Emissions, Fate and Transport of Persistent Organic Pollutants to the Arctic in a Changing Global Climate

Henry Wöhrenschimmel,† Matthew MacLeod,*‡ and Konrad Hungerbuhler†

†Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology Zurich, Wolfgang-Pauli Strasse 10, 8093 Zurich, Switzerland
‡Department of Applied Environmental Science, Stockholm University, Svante Arrhenius väg 8, 11418 Stockholm, Sweden

Supporting Information

ABSTRACT: Climate change is expected to alter patterns of human economic activity and the associated emissions of chemicals, and also to affect the transport and fate of persistent organic pollutants (POPs). Here, we use a global-scale multimedia chemical fate model to analyze and quantify the impact of climate change on emissions and fate of POPs, and their transport to the Arctic. First, climate change effects under the SRES-A2 scenario are illustrated using case-studies for two well-characterized POPs, PCB153, and α-HCH. Then, we model the combined impact of altered emission patterns and climatic conditions on environmental concentrations of potential future-use substances with a broad range of chemical properties. Starting from base-case generic emission scenarios, we postulate changes in emission patterns that may occur in response to climate change: enhanced usage of industrial chemicals in an ice-free Arctic, and intensified application of agrochemicals due to higher crop production and poleward expansion of potential arable land. We find both increases and decreases in concentrations of POP-like chemicals in the Arctic in the climate change scenario compared to the base-case climate. During the phase of ongoing primary emissions, modeled increases in Arctic contamination are up to a factor of 2 in air and water, and are driven mostly by changes in emission patterns. After phase-out, increases are up to a factor of 2 in air and 4 in water, and are mostly attributable to changes in transport and fate of chemicals under the climate change scenario.

1. INTRODUCTION

Global climate change is forecasted to significantly affect the environment and human society in the 21st century. In particular, higher temperatures, altered precipitation patterns and decreasing sea- and land-ice are anticipated. Climate change is expected to be strongest in the Arctic as a consequence of processes mostly related to snow and ice, and the fluxes of heat and water (see also Figures S1−S7 in the Supporting Information (SI)). These environmental changes will also impact the global fate and transport routes of persistent organic chemicals, and future primary emissions of chemical substances.

Some chemicals that were used and released in large quantities during the last century are very persistent and will therefore remain in circulation in the global environment for several decades, mostly stored in soils and water bodies from which they can be remobilized. Thus, despite being banned by international regulations such as the Stockholm Convention on Persistent Organic Pollutants (POPs), their fate is likely to be affected by climate change. Additionally, another ~100 000 chemicals are available in commerce, some hundreds of which might have POP-like behavior, and new chemical products are constantly being developed and brought to market. As human behavior and the economy adapt to the threats and opportunities that arise from a changing climate, also the magnitude, location, and timing of chemical emissions may alter. Climate change will therefore affect both the emission pattern and the fate and transport of these future-use substances.

A recent review commissioned by the United Nations Environment Programme concluded that our understanding of the mechanisms by which climate change may impact the fate of POPs is mostly qualitative, and that a more quantitative description of potential effects is needed. A few modeling studies have so far quantitatively addressed the changes in large-scale environmental fate of chemicals under climate change, and these were recently reviewed by Armitage et al. Notably, Ma and Cao used a generic multimedia fate model to investigate the dependence of chemical concentrations on temperature. Lamon et al. used steady state solutions to a global multimedia model to compare fate and transport of...
PCB28 and PCB153 under a realistic climate change scenario, and Gouin et al.6 computed steady state solutions for a range of hypothetical chemicals with a global multimedia model. Despite the different modeling approaches, a common finding is that the effect of climate change on environmental concentrations is typically up to factors between 1.5 and 2.5 change in modeled concentrations. Some of the climate change-induced effects that are forecasted by models have already been observed during the recent Arctic warming period, such as enhanced outgassing of α-HCH from the Arctic Ocean.14,15

The possible effects of climate change on anthropogenic emissions of chemicals are so far poorly described in the literature. Gouin et al.6 provide a qualitative review of potential drivers of change in chemical emissions, including changing land use patterns, migration of pests and infectious diseases, and an increase in the frequency of forest fires. The economic response to a future ice-free Arctic Ocean, especially the potential increase in transportation, fishing, and the extraction of oil, gas, and mineral resources16,17 will likely result in increased emissions of chemicals in the North. An increase in the Arctic and subarctic population seems likely as new shipping routes and resources become available, similar to the one that occurred in the Canadian Arctic in the 1950s and 1960s, when access to new resources triggered population growth of about 4.5% per year.18 Global crop production is also expected to be affected by climate change, with consequences for the use of agricultural chemicals. Crop yields are expected to change, driven by alterations in temperature, precipitation and CO2-concentrations.19 Also, regions with arable land are forecasted to shift polewards, while lower latitudes may experience a loss of suitable land for cultivation.20,21

In this study, we model both the effects of climate change on global transport and fate of persistent organic chemicals and the potential impacts on anthropogenic emissions of these substances. We apply the BETR Research multimedia chemical fate model, focusing on the Arctic (defined here as the region north of 75°N) as a receptor site of particular interest. We have modeled dynamic scenarios that describe the entire history of two representative POPs, PCB153, and α-HCH, and make forecasts for future-use patterns of a broad range of hypothetical chemicals. We further develop illustrative future emission scenarios for our hypothetical chemicals that consider the impact of climate change on the magnitude and geographic distribution of chemical emissions in selected economic sectors, and introduce these emission scenarios as additional forcing functions into our model.

2. MATERIALS AND METHODS

Multimedia Fate Model. BETR Research is a reimplementation of the BETR Global 2.0 model. It represents the global environment as 288 connected regions on a 1°×1° grid, with each region containing up to seven compartments (upper air, lower air, vegetation, fresh water, ocean water, soil, and sediment). The model expresses the mass fluxes of a chemical between individual regions and compartments as a system of first order differential equations. The kinetic model parameters are derived from studies of chemical mass transport and degradation reported in the literature, and from the environmental parametrization described below. Earlier versions of the model have been applied to describe the global fate and transport of a range of persistent organic pollutants.5,15,22–24 Further information and access to the last publicly available versions of BETR Research and BETR Global is provided in MacLeod et al.25

Environmental Parametrization. The parametrization of the environment in our 20th century base-case scenario is mostly identical to the BETR Global defaults described in MacLeod et al.25 (see also SI Table S1). However, for this work, air, land, and ocean surface temperatures, precipitation, atmospheric and oceanic circulation, as well as land-ice and sea-ice cover were extracted from ECHAM/MI-OM model outputs for the 20C3M and the SRES-A2 scenarios, respectively.26 Sea-ice and land-ice were implemented in the model as a barrier to diffusive air–surface exchange of chemicals, but without any storage capacity for chemicals. In addition, the database for organic carbon content in soils was updated with data reported in Fischer et al.22 Further details on data sources and the downscaling method are given in Section 1 of the SI.

For our 20th century base-case climate runs we used monthly averages of time-variable parameters from 1981 to 2000 to represent generic average conditions, whereas for the climate change scenario we used time-evolving fields between 1900 and 2100 (see also Figures S1–S7 in the SI).

Chemical Properties. Chemical properties of PCB153 and α-HCH are presented in SI Table S2 with literature sources. Our set of hypothetical future-use chemicals is composed of 198 combinations of partitioning and persistence properties that result from combining octanol–air partition coefficient from 102 to 1012 and air–water partition coefficient from 10−5 to 10−2 in steps of factor 10, with two sets of representative degradation half-lives (Table 1). Hypothetical chemicals with...
Eₐ set at values selected for PCB180 in previous modeling studies.²⁸,²⁹ In a sensitivity analysis we repeated some model runs with doubled activation energies. Thus, we address the uncertainty inherent in the estimates of Eₐ and the potential for multiple degradation pathways with different Eₐ, such as biodegradation and hydrolysis. The internal energy of phase transition ΔU₁₀⁻⁰ was estimated from Trouton’s rule and the empirical relationship between vapor pressure and KₒMA reported in eq 6.10 of MacLeod et al.¹¹

Emission Inventories. The emission inventories of PCB153 and α-HCH were derived from Breivik et al.³³ and Li et al.³⁴ respectively. They have been previously reported and used with earlier versions of BETR Research and/or BETR Global to evaluate the model against observations.¹³,¹⁵ Given the high uncertainties in present and future α-HCH emissions from stockpiles, this source was not considered in our modeling, and our forecasts thus represent an ideal case of complete remediation of former industrial sites. Further detail is provided in Sections 3.1 and 3.2 of the SI.

For our hypothetical future-use chemicals, we defined four different spatially and temporally resolved generic emission scenarios, covering the period 2020–2050. Two of the scenarios represent the base-case for emissions of chemicals associated with population and economic activity (ECON1) and agricultural crops (CROP1), respectively. Atmospheric emissions in ECON1 are distributed in proportion to nighttime emissions and those in CROP1 according to crop-land data.¹⁹ The temporal evolution follows a plausible pattern for substances that are introduced in 2020 and successfully merchandised up to the saturation of the market in 2035, and then phased out over the next 15 years because of concerns about harm to human health and/or the environment, or because they will be substituted by a superior product (see solid lines in SI Figures S10 and S12). These scenarios were used together with both the present climate and with the climate change parametrization of BETR Research.

Two modified scenarios, ECON2 and CROP2, were also constructed where we include possible increases in primary emissions that may result from altered human behavior induced by climate change. Scenario ECON2 introduces a higher usage of industrial chemicals in the Arctic and subarctic due to enhanced economic activity in response to ice-free conditions, as suggested in the literature.¹⁷ We adopted a bounding case with an annual increase in emissions of 5% between the years 2020 and 2050 north of 60°N, relative to scenario ECON1 (see dotted line in SI Figure S10). Emissions north of 60°N integrated over the 30-year period would thus nearly double, and global emissions would increase by about 7%. This scenario is illustrative, but it reflects current forecasts about the future development of Arctic population and economy under climate change.¹⁷ Scenario ECON2 was used only in combination with the climate change parametrization in BETR Research, since climate-change induced sea-ice melting is a precondition for this scenario.

Scenario CROP2 reflects altered global patterns in the application of agrochemicals that result from changes in crop yields and a shift of potential arable land to higher latitudes. We constructed a time-evolving scenario by combining spatially resolved forecasts for crop yields and potential arable land, using data from Haberl et al.¹⁹ Müller et al.,³⁶ and Zhang and Cai,³⁷ observed global emissions of agrochemicals over the period 2020–2050 increase by 13%. Like scenario ECON2, scenario CROP2 was used only in combination with the climate change parametrization of BETR Research.

More detail on the ECON and CROP scenarios is provided in Section 3.3 of the SI. All model runs were carried out dynamically from the first year of emission of the respective chemical and until the year 2100.

Uncertainty Evaluation. In our case studies for PCB153 and α-HCH we used first-order error propagation in the form

\[ C_f^{out} = \exp \left( \sum_i (\ln C_f^i)^2 \times S_i^2 \right) \]

as derived in MacLeod et al.³⁸ to calculate the uncertainty in modeled concentrations (C_f^{out}) due to estimated uncertainties in input parameters (C_f^i). C_f^{out} and C_f^i are the confidence factors that span the 95% confidence interval around the median of a log-normally distributed variable, and S_i is the relative sensitivity of the model output toward a change in parameter i. Besides total output uncertainty, we also calculated the contribution of uncertainty in each input parameter to total output uncertainty in order to identify the parameters that contribute most to uncertainties in our estimate of the climate change effect. With the same method, we also calculated uncertainty in the modeled ratio of concentrations in the climate change scenario relative to the 20th century scenario.

The input parameter uncertainties that we used for chemical properties and environmental parameters are listed in SI Tables S1 and S2. We assigned uncertainties of factor 10 and 2, respectively to emissions of PCB153 and α-HCH, in agreement with the uncertainties suggested in Breivik et al.³⁹ and Li et al.³⁴ We attributed no uncertainty to climate parameters (in particular temperatures of air, earth and ocean surface, precipitation, and sea ice), but rather compared a 20th century climate against a specific climate change scenario.

3. RESULTS

Case Study Chemicals: PCB153 and α-HCH. Concentrations of PCB153 and α-HCH in Arctic air and surface ocean decrease strongly throughout the 21st century in response to the phase-out of both chemicals (Figure 1). The uncertainties in our modeled concentrations for PCB153 in both environ-
mental compartments are within factors of 5–10 during the entire model period. For $\alpha$-HCH, the uncertainties are within factors of 3–5 during ongoing primary emissions, but increase to several orders of magnitude between 2010 and 2100, when secondary emissions from soil and ocean control our modeled environmental concentrations. Those overall uncertainties mostly result from uncertainties associated with primary emissions and with the removal rates from surface media (SI Figure S14).

The effect of climate change under the SRES-A2 scenario on modeled environmental concentrations of PCB153 and $\alpha$-HCH becomes notable mostly in the second half of the 21st century. By the year 2100, the effect on PCB153 in the Arctic is a relative increase by factors of 1.8 and 3.9 in air and ocean water, respectively. In contrast, a relative decrease of $\alpha$-HCH concentrations by factors of 0.7 and 0.4, respectively occurs at the end of the model scenarios. These climate-induced changes are small compared to the decline in concentrations over time, and compared to the uncertainties in our forecasts for absolute concentrations. However, when applying the method of error propagation to the concentration ratio under climate change versus 20th century climate, the effect was found to be significant for PCB153 in air and ocean water, and for $\alpha$-HCH in ocean water (see gray areas in Figure 2).

![Figure 2. Ratio of modeled concentrations in the Arctic under the full SRES-A2 climate change scenario compared to the 20th century climate (black line) and concentration ratios for changes in individual climate parameters (colored lines) for PCB153 and $\alpha$-HCH. The 95% confidence interval from uncertainty analysis of the full climate change effect was found to be significant for PCB153 in air and ocean water, and for $\alpha$-HCH in ocean water (see gray areas in Figure 2).](image)

Uncertainties in the concentration ratios are considerably smaller than uncertainties in the absolute concentrations because input parameters affect the outputs in the same direction under both climate scenarios. A main contributor to total uncertainty for both substances is the degradation rate in soil (SI Figure S15).

The differences in the responses of PCB153 and $\alpha$-HCH to climate change and the role of the underlying processes can be understood by analyzing how changes in temperature, precipitation, sea-ice cover, and atmospheric and oceanic circulation individually affect concentrations in Arctic air and ocean water (colored lines in Figure 2).

PCB153 concentrations in air increase mainly due to the higher temperature-controlled volatilization from primary and secondary sources and subsequent atmospheric transport to the Arctic, which dominates over more rapid degradation with higher temperatures. In Arctic Ocean water, the effect of environmental temperatures is not strong, indicating a balance between increased deposition of PCB153 from other regions, and outgassing and degradation in the Arctic Ocean. Instead, concentrations in Arctic Ocean water are additionally increased by retreating sea-ice, which allows for a higher mass transfer of PCB153 from air into the surface ocean. Changes in atmospheric and oceanic circulation do not strongly affect considerably the concentrations of PCB153 in the Arctic.

In contrast to PCB153, warmer temperatures in the climate change scenario decrease $\alpha$-HCH concentrations in both air and ocean water. In air, enhanced degradation dominates increased volatilization from surface media. Oceanic concentrations of $\alpha$-HCH are decreased by reduced transfer from air, but even more so by changes in oceanic circulation (see also SI Figures S6–S7). In particular, we noted an influence of east-west flows in the Eastern Arctic Ocean—where persistent and water-soluble pollutants tend to accumulate—on modeled $\alpha$-HCH in the Arctic Ocean. Our model is not appropriate to describe the complex flow patterns of the Arctic Ocean in detail, however a recent tracer modeling study showed that changes in ocean surface circulation are occurring in response to atmospheric forcings and on a time scale of less than a decade, and that this leads to altered transport of contaminants.40

**Hypothetical Future-Use Substances.** We investigated the effect of a changing climate on hypothetical substances with a broad range of partitioning properties and persistencies, and under different illustrative future emission scenarios. As above, we use the ratio of modeled chemical concentrations in the Arctic under the climate change scenario versus under the 20th century climate conditions as a metric of the influence of climate change. We consider two time windows, 2030–2050, which includes the period of peak primary emissions and the phase-out period, and 2080–2100, which is a period decades after primary emissions have ceased.

During the phase of ongoing primary emissions, the effect of climate change on transport and fate is relatively small, given that most large-scale changes in climate parameters only become notable in the second half of the 21st century. Changes in chemical concentrations remain therefore mostly below 10% in air and 30% in ocean water under our two baseline scenarios ECON1 and CROP1 (see SI Figures S16–S17).

Under our illustrative scenarios of climate change-modulated primary emissions, however, we find more substantial increases in chemical concentrations for this period. Higher emissions of chemicals related to enhanced economic development in the Arctic region (scenario ECON2) lead to ratios of up to 1.9 in air and 2.1 in ocean water (Figure 3). The illustrative changes in the use of agrochemicals (scenario CROP2) produced ratios of up to 1.5 and 1.6, respectively (SI Figure S18).

The magnitude of increase in concentrations under scenarios ECON2 and CROP2 is sensitive to chemical properties. For example, for borderline-persistent chemicals in air the response becomes stronger with increasing volatility (decreasing LogKOA), while for highly persistent chemicals in ocean water the response is strongest for low-volatility compounds. In general, the impact of additional emissions at high latitudes is most pronounced for chemicals with stronger removal processes in the atmosphere that limit their long-range transport from lower latitudes to the Arctic. Those chemicals have been previously characterized as substances with low Arctic Contamination Potential (see Figure 1 in Czub et al.41).
In the period 2080–2100, when primary emissions have ceased but chemical pollutants continue cycling in the global environment, the changes in climate parameters and with it the altered fate and transport processes become stronger. Climate change leads now to a relative decrease for a wider range of chemicals, even under the scenarios with enhanced emissions (Figure 4 and SI Figure S21). In particular, concentrations of borderline-persistent chemicals decrease across the whole chemical space. Also highly persistent volatile chemicals with intermediate solubility in water (LogK_{OA} < 5; -3 < LogK_{AW} < 1) decrease to ratios less than 1/10. In contrast, there is also a pronounced relative increase for highly persistent chemicals with low vapor pressure (7 < LogK_{OA} < 11), up to ratios of 1.8 in air and 4.2 in ocean water.

These changes in concentrations in the Arctic are mainly due to altered transport in ocean and global fate processes, as our
model results for scenarios ECON2 and CROP2 do not differ substantially from modeled concentrations under ECON1 and CROP1 (SI Figures S19–S20). Which of the individual climate change processes determines the direction and magnitude of change depends again on the chemical properties, and is summarized in Table 2 and SI Figures S22–S23.

The results for borderline persistent chemicals are strongly sensitive to the estimated values of $E_A$ that describe the temperature dependence of degradation. Borderline-persistent chemicals with doubled activation energies become more persistent in the Arctic. The decrease of these substances under climate change is less pronounced than with default values for $E_A$ and for some low-volatility chemicals the effect of climate change becomes even positive (see SI Figure S24, upper panels).

<table>
<thead>
<tr>
<th>chemical classification</th>
<th>dominant fate process in climate change</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/E volatile flyer</td>
<td>temperature $\uparrow \Rightarrow$ degradation $\uparrow$</td>
</tr>
<tr>
<td>B/F volatile water-soluble multiple-hopper</td>
<td>sea-ice $\Rightarrow$ volatilization from Arctic Ocean $\uparrow$</td>
</tr>
<tr>
<td>C borderline-persistent multimedia multiple-hopper</td>
<td>temperature $\uparrow \Rightarrow$ degradation $\uparrow$</td>
</tr>
<tr>
<td>D borderline-persistent single hopper</td>
<td>temperature $\uparrow \Rightarrow$ degradation $\uparrow$</td>
</tr>
<tr>
<td>G highly persistent multimedia multiple-hopper</td>
<td>temperature $\uparrow \Rightarrow$ volatilization from surface and particles $\Rightarrow$ atmospheric transport to the Arctic $\uparrow$ sea-ice $\Rightarrow$ deposition into Arctic Ocean $\uparrow$</td>
</tr>
<tr>
<td>H highly persistent single hopper</td>
<td>sea-ice $\Rightarrow$ deposition into Arctic Ocean $\uparrow$</td>
</tr>
</tbody>
</table>

"According to Gouin and Wania42

4. DISCUSSION

We have used a global multimedia chemical fate model to forecast the effect of climate change during the 21st century on the concentrations of POPs and hypothetical future-use persistent chemicals in the Arctic. The maximum increase in atmospheric concentrations that we modeled under climate change conditions was close to a factor of 2 compared to the 20th century climate scenario, for both the phase of primary emissions and the phase of secondary releases. This result is similar to findings in previous global modeling studies that assumed steady state conditions,4,13 despite differences in emission histories and modeling approaches. The maximum overall increase of a ratio more than 4 in ocean water is considerably higher than suggested in previous work, and the modeled relative decrease for water-soluble substances is even more pronounced.

Both of these pronounced effects in ocean water are a result of sea-ice processes that we introduced into our modeling framework, and for which we show evidence in Section 8 of the SI. We conclude that sea-ice melting is a crucial aspect of forecasting chemical fate in the Arctic under a warming climate, particularly for chemicals in regions F, G, and H of the chemical space (Figure 4). In future versions of our model it would be desirable to include sea- and land-ice as a compartment of its own, so that other ice-related processes, such as runoff from melting sea-ice, can be considered in addition to air–surface diffusion.

Aside from sea-ice cover, it was temperature and—for water-soluble chemicals—oceanic flow that were the dominant parameters through which climate change affects environmental concentrations of chemicals in our model. The effect of changes in atmospheric circulation was rather small.

A notable feature of our modeling analysis is that the relative increases in ambient concentration do not necessarily happen at the same pace as climate change. Instead, changes may be more immediate, triggered by human behavior in response to climate change. In terms of risk, the increases that occur as a result of altered anthropogenic emissions might be particularly relevant, given that they take place when ambient levels are highest.

For phased-out chemicals the relative increases are small in comparison to the expected removal from the global environment over the same period. Nevertheless, the factor of 4 modeled for oceanic concentrations may delay to some extent the removal of the chemicals with properties near region G of the chemical space (Figure 4) from the Arctic Ocean, and with that the background exposure of populations that base their diet on foods derived from the Arctic Ocean.

Our analysis contributes to identifying chemicals with critical properties, for which a more detailed risk analysis should be conducted before introducing them to the market. An important part of such an analysis is a deeper and substance-specific evaluation of uncertainty. In particular the uncertainties associated with removal rates in the environment and their temperature dependence should be a focus of additional experimental research.

Large uncertainties remain also in the forecasts of future climate and the economic response to those changes. Here we have proposed two generic emissions scenarios that reflect plausible alterations of emissions of chemicals under climate change. These scenarios are a first step toward a more comprehensive assessment of climate change-induced alterations in anthropogenic chemical emissions.

ASSOCIATED CONTENT

Supporting Information

Model parameterization and input parameter uncertainties, climate change anomalies, emission scenarios for PCB153, $\alpha$-HCH and hypothetical chemicals, uncertainty analysis, effect of climate change and its components on hypothetical chemicals, sensitivity of modeled concentrations to activation energy, effect of sea-ice melting. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Phone: +46 8 674 7168; e-mail: matthew.macleod@itm.su.se.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the European Community’s Seventh Framework Programme FP7/2007–2013 — Environment (including Climate Change) FP7-2008-1, under Grant Agreement no 226534-ArcRisk. We thank Alberte Bondeau and Christoph Müller from Potsdam Institute for Climate Impact Research, Germany, for providing spatially resolved model forecasts for crop yields, and Xiao Zhang and Ximing Cai from
University of Illinois at Urbana–Champaign, USA, for their model forecasts on potential arable land under climate change.

REFERENCES


(22) Armitage, J. M.; MacLeod, M.; Cousins, I. T. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. Environ. Sci. Technol. 2009, 43, 1134–1140.


(37) Zhang, X. A.; Cai, X. M. Personal communication. 2012.

(38) MacLeod, M.; Fraser, A. J.; Mackay, D. Evaluating and expressing the propagation of uncertainty in chemical fate and...


