Evidence of Latitudinal Fractionation of Polychlorinated Biphenyl Congeners along the Baltic Sea Region

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Annual cycles of the atmospheric concentrations of PCBs were determined at 16 (mostly rural) stations around the Baltic Sea between 1990 and 1993. The concentration levels of individual congeners were found to be influenced by their physical-chemical properties, ambient temperature, and geographical location. Median levels of PCBs were similar at all stations except at one urban site near Riga. A latitudinal gradient with higher levels in the south was found for the sum of PCB as well as for individual congeners, and the gradient was more pronounced for the low volatility congeners. As a result, the high volatility congeners increased in relative importance with latitude. Generally, PCB concentrations increased with temperature, but slopes of the partial pressure in air versus reciprocal temperature were different between congeners and between stations. In general, the low volatility congeners were more temperature dependent than the high volatility PCB congeners. Steep slopes at a sampling location indicate that the concentration in air is largely determined by diffusive exchange with soils. Lack of a temperature dependence may be due to the influence of long-range transported air masses at remote sites and due to the episodic or random nature of PCB sources at urban sites.

Introduction

During the last two decades several studies on persistent organic pollutants (POPs) in air have been conducted both in remote and rural areas (*1* and references therein). Emphasis has traditionally been on spatial distribution, but during recent years the focus has shifted to mechanistic approaches using data covering longer time periods (*1*−*5*). These studies have shown that many POPs show cyclic fluctuations over the year, with atmospheric concentrations peaking during the summer. Higher summer temperatures enhance volatilization from surface media, i.e., water, ice, snow, plants, soil, and bedrock. Once airborne, POPs may migrate through the atmosphere as gases and sorbed to aerosols. Deposition from the atmosphere is enhanced in low-temperature regions. Possibly a fractionation process occurs so that less volatile compounds are deposited close to the source and more volatile compounds travel further toward the poles. A contaminant mixture with both high and low volatility compounds, such as the PCBs, will change its composition along a temperature or latitudinal gradient (*6*). This means that the proportion of high volatility PCBs in air should increase relative to low volatility PCBs when approaching the polar regions.

Latitudinal gradients have been observed for PCBs in fish liver (*7*) and in sediments (*8*), for HCB and HCHs in foliage (*9*), and for HCB, α-HCH, γ-HCH, and pentachloroanisol in treebark (*10*). Lead et al. (*11*) argue that to test the global fractionation hypothesis, concentration data are required for longer time periods at different latitudes. They conclude that for latitudinal data obtained at only one sampling occasion, only the effect of temperature and a compound's physicochemical properties on air-vegetation partitioning can be observed. They measured the concentration of PCBs in moss (*Hylocomium splendens*) collected in remote areas in Norway in 1977, 1985, and 1990. A change in congener profile was observed, in that over time, the low volatility groups decreased more in the South then they did in the North. These observations are tentatively suggested to provide evidence for the process of global fractionation.

A field study was initiated in October 1990 in order to determine polychlorinated biphenyls (PCBs) in air at 16 sampling stations, located on islands or close to the coast of the Baltic Sea. Sampling was carried out continuously during one year for most of the stations, and up to two years for some stations. Establishing the spatial and temporal variability of the atmospheric concentrations of PCBs over the Baltic Sea is important because in large water bodies the water is responding fairly rapidly to contaminant levels in the atmosphere (*12*). This study is the first to combine long-term temporal measurements of air concentrations with large spatial coverage (latitude 54°00′ to 65°44′) that allows the investigation of latitudinal trends in atmospheric concentrations.

Recently, Wania et al. (*13*) presented two models to explain how air concentrations depend on temperature. The first assumes equilibrium between the atmosphere and the Earth's surface. The second also include the kinetics of air-surface exchange and predicts atmospheric concentrations when advection in air and reversible exchange with a surface is taken into account. Based on these models it is hypothesized that the relationship between the logarithm of the partial pressure of PCBs in air ($\ln p_A$) and inverse temperature ($1/T$) can be used to determine how air concentration is controlled by local (re-) evaporation vs by advection of contaminated air masses. Hoff et al. (*14*) came to a similar conclusion when analyzing data from the Great Lakes region. In this paper we attempt to evaluate this hypothesis by testing it on our field data.

Experimental Section

Sixteen sampling stations were located as close to the sea as possible and preferentially in the vicinity of meteorological stations (Figure 1). Nine stations were situated on the mainland within 5 km of the shoreline, and five stations were on islands. Air was sampled with high-volume samplers at 2 m above the ground. Approximately 1000 m^3 of air was drawn through two polyurethane foam (PUF) plugs in series by means of an electric pump at a rate of 30−50 L/min

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10.1021/es980867l CCC: $18.00
Published on Web 02/27/1999

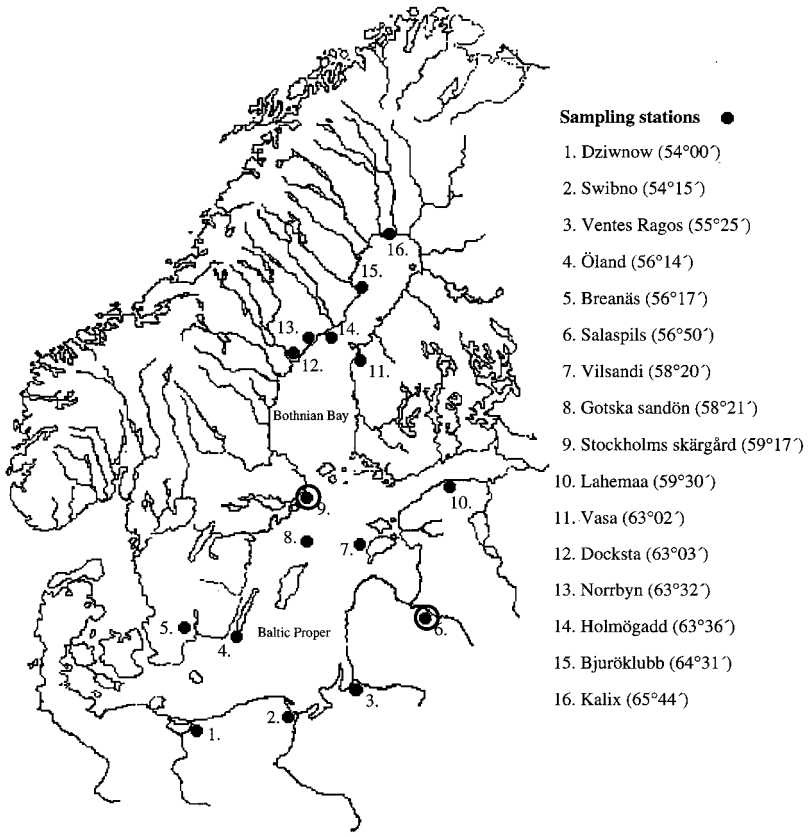


FIGURE 1. The sampling locations were located all around the Baltic Sea. Latitudes are given in parentheses after the name of the station. Encircled are the stations discussed in Figure 5.

(registered by a flow meter, see ref *15* for more details). PUF-plugs were precleaned in a modified Soxhlet apparatus with acetone:*n*-hexane and kept frozen until use. No separation of vapor and particle-sorbed PCBs was performed in this study. Reported levels are thus for total PCBs. The PUF-plugs were changed every 2 weeks. During the study, a total of 299 air samples was obtained.

Sample Preparation and Analysis. The methods for sample preparation and analysis are described in detail elsewhere (*16*). Briefly, PCBs adsorbed on the PUF from air were extracted in a modified Soxhlet apparatus with a mixture of acetone and *n*-hexane. Octachloronaphthalene and pentachlorobenzene were used as internal standard and chromatographic standard, respectively. Concentrated extracts were cleaned and fractionated on acid/basic double layer silicagel columns. Samples were analyzed for PCBs by capillary-gas chromatography/ECD (Shimadzu GC-14) with split/split less injector, 20 m DB5 quartz capillary column (i.d. 0.18 mm). PCB components were identified and quantified according to Mullin et al. (*17*) and Schulz et al. (*18*). The concentration of total PCB (sPCB) was calculated from 51 identified peaks: PCB-7/9, 6, 18/17/15, 24/27, 16/32, 26,25, 31/28, 20/33/53, 51/22, 45, 46, 52, 49, 47/48/75, 35, 44, 37/59/42/, 41/64, 40, 63, 74, 70, 66/95, 92, 84, 90/101, 99, 97, 87/115, 77/110, 82/151, 123/149/118, 146, 132/153/105, 141/179, 160/138/158, 129/126/178, 187, 183, 128, 174, 177, 202/171/156, 180, 200, 170/190, 199, 203/196, 208/195, and 194.

Quality Control. The analytical performance was regularly controlled with pesticide standards, PCB standards, Aroclor 1242, and Clophen A60. Extraction efficiency of the internal standard octachloronaphthalene was 91 ± 23%. All samples were corrected individually for recovery. For 12 samples, we extended the control of recovery by adding PCB-14, 65, and 166 to the PUF-plugs before extraction. Recoveries were 93 ± 21%, 88 ± 23%, and 105 ± 28%. Blanks (field and analytical) were examined every 12 samples, and as blank values were always negligible compared to the samples, no blank correction was performed.

To examine collection efficiency, 12 samples collected at the Salaspils station (no. 6) in Latvia (the most heavily contaminated station) during the time period November 28, 1991 to June 18, 1992, were used. The two PUF-plugs were cut in half, and the resulting four parts analyzed individually. No breakthrough was detected except for periods when the temperature was >10 °C. Then the breakthrough of some PCBs, up to tetrachlorobiphenyl, was extensive, with equal amounts of the congeners on each of the four plugs. However, during these high summer temperatures, congeners showing breakthrough constituted only about 27% of the total PCB concentration and were therefore included in the calculations of sum PCB. PCB-28/31 (tri-PCB) and 52 (tetra-PCB) showed breakthrough behavior, but PCB-20/33/53 and 41/64 did not. These latter congeners were therefore used to illustrate the behavior of tri- and tetrachlorinated PCBs.

Statistical Analysis. Analysis of covariance (ANCOVA) was employed to validate and summarize the data (*19*). To obtain a comparable set of data from each station with a minimum of bias of season for the analysis of latitudinal gradients, median, minimum, and maximum value, we limited the time period from which data were selected to approximately one year. On average, 315 ± 90 days of sampling were included in the statistical analysis. Due to an insufficient number of samples the two Polish stations, Dziwnow (no. 1) and Swibno (no. 2), were omitted from this analysis as was the station Salaspils (no. 6) in Latvia which is considered to be an urban rather than a background station. For three stations there were periods during which no air samples were taken: spring samples for Lahemaa (no. 10), summer samples for Ventes Ragos (no. 3), and winter samples for Vilsandi (no. 7). These data are thus less reliable. All PCB concentration data used

in the statistical analysis were natural log(ln) transformed to obtain normally distributed values. Temperature data were received from the meteorological database at the Swedish Meteorological and Hydrological Institute (SMHI, *15*).

Results and Discussion

Concentrations of PCBs. Median concentrations of sPCB and seven congeners for all 16 stations are reported in Table 1. Results for individual congeners are available from the authors on request. Overall, the median concentration of sPCB in air was 57 pg/m^3 (n = 299) and ranged from 32 to 80 pg/m^3 for the 15 "background stations". On a congener specific level, the median concentrations were between 0.4 and 2.3 pg/m^3 with PCB-101 having the highest and PCB-180 the lowest median. Salaspils (no. 6) in Latvia consistently showed higher values of PCBs than any other station, with a median of 454 pg/m^3 sPCB and with congener levels between 1.5 and 28.4 pg/m^3. Thus, this station was considered to be an "urban station" (Table 1). The PCB levels in air measured in this study are comparable with those reported in previous studies. Axelman et al. (*20*) found sPCB concentrations of 5−40 pg/m^3 (seven congeners) with a median of 21 pg/m^3 in 10 samples collected along a latitudinal gradient in the Baltic Sea during 1992. A comparison between the present data and those from earlier studies indicates that there has been no major decline in atmospheric PCB concentration. Larsson and Okla (*21*) reported median atmospheric concentrations of PCBs at five coastal stations in Sweden to be 62 pg/m^3 between 1984 and 1985. In the Skagerak region, concentrations were approximately 100−200 pg/m^3 of sPCB, and the median concentrations of congeners PCB-28, 52, 101, 118, 153, 138, and 180 were between 0.65 and 5.5 pg/m^3 (*22*).

To exemplify the annual cycles of a high and a low volatility PCB (PCB-33 and PCB-138) and illustrate how these substances vary in the atmosphere over the latitudinal gradient, atmospheric concentrations were plotted against time for five selected stations: Öland (no. 4), Gotska sandön (no. 8), Stockholm's skärgård (no. 9), Holmögadd (no. 14), and Kalix (no. 16) (Figure 2). Overall, concentration of both congeners showed similar patterns for all sampling stations over the study period. The levels seemed to oscillate, with high levels from August to October of 1991, lower levels November to January of 1991−1992. All stations showed an increase in levels during late winter, starting in January at the most southerly station (Öland) and in February further north (Stockholm's skärgård, Holmögadd, and Kalix). During the summer of 1992, all stations showed high levels of PCB-138 and low levels of PCB-33. Also worth noting is the comparably limited oscillations at the station Gotska sandön (no. 8), which is a small island situated in the middle of the Baltic Proper. The similarity of the concentration curves for PCB-33 during the sampling period indicates that it is the same air mass that travels over the latitudinal gradient. Differences between the stations may be attributed largely to whether it is a site that experiences air masses originating mostly from the open sea (i.e. like the maritime station Gotska sandön no. 8), from uncontaminated terrestrial surfaces, or from more contaminated terrestrial surfaces as for the station Öland (no. 4). The latter station showed the largest increase in PCB-138 during the summer months of 1992 although a similar response on the concentration curve was evident at most stations.

Latitudinal Relationships and Global Fractionation. We calculated the regression between the mean concentration of each station (expressed as the logarithm of the partial pressure in air in Pa, ln p) and latitude. All congeners except PCB-41/64 showed a negative relationship with latitude (Figure 3). The slopes (m) of the regression-lines decreased with decreasing volatility so that PCB-180 had a slope of −0.09 and PCB-33 had a slope of −0.04. The r^2 values varied between 0.38 and 0.70, and it was highest for PCB-101.

The dataset was further examined by calculating the ratio, R, between the concentration of PCB-20, 33, 53 and PCB-138 (expressed as p). R is thus a measure of the relative PCB composition. High R consequently means a large proportion of the high-volatility congener, a ratio that is predicted to increase with latitude according to the global fractionation hypothesis (*23*). This was clearly seen in the data as the median of ln R for each station was positively related to latitude (Figure 4, m = 0.06, n = 13, r^2 = 0.61, p < 0.002).

The decrease of concentration with latitude was strongest for the low volatility PCBs. This was also reflected in the relative PCB composition as an increase of the proportion of high volatility congeners (ratio R) with latitude. This behavior can be explained by the more efficient deposition of the low volatility congeners, which are lost from the atmosphere closer to the source regions. The high volatility PCBs remain airborne for a longer time, are transported greater distances, and can be assumed to show more uniform atmospheric concentrations. The results could, however, partly be explained by higher decomposition of PCB in the south than in the north, both in soil and atmosphere. Higher degradation in soil, caused by higher microbial activity due to higher mean temperature in the south, would mainly affect high volatility PCBs (*24*−*26*). One effect of high degradation would be that less of the high volatility PCBs is available for volatilization from soils, which in turn would lower the proportion of these congeners in the atmosphere. This would result in a lower mean R-ratio in the south relative to the north. Chemical reactions with OH radicals in the atmosphere increase with temperature and volatility (*27*). Thus, higher OH-radical degradation of high volatility PCBs would also lead to a lower mean R-ratio in the south relative to the north. However, at present very limited field data is available on the relative importance of these degradation pathways for PCBs. Recently, Bignert et al. (*28*) could find no evidence for global fractionation when analyzing concentrations in biota samples along a South−North transect in Sweden. Namely, the concentration decrease observed during the time period from 1968 to 1995 was the same for fish in lakes in the South of Sweden (Lake Bolmen) and in the Swedish Arctic (Lake Storvindeln). This was interpreted as evidence for a one-step transport mode from source regions to the Arctic, controlled by the winds and the deposition conditions prevailing during a specific year, rather than global fractionation. The contrasting results of this and our study may be due to the different nature of the sampling matrix. The atmosphere provides a short-term picture at high resolution whereas biota integrates conditions over a much longer time span.

Temperature Relationships: Long-Range Transport vs Local Surfaces as Source of PCB to the Atmosphere. It has been hypothesized that the slope (m) of the relationship between ln p and reciprocal temperature can be used to determine which processes control atmospheric concentrations of POPs (*13*, *14*). Low slope or lack of slope is an indication that advection of air masses from areas experiencing little effect of temperature is the driving force behind atmospheric concentration. The reasons for the lack of a temperature effect in these air masses may be that they have (a) passed over cold and/or uncontaminated terrestrial surfaces where the pollutants are lost to the surface, resulting in low stable levels in the air, or (b) that the air masses have passed over the relatively isothermal open sea with no point sources, resulting in stable concentrations. Steep slopes at a sampling location, on the other hand, indicate that the concentration in air is largely determined by diffusive exchange with contaminated terrestrial surfaces which experience major temperature fluctuations (*13*).

TABLE 1. Concentrations and Temperature Dependence of Selected PCB Congeners and sPCB at the Sampling Stations

S	median	min.	max.	*m*	r^2	*p*	*S*	median	min.	max.	*m*	r^2	*p*
							PCB-33						
1	1.8 (5)	0.8	10				10	1.3 (16)	0.7	1.9	−328 (24)	0.00	ns
2	2.5 (6)	1.0	11				11	1.1 (26)	0.4	2.7	6122 (30)	0.58	***
3	1.3 (10)	0.9	9.3	−4 (17)	0.00	ns	12	1.2 (24)	0.4	4.7	2001 (26)	0.05	ns
4	2.3 (18)	0.3	5.2	1606 (18)	0.02	ns	13	1.2 (23)	0.4	3.8	−515 (27)	0.01	ns
5	1.7 (21)	0.5	4.7	4859 (21)	0.44	**	14	1.5 (23)	0.2	7.2	992 (24)	0.01	ns
6	5.7 (20)	2.3	29	−1390 (20)	0.04	ns	15	1.2 (23)	0.1	5.1	2956 (31)	0.08	ns
7	1.2 (9)	0.5	1.7	−1884 (9)	0.11	ns	16	1.2 (24)	0.3	4.9	2122 (25)	0.05	ns
8	1.7 (24)	0.8	6.2	2856 (29)	0.20	*	AS	1.4 (293)	0.1	29			
9	1.3 (21)	0.8	4.0	2656 (21)	0.17	ns							
							PCB-41/64						
1	0.9 (5)	0.3	12				10	1.2 (16)	0.3	3.4	−1986 (24)	0.07	ns
2	1.5 (6)	0.4	12				11	0.9 (27)	0.3	3.3	3647 (31)	0.20	*
3	0.9 (10)	0.3	12	−1216 (17)	0.00	ns	12	1.3 (24)	0.5	3.9	−469 (26)	0.00	ns
4	2.1 (20)	0.7	6.8	539 (20)	0.00	ns	13	1.3 (23)	0.4	5.3	−3957 (27)	0.26	**
5	2.3 (21)	0.8	7.8	5108 (21)	0.55	**	14	1.6 (23)	0.6	10	−2745 (25)	0.06	ns
6	14 (20)	1.8	86	−4209 (20)	0.18	ns	15	1.4 (23)	0.2	6.3	2102 (31)	0.04	ns
7	2.1 (9)	0.9	3.1	−6721 (9)	0.74	**	16	1.1 (24)	0.3	5.1	109 (25)	0.00	ns
8	2.0 (23)	1.4	8.5	−652 (28)	0.01	*	AS	1.7 (295)	0.2	86			
9	2.4 (21)	1.1	4.9	−1644 (21)	0.07	ns							
							PCB-101						
1	1.7 (5)	0.4	12				10	1.7 (16)	1.0	5.8	−2443 (24)	0.12	ns
2	1.9 (6)	0.7	8.4				11	1.3 (27)	0.7	2.9	66 (30)	0.00	ns
3	2.6 (10)	0.7	11	−1385 (17)	0.01	ns	12	2.1 (24)	0.7	8.0	−2003 (26)	0.06	ns
4	3.4 (21)	0.8	9.4	−6205 (21)	0.45	***	13	2.6 (24)	0.2	6.1	−6664 (28)	0.33	**
5	2.8 (21)	1.2	7.9	964 (21)	0.03	ns	14	2.1 (23)	0.6	6.7	−6398 (25)	0.48	***
6	28 (20)	4.3	245	−2856 (20)	0.08	ns	15	1.4 (24)	0.6	3.4	−45 (32)	0.00	ns
7	2.2 (9)	1.0	4.9	−4812 (9)	0.35	ns	16	2.0 (24)	0.2	3.4	−5478 (25)	0.46	***
8	2.7 (24)	1.5	5.9	−2164 (29)	0.23	**	AS	2.3 (299)	0.2	245			
9	3.0 (21)	0.7	7.5	−7244 (21)	0.65	***							
							PCB-118						
1	1.3 (5)	0.3	6.2				10	1.1 (16)	0.5	2.6	−2060 (24)	0.11	ns
2	1.2 (6)	0.5	3.6				11	1.1 (27)	0.4	2.4	−1683 (31)	0.09	ns
3	1.3 (8)	0.4	3.3	−2125 (17)	0.04	ns	12	1.3 (22)	0.3	11	−4944 (24)	0.28	**
4	2.1 (18)	0.4	11	−11850 (18)	0.86	***	13	1.8 (22)	0.3	6.6	−8150 (26)	0.58	***
5	2.8 (19)	0.5	9.8	−1509 (21)	0.04	ns	14	1.3 (20)	0.4	3.1	−5124 (21)	0.35	**
6	34 (3)	6.8	158				15	0.9 (24)	0.5	2.0	−1454 (32)	0.14	*
7	1.5 (9)	0.7	3.4	−5614 (9)	0.37	ns	16	1.1 (24)	0.2	5.0	−7755 (25)	0.65	***
8	1.7 (22)	1.1	5.3	−4999 (29)	0.71	***	AS	1.4 (266)	0.2	158			
9	2.7 (21)	0.4	9.5	−9572 (21)	0.69	***							
							PCB-153						
1	2.5 (5)	0.4	7.6				10	1.1 (16)	0.5	3.3	−1793 (24)	0.05	ns
2	1.1 (6)	0.5	3.8				11	1.2 (27)	0.5	2.6	−1281 (31)	0.05	ns
3	1.7 (10)	0.4	3.8	−1767 (17)	0.02	ns	12	1.4 (24)	0.4	5.0	−3859 (26)	0.18	*
4	4.0 (21)	0.5	10	−10195 (21)	0.76	***	13	1.9 (22)	0.3	5.2	−7603 (26)	0.59	***
5	2.1 (21)	0.5	5.3	−3164 (21)	0.19	*	14	1.4 (23)	0.5	3.6	−5193 (25)	0.41	***
6	12 (20)	2.6	84	−1448 (20)	0.03	ns	15	1.2 (24)	0.6	2.1	−1265 (32)	0.08	ns
7	1.7 (9)	0.6	3.2	−4568 (9)	0.33	ns	16	1.4 (23)	0.2	4.0	−7461 (24)	0.72	***
8	1.8 (24)	1.2	3.8	−4355 (29)	0.64	***	AS	1.6 (296)	0.2	84			
9	2.6 (21)	0.5	6.4	−8132 (21)	0.68	***							
							PCB-138						
1	2.3 (5)	0.6	8.6				10	1.5 (16)	0.6	6.4	−2218 (24)	0.08	ns
2	1.7 (6)	0.6	3.8				11	1.1 (27)	0.5	3.0	−1257 (31)	0.05	ns
3	2.3 (10)	0.7	4.3	−1897 (17)	0.03	ns	12	1.5 (24)	0.4	6.7	−2732 (26)	0.08	ns
4	5.8 (21)	0.8	15	−10566 (21)	0.77	***	13	2.0 (23)	0.2	5.9	−8835 (27)	0.45	***
5	2.0 (21)	0.9	4.2	−1824 (21)	0.10	ns	14	1.7 (23)	0.5	4.8	−5838 (25)	0.43	***
6	21 (20)	3.9	120	−1188 (20)	0.02	ns	15	1.3 (24)	0.6	2.4	−961 (32)	0.03	ns
7	1.8 (9)	0.6	5.3	−4298 (9)	0.17	ns	16	1.7 (23)	0.2	5.0	−8328 (24)	0.71	***
8	2.1 (24)	1.0	5.6	−3269 (29)	0.35	***	AS	1.9 (297)	0.2	120			
9	2.3 (21)	0.6	6.6	−7193 (21)	0.62	***							
							PCB-180						
1	0.4 (5)	0.3	2.7				10	0.2 (15)	0.1	0.8	−2320 (21)	0.11	ns
2	0.5 (4)	0.2	1.4				11	0.2 (26)	0.1	0.6	318 (28)	0.00	ns
3	0.6 (9)	0.1	1.6	−2022 (16)	0.01	ns	12	0.2 (11)	0.1	0.5	−1150 (13)	0.03	ns
4	1.0 (19)	0.2	3.9	−10408 (19)	0.78	***	13	0.5 (17)	0.1	1.1	−6259 (21)	0.48	***
5	0.7 (9)	0.3	0.9	−2955 (9)	0.22	ns	14	0.2 (15)	0.1	0.6	−3257 (17)	0.32	*
6	1.5 (20)	0.5	6.6	−1524 (20)	0.05	ns	15	0.2 (24)	0.1	0.5	−1336 (32)	0.08	ns
7	0.4 (4)	0.1	1.0	−12975 (4)	0.71	ns	16	0.3 (21)	0.1	1.0	−7101 (22)	0.77	***
8	0.4 (15)	0.2	0.6	−3129 (20)	0.36	**	AS	0.4 (230)	0.1	6.6			
9	0.6 (16)	0.3	1.2	−4817 (16)	0.45	**							

TABLE 1. (Continued)

S	median	min.	max.	m	r^2	p	S	median	min.	max.	m	r^2	p
							sPCB[b]						
1	55 (5)	26	277				10	49 (16)	32	129	−1427 (24)	0.05	ns
2	69 (6)	34	249				11	32 (27)	16	66	2055 (31)	0.21	**
3	61 (10)	31	220	120 (17)	0.00	ns	12	50 (24)	19	119	−680 (26)	0.01	ns
4	76 (21)	30	178	−3822 (21)	0.29	*	13	48 (24)	8.6	106	−4620 (28)	0.33	**
5	79 (21)	38	204	2465 (21)	0.25	*	14	57 (23)	20	190	−3270 (25)	0.17	ns
6	454 (20)	93	2464	−2813 (20)	0.11	ns	15	38 (24)	14	104	1400 (32)	0.05	ns
7	79 (9)	34	122	−3084 (9)	0.20	ns	16	47 (24)	8.7	107	−2573 (25)	0.17	*
8	60 (24)	38	155	−780 (29)	0.04	ns	AS	57 (299)	8.6	2464			
9	80 (21)	25	137	−3800 (21)	0.41	**							

[a] Given is the median (pg/m^3) with the number of observations in parentheses, minimum (pg/m^3), and maximum value (pg/m^3), the slope m of the relationship $\ln(p_a/\text{Pa}) = m/(T/K) + b$ with the number of observations in parentheses, the regression coefficient r^2, the level of significance p. AS = all stations. [b] Assumed average molecular mass of 326.4 g/mol.The level of significance where * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$, and ns = not significant.

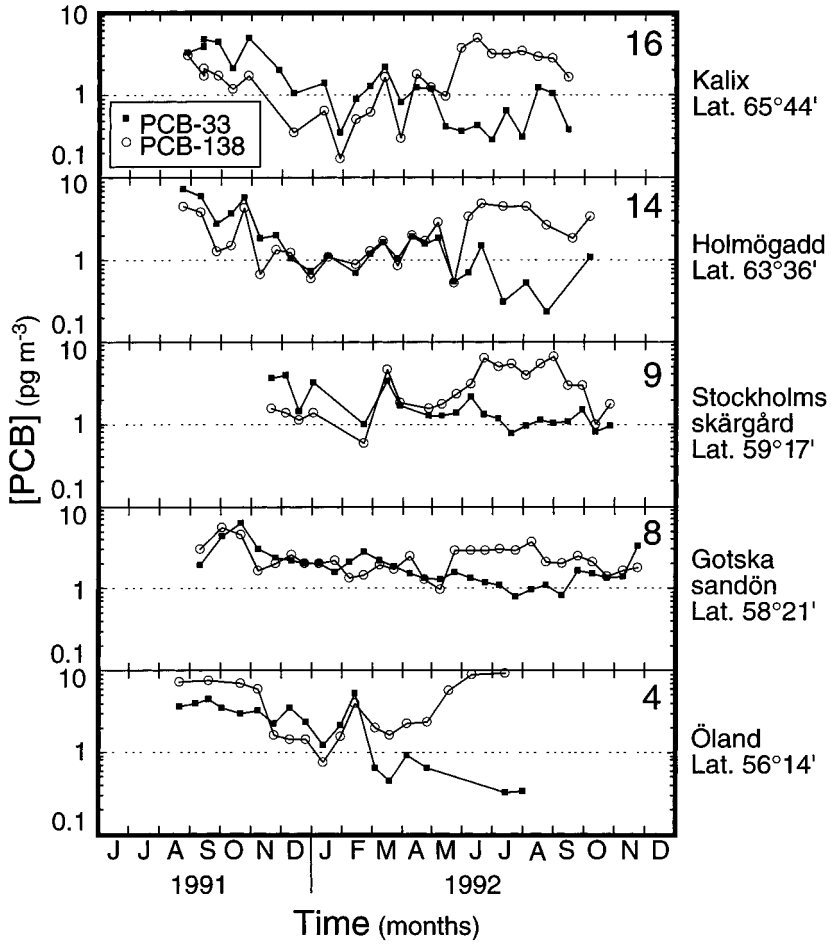
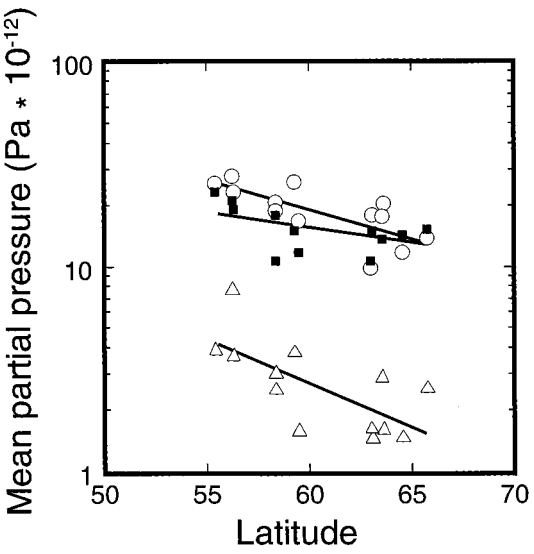


FIGURE 2. Annual cycles of the atmospheric concentration of PCB-33 and PCB-138 for five selected stations.

Not all congeners showed a significant relationship with temperature at all stations (Table 1). However, an analysis of covariance (ANCOVA using $1/T$ as a covariate), including all data collected, revealed that the concentration of all congeners in air (expressed as ln p) was related to temperature. This relationship varied between stations (i.e. significant interaction terms, Table 2), except for PCB-33 for which a common positive slope ($m = 1880$) could be calculated and concentrations overall decreased with temperature. For the rest of the congeners, the $1/T$ relationship had different slopes for the different stations (for individual station regression parameters see Table 1), although, in general, concentrations increased with temperature. This observed difference in slopes for the same congener between stations reflects the relative importance of long range transported air masses vs local surfaces as sources for PCB. The different slopes may also reflect that local surfaces are different with regards to soil type, land use, vegetation type and coverage, and snow coverage which affects volatilization and, thus, the slope at a site. However, generally, when applying the hypothesis formulated by Hoff et al. (*14*) and Wania et al. (*13*) on our data, the concentration for the higher volatility congeners in the atmosphere seems largely to be controlled by advection from air masses where local temperature have little influence on the concentrations found. For PCB-33 the common negative relationship with temperature may in part be explained by higher degradation during warm periods, but different source regions over the year may be of importance for this congener. For low volatility congeners, showing steep slopes, local air temperatures are driving the



PCB congener		m	r^2	p
20/**33**/53	■	-0.04	0.57	**
41/64		-0.03	0.17	ns.
90/**101**	○	-0.07	0.71	***
123/**118**/149		-0.07	0.38	*
132/**153**/105		-0.06	0.45	**
160/**138**/158		-0.08	0.59	**
180	△	-0.09	0.50	**
sPCB		-0.07	0.68	***

FIGURE 3. Relationship between ln(p_a/Pa) and latitude exemplified by congeners PCB-33, PCB-101, and PCB-180. Given is the slope *m*, the regression coefficient r^2, and the level of significance *p* where *=$p < 0.05$, **=$p < 0.01$, ***=$p < 0.001$, and ns = not significant.

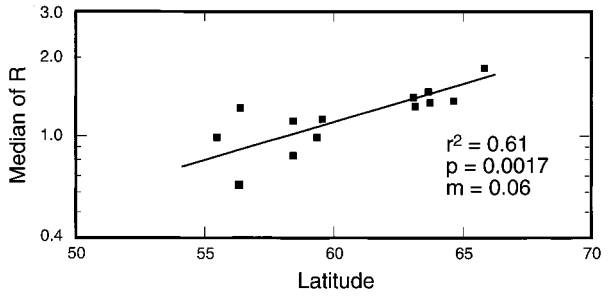


FIGURE 4. Relationship between latitude and the median ratio between PCB-33 and PCB-138 (ln *R*). Given is the regression coefficient r^2, the level of significance *p*, the number of observations *n*, and the slope *m*.

PCB partial pressure inferring local surfaces as the most likely source to the overlying atmosphere. This is summarized in Figure 5 where the number of stations that showed a significant temperature relationships decreased with volatility: for PCB-153 and PCB-118 eight out of 14 stations showed significant relationships with temperature, whereas for PCB-33, only three stations where significant. Figure 5 also shows that the steepness of the slope (*m*) increases for the low volatility congeners. This behavior has also been observed in other studies of PCB in temperate regions on PCBs (*13*, *14*, *22*, *29*, *30*).

For some stations (Lahemaa no. 10, Vasa no. 11, Bjuröklubb no. 15, Salaspils no. 6, Breanäs no. 5 and Ventes Ragos no. 3) relationships between PCBs and temperature were poor, even for low volatility congeners. This indicates minor influence of evaporation from surfaces and consequently low contamination of PCBs in surrounding surface media at these sites. For three of these stations, Lahemaa, Vasa, and Bjuröklubb, the concentration of the different congeners of PCB was always lower than the overall median concentration for all stations. These stations also showed less steep slopes in regressions between temperature and the ratio (*R*) between PCB-33 and PCB-138 compared with the rest of the stations (Figure 6). This was most likely due to a comparably low evaporation of PCB-138 even at high temperatures, as indicated by the poor relationships with temperature found for this congener at these sites (Table 1).

"Fresh" Sources of PCB to the Atmosphere. The concentrations of the different congeners of PCB at Salaspils, Breanäs, and Ventes Ragos were always higher than the overall median. Salaspils, the only station that could be considered urban, had levels which were 10 times higher than the concentration at the other stations. Nevertheless, levels of PCBs at Salaspils were not temperature dependent. Neither was there any tendency toward a stronger temperature dependence for low volatility congeners, as was found in a study of four urban centers in the United Kingdom (*3*). Finally, the ratio between PCB-33 and PCB-138 at Salaspils was not affected by temperature. For illustrative purposes, the relationship between ln *R* and temperature was compared between the stations Salaspils (no. 6) and Stockholm's skärgård (no. 9, Figure 6). Theses two stations were both located rather close to a large city, 20 km from Riga (0.9 million inhabitants) and 80 km from Stockholm (1.5 million inhabitants). The ratio between PCB-33 and PCB-138 at Salaspils was not related to temperature, whereas for Stockholm's skärgård and most other stations, this relation-

TABLE 2. Effects of Sampling Station and Temperature on Partial Pressure for Selected PCB Isomers

PCB no.	source	slope	df	*F*-ratio	r^2	*p*
	station		13	10.00		***
20/**33**/53	**1/temp (K)**	**1880**	**1**	**15.18**	**0.31**	***
	station		13	2.66		**
41/64	1/temp (K)		1	2.15		ns
	station * 1/temp		**13**	**2.53**	**0.45**	**
	station		13	3.58		***
90/**101**	1/temp (K)		1	48.74		***
	station * 1/temp		**13**	**3.53**	**0.65**	***
	station		13	6.15		***
123/**118**/149	1/temp (K)		1	54.83		***
	station * 1/temp		**13**	**6.10**	**0.64**	***
	station		13	4.60		***
132/**153**/105	1/temp (K)		1	101.50		***
	station * 1/temp		**13**	**4.60**	**0.67**	***
	station		13	4.70		***
160/**138**/158	1/temp (K)		1	78.52		***
	station * 1/temp		**13**	**4.73**	**0.67**	***
	station		13	4.51		***
180	1/temp (K)		1	51.87		***
	station * 1/temp		**13**	**4.36**	**0.68**	***

[a] Analysis performed with ANCOVA using temperature as a covariate. Given is the source, the number of degrees of freedom df, the *F*-ratio, the regression coefficient r^2, and the level of significance *p*. The level of significance where *=$p < 0.05$,**=$p < 0.01$, ***=$p < 0.001$ and ns = not significant. The stations Dziwnow (no. 1) and Swibno (no. 2) were omitted from this analysis due to an insufficient number of samples.

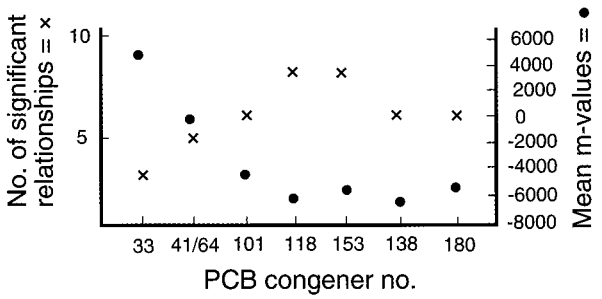


FIGURE 5. Number of stations (out of a total of 14) that showed a significant relationship ln (p_a/Pa) = m/T/K) + b for the different PCB congeners. Also shown is the mean slope m, of the significant stations.

Station	Lat.	Ln(R)			
		m	n	r^2	p
Ventes R.	55°25'	-0.026	17	0.02	ns.
Öland	56°14'	-0.160	18	0.57	***
Breanäs	56°17'	-0.084	21	0.44	***
Salaspils	**56°50'**	**0.000**	**20**	**0.00**	**ns.**
Vilsandi	58°20'	-0.030	9	0.07	ns.
Gotska s.	58°21'	-0.080	29	0.20	***
S-holms s.	**59°17'**	**-0.120**	**21**	**0.68**	***
Lahemaa	59°30'	-0.024	24	0.17	*
Vasa	63°02'	-0.097	30	0.65	***
Docksta	63°03'	-0.060	26	0.43	***
Norrbyn	63°32'	-0.100	26	0.57	***
Holmögadd	63°36'	-0.090	24	0.30	**
Bjurökl.	64°31'	-0.050	31	0.19	*
Kalix	65°44'	-0.130	24	0.57	***

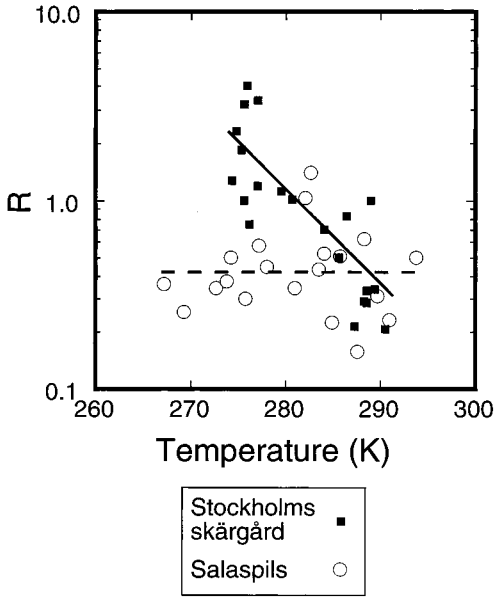


FIGURE 6. Relationship between temperature (K) and the ratio between PCB-33 and PCB-180 (ln R) exemplified by the stations Stockholms skärgård (no. 9) and Salaspils (no. 6). Given is the slope m, number of observations n, the regression coefficient r^2, and the level of significance p where *=p < 0.05, **=p < 0.01, ***=p < 0.001, and ns = not significant.

ship was highly significant. Therefore, the source of PCB was probably "fresh" material emitted directly to the air for the sampling station situated in Salaspils. An "aging effect" such as different volatilization behavior of the PCB congeners from condensed media was therefore not observed.

At Breanäs, the elevated levels of PCB-138 occurred primarily during low temperatures and resulted in a lack of temperature dependence for this congener. Summer concentrations, on the other hand, did not seem to be affected by an episodic source for PCB-138. The concentration of PCB-33 on the other hand, was significantly related to temperature, with levels being lowest during warm weather. Taken together this resulted in a strong negative temperature dependence for the ratio (R) between PCB-33 and PCB-138. This relationship was consequently similar to those at other stations, but the underlying mechanisms differed. If air concentrations at a site are high and not dependent on temperature, it is unreasonable to assume that long range transport or local re-evaporation controls these concentration levels. Therefore, other reasons need to be invoked to explain these observations. PCB sources to the atmosphere may be highly irregular over time, e.g. because of leakage/evaporation from dumps or PCB contaminated buildings, or because of accidental burning of PCB contaminated oil. Such episodic local sources may obscure any temperature dependence of air concentrations. This is a probable explanation for the station Breanäs. At Ventes Ragos, a lack of samples collected at high temperatures probably explains the lack of a temperature relationship.

To further examine the relative impact of local and distant sources, Wania et al. (*13*) suggest simultaneous measurements of atmospheric and surface concentrations (i.e. soils, plants, snow, water surfaces). In addition, we suggest that more research should be focused on how decomposition of PCBs in soil and air is influenced by climate. Also, potential sources of "fresh" PCBs to the atmosphere, presumably located predominately in urban and industrial areas, need to be characterized more thoroughly in terms of their release characteristics (e.g. episodic vs continuos vs cyclical release, or regarding differences in congener composition), if spatial and temporal variability of these contaminants in air is to be more fully understood. Finally, temperature alone is not sufficient to predict atmospheric concentrations of especially high volatility PCBs at remote or uncontaminated locations. It is therefore important to know for how long and for what distance the temperature-related fluctuations of atmospheric PCB concentrations are preserved in a moving air mass. This would make it possible to distinguish between the influence of advection of background air vs that of local evaporation from nearby sources.

Acknowledgments

All personnel at the sampling stations are gratefully acknowledged for their invaluable work with obtaining the samples in the program. We further want to express our gratitude to G. Bremle for assistance with chemical analysis, J. Agrell and A. Hollsberg for help with statistics, and J. Agrell, O. Berglund and an unknown referee for constructive comments on this manuscript. This work was supported by grants from the Swedish Environmental Protection Board, the Futura Foundation and the Magnus Bervall's Foundation. F.W.'s contribution to this work was supported by the Environment and Climate Research Program of the European Union (Contract ENV4-CT96-0214).

Supporting Information Available

Table showing concentrations of PCB-33, 41/64, 101, 118, 153, 138, 180, sum PCB, and temperature for all sampling periods and stations during 1990−1993. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review August 24, 1998. Revised manuscript received November 30, 1998. Accepted January 7, 1999.

ES980867L