

THE FATE OF POLYCHLORINATED BIPHENYLS IN ALPINE GLACIERS

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Introduction

Polychlorinated biphenyls (PCBs) are poorly degradable, hazardous chemicals that were banned in many countries almost three decades ago. Today, they are still ubiquitous in the environment and can be found far away from their initial source areas¹. PCBs have been shown to be released from Alpine glaciers^{2,3,4}, which is of crucial importance as the chemicals reach highly sensitive ecosystems and the freshwater system. However, the amount and the timing of present and future release of persistent organic pollutants from Alpine glaciers is unclear. Here, we present a dynamic multimedia chemical fate model describing the fate of PCBs in an Alpine glacier. This work is still ongoing and part of an interdisciplinary research project connecting the fields of analytical chemistry, glaciology and chemical fate modeling, aiming at determining the importance of Alpine glaciers as a secondary source of persistent organic pollutants to the Alpine environment.

Materials and methods

A glacier is a mass of ice that slowly flows downhill due to internal deformation and driven by gravity. The ice mass is fed by snow accumulating on the glacier surface, while mass is lost by ice melt. This change in ice mass is described by the glacier mass balance. A positive mass balance indicates that more mass is accumulated than melted; a negative mass balance means that melting exceeds accumulation (the glacier recedes). A glacier can be divided into two parts, the accumulation area in the upper part of the glacier where the yearly local mass balance generally is positive and the ablation area in the lower part of the glacier where the yearly local mass balance generally is negative. However, accumulation and ablation areas vary from year to year depending on the climate. The fate of a chemical in this system strongly depends on the location on the glacier where the chemical is deposited. Therefore, in our model, we split the glacier surface in 170 sections (Figure 1). For every section, three main parameters are defined according to the altitude of the section: 1) the air temperature defining the length of the winter (air temperature < 0 °C) and the summer (air temperature > 0 °C) seasons; 2) the winter mass balance describing the total amount of snow accumulated during the winter season every year; 3) the yearly mass balance describing the total amount of snow accumulated over the entire year.

We model PCB incorporation for every section on the glacier in a monthly resolution from 1930 to 2007. Every year consists of a winter and a summer season (Figure 2). The incorporation model is composed of an atmospheric compartment and a set of vertically aligned glacier compartments. During every winter month, snow accumulating on the glacier surface forms an additional compartment consisting of solid ice, pore air and particles. During summer, the snow on the glacier surface melts, and the snow compartments on the surface decrease in size and are removed one after the other. The melt water, now included in the compartments, percolates downwards, partly refreezing and leaving the system as melt runoff.

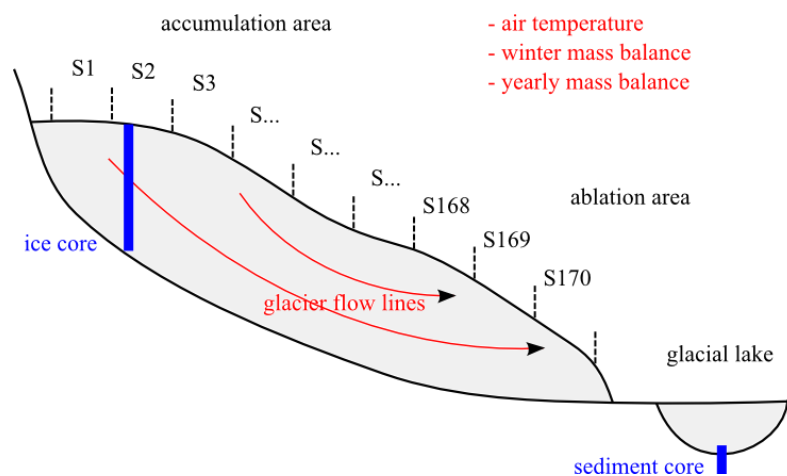


Figure 1. Scheme of the glacier sections (S1 to S170) and the glacial lake. Input parameters used in the model (air temperature, winter mass balance, yearly mass balance and glacier flow lines) are shown in red, while validation data (ice core, sediment core) is shown in blue.

Figure 2 illustrates the setup of the incorporation model for three example years. In year 1, the yearly mass balance on the section is positive. This means that after the summer season a part of the snow compartments is still active on the glacier surface. The amount of ice, particles and chemicals stored in these compartments is now defined as incorporated into the glacier. In year 2, the yearly mass balance of the section is lower than in year 1, but it is still positive. Consequently, the remaining amount of ice, particles and chemicals is incorporated into the glacier. In year 3, the mass balance on the section is negative. This means that none of the glacier compartments remain on the glacier surface after the summer season. Therefore, no ice is incorporated into the glacier ice, but particles and chemicals partly remain on the surface. A negative mass balance also leads to a partial release of ice, particles and chemicals that have been incorporated in the previous year.

Processes described in the incorporation model include advective inflow/outflow by wind, snowflake-air and aerosol particle-air partitioning, degradation by OH radicals in the atmosphere, wet deposition by snow (winter) and rain (summer) and dry deposition of gaseous and particle-bound chemicals. In addition, in the glacier compartments, modeled processes include re-volatilization from snow to air, diffusion between pore air and liquid water of adjacent glacier compartments, ice-pore air, particle-pore air and liquid water-pore air partitioning, and photochemical degradation in the glacier surface. The incorporation model is validated against PCB levels measured in ice cores within our research project. Up to today it was applied to an ice core from a cold Alpine glacier (Fiescherhorn Glacier in the Swiss Alps with ice temperature below 0°C, no significant melt processes)^{5,6}, an ice core from an Arctic glacier (Lomonosovfonna Glacier on Svalbard, Norway)⁶ and an ice core from a temperate Alpine glacier (Silvretta Glacier in the Swiss Alps)⁷.

Once incorporation is calculated for every section on the glacier and every year, the sections are connected by a full-Stokes glacier flow model, describing the flow lines of ice from the upper to the lower part of the glacier⁸ (Figure 1). This means that the incorporated chemicals are stored within the glacier for a certain time period according to the section on the glacier, the year of incorporation and the flow line they were deposited onto. After this storage time, when a flow line arrives at the glacier surface, the chemicals are transferred to the section where the flow line ends and are either stored on the glacier surface, re-volatilized to air or they run off with melt water to reach the glacial lake. In the last step, the fate of chemicals in the glacial lake is described by using a multi-compartment chemical fate model including the atmosphere, lake water and lake sediment. Model results are then validated against PCB levels measured in the lake sediments.

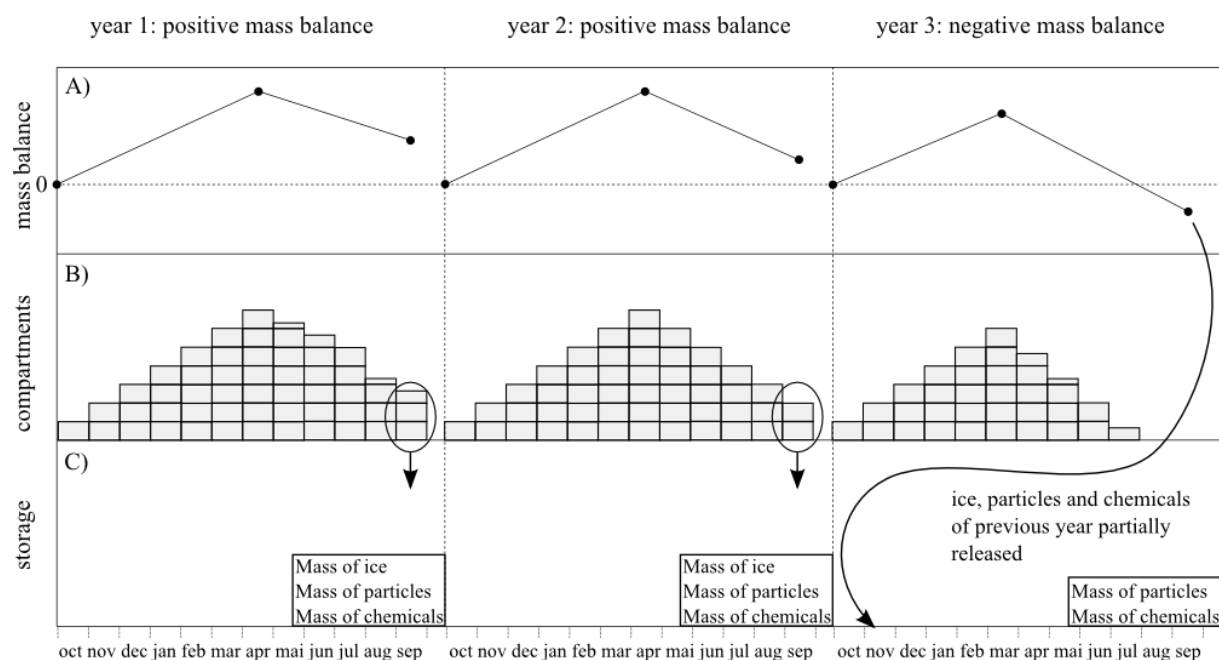


Figure 2. Setup of the incorporation model for three different years. A) Positive winter mass balances and varying yearly mass balances (dots) and interpolated monthly values (lines) for the three years. B) Setup of glacier compartments over the course of the year. One year consists of one winter and one summer season. The duration of a year is defined by air temperature and might be shorter or longer than 12 months. C) Incorporation of ice, particles and chemicals into the glacier after the summer season.

We apply the model to the Silvretta glacier. The Silvretta glacier is located in the Swiss Alps (46°50' N, 10°0' E), expands over an altitude of 2500–3000 m above sea level and is connected to two glacial lakes. The Silvretta glacier is a temperate glacier, which means that the ice temperature is approximately 0 °C, indicating the occurrence of melt processes. The glacier is part of the Swiss Glacier Monitoring Network⁹ in which detailed measurements of the mass balance of a glacier are carried out, and which indicates for the Silvretta glacier a considerable mass balance decrease since 1900, especially in the 1950s and since the 1990s. An ice core from an elevation of 2950 m above sea level as well as sediment cores from both glacial lakes were extracted and analyzed for PCBs (Pavlova P.A., unpublished results). Global emissions of PCBs were taken from Breivik et al.¹⁰, and the global PCB distribution was calculated using the BETR Research model¹¹. BETR Research is a global model, describing chemical concentrations in tropospheric air, boundary layer air, vegetation, fresh water, coastal water, soil and sediment. We use a seasonally varying mixture of tropospheric and boundary layer air above central Europe as input into the model.

Results and discussion

The amount of PCBs incorporated into the glacier is highly variable depending on the section and year. First results show a high incorporation on sections where the local mass balance is high and the winter season is long. A high winter mass balance means that the glacier compartments formed on the glacier surface are deep, decreasing diffusion and thus, decreasing re-volatilization to the atmosphere. A high yearly mass balance means that a high number of glacier compartments is still active after the summer period. These compartments then get covered by new compartments during the following winter and are buried within the glacier, storing the chemicals contained within. A long winter season means that the air temperature is negative during several months. This leads to increased deposition of chemicals to the glacier surface due to deposition by snow (higher scavenging ratio than rain) as well as increased sorption to the condensed phase, in this case snowflakes and aerosol particles.

Incorporation into the glacier is strong for chemicals with low volatility, such as the higher chlorinated PCBs, because their re-volatilization to the atmosphere is low. On the other hand, an important fraction of chemicals with a high volatility, as for example the lower-chlorinated PCBs, is re-volatilized to the atmosphere after deposition. In addition to volatility and sorption to solid ice and particles, the following properties of the glacier compartment have an effect on re-volatilization: density of the compartment influencing porosity and specific surface area of the snow, compartment size and compartment depth (controlled by the mass balance).

Preliminary results show the total incorporation of PCBs into the glacier to strongly follow the emissions of these chemicals, increasing after 1950, peaking in the 1970s and reaching low values after 1990. However, strong yearly fluctuations are observed. In a warm year, the mass balance of the glacier is low. This means the majority of the sections has a negative mass balance and only a small part of all the newly formed glacier compartments is still active on the surface after the summer season and can be buried. In addition, in sections where the local mass balance is strongly negative, even previously stored chemicals might be released.

As mentioned above, fractionation of chemicals happens during their incorporation into the glacier surface. During the time where chemicals are stored within the glacier (transported along a flow line) no degradation or volatilization occurs and therefore no fractionation happens. Subsequently, when chemicals are released from the glacier surface, chemicals with a strong sorption to solid ice or organic particles stay on the glacier surface while other chemicals re-volatilize to the atmosphere or are washed off by melt water runoff. A key parameter in this system is the fraction of particles running off with melt water, which is particularly important for strongly sorbing chemicals such as the highly chlorinated PCB 180.

After release from the glacier the chemicals reach the glacial lake, where they deposit to the lake sediment. We then validate the modeled sediment concentrations against PCB levels measured in the lake sediment. By adding future scenarios of the chemical fate and glacier flow models we will be able to calculate future release of PCBs from Alpine glaciers.

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