Influence of snow and ice on the distribution of POPs in a global multi-media model

Judith Stocker[1], Fabio Wegmann[1], Martin Scheringer[1], Konrad Hungerbühler[1]

[1]Swiss Federal Institute of Technology

Introduction

Snow and ice influence the environmental behavior of organic chemicals at high altitudes and latitudes as well as in low latitudes in the winter season [1]. Organic pollutants were found in snow and ice of cold regions and research is conducted in order to understand the processes which cause the occurrence of these chemicals in these regions [2, 3, 4].

To analyze trends in field data within a model framework, we have added a snow and ice compartment to CliMoChem, a global multimedia model. The long-range transport of persistent organic pollutants (POPs) is investigated with this model and results are presented for a variety of organic compounds. The interpretation of the results focuses (i) on the influence of the snow and ice compartment on the interplay between phase partitioning, degradation and long range transport and (ii) on the sensitivity of this interplay to a variation of substance properties (e.g. snow surface/air partition coefficient, degradation rate) and environmental parameters (e.g. specific snow surface area, organic matter content of snow).

Materials and Methods

CliMoChem is a dynamic global multi-compartment box model with a flexible number of latitudinal zones (typically 10–30) having different temperatures and compartment volumes (Figure 1). Environmental compartments included are atmosphere, water, and vegetation as well as vegetation covered and bare soil. Here, only a brief description of the model is given as details can be found elsewhere [5, 6].

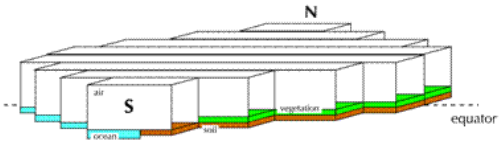

Figure 1: Geometry of the CliMoChem model with 8 zones (Zone 1 represents the Arctic ("N"), zone 8 the Antarctic ("S").

Intrazonal processes are wet and dry gaseous and particulate deposition, runoff and leaching from bare soil to water, leaf fall, deposition to deep sea and degradation. These processes were modified if necessary when including the snow and ice compartment in CliMoChem, e.g. there is no exchange between the atmosphere and a snow-covered compartment.

Interzonal processes include long range transport in the atmosphere and in the ocean. The temporal resolution is one month to one year and the spatial resolution is determined by the number of latitudinal zones.

Model outputs are concentrations, masses and mass fluxes, exposure as time integrated concentration, cold condensation quotients, persistence and spatial range.[5]

Global seasonal snow cover and depth was averaged from satellite data obtained from the National Snow and Ice Data Center (NSIDC) at the University of Colorado and are documented by Chang et al.[7] Figure 2 shows the average zonal snow depth and the average zone-specific surface fraction of water, permanent ice and areas with/without snow cover in winter. An effective diffusion depth of 0.2 m was used for the surface layer of the permanent ice from which chemicals are transported to deeper ice.

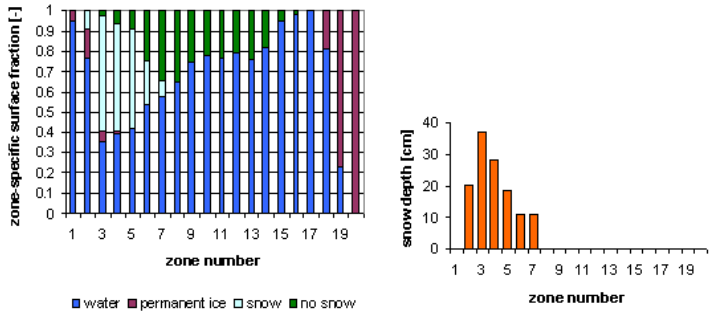

Figure 2: Average zone-specific surface fraction and average zonal snow depth [cm] in winter (January to March).

Chemicals are deposited from the atmosphere to the underlying snow or ice surface by wet and dry deposition (particulate and gaseous). The advective deposition processes are parameterized according to Lei and Wania, and the diffusive process is based on a two-resistance model [8]. The deposited chemicals revolatilize or remain in the snowpack and are subsequently degraded or transferred to soil and water during snow melt. The degradation rate in snow and ice is assumed to be equal to that in water and adjusted to ice or snow temperature.

The partition coefficient between snow or ice and air is calculated as described by Roth et al.[9]:

$$\log K_{ssf/air} = c \cdot \log K_{hexadecane/air} + a \cdot \sum\beta + b \cdot \sum\alpha - 6.85 \quad (1)$$

where $K_{ssf/air}$ is the coefficient for sorption equilibrium between snow surface (ssf) and air [m], $\log K_{hexadecane/air}$ is the hexadecane/air partition coefficient at 298.15 K, and Σα and Σβ are the sum of the electron acceptor and electron donor characteristics of the chemical, respectively. The regression coefficients a (= 3.38), b (= 3.53) and c (=0.639) are related to the properties of the snow surface.

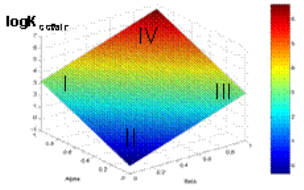

Figure 3: Eq. 1 is plotted for a combination of Σα and Σβ between 0 and 1. The slope of the plane is defined by a and b while $\log K_{hexadecane/air}$ shifts the plane up and down along the vertical axis. A chemical's position on the plane depends on its polarity (area I to IV). POPs are mainly in area II (e.g. PCBs or DDT), in area III (e.g Atrazine or Terbutylazine) or in between (e.g. 2,3,7,8-TCDD).

The sensitivity of the model outputs to environmental parameters is analyzed by varying the specific snow surface area, A_S [m^2/kg] and the snow density, ρ_S [kg/ m^3], in the expression for the bulk air/snow partition coefficient K_{asp}^{bulk} [m]:

$$K_{asp}^{bulk} = \frac{1 - f_{paA} + f_{paA} \cdot K_{PA} \cdot \rho_{PA}}{(1 - f_{wS} - f_{aS} - f_{ocS}) \cdot A_S \cdot \rho_S \cdot K_{ssf/air} + f_{wS} \cdot K_{WA} + f_{aS} + f_{ocS} \cdot K_{OA}} \quad (2)$$

where ρ_{PA} is the density and f_{aS} is the volume fraction of aerosol particles in air. The particle/air partition coefficient K_{PA} (m^3/μg) is modeled as in Finizio et al.[10] The octanol/air partition coefficient, K_{OA}, is approximated as $K_{OA} = K_{OW}/K_{AW}$ where K_{OW} is the octanol/water partition coefficient and K_{AW} the air/water partition coefficient., and f_{wS}, f_{aS} and f_{ocS} are the volume fractions of water, air and organic carbon in the snow pack, respectively.

Results and Discussion

Substance properties. Snow is a highly polar medium and the polar properties of a chemical have a dominant influence on its sorption to snow. This is reflected by the steep slope of the plane in Figure 3. The $K_{ssf/air}$ of polar substances is three orders of magnitude higher than that of non-polar chemicals. Hence, polar chemicals are efficiently scavenged from the atmosphere as they sorb strongly to snow. This effect may influence the long range transport potential of these compounds.

Environmental properties. A_S and ρ_S are altered by different processes such as snow metamorphism caused bysublimation, vapor transfer, and crystal deformation within the snow. Additionally, weight of subsequent layers, wind and snow permeability affect A_S and ρ_S in aging snow. Figure 4 shows $-\log K_{asp}^{bulk}$ for atrazine, α-HCH and PCB153 in new and aged snow. Results are shown for snow having high and low f_{ocS}, respectively [11, 12]. The values of A_S and ρ_S are based on Cabanes et al. and Legagneux et al.[13,14]

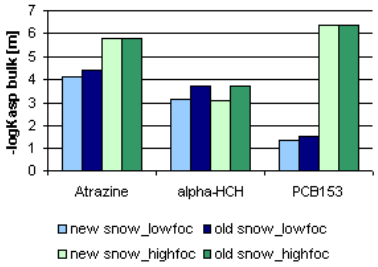

Figure 4: $-\log K_{asp}^{bulk}$ [m] for atrazine, α-HCH and PCB153 in snow with low f_{ocS} ($1.3 \cdot 10^{-7}$) and high f_{ocS} ($2 \cdot 10^{-2}$), new snow: A_S = 80 m^2/kg, ρ_S = 100 kg/m^3, old snow: A_S = 20 m^2/kg, ρ_S = 400 kg/m^3.

Generally, A_S decreases and ρ_S increases in aging snow causing a range of a factor of ten between minimum and maximum values of the term $(1-f_{wS}-f_{aS}-f_{ocS})\cdot A_S\cdot\rho_S$ in eq. 2. Thus, snow aging has only a moderate effect on K_{asp}^{bulk}, or even no effect for high f_{ocS} and high K_{OA} (Figure 4) because in this case $f_{ocS}\cdot K_{OA}$ is the dominant term in the denominator.

Model results on long range transport. We investigated the effect of the snow and ice compartment on the long range transport of POPs by

analyzing mass fluxes within and between zones for a single pulse emission in the northern temperate zone.

Results obtained with the CliMoChem model show that adding a snow and ice compartment alters the transport efficiency of POPs to polar and boreal regions. The temporal course of the environmental exposure is governed by different processes according to season. In winter, transport and snow scavenging are the dominant processes. In sprint, snow melt and subsequent revolatilization mainly contribute to environmental exposure and released compounds may be transported to adjacent zones (grasshopper effect).

Aknowledgments

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References

1. Wania F., Hoff J., Jia C., Mackay D. (1998) *Environ. Pol.* **102**, 25-41.

2. Carrera G., Fernandez P., Grimalt J., Ventura M., Camarero L., Catalan J., Nickus U., Thies H., Psenner R. (2002) *Environ. Sci. Technol.* **36**, 2581-2588.

3. Halsall C., Bailey R., Stern G., Barrie L., Fellin P., Muir D., Rosenberg B., Rovinsky F., Kononov E., Pastukhov B. (1998) *Environ.Pol.***102**, 51-62.

4. Garbarino J., Snyder-Conn E., Leiker T., Hoffman G. (2002) *Water Air Soil Pol.***139**, 183-214.

5. Wegmann F. (2004) Dissertation, Swiss Federal Institute of Technology, Nr. 15427, Zürich.

6. Scheringer M. (2002) Persistence and spatial range of environmental chemicals: new ethical and scientific concepts for risk assessment, Wiley-VCH, Weinheim.

7. Chang A. T. C., Foster J. L., Hall D. K. (1987) *An. Glaciol.* **9**, 39 - 44.

8. Lei Y., Wania F. (2004) *Atmos. Env.* **38**, 3557-3571.

9. Hock R. (2003) *J. Hydrol.* **282**, 104-115.

10. Roth C., Goss K., Schwarzenbach R. (2004) *Environ.Sci. Technol.* **38**, 4078-4084.

11. Finizio A., Mackay D., Bidleman T., Harner T. (1997) *Atmos.Environ.* **31**, 2289-2296.

12. Davies T., Tranter M., Jickells T., Abrahams P., Landsberger S., Javis K., Pierce C. (1992) *Atmos. Environ.* ***26***, 95-112.

13. Reimnitz E., Barnes P., Weber W. (1993) *J. Glaciol.***39**, 186-198.

14. Cabanes A., Legagneux L., Domine F. (2002) *Atmos. Environ.* **36**, 2767-2777.

15. Legagneux L., Cabanes A., Domine F. (2002) *J. Geophys. Res.Atm.***107**, 4335-4349.