Atmospheric Pollution Research

Global multimedia source–receptor relationships for persistent organic pollutants during use and after phase–out

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ABSTRACT

Chemicals that are persistent in the atmosphere can be transported long distances and across international boundaries. Therefore, information about the fraction of local versus imported air pollution is required to formulate regulations aimed at controlling pollutant levels. The objective of this work is to illustrate the capabilities of a dynamic global–scale multimedia model to calculate source–receptor relationships for persistent organic pollutants that cycle between air, water, soil and vegetation in the global environment. As exemplary case studies, we present model calculations of time–evolving source–receptor relationships for PCB28, PCB153, α–HCH and β–HCH over the duration of their usage, phase–out and a post–ban period. Our analysis is geographically explicit, and elucidates the role of primary versus secondary sources in controlling the levels of air pollution. Our case studies consider source–receptor relationships between the four regions defined by the Convention on Long–range Transboundary Air Pollution Task Force on Hemispheric Transport of Air Pollution, as well as the Arctic as a remote receptor region. We find source–receptor relationships that are highly variable over time, and between different regions and chemicals. Air pollution by PCBs in North America and Europe is consistently dominated by local emissions, whereas in East– and South–Asia extra–regional sources are sometimes major contributors. Emissions of α–HCH peak at different times in the four regions, which leads to a phase of high self–pollution in each region, and periods when pollution enters mainly from outside. Compared to α–HCH, air pollution with the less volatile and more persistent β–HCH is more strongly determined by secondary emissions near source areas throughout its use history. PCB concentrations in Arctic air are dominated by emissions transported from North America and Europe from 1930 to 2080, whereas for HCHs each of the source regions contributes a high share at some point between 1950 and 2050.

1. Introduction

Economic activities in industrial regions all over the world introduce volatile and semi–volatile pollutants into the air. Air pollutants that are persistent and transported over long distances through the atmosphere are an international concern because policy makers must address the potential negative effects of imported air pollution in addition to their own emissions. In this context the Arctic, which has very few local sources of pollutants, has become a focus of attention of international policy making. Both the Stockholm Convention on Persistent Organic Pollutants (POPs) and the Protocol on POPs of the UNECE Convention on Long–range Transboundary Air Pollution (CLRTAP) aim at reducing or eliminating POP emissions that may impact remote ecosystems like the Arctic. However, the time–dependent share of local versus imported pollution for both source and receptor regions is difficult to evaluate. To confront this problem, the CLRTAP's Task Force on Hemispheric Transport of Air Pollution (HTAP) was established to develop a better understanding of intercontinental transport of air pollution in the Northern Hemisphere (HTAP, 2012).

A quantitative accounting of global source–receptor relationships can be obtained through fate and transport modeling that has been evaluated against observational data. Global modeling studies addressing PCB28, PCB118, PCB153 and PCB180 deposition in the Arctic during 1996 suggested that the major

contribution to the total burden of this industrial chemical derived from emissions in Europe and Russia, and in third place from the Americas (Malanichev et al., 2004). Toose et al. (2004) used the BETR World model to analyze the global fate of α–HCH, which beside β– and γ–HCH is the main constituent of the pesticide "technical HCH". They found that 30–40% of the total historical loading of α–HCH to the Arctic originated in Europe, and 20–30% in Russia and Asia. Gusev et al. (2007) further explored source–receptor relationships of PCB153 and α–HCH between North America, Europe, South– and East Asia for the year 2005, and modeled the effect of hypothetical emission reductions in selected regions. A further study, including both PCBs and α–HCH, showed that between 75% and 90% of the atmospheric burden of PCBs in 2001 in North America, Europe, South– and East Asia was caused by emissions from within the source region, while 10% to 25% was imported from outside (Shatalov et al., 2010).

Here, we seek to expand upon earlier modeling studies by including the dynamic aspect of source–receptor relationships, and explicitly separating primary and secondary emissions. We model source–receptor relationships for PCB28, PCB153, α–HCH and β–HCH over the whole history of their usage, phase–out and post–ban period, and compare primary emissions to the atmosphere against re–emission of past releases that are still cycling in the environment. The substances selected as case studies cover a range of chemical properties, and include both industrial and

agricultural applications. Our analysis is focused on atmospheric pollution in the four geographic regions defined by the HTAP Task Force, and the Arctic. We quantify the relative contributions of anthropogenic emissions that have their origin within and outside these regions, respectively. Then, we consider the Arctic in more depth as a receptor region of interest and quantify the contributions of global source regions to Arctic pollution over time.

This study explicitly addresses research priorities that are included in the workplan for the HTAP Task Force during the 2011–2015 period (HTAP, 2012). In particular we provide quantitative model results to inform decisions about two policy–relevant scientific questions formulated under Objective 1 of the workplan: (i) What is the relative contribution of contemporary regional anthropogenic emissions, contemporary anthropogenic emissions in other regions, or re–emitted POPs that were previously deposited from past anthropogenic emissions? (ii) How do the magnitudes of these contributions differ in different regions of the world and how have they changed over time?

2. Methods

2.1. The *BETR Research* model

We modeled source–receptor relationships between the four HTAP regions and the Arctic for PCB28, PCB153, α–HCH and β–HCH over their whole period of usage, phase–out and a multi–decade post–ban period, using the *BETR Research* model. *BETR Research* is an implementation of the *BETR Global* multimedia chemical fate model. It represents the Earth as a 15° x 15° grid of regional environments, with each region containing up to seven compartments (upper and lower air, vegetation, fresh water, surface ocean, soil and sediment). Advective fluxes and intermedia exchanges are calculated from the emission inventory of the chemical of interest, its chemical properties, and a global environmental parameterization. The last public versions of *BETR Global* and *BETR Research* are described in MacLeod et al. (2011), and can be downloaded from https://sites.google.com/site/betrglobal/home and http://betrs.sourceforge.net/, respectively.

The chemicals considered in this study have been modeled previously with *BETR Global* or *BETR Research*, and model results and measurements have been compared at remote receptor sites. Lamon et al. (2009) found that 64% of modeled concentrations of

PCBs in the atmosphere are within a factor of 3.2 of measured values. Wöhrnschimmel et al. (2012) found that 70% of modeled concentrations of α– and β–HCH agree within a factor of 3 and 8, respectively. In this work we have adopted the same chemical properties (see the Supporting Material, SM, Table S1) and emission scenarios that were used in these earlier studies.

Emissions of PCBs are 100% to air and correspond to the higher emission scenarios from Breivik et al. (2007), which include historical and country–specific data for production, consumption and trade, as well as assumptions on the use–life expectancy of PCB containing products. Emissions of HCHs have been derived from Li et al. (2000; 2002), and are based on country–specific usage data for technical HCH. Consistent with previous modeling studies, we assume that 92.5% of total HCH emissions go into soil, 5% are released to the atmosphere, and 2.5% to freshwater. Global usage of technical HCH is assumed to cease after 2010 (Li, personal communication). Details on our parameterization of the global environment are provided in the SM.

We have analyzed source–receptor relationships in the model results for PCB28 and PCB153 in the period from 1930 to 2080, and for the HCH isomers in the period from 1950 to 2050. These periods extend from the early years of each chemical's emission history until several decades after the use–life expectancy of PCB containing products (about 2040–2050) and the global phase–out of technical HCH, respectively (Breivik et al., 2007; Li et al., 2000).

2.2. Global source–receptor relationships

Four Northern Hemisphere regions have been defined by the HTAP Task Force for use in source–receptor modeling: North America, Europe, East Asia and South Asia. We have adopted these four regions, as well as the Arctic as a receptor region, in this study (Figure 1).

Source–receptor relationships were modeled by running the model first with the full emission inventory, and then with inventories where primary emissions occur in only one region at a time. Our model explicitly considers secondary emission of pollutants that have previously been deposited into a surface compartment. Such emissions can occur from any location on Earth, but are still attributed in our source–receptor analysis to the region where the pollutant was originally released.
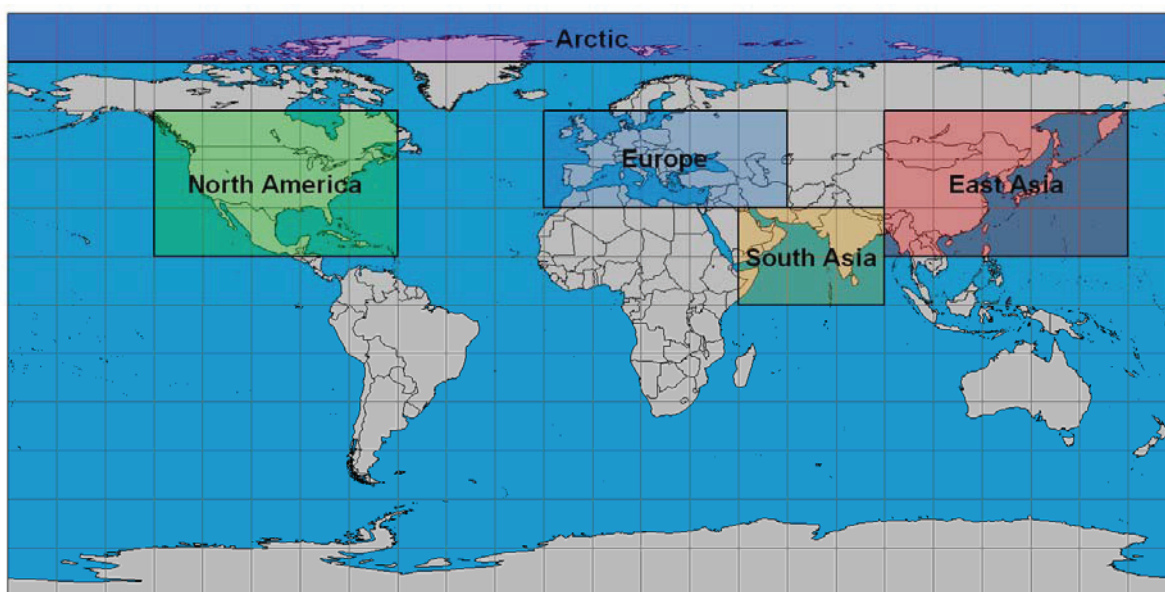

Figure 1. HTAP regions and the Arctic on the BETR grid, used for determining source-receptor relationships.

To further distinguish primary from secondary emissions, all model runs were repeated with a modified algorithm of *BETR Research* where re–emission from surface compartments was blocked. This was achieved by setting all mass transfer coefficients from surface compartments to air to zero. The blocked processes include diffusion from soil, water and vegetation to air, and re–suspension from soils via dust and from ocean via marine aerosol production. In the Supporting Material we demonstrate how the source–receptor relationships presented in this work are calculated from the above described model runs.

To produce source contribution maps for specific years, as discussed in Section 0 and illustrated in Figure 5, the model was run repeatedly, one time for each of the 288 grid cells of the 15° x 15° grid, with initial conditions from a long–term model run. In each model run, only the primary and secondary emissions from the grid cell under consideration were modeled by setting to zero both the emission inventory and environmental concentrations in all other grid cells.

An interesting aspect of secondary emissions of persistent semi–volatile pollutants is the potential for delayed re–emissions of so–called legacy pollutants from surface media years after they were first emitted (e.g. Harner et al. 1995; Jones and de Voogt, 1999). Delayed re–emission will occur from compartments that are slow to respond to changes in atmospheric levels, like soils and oceans. However, secondary emissions also occur on much shorter time–scales from compartments that respond rapidly to changes in atmospheric levels, like vegetation. Our model computes secondary emissions from all compartments, with no distinction between fast re–emission from vegetation and delayed re–emissions. However, we can identify periods when delayed re–emission begins to control atmospheric levels because the rates of primary and secondary emissions to the global atmosphere cease to be proportional to each other.

3. Results and Discussion

3.1. History of emissions and atmospheric pollution

PCBs. Atmospheric concentrations of PCB28 and PCB153 between 1930 and 2050 follow the trends of estimates of primary emissions (upper panels of Figure 2). Globally, a phase of strong increase until the 1970s is followed by a decrease, reflecting the bans on PCB production and use in developed countries (see also SM, Table S2). However, even after the bans enter into force, emissions from in–use products are forecasted to continue until about the middle of the 21st century. During most of this period, atmospheric concentrations are highest over North America and Europe, but after about 2030 the concentration of PCB28 in the Arctic surpasses levels in North America (lower panels of Figure 2). After 2050, primary emissions of PCB153 are forecasted to decrease at a modest pace, and the trend in reduction of primary emissions continues to dictate the trend of atmospheric concentrations. In contrast, primary emissions of PCB28 decrease more quickly and atmospheric concentrations become controlled by delayed secondary emissions. After 2050, the Arctic is the region with highest concentrations of PCB28 in air, which reflects delayed re–emission from cold Northern latitude reservoirs where PCBs are more persistent.

HCHs. Atmospheric concentrations of α– and β–HCH follow the trends of their respective emission histories between 1950 and the 1990s (Figure 2). Bans implemented worldwide between the 1970s and the end of the 1990s (Table S2) led to a complete cessation of primary emissions of HCHs, leaving atmospheric concentrations under the control of delayed secondary emissions. Differences in the chemical properties of α– and β–HCH result in different removal rates from the environment, but also in different global distributions of the two isomers. Background concentrations of α–HCH are forecasted to become highest in the Arctic relative to the

other regions after 2020, whereas atmospheric levels of β–HCH remain highest over former source regions for a longer time. These results are in agreement with previous measurement and modeling studies, which indicate that the more volatile α–HCH distributes efficiently in the atmosphere, whereas the more water–soluble β–HCH tends to remain close to its primary emission sources (Li et al., 2002; Wöhrnschimmel et al., 2012). Long–range transport of β–HCH into the Arctic has been hypothesized to also occur on the oceanic pathway through the Bering Strait and/or the Northern Atlantic Current (ibid.), but did not play a prominent role in our model scenarios.

3.2. Air pollution in source regions

PCBs. In North America, regional emissions of PCB28 account for over 80% of the concentration in air between 1930 and the 1970s, and more than 50% until the 2020s (Figure 3). During this period, the proportion of primary versus secondary regional sources remains about constant, indicating that re–emission is mostly a consequence of rapid cycling of recently deposited pollutants. Levels of PCB28 in air in this period therefore result from ongoing use rather than a re–emission of legacy pollutants. After 2030, however, primary emissions from within North America are forecasted to decrease quickly, and regional legacy sources and extra–regional emissions become the dominant contributors. After 2050, global primary emissions of PCB28 become insignificant, and pollution in North America is caused by regional (~40%) and extra–regional (~60%) secondary sources. The evolution of PCB153 is similar until the middle of the 21st century. After 2050, however, regional concentrations are forecasted to continue to be dominated by ongoing regional primary emissions and rapid re–emission, which contribute about 60% to the total levels.

In Europe, regional primary and secondary sources of PCB28 dominate pollution beginning in the mid 1950s, which corresponds to increasing emissions in this region. In contrast to North America, the total share of local pollution does not drop below 60% before the end of our modeling period in 2080. At that time, PCB28 air pollution over Europe is forecasted to be almost entirely due to delayed re–emission. PCB153 is forecasted to be 80% of regional origin in Europe at the end of our modeling period, however, with primary emissions still contributing a major fraction.

Like in Europe, in East– and South– Asia there is a phase of enhanced contribution of regional emissions of PCB28 and PCB153 starting in the 1960s that corresponds to increasing PCB emissions outside of North America. However, the regional fractions of primary emissions hardly exceed 30%, which can be explained by the smaller amount of PCBs used in comparison to Europe and North America (see also SM, Figure S1). Correspondingly, secondary regional emissions play a smaller role in South– and East–Asia.

HCHs. For North America, the regional contribution to atmospheric levels of both HCHs starts high, but declines rapidly during the 1950s and 1960s as emissions shift to other regions (Figure 3 and Figure S2). The spike in the contribution of local North American sources of both isomers that occurs in the early 1970s is due to a brief period of increased use of technical HCH in the United States after the use of DDT in agriculture was recommended for phase–out in 1969, and finally banned in 1972. By 1980, mostly as a consequence of the ban on technical HCH imposed by the United States in 1976, local sources in North America contribute less than 5% and 20% to regional air pollution with α–HCH and β–HCH, respectively. After the year 2000, atmospheric pollution by α–HCH is almost entirely made up by extra–regional secondary emissions. In contrast, β–HCH in the year 2000 is still 20% of regional origin. The low volatility of β–HCH in comparison to α–HCH and its relatively high persistence mean that the fraction of local β–HCH decreases more slowly than α–HCH, to about 10% in the year 2050.

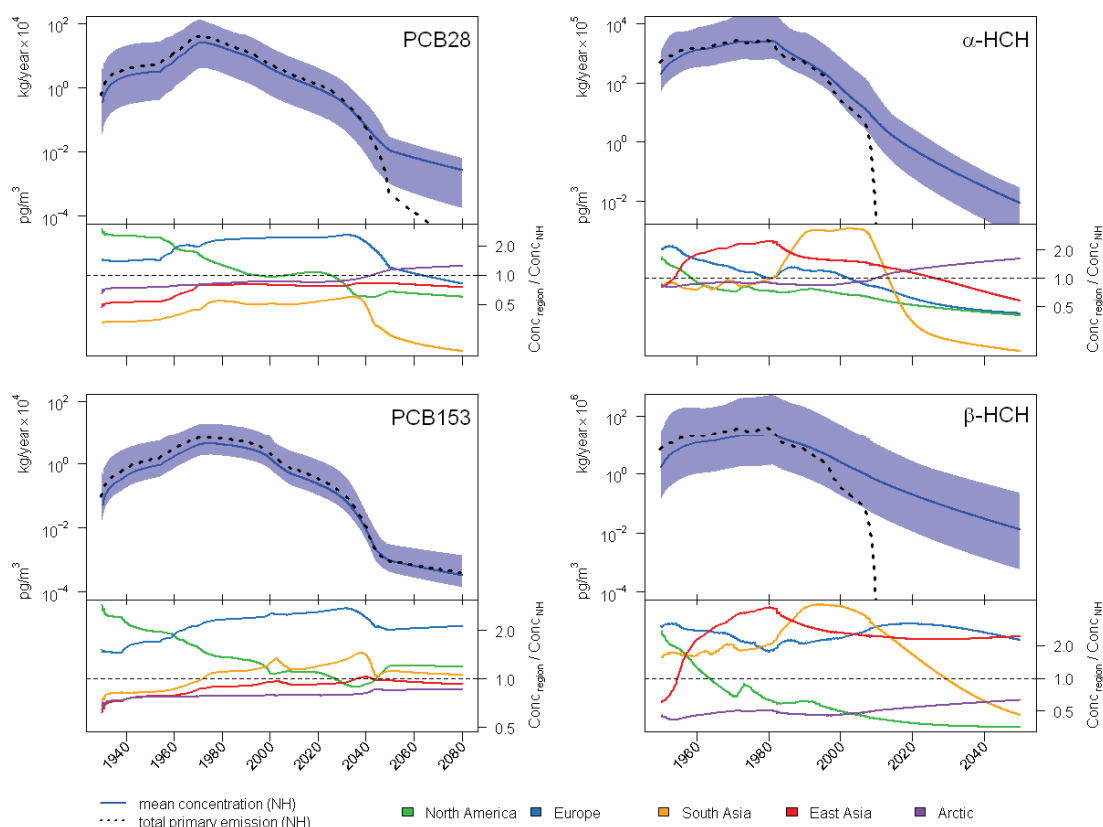*Figure 2. Time series of mean atmospheric concentration and total primary emission of PCB28, PCB153, α-HCH and β-HCH in the Northern Hemisphere (NH, upper panels). The shading indicates the range of concentrations in each model grid-cell. The ratio of concentrations in North America, Europe, South Asia, East Asia and the Arctic relative to the Northern Hemispheric mean concentration is shown in the lower panels.*

In Europe, the contribution of regionally produced HCHs is similar to that of North America at the beginning of the model simulation. The decline of local contributions over time, however, is much slower as a result of higher overall–usage and the later introduction of bans of HCH in Europe compared to the United States. In 2050, 10% of the air pollution with α–HCH and 90% of β–HCH over Europe is forecasted to be from regional re–emissions.

In East– and South–Asia, the contribution of regionally emitted α– and β–HCH reaches between 80% and 90%, after the 1960s, and the 1980s, respectively. Such a high share is due to ongoing emissions in these countries when other countries have stopped the application of technical HCH. After phase–outs in the early 1980s in East Asia and in the 1990s in South Asia, the regional contribution to atmospheric α–HCH levels drops to 40% and 10%, respectively, and is attributable to delayed secondary emissions. For the more persistent β–HCH, regional secondary sources are more prominent, similar to the situation in North America and Europe. In South–Asia, however, the contribution of local secondary emissions of β–HCH decreases much faster over the following decades than in other regions because higher temperatures enhance the rate of degradation in soils and surface water.

3.3. Air pollution in the Arctic

PCBs. North America and Europe contribute over 80% of the Arctic air pollution with PCB28 and PCB153 during the entire modeling period from 1930 to 2080 (Figure 4). This dominant influence is not only due to both regions' leading position in PCB usage, but also due to their relative proximity to the Arctic. During the period between 1950 and 2040 primary emissions are the dominant driver for the global levels of PCBs in the atmosphere, and the relative contribution of North America and Europe to Arctic air pollution depends largely on the relative rate of primary emissions

in the two regions. After 2050, when delayed re–emission of PCBs becomes important, the proportion of Arctic contamination from North America and Europe – corresponding to about 40% and 60%, respectively – largely reflects the integrated emission history of the past several decades in the two regions.

HCHs. Regional contributions to Arctic pollution with HCHs follow a very different pattern than the PCBs. Prior to 1960, North America and Europe are the dominant polluters of Arctic air, but their share decreases quickly as emissions shift to other parts of the world (Figure 4). The North American contribution becomes insignificant by the 1970s, whereas the European contribution falls to about 15–25% in the year 2000. Between 1970 and 2000, East– and South–Asia are the principal source regions for Arctic pollution with HCHs. Ongoing emissions in both source regions have their biggest relative impact around the year 1980 and around the turn of the century, respectively. After 2010, primary emissions world–wide have ceased, and the integrated emission history attenuated by travel times in the atmosphere to the Arctic determines the relative regional contributions of delayed secondary sources. East–Asia plays a dominant role for α–HCH, whereas for β–HCH Europe also contributes a significant, but declining share.

3.4. Lags between emission and presence of POPs in Arctic air

Due to their persistence and potential for delayed re–emission from secondary sources, there may be temporal and spatial lags between emissions of persistent pollutants in source regions and accumulation at global receptor sites. To illustrate and quantify the lags between actions to reduce emissions and changes in source-receptor relationships, we have calculated the global distribution of the sum of primary and secondary emissions to the atmosphere and plotted the spatial variability of relative contributions to Arctic air pollution in 1990 and 2050.
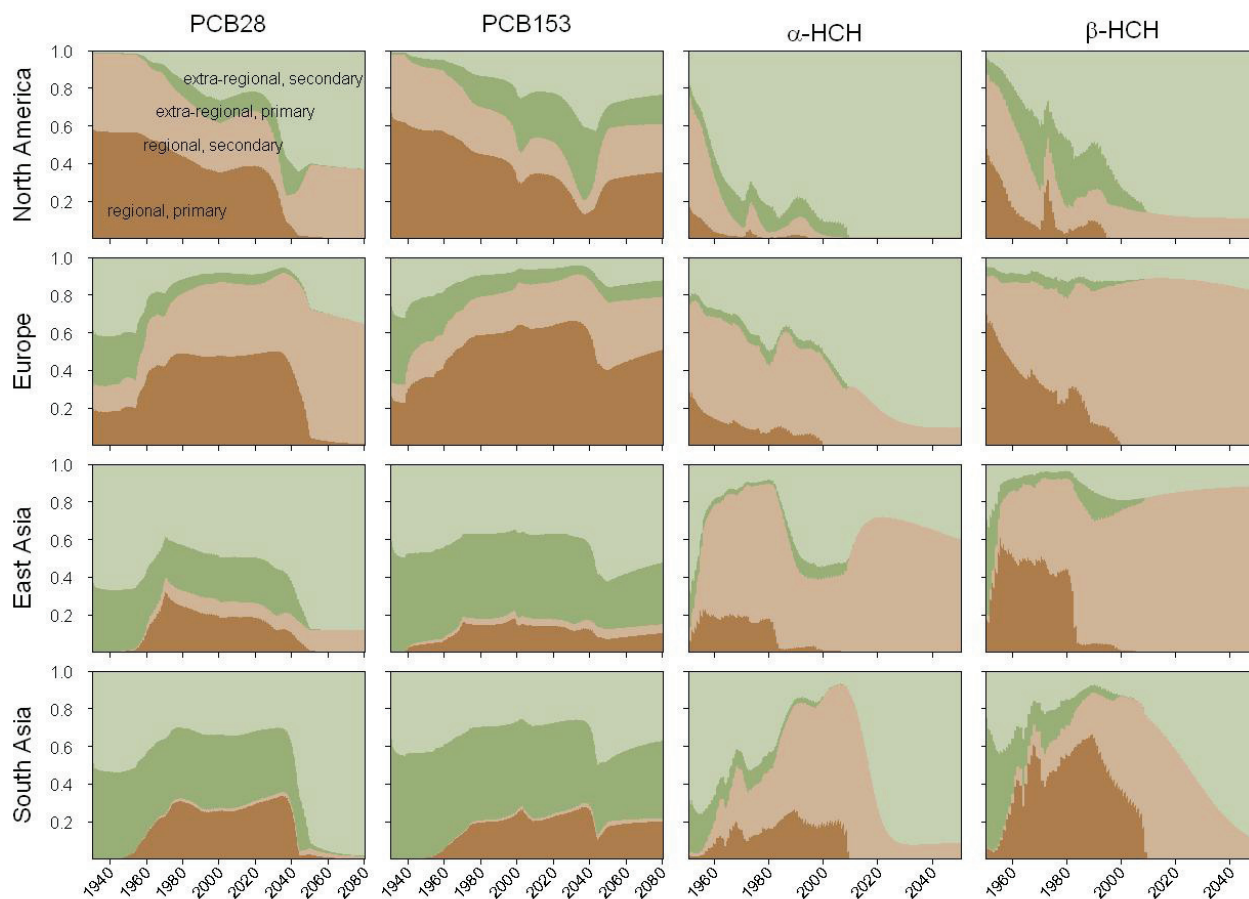
Figure 3. *Relative contributions of regional and extra-regional PCB28, PCB153, α-HCH and β-HCH emissions (primary and secondary) to concentrations in air in the 4 HTAP regions.*
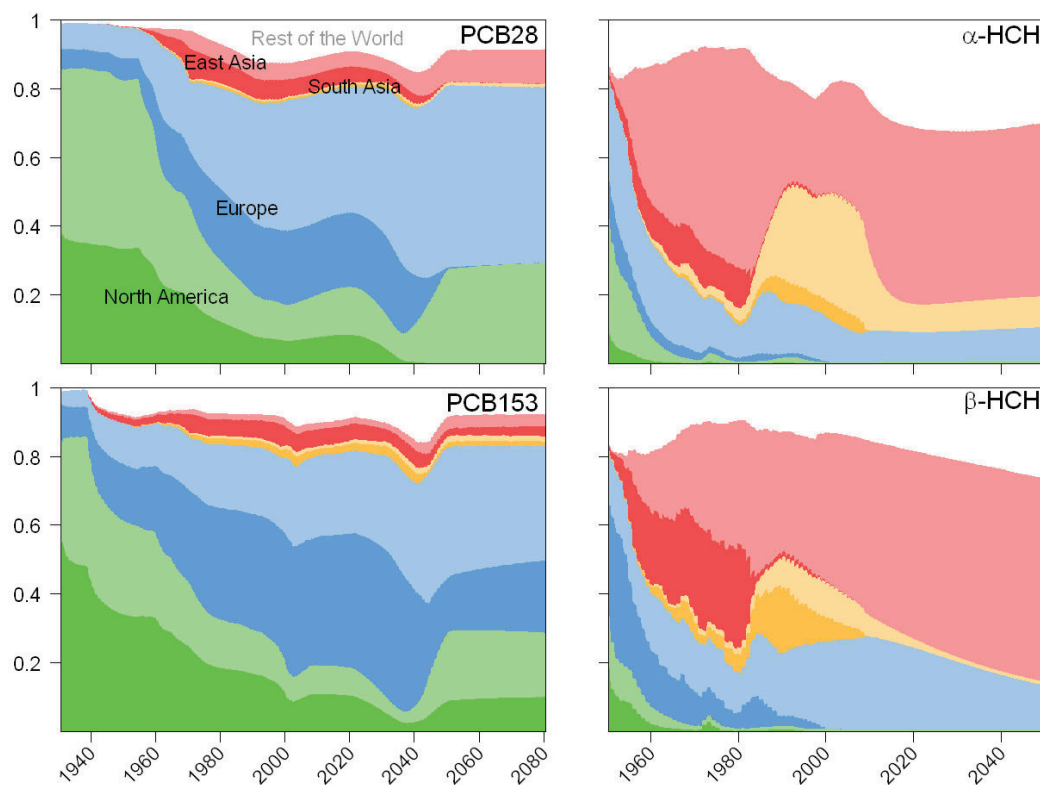

Figure 4. *Relative contributions of PCB28, PCB153, α- and β-HCH emissions from North America (green), Europe (blue), South Asia (orange), East Asia (red) and the rest of the world (white) to atmospheric pollution in the Arctic. Primary emissions are dark shaded; secondary emissions are light shaded.*
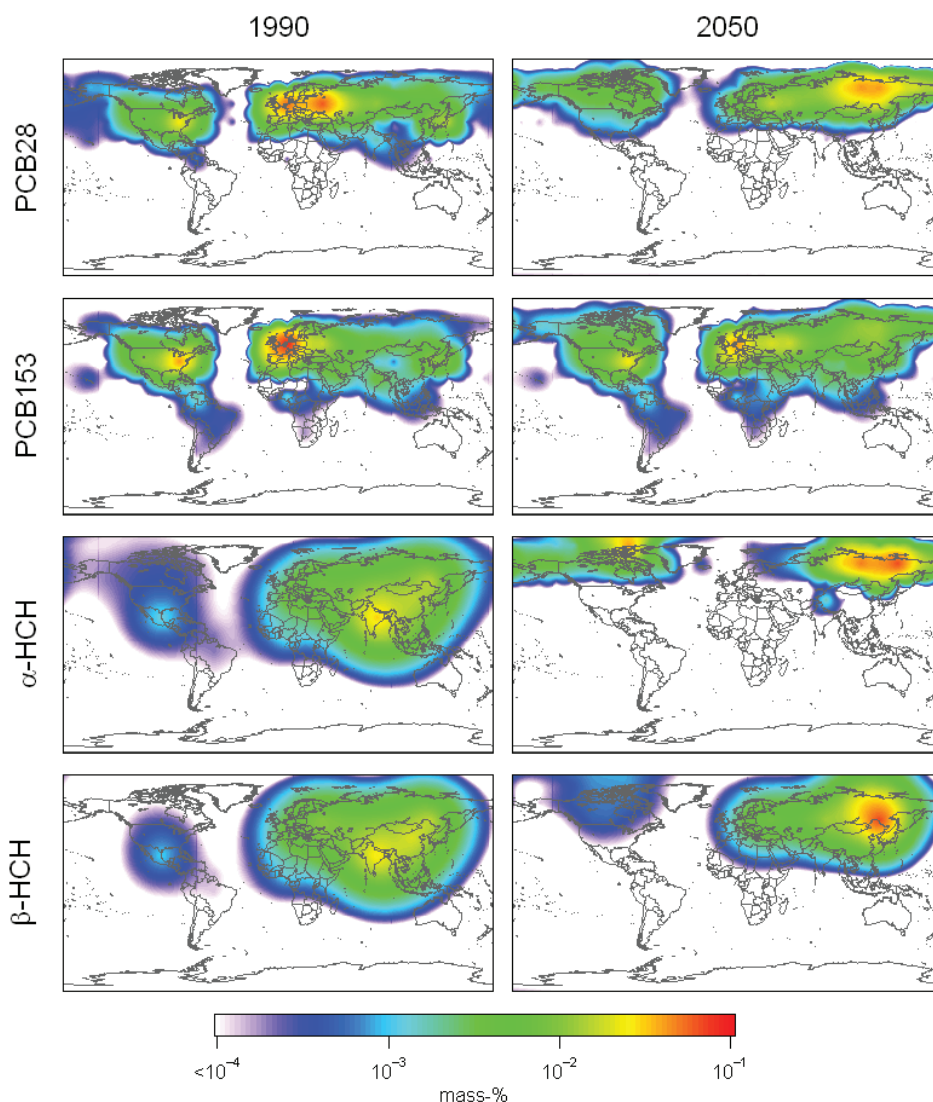
Figure 5. *Global contributions to PCB28, PCB153, α-HCH and β-HCH in the Arctic atmosphere, for 1990 and 2050.The raw model output has been interpolated to a 1°x1° grid using the Krig-function in the fields package of the R statistical software. Non-interpolated results are provided in the SM, Figure S3.*

The source contribution maps for 1990 indicate that Arctic air pollution originates mainly from locations of ongoing primary emissions (Figure 5). For PCBs this is North America and Europe, while for HCHs South–Asia is the dominant contributor.

By 2050, when secondary sources become important, the contributing locations shift away from these sources, mainly towards northern latitudes. In particular, soils in Northern Russia, Alaska and Northern Canada, which are reservoirs of POPs close to the Arctic, are forecasted to become influential secondary sources. An exception among our four case–study chemicals is β–HCH, which affects the Arctic in 2050 via secondary emissions from East–Asian soils. Again, this particular behavior can be attributed to the relative immobility of β–HCH.

4. Conclusion and Outlook

We have shown that global source–receptor relationships of POPs are highly dynamic, and that they depend strongly on the chemical and its global emission pattern. Dramatic changes in source–receptor relationships are possible when the dominant location of emissions shifts between regions, or during the transition from primary– to secondary–source dominated regimes.

Our case study chemicals provide an example of the variability that is possible in the global environmental fate of persistent pollutants, in particular after their phase–out. The model results

forecast the time–scale for removal of pollutants from the global environment once production and use is banned; decades for the HCHs, and even longer for the PCBs, which continue volatilizing from industrial capacitors, transformers, and building materials long after the ban. Furthermore, the accumulation of pollutants in high latitude surface media causes delayed secondary emissions long after the cessation of primary emissions. Regions with higher historic emissions can therefore buffer global pollution levels long after bans or remediation measures have been implemented. Such lags must be considered in the design of regulatory actions and during the evaluation of their effectiveness at reducing ambient concentrations of chemicals.

Our results demonstrate that global–scale multimedia contaminant fate models like *BETR Research* can provide answers to the policy-relevant scientific questions about source-receptor relationships raised by the Task Force on Hemispheric Transport of Air Pollutants. However, the source–receptor relationships calculated by models cannot be more accurate than the emission estimates that are used to drive the model calculations, and uncertainties in chemical properties and estimated degradation half–lives used as inputs to the model will also limit the accuracy of model results. The limiting factor on providing source–receptor information for other chemicals is the availability of geographically explicit emission inventories. To improve the availability of emission information, novel methods such as the regional–scale measurement–modeling approach described by Gasic et al. (2009)

should be further exploited for candidate POPs of regulatory interest.

Supporting Material Available

Chemical properties of PCB28, PCB153, α–HCH and β–HCH; details on the parameterization of the BETR Research model; emissions of PCBs and HCHs for each HTAP region; year of ban for PCBs and technical HCH in selected countries; calculation of source-receptor relationships from model output; non-interpolated version of Figure 5; properties of our four case study chemicals; details on the parameterization of the *BETR Research* model; year of ban for HCHs and PCBs for selected countries. This information is available free of charge via the Internet at http://www.atmospolres.com.

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