

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

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Reviewer comments are shown below, first, with author responses following.

Reviewer: General comments Friedman and Selin have made a model study using an adjusted version of the global atmospheric transport model GEOS-CHEM to study the most important drivers of Arctic atmospheric concentrations of seven PCB congeners. The authors describe the new model version with a comprehensive and thorough supplementary material, although three references are not cited in the main manuscript. The model set-up is well described and the scientific methods and assumptions are valid and clearly outlined. The results are generally sufficient to support the interpre-

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tations, although some of them could be discussed in more detail. Substantial conclusions are reached and the study is in general transparent and traceable. The title clearly reflects the contents of the paper and the abstract provides a concise and complete summary. The manuscript is well structured and clear and the language fluent and precise. Proper credit is given to related work. A similarly thorough model sensitivity analysis of the most important processes determining the atmospheric transport of PCBs to the Arctic has not been published previously, and the manuscript provides valuable new insight within the field. I think this will be of great interest to the readers of Atmospheric Chemistry and Physics and I suggest to publish the manuscript subject to minor revisions. I have added a few specific comments below that the authors should take into account in their revised manuscript.

Specific comments Partitioning to particles Page 30862, line 17-18: “there is no such conclusive evidence that PCBs adsorb more strongly to BC than they do to OM”. Has this been investigated and can the authors supply references for this claim? If not, please discuss why you expect PCBs to behave differently to PAHs with respect to adsorption to BC. This is mentioned again on page 20870, line 21.

Author response: This has been investigated in the marine sediment environment with respect to assessing risks posed by highly contaminated sites, but to our knowledge, it has not been investigated explicitly in the atmosphere. The marine sediment literature suggests that while there may be enhanced PCB adsorption to BC compared to absorption into OM, that it is primarily only for planar, dioxin-like PCB congeners (i.e., non-ortho substituted congeners) and that it is not to the same degree as the sorption of PAHs to BC. All of the congeners we simulate are ortho-substituted (non-planar). We have revised the line quoted above to add more detail and point readers to the specific literature that led us to omit adsorption to BC from the PCB model:

“While PAHs have been shown to adsorb strongly to BC in the field (e.g., Accardi-Dey and Gschwend, 2002; Arp et al., 2008; Lohmann et al., 2005), and modeling studies have suggested PAH association with BC particles can explain LRT patterns (Fried-

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man et al., 2014a), literature from contaminated marine sediment studies suggests enhanced sorption to BC occurs primarily for non-ortho substituted PCB congeners (i.e., those that assume a planar conformation; (Cornelissen et al., 2005; Koelmans et al., 2006)), which we do not simulate here. Furthermore, in contrast to PAHs, there is little evidence directly from the atmospheric literature to suggest PCBs show enhanced sorption to BC compared to OM (Arp et al., 2008)."

The Cornelissen and Koelmans papers discuss the effect of BC on the sorption of different types of hydrophobic contaminants, while the Arp et al. paper demonstrates that the aerosol partitioning of many POPs, with the exception of PAHs, can be reasonably estimated with a polyparameter linear free energy relationship that is largely based on the hexadecane-air partition coefficient (which is similar to the octanol-air partition coefficient, which we use).

Reviewer: I think there may be a general problem with the parametrization of the gas-particle partitioning in the model, where the fraction sorbed to particles appears to be quite low (0.02

Author response: We agree with the reviewer that for CB180, at least, there is a discrepancy between our model results for the particulate fraction versus the measurements from the cited studies (CB28 compares well). However, we do not believe there is a problem with the parameterization. The discrepancy is likely due to a combination of factors: 1. Gas-particle partitioning model: The gas-particle partitioning model within GEOS-Chem is, by default, an equilibrium partitioning model. We have shown in previous work (Friedman, Pierce, and Selin, 2014 EST, 48:3293), with PAHs at least, that other models fit observed data better; however, there is very little empirical experimental data to support the wide-spread use of alternative models. For example, for PAHs, we took results from a single laboratory study looking at the entrapment of PAHs in secondary organic aerosols (SOA) and embedded it in the model. We were able to show that while PAHs likely do not become entrapped in SOA, they may, however, become entrapped in BC and slowly desorb as they travel. It is possible that

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regardless of whether PCBs travel in/on SOA, OM, or BC, they also follow an "entrapment and slow release" ab/adsorption model, versus an equilibrium model. This would lead to higher particulate fractions than the results we have here. However, there are no such laboratory experiments for PCBs or evidence that PCBs adhere strongly to BC the way PAHs do (see above), so we have maintained the default partitioning model in this study. 2. Comparison of a global average to urban measurements: particulate fractions reported here are global averages. There are indeed higher particle phase fractions in urban areas in the model, but they are masked by these averages. Our understanding is that attributing total POP concentrations to particulate versus vapor phases at remote locations is usually not possible because of the very high vacuum pump flow rates and long sampling times required for a detectable signal, which result in blow-off from the filter into the PUF. Therefore, we make comparison of total PCB concentrations the focus of our model-measurement evaluation.

Since gas-particle speciation is not a focus of this paper, total PCB concentrations compare well, and because we have conducted extensive particle phase/partitioning sensitivity studies previously (see paper mentioned above as well as sensitivity simulations regarding the temporal resolution of aerosols in Friedman, Zhang, and Selin, EST 2014, 48:429-437 (using daily average aerosol concentrations instead of monthly averages only changed PAH concentration by less 1

To address the reviewer's concerns, we now include the following text to give readers more insight into these thoughts and comparisons:

In section 3.2, second paragraph: "While these fractions are low compared to measured PCB particulate fractions, especially for the heavier congeners like CB180, most measurements of particulate fractions are in urban areas (e.g., Simcik et al., 1998); the fractions we report here are global averages and are thus lower than particulate fractions found near urban locations."

and in the third paragraph of the Discussion:

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“Also, model particulate fraction results are biased low for the higher molecular weight congeners compared to measurements; a greater fraction of PCB in the particulate phase may reduce the overall mass lost from oxidation”

Reviewer: Other specific comments Page 30868, second paragraph/Table 3. I think the statistics should be revised in this section. What is of interest in a model evaluation is how well the predicted concentrations fit to the measured concentrations on a 1:1 line. Instead the authors show the best possible linear fit, which is of no use in the interpretation of the results unless discussed further. This results in larger correlation coefficients than with a 1:1 fit. I therefore suggest that the authors replace the calculated correlation coefficients with a fit to the 1:1 line and also include a proper calculation of the bias and/or the mean error. This will improve the interpretation of how well the model predicts atmospheric concentrations. Please also specify if this is seasonal mean or monthly mean.

Author response: We have now included a calculation of the mean bias and root mean square error in Table 3. We feel, however, that showing plots of each linear correlation for the annual means takes up valuable space, and in their absence the presentation of the equation of linear best fit gives an approximation of the fit to a 1:1 line. Deviations in the slope from one and the intercept from zero provide the reader with an estimation of how closely the modeled and measured concentrations match on average. Further, Fig. 2 provides a fit to a 1:1 line for CBs 28 and 153 (the two congeners we look at in the most detail), and is generally representative of the degree of fit for the other congeners as well. Though the Pearson correlation coefficient (r) doesn't provide a measure of how well the data corresponds to a 1:1 line, it does provide a measure of how well the model is able to reproduce variability seen in the measurements, which is critical for evaluating a model that includes meteorology since the assumption is that the meteorology will enhance that capability – and it does – see Fig. 2 and our comparison to the BETR-Global model, which does not use assimilated met data, in the results. We've added discussion to this end at the end of section 3.1.1:

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“Pearson correlation coefficients, which provide a measure of how well the model is able to reproduce variability in the measurements, range from 0.53 (CB 118) to 0.75 (CBs 180). There was no systematic bias in the model with congener volatility. Slopes and intercepts of linear best fit equations range from 0.17 to 1.15 and 0.07 to 1.28, respectively, indicating measured and modeled data are well within an order of magnitude of one another.”

The discussion of Table 3 takes place in the “Annual mean concentrations” section of the results (Section 3.1.1). To further clarify that these are annual means, we have added “annual” to this sentence in that section:

“Table 3 provides linear relationships and correlations between simulated and observed mean annual concentrations for all NH non-urban locations (i.e., NUML + Arctic sites), with Pearson correlation coefficient (r) values ranging from 0.55 (CB 118) to 0.77 (CBs 153 and 180).”

and included the word “annual” in the caption of Table 3.

Reviewer: Page 30869, line 24 and Page 30870, line 1: It is not quite clear to the reader that the “temporal average” in this case refers to the “monthly concentrations averaged over time” like in the previous paragraph. Please specify this.

Author response: We have changed “temporal average” to “monthly concentrations averaged over time” in both instances.

Reviewer: Figure 3 4. It is interesting to note that there is a clear decreasing trend in the simulated monthly concentrations of CB 28 at both sites that appear to be declining more rapidly than the observations. The results for CB 153 (Figure 4) show the same pattern although as clear. Please comment on this (something with the emission input?).

Author response: This effect is most likely related to emissions. The emissions profile shows a fairly linear decrease from year-to-year after the 1970s that is mirrored in the

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concentrations results. We also add “The model also reproduces the slow decline in concentrations observed in the measurements, though in the case of CB 28 at a slightly faster rate; this rate is primarily dictated by the rate of decline in primary emissions.” to the third paragraph in section 3.1.2.

Reviewer: Table 2. Another interesting result that is not discussed is the similar Sim/Obs ratios for the Arctic and the NUML sites as well as for the Antarctic site, with higher simulated mean concentrations for CB 28 and 118 and lower for the other congeners. This could also be related to the emission input. Please comment on this.

Author response: This is indeed an interesting result, and we are not able to definitively diagnose why CB28 and CB118 are consistently greater than one while the others are less than one. It may have to do with high estimates for CB28 and CB118 emissions compared to other congeners, but it is difficult to test that. There is no particular physicochemical characteristic of these two congeners compared to the others that would set them apart. Given that these are means of annual means and in some cases across a large spatial range, there is considerable uncertainty surrounding the exact value of the ratio. We have addressed this comment by pointing out the result as well as the uncertainty surrounding the ratios in the first paragraph of section 3.1.1:

“Simulated to measured ratios for CB 28 and CB 118 are greater than one for all locations while for all other congeners the ratio is consistently less than one, though there is substantial uncertainty in these values given that they are spatial and temporal averages.”

Reviewer: There are 3 references in the supplementary material that are not cited in the main manuscript (Gouin et al., 2013; Li et al., 2003; Mackay et al., 2006). Proper credit should be given to these studies.

Author response: We have added this statement to the end of methods section 2.1 to cover the above-mentioned citations that didn't quite fit with descriptions in previous paragraphs: “Degradation reaction rate constants in all environmental media are

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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.”

Reviewer: Technical corrections Page 30868, line 18: Please insert “seasonal” into this sentence: “. . .the model predicts seasonal observed concentrations. . .”

Author response: Done.

Reviewer: Page 30869, line 22: Please change “minimum” to “maximum” and vice versa. Table 2, line 3: Please insert (NUML): “. . .and non-urban mid-latitude (NUML) sites. . .”

Author response: We thank the reviewer for catching these errors. The suggested changes have been made.

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

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