Supporting Information

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

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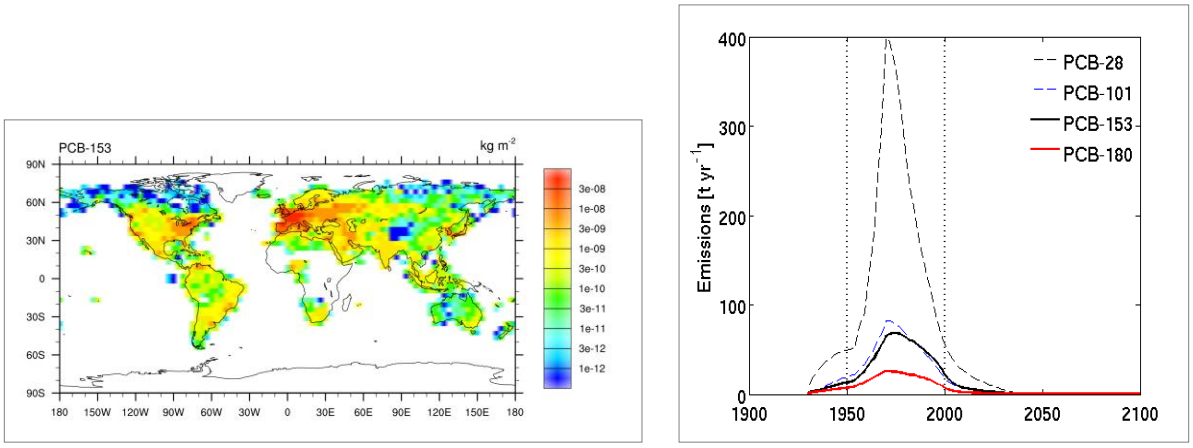
S1. Methods

S1.1 Emissions

The accumulated global emissions of PCB28, -101, -153 and -180, for the period 1930-2000 amount to 11568, 2894, 2596 and 1037 t, respectively (high emission estimate; Breivik et al., 2002). The emissions of PCB153 for the years 1950-2000, 2385 t, were used for all congeners. The geographic distribution is shown in Fig. S1.

Fig. S1: Global spatial (a) and temporal (b) primary emission distribution of PCB153.

a. b.



1.2 Physico-chemical properties

Table S1. Physico-chemical properties of PCBs. Data given for 298 K unless otherwise stated.

Property	PCB28 ($C_{12}H_7Cl_3$)	PCB101 ($C_{12}H_5Cl_5$)	PCB153 ($C_{12}H_4Cl_6$)	PCB180 ($C_{12}H_3Cl_7$)
Saturation vapour pressure p_{sat} [Pa]	0.027[a]	0.025[a]	0.0006[a]	0.0002[a]
Enthalpy of vapourisation H_{vap} [kJ mol^{-1}]	89.3[b]	95.6[c]	103.5[c]	111.9[c]
Water solubility s [g L^{-1}]	0.23 [a]	0.033[a]	0.011[a]	0.0052[a]
Henry constant [M atm^{-1}]	3.36[a]	4.22[a]	5.08 [a]	11.9 [a]
Enthalpy of solution H_{sol} [kJ mol^{-1}]	27 [d]	27[d]	27[d]	27[d]
Octanol-air partitioning coefficient log K_{OA}	7.57 [e]	8.34[e]	8.97[e]	9.64[e]
Soil organic carbon partitioning coefficient log K_{OC} [L g^{-1}]	5.27 [f]	5.94[f]	6.48[f]	6.77[f]
OH gas-phase reaction rate coefficient k_{OH} [10^{-12} cm^3 $moles^{-1}$ s^{-1}] [j]	1.06 [g]	0.33 [g]	0.16 [g]	0.10 [g]
OH particulate-phase reaction rate coefficient k_{OH} [10^{-12} cm^3 $moles^{-1}$ s^{-1}] [j]	0 [d]	0 [d]	0 [d]	0 [d]
First-order degradation rate coefficient in sea-water k_{oc} [s^{-1}]	$3.5 \cdot 10^{-8}$, [h]	$6.21 \cdot 10^{-9}$, [h]	$3.5 \cdot 10^{-9}$ [h]	$3.5 \cdot 10^{-9}$ [h]
First-order degradation rate coefficient in ocean sediment k_{sed} [s^{-1}]	$1.13 \cdot 10^{-8}$ [h]	$3.50 \cdot 10^{-9}$ [h]	$1.13 \cdot 10^{-9}$ [h]	$1.13 \cdot 10^{-9}$ [h]
First-order degradation rate coefficient in topsoil and on vegetation surfaces k_{soil} [s^{-1}]	$1.93 \cdot 10^{-8}$ [h]	$1.93 \cdot 10^{-9}$ [h]	$3.5 \cdot 10^{-10}$ [h]	$1.93 \cdot 10^{-10}$ [h]

[a] Li et al., 2003
[b] Puri et al., 2001
[c] Puri et al., 2002
[d] estimate
[e] from K_{ow}/K_{aw}, K_{ow} from Li et al., 2003, K_{aw} based on water solubility and vapour pressure
[f] $0.41 \times K_{ow}$ (Karickhoff), K_{ow} from Li et al., 2003
[g] Anderson and Hites, 1996
[h] adopted from Wania and Daly, 2002

S2. Results

S2.1 PCB congener budgets

Table S2: Selected global burdens in compartment j, b_j, removal and intercompartmental exchange fluxes, F_i, and characteristic removal and residence times, τ_i. γ_a is the feedback correction factor for emission (100% into air) 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). Annual means of 2 selected years, 1970 and 1995. deg = degradation, dep = total deposition, vol = volatilisation.

	PCB28		PCB101		PCB153		PCB180	
Year	1970	1995	1970	1995	1970	1995	1970	1995
b_{total} (t)	45	32	255	533	444	1198	613	1461
b_{air} (t)	3.84	2.32	9.66	7	9.15	6.95	5.71	4.25
$b_{seawater.}$ (t)	4.82	4.02	35.38	68.61	84.53	223.42	118.83	319.08
$b_{seawater\ +sea\ ice}$ (t)	6.54	5.2	41.44	74.34	90.8	229.71	122.48	322.58
$b_{soil+vegetation}$ (t)	31.04	23.12	194.59	435.79	330.68	938.69	376.63	1123.3
$b_{land\ ice\ +\ snow}$(t)	3.13	2.71	9.79	16.36	13	22.43	8.1	11.36
$F_{deg\ soil\ +\ vegetation}$ (t a^{-1})	10.5	6.9	4.5	8.1	2.3	5.7	1.7	4.6
$F_{deg\ air}$ (t a^{-1})	46.31	27.73	35.16	24.92	15.33	11.41	5.78	4.19
$F_{deg\ ocean}$ (t a^{-1})	1.38	1.11	1.88	3.49	2.68	6.66	3.97	9.86
F_{dep} (t a^{-1})	66.4	40.17	133.94	105.28	148.96	121.33	121.41	91.09
$F_{vol\ soil\ +\ vegetation}$ (t a^{-1})	21.90	12.71	38.91	28.78	35.56	28.95	29.83	25.11
$F_{vol\ seawater+sea\ ice}$ (t a^{-1})	14.95	9.31	44.01	37.62	52.99	48.49	27.63	22.82
$F_{vol\ snow\ and\ land\ ice}$ (t a^{-1})	14.26	9.68	19.3	21.55	9.23	12.87	4.8	5.22
F_{dep}/F_{vol} (%) [1]	57	58	80	84	92	95	96	100
γ_a	0.30	0.36	0.69	1.00	0.84	0.76	0.98	0.76
τ_{air} (d) [2]	12.46	12.5	20.85	19.62	20.32	19.12	16.4	16.28
$\tau_{air\ dep}$ (d)	21.19	21.12	26.33	24.26	22.41	20.92	17.18	17.03
$\tau_{air\ deg}$ (d)	30.25	30.6	100.29	102.47	217.74	222.49	360.8	370.53
$\tau_{soil+vegetation}$ (a) [2]	0.96	1.18	4.49	11.81	8.73	27.05	11.95	37.85
$\tau_{snow+land\ ice}$ (d) [2]	28.31	39.28	54.18	110.17	76.05	157.2	53.66	96.22
$\tau_{ocean+sea\ ice}$ (a) [2]	0.40	0.50	0.90	1.81	1.63	4.16	3.88	9.87
$\tau_{overall}$ (a)	0.77	0.93	6.16	14.6	21.8	50.28	44.84	78.46

[1] F_{vol} refers to total volatilisation, i.e. sum of primary and secondary sources

[2] compartmental residence time considers, besides degradation, intercompartmental transfer fluxes and it is defined as $\tau_j = 1/(1/\tau_{deg} + 1/\tau_{transfer})$

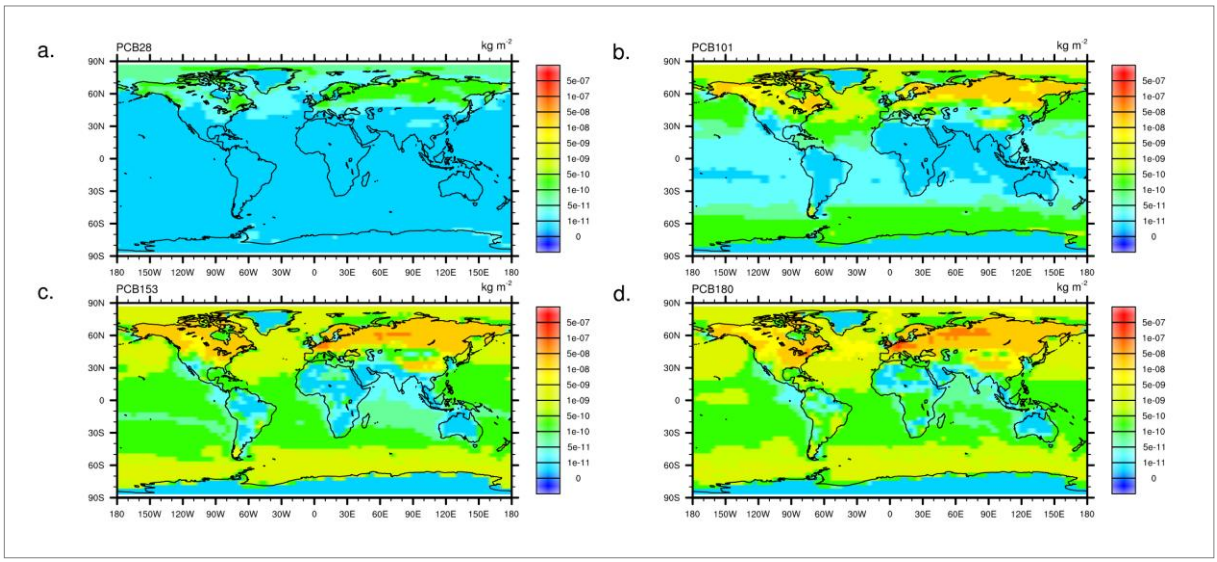
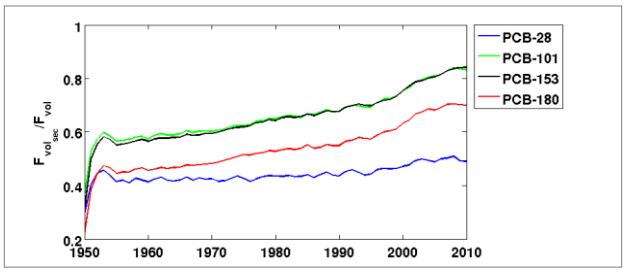
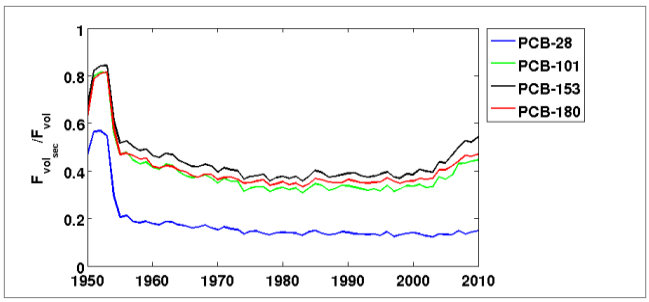


Fig. S2: Global distribution of the total environmental burdens of (a) PCB 28, (b) PCB101, (c) PCB153 and (d) PCB180 excluding the atmosphere (kg m^{-2}). Mean of the year 2010.

a.



b.



c.

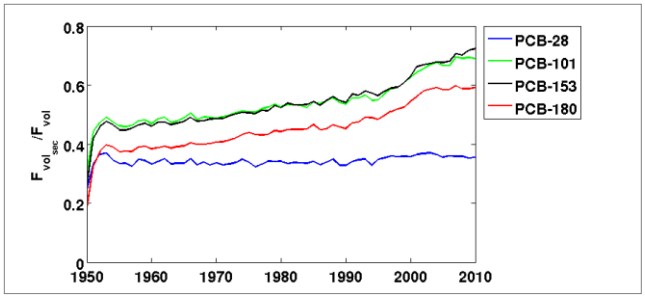


Fig. S3. Time series of the fraction of PCB congeners' secondary emissions over all sources (primary + secondary) (a) globally, (b) in the latitudinal band 0°N-30°N and (c) 30°N-60°N. Annual means.

S2.2 Fractionation in meridional direction and long-term chemodynamics

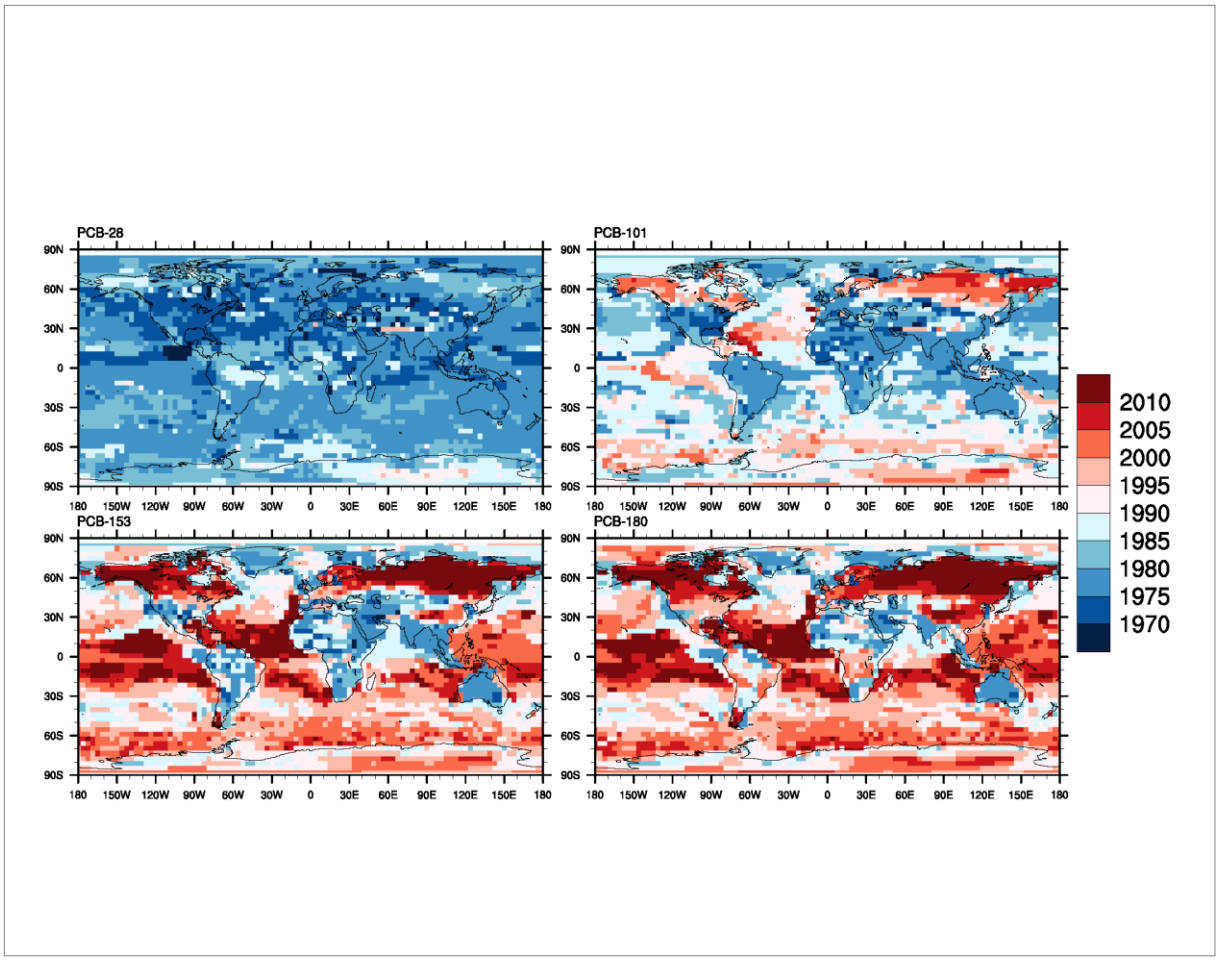


Fig. S4: Mapped year of peak total environmental burden. Identical emission distributions used (historic only for PCB153, see text).

S3. Comparison between modeled and observed levels, congeners' fractions and trends

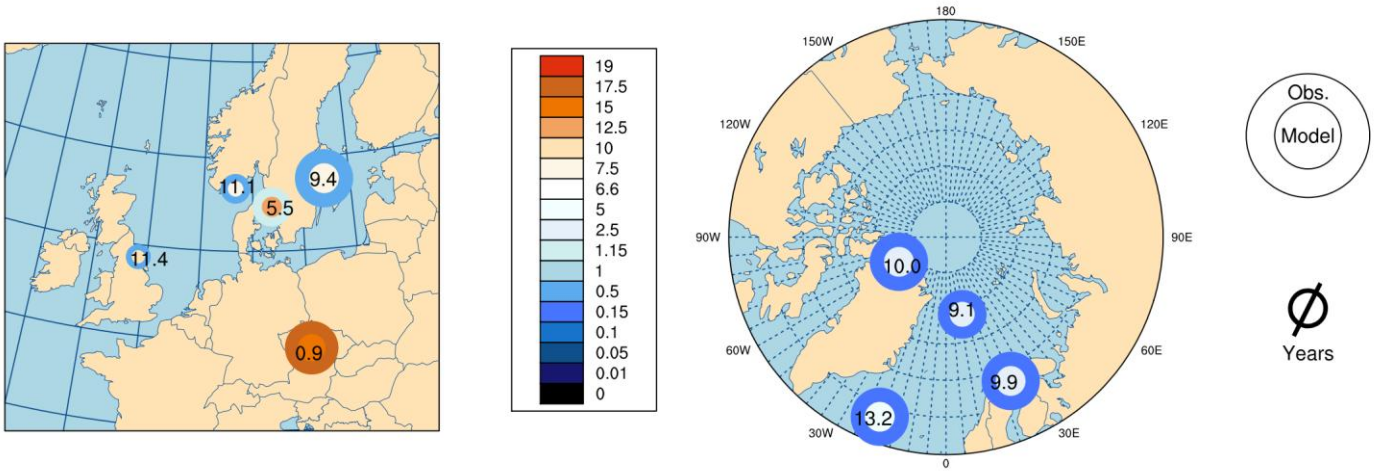


Fig. S5. Comparison of observed and model predicted near-ground atmospheric concentrations of PCB153 at monitoring stations in Europe (EMEP, 2011) and in the Arctic (Hung et al., 2010) [pg m^{-3}]. Multi-annual mean, number of years (5-12) depicted by size of symbol. Numbers in the circles denote ratio between predicted and observed concentrations.

Perfect agreement is found for one central European station (Kosetice, Czech Republic), discrepancy of a factor of 5 for one northern European station (in Sweden) and a factor of ≈10 for other western and northern European stations (in England, Sweden, and continental Norway) and on Svalbard) and the Arctic. No direct comparison between levels in soil is possible, because measurements refer to the concentration in topsoil of decimeter of depth, while no depth is allocated to the soil compartment in the model.

In the following, fractions of congeners among the sum of 4 PCB congeners (PCB28, -101, -153, -180) are compared. When observational data were not available on an individual congener basis, comparison is done between observed homologues' quantity and one predicted congeners' quantity. I.e., comparability between predicted and observed is limited by the implicit assumption that the indicator congeners' degradation rates are representing the characteristic mean degradation rate of

the respective group of homologues. Similar degradation rates in soil are usually adopted for PCB homologues. In air, however, lifetimes vary by a factor of three among tri- and penta-chloro homologues (Anderson and Hites, 1996). Furthermore, historic emissions were simulated for only one congener, PCB153, while the emissions of the other congeners were set equal to those of PCB153 deviating from the historic emission distribution (Section 2.).

For fractionation in soil a strong spatial trend is predicted in contrast to a weak one observed (Fig. S6c, d). This is related to the prediction of a low mobility of PCB180 in Europe unlike the other congeners (Fig. S1d).

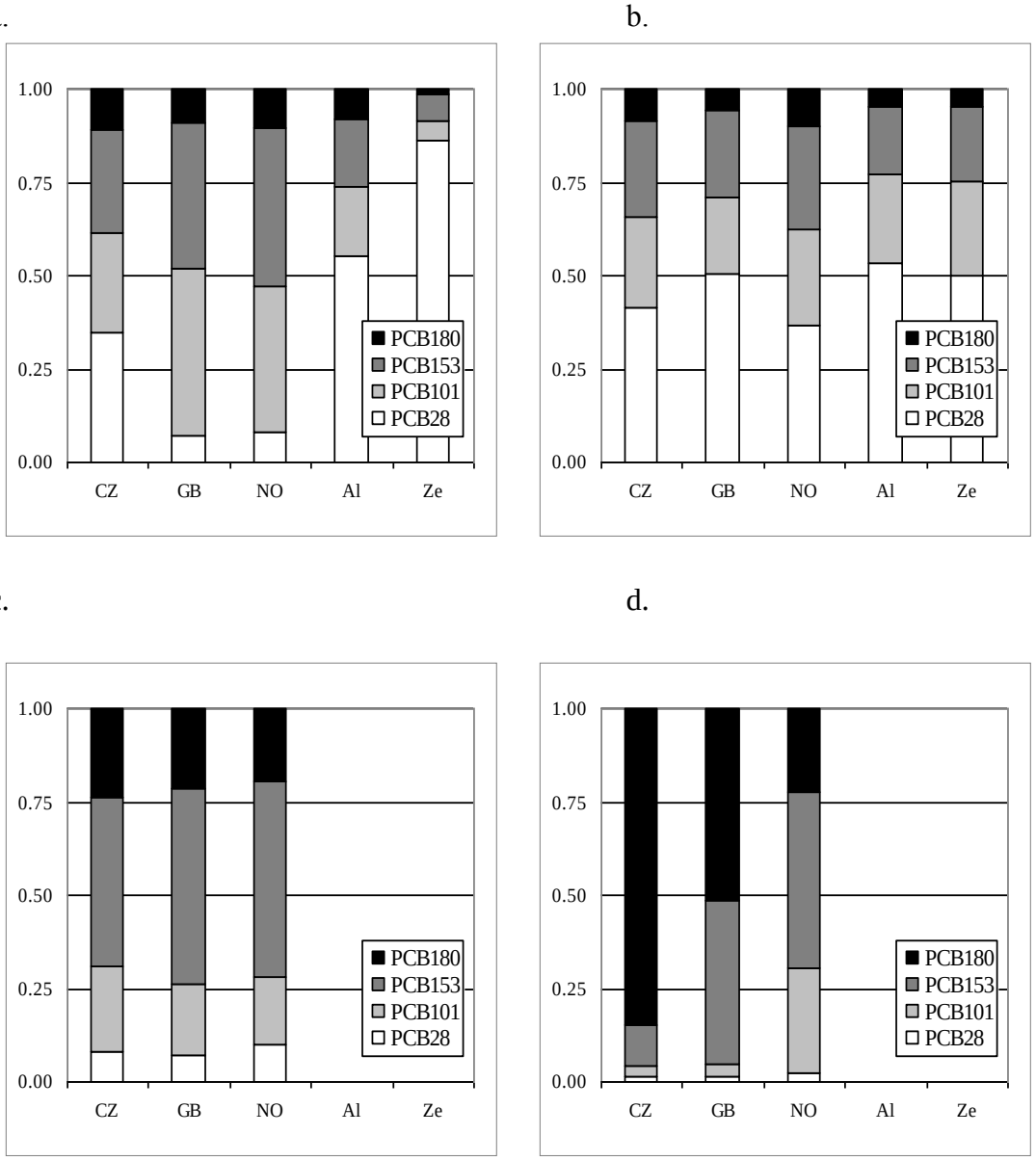


Fig. S6. Observed (a, c) and predicted (b, d) PCB fractionation in temperate (Czech Republic, GB), boreal (Norway) and Arctic (Alert, Zeppelin) (a, b) near-ground atmosphere 1998-2000 (except CZ: 1999-2000; Meijer et al., 2003a; Holoubek et al., 2007a; Hung et al., 2010; Klánová, personal communication) and (c, d) soils 1998-2000 (except CZ: 2000-2002; Meijer et al., 2002; Holoubek et al. 2007b; Hung et al., 2010; Klánová, personal communication). Given as fraction of individual congeners' concentration over sum of four PCB congeners' concentrations or of the fraction of homologues with 3, 5, 6 or 7 chlorine atoms over their sum. Soil sites were 1 mixed forest and agricultural site in the Czech Republic (9 localities), 14 grassland sites in Great Britain and 9 in Norway. Model predicted concentrations of PCB28, -101 and -180 were weighted with the corresponding accumulated global emissions (Breivik et al., 2002) in order to account for non-historic emissions used for these 3 congeners.

Table S3: Modelled and observed time trends (linear regressions of annual or monthly data, % a^{-1}) of the fraction of individual congeners' concentration over sum of four PCB congeners' concentrations (predicted all sites, observed Košetice, Czech Republic) or of the fraction of homologues with 3, 5, 6 or 7 chlorine atoms over their sum (observed Alert and Zeppelin) in (a.) the near-ground atmosphere of one mid latitude (Košetice, Klánová, personal communication) and two Arctic (Alert, Zeppelin, based on Fig. 2 of Hung et al., 2010) stations and (b.) soil of the mid latitude station. Model predicted concentrations of PCB28, -101 and -180 were weighted with the corresponding accumulated global emissions (Breivik et al., 2002).

a.

	Observed			Predicted		
	Košetice 1999-2008	Alert 1993-2005	Zeppelin 1998-2006	Košetice 1999-2008	Alert 1993-2005	Zeppelin 1998-2006
PCB28 / trichlorobiphenyls	+2.5	-1.20	-0.25	-0.94	-0.84	-1.44
PCB101 / pentachlorobiphenyls	-1.6	+0.92	+0.36	+0.24	+0.36	+0.72
PCB153 / hexachlorobiphenyls	-0.45	+0.48	-0.10	+0.42	+0.36	+0.60
PCB180 / heptachlorobiphenyls	-0.45	-0.13	-0.02	+0.28	+0.08	+0.05

b.

	Observed	Predicted
	Košetice 1999-2008	Košetice 1999-2008
PCB28	-0.46	-0.12
PCB101	-1.3	-0.19
PCB153	-0.29	-0.61
PCB180	+2.0	+0.93

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