Interhemispheric Exchange of Hexachlorocyclohexanes, Hexachlorobenzene, Polychlorobiphenyls, and 1,1,1-Trichloro-2,2-bis(p-chloro phenyl)-ethane in the Lower Troposphere

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Interhemisphere Exchange of Hexachlorocyclohexanes, Hexachlorobenzene, Polychlorobiphenyls, and 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane in the Lower Troposphere

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■ Two nearly independent hemispheric compartments exist in the atmosphere for hexachlorobenzene [HCB; south/north (S/N) ratio of 0.06] and α-hexachlorocyclohexane (α-HCH; S/N = 0.09), as base-line measurements in both hemispheres indicate. The interhemispheric differences in the profile of the α and γ isomers of hexachlorocyclohexane can be explained best by the different HCH products applied worldwide. Both isomers occur in technical HCH, the so-called benzene hexachloride (BHC), which is preferably used in the Northern Hemisphere, and the purified HCH "lindane", consisting of >99% γ-HCH, which is used worldwide. The distribution of the PCB congeners between gas phase and aerosol particles in dependence of the degree of chlorination is examined in urban air at a temperature of -8 °C, which is close to the global medium temperature of -11 °C at 4000 m. In clean air the interhemispheric contrast, the south/north ratio, is ~0.7 or even close to unity for the PCB. 4,4'-DDT is detected at 8 times higher levels in the southern as compared to the Northern Hemisphere. 4,4'-DDE, the transformation product of 4,4'-DDT, follows the same pattern (S/N = 3). The quotient of Henry constant and octanol–water distribution coefficient H/K_{ow} correlates to the S/N ratio of semivolatiles in the troposphere. These results require the conclusion that the interhemispheric exchange of other compounds with similar physicochemical data as given by HCB and α-HCH must be very slow in the atmosphere if it occurs at all at a significant level. This can have far-reaching consequences in the understanding of both the interhemispheric and finally the global distribution of xenobiotics, as the oceanic system has to be discussed as the major long-range transport medium.

1. Introduction

During the last two decades organochlorines were recognized as pollutants to be found in even the most remote regions of the globe (*1–3*). Dispersion of xenobiotics can occur (1) via trade, (2) via the mass flow in the atmosphere and (3) in the oceans, and (4) by the mobility of biota.

The global environmental fate—dispersion, accumulation, and transformation—of chemically stable semivolatile organochalogens, which react little or not all with OH, O_3, or H_2O [e.g., 1,2,3,4,5,6-hexachlorocyclohexanes (HCH), hexachlorobenzene (HCB), polychlorobiphenyls (PCB), and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethene (DDE)], depends mainly on their mobility in the different environmental compartments.

In this paper we discuss the levels and the mobility in the lower troposphere of the α and γ isomers of 1,2,3,4,5,6-hexachlorocyclohexane (α-HCH, γ-HCH), hexachlorobenzene, seven principal polychlorobiphenyl congeners, and the DDT group of compounds, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (4,4'-DDT) and 1,1-dichloro-2,2-bis(p-chlorophenyl) ethene (4,4'-DDE), under hemispheric and interhemispheric dimensions.

In the atmosphere as well as in the oceans the mobility of sparsely water soluble, semivolatile compounds will be mainly regulated by the ratio of particle-bonded to non-particle-bonded molecules. This ratio is regulated in the atmosphere by the surface of particles offered per volume unit and the mean temperature of the specific environment (*4*). The adsorbed portion will follow the transport routes of the aerosols, which after aggregation are mainly regulated, besides dry deposition, by the process of wet deposition as condensation nuclei together with impact scavanging by the rain droplets. Most authors favor dry sedimentation as the carry-down process for semivolatile compounds in the atmosphere (*5–8*). In areas and at times of no precipitation, dry sedimentation is surely a correct approach.

The discussion of the mobility in the troposphere is based in this paper on results obtained from depositions on snow and air samples of the Northern (*9*) and Southern Hemisphere (*10*), including previous measurements of other authors.

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Table I. Physicochemical Data of Semivolatile Organochloro Compounds

	MW	mp, °C	vp (25 °C), Pa	water sol., mol/m^3	H, Pa m^3/mol	log K_{ow}
Hexachlorocyclohexanes (HCH)						
α-HCH (65–70%)	290.8	158	7.3 × 10^{-3} (20 °C)[a]	5.2 × 10^{-3} (20 °C)[a]	1.1	3.89[b]
β-HCH (7–10%)	290.8	309	4.9 × 10^{-5} (20 °C)[a]	7 × 10^{-4} (20 °C)[a]	0.07	3.96[b]
γ-HCH (14–15%)	290.8	112.8	1.9 × 10^{-2} (20 °C)[a]	2.1 × 10^{-2} (20 °C)[a]	0.1	3.85[b]
δ-HCH (7%)	290.8	138.5		3.1 × 10^{-2} (20 °C)[a]		
Polychlorobenzenes						
1,2,3,4-tetrachlorobenzene	215.9	47.5	5.6[c]	3.6 × 10^{-2}[c]	160[c]	4.5[c]
pentachlorobenzene	250.3	86	8.8 × 10^{-1}[c]	2.6 × 10^{-3}[c]	340[c]	5.0[c]
hexachlorobenzene (HCB)	284.8	230	2.4 × 10^{-3}[c]	1.8 × 10^{-5}[c]	139[c]	5.5[c]
Polychlorobiphenyls (PCB)						
PCB 28 (2,4,4′)	257.8	57	2.6 × 10^{-2}[d]	7.9 × 10^{-4}[f]	33[d]	5.5[f]
			(3.4 × 10^{-2})[e]	(1.0 × 10^{-3})[g]	32[i]	
PCB 52 (2,2′,5,5′)	292.0	87	1.3 × 10^{-2}[d]	8.1 × 10^{-5}[f]	160[d]	5.8[f]
			(1.6 × 10^{-2})[e]	(1.4 × 10^{-4})[g]	34[i]	
PCB 101 (2,2′,4,5,5′)	326.4	77	2.6 × 10^{-3}[d]	1.2 × 10^{-5}[f]	217[d]	6.4[f]
			(3.3 × 10^{-3})[e]	(5.0 × 10^{-5})[g]	25[i]	
PCB 118 (2,3′,4,4′,5)	326.4	106	8.4 × 10^{-4}[d]	4.7 × 10^{-5}[f]	18[d]	6.6[f]
			(1.2 × 10^{-3})[e]	–[j]		
PCB 138 (2,2′,3,4,4′,5)	360.7	77.5	3.3 × 10^{-4}[d]	4.8 × 10^{-6}[f]	69[d]	6.7[f]
			(5.0 × 10^{-4})[e]	–[j]		
PCB 153 (2,2′,4,4′,5,5′)	360.7	103	5.6 × 10^{-4}[d]	2.5 × 10^{-6}[f]	224[d]	6.8[f]
			(6.8 × 10^{-4})[e]	(7.7 × 10^{-6})[g]	13[i]	
PCB 180 (2,2′,3,4,4′,5,5′)	395.3	178	8.1 × 10^{-5}[a]	7.9 × 10^{-7}[f]	102[d]	7.2[f]
			(1.3 × 10^{-4})[e]	–[j]		
DDT group						
4,4′-DDT	354.0	109	3.3 × 10^{-5}[h]	5.6 × 10^{-6}[h]	6 (0.8)[i]	6.0[b]
4,4′-DDE	319.0	88.5	8.6 × 10^{-4}(30 °C)[h]	2.5 × 10^{-5}[b]	34	5.7[b]
4,4′-DDD	321.0	109.5	1.3 × 10^{-4} (30 °C)[h]	1.5 × 10^{-5}[b]	9	6.0[b]
2,4′-DDT	319.0			4.8 × 10^{-5}[b]		5.8[b]

[a]Reference 29. [b]Reference 61. [c]Reference 62. [d]Reference 10. [e]Reference 63. [f]Reference 18. [g]Reference 64. [h]Reference 65. [i]Reference 66; see also ref 67. [j]–, no data.

The sources for the occurrence of HCB in the environment are not fully understood. They are often correlated to burning or other technical high-temperature processes involving chlorine gas and organics including plain carbon (8, 11). DDT and HCH are used worldwide as insecticides and are deliberately spread out. Several countries stopped the production and banned the use of DDT, though in global terms this will have little effect for the next years as a substantial reduction in total environmental input is questionable (10). The HCH is either used as the multicomponent mixture benzene hexachloride ("BHC") or as the purified γ isomer ("lindane"). Technical PCB mixtures are preferentially produced and used in the industrialized countries (12). For environmental concern the ~100 occurring PCB congeners of the total of 209 are often summarized as groups with a mean degree of chlorination, as the so-called technical mixtures. Treating chemicals as their technical mixture is rarely done for the HCH isomers, the chlordane compounds, or the DDT group and valuable information is lost. In a multicomponent mixture like PCB, typical and representative congeners, e.g., representing the degree of chlorination or typical structural parameters such as the degree of coplanarity, must be chosen (9, 10), rather than discussing the environmental fate of mixtures, which are by definition ill-defined in their physicochemical data. Particularly when the correlation of physicochemical data and environmental fate (e.g., translocation and transformation) is under discussion, a single-component approach is mandatory.

2. Experimental Section

The physicochemical constants of the compounds studied in this work are listed in Table I. For the PCB, seven major representative congeners (PCB 28, 52, 101, 118, 138, 153, and 180) have been selected. Recent compilations of basic physicochemical data such as water solubility, octanol–water partition coefficient (K_{ow}), and vapor pressure of semivolatile compounds reveal discrepancies in the data of up to 2 orders of magnitude.

The data in Table I for the water solubility and the K_{ow} coefficient have been taken from a critical review of literature data (6, 13–17) and from our own measurements based on HPLC k′/K_{ow}/S_{H_2O} correlations (18). The vapor pressure data are from the literature (19) and partly from our own measurements based on HRGC (retention time)/P_o correlations (10). The pollutants in the environment never occur as pure compounds but always in mixtures together with others; there are therefore good reasons to use only data of the liquid or subcooled liquid state for both the vapor pressure and the water solubility data when the environmental distribution of xenobiotics is discussed (8, 16, 17, 19).

The Henry's law coefficients, H, require special attention, as the coefficients derived from separate vapor pressure and water solubility measurements differ quite markedly from those determined directly by dynamic methods. Where available, both sets of data are given for H. The necessity of using uniformly liquid/subcooled liquid data for deriving H has been pointed out. The values for H for the PCB correlate to the coplanarity of both rings, which is directed by the number of ortho substituents to the phenyl–phenyl carbon bond (2,2′,6,6′-position) (10, 20–22).

High-volume air sampling by adsorption on silica gel, sample preparation, cleanup, separation by high-resolution gas chromatography, detection, and quantitation by electron capture and mass selective detection are described elsewhere (9, 10). One air and one snow surface sample

Table II. Date, Time, and Meteorological Conditions of Air and Snow Sampling at Ulm, Germany

	sample	
	A	S
sampling location[a]	downtown	suburban
kind of sample	air sample	snow surface
sampling period	9/12/87–10/12/87	8/1/87–23/1/87
sample vol	1000 m^3	17 m^2 surface $\simeq$ 22 L of molten water
temp, °C	−13 to −4	below 0
air pressure, hPa	1019–1024	1015–1025, inversion
wind	NW (2 km/h)	different directions (2–20 km/h)
precipitation, mm	no	1.7
sunshine	yes	16.7 h (130 h possible)
origin of air masses	local	regional
snow height total, cm		9–13

[a] Sampling locations: (A) downtown, near road with heavy traffic; (B) suburban area, rural.

were taken near Ulm during wintertime 1987 to examine the vapor/particle distribution of semivolatile organohalogens at temperatures below the freezing point of water.

The air sample (A) was a high-volume air sample, taken at a mean ambient temperature of −8 °C (range −4 to −13 °C) near a road with heavy traffic at the edge of a small village. The mean temperature in the troposphere at 4000 m is −11 °C. To a degree the air sample mimics this condition.

The snow (S) was a sample of a snow surface, taken near the university campus in Ulm, ~500 m away from a building and 50 m from a small street with occassional traffic (~10 cars/h). Table II presents weather conditions and time of sampling.

3. Results

Table III summarizes the measured concentrations of the compounds analyzed in the cold air and in the snow sample. The values of the snow sample approximate the deposition per day and meter squared. After a period of 15 days of dry and sunny anticyclonic weather, 17 m^2 of snow surface was collected. Correlating the deposited amount to the particle flux, a mean settling velocity of 100 m/day would fit the PCB concentrations in the air sample A. The isomer-specific analysis of the PCB congeners by high-resolution gas chromatography and mass selective detection (HRGC/MSD) clearly demonstrated the shift of the higher chlorinated PCB congeners to the particle phase, as well as the deviation from the standard mixture particularly for the pentachlorobiphenyls (9).

Table IV summarizes the results of our own previous measurements in coastal air at Réunion/South Indian Ocean used in this paper.

4. Discussion

The following results are used to discuss the mobility of HCH, HCB, PCB, and 4,4'-DDT in the lower troposphere of both hemispheres: (1) two samples described in this report (Table III) and three air samples discussed in (9), representing base-line levels in the westerlies of the northern hemisphere, (2) seven air samples from Réunion, representing base-line levels in the trade winds of the Southern Hemisphere (Table IV) (10), and (3) reports from other authors (2, 8, 23–28).

4.1. Hexachlorocyclohexanes and Hexachlorobenzene in the Troposphere. Hexachlorocyclohexanes are applied either as lindane (>99% γ-HCH), purified HCH (60–98.9% γ-HCH) or benzene hexachloride (65–70% α-HCH, 12–16% γ-HCH). Total global annual production and use of BHC amounts to 200 000 t (29).

Table III. Semivolatile Chlorinated Hydrocarbons in Air (Sample A) and in the Snow Surface (Sample S) in Central Europe (Ulm, Germany)[a]

	total, pg/m^3	sample A			sample S snow surface, pg/m^2
		gas phase, pg/m^3	partic phase, pg/m^3	adsrbd fractn, % (−8 °C)	
α-HCH (C$_6$H$_6$Cl$_6$)	113	110	3	3	2500[c]
γ-HCH (C$_6$H$_6$Cl$_6$)	173	160	13	8	9500[d]
HCB (C$_6$Cl$_6$)	114	110	4	4	1500[e]
Polychlorobiphenyl Congeners					
PCB 28 (Cl$_3$) (2,4,4')	10	10	<1	<10	700[e]
PCB 52 (Cl$_4$) (2,2',5,5')	24	19	5	20	1000[e]
PCB 101 (Cl$_5$) (2,2',4,5,5')	47	15	32	68	2800[e]
PCB 118 (Cl$_5$) (2,3',4,4',5)	17	3	14	83	1400[e]
PCB 138 (Cl$_6$) (2,2',3,4,4',5')	52	7	45	87	5700[e]
PCB 153 (Cl$_6$) (2,2',4,4',5,5')	52	7	45	87	5900[e]
PCB 180 (Cl$_7$) (2,2',3,4,4',5,5')	23	3	20	87	3900[e]
PCB 209 (Cl$_{10}$)	<1	<1	<1		300[e]
Sum of PCB Isomers					
Σ(C$_{12}$H$_7$Cl$_3$)	40	40	<1	<5	
Σ(C$_{12}$H$_6$Cl$_4$)	47	40	7	12–20[b]	
Σ(C$_{12}$H$_5$Cl$_5$)	190	60	130	54–83[b]	11000[e]
Σ(C$_{12}$H$_4$Cl$_6$)	280	40	240	79–90[b]	21000[e]
Σ(C$_{12}$H$_3$Cl$_7$)	110	10	100	82–92	11000[e]
Σ(C$_{12}$H$_2$Cl$_8$)	<1	<1	<1		
Σ(C$_{12}$HCl$_9$)	<1	<1	<1		
ΣPCB (Cl$_3$–Cl$_9$)	670	190	480	72	
4,4'-DDT	<1	<1	<1		
4,4'-DDE	4	1	3	75	

[a] Sampling temperature for sample A, −8 °C. The values for sample S also correspond to the deposited amount per day. [b] Range for isomers. [c] Only water phase, particle phase < 50 pg/m^2. [d] Water phase and particle phase (particles contained 16% of the total amount). [e] Mainly particle phase.

Table IV. Semivolatile Chlorinated Hydrocarbons in Coastal Air at Reunion/South Indian Ocean (March 1986) (10)

	mean, pg/m^3	n	range, pg/m^3
α-HCH (C$_6$H$_6$Cl$_6$)	13	6	6–21
γ-HCH (C$_6$H$_6$Cl$_6$)	406	3	320–530
HCB (C$_6$Cl$_6$)	7	4	4–12
Polychlorobiphenyls			
PCB 28 (C$_{12}$H$_7$Cl$_3$) (2,4,4′)	3.2	7	2–4
PCB 52 (C$_{12}$H$_6$Cl$_4$) (2,2′,5,5′)	4.9	7	3–8
PCB 101 (C$_{12}$H$_5$Cl$_5$) (2,2′,4,5,5′)	6.0	7	3–8
PCB 138 (C$_{12}$H$_4$Cl$_6$) (2,2′,3,4,4′,5′)	5.0	7	4–9
PCB 153 (C$_{12}$H$_4$Cl$_6$) (2,2′,4,4′,5,5′)	5.0	7	3–7
PCB 180 (C$_{12}$H$_3$Cl$_7$) (2,2′,3,4,4′,5,5′)	1.5	7	0.2–4
Σ(6PCB 28–180)	26	7	18–35
ΣPCB total (Cl$_3$–Cl$_9$)	125	1	
4,4′-DDT	8	7	6–13
4,4′-DDE	18	5	13–21

This report discusses only the two main components of BHC: α-HCH and γ-HCH.

The sources for HCB are not yet completely assigned. In most cases HCB is connected with burning events and metallurgical processes involving the use of chlorine (12). It could be shown that in the case of the Ebro delta in the western Mediterranean the river is a major source of HCB to the coastal environment (30). The HCB was mainly associated with the particulate phase. In the marine bay water, mean levels were 1.0–4.1 pg/L dissolved in the water and 12–31 pg/L associated with the particulate phase. Surface water in the North Atlantic Ocean gave levels for HCB of 3 pg/L, while in the eastern North Indic Ocean levels were below the detection limit of 1 pg/L (3).

Due to the relative high vapor pressure (Table I), the extent of adsorption of α-HCH, γ-HCH, and HCB on aerosol particles is rather small. Even at –8 °C, the adsorbed fraction is in the range of 3–8% only (Table III). The relatively high deposited amounts of α-HCH, γ-HCH, and HCB on snow correspond to the measured adsorbed fractions of the high-volume air sample (Table III). This keeps the question open of whether wash out is the most important or only an additional mechanism for the depletion of HCH from the atmosphere. The Henry constants (Table I) would allow such scavenging by wash out as suggested by several authors. The differences in water solubility of α-HCH and γ-HCH and of HCB are clearly shown in sample S (Table III). The melted snow contained the HCH isomers preferentially in the water phase while the HCB was found mainly adsorbed on the particles. One has to keep in mind, however, that the equilibria in air and in the melted snow water are different, that is, a gas/solid versus liquid/solid distribution. Wrong conclusions might be drawn by simply comparing the results directly.

The mean ratio of α-HCH to γ-HCH in all air samples from Réunion was 1:30 (Table IV). This indicates that the input into the air nearly exclusively consists of lindane. It is known that in the northern hemisphere the HCH input derives from lindane (γ-HCH) and BHC (α- and γ-HCH) as well. In background areas, the concentration of α-HCH in air surpasses that of γ-HCH; a ratio of α/γ of 15:1–20:1 is found (2, 32). A hemispheric south/north ratio of 0.09 (0.05) can be calculated for α-HCH (Table V).

An often discussed point is the conversion of γ-HCH into α-HCH in the environment (32). The air samples from Réunion in the southern hemisphere are polluted by nearly pure γ-HCH. Significant conversion of the γ isomer into the α isomer under tropical conditions is most unlikely considering the observable γ- to α-HCH ratios. The thermodynamically possible conversion of γ-HCH into α-HCH catalyzed by water-free FeCl$_3$ at 200 °C thus is a questionable sink for γ-HCH in the atmosphere.

A similar hemispheric south/north ratio as for α-HCH is calculated for hexachlorobenzene (S/N = 0.06) on the basis of base-line air samples from southern Germany and the island Réunion (Table V) (10).

The separation of the global troposphere into two independent hemispheric parts, already indicated for some chlorinated C$_2$ compounds (33), also holds for α-HCH and HCB. The exchange time of air, meaning molecules in the true gaseous state, between the two hemispheres is in the range of 1 year (4, 34, 35). Thus, the net residence time of α-HCH or HCB in the atmosphere must be significantly smaller than 1 year and it is clearly based on physical translocation and not on chemical transformation. Even if the residence time would be on the order of 2 or 3 months, an equilibrium with definitely higher levels of α-HCH and HCB in the Southern Hemisphere should be observed.

There are good reasons to assume a "physical" residence time of α-HCH and HCB regulated by the residence time of particulates and water in the troposphere. The residence time of molecules with the partition ratio ϕ is particle residence time divided by partition ratio (days). On

Table V. Base-Line Concentrations (pg/m^3) of Semivolatile Organochloro Compounds in the Lower Troposphere[a]

	central Europe rural 1985 (9) (a)	north Pacific 1979 (48) (b)	south Indic 1986 (10)	S/N ratio (a)	S/N ratio (b)
α-HCH (C$_6$H$_6$Cl$_6$)	150	250	13	0.09	(0.05)
γ-HCH (C$_6$H$_6$Cl$_6$)	430	15	406	0.94	(27)
HCB (HCH)	120	100	7	0.06	(0.07)
Polychlorobiphenyls C$_{12}$H$_{(10-x)}$Cl$_x$					
PCB 28 (C$_{12}$H$_7$Cl$_3$) (2,4,4′)	5	–	3	0.6	–
PCB 52 (C$_{12}$H$_6$Cl$_4$) (2,2′,5,5′)	8	–	5	0.6	–
PCB 101 (C$_{12}$H$_5$Cl$_5$) (2,2′,4,5,5′)	–	–	6	–	–
PCB 118 (C$_{12}$H$_5$Cl$_5$) (2,3′,4,4′,5)	4	–	–	–	–
PCB 138 (C$_{12}$H$_4$Cl$_4$) (2,2′,3,4,4′,5)	18	–	5	0.3	–
PCB 153 (C$_{12}$H$_4$Cl$_6$) (2,2′,4,4′,5,5′)	12	–	5	0.5	–
PCB 180 (C$_{12}$H$_3$Cl$_7$) (2,2′,3,4,4′,5,5′)	4	–	1.5	0.4	–
ΣPCB (3–9)	170	(600)	125	0.7	
4,4′-DDT	1	–	8	8	
4,4′-DDE	6	3	19	3	(6)

[a] –, no data.

Table VI. Particle-Phase/Gas-Phase Distribution ϕ According to the Junge eq 4

	ϕ, %		
P_o, Pa	$\theta_1{}^a$	$\theta_2{}^b$	$\theta_3{}^c$
10^{-2}	0.001	0.01	0.1
10^{-3}	0.01	0.1	1
10^{-4}	0.1	1	9
10^{-5}	1	9	50
10^{-6}	9	50	100
10^{-7}	50	100	100

$^a\theta_1$, surface of clean air aerosol 10^{-7} cm^2/cm^3. $^b\theta_2$, surface of rural air aerosol 10^{-6} cm^2/cm^3. $^c\theta_3$, surface of urban air aerosol 10^{-5} cm^2/cm^3.

the basis of a mean temperature of −11 °C at 4000 m and the values for ϕ as calculated in Table VI, residence times can be estimated. The estimations for particle residence times range from 1.9 days for submicron particles (36) to a general particle residence time of 6 (37) or 9 days (4). A partition ratio of 0.01 results in residence times of 190–900 days, while a partition ratio of 0.1 gives residence times of 19–90 days. The global distribution pattern requires the lower values at least for the interhemispheric exchange in the atmosphere.

4.2. Correlation of Physicochemical Properties and Hemispheric Distribution of HCH and HCB.

A correlation of vapor pressure, water solubility, and the south/north ratio in the troposphere of α-hexachlorocyclohexane, and hexachlorobenzene including tetrachloromethane, hexachloroethane, and hexachlorobutadiene, (Table VII) indicates which set of physicochemical data can define a strongly reduced interhemispheric exchange. The H/K_{ow} ratio summarizing the vapor pressure and the lipophilic character of a compound correlates with the south/north ratio. The H/p ratio has been discussed under similar aspects (19). The H/K_{ow} ratio retains the dimension of the Henry constant, thus expressing a gas-phase/liquid-phase distribution, in this case based on the lipophilic octanol and not on water. The ratio K_{ow}/H was used to describe the air to plant bioconcentration factors of semivolatile organochlorine compounds (38).

The conclusion of a strongly reduced interhemispheric crossing in the atmosphere of the α-HCH is supported by earlier measurements by Tanabe and Tatsukawa in the northern Indian Ocean and the western Pacific (2). The latitudinal distribution of $\sum$HCH in air gives a definite downward trend toward the equator with an about even level south of the intertropical convergence zone (ITCZ) and the southern westwind belt (40–60° S) (2). They also observed an even distribution over the North Pacific for both the $\sum$DDT and $\sum$HCH from 150° E to 100° W at 40–20° N in both the surface water and the air above it (39). This is in contrast to the exponential decline of PCB in air measured by Bidleman and Olney on the cruise from New York to the Bermudas in 1972, which however could present a mesoscale phenomenon (41).

The even distribution of HCH and DDT in the air above the ocean requires the assumption of equilibrium conditions in air buffered by the concentration in and volatilization from the oceanic surface waters either by water codistillation, film droplet formation, or a mixture of both processes. The concentrations in air depend, according to this model, on the concentration of the semivolatile compound in the underlying water masses. The reverse assumption defining the concentration in water by the concentration in air was made by Tanabe and Tatsukawa in 1980 (39). However, the load of semivolatiles in only the upper 10–30 m of the ocean water (range ng/m^3) corresponds to the load of the whole tropospheric air column (range pg/m^3) above the ocean water. Mixing in both compartments occurs within hours to a few days. The global long-range transport of semivolatiles could be understood by a "up and down" type mechanism with a mesoscale part in the air and a long-range part in the oceans. Transport in the ocean water would be relatively slow but steadily following the established flow patterns of surface and subsurface currents (31).

4.3. Polychlorobiphenyls (PCB) in the Troposphere.

PCB have different possible sources. The main source is the FeCl$_3$-catalyzed chlorination of biphenyl, which leads to the widely used technical PCB mixtures (12). Thermal dimerization of chlorobenzenes as a result of combustion chemistry also leads to complex PCB mixtures with a predominance of the higher chlorinated and the coplanar congeners (12, 42).

Technical PCB mixtures are mostly produced with 42% chlorine (e.g., Aroclor 1242, Clophen A30), 54% chlorine (e.g., Aroclor 1254, Clophen A50), and 60% chlorine (e.g., Aroclor 1260, Clophen A 60). Until 1950 askarales (transformer fluids) contained only the 60% chlorine PCB, from 1950 to 1977 it was a mixture of 20% of the 54% chlorine PCB with 50% of the 60% chlorine PCB together with 30% of trichlorobenzenes. From 1963 to 1977 a 1:1 mixture of 54% and 60% chlorine PCB was used. Only after 1977 was the use of 60% chlorine PCB abandoned in transformer fluids (12).

The isomer patterns of the three major PCB mixtures are very similar; e.g., the tetrachlorobiphenyl pattern of PCB 42% chlorine and PCB 54% chlorine are nearly the same, while PCB 60% chlorine contains only traces of tetrachlorobiphenyls. Thus, mixtures of PCB of 42%, 54%, and 60% chlorine can be used to describe input of technical PCB for the isomeric pattern of PCB with three to seven chlorine atoms. The chloro isomer pattern of environmental samples as detected by capillary gas chromatography and mass selective detection (HRGC/MSD) can be matched best by a 1:1:1 mixture of PCB with 42%, 52%, and 60% chlorine (9).

The concentration of PCB calculated as the sum of chlorohomologues in the air near the city of Ulm, 100 km north of the Alps in central Europe, taken as representatives of base-line levels of the westerlies of the northern hemisphere, ranged from 125 to 2600 pg/m^3 in the vicinity of a road with heavy traffic. A mean of 170 pg/m^3 was

Table VII. Atmospheric South/North Ratios of Chlorinated Compounds with Preferable Input in the Northern Hemisphere

	MW	mp, °C	vp (25 °C), Pa	water sol., mol/m^3	H,^{a} Pa m^3/mol	K_{ow}	H/K_{ow}, Pa m^3/mol	S/N ratio
tetrachloromethane	153	−23	1.2×10^4	7.8	1.5×10^4	5×10^2	30	1.0^b
hexachloroethane	237	193	12.7	2.8×10^{-3}	4.5×10^3	7.9×10^3	5.6×10^{-1}	0.89^b
hexachlorobutadiene	261	−19	0.84	7.7×10^{-3}	1.1×10^3	6.3×10^4	1.7×10^{-2}	0.41^b
α-hexachlorocyclohexane	291	158	7.3×10^{-3}	2.7×10^{-3}	1.1	7.9×10^3	1.4×10^{-4}	0.09
hexachlorobenzene	285	230	2.4×10^{-3}	1.8×10^{-5}	1.4×10^2	3.2×10^5	4.3×10^{-4}	0.06

$^a H = P_L/C_L$; $C_{air}/C_{water} = H/RT$; $RT = 2477$ (25 °C); $C_{air} = C_{water}H/2477$ (25 °C; vapor pressure in pascals). ^{b} Reference 33.

found for rural air conditions (9). A sample collected at Réunion, South Indic Ocean, gave a PCB concentration of 125 pg/m³ (10).

Seasonal variations in the atmospheric concentrations of PCB were studied for a period over 1 year in a remote site in the Great Lakes watershed in northern Wisconsin (43). Total PCB concentrations varied in the same range as in central Europe from 135 pg/m³ in winter to 1820 pg/m³ in summer.

4.4. Particle-Phase/Gas-Phase Distribution of PCB. The vapor pressures of the PCB congeners under discussion are summarized in Table I. The Junge diagram correlating gas-phase/particle-phase distribution to the vapor pressure for a given particle surface per volume clearly reveals that there exists a range of vapor pressures where, under urban conditions, a distinct difference in the gas-phase/particle-phase distribution for chlorohomologues as well as for the isomers can be measured (Table III). Regions with the PCB in respect to the particle phase "all on" (high surface area per volume, low temperature) or "all off" (low surface area per volume, high temperatures) give no differences in the homologues and isomeric patterns as compared to standards when the particle phase and the gaseous phase are analyzed separately. In a remote site in Wisconsin, PCB were found at an average of 92% in the gas phase (43). A residence time of ~100 days is calculated by using the partition ratio ϕ defined by Junge (4) and an average residence time of atmospheric particles of 6 days (37).

Analyzing the PCB dry depositions in La Jolla, CA, led McClure to the conclusion that aerosol transport of semivolatile organochlorines is a mesoscale (100–500 km) rather than a hemispheric or even global phenomenon (5). Eisenreich calculated the flux of PCB to Lake Superior by the different input pathways from the atmosphere and came to the conclusion that 60–80% resulted from dry depositions, while for the wet deposition, vapor partitioning was the major process and only a smaller contribution came from particle washout (6). Measurements of the atmospheric loadings to Lake Huron indicate a prevalence of wet depositions (7). Recent sampling of PCB in air and rain within the city of Kiel, FRG, underlined the effectiveness of PCB scavenging from air by the particle-based rain-out process under urban air conditions (44).

4.5. Interhemispheric Transport of PCB in the Troposphere. The overwhelming part of the PCB input into the environment surely takes place in the Northern Hemisphere. The troposphere of the Southern Hemisphere shows, however, only slightly lower PCB concentrations than unpolluted air of the westerlies of the Northern Hemisphere (9, 10, 43). The about equal and at the same time low concentrations of PCB in the troposphere of the Northern and the Southern Hemispheres at base-line conditions make the presence of efficacious transport mechanisms to the surface for the PCB necessary. Reentry into the troposphere must be nearly independent from the concentrations in the liquid-phase/solid-phase reservoir at the surface.

An interhemispheric transport in the troposphere is most unlikely for the PCB, though the south/north ratio is 0.7 or even close to 1 in the troposphere. Nevertheless, the results of α-HCH and HCB, for which an interhemispheric exchange in the atmosphere must be of minor extent, require the same conclusion for the PCB considering their physicochemical parameters.

4.6. Photolytic Transformation of PCB in the Troposphere. The photochemical destruction of PCB in the troposphere appears to be very slow (45), though re-

cently a half-live in the order of 1 week has been derived from laboratory measurements for direct photolysis by sunlight (46). Selective changes of the PCB pattern in the lower troposphere due to photodecomposition, particularly of congeners with a substitution in the 2,2′,6,6′-positions, were not observed in the air samples from Réunion. But a nonselective mechanism cannot be recognized in this way. An enrichment of the pentachlorobiphenyls PCB 90 (2,2′,3,4′,5) and PCB 101 (2,2′,4,5,5′) relative to PCB 110 (2,3,3′,4′,6) in correlation to the distance of possible sources has been observed in air (10). PCB 110 is more photolabile than PCB 90 and 101 (47), but the latter are also more biopersistent than PCB 110, so a clear decision as to the cause of the observation cannot be made. A detailed analysis of 2,2′,6- and 2,2′,6,6′-type PCB congeners, preferably those that are among the biopersistent congeners, might add information about the often claimed PCB photodegradation under environmental conditions. PCB 136 (2,2′,3,3′,6,6′) belongs to the photolabile "2,6"-group, but in our experience other than in biological samples it is never clearly diminished (10).

4.7. 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (4,4′-DDT) and 1,1-Dichloro-2,2-bis(p-chlorophenyl)ethene (4,4′-DDE) in the Troposphere. The ban of 4,4-DDT in most western countries and the continuing application in eastern Europe and in tropical regions explain the observed global distribution (2). Most of the DDT applied is already transformed to 4,4′-DDE or has to be looked for in other environmental compartments than the air. The ratio of DDE/DDT can be used to distinguish any recent DDT input. 4,4′-DDE has not only to be discussed as a transformation product of 4,4′-DDT, but also as a byproduct of dicofol (Kelthan), 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol. Dicofol is a widely used acaricide and is produced via 4,4′-DDE.

In central Europe the base-line level for 4,4′-DDT is in the range of 1 pg/m³ and lower (Tables III and V). In air sample A, the concentration of 4,4′-DDT was below 1 pg/m³ while 4,4′-DDE was detected at a level of 4 pg/m³ with 75% in the particle fraction (Table III). Air samples collected in summer 1979 in the North Pacific Ocean gave a concentration of 3 pg/m³ for 4,4′-DDE (48). A level of 5 pg/m³ for 4,4′-DDE over the Sargasso Sea could be explained by elevated concentrations of 83 pg/m³ in the air above the Gulf of Mexico (48). The base-line load of 1–3 pg/m³ in the northern hemisphere for 4,4′-DDE appears to be stable during the last decade.

4,4′-DDT was recently measured in the air above the South Indian Ocean (Réunion) at levels of 6–13 pg/m³ with a mean at 8 pg/m³, while for 4,4′-DDE a level of 19 pg/m³ was found (Table IV). In the southern westwind belt between Australia and the Antarctic, levels for 4,4′-DDT and 4,4′-DDE were 100 and 232 pg/m³, respectively, in 1980/1981 (2).

A south/north ratio of approximately 7–8 for 4,4′-DDT and a value of ~3 for 4,4′-DDE seems to be valid in 1986, though such a general conclusion should be based on more data.

4.8. Environmental Fate in the Troposphere: Global Aspects. The general concentrations for the semivolatiles measured in the troposphere are very low, compared with the industrial output of the last 50 years (1, 2, 9, 10). Despite the low standing load of the semivolatile organohalogens, the troposphere can act as an effective and fast medium for long-range transport if the compounds truely occur in the gas phase. The complete mixing of the troposphere within a hemisphere with a substance starting in the westerlies takes ~1 month (49),

whereas the time constant of the interhemispheric exchange, if such an exchange follows true molecular spreading, is ~1 year (4). The global transport processes in the atmosphere are discussed and summarized in a review by Holton (34). The processes controlling the transport and dynamic phenomena at interfaces of organic compounds in the environment are summarized in a symposium report (35). Basic chemistry and physics of air pollutants in the atmosphere are well presented in a textbook by Seinfeld (35) and in a recent publication by Mackay et al. (19). During their residence in the atmosphere, air pollutants can be transformed by UV light induced reactions involving NO_2, ozone, or OH radicals. Thus, residence time both in terms of chemical stability and geophysical spreading, including interhemispheric exchange, rules the hemispheric concentration for a given input as pointed out by Junge about two decades ago (4).

The influence of the global mass flow in the troposphere, the so-called general circulation, on the spreading of pollutants in the gaseous state in the troposphere has already been modeled (4, 35) and recently discussed in detail for a broad spectrum of volatile organohalogens (33). Our aim is to understand the global spreading of anthropogenic compounds on the basis of the real world mass flow followed up by representative but selected measurements (1). This analytical approach is the final test for any physicochemical model (19, 50).

In global terms, for the process of dry deposition there is a 71% probability of contacting a water surface and a 29% probability of reaching soil. For the Northern Hemisphere this ratio becomes water 60.7% to soil 39.3%, while for the Southern Hemisphere the ratio is 80.9% to 19.1%, respectively. Thinking in equilibria or at least in kinetically controlled exchange processes, the water surface of the oceans is the main source for an exchange step on the global scale.

For the processes of wash out and rain out, probabilities follow the mean global precipitation pattern, which favors deposition on the oceans' surface. The total global precipitation of 511.11×10^3 km^3 divides into 411.61×10^3 km^3 rain hitting the oceans and only 99.5×10^3 km^3 reaching the continents (51). There are three maxima in this global pattern, both the cyclonic westwind belts of the hemispheres and the tropics (36, 37). Most of the rain in the global scale comes down between 20° N and 20° S. In the tropics, rain is mainly formed in high-reaching cumulus clouds (6–10 km or more) as zenital or convective rain. In the midlatitudes, cyclonic rain is dominating, which originates in heights of 1000–2000 m (51). The intertropical convergence zone is in itself an area of ascending motion and copious precipitation with the existence of a dry zone along the equator particularly across the Pacific (52). Second, each summer the ITCZ moves far to the north over the Indian Ocean, as the result of the turnover of the northeast tradewinds to the southwest monsoon. This input of air in the lower northern troposphere is counterbalanced in higher troposphere regions.

Soil and water surfaces will act in different ways as sources for the pollutants returning to the atmosphere. While the mechanism of evaporation and water codistillation has to be discussed for water removal on the molecular level (volatilization), on the microscopic level, film drops and jet drops as the basis for marine particulate formation will play an important and continuous role for semivolatile compounds. The flux back from the soil can be regarded as a counteracting mechanism of both temporary water codistillation and solid-phase/gas-phase desorption.

4.9. Adsorption Processes in the Troposphere: Global Considerations. The application of the BET isotherm to tropospheric gas/particle distribution is given by Junge, resulting in eq 1, which is based on reasonable

$$\phi_{(T)} = c\theta/(P_o + c\theta) \qquad (1)$$

approximations (4, 53), where $\phi_{(T)}$ is the fraction adsorbed on aerosol particles at temperature T, θ is the aerosol surface area per volume (cm^2/cm^3), c is a constant, and P_o is the saturation vapor pressure at a given temperature T.

The so-called Yamasaki equation includes the temperature dependence of the partition between gaseous and particulate phases based on three experimental parameters (54): the adsorbed retained portion (gas phase, in mg/m^3), the total suspended particulates (μg/m^3), and the filter-retained portion (particulate phase in mg/m^3) at a given temperature.

The influence of the temperature on ϕ at a given aerosol surface area per volume by changing the vapor pressure is easily calculated (Table VI). The available surface per volume unit is less definitive to evaluate (55). Urban air is set to have 10^6 particles/cm^3 while marine air is set to have 10^2 particles/cm^3. Furthermore, the number of particles per volume has to be correlated to the size distribution to obtain realistic numbers for the surface available for adsorption. The occurrence of carbon black (soot) as a substantial part of the aerosol surface (56) increases the capability of the aerosol particles to selectively adsorb planar molecules, thus modifying the concept of general adsorption.

In global terms, particles derived from the ocean surface will be the most prevalent despite such visible events as movements of Sahara dust or similar phenomena. The global atmospheric sea-salt production is estimated at 1×10^{15} g/year correlating to an annual input of organic carbon from the sea to the atmosphere of 5×10^{13} g (57). A portion of the particles derived from the bubble bursting (radius 0.05–1 μm) will undergo quasi molecular distribution in the lower troposphere prior to aggregation to larger particles. The total residence time for submicron particles (10^{-12} g wt for individual particles) over the ocean has been estimated to be close to 1.9 days while particles with 10^{-9} g wt corresponding to an inner diameter of ~10 μm have a residence time of only 0.3 days (36). The submicron particles could be transported over 1000–2000 km in their residence time.

Substances with vapor pressures in the 10^{-6}–10^{-7}-Pa range at a given temperature are adsorbed in urban air up to 100% while in clean air absorption is more than 10%. 4,4'-DDT and PCB congeners with seven chlorine atoms and more have vapor pressures below $P_o = 10^{-4}$ Pa at 25 °C as subcooled liquids, leading to an estimation of the adsorbed portion of up to 10–50% of the concentration in urban air. In clean air at 25 °C, however, 4,4'-DDT and the hepta- to decachlorobiphenyls should be present to more than 99% in the gas phase as the mean aerosol surface area decreases from 10^{-5} to 10^{-7} cm^2/cm^3. Hexachlorocyclohexane, hexachlorobenzene, and PCB with less than seven chlorines per molecule should always occur at greater than 99% in the gas phase at 25 °C. The relative amount of decane ($P_o = 66.6$ Pa, 20 C) bounded to particles was found to be 0.5% at 20 °C while the octaeicosane (C_{28}) ($P_o = 5.3 \times 10^{-8}$ Pa, 20 °C) was at the 4% level associated with particles in the lower troposphere (58). These two alkanes cover the vapor pressure range of the semivolatiles under discussion in this paper.

In global terms the clean air condition prevails, which should favor the presence of the semivolatiles in the gas

phase. A mean tropospheric temperature of 15 °C is assumed at sea level while at 2000-m height a temperature of +2 °C and at 4000-m height a temperature of –11 °C is set for the standard atmosphere (ICAO atmosphere). Formation of rain occurs mostly at temperatures even below that point. The air sample collected at –8 °C (Table III) roughly approximates these standard conditions in terms of gas-phase/particle-phase distribution for urban conditions. The mean temperature at 4000 m and above this height, however, clearly moves the semivolatile compounds to the adsorbed state even under clean air conditions.

The tropic rain belt (20 °N–20° S) together with the ascending air at the ITCZ thus could act as an effective barrier for these compounds by the mechanism of rain out, strongly reducing an atmospheric interhemispheric exchange of molecules connected to gas-phase/particulate-phase equilibria. The rain can be considered as wetted dust. The role of cloud physics in atmospheric multiphase systems has been summarized by Pruppacher (59). He outlined the role of aerosol particles of specific characteristics that lead the water from the vapor phase to drops. Already the intrahemispheric spreading should be limited, as the main industrial and agricultural activities are taking place in the rain belt of the westerlies of the northern hemisphere. Also, the cold climates would favor the deposition from the atmosphere by snowfall.

5. Conclusions

Adsorption of molecules on aerosols and subsequent output to the earth surface depends on the vapor pressure at standard conditions, the amount and surface area of aerosol particles, and the relevant environmental temperature. For the environmental fate of the semivolatile organohalogens HCH, HCB, PCB, and DDT, the adsorption on atmospheric aerosol particles must play an important role even under clean air conditions considering the mean temperature of the troposphere, which is, e.g., –11 °C at 4000 m for standard conditions. Hexachloro and higher chlorinated PCB congeners and DDT can be adsorbed to a considerable extent to aerosol particles, whereas the HCH isomers, HCB, and the trichloro- to pentachlorobiphenyls are mainly in the gaseous phase even at a temperature of –10 °C.

The interhemispheric exchange of α-HCH and HCB in the atmosphere is clearly restricted, however, which allows the conclusion that all the other semivolatile organohalogens will follow the same distribution pattern in the atmosphere. The barrier for an interhemispheric exchange in the atmosphere is apparently an effective wash out and rain out in the 20° N–20° S region of the tropics; if not, transport in air is mainly a mesoscale event. Interhemispheric exchange of the semivolatile organohalogens will thus mainly occur in the oceans. This would also explain why the HCB/PCB concentrations in the northern Indian Ocean are much lower than in the North Atlantic (31, 60).

The results also open the question of whether regional (10–100 km), mesoscale (100–1000 km), and hemispheric (1000–40000 km) transport have to be discussed under different aspects to understand the global long-range transport of semivolatile compounds in total. Table VII summarizes the physicochemical data of persistent organochlorine compounds, which apparently define the long-range homogenous spreading as occurs for tetrachloromethane on the one hand and a compartmental distribution of hexachlorocyclohexane and hexachlorobenzene on the other. As a first approximation, the south/north ratio correlates to the H/K_{ow} ratio. The latter ratio contains as basic elements, first, the solubility in octanol as a measure of lipophility and, second, the vapor pressure of a compound. Decreasing values of the H/K_{ow} ratio indicate preference of lipophilic surfaces and bulks, i.e., particle retention, which means deposition close to the source in global terms.

The south/north ratios of Table VII give a first indication where an intermediate behavior can be anticipated. Among others, the alkyl and chloro derivatives of benzene and naphthalene offer good model systems for such environmental studies. Both groups of compounds are among the major emitted anthropogenic chemicals.

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