1   Response to reviewer comments
2   Author responses are shown in red.

3   <u>Reviewer 1</u>

4   General comments

5   Friedman and Selin have made a model study using an adjusted version of the global
6   atmospheric transport model GEOS-CHEM to study the most important drivers of Arctic
7   atmospheric concentrations of seven PCB congeners. The authors describe the new model
8   version with a comprehensive and thorough supplementary material, although three
9   references are not cited in the main manuscript. The model set-up is well described and the
10   scientific methods and assumptions are valid and clearly outlined. The results are generally
11   sufficient to support the interpretations, although some of them could be discussed in more
12   detail. Substantial conclusions are reached and the study is in general transparent and
13   traceable. The title clearly reflects the contents of the paper and the abstract provides a
14   concise and complete summary. The manuscript is well structured and clear and the
15   language fluent and precise. Proper credit is given to related work.

16   A similarly thorough model sensitivity analysis of the most important processes
17   determining the atmospheric transport of PCBs to the Arctic has not been published
18   previously, and the manuscript provides valuable new insight within the field. I think this
19   will be of great interest to the readers of Atmospheric Chemistry and Physics and I suggest
20   to publish the manuscript subject to minor revisions. I have added a few specific comments
21   below that the authors should take into account in their revised manuscript.

22   Specific comments

23   Partitioning to particles

24   Page 30862, line 17-18: "there is no such conclusive evidence that PCBs adsorb more
25   strongly to BC than they do to OM". Has this been investigated and can the authors supply
26   references for this claim? If not, please discuss why you expect PCBs to behave differently to
27   PAHs with respect to adsorption to BC.

28   This is mentioned again on page 20870, line 21.

29   This has been investigated in the marine sediment environment with respect to assessing
30   risks posed by highly contaminated sites, but to our knowledge, it has not been investigated
31   explicitly in the atmosphere. The marine sediment literature suggests that while there may
32   be enhanced PCB adsorption to BC compared to absorption into OM, that it is primarily only
33   for planar, dioxin-like PCB congeners (i.e., non-ortho substituted congeners) and that it is
34   not to the same degree as the sorption of PAHs to BC. All of the congeners we simulate are
35   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 (Friedman 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).

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%-1.4%). Although the particle fraction of PCBs has not been reported in any model studies, this has been studied in several measurement experiments, e.g. Simcik et al., ES&T, 32, 1998 reported particle fractions of 0.2%-0.7% for CB 28 and 5%-10% for CB 180 in July for Lake Michigan, depending on the wind direction, 1.1%-1.4% and 16.2%-21.2% for the two congeners in July and 2.9% and 49.4% in January in Chicago. Lohmann et al., ES&T, 34, 2000, reported PCB particle concentrations up to 70% for an urban site in the UK during winter, and in a more recent study Li et al., Aerosol and Air Quality Research, 15, 2015 reported 6-44% in Tianjin, China. The higher fractions for the urban site can be due to larger particle concentrations in the urban area, which is not reflected in the GEOM-CHEM model due to the spatial resolution, but even at the remote sites the measured fractions are well above the modelled fractions in this study. A larger particle phase fraction will also influence the loss from oxidation due to the neglected particle phase oxidation (the discussion on page 30874, second paragraph). Please comment on this, and if possible, introduce a sensitivity study of the effect of gas-particle partitioning in the model.

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 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, ES&T 2014, 48:429-437 (using daily average aerosol concentrations instead of monthly averages only changed PAH concentration by less ~1% at most)), we have not included a sensitivity study here.

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: "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"

Other specific comments

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

10 We have now included a calculation of the mean bias and root mean square error in Table 3.
11 We feel, however, that showing plots of each linear correlation for the annual means takes
12 up valuable space, and in their absence the presentation of the equation of linear best fit
13 gives an approximation of the fit to a 1:1 line. Deviations in the slope from one and the
14 intercept from zero provide the reader with an estimation of how closely the modeled and
15 measured concentrations match on average. Further, Fig. 2 provides a fit to a 1:1 line for
16 CBs 28 and 153 (the two congeners we look at in the most detail), and is generally
17 representative of the degree of fit for the other congeners as well. Though the Pearson
18 correlation coefficient (r) doesn't provide a measure of how well the data corresponds to a
19 1:1 line, it does provide a measure of how well the model is able to reproduce variability
20 seen in the measurements, which is critical for evaluating a model that includes
21 meteorology since the assumption is that the meteorology will enhance that capability –
22 and it does – see Fig. 2 and our comparison to the BETR-Global model, which does not use
23 assimilated met data, in the results. We've added discussion to this end at the end of section
24 3.1.1:

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

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

33 "Table 3 provides linear relationships and correlations between simulated and observed
34 mean annual concentrations for all NH non-urban locations (i.e., NUML + Arctic sites), with
35 Pearson correlation coefficient (r) values ranging from 0.55 (CB 118) to 0.77 (CBs 153 and
36 180)."

37 and included the word "annual" in the caption of Table 3.

4

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.

We have changed "temporal average" to "monthly concentrations averaged over time" in both instances.

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?).

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 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.

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.

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."

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.

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:

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

7   Technical corrections
8   Page 30868, line 18: Please insert "seasonal" into this sentence: ". . .the model predicts
9   seasonal observed concentrations. . ."

10   Done.

11
12   Page 30869, line 22: Please change "minimum" to "maximum" and vice versa.
13   Table 2, line 3: Please insert (NUML): ". . .and non-urban mid-latitude (NUML) sites. . ."

14   We thank the reviewer for catching these errors. The suggested changes have been made.

15

16

17   Reviewer 2

18   Reviewer: Dear Ladies, Sirs,

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

22   General comments

23   1.) The ability of PCB to cycle through different environmental phases is described.
24   However, the importance of "lipophilicity" as inherent property required to follow the lipid
25   transfer along the food web should be mentioned here as an important feature for the
26   transfer along the Arctic food webs but in particular as prerequisite for the elevated levels
27   found in indigenous people of the North like the Inuit heavily relying on local lipid rich
28   (fatty) marine food sources (mentioned in the introduction).

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

6

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, temperature 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; K_{OW} values for PCBs are quite high ($\sim10^5$ to 10^7), and since dry deposition is mediated by K_{OA} while wet deposition is mediated by K_{AW}, the overall 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, C12H7Cl3) and later PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl, C12H4Cl6) was selected as model congeners for the sensitivity simulations and discuss the strategy for the parameter tests (single pa- rameter 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 specific 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 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 2's concerns, we added the following sentence to the last paragraph is 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 lack of sig- nificant 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."

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., Lammel 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-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

1   P30858/L24 "Consequently, their production was banned internationally when the

2   Stockholm Convention was adopted (2001) and entered into force (2004)." This pos- tulate

3   is not entirely correct! The international regulation and ban of PCBs started in the early

4   1970s already by the official regulation of the US and EU legislation. PCBs as environmental

5   pollutants were, however, adopted and implemented by Stockholm convention and, thus,

6   recognized as global pollutants. Please consider revision.

7   Author response: We have changed the original sentence referenced above to:

8   "Consequently, their production was banned by national actions as early as the 1970s.

9   Under the global Stockholm Convention, which entered into force in 2004, parties

10   committed to eliminate PCB production."

11   Reviewer: P30865/L 10 "The fraction of snow/ice in a grid box is estimated by adding the

12   fractions of snow, sea ice, and land ice (provided by meteorological data)" Please provide

13   information about the origin of this information or refer to an appropriate publication.

14   Author response: Details on the fractionation of grid boxes into different land types for the

15   GMAO MERRA dataset, and how it compares to previous data sets (namely, GEOS5), can be

16   found in this document:

17   http://gmao.gsfc.nasa.gov/products/documents/MERRA_File_Specification.pdf.

18   We have now supplied this link in the sentence pointed to by the reviewer.

19   Reviewer: Final recommendation: I, thus, recommend the here submitted and discussed

20   manuscript for publication in "Atmospheric Chemistry and physics" after major revi- sions,

21   for details please see above.

22

23

PCBs in the Arctic atmosphere: Determining important driving forces using a global atmospheric transport model

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Abstract

We present a spatially and temporally resolved global atmospheric PCB model, driven by meteorological data, that is skilled at simulating mean atmospheric PCB concentrations and seasonal cycles in the northern hemisphere mid-latitudes, and mean Arctic concentrations. However, the model does not capture the observed Arctic summer maximum in atmospheric PCBs. We use the model to estimate global budgets for seven PCB congeners, and demonstrate that congeners that deposit more readily show lower potential for long-range transport, consistent with a recently-described "differential removal hypothesis" regarding the hemispheric transport of PCBs. Using sensitivity simulations to assess processes within, outside, or transport to the Arctic, we examine the influence of climate- and emissions-driven processes on Arctic concentrations and their effect on improving the simulated Arctic seasonal cycle. We find evidence that processes occurring outside the Arctic have a greater influence on Arctic atmospheric PCB levels than processes that occur within the Arctic. Our simulations suggest that re-emissions from sea ice melting or from the Arctic Ocean during summer would have to be unrealistically high in order to capture observed temporal trends of PCBs in the Arctic atmosphere. We conclude that mid-latitude processes are likely to have a greater effect on the Arctic under global change scenarios than re-emissions within the Arctic.

1 Introduction

Polychlorinated biphenyls (PCBs) are chemicals that were manufactured for industry beginning in the 1930s (Breivik et al., 2002). Since the peak of their manufacture and use, PCBs have been shown to be toxic, bioaccumulative, persistent, and travel long distances in the environment. 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. PCBs continue to pose health risks,

1 however, because of their recalcitrance and ability to cycle through environmental phases.

2 Indigenous peoples and top marine predators in the Arctic are especially exposed to health

3 risks from PCBs. Because of their high lipophilicity, PCBs are readily accumulated by marine

4 mammals, and the traditional diets of the Arctic indigenous rely heavily on these animals.

5 The surprisingly high body burdens in indigenous populations, given that PCBs generally

6 were not used in the region, were first documented in the literature decades ago (e.g.,

7 Dewailly et al., 1989). However, there remain important uncertainties about the driving

8 factors of Arctic concentrations, particularly in the context of reduced primary production

9 and changing climate. Here, we use a chemical transport model to assess factors affecting

10 the long-range atmospheric transport of PCBs to the Arctic.

11 Evidence of long-range atmospheric PCB transport to the Arctic from the Northern
12 Hemisphere mid-latitudes, where their manufacture and use was concentrated, has been
13 well-documented (e.g., Hung et al., 2001, 2005, 2010). The warmer temperatures of the
14 mid-latitudes facilitate PCB volatilization and their subsequent transport via the
15 atmosphere to the Arctic. Several hypotheses have been proposed to mechanistically
16 describe the transport process and the observed global fractionation of PCBs. The most well
17 known is the "global distillation hypothesis" (Wania and Mackay, 1993, 1996), whereby
18 PCBs and other persistent organic pollutants (POPs) fractionate globally along a latitudinal
19 temperature gradient depending on their volatility, similar to a gas chromatographic
20 separation. A relatively new hypothesis, the "differential removal hypothesis", expands on
21 the global distillation hypothesis with an interpretation of observational and modeling data
22 that accounts for the correlation between latitudinal temperature and remoteness. This
23 latter hypothesis proposes that the observed global fractionation of PCBs is due primarily to
24 different loss rates that act along a gradient of remoteness from emission source, rather
25 than temperature differences (von Waldow et al., 2010).
26 Whether or not remoteness is the primary driver of PCB transport compared to
27 temperature fractionation, as suggested by the differential removal hypothesis,
28 temperature nevertheless still plays a strong role in determining the environmental
29 behavior of PCBs globally. Higher temperatures lead to greater fractions of PCBs in the
30 atmospheric gas phase versus the particle phase (which alters overall loss rates), and a shift
31 in partitioning between other environmental media (including increased fluxes from
32 surface media to the atmosphere). Temperature can also affect emissions, including both
33 primary and secondary emissions (i.e. revolatilization of previously deposited PCBs from
34 surface phases), and degradation rates (Hansen et al., 2015; Lamon et al., 2009;
35 Wornschimmel et al., 2013). For this reason, the impact of global climate change on the
36 environmental cycling of PCBs has received much interest. Results from a number of recent
37 modeling studies collectively suggest that predicted climate change will affect atmospheric
38 PCBs by roughly a factor of two (Hansen et al., 2015; Lamon et al., 2009; Wornschimmel et
39 al., 2013). Whether concentrations increase or decrease depends on the congener modeled,
40 the model used, and model inputs. In general, however, previous studies have shown that

predicted changes in emissions will have a stronger impact on future concentrations than climate, and that uncertainties in model inputs are substantial enough to make interpretation of climate impact data challenging. For example, Wornschimmel et al. (2013) found that atmospheric concentrations of PCB 153 increased by a factor of 1.8 between 2010 and 2100 using the BETR-Research model, but estimated uncertainties in absolute predicted concentrations within a factor of five to 10. Despite uncertainties, studies of global and hemispheric atmospheric PCBs in a future climate generally identify temperature as a key driving factor.

The mechanisms affecting the climate-driven variability of PCB concentrations in the Arctic, however, are less certain. In the Arctic, temperatures are increasing at rates faster than the global average and sea ice coverage is declining rapidly. The uncertainty in mechanisms of PCB variability due to climatic drivers primarily results from a lack of empirical data characterizing the behavior of PCBs in Arctic surface media, such as snow, ice, and seawater, and their interaction with the atmosphere. Conclusions from existing modeling studies and observational data can be contradictory. For example, Ma et al. (2011) suggest that slight increases in atmospheric PCB concentrations at the Alert (Canada) and Zeppelin (Svalbard, Norway) from the early-to-mid 2000s are likely due to revolatilization of PCBs from melting sea ice and the Arctic Ocean. Zhao et al. (2015) propose that step change increases in Arctic atmospheric PCBs in recent years coincide with lower sea ice coverage. In contrast, Gioia et al. (2008) argued that PCBs are under a net deposition regime across the North Atlantic and Arctic Oceans; i.e., PCBs are being absorbed by the Arctic Ocean rather than volatilizing. Sobek and Gustafsson (2014) also presented evidence of the Arctic Ocean acting mainly as a sink rather than a source of PCBs to the atmosphere. They constructed a budget of PCBs in the Arctic Ocean and concluded that sea ice and surface waters contained insignificant masses of PCBs compared to other compartments. Lastly, studies focusing on the impact of surface snow and/or ice on atmospheric concentrations have shown that snow and ice can increase atmospheric concentrations relative to no or less snow/ice cover for volatile compounds (Hansen et al., 2006; Stocker et al., 2007; Wornschimmel et al., 2013). In summary, the role of typical Arctic surface media on atmospheric concentrations of POPs is unclear, even in the absence of rapid change.

Here, we use information about the spatial and temporal variability of mid-latitude and Arctic PCB concentrations to constrain the relative importance of climate-driven processes to Arctic PCB concentrations. To do this, we construct a spatially and temporally resolved PCB model, driven by meteorological data, that can reproduce global measured atmospheric PCB concentrations, and to then manipulate the model to see how changing specific environmental and chemical parameters impacts the model's ability to reproduce historical measurements in the Arctic. We use this comparison to examine the relative importance of local versus global PCB sources and dynamics to Arctic atmospheric PCB concentrations. We first evaluate the new model by comparing simulated concentrations to measurements from 1991-2010, and use the model to calculate global and Arctic budgets for the International Council for the Exploration of the Sea (ICES) 7 PCB congeners (CBs 28, 52, 101, 118, 138, 153, and 180). We then conduct sensitivity simulations for CB 28 by manipulating model parameters associated with three distinct spatial categories of Arctic drivers to determine which factors controlling PCBs have the greatest impact on Arctic

1 concentrations and seasonal cycles. We conclude by discussing implications of our work for
2 studies of PCB concentrations under future climate.
3

2 Methods

2.1 GEOS-Chem PCB Model

6 The GEOS-Chem POPs model has been previously developed and applied to PAHs
7 (Friedman et al., 2014a, 2014b; Friedman and Selin, 2012); here, we extend it to address
8 PCBs. The GEOS-Chem POPs simulation (v9-01-03) includes oxidation of gas-phase species
9 by hydroxyl radical (OH; scaled for diurnal variation), wet and dry deposition of both gas
10 and particle phases, and temperature-dependent partitioning between the gas and particle
11 phases. For PCBs, we neglect particle phase oxidation, as there is no evidence in the
12 literature that these are important processes. Second, we partition PCBs to one bulk organic
13 matter (OM) phase, which combines the two different types of particle phases used
14 previously in simulating PAHs: an OM phase and a black carbon (BC) phase. While PAHs
15 have been shown to adsorb strongly to BC in the field (e.g., Accardi-Dey and Gschwend,
16 2002; Arp et al., 2008; Lohmann et al., 2005), and modeling studies have suggested PAH
17 association with BC particles can explain LRT patterns (Friedman et al., 2014a), literature
18 from contaminated marine sediment studies suggests enhanced sorption to BC occurs
19 primarily for non-ortho substituted PCB congeners (i.e., those that assume a planar
20 conformation; (Cornelissen et al., 2005; Koelmans et al., 2006)), which we do not simulate
21 here. Furthermore, in contrast to PAHs, there is little evidence directly from the
22 atmospheric literature to suggest PCBs show enhanced sorption to BC compared to OM
23 (Arp et al., 2008). Therefore, the model assumes PCBs partition between the gas and
24 particle phase following their octanol-air partition coefficients (K_{OA}, see supplementary
25 information, SI, for details). A separate NO_X-O_X-hydrocarbon-aerosol simulation of GEOS-
26 Chem (v9-01-02) is used to generate monthly mean concentrations of OM and OH, which
27 are archived and read into the POPs simulation as input. OM particles to which PCBs
28 associate convert from hydrophobic to hydrophilic with a lifetime of 1.2 days (Park et al.,
29 2003); this serves to increase the efficiency of particle-phase PCB wet scavenging over time.
30 We use the "high" annual PCB emissions inventory from Breivik et al. (2007), compiled on a
31 national basis and spatially allocated on a 1°x1° grid globally, as input emissions from 1930
32 to 2010. Primary emissions depend on ambient temperature following the van't Hoff
33 equation:
34 $$E_{T2} = E_{T1} \times \exp\left[\frac{-\Delta H}{R} \times \left(\frac{1}{T2} - \frac{1}{T1}\right)\right] \qquad (1)$$
35 where E_{T2} is the emissions rate (kg/s) at the ambient surface air temperature T_2 (K), E_{T1} is
36 the emissions rate (kg/s) given by the emissions inventory at an assumed mean global
37 surface temperature (T_1) of 288 K, ΔH is the internal phase transfer energy (J/mol) for the
38 transfer from the gas phase to the particle phase, and R is the gas constant (J K^{-1} mol^{-1}) . For
39 simulated years 1930 (the start of PCB production and hence emissions; Breivik et al.,
40 2007) to 1978, we use assimilated meteorology from the NASA Global Modeling and
41 Assimilation Office (GMAO) data set degraded to 6 hrs temporally, 4°x5° horizontally, and

1. 47 levels vertically. The GEOS5 product includes data from years 2004-2012; hence, we
2. repeat a subset of meteorological years (2006-2008) for the 1930-1978 "spin-up" of the
3. model. For simulated years 1979-2010 we use the NASA GMAO Modern Era Retrospective-
4. analysis for Research and Applications (MERRA) data set, which is consistent over the 30+
5. year historical period. MERRA data are also downgraded from their native resolution to fit
6. the model resolution. GEOS5 data are averaged at 3 or 6 hr intervals, while MERRA data are
7. averaged at 3 or 1 hr intervals, depending on the variable. The native spatial resolution of
8. both GEOS5 and MERRA products is ½°x 2/3° with 72 vertical levels.
9. PCB simulations include an improved mechanism in the GEOS-Chem POPs model for
10. surface-atmosphere interactions. PCB dynamics in surface compartments, which include
11. soils, vegetation, lakes, oceans, and snow/ice, are parameterized with level IV fugacity box
12. models embedded within GEOS-Chem. The parameterization of each surface compartment
13. and methods for estimating the fractional coverage of a grid box by a given surface medium
14. are described in detail in the SI, with references therein, along with tabulations of
15. physicochemical constants used for each process and congener, but we provide a brief
16. summary here.
17. The fraction of soil coverage within a grid box is estimated by subtracting the fraction of
18. snow from the fraction of land, which are both provided by the MERRA data set. Once
19. deposited, PCBs are assumed to distribute within the top 5 cm. Sorption to soils is
20. dependent on a soil-air partition coefficient (K_{SA}), which in turn depends on the fraction of
21. organic carbon (OC) in the soil (f_{OC}) and K_{OA}. The f_{OC} is generated with a version of the CASA
22. biogeochemical model previously coupled to GEOS-Chem (Smith-Downey et al., 2010) at
23. latitudes between 60N and 60S; at the poles, a mean Arctic tundra lowlands soil carbon
24. content (15.1 kg C/m^2) from the organic-enriched surface horizon (Ping et al., 2008) is used
25. to estimate f_{OC}, as f_{OC} is not well defined by CASA in seasonally ice-covered regions. Losses
26. of PCBs from soils include re-emissions, degradation, runoff, and leaching. Transfer of PCBs
27. to soils can come from direct atmospheric deposition, from snow/ice melt, from vegetative
28. litterfall, or from a fraction of wet deposition that has washed off vegetation. Additional
29. citations used in creating the soil module include Mackay (2001), Mackay and Paterson
30. (1991), Potter et al. (1993), and Ribes et al. (2003).
31. The fraction of a grid box covered in vegetation is estimated by multiplying the fraction of
32. soil by a greenness index (values between 0 and 1), provided by the meteorological data.
33. Deposition to vegetation includes all dry deposition and 10% of wet deposition. The other
34. 90% of wet deposition is passed directly to soils (following Cousins and Mackay, 2000). All
35. vegetation is assumed to consist of leaves having a surface thickness of 2x10^{-6} m and an
36. internal reservoir of 0.01 m thickness, and a total vegetation volume in a grid box is
37. estimated by multiplying total leaf thickness by the leaf area index (LAI). The sequestration
38. of PCBs in vegetation is controlled by both the air-water partition coefficient (K_{AW}) and the
39. K_{OA}. PCB losses from vegetation include re-emissions, litter loss, and degradation. Citations
40. used in creating the vegetation module include Cousins and Mackay (2000, 2001), Mackay
41. (2001), and Mackay and Paterson (1991).
42. The behavior of PCBs in freshwater and seawater is parameterized similarly. The fraction of
43. lake in a grid box is given by the meteorological data, while the fraction of open ocean is
44. estimated by subtracting the fraction of sea ice from the total fraction of ocean (both also
45. provided by meteorological data). Deposition to both comes directly from the atmosphere

1 or from melting snow/ice. Lakes are assumed to be 10 m deep while oceans are assumed to
2 be 1000 m deep. We assume a volume fraction of 5×10^{-6} for particles in freshwater, with
3 20% OC content. In seawater, we assume a particle volume fraction of 1×10^{-6} also with 20%
4 OC content. Sorption to particles is governed by the K_{OA}. Losses from both include re-
5 emissions, degradation, and deposition to sediments with particles. Literature used in
6 creating the lake and ocean modules includes Mackay (2001), Mackay and Paterson (1991),
7 and Schwarzenbach et al. (2003).
8 The fraction of snow/ice in a grid box is estimated by adding the fractions of snow, sea ice,
9 and land ice (provided by meteorological data; see
10 http://gmao.gsfc.nasa.gov/products/documents/MERRA_File_Specification.pdf for more
11 details). PCBs are deposited directly from the atmosphere to the ice/snowpack. Sorption of
12 PCBs in snow depends on a snow surface-air adsorption coefficient (K_{CA}), which in turn
13 depends on the density of the snow and the temperature-dependent specific snow surface
14 area (surface area per unit mass). Losses from snow include re-emissions, degradation,
15 meltwater runoff, and particle flushing. Literature used in creating the snow/ice module
16 includes Abraham and Al-Hussaini (2005), Daly and Wania (2004), Hansen et al. (2006),
17 Roth et al. (2004), and Stocker et al. (2007).
18 Degradation reaction rate constants in all environmental media are temperature dependent
19 following the Arrhenius equation. Surface media half lives and molar masses were chosen to
20 be consistent with those used in other modeling studies (Li et al., 2003; Mackay et al., 2006).
21 Activation energies were also chosen to be consistent with previous PCB modeling studies
22 (Gouin et al., 2013; Lamon et al., 2009). Details are presented in the SI.

23 ## 2.2   Model evaluation

24 We evaluate the performance of the model by comparing simulated interannual mean total
25 (gas plus particle phase) concentrations to measured total concentrations at specific sites
26 globally, for all ICES congeners. We then compare the simulated total versus measured total
27 seasonal average concentrations globally for CBs 28 and 153 from 1991 to 2010. We chose
28 these two congeners for seasonal comparisons because they have been the focus of
29 previous PCB work (e.g., Lamon et al., 2009) and because they span a wide range of
30 volatilities. Finally, we compare the monthly mean total concentrations and long-term
31 monthly averages of these two congeners for sites representative of model skill at Arctic
32 and remote mid-latitude measurement stations: Zeppelin (Norway), and Burnt Island
33 (Canada), respectively. We choose Zeppelin as an Arctic representative site because of its
34 extensive monitoring history (from 1998 onward), its high Arctic location (80 N), and
35 because time series data from the only other station at such a high latitude (Alert, Canada)
36 were affected by a laboratory switch in 2002 (Su et al., 2011). We choose Burnt Island
37 because of its long monitoring history (since 1992), because its location is more distant
38 from the mid-latitude/Arctic boundary (66 N) than European stations with similarly long
39 monitoring histories, and because data was available for both CB 28 and 153.

2.3 Sensitivity simulations

We conduct 10 sensitivity simulations in which individual model processes are either removed or altered to assess their impact on mean simulated Arctic PCB 28 concentrations and seasonal cycles from 1992 to 2009. These 10 sensitivity simulations are grouped into three general "Arctic driver" categories, depending on what was altered in the model: mid-latitude/emissions parameters ("ML"), removal/transformation parameters ("RT"), or local Arctic parameters ("ARC"). In each of the 10 sensitivity simulations, only one process is effectively 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.
In the ML category, sensitivity simulations address the effect of (1) ocean emissions, (2) temperature dependency of primary emissions, and (3) re-emissions from all surfaces to the atmosphere. For (1), we increase ocean concentrations by ~100x. We do this by re-running the 1930-1978 with the ocean depth decreased by a factor of 10 (from 1000 m to 100 m). Additionally, we artificially increase ocean concentrations globally in 1979 by a factor of 10. We categorize this as an ML sensitivity simulation because ocean concentrations are highest in the mid-latitudes. To address (2), our sensitivity simulation removes the temperature-dependency of the primary emissions rate (shown above in equation 1) such that $E_{T2} = E_{T1}$. For (3) we assume all deposited PCB 28 is re-emitted to the atmosphere by turning off all loss processes in surface media except for re-emissions, as a way to artificially increase secondary emissions to an upper-limit level.
In the RT category, our sensitivity simulations examine the effect of: (1) dry deposition, (2) slower oxidation, (3) faster oxidation, and (4) temperature sensitivity. For (1), we turn off dry deposition, and for (2) we turn off oxidation processes in the model, to assess upper-limit (i.e., extreme and not necessarily realistic) manipulations on the main loss/transformation routes of CB 28. For (3), there is substantial uncertainty associated with measured PCB OH reaction rate constants (Anderson and Hites, 1996), and we test the impact of that uncertainty by replacing the average measured k_{OH} value (1.1×10^{-12} cm^3/s) with the upper 95% confidence limit value (1.4×10^{-12} cm^3/s). This serves to test the opposite effect of turning off all oxidation (#2 above), but also in a more realistic way. For (4), to test whether Arctic dynamics of CB 28 depend on its sensitivity to temperature changes, we replace ΔH for CB 28 with that of CB 153, which has a larger absolute value (94.8 kJ/mol versus 78.4 kJ/mol; both values from Schenker et al. (2005)), and thus will induce stronger changes in both primary and secondary emissions rates depending on temperature changes (e.g., Lamon et al., 2009).
In the ARC category, we assess: (1) the influence of Arctic (both primary and secondary) emissions, (2) scavenging by snow, and (3) re-emissions from snow. For (1), we turn off all (primary and secondary) Arctic emissions, to quantify the contribution of local emissions to Arctic CB 28 concentrations. For (2), we turn off snow scavenging of PCBs in the atmosphere, to assess whether scavenging by snow, which is more prevalent at the high latitudes than mid-latitudes, has a substantial effect on Arctic concentrations and seasonal cycles. For (3), we increase snow re-emissions by increasing the wind pumping factor in the snowpack by 100x. Previous studies have shown that when wind blows across the snowpack surface, interstitial air in the snow is ventilated and POP exchange between the

1 snow and the atmosphere is enhanced. For example, Hansen et al. (2006) demonstrated
2 that modeled snow concentrations decreased by as much as 185% for CB 28 when wind
3 pumping was included in the model.
4 We note that while several of our sensitivity simulations address the impact of temperature
5 on both primary and secondary emissions (e.g., ML2), as well as gas-particle partitioning
6 (e.g., RT4), degradation of PCBs is impacted by temperature changes as well (via the
7 Arrhenius equation). We did not explicitly test the impact of changes in degradation
8 parameters in this study.
9

10 ## 3 Results

11 We first present a global evaluation of the model for each of the ICES congeners by
12 comparing annual means of simulated and measured concentrations at specific
13 measurement sites. We look in closer detail at CBs 28 and 153, two congeners that span a
14 range of volatilities, by comparing simulated results to a 1991-2010 measured time series.
15 We then present global budgets and lifetimes for all congeners, and finally, assess the
16 results of sensitivity simulations to quantify the relative effects of parameters associated
17 with ML, RT, and ARC spatial/transport drivers on CB 28 concentrations in the Arctic.

18 ### 3.1 Model evaluation

19 ### 3.1.1 Annual mean concentrations

20 Figure 1 shows global simulated annual mean concentrations from 2006-2010
21 (background) compared to observations (circles). Observations come from non-urban long-
22 term measurement sites using high-volume air samplers, listed in Table 1. Table 2
23 compares the same data when averaged spatially. We present the results for the NH (Arctic
24 and NUML sites) and an Antarctic site separately. Simulated concentrations in the Arctic
25 range from 24% (CB 180) to 1.3 times (CB 118) observed Arctic concentrations, while
26 NUML simulated concentrations are between 34% (CB 101) and 1.6 times (CB 28)
27 observed. Simulated to measured ratios for CB 28 and CB 118 are greater than one for all
28 locations while for all other congeners the ratio is consistently less than one, though there is
29 substantial uncertainty in these values given that they are spatial and temporal averages.
30 Also shown in Table 2 are observed and simulated ratios of NUML to Arctic concentrations.
31 Both sets of ratios generally increase with increasing log K_{OA}, though the relationship is not
32 statistically significant at α=0.05 (p=0.14 and 0.08 for observations and model results,
33 respectively). The increase, however, indicates greater long-range transport potential for
34 congeners that do not deposit as readily (as deposition increases with increasing log K_{OA} in
35 the model). This is consistent with the "differential removal" hypothesis from von Waldow
36 et al. (2010). In the Antarctic, simulated concentrations range from 25% (CB 180) to 1.4
37 times (CB 28) observed concentrations, demonstrating that the model captures the
38 approximately order of magnitude difference observed between the Arctic and Antarctic for
39 all congeners.

20

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). 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.

3.1.2 Monthly and seasonal mean concentrations from 1991-2010 (CBs 28 and 153)

GEOS-Chem compares favorably to previous PCB models using the same emissions inventory (e.g., GEM-POPs and BETR-Global from Huang et al., 2007, and Lamon et al., 2009). For CBs 28 and 153, we find that the model predicts observed seasonal concentrations within a factor of $10^{0.5}$ 77 % of the time, and within a factor of 10 98% of the time (Figure 2). For comparison, the BETR-Global model predicted CB 28 and 153 observed concentrations within a factor of $10^{0.5}$ 64% of time and within a factor of 10 96% of the time (Lamon et al., 2009). This gives us confidence that GEOS-Chem has the ability to simulate site-specific changes in atmospheric concentrations.
The model captures episodic events and seasonal cycles well in the mid-latitudes, but has less skill in the Arctic. Figures 3 and 4 present monthly time series and long-term monthly averages of CBs 28 and 153, respectively, at Zeppelin (Norway) and Burnt Island (Canada). For both CB 28 and 153, the model reproduces the Burnt Island monthly time series in terms of mean concentrations (simulated concentrations are 1.6 and 1.3 times higher for CBs 28 and 153, respectively) and captures the observed seasonal cycle with a peak in concentrations in summer months and a trough in the winter. This seasonal cycle is observed at all mid-latitude stations. 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. The Pearson correlation coefficient (r) values for the monthly concentrations averaged over time are 0.97 (CB 28) and 0.99 (CB 153) at Burnt Island, and the overall trend agreement between the model and measurements at this NUML station can be seen in the upper right quadrants of Figs. 3 and 4.
The model has less skill at capturing the observed Arctic (Zeppelin) seasonal cycle, particularly for CB 28. Though absolute simulated concentrations are close to measured on average (simulated concentrations are 0.55 and 0.59 times observed concentrations of CB 28 and 153, respectively), the observed cycle of CB 28 is similar to that in the mid-latitudes, with a summer maximum and a winter minimum, while the model simulates the opposite pattern (summer minimum, winter maximum). Thus, there is a strong anticorrelation between observed and simulated concentrations (r = -0.75 for the monthly concentrations averaged over time). For CB 153, there is an observed general seasonal cycle with two maxima in the observations. Though not consistent, there is usually a peak in the late spring through late summer, and another in the late fall or early winter. This is true for the

1   simulated concentrations as well, with the larger peak arriving in June-August, and a
2   smaller peak in November-January. However, because the model predicts maxima roughly a
3   month before observed maxima, the correlation is not very strong (r = 0.25 for the monthly
4   concentrations averaged over time). This mismatch is explored further in our sensitivity
5   simulation with CB 28.

6   ## 3.2   Global atmospheric budgets and lifetimes

7   The budget from simulated years 2006-2010 indicates that for all congeners the
8   atmosphere, vegetation, lakes, and snow are at steady state, while the ocean and soils are
9   emitting legacy deposition. Table 4 summarizes the atmospheric portion of the budget. Dry
10 deposition of the gas phase and OH oxidation are the two main loss routes for all seven
11 congeners, though their relative importance changes across the congener spectrum. For
12 example, dry deposition accounts for 82% of the loss of CB 180, but only 30% for CB 28.
13 Conversely, OH oxidation accounts for 65% of the loss of CB 28, but only 13% for CB 180.
14 Though we predict substantially lower total masses of PCBs in the atmosphere compared to
15 other PCB modeling studies (e.g., Huang et al., 2007, whose simulated concentrations
16 generally biased high while ours generally bias low), the relative percentages of loss due to
17 oxidation versus deposition across congeners are similar. Wet deposition plays a relatively
18 minor role in the global budget; wet deposition accounts for only 4% (CB 138) to 7% (CB
19 180) of total losses and only 5% (CB 138) to 14% (CB 28) of total deposition. More than
20 99% of wet deposition, for all congeners, is of the gas phase. This is true for the Arctic in
21 particular as well.
22 The particle phase makes up only a very small fraction of the total budget for all congeners.
23 CB 28 has the least in the particle phase (0.02%) while CB 180 has the most (1.4%). While
24 these fractions are low compared to measured PCB particulate fractions, especially for the
25 heavier congeners like CB 180, most measurements of particulate fractions are in urban
26 areas (e.g., Simcik et al., 1998); the fractions we report here are global averages and are
27 thus lower than particulate fractions found near urban locations. The low PCB particulate
28 fractions are in contrast to GEOS-Chem simulations of PAHs, where 93% of benzo[a]pyrene
29 was found to be in the particle phase (Friedman and Selin, 2012). The difference can be
30 attributed to PAH preferentially strongly binding to BC, a process that has not been
31 observed to the same degree for PCBs and hence does not exist in the PCB model (BC and
32 OC particles are treated as one particle type for PCBs, with partitioning controlled by the
33 K_{OA} for both). The small fraction in the particle phase results in nearly all wet and dry
34 deposition (>99% for all congeners) being attributable to the gas phase.
35 The relative contribution of re-emissions to total atmospheric emissions generally
36 decreases with increasing degree of chlorination. CB 52 has the highest percentage of re-
37 emissions (9.2 %), while CB 180 has the least (1.9 %). Re-emissions can enhance transport
38 to remote regions, as they can occur anywhere PCBs have previously deposited; this is
39 consistent with the different distributions seen in the Arctic across congeners in Fig. 1 (i.e.,
40 a greater fraction of CB 28 in the Arctic atmosphere versus CB 180), and the increase in
41 measured NUML-to-Arctic ratios with increasing chlorination shown in Table 2, which is
42 generally captured by the model.

The model predicts short atmospheric lifetimes of PCBs, ranging from 4.5 to 9.4 hours (for CBs 180 and 28, respectively). We note that, in contrast to effective lifetimes often quoted in previous literature, these atmospheric residence times only take into account gross losses and do not consider re-emissions or storage in surface reservoirs.
We do not focus on surface media budgets here, other than to note that for all surface media except snow, re-emissions generally do not contribute substantially to losses from the surface. Degradation and deposition to sediments (for oceans and lakes) usually account for the largest losses. In the case of snow, re-emissions account for 22% (CB 180) to 56% (CB 52) of losses.

3.3 Sensitivity of Arctic concentrations to different spatial drivers

We focus our Arctic sensitivity analyses on CB 28 because a) its removal from the atmosphere is not dominated by one loss pathway; i.e., it is sensitive to changes in both dry deposition and oxidation, and b) it is one of the more volatile congeners of the ICES suite, so re-emissions of previously deposited chemical play a larger role in its LRT. This is important because re-emissions have been identified as important in a number of studies attempting to identify the source of recent observed increases in Arctic atmospheric PCBs (Ma et al., 2011; Zhao et al., 2015). In this section, all comparisons are for changes in surface atmospheric concentrations averaged over the entire Arctic (66-90N, 180W-180E). Our sensitivity analyses are divided into three different "Arctic driver" categories, depending on what was altered in the model: mid-latitude/emissions parameters ("ML"), removal/transformation parameters ("RT"), or local Arctic parameters ("ARC"). Table 5 shows the results of the changes from each category on both absolute concentrations as well as the seasonal variation, averaged over simulated time (1992-2009). As noted above, there is a mismatch between measured and simulated seasonal variation. Sensitivity simulations that simultaneously increase absolute concentrations and decrease modeled seasonal cycle amplitude bring the model closer to observations, indicating that associated process changes may be more influential in the Arctic than changes in mean Arctic concentrations alone. Figure 5 shows the impact on seasonal cycle for simulations resulting in changes of at least 10%. Concentrations in Figure 5 have been normalized to a running mean so that the change in seasonal cycle can be viewed without interference from long-term changes in concentrations.
In the ML category, removing the temperature dependency of primary emissions (simulation ML2) has a greater effect on Arctic surface concentrations than increasing surface re-emissions to the atmosphere (simulations ML1 and ML3). Removing the temperature dependency causes a 340% increase in mean Arctic surface concentrations compared to default simulations, while simultaneously increasing the seasonal cycle bias in the simulations (i.e., the winter-time high in the simulation is amplified). Thus, removing a key temperature-sensitivity parameter in the model increases the mismatch between observed and simulated Arctic PCB seasonal cycles and concentration magnitude. Extreme increases in re-emissions from all surfaces (simulation ML3) also has a relatively large effect on both mean concentrations and the seasonal cycle, with Arctic concentrations increasing by 260% and seasonal cycle amplitude decreasing by 34%. Increasing ocean

emissions alone, in a more realistic parameterization (simulation ML1), has a nearly negligible effect.

In the RT category, turning off dry deposition (RT1) and oxidation (RT2) demonstrates that these processes strongly influence mean Arctic concentrations. RT1 and RT2 result in 200% and 370% increases in mean Arctic concentrations, respectively and 11% and 27% decreases in the strength of the seasonal cycle, respectively. Conversely, increasing the oxidation rate (RT3) results in a decrease in concentrations (-13%) and an increase in the strength of the simulated seasonal cycle (8%). Altering the temperature sensitivity of emissions for CB28 (RT4) resulted in a small decrease in mean concentrations (-6%) and a decrease in seasonal cycle strength (-12%)

In the ARC category, turning off all local emissions causes a small decrease (-5%) in mean concentrations and a small increase (+4%) in seasonal cycle strength, demonstrating that their presence in the model is important to model-observation agreement. Removing snow scavenging from the atmosphere (simulation ARC2) causes minor increases in mean concentration and seasonal cycle strength (+7% and +5%, respectively). Finally, increasing snow emissions (ARC3) causes a small increase in the mean Arctic concentration, but no change in the seasonal cycle.

Overall, sensitivity simulations only reduce or increase the amplitude of the simulated CB 28 seasonal maxima but do not affect timing (Fig. 5), with the exception of Simulation ML2, which results in a slight shift in the timing of maxima (maxima occur approximately one month later).

We find that mean surface Arctic concentrations of CB 28 are positively correlated to the mean fraction of ice/snow in Arctic grid boxes (r = 0.46), and inversely correlated to both Arctic surface air temperatures (r = -0.59) and mid-latitude surface temperatures (r = -0.56).

4   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-November) and the minimum occurs during the summer (June-July-August). The opposition in observed and simulated seasonal cycles indicates that the model is missing an important process influencing the Arctic. We use our ML, RT, and ARC sensitivity simulations of CB 28 and their effect on simulated mean Arctic concentrations and seasonal cycles to assess the mismatch. We then discuss what our sensitivity simulations imply about the influence of relevant processes controlling PCB concentrations in a changing climate.

The direction of change induced by sensitivity simulations (Table 5) can be used in conjunction with the model-measurement mismatch to assess potential drivers of Arctic PCBs and indicate what processes the model is missing that might account for the summer high seen in observations. Sensitivity simulations that simultaneously increase the mean Arctic concentration and reduce the strength of the simulated seasonal cycle are those that

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bring modeled and measured concentrations and temporal patterns closer together. Thus, our sensitivity simulations suggest that less dry deposition, less oxidation, and higher re-emissions in the model would help close the model-measurement gap in the Arctic (i.e., simulations RT1, RT2, and ML3).

Supporting evidence beyond sensitivity simulations exists to indicate the model assumes oxidation and deposition rates that are too fast. In the case of oxidation, there are few measurements of PCB OH reaction rate constants. Most modeling studies rely on one set of measurements obtained decades ago (Anderson and Hites, 1996). A number of studies examining atmospheric PCB measurements and constructing global budgets have suggested that the rates measured by Anderson and Hites are too high to account for observed spatial distributions across congeners (e.g., Axelman and Gustafsson, 2002). 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. Similarly, while there are only three stations from Table 1 routinely measuring total deposition, a comparison between model results and measurements demonstrates that CB 28 deposition (which is dominated by dry deposition of the gas phase) is approximately an order of magnitude too high in the model (data not shown). Thus, reducing oxidation and dry deposition rates are reasonable changes to make to the model, though we note that these changes also increase concentrations in the mid-latitudes where the model is already skilled at predicting concentrations.

Simulation ML3, in which re-emissions are increased to an extreme upper-limit, shows that increasing secondary emissions in the model also helps close the model-measurement gap in the Arctic. However, other sensitivity simulations that also increase secondary emissions in the Arctic, but in a more realistic/less extreme manner, such as increased ocean and snow re-emissions (ML1 and ARC3, respectively), lead only to minor increases in atmospheric concentrations and have virtually no effect on the seasonal pattern. This suggests that secondary emissions would have to be unrealistically high in order to match Arctic observations without affecting the model-measurement match in the mid-latitudes. In the absence of secondary emissions as a likely source of model-measurement mismatch, local primary emissions that are not accounted for in the Breivik emissions inventory deserve attention. While Arctic monitoring stations are situated such that the impact of local contamination should be minimal, contamination issues have been observed in remote locations where measurement platforms rely on older building materials that potentially contain PCBs. For example, the continuous diffusive emissions of PCBs from older ships during remote ocean measurements has been documented (Lohmann et al., 2004), while hot spots of PCBs and other POPs have been observed near Antarctic research stations (Cabrerizo et al., 2012; Kennicutt II et al., 1995; Wild et al., 2015). The Alert station is located near a Canadian military station with buildings from at least the 1950s, while the Zeppelin station is just south of Ny-Ålesund, a research settlement formed in the 1960s but which has hosted mining operations since the early 1900s. Given the greater effect of temperature changes on primary volatilization emissions compared to secondary emissions found both here and in other modeling studies (Lamon et al., 2009), it seems plausible that the maxima seen in the remote Arctic summer could be attributed to unaccounted-for local primary emissions. We also note that while observed atmospheric concentrations of POPs have been shown to be positively correlated to both sea ice retreat and surface temperature

in the Arctic (Ma et al., 2011), the multicollinearity of sea ice retreat and surface temperature was not discussed; i.e., it is possible that the observed seasonal cycle is driven primarily by temperature alone. Thus, based on our model results and supporting data, we consider local primary emissions a more probable driver of summer concentration maxima compared to re-emissions from surface media.

Except for the possibility of unaccounted-for local primary emissions, even when the more probable missing model processes are considered, simulated Arctic PCB concentrations are mostly controlled by factors outside of the region. We hypothesize based on this result that the main factors driving observed variability in Arctic PCB concentrations result from processes outside the Arctic. The sensitivity simulations that minimize the model-measurement gap in the Arctic (ML3, RT1, and RT2) are those that alter processes that mainly take place outside the Arctic. Also, the ML and RT categories of sensitivity simulations generally cause a much larger percent change in mean concentrations and seasonal cycle compared to ARC sensitivity simulations. Much of the greater magnitude of change from the ML and RT scenarios is attributable to the fact that changes within these categories affect nearly all emitted PCBs globally, while ARC simulation changes affect primarily only PCBs emitted or deposited in the Arctic. This points to the importance of accurate quantification and spatial attribution of emissions globally for assessing changes in Arctic PCB levels.

If absent Arctic primary emissions are indeed the main cause of model-measurement mismatch, then our conclusion above that factors outside the region control PCB concentrations would need revising. With the model in its current form, simulated Arctic concentrations have a weak inverse correlation with mid-latitude temperatures. This suggests the simulated seasonal pattern mostly reflects strong winter-time transport rather than temporal variation in mid-latitude emissions, and thus that the simulated Arctic is mostly influenced by physical transport. 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. Primary emissions are sensitive to changes in temperature, and it is likely that with additional Arctic primary sources beyond those accounted for in the Breivik inventory, summer-time temperature increases would cause an increase in atmospheric concentrations that would dominate a long-range transport signal. As discussed above, we do not consider secondary emissions in the Arctic to be a probable cause of seasonal cycle mismatch because of the extreme increase required in the model in order to match observations. Additional evidence for secondary emissions as an unlikely cause of seasonal cycle is the positive correlation in our simulations between concentrations and ice/snow cover in the Arctic, which suggests surface media associated with lower temperatures (e.g. snow/ice) leads to higher atmospheric concentrations than surface media associated with warmer temperatures (e.g. open ocean/soil). Indeed, previous modeling studies (Hansen et al., 2006; Stocker et al., 2007) have suggested that the presence of a surface snowpack increases atmospheric concentrations of volatile POPs compared to a surface without snow, because of the tendency for volatile POPs to be re-emitted quickly (Daly and Wania, 2004). This means that a summer-time retreat in snow/ice is unlikely to be the source of higher concentrations in the Arctic.

Our results can be considered in the context of climate change and the current literature. Previous studies aimed at assessing the role of changing climate on Arctic PCB concentrations have suggested the break up of sea ice and exposure of the Arctic Ocean with warmer temperatures accounts for increases in Arctic atmospheric PCBs (Ma et al., 2011; Zhao et al., 2015). Most of the evidence presented by Ma et al., however, focuses on POPs that are more volatile than PCBs, such as α-HCH, and the concentration increases in PCBs cited at Arctic stations were more prominent for heavier congeners, which are less likely to volatilize. Both Ma et al. and Zhao et al. employed perturbation modeling, which assumes a closed system with simplifications of Arctic-specific processes and neglects transport from outside the region. In contrast, our results suggest that changes in long-range transport and/or volatilization of local primary sources would overwhelm release of legacy PCBs from sea ice or the Arctic Ocean. Changes in long-range transport due to climate change are likely to take the form of faster atmospheric degradation rates and increases in mid-latitude primary emissions relative to the present climate (Hansen et al., 2015; Lamon et al., 2009; Wornschimmel et al., 2013), processes which change PCB concentrations in opposite directions and thus make it difficult to predict the effect on the Arctic. There is also literature that supports the idea that Arctic secondary emissions will not play a major role in atmospheric PCB levels there with a changing climate. Gioia et al. (2008) conducted PCB measurements over the Arctic Ocean and their results suggest the Arctic is under a strong net PCB deposition regime, rather than net volatilization. Likewise, Sobek and Gustafsson (2014) recently constructed a budget of PCBs in the Arctic Ocean which suggests 98% of PCBs reside in the deep and intermediate waters, with surface water and ice containing insignificant masses in comparison. 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.

It should be noted that our model includes substantial uncertainties with regard to predicting secondary emissions, especially with respect to re-emissions from oceans and ice. The ocean in the GEOS-Chem model is an embedded box model, and thus does not consider lateral transport, which can be a key factor in moving soluble POPs from the mid-latitudes to more remote regions. It is possible that in an ocean model with resolved surface and subsurface layers, that also includes particle dynamics and lateral transport, we may see enhanced secondary emissions. Snow and ice are also combined as one substance in the model and treated as snow. Snow is more porous than ice and because of this, snow cover has been shown to increase atmospheric concentrations for volatile POPs (Hansen et al., 2006; Stocker et al., 2007; Wornschimmel et al., 2013). Ice has greater potential than snow to trap POPs and release them in melt water with warmer temperatures, as been shown in studies examining melting glaciers (Bogdal et al., 2010); however, the effect of melting ice on atmospheric PCB concentrations is not well studied. A more realistic parameterization of Arctic sea ice dynamics could also potentially increase simulated re-emissions in the Arctic; however, the increase would have to be substantial to invalidate our conclusions.

5   Conclusion

We constructed a spatially and temporally resolved global atmospheric PCB model, driven by meteorological data, that is skilled at simulating mean atmospheric PCB concentrations and seasonal cycles in the northern hemisphere mid-latitudes, and mean Arctic concentrations. The model does not capture observed Arctic summer time maxima. We use the model to estimate global budgets for the ICES 7 PCBs, and our simulations demonstrate that in accordance with the "differential removal" hypothesis (von Waldow et al., 2010), a greater fraction of emitted PCB is transported to remote regions (ie., the Arctic) for congeners that do not readily deposit compared to those that do. Using a number of sensitivity simulations, grouped into three categories depending on whether they affect processes within, outside, or transport to the Arctic, in conjunction with the model-measurement mismatch in the Arctic, we examined the influence of climate- and emissions-driven processes on Arctic concentrations. Based on these simulations, we find evidence for the hypothesis that processes outside the Arctic rather than within primarily affect Arctic atmospheric PCB levels. Our simulations suggest that re-emissions from sea ice melting or from the Arctic Ocean during summer would have to be unrealistically high in order to capture observed Arctic concentrations. We conclude that while previous studies have suggested climate change will induce re-emissions from Arctic sea ice and the Arctic Ocean, there is little evidence in our results to expect significant fluxes out of Arctic surface media compared to changes from transport from the mid-latitudes.

References

Abraham, M. H. and Al-Hussaini, A. J. M.: Solvation parameters for the 209 PCBs: calculation of physicochemical properties, J Env. Monit, 7, 295–301, 2005.

Accardi-Dey, A. and Gschwend, P. M.: Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments, Env. Sci Technol, 36(1), 21–29, 2002.

Anderson, P. N. and Hites, R. A.: OH radical reactions: The major removal pathway for polychlorinated biphenyls from the atmosphere, Environ. Sci. Technol., 30(5), 1756–1763, 1996.

Armitage, J. M. and Wania, F.: Exploring the potential influence of climate change and particulate organic carbon scenarios on the fate of neutral organic contaminants in the Arctic environment, Env. Sci Process. Impacts, 15, 2263–2272, 2013.

Arp, H. P. H., Schwarzenbach, R. P. and Goss, K.-U.: Ambient gas/particle partitioning. 2: The influence of particle source and temperature on sorption to dry terrestrial aerosols, Env. Sci Technol, 42, 5951–5957, 2008.

Axelman, J. and Gustafsson, O.: Global sinks of PCBs: A critical assessment of the vapor-phase hydroxy radical sink emphasizing field diagnostics and model assumptions, Glob. Biogeochem. Cycles, 16(4), art. no.–1111, 2002.

Bogdal, C., Nikolic, D., Lüthi, M., Schenker, U., Scheringer, M. and Hungerbühler, K.: Release of legacy pollutants from melting glaciers: model evidence and conceptual understanding, Env. Sci Technol, 44, 4063–4069, 2010.

Breivik, K., Sweetman, A., Pacyna, J. M. and Jones, K. C.: Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 2. Emissions, Sci Total Env., 290(1-3), 199–224, 2002.

Breivik, K., Sweetman, A., Pacyna, J. M. and Jones, K. C.: Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 3. An update, Sci Total Env., 377, 296–307, 2007.

Cabrerizo, A., Dachs, J., Barceló, D. and Jones, K.: Influence of organic matter content and human activities on the occurence of organic pollutants in Antarctic soils, lichens, grass, and mosses, Env. Sci Technol, 46, 1396–1405, 2012.

Cornelissen, G., Haftka, J., Parsons, J. and Gustafsson, O.: Sorption to black carbon of organic compounds with varying polarity and planarity, Env. Sci Technol, 39, 3688–3694, 2005.

Cousins, I. T. and Mackay, D.: Transport parameters and mass balance equations for vegetation in Level III fugacity models. Internal report published on the website of the Canadian Environmental Modelling Centre (http://www.trent.ca/envmodel/)., 2000.

Cousins, I. T. and Mackay, D.: Strategies for including vegetation compartments in multimedia models, Chemosphere, 44, 643–654, 2001.

Daly, G. L. and Wania, F.: Simulating the influence of snow on the fate of organic compounds, Env. Sci Technol, 38, 4176–4186, 2004.

Dewailly, E., Nantel, A., Weber, J.-P. and Meyer, F.: High levels of PCBs in breast milk of Inuit women from Arctic Quebec, Arch. Environ. Contam. Toxicol., 43(5), 641–646, 1989.

Friedman, C. L. and Selin, N. E.: Long-range atmospheric transport of polycyclic aromatic hydrocarbons: A global 3-D model analysis including evaluation of Arctic sources, Env. Sci Technol, 46, 9501–9510, 2012.

Friedman, C. L., Pierce, J. R. and Selin, N. E.: Assessing the influence of secondary organic verus primary carbonaceous aerosols on long-range atmospheric polycyclic aromatic hydrocarbon transport, Env. Sci Technol, 48(6), 3293–3302, 2014a.

Friedman, C. L., Zhang, Y. and Selin, N. E.: Climate change and emissions impacts on atmospheric PAH transport to the Arctic, Env. Sci Technol, 48, 429–437, 2014b.

Gioia, R., Lohmann, R., Dachs, J., Temme, C., Lakaschus, S., Schulz-Bull, D., Hand, I. and Jones, K. C.: Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean, J Geophys Res, 113, D19302, 2008.

Gouin, T., Armitage, J. M., Cousins, I. T., Muir, D. C. G., Ng, C. A., Reid, L. and Tao, S.: Influence of global climate change on chemical fate and bioaccumulation: The role of multimedia models, Env. Toxicol Chem, 32, 20–31, 2013.

Hansen, K. M., Halsall, C. J. and Christensen, J. H.: A dynamic model to study the exchange of gas-phase persistent organic pollutants between air and a seasonal snowpack, Env. Sci Technol, 40, 2644–2652, 2006.

Hansen, K. M., Christensen, J. H., Geels, C., Silver, J. D. and Brandt, J.: Modelling the impact of climate change on the atmospheric transport and the fate of persistent organic pollutants in the Arctic, Atmos Chem Phys, 15, 6549–6559, 2015.

Huang, P., Gong, S. L., Zhao, T. L., Neary, L. and Barrie, L. A.: GEM/POPs: a global 3-D dynamic model for semi-volatile persistent organic pollutants - Part 2: Global transports and budgets of PCBs, Atmos Chem Phys, 7, 4015–4025, 2007.

Hung, H., Halsall, C. J., Blanchard, P., Li, H. H., Fellin, P., Stern, G. and Rosenberg, B.: Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring, Environ. Sci. Technol., 35(7), 1303–1311, 2001.

Hung, H., Blanchard, P., Halsall, C. J., Bidleman, T. F., Stern, G. A., Fellin, P., Muir, D. C. G., Barrie, L. A., Jantunen, L. M., Helm, P. A., Ma, J. and Konoplev, A.: Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring, Sci. Total Environ., 342(1-3), 119–144, 2005.

Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J. M., Leppänen, S., Bossi, R., Skov, H., Manø, S., Patton, G. W., Stern, G., Sverko, E. and Fellin, P.: Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006., Sci Total Env., 408, 2854–2873, 2010.

Kallenborn, R., Christensen, G., Evenset, A., Schlabach, M. and Stohl, A.: Atmospheric transport of persistent organic pollutants (POPs) to Bjornoya (Bear island), J. Environ. Monit., 9(10), 1082–1091, 2007.

Kennicutt II, M. C., McDonald, S. J., Sericano, J. ., Boothe, P., Oliver, J., Safe, S., Presley, B. J., Liu, H., Wolfe, D., Wade, T. L., Crockett, A. and Bockus, D.: Human contamination of the marine environment - Aurther Harbor and McMurdo Sound, Antarctica, Env. Sci Technol, 29, 1279–1287, 1995.

Koelmans, A. A., Jonker, M. T. O., Cornelissen, G., Bucheli, T. D., Van Noort, P. C. M. and Gustafsson, O.: Black carbon: The reverse of its dark side, Chemosphere, 63, 365–377, 2006.

Lamon, L., von Waldow, H., MacLeod, M., Scheringer, M., Marcomini, A. and Hungerbuhler, K.: Modeling the global levels and distribution of polychlorinated biphenyls in air under a climate change scenario, Env. Sci Technol, 43, 5818–5824, 2009.

Li, N. Q., Wania, F., Lei, Y. D. and Daly, G. L.: A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls, J. Phys. Chem. Ref. Data, 32(4), 1545–1590, 2003.

Lohmann, R., Jaward, F. M., Durham, L., Barber, J. L., Ockenden, W., Jones, K. C., Bruhn, R., Lakaschus, S., Dachs, J. and Booij, K.: Potential contamination of shipboard air samples by diffusive emissions of PCBs and other organic pollutants: Implications and solutions, Environ. Sci. Technol., 38(14), 3965–3970, 2004.

Lohmann, R., MacFarlane, J. K. and Gschwend, P. M.: Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York, Harbor sediments, Env. Sci Technol, 39, 141–148, 2005.

Mackay, D.: Multimedia Environmental Models: The Fugacity Approach, 2nd ed., Lewis Publishers, Boca Raton., 2001.

Mackay, D. and Paterson, S.: Evaluating the multimedia fate of organic chemics: A level III fugacity model., Env. Sci Technol, 25, 427–436, 1991.

Mackay, D., Shiu, W. Y., Ma, K.-C. and Lee, S. C.: Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, 2nd. ed., CRC Press, Boca Raton., 2006.

Ma, J., Hung, H., Tian, C. and Kallenborn, R.: Revolatilization of persistent organic pollutants in the Arctic induced by climate change, Nat. Clim Change, 1, 255–260, 2011.

Octaviani, M., Stemmler, I., Lammel, G. and Graf, H. F.: Atmospheric transport of persistent organic pollutants to and from the Arctic under present-day and future climate, Env. Sci Technol, 49, 3593–3602, 2005.

Park, R. J., Jacob, D. J., Chin, M. and Martin, R. V.: Sources of carbonaceous aerosols over the United States and implications for natural visibility, J Geophys Res, 108(D12), 4355, 2003.

Ping, C.-L., Michaelson, G. J., Jorgenson, M. T., Kimble, J. M., Epstein, H., Romanovsky, V. E. and Walker, D. A.: High stocks of soil organic carbon in the North American Arctic region, Nat. Geosci, 1, 615–619, 2008.

Potter, C. S., Randerson, J. T., Field, C. B., Matson, P. A., Vitousek, P. M., Mooney, H. A. and Klooster, S. A.: Terrestrial ecosystem production: A process model based on global satellite and surface data, Glob. Biogeochem Cycles, 7, 811–841, 1993.

Ribes, S., Van Drooge, B., Dachs, J., Gustafsson, O. and Grimalt, J. O.: Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons, Env. Sci Technol, 37, 2675–2680, 2003.

Roth, C. M., Goss, K.-U. and Schwarzenbach, R. P.: Sorption of diverse organic vapors to snow, Env. Sci Technol, 38, 4078–4084, 2004.

Schenker, U., MacLeod, M., Scheringer, M. and Hungerbuhler, K.: Improving data quality for environmental fate models: A least-squares adjustment procedure for harmonizing physicochemical properties of organic compounds, Env. Sci Technol, 39(21), 8434–8441, 2005.

Schwarzenbach, R. P., Gschwend, P. M. and Imboden, D. M.: Environmental Organic Chemistry, 2nd ed., 2003.

Simcik, M. F., Franz, T. P., Zhang, H. X. and Eisenreich, S. J.: Gas-particle partitioning of PCBs and PAHs in the Chicago urban and adjacent coastal atmosphere: States of equilibrium, Environ. Sci. Technol., 32(2), 251–257, 1998.

Smith-Downey, N., Sunderland, E. and Jacob, D.: Anthropogenic impacts on global storage and emissions of mercury from terrestrial soils: insights from a new global model, J Geophys Res, 115, G03008, 2010.

Sobek, A. and Gustafsson, O.: Deep water masses and sediments are the main compartments for polychlorinated biphenyls in the Arctic Ocean, Env. Sci Technol, 48, 6719–6725, 2014.

Stocker, J., Scheringer, M., Wegmann, F. and Hungerbuhler, K.: Modeling the effect of snow and ice on the global environmental fate and long-range transport potential of semivolatile organic compounds, Env. Sci Technol, 41, 6192–6198, 2007.

Su, Y., Hung, H., Stern, G., Sverko, E., Lao, R., Barresi, E., Rosenberg, B., Fellin, P., Li, H. and Xiao, H.: Bias from two analytical laboratories involved in a long-term air monitoring program measuring organic pollutants in the Arctic: a quality assurance/quality control assessment, J Env. Monit, 13, 3111–3118, 2011.

von Waldow, H., MacLeod, M., Jones, K., Scheringer, M. and Hungerbühler, K.: Remoteness from emission sources explains the fractionation pattern of polychlorinated biphenyls in the northern hemisphere, Env. Sci Technol, 44, 6183–6188, 2010.

Wania, F. and Mackay, D.: Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions, Ambio, 22(1), 10–18, 1993.

Wania, F. and Mackay, D.: Tracking the distribution of persistent organic pollutants, Env. Sci Technol, 30, A390–A396, 1996.

Wild, S., McLagan, D., Schlabach, M., Bossi, R., Hawker, D., Cropp, R., King, C. K., Stark, J. S., Mondon, J. and Bengtson Nash, S.: An Antarctic research station as a source of brominated and perfluorinated persistent organic pollutants to the local environment, Env. Sci Technol, 49, 103–112, 2015.

Wornschimmel, H., MacLeod, M. and Hungerbuhler, K.: Emissions, fate and transport of persistent organic pollutants to the Arctic in a changing global climate, Env. Sci Technol, 47(5), 2323–2330, 2013.

Zhao, Y., Huang, T., Wang, L., Gao, H. and Ma, J.: Step changes in persistent organic pollutants over the Arctic and their implications, Atmos Chem Phys, 15, 3479–3495, 2015.

1   Table 1. Stations where observational data were obtained; first four sites considered Arctic.
2   References: (a) Hayley Hung/Northern Contaminants Program, personal communication;
3   (b) EMEP (Cooperative Programme for Monitoring and Evaluation of the Long-range
4   Transmissions of Air Pollutants in Europe); (c) Helena Dryfout-Clark/IADN (Integrated
5   Atmospheric Deposition Network), Environment Canada, personal communication. *Site
6   considered urban and not included in model-measurement comparison. %Site where total
7   deposition is measured. Sites listed in bold/italics were averaged as they occurred within
8   the same model grid box.

Latitude	Longitude	Elevation (m)	Station Name	Reference
82	-62	30	Alert Canada	a
78.9	11.9	474	Zeppelin Norway	b
69.3	16	380	Andoya Norway	b
68	24.2	340	Pallas (Matorova) Finland[%]	b
64.1	21.9	52	Reykjavik Iceland	b
58.8	17.38	20	Aspvreten Sweden[%]	b
58.4	*8.3*	*190*	*Birkenes Norway*	*b*
58.4	*8.3*	*219*	*Birkenes II Norway*	*b*
57.4	11.9	5	Rao Sweden[%]	b
54.9	8.3	12	Westerland Germany	b
54.4	12.7	1	Zingst Germany	b
54.3	-0.8	267	High Muffles Great Britain	b
53	70.6	334	Borovoe Kazakhstan	b
50.7	10.8	937	Schmucke Germany	b
49.6	15.1	534	Kosetice Czech Republic	b
47.9	7.9	1205	Schauinsland Germany	b
47.5	**-88.1**	**185**	**Eagle Harbor US**	**c**
46.5	28.3	166	Leova II Moldova*	b
45.8	**-89.2**	**184**	**Burnt Island Canada**	**c**
44.8	-86.1	241	Sleeping Bear Dunes US	c
43.8	-77.2	78	Point Petre Canada	c
42.7	-79.1	176	Sturgeon Point US	c
41.8	-87.6	199	Chicago US*	c
41.5	-81.7	204	Cleveland US*	c
-72	2.5	1309	Troll Norway	b

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Table 2. Observed versus simulated geometric mean concentrations averaged over all sites listed in Table 2 for years 2006-2010 (for some sites, only a subset of the 2006-2010 timeseries was available). Results for the Arctic and non-urban mid-latitude sites are presented separately. Geometric standard deviations are for geomeans across 2006-2010 annual means for all Arctic and non-urban mid-latitude (NUML) sites. For Troll, the geometric mean from years 2007-2009 is given for observations, while the geometric mean for 2006-2010 is given for simulations. Arctic means are of the first four sites listed in Table 1, except for CBs 28 and 138; Alert data was not considered for these congeners because of analytical interference by chromatographically co-eluting congeners. NUML means are of all non-urban, non-Arctic sites listed in Table 1.

PCB	Arctic geomean (range factor 1 SD)			NUML geomean (range factor 1 SD)			Mid-lat/Arctic Ratio		Antarctic (Troll) geomean		
	Obs	Sim	Sim/Obs	Obs	Sim	Sim/Obs	Obs	Sim	Obs	Sim	Sim/Obs
28	1.4 (0.70-2.8)	1.7 (1.5-1.9)	1.2	3.0 (1.9-5.0)	4.8 (2.9-7.8)	1.6	2.1	2.8	0.040	0.057	1.4
52	1.0 (0.63-1.6)	0.60 (0.51-0.70)	0.60	3.0 (1.8-5.1)	1.9 (1.2-3.3)	0.63	3.0	3.2	0.047	0.027	0.57
101	0.52 (0.37-0.72)	0.18 (0.17-0.20)	0.35	1.9 (0.98-3.7)	0.64 (0.32-1.26)	0.34	3.7	3.6	0.029	0.015	0.52
118	0.20 (0.17-0.24)	0.25 (0.23-0.28)	1.3	0.63 (0.31-1.3)	0.79 (0.42-1.5)	1.3	3.2	3.2	0.015	0.019	1.3
138	0.26 (0.15-0.43)	0.094 (0.083-0.11)	0.36	0.85 (0.32-2.3)	0.45 (0.18-1.1)	0.53	3.3	4.8	0.024	0.014	0.58
153	0.29 (0.20-0.42)	0.13 (0.10-0.15)	0.45	1.1 (0.41-2.7)	0.61 (0.24-1.6)	0.55	3.8	4.7	0.032	0.025	0.78
180	0.072 (0.036-0.14)	0.017 (0.012-0.025)	0.24	0.36 (0.13-1.0)	0.16 (0.055-0.48)	0.44	5.0	9.4	0.015	0.0037	0.25

1 Table 3. Linear relationships and correlations between simulated and observed mean
2 annual (2006-2010) concentrations for all NH non-urban locations (i.e., NUML + Arctic
3 sites) with Pearson correlation coefficient (r) values, mean bias, and root mean square error
4 (pg m^{-3}).

PCB	Linear relationship	r	Bias	RMSE
28	Y= 1.15x + 1.28	0.64	1.73	2.69
52	Y= 0.32x + 0.95	0.57	-1.12	2.05
101	Y= 0.17x + 0.32	0.56	-1.41	1.91
118	Y= 0.46x + 0.48	0.53	0.12	0.54
138	Y= 0.25x + 0.25	0.61	-0.57	1.00
153	Y= 0.40x + 0.19	0.73	-0.53	0.90
180	Y= 0.27x + 0.07	0.75	-0.27	0.47

5

1   Table 4. Mean 2006-2010 atmospheric budget of PCBs. For all congeners, total wet and dry
2   deposition was dominated by the gas phase (>99% attributable to the gas phase).

	Congener						
Quantity associated with atmospheric budget	**28**	**52**	**101**	**118**	**138**	**153**	**180**
Mass in atmosphere (kg)	58	26	12	16	10	15	3.4
Mean fraction in particle phase (%)	0.021	0.052	0.17	0.18	0.57	0.40	1.4
OH oxidation losses (%)	65	53	35	34	21	25	13
Dry deposition losses (%)	30	42	60	61	75	70	82
Wet deposition losses (%)	5.1	4.6	4.9	4.9	4.0	5.2	5.8
Re-emissions out of total emissions (%)	6.0	9.2	5.1	4.8	2.7	4.1	2.0
Mean atmospheric lifetime (gas + particulate; hrs)	9.4	8.1	6.7	6.5	5.3	5.9	4.5

3

1   Table 5. Results of sensitivity simulations on mean surface atmospheric CB 28 Arctic concentrations. *Measured by taking
2   the ratio of mean January normalized concentrations. Simulations that increase the mean concentration while
3   simultaneously decreasing the seasonal pattern amplitude (simulations ML3, RT1, and RT2) are those that bring model and
4   observational results closer together.

| Arctic driver	Simulation name	Simulation tests sensitivity to	Actual change to simulation	Effect on mean concentration	Effect on seasonal pattern amplitude*
ML/Emissions "ML"	ML1	Ocean re-emissions	Ocean concentrations increased ~ 100x	+2%	+1%
	ML2	Temperature	Emissions dependency on temperature removed	+340%	+230%
	ML3	All surface re-emissions	All losses from surface media turned off except re-emissions	+260%	-34%
Removal/Transformation "RT"	RT1	Reduced deposition	All dry deposition turned off	+200%	-11%
	RT2	Reduced oxidation	All oxidation turned off	+370%	-27%
	RT3	Increased oxidation	OH reaction rate constant increased	-13%	+8%
	RT4	Temperature	Substitute delta H of 153	-6%	-12%
Arctic "ARC"	ARC1	Arctic emissions	All Arctic emissions turned off	-5%	+4%
	ARC2	Reduced snow scavenging	Snow scavenging turned off	+7%	+5%
	ARC3	Increased snow re-emissions	Increase wind pumping factor 100x	+3%	No change

5
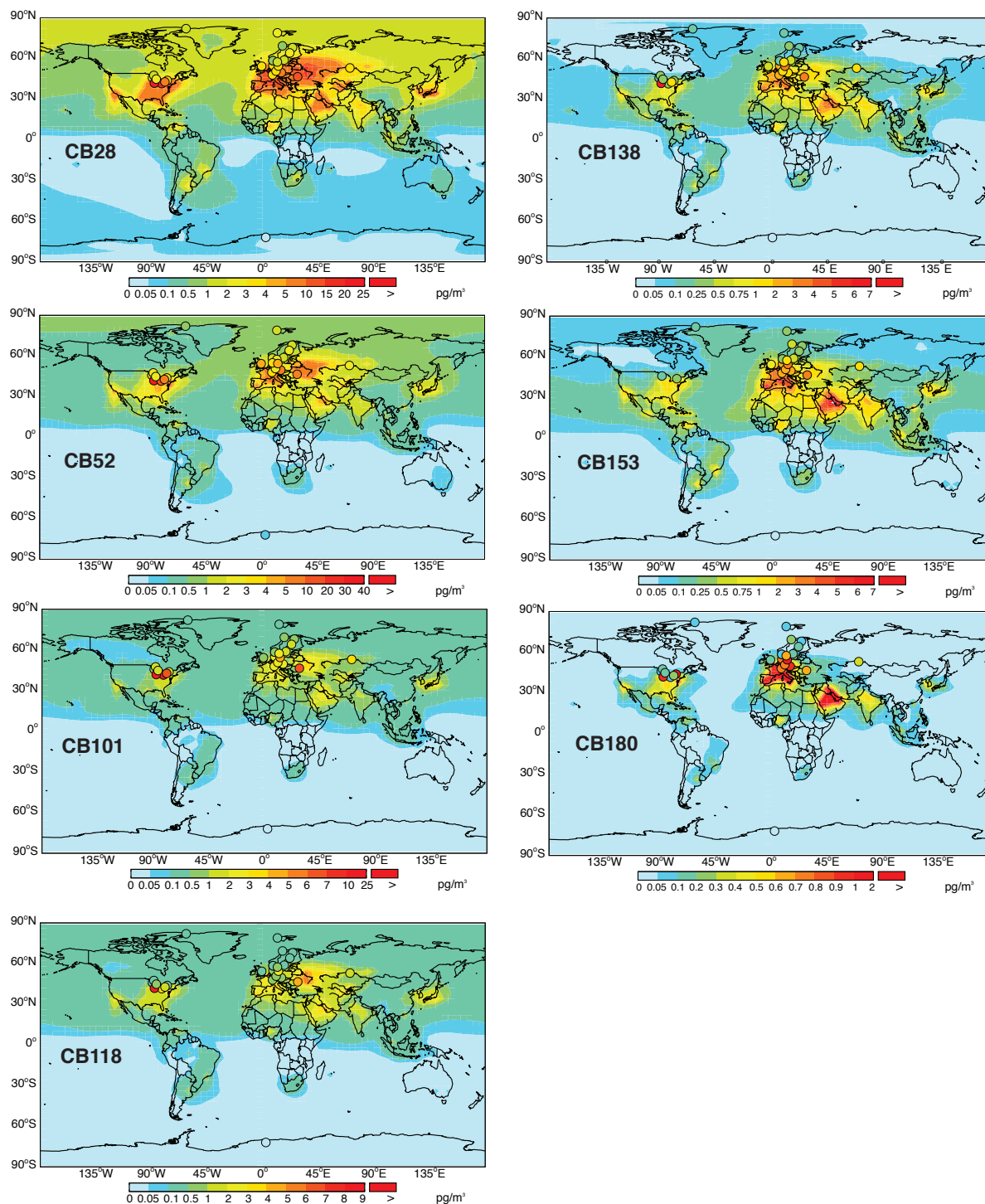
1
2 Figure 1. Average total (gas + particulate) simulated PCB concentrations in surface air from
3 2006 to 2010 (background) and land-based observations (circles) from measurement
4 stations listed in Table 1. Observations are interannual means from 2006 to 2010, except in
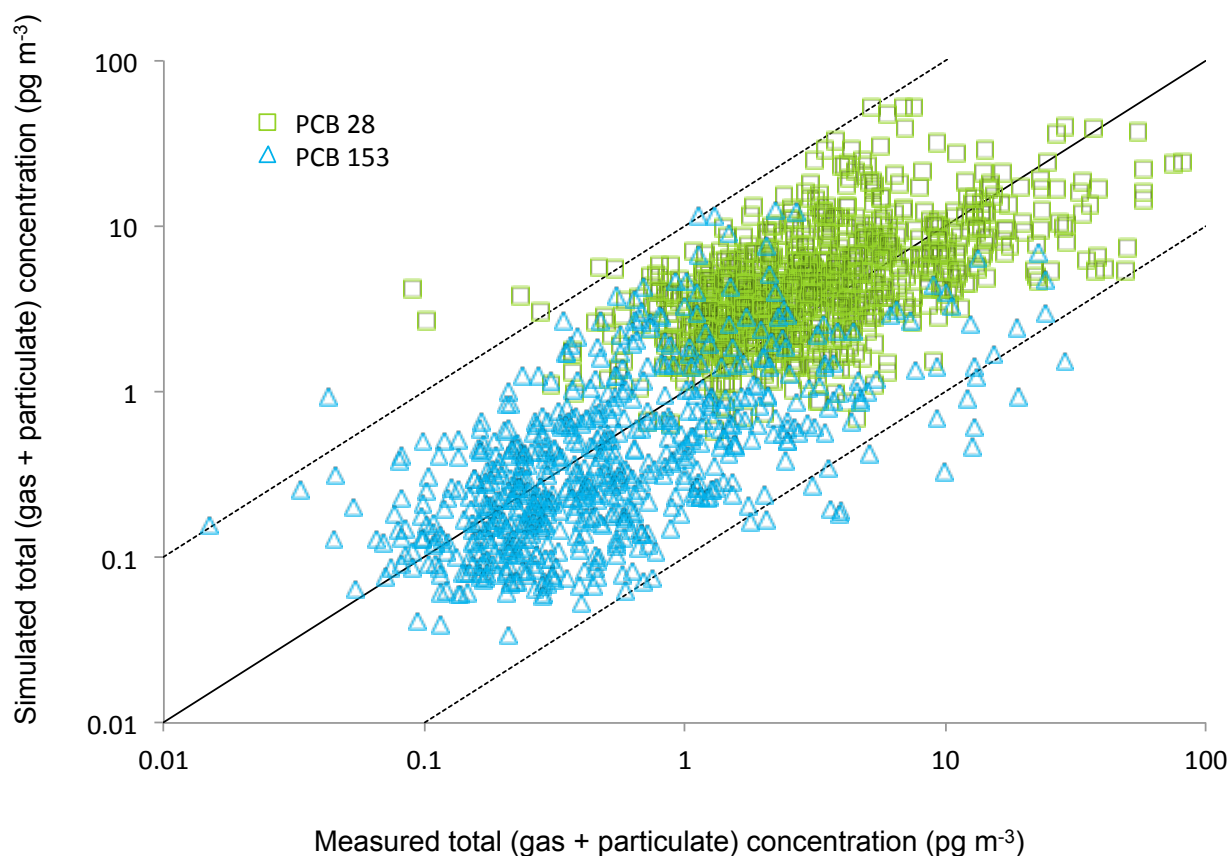5 some cases where only a subset of data was available.

Figure 2. Comparison of seasonal averages of simulated and measured total concentrations of CBs 28 and 153. Measurement data come from 23 different non-urban monitoring sites in the northern hemisphere, which correspond to 21 different GEOS-Chem grid boxes. The solid line represents a 1:1 relationship, while the dashed lines represent the boundaries where simulated concentrations are 0.1 and 10 times measured concentrations.
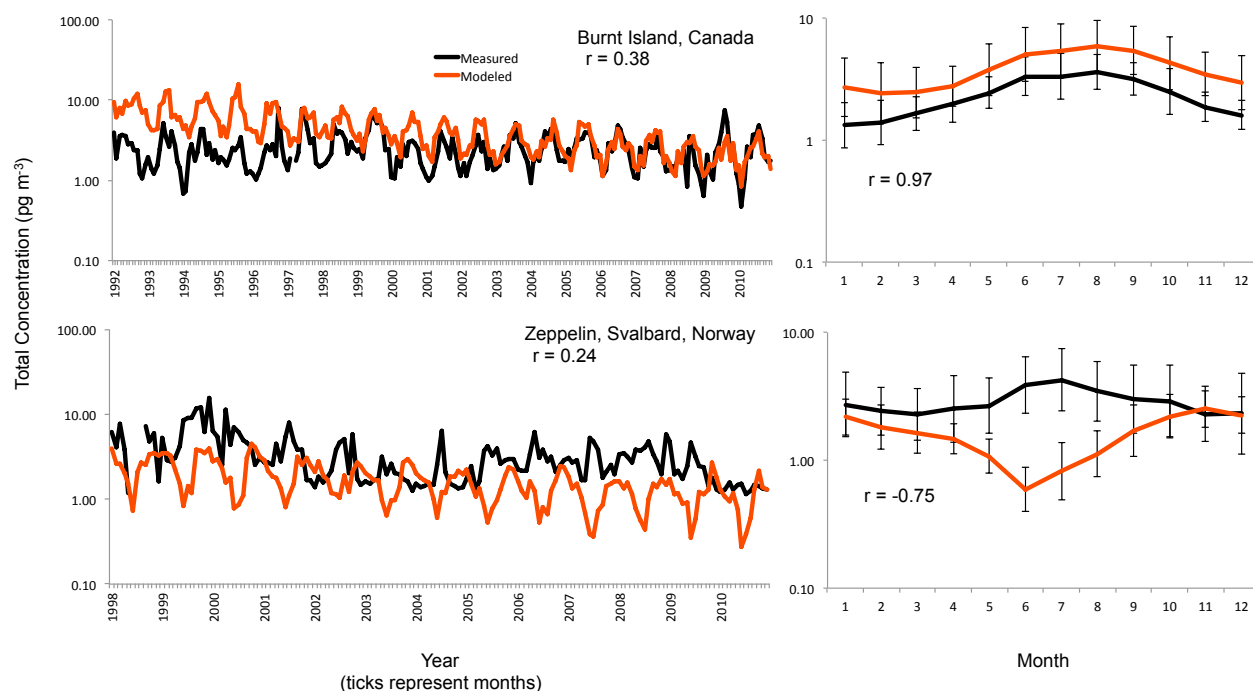
Figure 3. Total measured and simulated monthly mean concentrations of CB 28 at Burnt Island, Canada (top row) and Zeppelin, Norway (bottom row). The left-hand column is the full time series, while the right-hand column is an average of the data on the left over all years.
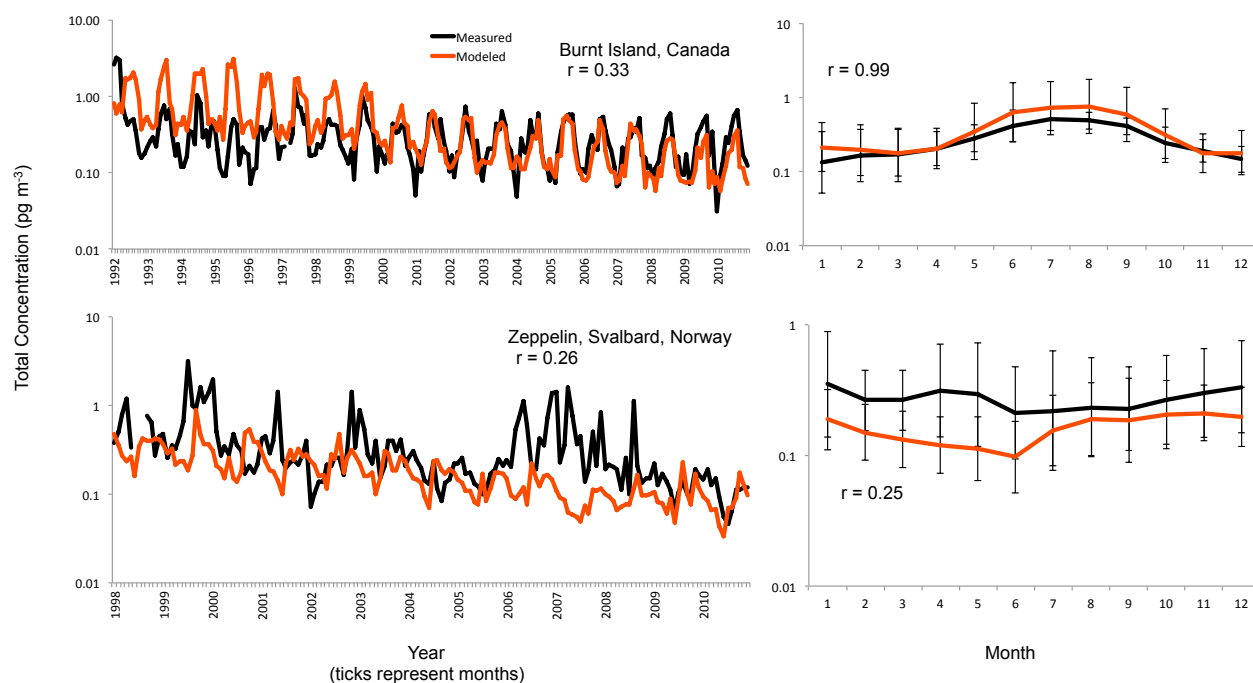
Figure 4. Total measured and simulated monthly mean concentrations of CB 153 at Burnt Island, Canada (top row) and Zeppelin, Norway (bottom row). The left-hand column is the full time series, while the right-hand column is an average of the data on the left over all years.
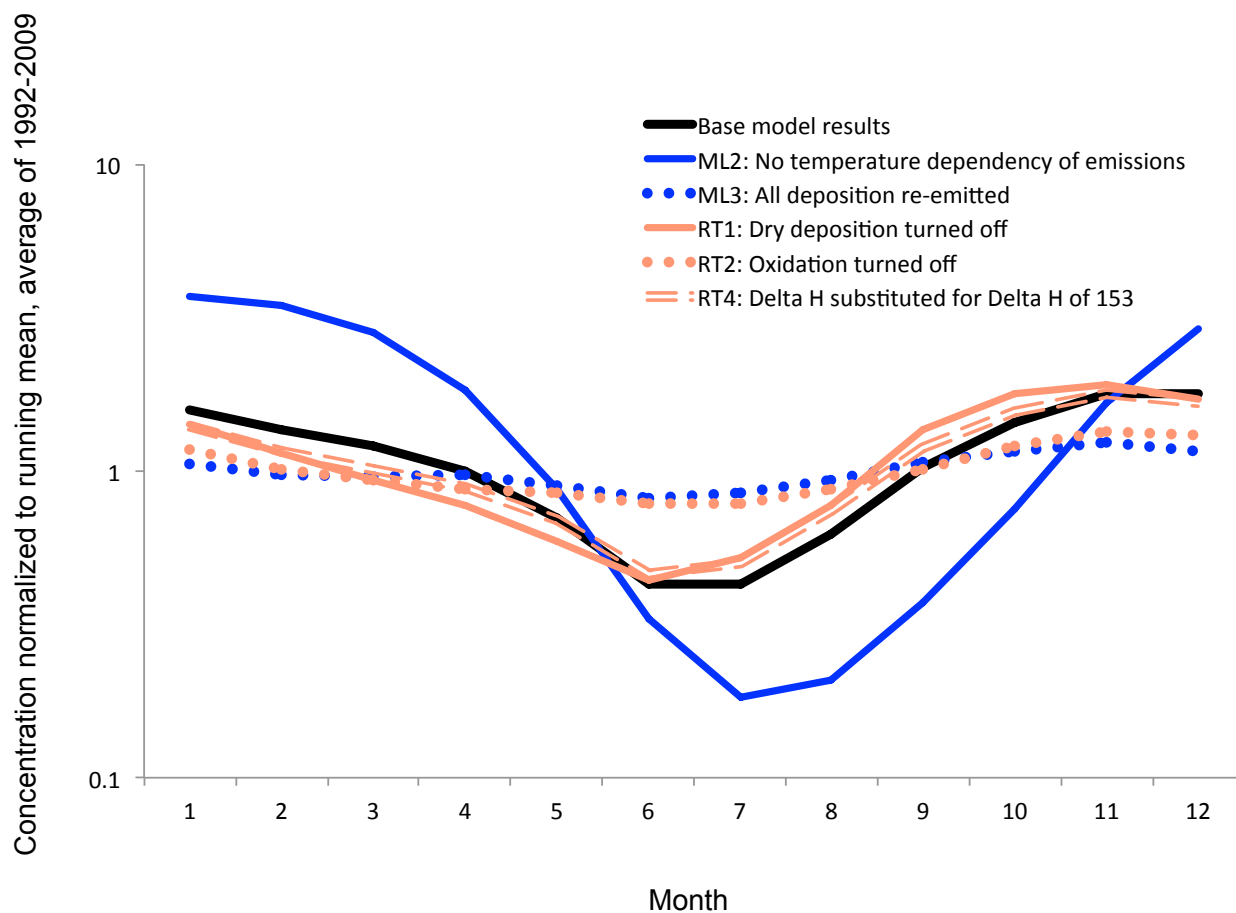
Figure 5. Changes in mean surface Arctic PCB 28 seasonal variation with sensitivity simulations, averaged over time (1992-2009). Simulated concentrations have been normalized to a running mean. Sensitivity simulations that flatten the simulated seasonal cycle are those that minimize the model-measurement gap in the Arctic.