Atmos. Chem. Phys. Discuss., 15, 6509–6535, 2015
www.atmos-chem-phys-discuss.net/15/6509/2015/
doi:10.5194/acpd-15-6509-2015
© Author(s) 2015. CC Attribution 3.0 License.

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Modelling impact of climate change on atmospheric transport and fate of persistent organic pollutants in the Arctic

K. M. Hansen[1], J. H. Christensen[1], C. Geels[1], J. D. Silver[1,*], and J. Brandt[1]

[1]Department of Environmental Science and Arctic Research Centre, Aarhus University, Frederiksborgvej 399, 4000 Roskilde, Denmark
[*]now at: School of Earth Sciences, University of Melbourne, Victoria, 3010, Australia

Received: 8 January 2015 – Accepted: 9 February 2015 – Published: 5 March 2015

Correspondence to: K. M. Hansen (kmh@envs.au.dk)

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

Abstract

The Danish Eulerian Hemispheric Model (DEHM) was applied to investigate how projected climate changes will affect the atmospheric transport of 13 persistent organic pollutants (POPs) to the Artic and their environmental fate within the Arctic. Two sets of simulations were performed, one with initial environmental concentrations from a 20 year spin-up simulation and one with initial environmental concentrations set to zero. Each set of simulations consisted of two ten-year time slices representing the present (1990–2000) and future (2090–2100) climate conditions. The same POP emissions were applied in all simulations to ensure that the difference in predicted concentrations for each set of simulations only arises from the difference in climate input. DEHM was driven using meteorological input from the global circulation model, ECHAM/MPI-OM, simulating the SRES A1B climate scenario. Under the applied climate and emission scenarios, the total mass of all compounds was predicted to be up to 20 % higher across the Northern Hemisphere. The mass of HCHs within the Arctic was predicted to be up to 39 % higher, whereas the change in mass of the PCBs was predicted to range from 14 % lower to 17 % higher depending on the congener and the applied initial environmental concentrations. The results of this study also indicate that contaminants with no or a short emission history will be more rapidly transported to and build up in the arctic environment in a future warmer climate. The process that dominates the environmental behaviour of POPs in the Arctic under a future warmer climate scenario is the shift in mass of POPs from the surface media to the atmosphere induced by the higher mean temperature. This is to some degree counteracted by higher degradation rates also following the higher mean temperature. The more dominant of these two processes depend on the physical-chemical properties of the compounds. Previous model studies have predicted that the effect of a changed climate on the transport of POPs to the Arctic is moderate relatively to the effect of proposed changes in emissions, which is confirmed in this study. However, the model studies do not agree on

ACPD
15, 6509–6535, 2015

whether climate change acts to reduce or increase environmental concentrations of POPs in the Arctic, and further work is needed to resolve this matter.

1 Introduction

The climate has changed in recent decades with the main sign being an increase in global mean temperature. In both the 4th and the recent 5th IPCC Assessment Report (AR4 and AR5), the multi-model ensembles project an increase in the global mean temperature in the range of 1–6 °C by the end of the 21st century, relative to pre-industrial temperature levels (IPCC, 2007; Rogelj et al., 2012). The broad range in the projected temperature increase is linked to the various greenhouse gas emission scenarios used as input to the climate simulations.

Within the Arctic these changes are projected to be larger than elsewhere. According to one of the intermediate emission scenarios applied in AR4, the SRES A1B scenario, the average temperature increase in the Arctic exceeds 9 °C by the end of the 21st century compared to the 1990s (Hedegaard et al., 2012). The increasing temperature leads to enhanced seasonal melting of the Arctic Ocean sea ice, retreating of glaciers and melting of the Greenland ice sheet. Changes are also projected for precipitation patterns as well as in weather patterns in general.

Climate change impacts the physical and chemical processes in the atmosphere, including atmospheric transport pathways, chemical composition, air–surface exchange processes, natural emissions, etc., see Jacob and Winner (2009) for a review. Changes in climate alone might lead to both lower or higher levels of specific pollutants in the atmosphere leading to a lower or higher exposure, which can be referred to as a "climate benefit" or "climate penalty", respectively. During the last decade a number of studies have examined the effects of climate change on air pollutants such as ozone (Hedegaard et al., 2008, 2012; Anderson et al., 2010; Langner et al., 2012) and particulate matter (Hedegaard et al., 2013; Colette et al., 2013; Simpson et al., 2014). So far the most robust signal is seen for ozone with an overall climate penalty projected for the

ACPD
15, 6509–6535, 2015

future; however, there are large uncertainties associated with for example the natural sources for ozone precursors and their sensitivity to climate changes (Langner et al., 2012). It has also been shown that this kind of study is very dependent on the applied climate input (Manders et al., 2012).

The environmental fate of persistent organic pollutants (POPs) is determined by many different environmental factors, several of which may be affected by climate change, thus making the combined effect difficult to predict. A report from an UNEP/AMAP expert group outlines qualitatively the effects of a warming of the climate on the cycling and fate of POPs in the environment (UNEP/AMAP, 2011): increasing temperatures can lead to changed partitioning between the different media as well as to enhanced re-volatilization from historically deposited compounds, which can lead to larger atmospheric transport. Higher temperatures also increase degradation rates in both air and surface media. Melting of polar ice caps and glaciers will result in larger air–surface exchange and the melting ice may release stored POPs to the marine and atmospheric environments. Higher wind speed may lead to enhanced atmospheric transport downwind of major source areas and increasing precipitation in the Arctic may lead to increasing deposition.

The effect of a changed climate on the transport and fate of POPs in the Arctic has been investigated in a few studies with a range of different modelling approaches and model setups (Lamon et al., 2009; Armitage et al., 2011; Gouin et al., 2013; Wöhrnschimmel et al., 2013; Armitage and Wania, 2013). Despite differences in modelling approaches, the studies generally predict that the effect of changed climate on simulated environmental concentrations is within a factor of two. However, the applied models in the previous studies have a low spatial resolution with 10 zonally averaged climate zones and 4 atmospheric layers (Armitage et al., 2011; Armitage and Wania, 2013), 25 geographically explicit compartments (Gouin et al., 2013) or $15^{\circ} \times 15^{\circ}$ regular grid and 2 atmospheric layers (Lamon et al., 2009; Wöhrnschimmel et al., 2013) as well as simplified representations of important atmospheric processes. It is thus important

ACPD
15, 6509–6535, 2015

to test whether the predictions from these studies are reliable using more advanced models.

The aim of this study is to investigate how a changed climate will affect the fate of POPs with special focus on the transport to and fate within the Arctic, and to determine if there will be a climate penalty or benefit on POPs in terms of higher or lower environmental concentrations and thus higher or lower potential exposure. The applied model has a much higher spatial resolution and with more detailed descriptions of atmospheric degradation and airborne particulate matter than previous model studies, and was previously applied to study the effect of climate change on future atmospheric levels of ozone and particulate matter (Hedegaard et al., 2008, 2012; 2013; Langner et al., 2012; Simpson et al., 2014).

2 Material and method

We applied the Danish Eulerian Hemispheric Model (DEHM), a 3-D dynamic atmospheric chemistry-transport model covering the Northern Hemisphere with a horizontal resolution of 150 km × 150 km and 20 vertical layers extending to a height of 10 hPa. DEHM comprises a comprehensive chemistry scheme including full ozone chemistry and particulate matter and is driven by meteorological data (temperature in air and surface media, pressure, wind velocity, humidity, solar radiation, cloud cover and sea ice cover) from a numerical weather prediction model. A detailed description of the model can be found in Christensen (1997), Frohn et al. (2002) and Brandt et al. (2012). DEHM has successfully been applied to study the transport and fate of a range of chemical compounds to the Arctic, including sulphur and sulphate (Christensen, 1997), mercury (Christensen et al., 2004; Skov et al., 2004), POPs (Hansen et al., 2004, 2008a, b) and Decamethylcyclopentasiloxane (Krogseth et al., 2013). Two-way air–surface gas exchange processes as well as intra-compartmental processes are included for the surface compartments soil, water, vegetation and snow (Hansen et al., 2004, 2008a). Model evaluations against measured air concentrations show reasonable agreement

ACPD
15, 6509–6535, 2015

with predicted concentrations for a range of persistent compounds (Hansen et al., 2004, 2006; 2008a, b; McLachlan et al., 2010; Genualdi et al., 2011; Krogseth et al., 2013).

Most of the environmental processes described in DEHM are climate-dependent and they will therefore affect the predicted fate of POPs under a changed climate. Temperature is the main driver that affects the partitioning between gas- and particle-phase POPs in air, degradation of gas-phase compounds in air, vegetation and snow, degradation in soil and water as well as the air–surface gas-exchange for the surface media. Changes in precipitation patterns will affect the scavenging of POPs from the atmosphere and the flush-through of water of the soil compartment and changes in the snow cover and sea ice cover will affect the air–surface gas-exchange for the surface media (Hansen et al., 2004, 2008a).

2.1 Model set-up

A total of 13 different POPs are included in the model simulations: α-, β-, and γ-HCH and 10 PCB congeners: PCB8, PCB28, PCB31, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180, and PCB194. In addition, the simulations are made with the regular chemistry scheme, including 67 compounds. This ensures a proper description of airborne particulate matter with which POPs can associate and the OH radicals, the primary degradation oxidant for POPs in the atmosphere.

We have performed two sets of simulations, one set with initial environmental concentrations from a 20 year spin-up simulation (the "W" simulations) and one set with zero initial environmental concentrations (the "WO" simulations). The spin-up simulation was initialized with zero environmental concentrations for all compounds except for α-HCH in which case environmental concentrations were taken from a previous study using a 45 year spin-up period (Hansen et al., 2008a). Each set of simulations consist of two ten-year time slices representing present (1990–2000, "W19" or "WO19") and future (2090–2100, "W20" or "WO20") climate. We have applied the same emissions in all simulations. With this set-up the difference in predicted concentrations for each

ACPD
15, 6509–6535, 2015

set of simulations arises only from the effect the difference in climate input has on the transport and deposition processes. As driver of the simulations we have applied meteorological data obtained from a model simulation made with the ECHAM5/MPI-OM model (Roeckner et al., 2003, 2006; Marsland et al., 2003;) simulating the SRES A1B scenario (Nakicenovic et al., 2000). The SRES A1B scenario projects the global average temperature to increase by ∼ 3 °C by the end of the 21st century with large seasonal and regional differences in the warming with annual temperature increase exceeding 6 °C in the sub-polar regions of Asia, North America and Europe. The average sea ice extent in the Arctic is estimated to retreat by approximately 40 %, and over the Barents Sea the sea ice is predicted to vanish completely by the end of the 21st century. The globally averaged precipitation changes only slightly, although there are large regional and seasonal differences. The winter precipitation over the temperate and arctic regions is projected to increase by 10–50 %. The global temperature change related to the SRES A1B scenario from AR4 is quite similar to the RCP6 scenario used in the IPCC AR5 (Rogelj et al., 2012). The SREAS A1B is only one of several climate change scenarios and represents an intermediate development of the climate. The projected changes in this study should be viewed in this context.

2.1.1 Input data

DEHM requires physical-chemical properties and emission data for each of the modelled compounds as input for the model simulations. Temperature dependent physical-chemical properties for the HCHs are from Xiao et al. (2004) and for the PCBs from Schenker et al. (2005), degradation rates in air are derived from Beyer et al. (2003), and reaction half lives in soil and water are from common model input properties for the ArcRisk project (Wöhrnschimmel, personal communication; Table S1). α-HCH emissions for the year 2000 are from Hansen et al., (2008), β-HCH emissions are calculated as 1/6 of the α-HCH emissions and γ-HCH are calculated emissions for the year 2005 (Li et al., 2008). For the PCBs, annual emissions from 2007 based on the high emission scenario from Breivik et al. (2007) are applied (Table S2).

ACPD
15, 6509–6535, 2015

3 Results

3.1 The Northern Hemisphere

We have calculated the total mass in each of the compartments in the entire model domain. The total mass of α-HCH decreases over the modelled decades for the "W" simulations with a more rapid decline for the 2090s than for the 1990s (Fig. S1 in the Supplement). The mass of β-HCH and the intermediately chlorinated PCBs (PCB101–PCB118) display the same pattern, whereas the mass of γ-HCH and the most chlorinated PCBs (PCB138–PCB194) increases through the modelled decades. The mass of the least chlorinated PCBs (PCB8–PCB52) increases for the 1990s and decreases for the 2090s (Fig. S1). For the "WO" simulations the mass of all compounds increases more rapidly for the 1990s than for the 2090s (Fig. S1).

To evaluate the difference between the modelled masses in the 1990s and the 2090s we have calculated the linear trend of the difference in annual averages of the total mass (Figs. S2 and S3). The mass within the entire model domain is lower in the 2090s than in the 1990s for all compounds except for β-HCH and γ-HCH where the mass is 2 and 0.2 % higher, respectively (Fig. 1). The largest differences are found for the least chlorinated PCB congeners (20 %).

Within the entire model domain around 90 % of the three HCHs are found in water in the 1990s for the "W" simulation (Fig. S4). The predominant medium for all PCB congeners is soil (45–90 %). For the least chlorinated PCB congeners the highest fraction found in air is 10 %, while the fraction in air is negligible for the intermediate and most chlorinated congeners. The fraction associated with water is lowest for the intermediate chlorinated congeners and higher (up to 35 %) for the least and most chlorinated congeners. For the "WO" simulations the inter-media distribution is almost the same for the HCHs and the least chlorinated PCBs, whereas for the more chlorinated PCBs (PCB101 and higher) more mass is found in vegetation and water, and less in soil (Fig. S4).

ACPD
15, 6509–6535, 2015

Relatively small differences in the inter-media distribution are found between the 1990s and the 2090s (Figs. S4 and S5). The most notable change is in the snow compartment, with 45–70 % lower masses, but since the mass in snow is small compared to the mass in other media this makes little change to the inter-media distribution (Fig. S4). The mass in air is higher in the 2090s than in the 1990s for the HCHs and the least chlorinated PCB congeners (Fig. S5).

The mass of α-HCH decreases with time in all compartments, with seasonal variations, for the "W" simulations, whereas it increases for the "WO" simulations (Fig. S6). The mass in soil and ocean water is lower in the 2090s than in the 1990s, but the mass in air is higher in the 2090s for both sets of simulations (Fig. S6). Highest air concentrations are seen over the countries and regions with most recent use, such as India, Southeast Asia, Tunisia and Nigeria at the end of the 1990s (Fig. 2). High concentrations are also seen over the Pacific and the North Atlantic Oceans with sharp land–sea contrasts, which show that re-volatilization from the oceans is a major source of atmospheric α-HCH in these areas. The pattern is similar at the end of the 2090s but with generally higher concentrations in the entire model domain. Largest relative differences between the two periods are found over the Arctic and North America (Fig. 2). The large relative differences over Africa and the Pacific Ocean at the border of the domain are not considered here because the concentrations are very low in these areas.

The averaged ocean water concentration in the Arctic decreases during the modelled decades and is lower in 2099 than in 1999 (Fig. 2). There are regional differences with lower concentrations around Svalbard, in the Eastern Arctic Ocean and in the Canadian Archipelago and higher concentrations in the central Arctic Ocean. The average soil concentrations within the Arctic also decreases during the simulated decades with a more rapid decline in soil concentrations for the 2090s than for the 1990s. Large regional differences are seen for the soil compartment (Fig. 2).

Monthly averaged masses in air, water and soil over the modelled decades (Fig. S6) are shown in the Supplement. The pattern of the total mass follows closely the pattern of the most dominant medium, i.e. water for the HCHs and soil for the PCBs (Fig. S6).

ACPD
15, 6509–6535, 2015

The mass of PCBs in air from the "W" and "WO" simulations cannot be distinguished from each other at the end of the simulated decades except for the most chlorinated congeners (PCB153 and higher). The masses of γ-HCH in air are very similar for both sets of simulations (Fig. S6).

3.2 The Arctic

The Arctic, the focus area in this study, is defined as the area north of the Arctic Circle (66.5° N). Sea ice/water covers 62 % of the area in the Arctic, the rest is land mass. The total mass of α-HCH within the Arctic decreases over the modelled decades for the "W" simulation with a more rapid decline for the 2090s than for the 1990s (Fig. S9). For the "WO" simulations the total mass within the Arctic increases, but contrary to the whole model domain the mass within the Arctic increases more rapidly in the 2090s than in the 1990s. Apart from PCB194, the most chlorinated PCB congeners (PCB52–PCB180) display the same pattern. The mass of β-HCH shows a similar pattern except that the mass decreases most rapidly for the 1990s for the "W" simulations. The mass of γ-HCH follows the same pattern as the mass of α-HCH for the "WO" simulations, but for the "W" simulations the mass for the 2090s increases, whereas the mass for the 1990s is almost constant. For the least chlorinated PCB congeners (PCB8–PCB31), the mass increases for both sets of simulations with most rapid increases for the 1990s (Fig. S7).

The total mass of the HCHs and the most chlorinated PCB congeners (PCB101 and higher) within the Arctic is higher in the 2090s than in the 1990s for the "WO" simulations, whereas it is lower for the least chlorinated PCB congeners. The pattern is almost the same for the "W" simulation except for α-HCH, PCB101 and PCB118 for which the total mass is lower in the 2090s (Fig. 1). The largest differences are found for the HCHs (20–40 %).

Within the Arctic, higher fractions of HCHs are found in soil than in the entire model domain for both sets of simulations, but water is still the predominant medium for the

ACPD
15, 6509–6535, 2015

HCHs in the Arctic (Fig. S8). Soil is also the predominant medium for the PCBs for the "W" simulations, while water is the predominant medium for the "WO" simulation.

The fraction found in snow is considerable for the "WO" simulation although there is no distinct pattern between the fraction in snow and the chlorination of the PCB congeners. For the "W" simulation, considerable fractions in snow are only seen for the least chlorinated PCB congeners. The fraction found in air is higher in the Arctic than in the entire domain for all compounds as well. The difference in inter-media distribution between both sets of simulations is larger than the difference for the whole domain. The effect of the different climate on the inter-media distribution is larger in the Arctic than the effect in the whole domain (Fig. S8). The masses of the least chlorinated PCB congeners in air are higher in the 2090s for both sets of simulations. For the most chlorinated PCB congeners the masses in soil are higher in the 2090s than in the 1990s, and for the HCHs the masses in water are higher in the 2090s than in the 1990s for the "WO" simulation (Fig. S9).

We also examined the fraction of the total mass in the model domain that is found within the Arctic for the different simulations (Fig. 3). The highest fraction (24 %) is found for α-HCH for the "W20" simulation. The fraction of the PCBs found within the Arctic is between 3 and 15 % with largest fractions for the least chlorinated congeners. The fraction found in the Arctic is higher in the 2090s than in the 1990s for all compounds and for both sets of simulations. For the HCHs and the least chlorinated PCB congeners, the fraction in the Arctic is slightly higher for the "W" simulations, but in general the differences are very small apart from α-HCH where the initial environmental concentrations reflects 45 years of previous accumulation in contrast to the 20 years for the other compounds.

3.3 Test of statistical significance

A statistical test was applied to assess the significance of differences in the modelled masses of POPs in the different media within the Arctic between the 1990s and 2090s. We have calculated the difference of the annual averaged mass in air, water and soil

ACPD
15, 6509–6535, 2015

and in total (Figs. S2 and S3) and tested if the slope of the annual differences over the modelled decade is significant compared to the variability around the slope using a Student's t test (Table S3). By evaluating the variability around the trend of the annual differences instead of the differences themselves we ensure that the data are independent which is an assumption needed for the t test. The mass is building up in the model due to the emissions, but the same emissions are applied in both set of simulations, so the trend of the annual differences in mass is a good measure for the climate change impacts. Although there are uncertainties in the model associated with the process parameterizations and the input parameters, these are evened out when comparing two model simulations with the same model set-up.

The difference in total mass within the entire model domain between the 1990s and the 2090s is statistically significant within a 1 % significance level for all compounds except γ-HCH for both set of simulations (Table S3). Within the Arctic the differences are only statistically significant within a 1 % significance level for the HCHs, PCB52 and PCB194 for the "W" simulation and for the HCHs and PCB101–PCB180 for the "WO" simulation (Table S3). The differences in soil are statistically significant within a 1 % significance level for most of the compounds. Statistically significant differences are found in ocean primarily for the HCHs and the most chlorinated PCB congeners, while the differences in air are only statistically significant for α-HCH, PCB180, and PCB194 (Table S3).

4 Discussion

The simulations all apply input from one possible climate change scenario and this should therefore be considered as a sensitivity study of how the results from the DEHM model responds to the changed climate input in that particular scenario. The studied compounds behave differently depending on their physical-chemical properties and emission history in the simulations.

ACPD
15, 6509–6535, 2015

4.1 α-HCH

The overall response of α-HCH to climate change is mainly driven by two processes, both of which are affected by the higher mean temperature in the 2090s than in the 1990s. Re-volatilization from the surface is higher in the 2090s indicated by more mass in air and less in the surface media, and environmental degradation (dominated by degradation in air) is higher, indicated by the lower total mass in the model domain in the 2090s than in the 1990s for both sets of simulations.

The higher concentrations in the air lead to a larger atmospheric transport of α-HCH to the Arctic. Larger atmospheric transport can also arise from changes in wind patterns, but this can not be quantified from these simulations. For the "W" simulations the larger degradation counteracts the increased transport, leading to lower overall mass in the Arctic in the 2090s than in the 1990s. For the "WO" simulations the larger atmospheric transport to the Arctic leads to rapid deposition to the relatively "clean" surface compartments, where the degradation is lower than in the atmosphere. Climate induced changes in the surface characteristics with less sea ice and snow cover enhances the possible transfer to soil and ocean water, both of which are surface media with more accumulation potential due to the lower degradation rates. The effect of this process is larger than the effect of the higher degradation rates, and the result is thus more mass in the Artic in the 2090s than in the 1990s for the "WO" simulation. The differences in mass of α-HCH are all statistically significant within a 1.1 % significance level except for air for the "WO" simulation.

4.2 β-HCH

β-HCH has a generally different behavior in the environment compared with α-HCH. It has a lower log K_{AW} and it is therefore more readily transferred to the oceans via wet and dry deposition (Li et al., 2002). It has a statistically significant higher overall mass in the 2090s than in the 1990s for the "WO" simulation. This is due to the statistically significant higher mass in water, which most probably arises due to a larger volatiliza-

ACPD
15, 6509–6535, 2015

tion to air from soil combined with changes in the precipitation patterns that can lead to a more rapid transfer of β-HCH to the oceans close to the source areas.

The fraction found in the Arctic in this study is very low for both sets of simulations. The reason for this is that β-HCH is primarily transported to the Arctic via ocean currents (Li et al., 2002). This process takes several decades and is therefore not adequately represented in the 10 year model simulations in this study. The spatial distribution of β-HCH in this study is thus not representative for the distribution of β-HCH in the environment.

4.3 γ-HCH

In contrast with α-HCH, the mass of γ-HCH increases during the modelled decades for both sets of simulations. The reason for this is that with the relatively short spin-up simulation, combined with a relatively high emission scenario, the concentrations are still building up in the modelled environment.

The total mass in the Artic for the "W" simulations is almost constant over the 1990s, whereas it increases in the 2090s. The reason for this is that while the mass in soil increases in both simulations the mass in sea water decreases in the 1990s, whereas it increases in the 2090s. This can be a result of a larger deposition to the sea in 2090s due to larger atmospheric transport to the Arctic and a larger sea surface available for deposition following the retreat of sea ice. The differences in mass of γ-HCH within the Arctic are all statistically significant within a 1 % significance level except for air for both simulations and for soil for the "WO" simulation.

4.4 PCBs

The physical-chemical properties of the PCB congeners span a range of four orders of magnitude in log K_{OA} (7–12) and almost one order of magnitude in log K_{AW} (−2–−3) from the least chlorinated PCB8 to the most chlorinated PCB194. With higher log K_{OA} values partitioning to particles in the air becomes an important process affecting the

ACPD
15, 6509–6535, 2015

environmental fate of PCBs and thus the effect of climate change on the fate, in addition to the two processes dominating the fate of the HCHs. Particle- and gas-phase compounds are transported differently in the atmosphere; their deposition patterns are different, and most importantly particle-phase compounds are less degradable, with zero degradation assumed in the DEHM model (Hansen et al., 2008a). A higher temperature shifts the gas-particle equilibrium towards the gas phase.

For the least chlorinated congeners (PCB8–PCB52), which are primarily found in gas-phase in the atmosphere, the effect of climate change on the fate is dominated by the higher degradation resulting in up to 20 % less mass within the model domain in the 2090s, all statistically significant within a 1 % significance level. The total mass of these congeners is almost equal at the end of the "W19" and "WO19" simulations and similarly for the "W20" and the "WO20" simulations. This indicates that the model relatively quickly reaches an overall steady-state between concentrations in air and in the surface compartments due to the relatively high environmental degradation rates for these congeners. The steady-state is not the same for the two decades, with the overall steady-state being lower for the 2090s than for the 1990s. This is due to the larger environmental degradation following the higher average temperature in the 2090s.

Degradation also dominates the fate of the intermediately chlorinated congeners (PCB101–PCB118) although not to the same extent as for the least chlorinated PCB congeners. The result is a relatively low, but still statistically significant, overall effect of climate change of less than 5 % lower mass in the 2090s.

For the most chlorinated congeners (PCB138 and higher) the overall steady state is not reached at the start of the "W" simulation, indicated by increasing environmental mass through the modelled decades. The effect of climate change is even smaller for these congeners, but still statistically significant.

The effect of climate change on the total mass in the Arctic is smaller than the effect in the entire model domain, with a maximum of 10 % difference for the least chlorinated congeners. This indicates that more mass is transported to the Arctic in the 2090s than in the 1990s. For the least chlorinated congeners (PCB8–PCB52) that are dom-

ACPD
15, 6509–6535, 2015

inated by the gas-phase, the result is a lower mass in the 2090s than in the 1990s due to the enhanced degradation. With increasing chlorination, the partitioning to particles is higher and the transport via the (non-degradable) particle-phase thus leads to a smaller effect of the changed climate on atmospheric transport of the PCB congeners to the Arctic. Differences between the congeners (e.g. larger difference in mass of PCB153 than of PCB180 in the Arctic for the "WO" simulation) can be due to the different emission patterns for the individual congeners.

The overall average mass in air in the entire model domain of each of the PCB congeners is almost the same at the end of all four simulations, regardless of the initial environmental concentrations and, to a less degree, the climate input (Fig. S6). This indicates that the dynamics of atmospheric concentrations of PCBs are dominated by primary emissions and that re-emissions from surfaces do not contribute considerably to the large-scale atmospheric transport and fate of PCBs. The differences are only statistically significant within a 1 % significance level for the PCB52 and PCB194 for the "W" simulation and for PCB101–PCB180 for the "WO" simulation, but the differences for most of the other PCB congeners are significant within a 5–10 % significance level, which is relatively high.

For the studied compounds where the model predicts higher mass in the Arctic in the 2090s for the "W" simulation, the difference in mass is larger for the "WO" simulation, except for PCB194 (Fig. 1). For the compounds with small negative difference for the "W" simulation the difference for the "WO" simulations are positive (Fig. 1). This indicates that climate change acts to enhance atmospheric transport and subsequent accumulation in the Arctic for new contaminants to a larger degree than for compounds with longer emission histories.

4.5 Comparison with previous results

Armitage et al. (2011) and Gouin et al. (2013) recently reviewed the few model studies that have investigated the effect of a changed climate on the transport and fate of POPs in the Arctic. Lamon et al. (2009) applied a global gridded multimedia model to

ACPD
15, 6509–6535, 2015

calculate steady-state solutions for PCB28 and PCB153 under the SRES-A2 climate scenario. SRES-A2 is a high-emission scenario with a predicted increase in global average temperature of approximately 1 °C more by the end of the 21st century than the SRES-A1B scenario applied in this study. They predicted about 20–30 % higher air concentrations within the Arctic under the influence of climate change alone.

A global geographically explicit multimedia model was applied to calculate steady state solutions for a range of hypothetical chemicals under the SRES-A1B scenario by Gouin et al. (2013) Within the Arctic the concentrations of a chemical corresponding to the physical-chemical properties of α-HCH are predicted to be about 20 % higher in air and about 20 % lower in soil and sea water. For a chemical corresponding to the physical-chemical properties of PCB153 the results show about 10 % higher concentrations in air, about 30 % higher concentrations in sea water and about 20 % lower concentrations in soil (Gouin et al., 2013).

Wöhrnschimmel et al. (2013) applied a global gridded multimedia model forced with the SRES-A2 climate scenario and with average climate input for the period 1980–2000 to predict the effect of climate change on the transport of α-HCH and PCB153 to the Arctic. The model was run continuously from 1900 to 2100 using historic emissions and future emission scenarios. According to the results, concentrations of α-HCH in arctic air are predicted to be about 30 % lower and in arctic sea water about 60 % lower at the end of the 21st century than for the period 1980–2000. The predicted concentrations of PCB153 in air are 80 % higher and in sea water 390 % higher (Wöhrnschimmel et al., 2013).

A zonally averaged multimedia model was applied by Armitage and Wania (2014) to study the impact of changed climate conditions on the fate of a range of hypothetical chemicals forced with a climate change scenario resembling the SRES-A1B scenario. They predict higher concentrations in air and lower concentrations in ocean water in the Arctic for chemicals corresponding to the physical-chemical properties of the HCHs.

The previous studies all apply models with different spatial resolution, different process parameterizations and input parameters as well as different climate change sce-

ACPD
15, 6509–6535, 2015

narios so a direct comparison of the results from this study with the previous model studies is therefore difficult. One common result is that the impact of climate change is moderate, with all studies but one predicting an effect of climate change on environmental concentrations of POPs within a factor of 2. The differences projected in this study are in the lower end compared to previous predictions.

While the different models in general agree on the moderate effect of climate change on the environmental concentrations of POPs in the Arctic, they do not always agree on the sign of the changes. Although there is some disagreement between the previous model studies most of them predict higher air concentrations and lower ocean water concentrations of PCB153 in the Arctic. The results in this study are opposite to most of the previous studies but the predicted differences are not statistically significant. Apart from one of the previous model studies all the studies including α-HCH predicts higher air concentrations and lower ocean water concentrations in the Arctic. The results in this study are in accordance with the previous findings and they are statistically significant.

5 Conclusions

We have studied the effect of climate change on the fate of a range of POPs. Under the applied climate and emission scenarios, the total mass of all compounds was predicted to be lower by up to 20 % across the Northern Hemisphere in a future warmer climate. The mass of HCHs within the Arctic was predicted to be higher by up to 39 %, whereas the change in mass of the PCBs was predicted to range from 14 % lower to 17 % higher mass depending on the congener and the applied initial environmental concentrations. These differences are statistical significant for the HCHs, while not all the results for the PCBs are statistical significant. It is not possible to state whether there in general is a climate penalty or benefit on the transport of POPs into the Arctic in terms of higher or lower environmental concentrations and thus higher or lower potential exposure since it depends on the physical-chemical properties of the compounds as well as the initial

ACPD
15, 6509–6535, 2015

environmental concentrations. The results of this study also indicate that contaminants with no or a short emission history will be more rapidly transported to and build up in the arctic environment in a future warmer climate.

From this study we have gained insight into how climate change affects the transport of a range of POPs to the Arctic and into which processes are dominating the environmental behaviour of POPs in the Arctic in a future warmer climate scenario. The most dominating process is the shift in mass of POPs from the surface media to the atmosphere induced by the higher mean temperature. This is to some degree counteracted by higher degradation rates also following the higher mean temperature. The more dominant of these two processes depend on the physical-chemical properties of the compounds.

The results in this study confirm findings from previous studies using less complex models that the effect of a changed climate on the transport of POPs to the Arctic is moderate. Larger differences in environmental concentrations are predicted due to changes in emissions than due to changes in climate parameters (Lamon et al., 2009; Wöhrnschimmel et al., 2013). While the different models in general agree on the moderate effect of climate change on the environmental concentrations of POPs in the Arctic, they do not always agree on the sign of the changes, i.e. whether there is a climate penalty or a climate benefit on the environmental fate of POPs. This is due to differences in process parameterizations and in the physical-chemical parameters, emissions scenarios and climate change scenarios applied as input data. To identify which parameters and processes are creating the discrepancies between the models a thorough model comparison such as the one conducted by Hansen et al. (2006) is needed.

The Supplement related to this article is available online at doi:10.5194/acpd-15-6509-2015-supplement.

ACPD
15, 6509–6535, 2015

Acknowledgements. We gratefully acknowledge the contributions of Arctic Research Centre (ARC), Aarhus University. The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 – Environment (including Climate Change) FP7-2008-1 under Grant Agreement no 226534-ArcRisk, as well as from the Danish Environmental Protection Agency as part of the environmental support program Dancea – Danish Cooperation for Environment in the Arctic. The authors are solely responsible for all results and conclusions presented in the report; these do not necessarily reflect the position of the Danish Environmental Protection Agency. This work is a contribution to the Arctic Science Partnership (ASP).

References

Andersson, C. and Engardt, M.: European ozone in a future climate: importance of changes in dry deposition and isoprene emissions, J. Geophys. Res., D02303, doi:10.1029/2008JD011690, 2010.

Armitage, J. M., Quinn, C. L., and Wania, F.: Global climate change and contaminants – An overview of opportunities and priorities for modelling the potential implications for long-term human exposure to organic compounds in the Arctic, J. Environ. Monitor., 13, 1532–1546, 2011.

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, Environ. Sci. Processes Impacts, 15, 2263–2272, 2013.

Beyer, A., Wania, F., Gouin, T., Mackay, D., and Matthies, M.: Temperature dependence of the characteristic travel distance, Environ. Sci. Technol., 37, 766–771, 2003.

Brandt, J., Silver, J. D., Frohn, L. M., Geels, C., Gross, A., Hansen, A. B., Hansen, K. M., Hedegaard, G. B., Skjøth, C. A., Villadsen, H., Zare, A., and Christensen, J. H.: An integrated model study for Europe and North America using the Danish Eulerian Hemispheric Model with focus on intercontinental transport, Atmos. Environ., 53, 156–176, 2012.

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 Environ., 377, 296–307, 2007.

ACPD
15, 6509–6535, 2015

Christensen, J. H.: The Danish Eulerian hemispheric model – A three-dimensional air pollution model used for the Arctic. Atmos. Environ., 31, 4169–4191, 1997.
Christensen, J. H., Brandt, J., Frohn, L. M., and Skov, H.: Modelling of Mercury in the Arctic with the Danish Eulerian Hemispheric Model, Atmos. Chem. Phys., 4, 2251–2257, doi:10.5194/acp-4-2251-2004, 2004.
Colette, A., Bessagnet, B., Vautard, R., Szopa, S., Rao, S., Schucht, S., Klimont, Z., Menut, L., Clain, G., Meleux, F., Curci, G., and Rouïl, L.: European atmosphere in 2050, a regional air quality and climate perspective under CMIP5 scenarios, Atmos. Chem. Phys., 13, 7451–7471, doi:10.5194/acp-13-7451-2013, 2013.
Frohn, L. M., Christensen, J. H., and Brandt, J.: Development of a high resolution nested air pollution model – the numerical approach, J. Comput. Phys., 179, 68–94, 2002.
Genualdi, S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K. M., van Egmond, R., Shoeib, M., and Lee, S. C.: Global distribution of linear and cyclic volatile methyl siloxanes in air, Environ. Sci. Tochnol., 45, 3349–3354, 2011.
Gouin, T., Armitage, J., Cousins, I., Muir, D., Ng, C. A., Reid, L., and Tao, S.: Influence of global climate change on chemical fate and bioaccumulation: the role of multimedia models, Environ. Toxicol. Chem., 32, 20–31, 2013.
Hansen, K. M., Christensen, J. H., Brandt, J., Frohn, L. M., and Geels, C.: Modelling atmospheric transport of α-hexachlorocyclohexane in the Northern Hemispherewith a 3-D dynamical model: DEHM-POP, Atmos. Chem. Phys., 4, 1125–1137, doi:10.5194/acp-4-1125-2004, 2004.
Hansen, K. M., Prevedouros, K., Sweetman, A., Jones, K. C., and Christensen, J. H.: A process-oriented inter-comparison of a box model and an atmospheric chemistry transport model: insights into model structure using α-HCH as the modelled substance, Atmos. Environ., 40, 2089–2104, 2006.
Hansen, K. M., Christensen, J. H., Brandt, J., Frohn, L. M., Geels, C., Skjøth, C. A., and Li, Y. F.: Modeling short-term variability of alpha-hexachlorocyclohexane in Northern Hemispheric air, J. Geophys. Res.-Atmos., 113, doi:10.1029/2007JD008492, 2008a.
Hansen, K. M., Halsall, C. J., Christensen, J. H., Brandt, J., Geels, C., Frohn, L. M., and Skjøth, C. A.: The role of the snowpack on the fate of alpha-HCH in an atmospheric chemistry-transport model, Environ. Sci. Technol., 42, 2943–2948, 2008b.
Hedegaard, G. B., Brandt, J., Christensen, J. H., Frohn, L. M., Geels, C., Hansen, K. M., and Stendel, M.: Impacts of climate change on air pollution levels in the Northern Hemi-

ACPD
15, 6509–6535, 2015

sphere with special focus on Europe and the Arctic, Atmos. Chem. Phys., 8, 3337–3367, doi:10.5194/acp-8-3337-2008, 2008.
Hedegaard, G. B., Christensen, J. H., Geels, C., Gross, A., Hansen, K. M., May, W., Zare, A., and Brandt, J.: Modelling the impacts of climate change on tropospheric ozone over three centuries, Atmos. Clim. Sci., 2, 546–561, 2012.
Hedegaard, G. B., Christensen, J. H., and Brandt, J.: The relative importance of impacts from climate change vs. emissions change on air pollution levels in the 21st century, Atmos. Chem. Phys., 13, 3569–3585, doi:10.5194/acp-13-3569-2013, 2013.
IPCC: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Core Writing Team, Pachauri, R.K and Reisinger, A., IPCC, Geneva, Switzerland, 104 pp., 2007.
Jacob, D. J and Winner, D. A.: Effect of climate change on air quality, Atmos. Environ., 43, 51–63, 2009.
Krogseth, I. S., Kierkegaard, A., Breivik, K., McLachlan, M. S., Hansen, K. M., and Schlabach, M.: Occurrence and seasonality of cyclic Volatile Methyl Siloxanes in Arctic air, Environ. Sci. Technol., 47, 502–509, 2013.
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, Environ. Sci. Technol., 43, 5818–5824, 2009.
Langner, J., Engardt, M., Baklanov, A., Christensen, J. H., Gauss, M., Geels, C., Hedegaard, G. B., Nuterman, R., Simpson, D., Soares, J., Sofiev, M., Wind, P., and Zakey, A.: A multi-model study of impacts of climate change on surface ozone in Europe, Atmos. Chem. Phys., 12, 10423–10440, doi:10.5194/acp-12-10423-2012, 2012.
Li, Y.-F., Macdonald, R. W., Jantunen, L. M. M., Harner, T., and Bidleman, T. F., Strachan, W. M. J.: The transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH, Sci. Total. Environ., 291, 229–246, 2002.
Li, Y. F., Ren, N. Q., and Tian, C.: China-North America project on reduction of lindane usage in China and its impact globally and on North America, in: Report to North America Commission for Environmental Cooperation (CEC), Environment Canada and US EPA, 2008.
Manders, A. M. M., van Meijgaard, E., Mues, A. C., Kranenburg, R., van Ulft, L. H., and Schaap, M.: The impact of differences in large-scale circulation output from climate models on the

ACPD
15, 6509–6535, 2015

regional modeling of ozone and PM, Atmos. Chem. Phys., 12, 9441–9458, doi:10.5194/acp-12-9441-2012, 2012.
Marsland, S. J., Haak, H., Jungclaus, J. H., Latif, M., and Roske, F.: The Max-Planck-Institute Global Ocean/Sea Ice Model with Orthogonal Curvilinear Coordinates, Ocean Model., 5, 91–127, 2003.
McLachlan, M. S., Kierkegaard, A., Hansen, K. M., van Egmond, R., Christensen, J. H., and Skjøth, C. A.: Concentrations and Fate of Decamethylcyclopentasiloxane (D5) in the Atmosphere, Environ. Sci. Technol., 44, 5365–5370, 2010.
Nakicenovic, N., Alcamo, J., Davis, G., de Vries, B., Fenhann, J., Gaffin, S., Gregory, K., Grbler, A., Jung, T., Kram, T., Rovere, E. L., Michaelis, L., Mori, S., Morita, T., Pepper, W., Pitcher, H., Price, L., Riahi, K., Roehrl, A., Rogner, H.-H., Sankovski, A., Schlesinger, M., Shukla, P., Smith, S., Swart, R., van Rooijen, S., Victor, N., and Dadi, Z.: Special Report on Emission Scenarios: a Special Report of Working Group III of the Intergovernmental Panel on Climate Change, Cambridge University Press, New York, 2000.
Roeckner, E., Bauml, G., Bonaventura, L., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kirchner, I., Korn-blueh, L., Manzini, E., Rhodin, A., Schlese, U., Schulzweida, U., and Tompkins, A.: The Atmospheric General Circulation Model ECHAM5, Part I, Max-Planck-Institute für Meteorologie, Hamburg, 2003.
Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblueh, E., Manzini, L., Schlese, U., and Schulzweida, U.: Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model, J. Climate, 19, 3771–3791, 2006.
Rogelj, J., Meinshausen, M., and Knutti, R.: Global warming under old and new scenarios using IPCC climate sensitivity range estimates, Nature Clim. Change, 2, 248–253, 2012.
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, Environ. Sci. Technol., 39, 8434–8441, 2005.
Simpson, D., Andersson, C., Christensen, J.H., Engardt, M., Geels, C., Nyiri, A., Posch, M., Soares, J., Sofiev, M., Wind, P., and Langner, J.: Impacts of climate and emission changes on nitrogen deposition in Europe: a multi-model study, Atmos. Chem. Phys., 14, 6995–7017, doi:10.5194/acp-14-6995-2014, 2014.
Skov, H., Christensen, J. H., Goodsite, M. E., Heidam, N. Z., Jensen, B. P. Wåhlin, B., and Geernaert, G.: Fate of elemental mercury in the Arctic during atmospheric mercury depletion

ACPD
15, 6509–6535, 2015

episodes and the load of atmospheric mercury to the Arctic, Environ. Sci. Technol., 38, 2373–2382, 2004.

UNEP/AMAP: Climate Change and POPs: Predicting the Impacts, Report of the UNEP/AMAP Expert Group, Secretariat of the Stockholm Convention, Geneva, available at: http://chm.pops.int/tabid/1580/language/en-US/Default.aspx, 2011.

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

Xiao, H., Li, N. Q., and Wania, F.: Compilation, evaluation, and selection of physical-chemical property data for α-, β-, and γ-hexachlorocyclohexane, J. Chem. Eng. Data, 49, 173–185, 2004.

ACPD
15, 6509–6535, 2015

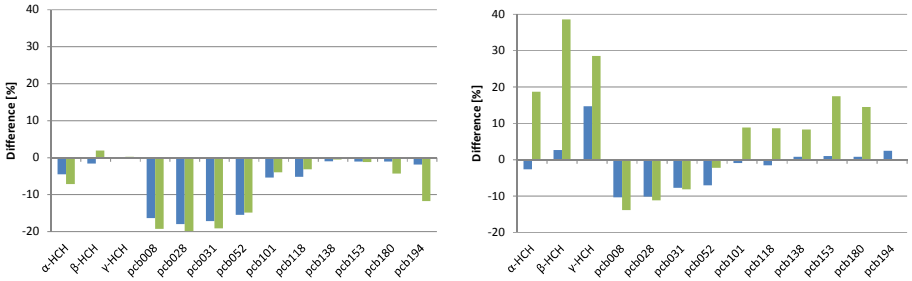

Figure 1. Difference in total mass between the 1990s and the 2090s calculated from the linear trend of the difference in annual averages compared to the average mass in 1999 in the entire model domain (left) and in the Arctic, defined as the area north of the Arctic Circle (66.5° N) (right), for the "W" simulation (blue) and the "WO" simulation (green).

ACPD
15, 6509–6535, 2015

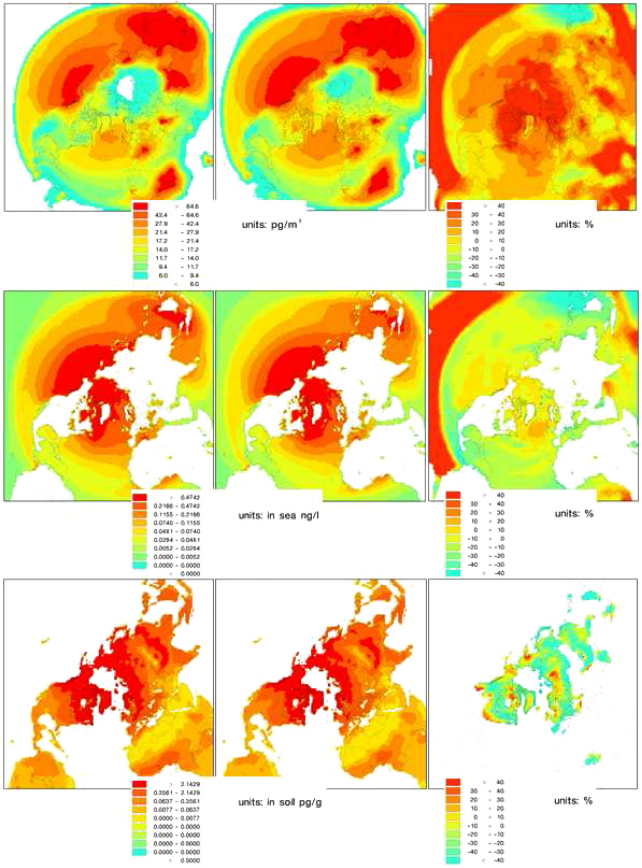

Figure 2. Annually averaged α-HCH concentrations in the lowermost atmospheric layer (top row) in ocean water (middle row) and soil (bottom row) for 1999 (left column) and 2099 (middle column) and the difference in percent between 1999 and 2099 (right column) for the "W" simulations.

ACPD
15, 6509–6535, 2015

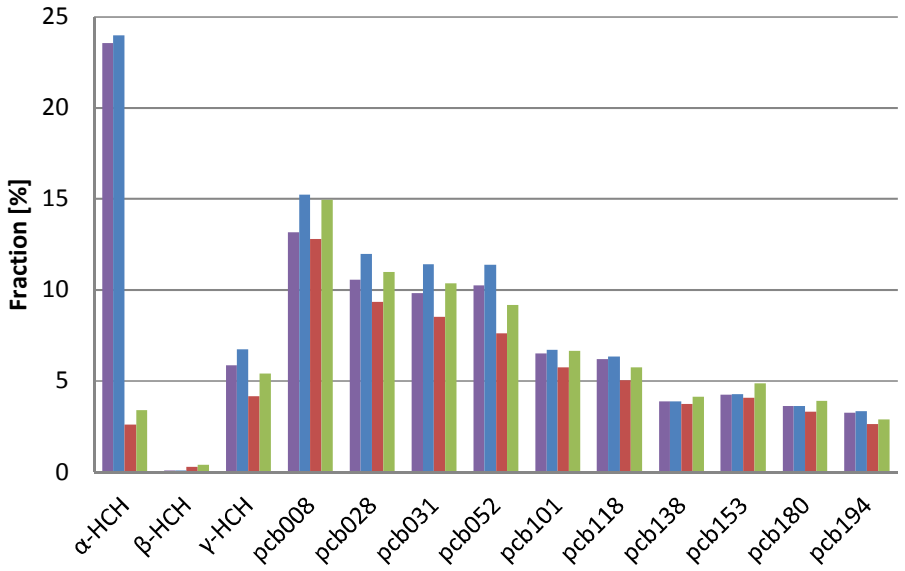

Figure 3. The fraction of the compounds found within the Arctic relative to the mass in the entire model domain calculated from the annual averages in the last simulated year for "W19" (purple), "WO19" (red), "W20" (blue) and "WO20" (green).

ACPD
15, 6509–6535, 2015