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Budget calculations for polychlorinated biphenyls (PCBs) in the Northern Hemisphere — a single-box approach

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ABSTRACT

Numerous studies show that the environmental concentrations of PCBs have been decreasing since the production and use of PCBs in most industrialised countries was banned in the 1970s. However, most of these studies have been conducted close to historical sources. The few studies conducted in remote locations detect no trend of decreasing concentrations over the past 20–30 years. These observations suggest that PCBs may be removed more slowly from the environment, when viewed from a global or hemispheric perspective. The present study estimates the mass fluxes of individual PCB congeners in the Northern Hemisphere in order to elucidate the most important removal processes and the rate of decrease one may expect with complete cessation of emissions. Atmospheric reaction lifetimes, open-ocean settling fluxes and the pools and mobility of PCBs in the terrestrial environment are shown to be crucial parameters. However, the calculations identify important gaps of knowledge regarding predictions of environmental half-lives of PCBs. The results suggest that highly chlorinated congeners such as PCB 153 and 180 may be persistent in the global environment with annual rates of decrease of less than 1%. The compiled environmental data also highlight large differences between the different PCB congeners. Although this paper is based on more than 800 PCB measurements it should be considered a starting point for further research aiming to quantify the global fate of toxic and persistent organic substances such as the PCBs.

1. Introduction

In the Great Lakes region, the concentrations of PCBs in biota (Gobas et al., 1995), lake water (Jeremiason et al., 1994), sediments (Eisenreich et al., 1989; Wong et al., 1995) and peat (Rapaport and Eisenreich, 1988) have been decreasing over the past decades. In the Baltic Sea, the concentrations of PCBs have declined in herring (Bignert et al., 1993) and studies have shown decreasing sediment burial fluxes over the last decades (Axelman et al., 1995; Kjeller and Rappe, 1995). In a peat core collected in the United Kingdom, Sanders et al. (1995) found a maximum in atmospheric deposition in layers corresponding to the mid 1960s. Long-term year-round measurements have also revealed trends of declining concentrations in air at two locations, near Lake Erie and near Lake Michigan (Hillery et al., 1997). All of these studies were conducted in contaminated regions where concentrations have been substantially higher than in the surrounding hemispheric environment. Volatilisation and a net flux of PCBs from soil and water surfaces to the atmosphere and could therefore have been the primary route of removal from these areas (Jeremiason et al., 1994; Alcock et al., 1993). This view implies that the PCBs are diluted into the remote areas of the earth rather than being permanently removed from global cycling. When more uniform concentrations over the globe are achieved, a slower

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removal rate could be expected in regions close to historical sources.

Panshin and Hites (1994a) measured PCB concentrations in oceanic air during one year (1992/1993) over Bermuda, compared the results with those of several studies in the 1970s at the same location and found no statistically detectable change over the past two decades. In fact, the 95% confidence limits of the regression between PCB concentrations and time obtained by comparing their own measurements with older measurements, suggested that the annual rate of decrease of PCBs in the atmosphere should be less than 3%. Hillery et al. (1997) concluded that the atmospheric concentrations of PCBs near Lake Superior, the most remote of the Great Lakes, have remained unchanged over a time period of 6 years. These authors compared their results with those of Panshin and Hites (1994a) and suggested that atmospheric PCB concentrations in remote areas may not decline to the same extent as in heavily populated or contaminated areas such as near Lake Michigan. Further indications of a slower decline of PCB concentrations in remote areas are the findings by Gregor et al. (1995), who found no statistically detectable decline of PCB concentrations in accumulated snow in the Agassiz ice cap (80°N) over the past three decades. We calculated the 95% confidence limits for the regression concentration vs. time and found a maximum rate of decline as low as 1% per year for the homologue group pentachlorobiphenyls. Finally, Muir et al. (1996) measured the historical concentrations of PCBs in sliced sediment cores in 11 Canadian lakes in a latitude range 49–81°N. In only three of those lakes the most recent sediment slice contained considerably lower (<70%) concentrations of PCBs than the slices with the maximum concentration. In addition, two out of these three were close to the Great Lakes area. Data from the rest of the lakes indicated no recent trend of decreasing concentrations.

The rapidly decreasing concentrations in the historical source regions imply that the majority of the PCB emissions have been significantly reduced and the lack of clear time trends in remote areas suggest that PCBs may be removed slower from the environment in a hemispheric perspective than has been observed in regions such as the Baltic Sea and the Great Lakes. It is therefore of great interest to compile a quantitative estimate of all possible removal processes and to compare those with an estimate of the hemisphere-scale pools of PCBs in compartments from which PCBs can be remobilised. Compiling and contrasting pools and sinks may not only give the first estimates of hemisphere-scale rates of removal but also valuable information on which loss processes and pools that plays the most important role for the long term fate of PCBs.

2. Methods

2.1. *Selection of compounds*

Evidently, PCBs are not transported through the environment as a chemical mixture that reflects the chemical composition of the commercial products. The PCBs are a series of congeners with different physiochemical properties and chemical stability and behave differently in many transport processes in the environment. The relative amounts of the different PCB congeners differ not only between different environmental matrices, but also between different locations. The difference in chemical properties implies that the fate in the environment could differ considerably among congeners. For example, Wania and Mackay (1993) suggested that a global fractionation process will cause a higher content of compounds with high vapour pressure relative to compounds with low vapour pressures at high latitudes.

In this study, we describe the budget of the following congeners: 2,4,4′-trichlorobiphenyl (PCB IUPAC no. 28); 2,2′,5,5′-tetrachlorobiphenyl (PCB 52); 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153) and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB 180). These congeners cover a wide range of physicochemical properties, both in terms of vapour pressure and hydrophobicity. Being dominant among PCBs in environmental samples, these congeners are among the most commonly reported. Depending on column and temperature program used in the gas-chromatography (GC) system, PCB 28 may co-elute with PCB 31 in single column GC-systems. In Aroclor 1242 these two congeners constitute approximately the same mass fraction (Schulz et al., 1989). In references where the two congeners are reported as a sum of the two, half of that value is used as an estimate of PCB 28. PCB 153 co-elutes with PCB 132 on many gas-chromatography columns. PCB 153 is the dominating congener. The mass relation of PCB 153 and PCB 132 is approximately 7:3 in sediment samples, water samples, and in Aroclor mixtures (Niimi et al., 1996). As Niimi et al. (1996) pointed out, concentrations of these congeners are commonly reported as mere "PCB 153" and this figure probably often also represent PCB 132. However, it is assumed that the possible errors caused by these uncertainties have negligible bearing on the results of this study; thus the sum of these two congeners is used as an estimate of PCB 153.

2.2. *Description of model — a one-box approach*

The aim of the paper was to elucidate the environmental removal rate of PCBs, expressed as the fraction of the total environmental pool removed per year assuming that the system exhibits apparent first order kinetics. To this end, it was necessary to estimate the sum of all the important sinks and the total environmental pool of PCBs. The majority of all data on the occurrence and fluxes of PCBs in different environmental media have been reported for the Northern Hemisphere (NH). The atmospheric lifetimes of the congeners studied in this paper are estimated to be in the range of weeks (Anderson and Hites, 1996), which means that they are transported over a hemispheric space scale. Therefore, the entire NH was selected as the system of interest. To meet the scope of this study where sinks and pools are directly contrasted on a hemispheric scale it was necessary to keep the framework as simple as possible. The entire NH was therefore treated as a single box. However, it was to some extent possible to take into account geographical differences within the box in some of the pool and sink estimates. The removal rate (k_i) was estimated from the total pool of this single box contrasted to the sum of all loss fluxes from the box as:

$$k_i = \frac{S_{\text{total}}}{m_{\text{total}}}, \tag{1}$$

where S_{total} (t yr^{-1}) is the sum of all significant environmental sinks and m_{total} (t) the total pool of a PCB congener in the NH. m_{total} in turn, is the sum of several different terms:

$$m_{\text{total}} = m_{\text{atmosphere}} + m_{\text{ocean}} + m_{\text{terrestrial}} + m_{\text{shelf}}, \tag{2}$$

where $m_{\text{atmosphere}}$ is the mass of the PCB congener in the atmosphere (t), $m_{\text{terrestrial}}$ the mass in the terrestrial environment (soils, biomass and litter) (t), m_{ocean}, the mass in the ocean surface water (t) and m_{shelf} the amount in the shelf sediments (t). The total sink (S_{total}) is the sum of four major loss fluxes:

$$S_{\text{total}} = S_{\text{HO}\cdot} + S_{\text{deep-sea}} + S_{\text{soil}} + S_{\text{shelf}}, \tag{3}$$

where $S_{\text{HO}\cdot}$ is the loss due to the gas-phase reaction in the atmosphere with the hydroxy radical (HO•) (t yr^{-1}), $S_{\text{deep-sea}}$ the loss due to sedimentation to deep-sea (t yr^{-1}), S_{soil} the loss due to burial on land (t yr^{-1}) and S_{shelf} the burial in shelf sediments (t yr^{-1}).

PCBs are hydrophobic compounds with octanol–water partition coefficients in the range of 10^5–10^8 (L water/L octanol) and are therefore readily sorbed to hydrophobic matrices. Organic carbon, rather than the mineral fraction, have been shown to account for practically all sorbing capacity of sediment and soil (Karickhoff et al., 1979). Burial of organic carbon in shelf sediments and sedimentation of organic carbon to deep-sea will be associated with a burial and sedimentation of PCBs. The biogeochemistry of organic carbon on a global scale therefore plays a potentially important role for the environmental fate of PCBs. The estimated pools and fluxes of organic carbon are generally given as global estimates in the literature. Recalculating these figures for the NH by going back to all source references in the global estimates is not motivated for this preliminary budget. Instead, averaged area-specific estimates (e.g., accumulated C m^{-2} buried annually) and percentage of areas of different types (e.g., cultivated soil) was assumed to be equal for both hemispheres.

It is necessary to define the word "environment" used in this study. By "PCBs in the environment" is meant PCBs that do participate or have a potential to participate in re-volatilisation and long-distance air transport, over the time scale of years to decades. It has previously been referred to as the "mobile environmental reservoir" of PCBs (NAS, 1979). For example, in the terrestrial environment this means that the PCBs buried in deep soil layers are not part of the environmental pool of PCBs, they are rather considered permanently removed. PCBs in any significant positive concentration gradient (in relation to background concentrations), e.g., in landfills or highly contaminated soils or sediments are considered as potential sources to the global remote environment.

There has been no consensus in the scientific community as to which congeners to focus on, or of the manner of reporting environmental concentrations. For example, most commonly only the sum of the congeners screened for in the particular study (in some cases also a general congener profile) are given. Even the number of congeners screened for varies considerably among studies. In this study we have selected to use congener specific data wherever possible. In many cases this means estimating concentrations from the reported ΣPCB and a diagram of the average congener profile. In studies where only ΣPCB is given, a typical congener profile derived for the same type of matrix is used to calculate the concentration of the congener of interest. In Table 2, the congener composition profiles used for calculating the concentrations of individual congeners are listed. Wherever a profile from another study was used for calculating congener specific concentrations in Tables 3 to 7, the profile is referred to by its number in the column "P".

Mean values of the concentration of individual congeners from the cited studies are listed in Tables 3–8 together with the number of samples on which the mean value is based. In the budget, values as representative as possible are needed. For all the matrices reported concentrations are missing from many regions of the NH. This excludes the possibility to calculate area-weighted NH mean based on different regions. Therefore, we have calculated the unweighted mean of the listed means for the different locations for each compartment, for which also a 95% confidence interval was given.

2.3. *Estimation of pools*

2.3.1. Mass of PCBs in the atmosphere. The vertical distribution of PCBs in the atmosphere is an important parameter since it affects the estimated amount of PCBs subjected to atmospheric reactions. Reaction lifetimes in the order of weeks (Anderson and Hites, 1996) are too short for PCBs to penetrate the tropopause and therefore only the troposphere was considered further. The vertical mixing time within the troposphere is on the order of 1 month (Rodhe, 1992). This implies that the concentrations at higher altitudes should be in the same range as in the boundary layer (0–1 km). Knap and Binkley (1991) analysed 24 samples taken at different altitudes in the lower 3000 m of the troposphere, for content of PCBs and other organic compounds with similar properties. No vertical concentration gradients were found by Knap and Binkley (1991). However, the large variation may have hidden a possible gradient. For simplicity, the concentrations of PCBs on a mass/mass basis were assumed to be vertically homogenous throughout the entire troposphere. A troposphere height of 6 km normalised to the temperature and pressure at sea level was used.

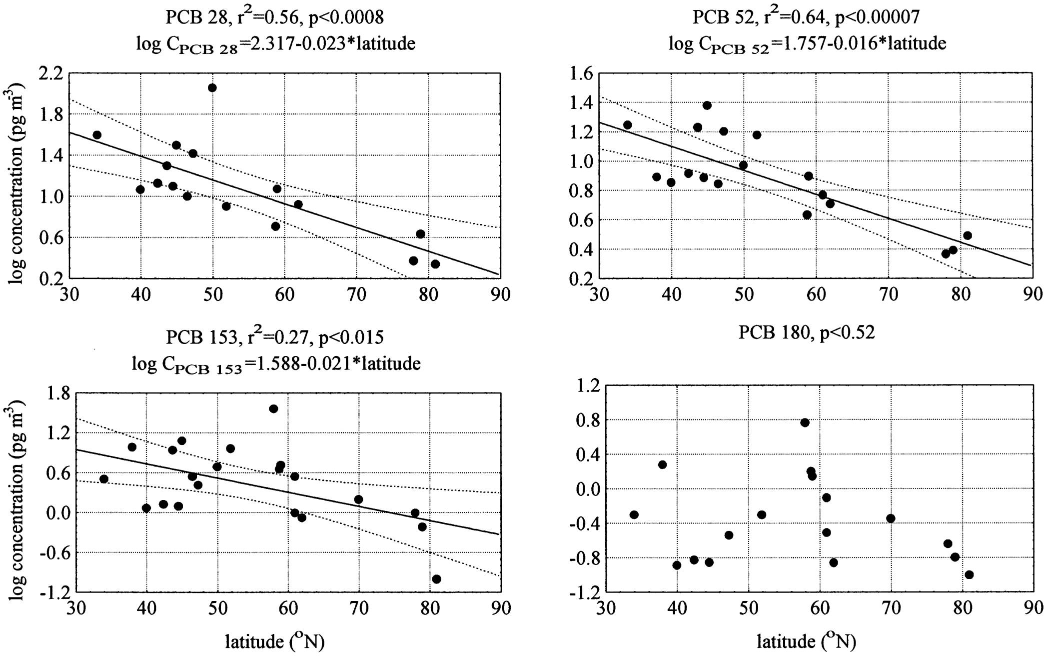
The set of data on atmospheric concentrations of PCBs was large enough to allow for investigation of the geographical distribution. The logarithm of station average concentrations of PCBs 28, 52 and 153 all showed a strong negative correlation with latitude, while PCB 180 showed no latitudinal trend (Fig. 1). No correlation between longitude and atmospheric concentration was found for any of the congeners. Only data originally reported congener specifically was used for these correlations.

The observed latitudinal trends imply that the pool of PCB congeners 28, 52, and 153 in air would best be estimated by integrating the atmospheric concentration equations in Fig. 1 from the equator to the pole. $m_{\text{atmosphere}}$ for these congeners were calculated as the sum of the pools in nine latitude bands 0–10°N, 10–20°N, 20–30°N, etc. as:

$$m_{\text{atmosphere}} = \sum_{0\text{–}10^\circ\text{N}}^{80\text{–}90^\circ\text{N}} (A^i \times C^i) \times h \times r_1 \tag{4}$$

where A^i the area of the latitude band (km^2) (Table 1), h the normalised tropospheric height (km) and C^i the estimated average tropospheric concentration pg m^{-3} based on the equations in Fig. 1. The unit conversion factor, r_1, is 10^{-9} t m^3 pg^{-1} km^{-3}.

It was assumed that concentrations in latitudes 0–30°N were similar to those in 30–40°N. An extrapolation of the regression based on concentrations between 35°N and 82°N in Fig. 1 implied 300% higher PCB concentrations at 0°N than at Bermuda. However, a few measurements by Ngabe and Bidleman (1992) ($n = 14$, Table 3, Brazzaville urban environment) indicated that maximum con-



PCB 28, $r^2=0.56$, $p<0.0008$
$\log C_{PCB\ 28}=2.317-0.023*\text{latitude}$

PCB 52, $r^2=0.64$, $p<0.00007$
$\log C_{PCB\ 52}=1.757-0.016*\text{latitude}$

PCB 153, $r^2=0.27$, $p<0.015$
$\log C_{PCB\ 153}=1.588-0.021*\text{latitude}$

PCB 180, $p<0.52$

Fig. 1. Relationship between latitude and the logarithm of the average PCB concentration at different sites. 95% confidence intervals were calculated with the computer software Statistica 5.5 (Statsoft, Inc. 1999).

centrations at 4°S are not higher than those measured at Bermuda (Panshin and Hites, 1994a).

Data from 558 different measurements were compiled, of which approximately 330 (depending on congener) were available as congener specific data (Table 3). PCBs are generally collected from air on glass or quartz fibre filters followed by some kind of hydrophobic adsorbent. In some of the cases filters and adsorbents are analysed together, in others filters and adsorbents were analysed separately (Table 3). PCBs in air-samples are normally found predominantly (>90%) in the operationally defined gas-phase, i.e., in the adsorbent. The error introduced by the mixed phases in some of the data in Table 3 is therefore considered insignificant. Particulate PCBs are not a significant part of the atmospheric PCB pool and are therefore not considered further in this study.

2.3.2. Mass of PCBs in the ocean. Data on PCB occurrence in open ocean have been reported for many different areas of the NH (Table 4). The sampling methodologies vary between the different studies. Schulz et al. (1988) and Petrick et al. (1996) used glass fiber filters and XAD-2 columns in series while Iwata et al. (1993) passed the seawater samples directly through an XAD-2 column. The concentrations of suspended particulate matter in open ocean areas are very low and the relative amounts of PCBs found to be associated with particles are therefore also low (<20%) (Schulz et al., 1988). Therefore, only the dissolved phase was considered for the estimate of the pool in seawater. The additional variation caused by the use of different methods was assumed to be insignificant. The pool of the different PCB congeners in the ocean surface waters m_{ocean} (t) was estimated from the concentrations listed in Table 4, C_{ocean} (pg dm^{-3}), and the total volume of this compartment V_{ocean}, km^3):

$$m_{\text{ocean}} = C_{\text{ocean}} \times V_{\text{ocean}} \times r_2, \tag{5}$$

where the unit conversion factor, r_2, is 10^{-6} t dm^3 pg^{-1} km^{-3}. In addition, the pool of PCBs in the deep-sea water column was estimated similarly using the concentrations measured in deep-sea water, $C_{\text{deep-ocean}}$ (pg dm^{-3}), listed in Table 5 and the total volume of the deep ocean

Table 1. *Properties of the Northern Hemisphere used in the budget calculations*

Property	Parameter	Value	Unit	Ref.
total area	A_{NH}	2.5×10^8	km^2	
area 0–10°N	A_{0-10}	44×10^6	km^2	
area 10–20°N	A_{10-20}	43×10^6	km^2	
area 20–30°N	A_{20-30}	40×10^6	km^2	
area 30–40°N	A_{30-40}	36×10^6	km^2	
area 40–50°N	A_{40-50}	31×10^6	km^2	
area 50–60°N	A_{50-60}	25×10^6	km^2	
area 60–70°N	A_{60-70}	19×10^6	km^2	
area 70–80°N	A_{70-80}	12×10^6	km^2	
area 80–90°N	A_{80-90}	4×10^6	km^2	
area of shelf sediment	A_{shelf}	1×10^7	km^2	
area of land	A_{land}	1.1×10^8	km^2	
NH land area as fraction of global land		0·75		
area of open ocean	A_{ocean}	1.3×10^8	km^2	
volume of surface ocean water	$V_{surf\text{-}ocean}$	6.5×10^6	km^3	
volume of deep ocean water	$V_{deep\text{-}ocean}$	4.8×10^8	km^3	
area of cultivated soils	$A_{cult\text{-}soils}$	2.4×10^7	km^2	estim. from The Times Atlas 10th ed.
total mass[a)] of cultivated soil	$M_{cult\text{-}soils}$	3.6×10^{12}	ton	
area of woodland, shrubland and grassland	$A_{w/s/g\text{-}soils}$	5.8×10^7	km^2	estim. from The Times Altas 10th ed.
total mass[b)] of woodland, shrubland and grassland soil	$M_{w/s/g\text{-}soils}$	4.4×10^{12}	t	
equivalent height of troposphere	H_{tropo}	1.6×10^9	km^3	
pool of OC[c)] in biomass and litter	$M_{OC\text{-}biomass}$	9.8×10^{10}	t	
burial of OC on land	$S_{OC\text{-}land}$	2.8×10^8	t yr^{-1}	estim. from data compiled by Schlesinger (1991)
burial of OC in shelf sediments	$S_{OC\text{-}shelf}$	8.6×10^6	t yr^{-1}	estim. from Berner (1989)

[a)] The active pool of PCBs is assumed to be the top 10 cm of the cultivated soils.
[b)] The active pool of PCBs is assumed to be the top 5 cm of the forest, scrubland and grassland soils.
[c)] Organic carbon.

(Table 1):

$$m_{deep\text{-}ocean} = C_{deep\text{-}ocean} \times V_{deep\text{-}ocean} \times r_2, \qquad (6)$$

$m_{deep\text{-}ocean}$ (t) is not a part of the environmental pool of PCBs according to eq. (2) but used in the discussion to validate the magnitude of the sedimentation sink.

2.3.3. Mass of PCBs in the terrestrial environment. The amount of PCBs associated with organic matter in the terrestrial environment is poorly investigated in comparison to the efforts made regarding the occurrence of PCBs in limnic and coastal aquatic systems. However, it is evident that the large amounts of organic matter in the terrestrial environment may be a significant pool for PCBs. For our budget, we aimed to assess the magnitude of the PCB pool that can be mobilised on yearly to decadal timescales. We did not aim to estimate the total pool in the terrestrial environment. Cultivated soils may serve as a large reservoir of mobile PCBs due to regular mixing (Harner et al., 1995). Recent work on PCB depth profiles in soils suggests that also forest and grassland soils may be of importance due to the effect of bioturbation (Cousins et al., 1999). Soil PCB concentrations have been measured in the UK (Alcock et al., 1993; Cousins et al., 1999), South-east Asia (Thao et al., 1993a; Thao et al., 1993b), Germany (Krauss et al., 2000) and Russia (Iwata et al., 1995) (Table 6). The overall variability is illustrated in Fig. 2 where all data points are plotted. Outliers, differing more than 4× the standard deviation from the mean value, have

Table 2. *Fractional content of congeners #28, #52, #153 and #180 in different matrices used to calculate congener specific concentrations from ΣPCB*

Profile #	Matrix	Location	Fraction of sum of	#28	#52	#153	#180	Ref.	Notes
1	sediment	Baltic Sea	3 congeners	0.14	0.09	0.52	0.20	1)	#138, #153 and #180
2	sediment	Baltic Sea	PCB #52	0.5				1)	to calculate PCB #28
3	sediment	Baltic Sea	50 congeners	0.03	0.02	0.14	0.05	1)	
4	soil	UK	24 congeners	0.045	0.023	0.037	0.082	2)	contemporary soils
5	soil	UK	homologue group	0.4	0.4	0.2	0.4	2)	fraction #28 of trichlorobiphenyls etc.
6	air	Bering Sea	38 congeners	0.09	0.06			3)	only <7 chlorine, #28 + #31 was 18%
7	air	Northern Pacific	38 congeners	0.06	0.04			3)	only <7 chlorine, #28 + #31 was 12%
8	air	Bermuda	119 congeners	0.10	0.046	0.0084	0.001	4)	#28 + #31 was 20%
9	water	North Atlantic	18 congeners	0.07	0.08	0.08	0.06	5)	based on three surface water samples
10	water	N.A. deep-sea	18 congeners	0.06	0.07	0.08	0.07	6)	based on two deep-water samples

1) Data unpublished in congener specific form. For details of sampling and analysis see Axelman et al. (2001).
2) Alcock et al. (1993).
3) Iwata et al. (1993).
4) Panshin and Hites (1994).
5) McConnell et al. (1996).
6) Schulz et al. (1988).

Table 3. *Concentration of congeners #28, #52, #153 and #180 in air $C_{atmosphere}$ (pg m^{-3}). One urban site is reported for comparison at the bottom of the table*

Location	Year	ΣPCB (pg m^{-3})	#28 (pg m^{-3})	#52 (pg m^{-3})	#153 (pg m^{-3})	#180 (pg m^{-3})	Ref.	*n*	*P*
Baltic Sea	92			5.9	3.5	0.8	[1]	10	
Wisconsin	84	483	115	9.4	4.9		[2]	17	
Bermuda	92	383	39	18	3.2	0.5	[3]	34	
Bermuda	74	506	46	20	4.6	0.5	[4]	12	8
Pacific	79	600	54	24	5.4	0.6	[5]	14	8
Gulf of Mexico	77	350	32	14	3.2	0.4	[6]	10	8
Barbados	77	57		4.6	1.0	0.1	[7]	16	8
Newfoundland	77	115		9	2.1	0.2	[7]	6	8
Bermuda	85	196	18	7.8	1.8	0.2	[8]	12	8
Adirondack Mtns., New York	86	951	86	38	8.6	1.0	[8]	4	8
Svalbard	92	13	2.4	2.3	1.0	0.2	[9]	18	
Svanvik, Norway	92	9.8			1.6	0.5	[9]	28	
Kårvatn, Norway	92	7.0			1.0	0.3	[10]	28	
Lista, Norway	92	146			36	5.8	[10]	9	
Svalbard, Arctic	93	13	4.3	2.5	0.6	0.2	[10]	50	
Ice Island, Arctic	88	49	2.2	3.1	0.1	0.1	[11]	10	
Chukchi Sea	90	85	7.7	4.7	0.7	0.09	[12]	2	6, 8[21]
Bering Sea	90	93	5.6	3.3	0.8	0.09	[12]	5	
Gulf of Alaska	90	130	8	4.6	1.1	0.1	[12]	4	7, 8[21]
Northern North Pacific	90	83	5.0	2.9	0.7	0.08	[12]	14	7, 8[21]
North Pacific	90	130	8	4.6	1.1	0.1	[12]	9	
Caribbean Sea	89	320	19	11	2.7	0.3	[12]	1	7, 8[21]
Gulf of Mexico	89	160	10	5.6	1.3	0.2	[12]	1	7, 8[21]
North Atlantic	89	290	17	10	2.4	0.3	[12]	4	7, 8[21]
Mediterranean	89	330	20	12	2.8	0.3	[12]	2	7, 8[21]
Red Sea	89	250	15	8.8	2.1	0.3	[12]	1	7, 8[21]
Bay of Bengal	89	270	16	9.5	2.3	0.3	[12]	7	7, 8[21]
Lake Baikal	92	100	4.0	8.0	5.0	0.3	[12]	6	8
Lake Baikal	91	196	8.0	15	9.2	0.5	[13]	5	
Chesapeak Bay	91	210		7.8	9.7	1.9	[14]	38	
Sault Ste. Marie, Michigan	91	198	10	7.0	3.5		[15]	12	
Saginaw, Michigan	91	469	20	17	8.7		[15]	12	
Traverse, Michigan	91	616	32	24	12		[15]	12	
Swedish West Coast	90	35	12	7.9	5.2	1.4	[16]	12	
Swedish West Coast	92	26	5.1	4.3	4.5	1.6	[17]	21	
Lake Superior	95	290	17	10	2.4	0.3	[18]	30	8
Lake Michigan	95	140	8	4.9	1.2	0.1	[18]	30	8
Lake Eire	95	150	9	5.3	1.3	0.2	[18]	30	8
Alert Station, Arctic	94		1.2	1.5	0.4	0.3	[19]	52	
sum								588	
average						0.58			
95% C.I.						0.33			
Brazzaville, Congo	89	550	28	40	8	7	[20]	14	

[1] Data unpublished in congener specific form. For methods see Axelman et al. (2001).

[2] Manchester-Neesvig and Andren (1989).

[3] Panshin and Hites (1994a).

[4] Bidleman and Olney (1974).

[5] Atlas and Giam (1981).

[6] Giam et al. (1980).

[7] Bidleman et al. (1981).

[8] Knap and Binkley (1991).

[9] Oehme et al. (1995).

[10] Oehme et al. (1996).

[11] Patton et al. (1991).

[12] Iwata et al. (1993).

[13] McConnell et al. (1996).

[14] Leister et al. (1994).

[15] Monosmith and Hermanson (1996).

[16] Brorström-Lundén et al. (1994).

[17] Brorström-Lundén (1996).

[18] Hillery et al. (1997).

[19] Stern et al. (1997).

[20] Ngabe and Bidleman (1992).

[21] First number indicates the profile used for PCBs #28 and #52 since Iwata et al. (1993) did not measure #153 and #180. For #153 and #180 profile number 7 was used.

Table 4. *Concentration of congeners #28, #52, #153 and #180 in ocean surface waters,* C_{ocean} *(pg l^{-1})*

Location	Year	ΣPCB (pg l^{-1})	#28 (pg l^{-1})	#52 (pg l^{-1})	#153 (pg l^{-1})	#180 (pg l^{-1})	Ref.	*n*	*P*	Depth
North Atlantic	86	21	0.6	0.9	2.7	1.7	1)	1		250 m
North Atlantic	86	8.3	0.5	0.9	0.5	0.6	1)	1		250 m
North Atlantic	86	6.6	0.8	0.6	0.3	0.3	1)	1		10 m
North Altantic	92	1.2	0.09	0.1	0.1	0.08	2)	1	9	200 m
North Atlantic	92	5	0.4	0.4	0.4	0.3	2)	1	9	50 m
Ice Island	86	7	0.5	0.6	0.6	0.5	3)	6	9	surface
Chukchi Sea	90	8.4	0.6	0.7	0.7	0.5	4)	3	9	surface
Bering Sea	90	12	0.9	1.0	1.0	0.8	4)	4	9	surface
Gulf of Alaska	90	12	0.9	1.0	1.0	0.8	4)	3	9	surface
Northern North Pacific	90	14	1.0	1.1	1.1	0.9	4)	12	9	surface
North Pacific	90	24	1.7	2.0	1.9	1.6	4)	8	9	surface
Caribbean Sea	89	18	1.3	1.5	1.5	1.2	4)	1	9	surface
Gulf of Mexico	89	16	1.1	1.3	1.3	1.0	4)	1	9	surface
North Atlantic	89	26	1.9	2.1	2.1	1.7	4)	4	9	surface
Mediterranean	89	27	1.9	2.2	2.2	1.7	4)	2	9	surface
Red Sea	89	9.3	0.7	0.8	0.7	0.6	4)	1	9	surface
Bay of Bengal	90	21	1.5	1.7	1.7	1.4	4)	5	9	surface
sum								55		
average			1.0	1.1	1.2	0.92				
95% C.I.			0.26	0.29	0.35	0.26				

1) Schulz et al. (1988).
2) Petrick et al. (1996).
3) Hargrave et al. (1989).
4) Iwata et al. (1993).

Table 5. *Concentration of PCB congeners in deep-sea waters,* $C_{deep\text{-}ocean}$ *(pg l^{-1})*

Location	Year	ΣPCB	#28 (pg l^{-1})	#52 (pg l^{-1})	#153 (pg l^{-1})	#180 (pg l^{-1})	Ref.	*n*	Depth	*P*
North Atlantic	86	1.56	0.08	0.09	0.13	0.1	1)	1	3500 m	
North Atlantic	86	1.57	0.1	0.09	0.14	0.11	1)	1	4000 m	
North Atlantic	86	2.0	0.13	0.17	0.15	0.13	1)	1	4000 m	
North Atlantic	92	1.5	0.09	0.10	0.12	0.10	2)	1	2000 m	10
North Atlantic	92	1.5	0.09	0.10	0.12	0.10	2)	1	3500 m	10
North Atlantic	92	0.06	0.004	0.004	0.005	0.004	2)	1	2000 m	10
North Atlantic	92	0.3	0.02	0.02	0.02	0.02	2)	1	750 m	10
sum								7		
average			0.07	0.08	0.10	0.08				
95% C.I.			0.03	0.04	0.04	0.04				

1) Petrick et al. (1996).
2) Schulz et al. (1988).

been excluded from the data set. Part of the variability between samples could be due to that concentrations are expressed per soil dry weight rather than per mass of organic carbon. Part of the variation in concentration between studies may also be due to differing numbers of analysed PCB congeners, being used for the parameter ΣPCB.

The calculated average concentration of the individual PCB congeners in soils is based on 121 measurements, which are not geographically well distributed over the NH. However, data with higher geographical resolution on the concentrations of PCBs in other terrestrial matrices (Table 7) indicates that PCBs within a region, such as Western Europe, occur relatively evenly

Table 6. *Concentration of congeners #28, #52, #153 and #180 in soils, C_{soils} (ng gdw^{-1})*

Matrix	Location	Year	ΣPCB (ng gdw^{-1})	#28 (ng gdw^{-1})	#52 (ng gdw^{-1})	#153 (ng gdw^{-1})	#180 (ng gdw^{-1})	Ref.	*n*	*P*
soil	Vietnam	91	7.8	0.4	0.2	0.3	0.6	3)	23	4
soil	Thailand	88, 90	7.6	0.3	0.2	0.3	0.6	4)	14	4
soil	Taiwan	90	28	1.3	0.7	1.0	2.3	4)	13	4
soil	Vietnam	90	3.0	0.1	0.1	0.1	0.2	4)	15	4
soil	UK	2)	28	1.3	0.6	1.0	2.3	5)	33	4
soil	Baikal	92	2.3	0.1	0.1	0.1	0.2	6)	3	4
soil	UK	2)	5.3	0.2	0.1	0.2	0.4	7)	4	
soil	Germany	2)	12	0.5	0.3	0.4	1.0	8)	16	4
peat core1)	USA	81–84	3–15					9)		
peat core1)	UK	90	18					10)		
sum									121	
average				0.53	0.27	0.44	0.97			
95% C.I.				0.3	0.2	0.3	0.6			

1) Shown only for comparison. Not used in calculations.
2) Sampling year not given.
3) Thao et al. (1993a).
4) Thao et al. (1993b).
5) Alcock et al. (1993).
6) Iwata et al. (1995).
7) Cousins et al. (1999).
8) Krauss et al. (2000).
9) Rapaport and Eisenreich (1988). Deduced from accumulation rates.
10) Sanders et al. (1995).

distributed, expressed as mean values of multiple samples. Still, the estimated pool of PCBs in soils should be considered as a very rough estimate with a significant potential error.

It was assumed that cultivated soils to a depth of 10 cm (with an assumed dry mass of 150 kg m^{-2}) will act as a pool for PCBs from which they can be mobilised. The area of cultivated soils in the Northern Hemisphere was estimated to 24 × 10^6 km^2 (calculated from Times Atlas of the World, 1999). Cousins et al. (1999) found a vertical decline in soil PCB concentrations in both grassland and forest soils. Concentrations in the top few centimeters were approximately 5–10 × higher than at 10 cm depth. Similarly, Krauss et al (2000) found soil PCB concentrations in the 0–5 cm depth layer to be on average 6 × higher than in the 15–20 cm depth layer. A very crude assumption for the calculation of the pool in grassland, forest and shrubland soils would be to include the top 5 cm (dry mass 75 kg m^{-2}), taking into account both the declining concentrations with depth and the possibility PCBs in deeper soil layers to reach the surface for air/soil exchange. From the reported concentration depth profiles follows that soils layers deeper than 10 cm probably not are important as a pool for PCBs in relation to the 0–10 cm layers. The upper uncertainty limit of the depth estimate is also difficult to assess, however, given the indications of an efficient downward mixing though bioturbation (Cousins et al., 1999), which in turn is most intense in the top most soil, the active soil layer should not be less than a few centimeters. An uncertainty range for the active soil depth could thus be 2–10 cm. A similar uncertainty factor for cultivated soils would give an interval of 4–20 cm.

PCBs in the terrestrial environment may also occur associated with biomass and litter. Eriksson et al. (1989) found relatively high concentrations of PCBs in pine needles all over Europe (Table 7). The high concentrations may be explained by the sorbing capacity of the 4% lipid rich cuticle and to some extent that the measurements were done already in 1984–86. Relatively little research has been conducted regarding how large is the organic matter pool in the terrestrial environment from which PCBs can volatilise. It is, however, clear that mixing will increase the size of the PCB pool avallable for exchange with the atmosphere.

The average amount of biomass on land has been estimated to 5.55 kg C m^{-2} (Whittaker and Likens, 1973). It can be expected that not all biomass is available for partitioning with air,

Table 7. *Geographical distribution in Europe of PCB concentration in moss and pine needles,* $C_{biomass}$ *(ng gdw^{-1})*

Matrix	Location	Year	ΣPCB	#28 (ng gOC^{-1})	#52 (ng gOC^{-1})	#153 (ng gOC^{-1})	#180 (ng gOC^{-1})	Ref.	*n*	*P*
moss	southern Norway	90	8.6	0.84	0.92	0.26	0.21	1)	19	5
moss	mid Norway	90	7.3	0.84	0.72	0.24	0.16	1)	13	5
moss	northern Norway	90	7.4	0.86	0.88	0.25	0.15	1)	15	5
pine needles	northern Sweden	85	12	0.55	0.28	0.45	1.0	2)	3	4
pine needles	Norway	85	11	0.50	0.25	0.41	0.90	2)	2	4
pine needles	central Sweden	85	11	0.49	0.25	0.40	0.89	2)	10	4
pine needles	east coast of Sweden	85	12	0.55	0.28	0.45	1.0	2)	8	4
pine needles	northern Germany and Denmark	85	14	0.65	0.33	0.53	1.18	2)	7	4
pine needles	Switzerland and southern Germany	85	12	0.55	0.28	0.45	1.0	2)	4	4
pine needles	southern France	85	14	0.65	0.33	0.53	1.18	2)	7	4
pine needles	southwestern Poland	85	17	0.75	0.38	0.61	1.36	2)	2	4
pine needles	southeastern Poland	85	3.4	0.15	0.08	0.13	0.28	2)	2	4
sum									96	
average				0.61	0.42	0.39	0.78			
average assuming 50% organic carbon content (ng gOC^{-1})				1.2	0.83	0.79	1.6			
95% C.I.				0.23	0.31	0.17	0.51			

1) Lead et al. (1996), only data from 1990 used.

2) Eriksson et al. (1989), values originally reported on fresh weight. Dry weight is approximately 50% of fresh weight.

although leaves also have been shown to contain significant concentrations of other semivolatile organics (Calamari et al., 1991). The surface-volume relation should play an important role in this context; thus needles and leaves can be expected to contain higher concentrations of PCBs than stems. In order to be conservative in the estimates of the pools, only 1/10 of the total biomass is therefore assumed be able to sorb PCBs to the same extent as pine-needles. It is also reasonable to assume that litter, which originates from biomass, contains significant concentrations of PCBs. The amount of litter is on average 0.38 kg C m^{-2} (Schlesinger, 1977). In total, biomass and litter was estimated to constitute some 0.9 kg C m^{-2} available as a sorbing pool for PCBs. The pool of PCBs in the terrestrial environment was estimated as:

$$m_{\text{terrestrial}} = C_{\text{soil}}(M_{\text{cult-soils}} + M_{\text{w/s/g-soils}}) \times r_3 + C_{\text{biomass}} \times M_{\text{OC-biomass}} \times r_3, \quad (7)$$

where C_{soil} (ng gdw^{-1}) and C_{biomass} (ng gOC^{-1}) are concentrations in soils and biomass (Tables 6 and 7, respectively). $M_{\text{cult-soils}}$, $M_{\text{w/s/g-soils}}$ (t) are the masses of cultivated soils and wetland, shrubland and grassland soils respectively (Table 1), and $M_{\text{OC-biomass}}$ (t) the organic carbon in biomass (Table 1). The unit conversion factor, r_3, is 10^9 g ng^{-1}.

2.3.4. Mass of PCBs in the shelf sediments. The sediment burial fluxes of PCBs have most likely varied in many areas close to historic sources. PCBs that deposit to the sediment surface are not always immediately buried in the sediments. Instead, they will be incorporated into a pool in the surface of the sediment from which PCBs can exchange with the overlying water column. The size of this pool depends on biological mixing activity and resuspension intensity and may thus vary significantly between different areas. In shelf areas the sediment accumulation flux is in the mm yr^{-1} order of magnitude. The mixed sediment layer depth is in the order of cm. A simplistic approach would then be to estimate the size of the "active" pool size from the sediment burial of OC during a decade (see Subsection 2.4.3 below). A more refined estimate would need an average mixed sediment depth and an average organic carbon content for the continental shelves. The pool of PCBs in the shelf sediments would thus be estimated as follows:

$$m_{\text{shelf}} = C_{\text{shelf}} \times S_{\text{OC-shelf}} \times 10 \text{ yr} \times r_3, \quad (8)$$

where C_{shelf} (ng g OC^{-1}) is the PCB concentration in shelf sediments (Table 8) and $S_{\text{OC-shelf}}$ (t yr^{-1}) the total burial of organic carbon in shelf sediments (Table 1).

2.4. *Estimation of sinks*

2.4.1. Atmospheric reaction. The magnitude of reactions between HO· and PCBs in the vapour phase in air has been investigated by Atkinson (1987) who estimated atmospheric lifetimes (τ) from 5–11 d for monochlorobiphenyls to 60–120 d for pentachlorobiphenyls. More recently, direct measurements of the reaction rate ($k_{\text{HO}\cdot}$) and its temperature dependence for biphenyl to pentachlorobiphenyl was done by Anderson and Hites (1996). We used the relationships between temperature and reaction rates given by Anderson and Hites (1996) to calculate reaction rate for an assumed average tropospheric temperature of $-10°$C, $k_{\text{HO}\cdot}^{-10°\text{C}}$ (Table 8). From these we estimated average reaction lifetimes, $\tau_{\text{HO}\cdot}$ (d), for homologue groups in nine latitude bands, based on annual average [HO·] concentrations for different latitudes calculated from the data of Spivakovsky et al. (2000) (Table 10):

$$\tau^i_{\text{HO}\cdot} = \frac{1}{k_{\text{HO}\cdot}^{-10°\text{C}} \times [\text{HO}\cdot]^i \times r_4}, \quad (9)$$

where the unit conversion factor, r_4, is 8.6×10^5 s yr^{-1}. For hexa and heptachlorobiphenyls we extrapolated $k_{\text{HO}\cdot}^{-10°\text{C}}$ from a linear regression between log $k_{\text{HO}\cdot}$ and number of chlorine atoms (Table 9) based on the temperature corrected dataset from Anderson and Hites (1996). The atmospheric gas-phase pools (eq. (4)) of the 4 congeners were then divided by the atnospheric lifetimes to give the reaction sink in each of the nine latitude bands. The HO·-reaction sink, $S_{\text{HO}\cdot}$, (t yr^{-1}) was thus estimated as:

$$S_{\text{HO}\cdot} = \sum_{0\text{–}10°\text{N}}^{80\text{–}90°\text{N}} \left(\frac{A^i \times C^i}{\tau^i_{\text{HO}\cdot}} \right) \times h. \quad (10)$$

Another atmospheric loss process may be the reaction of PCBs with HO· in cloudwater. Sedlak and Andren (1991) estimated PCBs to have reaction lifetimes 1–2 orders of magnitude lower in cloudwater than in the gas-phase of the atmosphere. Presently, the amounts of PCBs occurring

Table 8. *Organic carbon normalised concentrations of PCBs in shelf-sediments,* C_{shelf} *(ng gOC^{-1})*

Location	Year	ΣPCB	#28 (ng gOC^{-1})	#52 (ng gOC^{-1})	#153 (ng gOC^{-1})	#180 (ng gOC^{-1})	Ref.	*n*	*P*
Baltic Sea	90		8.6	17	57	35	1)	42	
North Sea	84–87		14	8.7	52	20	2)	29	1
Mediterranean	87–91		9.1	18	60	53	3)	11	2
Arctic	98	60	1.9	1.3	8.3	3.2	4)	44	3
sum								126	
average			8.4	11	44	28			
95% C.I.			4.8	7.8	24	21			

1) Data not published in congener specific form. See Axelman et al. (2001) for sampling and analysis details.
2) Lohse (1988). From a diagram with categorised data containing congeners #138, #153 and #180.
3) Tolosa et al. (1995). River-delta locations excluded.
4) AMAP (1998).

Table 9. *Reaction rate constants for $HO^{\bullet}$ and PCB-reaction corrected with the Arrhenius equation to an average ambient temperature of $-10°C$*

For individual congeners			For homologue groups	
congener IUPAC no.	no. Cl	$k_{HO^{\cdot}}$ $(-10°C)$ $(10^{-12}\,cm^3\,s^{-1})$	no. Cl	$k_{HO^{\cdot}}$ $(-10°C)$ $(10^{-12}\,cm^3\,s^{-1})$
PCB 0	0	7.8	0	7.8
PCB 1	1	2.3	1	3.1
PCB 2	1	4.5	2	1.7
PCB 3	1	2.5	3	0.76
PCB 4	2	1.4	4	0.53
PCB 7	2	2.1	5	0.32
PCB 15	2	1.5	6	0.15 1)
PCB 28	3	0.50	7	0.081 1)
PCB 29	3	1.0		
PCB 31	3	0.86		
PCB 33	3	0.69		
PCB 44	4	0.38		
PCB 47	4	0.69		
PCB 95	5	0.15		
PCB 110	5	0.38		
PCB 116	5	0.45		

The rate constants, and their temperature dependence, were measured in the laboratory by Anderson and Hites (1996). Reaction rates for hexa- and heptachlorinated PCBs were estimated from the linear regression fit ($r^2 = 0.98$) to the average $\log k_{HO^{\cdot}}$ for a homologue group vs. number of chlorines: $\log k_{HO^{\cdot}} = -0.27n - 11.25$ where n is the number of chlorine atoms.
1) Extrapolated value.

in cloudwater in the atmosphere are not known. Reported washout ratios for PCBs suggest that cloud droplets will contain 8000–40,000 times higher concentrations by volume than the surrounding air (Bidleman, 1988). Using the average area specific tropospheric cloud water content for different latitudes, given by Lelieveld et al. (1989), the total amount of liquid cloudwater in the NH was calculated to be 34–43 km^3 This means that the amount of PCB in cloudwater will be less than 0.1% of the atmosphere's total content of PCBs. In addition, some of the PCBs in cloudwater is associated to particles, which means that a smaller fraction of PCB will be subjected to reaction with

HO· in cloudwater. This indicates that cloudwater reaction is of less significance than the gas-phase reaction, and is therefore not considered in our budget.

2.4.2. Sedimentation to deep-sea. The sedimentation to deep-sea is potentially an important sink of PCBs since open ocean areas cover more than 60% of the surface of the NH. In the open ocean there is a well-mixed surface water layer down to 50–200 m depth. The surface layer is separated from deeper waters by a thermocline, which restricts transport of material that settles below the thermocline depth back to the surface waters. The residence time of deep-sea water is of the order of 500 yr (Stuiver et al., 1983). This means that the transport of PCBs back from deep-sea water can be considered to be insignificant in the timescales considered in our budget. PCBs settling from the ocean surface waters are therefore considered buried and removed from future cycling in the environment.

To the authors' knowledge, direct measurements of this flux in open ocean areas have been reported only three times in the literature (Knap et al., 1986; Dachs et al., 1996; Gustafsson et al., 1997) (Table 11). Although there were significant differences in terms of location, season, year of sampling, and techniques used, the values reported in the three studies are remarkably similar. The maximum deviation between the three measurements is a factor of three, which is less than was found between measurements in the study by Knap et al. (1986). While direct PCB flux measurements are rare, more data is available on the sealing flux of organic carbon in open ocean areas. The sealing of organic carbon, which is the governing process for this PCB sink, varies within almost two orders of magnitude between different ocean areas (Buesseler, 1998). The extremely small variation between the PCB-flux measurements may therefore be coincidental. Still, these estimates can provide an indication of the magnitude of this flux on a hemisphere scale. The total loss flux to deep-sea was calculated from the PCB sedimentation fluxes F_{seal} (ng m^{-2} yr^{-1}) Table 11 and the open ocean area of the NH, A_{ocean} (km^2) (Table 1):

$$S_{\text{ocean}} = F_{\text{seal}} \times A_{\text{ocean}} \times r_5, \qquad (11)$$

where the unit conversion factor, r_5, is 10^{-12} t m^2 ng^{-1} km^{-2}.

2.4.3. Burial in shelf sediments. It can be concluded from several studies with different approaches that bacterial degradation in background shelf sediments is an insignificant loss process. Although Øfjord et al. (1994) observed a rapid dehalogenation of PCB 153 by sediment bacteria cultures when the bacteria were exposed to PCB concentrations exceeding 1000 μg g^{-1} sediment, the effect was negligible when the cultures were exposed to lower concentrations, an

Table 10. *Modelled annual average concentrations of [HO˙] reported by Spivakovsky et al. (2000) and the annual average concentrations of [HO˙] for the nine latitude bands used in this paper*

Calculated from Spivakovsky et al. (2000)		[HO·] used in this paper	
latitude (°N)	annual average [HO·] · 10^5 cm^{-3}	Latitude band	annual average [HO·] · 10^5 cm^{-3}
4	14.9	0–10°N	15
12	15.2	10–20°N	15
20	14.0	20–30°N	13
28	11.6	30–40°N	11
36	10.6	40–50°N	8
44	8.3	50–60°N	5
52	5.4	60–70°N	4
60	4.3	70–80°N	2
68	3.7	80–90°N	2
76	2.2		
84	2.1		
90	0.6		

Table 11. *Sedimentation flux to deep-sea, F_{sed} (ng m^{-2} y^{-1}). Data for congeners #118, #128 and #174 is shown for comparison only*

Location	Year	#28 (ng m^{-2} y^{-1})	#52 (ng m^{-2} y^{-1})	#118 (ng m^{-2} y^{-1})	#128 (ng m^{-2} y^{-1})	#153 (ng m^{-2} y^{-1})	#174 (ng m^{-2} y^{-1})	#180 (ng m^{-2} y^{-1})	Ref.	n
Bermuda[1]	78–80	52	230	240	11	55	18	31	[4]	6
Mediterranean[2]	92	110	160	130		150		90	[5]	6
Bermuda[3]	93		250		30		17		[6]	1
sum										13
average		81	213			103		61		
95% C.I.		57	53			93		58		

[1] Sediment traps at 3000 m depth.
[2] Sediment traps at 250 m depth.
[3] ^{234}Th-derived surface water export flux.
[4] Knap et al. (1986).
[5] Dachs et al. (1996).
[6] Gustafsson et al. (1997).

observation also made by others (Sokol et al., 1995). In addition, Wong et al. (1995) found in Lake Ontario sediments that over a nine year period, no change in PCB congener profile nor any loss of PCB mass had occurred. In the Baltic Sea, Axelman et al. (1995) found no significant change in congener composition with depth in undisturbed sediments. Therefore, degradation within shelf sediments is not considered as a sink for PCBs.

In contrast to open ocean areas, a large part of the organic carbon that settles from the surface waters in coastal and shelf areas reaches the sediment surface. In shelf areas the actual burial flux of PCBs in the sediments is therefore more relevant than the flux from the surface waters. The approach in this study was to estimate the average organic carbon normalised concentrations of PCB congeners in shelf sediments and use the estimate of the global burial of organic carbon in shelf sediments by Berner (1989). According to Berner (1989) most of the global organic carbon burial occurs in terrigenous deltaic-shelf sediment, which is 104×10^6 t OC yr^{-1}. 75% of the continents are found in the NH. For simplicity, we assumed that also 75% of the global continental shelf area is in the NH. For the NH we therefore used a terrigenous deltaic-shelf sediment burial of 78×10^6 t OG yr^{-1}. In addition, another biogenous 10×10^6 t OC yr^{-1} (Berner, 1989) (7.5×10^6 t for the NH) is buried in shelf sediments in productive areas. The total PCB sink in shelf sediments, S_{shelf} (t yr^{-1}) would thus be:

$$S_{\text{shelf}} = C_{\text{shelf}} \times S_{\text{OC-shelf}} \times r_3, \qquad (12)$$

2.4.4. Burial on land. The accumulation of organic carbon on land is highly variable between ecosystems varying from 0.2 g C m^{-2} yr^{-1} in tundra (Evans and Cameron, 1979) to 15.3 g C m^{-2} yr^{-1} in boreal forests (Ugolini, 1968). For this purpose a very crude estimate of the burial of organic carbon in soils, $S_{\text{OC-soils}}$, of 2.5 g C m^{-2} yr^{-1} was calculated from data compiled by Schlesinger (1991). Reported accumulation rates for different ecosystem types were weighted with respect to their total area. Although the permanent removal of organic carbon in a longer time perspective may be considerably lower than this figure due to respiration in deeper soils layers, the PCBs may be considered buried once being accumulated into these layers. The cultivated soils most probably act as a reservoir rather than a sink for PCBs, since the accumulation of organic matter in these soils is negligible. The organic carbon normalised PCB concentrations estimated for litter (Table 7) were used for total sink in soils $S_{\mathrm{soil}}(\mathrm{t\ yr}^{-1})$:

$$S_{\mathrm{soil}} = C_{\mathrm{biomass}} \times S_{\mathrm{OC\text{-}soil}} \times r_3. \tag{13}$$

Removal into the ground via downward translocation with rainwater is probably a process of limited significance as the high partition coefficients make PCBs relatively resistant to mass transfer through soils. However, a certain vertical mass transfer in peat has been observed for trichlorobiphenyls and to a limited extent for tetrachlorobiphenyls (Sanders et al., 1995).

2.4.5. Net transport to the southern hemisphere. Assuming that the residence time of tropospheric air in the two hemispheres is one year (Rodhe, 1992) the annual gross flux from the NH to the Southem Hemisphere (SH) should equal the product of the concentration of the PCB congeners in the southerly latitudes and the total atmospheric volume of the NH. This amount is 50, 24, 11 and 0.9 t for PCB 28, 52, 153 and 180 respectively, i.e., 20–30% more than the NH atmospheric pool. Tanabe et al. (1983) measured in 1981 atmospheric concentrations of PCBs at several locations in the SH and reported a ΣPCB concentration of 200–250 pg m^{-3} between the latitudes 20°–45°S, which was in the same range as those observed in the NH. Although there probably is a net loss from the NH to the SH, these figures imply that the annual net loss may be considerably less than estimated gross fluxes above. This loss route is not considered in the calculation of k_i.

2.5. *Estimation of emissions*

Emissions are not used in eq. (1), where the earth's cleaning time is in focus. However, hemisphere-scale emission estimates, accumulated historical emissions as well as current emissions, may serve as validations of the estimates of m_{total} and S_{total}.

2.5.1. Total amount of PCBs released to the environment. The total amount of PCBs released to the environment serves as a comparison for m_{total}. Although significant effort was put into destruction of PCBs in closed applications and in contaminated sites a noteworthy fraction of the total is believed to have reached the ambient environment. A widely cited estimate of the total historical PCB release to the environment is 82,500 t (NAS, 1979). This figure is based on a total PCB use of 610,000 t in the USA (NAS, 1979). The USA had the largest production and use of PCBs, but the technical mixture was also produced elsewhere in significant amounts; 67,000 t PCBs were produced in the UK (Harrad et al., 1994), and in Japan some 60,000 t PCBs were manufactured (Ueda et al., 1976). The production of PCBs in the former Soviet Union has been estimated to 100,000 t (Ivanov and Sandell, 1992), and for China, this figure is approximately 8000 t (Jiang et al., 1997). The total global production could thus be more than 1,000,000 t, and the total amount released to the global environment would probably be more than 100,000 t. Considering that most industrialised countries are located in the NH, the figure 100,000 t was used as an estimate of the total PCB release to the NH.

Christensen and Lo (1986) compiled sales lists from 1957–1974 in the USA for each of the following Aroclor mixtures: 1242, 1248, 1254 and 1260. Together they comprised 90% of the total PCB sales in the USA. Although other mixtures were used in other countries, e.g., Clophen in Germany, Fenclor in Italy, and Kanechlor in Japan, this was considered the best available estimate for the relative contribution of different congeners for an estimate for the NH. The relative contributions of the four mixtures were 54%, 7%, 16% and 12% and these contributions, in combination with the relative content of the studied PCB congeners for different Aroclor mixtures reported by Schulz et al. (1989), were used to calculate the total emission of individual congeners from ΣPCB estimates.

2.5.2. Current emissions. Current emission estimates for a compound group such as the PCBs are associated with great uncertainties. PCBs are released from many different diffuse sources such as old transformers, old capacitors, landfills, paints, wood preservatives, plasticisers, hydraulic systems, carbonless copying paper, and sealants. Only few attempts have been made to estimate the release of PCBs to the environment after their production and use was banned. Murphy et al. (1985) estimated that by 1985, 10–100 kg ΣPCB yr^{-1} were released to the environment from sanitary landfills in the USA. Harrad et al. (1994) made a thorough investigation and estimated congener specific releases of PCBs to the environment in the UK taking into account a number of different possible sources, e.g., electrical equipment, sewage sludge and landfills. The estimate of ΣPCB annually released was 5 t. Using the population of 60 million people in the UK, a very crude estimate of the per capita specific release of individual PCB congeners in industrialised countries can be obtained. Another emission estimate of ΣPCB in Europe has been done by Berdowski et al. (1997) giving a per capita specific emission rate approximately 2 times higher. An assumption that 1 billion people reside in highly economically developed countries in the NH was used to recalculate the emission of ΣPCB to the NH, which would then be some 100–200 t yr^{-1}. In the following calculations the value 150 t yr^{-1} was used in conjunction with the specific congener content of the average PCB mixture (see Subsection 2.5.1 above). This approach likely underestimates the emission for the lighter congeners in relation to heavier congeners. However, a lack of data on this process prevents a further refinement of the congener specific emission estimates.

3. Results and discussion

The estimates of the sinks and pools of the individual PCB congeners are presented in Fig. 2. Vapour pressure has been suggested to control the global fate of semi-volatile persistent organic contaminants by cold condensation in polar regions resulting in a relative enrichment of less chlorinated PCBs in cold regions. Such a trend was observed by Muir et al. (1996) in 11 lake sediments in Canada. The compiled set of data does not show any increase of either PCB 28 or PCB 52 in air with increasing latitude in relation to PCB 153. The atmospheric concentrations of all congeners except 180 tended to decrease with increasing latitude. This was probably not an indication of a relative increase of PCB 180 in relation to the other congeners. Most likely, it was partly an effect of the analytical work. PCB 180 was present in concentrations much lower than the other three congeners. This makes quantification more uncertain, which may explain the high degree of variation, possibly obscuring an actual trend.

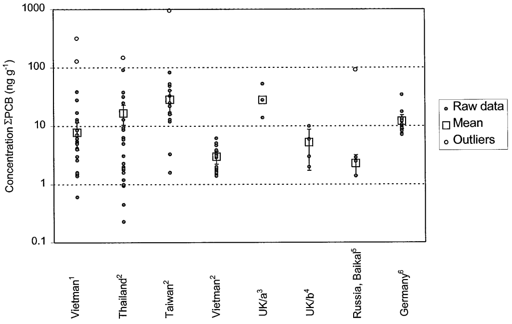


Fig. 2. Concentration of ΣPCB found in soil in different countries. Mean values for each country is given with errorbars representing standard deviation. Values differing from mean value with more than 4 standard deviations are defined as outliers.

Burial in the terrestrial environment seemed to be a relatively insignificant sink, less than 1% of the total sink for PCBs 28, 52 and 153 and 3% for PCB 180. Also burial in shelf sediments appeared to be a minor removal process, at least for the two light congeners 28 and 52. For PCBs 153 and 180 this sink corresponded to 6 and 18% of the total environmental sink, respectively. The uncertainty range (the maximum 95% confidence limit over the minimum 95% confidence limit) of the sediment concentration was 3.4 for PCB 153 and as much as a factor 7 for PCB 180, which means that at least for PCB the sediment burial flux could potentially be the dominating environmental sink.

Burial in deltaic shelf sediments may be significant compared to the background sediment burial. For example, Tolosa et al. (1995) estimated a ΣPCB burial of 1 t yr^{-1} in the Rhone pro-delta (NW Mediterranean), of which congeners 52, 153 and 180 contributed with approximately 20, 80 and 65 kg yr^{-1} respectively. The river Rhone had one order of magnitude higher concentrations of PCBs than the river Ebro (Tolosa et al., 1995) and was considered the major contributor of PCB discharge to Northwestern Mediterranean. Rivers with a high level of contamination can therefore occur as a possible sources to the remote environment.

The reaction of PCB 28 with the HO· in the atmosphere appeared to be overestimated. If this figure would reflect the actual loss, a selective emission of low chlorinated congeners that have balanced this loss through 20–30 yr must have occurred to maintain the concentration of this congener in relation to the highly chlorinated congeners. This is not supported by the estimated current emission fluxes (Fig. 3). The reaction loss of PCB 28 was 1000 times larger than the reaction loss of PCB 180, and 50 times larger than for PCB 153. The estimated loss of PCB 28 via atmospheric reaction also complied poorly with the estimated environmental pool and even the estimated total amount ever emitted to the environment. Under the assumption that the current emissions have not been balancing the reaction loss it implied that the global environmental concentrations would decline with two orders of magnitude in 5 years. This is not consistent with any observed time-trend. The uncertainty in the average soil concentration estimate (Table 6) give a 95% confidence range for the total pool of 2100–6600 t. Uncertainties in the size of the available pool for PCBs also adds to this uncertainty. Increasing the soil pool size with a factor 2, and using the highest concentration according to the 95% confidence interval gave a maximum soil pool of PCB 28 of 13,000 t. Even this larger pool is inconsistently small in relation to the total sink. Over the past 2 decades the environmental concentrations would have declined 2 orders of magnitude, also this conflicting observed times-trends.

The ratio between the estimated pool and the estimated amount emitted to the environment for the PCBs 28, 52, 153 and 180 was 0.31, 0.86, 0.75 and 4.2, respectively. The accordance in terms of absolute numbers was good, considering the uncertain nature of the soil PCB pool and emission estimates. Interestingly, the ratio seemed to increase with increasing degree of chlorination. This implies that PCB 28 has undergone more removal from the environment than the heavier congeners, which is consistent with a dominating HO•-reaction sink. However, as mentioned above observed time-trends in the environment do not suggest a decrease in the relative content of lighter PCB congeners in relation to heavier ones (see, e.g., Muir et al., 1996). Another explanation for this trend could be that the active soil depth may be smaller for the heavier congeners due to reduced mobility in soil as an effect of lower vapour pressure and higher hydro-

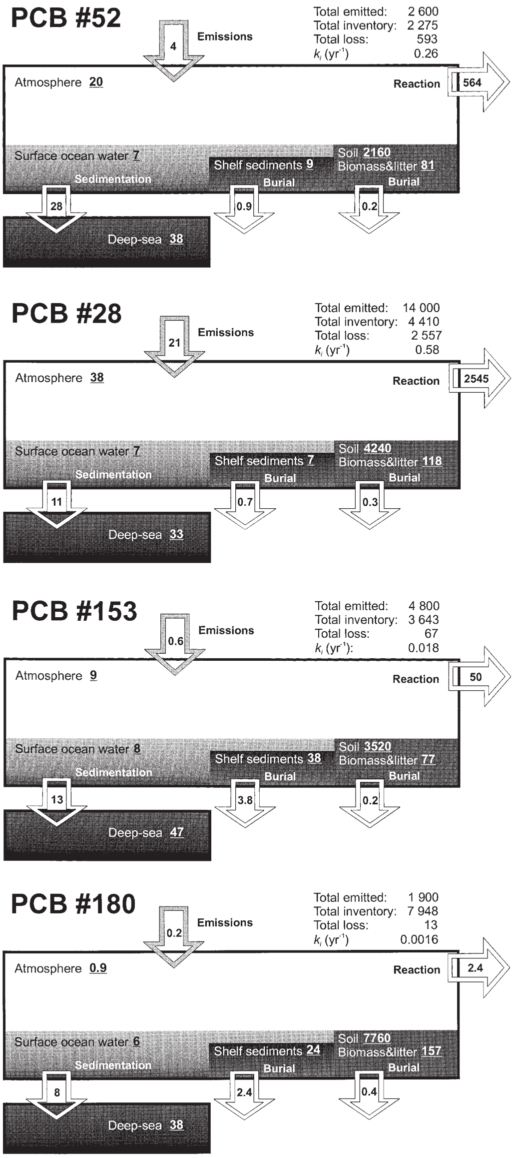


Fig. 3. Estimated inventories, loss fluxes, internal fluxes and emissions of the four PCB congeners PCB 28, 52, 153 and 180. The environmental pools are shown with underlined numbers and the sinks are represented by the numbers within white arrows. These estimates (except deep-sea pool) are used in the calculation of the rate of removal according to eqs. (1)–(3). The number within the arrow with a shaded outline represent the emission input to the box.

phobicity. Therefore, the pool size may be overestimated for PCB 180 and in the same time underestimated for PCB 28.

It is difficult to find a plausible explanation for the overestimation of the HO•-reaction term. HO• reaction rates of PCBs measured with different methods have been shown to be relatively well in agreement (Anderson and Hites, 1996). A partial explanation may be found in the distribution of PCBs between the gas phase and the particulate phase (G/P-distribution). The reaction between the PCB-molecule and HO• is a gas phase reaction. Present estimation of the G/P-distribution may be inaccurate due to difficulties in separating the two phases during sampling. The G/P-distribution is also strongly affected by temperature. At 3 km height the temperature is typically 20°C lower than at sea level. The particulate fraction of PCBs in large parts of the troposphere may thus be higher than normally found at sea level. However, even an error of a factor 20 in the estimate of the G/P-partition coefficient, e.g., an approximate G/P-distribution of 50–50% instead 95–5%, would not be sufficient to explain the apparent large reaction loss of PCB 28.

From these budget calculations, sedimentation to deep-sea clearly appeared to be a major loss process, in particular for PCB 180 but also for PCB 153 this loss was significant in relations to the HO•-reaction sink.

The fluxes and pools of PCB for the deep-sea were not consistent. The presented set of data suggested that the pool of PCBs in the deep-sea water column should be approximately one order of magnitude higher than what was found, under the assumption that the PCB sedimentation fluxes have been constant or declining. A minimum cumulative flux of PCB 52 would then be 800 t, which can be compared with the estimated deep-sea pool of 62 t. Since typically only a small fraction of the organic carbon produced in the ocean surface waters reaches the deep-sea, it is reasonable to assume that much of the PCBs should be desorbed during sedimentation. For example, Martin et al. (1987) estimated that the vertical flux of organic carbon at 1000 m depth was only 10% of the surface-water export flux. Since organic carbon is the primary carrier of particulate PCBs this may also apply to the PCB flux. It is difficult to generalise the vertical stratification of the ocean water column, but it is possible that most of the PCBs are desorbed before reaching the deepest water bodies and that a part of the desorbed PCBs are recycled to surface waters from intermediate water bodies with shorter residence time than the deep water bodies.

An alternative explanation would be that the PCBs are transported down to the sediments. Tolosa et al. (1995) found a mean ΣPCB burial flux of 200 ng m^{-2} yr^{-1} in the Eastern Deep Basin of the Northwestern Mediterranean, which means congener specific fluxes of approximately 10, 32 and 30 ng m^{-2} yr^{-1} for congeners 52, 153 and 180. Most likely, these fluxes are in the high range of what could be expected for remote open ocean areas due to the sampling points in that study were located only 100–300 km off the coast implying a significant input of horizontally transported material above the continental slope. For comparison the burial of organic carbon in the Northwestem Atlantic in deep-sea sediments during the Holocene (0.04 g C m^{-2} yr^{-1}, McCave, 1995), can be used in combination with the carbon normalised concentrations of individual PCB congeners in sediment trap material at 3200 m depth, deduced from Knap et al. (1986). These figures suggest sediment burial rates from 16 ng m^{-2} yr^{-1} for PCB 52 to 2 ng m^{-2} yr^{-1} for PCB 180, under the assumption that the ratio between PCBs and organic carbon remains constant during further settling and sediment diagenesis. Extrapolated to the ocean areas of the NH this corresponds to total deep-sea sediment burial rates from 2 t yr^{-1} for PCB 52 to 0.3 t yr^{-1} for PCB 180, which is not enough to explain the fate of PCBs after export from the surface waters, particularly not for PCB 180. In fact, even the sediment burial fluxes determined by Tolosa et al. (1995) are somewhat low to account for the sedimentation flux to deep-sea. Both the deep-sea pool and the sedimentation fluxes rely on only a few measurements, which makes it difficult to draw any strong conclusions. However, the measurements of deep-sea pools should be considered as maximum values, i.e., overestimating the concentration is the major concern when measuring concentration in the 0.1 pg l^{-1} range.

It was necessary to test the suitability of using the one-box approach for the entire NH. By roughly estimating the magnitude of the fluxes between the subcompartments it was assessed how well mixed the box was internally. To estimate the mixing potential of the box, gross fluxes, or "potential" fluxes, rather than net fluxes are needed. In an assumed situation of near-equilibrium conditions, the net flux between the atmosphere and the soil may be negligible but the potential for the soils to maintain atmospheric concentrations may still be significant, which in turn is indicated by the gross volatilization flux. If the potential internal fluxes are smaller than the net sinks it is not justified to use a single box approach. For instance, if the potential flux between the soils and the atmosphere is considerably smaller than the atmospheric reaction sink it is not justified to consider the reaction loss as a loss from the entire NH pool, including the soils. There is a number of different processes for the transport of PCBs between the atmosphere and the terrestrial environment/ocean. Atmospheric deposition occurs both by dry deposition and precipitation washout (wet-deposition), of which both processes act on particulate and gas-phase PCBs.

Below we will consider the magnitude of only the gas-phase exchange processes air/ocean and air/soil. If these are large enough it is not needed to consider other processes for the justification purpose. Models of the air soil exchange flux taking soil density, porosity, water content and organic carbon content into account have been developed by, e.g., Jury et al. (1990). Regardless which approach is used it is clear that any global scale estimate flux will be very crude. In lack of typical soil parameters we chose to use transfer velocities derived from gross volatilisation fluxes of PCBs directly measured in a simplistic way during a period of a few weeks in a forest location in the southern part of Sweden (Axelman and Broman, 1999). These are of the same order of magnitude as transfer velocities deduced from reported half lives of PCBs in 5 mm deep experimental soils (Cousins and Jones, 1998). For PCBs 52, 153 and 180 the average transfer velocities were 55, 2.3 and 0.6×10^9 cm s^{-1}, respectively. For PCB 28 no transfer velocity was reported for background soils. An approximate extrapolated value of 10^{-7} cm s^{-1} was therefore used for PCB 28. The transfer velocities were multiplied with the average soil concentrations, recalculated to a volumetric basis from an assumed bulk density of 1.5 g cm^{-3}, and applied to the total soil surface area in the NH (Table 1). The resulting gross gas-exchange fluxes were 1920, 536, 37 and 21 t yr^{-1} for the PCBs 28, 52, 153 and 180 respectively. For the lighter two congeners this flux is significantly larger than the net sedimentation sink and in the same range as the reaction sink. For the two heavier congeners the gross gas-exchange fluxes were in the same range as the sum of the major loss fluxes.

The magnitude of the air–ocean gas-exchange indicates how fast the atmosphere and ocean equilibrate, i.e., counteract a fugacity gradient over the air–ocean interface caused by for example a removal of PCBs via sedimentation. The net direction of this flux is govemed by the Henry's law constant K_H of the individual congeners. K_H, in turn, is dependent on vapour pressure and aqueous solubility of the PCB congener and the temperature in the ambient environment. Similar to the air/soil-exchange we were interested in the gross flux. This was estimated from the average ocean surface water concentration and an estimation method in Schwarzenbach et al. (1993) to calculate a typical air–water transfer velocity for PCB 153. The transfer velocity was 3.7×10^{-4} cm s^{-1} corresponding to an assumed wind speed of 4 m s^{-1} 10 m above the sea surface. The resulting flux were for the PCBs 28, 52, 153 and 180 15, 17, 18, 14 t yr^{-1}, respectively. These fluxes are significantly lower than the air/soil fluxes for PCBs 28 and 52, whereas they are similar to those of PCB 153 and 180. A comparison of the air/ocean fluxes and the sedimentation sink shows that it is justified to consider the atmosphere and the ocean surface waters to belong to the same box.

The estimated emission of the individual congeners suggests that current emissions (Fig. 3) are two orders of magnitude lower than the total sink. The cited emission figures mainly included emissions to the atmosphere. Significant additional emissions may reach the remote environment via river discharge. Although most of the particulate material settles out near the river mouth, the dissolved phase may be transported further out into the receiving ocean area. Montañes et al. (1990) reported approximately 20% of the PCBs to be in the apparently dissolved phase, which indicates that a significant fraction of PCBs in runoff water may reach remote areas. It is difficult to give an estimate of this figure for the entire NH but the data available indicates that diffuse emissions into run-off water may contribute significantly to the total emissions.

The world's total river water discharge is $\sim 40{,}000\ \mathrm{km}^3$ (Speidel and Agnew, 1982). A conservative assumption that 10% of the world's rivers have the same level of contamination as the moderately contaminated river Ebro in the Mediterranean, which contains approximately $0.5\ \mathrm{ng\,l}^{-1}$ of PCB 153 (Montañes et al., 1990), the total emission of this congener would be around 2 t. This is considerably smaller than the total removal figure, especially in the light of that a large part of the discharged PCBs probably will be buried in the sediments close to river deltas and will not reach the remote areas. On the other hand, single rivers are highly contaminated and may contribute significantly to new emissions. In 1987 the river Seine, France, contained a mean concentration of $115\ \mathrm{ng\,l}^{-1}$ ΣPCB (Chevreuil et al., 1990) corresponding to approximately $10\ \mathrm{ng\,l}^{-1}$ for PCB 153, which is more than one order of magnitude higher than the river Ebro. There are thus reasons to believe that diffuse emissions to run-off water may be of significance. Although emissions may not balance the total removal, more reliable emission estimates will be very useful in future global mass balances for PCBs.

It could be argued that if the PCBs have become more evenly spread throughout the global environment, the concentrations could actually have increased in the remote areas as PCBs have been transported from more contaminated areas to the surrounding global environment. However, the pool of PCBs in the vast remote areas is probably much greater than in the contaminated areas such as the Great Lake area. For example Oliver et al. (1989) and Wong et al. (1995) reported a total pool for Lake Ontario of 50 and 130 t ΣPCB, respectively. Eisenreich and Johnson (1983) estimated the total pool of ΣPCB in the entire Great Lakes area to be 442–504 t. This, in turn, equals approximately 10–50 t of the individual congeners discussed in this paper, which is a relatively insignificant figure in relation to the total NH pools of $\sim 10^3$ t. Hence, a net flux of PCBs from the highly contaminated areas would not significantly affect the concentrations in the remote areas of the environment.

4. Concluding remarks

These preliminary budget calculations indicate that the atmospheric gas phase reaction with HO-radicals followed by sedimentation to deep-sea are important loss processes for three (PCB 28, 52 and 153) of the 4 PCB congeners considered in this study. For PCB 180 sedimentation to deep-sea was found to be the most important sink followed by burial into shelf sediments. However, when contrasting the HO· reaction flux with the environmental pools and current emissions it became evident that the predicted observable rate of decline was far higher than what has been found in dated sediment cores and other historical records, in particular for PCB 28. This indicates that the HO·-reaction flux was significantly overestimated.

Most of the PCBs in the environment occur in the soils all over the NH, rather than in contaminated regions such as the Great Lakes and the Baltic Sea. This indicates that processes on a global scale will determine the long-term evolution of environmental concentrations. Moreover, contrasting the fluxes on a congener specific basis clearly illustrates that the environmental fate varies significantly with congener properties.

Finally, the results also show in particular that accurate estimates of the global pool and mobility of PCBs in the terrestrial environment are critical parameters in future attempts to make a global budget for PCBs. This should encourage further investigations regarding these processes since the rate of removal, or the overall environmental residence time, is a central parameter for the assessments of the environmental impact of all semi-volatile organic compounds.

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