# MODELING INCORPORATION AND POST-DEPOSITIONAL PROCESSES OF PCB IN ALPINE GLACIERS

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## Introduction

Glaciers and ice sheets contain records of past environmental conditions such as carbon dioxide or methane levels in the atmosphere. These archives can also provide information about atmospheric concentrations and emission trends of less volatile chemicals. However, for semi-volatile chemicals it is not clear how well they are preserved. They may be subject to diffusion and evaporation, but also other post-depositional processes such as melt can corrupt the records. Cold glaciers are suitable as natural archives, as ice temperature throughout the glacier is below 0°C and melt processes are negligible. However, in the Alps, cold glaciers are only present at altitudes above 4000 m a.s.l.[1] and are therefore not numerous. The majority of Alpine glaciers are temperate, meaning that except for seasonal freezing at the glacier surface, the ice is at 0°C. In this case, melt processes are crucial and have to be understood if ice cores are used as environmental archives.

Here we use persistent organic pollutants (POPs) as tracers for post-depositional processes in both a cold and a temperate glacier. We thereby focus on polychlorinated biphenyls (PCBs) as emission inventories are known and available[2]. PCBs are a group of 209 congeners with log Kow and log Kaw values ranging from 4.5 to 8.5 and -2.0 to -3.0, respectively[3]. This variety in properties leads to different behavior of the light (lower chlorinated) and the heavy (higher chlorinated) PCB congeners in the environment. We use this fractionation to identify key processes influencing the movement of PCBs in a cold and a temperate Alpine glacier as well as to determine the fate of POPs in a high-Alpine area.

We present a model describing (1) the transport from source areas in the lowlands to Alpine areas, (2) the deposition to the glacier surface by dry deposition and wet deposition in the form of snow or rain, and (3) the incorporation and storage at the glacier surface, including the partitioning between the solid ice matrix, pore air, organic particles and liquid water. We validate our model with the concentration records measured in an ice core from a cold glacier (Fiescherhorn) and from a temperate glacier (Silvretta).

## Materials and methods

*Study site.* The ice core from Fiescherhorn glacier was extracted in December 2002 (46°33’ N, 08°04’ E), Bernese Oberland, Switzerland. The drilling site is in the accumulation area of the glacier at an altitude of 3900 m a.s.l., approximately 6 km east of the high-Alpine research station Jungfraujoch. Local mass balance was determined by dating of the ice core and had an average of 1.7 m water equivalent/year between 1900 and 2000. Details about sampling and dating of the ice core can be found in Jenk[4]. The ice core from Silvretta glacier was extracted in April 2010 (46°50’ N, 10°5’ E), Grisons, Switzerland. The drilling site is close to the equilibrium line at an altitude of 2950 m a.s.l. Seasonal mass balance observations are reported in Huss et al.[5] and interpolated to monthly values according to positive and negative air temperature.

*Chemical analysis and properties.* PCBs were analyzed in the ice core by extraction into a polydimethylsiloxane coated trap capillary and quantitative determination by gas chromatography mass spectrometry[6]. Temperature dependence of partitioning and degradation was modeled according to MacLeod et al.[7] and adsorption to ice was estimated using the poly-parameter linear free energy relationship introduced by Roth et al.[8], where the ice surface-air partition coefficient is a function of the hexadecane-air partition coefficient and the electron donor/acceptor properties of the chemical.

*Model setup.* The model is a dynamic multimedia chemical fate model consisting of two submodels. One submodel is parameterized for the lowlands, the other for the glacier surface of the cold or the temperate glacier (Figure 1). The lowlands model (Figure 1, middle part) is a five-box model consisting of soil, water, sediment and a lower and upper air compartment and includes the part of western Europe lying between longitudes 1° W and 14° E and latitudes 44-50° N. The lower air compartment corresponds to the planetary boundary layer and is in contact with the earth surface, whereas the upper air compartment describes the free troposphere. PCBs are emitted to the planetary boundary layer in the lowlands submodel according to existing emission inventories[2]. After distribution between the five compartments, air with a certain chemical load is advected to the high-Alpine area by wind. The air originates from the upper or the lower air compartment according to how often the drilling site is exposed to the free troposphere or the planetary boundary layer.

The 1-dimensional glacier surface model consists of an air compartment and a set of vertically aligned firn and glacier ice compartments. Temperature, precipitation and local mass balance are parameterized for the drilling sites on Fiescherhorn and Silvretta glacier. Firn compartments are formed on the surface during periods of positive mass balance and inactivated when they melt away while the mass balance is negative. When a compartment is covered with fresh snow, the density of this compartment increases as a function of depth. On Fiescherhorn (Figure 1, left part), the mass balance is always positive, therefore no melt processes occur and no compartment is inactivated. In contrast, on Silvretta (Figure 1, right part), the mass balance can be positive or negative, causing meltwater to run off from the surface or percolate through the firn. This meltwater percolates to the bottom of the firn of the previous winter season and partly refreezes in a layer, whose density subsequently increases (grey shaded layers in Figure 1). The other part runs off just above this dense layer.

Modeled processes in the atmosphere include degradation by OH-radicals and advective loss by wind. Wet and dry deposition of gaseous and particle-bound chemicals is modeled, where the former is initiated by snow on Fiescherhorn and by snow or rain on Silvretta. Post-depositional processes include diffusion of chemicals between pore air and ambient air, as well as between pore air of adjacent firn layers; pore air advection within the firn; and photochemical degradation in the top 15 cm of the firn. In the temperate glacier, the model additionally includes partitioning of chemicals into liquid water, transport with meltwater and refreezing in the dense layers as well as runoff from the surface and above the dense layers. The Fiescherhorn model is yearly resolved between the years 1933 and 2002, while the Silvretta model is monthly resolved from 1960-2007.

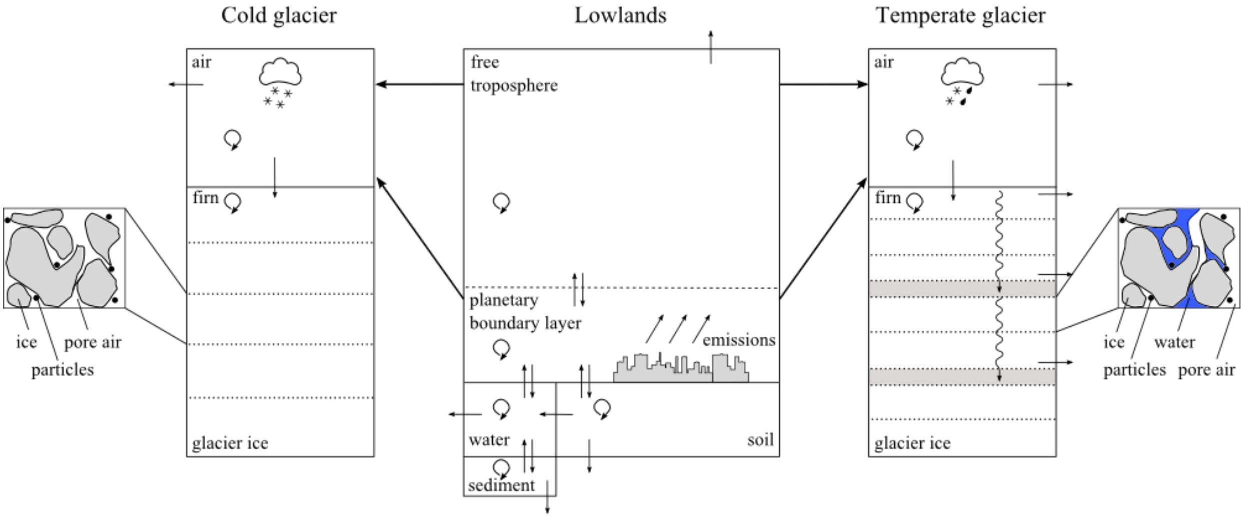

**Figure 1: Model setup: POPs are emitted in the lowlands and transported to the glacier surface by air advection. In the cold glacier, post-depositional processes include diffusion and air advection (not shown here) and degradation. In the temperate glacier, additional processes, such as density layering (grey shaded layers), percolation of meltwater and meltwater runoff are included.**

## Results and discussion

Modeled and measured concentration profiles of the two ice cores are compared in Figure 2. For the cold glacier (Fiescherhorn), the modeled temporal trend of the PCB congeners PCB 101 and PCB 180 agrees well with the measured profiles. The modeled concentrations peak at a depth of 60 m, corresponding to the 1970s when emissions of these chemicals were highest. Modeled and measured absolute concentrations agree well for PCB 101. For PCB 180 we observe higher modeled concentrations than measured, which may be explained by the direct transport from the lowlands to the high Alps, probably underestimating the losses of highly chlorinated congeners during this passage. In contrast to the modeled profile, the measured concentration of PCB 28 peaks in a depth of 100 m. This may be due to surface melt events during the summer months which we have not accounted for in our yearly resolved model. Such melt events have been identified in the record of major ions in the Fiescherhorn ice core[4].

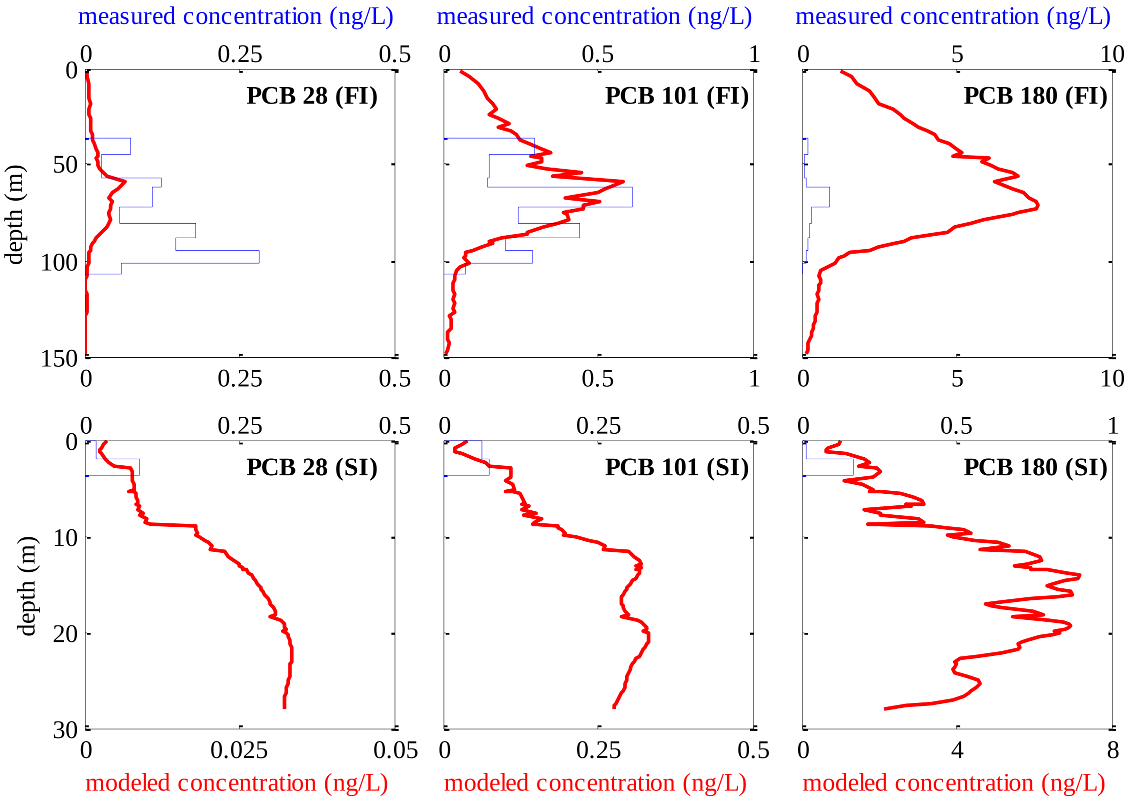

**Figure 2: Preliminary depth concentration profiles of the cold glacier (Fiescherhorn, FI, upper row) and the temperate glacier (Silvretta, SI, lower row) for PCB 28, PCB 101 and PCB 180. All concentrations are in ng/L. The red lines correspond to modeled profiles (bottom axis), the blue bars to measurements (upper axis). Note that in the lower row, upper and lower axis are different. So far, measured concentrations of Silvretta are only available for the top 4 m.**

The modeled concentration profiles of the temperate glacier (Silvretta) show less distinct peaks than the profiles of the cold glacier. The concentrations peak in a depth of 15-20 m for PCB 101 and PCB 180. The concentration of the light congener PCB 28 peaks further down at a depth of 20-25 m, indicating an increased influence of melt processes on lower chlorinated congeners. In contrast to the Fiescherhorn profile, the profile of Silvretta reaches only a depth of 30 m. This originates from the much lower mass balance on Silvretta, which is positive and negative in different years, accumulating a smaller amount of new firn on the surface than on the cold glacier. Absolute concentrations are smaller than on the cold glacier, due to the greater losses on Silvretta (see next paragraph). So far, measured concentrations of Silvretta are only available for the top 4 m.

Besides the concentration profiles, we are able to reveal information about the fate of PCBs in a high-Alpine system and its dependence on the characteristics of the system as well as the chemicals. In the cold glacier, only 27% of the deposited amount of PCB 28 is actually preserved, whereas this percentage is as high as 96% for PCB 180. The rest is lost to the atmosphere through the air phase, including diffusion in air and air moving out of the glacier due to decreasing pore size with aging snow. For the Silvretta system, only 4% of what was deposited on the surface remains in the glacier for PCB 28, whereas 22% of PCB 180 is retained in the ice. The rest is lost to the atmosphere through the air phase (72% for PCB 28 and 6% for PCB 180), and by melt runoff (24% for PCB 28 and 71% for PCB 180).

Calculated air concentrations of the lowland model closely follow the emission trends, both peaking in the 1970s. For the year 2006, the model predicts atmospheric concentrations of PCB 28 and PCB 180 of 1.9 and 0.9 pg/m$^3$ reaching Fiescherhorn glacier. During summer 2006, concentrations of 2.7 and 1.5 pg/m$^3$ were measured at the adjacent Jungfraujoch for the two chemicals[9]. As expected, these summer concentrations are higher than the concentrations used in the yearly resolved model, as the planetary boundary layer can reach high altitudes during this season[10]. A sensitivity analysis shows that properties of the atmosphere, such as aerosol fraction, fraction of organic matter in aerosols and scavenging ratio are the most sensitive environmental parameters in the calculation of air concentrations in the lowlands. The most sensitive chemical parameters are the octanol-air partition coefficient and the degradation rate constant in air. The uncertainty limits of the air concentration in the upper air compartment are within factors of 7.3 and 3.0 for PCB 28 and PCB 180, respectively. For the lower air compartment, the uncertainty limit is lower, reaching at maximum a factor of 2.5 for PCB 28.

Our study reveals information about the fate of PCBs in a high-Alpine environment and its variance depending on the chemical and the glacial system. We can conclude that for PCB 28, the most important post-depositional process is release to the atmosphere through the air phase, whereas for PCB 180, significant amounts are lost by melt runoff. In a cold glacier, the record of a highly chlorinated PCB congener is only slightly disturbed by post-depositional processes; the total amount as well as the temporal trend is close to deposition characteristics. However, this is not true for more volatile congeners, as they are relocated through the air phase. In a temperate glacier, neither the total amount, nor the time trend is preserved for a light PCB congener. The profile of a highly chlorinated congener is disturbed, but still discernible. However, to determine total amounts preserved in the archive, post-depositional processes influencing the concentration of highly chlorinated congeners have to be accounted for. Our study shows that a comprehensive understanding of post-depositional processes influencing the fate of POPs in ice is indispensable for the interpretation of ice core records, both for cold and for temperate systems.

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