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GLOBAL BASELINE POLLUTION STUDIES XI*: CONGENER SPECIFIC DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCB) AND OCCURRENCE OF ALPHA- AND GAMMA-HEXACHLOROCYCLOHEXANE (HCH), 4,4'-DDE AND 4,4'-DDT IN CONTINENTAL AIR

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Summary

The hexachlorocyclohexane-isomers (HCH), hexachlorobenzene (HCB), the polychlorinated biphenyls (PCB), 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) have been measured in urban and rural air around the city of Ulm (F. R. G., 48.4° N, 10.0° E). The sampling stations are typical for continental air in the westerlies of the northern hemisphere including local and regional influences. The analytical method consists of adsorptive sampling of large volumes (1000 m^3) of air on silica gel, solvent desorption with CH_2Cl_2, preseparation of the collected chlorinated C_6/C_{14} hydrocarbons by liquid adsorption chromatography on silica gel, and high resolution capillary gas chromatography with electron capture-(HRGC/ECD) or mass-selective detection (HRGC/MSD). The concentrations found in the lower troposphere under different meteorological conditions reflect regional input and long range transport. The levels found range from 1 pg/m^3 for 4,4'-DDT to 10 ng/m^3 for gamma HCH.

1. Introduction

Chlorinated hydrocarbons have been produced since the early thirties for different purposes /1/. Reports about the occurence of the polychlorinated biphenyls (PCB), the insecticides 1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane (DDT) and 1,2,3,4,5,6-hexachlorocyclohexane (HCH) in air are numerous /2 - 11/. All these compounds, in contrast to C_1 / C_2 chlorinated solvents, have vapor pressures smaller than 1 Pa at 25° C. While solvents usually are

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*Part X: Class T., Ballschmiter K.
Fresenius Z. Anal. Chem. (1987), 327: 198-204

released into the air as a way of disposal, insecticides are on purpose brought into the environment. Like all environmental chemicals they are distributed between atmosphere, hydrosphere, sediments and biosphere on a regional and finally global level and may undergo various abiotic or biotic transformations. These complex processes of distribution, accumulation, redispersion and transformation are summarized as environmental behavior. It is governed by the physico-chemical and chemical properties of the individual substances and the specific physico-chemical properties of and the mass flow in the respective environmental compartment /12/. Usually the atmosphere is considered to be the major pathway for chlorinated hydrocarbons, the PCB and DDT included /6, 7, 10/. This transport will be governed, however, by the extent of gas phase / particle phase distribution, since the deposition mechanisms and therefore the ultimate range of transport depend on it.

One method for a rough estimation of the distribution between gas phase and particles is given by the Junge approach /13/. In remote or rural areas (particle surface $<10^{-4}$ m^2 per m^3 air), substances with a vapor pressure larger than 10^{-4} Pa, e. g. all PCB congeners with 3 to 7 chlorine atoms, HCB, HCH isomers, DDT, and DDE can be expected to occur to more than 80 $^o/o$ in the gas phase. In urban areas (particle surface $\geq 10^{-3}$ m^2 per m^3) a considerable adsorption of 4,4'-DDT and of PCB congeners with 7 or more chlorine atoms ($p < 5 \cdot 10^{-4}$ Pa) can occur. Besides the increased surface area per cubic meter of air the increased amounts of black carbon (soot) in urban air have to be considered /14/. The high adsorptivity of this material for organics will move the gas phase / particle distribution to the particle side. Substances with a vapor pressure exceeding 10^{-2} Pa, e. g. the PCB congeners with 1, 2 or 3 chlorine atoms, HCB and HCH are expected to be adsorbed only to a small extent.

The chlorinated hydrocarbons, as discussed in this report, are present in the lower troposphere in concentrations of a few nanograms per m^3 or less. Problem-orientated methods are necessary to monitor concentrations down to 1 picogram per m^3 air (Table 1). The adsorptive enrichment of these substances by pumping a large volume of air (about 1000 m^3) through a proper adsorbent is a widely used technique to achieve the neccesary preconcentration.

2. Experimental

2.1. Air sampling by adsorption

Several adsorbents are reported in the literature for high volume air sampling (Table 2) /4 - 11, 15, 16/. In this work, silica gel was selected as the adsorbent because of its very low and easily controlled blank value, its good mechanical properties, combined with a high surface area, sufficient permeability and low cost.

Table 1: Concentrations of less volatile chlorinated hydrocarbons found in air of the westerlies of the northern hemisphere. The lowest and the highest values are cited.

	Remote areas pg/m^3	Urban areas pg/m^3
alpha-HCH	410 /8/	347 /7/ - 1700 /2/
gamma-HCH	29 /8/	154 /4/ - 410 /4/
HCB	126 /8/	55 /7/ - 403 /21/
4,4'-DDT	2 /3/ - 19 /8/	12 /20/ - 270 /2/
4,4'-DDE	9 /8/	60 /2/ - 300 /2/
Sum of PCB(3-10)	58 /8/	100 /11/ - 7950 /11/

The silica gel was baked out before use by heating to 600° C for 20 hours. It had a pore diameter of 6.0 nm. Two different particle sizes were examined to test the breakthrough of substances during sampling: silica gel, 0.2 mm - 0.5 mm diameter, purchased from Merck (Darmstadt, F. R. G.) and silica gel, 0.5 mm - 1.0 mm diameter, purchased from Machery and Nagel (Düren, F. R. G.). The 0.2 mm - 0.5 mm diameter silica gel gave under identical sampling conditions less breakthrough for e.g. gamma-HCH. Therefore it was used for further analyses. Sampling of particles was executed with glass fiber filters /10/ (Sartorius, Göttingen, F. R. G., type SM 134 00). The separation efficiency of these filters is given as 98 ^{o}/o for oil droplets greater than 0.3 um.

Sampling was done by pumping air first through a glass fiber filter, followed by a layer of 100 g silica gel, a second glass fiber filter covering a second bed of 100 g silica gel for determination of the breakthrough of substances. Filter and adsorbent were placed inside a test sieve (Retsch, Haan, F. R. G.), 20 cm in diameter and 5 cm high. The test sieve was placed in the aluminium filter holder (unheated, open design) with a rain shelter of a high-volume air sampling system, Turbine EM 101 (Ströhlein, Kaarst, F.R.G.). About 1000 m^3 air were sampled during 20 - 22 hours. The air flux was adjusted to 50 m^3 per hour (14 l per second). 0.2 ml of the internal standard solution, containing 190 ng 1,2,3,4-tetrachloronaphthalene, was added on top of the particle filter before sampling.

Prior to and after sampling, the silica gel was transported and stored in screw cap jars or special glass flasks, which could be flame sealed.

2.2. Sampling locations

Samples were taken in a garden near a road with heavy traffic (location A) as well as in a suburban residential area with a rural surrounding (location

Table 2: High volume sampling of organic traces in air using adsorbents

Adsorbent	Amount	Flow rate m^3/h	Solvent Extraction	References
Polyurethane foam	8 g	21 - 30	Petroleum Ether + Acetone	5
	472 cm^3	13 - 25	Hexane	4,7
Amberlite XAD 2	20 g	21 - 30	MeOH, Acetone	5
	70 g	30 - 42	Hexane	11
Tenax GC	10 g	21 - 30	Petroleum Ether + Acetone	5,15
Florisil	60 g	24 - 32	CH_2Cl_2	8,9,15
Porous glass	76 cm^3	0,6	CH_2Cl_2	10
Silica gel	8 g	2,5	Benzene	16
Silica gel	100 g	40 - 50	CH_2Cl_2	this work

B) 5 km north of downtown Ulm (48.4° N, 10.0° E) in West Germany. The locations were selected in order to recognize local influences, mainly of traffic, and long range transport phenomena during constant continental weather conditions of the cyclone and anticyclone type.

2.3. Extraction and preseparation

The glass fiber filters were extracted continuously with dichloromethane for 20 hours in a Soxhlet apparatus. The silica used for adsorptive enrichment was extracted in a column (diameter 4 cm, length 20 cm) by elution with 250 ml dichloromethane. All chlorinated hydrocarbons of interest were eluted this way. The extract and the eluate were evaporated after adding 1 ml of heptane each to 1 ml using a Rotavapor.

Preseparation of the extracts was done on 4.5 g silica gel 60, (3 % H_2O) 0.2 mm - 0.5 mm diameter (Merck, Darmstadt, F. R. G.) /17, 18/. The first fraction (LC 1) was eluted with 30 ml hexane and included all chlorinated benzenes, polychlorinated biphenyls, polychlorinated naphthalenes and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethene (4,4'-DDE). The second fraction (LC 2) was eluted with a mixture of 30 ml hexane and 10 ml dichloromethane. This fraction included all isomers of HCH and DDT. The fractions obtained were evaporated to 0.1 ml using 0.1 ml of isooctane as keeper.

The group separation by adsorption chromatography gives both a separation into classes of different polarity and a separation from undesired polar organic substances, e. g. phenols and organic acids. The less volatile chlorinated hydrocarbons from about 1 ton of air are brought into 100 ul hexane solution this way. The enrichment factor is 10^7.

The second layer of adsorbent was used to control the breakthrough and worked up accordingly.

2.4. High resolution gas chromatography

The eluates, obtained by liquid adsorption chromatography, were analyzed qualitatively and quantitatively by high resolution capillary gas chromatography. Injection volumes were 1 ul to 3 ul. The injected solutions are equivalent to 1 m^3 or 30 m^3 air.

Two different detection systems were used: An electron capture detector (HRGC/ECD) and a mass selective detector (HRGC/MSD). Separation in both cases was done on crosslinked SE 54 fused silica capillaries.

The ECD was installed in a Fractovap 2350 gas chromatograph (Carlo Erba, Milano, Italia). Column: 25 m, i.d. 0.20 mm, fused silica, film thickness 0.5 um, Hewlett Packard (Palo Alto, U. S.). Temperature program: 120° C, 3 min, 4° C/min, until 270° C. The injector was set at 250° C and the detector at 275° C. Carrier gas was hydrogen at 1.0 m/sec.

The HRGC/MSD equipment was a HP 5995 gas chromatograph/mass-selective detector with electron impact source, quadrupol analyzer, and a HP 9816 work station (Hewlett-Packard, Palo Alto, U. S.). Capillary column: 60 m, i.d. 0.25 mm, fused silica, film thickness 0.25 um. The injector temperature was set at 280° C, oven temperature was held at 120° C for 5 minutes, then raised at a rate of 2° C/min to 280° C. Carrier gas was helium at 27 cm/sec. PCB with 3 to 10 chlorine atoms were monitored in a selected ion mode. The following masses were used: PCB (3): 255.95 amu and 257.95 amu, PCB (4): 289.90 amu and 291.90 amu, PCB (5): 323.90 amu and 327.90 amu, PCB (6): 359.85 amu and 361.85 amu, and PCB (7): 393.80 amu and 395.80 amu. The hexachlorocyclohexanes (HCH) were monitored using the masses 216.90 amu and 218.90 amu (equivalent to $C_6H_5Cl_4$), and 217.90 as control. The ions for DDT were 234.90 amu, and 236.90 amu ($C_{13}H_9Cl_2$) (235.90 as control) and those for DDE were 315.90 amu, and 317.90 amu ($C_{14}H_8Cl_4$) (316.90 as control). Hexachlorobenzene was also detected in the scan mode. Reference substances were used to monitor the retention times. External quantitation was done using the peak heights.

2.5. Quantitation procedure

The quantitation of PCB is a complex and difficult problem, particularly if the PCB pattern found in the samples deviates from that of defined technical mixtures or combinations of such mixtures. Because the PCB pattern found in air cannot be described in terms of defined technical mixtures, a simplified procedure using selected congeners was carried out /19/. The surrogate congeners PCB 28-PCB(3), PCB 52-PCB(4), PCB 118-PCB(5), PCB 138-PCB(6) and PCB 180-PCB(7) were externally calibrated. Next the PCB congeners of each degree of chlorination were quantified, using the response factors determined before /19/. The quantitation procedure for the PCB is regarded to be sufficiently accurate for comparative purposes. The detection limit for a single PCB congener was 1 - 3 picograms per m^3 depending on the specific congener.

3. Results and discussion.

Concentrations measured in both the particle and the gas phase under different meteorological conditions (Table 3) are summarized in Table 4. The particles contain only amounts near the blank value. For comparison, values found in the literature are cited in Table 1.

3.1. Isomer-specific identification of PCB in air.

PCB congeners with 3 to 7 chlorine atoms could be isomer-specifically identified and have been quantified in all air samples taken in rural and urban areas around Ulm. More than 95 °/o of the PCB were sampled on the silica adsorbent. From this one can conclude that they were originally present in the gas phase. The particles retained on the filter and the filter itself con-

Table 3: Time, site, and general meteorological conditions of the sampling

Sample number	A1	A2	A3	B1	B2	B3
Location of sampling	A	A	A	B	B	B
Date of sampling (begin)	01.07.86	18.08.86	21.10.86	01.10.86	02.10.86	23.10.86
Temperature (°C)	11-24	14-27	8-10	5-24	7-25	1-11
Air pressure (hPa)	1017-1022	1007-1008	1003-1016	1025	1025	1001-1019
Preciptation (mm)	no	rain (20)	rain (2)	no	no	rain (2)
Wind (km/h)	NNW (6)	SSW (11)	SW (24)	SSW (2)	no wind	SSW (9)
Origin of air masses	continental	mixed	marine	local, higher troposphere		marine

sampling locations: A) downtown, near road with heavy traffic,
B) suburban area, rural

Table 4: Chlorinated C_6 / C_{14} hydrocarbons found in continental air near the city Ulm (F.R.G., 48.4° N, 10.0° E). Values of the gas phase in picograms per m^3 (> 95 % total value in air). Meteorological conditions see table 3.

Sample number	A1	A2	A3	B1	B2	B3	mean value
alpha-HCH ($C_6H_6Cl_6$)	1300	160	220	520	1100	110	570
gamma-HCH ($C_6H_6Cl_6$)	11000	840	520	820	1100	180	2400
HCB (C_6Cl_6)	520	100	70	270	340	190	250
4,4'-DDT ($C_{14}H_9Cl_5$)	40	9	7	1	1	1	10
4,4'-DDE ($C_{14}H_8Cl_4$)	19	39	11	7	4	7	15
Single PCB congeners							
PCB 28 ($C_{12}H_7Cl_3$)	36	68	19	5	4	5	23
PCB 52 ($C_{12}H_6Cl_4$)	230	88	23	7	7	9	61
PCB 101 ($C_{12}H_5Cl_5$)	230	96	24	27	10	10	66
PCB 118 ($C_{12}H_5Cl_5$)	68	29	6	7	3	2	19
PCB 138 ($C_{12}H_4Cl_6$)	110	52	12	15	7	6	34
PCB 153 ($C_{12}H_4Cl_6$)	130	73	16	21	8	7	43
PCB 180 ($C_{12}H_3Cl_7$)	27	13	2	2	8	1	9
Sum of PCB chloroisomers							
Sum PCB (3) ($C_{12}H_7Cl_3$)	170	310	80	20	20	30	110
Sum PCB (4) ($C_{12}H_6Cl_4$)	810	460	110	30	30	30	250
Sum PCB (5) ($C_{12}H_5Cl_5$)	880	330	70	70	30	30	240
Sum PCB (6) ($C_{12}H_4Cl_6$)	590	350	80	100	40	30	200
Sum PCB (7) ($C_{12}H_3Cl_7$)	150	70	10	10	30	4	46
Sum PCB (8) ($C_{12}H_2Cl_8$)	1	1	1	1	1	1	1
Sum PCB (9) ($C_{12}HCl_9$)	1	1	1	1	1	1	1
Sum of PCB(3-9)	2600	1520	350	232	152	125	830

Abbreviations: alpha-HCH: Alpha-isomer of hexachlorocyclohexane
gamma-HCH: Gamma-isomer of hexachlorocyclohexane
4,4'-DDT: 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane
4,4'-DDE: 1,1-Dichloro-2,2-bis(p-chlorophenyl)ethene

tained only amounts of PCB at a level near the blank value. Congeners with 8, 9 or 10 chlorines per molecule (PCB (8-10)) were below the detection limit.

Different meterological situations significantly changed the total amount of PCB present in the lower troposphere, Table 4. If the air sampled was

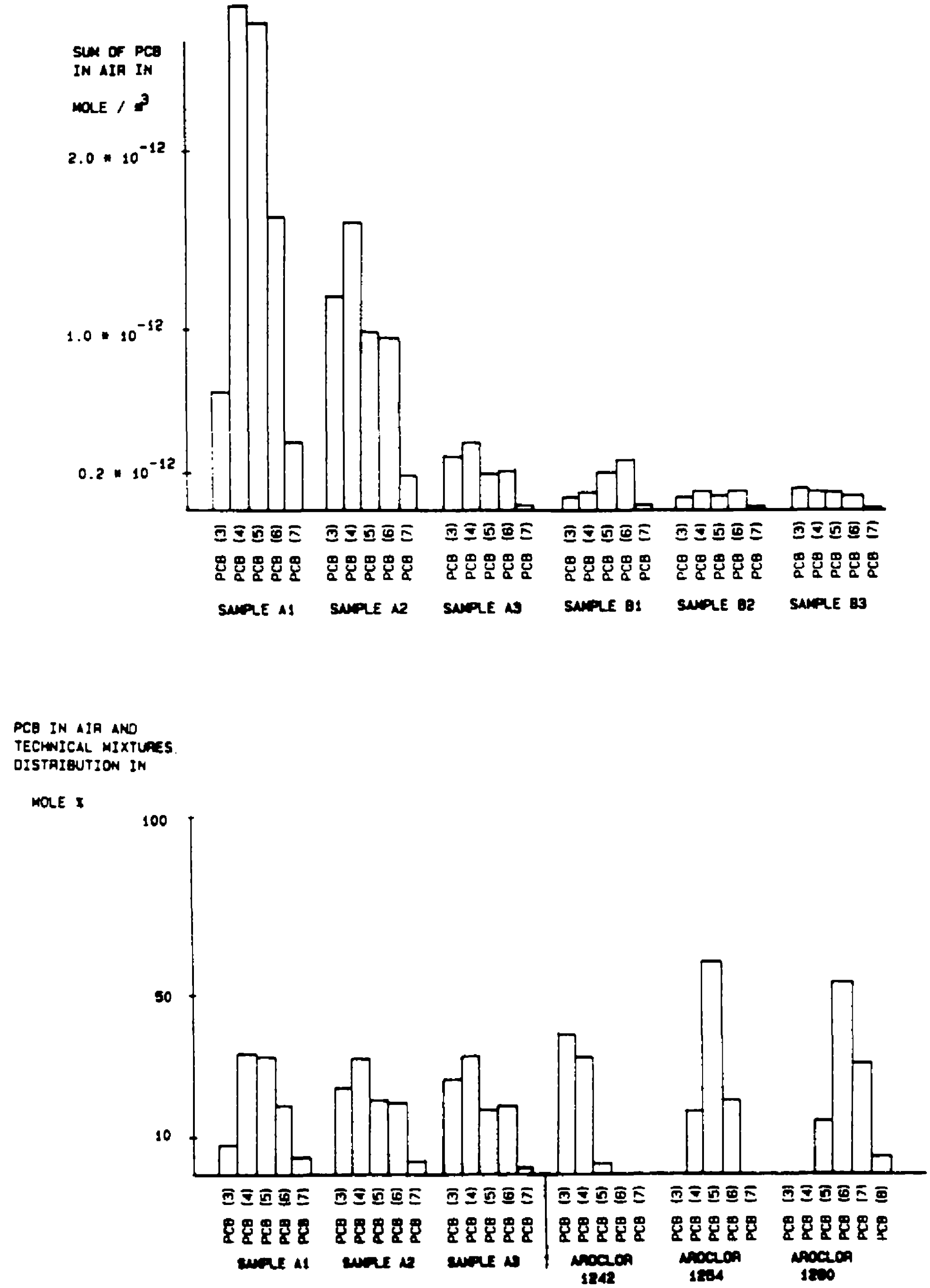

Figure 1: Upper part: Distribution of PCB homologues in air samples A1 - B3 in moles per m^3. Lower part: Distribution of PCB homologues in air samples A1 - A3 and Aroclor 1242, 1254, 1260 in mole %.

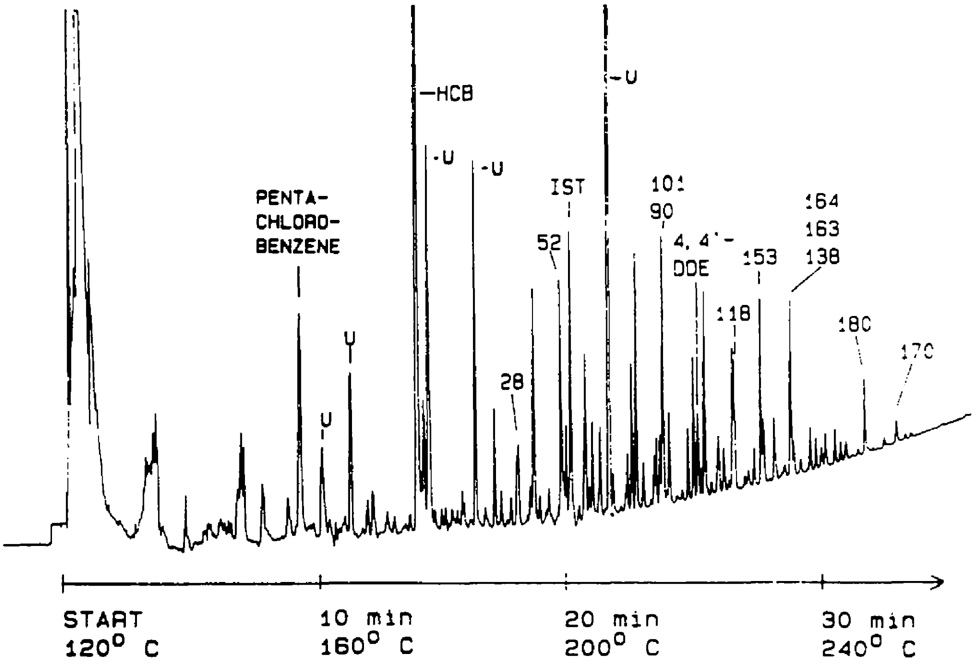

Figure 2: HRGC/ECD-Chromatogram (SE 54) of LC 1 (SiO_2 / Hexane). Injection volume equivalent to 1 m^3 air.

carried over from the Atlantic Ocean by a storm, the total amount of PCB in the lower troposphere was small, totalling 120 pg per m^3 air. When the air was of continental origin, the total amount of PCB increased by a factor of more than ten, to several nanograms per m^3 air. An influence of the sampling site can be deduced from comparing samples A3 and B3. The distribution of the chloroisomers of the same degree of chlorination did not change significantly, however. Figure 1 depicts the distribution of the PCB chlorohomologues obtained at various samplings, and for comparison the technical mixtures Aroclor 1242, 1254 and 1260 /22/. An air sample of continental history, monitored with HRGC/ECD, is depicted in Figure 2. A more detailed analysis is possible using the HRGC/MSD technique /23, 24/. An example of the resulting ion chromatograms and a corresponding reference mixture of PCB with 42 %, 54 % and 60 % chlorine (1 : 1 : 1) is depicted in Figures 3 - 5. The identification of PCB-congeners in technical mixtures has been reported /24/.

The HRGC/MSD chromatograms clearly reveal that the pattern of PCB in the lower troposphere only partly corresponds to a specific technical mixture of PCB. In air and in the technical PCB mixtures the same congeners are found, but the relative distribution is different.

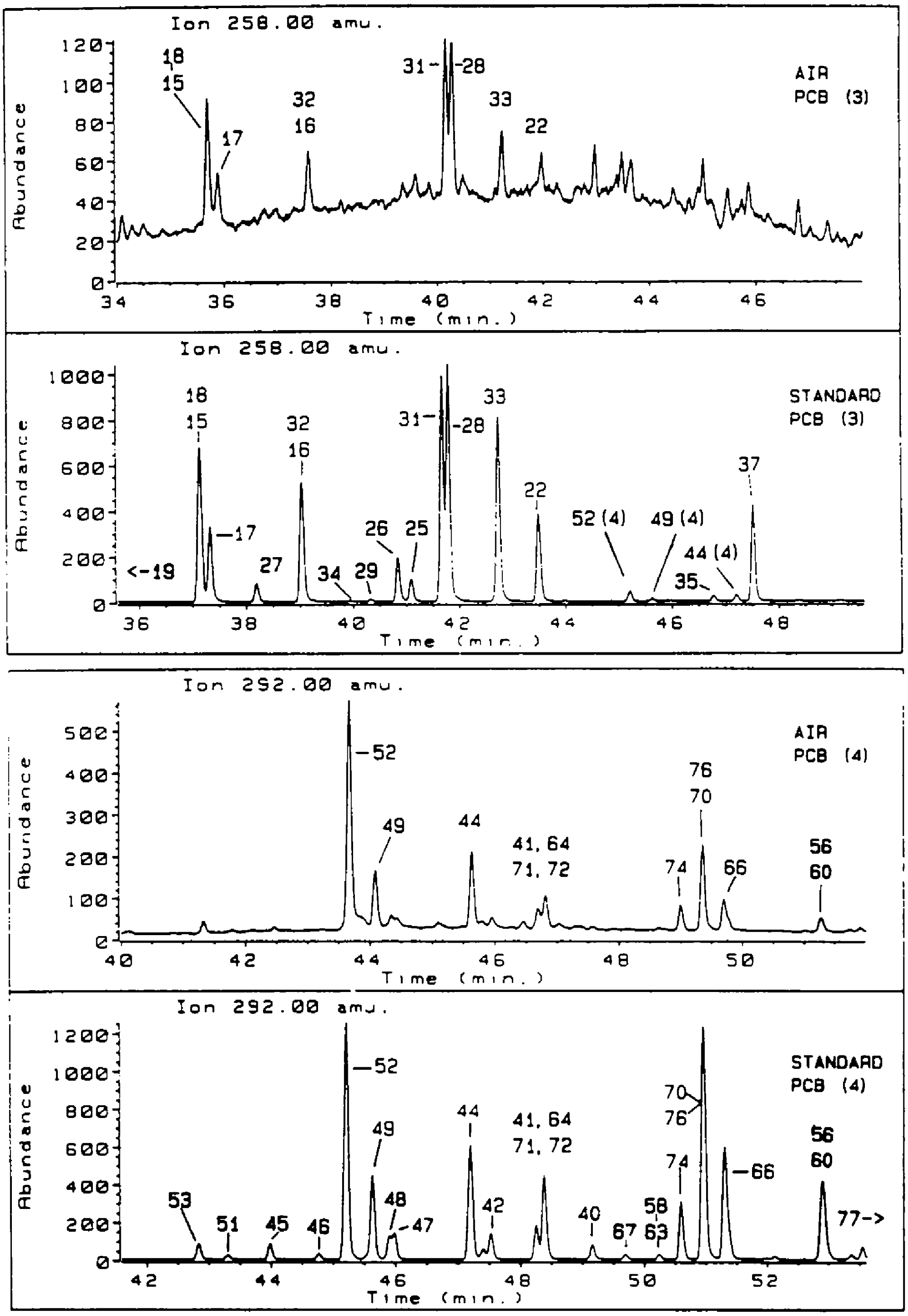

Figure 3: HRGC/MSD-Chromatogram (SE 54) of LC 1 (SiO_2 / Hexane). Detection of trichlorobiphenyls (256 amu) and tetrachlorobiphenyls (292 amu) Upper trace equivalent to 30 m^3 air, lower trace PCB reference mixture of 42 %, 54 % and 60 % chlorine content (1 : 1 : 1).

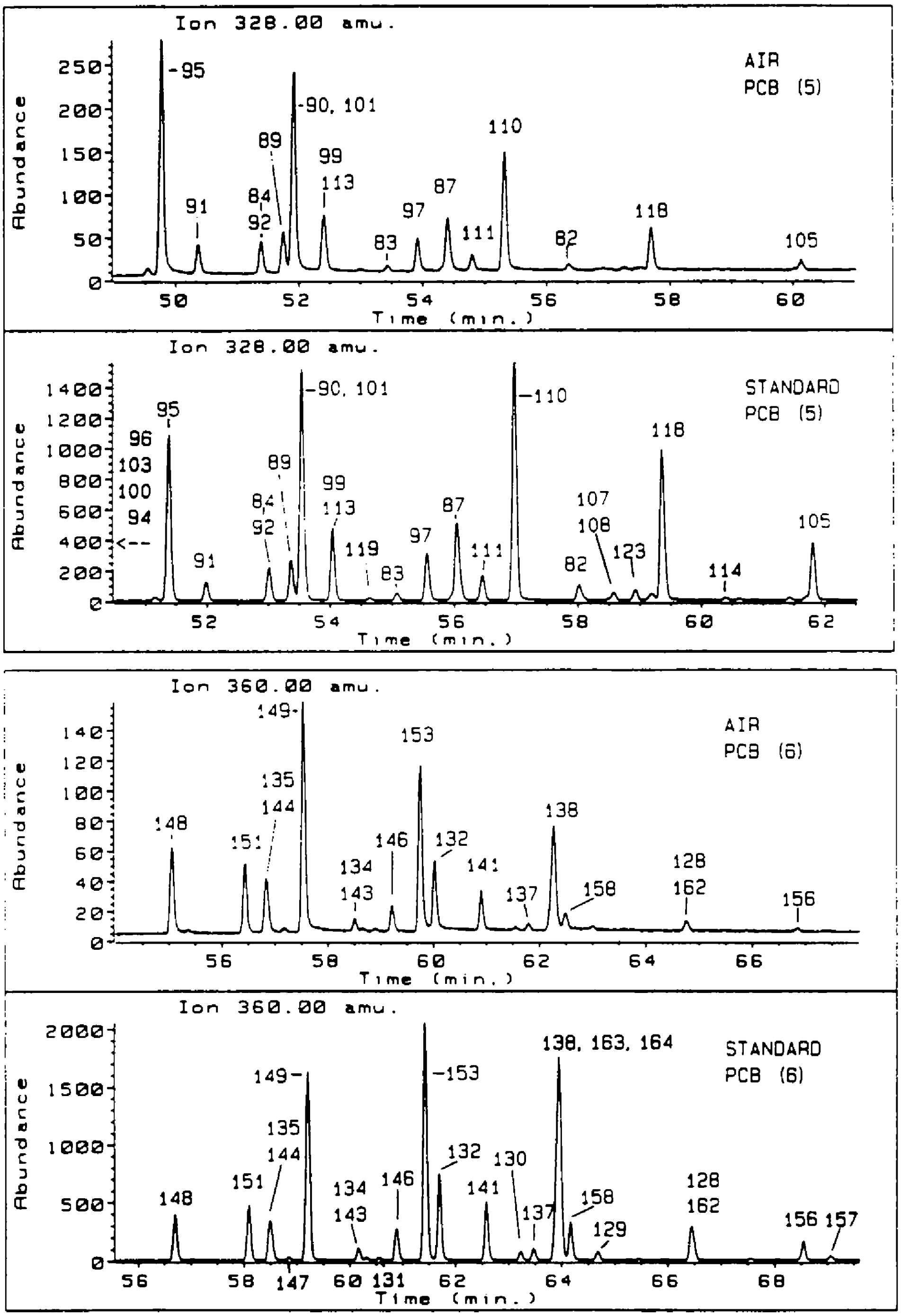

Figure 4: HRGC/MSD-Chromatogram (SE 54) of LC 1 (SiO$_2$ / Hexane). Detection of pentachlorobiphenyls (328 amu) and hexachlorobiphenyls (360 amu). Upper trace equivalent to 30 m^3 air, lower trace PCB reference mixture of 42 %, 54 % and 60 % chlorine content (1 : 1 : 1).

As a first step towards the analysis of the deviations of the relative distributions of the PCB found in the lower troposphere from those found in technical mixtures, an approximation to a composite mixture of technical PCB was tried. Typical indicator congeners were used to calculate a possible mixed composition /25/. PCB 28 was selected as a basis for PCB with 42 % chlorine (equal to Clophen A 30, Aroclor 1242), PCB 99 and 113 for PCB with 54 % chlorine (Clophen A 50, Aroclor 1254), and PCB 138 for PCB with 60 % chlorine (Clophen A 60, Aroclor 1260). This approach, however, could not simulate the PCB pattern found in the air samples.

In a second step the approximation was attempted for each of the chlorohomologues only, as the deviation of the pattern of the chlorohomologues is small for the different PCB mixtures. A reference mixture of PCB with 42 %, 54 % and 60 % chlorine (1 : 1 : 1) was chosen to simulate overlapping inputs of congeners occuring in different PCB preparations. The peak heights of PCB 28 (tri-), PCB 66, 80 (tetra-), PCB 118 (penta-), PCB 138 (hexa-) and PCB 180 (heptachlorobiphenyl) were set to one and this standard mixture was compared to the PCB in air. The ratios of the peak height for the PCB-congeners in air and in the above reference mixture vary between 0.5 to 6, however indicating a

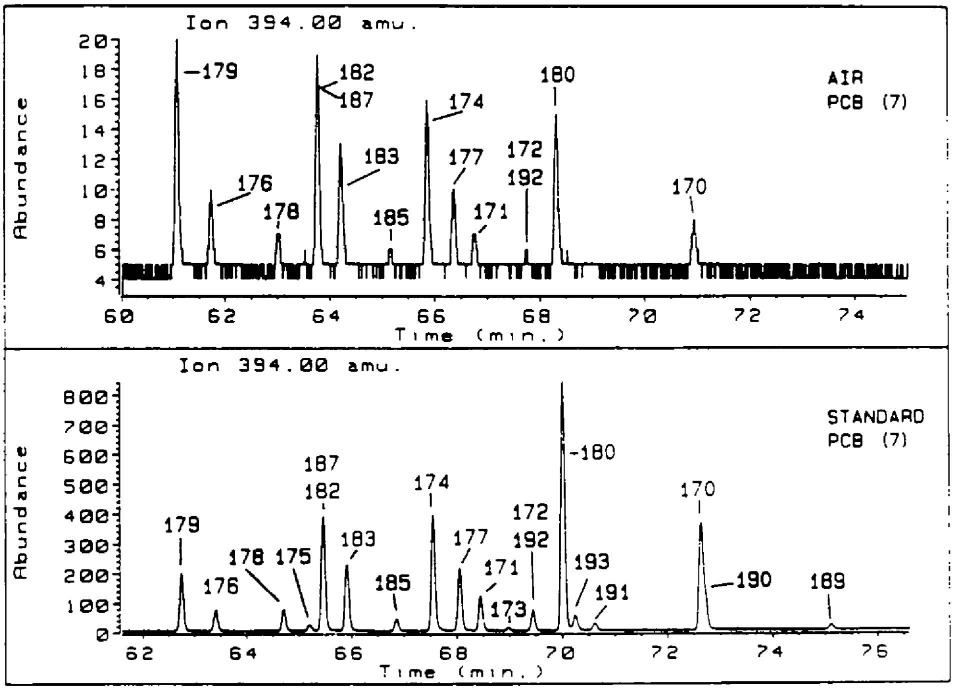

Figure 5: HRGC/MSD-Chromatogram (SE 54) of LC 1 (SiO_2 / Hexane). Detection of heptachlorobiphenyls (394 amu).
Upper trace equivalent to 30 m^3 air, lower trace PCB reference mixture of 42 %, 54 % and 60 % chlorine content (1:1:1).

distinct trend. The plot is shown in Figure 6. Obvious is the enrichment of isomers with higher vapor pressure compared to those with lower vapor pressure for the same degree of chlorination in the air samples. Only the PCB isomers with 3 chlorine atoms do not show this effect. The deviations of the pattern of chlorohomologues in air and in technical mixtures did not change much with different meteorological conditions, though the relative distribution for the chlorohomologues (Fig. 1) and the absolute amounts of PCB changed (Table 4).

In a third step to simulate the pattern of PCB in the lower troposphere, the vapor pressure as an important physico-chemical property was taken into consideration. The peak ratios of step two were corrected by the vapor pressure of each congener. This will correct for the input by evaporation from solid surfaces and also for the output by adsorption on particles and their dry and wet deposition.

Again, the vapor pressure corrected peakheights of the PCB 28 (tri-), PCB 66,80 (tetra-), PCB 118 (penta-), PCB 138 (hexa-) and PCB 180 (heptachlorobiphenyl) are set to one. Then all other congeners of one degree of chlorination are normalized to the corresponding PCB-congener. The ratio r_i

$$r_i = \frac{H_{i,air}}{H_{i,ref}} \cdot \frac{1}{p_{i0}}$$

$H_{i,air}$	Peak height of PCB congener i in air sample
$H_{i,ref}$	Peak height of PCB congener i in a 1:1:1 mixture of 42 %, 54 % and 60 % chlorine, normalized
p_{i0}	Vapor pressure of the PCB congener i

amounts to 1.0 ± 0.2 (range 0.7 to 1.5) for the PCB congeners with 4 - 7 chlorine atoms (Figure 7). A good agreement between the PCB pattern in air samples and technical mixtures was obtained by this vapor pressure correction. This good agreement makes any specific photodegradation of PCB often discussed in the literature unlikely.

3.2. Hexachlorobenzene (HCB)

HCB is used as fungicide and is found as a by-product in several chlorinated industrial chemicals and wastes. It is also produced during combustion processes. Its environmental input is complex and diffuse. Combining this with its chemical stability and apparently poor adsorption properties explains the small changes in concentrations observed in the troposphere, compared to e. g. gamma-HCH or the hexachlorobiphenyls. The amount found in the lower troposphere in our measurements ranged from 0.07 to 0.5 nanograms per m^3 and is in agreement with other reports (Table 1) /2,5,7,8,21/. The values for the suburban/rural area always show a higher trend. This makes a local input likely.

3.3 Hexachlorocyclohexane (HCH)

Hexachlorocyclohexanes are applied either as "Lindane" (99 % gamma-isomer),

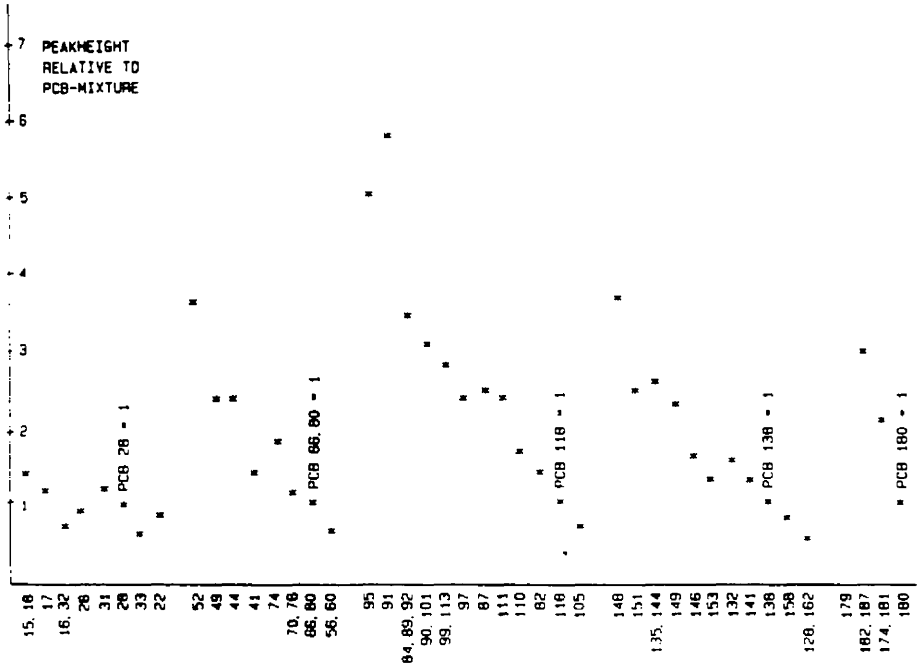

Figure 6: Plot of the normalized ratio r versus chlorination degree and retention on a non-polar GC-phase (SE 54).
Reference mixture consists of PCB 42 %, 54 % and 60 % chlorine content (1:1:1).

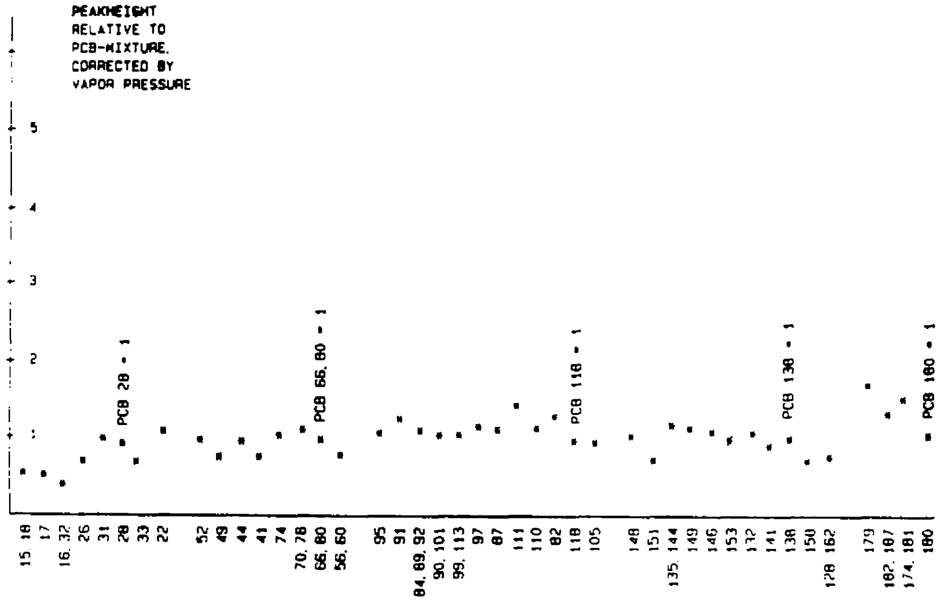

Figure 7: Plot of normalized ratio r_i, corrected for vapor pressure, versus chlorination degree and retention on a non-polar GC-phase (SE 54).
Reference mixture consists of PCB 42 %, 54 % and 60 % chlorine content (1:1:1).

purified HCH (16.1 % - 98.9 % gamma-isomer) or technical HCH (benzene-hexachloride: 12 % - 16 % gamma-isomer) and are known to exist in eight isomeric forms /27/. The most pronounced insecticidal properties are exhibited by the gamma-isomer. In this report only alpha- and gamma-HCH are considered. The ratio of the alpha- and gamma-isomers of HCH found in the air of the lower troposphere should reflect the kind of mixtures applied for insecticide control, its modification by dry and wet deposition and by abiotic degradation, too. In remote areas of the northern hemisphere the amount of the alpha-isomer surpasses that of the gamma-isomer several times; the ratio is 3 :1 up to 50 : 1 /3,7,8/. In urban and rural areas around Ulm we found the situation reversed. Depending on the origin of the air masses, the total amount of HCH and the ratio alpha to gamma changed. Air masses coming in from the North Atlantic by storms and showing heavy rainfalls, gave levels for gamma-HCH of about 0.20 nanograms per m^3 and an alpha to gamma ratio of 1 : 1 to 1 : 2. In contrast, air masses from the continent in a high pressure situation without precipitation gave alpha to gamma ratios as low as 1 : 8, with an increase of the total amount of HCH up to 12.3 nanograms per m^3. The use of Lindane, the gamma isomer, in forestial applications is strongly reflected in these results. The occurence of gamma-HCH in the groundwater in West Germany is well documented /28/ and surely a result of its general occurence. The water / air distribution coefficient (K_W) for gamma-HCH $K_W = c_{water} / c_{air} = 300$ /29/ indicates a rather effective washout by rain.

3.4. 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (4,4'-DDT)

DDT is still extensively produced worldwide for use as an insecticide. It is usually applied as a technical mixture containing 70 % 4,4'-DDT, 20 % 2,4'-DDT and 10 % other products /27/. Only minor amounts of 4,4'-DDE are present in the mixture called "DDT" /27/.

The worldwide occurence of 4,4'-DDT and 4,4'-DDE in the troposphere is well documented. Up to 600 picograms 4,4'-DDT per m^3 air have been determined in tropical regions /3, 30/. In remote areas of the westerlies of the northern hemisphere concentrations below 25 picograms 4,4'-DDT per m^3 air are found /3, 7, 8/. 4,4'-DDE is reported to occur at levels between 10 to 100 picograms per m^3 air in remote areas worldwide /6, 8, 30/.

In the air around Ulm we found levels of 4,4'-DDT from 1 to 40 picograms per m^3 air. Lower values were always found at sampling location B indicating a local source for sampling location A. Cyclonic marine air gave low results, anticyclonic continental air gave high results, as also found for the PCB. The level of 4,4'-DDE in air changed independently from that of 4,4'-DDT. Amounts of 4 - 39 picograms 4,4'-DDE per m^3 have been determined. Again the lower values were found at the suburban/rural sampling location B. "DDT" is not allowed to be applied in West Germany since 1971 /31/. It must be transported from areas, where this insecticide is still in use. The occurence of the transformation product 4,4'-DDE and the independent changes of 4,4'-DDE relative to 4,4'-DDT indicate the presence of an standing air load of the former.

Conclusions

The atmospheric concentrations of the less volatile chlorinated hydrocarbons HCH, PCB and DDT are due to the input of defined technical products, whereas HCB originates from different sources. As shown for the PCB the vapor pressure of the individual substance is an important physico-chemical parameter that governs both the distribution between particle and gas phase, and second the deviations found between the pattern in air and in technical mixtures. Different meteorological situations result in varying concentrations of the chlorinated hydrocarbons considered. The movement of air masses over the European continent distributes the chlorinated hydrocarbons, released from different sources, according to the meteorological conditions. Transport of air masses over longer distances superimposes local input. Though the results by no means allow a statistical evaluation, it may be of interest to calculate the order of the aerial load. For this purpose we used the small data basis of this work. The means of other investigators coincide well with our results (Table 1). The results for the troposphere between 30° N and 70° N are summarized in Table 5.

Table 5: Estimation of the total load of selected halogenated hydrocarbons in the troposphere between 30° N and 70° N.

Substance	Assumed average concentration	Calculated tropospherical load (30° N - 70° N)*
HCB	250 pg/m^3	170 tons
HCH**	3000 pg/m^3	2000 tons
DDT	10 pg/m^3	7 tons
DDE	15 pg/m^3	10 tons
Sum PCB (3-7)	830 pg/m^3	560 tons

* (22 % of the surface of the earth, height of troposphere 6 km STP)

** Sum of alpha- and gamma-isomer

The results of Table 5 indicate that relative to the known production figures the tropospheric load is negligible. The troposphere may act as a very effective medium for long range transport, but the prevailing part of the production always arrived in the environment has to be sought in other environmental compartments (water, soil, sediments, biota). In the case of e.g. the PCB, the substances may not yet have entered the environment to a substancial part at all.

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