

Distribution of Persistent Organochlorines in the Oceanic Air and Surface Seawater and the Role of Ocean on Their Global Transport and Fate

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Concentrations of organochlorines such as hexachlorocyclohexanes (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 Hemisphere, 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 near tropical Asia. Chlordanes and PCBs exhibited rather uniform distributions in both the hemispheres. Estimations of fluxes by gas exchange across the air-water interface gave 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 the reports documented that these contaminants are transportable widely through atmosphere and eventually contaminated all over the world including polar regions (1-8). The concern about these organochlorines has also extended to the ecotoxicological context as to which of their residues poses a toxic threat to humans and wildlives, particularly marine mammals (9, 10). Among these findings and views, recent studies highlight the concern in the Arctic region where unexpectedly higher contamination by organochlorines were observed in air, seawater (8, 11), precipitation (12), plankton (13), and wild animals (14, 15). 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 the most-developed nations since the 1970s, their usage and disposal are still continuing or increasing in developing countries near tropical regions (16, 17). Although such a geographical transition in chemical usage is expected to affect the current status of global contamination, a worldwide survey of 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 (2, 18, 19). However, such a role of the oceans is 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 a smaller number of surveys in limited areas (20, 21), which still make the role of oceans on global transport and fate of persistent organochlorines disputable. 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 (22). 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), chlordanes (CHLs), and PCBs. Based on these data, their global distribution in the atmosphere and hydrosphere were described, and temporal variations of residue levels were also discussed by comparing them 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 Southern Ocean (Figure 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 V and VI, respectively, in the supplementary material.)

Preparation for Sampling. Polyurethane foam plugs (PUF, Model HA, Achilles Co. Ltd., Japan, diameter 31 mm, length 50 mm, density $20 \pm 1.6 \text{ kg/m}^3$) were used as adsorbents for collection of persistent organochlorines in the atmosphere. Smaller size PUFs (diameter 18 mm, length 50 mm) were used only in the Kagoshima-Maruru cruise (Figure 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 (2000 mL) for more than 7 days. During the Soxhlet cleaning, the acetone was changed four times. About 1500 mL of acetone in the fourth PUF cleaning was concentrated to 5 mL and used to check the contamination and interfering substances using high-resolution gas chromatograph ^{63}Ni electron capture detector (HRGC-ECD). The cleaned PUF plugs were immediately dried

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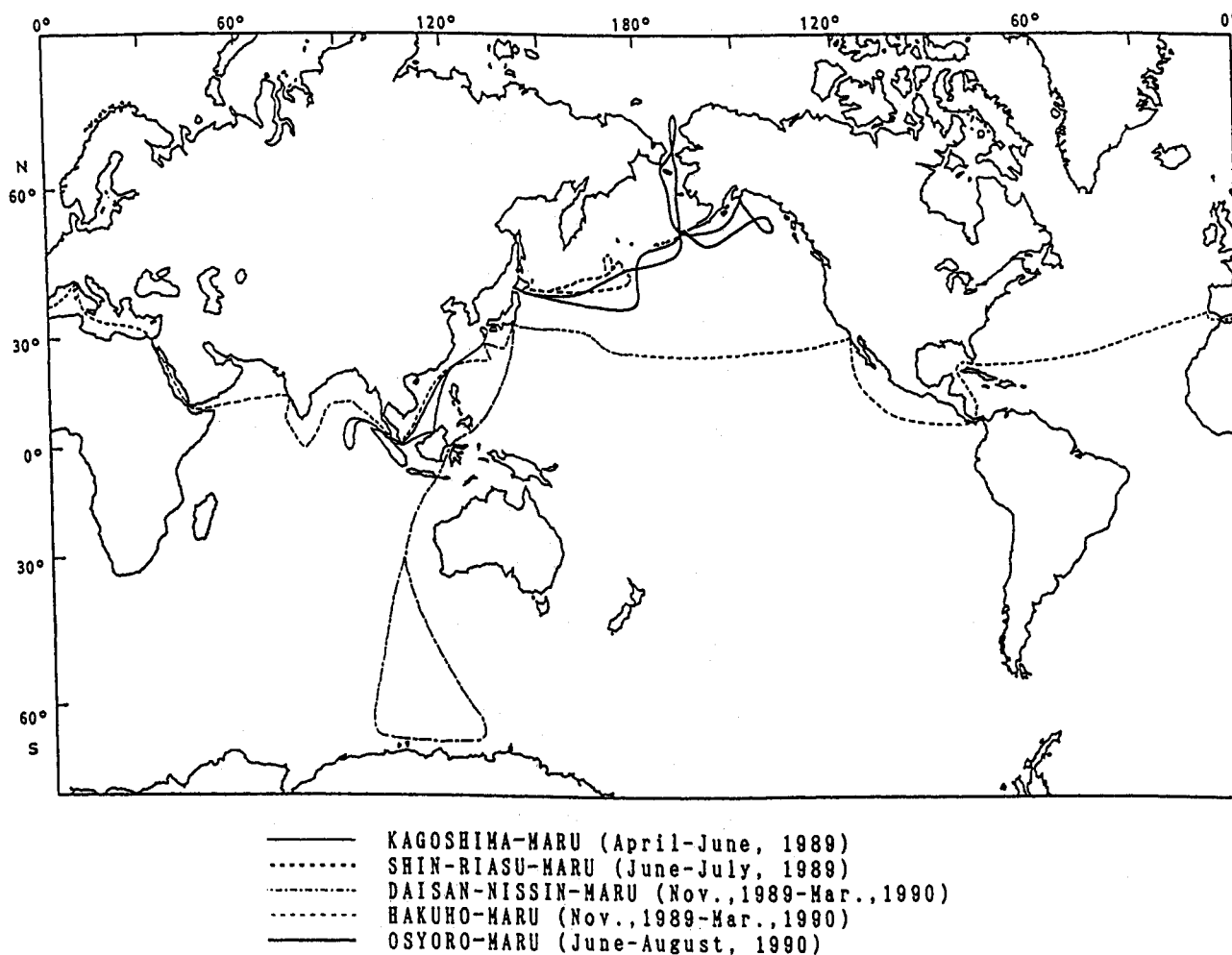


Figure 1. Survey cruise routes.

in a heated vacuum desiccator. If the PUF plugs were found to contain organochlorine residues or interfering 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 both ends and sealed in polyethylene bags until sampling. In the case of sampling by the Kagoshima-Maru cruise, three small PUFs were packed in a small glass column (i.d. 15 mm, length 200 mm).

Amberlite XAD-2 (styrene-divinylbenzene copolymer macroporous) resin as adsorbents of organochlorines in seawater was employed to enable the sampling of several hundred liters of water. Prior to use, it was thoroughly washed by shaking with water and then with ethanol. The further cleanup 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 coupling.

Sample Collection. Air sampling was performed on the upper deck of the 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, and the shelter was fixed using acrylic resin rope. Atmospheric collection was continued for 2 days per sample. About 100 m³ of air (flow rate 32–37 L/min) was passed through the PUF column. At the beginning and end of the sampling, the flow rate was checked using a flowmeter (Model RK1400, KOFLOC, KOJIMA Co. Ltd., Japan). The collection efficiency in

the present method, using a larger column, was preliminarily examined three times during the summer season in Japan (temperature 21.8–34.1 °C) to check the breakthrough of organochlorines. A sample of 500 ng of individual organochlorine pesticides and 5 µg of PCBs was spiked on the PUF and extracted by the same method used for samples, after 100 m³ of air was collected. Average adsorption efficiencies for 100 m³ 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 PUF, and hence the data collected during the Kagoshima-Maru cruise were omitted from the following consideration.

About 150–400 L of surface seawater was taken by pumping from a seawater faucet of each vessel. In some cases, a metal bucket was used for the water collection during the cruise in the northern North Pacific. However, results from both 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 on both ends and packed in polyethylene bags again. These samples were shipped to the laboratory and stored below –20 °C until analysis.

Chemical Analysis. Organochlorines adsorbed on PUF were Soxhlet extracted using mixed solvents of 300 mL of acetone and 100 mL of hexane for 3 h. The extracts were microconcentrated by using a Kuderna–Danish (KD) concentrator and by passing a stream of nitrogen. Five

milliliters 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% 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 μ L and then subjected to further cleanup and fractionation of high-performance liquid chromatography (HPLC, LC-6A Series, Shimadzu Co. Ltd., Japan). A silica gel column packed with Simpack-SIL (i.e. 4.6 mm, length 250 mm, 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 cleanup of samples are 4.5, 4.5, and 2.5 mL, respectively. Eluates from the HPLC column were separated into four fractions. Hexachlorobenzene was eluted in the first fraction (1 mL) but not quantified in this work. The second fraction (3.5 mL) included PCB isomers and congeners and *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, and *trans*-nonachlor were contained in the third fraction (3.5 mL), and other pesticides examined were eluted in the fourth fraction (3.5 mL). 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 i.d. \times 30-m length) consisted of DB-1701 (J & W Scientific Co. Ltd., Folsom, CA, 14% cyanopropyl phenyl polysiloxane, 0.25- μ m bonded phase) for organochlorine pesticides and DB-1 (J & W Scientific Co. Ltd., Folsom, CA, 100% dimethylpolysiloxane, 0.25- μ m 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 the carrier (20–30 cm/s) and the make-up gas 60 mL/min, respectively. Injector temperature was kept at 200 °C or 250 °C, and the detector was maintained at 300 °C. Data on the chromatogram from HRGC-ECD were collected with an 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 (23).

Seven blanks for air samples and six for seawater samples were also analyzed. Procedural blanks, including adsorbent extraction, ranged from 0.05 to 1 pg/m³ (or pg/L in case of water) for organochlorine pesticides and from 0.01

to 0.1 pg/m³ (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, the loss of organochlorines through analytical procedure has also been checked by spiking about 5 ng of pesticides and 50 ng 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 are given in Tables I and II, 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 (Figure 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 Hemisphere. In the atmospheric samples, considerably higher concentrations over 10 ng/m³ 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 (1300 pg/m³) and East China (640 pg/m³) Seas and the northern North Pacific (28–1300 pg/m³). It should also be noted that the HCH contamination extends over the Atlantic Ocean, Mediterranean Sea, and polar regions. Regarding HCH residues in surface seawater (Table II and Figure 2), much higher concentrations, more than 1000 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 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 (8, 11). 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 (24) also found a similar 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 South China Sea (Figure 3). Particularly, 1000 pg/m³ of DDTs was found in an air sample from the Arabian Sea located off the west coast of India where DDT usage is still continuing for agriculture and vector control (25). It was apparent that DDT concentrations drastically decreased with distance from the point source areas.

CHL residues (sum of *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor) in atmosphere, as shown in Figure 4, were also higher in the Northern Hemisphere (<1.0–160 pg/m³) than in the Southern Hemisphere (<0.5–14 pg/m³). Considering the fact that the atmospheric dis-

Table I. Range and Mean Concentrations of Persistent Organochlorines (pg/m³) in Air from Various Seas and Oceans^a

| sampling location | α -HCH | γ -HCH | Σ HCHs | <i>t</i> -chlor | <i>c</i> -chlor | <i>t</i> -nona | Σ CHLs | <i>p,p'</i> -DDE | <i>o,p'</i> -DDT | <i>p,p'</i> -DDT | Σ DDTs | Σ PCBs |
|---|---------------|---------------|---------------|-----------------|-----------------|----------------|---------------|------------------|------------------|------------------|---------------|---------------|
| Chukchi Sea (<i>n</i> = 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 (<i>n</i> = 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 (<i>n</i> = 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 |
| Northern North Pacific (<i>n</i> = 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 |
| North Pacific (<i>n</i> = 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 (<i>n</i> = 1) | | | | | | | | | | | | |
| mean | 96 | 27 | 120 | 1.4 | 0.3 | 0.2 | 1.9 | 6.4 | 2.1 | 4.6 | 13 | 320 |
| range | 61 | 16 | 78 | <0.5 | <0.3 | <0.2 | <1.0 | 9.1 | 17 | 22 | 48 | 160 |
| Gulf of Mexico (<i>n</i> = 1) | | | | | | | | | | | | |
| 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 (<i>n</i> = 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 |
| Red Sea (<i>n</i> = 1) | | | | | | | | | | | | |
| mean | 61 | 24 | 86 | 0.6 | <0.3 | <0.2 | 0.6 | 5.8 | 3.5 | 6.8 | 16 | 250 |
| East China Sea (<i>n</i> = 1 for HCHs, <i>n</i> = 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 (<i>n</i> = 1 for HCHs, <i>n</i> = 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 |
| Strait of Malacca (<i>n</i> = 1) | | | | | | | | | | | | |
| mean | ND | ND | ND | 7.3 | 8.5 | 4.0 | 20 | 180 | 180 | 220 | 580 | 30 |
| range | 95 | 23 | 120 | 3.3 | 2.8 | 1.8 | 7.9 | 0.7 | 13 | 23 | 37 | 22 |
| Celebes Sea (<i>n</i> = 1) | | | | | | | | | | | | |
| mean | 56 | 19 | 75 | 1.2 | 1.3 | 1.4 | 3.9 | 1.5 | 14 | 23 | 39 | 36 |
| range | | | | | | | | | | | | |
| Java Sea (<i>n</i> = 1) | | | | | | | | | | | | |
| 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 |
| Bay of Bengal and Arabian Sea (<i>n</i> = 5 for HCHs, <i>n</i> = 7 for others) | | | | | | | | | | | | |
| 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 |
| Eastern Indian Ocean (<i>n</i> = 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 |
| Southern Ocean (<i>n</i> = 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 |

^a *t*-chlor = *trans*-chlordane; *c*-chlor = *cis*-chlordane; *t*-nona = *trans*-nonachlor. Values below detection limit are calculated as zero for arithmetic means. ND = not determined.

tribution 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 levels 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 Figure 7) in the atmosphere showed higher levels in the Northern Hemisphere and smaller difference between both the hemispheres in the

surface seawater (Figure 5). In comparing the PCB concentrations in the North Pacific (12-390 pg/m³) and in the North Atlantic (72-600 pg/m³), samples revealed more than two times higher levels on an average in the atmospheric samples (Table I). A recent study using aircraft reported 265 pg/m³ of PCBs in Bermuda (26), which is comparable to our data. There have also been recent reports about PCB contaminations in open ocean water samples. For example, 7 pg/L of mean PCB residues (quantified as Arochlor 1254) was detected in the seawater from the Arctic Ocean in 1986 (8). Our samples from the Chukchi Sea contained 8.4 pg/L of PCBs as the mean values of the sum of isomers and congeners. Moreover

Table II. Range and Mean Concentrations of Persistent Organochlorines (pg/L) in Surface Seawater from Various Seas and Oceans^a

| sampling location | α -HCH | γ -HCH | Σ HCHs | <i>t</i> -chlor | <i>c</i> -chlor | <i>t</i> -nona | Σ CHLs | <i>p,p'</i> -DDE | <i>o,p'</i> -DDT | <i>p,p'</i> -DDT | Σ DDTs | Σ PCBs |
|---|---------------|---------------|---------------|-----------------|-----------------|----------------|---------------|------------------|------------------|------------------|---------------|---------------|
| Chukchi Sea (<i>n</i> = 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 (<i>n</i> = 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 (<i>n</i> = 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 |
| Northern North Pacific (<i>n</i> = 12) | | | | | | | | | | | | |
| mean | 870 | 170 | 1000 | 2.9 | 3.9 | 1.3 | 8.3 | 1.0 | 0.3 | 1.4 | 2.5 | 14 |
| range | 330-1400 | 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 |
| North Pacific (<i>n</i> = 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 (<i>n</i> = 1) | 180 | 36 | 220 | 2.8 | 2.1 | 1.1 | 6.0 | 0.5 | 0.8 | 2.6 | 3.9 | 18 |
| Gulf of Mexico (<i>n</i> = 1) | 44 | 14 | 58 | 5.6 | 2.6 | 1.0 | 9.2 | 0.3 | 0.6 | 1.4 | 2.2 | 16 |
| North Atlantic (<i>n</i> = 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 (<i>n</i> = 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 |
| Red Sea (<i>n</i> = 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 (<i>n</i> = 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 (<i>n</i> = 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 |
| Strait of Malacca (<i>n</i> = 1) | 360 | 120 | 480 | 2.6 | 5.0 | 1.8 | 9.4 | 0.9 | 2.6 | 2.9 | 6.4 | 20 |
| Celebes Sea (<i>n</i> = 1) | 240 | 43 | 280 | 1.0 | 2.5 | 1.6 | 5.1 | 1.0 | 0.5 | 1.1 | 2.6 | 20 |
| Java Sea (<i>n</i> = 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 (<i>n</i> = 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 |
| Eastern Indian Ocean (<i>n</i> = 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 (<i>n</i> = 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 |

^a *t*-chlor = *trans*-chlordane; *c*-chlor = *cis*-chlordane; *t*-nona = *trans*-nonachlor. Values below detection limit are calculated as zero for arithmetic means.

Schultz et al. (27) also found that the PCB residues in the North Atlantic surface water (10-250 m depth) ranged from 6.6 to 21 pg/L, which was rather comparable to our data (21-29 pg/L) (Table II).

The present distribution of these organochlorines in the world's oceans suggested the drastic change of the contamination pattern during the last decade. There was a much higher contamination by organochlorines (HCHs, DDTs, and PCBs) in the mid-latitude ocean of the Northern Hemisphere until the 1980s, reflecting the large amount of organochlorine usage in the developed countries such as Japan, Europe, and the U.S. (6, 28). However, such a pattern was not seen in the present status of their contamination (Figures 2-5). 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 (2) predicted the

transition of the major usage area for DDTs from the developed to the developing countries as the so-called "southward tilt". In fact, some tropical Asian countries, for example, India, are still using HCHs and DDTs in large quantities as insecticides for mosquito control and against crop pests (29, 30). The amount of annual usage in India was estimated to be about 47 000 tons for HCHs and 20 000 tons for DDTs (25). Much higher concentrations, more than 100 ng/m³, of HCHs and DDTs have been reported in urban air from new Dehli (29) and in rural air from south India (30). Moreover, Wolfe et al. (31) reported the extensive usage of HCHs and DDTs in China, even though this country had officially ceased the production of these contaminants in March 1983. According to a study over the Arabian Sea in 1976-1977 (32), HCH residue levels in the air exceeded more than 1 ng/m³, and *p,p'*-DDT concentrations ranged from 4.7 to 580

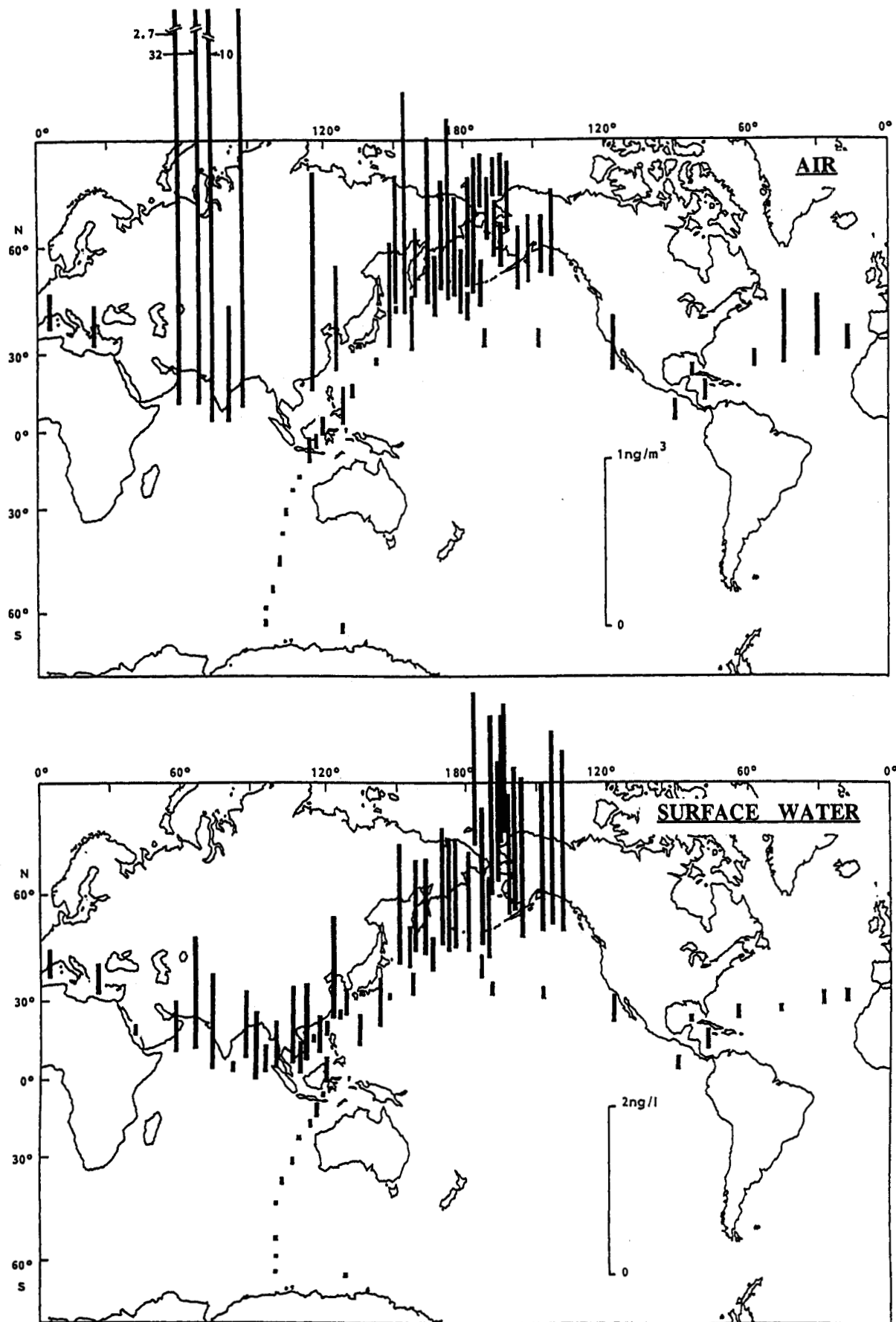


Figure 2. Distribution of HCH (sum of α - and γ -isomers) concentrations in air and surface seawater (1989–1990).

pg/m^3 . These values are quite close to the present residue levels in the Bay of Bengal and the 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 is still continuing in some countries near the northern Indian Ocean since the 1970s. On the contrary, the levels of DDTs in air over

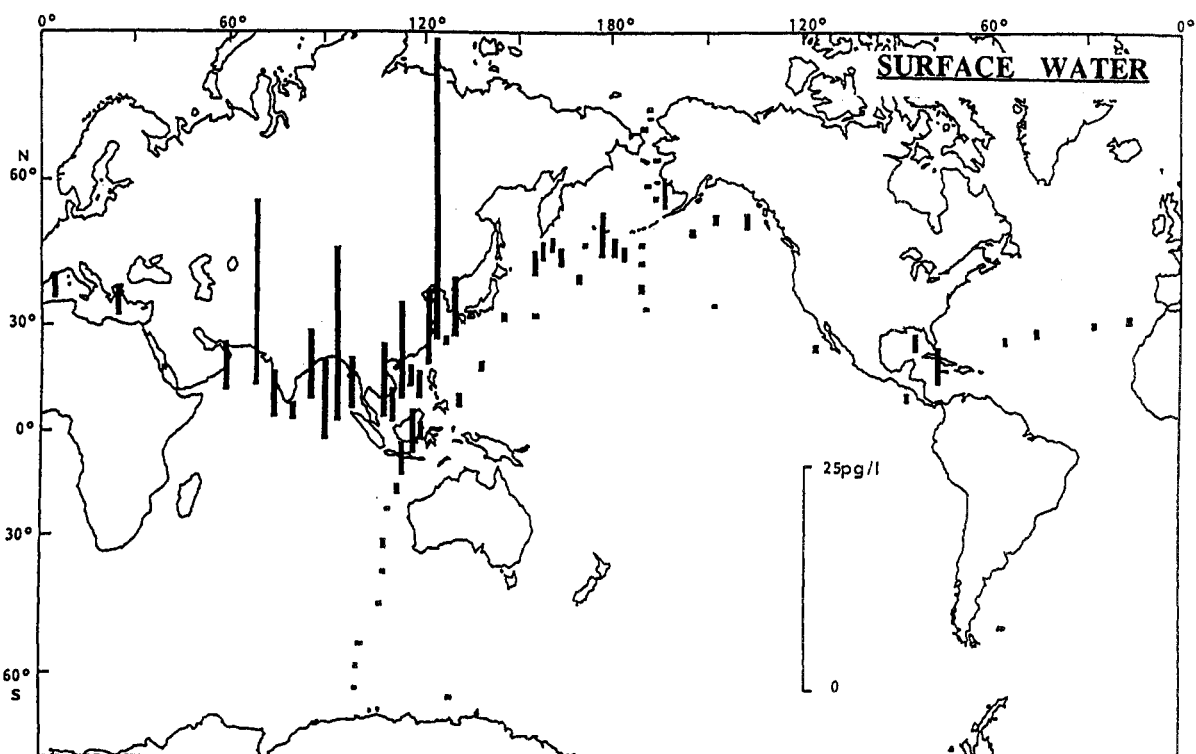
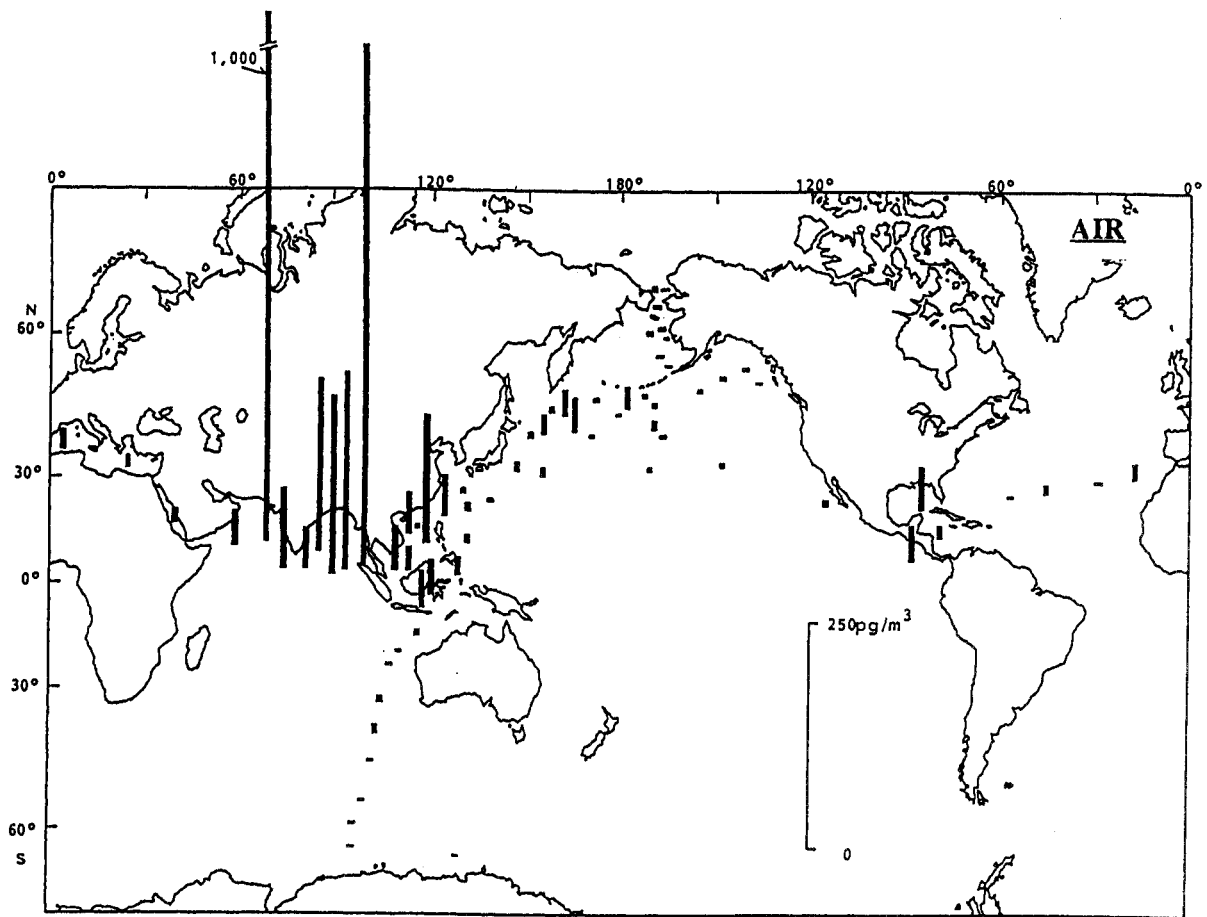


Figure 3. Distribution of DDT (sum of *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT) concentrations in air and surface seawater (1989–1990).

the eastern Indian Ocean and the Southern Ocean are much lower than those found by Tanabe et al. (6) 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 suggests

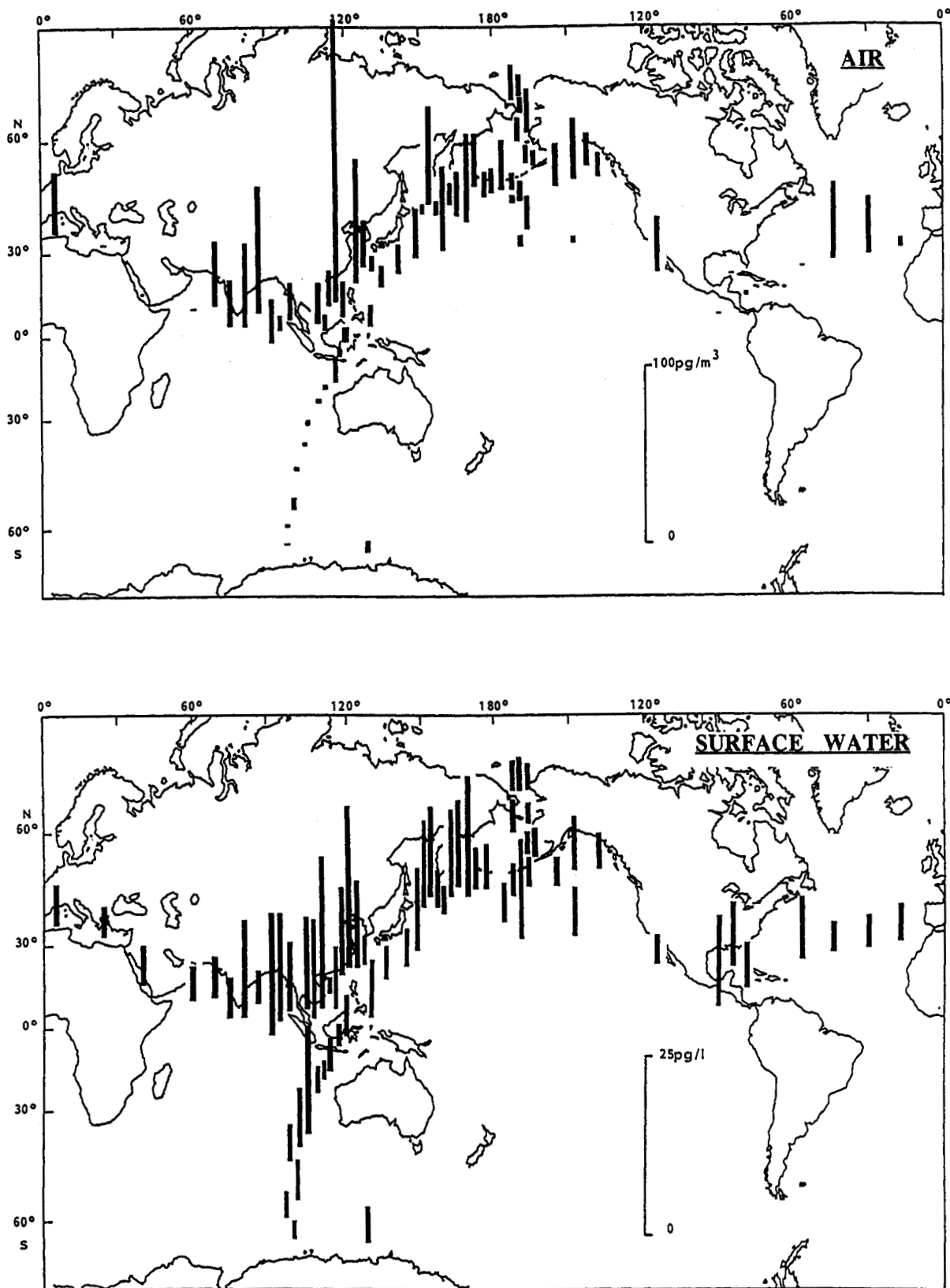


Figure 4. Distribution of CHL (sum of *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor) concentrations in air and surface seawater (1989–1990).

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 tropical Asia is a significant emission source of persistent organochlorines on global contamination.

Besides HCHs and DDTs, more than 70 000 tons of CHLs has been produced in the U.S. between 1960 and 1988 (33) and has been used to control termites and other

pests and as a wood preservative in freight containers (34). A significant quantity of this pesticide has been exported to Japan and other nations. Although its use has been stopped in the U.S. and Japan in recent years, continuous consumption in some other countries is suspected (33). Similar to other organochlorines, CHLs are also known as worldwide contaminants, as evidenced by their detection in the Arctic and Antarctic samples (34, 35). However,

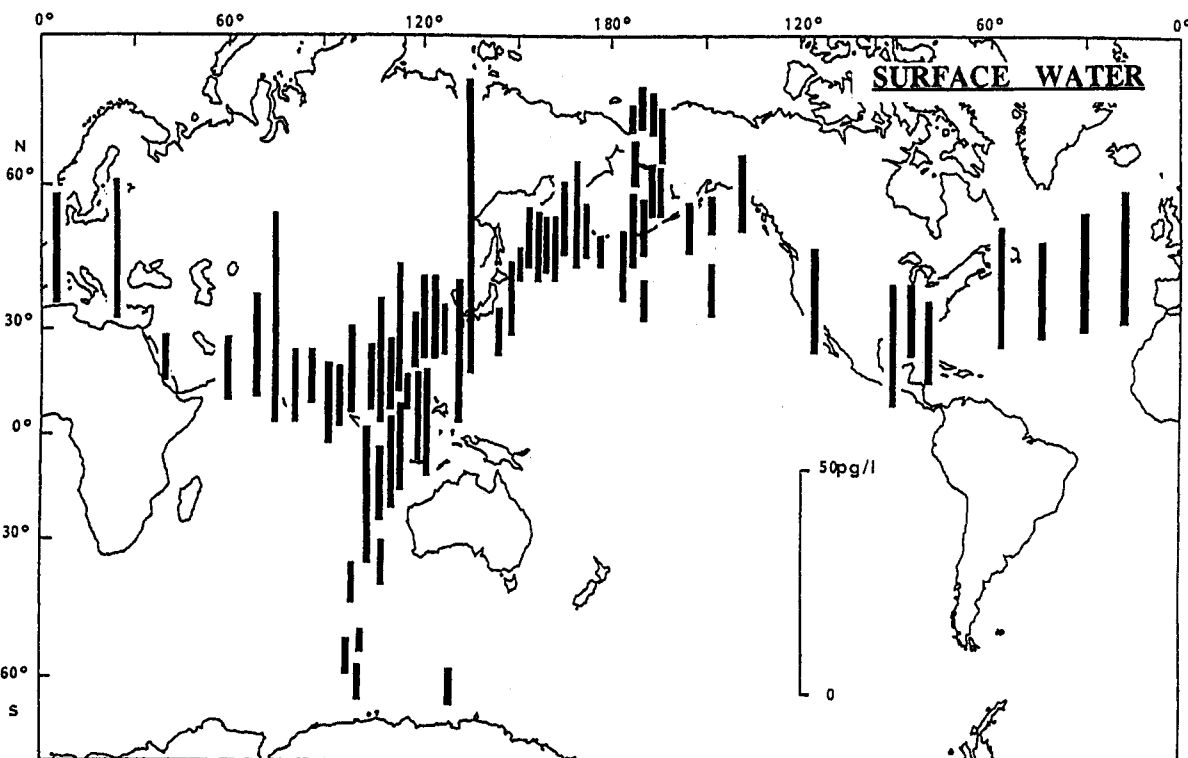
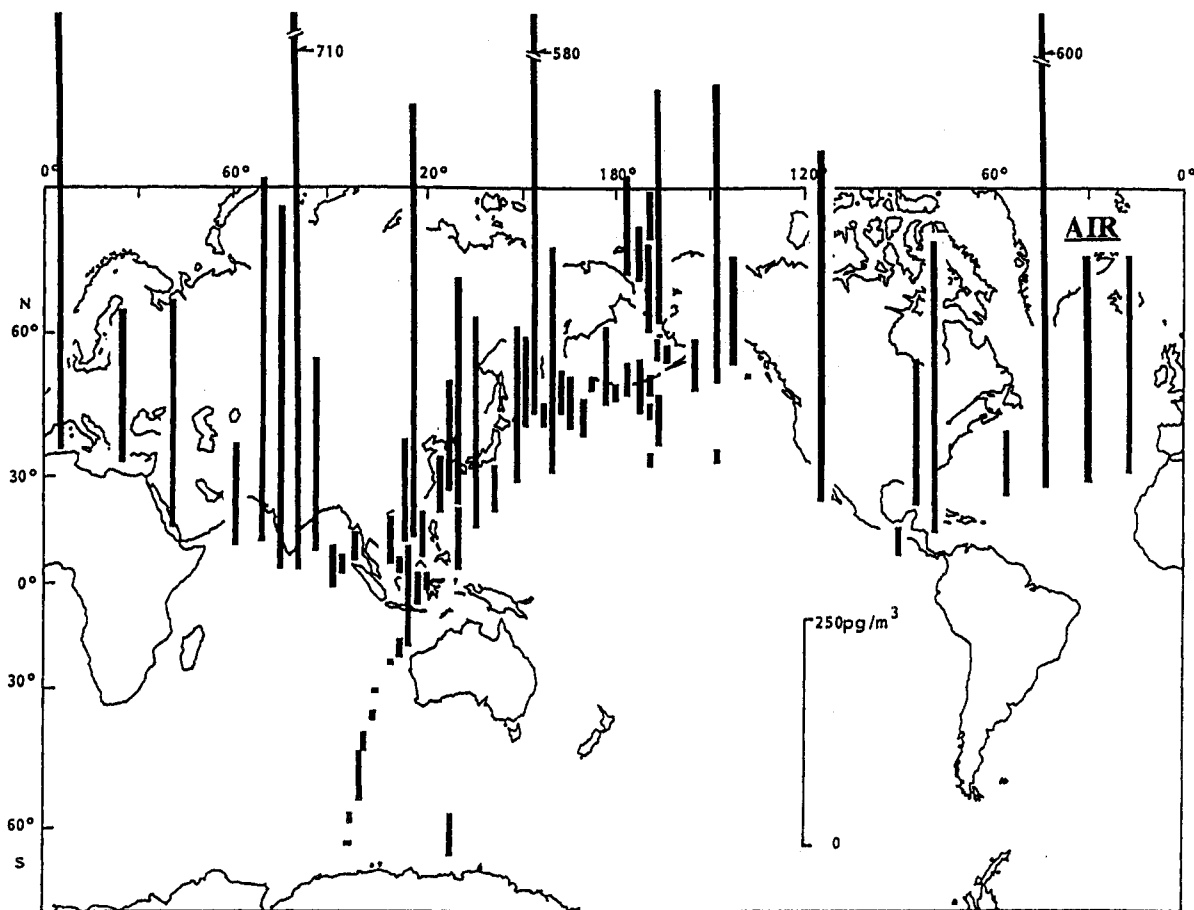


Figure 5. Distribution of PCB concentrations in air and surface seawater (1989-1990).

little is known about their distribution in the tropical marine environment. In the present atmospheric distribution of CHL concentrations (Figure 4), smaller geo-

graphical variation in the Northern Hemisphere may suggest the expansion of their point source areas of contamination including the tropical developing countries.

Table III. Concentration Ratios of HCHs and CHLs in Atmospheric Samples from Various Seas and Oceans^a

| sampling location | α/γ | N/C | sampling location | α/γ | N/C |
|-------------------------|-----------------|-----------|-------------------------------|-----------------|-----------|
| Chukchi Sea | | | Mediterranean | | |
| <i>n</i> | 2 | 2 | <i>n</i> | 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 | | |
| <i>n</i> | 5 | 5 | <i>n</i> | 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 | | |
| <i>n</i> | 4 | 4 | <i>n</i> | 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 |
| Northern North Pacific | | | Bay of Bengal and Arabian Sea | | |
| <i>n</i> | 14 | 14 | <i>n</i> | 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 |
| North Pacific (coastal) | | | Eastern Indian Ocean | | |
| <i>n</i> | 7 | 6 | <i>n</i> | 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 |
| North Pacific (central) | | | Southern Ocean | | |
| <i>n</i> | 2 | 2 | <i>n</i> | 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 |
| North Atlantic | | | | | |
| <i>n</i> | 4 | 3 | | | |
| mean | 3.6 | 0.60 | | | |
| range | 2.0-6.2 | 0.15-1.2 | | | |
| SD | 1.9 | 0.54 | | | |

^a α/γ = α -HCH/ γ -HCH; N/C = *trans*-nonachlor/*trans*-chlordane; *n* = number of samples; mean = sum of ratios for individual samples divided by number of samples; SD = standard deviation.

The fact that CHL concentrations in the Bay of Bengal and the Arabian Sea in the present study (ranging from <1.0 to 69 pg/m³) were found to be several times higher than those in 1976-1977 (32) is likely to support the southward expansion of CHLs usage on a 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 (28). However, such a pattern was rather unified during the last decade, which was evidenced with a smaller variation of PCB residue levels over all the oceans surveyed (Figure 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 (9) 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 the recent decade.

Regarding the previous survey of atmospheric PCBs, Bidleman et al. (36) reported the mean concentrations of 115 and 57 pg/m³ of PCBs (as Arochlor 1254) over Barbados and Bermuda in 1977-1978, 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/m³ on the average). Moreover, in the North Pacific, mean PCB levels in the atmosphere were found to be 540 pg/m³ in 1979 (5), 250 pg/m³ in 1980-1981 (37), and 130 pg/m³ in 1989 (present study). Despite the small number

of samples, it is apparent that atmospheric PCB concentrations over the ocean are not decreasing rapidly since the 1980s.

Composition of Residues. Beside the residue concentrations, the composition of organochlorines and their related compounds such as isomers and metabolites could be used as complementary and available tools to understand the emission source areas of global contamination. As shown in some literature (38-42), 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 the 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 concentrations of γ -HCH in almost all the air samples (Table I), the ratios (α/γ) were apparently different according to the seas and oceans (Table III). In general, lower α/γ ratios were observed in the South China Sea, Mediterranean Sea, North Atlantic, and Southern Hemisphere. The observed lower ratio may indicate the presence of a possible sporadic emission source of lindane nearby these seas and oceans. According to the earlier survey conducted in 1980, Tanabe et al. (7) 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 significant than the previous survey. The

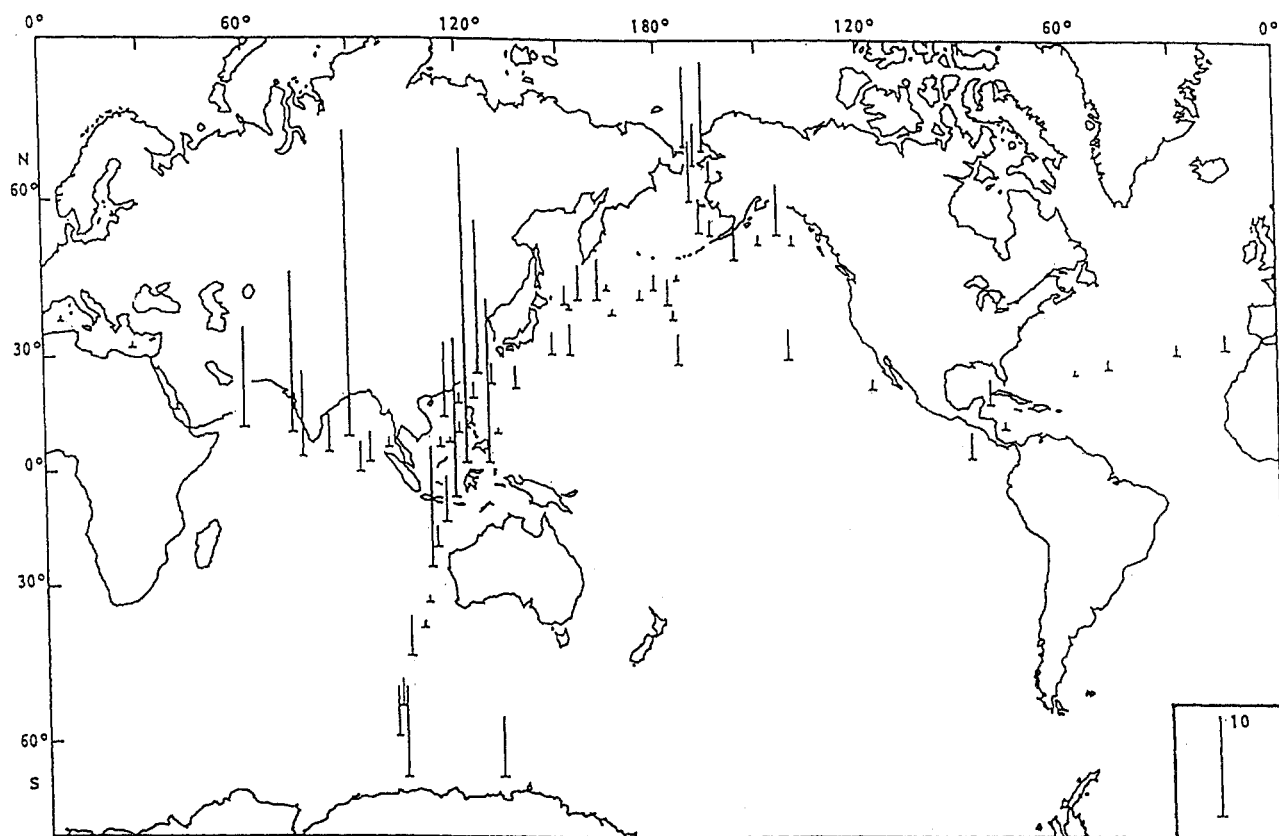


Figure 6. Distribution of the concentration ratios of p,p' -DDT/ p,p' -DDE in air (1989–1990).

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, and northern and central part of North Pacific (Table III), similar to those reported from summer to fall over the Canadian Arctic atmosphere (11). An extraordinarily high α/γ ratio was also found in the northern North Pacific ($\alpha/\gamma = 40$). The same phenomena has also been recorded in the Norwegian Arctic air during the summer season (38–41). Such a high ratio cannot be explained by the effect arising out of the usage of technical formulation which consists of 60–70% α -, 5–12% β -, and 10–15% γ -HCH and other minor isomers (43). Hence, the photochemical transformation of γ - to α -isomer in the atmosphere has been given as one of the plausible explanations (40, 41). Significant isomerization of the solid γ -isomer into the α -isomer has been experimentally demonstrated under conditions in the presence of ferrous salts and sunlight (44). If γ -HCH significantly isomerizes into α -HCH under natural conditions, a specific higher proportion of the 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 the Arctic and nearby northern oceans because the higher ratio was also observed in the central North Pacific (Table III). 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 with 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 near India and southeast Asian countries (Figure 6). This result also indicates the presence of a significant source of DDT in tropical Asia 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 contamination sources like the 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 UV light and the metabolism by organisms during the atmospheric transport (42). 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 physicochemical properties.

A previous study in 1980–1981 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 (6). A higher proportion of p,p' -DDT implies the worldwide usage of this insecticide until the early 1980s. The present results, showing a 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 the atmosphere. This result may suggest the DDT usage in some high latitudinal countries near polar regions. In fact, Bidleman et al. (45) detected a maximum 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 (46) 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. (47) also noted the higher proportion of p,p' -DDT

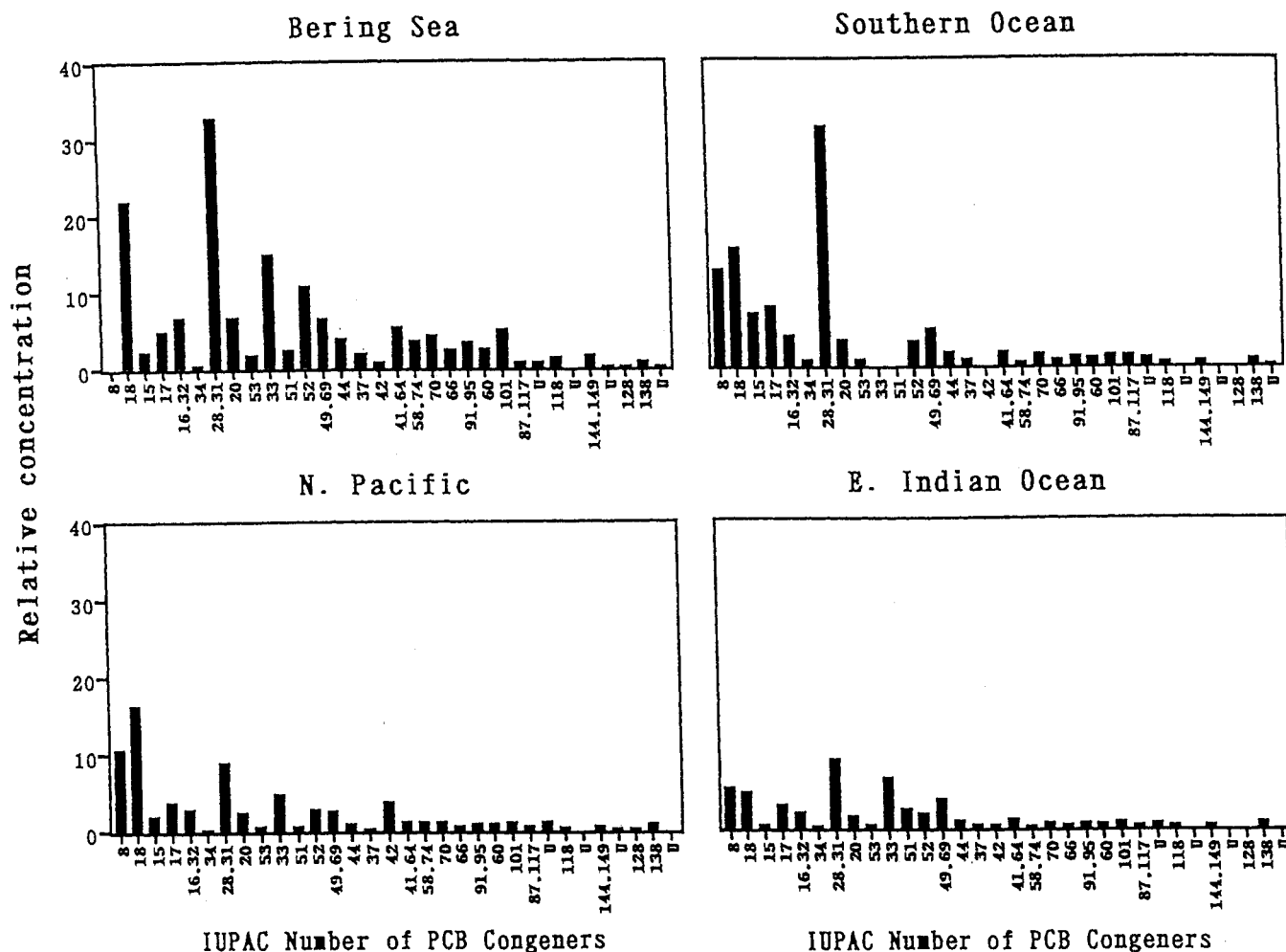


Figure 7. Relative concentrations of PCB isomers and congeners in open ocean atmosphere. Concentration of IUPAC no. 138 was defined as 1.0. Upper and lower figures represent higher and lower latitude areas, respectively. U means the PCB peaks with no IUPAC number.

and suggested the continuous supply of DDT to the Northwestern Territories in the 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 the 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, a recent report suggests that DDT is still being used for limited agricultural purposes in some Australian states (48). 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 (49).

As suggested from the distribution of CHL concentrations (Figure 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 (50). 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 III, 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 North 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, the U.S., 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 the above possible sources. Some authors also pointed out the higher ratios of N/C in remote areas like the Canadian Arctic (11, 51). Although they believed that the higher N/C ratios were related to the preferential depletion of *trans*-chlordane, a 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 (52, 53). 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 physicochemical properties. According to the isomer-specific analysis of PCBs in atmosphere, high latitude oceans such as the Bering Sea and Southern Ocean revealed a relatively larger proportion of less chlorinated members when compared to those in mid and low latitude waters such as the North Pacific and eastern Indian Ocean (Figure 7). PCB compositions in the open ocean atmosphere have been determined by some authors, and it is rather common for them to largely contain the less chlorinated members (5, 54). However, to our knowledge, this is the first report to note that PCB compositions in

oceanic atmosphere are different between high and low latitude. These 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 section.

Role of Oceans on 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 (55) and has been applied to estimate the mass transfer of many substances, including persistent organochlorines (56–61). Flux of contaminants (F) by gas exchange between air and water is expressed as (62)

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

where $C_{diss,w}$ and C_g are the dissolved solute concentration in water (pg/L) and the gas-phase concentration in air (pg/m³), respectively. Organochlorine concentrations in air and seawater simultaneously collected at each sampling point were only used for this calculation. Using eq 1, a plus (+) value of F indicates the tendency of contaminant transfer from water to air. On the contrary, a minus (–) value of F means the leaning of contaminants in air, and hence, they tend to flow toward the water phase from atmosphere. T is the absolute temperature (K) at the air–water interface, R is the universal gas constant (Pa m³ mol^{–1} K^{–1}), and K_{ol} is the overall mass transfer coefficient (m/s). H is the Henry's law constant (HLC, Pa m³ 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 equations (61):

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

$k_g =$

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

$k_l =$

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

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 \times diffusivity), ranging from 1.8 to 2.2 for S_{cg} and from 800 to 1200 for S_{cl} in organic solutes (63). In this study, 2.0 for S_{cg} and 1000 for S_{cl} were used for all organochlorines examined. Wind speed was approximated to 7 m/s (>60° latitude), 5 m/s (20–60° latitude), and 3 m/s (0–20° latitude) at each latitude of the sampling site, referring to the wind velocity data during the cruises of Kagoshima–Maru and Osyoro–Maru (see Figure 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° latitude), 10 °C (40–60° latitude), 20 °C (20–40° latitude), and 30 °C (0–20° latitude) in each sampling site, which is based on the seasonal average water temperature in the Pacific Ocean from ref 64. Table IV presents the comparison of HLCs of organochlorines which have already been reported in other papers. These HLCs were mainly based on the

review by Suntio et al. (65), a combination of reported solubilities and vapor pressures (66–68), direct measurements (69–72) such as bubble stripping and wetted-wall column techniques, and the quantitative structure–property relationship models (73). The HLCs for HCHs (at 20–25 °C) were within 2–3 factors among these presented values. Kucklick et al. (72) 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 (65, 69) 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 (66, 70) 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. A recent study (35) which offered the vapor pressures and the water solubilities for CHLs allowed the calculation of their HLCs. The HLCs seem to be considerably close to the estimations and measurements by other authors, except for those by Atlas et al. (69). 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 number of chlorine substitutes. In this study, the most recent data by Dunnivant et al. (73) were used. The constants of all the organochlorines at diverse temperatures were obtained using the slope (m) of the following eq 5.

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

As for HCHs, the slopes determined by a recent study (72) were applied ($m = -2969$ for α -HCH and $m = -2703$ for γ -HCH). The slope ($m = -7868$) obtained for PCBs earlier (68) 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 $U_{10} = 5$ m/s are summarized in Table IV.

The fluxes were estimated in the different seas and oceans. In this process, the particle binding fraction of organochlorines was taken into consideration. Generally, atmospheric persistent organochlorines are distributed in both gas and aerosol phases, depending on the air temperature (74). 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 (22, 45, 75). Moreover, even under the condition of low temperature in the Arctic region, organochlorines in aerosol phase could not be detected (11). Taking these facts into account, 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 (19, 76, 77). However, the filtration of water samples was not carried

Table IV. Henry's Law Constants (HLC, Pa·m³/mol) and K_{ol} (m/day) for Organochlorines

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

^a Estimated under the conditions of T = 20 °C and U₁₀ = 5 m/s. ^b After ref 69. ^c Measurement using seawater. ^d After ref 65. ^e After ref 72. ^f Selected for flux estimation. ^g After ref 66. ^h After ref 70. ⁱ Isomer not specified. ^j Calculated from the subcooled liquid vapor pressure and the water solubility after ref 35. ^k After ref 67. ^l After ref 68. ^m After ref 71. ⁿ Including the HLC for other congener. ^o After ref 73. ^p NA = not available. ^q Represented with the HLC for one congener. ^r Averaged with the HLC for two congeners.

out in the present study because of the methodological difficulties in separating the dissolved and colloidal phases by conventional filtration and centrifugation (22, 76, 77). 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 eq 1) or adsorbed fraction (case 2, C_{diss,w} = 0 in eq 1). Cases 1 and 2 mean no binding and 100% binding to particles of organochlorines in water, respectively. The ranges of fluxes in both cases in seas and oceans surveyed are graphically presented in Figures 8–11. (The arithmetic mean and ranges of fluxes in both cases in seas and oceans surveyed are available in Table VII in the supplementary material.)

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 (Figure 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 av, -2500 ng m⁻² day⁻¹; case 2 av, -2600 ng m⁻² day⁻¹), East China Sea (-260 ng m⁻² day⁻¹; -270 ng m⁻² day⁻¹), and South China Sea (-350 ng m⁻² day⁻¹; -360 ng m⁻² day⁻¹), 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 (-56 ng m⁻² day⁻¹; -190 ng m⁻² day⁻¹), Bering Sea (-73 ng m⁻² day⁻¹; -220 ng m⁻² day⁻¹); Gulf of Alaska (-43 ng m⁻² day⁻¹; -190 ng m⁻² day⁻¹), and northern North Pacific (-150 ng m⁻² day⁻¹; -240 ng m⁻² day⁻¹).

It has already been indicated in recent studies that HCHs are removed rapidly from the inland water (72, 73) and agricultural fields (74) in the tropical region and emitted largely to the atmosphere. The present study suggests the active transfer of these atmospheric HCHs into the water phase of seas and oceans close to the tropical contamination source. If the 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 Figure 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 near coastal areas such as the Bay of Bengal, Arabian Sea (case 1 av, -33 ng m⁻² day⁻¹; case 2 av, -33 ng m⁻² day⁻¹), and

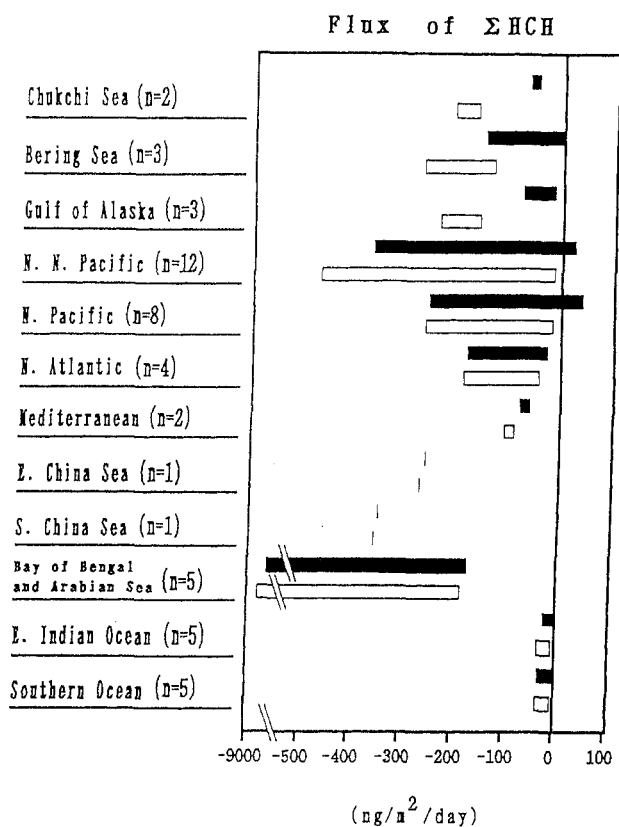


Figure 8. Fluxes by gas exchange of HCHs (sum of α - and γ -isomers) across the air-water interface in various seas and oceans. Figures in parentheses are the number of pairings for air and surface water samples. Length of a bar shows the range of flux. Solid and open bars represent the flux for cases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

South China Sea ($-7.8 \text{ ng m}^{-2} \text{ day}^{-1}$; $-9.1 \text{ ng m}^{-2} \text{ day}^{-1}$) (Figure 9). This also indicates that larger quantities of DDTs rapidly transfer into the water bodies near 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 the direction of the flux estimation for DDTs into account, it was noted that the concentrations of DDTs and HCHs in surface seawater surely depend on the concentration in the overlying air in all seas and oceans surveyed.

In the case of CHLs (Figure 10), apparently negative flux values were observed in high latitude waters like the Chukchi Sea (case 1 av, $-6.6 \text{ ng m}^{-2} \text{ day}^{-1}$, case 2 av, $-8.1 \text{ ng m}^{-2} \text{ day}^{-1}$), Bering Sea ($-6.2 \text{ ng m}^{-2} \text{ day}^{-1}$, $-8.0 \text{ ng m}^{-2} \text{ day}^{-1}$), Gulf of Alaska ($-4.7 \text{ ng m}^{-2} \text{ day}^{-1}$; $-7.4 \text{ ng m}^{-2} \text{ day}^{-1}$), and northern North Pacific ($-1.4 \text{ ng m}^{-2} \text{ day}^{-1}$; $-6.0 \text{ ng m}^{-2} \text{ day}^{-1}$), 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 positive and negative values, depending on the rate of particle and colloid binding fractions of CHLs (Figure 10). There are two possible scenarios to explain this result. First, one designates the case to present in the dissolved state for most of the CHLs

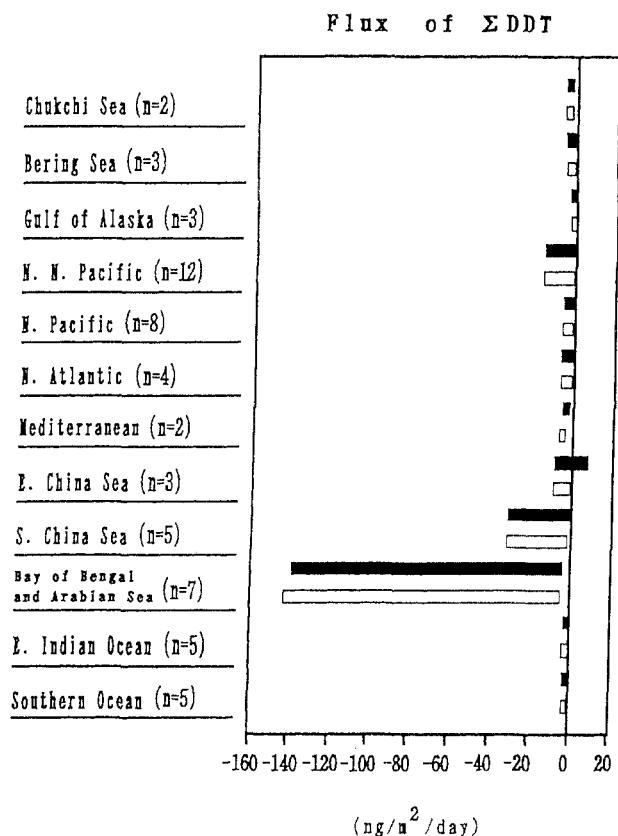


Figure 9. Fluxes by gas exchange of DDTs (sum of p,p' -DDE and p,p' -DDT) across the air-water interface in various seas and oceans. Symbols are the same as in Figure 8.

means volatilization of the organochlorines from the surface waters, which is graphically shown as case 1 in Figure 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 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 the next events as pointed out by Mackay et al. (66). Knap et al. (81) 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 to $0.32 \text{ ng m}^{-2} \text{ day}^{-1}$. In the present study, flux from seawater to air by gas exchange of CHLs (sum of *cis*- and *trans*-chlordane) was estimated to be $0.46 \text{ ng m}^{-2} \text{ day}^{-1}$ 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 be 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 is 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 environ-

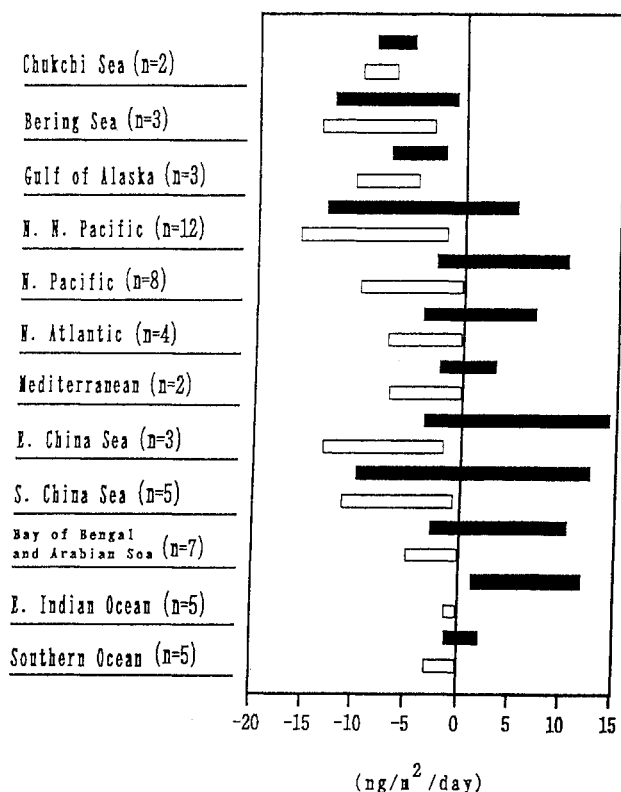
Flux of Σ CHL

Figure 10. Fluxes by gas exchange of CHLs (sum of *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor) across the air-water interface in various seas and oceans. Symbols are the same as in Figure 8.

ment is close to the equilibrium state of the gas exchange process. However, even if the results of a laboratory experiment (76) on the adsorption effect of aqueous hydrophobic organochlorines to microparticle are considered, the contribution of the microparticle to retain the organochlorines in ocean water seems to be quite small. Cotham and Bidleman (20) estimated the truly dissolved fraction of organochlorines in the Arctic Ocean using the three-phase (dissolved, macroparticle, and microparticle phases) equilibrium partitioning model (76, 77). 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 (the 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 the negative ones can be seen in higher latitudes (Figure 11). This result for PCBs may again lead to a similar conclusion with CHLs that the volatilization is in the tropical waters and the loading is 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 (Figure 12). In high latitude oceans such

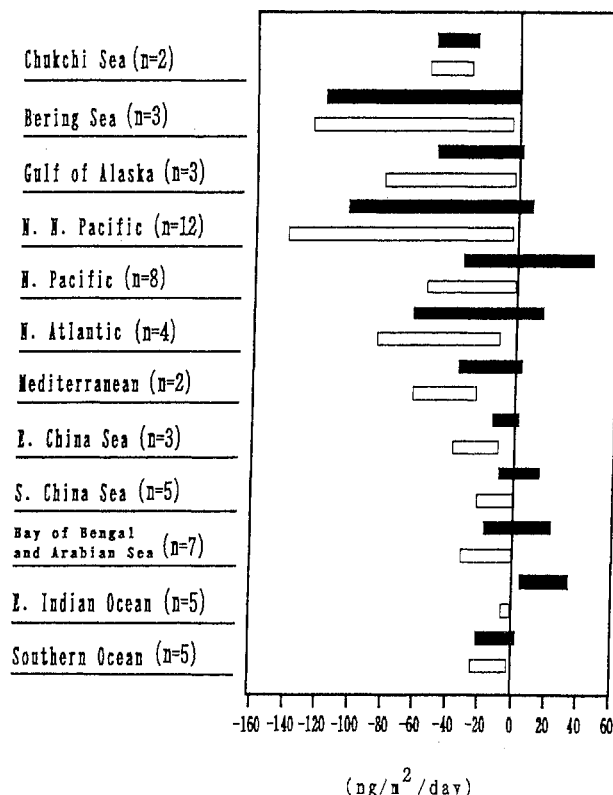
Flux of Σ PCB

Figure 11. Fluxes by gas exchange of PCBs across the air-water interface in various seas and oceans. Symbols are the same as in Figure 8.

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 a 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 transferable 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 Figure 7.

The above rule obtained in PCB isomers and congeners might also be the explanation for the different ratio of α - and γ -HCH between high and low latitude oceans. α -HCH has a two times higher HLC than γ -HCH (Table IV), which is considered to be more transportable through the ocean atmosphere. This may result in the higher α/γ ratio in the Arctic atmosphere than in the lower latitudes, when the HCH residues in cold waters 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 in a column (1 m²) of air (6300 m) and surface water (100 m). On the assumptions that HCHs are not in the equilibrium but in the steady state and that the gas exchange process is the main route of HCHs mobilization in the column, the temporal variation for HCH concentrations in the oceanic

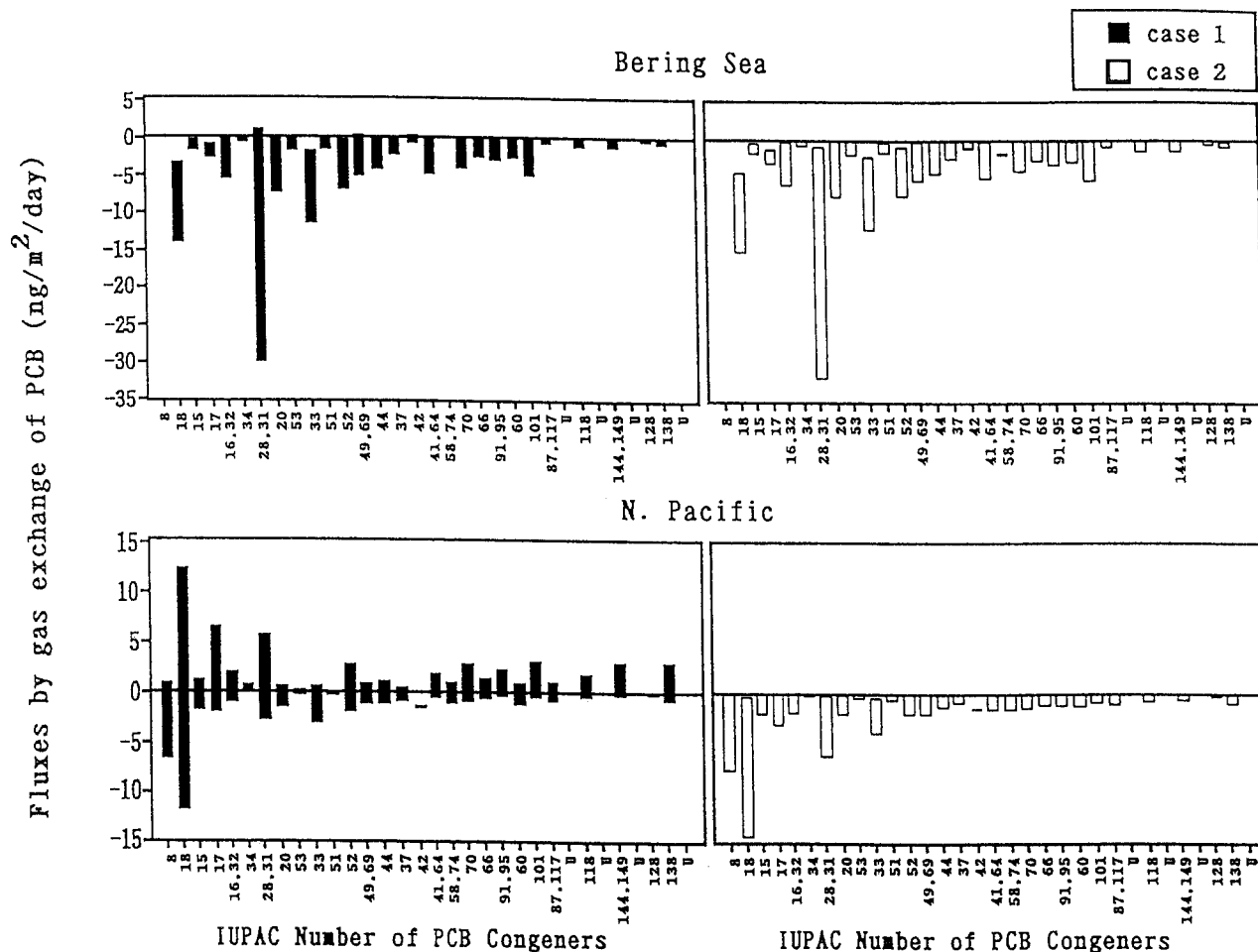


Figure 12. Fluxes by gas exchange of PCB isomers and congeners across the air-water interface in the Bering Sea and the North Pacific. U means the PCB peaks with no IUPAC number.

air and surface water can be expressed as follows:

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

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

Using these two equations and eq 1, $C_g(n)$ can be converted into eq 8:

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

where $a = 1 - K_{ol}/100 - (K_{ol}/6300)RT/H$ and the number in the parentheses means the exposure time after the air collection date. $C_g(0)$ (α -HCH, 5000 pg/m³; γ -HCH, 1000 pg/m³) and $C_{\text{diss,w}}(0)$ (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. HLCs and K_{ol} 's at 30 °C for HCH isomers calculated by the method mentioned above were given. The result shows that the atmospheric α/γ ratio [$C_g(n)$ for α -HCH/ $C_g(n)$ for γ -HCH] converges from 5.0 to 9.9 with an increase in the exposure time. In contrast with the air, the hydrospheric α/γ ratio almost remains constant (5.0). The time interval until closing with the equilibrium state (exceeds more than 9.8 of α/γ ratio) varies according to the prevailing wind speed, since K_{ol} depends on it. The interval resulted in 45 days under 10 m/s of wind speed, while showing 153 days under 3 m/s. This estimation by the simple model might give enough reliability to the hypothesis. If the higher α/γ ratios in remote oceanic atmosphere are explained by the preferential transport of the α -isomer from emission sources, a 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 (Figure 6 and Table III). 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 IV).

The 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 eqs 2-4, the most influential factor under possible hypothetical conditions seems to be U_{10} . For example, while K_{ol} 's under still-air conditions for PCB isomers and congeners range within only a factor of 1.5-3.0 with an increase of T from 0 to 30 °C, these values at 10 m/s are approximately 35 times greater than those at 0 m/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 CO₂ gas in high wind conditions was experimentally demonstrated by the application of tracer techniques (82).

Uncertainties in the magnitude of the HLCs for some organochlorines still remain possibilities 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. (69) (Table IV) 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 the ocean will be controlled by the concentrations in the underlying surface waters, and hence, the 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 nonpoint 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 Hemisphere. In the Northern Hemisphere, higher residue levels of HCHs and DDTs were observed in tropical Asia. In contrast to these patterns, the 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 near tropical Asia. CHLs and PCBs revealed a rather 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 the 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 are promptly absorbed in the water bodies near the 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 the 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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Supplementary Material Available

Table V containing details of air samples, Table VI containing details of surface seawater samples, and Table VII containing fluxes by gas exchange of organochlorines across the air-water interface in seas and oceans surveyed (11 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$22.00 for photocopy (\$24.00 foreign) or \$10.00 for microfiche (\$11.00 foreign), are required. Canadian residents should add 7% GST.

Literature Cited

- (1) Bidleman, T. F.; Olney, C. E. *Science* 1974, 183, 516–518.
- (2) Goldberg, E. D. *Proc. R. Soc. London, Ser. B* 1975, 189, 277–289.
- (3) Risebrough, R. W.; Walker, W., II; Schmidt, T. T.; de Lappe, B. W.; Connors, C. W. *Nature (London)* 1976, 264, 1098–1102.
- (4) Tanabe, S.; Tatsukawa, R. *J. Oceanogr. Soc. Jpn.* 1980, 36, 217–226.
- (5) Atlas, E.; Giam, C. S. *Science* 1981, 211, 163–165.
- (6) Tanabe, S.; Tatsukawa, R.; Kawano, M.; Hidaka, H. *J. Oceanogr. Soc. Jpn.* 1982, 38, 137–148.
- (7) Tanabe, S.; Hidaka, H.; Tatsukawa, R. *Chemosphere* 1983, 12, 277–288.
- (8) Hargrave, B. T.; Vass, W. P.; Erickson, P. E.; Fowler, B. R. *Tellus* 1988, 40B, 480–493.
- (9) Cummins, J. E. *Ecologist* 1988, 18, 193–195.
- (10) Tanabe, S. *Environ. Pollut.* 1988, 50, 5–28.
- (11) Patton, G. W.; Hinckley, D. A.; Walla, M. D.; Bidleman, T. F.; Hargrave, B. T. *Tellus* 1989, 40B, 480–493.
- (12) Gregor, D. J.; Gummer, W. D. *Environ. Sci. Technol.* 1989, 23, 561–565.
- (13) Bidleman, T. F.; Patton, G. W.; Walla, M. D.; Hargrave, B. T.; Vass, W. P.; Erickson, P.; Fowler, B.; Scott, V.; Gregor, D. J. *Arctic* 1989, 42, 307–313.
- (14) Norstrom, R. J.; Simon, M.; Muir, D. C. G.; Schweinsburg, R. E. *Environ. Sci. Technol.* 1988, 22, 1063–1071.
- (15) Muir, D. C. G.; Norstrom, R. J.; Simon, M. *Environ. Sci. Technol.* 1988, 22, 1071–1079.
- (16) Mowbray, D. L. *Ambio* 1986, 15, 22–29.
- (17) Forget, G. J. *Toxicol. Environ. Health* 1991, 32, 11–31.

- (18) Knap, A. H.; Binkley, K. S.; Deuser, W. G. *Nature* 1986, 319, 572-574.
- (19) Tanabe, S.; Tatsukawa, R. *J. Oceanogr. Soc. Jpn.* 1983, 39, 53-62.
- (20) Cotham, W. E., Jr.; Bidleman, T. F. *Chemosphere* 1991, 22, 165-188.
- (21) Kurtz, D. A.; Atlas, E. L. In *Long Range Transport of Pesticides*; Kurtz, D. A., Ed.; Lewis Publishers: Chelsea, MI, 1990; pp 143-160.
- (22) Baker, J. E.; Eisenreich, S. J. *Environ. Sci. Technol.* 1990, 24, 342-352.
- (23) Tanabe, S.; Tatsukawa, R.; Phillips, D. J. H. *Environ. Pollut.* 1987, 47, 41-62.
- (24) Krämer, W.; Ballschmiter, K. *Fresenius Z. Anal. Chem.* 1988, 330, 524-526.
- (25) Ray, P. K.; Parasad, A. K.; Nandan, R. *Sci. Cult.* 1985, 51, 363-371.
- (26) Knap, A. H.; Binkley, K. S. *Atmos. Environ.* 1991, 25A, 1507-1516.
- (27) Schulz, D. E.; Petrick, G.; Duinker, J. C. *Mar. Pollut. Bull.* 1988, 19, 526-531.
- (28) Tanabe, S.; Mori, T.; Tatsukawa, R.; Miyazaki, N. *Chemosphere* 1983, 12, 1269-1275.
- (29) Kaushik, C. P.; Pillai, M. K. K.; Raman, A.; Agarwal, H. G. *Water, Air, Soil Pollut.* 1987, 32, 63-76.
- (30) Ramesh, A.; Tanabe, S.; Tatsukawa, R.; Subramanian, A. N.; Palanichamy, S.; Mohan, D.; Venugopalan, V. K. *Environ. Pollut.* 1989, 62, 213-222.
- (31) Wolfe, D. A.; Champ, M. A.; Cross, F. A.; Kester, D. R.; Park, P. K.; Swanson, R. L. *Mar. Pollut. Bull.* 1984, 15, 207-212.
- (32) Bidleman, T. F.; Leonard, R. *Atmos. Environ.* 1982, 16, 1099-1107.
- (33) Dearth, M.; Hites, R. *Environ. Sci. Technol.* 1991, 25, 1279-1285.
- (34) Kawano, M.; Inoue, T.; Wada, T.; Hidaka, H.; Tatsukawa, R. *Environ. Sci. Technol.* 1988, 22, 792-797.
- (35) Kawano, M. Ph.D. Dissertation, Kyusyu University, 1991.
- (36) Bidleman, T. F.; Christensen, E. J.; Billings, W. N.; Leonard, R. *J. Mar. Res.* 1981, 39, 443-464.
- (37) Tanabe, S.; Kawano, M.; Tatsukawa, R. *Trans. Tokyo Univ. Fish.* 1982, 5, 97-109.
- (38) Oehme, M.; Ottar, B. *Geophys. Res. Lett.* 1984, 11, 1133-1136.
- (39) Oehme, M.; Stray, H. *Fresenius Z. Anal. Chem.* 1982, 311, 665-673.
- (40) Oehme, M.; Mano, S. *Fresenius Z. Anal. Chem.* 1984, 319, 141-146.
- (41) Pacyna, J. M.; Oehme, M. *Atmos. Environ.* 1988, 22, 243-257.
- (42) Atlas, E.; Giam, C. S. *Water, Air, Soil Pollut.* 1988, 39, 19-36.
- (43) Demozay, D.; Marechal, G. In *Lindane: Monograph of an Insecticide*; Ulmann, E., Ed.; Verlag K. Schillinger: Freiburg i. Br., 1972; pp 15-21.
- (44) Malaiyandi, M.; Shah, S. M. *Environ. Sci. Health* 1984, A19, 887-910.
- (45) Bidleman, T. F.; Wideqvist, U.; Jansson, B.; Soderlund, R. *Atmos. Environ.* 1987, 3, 641-654.
- (46) Larsson, P.; Okla, L. *Atmos. Environ.* 1989, 23, 1699-1711.
- (47) Addison, R. F.; Zinck, M. E.; Smith, T. G. *Environ. Sci. Technol.* 1986, 20, 253-256.
- (48) Corrigan, P. J.; Seneviratna, P. *Aust. Vet. J.* 1990, 67, 56-58.
- (49) Weber, R.; Montone, R. C. In *Long Range Transport of Pesticides*; Kurtz, D. A., Ed.; Lewis Publishers: Chelsea, MI, 1990; pp 185-197.
- (50) Sovocool, G. W.; Lewis, R. G.; Harless, R. L.; Wilson, N. K.; Zehr, R. D. *Anal. Chem.* 1977, 49, 734-740.
- (51) Hoff, R. M.; Chan, K. W. *Chemosphere* 1986, 15, 449-452.
- (52) Subramanian, A. N.; Tanabe, S.; Tatsukawa, R. *Mar. Pollut. Bull.* 1988, 19, 284-287.
- (53) Subramanian, A. N.; Tanabe, S.; Tatsukawa, R. *Mar. Environ. Res.* 1988, 25, 161-174.
- (54) Tanabe, S.; Tatsukawa, R. In *PCBs and Environment*; Waid, J. S., Ed.; CRC Press: Boca Raton, FL, 1986; Vol. I, pp 143-161.
- (55) Whitman, W. G. *Chem. Metall. Eng.* 1923, 29, 146.
- (56) Liss, P. S.; Slater, P. G. *Nature* 1974, 247, 181-184.
- (57) Smith, J. H.; Bomberger, D. C.; Haynes, D. L. *Environ. Sci. Technol.* 1980, 14, 1332-1337.
- (58) Zafiriou, O. C.; Alford, J.; Herrerra, M.; Peltzer, E.; Thompson, A. M.; Gagosian, R. B. *Geophys. Res. Lett.* 1980, 7, 341-344.
- (59) Rudolph, J.; Ehhalt, D. H. *J. Geophys. Res.* 1981, 86, 11959-11964.
- (60) Gammon, R. H.; Cline, J.; Wisegarver, D. *J. Geophys. Res.* 1982, 87, 9441-9454.
- (61) Mackay, D.; Yeun, A. T. K. *Environ. Sci. Technol.* 1983, 17, 211-217.
- (62) Eisenreich, S. J.; Looney, B. B.; Thornton, J. D. *Environ. Sci. Technol.* 1981, 15, 30-38.
- (63) Strachan, W. M.; Eisenreich, S. J. In *Mass Balancing of Chemical Pollutants in The Great Lakes, The Role of Atmospheric Deposition*; International Joint Commission Report: Windsor, Ontario Regional Office, 1988.
- (64) Barkley, R. A. In *Oceanographic Atlas of the Pacific Ocean*; Barkley, R. A., Ed.; University of Hawaii Press: Honolulu, 1968.
- (65) Suntio, L. R.; Shiu, Y.; Mackay, D.; Seiber, J. N.; Glotfety, D. *Rev. Environ. Contam.* 1988, 103, 1-59.
- (66) Mackay, D.; Paterson, S.; Schroeder, W. H. *Environ. Sci. Technol.* 1986, 20, 810-816.
- (67) Murphy, T. J.; Mullin, M. D.; Meyer, J. A. *Environ. Sci. Technol.* 1987, 21, 155-162.
- (68) Tateya, S.; Tanabe, S.; Tatsukawa, R. In *Toxic Contamination in Large Lakes*; Schmidtke, N. W., Ed.; Lewis Publishers: Chelsea, MI, 1988; Vol. 3, pp 237-281.
- (69) Atlas, E.; Foster, R.; Giam, C. S. *Environ. Sci. Technol.* 1982, 16, 283-286.
- (70) Fendinger, N. J.; Glotfelty, D. E.; Freeman, H. P. *Environ. Sci. Technol.* 1989, 23, 1528-1531.
- (71) Brunner, S.; Hornung, E.; Santl, H.; Wolf, E.; Piringer, O. G.; Altschuh, J.; Brüggeman, R. *Environ. Sci. Technol.* 1990, 24, 1751-1754.
- (72) Kucklick, J. R.; Hinkley, D. A.; Bidleman, T. F. *Mar. Chem.* 1991, 34, 197-209.
- (73) Dunnivant, F. M.; Eizerman, A. W.; Jurs, P. C.; Hasan, M. N. *Environ. Sci. Technol.* 1992, 26, 1567-1573.
- (74) Yamasaki, H.; Kuwata, K.; Miyamoto, H. *Environ. Sci. Technol.* 1982, 16, 189-194.
- (75) Nakano, T.; Tsuji, M.; Okuno, T. *Atmos. Environ.* 1990, 24A, 1361-1368.
- (76) Gschwend, P. M.; Wu, S. *Environ. Sci. Technol.* 1985, 19, 90-96.
- (77) Baker, J. E.; Capel, D.; Eisenreich, S. J. *Environ. Sci. Technol.* 1986, 20, 1136-1143.
- (78) Ramesh, A.; Tanabe, S.; Iwata, H.; Tatsukawa, R.; Subramanian, A. N.; Mohan, D.; Venugopalan, V. K. *Environ. Pollut.* 1990, 67, 289-304.
- (79) Takeoka, H.; Ramesh, A.; Iwata, H.; Tanabe, S.; Subramanian, A. N.; Mohan, D.; Magendran, A.; Tatsukawa, R. *Mar. Pollut. Bull.* 1991, 22, 290-297.
- (80) Tanabe, S.; Ramesh, A.; Sakashita, D.; Iwata, H.; Mohan, D.; Subramanian, A. N.; Tatsukawa, R. *Int. J. Environ. Anal. Chem.* 1991, 45, 45-53.
- (81) Knap, A. H.; Binkley, K. S.; Artz, R. S. *Atmos. Environ.* 1988, 22, 1411-1423.
- (82) Watson, A. J.; Upstill-Goddard, R. C.; Liss, P. S. *Nature* 1991, 349, 145-147.

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