

PCBs in the Arctic atmosphere

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

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Received: 21 August 2015 – Accepted: 14 October 2015 – Published: 5 November 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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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 the International Council for the Exploration of the Sea 7 PCBs, 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 internationally when the Stockholm Convention was adopted (2001) and entered into force (2004). PCBs continue to pose health risks, however, because of their recalcitrance and ability

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to cycle through environmental phases. Indigenous peoples and top marine predators in the Arctic are especially exposed to health risks from PCBs. Marine mammals bioaccumulate PCBs, and the traditional diets of the Arctic indigenous rely heavily on these animals. The surprisingly high body burdens in indigenous populations, given that PCBs generally were not used in the region, were first documented in the literature decades ago (e.g., Dewailly et al., 1989). However, there remain important uncertainties about the driving factors of Arctic concentrations, particularly in the context of reduced primary production and changing climate. Here, we use a chemical transport model to assess factors affecting the long-range atmospheric transport of PCBs to the Arctic.

Evidence of long-range atmospheric PCB transport to the Arctic from the Northern Hemisphere mid-latitudes, where their manufacture and use was concentrated, has been well-documented (e.g., Hung et al., 2001, 2005, 2010). The warmer temperatures of the mid-latitudes facilitate PCB volatilization and their subsequent transport via the atmosphere to the Arctic. Several hypotheses have been proposed to mechanistically describe the transport process and the observed global fractionation of PCBs. The most well known is the “global distillation hypothesis” (Wania and Mackay, 1993, 1996), whereby PCBs and other persistent organic pollutants (POPs) fractionate globally along a latitudinal temperature gradient depending on their volatility, similar to a gas chromatographic separation. 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. This latter hypothesis proposes that the observed global fractionation of PCBs is due primarily to different loss rates that act along a gradient of remoteness from emission source, rather than temperature differences (von Waldow et al., 2010).

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 be-

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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 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 vs. 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 concentrations and seasonal cycles.

We conclude by discussing implications of our work for studies of PCB concentrations under future climate.

2 Methods

2.1 GEOS-Chem PCB model

5 The GEOS-Chem POPs model has been previously developed and applied to PAHs (Friedman et al., 2014a, b; Friedman and Selin, 2012); here, we extend it to address PCBs. The GEOS-Chem POPs simulation (v9-01-03) includes oxidation of gas-phase species by hydroxyl radical (OH; scaled for diurnal variation), wet and dry deposition of both gas and particle phases, and temperature-dependent partitioning between the
10 gas and particle phases. For PCBs, we neglect particle phase oxidation, as there is no evidence in the literature that this is an important process. Second, we partition PCBs to one bulk organic matter (OM) phase, which combines the two different types of particle phases used in simulating PAHs: an OM phase and a black carbon (BC) phase. 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
15 have suggested PAH association with BC particles can explain LRT patterns (Friedman et al., 2014a), there is no such conclusive evidence that PCBs adsorb more strongly to BC than they do to OM. PCBs partition between the gas and particle phase following their octanol–air partition coefficients (K_{OA} , see Supplement, SI, for details). A separate NO_x – O_x –hydrocarbon–aerosol simulation of GEOS-Chem (v9-01-02) is used to
20 generate monthly mean concentrations of OM and OH, which are archived and read into the POPs simulation as input. OM particles to which PCBs associate convert from hydrophobic to hydrophilic with a lifetime of 1.2 days (Park et al., 2003); this serves to increase the efficiency of particle-phase PCB wet scavenging over time. We use the
25 “high” annual PCB emissions inventory from Breivik et al. (2007), compiled on a national basis and spatially allocated on a $1^\circ \times 1^\circ$ grid globally, as input emissions from

1930 to 2010. Primary emissions depend on ambient temperature following the van't Hoff equation:

$$E_{T_2} = E_{T_1} \times \exp \left[\frac{-\Delta H}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad (1)$$

where E_{T_2} is the emissions rate (kg s^{-1}) at the ambient surface air temperature T_2 (K), E_{T_1} is the emissions rate (kg s^{-1}) given by the emissions inventory at an assumed mean global surface temperature (T_1) of 288 K, ΔH is the internal phase transfer energy (J mol^{-1}) for the transfer from octanol to the vapor phase, and R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$). For simulated years 1930 (the start of PCB production and hence emissions; Breivik et al., 2007) to 1978, we use the GEOS5 assimilated meteorology data set from the NASA Global Modeling and Assimilation Office (GMAO) degraded to $4^\circ \times 5^\circ$ horizontally and 47 levels vertically. The GEOS5 product includes data from years 2004–2012; hence, we repeat a subset of meteorological years (2006–2008) for the 1930–1978 “spin-up” of the model. For simulated years 1979–2010 we use the NASA GMAO Modern Era Retrospective-analysis for Research and Applications (MERRA) data set, which is consistent over the 30+ year historical period. MERRA data are also downgraded from their native resolution to fit the model resolution. GEOS5 data are averaged at 3 or 6 h intervals, while MERRA data are averaged at 3 or 1 h intervals, depending on the variable. The native spatial resolution of both GEOS5 and MERRA products is $1/2^\circ \times 2/3^\circ$ with 72 vertical levels.

PCB simulations include an improved mechanism in the GEOS-Chem POPs model for surface–atmosphere interactions. PCB dynamics in surface compartments, which include soils, vegetation, lakes, oceans, and snow/ice, are parameterized with level IV fugacity box models embedded within GEOS-Chem. The parameterization of each surface compartment and methods for estimating the fractional coverage of a grid box by a given surface medium are described in detail in the SI, with references therein, along with tabulations of physicochemical constants used for each process and congener, but we provide a brief summary here.

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The fraction of soil coverage within a grid box is estimated by subtracting the fraction of snow from the fraction of land, which are both provided by the MERRA data set. Once deposited, PCBs are assumed to distribute within the top 5 cm. Sorption to soils is dependent on a soil–air partition coefficient (K_{SA}), which in turn depends on the fraction of organic carbon (OC) in the soil (f_{OC}) and K_{OA} . The f_{OC} is generated with a version of the CASA biogeochemical model previously coupled to GEOS-Chem (Smith-Downey et al., 2010) at latitudes between 60° N and 60° S; at the poles, a mean Arctic tundra lowlands soil carbon content (15.1 kg C m^{-2}) from the organic-enriched surface horizon (Ping et al., 2008) is used to estimate f_{OC} , as f_{OC} is not well defined by CASA in seasonally ice-covered regions. Losses of PCBs from soils include re-emissions, degradation, runoff, and leaching. Transfer of PCBs to soils can come from direct atmospheric deposition, from snow/ice melt, from vegetative litterfall, or from a fraction of wet deposition that has washed off vegetation. Additional citations used in creating the soil module include Mackay (2001), Mackay and Paterson (1991), Potter et al. (1993), and Ribes et al. (2003).

The fraction of a grid box covered in vegetation is estimated by multiplying the fraction of soil by a greenness index (values between 0 and 1), provided by the meteorological data. Deposition to vegetation includes all dry deposition and 10 % of wet deposition. The other 90 % of wet deposition is passed directly to soils (following Cousins and Mackay, 2000). All vegetation is assumed to consist of leaves having a surface thickness of $2 \times 10^{-6} \text{ m}$ and an internal reservoir of 0.01 m thickness, and a total vegetation volume in a grid box is estimated by multiplying total leaf thickness by the leaf area index (LAI). The sequestration of PCBs in vegetation is controlled by both the air–water partition coefficient (K_{AW}) and the K_{OA} . PCB losses from vegetation include re-emissions, litter loss, and degradation. Citations used in creating the vegetation module include Cousins and Mackay (2000, 2001), Mackay (2001), and Mackay and Paterson (1991).

The behavior of PCBs in freshwater and seawater is parameterized similarly. The fraction of lake in a grid box is given by the meteorological data, while the fraction of

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open ocean is estimated by subtracting the fraction of sea ice from the total fraction of ocean (both also provided by meteorological data). Deposition to both comes directly from the atmosphere or from melting snow/ice. Lakes are assumed to be 10 m deep while oceans are assumed to be 1000 m deep. We assume a volume fraction of 5×10^{-6} for particles in freshwater, with 20 % OC content. In seawater, we assume a particle volume fraction of 1×10^{-6} also with 20 % OC content. Sorption to particles is governed by the K_{OA} . Losses from both include re-emissions, degradation, and deposition to sediments with particles. Literature used in creating the lake and ocean modules includes Mackay (2001), Mackay and Paterson (1991), and Schwarzenbach et al. (2003).

The fraction of snow/ice in a grid box is estimated by adding the fractions of snow, sea ice, and land ice (provided by meteorological data). PCBs are deposited directly from the atmosphere to the ice/snowpack. Sorption of PCBs in snow depends on a snow surface–air adsorption coefficient (K_{CA}), which in turn depends on the density of the snow and the temperature-dependent specific snow surface area (surface area per unit mass). Losses from snow include re-emissions, degradation, meltwater runoff, and particle flushing. Literature used in creating the snow/ice module includes Abraham and Al-Hussaini (2005), Daly and Wania (2004), Hansen et al. (2006), Roth et al. (2004), and Stocker et al. (2007).

2.2 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 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 $\sim 100\times$. We

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do this by re-running the 1930–1978 with the ocean depth decreased by a factor of 10 (from 1000 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 Eq. 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 ($1.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) with the upper 95 % confidence limit value ($1.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$). 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 vs. 78.4 kJ mol⁻¹; 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 con-

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to Arctic concentrations. Both sets of ratios generally increase with increasing $\log K_{OA}$, though the relationship is not statistically significant at $\alpha = 0.05$ ($p = 0.14$ and 0.08 for observations and model results, respectively). The increase, however, indicates greater long-range transport potential for congeners that do not deposit as readily (as deposition increases with increasing $\log K_{OA}$ in the model). This is consistent with the “differential removal” hypothesis from von Waldow et al. (2010). In the Antarctic, simulated concentrations range from 25 % (CB 180) to 1.4 times (CB 28) observed concentrations, demonstrating that the model captures the approximately order of magnitude difference observed between the Arctic and Antarctic for all congeners.

Table 3 provides linear relationships and correlations between simulated and observed mean concentrations for all NH non-urban locations (i.e., NUML + Arctic sites), with Pearson correlation coefficient (r) values ranging from 0.55 (CB 118) to 0.77 (CBs 153 and 180). There was no systematic bias in the model with congener volatility.

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 concentrations within a factor of $10^{0.5}$ 77 % of the time, and within a factor of 10 98 % of the time (Fig. 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, 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 representa-

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tive 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.

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 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 (winter minimum, summer maximum). Thus, there is a strong anticorrelation between observed and simulated concentrations ($r = -0.75$ for the temporal averages). 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 simulated concentrations as well, with the larger peak arriving in June–August, and a smaller peak in November–January. However, because the model predicts maxima roughly a month before observed maxima, the correlation is not very

strong ($r = 0.25$ for the temporal averages). This mismatch is explored further in our sensitivity simulation with CB 28.

3.2 Global atmospheric budgets and lifetimes

The budget from simulated years 2006–2010 indicates that for all congeners the atmosphere, vegetation, lakes, and snow are at steady state, while the ocean and soils are emitting legacy deposition. Table 4 summarizes the atmospheric portion of the budget. Dry deposition of the gas phase and OH oxidation are the two main loss routes for all seven congeners, though their relative importance changes across the congener spectrum. For example, dry deposition accounts for 82 % of the loss of CB 180, but only 30 % for CB 28. Conversely, OH oxidation accounts for 65 % of the loss of CB 28, but only 13 % for CB 180. Though we predict substantially lower total masses of PCBs in the atmosphere compared to other PCB modeling studies (e.g., Huang et al., 2007, whose simulated concentrations generally biased high while ours generally bias low), the relative percentages of loss due to oxidation vs. deposition across congeners are similar.

The particle phase makes up only a very small fraction of the total budget for all congeners. CB 28 has the least in the particle phase (0.02 %) while CB 180 has the most (1.4 %). This is in contrast to GEOS-Chem simulations of PAHs, where 93 % of benzo[a]pyrene was found to be in the particle phase (Friedman and Selin, 2012). The difference can be attributed to PAH preferentially strongly binding to BC, a process that has not been observed to the same degree for PCBs and hence does not exist in the PCB model (BC and OC particles are treated as one particle type for PCBs, with partitioning controlled by the K_{OA} for both). The small fraction in the particle phase results in nearly all wet and dry deposition (> 99 % for all congeners) being attributable to the gas phase.

The relative contribution of re-emissions to total atmospheric emissions generally decreases with increasing degree of chlorination. CB 52 has the highest percentage of re-emissions (9.2 %), while CB 180 has the least (1.9 %). Re-emissions can en-

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hance transport to remote regions, as they can occur anywhere PCBs have previously deposited; this is consistent with the different distributions seen in the Arctic across congeners in Fig. 1 (i.e., a greater fraction of CB 28 in the Arctic atmosphere vs. CB 180), and the increase in measured NUML-to-Arctic ratios with increasing chlorination shown in Table 2, which is generally captured by the model.

The model predicts short atmospheric lifetimes of PCBs, ranging from 4.5 to 9.4 h (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 (66–90° N, 180° W–180° E).

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

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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 Fig. 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 temper-

ature 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 compared to observations at Arctic stations for the more volatile PCBs. 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.

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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 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). 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

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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). The concentration increases at Arctic stations cited by Ma et al., however, were more prominent for heavier PCB 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

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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.

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

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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.

**The Supplement related to this article is available online at
doi:10.5194/acpd-15-30857-2015-supplement.**

Acknowledgements. We acknowledge support from the U.S. National Science Foundation's Arctic Natural Sciences program #1203526, Dynamics of Coupled Natural Human Systems program #13113755, and Atmospheric Chemistry program #1053648. C. L. Friedman was partially supported under NIH Training Grant T32-ES007-020. We thank Colin Thackray (MIT) and Helen Amos (Harvard University) for helpful discussions and computing assistance, and Hayley Hung (Environment Canada and Northern Contaminants Program) for helpful discussions regarding Alert PCB data interpretation.

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Table 1. Stations where observational data were obtained; first four sites considered Arctic.

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
<i>58.4</i>	<i>8.3</i>	<i>190</i>	<i>Birkenes Norway</i>	<i>b</i>
<i>58.4</i>	<i>8.3</i>	<i>219</i>	<i>Birkenes II Norway</i>	<i>b</i>
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

References: (a) Hayley Hung/Northern Contaminants Program, personal communication, 2013; (b) EMEP (Cooperative Programme for Monitoring and Evaluation of the Long-range Transmissions of Air Pollutants in Europe); (c) Helena Dryfot-Clark/IADN (Integrated Atmospheric Deposition Network), Environment Canada, personal communication, 2013. ^{*} Site considered urban and not included in model-measurement comparison. [%] Site where total deposition is measured. Sites listed in bold/italics were averaged as they occurred within the same model grid box.

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Table 2. Observed vs. simulated geometric mean concentrations averaged over all sites listed in Table 1 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 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)		Sim/Obs	NUML geomean (range factor 1 SD)		Sim/Obs	Mid-lat/Arctic ratio		Antarctic (Troll) geomean		Sim/Obs
	Obs	Sim		Obs	Sim		Obs	Sim	Obs	Sim	
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

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N. E. Selin**Table 3.** Linear relationships and correlations between simulated and observed mean concentrations for all NH non-urban locations (i.e., NUML + Arctic sites) with Pearson correlation coefficient (r) values.

PCB	Linear relationship	r
28	$Y = 1.15x + 1.28$	0.64
52	$Y = 0.32x + 0.95$	0.57
101	$Y = 0.17x + 0.32$	0.56
118	$Y = 0.46x + 0.48$	0.53
138	$Y = 0.25x + 0.25$	0.61
153	$Y = 0.40x + 0.19$	0.73
180	$Y = 0.27x + 0.07$	0.75

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**PCBs in the Arctic
atmosphere**C. L. Friedman and
N. E. Selin**Table 4.** Mean 2006–2010 atmospheric budget of PCBs. For all congeners, total wet and dry deposition was dominated by the gas phase (> 99 % attributable to the gas phase).

Congener	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; h)	9.4	8.1	6.7	6.5	5.3	5.9	4.5

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Arctic driver	Simulation name	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 $\sim 100\times$	+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 δH 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 $100\times$	+3 %	No change

* Measured by taking the ratio of mean January normalized concentrations. Simulations that increase the mean concentration while simultaneously decreasing the seasonal pattern amplitude (simulations ML3, RT1, and RT2) are those that bring model and observational results closer together.

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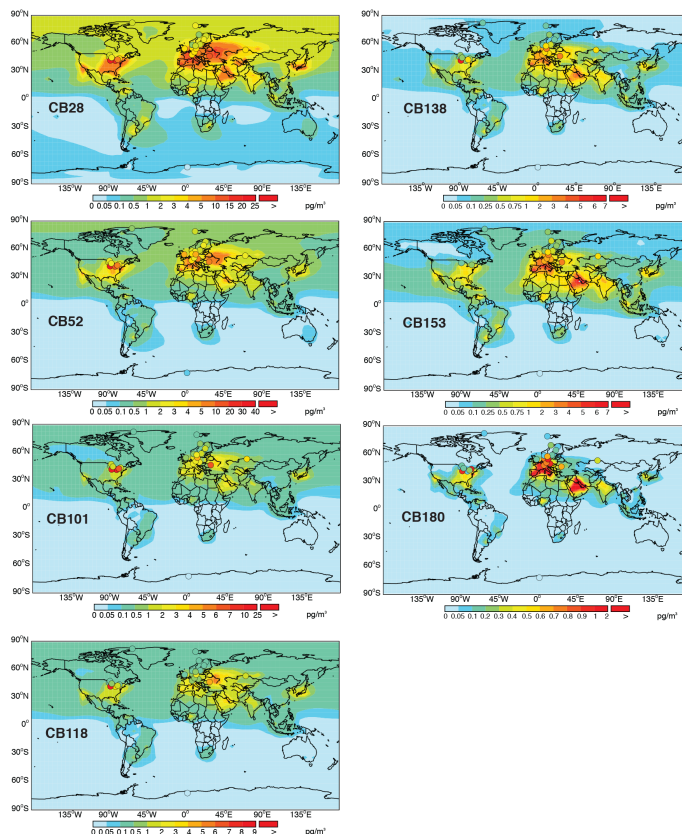


Figure 1. Average total (gas + particulate) simulated PCB concentrations in surface air from 2006 to 2010 (background) and land-based observations (circles) from measurement stations listed in Table 1. Observations are interannual means from 2006 to 2010, except in some cases where only a subset of data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

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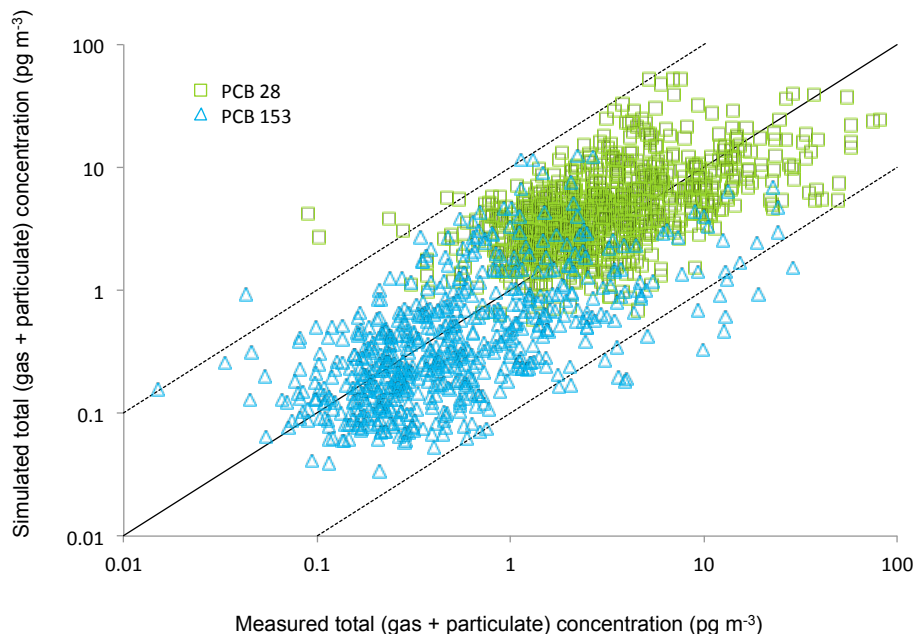


Figure 2. Comparison of seasonal averages of simulated and measured total concentrations of CBs 28 and 153. Measurement data come from 23 different non-urban monitoring sites in the Northern Hemisphere, which correspond to 21 different GEOS-Chem grid boxes. The solid line represents a 1 : 1 relationship, while the dashed lines represent the boundaries where simulated concentrations are 0.1 and 10 times measured concentrations.

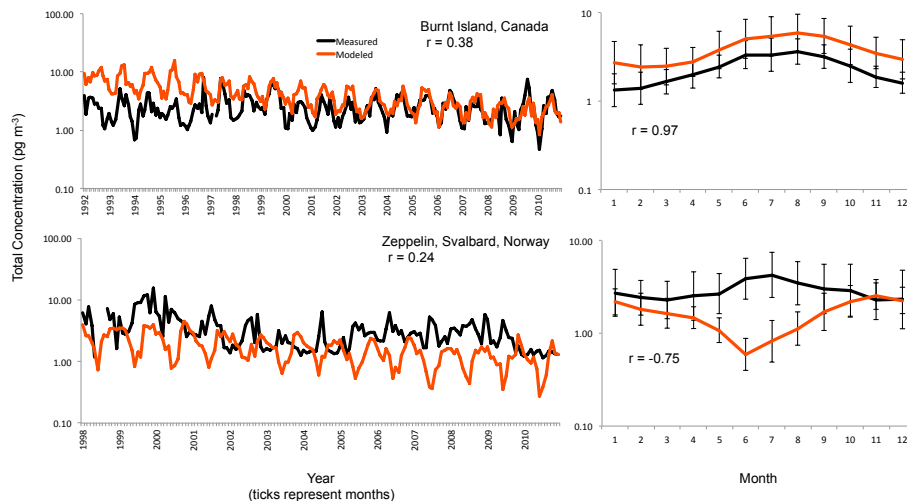
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Figure 3. Total measured and simulated monthly mean concentrations of CB 28 at Burnt Island, Canada (top row) and Zeppelin, Norway (bottom row). The left-hand column is the full time series, while the right-hand column is an average of the data on the left over all years.

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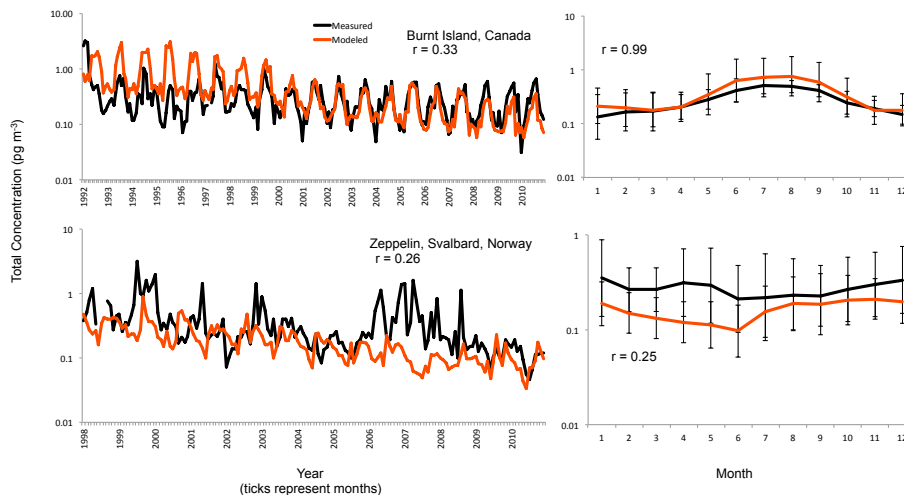
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Figure 4. Total measured and simulated monthly mean concentrations of CB 153 at Burnt Island, Canada (top row) and Zeppelin, Norway (bottom row). The left-hand column is the full time series, while the right-hand column is an average of the data on the left over all years.

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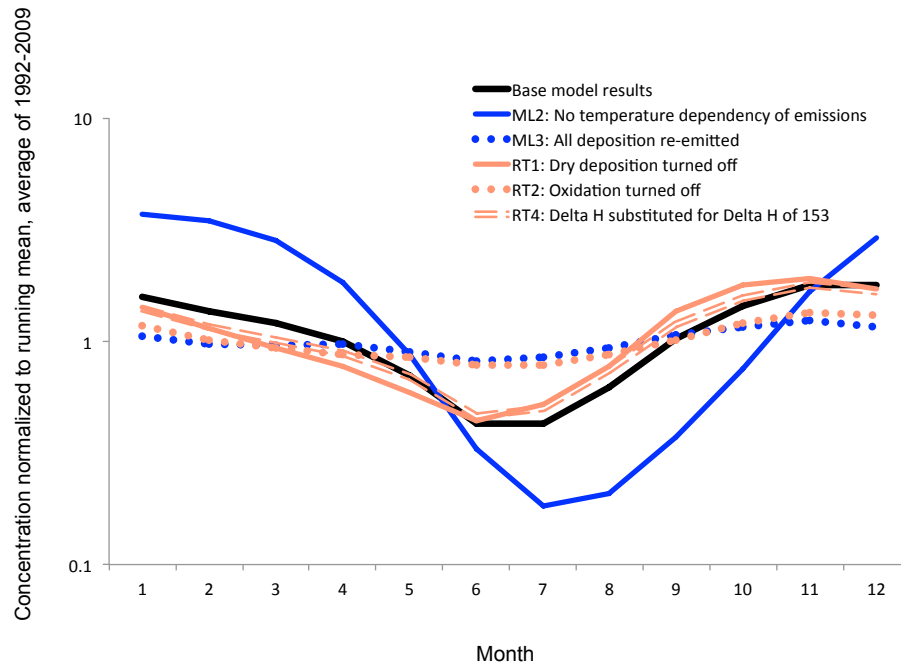


Figure 5. Changes in mean surface Arctic PCB 28 seasonal variation with sensitivity simulations, averaged over time (1992–2009). Simulated concentrations have been normalized to a running mean. Sensitivity simulations that flatten the simulated seasonal cycle are those that minimize the model-measurement gap in the Arctic.