



Fractionation and current time trends of PCB congeners: evolution of distributions 1950–2010 studied using a global atmosphere-ocean general circulation model

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Abstract. PCBs are ubiquitous environmental pollutants expected to decline in abiotic environmental media in response to decreasing primary emissions since the 1970s. A coupled atmosphere-ocean general circulation model with embedded dynamic sub-models for atmospheric aerosols and the marine biogeochemistry and air-surface exchange processes with soils, vegetation and the cryosphere is used to study the transport and fate of four PCB congeners covering a range of 3–7 chlorine atoms.

The change of the geographic distribution of the PCB mixture reflects the sources and sinks' evolution over time. Globally, secondary emissions (re-volatilisation from surfaces) are on the long term increasingly gaining importance over primary emissions. Secondary emissions are most important for the congeners with 5–6 chlorine atoms. Correspondingly, the levels of these congeners are predicted to decrease slowest. Changes in congener mixture composition (fractionation) are characterized both geographically and temporally. In high latitudes enrichment of the lighter, less persistent congeners and more delayed decreasing levels in response to decreasing emissions are found. The delivery of the contaminants to high latitudes is predicted to be more efficient than previously suggested. The results suggest furthermore that the effectiveness of emission control measures may significantly vary among substances. The trends of decline of organic contaminant levels in the abiotic environmental media do not only vary with latitude (slow in high latitudes), but do also show longitudinal gradients.

1 Introduction

Polychlorinated biphenyls (PCBs) are semivolatile organic compounds (SOCs), industrial chemicals that have been used widely in the last century as transformer and capacitor insulating material, adhesives, paints, flame retardants, and sealing materials (Breivik et al., 2002). The cumulative global production of PCBs 1930–1993 was estimated to 1.3 million tons (Breivik et al., 2007) with a peak production in the 1970s. The majority of PCBs have been used in the Northern Hemisphere, mostly between 30° N and 60° N (Breivik et al., 2002). PCBs are toxic and persistent and have been observed to cycle far from source areas (Atlas and Giam, 1981; Simcik et al., 1999), in the Arctic (Gubala et al., 1995; Stern et al., 1997; Harner et al., 1998; Bidleman et al., 1999; Macdonald et al., 2000; Hung et al., 2010) and Antarctic (Tanabe et al., 1983; Kallenborn et al., 1998; Baek et al., 2011) abiotic environments and to bioaccumulate and biomagnify in Arctic (Allen-Gil et al., 1997; Kucklick and Baker, 1998; Halsall et al., 1998; Sobek et al., 2010) and Antarctic (Taniguchi et al., 2009) terrestrial and marine food chains for decades. The atmosphere has been regarded as the most important and rapid route of transport for PCBs to polar regions.

Global distribution of PCBs depends on the physical-chemical properties and on environmental parameters. PCB transport goes along with phase changes such as partitioning to aerosol particulate matter in air and partitioning to organic matter in seawater. Partitioning to aerosols leads to faster dry deposition (Bidleman, 1988; Wania and Daly, 2002; Tasdemir et al., 2004). In seawater PCBs sorbed to particulate

organic carbon are subject to gravitational sinking (Dachs et al., 2002; Wania and Daly, 2002). Both processes limit the substances' residence times in the mobile media and, hence, retard global distribution of PCBs. The influence of air-soil exchange on atmospheric LRT is more complex: The depth of the layer of air in chemical equilibrium with the soil multi-phase system (air, water, organic and mineral phases) is limited by vertical mixing, which is spatially and temporally highly variable, and also influenced by ventilation of the soil. Organics transferred to soil are retained by sorption to organic matter (Cousins et al., 1999), but incompletely subject to re-volatilisation due to the long-term dynamics of sorption ("aging"; e.g. Gevaio et al., 2003; Lehnik-Habrink et al., 2010), a process that is hardly understood. PCBs undergo multiple deposition and (re-)volatilisation cycles on land and sea (Wania and Mackay, 1993; Klečka et al., 2000; Gouin and Wania, 2007). Under declining primary emissions, secondary emissions (re-volatilisation) will gain importance as sources for SOCs transported in air. PCB levels were recently reported to be still dominated by primary emissions in a source region (UK; Schuster et al., 2010).

According to the global distillation hypothesis (Wania and Mackay, 1993) the composition of a mixture of SOCs will progressively shift towards the more volatile substances during poleward travel, as the equilibria are shifted towards the condensed phases at the expense of the gas-phase, i.e. with increasing latitude the mass fractions of lighter PCBs in the congener mixture is expected to increase, while the less volatile congeners would be deposited closer to the sources (in warmer regions). This would result in fractionation, namely an enrichment of the more volatile (less chlorinated) congeners in the PCB mixture in polar areas over time. A number of field studies have found evidence of fractionation of PCBs in air, seawater and biota (Bignert et al., 1998; Agrell et al., 1999; Ockenden et al., 2003; Jaward et al., 2004; Sobek and Gustafsson, 2004; Gioia et al., 2006). However, Ockenden et al. (2003) who sampled worldwide soils at background sites did not find clear evidence of temperature driven fractionation of PCBs on the global scale, but merely in a subset of samples (north of 60° N). Wania and Su, 2004, studied the significance of partitioning, persistence and emissions in establishing PCB patterns using a zonally averaging multimedia model. They concluded that the processes contributing most to PCB fractionation in meridional (latitudinal) direction are partitioning to aerosol particles, and related dry deposition along atmospheric transport, and degradation rates (in various media).

International conventions aim to reduce the exposure of ecosystems towards hazardous, long-lasting chemicals, including PCBs, by introducing and or applying measures of emission control. Even if regulatory measures are taken, the levels of persistent contaminants in the abiotic environment are expected to decline with a multi-year delay. How this differs among compounds is extremely important for policy success. For persistent pollutants this has been studied re-

gionally based on field data (Hung et al., 2005; Dvorská et al., 2009; Hung et al., 2010) and globally using a zonally averaging multimedia model (Gouin and Wania, 2007). For PCBs in the Arctic a delay is observed and expected (Macdonald et al., 2000; Gouin and Wania, 2007). Observations at various Arctic sites do not follow the same temporal trend, however (Hung et al., 2010).

The aim of this study is to investigate the effect of substance properties of PCBs on their global distributions and long-term trends using for the first time a model system, which dynamically captures the three-dimensional multi-phase systems in air and sea-water and the transports in both air and ocean and their variability, including episodic transport in air. In this way biogeochemical and geophysical cycles, needed to understand and predict the global fate of persistent pollutants accurately (Lohmann et al., 2007), are represented according to the state of the art. Differences in PCB congener profiles between air samples from different latitudes are more likely to reflect differences in the congeners mixture composition of local and regional PCB sources than global transport and degradation processes (Wania and Su, 2004). We use therefore an artificial emission scenario, namely same emissions for all congeners, in order to study substance specific transport and fate. The model results provide insights into spatially varying PCBs distributions' time trends and can be used to test the global distillation hypothesis (fractionation). The model performance has been evaluated against observational data of non-PCB SOCs (Semeena et al., 2006; Stemmler and Lammel, 2009; Hofmann et al., 2011) and compared with other models (Lammel et al., 2007).

2 Materials and methods

2.1 Model description

The multicompartment chemistry-transport model MPI-MCTM (Semeena et al., 2006; Guglielmo et al., 2009) is based on the three-dimensional coupled atmosphere-ocean general circulation model ECHAM5-MPIOM (Roeckner et al., 2003; Marsland et al., 2003) with embedded submodels for atmospheric aerosols (HAM; Stier et al., 2005), marine biogeochemistry (HAMOCC5; Maier-Reimer et al., 2005) and two-dimensional top soil and vegetation surfaces. Organic substances in the model world cycle in the compartments air (gas, aqueous and particulate phases), ocean (dissolved, colloidal and particulate phases), soil, vegetation surfaces, snow, sea and land ice. The cycling includes intra-compartmental (advective and diffusive transport in atmosphere and ocean, degradation, phase partitioning) and inter-compartmental (deposition, gas exchange) processes. Wet deposition includes scavenging of gaseous and particulate phases by large-scale and convective precipitation. Dry deposition of both gases and particles is based on

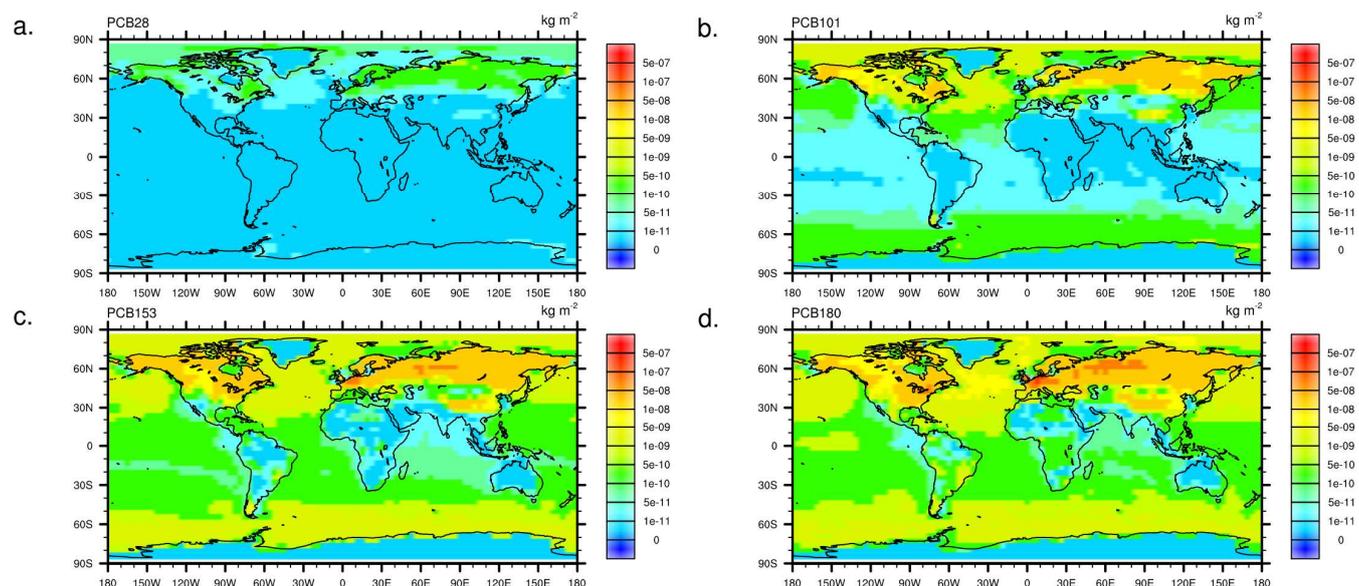


Fig. 1. Global distribution of the total environmental burdens of (a) PCB 28, (b) PCB101, (c) PCB153 and (d) PCB180 excluding the atmosphere (kg m^{-2}). Mean of the year 2010.

serial resistance approaches. The related degradation and exchange processes have been described previously (Seemena et al., 2006; Guglielmo et al., 2009; Hofmann et al., 2012). Riverine transports and runoff are neglected. The sub-model HAM describes nucleation, coagulation, condensation, and deposition of primary and secondary aerosols transported as four particle size modes. HAMOCC5 is a nutrient-phytoplankton-zooplankton-detritus ecosystem model (Six and Maier-Reimer, 1996; Maier-Reimer et al., 2005). In the ocean, in addition to advection and diffusion, chemicals in the particulate phase are subject to gravitational settling. As settling velocity that of detritus is adopted (Maier-Reimer et al., 2005).

Evaluation of this version of the MPI-MCTM by comparison of model results with observations with regard to the simulation of the cycling of organochlorine pesticides was provided earlier (Guglielmo et al., 2009 and 2012; Stemmler and Lammel, 2009; Hofmann et al., 2012) and with regard to PCB cycling is provided in the Supplement, i.e. Sect. S3.

2.2 Physico-chemical properties and emissions

In this study, the global emission estimates for PCB153 compiled by Breivik et al. (2002b, 2007) were used for four congeners, PCB28 ($\text{C}_{12}\text{H}_7\text{Cl}_3$), PCB101 ($\text{C}_{12}\text{H}_5\text{Cl}_5$), PCB153 ($\text{C}_{12}\text{H}_4\text{Cl}_6$), and PCB180 ($\text{C}_{12}\text{H}_3\text{Cl}_7$) (see below, 2.3). These estimates are based on a mass-balance approach and include emissions during use, accidental release, and disposal of technical mixtures. In line with earlier modelling studies (Wania and Daly, 2002; Hauck et al., 2009), the maximum emission scenario (Breivik et al., 2007) was adopted as being closer to real emissions than the mid or minimum

scenarios. The data ($1^\circ \times 1^\circ$) were re-gridded onto the model grid. The emissions (release) were into air, 100 %.

Physico-chemical properties relevant for the multimedia fate of the selected PCB congeners are listed in the Supplement, Table S1.

2.3 Experiments

To discern the impact of the physico-chemical properties on PCBs fate only, the four congeners were released into the environment using identical emissions, i.e. PCB153 emissions (Breivik et al., 2007). Choosing PCB153 emissions implies underestimating the real emissions for PCB28 and PCB101, and overestimating the ones of PCB180.

The model was run from 1950 to 2010 with a resolution of $\approx 3.75^\circ$ (T31) and 19 vertical levels (≈ 1000 – 10 hPa) in the atmosphere and a mean resolution of 3° (GR30) and 40 vertical levels (10–600 m deep, from surface to deep ocean) in the ocean. The resolution in ocean is highest close to the poles, with the North Pole being shifted onto Greenland.

3 Results and discussion

3.1 Migration of distributions

The total environmental distributions of the four PCB congeners (mapped for one selected year in Fig. 1) differ, despite similar emissions, due to different properties and degradation rates in the compartments (Table S1 in the Supplement) and to different (compartmental) sinks along atmospheric and oceanic transports. After peak emission, ≈ 1970 , most of each total environmental burden, 77–85 %, was stored in

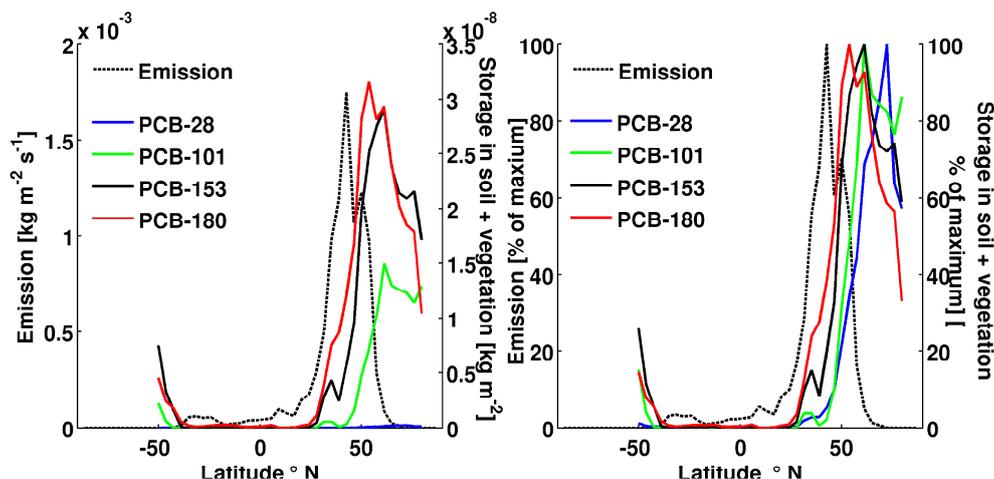


Fig. 2. Global, zonally (longitudinally) averaged soil and vegetation burdens together with accumulated emissions 1950–2010 (grey), absolute terms (left) and normalized to maximum (right). Mean of the year 2010.

the terrestrial ground compartments (characteristic numbers of the distributions and fluxes for selected years are listed in Table S2 in the Supplement). These burdens all have migrated northward from their initial distributions, i.e. those of the emissions (Fig. 2). The emissions themselves, migrated, too, but only within 3° , and without an obvious trend. Also, for all four PCB congeners long-range transport (LRT) to and accumulation in southern high latitudes is obvious (Figs. 1, 2). Still, most of the estimated soil PCB burden remains in the global source region of the Northern Hemisphere ($30\text{--}60^\circ\text{N}$) or in soils rich in organic matter north of that region. This had been stressed earlier (Meijer et al., 2003; Wania and Su, 2004).

At the end of the simulation, 2010, with $11\text{--}12^\circ$ the centres of gravity (COGs; Leip and Lammel, 2004) of the lighter congeners' geographic burdens' distributions on land surfaces (soil, vegetation, snow, ice) have migrated further north from the location of the emission distribution. Larger fractions of their terrestrial burdens are stored north of 65°N than of the burdens of the heavier congeners, PCB153 and PCB180 (zonal displacement of the COG, $\text{ZD}=6\text{--}8^\circ$, Table 1; Leip and Lammel, 2004). However, this shift comes with a significant zonal spreading of the distribution by $\text{ZS}=8\text{--}11^\circ$ only in the cases of the two heavier congeners' (hexachloro- and heptachlorobiphenyl) distributions (zonal spreading, ZS, which refers to the 5th and 95th percentiles of the cumulative meridional distributions; Leip and Lammel, 2004), whereas the distributions of PCB28 and PCB101 migrate northward without significant spreading ($\text{ZS}=\pm 1^\circ$). The evolution of these shifts during 50 years is such, that the soil burdens migrate northward, fast within the first few years and then slowly and steadily (Fig. 3). This can be explained by degradation in soil being faster at higher temperatures, which prevail in subtropical and tropical latitudes, and by the meridional distribution of total depositions. The

COGs of the distributions of PCB101, –153 and –180 in ocean migrate southward, forced by the atmospheric transports which lead to depositions also in the inner tropics and in the Southern Hemisphere. This is reflected by a steady southward migration of the southern margin of the distributions (5th percentile of the cumulative meridional distribution, not shown) from $\approx 20^\circ\text{S}$ in 1950 to $\approx 40^\circ\text{S}$ in 2010. Furthermore, the meridional distribution in ocean is in some regions influenced by southward ocean currents, both at the surface and below. Note that the COGs of the atmospheric distribution have a slow long-term southward trend (with strong seasonality; Fig. 3, see also ZD of the atmospheric distribution in Table 1). In the case of PCB28 the ocean distribution follows the distribution in soil. This is because of its shorter atmospheric lifetime which causes the COG of the meridional atmospheric distribution to remain around 45°N (Table 1). For PCB28 ocean currents are less effective, because of its relatively short residence times in seawater (a factor of 2–20 shorter than for the other congeners), mostly limited by its high volatility. High volatility of PCB28 is also reflected in the strong seasonality of the latitude of the COG of the distributions in both ocean and soil (Fig. 3). The atmospheric distribution's meridional shifts (ZD, Table 1) are significant and southward for PCB101, –153 and –180, but negligible for PCB28. This reflects the main characteristics of PCB28 cycling: Because of higher partial pressure PCB28 has a stronger tendency to return to air upon deposition to soil (secondary emission or re-volatilisation). For PCB28 degradation in air, a factor of 3–10 faster than for the other congeners ($\tau_{\text{air deg}}$, Table S2), is almost as limiting as deposition for residence in air. Consequently, the total residence time in air, τ_{air} , is shorter ($\approx 12\text{d}$ instead of $18 \pm 2\text{d}$ for the higher PCBs; Table S2 in the Supplement) and the effective total (= primary + secondary) emission into air, F_{vol} , is smaller ($\approx 1/3$ of the primary emission instead

Table 1. Indicators for meridional distribution, fractionation and long-range transport (LRT). ZD = zonal displacement, ZS = zonal spreading, eACP = Arctic contamination potential normalized to accumulated emissions. Distribution refers to the total compartmental burden. Mean of last year of the simulation, 2010. ZD and ZS of the emissions are 0.79 and 33.29° N for all substances.

	PCB28	PCB101	PCB153	PCB180
ZD of the atmospheric distribution (° N)	0.29	−15.48	−20.12	−19.51
ZS of the atmospheric distribution (° N)	52.3	68.89	65.93	54.16
ZD of the land surface distribution (° N)	12.29	11.9	8.38	6.47
ZS of the land surface distribution (° N)	0.98	−1.43	8.11	10.62
Fraction of atmospheric burden stored >65° N	0.16	0.11	0.08	0.07
Fraction of PCB mixture in air >65° N (DJF/JJA)	0.20/0.09	0.39/0.41	0.29/0.32	0.12/0.17
Fraction of ocean burden stored >65° N	0.46	0.24	0.12	0.11
Fraction of PCB mixture in ocean+sea ice >65° N	0.01	0.19	0.35	0.45
Fraction of terrestrial burdens stored >65° N	0.44	0.39	0.26	0.20
Fraction of PCB mixture in terrestrial surfaces >65° N	<0.01	0.22	0.39	0.39
Mean number of hops 1950–2010	0.9	2.7	4.8	4.0
eACP ₁₀ ^{air} (%)	3.0	10.9	13.9	12.4
eACP ₅₀ ^{air} (%)	0.14	6.7	11.9	11.7

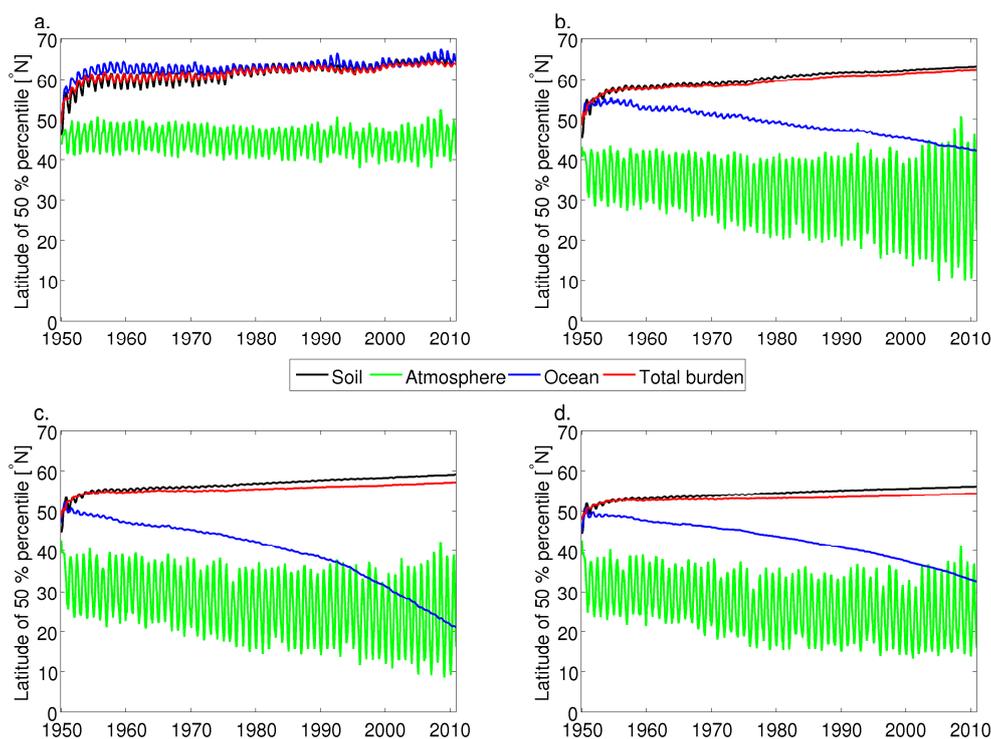


Fig. 3. Meridional shifts of the center of gravity (COG) of the cumulative meridional distributions of the compartmental burdens of (a) PCB28, (b) PCB101, (c) PCB153 and (d) PCB180, 1950–2010.

of $>2/3$ (Table S2; feedback correction factor for emission with respect to air-surface exchange $\gamma_a = 1/(1 - f_{as}^2)$, with $f_{as} = k_{netdep}/(k_{netdep} + k_{deg\ a})$; Margni et al., 2004). In conclusion, different volatilisation/condensation and degradation among congeners, together with geospheric transports shape their geographic distributions. The significance of secondary emissions for PCB sources is congener specific: High vapour pressure and slow degradability in air favour the importance of secondary emissions. Time series

of the fraction of secondary emissions over all sources (primary + secondary) are shown in Fig. 4. For the global environment this fraction is increasing in the long-term for all congeners. It is at all times highest and fastest increasing for the congeners of medium hydrophobicity, PCB101 and PCB153, slower for PCB180 (lowest vapour pressure, Table S1 in the Supplement) and slowest for PCB28 (shortest τ_{air} , Table S2) (Fig. 4a). From land surfaces PCB101 re-volatilisation exceeds that of PCB153, and vice versa from

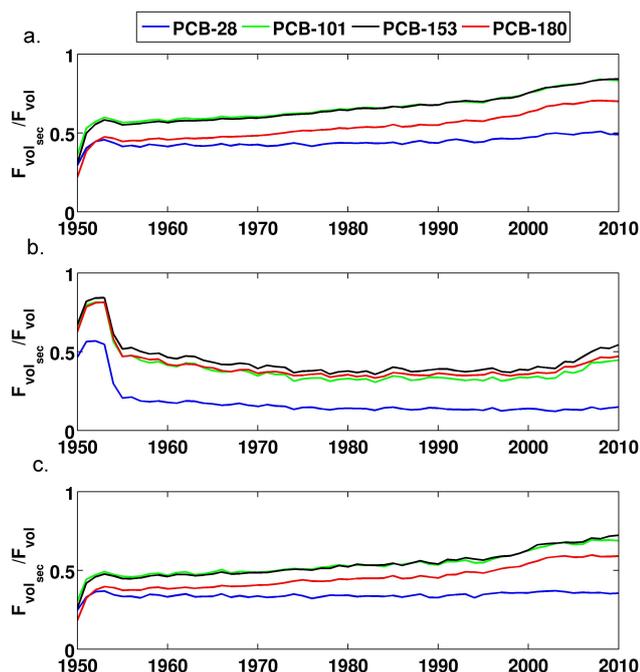


Fig. 4. Time series of the fraction of the PCB congeners' secondary emissions in all sources (primary + secondary) (a) globally, (b) in the latitudinal band 0° N–30° N and (c) 30° N–60° N. Annual means.

sea surfaces (not shown). This global picture is dominated by the northern mid latitudes (Fig. 4b), because PCBs have been released and mostly distributed there. Congeners' order is somewhat reversed in the tropics (Fig. 4c), both on land and on sea (not shown), with PCB180's secondary emissions significance slightly exceeding that of PCB101. In the tropics higher temperatures enhance volatilisation, less PCB has been used and usage trends were somewhat delayed (Breivik et al., 2002).

The efficiency of LRT in air depends on source distribution, atmospheric circulation, precipitation patterns, aerosol abundance, and temperature variation. All of these influences are non-uniformly distributed and temporally variable on various scales. The northward shift of the COG in soils and vegetation corresponds to and is determined by a decrease of the fractions volatilised from and degraded in soils. This is most pronounced for the lighter congeners and, in turn, leads to longer residence times of PCBs in the terrestrial environment in 1995 compared to 1970 (Table S2 in the Supplement). The same differences in residence times result for the ocean compartment including sea ice. As soils and ocean together store the highest shares of PCBs in the environment, a longer overall residence time is implied.

The LRT potentials in air of the four congeners studied are similar (because of similar τ_{air}), but the geographic distributions of the secondary emissions and, hence, the source distributions (for the atmosphere) differ: As a consequence

of higher burden in ground compartments (accumulating because of slow degradation there) but lower vapour pressure of the heavier PCBs (Tables S1 and S2 in the Supplement), secondary volatilisation is higher and faster for PCB101 and PCB153 than for the lightest and the heaviest studied congener (Fig. 3).

The northward shift of the global distributions is reflected in storages in the Arctic higher than its global area share (which is 8 %) would suggest: Highest values are reached for PCB28, distinctly less for PCB101 and the heavier congeners (see fractions of burden stored >65° N after 50 years, i.e. in 2010, Table 1). The model predicts high mass fractions of PCB28, but not of the other congeners, stored in the Arctic soils and in ocean and inverse concentration profiles in soils between Northern Hemisphere sources and remote regions.

3.2 Meridional long range transport potential and re-volatilisation

Indicators for the LRT potential are listed in Table 1. 94–98 % of the total environmental burdens of the PCBs are stored in the land surface compartments (not shown). The distribution of PCB28 migrates farthest to the north (quantified by ZD of the land surface burden, see also Fig. 2), while PCB180 stays closest to the emission sources. PCB153 and PCB180 stretch over the widest range of latitudes (quantified by ZS, Fig. 3). This transport pattern is also evident when looking into the fractions of compartmental burden found in the Arctic (>65° N). The highest shares of atmospheric, soil and vegetation, and oceanic burdens in the Arctic are found for PCB28 (Table 1). Similarly, the zonally averaged burdens of PCB28, PCB101, PCB153 and PCB180 in Antarctica reach up to approximately 30, 10, 10 and 5 %, respectively, of the maximum of the zonally averaged burdens in the Northern Hemisphere (Fig. 2).

The Arctic contamination potential, $eACP_{50}^{\text{air}}$, i.e. the fraction stored in surface compartments (total environment without the atmosphere) after 50 years of continuous release into air (Wania, 2006), is found here highest for PCB180 and PCB153 ($\approx 12\%$ in 2010), and lowest for PCB28 (0.14 % in 2010). PCB101 has an $eACP_{50}^{\text{air}}$ of 7 %. After 10 years ($eACP_{10}^{\text{air}}$) we find 3.0, 10.9, 13.9 and 12.4 %, respectively. These values exceed earlier predictions (Wania, 2006), namely ≈ 0.25 , ≈ 1.0 , ≈ 1.0 and $\approx 0.7\%$, respectively, by one order of magnitude. The metrics is not exactly the same, as Wania, 2006 has used a generic emission scenario with constant emissions, while we used transient ones (which are also longitudinally resolved). This difference in the scenarios used may explain part of the ACP discrepancies in the predictions. Furthermore, the discrepancy between ACP predictions is certainly influenced by a very different representation of the atmospheric dynamics in the models used: Episodic transport and vertical mixing in air are represented by our model, but not or very limited by the zonally averaging multimedia model. Furthermore, deposition processes,

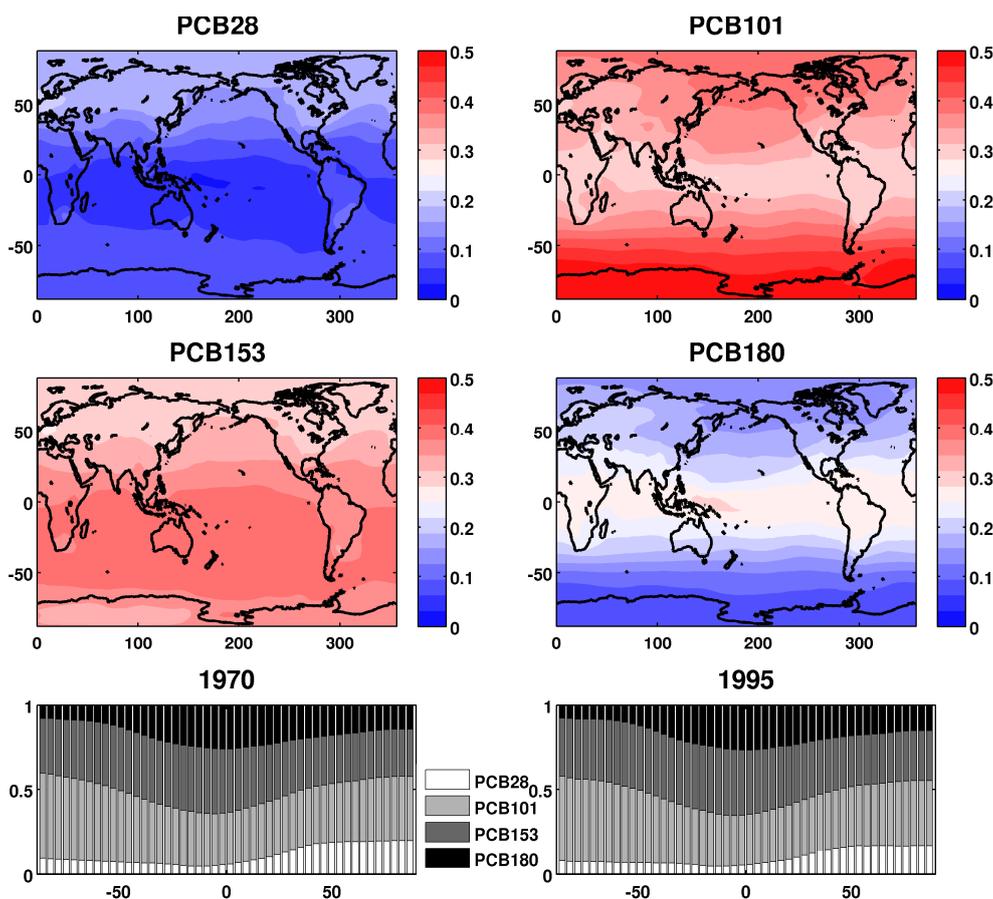


Fig. 5. Fractionation: Geographic (mean of year 1995, upper two panels) and meridional (mean of years 1970 and 1995, lower panel) distributions of the fraction (between 0 and 1) of the individual congener's burden in the mixture of four PCB congeners' burdens in the atmosphere.

their nature, mean and statistics, and geographic explicitness of the models are very different. In consequence, PCB cycling is more intense in the MPI-MCTM than in GloboPOP and, correspondingly, the substances undergo more cycles through the atmosphere (hops), which is enhancing the efficiency of the overall meridional transports. The mean number of hops n_{hop} between atmosphere and surface compartments, i.e. the number of full deposition-(re-)volatilisation cycles, was derived following Guoin et al., 2004:

$$n_{hop} = (N_{SA} \times N_{AS}) / (N_{RS} \times N_{RA} + N_{RS} \times N_{AS} + N_{RA} \times N_{SA}).$$

In the formula N_{SA} denotes the volatilisation from all surfaces (soils, vegetation, ocean, snow, sea and land ice), N_{AS} the deposition flux (dry and wet deposition of both gaseous and particulate phases), N_{RS} the degradation in surface media (soils, vegetation, and ocean including deep sea), and N_{RA} the degradation in air (in t month^{-1} globally). The mean number of hops averaged over the period 1950–2010 is 4.0, 4.8, 2.7, and 0.9 for PCB180, PCB153, PCB101 and PCB28, respectively (Table 1). The time series of the mean number of hops shows a strong seasonal cycle for the four PCBs with

minima in northern summer and maxima in northern winter (not shown). Thereby the minimum values for PCB28 (0.4), PCB101 (1.5), and PCB153 (3.4) are almost constant throughout the experiment, whereas the minimum value for PCB180 decreased during the simulation period from 7 to 1. The maximum number of hops of PCB180, PCB153, PCB101 is decreasing continuously, but in case of PCB28 it is almost constant at 2.5.

3.3 Global fractionation

The fractionation of the PCB mixture in meridional direction is shown after 20 and 45 yr (Fig. 5) and the long-term fractionation trends 1950–2010 for individual zones (Fig. 7): The emission scenario used was artificial in the sense that the congeners were released into the environment in equal amounts, i.e. the mass fraction of each congener in the sum of the four congeners was initially 0.25. In the atmosphere (Fig. 5) as well as in the ground compartments (including ocean, Fig. 6) PCB153 and PCB180 are enriched in all latitudes, PCB180 clearly most in the tropics and subtropics (see also Fig. 7).

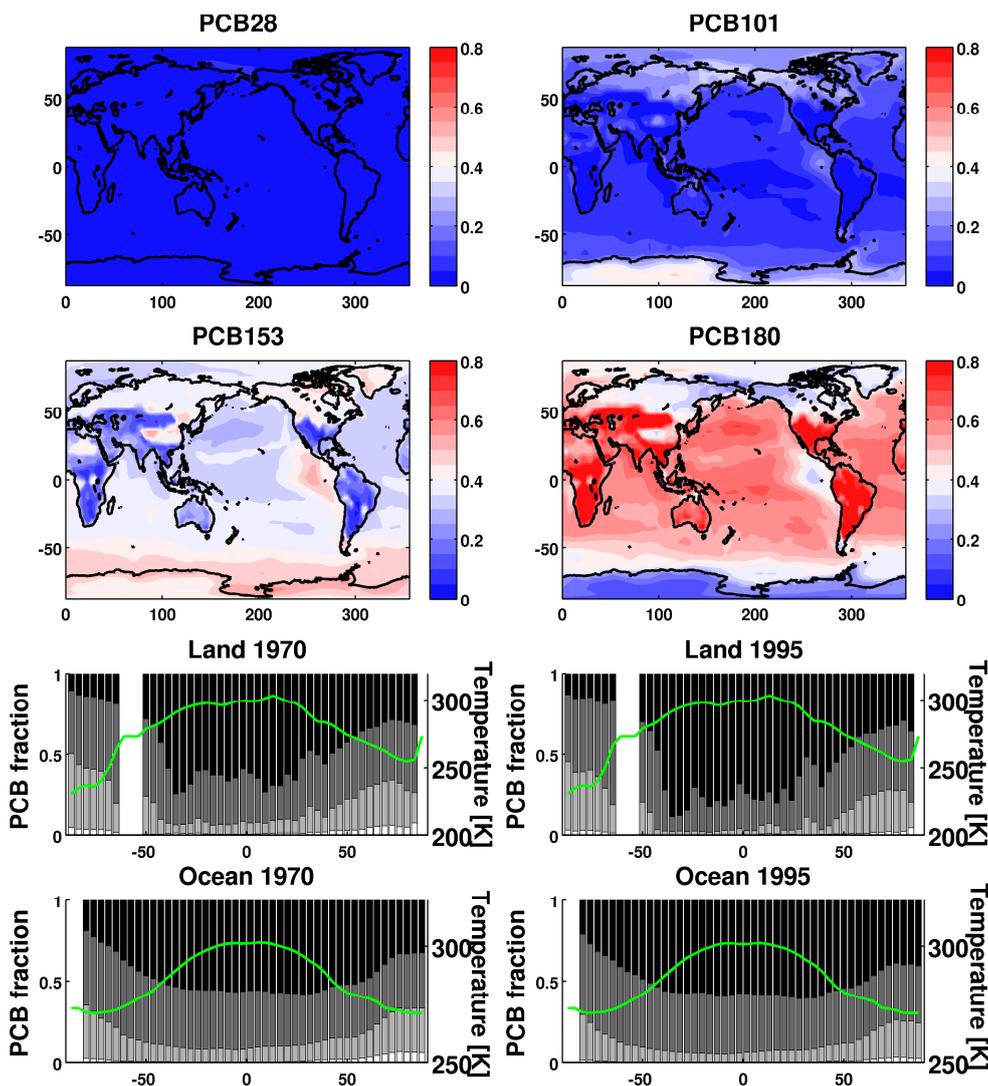


Fig. 6. Same as Fig. 5 but ground compartments, meridional trends for land (soil, vegetation, ice and snow) and ocean (seawater and sea ice) together with surface temperature (green line).

PCB28 becomes a minor component due to its fastest degradation.

3.3.1 Temporal trends

Long-term trends

PCB101's fraction in the ground compartments (Fig. 6) shows a strong latitudinal gradient, low in the tropics and subtropics (mostly influenced by rapid degradation), but relatively high in southern and northern high latitudes. The long-term trend of the substance pattern is dominated by the decline of the lighter PCBs at the expense of the fraction of the heavier ones in the mixture (Fig. 7). In high latitudes (in southern somewhat more pronounced than in northern) this trend is less pronounced as partly compensated for by advec-

tion carrying higher shares of the lighter PCBs. The decline of the lighter congeners is driven by both degradability and by the emission trends, while the compensating process is driven by higher mobility (higher fraction stored in the atmosphere) (Fig. 5). Note, however, that (due to persistence) in absolute terms the PCBs' total environmental burden is increasing far beyond the year of peak emission, namely until ≈ 2000 , or a few years before in the Southern Hemisphere (Fig. 7). Inter-hemispheric differences are dominated by the land-sea distribution and by different trends of soil and seawater burdens. The model predicts a slower response of the exposure to declining global emissions in high latitudes than in low latitudes (Table 2 and blue lines in Fig. 7). For example PCB101's mean decadal trend in 2001–2010 was -5.0 and $-4.5\% \text{ yr}^{-1}$ in the Arctic and Antarctic atmosphere, respectively, while it was $-5.8\% \text{ yr}^{-1}$ in the atmosphere of

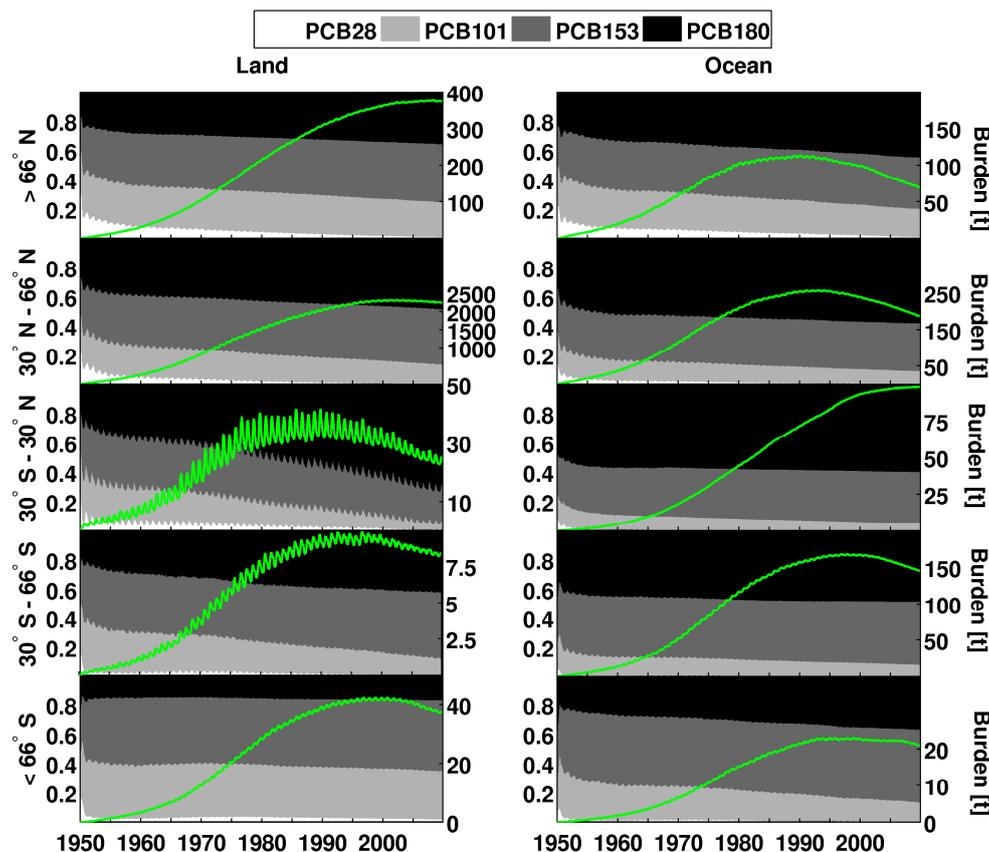


Fig. 7. Fractionation: 1960–2010 trends of the fractions of the individual congener's total environmental burden in the sum of four PCB congeners' burdens together with the absolute total environmental burden trend (sum of 4 congeners; green line), in land (left) and sea (right) areas of 5 latitudinal bands, i.e. Arctic (>66° N), 30–66° N, tropics (30° N–30° S), 30–66° S and Antarctic (>66° S).

Table 2. Decadal, i.e. 2001–2010, burden trends (% yr⁻¹) in air and soil for various (a) zonal and (b) meridional bands. Linear regressions of annual means.

(a)	PCB28		PCB101		PCB153		PCB180	
	air	soil	air	soil	air	soil	air	soil
Arctic (>66° N)	-6.9	-6.7	-5.0	-0.4	-5.1	+0.6	-6.4	+1.0
30–66° N	-6.9	-7.3	-5.5	-1.7	-5.1	-0.1	-6.4	+0.3
Tropics (30° N–30° S)	-7.3	-8.0	-5.8	-6.9	-5.5	-2.8	-6.5	-0.9
30–66° S	-8.3	-8.8	-5.4	-1.7	-5.3	+0.2	-6.6	-0.3
Antarctic (>66° S)	-7.4	(1)	-4.5	(1)	-4.2	(1)	-5.0	(1)

(b)	PCB28		PCB101		PCB153		PCB180	
	air	soil	air	soil	air	soil	Air	Soil
80°–170° W N America	-7.1	-7.5	-5.3	-1.8	-5.2	-0.2	-6.3	+0.1
30°–80° W S America	-7.0	-7.1	-5.5	-2.0	-5.1	-0.3	-6.5	+0.1
30° W–60° E Europe, Africa	-7.1	-7.2	-5.5	-1.4	-5.3	+0.0	-6.4	+0.4
60°–100° E W Asia	-7.3	-6.8	-5.8	-1.2	-5.4	+0.2	-6.6	+0.5
100°–170° E E and SE Asia, Australia	-2.4	-7.4	-5.6	-0.8	-5.4	-0.4	-6.4	+0.8

(1) no soil in the zone

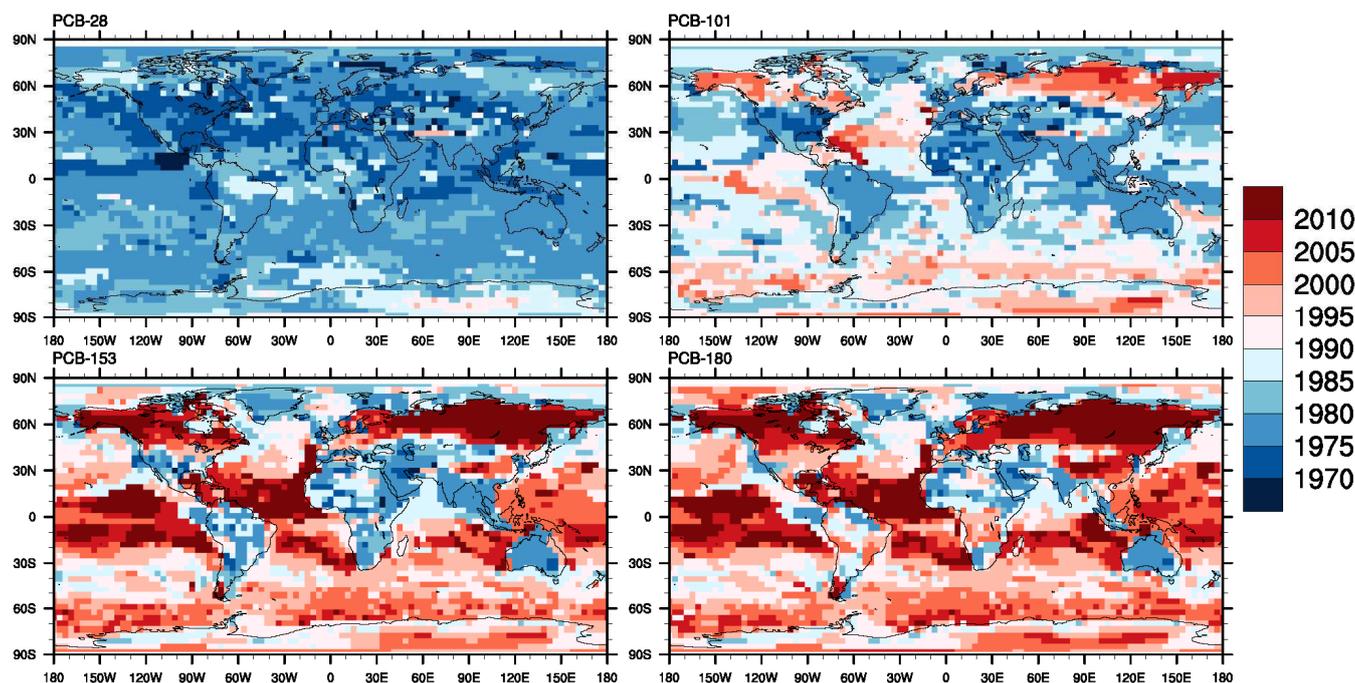


Fig. 8. Mapped year of peak total environmental burden. Identical emission distributions used (historic only for PCB153, see text).

the tropics. The slowest downward trends for PCB101, –153 and –180 are predicted for the Antarctic. Similar but more pronounced trends are found for the soils (Table 2). Between northern mid latitudes and the tropics the trends for PCB101 and –153 differ by a factor of 4 and ≈ 20 , respectively. For the more hydrophobic congeners soil burdens were even still increasing in the Arctic, namely $+0.6\% \text{ yr}^{-1}$ for PCB153 and $+1.0\% \text{ yr}^{-1}$ in the case of PCB180, and in northern mid latitudes, i.e. $+0.3\% \text{ yr}^{-1}$ for PCB180. Such a delayed response to declining emissions in high latitudes was hypothesized as resulting from higher persistency in the cold regions and on-going global distillation (Harner, 1997) and predicted to be of ≈ 15 years in the Arctic for organics which undergo multiple deposition-(re-)volatilisation cycles and exchange with seawater (Gouin and Wania, 2007). However, the geographic pattern of trend reversal from increasing to declining burdens is complex, as resulting from the combination of emission, transport and physical (deposition, sedimentation) and chemical (degradation) sink patterns (mapped in Fig. 8). Trend reversal occurred first in subtropical and tropical soils and northern high latitude seas. Burdens peak particularly late (partly not before 2010) in boreal and part of the temperate soils, as well as in tropical seas. They peak somewhat earlier in the Southern Ocean than in the ocean of the inner tropics. In general, the burdens peak once degradation overcompensates for primary emission. Therefore, the differences between the four geographic distributions of peak year of all congeners' burdens (Fig. 8) are dominated by the dif-

ferences in the residence times in soils and ocean. They are most pronounced in remote regions.

In the Arctic even small positive trends are found for PCB153 and –180 in soil. In the tropics (30° S – 30° N) the decadal trend is -8.0 , -6.9 , -2.8 and $-0.9\% \text{ yr}^{-1}$ for PCB28, –101, –153 and –180, respectively. In the Arctic these trends are slower or even still increasing, namely -6.7 , -0.4 , $+0.6$ and $+1.0\% \text{ yr}^{-1}$ for PCB28, –101, –153 and –180, respectively (Table 2). Qualitatively, similar trends had been suggested for PCB congeners in tropical, temperate and polar soils based on a zonally averaging multimedia model for the decades before 2000 and for the Northern Hemisphere (Wania and Su, 2004).

Fractionation is also reflected in differences in decreasing trends in response to declining emissions: The congeners of medium chlorination (and hydrophobicity), PCB101 and PCB153, show the slowest decreasing trends, e.g. -5.0 – $-5.1\% \text{ yr}^{-1}$ in Arctic air in 2001–2010, in contrast to -6.4 – $-6.9\% \text{ yr}^{-1}$ for PCB28 and PCB180 (Table 2). Observed trends of PCB fractionation in near-ground Arctic air have been reported for the period 1993–2006 (Hung et al., 2010). In agreement with these observations the model predicts the lowest (and negative) trends for PCB28's and the highest (and positive) trends for PCB101's shares (Table S3 in the Supplement). The temporal variability at Arctic monitoring stations is incompletely understood and even the annual mean levels are strongly influenced by the statistics of episodic emission events, such as boreal fires, in combination with atmospheric circulation and sea ice retreat, besides any

long-term trends (Hung et al., 2010). As the model does not capture episodic emission events nor the phase of interannual climate variability, full agreement cannot be expected.

The PCB congener ranking in the terrestrial ground compartments has not been changing from 1955 onwards, but the fractions of PCB153 and PCB180 have been increasing, whereas the ones of PCB101 and PCB28 have been decreasing (Fig. 6). Highest share of the PCB mixture is held by PCB153 (34–40%), followed by PCB180 (28–38%), and minor shares for PCB101 and PCB28.

The comparison of model results with levels observed in Europe and the Arctic (Fig. S5, Table S3a in the Supplement) suggests that the fractions of congeners in the PCB congeners' mixture in air is not fully captured by the model on the regional scale: While a very good agreement is found for a central European and one Arctic station, the fraction of low chlorinated congeners is overestimated for British and Norwegian sites and underestimated for a second Arctic station. Comparability is imperfect, however, due to the lack of observed data at the individual congeners' level and the non-historic emissions used for 3 of the 4 congeners.

Seasonal trends

In winter, PCB28 dominates the atmospheric composition (40%), followed by PCB101 (30%), PCB153 (20%), and PCB180 (10%). In summer the ranking is almost inverted, PCB28 holds 10%, PCB101 27%, PCB153 43%, and PCB180 25% of the atmospheric mixture. The annual mean mass fractions in air are shown in Fig. 5. PCB28's highest share is found in the northern mid and high latitudes, PCB101's in both northern and southern high latitudes, PCB153's throughout most of the Southern Hemisphere, and PCB180's throughout the tropics, with a pronounced maximum in the western equatorial Pacific Ocean (Fig. 5). The largest change in composition of the PCBs mixture occurs between tropical and subtropical air. This had been predicted before based on a zonally averaging multimedia model (Wania and Su, 2004). The shift is less pronounced in 1995 than in 1970 (Fig. 5). This is probably related to the lesser significance the less persistent (small τ_{ov}) congeners have under decreasing primary emissions.

3.3.2 Spatial trends

PCB153 shows highest share in soils in Antarctica, Greenland, the Canadian Arctic Archipelago and in a mid latitude region, namely large parts of China, stretching from Tibet until eastern and northeastern provinces. PCB101 shows its highest share in soils in high latitudes (Antarctica, Siberia, Alaska, Yukon and Nunavut). The largest change is located between temperate and boreal zone, similar in 1970 and in 1995 (Fig. 6). The same was predicted using a multimedia model (Wania and Su, 2004). Again, fractionation in soils is

also reflected in differences in long-term trends: The less hydrophobic the congener the faster is its soil burden decreasing toward the end of the simulation, 2001–2010.

The model suggests ranking of PCB congeners in the ocean compartment to have been stable from 1962 onward. Also in the ocean the fraction of PCB153 and PCB180 in the total PCB mass have been increasing, while the ones of PCB101 and PCB28 have been decreasing: the highest share of the PCB mixture in ocean is held by PCB180 followed by PCB153. PCB180 shows maxima in the tropics and subtropics, while PCB153's maxima are found in high latitudes, in particular in the Southern Ocean, and one extended region in the eastern Pacific, i.e. south of Central America and west of Colombia and Ecuador (Fig. 6). This geographic pattern results as the superposition of substance association with suspended particulate matter, temperature dependent degradation and deposition, all congener-specific processes.

The non-homogeneous zonal distribution of the individual congeners' mass fractions (e.g. the relative minimum of the fraction of PCB180 at ca. 70° N; Fig. 6) is strongly influenced by the land-sea distribution: the terrestrial compartmental distributions dominates the substance mix at 60–80° N, the substance mix in ocean at 80–90° N.

The model anyway suggests that trends are not uniform across hemispheres: Negative trends are faster in southern mid latitudes than in northern. This is most pronounced for PCB28 in both Southern Hemisphere air and soil (ca. 20% faster in southern mid latitudes than in northern mid latitudes). These inter-hemispheric differences are not found for PCB101 in air and soil (same in both hemispheres) and for PCB153 (positive in the Southern Hemisphere) in soil. The fraction of PCB180 in environmental compartments is higher in northern than in southern high latitudes (Figs. 5, 6). This model prediction is in agreement with the finding that the enrichment of low chlorinated congeners found in Arctic air is less pronounced in southern high latitudes (measurement at 61° N in 1994–1995; Kallenborn et al., 1998).

Across continents (Table 2) similar trends in air and in soils are found for the Americas, Europe together with Africa and West Asia, i.e. fastest negative trends in air for PCB28 and -180, in soil for PCB28. PCB180 and, in some longitudinal bands, PCB153 are still increasing in soils. East and Southeast Asia together with Australia is the zone with the slowest negative trends for PCB28 in air (-2.4 instead of $-(7.1 \pm 0.2) \% \text{ yr}^{-1}$), for PCB101 in soil (-0.8 instead of $-(1.6 \pm 0.4) \% \text{ yr}^{-1}$), but fastest positive PCB180 trend in soil ($+0.8$ instead of $+(0.3 \pm 0.2) \% \text{ yr}^{-1}$).

4 Conclusions

4.1 Levels and exposure

The model simulation suggests that secondary emissions (re-volatilisation from surfaces) are most important for the

cycling of congeners of medium hydrophobicity (5–6 chlorine atoms) and that these congeners' levels would decrease slowest in the abiotic environment.

Fractionation implies that ecosystems and habitats at different remote locations are exposed to different PCB mixtures (Bignert et al., 1998). The exposure of the marine ecosystems towards pollutants is heterogeneous in three dimensions due to the location and dynamics of sedimentation fluxes (Dachs et al., 2002) and currents including deep water formation and upwelling. This remains to be studied in detail. Apart from exposure levels, also the substance mixture entering the marine food chains is relevant for effects at higher trophic levels. However, the significance of varying substance mixture on toxicity and overall effects in wildlife is far from understood.

4.2 Trend reversal and implications for the effectiveness of emission control

Environmental response to regulatory measures in control of persistent chemicals is slow and substance specific. These results suggest that PCBs' total environmental burden is increasing far beyond the year of peak emission, namely until ≈ 2000 , or a few years before in the Southern Hemisphere. The differences between congeners' distributions have been evolving dynamically and non-linearly. Pseudo-linearity and pseudo-steady states, however, do occur in this chemodynamics. Both the emission distribution and the geospheric features, which, in combination determine the spatial variability of PCBs' chemodynamics are similar for many of the regulated persistent pollutants. The findings of this modelling study which used identical emissions for four PCBs which range several orders of magnitude in the most prominent physico-chemical properties illustrate that the effectiveness of emission control measures may significantly vary among substances. This is reflected as latitudinal gradients with delays expected for the high latitudes (as had been stressed earlier, Harner, 1997; Gouin and Wania, 2007). It is also reflected as longitudinal gradients, on both land and sea. This model simulation indicates that trend reversal occurred first in subtropical and tropical soils and northern high latitude seas and is most out of phase among the congeners in remote areas. Regional time trends will deviate even more between individual substances more distanced from each other in a chemical properties' phase space than the PCB congeners.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/12/7199/2012/acp-12-7199-2012-supplement.pdf>.

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