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Global Modelling of Polychlorinated Biphenyls

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Introduction

Substantial interest in the long term behaviour and final fate of persistent organic pollutants (POPs) arises from the continued presence of such substances in the global environment. They often have been restricted decades ago, yet continue to be detected in considerable concentrations in the environment, even far from their points of initial release. By providing only snapshots of the overall situation in space and time, measurements alone can not hope to grasp the full complexity of POPs fate in the global multi-compartmental environment. A zonally averaged global distribution model has previously been shown to elucidate many facets of the global behaviour of α -hexachlorocyclohexane (Wania et al. 1999) over the entire five decades of its large scale environmental release, including the capability for simple pathway analysis, source apportionment and trend prediction (Wania and Mackay, 1999). Objective of the present study is to conduct a similar comprehensive study of the global historical fate of polychlorinated biphenyls (PCBs) using this global distribution model, with a particular focus on changes in the relative homologue composition with latitude and between different compartments. This report gives an account of the progress of this ongoing investigation, rather than the final product.

The Model and the Model Input Parameters

Model Description and Modification

The model is a fugacity-based mass balance model that describes the global environment through ten latitudinal bands (or climate zones), each of which is divided into a set of well-mixed compartments, representing environmental phases such as the atmosphere, the terrestrial, the fresh water and the marine environment. Provided with historical emission estimates on a global scale, it calculates fugacities, amounts and concentrations in each of these compartments and chemical fluxes between them. A detailed description of the model can be found in Wania and Mackay (1995) and Wania et al. (1999a). Several improvements and modifications have been made to the model compared to the version used for the α -HCH simulation (Wania et al. 1999a). Briefly, these are:

1. A forest canopy compartment has been included into the model. A detailed account of the description of equilibrium partitioning into the canopy compartment, as well as the kinetics of the chemical transfer processes between the atmosphere, the canopy compartment and the uncultivated soil compartment is given in Wania et al. (1999b).
2. The diffusion distance in agricultural soil is no longer a fixed fraction of the soil depth, but a time-variable function of the soil-air partition coefficient. This accounts for the large capacity of the surface soil micro-layer for hydrophobic substances such as PCBs, which often eliminates the need of these chemicals to diffuse through the bulk soil to the soil surface. Again, details can be found in another publication (McLachlan and Wania, in prep.).
3. Atmospheric hydroxyl radical concentrations in the model are based on a two dimensional (i.e. zonally averaged) distribution of OH radicals in the global atmosphere calculated by Rodriguez et al. (1996). Monthly averages are interpolated in the model to give daily values.

4. The particle settling rate on the oceans has been reduced by an order of magnitude. An earlier exercise which used the global model as a predictive tool to identify the physical-chemical properties that make chemicals susceptible to long range transport to Arctic regions (Wania, 1998) had revealed that the model overestimates the transfer of particle-sorptive chemicals from the surface ocean to the deep sea. This process does not affect the global fate of α -HCH (thus not compromising the earlier simulations), but may be a significant loss process for the PCBs.
5. Due to the lack of measured Henry's law constants (HLC) of PCBs in sea water, no distinction between the HLC in fresh and sea water is made, i.e. the fresh water HLC is used for the fresh water and the marine environment.
6. The calculation of gas-particle partitioning is based on the K_{OA} -relationship presented by Finizio et al. (1996) and no longer on the classical Junge-Pankow relationship with sub-cooled liquid vapour pressure. This modification eliminates the need to specify a vapour pressure.
7. The calculation of the degradation rate in media other than the atmosphere is based on a degradation rate at a reference temperature 25 °C and an activation energy in J/mol. No dependence on pH is assumed to apply.

Global Emission Estimates for PCBs

An estimate of the historical emissions of the seven most commonly measured PCB isomers (28, 52, 101, 118, 153, 138, and 180) into the global environment from 1930 to 1994 was supplied for five year periods by Sweetman and Jones (pers. comm.). The data are based on production records in the following countries: UK, Germany, Italy, France, Spain, USA, Japan, Australia, New Zealand, and the former USSR. Different use categories, such as large capacitors, small capacitors and open uses (plasticiser, petroleum additives, etc.) and their different release characteristics were taken into account. The assignment of the country-specific release records to the ten climatic zones used in the global distribution model revealed that only releases into the Northern temperate and subtropical region, estimated at 48 kt and 11 kt respectively, seem to be of global significance. The composition of these emission was assumed to be (1) constant throughout the emission period, and (2) identical in the N-Temperate and N-Subtropical zone. Namely, the release rate of PCBs was assigned to the seven congeners according to Table 1. All release was assumed to occur into the atmosphere.

The data for the five year periods reported by Sweetman and Jones were distributed into annual emission rates of the sum of seven PCBs, and extrapolated until the year 2000 (Figure 1). The temporal profile of the estimated emissions has a triangular shape, suggesting a peak release in the early 1970s with a linear increase before and a linear decrease after that. No significant shift in the isomeric composition of the releases is believed to have occurred.

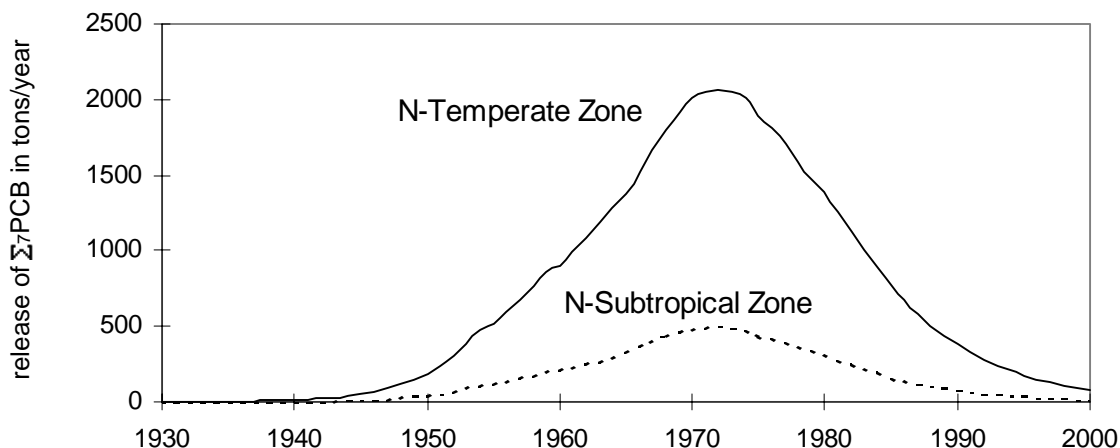


Figure 1 Estimated release of the sum of seven PCB isomers into the global environment (from Sweetman and Jones, pers. comm.). The total amount emitted between 1930 and 1994 was 48.12 kt into the northern temperate zone and 11.1 kt in the northern subtropical zone.

Table 1 Relative composition (from Sweetman and Jones, pers. comm.) and physical-chemical properties (from Paasivirta et al. 1999) of the seven PCB congeners used in the global model simulations.

Congener	Structure	% of $\Sigma_7\text{PCB}$	MW g/mol	log K_{OW}	log H $\text{Pa m}^3 \cdot \text{mol}^{-1}$
PCB-28	2,4,4'-triCB	18.1	257.5	5.67	11.97 - 3100 / T
PCB-52	2,2',5,5'-tetraCB	19.0	292	6.10	13.15 - 3352 / T
PCB-101	2,2'4,5,5'-pentaCB	18.6	326.4	6.37	13.55 - 3531 / T
PCB-118	2,3'4,4',5-pentaCB	14.3	326.4	6.60	13.44 - 3535 / T
PCB-138	2,2',3,4,4',5'-hexaCB	14.9	360.9	6.65	13.93 - 3757 / T
PCB-153	2,2',4,4',5,5'-hexaCB	10.0	360.9	6.88	14.05 - 3662 / T
PCB-180	2,2'3,4,4',5,5'-heptaCB	5.2	395.3	7.20	14.71 - 3910 / T

Table 2 Degradation rates with OH radicals in the vapour phase (k_{OH} in $\text{cm}^3/(\text{molecules} \cdot \text{s})$) and degradation half-lives (HL in hours) for the seven PCB congeners used in the global model simulations.

Congener	k_{OH}	HL _{canopy}	HL _{soil}	HL _{water}	HL _{sediment}
PCB-28	$1.04 \cdot 10^{-12}$	5500	10000	5500	17000
PCB-52	$0.59 \cdot 10^{-12}$	10000	17000	10000	55000
PCB-101	$0.30 \cdot 10^{-12}$	31000	100000	31000	55000
PCB-118	$0.30 \cdot 10^{-12}$	31000	100000	31000	55000
PCB-138	$0.16 \cdot 10^{-12}$	55000	170000	55000	170000
PCB-153	$0.16 \cdot 10^{-12}$	55000	550000	55000	170000
PCB-180	$0.10 \cdot 10^{-12}$	55000	1000000	55000	170000

Physical-Chemical Property Data for PCBs

As a result of the modifications to the model only three physical-chemical properties are required: molecular mass, octanol-water partition coefficient and the temperature dependent Henry's law constant (HLC). When modelling a group of related substances, such as several PCB congeners, it is imperative to have a consistent set of temperature dependent physical-chemical property data for all these substances. Only then will it be possible to analyse and evaluate calculated congeneric patterns, in addition to the results for individual PCB congeners. Temperature dependent physical-chemical property data for the selected PCB isomers were recently compiled by Paasivirta et al. (1999). HLCs as function of temperature for these congeners were estimated by combining vapour pressure data which had been measured as functions of temperature by Falconer and Bidleman (1994) with water solubilities which were estimated as a function of temperature using a modification of a method based on mobile order theory by Rülle and Kesselring (1997). A comparison of these data sets with measured Henry's law constants of PCBs (ten Hulscher et al. 1992, Dunnivant et al., 1988) revealed that this methodology gave reasonable estimates of the Henry's law constant at 25 °C. The octanol-water partition coefficients K_{OW} , which was assumed to be constant with temperature, were also taken from the compilation by Paasivirta et al. (1999).

Estimation of Degradation Half-lives for PCBs

The previous calculations on α -HCH (Wania et al. 1999) had revealed the immense importance of degradation processes on the global fate of persistent organic chemicals. In the case of the PCBs this issue is further complicated by the variable persistences of the different isomers. Internally consistent sets of degradation half-lives are necessary for a meaningful prediction of PCB homologue composition.

Based on a correlation for the rate constants for OH radical addition to aromatic rings k_{OH} with the sum of the electrophilic substituent constants $\Sigma\sigma^+$ given by Atkinson (1996), gas-phase reaction rate constants k_{OH} at 25°C in $\text{cm}^3/(\text{molecules}\cdot\text{s})$ for the selected PCB congeners were calculated (Table 2). The activation energy for these reactions was assumed to be 10 and 30 kJ/mol depending on the degree of chlorination. In the global model these chemical specific data are combined with spatially and temporally variable atmospheric temperatures and OH radical concentrations to calculate a time-dependent degradation rate.

Similar sets of degradation rates (or rather half-lives) were derived for the other model compartments (water, soils and sediments) from the published literature, giving more emphasis on field based studies than on laboratory derived half-lives. Degree of chlorination as well as substitution pattern were taken into account. For example, there are indications that for aerobic degradation to occur, the PCB should have five or fewer chlorine substitutions and two adjacent unsubstituted carbons. No distinction was made between degradation in fresh and sea water, or between degradation in agricultural and forest soils. Due to the lack of better information, the degradation half-life in water was assumed to apply to the forest canopy compartment. A uniform activation energy of 30 kJ/mol was assumed to apply. The reader should be aware that there is a huge uncertainty in the selection of degradation half lives and activation energy.

Simulation Results

The simulation results presented in this section should be considered very preliminary. In particular, no thorough attempt to evaluate the results with observations has so far been undertaken. The primary purpose of the present report is to show what sort of information the model can provide. Typically, only results for the Northern hemisphere will be presented.

Absolute Levels and Time Trends in Various Compartments

Figure 2 shows the concentrations calculated for the sum of seven PCB isomers (Σ_7 PCB) in the atmospheric boundary layer, in sea water, in agricultural soils and in forest foliage. Several aspects of these curves can be interpreted, namely the absolute levels in the various compartments, the differences between concentrations and time trends calculated for different zones and compartments.

Absolute levels in the various compartments: Calculated average air concentrations of Σ_7 PCB during the peak emission period were 250 to 500 pg/m^3 in the zones experiencing emissions. In the 1990s, levels have fallen below 100 pg/m^3 . For the marine environment the model calculates zonally averaged Σ_7 PCB concentrations in the range 20 to 130 pg/L during the 1970s (in the temperate zone up to 300 pg/L), and below 50 pg/L in the 1990s. Σ_7 PCB concentrations calculated for agricultural soils and foliage are in the range of 0.3 to 1.1 ng/g and 5 to 50 ng/g , respectively, but somewhat lower in the tropics. A preliminary comparison of these values with measurements in the global environment, e.g. those compiled by Axelman and Broman (1997), suggests that they tend to be in the correct order of magnitude. When interpreting these data, it is imperative to keep in mind the zonal averaging characteristics of the model. The emission estimates suggest that most of the countries emitting substantial amounts of PCBs were and are in Europe and North America, yet there are large regions within the emitting zones, particularly in Asia, which experienced much lower PCB emissions. Most measurements of PCBs in the environment were conducted in emission regions and are thus likely too high when compared with zonally averaged simulation results.

Relative levels in the various zones: Highest levels are always calculated for the Northern temperate zone, but ocean and soil environment show relatively high levels in the two northernmost zones: the boreal zone has higher sea water concentrations than the subtropical zone, and soil concentrations in the polar and boreal zone are higher than those in the subtropical zone.

Time delay: Various compartments differ in the immediacy of their response towards emission changes. Emissions peaked in 1972, and so do the calculated air concentrations. Foliage concentrations lag only by about one to two years, whereas sea water concentrations lag by two to five years, with the delay increasing with latitude. The model suggests that soils are particularly slow to respond to the decrease in PCB emissions during the last three decades. Peak concentrations in soil are calculated for the mid-1980s, i.e. a delay of more than a decade, and the decrease since then has been slow.

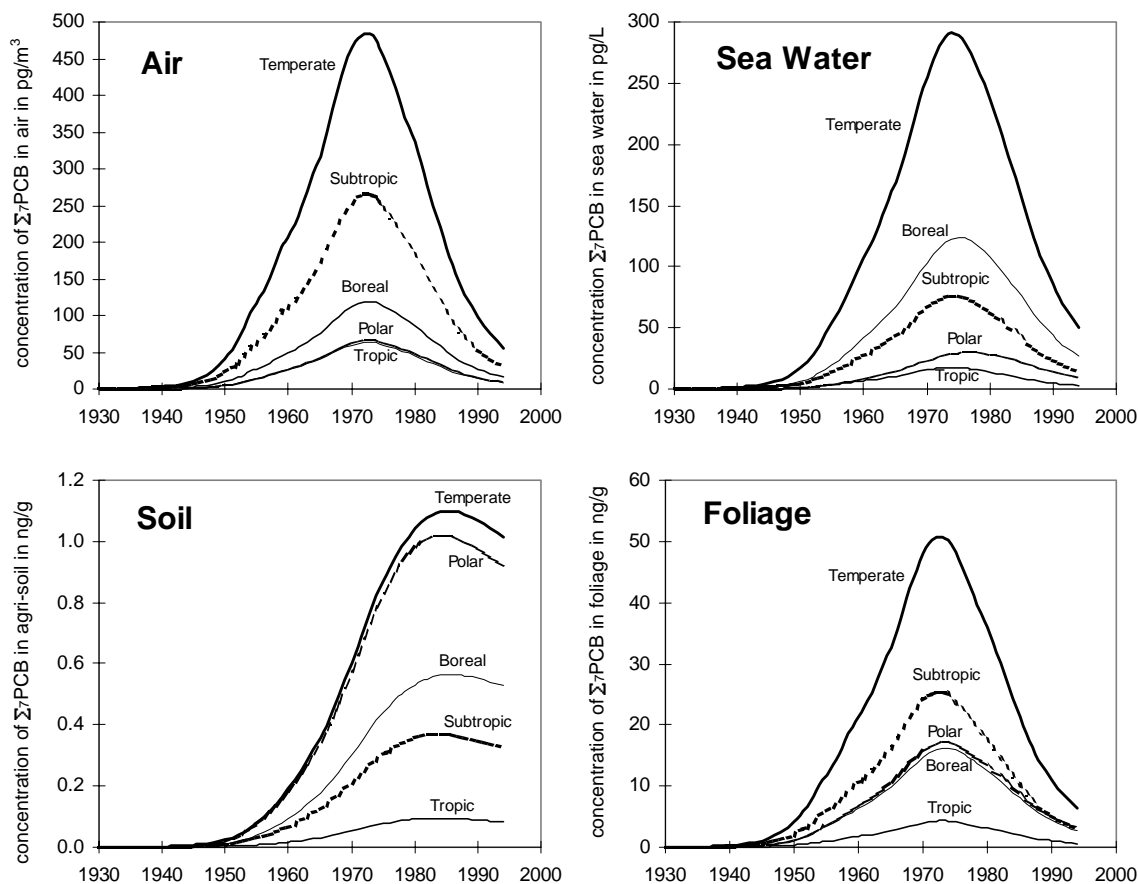


Figure 2 $\Sigma_7\text{PCB}$ concentrations in four compartments (lower atmosphere, sea water, agricultural soil and forest foliage) in the five zones of the northern hemisphere.

Table 3 Calculated percentage of the total accumulated emission of each PCB congener and $\Sigma_7\text{PCB}$, which has been degraded, transferred to the deep sea, buried in fresh water sediments, or is still dispersed in the global environment in 2000.

	dispersed in environment	degraded	deep sea transfer	fresh water sediment burial
PCB-28	0.4	97.9	1.2	0.5
PCB-52	1.0	95.4	2.6	1.0
PCB-101	15.7	68.5	14.5	1.3
PCB-118	19.4	53.2	26.1	1.3
PCB-138	28.1	35.4	34.8	1.6
PCB-153	38.3	25.5	34.6	1.7
PCB-180	41.1	15.5	41.8	1.6
$\Sigma_7\text{PCB}$	16.6	64.3	17.9	1.2

Overall Cumulative Fate of PCBs

The model simulation suggest that of the total amount of Σ_7 PCB released between 1930 and 2000, 64 % have been degraded, 18 % have been transferred to the deep sea and 1 % has been buried in fresh water sediments. 17 % of what has been emitted is still dispersed in the global environment today. However, the fate of the seven PCB congeners differs considerably in this respect. Table 3 gives the respective percentages. The model suggests that most of the lighter PCBs, such as PCB-28 and 52 have been degraded, and less than 1 % of the total accumulated emission is still in the environment today. The relative importance of degradation as a loss process rapidly decreases with increasing degree of chlorination, and deep sea transfer becomes a more important final loss process. A considerable fraction of the heavier congeners, such as PCB-153 and 180 is still dispersed in the environment today. From a global perspective fresh water sediment burial does not seem to be significant for any of the PCB congeners. The congeners not only differ in the extent of loss by degradation, but also in terms of where the degradation took place (Table 4). For the smaller congeners, the atmosphere is the primary medium of degradation, whereas for the higher chlorinated congeners the sea water environment is more important. The intermediate PCBs are degraded to a large extent in soils.

Table 4 Compartments where degradation of various PCB congeners took place between 1930 and 2000.

	Atmosphere	sea water	soils	fresh water	forest canopy
PCB-28	70.8	19.7	7.1	0.7	1.8
PCB-52	70.4	18.2	9.6	0.4	1.4
PCB-101	52.9	19.6	25.1	0.8	1.7
PCB-118	25.4	29.2	41.4	1.0	3.1
PCB-138	18.1	30.6	47.6	0.6	3.0
PCB-153	31.1	38.9	24.9	0.9	4.2
PCB-180	10.0	57.8	24.2	1.4	6.6

Congeneric Composition in Various Compartments and Zones

One of the main objectives of this modelling exercise is to investigate the compositional shifts that occur within the PCB profile along latitudinal and temporal gradients. We begin this task by taking a look at a few snapshot profiles calculated for the mid 1990s. Figure 3 shows the congeneric composition (i.e. percent of Σ_7 PCB) as calculated by the model for the atmosphere, the foliage, the agricultural soil and the sea water compartments of the tropical, temperate and polar zone of the Northern hemisphere in 1994. For comparison Figure 4 shows such profiles for the PCB emissions and for the total inventory of PCBs in the global environment in 1994. The profiles are very different in various compartments of the same climate zone and also in the same compartments of various climate zones. This reflects the variable environmental fate of PCB congeners, which differ by less than two orders of magnitude in K_{OW} , HLC (Table 1) and degradation half lives (Table 2). This confirms the need to perform such model calculations for individual molecular entities rather than for hypothetical chemicals with averaged property values.

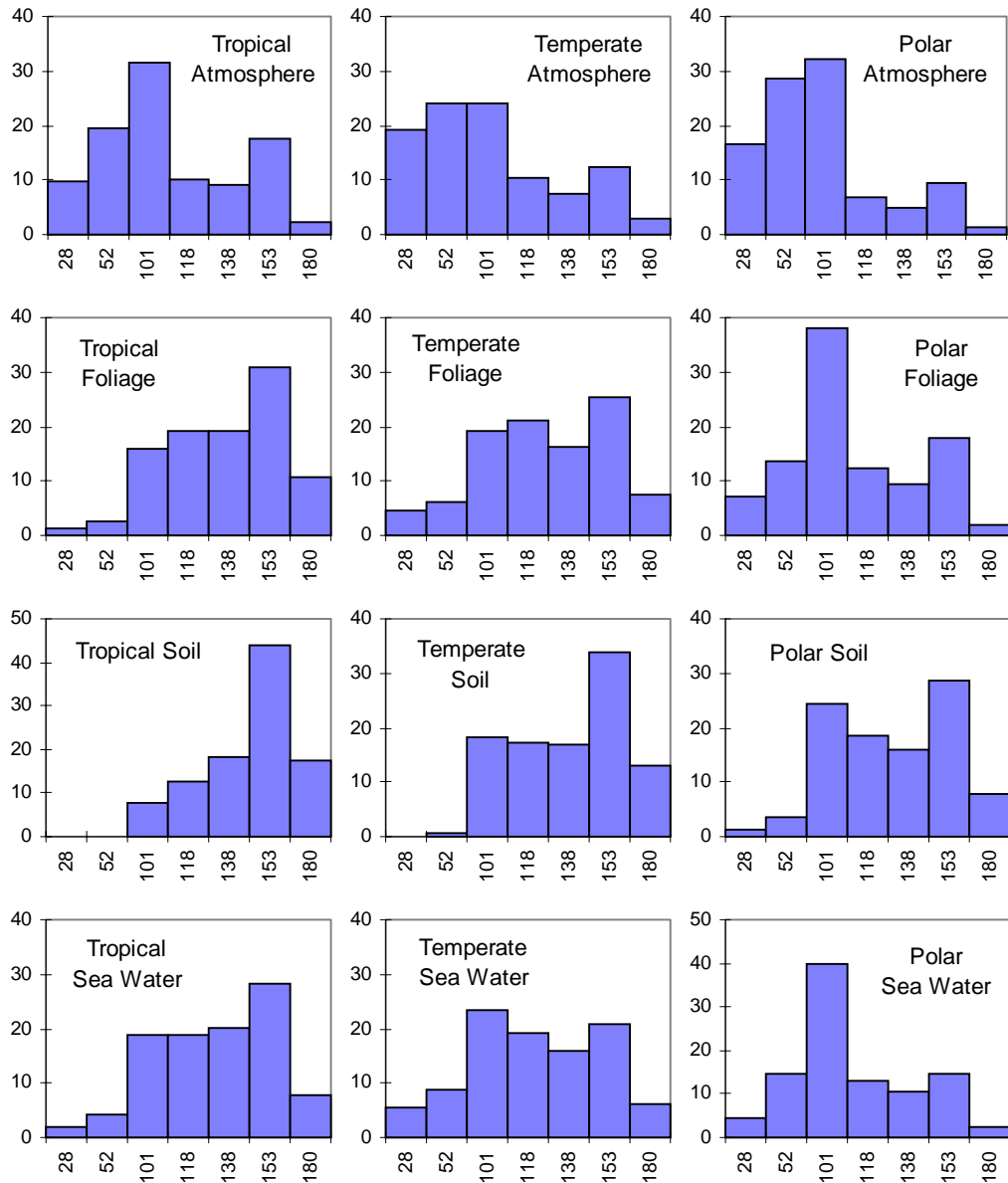


Figure 3 Calculated congeneric composition of PCBs in four different compartments and three different zones in 1994.

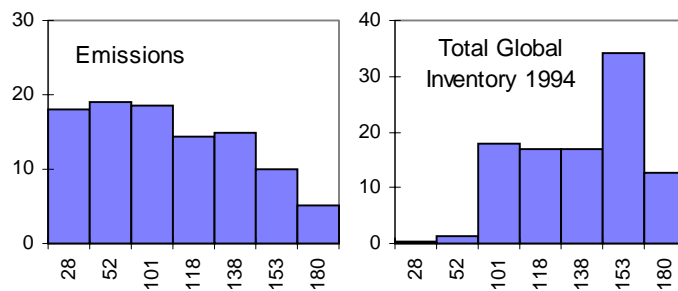


Figure 4 Congeneric composition of PCB emissions and of the total global environmental inventory in 1994.

The calculated atmospheric profiles are dominated by the three lighter PCB congeners and resemble most closely the emission profile, especially in the temperate zone. In the tropical atmosphere the two smallest congeners are relatively depleted, probably because of fast loss by degradation. In the polar atmosphere on the other hand, the heavy congeners are underrepresented, probably due to a reduced long range transport potential of these less volatile constituents.

The foliage profiles are dominated by the intermediate PCB congeners with 5 and 6 chlorine substitutions. We may speculate that this is a result of the uptake of the lighter PCBs such as 28 and 52 being limited by the capacity of the foliage, and that of heavy congener 180 being kinetically limited (McLachlan, 1999). There is also a clear shift towards lighter congeners with increasing latitude (see also below).

The soil profiles (especially in the temperate zone) resemble most closely that of the total inventory in 1994. This is not surprising, considering that the soils of the temperate zone are the major environmental reservoir for PCBs in 1994. These profiles are depleted in PCB-28 and 52 and enriched in PCB-153 and to a lesser extent also PCB-180.

Finally, the sea water profiles are dominated again by the penta- and hexachlorinated congeners. Congeners with less than five chlorine substitutions may be lost by degradation in the aqueous environment, and those with more than seven chlorine atoms by particle mediated transfer to the deep sea.

Conceptual Understanding of PCB Mobility in the Global Environment

In order to better understand the compositional shifts of PCBs in time and space, we may start out with a thought experiment. Let us assume that PCBs entered the global environment at only one point in time and at only one point in space (e.g. somewhere in the mid-latitudes). This pulse of PCB will be subject to several processes simultaneously (Figure 5):

1. According to the global distillation hypothesis the chemicals will gradually move from warmer to colder latitudes (Figure 5A).
2. The chemical gets dispersed from its initial entry point into the wider global environment (Figure 5B).
3. Due to degradation processes (and potentially other irreversible loss processes) chemicals is gradually lost from the global environment (Figure 5C).

The combined effect of these three processes is depicted in Figure 5D. The peak of chemical is moving northward, while at the same time decreasing in peak area and increasing in peak width. Different chemicals, and more specifically different PCB congeners will be subject to each of these processes to a different extent, depending on their degradability, and their partitioning properties between the atmosphere and the Earth's surface. We would expect lighter PCB isomers to move to polar regions more quickly, degrade faster and disperse more readily than the heavier ones (Figure 6).

Obviously, both assumptions made in this thought experiment are unrealistic:

1. PCB entered the global environment in many locations, rather than at a single spot. However, the global emission estimates (Figure 1) suggest that the bulk of the discharge did indeed occur in mid-latitudes.

2. PCB entered the global environment during a time period which lasted several decades and probably are still entering it to some extent. The peak of PCB emissions shown in Figure 1 could only be considered a pulse emission if a very long term perspective of several centuries is adopted.

Nevertheless, these hypothetical profiles may be helpful in understanding and interpreting the profiles calculated by the model.

Global Distribution of Various PCB Congeners

Figure 7 shows the calculated amount of the seven congeners and of their sum in the five climate zones of the Northern hemisphere at five points in time. In contrast to the conceptually derived profiles (Figure 6), the amounts tend to increase in time, at least for part of the displayed time period. This is simply because of the continued release of PCBs. After the emission decreased, the total global amounts do indeed decrease and this occurs considerably faster and earlier for the lighter PCBs. The northbound migration and general dispersion is not as obvious in Figure 7 as it is in the idealised plots. In contrast to Figure 6, all congeners have the maximum of their distribution still in the temperate zone. This is a reflection of the long-lasting and ongoing release of PCBs into that zone. Nevertheless, a “peak widening” towards the North, i.e. a more even global distribution can be seen for the congeners 52 and 28, in particular after 1980.

This effect is focused on in Figure 8, which shows the normalised zonal distribution of selected congeners in 1994, i.e. instead of amounts in each zone, the percentage of the total global amount of a congener that is in a particular zone is plotted. It serves to compare the calculated extent of Northbound migration and environmental dispersion from the site of entry for various congeners. The lighter a PCB congener, the more uniform its global distribution and the stronger the Northward tilt in its distribution. PCB-28 is an exception in that it shows less global mobility than PCB-52, which is probably due to its rapid degradation in the atmosphere.

Congeneric Composition in Foliage

Rather than assessing the total amount accumulated in various zones, normally chemical concentrations in various compartments are measured along latitudinal gradients. We therefore also take a look at the calculated latitudinal concentration profiles of selected PCB congeners in foliage of the Northern hemisphere as shown in Figure 9. Plotted are the annual mean concentrations profiles in 1950, 1960, 1970, 1980 and 1990 normalised to the average of the five zonal concentration at the time.

The model indeed suggests:

1. Dispersion from the sites of entry (temperate and subtropical zone) is larger for the lighter PCBs. PCB-180 has highest concentrations in the two emission zones, and below average concentrations in the other three zones. With decreasing degree of chlorination, the PCB congeners have a more “uniform” concentration profile with relatively higher levels particularly in the two Northernmost zones.
2. Lighter PCBs clearly show a stronger shift towards the Northern zones, with average or even above-average concentrations being established there. Degradation in the zones close to the equator obviously reduces the concentrations of light PCBs to below average levels.

3. In the course of time, all congeners experience a relative northward shift in the concentration profile. In foliage the shift in time is most pronounced for the PCB-101.

Figure 10 shows the resultant composition of PCB on the foliage as a function of latitude. A shift to the more volatile congeners at higher latitudes is very obvious. The fractions of 28, 52 and 101 increase sharply with latitude, whereas those of 118, 138, 153 and 180 decrease. This pattern did change little within the past 25 years, but the relative importance of the lighter PCBs in the Arctic increased during that time period.

The simulation results closely reproduce the compositional changes reported for PCBs in semipermeable membrane devices (SPMDs) exposed along a latitudinal band from 50 to 70 ° North along the European west coast during the 1990s (Ockenden et al., 1998, page 2800, Figure 5a). The SPMDs, which in many respect can be seen as “standardised foliage”, also showed a strong increase of the lighter PCBs, in particular the tetrachlorinated congeners with increasing latitude, at the expense of hexa- and heptachlorinated congeners.

Latitudinal Profiles of the Congeneric Composition in Other Compartments

The congeneric composition of PCBs in various environmental phases differs (Figure 3). Accordingly, shifts in the congeneric composition with latitude and in time are also different in different phases (Figure 11). Generally, however all phases show in some way or the other the shift from lower to higher congeners with increasing latitude. Differences between media are related to:

- the relative abundance of the various congeners (see also Figure 3).
- whether the shift occurs smoothly or whether it is more pronounced between some zones than others, and if the latter, between which zones the major shift occurs. For example, in the atmosphere the model calculates the strongest compositional changes between tropical and subtropical areas, whereas in the soil environment the most pronounced shift occurs between temperate and boreal environment.
- which congener shows the largest change in relative abundance. For example, the change in the relative abundance of PCB-180 in foliage and soil is rather pronounced, whereas it is very subtle in the atmosphere and in sea water.

The atmosphere is somewhat peculiar in that PCB-101 shows the lowest relative abundance in the temperate zones and increases towards both the tropical and arctic environment. This is probably a reflection of this congeners unusually high atmospheric long range transport (LRT) potential. The LRT potential of smaller congeners, such as PCB-52 and 28, is limited because of ready degradation in the atmosphere, that of heavier congeners is limited by surface-to-atmosphere partitioning.

A comparison of the profiles for 1970 and 1994 suggests that whereas overall changes have been minor, the fractionation effect has been increasing with time. The relative fraction of PCB-28, and 52 decreased in all zones and media, as a result of its rapid degradation.

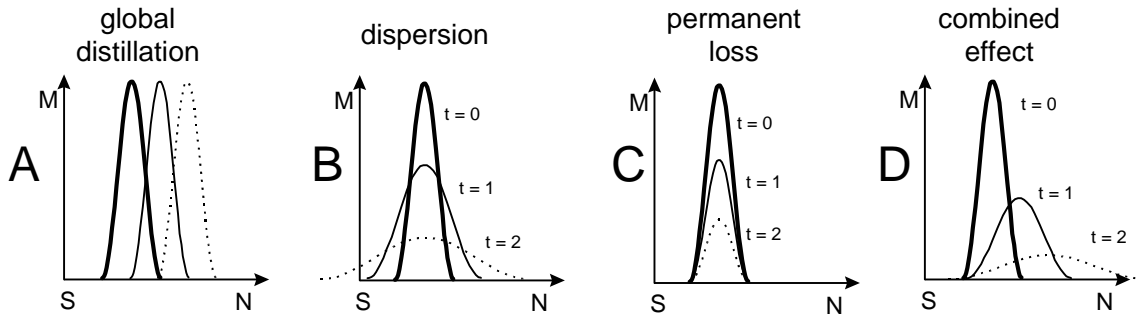


Figure 5 Conceptually derived zonal distribution of a chemical at different time periods after a short, localised pulse emission in the Northern hemisphere (M = amount, S = South, N = North).

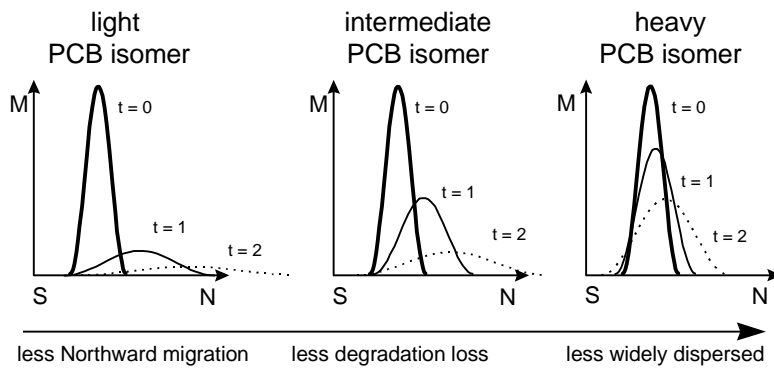


Figure 6 Conceptually derived zonal distribution of different PCB congeners.

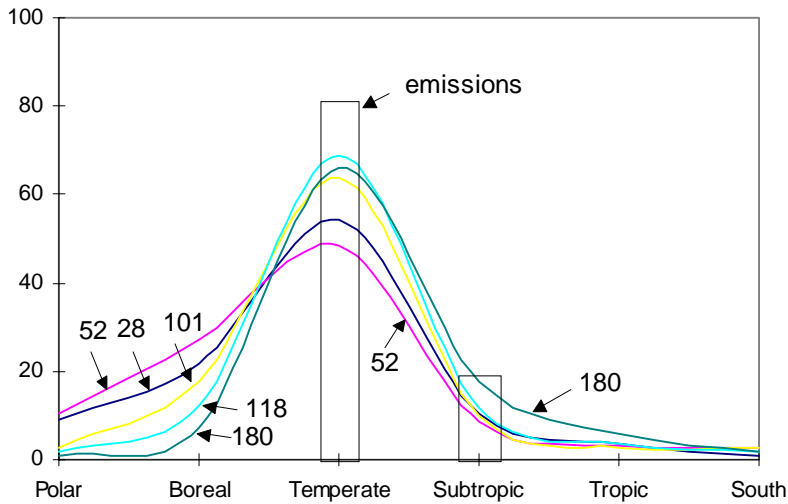


Figure 8 Relative distribution of selected PCB congeners among the climate zones in 1994. Also shown is the relative zonal distribution of the cumulative PCB emissions.

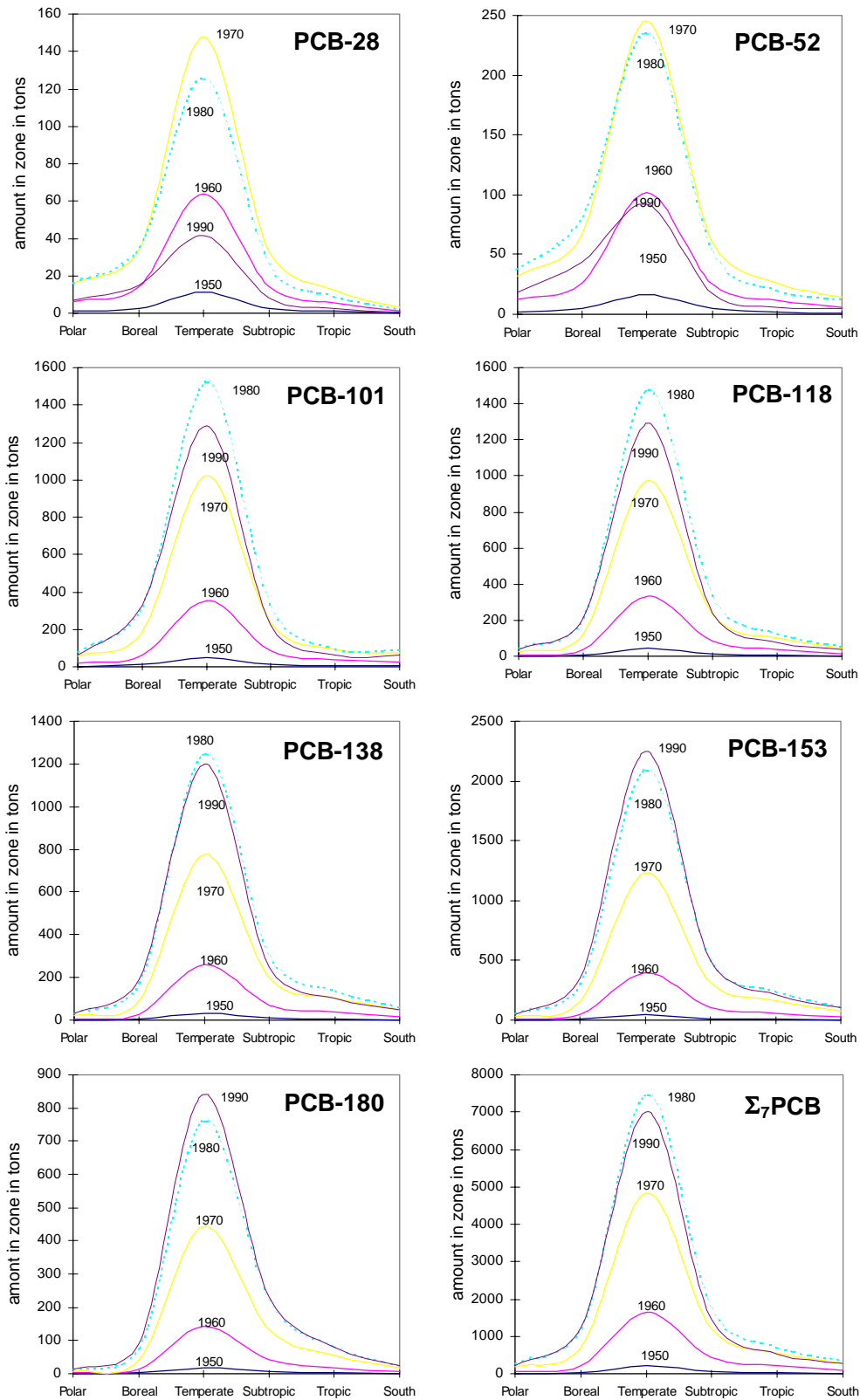


Figure 7 Calculated zonal distribution of seven PCB congeners and their sum in 1950, 1960, 1970, 1980 and 1990.

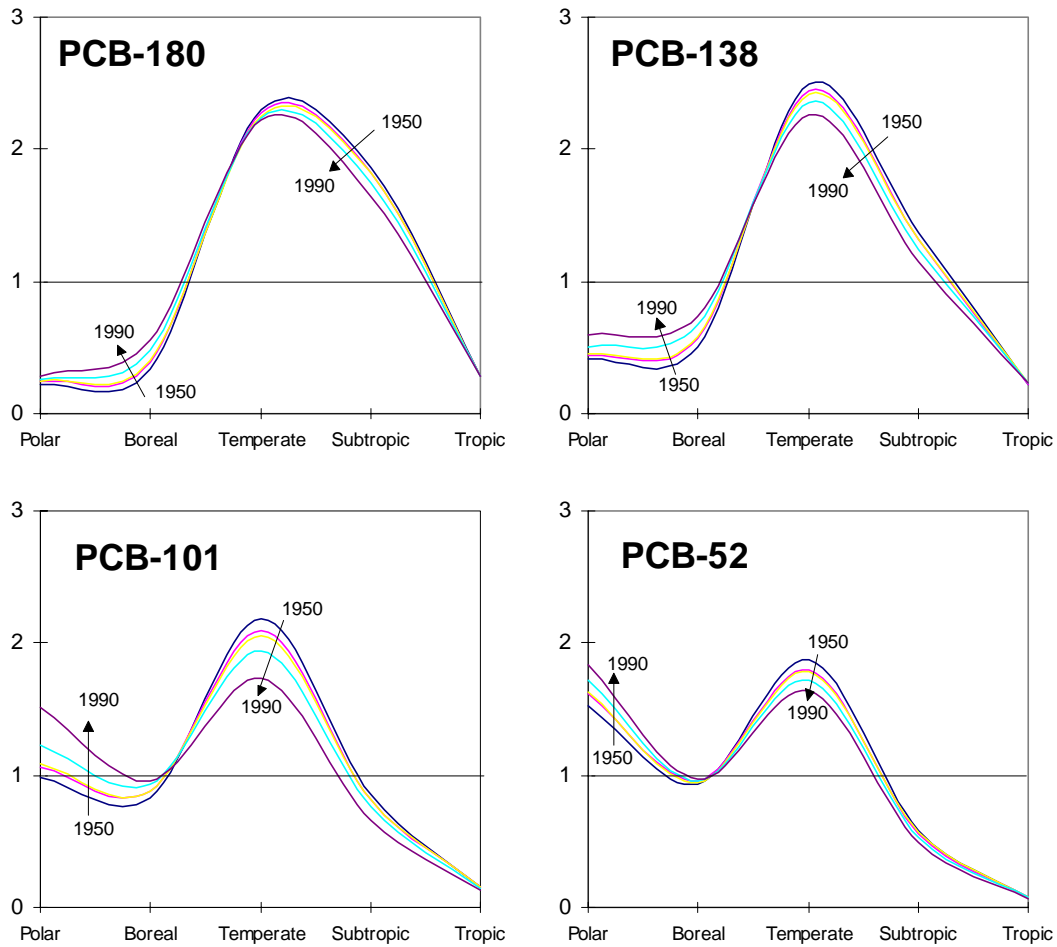


Figure 9 Latitudinal profiles of the annual mean concentrations (normalised to the hemispheric average) of selected PCB congeners in foliage of the Northern hemisphere in 1950, 1960, 1970, 1980 and 1990.

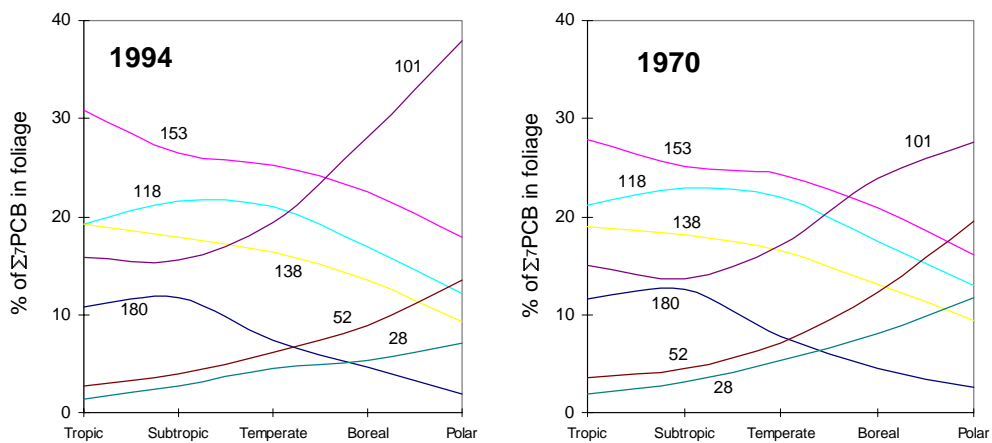


Figure 10 Calculated congeneric composition of PCBs on foliage as a function of latitude in 1994 and 1970.

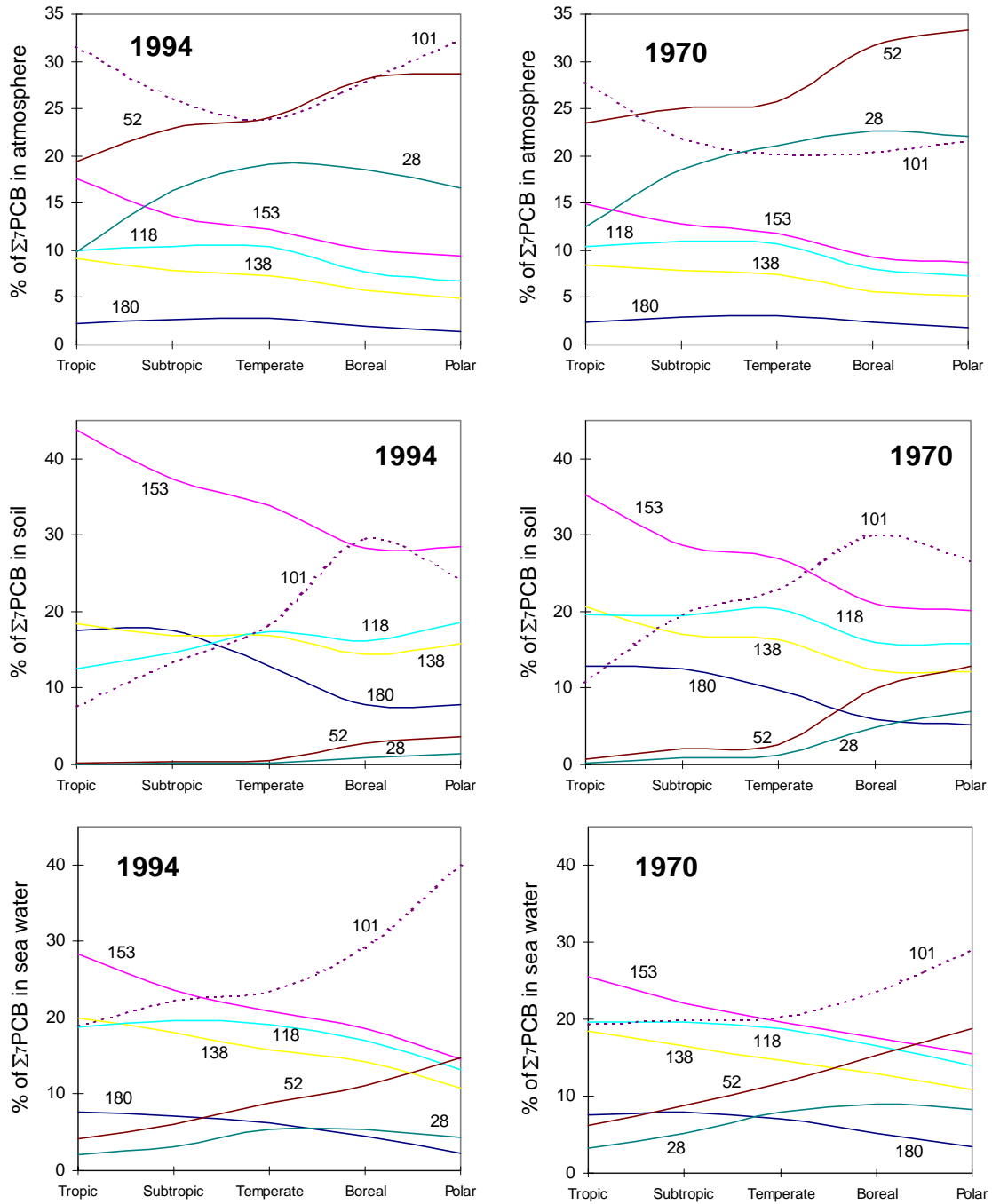


Figure 11 Calculated congeneric composition of PCBs in the atmosphere, in agricultural soil and in sea water as a function of latitude in 1994 and 1970.

Conclusions

The following conclusions can be drawn:

- The model is suitable to describe the fate of PCBs in a long term perspective, and in particular can be used to investigate compositional shifts among the PCB congeners between compartments, zones and different time periods.
- A preliminary evaluation suggests reasonable agreement between model results and measurements.
- The simulated fate of the various PCB congeners differs greatly, reaffirming the need to perform calculations for individual chemicals rather than chemical mixtures.
- The final destiny of PCBs in the global environment is degradation and transfer to the deep sea. The former is of primary importance to the lighter congeners, and the latter increases in relevance with the degree of chlorination. Burial in fresh water sediments is of little significance on a global scale.
- The model results reproduce shifts towards lighter PCB congeners with increasing latitude, as have been predicted by the global fractionation hypothesis and as have been observed in various measurement campaigns. The model further suggests that these shifts are rather complex, namely differ between various environmental media, have sometimes surprising anomalies, and change in time.
- The model further suggests that elevated PCB concentration levels in higher latitudes can be explained by relatively minor fractions of the global inventory of PCBs being transferred northward. This has already been found to apply to α -HCH.

Based on the preliminary results presented in this progress report, it is recommended that future efforts should be focused on a number of areas, namely:

- **revision of environmental input parameters.** In light of the large importance of the fate process “transfer to the deep sea” for the heavier congeners, the particle settling rates in the oceans are in particular need of closer scrutiny.
- **revision of chemical input parameters.** The chemical input parameters will need to be revised to account for the salinity effect on the HLCs. Due to the immense effect of degradation on model results, an effort will have to be made to improve the selection of degradation half-lives in various media and their temperature dependence.
- **sensitivity and uncertainty analysis.** Increased attention needs to be paid to testing the sensitivity of the model results to the most variable and uncertain input parameters, such as the emission and degradation rates.
- **thorough model evaluation.** A comparison of simulation results with measurements in the global environment will have to focus on the capability of the model to reproduce (i) measured absolute concentration levels and flux rates, (ii) measured congeneric compositions, and (iii) time trends in either of them.
- **model use.** Eventually, the model will be useful for tasks involving pathway analysis, source apportionment and trend predictions.

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