

## ***Interactive comment on “PCBs in the Arctic atmosphere: determining important driving forces using a global atmospheric transport model” by C. L. Friedman et al.***

**C. L. Friedman et al.**

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Reviewer: Dear Ladies, Sirs, I apologise for my late reply. Here now my review on the paper "PCBs in the Arctic atmosphere: determining important driving forces using a global atmospheric model" which I read with great interest.

General comments 1.) The ability of PCB to cycle through different environmental phases is described. However, the importance of “lipophilicity” as inherent property required to follow the lipid transfer along the food web should be mentioned here as an important feature for the transfer along the Arctic food webs but in particular as prerequisite for the elevated levels found in indigenous people of the North like the

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Inuit heavily relying on local lipid rich (fatty) marine food sources (mentioned in the introduction).

Author response: We agree with the reviewer. In the first paragraph of the introduction, we have changed “Marine mammals bioaccumulate PCBs, and the traditional diets of the Arctic indigenous rely heavily on these animals” to “Because of their high lipophilicity, PCBs are readily accumulated by marine mammals, and the traditional diets of the Arctic indigenous rely heavily on these animals”.

Reviewer: 2.) The “differential removal hypothesis” postulated by “von Waldow and co-authors” (2010) does not exclude ambient temperature as important driving force for the global distribution of POPs but rather includes a new defined “gradient of remoteness” into the list of driving factors of global POP distribution. It should, thus, be rather considered as an extension of the global fractionation theory than as a competing theory, as explained here.

Author response: We agree with the reviewer and have changed the following passage: “A relatively new hypothesis, the “differential removal hypothesis”, challenges the global distillation hypothesis with an interpretation of observational and modeling data that accounts for the correlation between latitudinal temperature and remoteness. to say “expands on” rather than “challenges”. We have also changed the following sentence, originally:

“While the driving factor in PCB transport to the Arctic may be its remoteness rather than temperature fractionation, as suggested by the differential removal hypothesis, temperature nevertheless still plays a strong role in determining the environmental behavior of PCBs globally.”

to

“Whether or not remoteness is the primary driver of PCB transport compared to temperature fractionation, as suggested by the differential removal hypothesis, tempera-

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ture nevertheless still plays a strong role in determining the environmental behavior of PCBs globally.”

Reviewer: 3.) The importance of deposition processes is stressed in the here discussed study. Deposition from the atmosphere is considered a key-process for the here discussed “differential removal hypothesis”. In order to appreciate these deposition processes, please discuss and compare wet and dry deposition (gas- and particle phase) equally as important processes for the transfer of PCBs from the atmosphere into the bio- sphere supported and illustrated by the here chosen model approach. The deposition pathways for PCBs is obviously dependent on the degree of chlorination and, thus, the volatility and the ad-/absorptive interactions of the respective congeners with the par- ticulate/ aerosol phase. The implication of dry deposition (Gaseous ad particulate) is mentioned and discussed. However, wet deposition should also be considered and dis- cussed (since it is not mentioned here) in the model when discussing PCB deposition properties. Wet deposition is a strong seasonal feature in the Arctic where deposition occurs as rain during the short summer period and mainly as snow during the colder season (around August – Mai). The scavenging effect of snow has been identified earlier as important seasonal property for PCB deposition already (i.e., Gregor D.J., Gummer W.D. (1989) *Env. Sci. Technol* 23/5: 561-565 and Herbert B.M.J. et al (2005) *Env. Sci. Technol.* 39/9: 2998-3005 and many others).

Author response: We agree that snow scavenging been identified as an important process in the Arctic, though it is unclear whether scavenging during precipitation events or by the snowpack is more significant. The model estimates that wet deposition makes up only 5% (CB 138) to 14% (CB 28) of total deposition globally, and that >99% of wet deposition is of the gas phase (more than 99% of dry deposition is in the gas phase too). This trend holds if we look at the Arctic specifically; total dry deposition (gas and particle phase) can be orders of magnitude higher than wet deposition. In the model, this makes sense; KOW values for PCBs are quite high (~105 to 107), and since dry deposition is mediated by KOA while wet deposition is mediated by KAW, the overall

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preference is for PCBs to partition to octanol (i.e., the Earth's surface) versus precipitation (all other variables being constant). We did not state this in the original draft, however, and have done so now. We have added the following sentences to the end of the first paragraph in section 3.2 (Global atmospheric budgets and lifetimes):

“Wet deposition plays a relatively minor role in the global budget; wet deposition accounts for only 4% (CB 138) to 7% (CB 180) of total losses and only 5% (CB 138) to 14% (CB 28) of total deposition. More than 99% of wet deposition, for all congeners, is of the gas phase. This is true for the Arctic in particular as well.”

Reviewer: 4.) Please provide a list of abbreviations in the Supplementary material section

Author response: Done (see page S1).

Reviewer: 5.) Explain why PCB 28 (2,4,4'-trichlorobiphenyl, C<sub>12</sub>H<sub>7</sub>Cl<sub>3</sub>) and later PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl, C<sub>12</sub>H<sub>4</sub>Cl<sub>6</sub>) was selected as model congeners for the sensitivity simulations and discuss the strategy for the parameter tests (single parameter modifications and/or combined modifications) in detail in order to understand fully your research concept.

Author response: The reviewer is referring to two separate sections. The first refers to our choice of CBs 28 and 153 to make monthly/seasonal concentrations comparisons between the simulations and measurements. The second refers to our choice of CB 28 as a model congener for conducting sensitivity simulations.

To address the first, we have added a section to the Methods (2.2: Model evaluation). This is in addition to a short preamble we originally had and have retained at the beginning of the Results section (Section 3). This new methods section includes the following new text:

“We evaluate the performance of the model by comparing simulated interannual mean total (gas plus particle phase) concentrations to measured total concentrations at spe-

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cific sites globally, for all ICES congeners. We then compare the simulated total versus measured total seasonal average concentrations globally for CBs 28 and 153 from 1991 to 2010. We chose these two congeners for seasonal comparisons because they have been the focus of previous PCB work (e.g., Lamon et al., 2009) and because they span a wide range of volatilities.”

As well as text from our original submission that was previously in Results, but seems more appropriate here:

“Finally, we compare the monthly mean total concentrations and long-term monthly averages of these two congeners for sites representative of model skill at Arctic and remote mid-latitude measurement stations: Zeppelin (Norway), and Burnt Island (Canada), respectively. We choose Zeppelin as an Arctic representative site because of its extensive monitoring history (from 1998 onward), its high Arctic location (80 N), and because time series data from the only other station at such a high latitude (Alert, Canada) were affected by a laboratory switch in 2002 (Su et al., 2011). We choose Burnt Island because of its long monitoring history (since 1992), because its location is more distant from the mid-latitude/Arctic boundary (66 N) than European stations with similarly long monitoring histories, and because data was available for both CB 28 and 153.”

In each of our sensitivity simulations, only one process was modified at a time. We have added two sentences to the end of the first paragraph in section 2.3 stating this:

“In each of the 10 sensitivity simulations, only one process is modified at a time. By grouping the sensitivity simulations into categories, we aim to assess the relative importance of difference mechanistic and spatial drivers on Arctic atmospheric PCB concentrations.”

Reviewer: 6.) When discussing the influence of ambient temperatures on PCB re-emission and seasonal trends, the inverse correlation to degradation, specifically biotransformation (Arrhenius), of lower chlorinated congeners should not be neglected in

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such a scenario assessment.

Author response: The reviewer usefully points out that there is a direct relationship between temperature and degradation rates in all environmental media (the Arrhenius relationship), and that lower chlorinated congeners have faster degradation rates than higher chlorinated congeners. The impact of temperature on degradation rates depends primarily on the assumed activation energy; for all congeners we assume 10 kJ/mol in the air and 30 kJ/mol in all other media (provided in the SI). To clarify that our simulations do include temperature-dependent degradation of all congeners, and to address one of reviewer 1's concerns, we added the following sentence to the last paragraph in section 2.1:

“Degradation reaction rate constants in all environmental media are temperature dependent following the Arrhenius equation. Surface media half lives and molar masses were chosen to be consistent with those used in other modeling studies (Li et al., 2003; Mackay et al., 2006). Activation energies were also chosen to be consistent with previous PCB modeling studies (Gouin et al., 2013; Lamon et al., 2009). Details are presented in the SI.”

We also added the following sentence to the sensitivity simulations section in the methods (last paragraph of section 2.3), to clarify that though both re-emissions and degradation can be significantly impacted by temperature, we have only manipulated the former:

“We note that while several of our sensitivity simulations address the impact of temperature on both primary and secondary emissions (e.g., ML2), as well as gas-particle partitioning (e.g., RT4), degradation of PCBs is impacted by temperature changes as well (via the Arrhenius equation). We did not explicitly test the impact of changes in degradation parameters in this study.”

Reviewer: 7.) How is the meteorology, and specifically the location of the “Polar Front system”, reflected in the here discussed seasonal PCB distribution patterns? As the

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lack of significant primary PCB emissions is postulated, the seasonality of the direct atmospheric transport into the Arctic should not be dependent on the position of the Polar front system (meteorological barrier) and, thus, the seasonality of LRTAP should be weakened (which is obviously not the case here).

Author response: The polar front moves toward the poles in the summer and toward the mid-latitudes in the winter. If primary emissions were indeed important in the Arctic, as we suggest may be the case, one might hypothesize that little seasonality would be observed due to this polar front behavior, when instead what we see is higher summer time concentrations in the observations and low summer concentrations in the model. For our sensitivity simulations, however, we are evaluating the Arctic as a whole and we see little evidence of impact from the polar front (this was the case for PAHs as well, where winter time concentrations were also higher than summer). Though the polar front will impact distinct Arctic stations differently, for our model evaluation in the Arctic we look at only one site in particular (the comparisons at Zeppelin for CBs 28 and CBs 153; Figs 3 and 4). Since we see different degrees of seasonal mismatch (for CB 153 the mismatch is not quite as drastic; in fact, the long-term averages suggest a positive linear correlation) and given that the polar front is captured by our use of assimilated meteorological data and both congeners are subject to the same meteorological behavior, the difference in seasonal mismatch is more likely due to a difference in physicochemical properties rather than a meteorological factor. We now point out, however, that the polar front may be a significant factor in deviations between specific Arctic stations, as has been found in previous studies (e.g., Kallenborn et al., *J. Environ. Monit.*, 2007, 9:1082) in the seventh paragraph of the discussion, where we discuss the potential role of primary emissions on overall concentrations in the Arctic:

“The polar front, which moves toward the poles in the summer and toward the mid-latitudes in the winter, has been implicated as a factor in deviations in PCB concentrations measured at distinct Arctic stations (Kallenborn et al., 2007); however, it does not appear to play a large role in simulated average Arctic PCB concentrations.”

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Reviewer: 8.) Similar model based simulations were conducted earlier also for PCBs in the Arctic atmosphere. It would therefore be worth considering a critical comparison with earlier investigations such as the recent paper by Octaviani M., Stemmler I., Lamme G., Graf H.F. (2015) *Env. Sci. Technol.* 49/6: 3593-3602, and an older study by Armitage J.M., Wania F. (2013) *Environ. Sci. Processes Impacts* 15:2263-2272 where also the role of the (organic) particulate phase in LRTAP into the Arctic atmosphere is discussed.

Author response: It is difficult to compare our results directly to these papers for the following reasons: the Octaviani paper looks explicitly at the impact of climate change on PCB fluxes into the Arctic (i.e., future compared to past), with no model evaluation against measurements for the present day, and the Armitage paper uses a fugacity model with coarser spatial and temporal resolution to predict the impact of climate change on hypothetical chemicals. Thus, we cannot directly compare simulated PCB concentrations. Each study does indeed contain information relevant to our study, however, so we have cited both in the revision. Octaviani et al. found that the seasonal dependency of PCB transport into and out of the Arctic depended on which region of the Arctic was being considered, a result that is very relevant to our finding of average Arctic wintertime highs and summer time lows. Armitage et al. found that particulate organic carbon in the Arctic Ocean may be one of the most important factors in controlling the concentrations of hydrophobic organic chemicals under climate change. We have incorporated a reference to the Octaviani paper into the first paragraph of the discussion:

“The model reproduces absolute concentrations of PCBs globally across congeners and simulates observed mid-latitude seasonal cycles with accuracy. However, the simulation predicts opposite seasonal cycles (high in winter, low in summer) compared to observations at Arctic stations for the more volatile PCBs. This is somewhat consistent with a modeling study by Octaviani et al. (2005) who showed that the highest flux of PCBs into the Norwegian Arctic occurs during the fall season (September-October-

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November) and the minimum occurs during the summer (June-July-August).”

and we have incorporated a reference to the Armitage paper into our discussion of the unlikelihood of high secondary emissions from the Arctic Ocean under future climate (second to last paragraph of discussion):

“Combined with evidence of increasing primary productivity and carbon export to sediments with climate change, the authors concluded a significant flux of PCBs out of the Arctic Ocean with warmer temperatures is unlikely; rather, it was suggested that net uptake from the atmosphere will increase in importance with changing climate. This is consistent with a study by Armitage and Wania (2013), who found that increases in particulate organic carbon in the Arctic Ocean may be one of the most important factors in controlling the concentrations of Arctic POPs under future climate.”

Reviewer: Detailed Comments P30858/L24 “Consequently, their production was banned internationally when the Stockholm Convention was adopted (2001) and entered into force (2004).” This postulate is not entirely correct! The international regulation and ban of PCBs started in the early 1970s already by the official regulation of the US and EU legislation. PCBs as environmental pollutants were, however, adopted and implemented by Stockholm convention and, thus, recognized as global pollutants. Please consider revision.

Author response: We have changed the original sentence referenced above to: “Consequently, their production was banned by national actions as early as the 1970s. Under the global Stockholm Convention, which entered into force in 2004, parties committed to eliminate PCB production.”

Reviewer: P30865/L 10 “The fraction of snow/ice in a grid box is estimated by adding the fractions of snow, sea ice, and land ice (provided by meteorological data)” Please provide information about the origin of this information or refer to an appropriate publication.

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Author response: Details on the fractionation of grid boxes into different land types for the GMAO MERRA dataset, and how it compares to previous data sets (namely, GEOS5), can be found in this document: [http://gmao.gsfc.nasa.gov/products/documents/MERRA\\_File\\_Specification.pdf](http://gmao.gsfc.nasa.gov/products/documents/MERRA_File_Specification.pdf). We have now supplied this link in the sentence pointed to by the reviewer.

Reviewer: Final recommendation: I, thus, recommend the here submitted and discussed manuscript for publication in “Atmospheric Chemistry and physics” after

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 30857, 2015.

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