with smaller number of chlorines notably revealed higher values of mass transfer, either positive or negative ones. It should be noted from these estimations that the less chlorinated members having higher HLCs are more transferrable across the air-water interface than the higher chlorinated ones. As a result, colder water bodies will serve as a more significant sink for the persistent contaminants with higher HLCs. Such a high exchangeability of less chlorinated PCBs might lead to a result of larger loading for these PCB components in the atmosphere of cold waters as shown in Fig. 3-7.

Gas-exchange model for HCH flux

The above rule obtained for PCB isomers and congeners, might be also explicable for the different ratio of α- and γ-HCH between high and low latitude oceans. It has been less disputed and evaluated whether the different kinetics of both isomers altered the ratio in

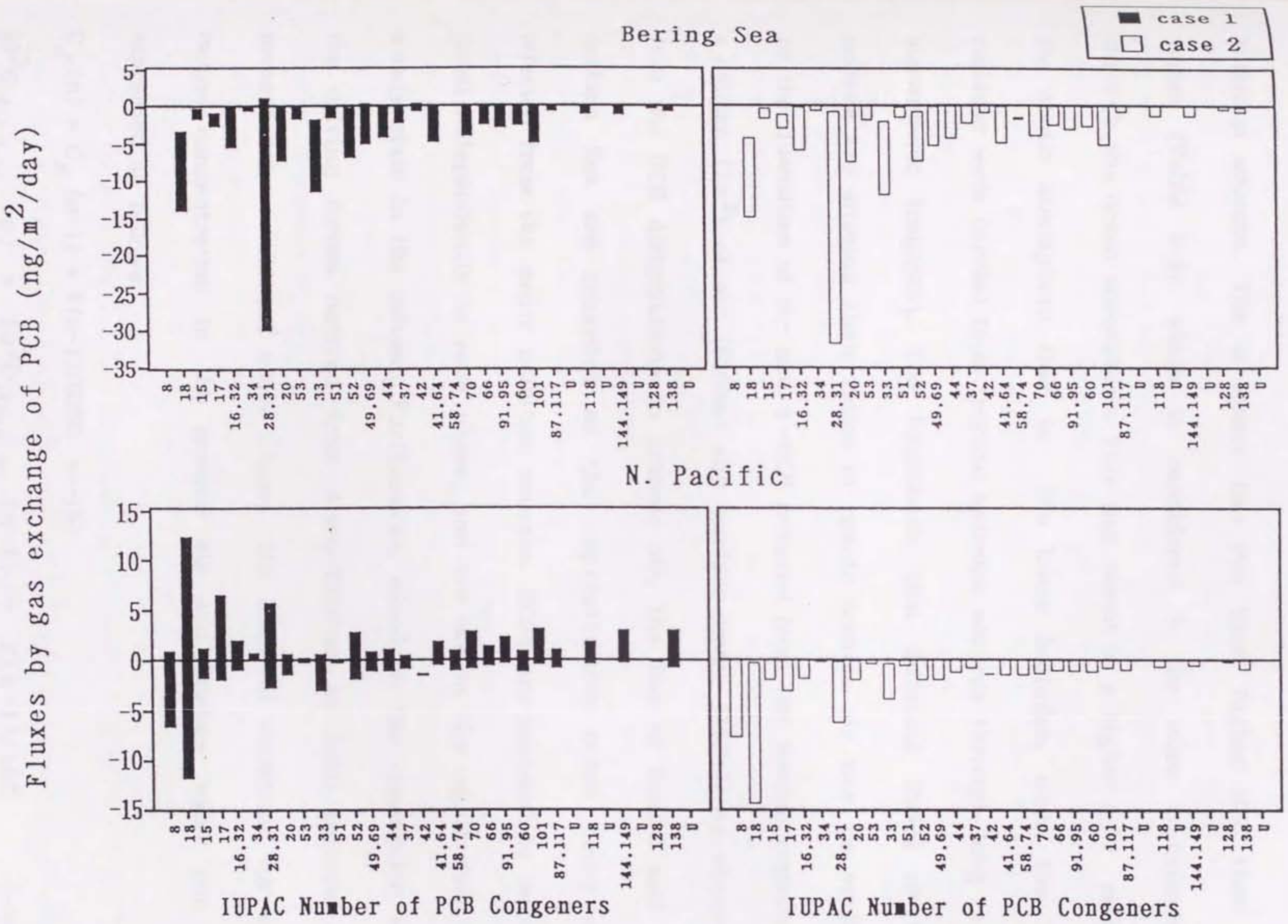


Fig. 3-12. Fluxes by gas exchange of PCB isomer and congeners across the air-water interface in the Bering Sea and the North Pacific.
Solid and open bars represent the flux for case 1 and 2 (see text), respectively.
U means the PCB peaks with no IUPAC number.

oceanic atmosphere. In this context, it would be worthy of notice that higher α/γ ratios were found largely in remote regions far away from pollution sources. The α-isomer has two times higher HLC than γ-isomer (Table 3-4), which is considered to be more transportable through the ocean atmosphere. This may result in a higher α/γ ratio in the Arctic atmosphere than in the lower latitudes, when the HCH residues were carried from tropical emission sources through long-range atmospheric transport. The hypothesis that differing fluxes of HCH isomers are altering their ratios in remote oceanic air may be verified by the quantities of α- and γ-HCH released from the source regions in a column ($1m^2$) of air (6300m) and surface water (100m). As observed from the HCH distributions in oceanic air, the Bay of Bengal and the Arabian Sea are regarded as the representative ocean being still affected from the major pollution sources. HCHs are assumed to be well mixed independently in each phase, and are not in the equilibrium but steady-state in the column. Furthermore, based on the assumption that the driving forces derived from disequilibrium of both isomers are present between air and water phase, the temporal variation for each isomer concentration in the oceanic air and surface water can be expressed as follows:

$$C_g(n) = C_g(n-1) + F(n-1)/6300 \quad ---(6)$$

$$10^3 C_{diss,w}(n) = 10^3 C_{diss,w}(n-1) - F(n-1)/100 \quad ---(7)$$

Using these two equations and equation (1), C_g (n) can be converted into eqn. (8).

$$C_g(n) = a(1-a^{n-1})[C_g(1) - C_g(0)]/(1-a) + C_g(1) \quad ---(8)$$

where $a = 1 - K_{ol}/100 - (K_{ol}/6300) \times RT/H$ and values in the parenthesis means the exposure time after the air collection date. C_g (0) (α-HCH; 5000 pg/m^3, γ-HCH; 1000 pg/m^3) and $C_{diss,w}$ (0) (α-HCH; 500 pg/l, γ-HCH; 100 pg/l) are determined, based on the HCH concentrations in the Arabian Sea and the Bay of Bengal. Temperature (T) at the air-water interface was determined to be 30 °C in these oceans. For the calculation of Kol (see eqns. (2), (3) and (4)), four cases of (3, 5, 7 and 10 m/s) of U10, which seems to be the most influential parameter under the suppositious conditions, were applied. The HLCs at 30°C for HCH isomers calculated by the method mentioned above (see eqn. (5)) were given into eqn. (8). The temporal variations of α/γ ratios for atmospheric concentrations, water concentrations and downward fluxes from air to water estimated under different wind speed are shown in Fig. 3-13.

Possible alteration of HCH isomer compositions

The atmospheric α/γ ratio [C_g (n) for α-HCH / C_g (n) for γ-HCH] converged from 5.0 to 9.9 with an increasing exposure time. In contrast with air, hydrospheric α/γ ratio almost remained constant ($\approx$ 5). Flux ratios of α-isomer to γ-isomer exhibited temporally increasing trend, because of the shorter residence time and the lower concentration of γ-

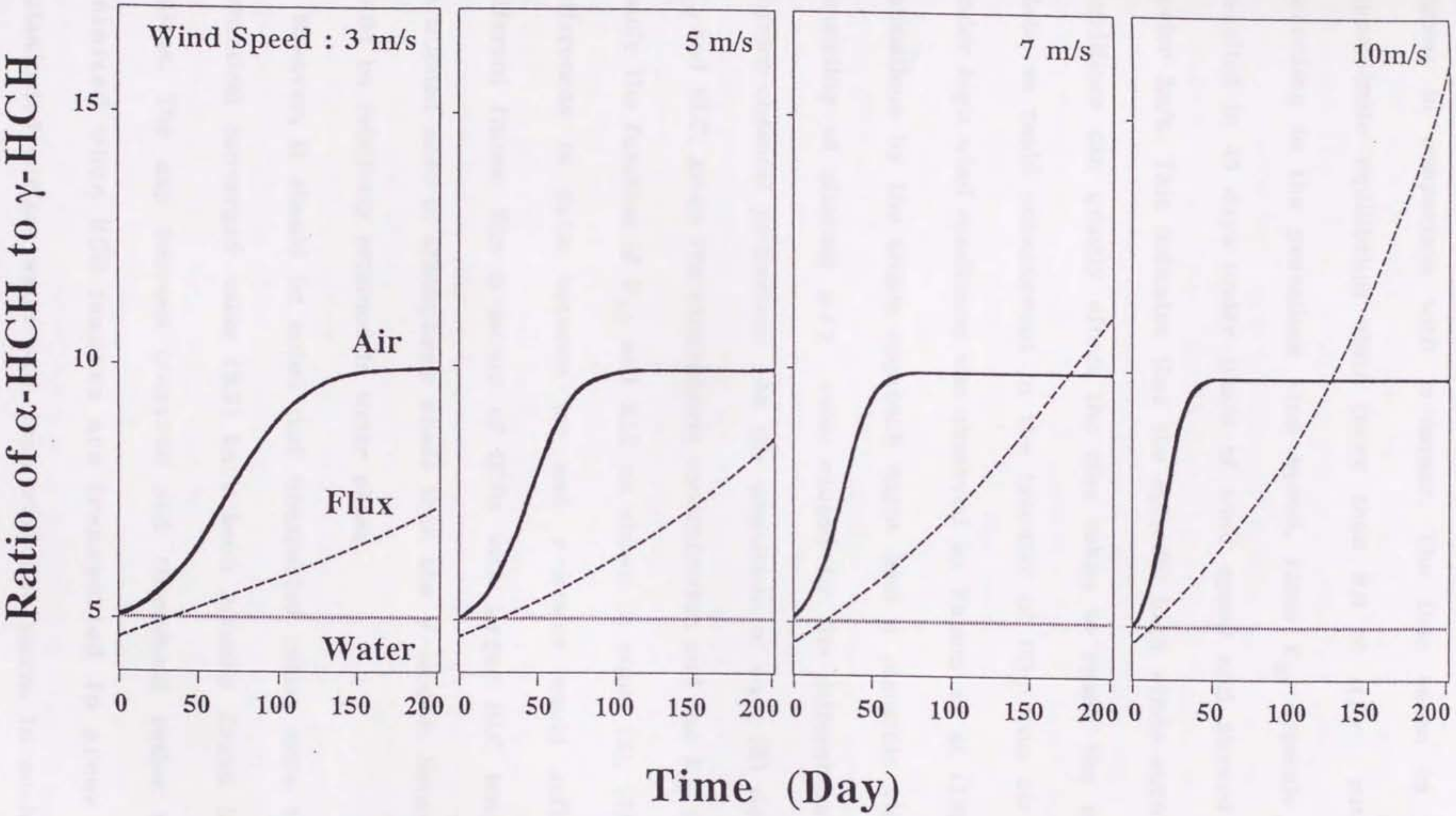


Fig. 3-13. Temporal variations of α / γ ratios for atmospheric concentrations, water concentrations, and downward fluxes from air to water by a gas exchange process estimated under different wind speed. This model based on data from the Bay of Bengal and Arabian Sea. HCHs are assumed to be well mixed independently in the air and surface seawater phases, and not in equilibrium but in a steady-state in the column which consists of air and seawater.

isomer in comparison with α-isomer. The time taken to reach the approximate equilibrium state (more than 9.8 of α/γ ratio) varies according to the prevailing wind speed, since K_{ol} depends on it. It resulted in 45 days under 10m/s of wind speed and showed 153 days under 3m/s. This indicates that the episodic high winds such as storm conditions can greatly affect the time taken to reach the equilibrium state, as rapid enhancement in the transfer of CO_2 from air to water under high wind conditions was observed by Watson *et al.* (1991). These estimations by the simple approach might lead a plausible view to the possibility of altering α/γ ratio caused by the differences in their physico-chemical properties. As the magnitude of eqn. (8) depends on K_{ol} and HLC, given the atmospheric concentration and the K_{ol} is further mainly the function of U_{10} and HLC as shown in eqns. (2), (3) and (4), differences in HLCs between α- and γ-isomer would reflect their different fluxes. The α-isomer of HCHs with larger HLC tends to be partitioned more in atmospheric phase than the γ-isomer. Hence, γ-HCH would be relatively retained in water phase.

However, it should be noted that unexpected ratios more than the theoretical converged value (9.9) have been actually found in remote regions. The gap between observed and theoretical ratios might be minimized when HCH isomers are transported to areas of less contaminated surface water with high wind like storm. In such a case, the theoretical α/γ ratio would be more than 10.

In the case of water phase, the estimated α/γ ratio in surface seawater (Fig. 3-13) is well consistent with the observation in the northern hemisphere where technical mixture of HCHs have been used (Tatsukawa *et al.*, 1990). Interestingly, the α/γ ratios in water phase were predicted to be rather constant, in spite of those larger variations in the atmospheric ratios. This is primarily due to larger load of HCHs in water phase than atmosphere in the column as well as different physico-chemical properties of α- and γ-isomers such as HLC. As a result, diversity of the α/γ ratio has been observed significantly only in oceanic air.

Similar partitioning between air and water might also be expected to the washout process of HCHs. This process is frequently described as the sum of scavenging of particle-bound and gaseous compounds (Ligocki *et al.*, 1985). Since both isomers of HCHs occurring in rain are likely scavenged in the gas phase rather than in the particle-bound phase and the gaseous non-reactive organic compounds attain equilibrium with a falling rain drop, the washout process can be expressed as the function of efficiency for gas phase scavenging (W_g) (Ligocki *et al.*, 1985; Swackhamer and Eisenreich, 1991):

$$W_g = C_{diss,r} / C_g = RT/H \quad \text{---(9)}$$

where $C_{diss,r}$ is the concentration of compound dissolved in rain. As the parameters for the scavenging are thus identical to those for gas exchange between air and surface seawater, and furthermore the precipitation for absorbing the organic contaminants may accelerate the transfer of γ-isomer to water phase, the time interval closing with the equilibrium state would be shorter according to the precipitation frequency and intensity.

As shown in Fig. 3-8, atmospheric concentrations for HCHs were higher than the equilibrium concentrations estimated from the surface water concentrations in almost all seas and oceans, suggesting a continuous downward flux from air to water during the atmospheric transport of HCHs. This indicates that the variable ratios of α/γ could be predicted not only in the Arabian Sea and the Bay of Bengal but also in other oceans. Nevertheless this discussion does not ignore the possibility of photoisomerization altering the α/γ ratio, it means that isomers with different HLCs may exhibit isomer-specific fluxes by gas exchange across air-water interface and ultimately result in divergent α/γ ratios in oceanic air.

If the higher α/γ ratios in remote oceanic atmosphere are explained by the preferential transport of α-isomer from emission sources, the similar rule is also applicable for higher ratios of *p,p'*-DDE to *p,p'*-DDT and *trans*-nonachlor to *trans*-chlordane in remote oceans (Fig. 3-6 and Table 3-3). In this regard, it should be noted that the ratios of HLCs of *p,p'*-DDE to *p,p'*-DDT and *trans*-nonachlor to *trans*-chlordane are 9.6

(8.0/0.83) and 2.9 (32/11), respectively (Table 3-4).

Magnitude of flux for organochlorines by gas exchange depends on K_{ol}, given the disequilibrium between air and surface water concentrations. Although K_{ol} is the function of U_{10}, S_{cg} , S_{cl} , T and H as shown in eqns. (2, 3 and 4), the most influential factor under possible suppositious conditions seems to be U_{10}. For example, while K_{ol} s under still air condition for PCB isomers and congeners range within only a factor of 1.5-3.0 with an increasing of T from 0°C to 30°C, these values at 10m/s are approximately 35 times greater than those at 0m/s. This indicates that episodic high winds such as storm conditions greatly affect the flux of organochlorines by gas exchange across the air-seawater interface, as rapid enhancement of transfer velocity for CO_2 gas in high wind conditions was experimentally demonstrated by the application of tracer techniques (Watson *et al.*, 1991).

Uncertainities in the magnitude of the HLCs for some organochlorines still remain a possibility to change the direction of the air-water gas exchange. Application of the higher HLCs for *p,p'*-DDE, *trans*-chlordane and *cis*-chlordane offered by Atlas *et al.* (1982) (Table 3-4) make the flux estimation plus values in the whole seas and oceans which mean the supersaturation of these contaminants in the water phase and the evaporation from water to air. In that case, atmospheric concentration over ocean will be controlled by the concentrations in the underlying surface waters and hence atmosphere probably results in a sink of such contaminants. Further efforts to determine the accurate HLCs and the truly dissolved fraction in natural water phase are necessary to understand the behavior of organochlorines and the role of ocean in the global scale.

Considering all these facts, it can be summarized that the distribution and behavior of persistent organochlorines are variable according to the seas and oceans, and such patterns would be controlled principally by the physico-chemical properties of contaminants and the meteorological conditions in nearby emission sources and non-point source areas. Moreover, the role of oceans in determining the fate of contaminants depends on the latitudinal degree such that the high latitude waters are likely to serve as a major sink.

Conclusions

In order to understand the present distribution, long-range atmospheric transport and global fate of hazardous man-made chemicals, persistent organochlorines such as HCHs, DDTs, CHLs and PCBs were determined in the air and surface water in various seas and oceans from 1989 to 1990.

In the atmospheric samples, the concentrations of these contaminants were found to be higher in the northern hemisphere than in the southern one. In the northern hemisphere, higher residue levels of HCHs and DDTs were observed in the tropical Asia. In contrast to these patterns, distributions of CHLs and PCBs were relatively uniform, suggesting that the usage of these chemicals is likely to be expanding to the tropical countries.

In the surface water samples, these contaminants revealed a specific pattern with respect to each chemical. HCH residues showed a considerable contamination over 40° N latitude in the North Pacific. Higher concentrations of DDT residues were found in seas and oceans nearby tropical Asia. CHLs and PCBs revealed rather an uniform distribution on the global terms.

As for the composition of organochlorine residues, higher ratios of α- to γ-HCH, *p,p'*-DDE to *p,p'*-DDT, *trans*-nonachlor to *trans*-chlordane and lower to higher chlorinated PCBs were found in remote oceans, suggesting the preferable atmospheric transport for the former chemicals with higher HLCs.

According to the approach using mass transfer of contaminants between air and water, it has been suggested that HCHs and DDTs having lower HLCs are less transportable through ocean atmosphere and promptly absorbed in the water bodies nearby emission source. While, the chemicals with higher HLCs such as CHLs and PCBs are likely to disperse to remote oceans through oceanic atmosphere.

Considering the present global distributions of organochlorines and the role of ocean on their transport and fate, the behavior of such chemicals released in the lower latitudes would be controlled by their physico-chemical properties and the meteorological conditions, and more transportable compounds of them may be loaded to the Arctic and the adjacent water bodies.

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Appendix.

Table 3-5. Details of air samples from various seas and oceans.

Sample No.	Sampling Date	Location			Sample Volume(m^3)
		Start	End		
K-1a	1989 Apr.25-27	29° 54'N 130° 33'E	22° 19'N 124° 18'E	East China Sea	92.2
K-2a	1989 Apr.28-30	19° 03'N 120° 35'E	12° 21'N 113° 21'E	South China Sea	92.2
K-3a	1989 May 01-03	10° 14'N 111° 25'E	02° 56'N 108° 22'E	South China Sea	92.2
K-5a	1989 May 12-14	05° 58'N 095° 04'E	00° 30'N 091° 06'E	Bay of Bengal and Arabian Sea	93.8
K-6a	1989 May 17-19	02° 09'S 091° 09'E	04° 29'N 091° 22'E	Bay of Bengal and Arabian Sea	92.2
K-7a	1989 May 29-31	06° 05'N 095° 37'E	03° 02'N 101° 22'E	Str. of Malacca	88.3
K-8a	1989 Jun.06-08	02° 44'N 107° 49'E	05° 49'N 114° 54'E	South China Sea	92.2
K-10a	1989 Jun.17-19	07° 32'N 116° 09'E	16° 34'N 119° 25'E	South China Sea	92.2
K-11a	1989 Jun.21-23	24° 26'N 123° 41'E	31° 10'N 130° 42'E	East China Sea	92.2
S-1a	1989 Jun.02-04	40° 38'N 145° 41'E	42° 30'N 158° 04'E	Northern North Pacific	109
S-2a	1989 Jun.04-06	42° 30'N 158° 04'E	43° 37'N 167° 28'E	Northern North Pacific	109
S-3a	1989 Jun.06-08	43° 37'N 167° 28'E	45° 24'N 177° 59'E	Northern North Pacific	105
S-4a	1989 Jun.09-11	45° 31'N 179° 50'E	45° 32'N 176° 04'W	Northern North Pacific	104
S-5a	1989 Jul.06-08	45° 25'N 179° 26'W	48° 49'N 169° 59'E	Northern North Pacific	104
S-6a	1989 Jul.10-12	49° 42'N 164° 39'E	49° 53'N 164° 31'E	Northern North Pacific	104
S-7a	1989 Jul.15-17	45° 00'N 169° 00'E	43° 44'N 157° 18'E	Northern North Pacific	104
S-8a	1989 Jul.17-19	43° 44'N 157° 18'E	40° 17'N 147° 47'E	Northern North Pacific	107
D-1a	1989 Nov.12-14	27° 19'N 135° 57'E	19° 40'N 132° 28'E	North Pacific	107
D-2a	1989 Nov.14-16	19° 40'N 132° 28'E	11° 37'N 128° 53'E	North Pacific	105
D-3a	1989 Nov.16-18	11° 37'N 128° 53'E	03° 58'N 124° 02'E	North Pacific	107
D-4a	1989 Nov.18-20	03° 58'N 124° 02'E	01° 57'S 118° 49'E	Celebes Sea	106
D-5a	1989 Nov.20-22	01° 57'S 118° 49'E	09° 36'S 115° 29'E	Java Sea	109
D-6a	1989 Nov.22-24	09° 36'S 115° 29'E	16° 15'S 113° 16'E	Eastern Indian Ocean	107
D-7a	1989 Nov.24-26	16° 15'S 113° 16'E	23° 00'S 110° 56'E	Eastern Indian Ocean	105
D-8a	1989 Nov.26-28	23° 00'S 110° 56'E	30° 25'S 108° 14'E	Eastern Indian Ocean	111
D-9a	1989 Nov.28-30	30° 25'S 108° 14'E	36° 33'S 105° 47'E	Eastern Indian Ocean	105
D-10a	1989 Nov.30-Dec.02	36° 33'S 105° 47'E	44° 10'S 102° 35'E	Eastern Indian Ocean	107
D-11a	1989 Dec.02-04	44° 10'S 102° 35'E	49° 41'S 099° 55'E	Southern Ocean	100
D-12a	1989 Dec.04-06	49° 41'S 099° 55'E	54° 41'S 097° 10'E	Southern Ocean	103
D-13a	1989 Dec.06-08	54° 41'S 097° 10'E	60° 02'S 097° 15'E	Southern Ocean	104
D-14a	1989 Dec.08-10	60° 02'S 097° 15'E	61° 47'S 095° 28'E	Southern Ocean	104
D-15a	1990 Mar.01-03	64° 08'S 122° 53'E	62° 08'S 117° 36'E	Southern Ocean	101

Table 3-5. To be continued.

H-1a	1989 Oct.31-Nov.02	32° 03'N 140° 02'E	32° 12'N 154° 04'E	North Pacific	107
H-3a	1989 Nov.09-Nov.10	27° 02'N 179° 22'W	27° 00'N 165° 20'W	North Pacific	108
H-5a	1989 Nov.12-14	27° 41'N 150° 59'W	29° 52'N 136° 25'W	North Pacific	106
H-8a	1989 Nov.23-25	26° 58'N 115° 43'W	20° 58'N 113° 57'W	North Pacific	107
H-10a	1989 Nov.30-Dec.02	09° 56'N 095° 01'W	07° 10'N 082° 01'W	North Pacific	107
H-11a	1989 Dec.04-06	13° 07'N 079° 27'W	18° 23'N 079° 39'W	Caribbean Sea	107
H-12a	1989 Dec.06-08	18° 24'N 079° 40'W	24° 22'N 083° 16'W	Gulf of Mexico	106
H-14a	1989 Dec.14-16	25° 38'N 074° 12'W	25° 01'N 060° 26'W	North Atlantic	107
H-15a	1989 Dec.17-19	25° 14'N 057° 53'W	26° 45'N 046° 57'W	North Atlantic	107
H-16a	1989 Dec.22-24	28° 35'N 036° 26'W	32° 03'N 023° 24'W	North Atlantic	107
H-17a	1989 Dec.25-26	33° 25'N 018° 30'W	36° 03'N 012° 40'W	North Atlantic	63.7
H-19a	1990 Jan.04-07	38° 46'N 004° 25'E	43° 40'N 007° 20'E	Mediterranean Sea	142
H-21a	1990 Jan.14-16	35° 05'N 022° 30'E	31° 49'N 031° 52'E	Mediterranean Sea	95.1
H-22a	1990 Jan.18-20	25° 38'N 035° 32'E	14° 20'N 042° 38'E	Red Sea	107
H-23a	1990 Jan.22-24	13° 19'N 053° 08'E	15° 01'N 060° 04'E	Bay of Bengal and Arabian Sea	107
H-24a	1990 Jan.26-27	15° 10'N 067° 19'E	15° 20'N 073° 29'E	Bay of Bengal and Arabian Sea	26.1
H-26a	1990 Feb.01-03	10° 43'N 073° 04'E	00° 27'N 079° 43'E	Bay of Bengal and Arabian Sea	107
H-27a	1990 Feb.03-05	00° 01'N 079° 59'E	06° 26'N 082° 09'E	Bay of Bengal and Arabian Sea	107
H-28a	1990 Feb.07-09	15° 03'N 085° 08'E	13° 06'N 090° 40'E	Bay of Bengal and Arabian Sea	107
H-30a	1990 Feb.22-24	*	20° 15'N 119° 43'E	South China Sea	107
H-31a	1990 Feb.27-Mar.01	29° 16'N 127° 52'E	29° 00'N 129° 49'E	East China Sea	107
H-32a	1990 Mar.02-03	28° 48'N 135° 01'E	32° 11'N 137° 35'E	North Pacific	53.4
0-1a	1990 Jun.05-07	39° 42'N 151° 51'E	38° 36'N 164° 20'E	Northern North Pacific	103
0-2a	1990 Jun.09-10	36° 59'N 179° 28'E	39° 03'N 179° 59'W	Northern North Pacific	109
0-3a	1990 Jun.14-16	42° 11'N 179° 55'W	46° 49'N 179° 60'W	Northern North Pacific	107
0-4a	1990 Jun.16-18	46° 52'N 179° 60'W	50° 48'N 179° 48'W	Northern North Pacific	104
0-6a	1990 Jun.22-24	55° 18'N 165° 38'W	55° 60'N 166° 00'W	Bering Sea	99.4
0-8a	1990 Jun.30-Jul.02	51° 07'N 160° 06'W	51° 52'N 155° 57'W	Gulf of Alaska	101
0-10a	1990 Jul.05-07	53° 07'N 151° 56'W	54° 35'N 147° 38'W	Gulf of Alaska	105
0-11a	1990 Jul.07-08	54° 35'N 147° 38'W	56° 21'N 144° 30'W	Gulf of Alaska	106
0-13a	1990 Jul.12-14	54° 01'N 140° 24'W	56° 08'N 143° 52'W	Gulf of Alaska	103
0-15a	1990 Jul.22-24	54° 19'N 164° 53'W	62° 33'N 169° 55'W	Bering Sea	97.9
0-17a	1990 Jul.24-26	62° 33'N 169° 55'W	62° 50'N 172° 60'W	Bering Sea	102
0-19a	1990 Jul.27-28	63° 50'N 172° 04'W	65° 47'N 168° 28'W	Bering Sea	90.1
0-21a	1990 Jul.28-30	65° 47'N 168° 28'W	68° 29'N 167° 07'W	Chukchi Sea	101
0-24a	1990 Jul.30-Aug.01	68° 28'N 167° 07'W	65° 50'N 168° 30'W	Chukchi Sea	93.7
0-28a	1990 Aug.01-03	64° 58'N 168° 28'W	54° 49'N 166° 45'W	Bering Sea	97.9
0-32a	1990 Aug.12-14	47° 16'N 172° 44'E	45° 25'N 161° 32'E	Northern North Pacific	104
0-33a	1990 Aug.14-16	45° 25'N 161° 32'E	43° 03'N 147° 43'E	Northern North Pacific	107

* Exact location was not recorded after the departure from Singapore.

Appendix.

Table 3-6. Details of surface seawater samples from various seas and oceans.

Sample No.	Sampling Date	Location		Sample Volume(l)
K-1w	1989 Apr.26-27	27° 33'N 129° 07'E	East China Sea	300
K-2w	1989 Apr.29-30	16° 58'N 118° 30'E	South China Sea	300
K-3w	1989 May 01	10° 18'N 111° 29'E	South China Sea	300
K-4w	1989 May 14-15	00° 48'N 091° 10'E	Bay of Bengal and Arabian Sea	300
K-8w	1989 May 18	03° 29'S 091° 12'E	Bay of Bengal and Arabian Sea	300
K-9w	1989 May 30	05° 08'N 098° 26'E	Str. of Malacca	300
K-10w	1989 Jun.07	04° 44'N 113° 20'E	South China Sea	300
K-11w	1989 Jun.18	10° 03'N 117° 48'E	South China Sea	300
K-12w	1989 Jun.20	19° 16'N 120° 35'E	South China Sea	300
K-13w	1989 Jun.22	27° 14'N 126° 48 E	East China Sea	300
S-1w	1989 Jun.03	41° 40'N 151° 52'E	Northern North Pacific	200
S-2w	1989 Jun.05	43° 30'N 163° 19'E	Northern North Pacific	200
S-3w	1989 Jun.10	45° 30'N 177° 27'E	Northern North Pacific	200
S-4w	1989 Jul.07	45° 56'N 176° 33'E	Northern North Pacific	200
S-5w	1989 Jul.11	49° 47'N 163° 12'E	Northern North Pacific	200
S-6w	1989 Jul.16	44° 58'N 162° 45'E	Northern North Pacific	200
D-1w	1989 Nov.12	27° 19'N 135° 57'E	North Pacific	180
D-2w	1989 Nov.14	19° 40'N 132° 28'E	North Pacific	150
D-4w	1989 Nov.18	03° 58'N 124° 02'E	Celebes Sea	200
D-5w	1989 Nov.20	01° 57'S 118° 49'E	Java Sea	200
D-6w	1989 Nov.22	09° 36'S 115° 29'E	Eastern Indian Ocean	200
D-7w	1989 Nov.24	16° 15'S 113° 16'E	Eastern Indian Ocean	200
D-8w	1989 Nov.26	23° 00'S 110° 56'E	Eastern Indian Ocean	200
D-9w	1989 Nov.28	30° 25'S 108° 14'E	Eastern Indian Ocean	200
D-10w	1989 Nov.30	36° 33'S 105° 47'E	Eastern Indian Ocean	200
D-11w	1989 Dec.02	44° 10'S 102° 35'E	Southern Ocean	200
D-12w	1989 Dec.04	49° 41'S 099° 55'E	Southern Ocean	200
D-13w	1989 Dec.07	56° 54'S 097° 10'E	Southern Ocean	200
D-14w	1989 Dec.09	61° 28'S 099° 28'E	Southern Ocean	200
D-15w	1990 Mar.02	64° 39'S 121° 47'E	Southern Ocean	180

Table 3-6. To be continued.

H-1w	1989 Nov.02	32° 10'N	150° 28'E	North Pacific	400
H-2w	1989 Nov.09	27° 01'N	178° 41'W	North Pacific	400
H-3w	1989 Nov.12	27° 50'N	150° 09'W	North Pacific	400
H-4w	1989 Nov.25	21° 02'N	113° 58'W	North Pacific	400
H-5w	1989 Dec.01	08° 45'N	089° 16'W	North Pacific	400
H-6w	1989 Dec.05	18° 08'N	079° 00'W	Caribbean Sea	400
H-7w	1989 Dec.07	21° 06'N	084° 16'W	Gulf of Mexico	400
H-8w	1989 Dec.14	25° 30'N	071° 14'W	North Atlantic	400
H-9w	1989 Dec.18	25° 52'N	052° 17'W	North Atlantic	400
H-10w	1989 Dec.23	30° 16'N	029° 59'W	North Atlantic	400
H-11w	1989 Dec.25	33° 46'N	017° 00'W	North Atlantic	400
H-12w	1990 Jan.05	39° 06'N	005° 05'E	Mediterranean Sea	400
H-13w	1990 Jan.14	35° 00'N	022° 44'E	Mediterranean Sea	400
H-14w	1990 Jan.19	19° 42'N	039° 10'E	Red Sea	400
H-15w	1990 Jan.23	13° 46'N	057° 28'E	Bay of Bengal and Arabian Sea	400
H-16w	1990 Jan.26	15° 10'N	067° 36'E	Bay of Bengal and Arabian Sea	400
H-17w	1990 Feb.01	08° 39'N	074° 24'E	Bay of Bengal and Arabian Sea	400
H-18w	1990 Feb.03	00° 01'N	079° 59'E	Bay of Bengal and Arabian Sea	400
H-19W	1990 Feb.08	15° 02'N	089° 59'E	Bay of Bengal and Arabian Sea	400
H-20W	1990 Feb.22	15° 06'N	115° 06'E	South China Sea	400
H-21W	1990 Mar.01	29° 10'N	129° 00'E	East China Sea	400
H-22W	1990 Mar.02	28° 49'N	135° 05'E	North Pacific	400
0-1W	1990 Jun.05	39° 40'N	152° 10'E	Northern North Pacific	400
0-2W	1990 Jun.09	36° 52'N	179° 38'W	Northern North Pacific	400
0-3W	1990 Jun.14	43° 16'N	179° 60'W	Northern North Pacific	400
0-4W	1990 Jun.18	50° 48'N	179° 60'W	Northern North Pacific	400
0-5W	1990 Jun.22	55° 26'N	165° 18'W	Bering Sea	400
0-6W	1990 Jun.30	51° 07'N	160° 06'W	Gulf of Alaska	400
0-7W	1990 Jul.04	53° 03'N	152° 00'W	Gulf of Alaska	400
0-9W	1990 Jul.13	53° 09'N	139° 45'W	Gulf of Alaska	400
0-10W	1990 Jul.24	62° 41'N	169° 31'W	Bering Sea	400
0-11W	1990 Jul.29	68° 10'N	168° 37'W	Chukchi Sea	400
0-12W	1990 Jul.30	68° 59'N	168° 39'W	Chukchi Sea	400
0-13W	1990 Jul.31	67° 20'N	168° 37'W	Chukchi Sea	400
0-15W	1990 Aug.01	65° 11'N	168° 29'W	Bering Sea	400
0-16W	1990 Aug.03	56° 42'N	167° 17'W	Bering Sea	400
0-18W	1990 Aug.12	46° 38'N	171° 03'E	Northern North Pacific	400
0-19W	1990 Aug.14	45° 10'N	159° 37'E	Northern North Pacific	400

Appendix.
Table 3-7. Fluxes by gas exchange of organochlorines across the air-water interface in various seas and oceans (ng/m²/day).

Sampling Location	α-HCH	γ-HCH	ΣHCHs	*t*-Chlor.	*c*-Chlor.	*t*-Nona.	ΣCHLs	*p,p'*-DDE	*p,p'*-DDT	ΣDDTs	ΣPCBs
Chukchi Sea											
n	2	2	2	2	2	2	2	2	2	2	2
case 1 mean	-47	-8.6	-56	-2.3	-2.7	-1.6	-6.6	-0.25	-2.9	-3.2	-37
range	-54～-41	-9.1～-8.1	-62～-50	-3.1～-1.5	-3.2～-2.1	-2.0～-1.3	-8.3～-4.9	-0.37～-0.13	-3.8～-2.1	-4.2～-2.2	-50～-25
case 2 mean	-170	-18	-190	-2.7	-3.3	-2.1	-8.1	-0.29	-2.9	-3.2	-41
range	-190～-150	-19～-17	-210～-170	-3.4～-2.0	-3.8～-2.8	-2.5～-1.7	-9.7～-6.6	-0.42～-0.17	-3.8～-2.1	-4.2～-2.2	-53～-30
Bering Sea											
n	3	3	3	3	3	3	3	3	3	3	3
case 1 mean	-57	-17	-73	-2.0	-2.9	-1.3	-6.2	-0.07	-1.7	-1.8	-53
range	-140～6.8	-32～-5.8	-150～1.1	-4.2～-0.04	-5.3～-0.86	-2.8～0.32	-12～-0.57	-0.95～1.0	-2.5～-0.29	-3.4～0.73	-120～1.3
case 2 mean	-190	-26	-220	-2.6	-3.5	-1.8	-8.0	-0.50	-1.7	-2.2	-59
range	-250～-120	-43～-15	-270～-130	-4.7～-1.0	-5.8～-1.6	-3.2～-0.17	-14～-2.8	-1.0～-0.15	-2.5～-0.30	-3.5～-0.45	-130～-4.3
Gulf of Alaska											
n	3	3	3	3	3	3	3	3	3	3	3
case 1 mean	-29	-16	-45	-2.5	-2.3	0.01	-4.7	-0.16	-0.58	-0.74	-17
range	-47～-6.8	-25～-8.9	-73～-16	-4.4～-0.89	-3.1～-1.6	-0.35～0.61	-6.8～-1.9	-0.34～-0.05	-1.1～-0.04	-1.2～-0.10	-49～2.7
case 2 mean	-170	-28	-190	-3.4	-3.4	-0.54	-7.4	-0.24	-0.63	-0.88	-33
range	-200～-140	-37～-23	-240～-160	-5.5～-1.8	-4.1～-2.3	-0.73～-0.17	-10～-4.3	-0.44～-0.11	-1.1～-0.12	-1.3～-0.23	-82～-2.9
N. N. Pacific											
n	12	12	12	12	12	12	12	12	9	12	12
case 1 mean	-130	-27	-150	-0.99	-1.1	0.64	-1.4	-0.76	-2.1	-2.3	-10
range	-330～21	-62～1.8	-370～23	-6.2～2.2	-5.0～1.2	-1.8～2.9	-13～5.2	-3.6～1.1	-12～-0.01	-14～1.1	-100～8.5
case 2 mean	-200	-35	-240	-2.6	-2.8	-0.63	-6.0	-1.2	-2.2	-2.8	-21
range	-420～-9.7	-73～-2.8	-470～-13	-7.3～-0.44	-5.8～-0.90	-2.5～-0.08	-16～-1.5	-4.1～-0.10	-12～-0.15	-14～-0.31	-140～-3.3
N. Pacific											
n	8	8	8	8	8	8	8	8	8	8	8
case 1 mean	-49	-13	-62	1.4	0.53	1.1	3.0	0.01	-1.1	-1.1	2.9
range	-210～40	-45～-0.08	-250～40	-1.1～7.6	-2.2～3.1	0.07～2.4	-2.2～10	-0.37～0.40	-3.7～-0.18	-4.0～0.23	-32～47
case 2 mean	-71	-16	-86	-1.3	-1.4	-0.28	-3.0	-0.30	-1.2	-1.5	-17
range	-220～-11	-45～-3.7	-260～-16	-4.3～0.0	-4.5～0.0	-0.80～0.0	-9.6～0.0	-0.66～-0.06	-3.8～-0.33	-4.3～-0.39	-54～-1.3
N. Atlantic											
n	4	4	4	4	4	4	4	4	4	4	4
case 1 mean	-69	-27	-96	0.62	-0.18	0.65	1.1	-0.42	-1.6	-2.0	-14
range	-130～-21	-52～-4.5	-180～-26	-1.9～3.8	-1.7～1.8	-0.70～1.6	-3.4～7.1	-1.1～0.0	-3.9～-0.42	-5.0～0.42	-62～17
case 2 mean	-82	-28	-110	-1.7	-1.5	-0.49	-3.6	-0.77	-1.6	-2.3	-40
range	-130～-36	-52～-6.1	-190～-43	-3.5～0.0	-2.8～0.0	-1.7～0.0	-6.9～0.0	-1.4～-0.30	-3.9～-0.45	-5.4～-0.75	-83～-10

Table 3-7. To be continued.

Mediterranean											
n	2	2	2	2	2	2	2	2	2	2	2
case 1 mean	-43	-24	-67	-0.03	-0.28	1.0	0.72	-1.4	-1.6	-3.0	-15
range	-63~-23	-38~-9.4	-72~-61	-1.7~1.6	-1.4~0.85	0.96~1.1	-2.0~3.4	-2.0~-0.87	-2.1~-1.1	-4.1~-1.9	-33~4.3
case 2 mean	-63	-32	-95	-1.8	-1.4	-0.23	-3.4	-2.3	-1.7	-4.0	-42
range	-84~-42	-47~-18	-100~-88	-3.5~0.0	-2.7~0.0	-0.45~0.0	-6.7~0.0	-2.7~-1.9	-2.2~-1.2	-4.9~-3.1	-61~-23
East China Sea											
n	1	1	1	3	3	3	3	3	3	3	3
case 1 mean	-210	-52	-260	1.5	1.0	1.9	4.4	1.4	-1.8	-0.39	-1.9
range	-	-	-	-1.4~5.1	-1.4~4.3	-0.44~5.1	-3.2~14	-1.4~5.9	-5.8~2.0	-7.2~7.9	-12~3.4
case 2 mean	-220	-52	-270	-2.6	-3.0	-0.85	-6.4	-0.83	-2.8	-3.7	-21
range	-	-	-	-5.3~0.63	-5.9~-0.74	-1.8~-0.15	-13~-1.5	-1.8~-0.02	-6.2~-0.63	-8.1~-0.65	-36~-8.9
South China Sea											
n	1	1	1	5	5	5	5	5	5	5	5
case 1 mean	-210	-140	-350	0.88	1.9	1.7	4.4	-2.2	-5.6	-7.9	5.3
range	-	-	-	-5.7~5.1	-4.0~4.3	-0.01~3.2	-9.6~13	-11~0.81	-19~0.53	-30~1.3	-7.6~17
case 2 mean	-220	-140	-360	-1.8	-1.5	-0.26	-3.6	-2.9	-6.2	-9.1	-6.6
range	-	-	-	-6.1~-0.21	-4.3~-0.30	-0.66~-0.04	-11~-0.55	-12~-0.28	-19~-0.87	-31~-1.2	-20~-0.75
Bay of Bengal and Arabian Sea											
n	5	5	5	7	7	7	7	7	7	7	7
case 1 mean	-2200	-310	-2500	1.8	1.5	1.1	4.4	-0.67	-32	-33	4.3
range	-7600~-140	-980~-32	-8600~-180	-1.5~5.0	-1.2~4.8	0.22~2.5	-2.5~11	-3.1~0.53	-140~-4.0	-140~-3.4	-17~24
case 2 mean	-2300	-310	-2600	-1.0	-0.83	-0.14	-2.0	-1.6	-33	-35	-11
range	-7700~-150	-990~-34	-8700~-190	-2.6~0.0	-2.0~0.0	-0.26~0.0	-4.7~0.0	-3.4~-0.17	-140~-4.5	-140~-4.6	-30~-0.83
E. Indian Ocean											
n	5	5	5	5	5	5	5	5	5	5	5
case 1 mean	-2.2	-5.2	-7.5	3.0	1.3	1.1	5.5	0.11	-0.35	-0.24	13
range	-10~2.7	-7.9~-1.9	-18~-1.6	-0.54~9.2	0.72~1.6	0.77~1.4	1.7~12	-0.80~0.56	-0.46~-0.12	-1.2~0.23	6.2~35
case 2 mean	-9.6	-6.3	-16	-0.16	-0.12	-0.04	-0.32	-0.43	-0.48	-0.91	-1.7
range	-22~-4.5	-9.9~-2.7	-32~-7.5	-0.54~-0.01	-0.31~-0.02	-0.07~0.0	-0.92~-0.02	-1.3~-0.01	-0.92~-0.19	-1.8~-0.22	-4.7~-0.50
Southern Ocean											
n	5	5	5	5	5	5	5	5	5	5	5
case 1 mean	-11	-6.1	-17	0.43	0.28	0.49	1.2	0.11	-0.63	-0.52	-2.7
range	-20~-0.98	-8.7~-3.1	-29~-4.1	-0.64~1.0	-0.31~0.72	0.06~1.0	-0.89~2.3	-0.01~0.24	-0.96~-0.38	-0.97~-0.24	-19~3.4
case 2 mean	-13	-6.4	-20	-0.44	-0.27	-0.24	-0.96	-0.10	-0.65	-0.75	-9.0
range	-22~-2.9	-9.0~-3.4	-31~-6.4	-1.2~0.0	-0.69~-0.0	-0.71~0.0	-2.6~-0.0	-0.13~-0.07	-0.97~-0.40	-1.1~-0.52	-23~-1.7

t-Chlor.: *trans*-chlordane   *c*-Chlor.: *cis*-chlordane   *t*-Nona.: *trans*-nonachlor
n: Number of samples.
case 1 and case 2: See text.

4 Fate and Temporal Trend in the Ocean

Abstract

Three surface sediments and two sediment cores were collected from the Gulf of Alaska, Bering Sea and Chukchi Sea, and analysed for persistent organochlorines. The geographical distributions of organochlorines showed different patterns according to their physicochemical properties. The concentrations of HCHs and HCB revealed rather uniform distribution, suggesting their transportable nature in the long-range atmospheric transport. On the other hand, DDTs and PCBs were predicted to be less transportable via atmosphere due to the decreasing trends of residue levels in sediments from south to north. The organochlorine profiles in the sediment core from the Gulf of Alaska which seemed to be preserved without turbation revealed the elevated residue levels from bottom to surface layers. This implies that the aerial inputs of organochlorines in the cold ocean are still significantly continuing. The accumulation rates of organochlorines into sediments were rather smaller than the atmospheric inputs, indicating that the residue levels in water bodies are unlikely to decrease rapidly in near future.

Introduction

Organochlorine compounds, such as polychlorinated biphenyls (PCBs) and DDT have been noticed in various environmental media due to their ubiquitous, persistent and toxic nature. In spite of the restriction or ban on the usage of the organochlorines in some countries of the northern mid-latitudes since 1970s, these man-made chemicals are still present at the considerable levels over the world. Even nowadays, some of the organochlorine insecticides such as hexachlorocyclohexane (HCH) and DDT are being used in many tropical countries (Edwards, 1985; Mowbray, 1988; Forget, 1991). Therefore, the recent tropical air and water are fairly contaminated by such insecticides (Kausik *et al.*, 1987; Ramesh *et al.*, 1989; Ramesh *et al.*, 1990; Ngabe and Bidleman 1992; see Chapters 1 and 3). At the same time, significant quantities of PCBs still remain in older electrical equipment, although the production and new usage were ceased in 1970s to 80s in the industrialized mid-latitude countries (Tanabe, 1988). The recent research conducted in eastern and southern Asia and Oceania noted that the contamination areas by PCBs and chlordane compounds (CHLs) were expanding from mid- to low-latitudes (see Chapters 1 and 3).

The Arctic that has been regarded as the pristine area for anthropogenic pollutants has been a matter of great concern with the recent increase of evidences as a receptor of semivolatile organochlorines originating from southern countries (Barrie, 1986; Cotham and Bidleman, 1991; Barrie *et al.*, 1992; see Chapter 3). The considerable residues of organochlorines in the Arctic fish (Muir *et al.*, 1990), terrestrial (Norstrom *et al.*, 1988) and aquatic mammals (Muir *et al.*, 1988 and 1992a) suggest the significance of long-range atmospheric transport from lower latitudes. Some authors have documented the presence of organochlorines in the Arctic air (Tanabe and Tatsukawa, 1980; Oehme and Mano, 1984; Hargrave *et al.*, 1988; Patton *et al.*, 1989; see Chapter 3) and precipitation (Gregor and Gummer, 1989; Welch *et al.*, 1991). A recent study found much higher concentrations of HCHs in the surface seawater nearby Arctic (see Chapter 3), nevertheless the major contamination sources are unlikely to be present in this region. Levels of HCHs in the cold water bodies were about two times higher than those in the tropical waters such as the Bay of Bengal and the Arabian Sea nearby India which is one of the source country for HCHs contamination, although the atmospheric levels were highest in the latter areas. Calamari *et al.* (1991) also noted that the global distribution of hexachlorobenzene (HCB), using foliage samples, clearly depended on the temperature and the heavily contaminated samples were found mainly in cold areas. These facts strongly support that the cold areas including water bodies play a role as a sink for these semivolatile chemicals.

Organochlorines transported through atmosphere as gas and/or particulate phases enter the surface seawater by gas-exchange across air-water interface and by deposition along with aerosols, rain and snow. A portion of the hydrophobic organochlorines in surface seawater associates with biotic and abiotic macroparticles and then that is removed from surface to benthic layers by the settling of these particles into the water column. In this context, the sediments are regarded as one of the ultimate sink of the hydrophobic and persistent toxic compounds. Although large number of data on organochlorine residue levels in sediments are reported, most efforts have been conducted on point source regions such as rivers, estuaries and lakes and only a few reports are available on those in open sea sediments mainly due to the difficulties of sample collection. To our knowledge, no reports have been presented on the organochlorine residues in oceanic sediments nearby Arctic region.

In the present study, surface sediment samples were collected from the Chukchi Sea, Bering Sea and the Gulf of Alaska and were analyzed for the organochlorine residue levels in order to evaluate their current status of contamination and distribution. Sediment cores that will be a useful matrix to restore the historical inputs of organochlorines were also collected from the Bristol Bay in Bering Sea and the Gulf of Alaska and were examined for the temporal trends of organochlorine levels in the Arctic and subarctic regions. There are several studies for the temporal trends of these contaminants in the Arctic using the tissues of marine mammals (Addison *et al.*, 1986; Muir *et al.*, 1988; Norstrom *et al.*, 1988). However, the consistent conclusion has been led yet (Muir *et al.*, 1992b). Besides present and past status of contamination, this study also attempted to estimate the accumulation rates of organochlorines into sediments and discussed in terms of their behavior over the ocean on a global scale.

Materials and Methods

Sampling of Sediments

Sampling was conducted on board during June to July, 1990. Sampling locations of surface and core sediments are shown in Fig. 4-1. The northeastern part of the Bering Sea is known to be one of the eutrophic areas with high primary productivity among the world oceans. Hence, the benthos supplied with abundant food is correspondingly rich. On the other hand, the Chukchi Sea is characterized by lower productivity in comparison with the Bering Sea. The sampling areas in the Bering Sea and the Chukchi Sea are covered by ice sheet during winter season, while the Bristol Bay located in the southern Bering Sea is not frozen. These areas receive the inflow of riverine water from Alaska and resulted in low salinity of seawater. Sediments in these seas originate from ice-rafted material which is deposited when the ice melt. Sampling location in the Gulf of Alaska located on the continental shelf far off the northeastern part of Aleutian trench is affected by the eastern water mass from the Alaskan stream.

Details of samples are summarized in Table 4-1. Surface and core sediments were collected by a Smith-MacIntyre grab sampler and a

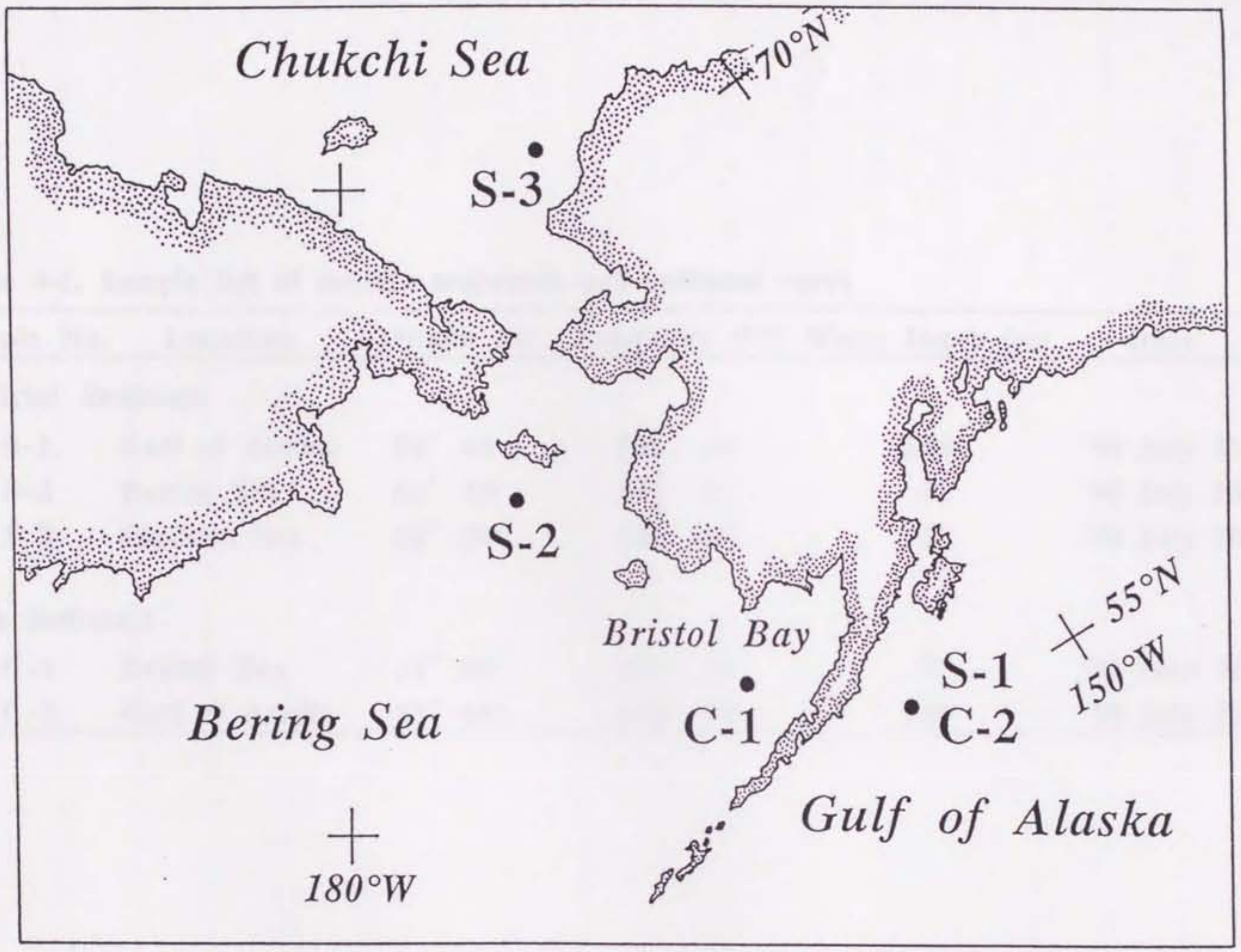

Fig. 4-1. Sampling locations of surface sediments and sediment cores.

Table 4-1. Sample list of surface sediments and sediment cores.

Sample No.	Location	Latitude (N)	Longitude (W)	Water Depth (m)	Date
Surficial Sediment					
S-1	Gulf of Alaska	55° 44'	156° 14'	249	'90 July 21
S-2	Bering Sea	62° 30'	171° 15'	47	'90 July 25
S-3	Chukchi Sea	68° 59'	167° 45'	27	'90 July 30
Core Sediment					
C-1	Bristol Bay	57° 00'	164° 58'	73	'90 June 23
C-2	Gulf of Alaska	55° 44'	156° 14'	249	'90 July 21

gravity core sampler (52mm i.d., 600mm length), respectively. Several centimeters of the surface sediment layer were taken by a stainless steel spatula. Two sediment cores were collected to a depth of 10 and 12 cm in the Bristol Bay and Gulf of Alaska, respectively. The cores were sectioned on board into 1 cm length with solvent-cleaned knives. All samples were sealed into polyethylene bags and stored at less than -20°C until analysis.

Chemical Analysis

The sediments were thawed out under a room temperature and then well mixed. Approximately 160 to 200 g (wet weight; w.w.) of surface sediments and 20 to 26 g (w.w.) of cores was extracted in glass-stoppered Erlenmeyer flasks with acetone by shaking for one hour. The following procedures of extraction were described in detail previously (see Chapter 1). The extracts were cleaned up with 5% v/v fuming sulfuric acid to destroy nitrogen- and oxygen-containing compounds and subsequently treated with copper chips to remove sulfur. The treated extracts were subjected to a high performance liquid chromatography (HPLC: LC-6A Series, Shimadzu Co. Ltd., Japan) for further clean-up and fractionation. The HPLC procedures employed in this study were followed to those reported previously (see Chapter 1). Extracts fractionated were injected to a high resolution gas chromatograph equipped with a moving needle type injection system (splitless and solvent cut mode, Shimadzu

Co. Ltd., Japan) and a ^{63}Ni electron capture detector (HRGC-ECD: Hewlett Packard 5890 series II) for identification and quantification of the chemicals. Fused silica capillary DB-1 and DB-1701 columns (J&W Scientific Co. Ltd., USA: 0.25 mm i.d., 30 m length) were used for the analysis of PCBs and the other organochlorines, respectively. The GC conditions and methods of quantification and peak identification of organochlorines were followed by previous reports (Tanabe *et al.*, 1987; see Chapter 3).

Total carbon and nitrogen contents in the surface sediments were also determined using a gas chromatograph (Shimadzu GC-8A: Shimadzu Co. Ltd., Japan) equipped with a thermal conductivity detector (GC-TCD) and a high sensitivity N.C.-analyser (Sumigraph NC-80: Sumitomo Chemical Industry Co. Ltd., Japan), after the sediment was dried and meshed homogeneously. Detector and column oven temperatures of GC-TCD were kept at 100 and 70°C, respectively. An electric current was used at 150 mA. Helium (80ml/min.) was used as a carrier gas. Reactive and reductive furances in the N.C.-analyser were kept at 850 and 550°C, respectively. Oxygen flow as a combustible gas was set at 300ml/min.

Results and Discussion

Residue levels in surface sediments

Organochlorine concentrations for three surface sediments were summarized in Table 4-2. At the same time, comparison of residue levels

Table 4-2. Organochlorine concentrations (pg / g dry wt.) and total carbon and nitrogen contents (%) in surface sediment samples from the Gulf of Alaska, Bering Sea and Chukchi Sea.

	Sampling Location		
Organochlorines	**Gulf of Alaska (S-1)**	**Bering Sea (S-2)**	**Chukchi Sea (S-3)**
α-HCH	**160**	**36**	**50**
β-HCH	**40**	**4.0**	**15**
γ-HCH	**48**	**3.3**	**10**
ΣHCH	**250**	**43**	**75**
***p,p'* -DDD**	**54**	**1.6**	**3.5**
***p,p'* -DDE**	**110**	**3.5**	**3.1**
***p,p'* -DDT**	**9.5**	**1.3**	**2.0**
ΣDDT	**170**	**6.4**	**8.6**
***trans* -chlordane**	**21**	**2.5**	**4.2**
***cis* -chlordane**	**19**	**5.0**	**5.1**
***trans* -nonachlor**	**15**	**3.4**	**4.1**
Σchlordane	**55**	**11**	**13**
Tri-CBs	**350**	**11**	**14**
Tetra-CBs	**730**	**45**	**47**
Penta-CBs	**600**	**35**	**49**
Hexa-CBs	**230**	**26**	**16**
Hepta-CBs	**89**	**10**	**13**
Octa-CBs	**37**	**1.7**	**1.9**
ΣPCB	**2,000**	**130**	**140**
HCB	**79**	**61**	**35**
Carbon	**1.36**	**0.335**	**1.33**
Nitrogen	**0.146**	**0.054**	**0.159**
C/N ratio	**9.32**	**6.20**	**8.36**

in various seas and oceans so far reported were given in Table 4-3. For all compounds detected, highest concentrations were observed in the Gulf of Alaska (Fig. 4-2).

HCH concentrations (sum of α-, β- and γ-isomers) were found to be in the range of 43-250 pg/g dry wt. in the survey areas. These residue levels correspond to the lower range of values in estuarine sediments from eastern and southern Asia and Oceania, except several areas from India and Vietnam which are influenced from the intensive sources of HCH contamination (see Chapter 1). It is also noteworthy that HCH levels found in the present study were comparable with those in the Mediterranean Sea that has been affected by the contamination of lindane from the runoff of European countries (Table 4-3). A previous study noted that HCHs are likely to be redistributed from the lower to higher latitudes through long-range atmospheric transport (see Chapter 1). The relatively uniform distribution of HCH concentrations not only among survey locations (Fig. 4-2) but also on wider scale (Table 4-3) may again support their possible redistribution from tropical to cold regions through atmosphere.

Regarding the composition of HCH isomers in the sampling locations, a high percentage of α-isomer was recorded whereas the concentrations of β- and γ-isomers were rather low (Table 2). The HCH compositions in this study were different from those in sediments from the highly contaminated areas like India, which showed larger proportion of β-

Table 4-3. Comparison of organochlorine residue levels in surface sediments collected from various seas and ocean after 1980.

Location	Organochlorines (ng/g dry wt.) HCHs	DDTs	CHLs	PCBs	HCB	Remarks	Reference
Chukchi Sea	0.075^{a}	0.0086^{c}	0.013	0.14^{f}	0.035	Grab sampler	This study
Bering Sea	0.043^{a}	0.0064^{c}	0.011	0.13^{f}	0.061	Grab sampler	This study
Bristol Bay	0.049^{a}	0.070^{c}	0.036	0.24^{f}	0.042	Core sampler (1cm)	This study
Gulf of Alaska	0.25^{a}	0.17^{c}	0.055	2.0^{f}	0.079	Grab sampler	This study
	0.17^{a}	0.092^{c}	0.018	0.47^{f}	0.067	Core sampler (1cm)	This study
North Sea				2.9-19^{f}		Grab sampler	(1)
Yellow Sea	0.44, 1.1^{a}	1.7, 3.3^{d}		0.92, 1.7^{f}		Core sampler (1cm)	(2)
East China Sea	0.21^{a}	0.34^{d}		0.81^{f}		Core sampler (1cm)	(2)
Mediterranean (Gulf of Lion)	0.012^{b}	0.047^{c}		0.8^{f}	0.039	Core sampler (5cm)	(3)
	0.080^{b}	0.89^{c}		1.0^{f}	0.085	Core sampler (1cm)	(3)
	0.180^{b}	0.43^{c}		0.7^{f}	0.064	Core sampler (2cm)	(3)
E. N. Pacific		3-195^{e}		<1-16^{g}		Grab sampler	(4)
Antarctica (Turtle Rock and Cinder Cone)		0.023^{c}		0.07^{h}		Core sampler (3cm)	(5)
		0.011^{c}		0.6^{h}		Core sampler (4cm)	(5)
		0.037^{c}		0.8^{h}		Core sampler (5cm)	(5)
		0.10^{c}		0.06^{h}		Core sampler (9cm)	(5)

(1) Klamer and Fomsgaard (1993); (2) Tanabe *et al.*, (1985); (3) Burns and Villeneuve (1987); (4) Thompson *et al.*, (1986); (5) Risebrough *et al.*, (1990). (a) sum of α, β and γ isomers; (b) γ isomer only; (c) sum of *p,p'* -DDD, *p,p'* -DDE and *p,p'* -DDT; (d)sum of *p,p'* -DDD, *p,p'* -DDE, *o,p'* -DDT and *p,p'* -DDT; (e)sum of *o,p'* -DDD, *p,p'* -DDD, *o,p'*- DDE, *p,p'* -DDE, *o,p'* -DDT and *p,p'* -DDT; (f)sum of congeners; (g)as Aroclor 1242 and 1254; (h)as Aroclor 1260.

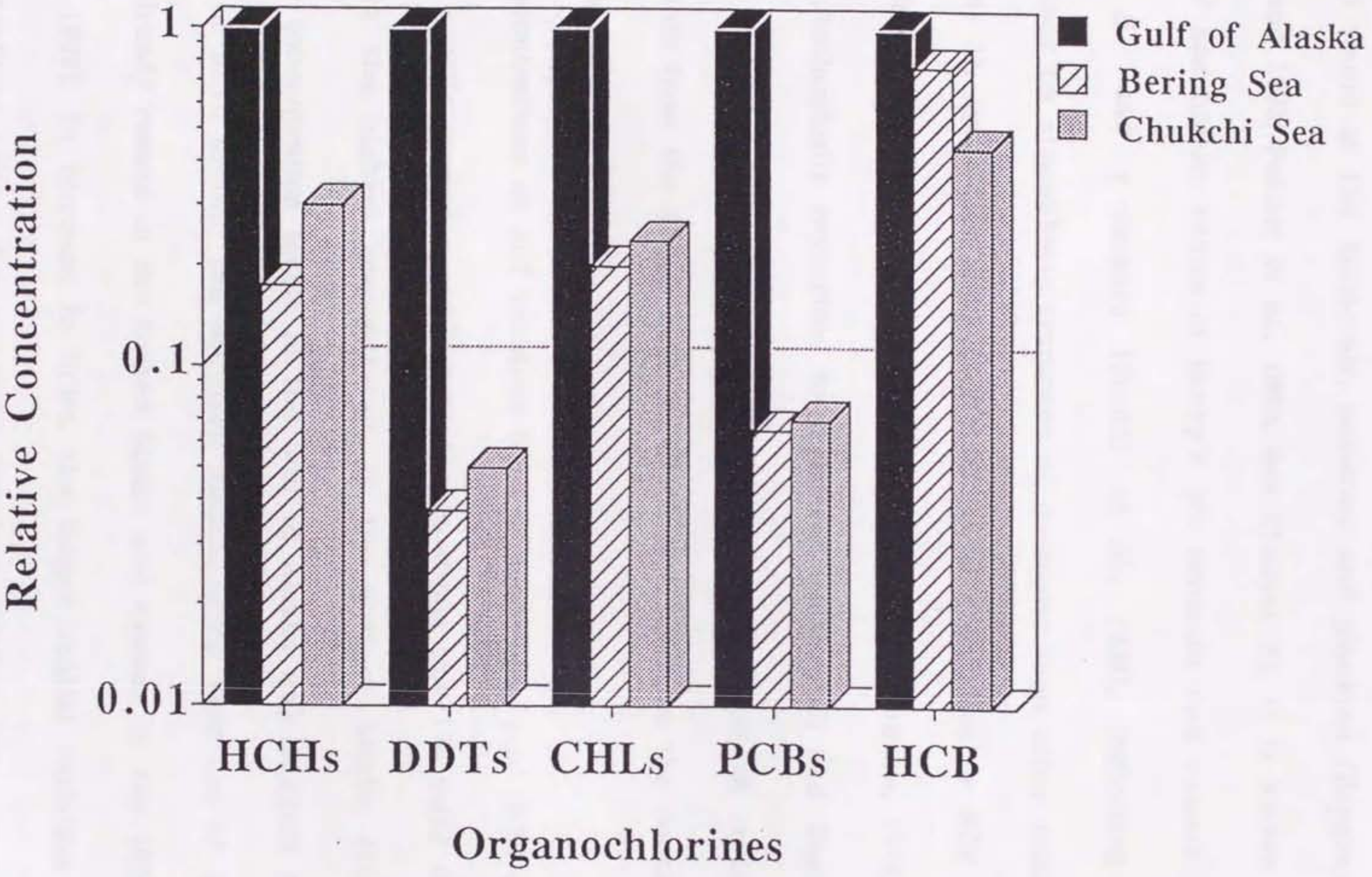

Fig. 4-2. Relative concentrations of organochlorines in sediments. The concentrations in the Gulf of Alaska are treated as 1.0.

isomer (Ramesh *et al.*, 1991; see Chapter 3). The α-HCH/γ-HCH ratios (3.3-11) obtained in this study (Table 4-2) were almost similar to those values found in the Arctic air, seawater and plankton (Hargrave *et al.*, 1989 and 1992; Patton *et al.*, 1989; see Chapter 3). It is known that α-isomer has higher values of Henry's law constant and vapour pressure than β- and γ-isomers (Suntio *et al.*, 1988), indicating greater efficiency by atmospheric transport of α-isomer than other isomers (see Chapter 3). Apart from such physicochemical properties, γ-HCH is noted to be degraded by microorganisms (Benezet and Matsumura, 1973) and to be photochemically isomerized to α-isomer (Malaiyandi and Shah, 1984). These factors may account for the higher proportion of α-isomer in sediments from the Arctic regions which are far from the contamination sources.

Concentrations of DDT residues (sum of *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT) greatly varied according to the locations (6.4-170 pg/g dry wt.), showing the highest concentration in the Gulf of Alaska (Fig. 4-2). Higher concentration levels in the Gulf of Alaska may suggest the past usage of DDTs around the southern Alaska, since most use of DDT has been already ceased in the United States and Canada in the 1970s (Hoff *et al.*, 1992). In contrast to HCHs, the larger spatial variation in DDT concentrations among the sampling locations implies less transportable potency of this contaminant through atmosphere. Comparison of DDT levels in the Chukchi Sea and Bering Sea with other data in temperate regions also indicates the apparent variation, showing a much lower concentration in cold waters (Table 4-3). The author (see Chapters 1 and 3) pointed out in the study of global scale that DDTs, unlike HCHs, have less efficiency for redistribution through atmosphere from lower to higher latitudes. The present results of DDT distributions in sediments again support our previous observation. The composition of DDT compounds in the oceanic sediments showed a higher percentage of *p,p'* -DDE than *p,p'* -DDT and *p,p'* -DDD in all the cases studied. Higher levels of *p,p'* -DDE which is a dehydrochlorination product of *p,p'* -DDT might be caused by the biological and photochemical transformation and/or preferential transport of *p,p'* -DDE as compared with other DDT compounds (Atlas and Giam, 1988; see Chapter 3). When comparing *p,p'* -DDE to *p,p'* -DDT ratios in sediment samples, much greater ratio was observed in the Gulf of Alaska (*p,p'* -DDE/*p,p'* -DDT=11.6) than the Bering Sea (2.7) and Chukchi Sea (1.6). A similar spatial variation of the ratio has been also observed in the atmosphere (see Chapter 3). The average *p,p'* -DDE/*p,p'* -DDT ratios for arctic shelf amphipods were reported to be 1.03 (Hargrave *et al.*, 1992) and hence appeared to be rather close to those in the sediments from the Bering and Chukchi Seas. Although the reason for such a spatial difference in the dominant percent of *p,p'* -DDE is still unknown, this may be attributed to the effect from various sources of DDT compounds between the Gulf of

Alaska and the other areas.

Among the 45 compounds included in technical chlordane (Sovocool *et al.*, 1977), the major three constituents (*trans* -chlordane, *cis* -chlordane and *trans* -nonachlor) were detected in the sediments. The sum of three chlordane compounds ranged 11-55 pg/g dry wt. Chlordane concentrations in the present study seemed to be one to two orders of magnitude lower than those from most of the Asian estuaries (see Chapter 1) and San Francisco Bay in the United States (Phillips and Spies, 1988) affected by urban runoff, although little information is available on CHL residues in sediments.

The composition of chlordane compounds in environmental samples has often been used as a tool to identify the contamination source and to understand the transport mechanism of toxic contaminants (Patton *et al.*, 1989; Hoff *et al.*, 1992; see Chapter 3). The ratios of *trans* -chlordane, *cis* -chlordane and *trans* -nonachlor (TC: CC: TN) in the Gulf of Alaska, Bering Sea and the Chukchi Sea were 1.1 : 1.0 : 0.79, 0.50 : 1.0 : 0.68 and 0.82 : 1.0 : 0.80, respectively. Considering the ratio in the technical mixture reported as 1.26 : 1.0 : 0.37 (Sovocool *et al.*, 1977), the composition in the Gulf of Alaska was found to be closer to that in the mixture than those in other locations. This may suggest that the Gulf of Alaska has been influenced relatively from the local source area. Nevertheless, the ratios in all the sampling locations surveyed showed the preferential depletion of *trans* -chlordane and *cis* -chlordane (larger contribution of *trans* -nonachlor). Similar pattern of the ratio has also been observed in the Arctic air (Hoff and Chan, 1986; Patton *et al.*, 1989; see Chapter 3). A higher Henry's law constant for *trans* -nonachlor (49.5 Pa m^3/mol at 25°C) than that for *trans* -chlordane (16.5 Pa m^3/mol) and *cis* -chlordane (11.2 Pa m^3/mol) may explain the efficient transport of *trans* -nonachlor and resulted in the relative abundance of this compound in remote areas (see Chapter 3). However, greater contribution of *cis* -chlordane than *trans* -chlordane may request another reason, since both the isomers have similar physicochemical properties. Krämer *et al.* (1984) and Kawano *et al.* (1988) found the predominance of *cis* -isomer to *trans* -isomer in marine organisms from the North Atlantic and the North Pacific and explained it by higher stability of the former isomer than the latter. Hargrave *et al.* (1988, 1992) also pointed out the possible degradation of *trans* -chlordane in the Arctic seawater and plankton. The present results found in the sediments might again support such a difference of environmental stability between *cis* - and *trans* -chlordanes.

PCB (sum of 36 isomers and congeners) concentrations also showed a larger gradient between the Gulf of Alaska and the other areas, which is similar to DDT distribution (Fig. 4-2). The residue levels in the Gulf of Alaska sediments seemed to be comparable with those from the Yellow Sea, East China Sea and the Mediterranean Sea and lower than that from the North Sea (Table 4-3). Compositions of PCB homologues found in these survey locations revealed the predominance of lower chlorinated biphenyls, accounting for 70-84 % of tri- to pentachlorinated congeners in total PCBs (Table 4-2). The enrichment of lower chlorinated members of PCBs in sediments from the colder waters were in agreement with the results found in the Arctic air (see Chapter 3), water (Tatsukawa and Tanabe, 1983) and biological samples (Tatsukawa and Tanabe, 1983; Muir *et al.*, 1990; Muir *et al.*, 1992a). This might be due to the efficient atmospheric transport of lower chlorinated biphenyls from the sources, which attributes to their higher vapor pressures and/or Henry's Law Constants (Dunnivant *et al.*, 1992). The author indicated larger fluxes of PCB congeners with smaller number of chlorines from air to surface seawater in cold oceans (see Chapter 3).

In contrast to DDT and PCB distribution patterns, HCB distribution was rather uniform with a narrow range (35-79 pg/g dry weight) among the three survey locations (Fig. 4-2). It should be also noted that HCB in the Mediterranean sediments exhibited the similar levels (Table 4-3), nevertheless the semi-closed sea appear to be directly influenced by the sources originating from the use of HCB as an agricultural fungicide and industrial byproduct formed in the production of chlorinated compounds. Atmospheric concentrations of HCB summarized from several literatures also ranged in a small variation on the global terms (Calamari *et al.*, 1991). The HCB distribution in sediments again verifies the previous finding. These geographical distributions imply the higher potency of this chemical on the long-range atmospheric transport.

Profiles in core sediments

Vertical profile of organochlorines in the sediment core from the Bristol Bay and Gulf of Alaska are shown in Figs. 4-3 and 4-4, respectively. In the sample from the Bristol Bay, organochlorines were detected in all the sediment core layers collected, showing no correlation of residues with sediment depth (Fig. 4-3). As biomass of benthic organisms would be expected to be high due to the abundant supply of nutrient on the shelf surface, the organochlorine profiles in sediments might be biologically disturbed by the activity of benthic organisms. Frequent fishing activities using trawl nets may also have affected the historical record of contaminants in this sediment core.

On the other hand, the sediment core from the Gulf of Alaska revealed a plausible pattern with an increasing trend from the bottom to upper layers (Fig. 4-4). As seen in the profiles of organochlorine concentrations in the sediment core, the chronology on organochlorine usages would be regarded to have started at the period when 5-6 cm of core layer was formed as a surface sediment. Hence, the recorded year of this core layer is estimated to be the period of 1930 to 1940 that almost corresponds to the starting year of the large scale production of DDTs and PCBs. Based on this conception, the average sedimentation rate

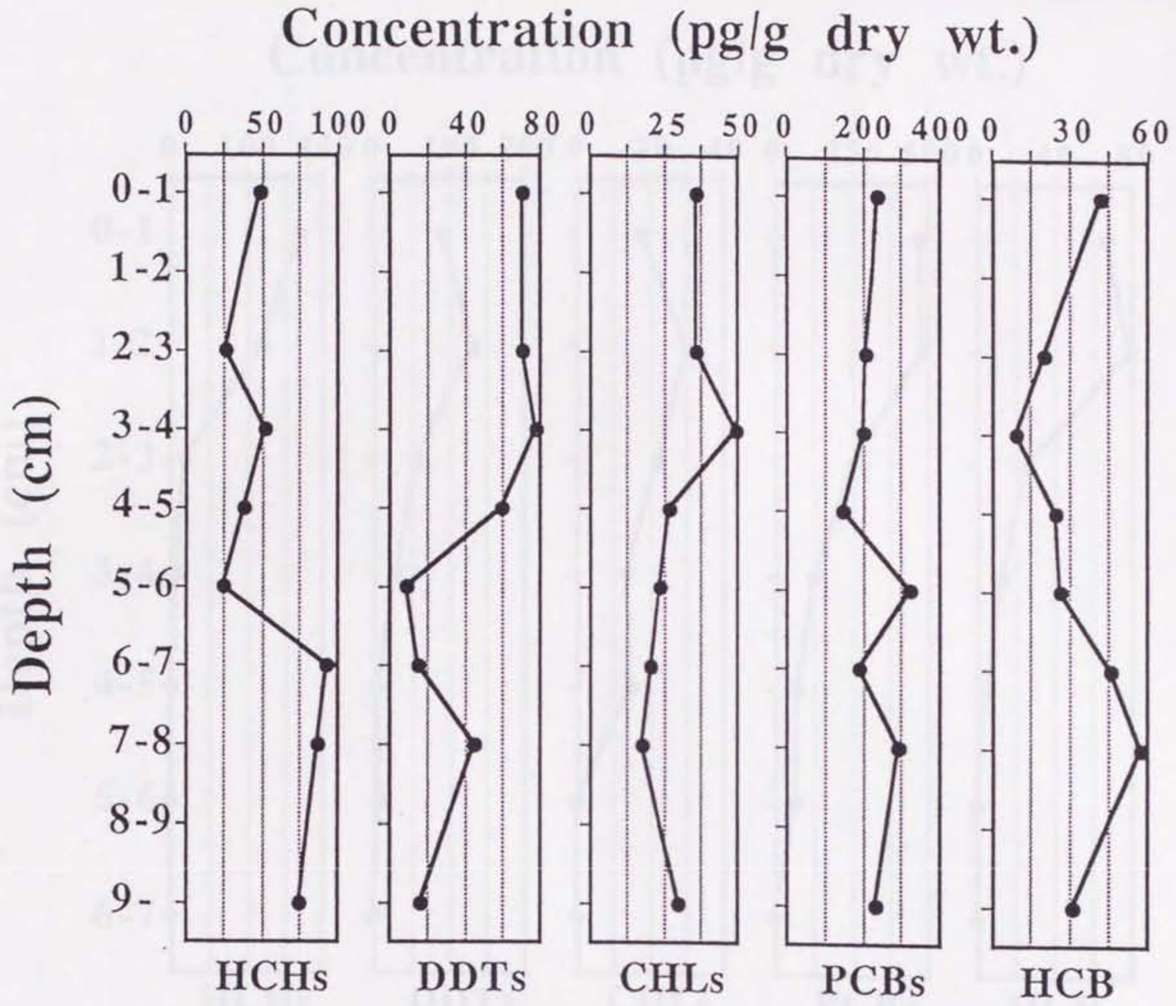

Fig. 4-3. Vertical profiles of organochlorine concentrations in the sediment core from the Bristol Bay.
Data for 1-2 and 8-9 cm cores are not available.

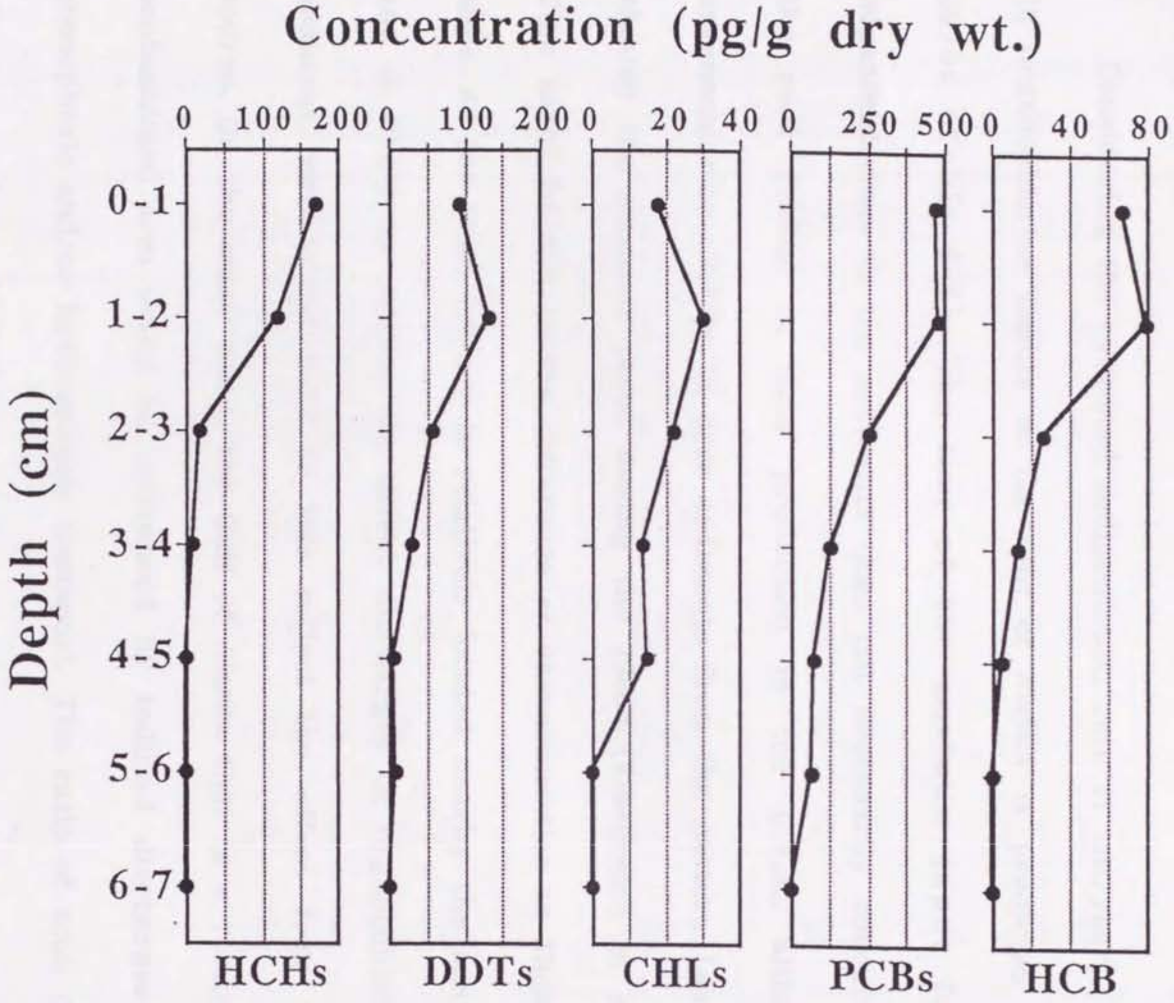

Fig. 4-4. Vertical profiles of organochlorine concentrations in the sediment core from the Gulf of Alaska.

in this location can be calculated to be about 1 mm/year. This sedimentation rate is two times higher than that in the Bering Sea basin at 3,600m depth (Tsunogai and Yamada, 1979). The higher rate estimated in this study may attribute to the proximity from shoreline and shallow water depth.

Considering the estimated sedimentation rate (1 mm/year), the peak in organochlorine inputs to the Gulf of Alaska is predicted after the 1970s (Table 4-4). The time of the maximum input for these organochlorines to the sediments does not necessarily concurrent with the peak (1960s) in their production in the U.S.A., although the organochlorine profiles in core sediments from the eastern Lake Ontario showed the maximum input during the 1960s (Eisenreich *et al.*, 1989). This might be due to the difference of characteristics in these survey sites. As the Lake Ontario is relatively located nearby the source areas and is likely to receive the direct discharges of organochlorines, the sediment core would more or less reflect the effect from the local source. On the other hand, the Gulf of Alaska that is a relatively less contaminated area would be influenced by indirect discharges through atmospheric and/or hydrospheric transport. The ratio of total carbon to nitrogen contents (C/N=9.3) in sediments from the Gulf of Alaska (Table 4-2) supports that the sediments derived from phyto- and zooplankton, not from land-derived materials such as terrestrial plants. The

Table 4-4. Temporal trends of organochlorine accumulation rates (pg/cm^2/yr.) into the sediments from the Gulf of Alaska.

Depth (cm)	Estimated Year	HCHs	DDTs	CHLs	PCBs	HCB
0-1	1980-1990	6.1	3.3	0.6	17	2.4
1-2	1970-1980	4.3	4.7	1.1	17	2.8
2-3	1960-1970	0.7	2.1	0.8	9.0	0.9
3-4	1950-1960	0.3	1.0	0.5	4.7	0.5
4-5	1940-1950	<0.2	0.3	0.5	2.6	0.2
5-6	1930-1940	<0.2	0.3	<0.2	2.4	<0.2
6-7	1920-1930	<0.2	<0.2	<0.2	<2.0	<0.2

organochlorine concentration profiles in the Gulf of Alaska core may integrate the input from numerous possible sources originating not only from the present but also in the past usage areas. Fukushima *et al.* (1988) found that PCB concentrations in water from less contaminated areas of the Yodo river in Japan had not changed significantly since 1974, despite the decrease of residues in the polluted area. Baker and Eisenreich (1990) reported the volatilization of PCBs from the surface water in the northern Great Lakes and concluded that the atmospheric PCB concentrations have remained constant during the last 10 years, whereas the sediment core in the eastern Lake Ontario clearly recorded a decreasing trend after 1970 (Eisenreich *et al.*, 1989). The author also reported that the present concentrations of atmospheric PCBs over the North Pacific and the North Atlantic Oceans were rather comparable with the previous data collected between the late 1970s and the early 1980s (see Chapter 3). These results mean that the oceanic water such as the Gulf of Alaska may have played the role as sink until now, while highly polluted waters such as lake, estuarine and coast located nearby human activities have served as secondary sources of organochlorine contaminations since 1970s. Losses of organochlorines through volatilization from these secondary sources are likely to be compensable inputs to the ocean (sink) through long-range atmospheric transport.

Accumulation rate into the sediments

Using the organochlorine concentrations in the sediment core (C_{SC} ;

pg/g wet wt.) from the Gulf of Alaska, their annual accumulation rates into the sediments can be estimated. The following equation was employed for estimating the rate (F; pg/cm^2/year):

$$F = SR \times CD \times C_{SC} \quad ---(1)$$

where SR and CD are the sedimentation rate (cm/year) and the sediment core density (g wet wt./cm^3), respectively. The SR was defined as 1 mm/year as described above. The CD was estimated from the average wet weight of sediment layers in unit volume and obtained to be 1.2 g wet wt./cm^3. Water content in the core sediments is assumed to be a constant 70%.

The estimated organochlorine accumulation rates into the sediments are presented in Table 4-4. Unfortunately, it was quite difficult to depict the geographical variation of organochlorine accumulation rates, because of the lack of comparable data so far reported. Nevertheless, PCB accumulation rates for various regions are only available in several regions. The present PCB accumulation rate in this study was one order of magnitude lower than those in the Lake Superior (Baker and Eisenreich, 1990) and the remote lakes such as the Crystal and Little Pine Lakes in Wisconsin of U.S.A. (Swackhamer and Armstrong, 1986), and two to three orders of magnitude lower than those in the Esthwaite Water in England (Sanders *et al.*, 1992), Lagoon of Venice (Pavoni *et al.*, 1987), Lake Michigan (Swackhamer and Armstrong, 1986) and Lake

Ontario (Eisenreich *et al.*, 1989). Considering the difference in magnitude of discharge from the source, sedimentation rate and water flow etc, the divergence of organochlorine accumulation rates into sediments seems to be plausible.

Atmospheric inputs of organochlorines to the surface water in the Gulf of Alaska reported previously (see Chapter 3) were compared with their accumulation rates into sediments. Average air to water fluxes for HCHs (α-HCH + γ-HCH), DDTs (*p,p'* -DDE + *p,p'* -DDT), CHLs (*cis* -chlordane + *trans* -nonachlor) and PCBs estimated from gradients between air and surface water concentrations in 1990 were 1,700, 27, 83 and 630 pg/cm^2/year, respectively. The ratios of these organochlorine accumulation rates into sediments to the atmospheric inputs corresponded to 0.37, 12, 0.72 and 2.7%, respectively. Similar phenomena have been reported in several investigations. Armstrong *et al.* (1987) and Baker *et al.* (1991) noted that, in the Crystal Lake and Lake Superior, the flux of particle-associated contaminants onto sediments in the water column was considerably greater than their accumulation rates into sediments. Swackhammer and Eisenreich (1991) also pointed out that only a small fraction of PCBs transported with sinking particles from surface to bottom layers in the water column in the Great Lakes were incorporated into the sediments (3-18% in the Lake Michigan and 0.3-1.4% in the Lake Superior). These incorporated rates into the sediments are in good agreement with those in the Gulf of

Alaska, implying the similar fate of organochlorines even in the oceanic environment. Vertical transfer of organochlorines from the surface to deep water layers in the ocean is mediated by incorporation with sinking particles arising out of biotic and abiotic processes. This was certainly evidenced by the significant detection of organochlorines in particulate matter collected with the sediment trap in the deep North Atlantic Ocean (Knap *et al.*, 1986). As an explanation of smaller accumulation rates of organochlorines into sediments, the removal of contaminants from the particulate to dissolved phases in the sediment-water interface, in accordance with the mineralization of the particulate organic carbon, should be taken into account (Swackhamer and Eisenreich, 1992). Barrie *et al.* (1992) also suggested the less potency of sediments as a sink in the Arctic Ocean by estimating the annual budget for HCHs. Ocean currents were considered as a primary carrier of the chemicals from the Arctic Ocean. The smaller accumulation rates of organochlorines into sediments indicate that the residues in water bodies are unlikely to decrease rapidly in near future.

Further studies are needed on the dynamics of organochlorines in the Arctic marine environment in order to fill the gaps in present knowledge and to understand their transport pathways on a global scale. In addition, comprehensive data of temporal trends would help to predict the future transition of these contaminants in cold water ecosystem.

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5 Factors Controlling Distribution, Dynamics and Fate on a Global Scale

Abstract

Semivolatile persistent organochlorines have been detected at significant concentrations in the environmental samples collected from various regions. Recent monitoring studies carried out on a global scale showed that the pattern of geographical distribution of organochlorines was rather different depending on the chemical species of organochlorines, as these compounds were inherently partitioned among compartments such as air, water, soil and plant etc, according to their physico-chemical properties. Based on the results on global monitoring studies, a combination of Henry's law constant (HLC) and HLC/octanol-water partition coefficient (H/K_{ow}) for organochlorines was found to be influential in explaining their present global distributions. Ambient temperatures and a proportion of water (oceanic) and lipophilic (terrestrial) surface areas in the environment would also be the factors concerned. It can therefore be concluded that these compounds are redistributed to their specifically designated regions on the heterogeneous earth.

Introduction

It can be defined that semivolatile persistent organochlorines are, on the whole, less degradable in nature and moderately partition between gas and water phases or between gas and solid phases. Providing these characteristics of organochlorines such as polychlorinated biphenyls (PCBs) and DDTs, numerous scientists have warned of their worldwide contaminations. Certainly, there are many indications that these organochlorines are widely distributed on the globe. Since the 1970s, technical improvement in the analytical chemistry enabled to give evidences that the Arctic and Antarctic which have been believed as pristine areas were also exposed to the organochlorine compounds. The large-scale transport of organochlorines through atmosphere was referred as "global distillation" by Goldberg (1975). In the latter 1970s to early 1980s, heavily contaminated regions were concentrated on the mid-latitudes of the northern hemisphere (Tanabe *et al.*, 1983). Large amount of organochlorines used mainly in the industrialized countries from 1940s to 70s influenced their geographical variations at that time. The higher levels in the mid-latitudes have veiled the concequences of contaminations in the higher latitude regions and delayed our evaluation to the significance of cold polar regions.

Recent interests have enthusiastically focused on organochlorine residues in the Arctic, because of the unexpectedly high contaminations were found in various environmental samples (Norstrom *et al.*, 1988; Muir *et al.*, 1988; Hargrave *et al.*, 1988; Patton *et al.*, 1989; Barrie *et al.*, 1992). However, due to the lack of global monitoring data of organochlorines, particularly those in lower latitude areas, depicting the specific features on their distribution, dynamics and fate in the cold region was difficult. During the recent years, the conceptual idea on the role of Arctic as a receptor of chemical pollutants (it is also called as cold condensation or trapping effect) was suggested based on the overview of scattered data from various laboratories (Barrie, 1986; Ottar, 1989). Apparent evidences for the role of natural cold receptor in the Arctic were then presented through two independent global monitoring programmes designed to elucidate the global distribution of organochlorines by Calamari *et al.* (1991) and our group (see Chapter 3). These authors found that the most contaminated region for HCB and HCHs was present in the Arctic. On the other hand, the geographical distribution for DDTs, chlordane compounds (CHLs) and PCBs showed higher concentrations in low- to mid-latitude areas. Fade-out of the notable contamination belt in the northern mid-latitudes disclosed both the southward shift of organochlorine sources to the tropics and the role of polar region as a receptor. In the low-latitude tropical regions, it is suspected that HCHs and DDTs are still being used for agricultural and vector control purposes, CHLs for termite control, and that PCBs are leaking out from old transformers and capacitors which were imported from the industrialized countries (see Chapter 1). The situation in the present tropics seems to be similar to that in the earlier northern mid-latitude countries where these hazardous chemicals have already been banned or restricted. It has been reported that the organochlorines released in the tropics would be rather redistributed to higher latitudes according to contaminant-specific efficiencies for the transportability than homogeneously diluted (see Chapters 1 and 3).

Nevertheless, it has not been inclusively understood how much (concentrations and burdens) of organochlorines is expected to be loaded in an environmental compartment, and what factors regulate their global behavior. One of the reasons for this is due to the existence of only a few monitoring data of organochlorines on a global scale. Ambiguous models and theories based on the limited knowledge and compiling localized data, which potentially slight requisites for unifying the information such as sampling year and analytical methodology, may lead to false perversions. For environmental chemists dealing with such toxic compounds which threaten the ecosystem on the globe, their ultimate purpose is to predict the fate of these contaminants and to evaluate the ecotoxicological impacts to organisms in their influential areas exerted.

In the former chapters, geographical distributions of some semi-volatile persistent organochlorines were presented on a global basis, and their worldwide dynamics and fate were discussed. Reviewing the global monitoring data that have been given in this study and others, the present chapter attempts to find significant factors controlling the behavior of these organochlorines. The factors considered here would include both the physico-chemical properties of compounds and extraneous parameters such as geographical features. Finally, the discussion is expanded to the other persistent organochlorines and the general conclusions are presented.

Air-Water and Air-Solid Partitioning

Anthropogenic pollutants released from their sources into the atmosphere to some extent would be trapped on water or solid phase which are defined as substances with lipophilic surface (aerosols, soils and plants). Hence, semivolatile persistent organochlorines are predicted to be properly partitioned among these (air, water and solid) phases.

Since Henry's law constant (HLC) is to describe the equilibrium partitioning of a compound between gas (P_v) and water ($C_{diss,w}$) following its definition ($P_v = H \times C_{diss,w}$), it could be a parameter to express the mobility (transportability) of a compound under the environment comprising atmosphere and hydrosphere. The compounds with higher HLCs would be more preferably partitioned in the gas phase than in the water phase and therefore it undergoes efficient diffusion through atmosphere. It has been reported that the HLC is available for estimating the gas exchange processes between air and surface seawater in the ocean and between air and rainwater during the rainfall (Liss and Slater, 1974; Ligocki *et al.*, 1985).

Besides, the parameter representing the transportability of a compound in the environment composed of gas and solid (lipophilic surface) may be expressed by the ratio of HLC to octanol-water partition coefficient (H/K_{OW}) as mentioned in Chapter 1. It was first used by Travis and Hattemer-Frey (1988) to determine the air-to-vegetation bioconcentration factor for semivolatile organochlorines. The compounds with higher H/K_{OW} values tend to transfer more in the gas phase than in the solid phase, and hence would be more transportable in the air-solid environment than those with the lower values. When this parameter is applied in the natural environment, partitioning between air and soils or air and aerosols can be proposed.

The relationships between HLC and H/K_{OW} of HCHs, DDTs, CHLs and PCBs were two-dimensionally plotted in Fig. 5-1 for featuring their physico-chemical characteristics. As the HLC is temperature-dependent, comparable values of HLC and H/K_{OW} obtained under 20-25°C are presented. In this study, it is assumed in the following discussion that the relative relationships of these parameters among chemical species are almost unchangeable at any temperatures.

The HLCs for HCHs including α- and γ-isomers were found to be lower than those of other organochlorines. Therefore, the isomers would be more favorably dissolved in the water phase. Judging from the higher concentrations of HCHs in cold water oceans as shown earlier

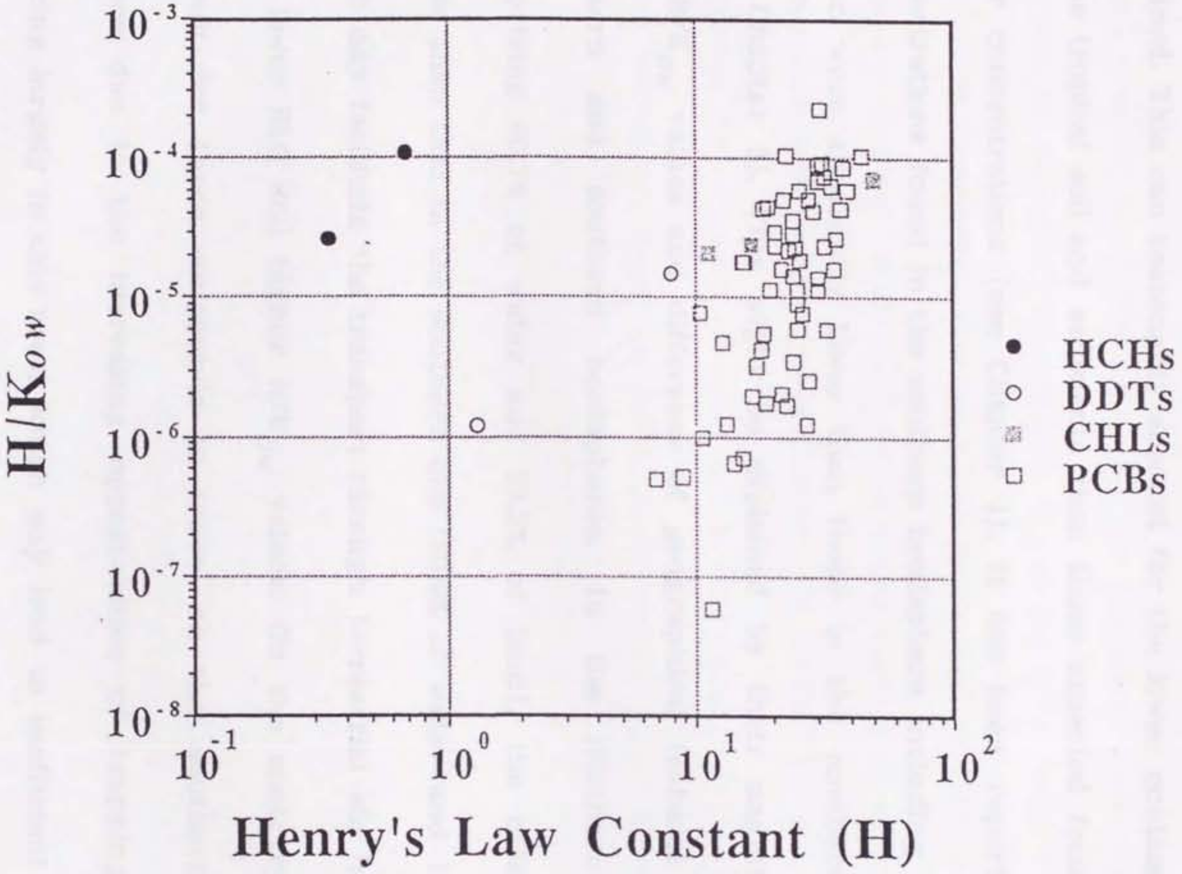

Fig. 5-1. Relationship between Henry's law constant (H) and H/K_{ow} of organochlorines.

Data are cited from Mackay *et al.* (1986), Shiu and Mackay (1986), Suntio *et al.* (1988), Kawano (1991), Kucklick *et al.* (1991) and Dunnivant *et al.* (1992).

(see Chapter 3), compounds with this magnitude of HLCs are evaluated to be retained in water at less than 10°C. As for the H/K_{OW}, HCHs showed relatively high values, indicating to be less adsorptive to the soil and aerosol phases in comparison to the other organochlorines examined. This can reasonably account for the lower contamination levels in the tropical soil and sediments than those expected from the air and water concentrations (see Chapter 1). It has been reported that HCH concentrations found in the southern hemisphere including the Antarctic region were apparently lower than those in the northern hemisphere (see Chapter 3). This might be explained by their magnitudes of HLC and H/K_{OW} values and difference of geographical features between the northern and southern hemispheres. In the northern hemisphere (comprising 60.7% of water and 39.3% of land), the ratio of land is higher than that in the southern one (80.9% of water and 19.1% of land) which may facilitate the transport through terrestrial air for compounds with lower HLC and higher H/K_{OW} values. On the contrary, it may be difficult for these compounds to travel on the southern hemisphere surface due to the increasing opportunities of trapping into water covering largely in this area, which may lead to inefficient amplification of HCH residues in the southern polar region. Regarding DDTs, higher HLCs and lower H/K_{OW} than those for HCHs were noticed. This result infers that these compounds are less adsorbable in water and are likely to be more retained on the lipophilic surface than HCHs. As far as DDT sources are present on land rather than ocean, this chemical would be trapped on various lipophilic surfaces nearby the source areas and not be subjected to long-range atmospheric transport. This is supported by the global distributions of DDTs in air, surface water and plant which showed higher concentrations in the samples from tropical areas (Calamari *et al.*, 1991; see Chapter 1 and 3). With respect to CHLs and PCBs, these compounds possess a tendency to be distributed more in the gas phase in ocean (air/water) environment than HCHs and DDTs, and an intermediate preference between HCHs and DDTs for lipophilic surface. The global distributions of CHLs and PCBs in ocean water, which showed smaller variations, might be due to their higher HLCs (see Chapter 3).

Generalization

In order to generalize the behavior and fate of various persistent organochlorines on a global scale, further inquiries using the HLC and H/K_{ow} are needed. Hence, hexachloroethane (HCE), hexachlorobenzene (HCB) and polychlorinated dibenzo-*p*-dioxins (PCDDs) with different magnitudes of HLC and H/K_{ow} values were also plotted in relation to HLC-H/K_{ow} and shown in Fig. 5-2.

As for HCE, it was found that both of the HLC and H/K_{ow} have higher values than any other organochlorines examined. This indicates that atmosphere serves as a sink for this compound rather than water and soil. The atmospheric distribution of HCE on a global basis has been

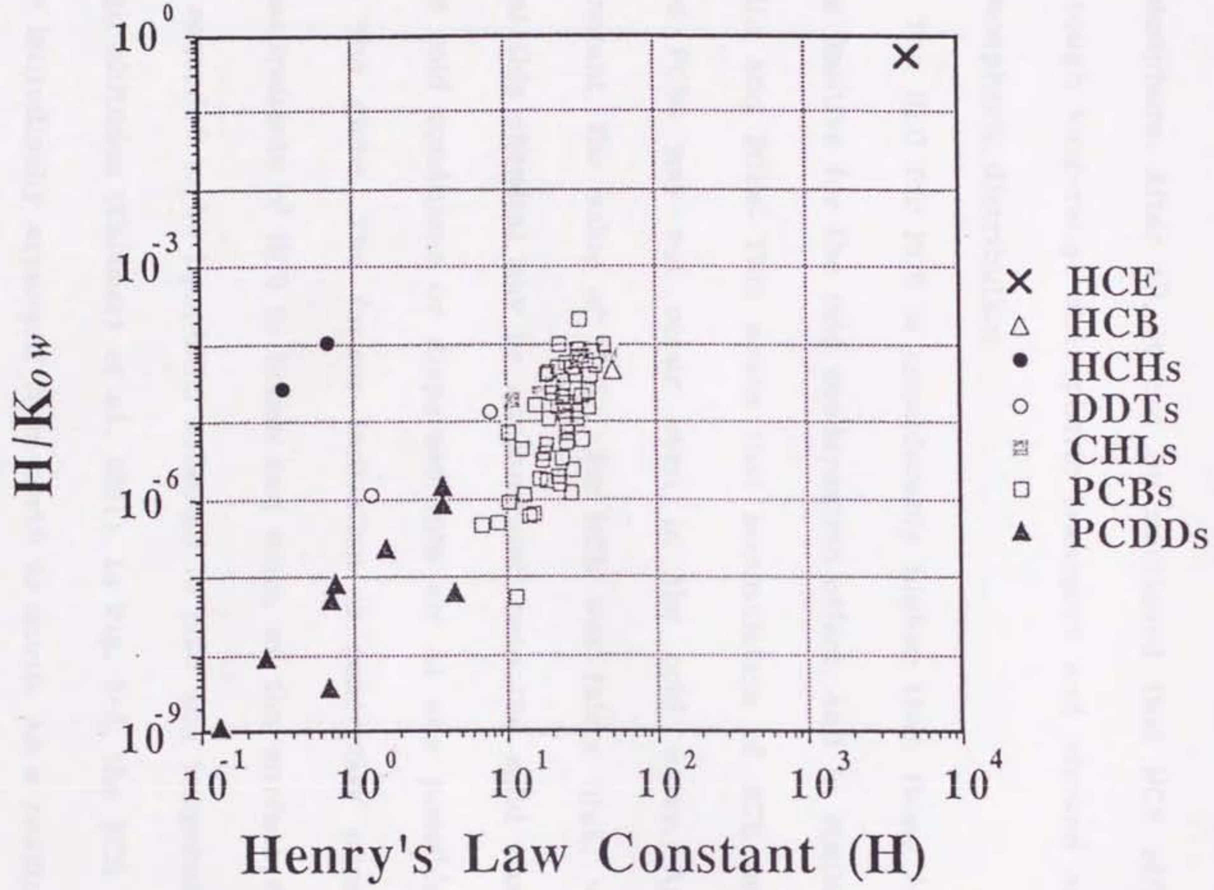

Fig. 5-2. Relationship between Henry's law constant (H) and H/K*ow* of organochlorines.

Data are cited from Mackay *et al.* (1986), Shiu and Mackay (1986), Shiu *et al.* (1988), Suntio *et al.* (1988), Ballschmiter and Wittlinger (1991), Kawano (1991), Kucklick *et al.* (1991), Dunnivant *et al.* (1992) and Hulscher *et al.* (1992).

reported by Class and Ballschmiter (1987) (Fig. 5-3). The uniform distribution in air implies that the removal from atmosphere through gas exchange and adsorption on lipophilic surface are minor processes. In other words, this chemical tends to be mostly partitioned to the atmosphere. After all, it can be mentioned that HCE efficiently spread through long-range atmospheric transport and showed an homogeneous atmospheric distribution.

The HLC for HCB is considerably higher than those for HCHs which are positive for the cold condensation effect, and is similar to those for CHLs and PCBs. This means that accumulation of HCB as well as CHLs and PCBs may not occur even in the cold water. Apart from the constant, the value of H/K_{OW} for HCB was fairly high, which indicates that this chemical may be concentrated onto the solid phase only under the cold conditions or dispersed into air at any possible temperatures on the globe. The former indication is concretely supported by the measurements of HCB in lichen and moss, as the surface of these plants is regarded to be lipophilic, collected in cold and temperate areas and at high altitudes (Calamari *et al.*, 1991). In Fig. 5-4, the HCB concentrations are latitudinally arranged from north to south. As a result, it was found that the plants collected in cold areas including higher latitudes and altitudes showed elevated concentrations.

The characteristic for PCDDs is that both of HLC and H/K_{OW} values

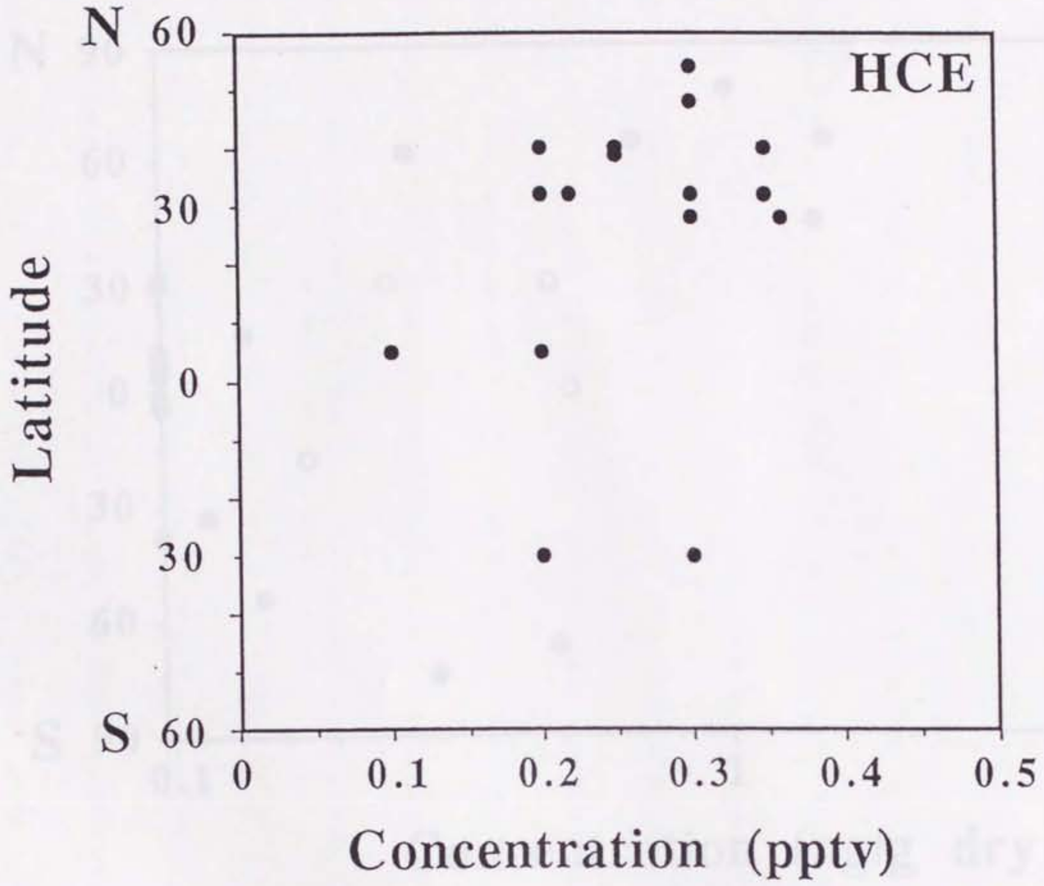

Fig. 5-3. Distribution of HCE concentrations in air as a function of the latitude.

Data are cited from Class and Ballschmiter (1987).

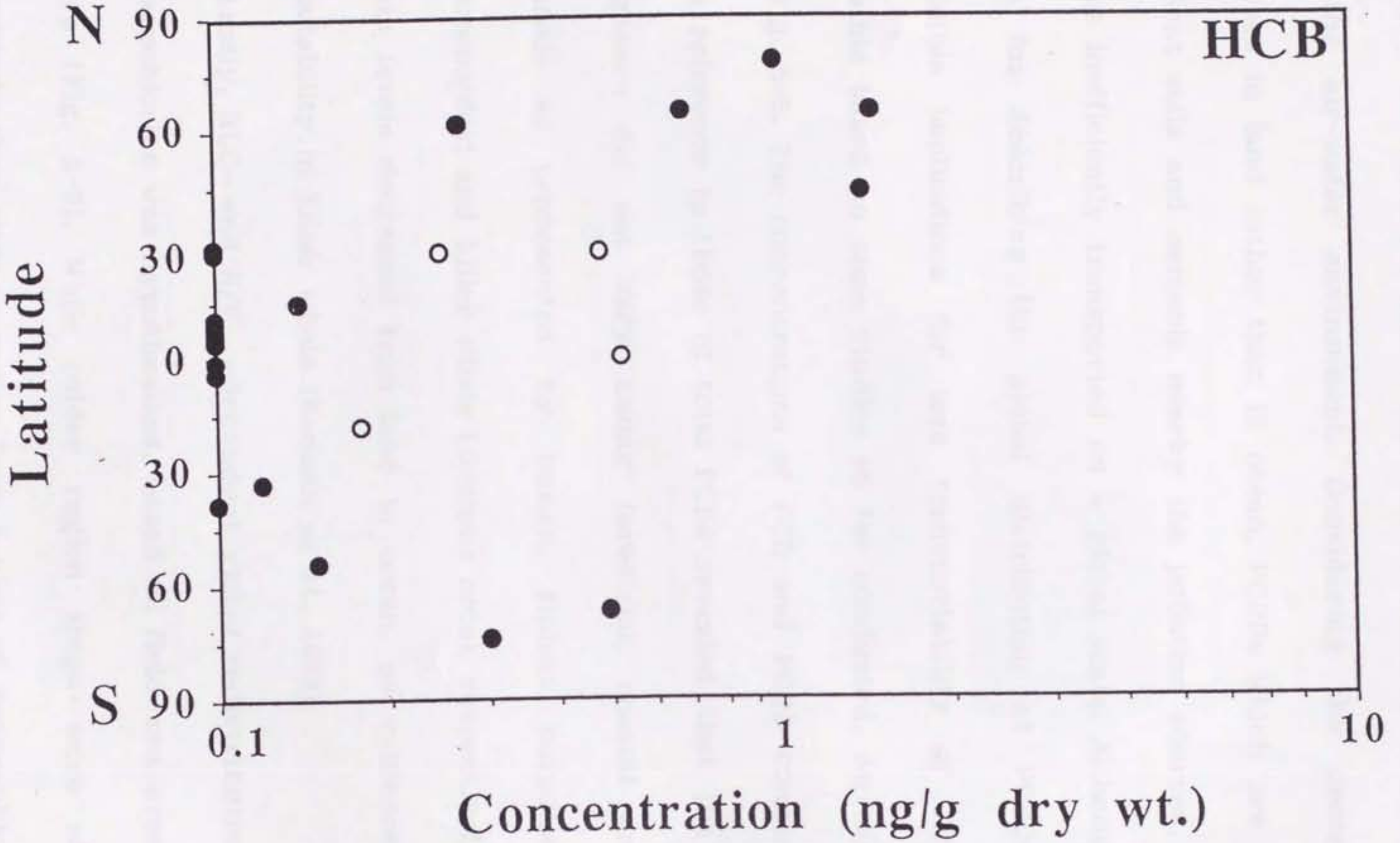

Fig. 5-4. Distribution of HCB concentrations in plants as a function of the latitude.

Open circles represent mountain sites.

Data are cited from Calamari *et al.* (1991).

are included in the lower range among OCs examined. Therefore, these compounds would be effectively adsorbed on lipophilic surfaces in the air-solid environment, while they will be possibly trapped in cold areas in the air-water environment. Considering the presence of PCDDs sources in land rather than in ocean, PCDDs which are intercepted by ambient soils and aerosols nearby the pollution sources, are forecasted to be inefficiently transported on a global scale. Although supplemental data for describing the global distribution of PCDDs are lacking, plausible implications for less transportability of PCDDs might be possible based on some studies so far conducted. An example is shown in Fig. 5-5. The concentrations of PCB and PCDD congeners normalized with reference to those of total PCBs revealed that the values of PCB congeners did not vary among terestrial, coastal and open ocean mammals as represented by human, finless porpoise (*Neophocoena phocoenoides*) and killer whale (*Orcinus orca*), respectively. However, the dioxin levels decreased from land to ocean, as evidenced by the non-detectability in killer whale (Kannan *et al.*, 1989).

Lastly, HLC- and H/K_{ow}-dependent global redistribution (fate) of each organochlorine was hypothesized, based on field measurements presented above (Fig. 5-6). While colder region traps more efficiently these compounds than warmer region from a view of geographical features, the latitudinal effect for condensation is variable according to the molecular species. The inherent pattern of each organochlorine distribution

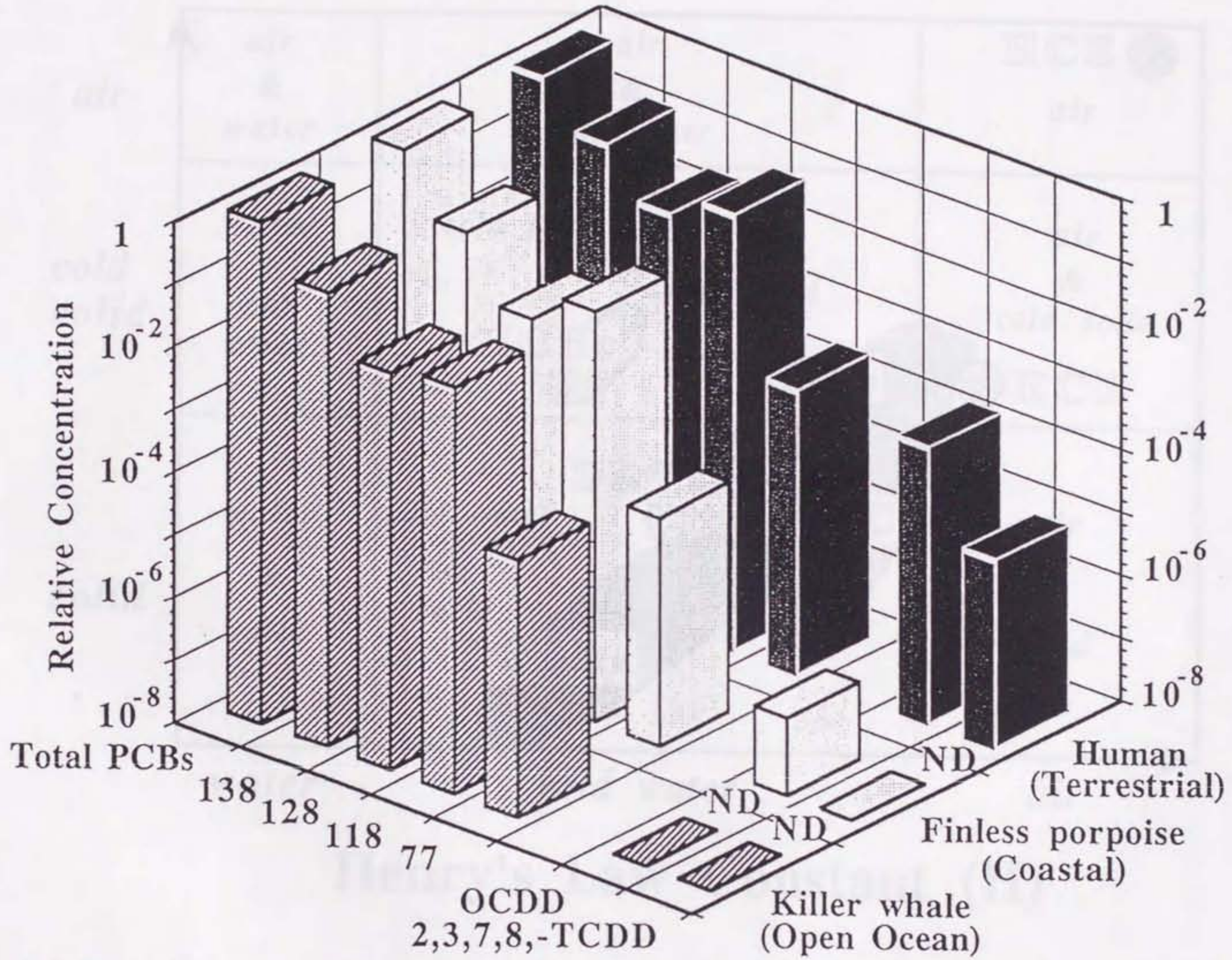

Fig. 5-5. Relative concentrations of PCB and PCDD congeners with reference to total PCBs in terrestrial, coastal and open ocean mammals.

Data are cited from Kannan *et al.* (1989).

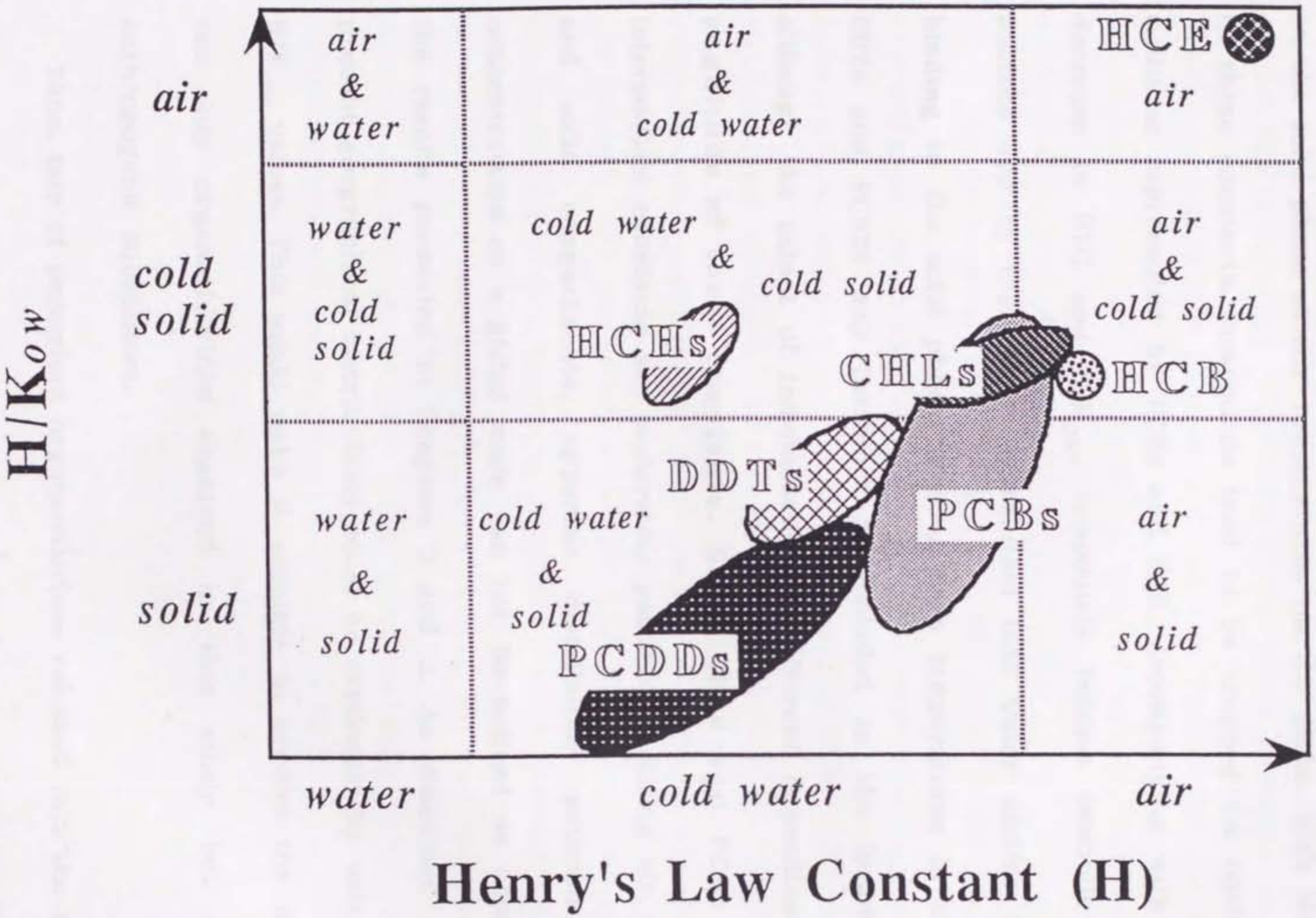

Fig. 5-6. Schematic representation of temperature-dependent redistribution of organochlorines on a global scale.

(behavior) would be regulated depending on the combination of HLC and H/K_{OW}. Persistent organochlorines with higher HLC and H/K_{OW} such as HCE are not effectively dissolved into surface water and not adsorbed on the solid phase at any temperatures on the globe. With the decrease in these constants, compounds tend to be trapped on colder surface media as represented by HCHs and HCB. Accompanying with a further decrease in HLC and H/K_{OW}, compounds become immobile from the sources due to the higher dissolution into water and/or the strong binding to the solid phase even at high temperatures in the tropics. DDTs and PCDDs may therefore be included in the immobile group, although the extent of immobilization is different depending upon the magnitude of these constants. Since CHLs and PCBs with the intermediate constants are moderately partitioned among air, cold water and solid compartments, apparent distribution patterns of their concentrations on a global scale can not be noticed as observed from the results presented in Chapters 1 and 3. As discussed above, the present geographical distributions could be explicable by using HLC and H/K_{OW} values. This would make it possible to predict the dynamics of not only organochlorines examined in this study but also other anthropogenic substances.

Thus, fate of persistent organochlorines released into the atmosphere from their sources would be latitudinally (temperature-dependently) redistributed according to their physico-chemical properties such as HLC and H/K_{OW}. Furthermore, dominance rate of water/solid surface (area proportion of ocean/land, aerosol density and precipitation intensity, etc) as geographical features may also affect their fate, as each function of the HLC and H/K_{OW} values for their global dynamics is different. Polar-ward winds also contribute to gather (fixate) the compounds with intermediate and low constants to colder regions more than those expected from their molecular diffusion.

It has been generally believed that the earth mixes and dilutes anthropogenic chemicals and leads them to a homogenous state. However, it requires a premise that molecular diffusion of these compounds can be well facilitated under any conditions on the globe. Persistent organochlorines dealt in this study except for HCE do not entirely fulfill the premise. The compounds like HCE with higher HLC and H/K_{OW} are mostly subjected to atmospheric diffusion. Organochlorines with such low to intermediate constants are redistributed to specifically designated regions (and/or compartments) on the heterogeneous world with latitudinal gradient temperatures.

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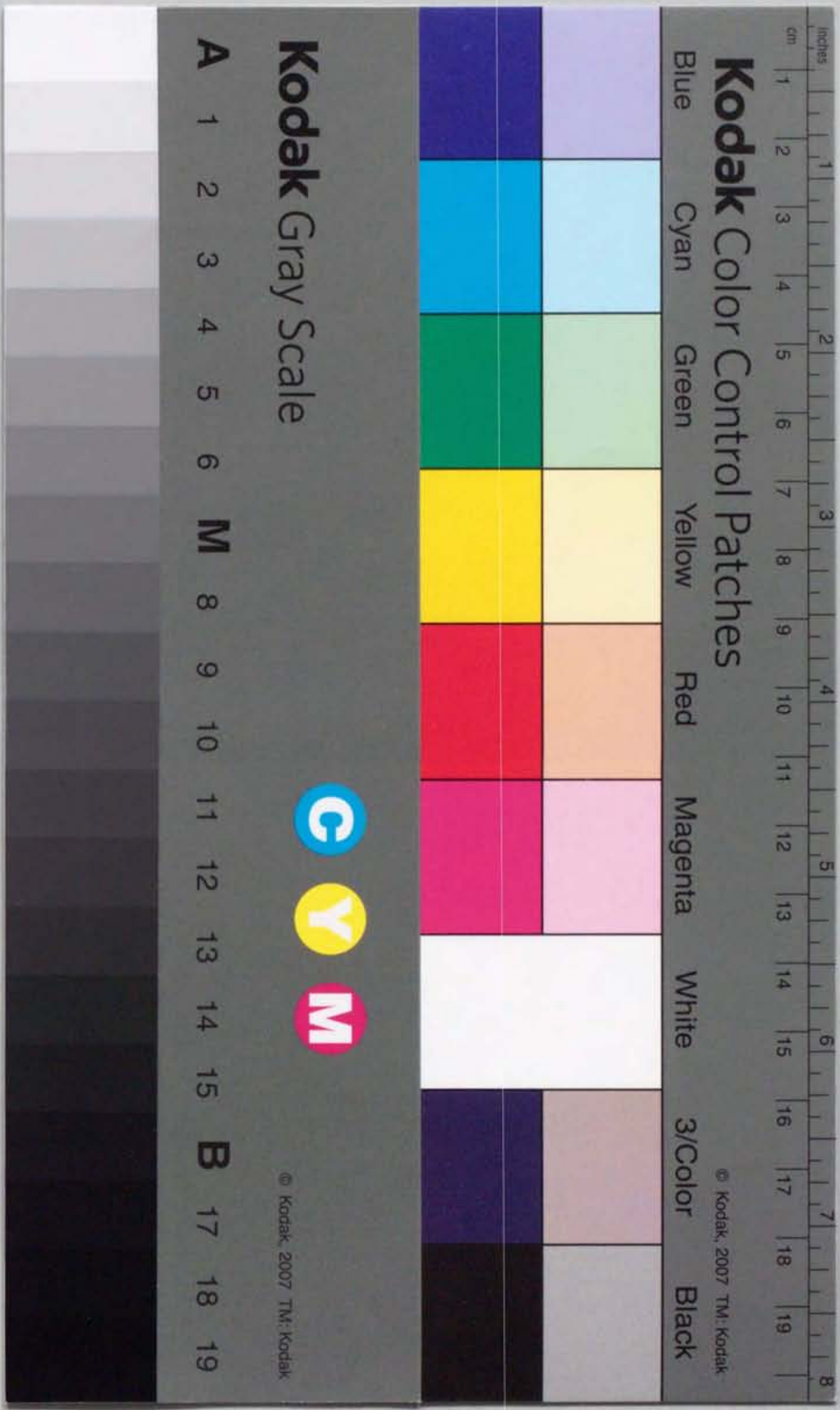
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