

Reply to referees:

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

We would like to thank the reviewers for their thoughtful comments. It helped to improve the paper.

Review #1

The paper addresses relevant scientific questions within the scope of ACP. The fractionation of 4 PCB congeners is investigated with the multicompartment chemistry transport model (MPI-MCTM), which is based on the coupled general ocean-atmosphere general circulation model (ECHAM5-MPIOM), and has embedded sub-dynamic models for atmospheric aerosols (HAM), marine biogeochemistry (HAMOCC5), and air-surface exchange processes with soils, vegetation and the cryosphere.

The approach and the results are novel in that fractionation of PCBs (and POPs) is modeled with a global 3-D model, which allows for variability in both the longitudinal and latitudinal directions. Previous models have been averaged in the longitudinal direction and fractionation in the latitudinal direction only has been investigated, see, e.g. Scheringer (2008), Gouin and Wania (2007).

The authors present some important and interesting conclusions that result from using their 3D model.

The study is very interesting and has important conclusions. In principle, the article is fit for publication in ACP. However, the language and the grammar need to be substantially improved throughout the manuscript, and the quality of the graphics is fair at best. Therefore, I have to say that the manuscript requires a major revision before it can be published in ACP.

I would be happy to accept the manuscript for publication once the authors have addressed these issues.

Please see some specific comments below.

1. Methods

a. The modeling approach is sound and the authors appear to have a very good handle on the numerical/scientific system.

b. Page 6, line 9: A model validation is very quickly presented in the supplementary material. Model results are generally an order of magnitude greater than observations. Please state briefly in the text what makes the model results reasonable.

It is not true that model results are generally an order of magnitude greater than observations. Ground level atmospheric concentrations predicted for one central European station are in perfect agreement, a discrepancy of a factor of 5 is found for one northern European station, while a factor of about 10 is found for 4 other European stations (in England, Sweden, and continental Norway, Iceland) and 2 Arctic stations (see section S3).

2. Results and Discussion

The results are very interesting and are well presented and discussed.

Just a few points:

a. Page 11708, line 7: The northward shift of the COG Etc. Please expand on this statement.

Will be expanded and rephrased in the revised version (new text: "...corresponds and is determined by...")

b. Page 11709, 2nd sentence: 94-98% of Please provide a figure describing this

We considered but are declined not to illustrate this feature by a figure: A figure would not provide more information than the number stated in the sentence. Furthermore, now that the manuscript includes 8 figures, 4 more than previously, due to suggestions on the existing art work (see below), we believe that such an additional figure would not provide sufficient information to deserve a higher priority than the ones added.

c. Page 11709, 2nd paragraph: please expand further on why your ACP predictions can be expected to be an order of magnitude greater than those of Wania (2006).

The two models differ in many features and processes which determine large-scale transports: the atmospheric dynamics, its mean and its statistics is totally different (only so-called large-scale Eddy coefficients, monthly climatological mean values represent meridional transport times in GloboPOP), geographic explicitness is very different (there is no longitudinal resolution and only mean fractions of land and sea in GloboPOP, rather than air-surface exchange as influenced by land-use categories and meteorological and hydrological parameters), deposition

processes, their nature, mean and statistics are very different. Also, the spatial distribution of the emissions are not identical in the two models as we resolve a longitudinal distribution. In consequence, PCB cycling is more intense in the MPI-MCTM than in GloboPOP, i.e. secondary emissions and deposition fluxes are higher, in high latitudes more than in low latitudes, and, correspondingly, the substances undergo more cycles through the atmosphere (hops), which is enhancing the efficiency of the overall meridional transports.

Accordingly, text in the revised version significantly expanded.

d. 3.3 Page 11710-11714: The results are interesting but the results can read more like a reporting of numbers. Try to split it into more paragraphs and improve language and grammar, to read more easily, and make it flow more easily for you and the reader.

In the revised version this paragraph will be split into several sub-paragraphs (temporal trends, spatial trends) to improve its readability. Re-ordering will allow to shorten slightly (as now 1 sentence is a repetition, i.e. "Negative PCB trends in high latitudes are in general weaker than in low latitudes (Table 2)."). Language improved by rephrasing (e.g. last lines of p. 11710).

3. Conclusions

4.1., 2nd paragraph: There is no mention of ecosystems in the results and discussion (sedimentation is briefly mentioned). Please address this.

Ecosystems are, of course, influenced by spatial and temporal trends of pollutant mix, hence, fractionation. Partitioning of the more lipophilic PCBs into plankton (zoo- and phytoplankton) introduces them into (the base of) marine food chains. Via bioaccumulation and biomagnification concentrations in higher trophic levels can reach levels, hazardous for wildlife (Bignert et al., 1998; Borgå et al., Environ. Toxicol. Chem. 2010) and even humans (according to diets; AMAP assessment report, 2009). On the other hand, a higher fraction of lighter PCBs reaches remote regions such as the Arctic. This implies that ecosystems and habitats at different remote locations are exposed to different PCB mixtures. The significance of varying substance mixture on overall effects in wildlife is far from understood. These topics need to be studied in detail, but are out of the scope of the study presented in this manuscript.

Accordingly, the text in the conclusions section is in the revised version expanded by referring to fractionation in biota (including a reference to literature, i.e. Bignert et al., 1998) and its relevance for effects.

4. The abstract is OK but the language is vague.

Now rephrased to improve language and clarity.

5. The language needs to be improved somewhat throughout the manuscript. The grammar can be poor. Some sentences are poorly written, and many sentences are not sentences at all. For example:

a. Page 11699, beginning line 8: sentences beginning on lines 11, 12 and 13 start with They, their and it, respectively. This language gets vaguer with every sentence.

In the revised version rephrased to improve language and clarity: "Globally, secondary emissions (re-volatilisation from surfaces) are on the long term increasingly gaining importance over primary emissions. Secondary emissions are most important for congeners of medium hydrophobicity (5-6 chlorine atoms). Levels of these congeners are predicted to decrease slowest. Congeners' fractionation is characterized both geographically and temporally. Fractionation causes enrichment of the lighter, less persistent congeners and more delayed decreasing levels in high latitudes in response to decreasing emissions."

b. Page 11700, beginning line 11. This is not a sentence. Perhaps something is missing after 'transport'

In the revised version split into several sentences and rephrased to improve language and clarity: "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."

c. The passive form of verbs is often used when active form is correct, e.g. PCBs are undergoing Should be ... PCBs undergo; ... are migrating southward Should be ... migrate southward This reappears throughout the text, please change.

Agree, will be corrected

d. Page 11702, lines 13-16. This sentence is not clear.

In the revised version slightly rephrased to improve language and clarity (new text: "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).")

e. End of page 11702, line 27: this sentence is not clear. Do you mean of PCBs on their global ...

Yes, reads in the revised version: "...their global distribution"

f. Page 11703, lines 9-11. Please rewrite this sentence.

Will be slightly rephrased to improve language and clarity (new text: "The model results provide insights into spatially varying PCBs distributions' time trends and can be used to test the global distillation hypothesis")

g. Page 11704, lines 5-6 ... the one of this appears throughout the text. Replace with ... that of

Done in the following sentences: "As settling velocity that of detritus is adopted (Maier-Reimer et al., 2005).", "From land surfaces PCB101 re-volatilisation exceeds that of PCB153, and vice versa from sea surfaces (not shown).", "Congeners' order is somewhat reversed in the tropics (Fig. S3c), both on land and on sea (not shown), with PCB180's secondary emissions significance slightly exceeding that of PCB101."

h. Page 11706, lines 3-8: please rewrite this sentence.

In the revised version cut into several sentences and slightly rephrased to improve language and clarity: "At the end of the simulation, 2010, the centres of gravity (COGs; Leip and Lammel, 2004) of the lighter congeners' geographic burdens' distributions on land surfaces 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 (Tab 1)."

i. Be careful with articles (the, a); sometimes they appear when they shouldn't be there and vice versa.

Will be corrected (in the abstract and figure captions, besides other)

j. Page 11707: replace 'In consequence' with 'Consequently'; rewrite lines 15-20.

"in consequence" will be replaced.

Lines 15-20 shortened and slightly rephrased to improve language and clarity (new text: "In conclusion, different volatilisation/condensation and degradation among congeners, together with geospheric transports shapes 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. 3. 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) and slowest for PCB28 (shortest tair, Table S2)").

k. Page 11708, line 7. Please change the language 'goes in line' to , for example, 'is consistent with a decrease in the ...'

In the revised version rephrased to improve language and clarity (new text: "The northward shift of the COG in soils and vegetation corresponds to and is determined by a decrease of...")

l. Page 11708, line 21. Please change the word 'migrate' to something like 'advection'/'transport'/'flux'/'shift'

Changed ('shift')

m. Page 11709, line 19: 'The metrics are not'

In the revised version somewhat expanded to improve language and clarity

n. Page 11709, line 26: Please rewrite this sentence: 'The mean number' – bad grammar after the equation.

In the revised version rephrased to improve language (new text: "The mean number of hops nhop between atmosphere and surface compartments, i.e. the number of full deposition-(re-)volatilisation cycles, was derived following Gouin et al., 2004:

$$\text{nhop} = (\text{NSA} \times \text{NAS}) / (\text{NRS} \times \text{NRA} + \text{NRS} \times \text{NAS} + \text{NRA} \times \text{NSA}).$$

In the formula NSA denotes the volatilisation from all surfaces (soils, vegetation, ocean, snow, sea and land ice), NAS the deposition flux (dry and wet deposition of both gaseous and particulate phases), NRS the degradation in

surface media (soils, vegetation, and ocean including deep sea), and NRA the degradation in air (in t month-1 globally).”).

o. *Page 11714, line 13, new paragraph: ‘The model suggests ...’, no, ‘The model results suggest’*

In the revised version rephrased accordingly

p. *Page 11714: change the language of ‘the shares of PCBs ...’ to something like ‘The fraction of the various PCBs contained in the total mass’*

In the revised version corrected

These problems persist throughout the text.

6. *The figures are of poor quality and need to be improved. Specifically,*

a. *Fig 2 is illegible; I cannot read the legend and I cannot tell one line from another.*

In the revised version improved layout

b. *Titles, labels and axes in Fig 3 are illegible. Please put the figure over two pages. The blue lines are barely legible. In Fig 3b, I would like to see an extra set of black/grey figures showing the fraction of each of the PCBs in ocean, soil, vegetation, ice and snow (Perhaps you could colour it and divide each of the colours, one per PCB, into different shades for each of the compartments). Fig 3 could be also displayed over 2 pages.*

In the revised version improved layout: split into 2 figures, line bright rather than dark blue. Expansion of the previously lower panel of (previous) Fig. 3b: will be shown separately for ground compartments on land (= soil and vegetation surfaces, snow cover and ice) and on sea (= seawater and sea ice).

c. *Fig 4 is barely legible, see b. above.*

In the revised version improved layout: more compact, line bright rather than dark blue.

d. *Please be more careful and complete with figure captions. They are vague and sometimes poorly worded.*

I have also suggested the authors provide a few additional figures, since there are now only 4.

Former Fig. 3 split into 2 (now Figures 5-6) and former Figures S2, S3 and S4 (now Figures 1, 4 and 8, respectively) moved from supplementary information to main text.

7. *The reference list is excellent.*

Anonymous Referee #2

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Page 11702, lie 25 “*The trends observed at various Arctic sites are not in phase*”

Please explain the “Phase” you are taking about? Solid phase, liquid phase,

The term “in phase” refers to the temporal behaviour of the observed time series here. In the revised version this sentence will be rephrased:

Observations at Arctic sites do not follow the same temporal trend, however (Hung et al., 2010).

Page 11703, line 21-24 “*Besides transports, cycling of organic substances in the model world includes the compartments air (gas, aqueous and particulate phases), ocean (dissolved, colloidal and particulate phases), soil, vegetation surfaces, snow, sea and land ice.*” This sentence is unclear, is the transport not considered as the combination exchange between compartments and the compartment specific latitudinal (directed towards the poles)/ longitudinal movement? Maybe you mean “*Pollutant transport in the model world includes the compartments air (gas, aqueous and particulate phases), ocean (dissolved, colloidal and particulate phases), soil, vegetation surfaces, snow, sea and land ice*”

In the revised version this sentence will be rephrased (new text: “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 (advection and diffusive transport in atmosphere and ocean, degradation, phase partitioning) and inter-compartmental (deposition, gas exchange) processes.”)

Page 11705, line 2-4 “*To discern the impact of the physico-chemical properties on PCBs fate only, the four congeners were released into the environment using identical emissions*” please refer to Breivik et al (2007) as you are supposed to apply the PCB 153 emission distribution to your model (previously mentioned)

Agree, will be corrected.

Page 11705, line 13 “..distributions of the 4 PCB congeners (mapped for one. . .” Just a minor issue: I suggest to use either umber or letter format, not both in one sentence: suggestion “..distributions of the four PCB congeners (mapped for one. . .

Agree, “4 PCB congeners” will be replaced by “four PCB congeners”.

References to be considered as additional reference: Kallenborn R., M. Oehme, D.D. Wynn-Williams, M. Schlabach and J. Harris (1998) Ambient air levels and atmospheric long-range transport of persistent organochlorines to Signy Island, Antarctica.. The Science of the Total Environment, 220, 167-180

In the revised version this reference is included in the introduction and in the discussion (i.e. new sub-section 3.3.2 on spatial fractionation trends)