EFFECTS OF SNOW AND POLAR ICE ON THE DEPOSITION AND LONG-RANGE TRANSPORT OF CURRENT-USE PESTICIDES AND OTHER ORGANIC POLLUTANTS

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Introduction

Organic pollutants have frequently been detected in snow and ice of cold regions. Field measurements and modeling studies are conducted in order to understand the processes which cause the occurrence of these chemicals in polar regions and mountainous areas.[1,2,3] Current modeling studies concentrate on the investigation of a chemical's fate in a regional snow pack but do not address the effects of snow and ice on the global distribution of chemicals.[4,5,6] 23% of the earth's surface is permanently or seasonally covered with snow or ice, which provides a large capacity for the sorption of chemicals. Furthermore, it has been found that the global fate of organic pollutants is strongly affected by globally varying environmental conditions, e.g. different temperatures in polar and temperate regions lead to different melt water transfer of the chemical to the underlying surface and the lower vapor pressure in colder regions leads to an accumulation of chemicals in the surface media (cold condensation[7,8]).

Therefore, there is a need to assess the influence of snow and ice on the global behavior of organic chemicals in order to complement ongoing field studies. To this end, we have incorporated a snow and ice compartment into CliMoChem, a global multimedia model.[7] Here, the effects of snow and polar ice on the partitioning and long-range transport of organic chemicals are investigated with this model and results are presented for a variety of organic compounds, including current-use pesticides and polybrominated diphenyl ethers. A variety of effects of snow and ice are observed for different chemicals and are interpreted in terms of the chemicals' physicochemical properties.

Materials and Methods

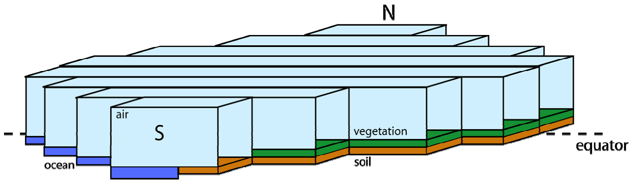

Figure 1: Geometry of the CliMoChem model (zone N represents the Arctic, zone S the Antarctic).

CliMoChem is a dynamic global multi-media 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.[9]
Multimedia partitioning processes taking place in the model are wet and dry gaseous and particulate deposition, runoff and leaching from soil to water, leaf fall and deposition to deep sea. These processes were modified if necessary when the snow and ice compartments were incorporated, e.g. there is no exchange between the atmosphere and snow-covered soil.
Degradation is described as (pseudo-) first-order loss process in all media. Long-range transport is described by large-scale eddy diffusion in the atmosphere and in the ocean. The temporal resolution is three months and the spatial resolution is determined by the number of latitudinal zones.
Model outputs are concentrations and masses in all compartments of the model, mass fluxes between all compartments, and different metrics of persistence and long range transport.[9]

The metamorphosis of fresh snow to ice includes six key stages[10]: fresh snow, old snow, firn, intermediate firn, glacier ice and ice. The snow compartment in CliMoChem includes fresh and old snow, the first two stages of the metamorphosis. The polar ice compartment consists of permanent ice and sea ice. Snow and ice are porous media including organic matter and pores filled with air and water.

Chemicals are deposited from the atmosphere to the underlying snow or ice surface by wet and dry deposition (particulate and gaseous). Washout by snow fall is parameterized according to Lei and Wania[11], and gaseous deposition and revolatilization are calculated with a two-resistance model. The partition coefficient between snow or ice and air, K_{ca}, is calculated as described by Roth et al.[12] The deposited chemicals revolatilize or remain in the snow or ice pack and are subsequently degraded or transferred to soil and water during snow or ice melt. In ice, chemicals are transported from the surface layer of the permanent ice to deeper ice. The degradation rate constant in snow and ice is assumed to be equal to that in water and is then adjusted to actual ice or snow temperatures. The melting rate is derived from a temperature index model.[13]

Global seasonal snow cover and depth was taken from satellite data obtained from the National Snow and Ice Data Center (NSIDC) at the University of Colorado.[14] Data on global ice cover were obtained from the Lawrence Livermore National Laboratory.[15]

Various chemicals with different affinities for snow and ice were selected to investigate the influence of snow and ice on their global distribution. They include current-use pesticides (chlorpyrifos, dieldrin, alachlor, dacthal), DDT, α-HCH, polybrominated diphenyl ethers (PBDE47, PBDE209), polychlorinated biphenyls (PCB28, PCB180) and HCB. The K_{ca} values of the investigated chemicals range from $2.17 \cdot 10^{-3}$ for HCB to $4.9 \cdot 10^{+4}$ for PBDE209.

Model calculations were performed with the original CliMoChem version and with the new version including snow and ice. Chemicals were released as a single pulse emission (10^9 kg) into the air compartment of the northern temperate zone (zone 3 of a total of 10 zones). The pulse release is used here because it shows in a transparent manner the processes governing the environmental fate of a chemical in the model. Because snow fall effectively transfers chemicals from air to snow, the mass balance of most chemicals is different in the two model versions directly after the pulse release took place. Therefore, we concentrate on the first year of the simulated period of time in the analysis of the model results.

Results and Discussion

In general, the observed effects are caused by direct interaction of the investigated chemicals with ice and snow or by the coverage of water and soil with snow and ice inhibiting exchange between the atmosphere and the covered compartments. The influence of snow on the fate of chemicals is important in temperate zones whereas the behavior of chemicals in polar zones is influenced by the ice compartment. Therefore, identified effects are described separately for snow and ice below. Depending on the partition coefficients and environmental half-lives of the different chemicals, various effects of snow/ice are observed.

Transfer from the atmosphere to the snow pack and subsequent storage. Chemicals with a high affinity for snow and ice and a high affinity for organic carbon are removed from the atmosphere by snow scavenging and stored in the snow pack. Only when the snow melts, the chemicals are released again and are mainly transferred to the soil. This reduces the amounts of these chemicals that are available for transport to the polar zones and leads to an accumulation of the chemicals in the emission zone compared to the model version not including snow and ice. This effect is observed for PBDE209, PBDE47 and PCB180, which have high to moderately high K_{ca} as well as a high K_{oa} and K_{ow}.

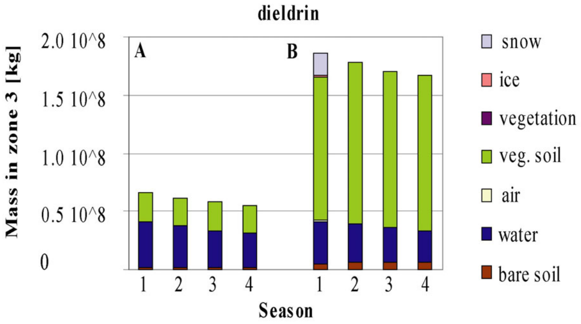

Figure 2: Mass of dieldrin in the environmental media of zone 3 in the first year after pulse release of $1\cdot10^9$ kg (A: model version without snow and polar ice; B: model version with snow and polar ice)

Transfer from the atmosphere to the underlying surface with snow melt. Alachlor and dacthal are efficiently removed from the atmosphere through vapor scavenging because of their high K_{ca} values. Alachlor and dacthal have very low K_{aw} values and are effectively removed with meltwater during snowmelt, which increases their mass stored in the vegetation soil in zones 2, 3 and 4 (a significant part of the vegetation soil is covered with snow in these zones). The half-life of alachlor and dacthal in vegetation soil is three orders of magnitude higher than that in air. Therefore, the increased transfer from air to soil via snow leads to a strong accumulation of alachlor and dacthal in temperate zones. This effect is also observed fordieldrin (shown in Figure 2), chlorpyrifos and DDT.

Inhibition of the exchange between air and vegetation soil and subsequent transfer to water. When the deposition from atmosphere to vegetation soil is blocked by snow, it depends on the relative magnitude of a chemical's K_{aw} and K_{ca} whether deposition flux is transferred to the snow pack or to water. The affinity of α-HCH for water is three orders of magnitude higher than for snow. The snow cover of the vegetation soil leads to higher deposition fluxes from the atmosphere to water than in model calculations without snow and ice. Figure 3 shows that the flux to vegetation soil is redirected to water rather than to snow in the case of α-HCH. Examples of chemicals transferred to snow rather than to water due to their larger K_{ca} have been given in the two paragraphs above.

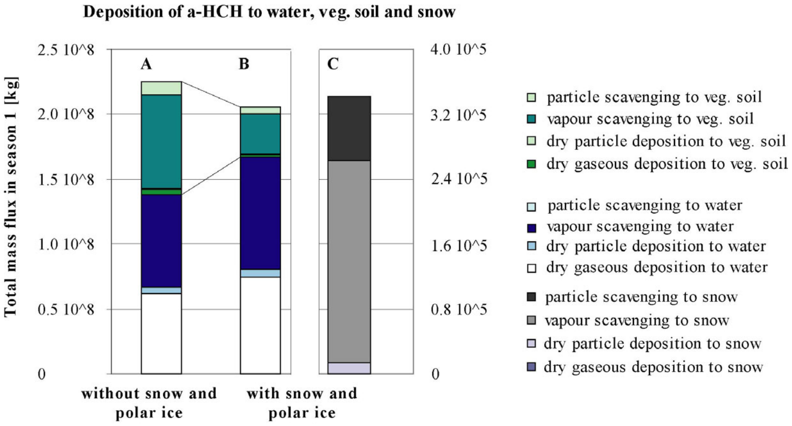

Figure 3: Total deposition flux from atmosphere to vegetation soil, water and snow in zone 3 in season 1 (A: model version without snow and polar ice; B and C: model version with snow and polar ice). Deposition to snow is shown on a smaller scale.

Inhibition of the exchange between air and vegetation soil and subsequent accumulation in air. PCB28 and HCB are relatively volatile chemicals and in the model version with snow, they are first deposited to the snow but revolatilize quickly. This leads to an increase of PCB28 and HCB in the atmosphere compared to the results of model calculations without snow and ice.

In conclusion, snow is a dynamic media due to seasonally varying snow fall and snow melt. Changes in snow volume are faster in warmer regions (zones 3 and 4) than colder regions (zones 1 and 2). The transport of chemicals with melt water to underlying surface described above is mainly observed in zones 3 and 4 as well as in zones 7 and 8. In zones 2 and 3, the fraction of snow-covered surface reaches its maximum and covers up to 70% of the total area in the winter. Therefore, the effects of the inhibited exchange between atmosphere and underlying surface are particularly important in these zones.

Inhibition of the exchange between air and underlying surface and subsequent accumulation in deeper ice. Polar ice covers large parts of zones 1, 2, 9 and 10. Chemicals are transported by water and air to these zones and polar ice has a strong influence on the fate of chemicals which are mainly transported through the atmosphere. Chemicals accumulate in polar ice and are subsequently transferred to deeper ice. Accumulation and transfer are higher for substances having a high K_{ca} such as PBDE209 and dieldrin than for chemicals having a lower K_{ca} (e.g. HCB and chlorpyrifos). Sea ice first inhibits deposition to water but releases deposited chemicals to the water when it melts.

In principle, a comparison between a distribution pattern of a chemical based on CliMoChem calculations and concentrations measured in the field is possible. Unfortunately, a lack of emission inventories for most chemicals impedes a comprehensive validation of model results with measurement data. Nevertheless, results obtained for PCB 28, PCB153 and PCB 180 showed similar trends as measured by Gustafsson et al.[16] They found decreasing concentration from PCB180 to PCB153 to PCB28 in melted ice samples of the Barents Seas and the North Pole, which is in agreement with our model results. Hermansson et al.[17] investigated current-use and legacy pesticides in the Austfonna Ice Cap. Concentration trends of methoxychlor and dieldrin showed a higher peak for dieldrin than for methoxychlor. Dieldrin was still measured in the ice core 10 years after it peaked while the concentration of methoxychlor had decreased close to zero. These observed trends were reproduced accurately with our model.

CliMoChem results show that the manner and magnitude of how snow and polar ice influence the fate of organic chemicals varies between different climatic zones and between chemicals having different substance properties. This underscores the need to assess the influence of snow and polar ice on the environmental fate of chemicals on a global scale.

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