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Atmospheric Chemistry and Physics Discussions

Interactive comment on "GEM/POPs: a global 3-D dynamic model for semi-volatile persistent organic pollutants – Part 2: Global transports and budgets of PCBs" *by* P. Huang et al.

P. Huang et al.

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We would like to thank the anonymous reviewer for the detailed review of our manuscript which gives us the opportunity to clarify some points. In the following we quoted each review question in the square brackets and added our response after each paragraph.

General comments: ["The contribution(s) lack(s) essential parts: Some environmental compartments (media) are captured by the models and others not, but the requirements and possible consequences of omittances are not identified. The model is introduced in part 1 and applied in part 2. The limitations of the methodology (essential) are not discussed in part 1 and the discussion of the results of the model experiment

is very deficient (part 2, see below). The way the study is presented is generally poor. Part 1 is so deficient that the quality of part 2 can hardly be assessed. Some of the text of part 1 is repeated in part 2. A reason to split the paper into two parts is not obvious for this reviewer."]

We appreciate the comments on the components of this modeling system for PCBs. In the modeling community of POPs, processes that influence the atmospheric distributions are relatively well identified. In the development of a modeling system, the key processes and components are the first priority to be implemented. In the mean time, the schemes for those key processes and components have to be well developed and evaluated. This is the philosophy behind our development of GEM/POPs. We agreed with the reviewer that a rational and consequences of neglecting some environmental compartments (media) in our model should be discussed. Details will be given in a reply to the specific comments below.

Specific comments:

[Introduction (parts 1 and 2): Large-scale multicompartmental modelling was developed in parallel on the atmospheric community and 'box-type' modellers' sides (unlike stated by the authors). The first global model of the first type of models was Strand & Hov, Water Air Soil Poll. 1996, and should be named here. As the historically first 3D global model, Koziol & Pudykiewicz, 2001, was from the same institution than the presented model, it should be explained how these two models relate to each other or what the main differences are (compartments, resolutions, exchange processes, initialization data). The Max Planck model was published earlier, Semeena & Lammel, Fresenius Environ. Bull. 2003. In the next sentence it is claimed that 'box-type models' proved 'extremely useful (Eˇ) in demonstrating the grasshopper effect and cold condensation'. It seems, that the authors mix up key hypotheses and processes of global scale environmental chemistry such as 'cold condensation', 'global fractionation' and 'global distillation': The latter is a consequence of the combination of 'cold condensation' and other features. It was hypothesized by Goldberg, Proc. R. Soc. London

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1975, and Wania & Mackay, Ambio 1993. The latter and later papers, e.g. Calamari et al., Environ. Sci. Technol. 1991, Ockenden et al., Environ. Sci. Technol. 1998, suggested that observed latitudinal trends could be explained by the grasshopper effect. The first attempt to verify/falsify the hypothesis by modelling was Semeena & Lammel, 2005.]

We have revised the introduction section of Part 1. Following is added:

"There are two parallel modeling frameworks for studying environmental POPs. One type of them divides the globe or a specific region into a few climate zones (MacLeod, 2001; Toose et al., 2004; Wania and Mackay, 1995) with environmental compartments described in each zone. These models could be used to explore rates of global migration of POPs released in certain zonal bands to other latitudes and have been proven useful as a heuristic and policy tool in demonstrating the "grasshopper" effect. However, these (multimedia) models are less suitable to predict the detailed spatial and short-term variability in the distribution of a compound. To overcome the limitation of box-type models, dynamical 3-D models have been developed to describe the atmospheric transport of POPs on both regional (Ma et al., 2003; van Jaarsveld et al., 1997), hemispheric (Gusev et al., 2005; Hansen et al., 2005) and global scales (Koziol and Pudykiewicz, 2001; Semeena and Lammel, 2005; Strand and Hov, 1996). These models include meteorological parameters such as wind speed, temperature and precipitation rate in finer spatial and temporal resolutions for more accurate transport, chemical reactions and removal processes of POPs. Species that have been simulated in these models include PCBs, DDTs and HCHs."

[The statement that 'the investigation of the budgets and deposition patterns lacks in these 3D studies' is not true, cf. e.g. Malanichev et al. 2004, Shatalov et al. 2005, Semeena et al. 2006.]

We regretted that the reviewer did not cite the entire sentence of this statement but just portion of it. The original statement is "One thing that lacks in these 3-D model

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studies was the investigation of the budgets and deposition patterns of inter-continental transports of various semi-volatile POPs". The budgets and deposition patterns of inter-continental transports is the focus of this paper, which has been lack in previous studies. The paper by Malanichev et al. (2004) focused more on the Arctic regions.

[Presentation of the substances chosen (introduction of part 2): One substance is called volatile, two semivolatile. Why ? Substance properties, chemical formulae and degradation rates should be listed including references. Which uncertainties are coming with e.g. the choice / uncertainty of Henry coefficients (cf. Bruhn et al., Atmos. Environ. 2003) ?]

Strictly speaking, any substance shows some volatile features. The definition of volatile and semi-volatile is based on the vapour pressure of the substances. In order to avoid confusion, a table has been added in Paper 1 to summarize the key properties of the three PCBs.

[Methodology / model description: Several compartments are not mentioned (parts 1 and 2), namely vegetation, sediments, land and sea ice. If ignored, what is the consequence ? Why is this simplification considered to be justified ? These questions should be discussed in the context of earlier studies of PCB cycling (Dachs et al., Environ. Sci. Technol. 1999, Axelman & Broman, Tellus 2001, Malanichev et al. 2004).]

There were three compartments neglected in the current modeling system: vegetation, sediments and sea ice. Land was considered in the model. Section 2.4 in our part 1 has been added to address the issues.

"2.4 Other processes In addition to the processes described above, there are other environmental compartments that POPs will be portioned in such as vegetation, ice and sediments (Malanichev et al., 2004). According to Malanichev et al. (2004), the emissions and accumulations of various PCBs from sea-water and vegetation take only a very small fraction of the total PCBs in the environmental media while the soil compart-

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ment is the dominant PCB sources in 1995. Consequently, the sea-ice and vegetation compartments are neglected in the current version of GEM/POPs in terms of the accumulation of PCB masses in these compartments. However, the deposition of POPs into these compartments is accounted for as the dry deposition scheme differentiates different land use categories."

[Emissions: Are PCBs industrial chemicals only or are they also formed in combustion processes? Which sources are considered in the emissions? Why were these substances chosen? Obviously, physico-chemical properties, observation and emission data are needed for such a modelling exercise. These would have been available for some pesticides, while for the chosen substances the emission data are certainly less well known than for pesticides (despite significant efforts to narrow these uncertainties down).]

The emissions for PCBs are from both sources. For details, please see (Breivik et al., 2002a; Breivik et al., 2002b). The substances were chosen for this study to evaluate the performance of the GEM/POPs for some representative POPs from less volatile to volatile species. We agreed that there are other pesticides with better emissions but the choice of these PCBs is within the scope of our researches. It should be noted that the framework of GEM/POPs could be used for other POPs as well.

[Atmosphere: Dry deposition of gases is obviously not covered although it is considered to contribute significantly to the overall atmospheric removal of SOCs. Why? What is the consequence of this simplification? Gas/particle partitioning: The Junge-Pankow approach is very deficient for lipophilic compounds (cf. e.g. Finizio et al., 1997). Therefore, the parameterisation is severely limiting the applicability of the model for the chosen study. At least needed is a justification why the Junge-Pankow approach was chosen instead of a Koa approach. Conclusions on the role of aerosols on the cycling of the heavier PCBs are not possible. Wet deposition: snow is not mentioned. What does this mean: No snow in the model world or is scavenging by snow treated like in rain? Clouds, although filling large parts of the troposphere, are not mentioned. Again,

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what does this mean? No clouds in the model world ? Ocean: How many vertical levels have been considered in the model experiment? How are vertical transports associated with marine particulate matter treated? This question should be discussed in the context of earlier studies of PCB cycling, e.g. Dachs et al., Environ. Sci. Technol. 1999, Axelman & Broman, Tellus 2001, Malanichev et al. 2004.]

(1) Dry deposition

Dry deposition of gases PCBs is treated in this model implicitly by soil-atmosphere and water-atmosphere modules where the resistance of gases PCBs transferred through aerodynamic and laminar layers was calculated. According to Jurado et al (2004), air-water exchange dominates the dry deposition mechanism for PCBs. One simplification in the current approach was that only two land use types were considered: water and soil. This is consistent with the assumption that vegetation compartment was not considered a large source of PCBs and neglected in this model.

(2) Partitioning

The Junge-Pankow approach has been used extensively for PCB partitioning between gases and particulate phases and reasonable results have been achieved (Malanichev et al., 2004). It is based on the adsorption scheme. We agreed that if the aerosol has a surface coating of organic matter, the absorption is expected to play a role in the partitioning process. However, there was limited study on the difference between these two schemes when applied to PCB simulations. Clearly, the aerosol surface areas and the organic contents play a more dominant role in determining the fraction of PCBs in particulate phase. This is the advantage of this model which provides the dynamic aerosol surface areas.

(3) Wet deposition

First of all, the model has all the components that the reviewer mentioned: snow and clouds. For aerosol-bound PCBs, the removal process is treated along with aerosol

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particles which are subject to different scavenging schemes by rain and snow. Both in-cloud and below cloud scavenging of aerosol-PCBs were considered. We acknowledge that for the gaseous PCBs, only rain scavenging was considered in the current model. This should have an influence on the deposition of PCBs in the cold environment but not so much on global scale.

(4) Ocean

There are 31 vertical levels considered in the model experiment.

(5) Marine particulate matter was not treated in the current model.

[Model run initialisation: 'spin-up run', 'assimilated' should be explained for nonmodellers in the readership. The way observational data were assimilated should be detailed.]

The points are well taken. However, we cannot explain all the terms in a paper. Please find their explanations on the web site of American Meteorological Society (http://amsglossary.allenpress.com/glossary/) and the other books. However, we have added more details on the way observational data were assimilated in the part1.

[Comparison with observations: These results should be discussed in the context of the input data uncertainties. As it is probably covered by the emission uncertainties, a discrepancy of a factor of 10 does not indicate a disagreement. (?) Table 1 of part 1: soil types and soil levels should be addressed in the caption. Table 2 of part 2: is it measured or modelled? Drop two or more digits. Fig. 2 of part 1: Caption needs to identify the parameter (probably atmospheric ground level concentration). Drop 'master'. Fig. 4 of part 1: Replace 'fractionation' in the caption by what it is supposed to be]

Thanks. We have made the revisions accordingly.

[Results: The results' presentation in part 2 is limited to the PCB concentration fields produced in one model simulation. Most of the results presented on intercontinental

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transport are well known as given by the large-scale atmospheric transports controlling the global scale distribution of tracers. The relevant knowledge should be briefly presented with appropriate citations.]

As it is well known that the intercontinental transports are regulated by the large-scale atmospheric transports controlling the global scale distribution of tracers, we briefly presented the relevant knowledge on transport flux in section 3 as follows:

The global transports of PCBs are investigated based on the analyses of transport flux which is calculated in zonal and meridional components by multiplying PCB-concentration and zonal/meridional wind velocity components. Therefore positive (negative) transport flux components of PCBs indicate eastward (westward) transport in zonal direction or northward (southward) transport in meridional direction depending on the directions of wind velocity components. As a vector variable, transport flux is used to estimate the amount and direction of PCB transport in this section.

[Then the new, in particular the substance specific insights should be presented. How do these contrast with the distributions of conventional pollutants?]

The global transports of PCBs with following conclusions were presented in the abstract and section 3, which should be the specific insights for the PCB-transports in contrast to the transports of conventional pollutants:

Dominant pathways were identified for PCB transports in the atmosphere with a peak transport flux below 4 km and 6 km for gaseous and particulate PCB 180, 8 km and 14 km for gaseous and particulate PCB 28. The inter-continental transports of PCBs in the Northern Hemisphere are dominated in the zonal direction with their route changes governed by the seasonal variation of westerly jet. More gas for PCB28 and more particles for PCB180 were involved in LRT. The transport pathways from Europe and North Atlantic to Arctic contributed the most PCBs to Arctic. There were the important routines of inter-continental transports across Arctic in the Northern Hemisphere. The PCBs transported across the equator between both Hemispheres in three different

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flow-paths from three regions of Europe, Asia and North America, accompanying with easterly jet, Asian monsoon winds and trade winds. The PCBs from the Southern Hemisphere could export into the Northern Hemisphere.

[The study would greatly merit from discussing the results in the context of previous studies into PCB regional and global fate (e.g. Wania & Daly, Atmos. Environ. 2002). In Section 3.1 some findings are mixed with expectations in a confusing way. The vertical distributions of the tracers are a major asset of the study. It would greatly benefit from a table which quantifies the fractions accumulated above certain levels (including the tropopause).]

This is a good suggestion to compare with other studies of PCB budgets. However, it is rather difficult to compare with the results of other compartment models (e.g. Wania and Daly 2002) as the processes included in the models are very different. Furthermore, GEM/POPs is a 3-D dynamic model while box-type models do not yield the same spatial and temporal distributions. We have revised the manuscript trying to include results from other models but direct comparisons are not given.

To quantify the fractions accumulated above certain levels we have added a new table (table 3) in the new section 4.5 (vertical distributions of PCB burdens).

We have also added following discussion in section 4.5 and the corresponding summary in abstract:

Table 3 quantified the fractions of PCB burdens accumulated within boundary layer below 1 km, in the lower (1-6 km), upper (6-15 km) troposphere and the stratosphere over 15 km to the total loading in the atmosphere. For all three congeners, particulate PCBs concentrated in the higher levels than gaseous PCBs due to the more particle condensation in the cold air of higher levels. The lighter congener (PCB28) with more than half particulate PCB28 could reach up to the stratosphere, while the heavier congeners (PCB153 and PCB180) mostly stayed in the troposphere including boundary layer, and even more than 99% gaseous PCB180 were below 6 km in the lower levels.

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[The long-range transport potential is addressed, partly in quantitative terms. Movements, e.g. meridional in Section 3.1, however, are not quantified.]

Yes, the long-range transport potential is addressed, partly in quantitative terms. But movements in the meridional direction are quantified in Fig. 1h, 1f, 1g and 1h in Section 3.1.

[Migrations in degree north as a function of season and relative to the distributions of emission would be the adeaquate way. The last sentence of Section 3.1 addresses the very difference between environmental chemistry and passive tracer transport studies: It needs to be detailed and elaborated: which processes and properties favour which distribution trends ?]

In part 1 (section 2.2.4) of this paper, we presented the gaseous and particulate processes of PCBs. The differences of the chemical degradation and deposition between the different PCBs are shown in Table 2. This sentence was modified as:

“These differences in the PCB transport amounts and layers of lighter PCB28 and heavier PCB180 could be related with their magnitude of emission, chemical degradation, deposition (table 2) and the gaseous and particulate processes of PCBs(Gong et al. 2007).”

[The seasonal variations (end of Section 3.2) should be discussed in the context of the seasonal variations of the emission patterns.]

This is very good suggestion. We did try to find some relationship of the seasonal variations between transports and emission patterns. It is hardly to find any clue which connects seasonal variations of transports with seasonal variations of emission patterns directly and to draw some general conclusions, because the primary emissions, i.e. anthropogenic PCB emissions, are available in this study only as the annual emission data currently and air concentrations of PCBs are mostly controlled by the primary emissions (Harrad et al 1994, Jaward et al. 2004 and Hung et al. 2005).

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[Generally, as none of the common LRTP indicators are used, the results on LRTP cannot be used to compare with the results of other studies of the same substances or between substances.]

Yes, we did not discuss any LRTP indicators in this study. The long-range transport potential is addressed in quantitative terms in Section 3.1 as follows: The lighter PCB (i.e. PCB28) is transported with stronger westerlies at the higher layers than the heavier PCB (i.e. PCB180) at the lower layers, which implied that the lighter PCB exhibits a more LRT-potential than the heavier PCB.

[The long-range transport potential may be higher or lower but not 'more' (last sentence of abstract, part 2). It seems that a native speaking scientist and/or a professional language editor was not involved prior to submission, which is somewhat disappointing. Typos: 'behaviours', 'potentials', PM2.5 (use capitals), 'meridinal', 'metrological', 'over three following areas', many hyphens are misplaced many articles are lacking.]

Thanks for the reviewer. We have corrected the grammatical errors and typos mentioned above.

[Figure captions: units should be harmonized (g and s or kg and years). (a), (b) not visible in Fig. 3. Table 1 of part 2: Caption needs specifications: is it about fluxes ?]

Changes have been made.

Global budgets (Section 4 of part 2): The first sentence(s) of Section 4.1 should be part of a methodological section of the manuscript. The emission estimates' uncertainties should be quantified. The scenarios should be explained more detailed.

Yes. These have been addressed in the revised manuscript.

[More technical corrections: Sloppy written: Terminological and notation rules largely ignored and frequently poor grammar. Science communication requires to restrict to precise wording otherwise we are lost, which is what happens sometimes in this manuscript. The authors are advised to refer to accepted standard terminology (e.g.

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IUPAC, SI). Some examples for this type of weakness are: “physiochemical” and “physico/chemical” are there but none of these is an English word, sorry; “partition” is used as a verb, a noun and an adverb (please use “partitioning” as the noun exclusively in the title of 2.2.4 of part 1 and elsewhere); ‘ND’ should be replaced by upper bounds / limits of quantification in caption of table 1 of part 1 (cf. IUPAC rules); “exchange”, although bidirectional by definition, is used unidirectional, too (title of Section 2.2.3 in part 1); concentrations are formulated as C, as (x) (even in the same equation, i.e. (2) of part 1) and called either concentrations or loadings (the latter is not recommendable as used with different meanings in different sub-communities); two Henry coefficients are used (in Section 2.2.2 of part 1) of which only one is identified (as dimensionless) but not really told what it is standing for; “fraction” and “fractionation” are used often without telling what it is: quotient (of what?), spatial or temporal trend ? Section 4.2 of part 1 (in combination with Fig. 4) is titled ‘Fractionation of PCBs’ but there is no chance for the reader to guess what it is about. In this case it does not help that the introduction seems to refer to global fractionation, although without explicitly saying so (mixed up with cold condensation ? see above). Section 4.3 of part 1 refers to ‘spring’ - even in the tropics. The following sentence lacks any logic. The long-range transport potential may be higher or lower but not ‘more’ (last sentence of abstract, part 2), the tropics inner or outer but not ‘most’. Please accept that particles together with the gas-phase are the aerosol and that the atmosphere contains gas, particulate matter and cloud water and ice. Hence, the word aerosol should be used when both phases are meant, ‘particulate phase’ when the condensed phase is meant only. ‘particles of 79 kg’, ‘total gas of 148 kg’ is inacceptable. Please use ‘multicompartmental” instead of “multi-compartment”. English grammar: almost no sentence which is grammatically correct. It is also unclear whether it is meant to be British, American or an other variety of the language (e.g. usage of ‘vapour’ and ‘vapor’ in the same text). It seems that a native speaking scientist and/or a professional language editor was not involved prior to submission, which is somewhat disappointing. Typos: ‘behaviours’, ‘potentials’, PM2.5 (use capitals), ‘meridinal’, ‘metrological’, ‘over three following areas’, many hyphens

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are misplaced many articles are lacking.]

The grammatical and print errors above mentioned in this paper have been corrected.

Reference:

Breivik, K., Sweetmen, A., Pacyna, J. M. and Jones, K. C.: Toward a global historical emission inventory for selected PCB congeners - a mass balance approach, 1 - Global production and consumption. Sci. Tot. Env., 290, 181-198, 2002a. Breivik, K., Sweetmen, A., Pacyna, J. M. and Jones, K. C.: Toward a global historical emission inventory for selected PCB congeners - a mass balance approach, 2 - Emissions. Sci. Tot. Env., 290, 199-224, 2002b. Malanichev, A., Mantseva, E., Shatalov, V., Strukov, B. and Vulykh, N.: Numerical evaluation of the PCB transport over the Northern Hemisphere. Env. Poll., 128, 279-289, 2004.

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