

**Article 9.****CONGENER SPECIFIC ASSESSMENT OF GLOBAL ATMOSPHERIC PCB POOL**

Barend L. van Drooge<sup>1</sup>, Joan O. Grimalt<sup>1</sup>, Johan Axelman<sup>2</sup>, Ørjan Gustafsson<sup>2</sup>,  
Kevin C. Jones<sup>3</sup>, Euripides Stephanou<sup>4</sup>

<sup>1</sup> Department of Environmental Chemistry, ICER-CSIC, Barcelona, Catalonia, Spain

<sup>2</sup> Institute of Applied Environmental Research, Stockholm University, Stockholm, Sweden

<sup>3</sup> Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, United  
Kingdom

<sup>4</sup> Department of Chemistry, University of Crete, Crete, Greece

submitted to Environmental Science & Technology



**Congener specific assessment of the global atmospheric PCB pool**

BAREND L. VAN DROOGE, AND JOAN O. GRIMALT

*Institute of Chemical and Environmental Research (IIQAB-CSIC), 08034 Barcelona. Catalonia. Spain*

JOHAN AXELMAN, AND ØRJAN GUSTAFSSON

*Institute of Applied Environmental Research (ITM), Stockholm University, 10691 Stockholm, Sweden*

KEVIN JONES

*Institute of Environmental and Natural Sciences, Lancaster University, Lancaster LA1 4YQ, U.K.*

EURIPIDES STEPHANOU

*Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, GR 71409 Heraklion, Greece***Abstract**

An attempt has made to establish a Global atmospheric inventory on PCBs, based on atmospheric field data from 1990 until 2000 of individual PCB congeners. Different approaches have been applied in order to obtain an overview on the possible advantages and disadvantages of these approaches on the model. On the Northern Hemisphere a negative latitudinal correlation is observed, which is in agreement with the pseudo-enthalpies for evaporation of the congeners. On the Southern Hemisphere, due to lack of sufficient data, this correlation is not observed. Moreover, new data from the Islands of Hawaii shows very low PCB concentrations in this part of the Pacific Ocean. Since it seems that remote sites on the Northern Hemisphere are under influence of potential source areas, the Northern Hemisphere is divided in a part of 'continental influence' and one without this influence. Further more, a vertical gradient on PCB concentration was applied. The calculated Global inventories show in general 2-3 times higher PCB amounts on the Northern Hemisphere than on the Southern Hemisphere. The Global inventory for  $\Sigma$ PCB is 63 tonnes and 32 tonnes for the model without and with the vertical PCB gradient. Implication of OH radical concentrations and calculated reaction rates between PCB and OH give very high PCB sink, which is primarily caused by both high PCB and OH concentrations in the tropical zones. These sinks have to be compensated by very high PCB emission, which does not occur. Implication of calculated residence times shows PCB loss which are closer to the annual estimated emission.

## 1. Introduction

In the last decades persistent organic pollutants such as polychlorinated biphenyls (PCB) have been banned in most industrialised countries. Accordingly, PCB decreases in lake waters, soils, peat and sediments have been identified in potential source areas where PCBs were produced and used [Gobas *et al.*, 1995; Jeremiason *et al.*, 1994; Eisenreich *et al.*, 1989; Wong *et al.*, 1995; Rapaport and Eisenreich, 1988; Kjeller and Rappe, 1995; Sanders *et al.*, 1995]. However, these compounds are still omnipresent and the observed decreases in remote areas have been small if any [Baker and Eisenreich, 1990; Panshin and Hites, 1994; Hillery *et al.*, 1997; Hung *et al.*, 2001].

Elucidation of the temporal concentration trends of these compounds at a planetary scale and, subsequently, anticipation of their future effects in remote ecosystems requires an improved understanding of the processes controlling their losses in the environment. Volatilization is responsible for a significant proportion of PCB decline in the source areas, involving a net flux of compounds from soils and waters to the atmosphere [Jeremiason *et al.*, 1994; Alcock *et al.*, 1993]. In this sense, PCBs are possibly not eliminated from the environment but merely translocated by atmospheric transport to other areas. This atmospheric compartment is the most important medium for the long range distribution of PCBs, including transport to the marine system, the arctic and high mountain areas [Duce *et al.*, 1991; Ballschmiter, 1992; Iwata *et al.*, 1993; Tolosa *et al.*, 1997; Wania and Mackay, 1993; Grimalt *et al.*, 2001].

In this respect, quantification of PCB loss should focus onto the processes that involve PCB destruction which essentially concern burial in deep sea sediments and degradation in the atmosphere [Gustafsson *et al.*, 1997; Axelman and Broman, 2001; Wania and Daly, 2002].

OH reaction has been proposed to be the most important parameter controlling atmospheric lifetime and long range PCB transport [Beyer *et al.*, 2000]. The importance of OH radicals on the degradation of gaseous PCBs has been assessed in laboratory experiments [Anderson and Hites, 1996]. Preliminary application of these reaction rate constants to environmental data resulted into a very large OH radical sink for PCBs in the Northern Hemisphere (NH), which led to question the reliability of the reaction rate constants [Axelman and Broman, 2001]. Recent GLOBO-POP model calculations [Wania and Daly, 2002] also showed the importance of PCB degradation by OH radicals but their losses were considerably lower than those calculated by Anderson and Hites [1996].

Gasses with long residence times have smaller variations in space and time than more reactive gases. Theoretical considerations led to propose a reverse relationship between relative standard deviation (RSD) and residence time [Junge, 1974].

$$T_i = 0.14/RSD_i \quad (1)$$

where  $T_i$  is the residence time and RSD is the relative standard deviation of the measured concentrations of compound  $i$

This relationship does not represent time fluctuations at a particular point but spatial variability of the concentrations [Slim, 1988]. Thus, the measured concentrations should be representative of the whole annual period. This approach may be useful for the calculation of the residence times of gas-phase PCB since distortion effects by point source emissions [Hamrud, 1983] are negligible after more than two decades of PCB banning.

No attempt has been made to date to estimate the global scale atmospheric sink of PCBs based on atmospheric field data. In the present study, the global atmospheric loss of PCBs has been estimated based on new and already existing data from remote locations in both hemispheres. Latitudinal trends and longitudinal and altitudinal differences have been identified and used to obtain best estimates for congener specific global atmospheric concentrations at the different zones. Seven PCB congeners (IUPAC no 28, 52, 101, 118, 138, 153, and 180) have been taken to model the diverse behaviour of the PCB mixtures. Previously reported OH reaction rate constants and PCB field data have been used to estimate the atmospheric PCB degradation and residence time.

## 2. Methods

### 2.1. Compound selection

The environmental distribution of PCB congeners is determined by their specific vapor pressures and hydrophobicities, not by the composition of the commercial mixtures produced initially. In the present study, the congeners selected for description of the atmospheric inventory and sink, 2,4,4'-trichlorobiphenyl (PCB IUPAC No. 28), 2,2',5,5'-tetrachlorobiphenyl (PCB 52), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), 2,3',4,4',5-pentachlorobiphenyl (PCB 118), 2,2',3,4,4',4-hexachlorobiphenyl (PCB 138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153) and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180), cover a wide range of these constants and are predominant in environmental samples. They are often taken as reference PCB congeners in many literature studies.

### 2.2. Data selection

Literature data has been selected after evaluation of sample site remoteness, sampling time, and congener specific information (Table 1). PCB concentrations on a global scale were calculated considering the globe as a remote system. Bias associated to sampling period duration or seasonality has been avoided by selection of long-term studies encompassing sampling over one year or more. Arithmetic means were calculated and incorporated into the model since they reflect better average environmental concentrations than geometric means [Parkhurst, 1998]. Data before 1990 was not considered. Old PCB data is often only reported as total PCB without congener specific PCB information. In addition to literature data, unpublished atmospheric concentrations from Hawaii, Moody Brook, Halley Base, Crete and Malawi Lake have been added (Table 1).

Table 1. Mean concentrations of PCB congeners in the sampling sites included in the model calculations. The tabulated values are arithmetic means of yearly sampling periods ( $\text{pg}\cdot\text{m}^{-3}$ ).

	Latitude	Longitude	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	Reference
Punto de Hidalgo, Tenerife	28	16	24	28	18.5	7.7	8.3	8.8	2.7	van Drooge et al. (2002)
Svalbard GSC	79	12	6.2	1.9		0.4		1.3	0.4	not published
Pallas, Finland	68	24	3.2	1.9	1.5	0.5	1.4	1.5	0.9	not published
Kalix, Sweden	66	23			1.9	1.9	1.9	1.8	0.4	Agrell et al. (1999)
Bjuröklubb, Sweden	65	22			1.6	1.0	1.3	1.1	0.2	Agrell et al. (1999)
Holmögadd, Sweden	64	21			2.8	1.4	2.3	1.7	0.3	Agrell et al. (1999)
Gotska sandön	58	19			2.9	2.2	2.4	2.1	0.4	Agrell et al. (1999)
Poland, coastal	54	19			3.6	1.7	2.1	1.7	0.6	Agrell et al. (1999)
Lithuania, coastal	55	21			2.9	1.4	1.9	1.5	0.5	Agrell et al. (1999)
Hazelrigg, UK	54	-3	16	20	1.3	2.2	3.3	0.7	0.7	www.aeat.co.uk/netcen/airqual/
High Murfles, UK	54	0	18.5	13	1.6	3.8	5.9	1.8	1.8	www.aeat.co.uk/netcen/airqual/
Stoke Ferry, UK	53	1	11	14	1.6	2.5	3.8	1.0	1.0	www.aeat.co.uk/netcen/airqual/
Bayreuth, Germany	50	12	13	7.4	5.9	3.0	3.0	5.6	1.3	McLachlan M. et al. (1998)
Signy Island	-61	-46	10	6.0	2.6	0.5	0.6	0.8	0.3	Kallenborn, R. et al. (1998)
Te Wera, New Zealand	-39	175	2.9	1.2	1.7	0.7	2.0	1.4	0.2	Buckland et al. (1999)
Baring Heads, New Zealand	-41	175	3.5	1.4	1.0	0.4	0.6	0.5	0.1	Buckland et al. (1999)
Nelson Lakes, New Zealand	-42	173	2.9	1.2	1.3	0.6	0.6	0.4	0.0	Buckland et al. (1999)
Culverden, New Zealand	-43	173	3.5	1.2	0.6	0.2	0.3	0.2	0.0	Buckland et al. (1999)
Halley base, Antarctica	-76	-26	1.8	0.2			0.2		0.1	not published
Moody Brook, Falkland Islands	-52	-58	2.6	0.7			0.2		0.1	not published
Baltic	61	18		5.9				3.5	0.8	see Axeliman and Broman (2001)
Wisconsin	50	-89		9.4		1.0		4.9	0.5	Manchester-Neesvig and Andren (1989)
Bermuda	34	-65	39	18	10.2			3.2	0.5	Panshin and Hites (1994)
Svalbard	79	12	2.4	2.3	1.9	0.8	1.8	1.0	0.2	Oehme (1995)
Svanvik	70	29			2.3	1.6	3.1	1.6	0.5	Oehme (1995)
Karvatn	61	6			2.4	0.8	2.1	1.0	0.3	Oehme (1995)
Svalbard	79	12	4.3	2.5				0.6	0.2	see Axeliman and Broman (2001)
Ice Island	81	-90	2.2	3.1				0.1	0.1	see Axeliman and Broman (2001)
Chesapeake Bay	38	-76		7.8				9.7	1.9	see Axeliman and Broman (2001)
Sault Ste. Marie, WI	47	-84	10	7.0	5.0		2.0	3.5	3.5	Monosmith and Hermanson (1996)
Saginaw, MI	44	-83	20	17	8.0		3.5	8.7	8.7	Monosmith and Hermanson (1996)
Traverse, MI	45	-86	32	24	20		5.0	12	12	Monosmith and Hermanson (1996)
Swedish West Coast	59	11	12	7.9	6.6	2.3	4.6	5.2	1.4	Brorstrom-Lunden et al. (1994)
Swedish West Coast	59	11	5.1	4.3				4.5	1.6	see Axeliman and Broman (2001)
Alert station	82	-62	1.1	1.4				0.4	0.3	see Axeliman and Broman (2001)
Finokalia, Crete	35	25	5.0	4.4	1.5	1.3		1.4	0.4	Mandalakis and Stephanou (In press.)
Hawaii	21	-156	1.6	1.3	1.1	0.2	0.7	0.6	0.2	not published
Brazzaville, Congo	-4	14	28	40				8.0	7.0	Ngabe and Bidleman, (1992)
Lake Malawi, Senga	-14	35	23	15	7.8	11		5.6	1.1	D. Muir pers. comm. (2002)

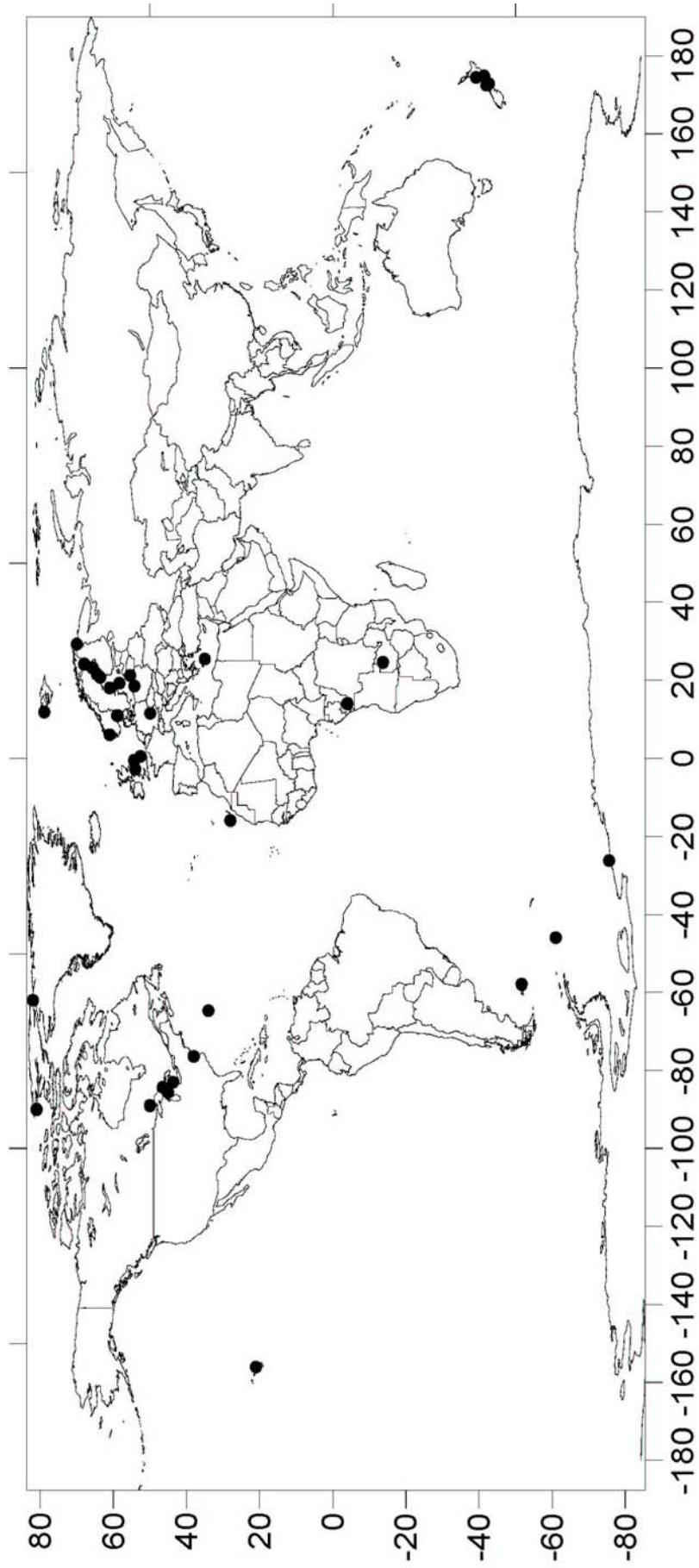


FIGURE 1. Map showing the sites from which PCB atmospheric concentrations covering more than one year period were available.





The atmospheric data selected from the literature was obtained using similar sampling and analytical methods. Sampling was performed by passing air through a glass fiber filter and then through a cartridge packed with an adsorbent material. Particulate phase bounded PCBs were retained in the filter while the gas phase PCBs were adsorbed in the cartridges. In some studies PCBs were sampled as bulk, without differentiation between gas and particulate phases. Most PCBs are present in the gas phase, the particulate phase only playing a minor role [van Drooge *et al.*, 2002; Mandalakis and Stephanou, 2003]. Furthermore, it is assumable that OH radical reactions on PCBs only take place in the gas phase. For these reasons, only the gas phase PCB concentrations have been considered. Introduction of the particulate phase would complicate the model unnecessarily, since a global distribution of aerosols and their organic content would be required for description of PCB partitioning between gas and particulate phase.

### 3. Results and discussion

#### 3.1. Geographic distributions.

The sample sites selected for estimation of the atmospheric concentration pool are represented in Figure 1. The NH is better represented than the Southern Hemisphere (SH). Within the NH the atmospheric samples around the North Atlantic exhibit PCB levels that are more than one order of magnitude higher than the rest (Figure 2). These higher values are in agreement with the areas of higher use of these compounds [Breivik *et al.*, 2002a]. However, in all PCB congeners the concentration differences are within less than two orders of magnitude. Having in mind that the sites represented in Table 1 encompass areas as distant as western Europe and New Zealand or Antarctica, and previously reported geographical distributions of PCB use [Breivik *et al.*, 2002a], the observed concentrations indicate that there is a significant degree of atmospheric mixing.

The logarithms of the concentrations in the North Atlantic area show a strong negative linear correlation with latitude between 30°N and 80°N for all PCBs (Figure 2 and Table 2). According to these correlations higher concentrations are found at lower latitudes. About 86% of the total historical usage of PCBs has been concentrated in a latitudinal band between 30°N-55°N with maxima at 40°N [Breivik *et al.*, 2002a]. The emissions of PCBs obtained from a mass balance model which link consumption and emissions also correspond to this band but with a displacement to higher latitudes [Breivik *et al.*, 2002b]. Furthermore, the global PCB distribution in background surface soils exhibit highest concentrations in the latitudinal band between 40°N-70°N with maxima around 50°N [Meijer *et al.*, 2003]. Among other factors, this northern displacement of the latitudinal soil PCB band with respect to the area of highest use in the past reflect the higher organic carbon content of soils in Scandinavia, south Canada and Siberia where PCB accumulated preferentially [Meijer *et al.*, 2003]. In any case, the highest concentrations of atmospheric PCBs at 30°N as indicated by the linear correlations obtained from Table 1 encompasses a net transfer of PCBs from higher to lower latitudinal locations. That is, a flux in the opposite direction to that predicted in the

global distillation theory [Wania and Mackay, 1993]. However, this flux is not in contradiction with the assumption of the global distribution model because no condensation effects are involved.

In any case, the concentrations of these compounds in the atmosphere are distributed paralleling a temperature gradient (Table 3). Previous studies on diurnal temperature profiles have shown that PCB air concentrations exhibit positive temperature correlations involving higher daytime than night-time values [Hornbuckle and Eisenreich, 1996; Wallace and Hites, 1996; Lee *et al.*, 1998]. In Table 2, recalculation of the slopes in function of the temperature gradients ( $\log(\text{conc.})$  vs.  $1/\text{Temp}$  ( $^{\circ}\text{K}$ )) and estimation of the phase-change enthalpies ( $\Delta H$ ):

$$\Delta H = \text{slope} \cdot R \cdot \ln(10) \quad (2)$$

where  $R$  is the gas constant  $8.314 \text{ J} \cdot ^{\circ}\text{K}^{-1} \cdot \text{mol}^{-1}$  and  $\ln(10) = 2.303$ , gives values in the order of 36-63  $\text{kJ} \cdot ^{\circ}\text{K}^{-1} \cdot \text{mol}^{-1}$ . These experimental enthalpies are a bit lower than the octanol-air phase transfer constants determined in laboratory experiments, 66-93  $\text{kJ} \cdot ^{\circ}\text{K}^{-1} \cdot \text{mol}^{-1}$  [Finizio *et al.*, 1997], but not too different which suggests that evaporation from the ground is a significant process determining the global atmospheric distribution of these compounds. In addition to this latitudinal dependence, longitudinal differences giving rise to higher atmospheric concentrations in the areas of higher PCB use in the past [Breivik *et al.*, 2002a] are also observed. Thus, the air levels in Hawaii are about one order of magnitude lower than in the North Atlantic area (Figure 3). According to these differences, the inventories in the northern hemisphere have been calculated using two types of latitudinal dependent linear regressions. Assuming a uniform N-S latitudinal gradient, all data between  $40^{\circ}\text{E}$  and  $90^{\circ}\text{W}$  have been used for curve fitting of the latitudinal dependence. The resulting slopes and intercept have been used for calculation of the concentrations in this longitudinal sector and between  $120^{\circ}$ - $150^{\circ}\text{E}$ , the area of Japan influence. In the rest of the northern hemisphere, the concentrations were calculated using the same slopes but the concentrations from Hawaii for intercept calculation. The use of these equations involves the assumption of a steady state concentration of these compounds in the atmosphere as consequence of their general release into the environment and physico-chemical structure of the atmospheric column.

In the SH, the logarithm-transformed average concentrations do not show a significant latitudinal linear dependence. From the amount of data available for this study it is not clear whether the lack of dependence is really characteristic of the SH atmospheric PCB distribution or due to lack of sufficient sampling sites. In practical terms, calculation of the PCB inventories has been performed by averaging the concentrations of all sample sites in this Hemisphere.

### 3.1. Maximum PCB inventory

For inventory calculations the globe surface was divided in 18 latitudinal bands of  $10^{\circ}$  uniformly distributed in the NH and SH. The atmospheric altitude in each band was taken to be 10 km and divided in 10 layers. The resulting model contained 180 boxes, each encompassing  $10^{\circ}$  of

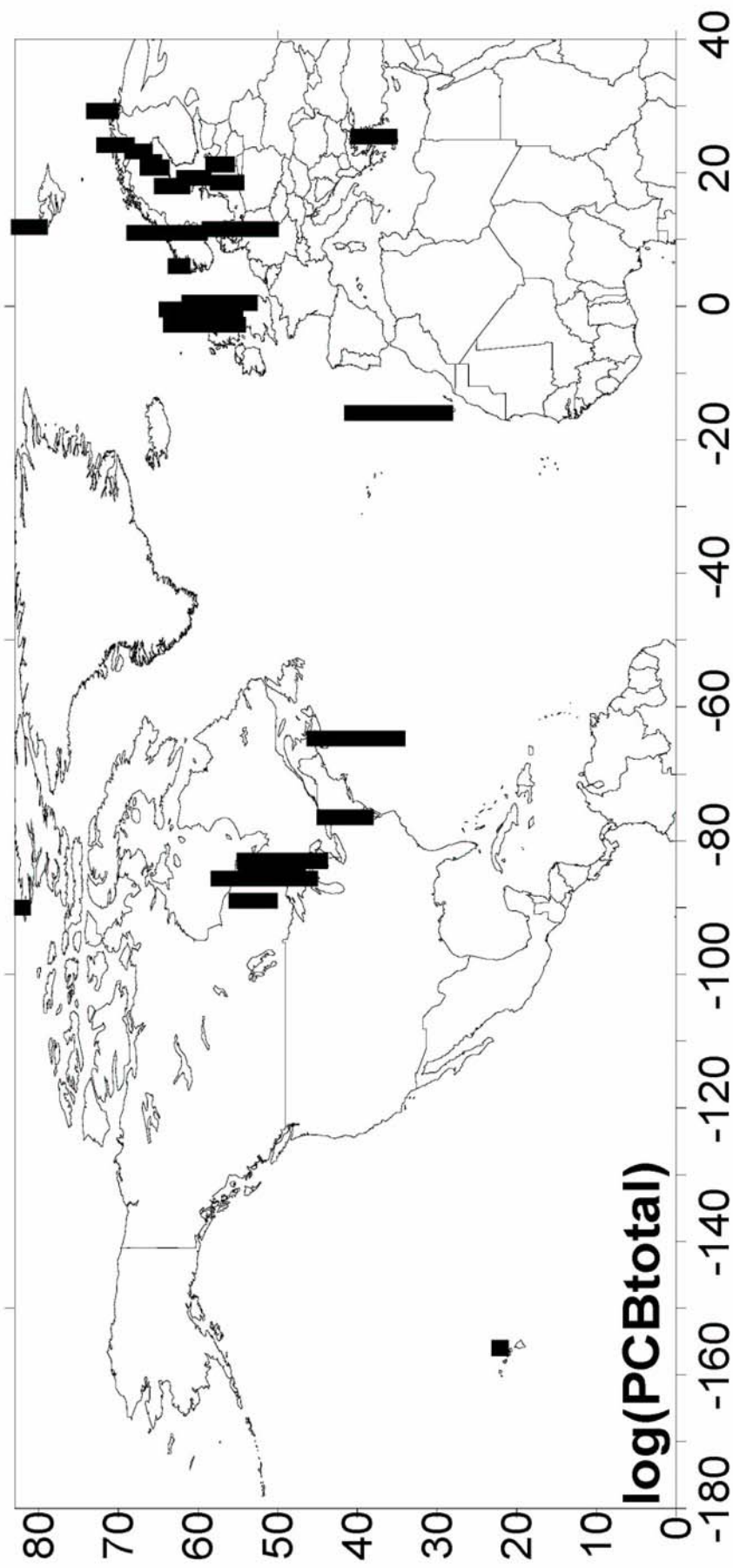


FIGURE 3. Annually-averaged total PCB concentrations in the Northern Hemisphere (log-scale)

latitude and 1000 m of height (Table 3). Similar approaches have been undertaken in previous studies such as the Globo-POP model in which the atmosphere was divided in 10 latitudinal zones and four vertical layers encompassing the lower 33 km [Wania *et al.*, 1999].

The above described latitudinal regressions for the NH (Table 2) were used to assign to each box its corresponding PCB levels. These equations predict an increasing concentration down to the equator. However, no data are available between 0-30°N. Lower PCB emissions are expected in this latitudinal range according to the previous use of these compounds (Breivik *et al.*, 2002a). In addition, the above reported parallelism between soil organic carbon distribution and PCB accumulation [Meijer *et al.*, 2003] should also involve some degree of exchange between soil and atmosphere. Considering these aspects, and the observed longitudinal differences in airborne PCB between areas from high and low use of these compounds, extrapolation of the curve fitted values between 30°N and 80°N to the 0°N-30°N sector seems inadequate. Thus, the boxes within this sector have been considered to contain PCB concentrations as those at 30°N. With this approach, the concentrations assigned to these sectors are similar to those determined in Africa at the same latitudes but in the SH (Table 1 and Figure 2).

In the absence of other data, assumption of PCB mixing throughout the entire troposphere involves estimation of concentration-pressure dependence only due to pressure correction. As described elsewhere [Anderson and Hites, 1996].

$$p(h_k) = 104144 \exp(-0,1342h_k) \quad (3)$$

where  $p$  is the atmospheric pressure in Pa and  $h_k$  is the height above sea level in km at the altitude box  $k$

Then, the PCB level for each box was calculated as

$$C_{ijk} = 10^{(a+b \cdot l)} \cdot x_{jk} \quad (4)$$

where  $C_{ijk}$  is the average concentration of congener  $i$  at latitude  $j$  and altitude  $k$

$a$  is the intercept in the air concentration vs. latitude regression

$b$  is the slope in the air concentration vs. latitude regression

$l$  is the average latitude in the box and  $x_{jk}$  is the ratio between the mean atmospheric pressure of the box and surface pressure.

In the SH the PCB concentrations were calculated from the estimated average values.

$$C_{ijk} = Ca_{ij} \cdot x_{jk} \quad (5)$$

where  $\bar{C}_{aj}$  is the average air concentration of congener  $i$  in the latitude sector  $j$  and  $C_{ijk}$  and  $x_{jk}$  are defined as in (3).

The results of these inventory calculations are summarized in Table 4. Consistently with the concentration differences observed between NH and SH samples, the amount in the former is more than two times higher. The average estimate of PCB concentrations resulting from this approach is  $13 \text{ pg}\cdot\text{m}^{-3}$  which is sensibly lower than the estimated of  $200 \text{ pg}\cdot\text{m}^{-3}$  from *Anderson and Hites* [1996].

Table 4. Global PCB atmospheric inventories and sinks for different options assuming complete concentration mixing or vertical gradient in the troposphere (10 km).

<i>Maximum</i>								
<b>PCB Congener No.</b>	<b>28</b>	<b>52</b>	<b>101</b>	<b>118</b>	<b>138</b>	<b>153</b>	<b>180</b>	<b><math>\Sigma</math>PCB</b>
Inventory NH (tons)	14	10	5	2,2	3,3	4,0	0,9	40
Inventory (tons)SH	9	5	3,6	0,7	2,8	2,1	0,4	24
<b>Total Inventory</b>	<b>23,2</b>	<b>15,3</b>	<b>8,4</b>	<b>2,8</b>	<b>6,1</b>	<b>6,1</b>	<b>1,2</b>	<b>63</b>
OH sink NH (tons $\cdot$ yr $^{-1}$ )	996	453	129	58	54	69	9	1768
OH sink SH(tons $\cdot$ yr $^{-1}$ )	552	186	86	16	42	32	3	918
<b>Total OH degradation (tons<math>\cdot</math>yr<math>^{-1}</math>)</b>	<b>1548</b>	<b>639</b>	<b>215</b>	<b>74</b>	<b>96</b>	<b>101</b>	<b>13</b>	<b>2686</b>
<i>Vertical gradient</i>								
<b>PCB Congener No.</b>	<b>28</b>	<b>52</b>	<b>101</b>	<b>118</b>	<b>138</b>	<b>153</b>	<b>180</b>	<b><math>\Sigma</math>PCB</b>
Altitudinal coefficient (d; km $^{-1}$ )	-0.40	-0.45	-0.27	-0.24	-0.26	-0.28	-0.068	
Inventory NH (tons)	6,1	4,0	2,9	1,5	2,1	2,3	1,1	20
Inventory SH (tons)	3,9	1,9	2,2	0,5	1,7	1,3	0,5	12
<b>Total Inventory</b>	<b>10,0</b>	<b>5,9</b>	<b>5,1</b>	<b>1,9</b>	<b>3,8</b>	<b>3,6</b>	<b>1,6</b>	<b>32</b>
OH sink NH (tons $\cdot$ yr $^{-1}$ )	446	185	83	41	37	44	11	846
OH sink SH(tons $\cdot$ yr $^{-1}$ )	234	71	54	11	27	20	4	422
<b>Total OH degradation (tons<math>\cdot</math>yr<math>^{-1}</math>)</b>	<b>680</b>	<b>256</b>	<b>137</b>	<b>52</b>	<b>64</b>	<b>63</b>	<b>15</b>	<b>1268</b>
<i>Other budgets (tons)</i>								
<b>Soils<sup>a</sup></b>	<b>190</b>	<b>210</b>	<b>170</b>	<b>400</b>	<b>530</b>	<b>1200</b>	<b>580</b>	<b>3280</b>
<b>Continental shelf sediments<sup>b</sup></b>	<b>460</b>	<b>700</b>				<b>1200</b>	<b>760</b>	
<b>Total production<sup>c</sup></b>	<b>57000</b>	<b>38000</b>	<b>32000</b>	<b>43000</b>	<b>25000</b>	<b>38000</b>	<b>14000</b>	<b>247000</b>

Footnotes: <sup>a</sup>from [Meijer et al., 2003]; <sup>b</sup>from [Jonsson et al., 2003]; <sup>c</sup>from [Breivik et al., 2002a]

### 3.2. Vertical-gradient inventory

In this second option, the vertical PCB distribution is assumed to represent a vertical gradient in addition simple air dilution. The vertical profile has been extrapolated from the one measured by congener specific PCB analysis in the island of Tenerife at 2367 m and sea level [*van Drooge et al.*, 2002]. These vertical profiles show a higher altitudinal decrease for the less chlorinated PCBs than for the higher chlorinated congeners. The observed differences are consistent with other independent studies performing airplane measurements at 500 and 3000 m above sea level [*Knap*

and Binkley, 1991]. An exponential decline function was assumed with increasing altitude. Now, the PCB concentrations for each box,  $C_{ijk}$ , in the NH and SH can be calculated as follows

$$\text{NH: } C_{ijk} = 10^{(a+b \cdot l)} \cdot e^{d \cdot b} \quad (6)$$

$$\text{SH: } C_{ijk} = Ca_{ij} \cdot e^{d \cdot b} \quad (7)$$

where  $d$  is the coefficient for the altitudinal PCB level decline (Table 5) and the other terms are defined as in the previous equations.

Table 5. Altitudinal coefficient, pre-exponential factors and activation energies ( $E_a$ ) for the reaction of PCB congeners with hydroxy radicals (after Axelman and Broman, 2001).  $R = 8.314 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$ .

Congener No.	Altitudinal Coefficient (d; $\text{km}^{-1}$ )	Pre-exponential factor ( $\text{s}^{-1}$ )	$E_a/R$ ( $^\circ\text{K}$ )
28	-0.40	57	959
52	-0.45	108	1265
101	-0.27	205	1571
118	-0.24	205	1571
138	-0.26	389	1877
153	-0.28	389	1877
180	-0.068	739	2183

Once the PCB concentrations for each box are defined, the inventories can be calculated as follows

$$M_{ijk} = C_{ijk} \cdot V_{jk} \quad (8)$$

where  $M_{ijk}$  stands for the amount of congener  $i$  in the box  $jk$  (in kg)

$V_{jk}$  is the volume of box  $jk$  and  $C_{ijk}$  is defined as in (6) and (7)

In this approach, a stronger vertical gradient is observed for the lighter than for the heavier congeners (Figure 4). The estimated inventories represent about half of the amounts obtained in the previous inventory calculations (Table 4). As in the previous case (maximum amount) the value for the NH is two times higher than in the SH. The average estimate of PCB concentrations corresponding to this approach is  $6.5 \text{ pg} \cdot \text{m}^{-3}$ . These values compare well to those obtained in the model of *Wania and Daly* [2002] who estimated a global concentration interval for 1999 ranging between 0.5 and  $55 \text{ pg} \cdot \text{m}^{-3}$ .

The resulting inventories are about 0.3-5% of the inventories calculated for the PCB amounts stored in soils (Table 4; [Meijer *et al.*, 2003]). As expected the atmospheric budgets of the more volatile congeners, e.g. #28, 52 and 101, represent higher relative amounts, 3-5%, of the soil budgets than those of the less volatile compounds, e.g. 0.3-0.7% for #118, #138, #153 and #180.

Comparison to the PCB amounts stored in the continental shelf sediments (Table 4; [Jonsson *et al.*, 2003]) show even lower proportions (0.2-2%) since the calculated budget of PCBs in this environmental compartment is even higher than the one in soils.

### 3.3. Reaction rates and sinks due to OH radicals

The concentrations of OH radicals in the global troposphere are difficult to measure due to the short lifetime and low levels. However, there have been some attempts to give annual global tropospheric means [Spivakovskiy *et al.*, 2000; Hein *et al.*, 1997]. In the calculations of Spivakovskiy *et al.* [2000] the mid troposphere OH radical concentrations range between  $23.4 \times 10^5$  molecules·cm<sup>-3</sup> in the tropics and  $0.9 \times 10^5$  molecules·cm<sup>-3</sup> at the North Pole, with mean concentrations of  $8.5 \times 10^5$  molecules·cm<sup>-3</sup> and  $8.8 \times 10^5$  molecules·cm<sup>-3</sup> in the NH and SH, respectively. The approach of this study was used to obtain latitudinal and altitudinal OH radical concentrations.

As described in Axelman and Broman [2001] the OH reaction rates  $k_{OH}$  (s<sup>-1</sup>) for PCBs were based on an Arrhenius temperature dependence equation for each congener (Table 5) using the raw data from Anderson and Hites [1996].

$$k_{OHijk} = 8.2865 \exp(0.6415 Cl_i) \exp(-(306.05 \cdot Cl_i + 40.714))(1/T_{boxjk}) \quad (9)$$

where  $Cl_i$  is the number of chlorine substituents in each congener  $i$ , and  $T_{boxjk}$  is the average temperature of the box  $jk$  (°K),

Calculation of  $k_{OHijk}$  from equation 9 was performed using the average annual ambient temperature at the surface of each box and then decreasing at 5°C km<sup>-1</sup>. The OH radical concentrations were estimated from the model of Spivakovskiy *et al.* [2000]. Highest potential degradation rates  $k_{OHijk} \cdot [OH]_{jk}$  were obtained in the warmer zones, like the tropics (Figure 4). However, the calculations also show that in this warm area higher degradation potential is found at higher altitudes due to the higher amounts of OH radicals (Figure 4).

The sink of each PCB congener ( $i$ ) in each box ( $jk$ ) ( $S_{ijk}$  (kg y<sup>-1</sup>)) was calculated as

$$S_{ijk} = k_{OHijk} \cdot [OH]_{jk} \cdot M_{ijk} \quad (10)$$

where  $k_{OHijk}$ ,  $[OH]_{jk}$  and  $M_{ijk}$  are calculated as defined above.

All PCB congeners show highest degradation rates at low latitudes (0-30°N/S; Figure 4). The lighter PCB congeners are degraded at higher rate near surface. However, highly chlorinated congeners such as #180 are degraded at higher extend at altitudes around 1-4 km due to their lower vertical gradient

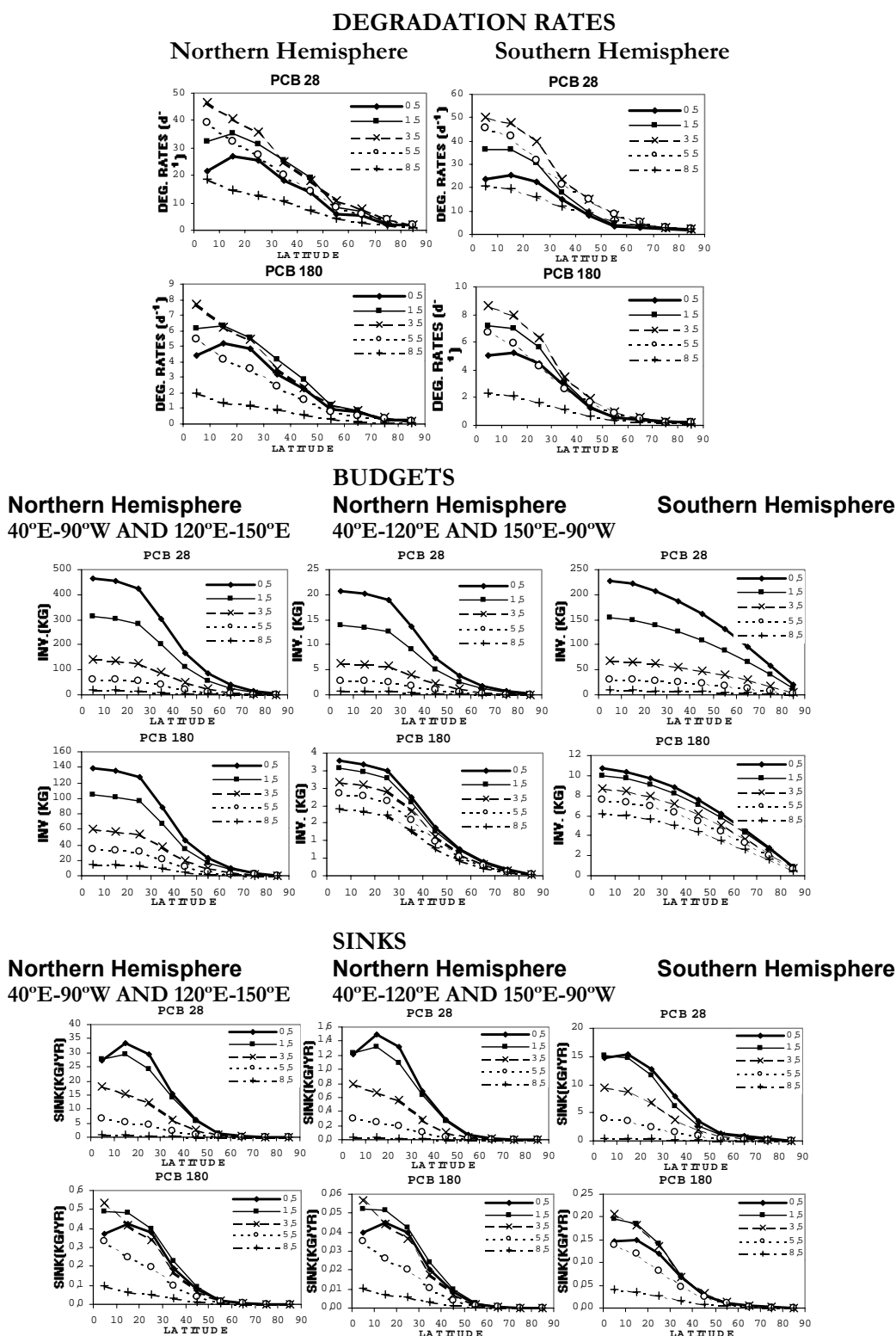


FIGURE 4. Examples based on PCB congeners #28 and #180 of calculated degradation rates, budgets and sinks of the mass balance box model assuming a vertical gradient (see text). According to the differences between PCB concentrations (Table 1) the planet is divided in three regions, two in the northern hemisphere (40°E-90°W and 120°E-150°E) and (40°E-120°E and 150°E-90°W) and one in the southern hemisphere (whole).and the higher OH concentrations at these elevations



(Figure 4). In any case, the heavier PCB congeners are degraded at a much lower rate (45 times for #28 than #180; Table 4).

In the vertical gradient model the sinks, 1300 t·y<sup>-1</sup>, are about half than those in the maximum inventory, 2700 t·y<sup>-1</sup> (Table 4). Although these amounts are significant, they are much lower than the sink predicted by *Anderson and Hites* (1996) who estimated 8271 t·y<sup>-1</sup> for total PCBs. In contrast, the estimated loss in the present study, e.g. vertical gradient, is still six times higher than the 218 t·y<sup>-1</sup> estimated by *Wania and Daly* (2002).

In any case, the sinks obtained in the present study are huge in comparison to the total inventories. Thus, in the case of congener #180 they are more than nine times higher than the global atmospheric inventory and in the case of congener #28 they are 68 times higher. These large numbers involve the need of a high emission flux of PCBs to the atmosphere in order to maintain the observed concentrations (Table 1). Thus, in the case of PCB #28 it involves an approximate renewal time of five days. This period is of 39 days for PCB #180.

The sink estimates reported in Table 4 have been obtained by combination of the information derived from air concentration measurements and experimental models for OH reaction rates. As indicated above, there are uncertainties in the concentration values, namely for large world areas from which no reliable data are available. However, the consistency of the data already obtained from different studies (Table 1) precludes that major differences in the atmospheric pool such as one order of magnitude could be expected from a model derived with a larger number of determinations. On the other hand, equation 9 used for estimation of the degradation rates compares well to the experimental values obtained in Finokalia (Crete, Greece). Thus, similar  $k_{OH}$  rates have been obtained based on the experimental measurement of PCB depletion and OH radical species [*Mandalakis et al., 2003*].

Overall, the data summarized in Table 4 points to a major PCB emission process to account for the large photochemical degradation in the atmosphere. These emissions must originate from environmental compartments other than soils or continental shelf sediments. Otherwise, the volatile PCB congeners contained in these reservoirs would be eliminated in short periods (a few years) if they would be the only source of PCB to the atmosphere.

The sink values of Table 4 are considerably higher than the estimated emissions based on a global mass balance of PCB production, historical usages, disposal and accidental release [*Brevik et al., 2002b*]. Thus, the 70 years averaged release rate of PCB#28 is 12 t·y<sup>-1</sup> (minimum and maximum values 0.65 and 167 t·y<sup>-1</sup>, respectively) whereas the atmospheric sink of this congener is 680 t·y<sup>-1</sup> (Table 4, vertical gradient). Similarly, for PCB#180 the average emission rate is 1.3 t·y<sup>-1</sup> (minimum and maximum values 0.083 and 15 t·y<sup>-1</sup>, respectively) [*Brevik et al., 2002b*] whereas the sink rate estimated in this study is 15 t·y<sup>-1</sup> (Table 4, vertical gradient). The differences between estimated emissions [*Brevik et al., 2002b*] and sinks are therefore significant. Higher differences are found as lower is the degree of chlorination of the PCB congeners which reflects the higher degradation

sinks at lower degree of chlorine substitution. Thus, the PCB#28/180 sink rate is 45 whereas the PCB#28/180 average emission rate is 28.

In addition, the finding of the highest PCB concentrations in the tropical zones where degradation rates and occurrence were highest involve that PCB transport from the areas of highest use to the tropics must have been very significant.

### 3.4. PCB loss by atmospheric residence times

The RSD from the data series summarized in Table 1 have been calculated. Average values corresponding to NH and SH have been obtained. The RSD due to analytical error have been estimated from the results of the GLOBAL-SOC intercalibration exercise on atmospheric PCB performed in 1998. The RSD corresponding to the pooled results of IIQAB-CSIC and the Lancaster University have been taken as reference. For most PCB congeners they involved values in the order of 20% of the field data RSD. These analytical RSD have been subtracted from the air concentration RSD values obtained from Table 1 and the resulting dispersion values have been used to obtain residence times using equation (1).

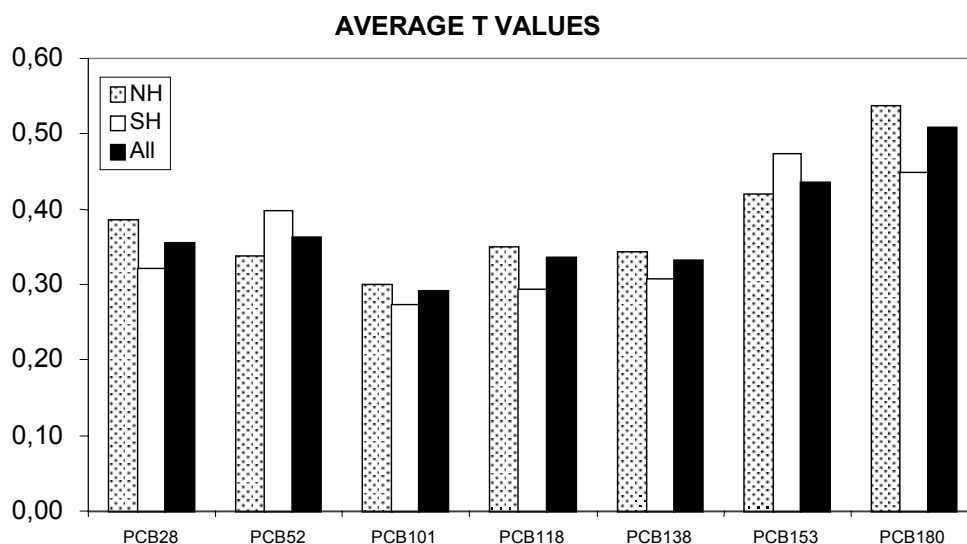


FIGURE 5. Average residence times for the PCB congeners calculated from the databases reported in Table 1.

The resulting values for the NH and SH are shown in Figure 5. Slightly lower loss rates for the more chlorinated congeners are found, namely PCB#153 and PCB#180. The differences between NH and SH are small. Accordingly, all values have been averaged and the means used for the calculation of PCB losses.

The sink of each PCB congener ( $i$ ) in each box ( $j$ ) ( $S_{ijk}$  ( $\text{kg y}^{-1}$ )) was calculated as

$$S_{ijk} = 1/T_i \cdot M_{ijk} \quad (11)$$

where  $T_i$  are reported in Figure 5 and  $M_{ijk}$  are calculated as defined above in equation (8).

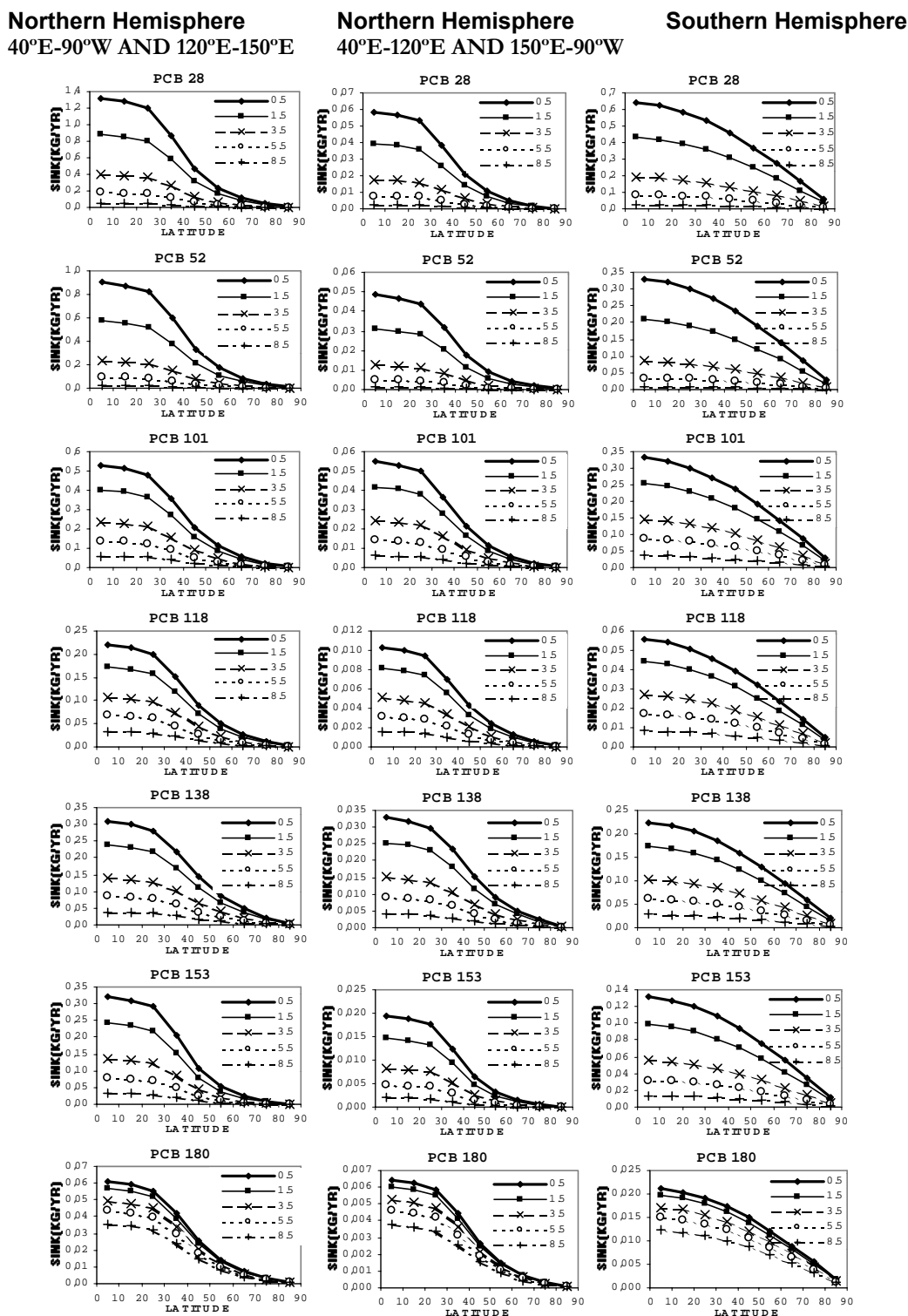


FIGURE 6. Examples based on PCB congeners #28 and #180 of calculated degradation rates, budgets and sinks of the mass balance box model assuming a vertical gradient (see text). According to the differences between PCB concentrations (Table 1) the planet is divided in three regions, two in the northern hemisphere (40°E-90°W and 120°E-150°E) and (40°E-120°E and 150°E-90°W) and one in the southern hemisphere (whole).

All PCB congeners show highest degradation rates where they are found in higher concentration. That is, at low latitudes and altitudes (Figure 6). The altitudinal differences are higher for the less than the more chlorinated PCB congeners. In the vertical gradient model the sinks, 90  $\text{t yr}^{-1}$ , are about half than those in the maximum inventory, 180  $\text{t yr}^{-1}$  (Table 6). Although these amounts are significant, they are much lower than the sink predicted by *Anderson and Hites* (1996) who estimated 8271  $\text{t yr}^{-1}$  for total PCBs and even lower than those estimated by *Wania and Daly* (2002), 218  $\text{t yr}^{-1}$ . The estimated values are also consistent with the estimated emission values reported by Breivik et al (2002b) based on historical emissions. As shown in Table 6, the loss values of all PCB congeners estimated in the present study fall within the range of average PCB emission for the 1930-2000 years period.

Table 6. Global PCB atmospheric inventories and sinks for different options assuming complete concentration mixing or vertical gradient in the troposphere (10 km).

<b>Maximum</b>								
<b>PCB Congener No.</b>	<b>28</b>	<b>52</b>	<b>101</b>	<b>118</b>	<b>138</b>	<b>153</b>	<b>180</b>	<b><math>\Sigma</math>PCB</b>
Inventory NH (tons)	14	10	5	2.2	3.3	4.0	0.9	40
Inventory (tons)SH	9	5	3.6	0.7	2.8	2.1	0.4	24
<b>Total Inventory</b>	<b>23</b>	<b>15</b>	<b>8.4</b>	<b>2.8</b>	<b>6.1</b>	<b>6.1</b>	<b>1.2</b>	<b>63</b>
NH loss ( $\text{tons}\cdot\text{yr}^{-1}$ )	40	29	16	6	10	9	2	110
SH loss ( $\text{tons}\cdot\text{yr}^{-1}$ )	26	13	12	2	8	5	1	67
<b>Total Loss (<math>\text{tons}\cdot\text{yr}^{-1}</math>)</b>	<b>65</b>	<b>42</b>	<b>29</b>	<b>8</b>	<b>18</b>	<b>14</b>	<b>2</b>	<b>180</b>
<b>Vertical gradient</b>								
<b>PCB Congener No.</b>	<b>28</b>	<b>52</b>	<b>101</b>	<b>118</b>	<b>138</b>	<b>153</b>	<b>180</b>	<b><math>\Sigma</math>PCB</b>
Altitudinal coefficient ( $\text{d}; \text{km}^{-1}$ )	-0.40	-0.45	-0.27	-0.24	-0.26	-0.28	-0.068	
Inventory NH (tons)	6.1	4.0	2.9	1.5	2.1	2.3	1.1	20
Inventory SH (tons)	3.9	1.9	2.2	0.5	1.7	1.3	0.5	12
<b>Total Inventory</b>	<b>10</b>	<b>5.9</b>	<b>5.1</b>	<b>1.9</b>	<b>3.8</b>	<b>3.6</b>	<b>1.6</b>	<b>32</b>
NH loss ( $\text{tons}\cdot\text{yr}^{-1}$ )	17	11	10	4	6	5	2	56
SH loss ( $\text{tons}\cdot\text{yr}^{-1}$ )	11	5	8	1	5	3	1	34
<b>Total Loss (<math>\text{tons}\cdot\text{yr}^{-1}</math>)</b>	<b>28</b>	<b>16</b>	<b>17</b>	<b>6</b>	<b>12</b>	<b>8</b>	<b>3</b>	<b>90</b>
<b>Other budgets (tons)</b>								
<b>Soils<sup>a</sup></b>	<b>190</b>	<b>210</b>	<b>170</b>	<b>400</b>	<b>530</b>	<b>1200</b>	<b>580</b>	<b>3280</b>
<b>Continental shelf sediments<sup>b</sup></b>	<b>460</b>	<b>700</b>				<b>1200</b>	<b>760</b>	
<b>Total production<sup>c</sup></b>	<b>57000</b>	<b>38000</b>	<b>32000</b>	<b>43000</b>	<b>25000</b>	<b>38000</b>	<b>14000</b>	<b>247000</b>
<b>Average emissions (1930-2000)<sup>d</sup> (<math>\text{tons}\cdot\text{yr}^{-1}</math>)</b>	<b>0.65-170</b>	<b>0.35-83</b>	<b>0.19-41</b>	<b>0.26-43</b>	<b>0.15-32</b>	<b>0.16-37</b>	<b>0.083-15</b>	<b>1.8-420</b>

Data from <sup>a</sup>[Meijer et al., 2003], <sup>b</sup> [Jonsson et al., 2003], <sup>c</sup> [Breivik et al., 2002a], <sup>d</sup> [Breivik et al., 2002b]

In contrast, extrapolation at a global scale of the PCB deposition values measured in remote sites such as Teide (Canary Islands; *van Drooge et al., 2000*), Pyrenees, Alps and Norway [*Carrera et al., 2002*] and the Swedish west coast [*Brorstrom-Lunden et al., 1994*] gives higher loss values (390  $\text{t yr}^{-1}$  for the sum of the seven PCB considered in this study) than those estimated with the present model.

These higher deposition values are perhaps reflecting that all the sites from which yearly deposition data are available correspond to the sector between 30°N and 60°N and 40°E and 90°W. The one having highest PCB use in the past [Breivik *et al.*, 2002b] and highest PCB accumulation in soils [Meijer *et al.*, 2003].

The sink estimates reported in Table 6 have been obtained by combination of the information derived from air concentration measurements and experimental models for OH reaction rates. As indicated above, there are uncertainties in the concentration values, namely for large world areas from which no reliable data are available. However, the consistency of the data already obtained from different studies (Table 1) precludes that major differences in the atmospheric pool such as one order of magnitude could be expected from a model derived with a larger number of determinations.

Overall, the data summarized in Table 6 points to a major PCB emission process to account for the large loss in the atmosphere. These emissions involve a renewal time of about four months for the global burden of atmospheric PCB. As indicated above, this rate is consistent with the average emission losses estimated from the PCB use in the past. Emissions from soils or continental shelf sediments are also feasible sources for the observed concentrations of PCB in the atmosphere.

#### 4. Conclusions

The obtained results show large differences between the sink of PCBs by OH radicals and the estimated atmospheric residence time. The observed differences in vertical gradient between PCB congeners and the differences in reaction rates between PCBs and OH radicals indicates that the OH reactions have influence on the less chlorinated PCBs. However, the reaction rates may not be the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not resolve the question which fraction is removed irreversibly from the troposphere (photo-degradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and form part again of the troposphere. Application of the Anderson and Hites (1996b) reaction rates may distinguish for the loss of PCBs from the troposphere, however, the very high PCB loss is not realistic in compare with other loss process and emission data. Moreover, there are no evidences in environmental data that such a depletion takes place. Highest atmospheric PCB concentrations are calculated in the tropical zone, without having data from this area. Since this area occupies a large volume in the Global inventory it is of importance to obtain data from remote tropical sites. The importance of this area is furthermore underlined by the fact the highest OH radical concentrations are estimated here. One way or another, the findings of the presented study suggest that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these 'well-studied' compounds.

### Acknowledgements

This study was supported by funding from EU DG XII, contract no. ENV4-CT97-0638 (GLOBAL-SOC).

### References

- Agrell, C., L. Okla, P. Larsson, C. Backe, and F. Wania, Evidence of Latitudinal Fractionation of Polychlorinated Biphenyl Congeners along the Baltic Sea Region. *Environ. Sci. Technol.*, *33*, 1149-1156, 1999.
- Alock, R. E., A. R. Johnson, S. P. McGrath, M. L. Berrow, and K. C. Jones, Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. *Environ. Sci. Technol.* *27*, 1918-1923, 1993.
- Anderson, P. N., and R. A. Hites, OH radicals reactions: The major pathway for polychlorinated biphenyls from the atmosphere. *Environ. Sci. Technol.* *30*, 1756-1763, 1996a.
- Axelman, J., and D. Broman, Budget calculations for polychlorinated biphenyls (PCBs) in the Northern Hemisphere - a single-box approach. *Tellus*, *53 B*, 235-259, 2001.
- Baker, J. E., and S. J. Eisenreich, Concentrations and Fluxes of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls across the Air-Water Interface of Lake Superiour. *Environ. Sci. Technol.*, *24*, 342-352, 1990.
- Ballschmiter, K. Transport and fate of Organic Compounds in the Global Environment. *Angew. Chemie*, *31*, 487-515, 1992.
- Beyer, A., D. Mackay, M. Matthies, F. Wania, and E. Webster, Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.*, *34*, 699-703, 2000.
- Brevik, K., A. Sweetman, J. M. Pacyna, and K. C. Jones, Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 1. Global production and consumption. *Sci. Total Environ.*, *290*, 167-184, 2002a.
- Brevik, K., A. Sweetman, J. M. Pacyna, and K. C. Jones, Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 2. Emissions. *Sci. Total Environ.*, *290*, 199-224, 2002b.
- Brorström-Lundén, E., A. Lindskog, and J. Mowrer, Concentrations and fluxes of organic compounds in the atmosphere of the Swedish west coast. *Atmos. Environ.*, *28*, 3605-3615, 1994.
- Buckland, S. J., H. K. Ellis, and R. T. Salter, PCDDs, PCDFs and PCBs in ambient air in New Zealand. *Organohalogen Comp.*, *43*, 117-122, 1999.
- Carrera, G., P. Fernandez, J.O. Grimalt, M. Ventura, L. Camarero, J. Catalan, U. Nickus, H. Thies, and R. Psenner, Atmospheric deposition of organochlorine compounds to remote high mountain lakes of Europe. *Environ. Sci. Technol.* *36*, 2581-2588 (2002)

- Duce, R. A., P. S. Liss, J. T. Merrill, E. L. Atlas, P. Buat-Menard, B. B. Hicks, J. M. Miller, J. M. Prospero, R. Arimoto, T. M. Church, W. Ellis, J. N. Galloway, L. Hansen, T. D. Jickells, A. H. Knap, K. H. Reinhardt, B. Schneider, A. Soudine, J. J. Tokos, S. Tsunogai, R. Wollast, and M. Zhou, The atmospheric input of trace species to the world ocean. *Global Biogeochem. cycles*, *5*, 193-259, 1991.
- Eisenreich, S. J., P. D. Capel, J. J. Richard, and R. Bourbonniere, Accumulation and Diagenesis of Chlorinated Hydrocarbons in Lacustrine Sediments. *Environ. Sci. Technol.*, *23*, 1116-1126, 1989.
- Finizio, A., D. Mackay, T. Bidleman, and T. Harner, Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols, *Atmos. Environ.*, *31*, 2289-2296, 1997.
- Gobas, F. A. P. C., M. N. Z'Graggen, and X. Zhang, X. Time responses of the Lake Ontario ecosystem to virtual elimination of PCBs. *Environ. Sci. Technol.* *29*, 2038-2046, 1995.
- Grimalt, J. O., P. Fernandez, L. Berdie, R.M. Vilanova, J. Catalan, R. Psenner, R. Hofer, P.G. Appleby, B.O. Rosseland, L. Lien, J.C. Massabuau, and R.W. Batterbee, Selective trapping of organochlorine compounds in mountain lakes of temperate areas. *Environ. Sci. Technol.*, *35*, 2690-2697, 2001.
- Gustafsson, Ö., P. M. Gschwend, and K.O. Buesseler, Settling removal rates of PCBs into the Northwestern Atlantic derived <sup>238</sup>U-<sup>234</sup>Th disequilibria. *Environ. Sci. Technol.* *31*, 3544-3550, 1997.
- Hamrud, M., Residence time and spatial variability for gases in the atmosphere. *Tellus 35B*, 295-303, 1983.
- Hein, R., P. J. Crutzen, and M. Heimann, M. An inverse modelling approach to investigate the global atmospheric methane cycle. *Global Biogeochem. Cycles*, *11*, 43-76, 1997.
- Hillery, B. R., I. Basu, C.W. Sweet, and R.A. Hites, Temporal and spatial trends in a long-term study of gas-phase PCB concentrations near Great Lake. *Environ. Sci. Technol.* *31*, 1811-1816, 1997.
- Hornbuckle, K., and S. J. Eisenreich, Dynamics of gaseous semivolatile organic compounds in a terrestrial ecosystem- effects of diurnal and seasonal climate variations. *Atmos. Environ.*, *30*, 3935-3945, 1996
- Hung, H., C. J. Halsall., P. Blanchard, H. H. Li, P. Fellin, G. Stern, B. Rosenberg, Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. *Environ. Sci. Technol.* *35*, 1303-1311, 2001.
- Iwata, H., S. Tanabe, N. Sakai, and R. Tatsukawa, Distribution of Persistent Organochlorines in the Oceanic Air and Surface Seawater and the Role of Ocean on Their Global Transport and Fate. *Environ. Sci. Technol.*, *27*, 1080-1098, 1993.
- Jeremiason, J. D., K. C. Hornbuckle, and S. L. Eisenreich, Decreases in water concentrations reflect loss by volatilisation. *Environ. Sci. Technol.*, *28*, 903-914, 1994.
- Jonsson, A., Ø. Gustafsson, J. Axelman, and H. Sundberg, Global accounting of PCBs in the continental shelf sediments. *Environ. Sci. Technol.*, in press.
- Junge, C.E., Residence time and variability of tropospheric trace gases. *Tellus*, *26*, 477-487, 1974.

- Kallenborn, R., M. Oehme, D. D. Wynn-Williams, M. Schlabach, and J. Harris, Ambient air levels and atmospheric long-range transport of persistent organochlorines to Signy Island, Antarctica. *Sci. Total Environ.*, 220, 167-180, 1998.
- Kjeller, L.-O., and C. Rappe, Time trends in levels, patterns, and profiles for polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic proper. *Environ. Sci. Technol.*, 29, 346-355, 1995.
- Knap, A. H., and K. S. Binkley, Chlorinated organic compounds in the troposphere over the Western North Atlantic Ocean measured by aircraft, *Atmos. Environ.*, 25A, 1507-1516, 1991.
- Lee, R.G.M., H. Hung, D. Mackay, and K.C. Jones, Measurement and modeling of the diurnal cycling of atmospheric PCBs and PAHs, *Environ. Sci. Technol.*, 32, 2172-2179, 1998.
- Manchester-Neesvig, J. B., and A.W. Andren, Seasonal Variation in the Atmospheric concentration of Polychlorinated Biphenyls Congeners. *Environ. Sci. Technol.*, 23, 1138-1148, 1989.
- Mandalakis M., and E.G. Stephanou, Study of atmospheric PCB concentrations over the eastern Mediterranean Sea. *J. Geophys. Res.*, 107,
- Mandalakis, M., H. Berresheim, and E.G. Stephanou, Direct evidence for destruction of polychlorobiphenyls by OH radicals in the subtropical troposphere, in press
- McLachlan, M., et al. Untersuchung der atmosphärischen belastung, des weiträumiges transports und des verbleibs von PCDD/F und coplanaren biphenylen in ausgewählten gebieten Deutschlands. *Schlussbericht, Universität Bayreuth*. 1998.
- Meijer, S. N., W. A. Ockenden, A. Sweetman, K. Breivik, J. O. Grimalt, and K. C. Jones, Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes. *Environ. Sci. Technol.* 37, 667-672, 2003.
- Monosmith, C. L., and M. H. Hermanson, Spatial and temporal trends of atmospheric organochlorine vapors in the central and upper Great Lakes. *Environ. Sci. Technol.* 30, 3464-3472, 1996.
- Ngabe, B., and T. F. Bidleman, Occurrence and vapor particle partitioning of heavy organic compounds in ambient air in Brazzaville, Congo. *Environ. Pollut.*, 76, 147-156, 1992.
- Oehme, M., J.E. Haugen, and M. Schlabach, Ambient air levels of persistent organochlorines in spring 1992 at Spitsbergen and the Norwegian mainland: Comparison with 1984 results and quality control measures. *Sci. Total Environ.*, 160/161, 139-152, 1995.
- Panshin, S. Y., and R. A. Hites, R.A. Atmospheric Concentration of Polychlorinated Biphenyls at Bermuda. *Environ. Sci. Technol.*, 28, 2001-2007, 1994.
- Parkhurst, D. F. Arithmetic versus geometric means for environmental concentration data. *Environ. Sci. Technol.*, 32, 92-98, 1998.
- Rapaport, R. A., and S. J. Eisenreich, Historical atmospheric inputs of high molecular weight hydrocarbons to the eastern North America. *Environ. Sci. Technol.*, 22, 931-941, 1988.
- Sanders, G., K. C. Jones, and J. Hamilton-Taylor, PCB and PAH fluxes to a dated UK peat core. *Environ. Pollut.*, 89, 17-25, 1995.



- 
- Slinn, W.G.N., A simple model for Junge's relationship between concentration fluctuations and residence times for tropospheric trace gases. *Tellus*, 40B, 229-232, 1988.
- Spivakovsky, C. M., J. A. Logan, S. A. Montzka, Y. L. Balkanski, M. Foreman-Foyler, D. B. A. Jones, L. W. Horowitz, A. C. Fusco, C. A. M. Brenninkmeijer, M. J. Prather, S. C. Wofsy, and M. B. McElroy, M.B. Three-dimensional climatological distribution of tropospheric OH: Update and evaluation. *J. Geophys. Res.*, 105, 8931-8980, 2000.
- Tolosa, I., J. W. Readman, S. W. Fowler, J. P. Villeneuve, J. Dachs, J. M. Bayona, and J. Albaiges, PCBs in the western Mediterranean. Temporal trends and mass balance assessment. *Deep-Sea Res. II*, 44, 907-928, 1997.
- van Drooge, B.L., J.O. Grimalt, C.J. Torres-García and E. Cuevas, Deposition of semi-volatile organochlorine compounds in the free troposphere of the Eastern North Atlantic Ocean. *Mar. Pollut. Bull.* 42, 628-634 (2001)
- van Drooge, B. L., J. O. Grimalt, C. J. Torres-García, and E. Cuevas, Semivolatile organochlorine compounds in the free troposphere of the northeastern Atlantic. *Environ. Sci. Technol.*, 36, 1155-1161, 2002.
- Wallace, J.C., and R.A. Hites, *Environ. Sci. Technol.*, 30, 3935, 1996.
- Wania, F., and D. Mackay, Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio*, 22, 10-18, 1993.
- Wania, F., D. Mackay, Y.-F. Li, T.F. Bidleman, and A. Strand, Global chemical fate of  $\alpha$ -hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environmental Toxicology and Chemistry*, 18, 1390-1399, 1999.
- Wania, F., and G. L. Daly, Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. *Atmos. Environ.*, 36, 5581-5593, 2002.
- Wong, C. S., G. Sanders, D. R. Engstrom, D. T. Long, D. L. Swackhamer, and S.L. Eisenreich, Accumulation, inventory, and digenesis of polychlorinated hydrocarbons in Lake Ontario sediments. *Environ. Sci. Technol.*, 29, 2661-2672, 1995.



## **Chapter 7    Discussion**

---

---

**Chapter 7. Discussion****7.1 Atmospheric transport and fate of POP in the subtropical troposphere****7.1.1 Organochlorine compounds**

The subtropical troposphere is here represented by the Atmospheric Observatory of Izaña. The concentrations of the organochlorine compounds are rather uniform and the troposphere is showing a well mixing of these pollutants. All OC show concentrations that are in the lower range of atmospheric samples from remote areas. The majority of them were detected in the gas phase and only the more chlorinated PCBs exhibit temperature dependence with shallow slopes in the plot of concentration versus inverse of temperature. Absence of temperature dependence or shallow slopes in the plots is related to long range transport (Wania et al., 1998). This is consistent with the results of the back-trajectories of the collected atmospheric samples showing that the origin of the air masses has no relevance for the load of contaminants. These results indicate that mixing and weathering processes like photo-degradation and deposition have homogenised the content of OC in the air mass. HCB is the individual organochlorine compound with the highest concentration, which is coherent with its theoretically long atmospheric life time, due to its high vapor pressure and resistance against degradation. Some evidence is found for the possible degradation of PCBs by OH-radicals. The levels of OC found at sea level (Punta de Hidalgo) are significantly higher for most of the compounds. The fact that tri- and tetra-CBs are dominating the PCB composition near sea level, while the penta-CBs dominate the air masses above the inversion layer, points to a possible effect of degradation by OH-radicals on the less chlorinated, and more reactive, PCBs during long-range atmospheric transport.

In contrast to the homogeneous atmospheric OC composition, the atmospheric deposition shows variability that is related to the mode of deposition. In the dry periods (dry deposition only and gas exchange with surface) there is a relatively constant deposition flux. This flux is in the lower range of the deposition observed in other remote areas. In episodes of wet deposition significantly higher loads are observed for most compounds. The increase is largest for the more volatile and water-soluble compounds, such as HCHs and less chlorinated PCBs. Since these compounds are predominantly detected in the gas phase, findings illustrate that there is an efficient exchange of gas phase to rain for these compounds. Correction for the average annual precipitation modes at the Atmospheric Observatory of Izaña shows that the episodes of wet deposition are responsible for 90% of the total deposition of HCHs, while this is 76% and 82% for HCB and 4,4'-DDE, respectively, and about 60% for the more volatile PCBs (#18, #28, and #52). For the less volatile PCBs (#70 and more chlorinated) the wet deposition represents between 40% and 50% of the total annual deposition load in the free troposphere in this part of the North Atlantic Ocean.

### 7.1.2 Polycyclic aromatic hydrocarbons

The analysis of the PAH in the free troposphere show very low concentrations of these compounds. They are in the lower range of those found in other remote areas. This is directly related to the remoteness of the sampling site, the absence of local or regional pollution sources and the influence of weathering processes during long-range atmospheric transport. The results also illustrate a great homogeneity in individual PAH composition. Similar distributions are found in other remote areas and are characteristic for air masses after long-range transport and independent of emission sources (Fernández et al., 2002).

Paralleling the differences in atmospheric composition, lower PAH concentrations were observed in soils above the inversion layer (1800m-3400m), than soils within the inversion layer (10m-1800m). The relative composition of PAH in the gas phase and in soils suggests that the mechanisms of input and conservation of PAH in soils is different within and above the inversion layer. In the former case soils are characterised by a high organic carbon content due to the support of local vegetation, while in the second soils lack the input of organic carbon from local vegetation.

The soil-air partitioning model based on the organic carbon content of the soil and the octanol-air partitioning coefficient ( $K_{oa}$ ) predicts very well the distribution of the studied PAH within the inversion layer, while this model underestimates the partitioning coefficient ( $K_p$ ) obtained empirically. Incorporation of the soot-carbon model ( $f_{sc}K_{sa}$ ) to the soil-air partitioning model shows that the predicted  $K_p$  is in good agreement with the measured  $K_p$  above the inversion layer. These findings show that the partitioning of PAH between air and soil depends largely on the composition of the soils. Dachs and Eisenreich (2000) proposed that if the organic fraction ( $f_{oc}$ ) is more than 2 orders of magnitude higher than the soot-carbon fraction ( $f_{sc}$ ), absorption of PAH into organic matter is the dominant sorption mechanism. In fact, this is the case in the soils located within the inversion layer of the lower part of the island. Abundant vegetation and high organic matter content may cover the soot-carbon content in these soils. Conversely, in the soils situated above the inversion layer,  $f_{sc}$  is relatively high in comparison to the  $f_{oc}$ . Therefore the adsorption of PAH to soil SC is the dominant process. This will also be the probable scenario for soils poor in organic matter that receive deposited aerosols, such as the soils in high-mountain areas. In fact the implication of the soot-carbon model to the gas-particle partitioning of PAH in atmospheric samples from European high-mountain areas show that soot-carbon is the main factor of the long-range atmospheric transport of particle-bounded PAH to these areas (Fernández et al., 2002).

## 7.2 Atmospheric transport and fate of POP in European high-mountain areas

### 7.2.1 Organochlorine compounds

#### 7.2.1.1 Active air sampling: HiVol

The relative composition of OC in the atmospheric samples determined by HiVol pumping in the High Tatras (Skalnate Pleso) and the Central Pyrenees (Estany Redon) is very similar. Most of the studied compounds are present in the gas phase, which is consistent with observations in other studies, like the free-troposphere on Tenerife (see article 1 and 7.1). At both sites HCB, which is only present in the gas phase, is the OC with the highest individual concentration. This compound is followed by  $\gamma$ -HCH,  $\alpha$ -HCH, 4,4'-DDE, and the individual PCB congeners. In terms of concentrations  $\gamma$ -HCH was the pre-dominant OC in the particulate phase. The less volatile PCB congeners, e.g. #149, #118, #153, 138, and #180, had similar or higher concentration in the particulate phase than in the gas phase, which is in agreement with reported gas-particulate phase distributions (Pankow, 1987).

The atmospheric levels observed near the lakes are in the lower range among those previously observed in other remote sites. Only PCB congeners and 4,4'-DDE show lower concentrations in the Arctic (Oehme et al., 1995).  $\gamma$ -HCH and endosulphanes observe high levels in the warmer periods. The ratios of  $\alpha/\gamma$ -HCH and  $\alpha/\beta$ -endosulphanes indicate that these high levels are directly related to the application of the compounds for agricultural purposes on the European continent. Thus, their observed atmospheric variability is related to use. Other OC compounds show an atmospheric variability that is related to ambient temperature. This was also observed for the OC in atmospheric deposition and lake waters in the European high-mountains (Vilanova et al., 2001c; Carrera et al., 2002). However, in the atmosphere this relationship was only significant for the less volatile compounds, e.g. PCB52 and more chlorinated PCB congeners and 4,4'-DDE.

Better correlation coefficients between concentration and reciprocal of temperature were found for Skalnate Pleso than for Estany Redon. Atmospheric gas phase concentrations drop with decreasing ambient temperatures. This points to evaporation/condensation effects or solid-gas phase exchange as the main factors for OC occurrence in the gas phase. Calculated pseudo-enthalpies range between 27 and 55 kJ mol<sup>-1</sup> for the individual OC in Skalnate Pleso with a small error for the less volatile PCB congeners and 4,4'-DDE. These values are lower than the laboratory-derived enthalpies, which indicates that long-range atmospheric transport (LRAT) is the main mechanism controlling the atmospheric OC (Wania et al., 1998).

Back-trajectories in Skalnate Pleso show that the oceanic air masses contain lower OC levels than the air masses that have travelled for a longer time over the European continent. Only HCB has similar concentrations in both cases. These higher concentrations in the continental group of samples is consistent with emissions from the continent, where some OC were produced and

used in the past (PCBs and 4,4'-DDE) and others are still being used (HCHs and endosulphanes). Although, the low pseudo-enthalpies point to LRAT as the main factor controlling the atmospheric gas phase, the European continent may be a source for these compounds. In the case of the back-trajectories of the air masses sampled near Estany Redon, the differences between continental and oceanic trajectories is less defined, which is due to its situation on the periphery of the European continent. Classification of the samples shows that the continental air masses contain higher levels for most of the OC than the oceanic air masses. However, the differences are not as clear as they were in the case of Skalnaté Pleso. Air masses from high altitudes (>6000m) show very low levels. Besides lower ambient temperatures these trajectories are more exposed to weathering processes and further away from potential emission sources. High altitude air masses and air masses with an oceanic trajectory are more related to the colder season, which is in coincidence with a more stable atmospheric situation in winter than in summer (Barry, 1992). The transport of OC to these high-mountain areas is related to LRAT, but the origin of the compounds is mainly related to surface sources located in Europe.

#### 7.2.1.2 Passive air sampling:

##### 7.2.1.2.1 *Pinus uncinata*

Needles of *Pinus uncinata* have demonstrated to be very useful in the determination of atmospheric PCB levels. The method is cheap and fast and can be applied on a large spatial scale and repeated temporally. *Pinus uncinata* is the uppermost growing tree species in the Pyrenees with growing heights up to 2400m. The analysis of the leaves on its PCB content show that the highest levels of most of the PCB, except PCB#28, were found at the highest sample site (e.g. Estany Redo, 2250m) and at lowest ambient temperature. This finding indicates that the temperature is the main factor controlling the concentrations in pine leaves. Probably temperature also controls the solid-gas phase exchange, as it did in fish muscle and sediments from high-mountain lakes (Grimalt et al., 2001; Vives et al., 2004). This result is in agreement with the global distillation theory (Wania and Mackay, 1993). This relationship disappears for most of the PCB congeners, except the less volatile one, PCB180, when pine needle concentrations were corrected for lipid content. Pseudo-enthalpies obtained from the plots of the log dry weight concentrations versus inverse of the ambient temperature indicate that the values observed in the pine needles are in good agreement with the laboratory derived enthalpies of vaporisation. The pine needle-air partitioning coefficient ( $K_{pa}$ ) exhibits a good relationship with the octanol-air partitioning coefficient ( $K_{oa}$ ). However,  $K_{pa}$  shows a stronger temperature dependence than  $K_{oa}$ , which is also observed in other species (Kömp and McLachlan, 1997a). In this sense the  $K_{oa}$  can not automatically be used in model calculations to obtain atmospheric levels from plant leaf concentrations. Estimations of atmospheric PCB levels at different altitudes using the obtained  $K_{pa}$  temperature relationship and the pine needle

concentrations at these altitudes show that atmospheric levels decrease slightly with increasing altitude, which is consistent with atmospheric measurement with HiVol pumping in January 2003 at 2250m (Estany Redon) and 1600m (CRAM). Moreover, the estimated atmospheric levels are in the same range as those obtained by conventional HiVols.

#### 7.2.1.2.2 SPMDs

Semipermeable Membrane Devices (SPMDs) have demonstrated in the study near Estany Redon that they can be used as monitoring devices for atmospheric OC levels. In a sense, they can be compared with pine needles, as they have a large surface/volume ratio. However, due to the fact that SPMDs are only exposed to the atmosphere over a period of few months, not all OC will achieve equilibrium. The uptake of chemical compounds has to be calculated using SPMD-air partitioning coefficients ( $K_{sa}$ ) and assuming that the exchange is boundary controlled. This could introduce a number of errors that may have influence on the finally calculated atmospheric levels by SPMDs. In contrast to the observed OC concentrations in pine needles, the SPMDs show very similar OC amount along a vertical gradient of 1000m, between 1600m and 2600m. Sampling rates of OC are modelled by using the calculated value of the performance reference compound PCB155. These values, together with physico-chemical properties of HCB and PCB congeners, were used to estimate the atmospheric levels at 1600m, 2250m, and 2600m. There is a slight altitude effect observed in the first sampling period, with lower atmospheric levels at higher altitude. However, in the other samplings this effect is not present. Although analytical errors and errors in the values of physico-chemical properties may have influenced the obtained results, comparison of the atmospheric levels by SPMDs and levels obtained by HiVols shows that both techniques give similar results. Like *Pinus uncinata*, the SPMDs can be used as passive air samplers on a broader spatial and temporal scale. Both techniques are cheap and fast to deploy on remote sites, like high-mountain areas. In this sense they could be used as monitoring systems to study the evolution of atmospheric OC levels in this sites. For the calibration of the uptake kinetics of SPMDs, PCB#155 can be used for exposure times of a few months. Exposure times of more than 3 months is recommended to obtain detectable OC levels.

#### 7.2.1.3 Fate of OC in soils and lake sediment

The low concentrations of OC observed in the soils and sediments from the high-mountain lake areas indicate the absence of local pollution sources in their vicinity. The concentrations are in the same range as rural areas elsewhere and lower than in industrial areas, or rural areas in the UK. However, sediment concentrations are higher than soil concentrations. Studies of fallout of radionuclides have shown that the flux of  $Pb^{210}$  is slightly higher in soils than sediments, which indicates that the higher OC levels in sediments can not be explained by a soil erosion effect of particles from the catchment to the lake. Leaching of OC from the soils to the



lakes is also not probable since soil have relatively higher organic matter content than the sediments and OC have high  $K_{OW}$ . This points to retention of organochlorine compounds to the soils. In general, the soils and sediments have the same OC input (atmospheric deposition and gas exchange), so higher concentrations of OC in sediments could be explained by a higher retention efficiency of the sediments over the soils. The lake water column impedes re-volatilisation of OC once they have entered the lake, and no significant transformation processes occur in the water column (Vilanova et al., 2001a). In contrast, re-volatilisation in soil could take place. The temperatures of the bottom-water in the lakes is around 4°C during whole the year, while soils can have values higher than 10°C in warm periods (Catalan, 1992). These higher temperatures may enhance biological activities as well as re-volatilisation to the atmosphere after condensation or deposition.

The relative distribution of OC compounds in the vertical profile of soils and sediments points to a recent input of these compounds to the compartments (last 50 years). However, soils exhibit a wider spread in their profiles than sediments. In the later, OC are concentrated in a thin layer. The wider spread of OC in soils than sediments suggests biological activities, such as bioturbation, in the soils. The upper sections of the soils and sediments are dominated by the less volatile, or heavier molecular weight compounds. The predominance of these compounds could be a consequence of their predominant condensation at ambient temperature (Grimalt et al., 2001), since an important part of these compounds is in the atmospheric gas phase. However, another part of these compounds is in the particulate phase of the atmosphere, and may enter the lake area by deposition. The relative abundance of more volatile, or lighter molecular weight compounds in the deeper soil sections, and in some cases deeper sediment sections, can not be explained by differences in input mechanisms through time. It might be associated to vertical transport of these compounds in the soil and sediment column, caused by chemical diffusion, or rainfall dissolution and water table oscillations (Rapaport and Eisenreich, 1988). In addition, *in situ* formation of less chlorinated PCBs could also be one of the possibilities of the presence of these compounds in the deeper soil sections, after dechlorination of higher chlorinated PCBs under anaerobic conditions.

Radiometric analyses observe that all sediment cores have a rather uniform sedimentation within the lakes, but different sedimentation rates between lakes. The sediment cores are good stores of the historical pollution records, since no mixing has been observed. The sedimentation rates are not the same in all lakes, so the profiles of OC have different time resolutions. Ladove pleso shows a biannual resolution profile of PCBs increasing rapidly between 1949 and 1957. Before this time the levels were below limit of detection. Then, there is another increase between 1963 and 1970, a period that probably reflects the historical use of PCBs in Europe after WWII. HCB shows a similar trend. DDTs have a steep increase between 1955 and 1978. Then there is a strong drop between 1978 and 1990. The second increase between 1992 and 1997 could indicate a new period of DDT use in some parts of Europe or re-mobilisation of compound stored in environmental compartments. After 1997 the OC concentrations drop significantly. The sediment

cores from the other lakes, Estany Redon, Starolesnianske pleso and Dlugi staw, do not show this clear decrease. However, these sediment cores, which have their highest OC concentration in the top layer section, represent sedimentation inputs until 1994. Thus, before the drop in Ladove pleso took place. The vertical profile of OC concentrations in the sediments reflects the increase of OC production and use in Europe after WWII. Sediments from Ladove pleso may represent a drop in concentrations after 1997. This result suggests that the input of OC to the remote high-mountain lakes may be decreasing, at least in this part of Europe. The decrease of OC levels in sediments of industrial areas of the UK was related to the decrease of emissions after the prohibition of production and use of these products (Sanders et al., 1994).

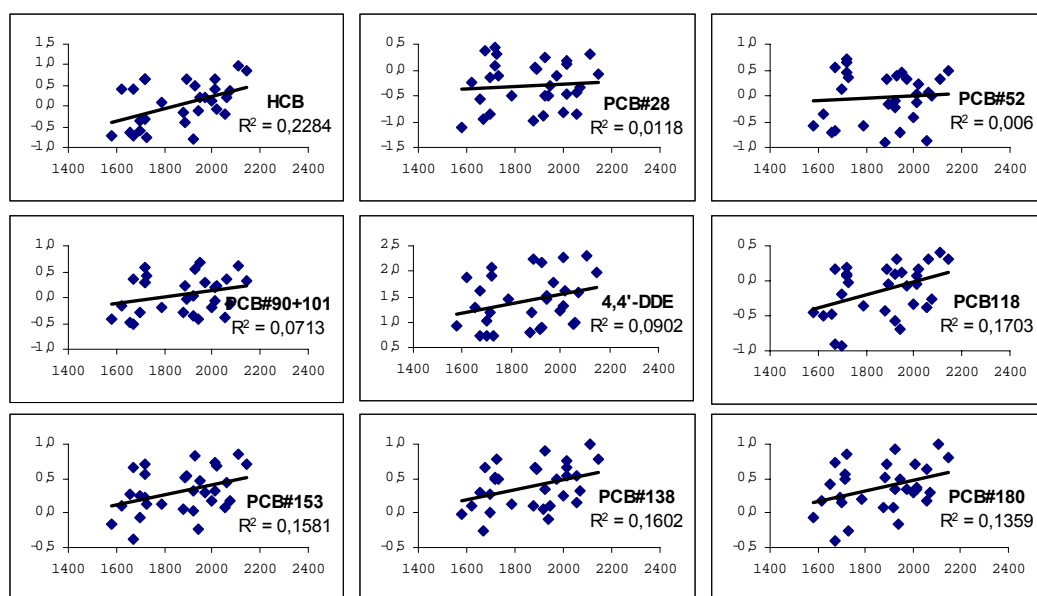


Figure 24. Log concentrations of OC in lake sediments ( $\text{ng g}^{-1}$  DW) (y-as) versus lake altitude (m) (x-as) of 30 high-mountain lakes in the High Tatras

A survey of 30 high-mountain lake sediments from the High Tatras sampled in 2001 shows a wide spread of OC concentrations in the top layer section (0-0.5cm) over this mountain range (Table 8; Figure 24). Ladove pleso (2057m) (**fat**) represents more or less the average OC concentrations in the lakes, with  $\Sigma$ PCB concentrations above the average and 4,4'-DDE concentrations under the average. Lake Vyšné Terianske (2109m) shows highest OC concentrations while Zielony Staw Gąsienicowy (1672m) is the lake with the lowest  $\Sigma$ PCB concentrations and one of the lowest 4,4'-DDE levels. These observations suggest that a selective trapping, or cold condensation effect takes place in this mountain range, since higher OC concentrations are found at higher (colder) altitudes than at lower altitudes. Moreover, the plots of the log concentrations of OC versus altitude of the lakes show positive slopes for most of the compounds (Figure 24). However, the altitude dependence of OC concentration in the lake sediments is not as clear as was observed in the comparison of lake sediments and fish muscle from lakes of different regions in Europe (Grimalt et al., 2001; Vives et al., 2004).

Table 8. OC concentrations (ng g<sup>-1</sup> DW) in top layer (0-0.5cm) of high-mountain lake sediments of High Tatras (2001).

	Latitude °N	Longitude °E	Altitude (m)	ng/g DW										
				HCB	#28	#52	#90+101	4,4'-DDE	#118	#153	#138	#180	Σ PCB	
Horné Roháčske	49,206	19,627	1718	4,5	1,2	2,9	1,9	80,8	1,2	3,7	3,2	3,7	3,7	17,8
Nízné Jamnicke	49,203	19,772	1728	0,2	0,8	2,3	2,7	5,2	0,9	1,4	3,1	0,6	0,6	11,8
Výšné Račkovce	49,200	19,807	1697	0,3	0,7	1,3	0,5	10,6	0,7	1,7	1,8	1,7	1,7	8,5
Zielony Staw Gašienicowy	49,229	20,001	1672	0,2	0,1	0,2	0,3	5,4	0,1	0,4	0,5	0,4	0,4	2,1
Zelené krivánske	49,159	20,009	2017	0,8	1,3	1,7	1,7	42,2	1,5	4,8	4,5	2,3	2,3	17,8
Nízné Tetianske	49,170	20,014	1941	0,8	0,3	0,2	0,4	28,7	0,2	0,6	0,8	0,7	0,7	3,2
Zadni Staw Polski	49,213	20,014	1890	4,6	1,0	0,7	0,9	168,3	0,9	3,6	4,4	5,1	5,1	16,5
Czamy Staw Gašienicowy	49,231	20,020	1620	2,5	0,6	0,4	0,7	76,7	0,3	1,2	1,3	1,5	1,5	6,0
Výšné Tetianske	49,168	20,022	2109	9,3	2,0	2,0	4,2	200,6	2,5	7,3	9,7	10,1	10,1	37,9
Zmarzly Staw Gašienicowy	49,224	20,024	1787	1,3	0,3	0,3	0,6	28,9	0,4	1,4	1,4	1,6	1,6	6,0
Výšné Wahlenbergovo	49,164	20,027	2145	6,9	0,8	3,1	2,1	97,8	2,1	5,0	6,0	6,4	6,4	25,6
Czamy Staw Polski	49,205	20,028	1722	4,4	2,0	4,4	3,7	116,8	1,5	5,2	6,2	7,3	7,3	30,3
Nízné Temnosmrečinské	49,193	20,031	1674	2,5	2,3	3,7	2,2	41,2	1,5	4,6	4,5	5,3	5,3	24,1
Capie	49,168	20,038	2072	2,3	0,5	1,0	0,8	38,8	0,5	1,5	2,1	2,0	2,0	8,3
Výšné Temnosmrečinské	49,189	20,040	1716	0,5	2,7	5,0	2,0	16,0	1,2	1,7	3,1	3,1	3,1	18,8
Wielki Staw Polski	49,213	20,040	1655	0,2	0,3	0,2	0,3	19,1	0,3	1,9	2,0	2,6	2,6	7,7
Malé Hincovo	49,174	20,059	1923	LQ	0,3	0,8	1,0	7,9	1,2	2,1	2,2	2,2	2,2	9,9
Veľké Hincovo	49,180	20,061	1946	1,6	0,5	2,8	4,7	33,1	1,3	2,9	1,3	3,2	3,2	16,6
Czamy Staw pod Rysami	49,189	20,078	1580	0,2	0,1	0,3	0,4	8,7	0,3	0,7	1,0	0,9	0,9	3,6
Veľké Žabie	49,172	20,079	1919	0,2	0,1	0,6	0,4	7,5	0,3	1,1	1,1	1,2	1,2	4,8
Dračie	49,166	20,088	1998	1,3	0,2	0,4	0,6	16,3	0,5	1,5	1,8	1,9	1,9	6,9
Výšné Žabie bielovodské	49,194	20,094	1699	0,4	0,1	LQ	LQ	5,3	0,1	0,9	1,0	1,4	1,4	3,6
Ľadové pleso v Zlomiskách	49,163	20,108	1925	3,2	1,7	2,5	3,6	147,4	2,0	6,9	8,1	8,4	8,4	33,2
Batizovské	49,152	20,132	1879	0,7	0,1	0,1	0,5	6,1	0,4	1,1	1,3	1,2	1,2	4,7
Pusté	49,182	20,155	2055	0,6	0,1	0,1	0,4	8,9	0,4	1,2	1,4	1,5	1,5	5,2
Výšné zbojnícke	49,179	20,160	1972	1,6	0,8	2,2	2,0	60,5	0,9	2,0	3,0	2,2	2,2	13,0
<b>Ľadové pleso</b>	<b>49,184</b>	<b>20,163</b>	<b>2057</b>	<b>1,7</b>	<b>0,4</b>	<b>1,2</b>	<b>2,2</b>	<b>9,9</b>	<b>2,1</b>	<b>2,7</b>	<b>3,5</b>	<b>4,2</b>	<b>4,2</b>	<b>16,3</b>
Žabie javorové	49,191	20,170	1886	0,4	1,1	2,1	1,7	15,3	1,5	3,4	4,6	3,4	3,4	17,7
Prostredné sivé	49,184	20,177	2011	4,7	1,5	1,0	1,6	179,8	1,2	5,5	5,9	5,2	5,2	21,9
Veľké spišské	49,193	20,196	2014	2,5	0,3	0,7	0,9	20,8	0,9	2,1	3,4	2,2	2,2	10,5

The absence of a significant altitude / temperature dependence in the High Tatras can be caused by different factors. In the case of the High Tatras the top layers of the sediments were sampled in 2001. All studied lakes have different sedimentation rates. Since no radiometric measurements were done on the top layers of the lake sediments it is not known if all top layers represent the period between 1997 and 2001. Probably they do not. Thus, lakes with high sedimentation rates will be more diluted for OC levels than lake with low sedimentation rates.

### 7.2.2 Fate of polycyclic aromatic hydrocarbon in soils and sediments

Polycyclic aromatic hydrocarbons are emitted to the atmosphere constantly during combustion processes. Although they have relatively short atmospheric residence times they have been observed in considerable quantities in the high mountain atmosphere.

Table 9. Summary of average PAH concentrations observed at Skalnaté Pleso (High Tatras) (left) and Estany Redon (right).

	Gas (pg/m <sup>3</sup> )	Particulate (pg/m <sup>3</sup> )	Gas (pg/m <sup>3</sup> )	Particulate (pg/m <sup>3</sup> )	
TSP (µg/m <sup>3</sup> )		16,9		14,3	
Fluorene	915	29,1	88	1,4	
Phenanthrene	3067	52,7	124	8,5	
Anthracene	21	18,2	5	0,9	
Fluoranthene	310	101,2	31	8,9	
Pyrene	100	77,3	19	6,8	
Benzo(a)anthracene	8	31,3	2	2,6	
Chrysene+Triphenylene	20	63,9	4	8,6	
Benzo(b)fluoranthene	dl	68,3	dl	7,6	
Benzo(k)fluoranthene	dl	41,5	dl	4,1	
Benzo(e)pyrene	dl	46,2	dl	7,5	
Benzo(a)pyrene	dl	41,4	dl	4,9	
Indene(1,2,3cd)pyrene	dl	62,3	dl	6,7	
Benzo(ghi)perylene	dl	55,3	dl	7,4	
Dibenzo(ah)anthracene	dl	19,2	dl	2,9	
ΣPAH	4442,8	707,8	290,1	85,1	
June 2001	1971	420	November 2000	289,3	31,8
September 2001	3961	451	May. 2001	409,6	123,8
December 2001	11950	4571	February 2002	229,5	100,8
June 2002	4774	323	March 2002	232,3	454,1
			June. 2002	402,2	71,7
			January 2003	152,1	105,3

Table 9 shows the geometric means of PAHs at Skalnaté Pleso (High Tatras) and Estany Redon. The gas phase levels of the High Tatras are about 15 times higher than the levels in the Central Pyrenees. Particulate phase levels are about 8 times higher. The PAH levels of the High Tatras are also about 3 times higher than those of the Tyrolean Alps and the Norwegian mountains (Fernández et al., 2002). In the High Tatras the highest atmospheric PAH concentrations were

observed in the colder periods, which is consistent with the observations by Fernández et al. (2002). The PAH are about 4 times higher in winter than in summer. The increase of PAH in colder periods can be explained by the increase of PAH emissions from source areas, less dispersion due to stable atmospheric situations and a reduced photo-degradation in winter time. In the Central Pyrenees this seasonal differences are not that clear.

The upper sections of the soil and sediment cores from the High Tatras and Central Pyrenees are always dominated by the pyrolytic parent PAH, with a higher abundance of the heavier weight compounds of catacondensed structures. The levels are higher in the High Tatras than in the Central Pyrenees, which is consistent with observed atmospheric levels. But despite the variability in sources and total PAH load, the distributions of the PAH in the sediments are very similar. The uniform sedimentary PAH profile exhibits a high parallelism with the PAH composition of the aerosols at these sites (Fernández et al., 2002). This composition is source independent and PAH load, and is very typical of air masses at remote locations.

Comparison between sediments and soils shows that the PAH ratios observed in the later are closer to the ones observed in aerosols. The transport through the water column to the sediments may be responsible for transformation of the PAH composition. However, the down core PAH ratios are less variable in the sediments than in the soils. Once the PAH have been buried the PAH are better preserved in the sediments than in the soils.

Radiometric dating of the sediment cores give different sedimentation rates for the lakes and thus different time resolutions of the vertical PAH profile in the cores (see 7.2.1.3). Ladove Pleso shows a biannual record between from 1924 and 2001, while the other lakes have lower temporal resolutions. The sediments from Ladove Pleso shows that the PAH levels between 1924 and 1954 were much lower than after 1954. In the other lakes the PAH levels maintain rather constant values from 1821 (earliest sample year) to the beginning of the 20<sup>th</sup> century. The steep increase of sedimentary PAH in the first half of the 20<sup>th</sup> century is observed in all lakes and can be interpreted as the effect of the increasing combustion of fossil fuels in this period, in coincidence with the industrial revolution and further intensification of the industry. Especially in the Tatras, high PAH levels are observed, which reaching concentrations 10 times higher than before the increase. There is a maximum in the Ladove Pleso core between 1980 and 1988 and between 1963 and 1966. The strong decrease of PAH levels from 1988 to 2001 (latest sample year) is consistent with the improvement of combustion techniques in central Europe and thus may indicate a decrease of atmospheric PAH emissions. The absence of the PAH decrease in the other lakes may be caused by the fact that their temporal resolution is lower than Ladove Pleso and their latest sample year is 1994, instead of 2001.

All pyrolytic PAH show a very similar temporal trend, reflecting similar atmospheric input through time to European mountain areas. However, perylene and retene exhibit a different profile with time in Estany Redon for the former and in all lake for the later. Perylene shows its highest concentrations in the oldest sediment sample in Estany Redon, while retene levels do not differ too

much between new and old sediments. The increase of perylene in the Redon sediments with depth is probably caused by in situ production of this compound. Although its precursor is still unknown, it is likely to be related to higher plant residues. The lack of anoxic conditions in the soil may be responsible for the absence of a perylene increase with depth in the soils. Retene has been used as a marker for wood combustion, while benzo(b)naphto[2,1-d]thiophene (BNT) is a specific marker for coal combustion. The relative constant retene concentrations in the sediment cores of the lakes may indicate a constant input of this compound after wood combustion. The increase of pirolytic PAH after combustion of fossil fuels may be represented by BNT. So, the ratio between these two 'markers' may indicate the downcore variation between 'natural' and 'industrial' combustion. A similar index is proposed for 1,7-dimethylphenanthrenes vs 2,6-dimethylphenanthrene, the first being a marker for wood combustion and the later a marker for fossil fuel combustion. The retene/(retene+BNT)-index increase with depth in Redon soils and in sediments and sediments from Ladove Pleso, while the 1,7DMPhe/(1,7DMPhe+2,6DMPhe)-index is constant with depth in soils and sediments. The downcore increase of the retene/(retene+BNT)-index indicates a diagenetic production of retene in the sediments. Thus, in these mountain environments this compound can not be used as marker for wood combustion.

### 7.3 Global atmospheric fate of POP with PCBs as model compounds

The atmospheric residence times of PCBs with the Junge model are higher than the residence times estimated by using the OH radical reactions of Anderson and Hites (1996b). Application of the reaction rates, as observed by Anderson and Hites (1996b), on environmental data would result in orders of magnitude faster depletion of the less chlorinated PCBs (more reactive) in comparison with the more chlorinated PCBs (less reactive). If this fast depletion of less chlorinated PCB really takes place in the troposphere, then this should be observed in the samples from environmental compartments. However, there are no temporal and spatial trends that give evidence for such enhanced depletion of less chlorinated PCBs. For example, the composition of PCB congeners is more or less the same along historical samples, such as sediment cores (Sanders et al., 1995; article 7). Moreover, the estimated quantity of degraded PCBs is of such an order that it outnumbers the loss of PCBs from the environment by other processes, such as sink to oceanic sediments. But maybe more important is the fact that PCBs are still detected in remote atmospheres (article 1, 4). This means that a constant flux of PCBs from sources to the atmosphere is required to maintain these actual ambient PCB concentrations. Even in a scenario of maximum annual PCB emissions (Breivik et al., 2002) this would not be enough by orders of magnitude to compensate for the annual loss of PCBs by the presumed OH radical reactions. On the other hand, even if atmospheric PCB levels are decreasing, it seems that this decrease is similar for the different PCB congeners (article 7).

---

As mentioned before, the experimental conditions under which the PCB-OH reaction rate constants were obtained are to far from the environmental conditions. Application of these rate constants may therefore lead to overestimation of the atmospheric loss of PCBs, especially the more volatile and reactive congeners.

Calculations of the  $\tau_{\text{total}}$  with the Junge model indicates that less chlorinated PCBs (3CB, 4CB and 5CB) have similar or slightly lower residence times than the more chlorinated PCB (6CB and 7CB, and probably 8CB) (article 11, Fig. 5). These results might indicate that the OH reactions have influence on the less chlorinated PCBs, but that the reaction rates are not the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not allow to elucidate which fraction is removed irreversibly from the troposphere (photo-degradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and return to the tropospheric PCB pool. However, there is no evidence based on field measurements that such depletion takes place. One way or another, the findings show that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these compounds. Among other requirements, more measurements in the tropical zone on both hemispheres are needed to obtain better estimates on global atmospheric levels, and consequently, better approaches on PCB losses.

## **Chapter 8    Conclusions**

---



---

**Chapter 8. Conclusions**

- 1) In the free-troposphere of the tropospheric Atlantic, the atmospheric organochlorine compounds and polycyclic aromatic hydrocarbons are well mixed and predominantly present in the gas phase. Back-trajectories show little influence from potential regional source areas, such as the European continent. The atmospheric OC levels and composition of the air masses origin from long-range atmospheric transport in the subtropical part of the free-troposphere.
- 2) In the European high-mountain atmosphere, HCB, PCBs, 4,4'-DDE are also relatively well mixed. HCB and the more volatile PCB-congeners are pre-dominantly present in the gas phase. The transport of these OC to these high-mountain areas is related to LRAT, but the origin of the compounds is mainly related to surface sources located in Europe.
- 3) In the European high-mountain atmosphere, the atmospheric variability of HCHs and endosulphanes is related to the application of these products for agricultural purposes in the European continent.
- 4) Some evidence is found for the degradation of PCBs by OH-radicals. The vertical gradient is decreasing with increasing chlorine number.
- 5) In the free-troposphere, there is a relatively constant settling flux of organochlorine compounds in the dry deposition mode. Variability in atmospheric deposition is essentially caused by episodes of wet deposition, which increases the settling flux of the more volatile and water soluble compounds.
- 6) In the free-troposphere (above the inversion layer of the subtropical Atlantic), where the soils are relatively poor in organic matter, adsorption of atmospheric PAH to soil soot-carbon is the dominant sorption process. Below the inversion layer the sorption of PAH to soils is controlled by their high organic matter content.
- 7) Leaves from *Pinus uncinata* are useful as passive atmospheric samplers for organochlorine compounds. The pine needle-air partitioning coefficients increase with decreasing temperatures, which explains the higher PCB concentrations in *Pinus uncinata* at higher altitude (lowest ambient temperature). A selective trapping / cold condensation effect is observed on these leaves.
- 8) SPMDs are useful as passive atmospheric samplers for organochlorine compounds. However, there are uncertainties related to the model calculation in order to obtain environmental OC levels.

---

In any case, the atmospheric OC concentrations obtained by SPMDs are in good agreement with the results obtained by HiVol pumping.

9) In the European high-mountain soils and lake sediments, organochlorine compounds are better preserved in the sediments than in the soils. All samples show an increase of OC after 1940, with higher absolute levels in the High Tatras than in the Central Pyrenees. The sediment core from Ladove Pleso shows a decrease of all OC in the last decade, indicating a decrease of atmospheric OC input to the High Tatras.

10) Higher PAH levels are observed in the soils and sediments of the High Tatras, than in the Central Pyrenees. The surface soils reflect better this difference than the sediments. Transport through the water column to the sediments may be responsible for the transformation of the PAH composition. However, once the PAH have been buried, PAH are better conserved in the sediments. The increase of PAH levels is related to the Industrial Revolution and the intensification of industrial processes in the European continent. The sediment core from Ladove Pleso shows a PAH decrease in the last decade, indicating a decrease of atmospheric input load to the High Tatras.

11) The Global atmospheric PCB pool shows 2-3 times higher amounts of PCBs in the Northern Hemisphere than in the Southern Hemisphere, which is in agreement with the historical production and use of these compounds. Modelisation of sink processes by OH radical degradation or estimated tropospheric residence times, gives rise to large annual sink differences between the two approaches. Extrapolation of laboratory derived reaction rates to tropospheric PCB levels yields large discrepancies between the annual atmospheric PCB sink and the annual emission and sinks in other environmental compartments.

## **Bibliography**

---

---

**Bibliography**

- AMAP. 1998. Arctic Pollution Issues: A State of the Arctic Environment Report. Arctic Monitoring and Assessment Programme, Oslo.
- Anderson, P.N., Atkinson, R. 1996a. System to measure relative rate constants of semivolatile organic compounds with hydroxyl radicals. *Environmental Science and Technology*. 30: 301-306.
- Anderson, P.N., Hites, R.A. 1996b. OH radicals reactions: The major pathway for polychlorinated biphenyls from the atmosphere. *Environmental Science and Technology*. 30: 1756-1763.
- Appleby, P.G. 2001. Chronostratigraphic techniques in recent sediments. In: *Tracking Environmental Change Using Lake Sediments Volume 1: Basin Analysis, Coring, and Chronological Techniques*. eds: W. M. Last & J. P. Smol, Kluwer Academic: 171-203.
- Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J., Battarbee, R.W. 1986. <sup>210</sup>Pb dating by low background gamma counting. *Hydrobiologia*. 141: 21-27.
- Appleby, P.G., Oldfield, F. 1978. The calculation of <sup>210</sup>Pb dates assuming a constant rate of supply of unsupported <sup>210</sup>Pb to the sediment. *Catena*. 5: 1-8.
- Appleby, P.G., Richardson, N., Nolan, P.J. 1992. Self-absorption corrections for well-type germanium detectors. *Nucl. Inst. & Methods B*. 71: 228-233.
- Argell, C., Okla, L., Larsson, P., Backe, C., Wania, F. 1999. Evidence of latitudinal fractionation of polychlorinated biphenyl congeners along the Baltic Sea region. *Environmental Science and Technology*. 33 (8): 1149-1156.
- Atkinson, R. 1987. Estimation of OH radical reaction rate constant and atmospheric lifetime of polychlorobiphenyls, dibenzo-p-dioxins, and dibenzofurans. *Environmental Science and Technology*. 21 (3): 305-307.
- Atkinson, R., Aschmann, S.M. 1985. Rate constants for the gas-phase reaction of hydroxyl radicals with biphenyl and the monochlorobiphenyls at 295 +/- 1K. *Environmental Science and Technology*. 19 (5): 462-464.

- 
- Atlas, E., Giam, C.S. 1981. Global transport of organic pollutants: ambient concentrations in remote marine atmosphere. *Science*. 211: 163-165.
- Axelmann, J., Gustafsson, Ø. 2002. Global sinks of PCBs: A critical assessment of vapor-phase hydroxy radical sink emphasizing field diagnostics and model assumptions. *Global Biogeochemical Cycles*. 16 (4): 1111.
- Bailey, R.E. 2001. Global hexachlorobenzene emissions. *Chemosphere*. 43: 167-182.
- Baker, J.E., Eisenreich, S.J. 1990. Concentrations and Fluxes of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls across the Air-Water Interface of Lake Superior. *Environmental Science and Technology*. 24 (3): 342-352.
- Baker, J.E., Eisenreich, S.J., Eadie, B.J. 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyls in Lake Superior. *Environmental Science & Technology*. 25: 500-509.
- Ballschmiter, K. 1992. Transport and fate of Organic Compounds in the Global Environment. *Angewandte Chemie*. 31 (5): 487-515.
- Ballschmiter, K., Wittlinger, R. 1991. Interhemisphere exchange of hexachlorocyclohexanes, hexachlorobenzene, polychlorobiphenyls, and 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane in the lower troposphere. *Environmental Science and Technology*. 25: 1103-1111.
- Barron, M. 1990. Bioconcentration. *Environ. Sci. Technol.* 24: 1612-1618.
- Barry, R.G. 1992. *Mountain Weather and Climate*. Routledge. .
- Baudo, R., de Bernardi, R., Tartari, G. 1998. Perspectives for a high altitude observatory for monitoring global changes. In: *Top of the World Environmental Research: Mount Everest-Himalayan Ecosystem*. Eds: R. Baudo, G. Tartari and M. Munawar.
- Baumard, P., Budzinski, H., Garrigues, P., Sorbe, J.C., Burgeot, T., Bellocq, J. 1998. Concentrations of PAHs (Polycyclic Aromatic Hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. *Mar Poll Bull.* 36: 951-960.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E. 2000. Assessing long-range transport potential of persistent organic pollutants. *Environmental Science and Technology*. 34: 699-703.

- Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B. 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. *Nature*. 395: 585-588.
- Booij, K., Hofmans, H.E., Fischer, C.V., van Weerlee, E.M. 2003. Temperature-dependent uptake rates of non-polar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environmental Science & Technology*. 37: 361-366.
- Booij, K., Van Drooge, B.L. 2001. Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMD). *Chemosphere*. 44: 91-98.
- Brevik, K., Sweetman, A., Pacyna, J.M., Jones, K.C. 2002. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 2. Emissions. *the Science of the Total Environment*. 290: 199-224.
- Brubaker, W. W., Hites, R.A. 1998a. OH reaction kinetics of gas-phase  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane and hexachlorobenzene. *Environmental Science and Technology*. 32: 766-769.
- Brubaker, W.W., Hites, R.A. 1998b. OH reaction kinetics of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-p-dioxins and dibenzofurans. *Journal of Physics and Chemistry*. 102: 915-921.
- Bucheli, T.D., Gustafsson, Ø. 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. *Environmental Science and Technology*. 34: 5144-5151.
- Bunce, N.J. 1982. Photochlorination of PCB's: Current Status. *Chemosphere*. 11 (8): 701-714.
- Bunce, N.J., Landers, J.P., Langshaw, J., Nakal, J.S. 1989. An assessment of the importance of direct solar degradation of some simple chlorinated benzenes and biphenyls in the vapor phase. *Environmental Science and Technology*. 23 (2): 213-218.
- Burgoyne, T. W., Hites, R.A. 1993. *Environmental Science and Technology*. 27: 910-914.
- Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M., Vighi, M. 1991. Role of Plant Biomass in the Global Environment Partitioning of Chlorinated Hydrocarbons. *Environmental Science and Technology*. 25: 1489-1495.

- 
- Camarero, Ll., Catalan, J. 1996. Variability of precipitation in the Pyrenees (northeastern Spain): Dominance of storm origin and lack of altitude influence. *Journal of Geophysical Research*. 101: 29491-29498.
- Carrera, G., Fernandez, P., Grimalt, J.O., Ventura, M., Camarero, L., Catalan, J., Nickus, U., Thies, H., Psenner, R.,. 2002. Atmospheric deposition of organochlorine compounds to remote high mountain lakes of Europe. *Environmental Science and Technology*. 36: 2581-2588.
- Carrera, G., Fernandez, P., Vilanova, R., Grimalt, J.O. 2001. Persistent organic pollutants in snow from European high mountain areas. *Atmospheric Environment*. .
- Carson, R.L. 1962. *Silent Spring*. Houghton Mifflin Company, NY, USA. .
- Castellano-Gil, J. M., Macías-Martin, F.J. 1993. *History of the Canary Islands*. Centro de la cultura popular canaria.
- Catalan, J. 1987. *Limnologia de l'estany Redó (Pirineu Central): El sistema pelàgic d'un llac profund d'alta muntanya*. PhD-thesis, Dept. d'Ecologia, Universitat de Barcelona. .
- Catalan, J. 1988. Physical properties of the environment relevant to the pelagic ecosystem of a deep high-mountain lake (Estany Redo, Central Pyrenees). *Oecologia Aquatica*. 9: 89-123.
- Catalan, J. 1992. Evolution of dissolved and particulate matter during the ice-period in a deep, high-mountain lake. *Canadian Journal of Fish and Aquatic Sciences*. 49: 495-955.
- Chiou, C.T., Porter, P.E., Schmedding, D.W. 1983. Partitioning equilibria of nonionic organic compounds between soil organic matter and water. *Environmental Science & Technology*. 17: 227-231.
- Clark, K.E., Gobas, F.A.P.C., Mackay, D. 1990. Model of organic chemical uptake and clearance by fish from food and water. *Environmental Science and Technology*. 24: 1203-1213.
- Cotham, W.E., Bidleman, T.F. 1989. Degradation of malathion, endosulphane and fenvalerate in seawater and seawater/sediment microcosms. *Journal of Agricultural Food Chemistry*. 37: 824-828.

- Cotham, W.E., Bidleman, T.F. 1991. Estimating the atmospheric deposition of organochlorine contaminants to the arctic. *Chemosphere*. 22 (1-2): 165-188.
- Cuevas, E. 1995. Estudio del Comportamiento del Ozono Troposférico en el Observatorio de Izaña (Tenerife) y su Relación con la Dinámica Atmosférica. Tesis Doctoral. .
- Dachs, J. and S. Eisenreich. 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. *Environmental Science and Technology*. 34: 3690-3697.
- Danielsen, E.F. 1961. Trajectories: Isobaric, isentropic and actual. *J. Meteorol.* 18: 479-486.
- de Voogd, P., Wells, D.E., Reutergardh, L., Brinkman, U.A.Th. 1990. Biological activity, determination and occurrence of planar, mono-, di-ortho PCBs. *International Journal of Analytical Chemistry*. 40: 1-46.
- Douthwaite, R.J. 1991. Effect of DDT on the fish eagle (*Haliaeetus vocifer*) population of Laja Kariba in Zimbabwe. *Ibis*. 134: 250-258.
- Duce, R.A., P. S. Liss, et al. 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical cycles*. 5: 193-259.
- Dunnivant, F.M., Elzerman, A.W., Jurs, P.C., Hasan, M.N. 1992. Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environmental Science and Technology*. 26 (8): 1567-1573.
- Eisenreich, S.J., Capel, P.D., Richard, J.J., Bourbonniere, R. 1989. Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. *Environmental Science and Technology*. 23 (9): 1116-1126.
- Fernández, C.E., Tejedor-Salguero, M., Quantin, P. 1982. Suelos de Regiones Volcánicas Tenerife, Vol IV. Colección Viera y Clavijo. .
- Fernández, P., Carrera, G., Grimalt, J.O., Ventura, M., Camarero, Ll., Catalan, J., Nickus, U., Thies, H., Psenner, R. 2003. Factors governing the atmospheric deposition of polycyclic aromatic hydrocarbons to remote areas. *Environmental Science and Technology*. 37: 3261-3267.



- Fernández, P., Grimalt, J.O., Vilanova, R.M. 2002. Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe. *Environmental Science and Technology*. 36: 1162-1168.
- Fernández, P., Vilanova, R.M, Grimalt, J.O. 1999. Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. *Environmental Science and Technology*. 33: 3716-3722.
- Fernández, P., Vilanova, R.M., Martinez, C., Appleby, P., Grimalt, J.O. 2000. The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. *Environmental Science and Technology*. 34: 1609-1913.
- Finizio, A., Mackay, D., Bidleman, T.F., Harner, T. 1997. Octanol-air partitioning as a predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmospheric Chemistry*. 31: 2289-2296.
- Fischer, R.C., Kramer, W., Ballschmiter, K. 1991. Hexachlorocyclohexane isomers as markers in the water flow of the Atlantic Ocean. *Chemosphere*. 23 (7): 889-900.
- Font Tullot, I. 1956. *El Tiempo Atmosferico en las Islas Canarias*. Ministerio del Aire. Serie A (26).
- Galassi, S., Valsecchi, S., Tartari, G.A. 1997. The distribution of PCB's and chlorinated pesticides in two connected Himalayan lakes. *Water, Air and Soil Pollution*. 99: 717-725.
- Gobas, F.A.P.C., Z'Graggen, M.N., Zhang, X. 1995. Time respons of the Lake Ontario ecosystem to virtual elimination of PCBs. *Environmental Science and Technology*. 29: 2038-2046.
- Gobas, F.A.P.C., Zhang, X., Wells, R. 1993. Gastrointestinal magnification: the mechanism of biomagnification and food chain accumulation of organic chemicals. *Environ. Science and Technology*. 27: 2855-2863.
- Goldberg, E.D. 1975. Synthetic organohalides in the sea. *Proc.R.Soc.London B*. 189: 277-289.
- Gramatica, P., Consolaro, F., Pozzi, S. 2001. QSAR approach to POPs screening for atmospheric persistence. *Chemosphere*. 43: 655-664.
- Grimalt, J.O., Fernández, P., Berdie, L., Vilanova, R.M., Catalan, J., Psenner, R., Hofer, R., Appleby, P.G., Rosseland, B.O., Lien, L., Massabuau, L.C., Batterbee, R.W. 2001. Selective

- trapping of organochlorine compounds in mountain lakes of temperate areas. *Environmental Science and Technology*. 35: 2690-2697.
- Grimalt, J.O., Sunyer, J., Moreno, V., Amaral, O., Sala, M., Rosell, A., Albaiges, J. 1994. Risk excess of soft-tissue sarcoma and thyroid cancer in a community exposed to airborne organochlorinated compound mixtures with a high hexabenzene content. *International Journal of Cancer*. 56: 200-203.
- Guerin, T.F., Kennedy, I.R. 1992. Distribution and dissipation of endosulphane and related cyclodienes in sterile aqueous systems: Implications for studies on biodegradation. *Journal of Agricultural Food Chemistry*. 40: 2315-2323.
- Guilizonni, P., Lami, A., Smith, J.D., Belis, C., Bianchi, M., Bettinetti, R., Marchetto, A., Muntau, H. 1998. Paleolimnological analysis of four Himalayan lakes (Khumbu Valley, Nepal). In: *Top of the World Environmental Research: Mount Everest-Himalayan Ecosystem*. Ed: R. Baudo, G. Tartari and M. Munawar.
- Guitart, R., Puig, P., Cómez-Catalán, J. 1993. Requirement for a standard nomenclature criterium for PCBs: Computer-assited assignment of correct congener dnomination and numbering. *Chemosphere*. 27: 1452-1459.
- Gustafson, K.E., Dickhut, R.M. 1997. Particle/gas concentrations and distributions of PAHs in the atmosphere of southern Chesapeake Bay. *Environmental Science and Technology*. 31: 140-147.
- Gustafsson, Ø., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.-N., Reddy, C.M., Eglinton, T.I. 2001. *Global Biogeochemical Cycles*. 15: 881-890.
- Halsall, C.J., Barrie, L.A. , Fellin, P., Muir, D.C.G., Billeck, B.N., Lockhart, L., Rovinsky, F.Ya., Kononov, E.Ya., Pastukhov, B. 1997. Spatial and temporal variation of polycyclic aromatic hydrocarbons in the arctic atmosphere. *Environmental Science and Technology*. 31: 3593-3599.
- Hargrave, B.T., Barrie, L.A. , Bidleman, T.F., Welch, H.E. 1997. Seasonality in exchange of organochlorines between Artic air and seawater. *Environmental Science and Technology*. 31: 3258-3266.
- Harner, T., Bidleman, T.F., Jantunen, L.M.M., Mackay, D. 2001. Soil-air exchange model of persistent pesticides in the United States cotton belt. *Environmental Toxicology and Chemistry*. 20: 1612-1621.

- Hillery, B.R., Basu, I., Sweet, C.W., Hites, R.A. 1997. Temporal and spatial trends in a long-term study of gas-phase PCB concentrations near Great Lake. *Environmental Science and Technology*. 31: 1811-1816.
- Hinkley, D.A., Bidleman, T.F., Foreman, W.T., Tuschall, J.R. 1990. *J.Chem.Eng.Data*. 35: 232.
- Hoff, R.M., Brice, K.A., Halsall, C.J. 1998. Non-linearity in the slopes of Clausius-Clapeyron plots for SVOCs. *Environmental Science and Technology*. 32: 1793-1798.
- Howsam, M., Jones, K.C. 1998. Sources of PAHs in the environment. In: *The Handbook of Environmental Chemistry Vol. 3 Part I, PAHs and Related Compounds*. Eds. Neilson AH.
- Hung, H., Halsall, C.J., Blanchard, P., Li, H.H., Fellin, P., Stern, G., Rosenberg, B. 2001. Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. *Environmental Science and Technology*. 35: 1303-1311.
- Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, R. 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environmental Science and Technology*. 27: 1080-1098.
- Jensen, S. 1966. Report of a new chemical hazard. *New Scientist*. : 612.
- Jensen, S., Johnels, A.G., Olsson, M., Otterlind, G. 1969. DDT and PCB in marine animals from Swedish waters. *Nature*. 224: 247-250.
- Jeremiason, J.D., Hornbuckle, K.C., Eisenreich, S.L. 1994. Decreases in water concentrations reflect loss by volatilisation. *Environmental Science and Technology*. 28: 903-914.
- Junge, C.E. 1974. Residence time and variability of tropospheric trace gases. *Tellus*. 16: 477-488.
- Kalantzi, O.I., Alock, R.E., Johnston, P.A., Santillo, D., Stringer, R.L., Thomas, G.O., Jones, K.C. 2001. The global distribution of PCBs and organochlorine pesticides in butter. *Environmental Science & Technology*. 35: 1013-1018.
- Kamenik, C., Koinig, K.A., Schmidt, R., Appleby, P.G., Dearing, J.A., Lami, A., Thompson, R., Psenner, R. 2000. Eight hundred years of environmental changes in a high Alpine lake (Gossenköllesee, Tyrol) inferred from sediment record. *Journal of Limnology*. 59: 43-52.

- Karickhoff, S.W., Brown, D.S., Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research*. 13: 241-248.
- Khalili, N.R., Scheff, P.A., Holsen, T.M. 1995. PAH source fingerprints for coke ovens diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment*. 29 (4): 533-542.
- Kjeller, L.-O., Rappe, C. 1995. Time trends in levels, patterns, and profiles for polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic proper. *Environmental Science and Technology*. 29: 346-355.
- Kömp, P., McLachlan, M.S. 1997a. Interspecies variability of the plant/air partitioning of polychlorinated biphenyls. *Environmental Science and Technology*. 31: 2944-2948.
- Kömp, P., McLachlan, M.S. 1997b. Octanol/air partitioning of polychlorinated biphenyls. *Environmental Toxicology and Chemistry*. 16 (12): 2433-2437.
- Konček, M. 1974. *Klima Tatier*, Slovenska. Académia Vied. Ústav Meteorológie Klimatológie.
- Kopáček, J., Stuchlík, E., Vesely, J., Schaumburg, J., Anderson, R.C., Fott, J., Hejzlar, J., Vrba, J. 2002. Hysteresis in reversal of Central European mountain lakes from atmospheric acidification. *Water, Air, and Soil Pollution*. 2: 91-114.
- Lemaire, J., Cambell, I., Hulpke, H., Guth, J.A., Merz, W., Philip J., van Waldow, C. 1982. An assessment of test methods for photodegradation of chemicals in the environment. *Chemosphere*. 11: 119-164.
- Mackay, D., Powers, B. 1987. Sorption of hydrophobic chemicals from water: A hypothesis for the mechanism of the particle concentration effect. *Chemosphere*. 16.
- Mackay, D., Shui, W.Y., Ma, K.C. 1992. *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals*. Vol. I and II. Lewis Publishers, London.
- Meijer, S.N., Ockenden, W.A., Sweetman, A., Breivik, K., Grimalt, J.O., Jones, K.C. 2003. Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes. *Environmental Science and Technology*. 37: 667-672.

- 
- Merrill, J.T., Bleck, R., Boudra, D. 1986. Techniques of lagrangian trajectories analysis in isentropic coordinates. *Mon. Wea. Rev.* 114: 571-581.
- Newton, I. 1979. DDT and other organochlorines. In: *Population Ecology of Raptors*. Poyser.
- Niesink, R., de Vries, J., Hollinger, M. 1996. *Toxicology: Principles and Application*. CRC Press. .
- Ockenden, W.A., Sweetman, A.J. , Prest, H.F. Steinness, E. , Jones, K.C. 1998. Towards an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time-integrated passive samplers. *Environmental Science and Technology*. 32: 2795-2803.
- Oehme, M., Haugen, J.E., Schlabach, M. 1995. Ambient air levels of persistent organochlorines in spring 1992 at Spitsbergen and the Norwegian mainland: Comparison with 1984 results and quality control measures. *the Science of the Total Environment*. 160/161: 139-152.
- Oehme, M., Haugen, J.E., Schlabach, M. 1996. Seasonal changes and relations between levels of organochlorines in Arctic ambient air: First results of an all-year-round monitoring program at Ny-Alesund, Svalbard, Norway. *Environmental Science and Technology*. 30: 2294-2304.
- Pankow, J.F. 1987. Review and comparative analysis of the theories on partitioning between gas and aerosol particulate phases in the atmosphere. *Atmospheric Environment*. 21: 2275-2283.
- Pankow, J. F., Bidleman, T.F. 1992. Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle partitioning and vapor pressure-I. Theory and analysis of available data. *Atmospheric Environment*. 26A (6): 1071-1080.
- Panshin, S.Y., Hites, R.A. 1994. Atmospheric Concentration of Polychlorinated Biphenyls at Bermuda. *Environmental Science and Technology*. 28: 2001-2007.
- Petty, J.D., Huckins, J.N., Zajicek, J.L. 1993. Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere*. 27: 1609-1624.
- Porta, M., Malats, N., Jarrod, M., Grimlat, J.O., Rifà, J., Carrato, A., Guarner, L., Santiago-Silva, M., Corominas, J.M., Andreu, M., Real, F.X. 1999. Serum levels of organochlorine compounds and K-ras mutations in exocrine pancreatic cancer. *The Lancet*. 354: 2125-2129.

- 
- Prest, H.F., Huckins, J.N., Petty, J.D., Herve, S., Paasivirta, J., Heinonen, P. 1995. A survey of recent results in passive sampling of water and air by Semipermeable Membrane Devices. *Marine Pollution Bulletin*. 31: 306-312.
- Rapaport, R.A., Eisenreich, S.J. 1988. Historical atmospheric inputs of high molecular weight hydrocarbons to the eastern North America. *Environmental Science and Technology*. 22: 931-941.
- Ribes, A., Grimalt, J.O., Torres-García, C.J., Cuevas, E. 2002. Temperature and organic matter dependence of the distribution of organochlorine compounds in mountain soils from the subtropical Atlantic (Teide, Tenerife Island). *Environmental Science & Technology*. 36: 1879-1885.
- Ribes, S., Van Drooge, B., Dachs, J., Gustafsson, Ø., Grimalt, J.O. 2003. Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons. *Environmental Science and Technology*. 37: 2675-2680.
- Safe, S. 1991. Polychlorinated dibenzo-p-dioxins and related compounds: sources, environmental distribution and risk assessment. *Environmental Carcinogenic and Ecotoxicological Reviews*. 9: 261-302.
- Sanders, G., Eisenreich, S.J., Jones, K.C. 1994. The Rise and Fall of PCBs: Time-trend Data from Temperate Industrial Countries. *Chemosphere*. 29: 2201-2208.
- Sanders, G., Jones, K.C., Hamilton-Taylor, J. 1995. PCB and PAH fluxes to a dated UK peat core. *Environmental Pollution*. 89: 17-25.
- Simo, R., Grimalt, J.O., Albaiges, J. 1997. Loss of unburned-fuel hydrocarbons from combustion aerosols during atmospheric transport. *Environmental Science and Technology*. 31 (9): 2697-2700.
- Simonich, S.L., Hites, R.A. 1995. Organic pollutant accumulation in vegetation. *Environmental Science & Technology*. 29: 2905-2914.
- Spacie, A., McCarty, L.S., Rand, G.M. (1995). Bioaccumulation and bioavailability in multiphase systems. *Fundamentals of Aquatic Toxicology*. G. Rand. Washington, DC, Taylor & Francis: 493-521.

- Spivakovsky, C.M., Logan, J.A., Montzka, S.A., Balkanski, Y.L., Foreman-Foyler, M., Jones, D.B.A., Horowitz, L.W., Fusco, A.C., Brenninkmeijer, C.A.M., Prather, M.J., Wofsy, S.C., McElroy, M.B. 2000. Three-dimensional climatological distribution of tropospheric OH: Update and evaluation. *Journal of Geophysical Research*. 105: 8931-8980.
- Steidl, R.J., Griffen, C.R., Niles, L.J., Clark, K.E. 1991. Reproductive success and eggshell thinning of a reestablished peregrine falcon population. *Journal of Wildlife Management*. .
- Swackhamer, D.L., Skoglund, R.S. 1993. Bioaccumulation of PCBs by Algae: Kinetics versus Equilibrium. *Environmental Toxicology and Chemistry*. 12: 831-838.
- ten Hulscher, T.E.M., van der Velde, L.E., Bruggeman, W.A. 1992. Temperature dependence of Henry's law constants for selected chlorobenzenes, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry*. 11: 1595-1603.
- Umlauf, G., Hauk, G., Reissinger, M. 1994. The distribution of semivolatile organic compounds in conifer needles following gas phase contamination. *Chemosphere*. 28: 1689-1699.
- University, Open. 1989. *Ocean Circulation*, Oceanography Course Team. Open University. Ed: W. Hall, Keynes, M.: 13-16.
- Varanasi, U. (1989). *Metabolism of polycyclic aromatic hydrocarbons in the aquatic environment*. Boca Raton, FL, CRC Press, Inc.
- Vilanova, R.M., Fernandez, P., Grimalt, J.O. 2001a. Polychlorinated biphenyls partitioning in the waters of a remote mountain lake. *the Science of the Total Environment*. 279: 51-62.
- Vilanova, R.M., Fernandez, P., Martinez, C., Grimalt, J.O. 2001b. Polycyclic aromatic hydrocarbons in remote mountain lake waters. *Water Research*. 35: 3916-3926.
- Vilanova, R., Fernandez, P., Martinez, C., Grimalt, J.O. 2001c. Organochlorine pollutants in remote mountain lake waters. *Journal of Environmental Quality*. 30: 1286-1295.
- Vives, I., Grimalt, J.O., Catalan, J., Rosseland, B.O., Batterbee, R.W. 2004. Influence of altitude and age in the accumulation of organochlorine compounds in fish from high mountain lakes, *Environmental Science & technology*, in press

- 
- Vreugdenhil, H.J.I., Slijper, F.M.E., Mulder, P.G.H., Weisglas-Kuperus, N. 2002. Environmental Health Perspectives. 110: 593-598.
- Walker, K., Vallero, D.A., Lewis, R.G. 1999. Factors influencing the distribution of lindan and other hexachlorocyclohexanes in the environment. Environmental Science & Technology. 33 (24): 4373-4378.
- Wania, F., Haugen, J.E., Lei, Y.D., Mackay, D. 1998. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. Environmental Science and Technology. 32 (8): 1013-1021.
- Wania, F., Mackay, D. 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio. 22 (1): 10-18.
- Wania, F., Mackay, D. 1996. Tracking the distribution of persistent organic pollutants. Environmental Science and Technology. 30: 390- 396.
- Wells, N. 1997. The Atmosphere and Ocean: A Physical Introduction. John Wiley & Sons.