Doctoral Thesis

Glaciers as a temporary reservoir of persistent organic pollutants
Incorporation, transport, and release

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GLACIERS AS A TEMPORARY RESERVOIR OF PERSISTENT ORGANIC POLLUTANTS: INCORPORATION, TRANSPORT, AND RELEASE

A thesis submitted to attain the degree of DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by
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Summary

Persistent organic pollutants (POPs) are a group of poorly degradable, bioaccumulative, and toxic chemicals. After a period of widespread use in the 20th century, certain POPs were gradually phased out and banned at the end of the 20th century. Due to their persistence and semivolatile character, POPs are globally distributed and can reach remote areas where these pollutants have never been used and emitted.

In Alpine areas, POPs are transferred from the atmosphere to glaciers by dry deposition, or by deposition initiated by snow- or rainfall. As the snow ages, it transforms to firn, and subsequently to glacier ice. The pollutants can be incorporated into the glacier ice, revolatilize to the atmosphere, degrade, or run off with meltwater or particles. Impurities incorporated into the glacier ice are transported from the accumulation area (where new glacier ice is formed) to the ablation area (where the ice melts), a transport process which can last decades to centuries in Alpine glaciers. When the ice melts, the chemicals contained in the ice are released with meltwater and can reach the aquatic freshwater system. The fate of semivolatile organic pollutants in a glacier system has not been investigated in detail before.

This thesis studies the fate and dynamics of polychlorinated biphenyls (PCBs) in glaciers. The thesis aims at investigating the fate of the six indicator PCB congeners (iPCBs) in two types of glaciers. The PCB congeners 28, 52, 101, 138, 153, and 180 are used as representative model chemicals, as they cover a wide range of properties, and measured environmental concentrations of these congeners are available.

In the first study of this thesis, the fate of PCBs in the accumulation area of a cold glacier is investigated. In a cold glacier, the ice temperature is below 0°C, and melting is negligible in the accumulation area. Chemical fate is studied by developing a multimedia chemical fate model describing deposition, postdepositional processes, and incorporation of chemicals into the Alpine Fiescherhorn glacier (Switzerland) and the Arctic Lomonosovfonna glacier (Svalbard, Norway). The model is based on local snow accumulation data, and is validated by comparing modeled and measured PCB concentrations in ice cores. The ice core of the Fiescherhorn glacier was analyzed for PCBs in the doctoral study of Pavlina Pavlova, which was conducted parallel to this thesis. The modeled and measured PCB concentrations peak in the 1970s, the period of
highest PCB emissions. For the individual congeners, average modeled concentrations are between 50 and 400 pg L$^{-1}$ in the ice core of the Fiescherhorn glacier, and between 8 and 50 pg L$^{-1}$ in the Lomonosovfonna glacier. The model is able to reproduce and explain measured PCB levels in the ice cores. The model shows that the majority of the lower-chlorinated congeners is lost from the glacier by revolatilization (86% of PCB 28). In contrast, the higher-chlorinated congeners are stored in the glacier ice (98% of PCB 180).

In the second study, the incorporation model is applied to the accumulation area of a temperate glacier, where the ice temperature is around 0°C, and melt processes are important. The multimedia chemical fate model is extended by including meltwater and particle percolation and runoff. The model is validated by comparing modeled and measured PCB levels in an ice core from Silvretta glacier (Switzerland), which was also analyzed for PCBs by Pavlina Pavlova in the parallel doctoral study. Average modeled concentrations are between 20 and 200 pg L$^{-1}$ for the individual congeners, which is lower than the levels in the cold glacier. The lower concentrations are caused by higher losses attributed to revolatilization and particle runoff in the temperate glacier. Again, the PCB concentrations peak in the 1970s, but the concentrations also reach high levels in the 1950s and the 1990s, which were periods of strong melt. Strong melt induces an enrichment of particles and associated chemicals in layers located at the glacier surface during the melt period. As a consequence, the interpretation of temperate ice cores as environmental archives of past atmospheric conditions should include postdepositional processes.

In the third study, the incorporation model is applied to the entire glacier surface of the Silvretta glacier, and connected to a glacier flow model based on fluid dynamics, and a multimedia chemical fate model describing the glacial lake. The amount of chemicals incorporated into the glacier surface is passed on to the flow model, and transported along glacier flowlines. When ice traveling along a flowline reaches the glacier surface, the chemicals contained in the ice are released to the proglacial lake fed by glacier meltwater. In the lake, the chemicals can be deposited to the sediment, or leave the lake with water advection. The models are validated by comparing modeled and measured levels in the ice core, in a sediment core from the glacier lake, and in the stream water. Again, PCB levels in the sediment core and the stream water were determined by Pavlina Pavlova in the parallel doctoral study. The models are able to reproduce the measured concentrations of the higher-chlorinated congeners in the different matrices, with average modeled concentrations in the sediment between 150 and 170 pg g$^{-1}$ dry weight for the individual congeners. In contrast, the concentrations of the lower-chlorinated congeners in the sediment core are underestimated by the model (average modeled sediment concentrations between 4 and 14 pg g$^{-1}$). This deviation might be caused by overestimated revolatilization and missing processes in the ablation
area. The PCB storage in the Silvretta glacier increases until the 1980s, reaching a maximum of 70 g iPCBs. Thereafter, PCB storage decreases, with a strong release of chemicals in the 1990s and the 2000s. After 2010, the models predict a constant but low release of 1 g iPCBs per year, and an iPCB concentration in the glacial stream of 100 pg L$^{-1}$. This concentration is below toxic levels.

This thesis studies the fate of PCBs in glaciers depending on the properties of the PCB congener and the glacier type. Higher-chlorinated congeners tend to be more incorporated into the glacier ice than lower-chlorinated congeners, which are mainly lost from the glacier surface by revolatilization. PCB incorporation increases with the net snow accumulation (glacier mass balance), and is higher in cold glaciers than in temperate ones. In 2015, the models estimate that 200 g in total PCBs are stored in the Silvretta glacier. A simplistic extrapolation of the PCB mass stored in the Silvretta glacier to the glaciers in the European Alps based on the surface area results in 200 kg of PCBs. This is a small amount compared to contemporary sources. However, it leads to a constant, but small release of toxic chemicals to remote areas throughout the 21st century.

Future studies may investigate meltwater, particle, and revolatilization processes, as well as chemical fate in the ablation area. Further, the models could be applied to current-use chemicals, and to different glaciers, providing knowledge about the total storage of chemicals in the cryosphere. This could then be used to quantify potential present and future exposure of sensitive remote ecosystems to various persistent, bioaccumulative, and toxic pollutants.
Zusammenfassung


In der ersten Studie dieser Doktorarbeit wird das Umweltverhalten von PCBs im Akkumulationsgebiet eines kalten Gletschers untersucht. In einem kalten Gletscher liegt die Eistemperatur unter 0°C, so dass Schmelze im Akkumulationsgebiet vernachlässigbar ist. Das Verhalten und die Dynamik der Chemikalien wird in dieser Studie mit einem Kompartment-Modell untersucht, welches die Ablagerung, postdepositionale Prozesse


In der dritten Studie wird das Chemikalienmodell aus der zweiten Studie auf die gesamte Fläche des Silvrettagletschers angewendet und mit einem auf Fluidodynamik basierenden Gletscherfließmodell und einem Chemikalienmodell für den Gletschersee


Zukünftige Studien könnten die Schmelzwasser-, Partikel- und Diffusionsprozesse sowie das Umweltverhalten der Chemikalien im Ablationsgebiet weiter untersuchen. Ferner könnten die Modelle auf Chemikalien angewendet werden, welche heutzutage genutzt
werden. Auch die Anwendung der Modelle auf andere Gletscher wäre interessant. Dies könnte Erkenntnisse über die totale Menge an Chemikalien liefern, welche in der Kryosphäre gespeichert ist. Damit könnte man auch die mögliche aktuelle und zukünftige Exposition von sensitiven, abgelegenen Ökosystemen durch persistente, bioakkumulierende und toxische Schadstoffe abschätzen.
Related Publications


Chapter 1

Introduction

1.1 Persistent Organic Pollutants

The discovery of the synthesis of organic chemicals was a huge innovation for society in the beginning of the 19th century. While initially, synthesized chemicals were closely inspired by naturally occurring compounds, subsequent research focused on identifying new compounds with specific properties or effects. Some of these chemicals induced substantial advancements in pharmacy, industry, and agriculture, such as for example the use of the analgesic aspirin (acetylsalicylic acid) in medicine, or the application of the insecticide DDT (dichlorodiphenyltrichloroethane) in agriculture. Subsequently, the synthesis of chlorinated organic chemicals offered a new range of opportunities. As a consequence, the production and use of synthetic organic chemicals showed a tremendous increase in the 20th century, leading on the one hand to industrial innovation, higher agricultural yields, and improved life quality, but on the other hand also to extensive amounts of chemicals being unintentionally or intentionally released to the environment.

It was only in 1962, when the general awareness about potential risks synthetic chemicals can represent in the environment was raised by Rachel Carson, describing the consequences of the DDT use in her pioneering book *Silent Spring* [Carson, 1962]. In the decades that followed, research was initiated on the issue of anthropogenic organic chemicals in the environment. Some chemicals were shown to be poorly degradable in the environment and transported over long distances to remote areas, where these chemicals were never used. Toxic chemicals, utilized against specific insects or weeds, were shown to be toxic against nontarget organisms. Certain chemicals were identified to accumulate in organisms and be enriched over the food chain, leading to increased concentrations in higher trophic levels. Consequently, chemicals that are poorly degradable, bioaccumulative, and toxic were identified as persistent organic pollutants (POPs). The most problematic of these chemicals were the so-called *Dirty Dozen*, rep-
representing a group of particularly hazardous chlorinated organic compounds, including the pesticides aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, the industrial chemical polychlorinated biphenyl (PCB), and chemicals formed as by-products in industrial processes, namely polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). Following the reduction of production, use, and emissions of these chemicals in several industrialized countries, the Dirty Dozen was banned worldwide by the Stockholm Convention on Persistent Organic Pollutants in 2004 [UNEP, 2004]. Today, the identification of additional chemicals possessing the properties of persistence, bioaccumulation, long-range transport, and toxicity is an important field of research [Muir and Howard, 2006; Howard and Muir, 2010, 2011, 2013].

Among the most relevant POPs are PCBs, which represent persistent hydrophobic chemicals, that were widely used from the 1940s to the 1980s, mainly as dielectric fluids and flame retardants in capacitors and electrical transformers, and as plasticizers in plastics, sealants, rubber, and paints. Following their identification as toxic, bioaccumulative, and persistent chemicals, they were phased out in the 1970–80s, and banned worldwide by the Stockholm Convention in 2004. PCBs are semivolatile and have a rather low water solubility, which means that they partition reversibly between the atmosphere, the water bodies, and environmental surfaces, such as soil, snow, or
1.2 Emissions and Environmental Fate of PCBs

PCBs can unintentionally be released to the environment by usage in open or closed applications, by disposal in landfills, or by accidental release. Breivik et al. [2002a] estimated global emissions of 22 PCB congeners using estimates of global historical production and consumption in combination with a mass balance model. The authors investigated the historical intentional production, including open usage (e.g. paints and joint sealants), closed usage (e.g. transformers and capacitors), disposal in landfills, open burning, or spillage to soil. From these production estimates, annual emissions to the atmosphere between 1930 and 2000 were estimated on a $1^\circ \times 1^\circ$ grid, considering population density and temperature [Breivik et al., 2002b]. The main emission areas of PCBs are located between 30° and 60° N, where industrial production and population density are high. Future emissions up to the year 2100 were then assessed in a follow-up study (Figure 1.2) [Breivik et al., 2007]. The PCB congeners 28, 52, 101, 138, 153, and 180 are used as indicator PCBs (iPCBs), as these congeners had an important historical production [Breivik et al., 2002a].

From their emission sources, PCBs evaporate and reach the atmosphere. PCBs are semivolatile chemicals, meaning that they sorb to surfaces, but can revolatilize back to the air. Continuous sorption to surfaces followed by revolatilization induces an al-

![Figure 1.2: Estimated global emissions of the six indicator PCB congeners 28, 52, 101, 138, 153, and 180 between 1920 and 2060 [Breivik et al., 2007].](image-url)
1 Introduction

Table 1.1: Property data of the six PCB congeners 28, 52, 101, 138, 153, and 180 given at 25°C. Molar mass \((M)\), partition coefficients \((\log K)\) of octanol–water partitioning \((K_{OW})\), air–water partitioning \((K_{AW})\), and octanol–air partitioning \((K_{OA})\) [Schenker et al., 2005], halflifes of OH-radical degradation in air \((T_{1/2, \text{air}})\) [Anderson and Hites, 1996], and halflifes of biodegradation in water \((T_{1/2, \text{water}})\), and in soil \((T_{1/2, \text{soil}})\) [Mackay, 2006]. More information on property data used in this study can be found in the Chapters 2–4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>PCB 28</th>
<th>PCB 52</th>
<th>PCB 101</th>
<th>PCB 138</th>
<th>PCB 153</th>
<th>PCB 180</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>g mol(^{-1})</td>
<td>257.5</td>
<td>292.0</td>
<td>326.4</td>
<td>360.9</td>
<td>360.9</td>
<td>395.3</td>
</tr>
<tr>
<td>(\log K_{OW})</td>
<td>[-]</td>
<td>5.66</td>
<td>5.95</td>
<td>6.38</td>
<td>7.19</td>
<td>6.86</td>
<td>7.15</td>
</tr>
<tr>
<td>(\log K_{AW})</td>
<td>[-]</td>
<td>-1.93</td>
<td>-1.96</td>
<td>-2.08</td>
<td>-1.97</td>
<td>-2.13</td>
<td>-2.51</td>
</tr>
<tr>
<td>(\log K_{OA})</td>
<td>[-]</td>
<td>7.86</td>
<td>8.22</td>
<td>8.83</td>
<td>9.67</td>
<td>9.45</td>
<td>10.17</td>
</tr>
<tr>
<td>(T_{1/2, \text{air}}^*)</td>
<td>d</td>
<td>6.7</td>
<td>11</td>
<td>18</td>
<td>31</td>
<td>31</td>
<td>51</td>
</tr>
<tr>
<td>(T_{1/2, \text{water}})</td>
<td>d</td>
<td>230</td>
<td>420</td>
<td>1300</td>
<td>2300</td>
<td>2300</td>
<td>2300</td>
</tr>
<tr>
<td>(T_{1/2, \text{soil}})</td>
<td>d</td>
<td>420</td>
<td>700</td>
<td>4200</td>
<td>23000</td>
<td>23000</td>
<td>42000</td>
</tr>
</tbody>
</table>

\(^*\)Halflifes in air based on a pseudo first-order reaction with a concentration of OH radicals of \(9.7 \times 10^5\) molecules cm\(^{-3}\).

...ternation between the solid and the gaseous phase. This semivolatile character, in combination with low degradation rates, leads to long-range transport and global distribution of these chemicals. As a consequence, PCBs can be redistributed to areas where these chemicals have never been used or emitted. Sorption and revolatilization are temperature-dependent processes, as they are driven by the vapor pressure, which is a temperature-dependent property of a chemical. High temperature leads to stronger revolatilization, while low temperature leads to stronger sorption. As a consequence, PCBs tend to accumulate in cold areas compared to warm areas. This has been shown by studies reporting the occurrence of PCBs in remote sites of the Arctic [AMAP, 2009], Antarctica [Cabrerozo et al., 2013], or high-mountain areas such as the Himalaya [Gong et al., 2014; Ren et al., 2014], the Andes [Estellano et al., 2008], or the Alps [Offenthaler et al., 2009a; Halse et al., 2011; Jaward et al., 2005]. The environmental fate and global distribution differ for the six indicator PCBs, from the more volatile and water-soluble lower-chlorinated congeners (e.g. PCB 28), to higher-chlorinated congeners (e.g. PCB 180) with stronger sorption to surfaces (Table 1.1).

1.3 Multimedia Chemical Fate Modeling

Chemical risk assessment consists of the effect quantification (how dangerous a chemical is) and the exposure quantification (the amount of chemical present). Exposure can be quantified by measuring concentrations of chemicals in various media. In addition,
exposure can be assessed by investigating the concentrations and fluxes of chemicals in and between environmental media. The ultimate fate of a chemical is determined by the interaction of various processes: partitioning between different phases, such as between air and aerosol particles in the atmosphere, or between water and particles or living organisms in water systems; deposition from air to surfaces or from water to sediment; or revolatilization from water to air or resuspension from sediment to the water phase. Multimedia chemical fate modeling aims at understanding chemical fate, by including all the processes that are important for a specific system and a specific set of chemicals. Chemical fate models can be extended at discretion, however, every additional process or system extension clearly increases the complexity of the model. Increasing complexity introduces more uncertainty, as well as difficulty in the interpretation of results. Therefore, it’s important to be aware of the aim of every model [MacLeod et al., 2010], and to keep a chemical fate model as simple as possible for its designed purpose [Mackay, 2001]. Schwarzenbach et al. [2003] describe the purposefulness and simplicity of the models in environmental chemistry as:

The construction of models is like formulating hypotheses, which, in turn, must be tested by new observations. (...) According to the simplicity postulate, the most complex model is not necessarily the best one. To the contrary, a good model is like a caricature in which the cartoonist enhances the characteristics of a person’s face that, in a given context, are most relevant. [Schwarzenbach et al., 2003, pp 947–952]

In multimedia chemical fate models, the environmental system is divided into compartments, such as air, water, or soil. Each compartment is composed of several phases and has specific properties. All processes occurring in the system, such as losses from the system and intercompartmental transfer can be variable in time and specific for each compartment. A differential equation describing the mass of a chemical in each compartment is then set up and solved mostly numerically. The main assumptions in multimedia chemical fate models are (i) the homogeneity of the compartments, meaning that all compartments are assumed to be well-mixed, and the properties of the compartments, such as for example the particle content in a lake, or the organic carbon content of these particles; (ii) the thermodynamic equilibrium between the phases in a compartment; and (iii) the assumption that all processes in the model follow first-order kinetics. If the homogeneity assumption does not hold, the system can be split into more compartments, e.g. by including the epilimnion and the hypolimnion of a lake in terms of separate compartments. If the assumption of thermodynamic equilibrium is not supported, kinetically controlled sorption and desorption processes can be included, as recently proposed for nanomaterials [Praetorius et al., 2014]. For POPs, five important characteristics allow the use of multimedia chemical fate models to study
Introduction

their fate in the environment [Wania and Mackay, 1999]:

1. POPs have physical-chemical properties that make them occur in all environmental compartments and constantly move between the different phases.

2. POPs are very persistent in the environment, which allows the use of equilibrium partitioning between phases in a given compartment. This means that the subcompartments in a compartment are in equilibrium.

3. POPs are present in the environment in extremely small concentrations. This allows to treat them like ideal gases (no interaction between POP molecules in the environment), and to use first-order kinetics (no saturation effects).

4. Analyzing POPs in the different environmental media is difficult and expensive. Therefore, it is not possible to track experimentally the fate of POPs at a high spatial or temporal resolution. As a consequence, experimental data required to validate a highly resolved model are not be available.

5. The negative effects of POPs appear in the biota. This means that if the final goal is to perform a complete human risk assessment, biotic uptake and the fate of POPs in food chains have to be integrated in the models. The coupling of organisms to their environment is a specific strength of multimedia models.

The chemical mass balance equations can be described in terms of concentrations or fugacities. Even if the concentration of a chemical in the environment provides a relevant and well-known information, the concentrations of a chemical in two different phases do not automatically translate the behavior of the chemical. This means, a chemical does not necessarily move from the phase with a high concentration to the phase with a low concentration. In contrast, the behavior of the chemical rather depends on the properties of the phases. This is different when using fugacities, as the fugacity stands for the fleeing tendency of a chemical from a phase. This means, the chemical always moves from the phase with the higher fugacity to the phase with the lower fugacity. As an analogy, fugacity is in mass diffusion what temperature is in heat diffusion [Mackay, 1979]. The fugacity concept was adopted from the field of chemical engineering and introduced in environmental sciences by Donald Mackay [1979, 2001]. The fugacity concept allows to easily compare the importance of different transport or loss processes in a system, and to keep the equation systems linear, therefore helping in understanding the system.
1.4 Glaciers as a Temporary Reservoir of PCBs

Located at high elevations and having constantly cold temperature, glaciers were identified as a potential temporary reservoir of persistent semivolatile pollutants [Blais et al., 2001]. Compared to low elevation regions, in mountains, lower temperatures coincide with higher precipitation rates, leading to strong deposition of semivolatile chemicals to surfaces while revolatilization is decreased [Daly and Wania, 2005]. Additionally, precipitation occurring as snow instead of rain scavenges apolar organic chemicals more efficiently [Lei and Wania, 2004]. The consequential accumulation of chemicals in mountain areas is called mountain cold trapping. From glaciers, pollutants can be released to sensitive Alpine freshwater systems, which is of crucial importance as this water is eventually used for the drinking water supply of large regions.

However, the transport of chemicals from the source (i.e. lowlands) to the receptor (i.e. mountains) regions is often restricted due to atmospheric layering, decreasing the mixing between the planetary boundary layer and the free atmosphere [Hageman et al., 2015]. In the Alps, atmospheric layering is frequent in winter, while in summer, convective mixing induces exposition of mountain peaks to planetary boundary layer air, which was shown by seasonal monitoring of various environmental parameters such as for example black carbon or radon [Herrmann et al., 2015; Gabbi et al., 2015; Griffiths et al., 2014; Gäggeler et al., 1995]. As a consequence, the input of organic pollutants to Alpine regions varies seasonally, with high input in summer and low input in winter.

A glacier is a mass of ice that is formed from aged snow. In the upper part of the glacier (accumulation area), the ice mass is fed by snowfall onto the glacier surface (Figure 1.3). The snow is subsequently compacted and sintered, and aging snowflakes are transformed to rounded grains. Snow that is older than one year is called firn. Further aging and increasing pressure when covered by new snow, induces the firn density to increase with depth, until the pore connections are closed off, and pore air can no longer reach the atmosphere. At this density, firn has become glacier ice [Cuffey and Paterson, 2010]. In the lower part of the glacier (ablation area), ice mass is lost by melt. The accumulation and the ablation areas are separated by the equilibrium line, where snow accumulation and melt are equal. The difference between ice gain and ice loss is described by the glacier mass balance. The mass balance is positive in the accumulation area and negative in the ablation area. The mass balance of the entire glacier determines whether mass and volume of a glacier increase or decrease over time. The mass balance can vary over time, due to variations in weather and climate.

Due to gravity, the glacier ice mass slowly flows downhill, by internal deformation and basal sliding, while continuously deforming. Snow deposited onto the glacier at a high elevation is continuously covered with new snow, while moving downhill, and incorporated deep into the glacier (red line in Figure 1.3). This material can be stored in
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Figure 1.3: Illustration of the ice flow of the Oberaar glacier, located in the Swiss Alps. Ice is incorporated in the accumulation area, slowly flows downhill, until reaching the ablation area, where ice is lost by melt. The numbers in the figure correspond to the storage age in years. The figure is based on Bogdal et al. [2010].

The temperature of a glacier is of importance due to its influence on the deformation rate of ice or the formation of liquid water [Cuffey and Paterson, 2010]. In general, two types of glaciers can be distinguished: cold glaciers and temperate glaciers. In cold glaciers, the ice temperature is below 0°C. In contrast, temperate glaciers are at the pressure-melting temperature, i.e. the ice temperature is around 0°C [Cuffey and Paterson, 2010]. In temperate glaciers, seasonal melting occurs regularly, and meltwater may be present and percolate through the glacier. In the Alps, the majority of glaciers are temperate with exception of a few glaciers located above 3400 m a.s.l. (northerly aspects) and 4150 m a.s.l. (southerly aspects) [Suter et al., 2001].

One of the first studies investigating the release of POPs by glaciers was done by Blais et al. [2001] in the Banff National Park in Canada. The authors observed higher concentrations of organochlorine pesticides in a glacier-fed stream than in a non-glacier-fed stream. However, this difference could not be shown for PCBs. At the same time, Villa et al. [2001] measured the historical profile of PCBs in an ice core from Lys Glacier, in the Italian Alps. Maximum concentrations occurred in the early 1980s, with a dominance of lower-chlorinated PCB congeners. These studies demonstrated that glaciers play a role in the environmental cycling of POPs, but mechanistic details
of their role were not investigated.

In the following years, several studies were conducted on the effect of seasonal snow on the fate of POPs. Franz and Eisenreich [1998] quantified the scavenging of POPs by falling snow, a process which was further discussed by Wania et al. [1999a]. The postdepositional fate of POPs in seasonal snow was investigated by focusing on the diffusivity of organic chemicals, and the relative importance of revolatilization, runoff with meltwater, and sorption to the ice surface and to particles [Wania, 1997; Wania et al., 1999b; Albert and Shultz, 2002; Albert et al., 2002; Herbert et al., 2005, 2006a; Meyer et al., 2006, 2009a,b]. In these studies, the snow pack was described as a porous system consisting of pore air, liquid water, organic material, and solid ice. The authors concluded that the specific surface area of the snow, as well as the sorption of POPs to the ice surface are the main parameters describing the fate of semivolatile chemicals in the snowpack. Relevant experimental work provided information about the specific surface area of snow [Legagneux et al., 2002; Dominé et al., 2007], predictive tools for estimating sorption of POPs to the snow surface [Roth et al., 2004], or the quantification of photochemical degradation of PCBs in ice [Matykiewiczová et al., 2007]. Additionally, the role of snow and ice on the fate of POPs was discussed in several reviews [Wania et al., 1998; Halsall, 2004; Herbert et al., 2006b; Grannas et al., 2013]. These studies demonstrated clearly the importance of the cryosphere on the cycling of POPs, as well as the complex interactions between solid water and organic pollutants.

In order to compare the release of organic pollutants from seasonal snowpacks to their release from glacier ice, the concentrations of POPs in glacier- and non-glacier-fed streams were analyzed [Lafrenière et al., 2006; Bizzotto et al., 2009; Bettinetti et al., 2008]. The authors concluded that the relative importance of the two sources depend on the historical use of the chemical. For example, the release from glacier ice is important for DDT, because atmospheric levels of DDT have declined in recent time, leading to low levels in the non-glacier-fed stream. In contrast, the release of PCBs or HCB from seasonal snowpacks is influential as these chemicals are still emitted in urbanized areas in the vicinity of mountain regions [Bizzotto et al., 2009].

The storage of chemicals in mountain glaciers and their subsequent release to the freshwater system was addressed by Bogdal et al. [2009]. The authors compared sediment concentrations of various POPs in the glacial Lake Oberaar to levels measured in the relatively close-by lowland Lake Greifen [Zennegg et al., 2007]. While PCB levels in the Lake Greifen peak in the 1960s and remain on low levels thereafter, PCB levels in the Lake Oberaar decline after the 1970s, but increase again after the year 2000 (Figure 1.4). The authors explained this recent increase by the release of chemicals from the melting Oberaar glacier. Schmid et al. [2011] then presented a follow-up study, where the authors compared sediment records of Lake Engstlen and Lake Stein. The Lakes Engstlen and Stein are mountain lakes located at a similar elevation and in
the same meteorological catchment, with a glaciated and a non-glaciated hydrological catchment, respectively. While PCB levels in the sediment of the non-glaciated Lake Engstlen decrease after 1990, the concentrations in the sediment of the glacial Lake Stein increase after 2000.

In 2010, Bogdal et al. [2010] investigated PCB storage in the Oberaar glacier using chemical fate modeling. The main aim of their study was to confirm the ‘glacier hypothesis’, i.e. to investigate whether the concentration peak observed in the lake sediment could be explained by the release of contaminated meltwater by the glacier, with respect to the mass of ice and associated chemicals, as well as the age of the melted glacier ice. The model included deposition of chemicals to the glacier surface, their transport by ice flow through the Oberaar glacier, as well as various chemical fate processes in the glacial lake. The most important simplification of this model was that chemicals being deposited onto the glacier surface were considered to be immediately incorporated into glacier ice. Hence, postdepositional processes during the transformation from snow to firn and then to glacier ice were not considered. Despite this simplification, the model was able to reproduce the general fate of semivolatile organic chemicals in a glacial system and, thus, confirm the ‘glacier hypothesis’. However, it was strongly limited in providing understanding of detailed postdepositional fate processes of the individual PCB congeners.

To finally assess the risk of pollutants released from glaciers to aquatic systems, the exposure in biota living in the environment has to be investigated and compared to
1.5 Scope of the Thesis

The overall scope of this thesis is to investigate the fate and dynamics of PCBs in glaciers. The thesis investigates three major questions, (i) which are the key processes determining the fate of PCBs in a glacial system, (ii) what differences in chemical fate can be identified for the six indicator PCBs, and (iii) what differences can be observed for cold and temperate glaciers, and what is the influence of melt processes on chemical fate?

1.6 Approach

To answer these questions, the fate of PCBs is described in a glacial system, including the atmosphere, the glacier ice, and the glacial lake (Figure 1.5). From the atmosphere, PCBs are transferred to the glacier surface, where their fate is determined by postdepositional processes. Transfer and postdepositional processes are described using a multimedia chemical fate model developed in this thesis. This is the first model describing the fate of semivolatile organic pollutants in a snow-firn-ice system, including seasonal snowmelt processes. The transport of PCBs in the glacier ice is determined using flowlines originating from a fluid dynamics model describing the flow of ice. Finally, the fate of PCBs in the glacial lake is assessed using a multimedia chemical fate model, developed for the glacial lake studied in this thesis. PCBs are suitable for this study because chemical properties are known, estimates of historical emissions are available, and the chemicals are not in use anymore today. The models are run for the six indicator PCB congeners 28, 52, 101, 138, 153, and 180. These congeners had an important historical production [Breivik et al., 2002a], they cover a wide range of properties, and measured levels of these congeners in the environment are available.

This thesis was done as part of the project GlazioPOP, connecting the discipline of chemical fate modeling presented here, with the disciplines of chemical analysis and glaciology. The chemical analysis part provided measurements of environmental levels of POPs [Pavlova, 2014]. The glaciology part investigated the development of the glaciers studied in the project, including their mass balance and ice flow. The models presented in this thesis are validated by comparing modeled and measured PCB concentrations in different environmental matrices. PCB concentrations were measured in ice cores from the accumulation areas of the Fiescherhorn glacier (Swiss Alps), the
Lomonosovfonna glacier (Norwegian Arctic), and the Silvretta glacier (Swiss Alps) [Pavlova et al., 2014a; Garmash et al., 2013; Pavlova et al., 2015a]. In addition, PCB concentrations were determined in a sediment core from the glacial lake and in the glacial stream downstream of the Silvretta glacier [Pavlova et al., 2015b]. Also, PCB concentrations in air and PCB deposition were quantified in the Alps in the Monarpop project [Offenthaler et al., 2009a]. It is important to note that all the models presented in this thesis are completely independent of the measured PCB concentrations.

1.7 Outline of the Thesis

This thesis is composed of three chapters in form of publications (Chapters 2–4), and one chapter containing the main conclusions of the thesis and suggestions for future research (Chapter 5). The three Appendices (A, B, and C) report the Supporting Information of the corresponding publications in Chapters 2–4.

The first study in Chapter 2 investigates the incorporation of PCBs into cold glaciers. A chemical fate model describing air-to-glacier transfer, postdepositional processes, and incorporation into the glacier ice is presented. The model is applied to the accumulation areas of the high-Alpine Fiescherhorn glacier and the Arctic Lomonosovfonna glacier. Fiescherhorn glacier is a cold glacier, indicating that melt processes are negligible in the accumulation area, while the Lomonosovfonna glacier undergoes seasonal melting on the glacier surface. From both glaciers, ice cores have been drilled and analyzed for levels of PCBs [Pavlova et al., 2014a; Garmash et al., 2013]. The ice core from
the Fiescherhorn glacier was analyzed within the GlazioPOP project, and field data and model results have been published in two parallel publications, where the first one presents the measurements, and the second one the model results. The chemical fate model is validated by comparing modeled and measured concentration depth profiles in the ice cores.

The second study in Chapter 3 introduces a chemical fate model quantifying the incorporation of PCBs into a temperate glacier. The model is applied to the accumulation area of the Alpine Silvretta glacier, where seasonal melt processes are prevalent. Therefore, in contrast to the first study, the incorporation model includes meltwater and particle percolation and runoff. Within the GlazioPOP project, PCB levels in an ice core from the accumulation area of the Silvretta glacier were measured [Pavlova et al., 2015a] and used for model validation. Again, two publications present the measured levels and the model results in parallel.

The third study in Chapter 4 expands the work of the second study by applying the incorporation model of Chapter 3 to the entire surface of the Silvretta glacier. The amount of PCBs incorporated into the glacier is passed on to a glacier flow model, and transported along the glacier flowlines. When these flowlines arrive to the glacier surface, the chemicals are released and reach the glacial lake. A chemical fate model of the glacial lake then quantifies pollutant levels in the lake sediment and the glacial stream. This combination of models is validated by comparing modeled and measured levels of PCBs in the lake sediment and in the glacial stream. Also the PCB concentrations in the lake sediment and the stream water were analyzed within the GlazioPOP project [Pavlova et al., 2015b].

Finally, Chapter 5 discusses the main conclusions of this thesis and highlights potential future investigations.
Chapter 2

Polychlorinated Biphenyls in Glaciers. Model Results of Deposition and Incorporation Processes

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Abstract

In previous work, Alpine glaciers have been identified as a secondary source of persistent organic pollutants (POPs). However, detailed understanding of the processes organic chemicals undergo in a glacial system was missing. Here, we present results from a chemical fate model describing deposition and incorporation of polychlorinated biphenyls (PCBs) into an Alpine glacier (Fiescherhorn, Switzerland) and an Arctic glacier (Lomonosovfonna, Norway). To understand PCB fate and dynamics, we investigate the interaction of deposition, sorption to ice and particles in the atmosphere and within the glacier, revolatilization, diffusion and degradation, and discuss the effects of these processes on the fate of individual PCB congeners. The model is able to reproduce measured absolute concentrations in the two glaciers for most PCB congeners. While the model generally predicts concentration profiles peaking in the 1970s, in the measurements, this behavior can only be seen for higher-chlorinated PCB congeners on Fiescherhorn glacier. We suspect seasonal melt processes are disturbing the concentration profiles of the lower-chlorinated PCB congeners. While a lower-chlorinated PCB congener is mainly deposited by dry deposition and almost completely revolatilized after deposition, a higher-chlorinated PCB congener is predominantly transferred to the glacier surface by wet deposition and then is incorporated into the glacier ice. The incorporated amounts of PCBs are higher on the Alpine glacier than on the Arctic glacier due to the higher precipitation rate and aerosol particle concentration on the former. Future studies should include the effects of seasonal melt processes, calculate the quantities of PCBs incorporated into the entire glacier surface, and estimate the quantity of chemicals released from glaciers to determine the importance of glaciers as a secondary source of organic chemicals to remote aquatic ecosystems.

2.1 Introduction

Polychlorinated biphenyls (PCBs) were widely used industrial chemicals and belong to the class of persistent organic pollutants (POPs), a group of poorly degradable, hazardous chemicals, which were phased out almost three decades ago and banned worldwide in 2004 by the Stockholm Convention on POPs [UNEP, 2004]. PCBs have become ubiquitous environmental contaminants, also present in remote regions far away from their initial source areas [AMAP, 1998]. In remote regions, PCBs have been detected in environmental media such as air [Halse et al., 2011; Hung et al., 2010; Jaward et al., 2005], soil and sediments [Bogdal et al., 2009; Grimalt et al., 2004; Schmid et al., 2005; Tremolada et al., 2008], vegetation [Nizzetto et al., 2006; Offenthaler et al., 2009b], biota [Grimalt et al., 2001; Schmid et al., 2007], and snow [Carrera et al., 2001; Gustafsson et al., 2005; Herbert et al., 2005]. Additionally, PCBs have been detected
PCBs are carried to remote regions by atmospheric transport, followed by wet or dry deposition to glaciers. Snow remaining on the glacier surface undergoes an aging process and transforms to firn within a year. This porous material consists of rounded snow grains, and when covered with fresh snow, compaction and sintering lead to increasing density, until the air-containing pores are isolated and the firn becomes glacier ice [Cuffey and Paterson, 2010]. The behavior of this system depends predominantly on temperature and precipitation, and is therefore different for every glacier and every location on a glacier [Cuffey and Paterson, 2010]. In general, a glacier can be divided into the accumulation area, where snow accumulation is higher than melt, and the ablation area, where more ice melts than snow accumulates. Because of gravity and internal deformation, the ice slowly flows downhill from the accumulation to the ablation area, a process strongly dependent on inclination, glacier thickness, and temperature.

Several studies highlight the importance of snow physics (e.g. snow surface area or snow density) as well as chemical properties (e.g. snow–air partitioning or water solubility) on the fate of organic chemicals in seasonal snow [Hansen et al., 2006; Herbert et al., 2006b; Meyer and Wania, 2011; Wania et al., 1998]. Bogdal et al. [2010] modeled deposition of PCBs onto a glacier surface. However, for the sake of simplicity, deposited chemicals were instantaneously incorporated into the glacier ice in their model. Other potentially important processes such as revolatilization or sorption to the ice surface were not included in their model.

In an interdisciplinary research project, we investigate the fate of PCBs in Alpine glaciers. A comprehensive inventory of PCBs in a dated ice core from the Fiescherhorn glacier, Switzerland, is presented in an accompanying article [Pavlova et al., 2014a]. Ice cores are often investigated as archives of past environmental conditions; however, in the interpretation of chemical profiles in ice cores, postdepositional processes have to be considered. Here, we introduce a chemical fate model describing depositional and postdepositional processes of PCBs in the accumulation area of two glaciers. First, we focus on the Fiescherhorn glacier in the Swiss Alps. Second, we apply our model to the Lomonosovfonna glacier, Svalbard, Norway, which is located in the Arctic and from which an ice core has recently been analyzed for PCBs [Garmash et al., 2013]. To gain a thorough understanding of PCB fate and dynamics in glacial systems, we identify how glacier characteristics and chemical properties influence 1) the transfer of PCBs from the atmosphere to the glacier surface, 2) their incorporation into the glacier ice, and 3) their overall fate after deposition. It is important to note that our model is completely independent of the PCB data presented in our accompanying article [Pavlova et al.,
2.2 Methods

2.2.1 Study Sites

Fiescherhorn glacier is located in the Alps, Switzerland. The ice core drilling site (46.55° N; 8.07° E) is at an altitude of 3900 m above sea level (a.s.l.), approximately 6 km east of the high-Alpine research station Jungfraujoch. Fiescherhorn glacier consists of cold ice, which means that ice temperature is below 0°C (borehole temperature between −6 and −1°C [Schwerzmann et al., 2006]) and except for occasional seasonal melt on the surface, no important melt processes occur. The melt index, describing the percentage of melt features in an annual layer, was estimated to be 9% [Pavlova et al., 2014a]. The ice core was extracted in December 2002 from the accumulation area of the glacier, where the net accumulation in the last decade was around 1.7 m water equivalent per year (m weq yr⁻¹). Ice core dating and accumulation data were provided by Jenk et al. [2006] and Mariani et al. [2012], and shown in the Supporting Information of Pavlova et al. [2014a].

Lomonosovfonna glacier is the highest-elevation glacier on Svalbard, Norway, located approximately 80 km east of Svalbard airport. Average borehole temperature in the ice core is slightly higher than in Fiescherhorn glacier but still below 0°C (around −2°C). Seasonal melt on the surface occurs and the average melt index was estimated to be 31% [Wendl, 2014]. Two parallel ice cores were extracted in March 2009, at an elevation of 120 m a.s.l. (78.82° N; 17.43° E), where the net accumulation in the past decade was around 0.6 m weq yr⁻¹. Ice core dating, density profile, and accumulation data were provided by Wendl [2014].

2.2.2 Model Setup

The model is a dynamic multimedia chemical fate model. These models are based on a discretized version of the advection-dispersion equation. Thus, an environmental system is divided into well-mixed compartments each one having specific properties. The input of chemicals into the system, losses from the system, and intercompartmental transfers are modeled by first-order differential equations. These processes are time-dependent and compartment-specific. For each compartment a chemical mass balance equation is set up and solved numerically. More information on multimedia chemical
fate models is provided by Mackay [2001].

The model describes the vertical transport of chemicals; it consists of an air compartment and a set of glacier compartments (Figure 2.1). In every season, a new glacier compartment is formed on the surface, with a mass according to the net snow accumulation. A glacier compartment consists of solid ice, pore air, and particles, where the fractions of ice and air and the compartment height are determined by the compartment density. The particle fraction is defined by the amount of aerosol particles deposited by wet and dry particle deposition during the season. When a glacier compartment is covered by a new glacier compartment on top, the density of the lower compartment increases while the pore air fraction decreases. The model is seasonally resolved, with a winter season from October to March and a summer season from April to September. The Fiescherhorn model runs from October 1934 to September 2002, whereas the Lomonosovfonna model runs from October 1957 to September 2008; these are the periods covered by the ice cores and available meteorological data.

Figure 2.1: Model setup including the air compartment, the glacier compartments, and the processes included in the model. The air compartment consists of air and aerosol particles, the glacier compartments of ice, air, and particles. Properties of the glacier compartments change with depth (density increases, pore air fraction decreases, ice fraction increases). The particle fraction in the glacier compartments is a function of the deposited quantities of aerosol particles and snow. Global distribution of PCBs is calculated using BETR Research.
Processes modeled in the atmosphere include: advective in-/outflow by wind, degradation by OH radicals, snowflake–air and aerosol particle–air partitioning, as well as wet deposition by snow and dry deposition of gaseous and particle-bound chemicals. Postdepositional processes include revolatilization from snow to air, diffusion between pore air of adjacent firn layers, ice–pore air and particle–pore air partitioning, and photochemical degradation in the firn surface. Snow ventilation is accounted for by using a wind pumping factor for dry gaseous deposition and revolatilization [Daly and Wania, 2004]. Other potentially important processes, such as snowmelt, blowing snow, or sealing of the surface by refrozen meltwater are not included in the model. More information about the processes and their parametrization is available in Appendix A.

2.2.3 Environmental Parameters

Time-resolved parameters include net snow accumulation, air temperature, and aerosol particle concentration (Appendix A, Figure A.1). The net accumulation is yearly resolved, determined by ice core dating and corrected for layer thinning [Jenk et al., 2006; Mariani et al., 2012; Wendl, 2014]. The same accumulation is used for the winter and summer season. To maintain conservation of mass, precipitation is set equal to the net accumulation. Monthly air temperatures from Jungfraujoch and Svalbard airport were corrected for elevation differences using adiabatic lapse rates and averaged over the winter and summer seasons. On Fiescherhorn glacier, the annual average air temperature is $-10^\circ$C, (average in winter, $-14^\circ$C, summer, $-7^\circ$C), whereas on Lomonosovfonna glacier, the annual average air temperature is $-11^\circ$C (winter, $-17^\circ$C, summer, $-5^\circ$C) [MeteoSwiss, 2014b; MET, 2013]. The aerosol particle concentrations used in the model are 1.6 $\mu$g m$^{-3}$ and 4.2 $\mu$g m$^{-3}$ on Fiescherhorn [EMEP, 2014] and 0.4 $\mu$g m$^{-3}$ and 0.3 $\mu$g m$^{-3}$ on Lomonosovfonna glacier [Tunved et al., 2013] during winter and summer, respectively. In the model, aerosol particles have a density of 1000 kg m$^{-3}$ [FCAH, 2007] and a fraction of organic matter of 0.2 in the Alps [FCAH, 2007] and 0.1 in the Arctic [Ricard et al., 2002].

Depth-resolved parameters include the densities of the glacier compartments and the specific surface area of the firn. Density increases with depth according to a saturation function fitted to the measured density profiles in the ice cores (Appendix A, Figure A.2). The specific surface area of firn is derived from the density using a relationship reported by Domine et al. [2007]. Other environmental parameters are kept constant in the model and can be found in Appendix A (Tables A.1 and A.2).
2.2 Methods

2.2.4 Emissions and Global Distribution

Global emissions of PCBs were taken from the maximum emission inventory of Breivik et al. [2007]. Global distribution of PCBs was calculated using the BETR Research model [Wöhrnschimmel et al., 2013]. This model includes 288 connected regions on a 15° x 15° grid, and each region contains seven environmental compartments, including an upper and a lower air compartment representative of the free troposphere and the planetary boundary layer, respectively. The Fiescherhorn glacier is exposed to the free troposphere during winter due to atmospheric stratification, and to a mixture of 80% tropospheric air and 20% boundary layer air during summer. This mixing ratio during summer was estimated from sulfate concentrations in aerosol particles showing a clear seasonal trend at Jungfraujoch (Appendix A, Figure A.3). However, the value is uncertain, as processes such as local winds or gradual mixing could not be quantified. The Lomonosovfonna glacier is constantly exposed to the free troposphere [Garmash et al., 2013].

2.2.5 Chemical Parameters

Chemical parameters used in the model are reported in Appendix A (Table A.3). We modeled PCB 28, 52, 101, 138, 153, and 180. In the discussion we focus on the PCB congeners PCB 28, PCB 101 and PCB 180 as they cover a wide range of properties with increasing molar weight, sorption to organic material, and decreasing volatility and water solubility. The temperature dependence of the partition coefficients and degradation rate constants was included, and adsorption to ice was estimated using the polyparameter linear free-energy relationship introduced by Roth et al. [2004].

2.2.6 Sensitivity and Uncertainty Analysis

Analysis of model sensitivity and uncertainty was performed on the basis of the error propagation method of MacLeod et al. [2002], where log-normal distributions of independent input variables are assumed. Confidence factors of the input parameters are reported in Appendix A (Tables A.1–A.3).
2.3 Results

2.3.1 Concentrations in Air

Modeled concentrations in air decrease after 1970 and reach levels of 4.9, 1.3, and 0.5 pg m\(^{-3}\) for PCB 28, PCB 101, and PCB 180, respectively, in 2002 on Fiescherhorn (Figure 2.2, Appendix A, Table A.4). For comparison, Figure 2.2 includes available measured concentrations in air in the respective regions (sites Jungfraujoch (3450 m a.s.l.), Sonnblick (3100 m a.s.l.), Weissfluhjoch (2660 m a.s.l.), and Zugspitze (2650 m a.s.l.) for Fiescherhorn, and Zeppelin (474 m a.s.l.) for Lomonosovfonna) [EMEP, 2014; Offenthaler et al., 2009a]. In 2006, measured concentrations in air are in the same range as modeled concentrations for PCB 28 (2.7–29 pg m\(^{-3}\)) and PCB 180 (0.5–1.9 pg m\(^{-3}\)), whereas measured concentrations in air of PCB 101 are higher (1.5–8.2 pg m\(^{-3}\)) [EMEP, 2014; Offenthaler et al., 2009a]. Modeled concentrations in air on Lomonosovfonna glacier also decrease after 1970 and reach levels two times lower than on Fiescherhorn glacier, namely 2.6, 0.6, and 0.2 pg m\(^{-3}\) for PCB 28, 101, and 180, respectively, in 2002. Concentrations measured at the Zeppelin station [EMEP, 2014] are in the same range as the modeled concentrations for all congeners.

2.3.2 Air-to-Glacier Transfer

Modeled air-to-glacier transfer includes wet and dry particle and gaseous deposition. The modeled transfer fluxes follow the concentrations in air and decrease after 1970, reaching values of 369, 210, and 752 pg m\(^{-2}\) d\(^{-1}\) for PCB 28, PCB 101, and PCB 180, respectively, in 2002 on Fiescherhorn (Figure 2.2, Appendix A, Table A.4). Measured bulk deposition fluxes in 2006 (sites Sonnblick, Weissfluhjoch, and Zugspitze) are lower than modeled transfer fluxes for PCB 28 (144–175 pg m\(^{-2}\) d\(^{-1}\)), higher than modeled transfer fluxes for PCB 101 (258–572 pg m\(^{-2}\) d\(^{-1}\)), but in the same range for PCB 180 (373–1060 pg m\(^{-2}\) d\(^{-1}\)) [Offenthaler et al., 2009a]. On Lomonosovfonna glacier, the modeled transfer flux is lower than on Fiescherhorn glacier by factors of 2 (PCB 28), 5 (PCB 101), and 20 (PCB 180) with values in 2002 of 182, 47 and 37 pg m\(^{-2}\) d\(^{-1}\), for PCB 28, 101, and 180, respectively. Bulk deposition of PCBs has not been measured in the area.
Figure 2.2: (A) Yearly resolved PCB concentrations in air and air-to-glacier transfer fluxes on Fiescherhorn glacier. Concentrations in air: model results (red line); concentrations measured at Jungfraujoch (passive air sampling) during the summer months July, August, and September (filled blue dots) [EMEP, 2014]; concentrations measured at Sonnblick (black squares), Weissfluhjoch (black diamonds), and Zugspitze (black triangles), which are averages of five samples (active air sampling) between winter 2005/2006 and spring 2007 [Offenthaler et al., 2009a]. Air-to-glacier transfer: model results (red line); bulk deposition measured at Sonnblick (black squares), Weissfluhjoch (black diamonds), and Zugspitze (black triangles), which are averages of six samples between spring 2005 and spring 2007 [Offenthaler et al., 2009a]. (B) Yearly resolved PCB concentrations in air and air-to-glacier transfer fluxes on Lomonosovfonna glacier. Concentrations in air: model results (red line); concentrations measured at Zeppelin (passive air sampling during the summer months July, August, and September (filled blue dots), yearly averages of active air sampling (black circles) [EMEP, 2014]). Air-to-glacier transfer: model results (red line).
2.3.3 Depth Concentration Profiles

On Fiescherhorn glacier, modeled and measured [Pavlova et al., 2014a] absolute concentrations agree well for PCB 180 with average concentrations of 482 pg L$^{-1}$ (modeled) and 493 pg L$^{-1}$ (measured) over the peak period between 50 and 100 m depth (years 1945–1981) (Figure 2.3, Appendix A, Table A.4). In the same depth range, the measured concentration of PCB 28 (132 pg L$^{-1}$) is by a factor of 2 higher than the modeled concentration (65 pg L$^{-1}$), and the concentrations differ by almost a factor of 5 for PCB 101 (measured, 543 pg L$^{-1}$, modeled, 120 pg L$^{-1}$). The modeled temporal trends of the PCB congeners PCB 101 and PCB 180 are in line with the measured profiles, both peaking at a depth of 70 m, corresponding to the 1970s when emissions of these chemical were highest. However, the peak of PCB 28 at the same depth in the modeled profile is not visible in the measured profile.

On Lomonosovfonna glacier, modeled and measured [Garmash et al., 2013] absolute concentrations agree well for the lower-chlorinated congeners with average concentrations over the peak period (20–30 m depth, years 1967–1986) of 17 pg L$^{-1}$ (modeled) and 4.9 pg L$^{-1}$ (measured) for PCB 28, and 12 pg L$^{-1}$ (modeled) and 26 pg L$^{-1}$ (measured) for PCB 101. For PCB 180, the modeled concentration averaged over the same depth range is by more than a factor of 20 higher than the measured concentrations, namely 70 pg L$^{-1}$ (modeled) and 3.1 pg L$^{-1}$ (measured). For all PCB congeners, modeled and measured absolute concentrations on Lomonosovfonna glacier are lower than absolute concentrations on Fiescherhorn glacier. Modeled concentration profiles on Lomonosovfonna glacier peak at a depth of 30 m, corresponding to the 1970s. This difference in depth of the 1970 horizon on Lomonosovfonna glacier compared to Fiescherhorn glacier is a result of the lower snow accumulation on Lomonosovfonna compared to Fiescherhorn glacier.

2.3.4 Postdepositional Fate

On Fiescherhorn glacier, model results show that 14% of the total amount of PCB 28 transferred to the glacier surface is actually preserved (i.e. buried in deeper ice layers), whereas this percentage is 58% for PCB 101 and 98% for PCB 180 (Figure 2.4). In the year 1970, when the air-to-glacier transfer was highest (Figure 2.2), the incorporation flux on Fiescherhorn glacier increased to 488, 738, and 2610 pg m$^{-2}$ d$^{-1}$ for PCB 28, 101, and 180, respectively. The remainder, namely 86%, 42% and 2%, is lost to the atmosphere by revolatilization. With percentages smaller than 0.3%, degradation on the glacier surface is of minor importance. On Lomonosovfonna glacier, the stored amounts are smaller, with values of 3%, 8% and 59% for the three PCB congeners. The incorporation flux in 1970 on Lomonosovfonna glacier was 34, 20, and 163 pg m$^{-2}$ d$^{-1}$
Figure 2.3: (A) Depth concentration profiles on Fiescherhorn glacier. Yearly averaged modeled concentrations (red line); measured concentrations (gray bars) [Pavlova et al., 2014a]. Note that in contrast to the profiles shown by Pavlova et al. [2014a], the profiles are not equidistant in years but in depth. (B) Depth concentration profiles on Lomonosovfonna glacier. Yearly averaged modeled concentrations (red line); measured concentrations (gray bars) [Garmash et al., 2013]. Note the two concentration axes for PCB 180 in part B. Depth concentration profiles of PCB 52, PCB 138, and PCB 153 are shown in Appendix A (Figure A.9).

for PCB 28, 101, and 180, respectively. Revolatilization is more important, reaching 97% for PCB 28, 90% for PCB 101, and 34% for PCB 180. Degradation on the glacier surface accounts for a loss of <1% to 7% of the transferred amount.
Figure 2.4: Fate of PCB 28, PCB 101, and PCB 180 after transfer to the glacier surface of the Fiescherhorn glacier (A) and the Lomonosovfonna glacier (B): loss by photochemical degradation, revolatilization to air, and storage in glacier ice. All values are in percent of the total air-to-glacier transfer.

2.4 Discussion

2.4.1 Concentrations in Air

For all PCB congeners, modeled concentrations in air above Fiescherhorn glacier are at the lower end of the measured concentrations (Figure 2.2). The high values measured at Weissfluhjoch, Zugspitze, and Jungfraujoch might be caused by a stronger influence of the planetary boundary layer, due to the lower altitude of Weissfluhjoch (2660 m a.s.l.) and Zugspitze (2650 m a.s.l.) compared to that of the Fiescherhorn glacier (3900 m a.s.l.), and due to seasonal influence at Jungfraujoch (3450 m a.s.l.), as these concentrations were measured in July–September. In contrast, the concentrations measured at Sonnblick (3100 m a.s.l.), where air was sampled over the entire year, are in the same range as the modeled concentrations. Low modeled concentrations might be caused by an underestimation of the exposure of the drilling site to the planetary boundary layer, as the mixture of 80% tropospheric air and 20% planetary boundary layer air we use in the model during the summer season is uncertain (see above). In BETR Research, the PCB concentration in the planetary boundary layer in this region is higher than the PCB concentration in the free troposphere by a factor of 3.0, 3.2, and 2.5, for PCB 28, PCB 101, and PCB 180, respectively.

Measured PCB concentrations in air above Lomonosovfonna glacier are not available. Instead, we compare modeled results to measured concentrations at Zeppelin station (474 m a.s.l.). For all PCB congeners, modeled concentrations correspond to the mea-
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sured concentrations, with the exception of concentrations measured in the early 1990s.

2.4.2 Air-to-Glacier Transfer

The modeled air-to-glacier transfer of PCB 28 (369 pg m\(^{-2}\) d\(^{-1}\)) for Fiescherhorn is higher than the measured deposition (144–175 pg m\(^{-2}\) d\(^{-1}\)). Dry gaseous deposition is the main air-to-glacier transfer pathway for PCB 28 (see below). However, it is unclear how well dry gaseous deposition is captured by deposition samplers, because of the substantially different properties of the samplers compared to the glacier surface. If we compare the sum of the modeled wet particle, wet gaseous and dry particle deposition (104 pg m\(^{-2}\) d\(^{-1}\)) to measured bulk deposition, model and measurements are similar. The modeled air-to-glacier transfer of PCB 101 (210 pg m\(^{-2}\) d\(^{-1}\)) for Fiescherhorn is lower than the measured deposition (258–572 pg m\(^{-2}\) d\(^{-1}\)). It is unclear which transfer pathway is responsible for this underestimation, as PCB 101 is not specifically transferred by one pathway but rather by a mixture of wet particle, wet gaseous, and dry gaseous deposition (see below). The good agreement of modeled deposition on Fiescherhorn with measured deposition for PCB 180 shows that the input of PCB 180 onto the glacier surface is well described by the model. For Lomonosovfonna, unfortunately, no PCB deposition data are available for comparison.

For PCB 28, dry gaseous deposition is the main air-to-glacier transfer pathway on both glaciers (Appendix A, Figure A.4) similar to what has been shown for temperate regions by Stocker et al. [2007], who described the effect of snow and ice on the chemical fate in a global multimedia box model. Also Daly and Wania [2004] and Lei and Wania [2004], who investigated the behavior of organic chemicals during deposition to a snowpack and release by melt, came to the same conclusion. Dry gaseous deposition is also important for PCB 101 dominating the air-to-glacier transfer on Lomonosovfonna glacier. However, on Fiescherhorn glacier the most important deposition pathway of PCB 101 is wet particle deposition, accounting for 43% of total deposition. The main air-to-glacier pathway of PCB 180 is wet particle deposition, accounting for 86% of the total transfer on Fiescherhorn glacier and 36% on Lomonosovfonna glacier, while wet gaseous deposition of PCB 180 accounts for 10% on Fiescherhorn and 35% on Lomonosovfonna glacier. Whereas Stocker et al. [2007] reported wet gaseous deposition to be the main air-to-glacier transfer pathway for PCB 180 in polar and temperate regions, Daly and Wania [2004] showed wet gaseous and wet particle deposition to be equally important for PCB 180. Lei and Wania [2004] concluded that precipitation scavenging (wet particle and gaseous deposition) is increasingly important at low temperatures, especially for heavy PCBs, and that the dominant deposition mechanism depends strongly on the specific surface area of snow, the aerosol particle concentration, the deposition velocity, the precipitation rate, the scavenging factor, and the air
temperature. Generally, our results agree with findings of these studies.

2.4.3 Depth Concentration Profiles

On Fiescherhorn glacier, modeled and measured concentrations agree well for PCB 180, while the modeled concentrations of PCB 28 and PCB 101 are lower than the measured concentrations. However, modeled and measured concentrations of all PCB congeners are in the same order of magnitude, and given that the model is completely independent from the measurements, this is a good agreement. The low modeled concentration of PCB 101 in the glacier can partly be explained by the underestimated air-to-glacier transfer of this congener (see above). The remaining difference between modeled and measured concentrations might be explained by overestimated revolatilization of PCB 101 in the model. The same reason might also be responsible for the low modeled concentration of PCB 28 in the glacier. This overestimation could be caused by melt processes that are not included in the model. Melting ice can lead to the formation of ice layers, trapping volatile chemicals in deeper layers and thereby preventing their revolatilization to the atmosphere [Pavlova et al., 2014a].

On Lomonosovfonna glacier, the model is able to reproduce the measured absolute concentrations of PCB 28 and PCB 101. In contrast, the modeled concentration of PCB 180 is by more than a factor of 20 higher than the measured concentration. Possible explanations were investigated and showed that there is no single process that could account for the difference. Excluding wet deposition decreases the PCB 180 concentration in the glacier only by a factor of 3. Increasing the air mass transfer coefficient of diffusion by a factor of 10 decreases the PCB 180 concentration only by a factor of 2. In addition, the possibility of an unconsidered process in the model cannot be ruled out. The particle-bound fraction of chemicals might be lost from the glacier with particles washed out by meltwater runoff, an effect that might be critical for PCB 180 due to the strong sorption to particles. Studies showed that particles seem to be prevented from washout by the filtering characteristics of snow [Meyer et al., 2006; Meyer and Wania, 2008]; however, information is missing about particle washout from firn. The transformation of water from the solid to the liquid state during melt periods increases partitioning to the air phase within the glacier compartment, thereby increasing revolatilization. This effect is more important for PCB 180, because the difference between the ice–pore air and the liquid water–pore air partition coefficients is higher for PCB 180 than for PCB 28 or PCB 101.

Modeled concentration profiles in the Fiescherhorn glacier are similar for all PCB congeners with peaking concentrations agreeing with peaking emissions. These profiles correspond closely to the measured profiles, also peaking at around 70 m depth (year 1970). However, the measured profile of PCB 28 does not show a clear trend. Again,
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This divergence might be caused by the influence of ice layers formed during seasonal melt (see above). Because of its volatility, PCB 28 is the most susceptible to changes in porosity of the ice and pore connections. As discussed in the accompanying article melt processes can play an important role [Pavlova et al., 2014a]. For instance in the years 1990–92, melt was particularly important, which could explain the increased concentration of PCB 28 at about 30 m depth, due to relocation of PCB 28 from above or trapping of the volatile chemical by ice layers (see above). It is obvious that we do not see this effect in the model because the formation of ice layers is not considered.

Modeled concentration profiles in the Lomonosovfonna ice core show peaking concentrations in approximately 30 m depth (year 1967). In contrast, measured concentrations do not increase with depth. On the contrary, measurements showed highest concentrations of PCB 28 and PCB 101 close to the surface. This is unexpected, as PCB emissions have decreased in recent years [Breivik et al., 2007]. On the one hand, Garmash et al. [2013] mention that on Lomonosovfonna glacier PCB deposition does not only depend on emissions, but also on transport from sources to the Arctic. The authors discuss five-day backward air mass trajectories and relate high PCB deposition fluxes to high frequencies of long trajectories extending south of the Arctic Circle. On the other hand, similar to what we discussed for PCB 28 in the Fiescherhorn glacier, the formation of ice layers could be responsible for disturbed concentration profiles especially for volatile congeners. As seen in the melt index, seasonal melt processes are more important in Lomonosovfonna than in Fiescherhorn glacier.

Similar concentrations in air above Fiescherhorn and Lomonosovfonna glaciers lead to higher concentrations in the Fiescherhorn than in the Lomonosovfonna glacier. Besides higher revolatilization on Lomonosovfonna glacier (see below), this difference is caused by the higher air-to-glacier transfer on Fiescherhorn glacier due to a higher aerosol particle concentration and a higher precipitation rate (linked to ice accumulation) than on Lomonosovfonna glacier. This indicates that the transferred amount of PCBs increases more strongly with precipitation than the dilution due to a larger glacier compartment.

2.4.4 Postdepositional Fate

Whereas for PCB 101 and PCB 180, the main part of the deposited amount is stored in the glacier ice, an important part of PCB 28 diffuses back to the atmosphere. Modeled revolatilization is more important on Lomonosovfonna than on Fiescherhorn glacier, a difference which can be explained by two facts: First, the lower snow accumulation on Lomonosovfonna (0.6 m weq yr\(^{-1}\) compared to 1.7 m weq yr\(^{-1}\) on Fiescherhorn in the past decade) leads to the formation of a thinner glacier compartment on the surface of Lomonosovfonna. As a consequence, the distance for a chemical to reach the surface by diffusion is shorter. Second, the density on the surface of Lomonosovfonna glacier
is lower than on Fiescherhorn glacier (Appendix A, Figure A.2). Consequently, revolatilization is more important due to a higher pore air fraction and higher porosity in the surface compartment, thereby increasing the effective diffusivity in the porous medium. As the model slightly underestimates absolute concentrations of PCB 28 and PCB 101 in Fiescherhorn glacier and overestimates PCB 180 in Lomonosovfonna glacier, the percentage of PCB 28 and PCB 101 stored in Fiescherhorn glacier might be underestimated, while the percentage of PCB 180 stored in Lomonosovfonna glacier might be overestimated. Photochemical degradation is generally of minor importance due to the short residence of a compartment at the surface before being covered by fresh snow. However, the degradation rate constant used in the model is uncertain, as it was estimated from PCB 153 in a laboratory study [Matykiewiczová et al., 2007], but used for all PCB congeners in this model. Additionally, while this degradation rate constant only accounts for photoreductive dechlorination, other degradation pathways are unknown.

### 2.4.5 Congener Profiles

Most processes affecting the fate of PCBs in the environment are congener specific, therefore, the resulting congener profiles are altered accordingly. Averaged over the years 1958–2002, which is the overlapping runtime of the Fiescherhorn and the Lomonosovfonna model versions, the congener profiles of the modeled air concentrations are similar for both glaciers, with profiles for PCB 28:PCB 101:PCB 180 of 12:3:1 for Fiescherhorn and 14:3:1 for Lomonosovfonna (Appendix A, Figure A.5). During the air-to-glacier transfer, the congener profile is shifted towards the higher-chlorinated congeners, because air-to-glacier transfer is stronger for the congeners with a higher octanol–air partition coefficient (Figure 2.2). The ratios of the modeled air-to-glacier fluxes are 2:1:3 for Fiescherhorn glacier and 4:1:2 for Lomonosovfonna glacier. The weaker shift on Lomonosovfonna can be explained by the importance of dry gaseous deposition on the Arctic glacier, which accounts for stronger air-to-glacier transfer of the more volatile PCB congeners. The modeled congener profile within the glacier is further shifted towards the higher-chlorinated congeners, with ratios of 1:2:9 for Fiescherhorn and 1:1:7 for Lomonosovfonna glacier. After deposition, the lower-chlorinated congeners are more likely to revolatilize back to the atmosphere due to their lower sorption to ice and particles, thereby shifting the congener profile towards the heavier congeners. However, the modeled concentration of PCB 180 in the glacier might be overestimated in the Lomonosovfonna glacier, therefore, the reported congener shift toward the higher-chlorinated congeners might be overestimated.
2.4 Discussion

2.4.6 Sensitivity and Uncertainty Analysis

The sensitivity analysis reveals which parameters have a strong influence on the modeled PCB concentration in the glacier compartments (Appendix A, Figure A.6). Parameters increasing particle deposition (e.g. snow scavenging factor), wet gaseous deposition (e.g. snow surface area of snowflake), or sorption to the ice surface (e.g. hexadecane–air partition coefficient) have a positive effect on the PCB concentrations in the glacier. On the other hand, parameters increasing diffusion (e.g. mass transfer coefficient air–firn) have a negative effect on the PCB concentrations, as the effect on revolatilization is higher than the effect on dry gaseous deposition. The most influential parameter is the energy of phase change octanol–air, influencing the aerosol particle–air (in atmosphere) and particle–pore air (in glacier) partition coefficients via the temperature dependence of the octanol–air partition coefficient. Air and glacier ice temperatures have a positive sensitivity, as an increase in the temperature parameter, which is negative in our model, leads to a decrease in temperature, enhancing sorption to aerosol particles, particles in the glacier compartment, and ice. Last but not least, the PCB concentration in the inflowing air has a high sensitivity, as it directly influences the amount of chemical entering the system.

The combination of sensitivity and uncertainty analysis reveals the parameters that have a high contribution to variance of the output (PCB concentration in glacier compartments) (Appendix A, Figure A.7). Such parameters with a strong influence on the model results and, at the same time, high uncertainty are recommended to be investigated in further studies, for example, by measurements, as they are most relevant for the model output. In our model, the variance of the output is dominated by the PCB concentration in the inflowing air, contributing 45–66% of the variance. While the octanol–air partition coefficient (used to describe sorption to organic material [Harner and Bidleman, 1998]) contributes up to 28% of the variance on Fiescherhorn glacier, the hexadecane–air partition coefficient (used to describe sorption to ice [Roth et al., 2004]) is more important on Lomonosovfonna glacier (contribution up to 40%). This difference originates from the lower aerosol particle concentration on Lomonosovfonna glacier, increasing the relative importance of ice–pore air partitioning. Furthermore, the snow scavenging ratio is important for the higher chlorinated congeners (contribution up to 30%). In total, with a 95% probability, concentrations of PCBs modeled in the ice lie within two orders of magnitude (Appendix A, Figure A.8).

This study provides relevant information about the fate and dynamics of individual PCB congeners in two glacial systems. It was shown that the interaction of air-to-glacier transfer processes, revolatilization, and sorption to surfaces leads to a high storage rate of PCB 180, while only a minor part of PCB 28 actually remains in the glacier ice after deposition. The incorporated amounts of PCBs are higher on the Alpine
glacier than on the Arctic glacier. For future studies we recommend investigating the effects of seasonal melt processes on the fate of POPs in glacial systems. Also the quantification of POPs released from glaciers and the resulting importance of glaciers as a secondary source of hazardous chemicals to remote aquatic ecosystems deserves further attention.

Supporting Information

Further information on model setup, parameters and processes, as well as results of the uncertainty analysis and concentration profiles of PCB 52, PCB 138, and PCB 153 is available in Appendix A.

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Chapter 3

Polychlorinated Biphenyls in a Temperate Alpine Glacier. Model Results of Chemical Fate Processes

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Abstract

We present results from a chemical fate model quantifying incorporation of polychlorinated biphenyls (PCBs) into the Silvretta glacier, a temperate Alpine glacier located in Switzerland. Temperate glaciers, in contrast to cold glaciers, are glaciers where melt processes are prevalent. Incorporation of PCBs into cold glaciers has been quantified in previous studies. However, the fate of PCBs in temperate glaciers has never been investigated. In the model, we include melt processes, inducing elution of water-soluble substances and, conversely, enrichment of particles and particle-bound chemicals. The model is validated by comparing modeled and measured PCB concentrations in an ice core, collected in the Silvretta accumulation area. We quantify PCB incorporation between 1900 and 2010, and discuss the fate of six PCB congeners. PCB concentrations in the ice core peak in the period of high PCB emissions, as well as in years with strong melt. While for lower-chlorinated PCB congeners revolatilization is important, for higher-chlorinated congeners, the main processes are storage in glacier ice and removal by particle runoff. This study gives insight into PCB fate and dynamics, and reveals the effect of snow accumulation and melt processes on the fate of semivolatile organic chemicals in a temperate Alpine glacier.

3.1 Introduction

In the previous study in Chapter 2, we investigated deposition and incorporation of PCBs in the accumulation area of the Fiescherhorn glacier using a multimedia chemical fate model. Fiescherhorn is a cold glacier, that is, a glacier with ice temperature below 0°C. The model was validated against PCB concentrations measured in an ice core drilled at an elevation of 3900 m above sea level (a.s.l.) [Pavlova et al., 2014a]. It successfully predicted the concentration profiles of PCBs in the cold glacier, however, the majority of Alpine glaciers are temperate, that is, with an ice temperature at the pressure melting point. In temperate glaciers, seasonal melt on the glacier surface occurs regularly, and meltwater percolates through the firn, removing water-soluble trace chemicals and potentially also particles. Percolating meltwater can also refreeze deeper in the glacier, leading to the formation of ice layers with increased density. Until today, the role and relevance of meltwater on the fate of semivolatile chemicals in temperate glaciers has not been investigated [Hodson, 2014]. Chemicals such as PCBs deposited to the glacier surface might be stored in the glacier, revolatilize to the atmosphere, be relocated within the glacier by percolating meltwater, or leave the glacier with meltwater runoff. As a result, the combination of these processes governs the incorporation of PCBs into the glacial reservoir.
These postdepositional processes have been described in seasonal snow using multimedia chemical fate models [Wania, 1997; Wania et al., 1999b; Albert and Shultz, 2002; Albert et al., 2002; Herbert et al., 2005, 2006a; Meyer et al., 2006, 2009a,b]. In these studies, the snowpack was treated as a porous system consisting of pore air, liquid water, organic material, and solid ice. The authors concluded that the specific surface area of the snow and the sorption of POPs to the ice surface are the main parameters describing the fate of semivolatile chemicals in the snowpack. For glaciers, a multimedia chemical fate model was used to describe the deposition of POPs to the glacier surface [Bogdal et al., 2010]. However, no postdepositional processes were included in this model, and chemicals were assumed to be instantaneously incorporated into the glacier ice.

Here, we investigate the incorporation of PCBs into the Silvretta glacier, a temperate glacier in the Swiss Alps. We introduce a multimedia chemical fate model that calculates PCB incorporation into the ice. In contrast to the model describing PCB incorporation into a cold glacier (Chapter 2), we include additional processes, such as meltwater percolation, refreezing, and runoff, as well as particle relocation. To parametrize the model, we use density and black carbon profiles determined in an ice core from the accumulation area of the Silvretta glacier in a parallel study [Pavlova et al., 2015a]. It is important to note that the model is completely independent of the PCB concentration measured in the ice core. Concentrations of PCBs and black carbon as well as density measured in the Silvretta ice core are presented in an accompanying publication [Pavlova et al., 2015a].

We focus on PCBs as representative persistent hydrophobic and semivolatile organic chemicals, because chemical properties and historical emissions are available, and the chemicals are not in use anymore today. The model is run for the six indicator PCB congeners (iPCBs) 28, 52, 101, 138, 153, and 180, as they belong to the congeners with the most important historical production [Breivik et al., 2002a]. In addition, they cover a wide range of properties, from lower-chlorinated congeners (e.g. PCB 28) with higher mobility, to higher-chlorinated congeners (e.g. PCB 180) with strong sorption to surfaces. The unique combination of a glaciological model providing glacier mass balance data, ice core data enabling an independent model validation, together with chemical fate modeling provides an opportunity to describe the fate of hydrophobic chemicals in a complex system such as a temperate Alpine glacier.
3.2 Methods

3.2.1 Study Site

Silvretta glacier is located in the Alps in Eastern Switzerland (46.85° N, 10.08° E) and extends over an elevation range of 2500–3000 m a.s.l., with an approximate area of 3 km². Silvretta glacier is a temperate glacier with an ice temperature around 0°C. The glacier is part of the Swiss Glacier Monitoring Network, with a long record of mass balance measurements, reaching back to 1915 [Huss et al., 2008a; Huss and Bauder, 2009; VAW, 2014]. A considerable ice mass loss since 1900, especially in the 1950s and since the 1990s has been documented. An ice core from an elevation of 2950 m a.s.l. was drilled in April 2011 and analyzed for various parameters [Pavlova et al., 2015a].

3.2.2 Model Setup

The model is a dynamic multimedia chemical fate model, where the environment is divided into compartments, and losses and transfers of chemicals from and between the compartments are described by first-order differential equations. A chemical mass balance equation for each compartment is solved numerically. The model includes an air compartment and a set of glacier compartments, and describes the vertical transport of chemicals in the glacier (Figure 3.1). The winter version of the model is based on the model described in Chapter 2. The summer version includes additional processes. The model is run from 1900 to 2010 with a monthly resolution.

3.2.3 Environmental System

3.2.3.1 Input Parameters

Measured monthly air temperatures from Weissfluhjoch (1959–2010, 2700 m a.s.l., 20 km from Silvretta glacier) and Säntis (1900–1958, 2500 m a.s.l., 80 km from Silvretta glacier) are corrected for elevation differences using adiabatic lapse rates (Appendix B, Figure B.2) [MeteoSwiss, 2014b]. The air temperature determines winter (air temperature below 0°C) and summer (air temperature above 0°C) seasons, with the end of the summer season being around September and the end of the winter season being around April.

Measured monthly precipitation values from Weissfluhjoch (1959–2010) and Davos (1900–1958, 1600 m a.s.l., 20 km from Silvretta glacier) are normalized to the average annual precipitation measured on the Silvretta glacier forefield (2500 m a.s.l., measurements available for 1959–2010) [MeteoSwiss, 2014b]. In the model, precipitation
Figure 3.1: Model setup including the air compartment and the glacier compartments. The air compartment consists of air and aerosol particles, the glacier compartments of ice, pore air, and particles (winter and summer), and liquid water (only summer). Some processes occur only during winter (snowfall, blue font), only during summer (rainfall, meltwater and particle processes, red font), or perennially (black font).
occurs as snow during winter (70% of the total precipitation) and as rain during summer (30% of the total precipitation). We assume rain runs off directly without interacting with the glacier. As the purpose of the model is to assess chemical fate, hydrological processes occurring in the firn are simplified in this model, for instance by not considering accelerated melting by rain penetrating into the glacier surface [Cuffey and Paterson, 2010]. However, the amount of new snow on the glacier surface and meltwater lost from the glacier column is defined by the glacier mass balance, and the amount of meltwater refreezing in the glacier column is defined by the density profile measured in the ice core. Therefore, a more detailed description of rain penetration into the glacier surface would not lead to differences in the model. For conservation of mass, in winter, we set modeled precipitation equal to the snow accumulation. This leads to a total precipitation at the ice core drilling site of 19% higher than the precipitation measured on the glacier forefield, which is in agreement with increasing precipitation with elevation [MeteoSwiss, 2014b].

Annual snow accumulation (in meters of water equivalent per year, m weq yr\(^{-1}\)) was taken from a mass balance model of Silvretta glacier [Huss et al., 2008a; Huss and Bauder, 2009]. The mass balance model was calibrated with ice volume changes from high-resolution digital elevation models, extensive point-based mass balance measurements, and discharge records, using air temperature and precipitation data. Two data sets for snow accumulation are available (Appendix B, Figure B.4): the annual snow accumulation, describing the amount of snow remaining on the glacier surface at the end of the summer season, and the winter snow accumulation, indicating the amount of snow accumulated on the glacier surface at the end of the winter season. The snow accumulated in the remaining months is approximated by linear interpolation. We use the monthly accumulated snow as an input to the model, with positive values during winter (snow accumulation) and negative values during summer (snowmelt).

As aerosol particle data for the beginning of the 20th century are missing, we use particulate matter (PM10) as representative for aerosol particles. Measured monthly concentrations of PM10 from Jungfraujoch (3600 m a.s.l., 130 km from Silvretta glacier) are available between 1973 and 2010 [NABEL, 2014], and were extrapolated to previous decades relative to estimated black carbon emissions [Bond et al., 2007]. The relation of particulate matter to black carbon emissions is based on the assumption that combustion is a suitable indicator of total aerosol particle emissions.

Measured monthly wind speed from Weissfluhjoch is available for 1959–2010 [MeteoSwiss, 2014b]. For 1900–1958, monthly averaged values from the period 1959–2010 are used. Other environmental parameters are provided in Appendix B (Subsection B.4.1).
3.2.3.2 Compartment Setup

Monthly snow accumulation or melt determines the setup of the glacier compartments, consisting of four phases: solid ice, particles, pore air, and liquid water (Figure 3.1). In winter, a new compartment is formed on the glacier surface every month, analogous to the modeling framework presented in Chapter 2. The mass of this compartment corresponds to the monthly snow accumulation. The particle fraction is a function of the wet and dry aerosol particle deposition during the specific month. The pore air fraction depends on the compartment density. In summer, when snow melts, liquid water is present in the glacier column. As a result of the monthly snowmelt, the surface compartments decrease in size and are eliminated. Depending on the extent of the snowmelt and the mass of the compartments, part of a compartment up to several compartments can melt each month. At the ice core site, the modeled total number of compartments increased continuously from 1900 to 2000, reaching a maximum number of 444 compartments (Appendix B, Figure B.6). This compartment number is specific to the ice core site as it is calculated from local input data, such as the air temperature and the time-resolved glacier mass balance. The air temperature defines the number of compartments formed (one per winter month), while the glacier mass balance determines the mass of these compartments. A detailed description of the compartment setup is provided in Appendix B (Subsection B.4.2).

The density of the glacier compartments increases as a function of depth, when the compartment is buried, based on the saturation function presented in Chapter 2 (Appendix B, Subsection B.4.1). The density of specific layers can further increase by local refreezing of percolating meltwater [Cuffey and Paterson, 2010]. In addition, during summer, the density of the compartment located on the glacier surface increases due to high solar irradiation, leading to snow aging. The volume of all glacier compartments is then derived from the mass and the density of the compartments.

3.2.3.3 Meltwater and Particle Flow

In the model, the meltwater from the glacier surface percolates down through the glacier column before it leaves the glacier. While the amount of meltwater running off is defined by the monthly snowmelt, the apportionment of the runoff to the glacier compartments is a function of compartment depth, with more meltwater running off from compartments closer to the glacier surface (Appendix B, Subsection B.4.3). Besides meltwater runoff, additional snow on the glacier surface melts and percolates down to refreeze in lower compartments. The amount of refreezing meltwater is proportional to the monthly snowmelt, leading to stronger refreezing in months with high melt. The distribution of the refreezing meltwater to the glacier compartments is a function of compartment depth and density, with more refreezing in compartments having a high
density and a low depth. Upon refreezing, the meltwater mass is added to the compartment, and while the volume of the compartment remains constant, the compartment density increases. Functions and parameters of meltwater processes are selected in such a way that modeled and measured [Pavlova et al., 2015a] density profiles in the ice core are similar (Appendix B, Figure B.8).

Meltwater percolating through the glacier column elutes a certain fraction of particles contained in the glacier compartments. This fraction can leave the glacier column with meltwater runoff, or can be trapped in compartments further down. The relocated fraction is a function of compartment density and depth, decreasing with increasing density and depth. It is important to note that meltwater and particle flows occur only in summer and that there is no melt in winter. Again, functions and parameters of particle processes are defined so that modeled and measured [Pavlova et al., 2015a] particle profiles in the ice core are similar (Appendix B, Figure B.10).

### 3.2.4 Input of Chemicals into the system

The global distribution of PCBs (monthly resolution, 1930–2010) was calculated using the maximum emission inventory of Breivik et al. [2007] and the BETR Research model [Macleod et al., 2011]. BETR Research is a global multimedia chemical fate model consisting of 288 connected regions. Each region is composed of seven environmental compartments, including two air compartments, that represent the planetary boundary layer and the free troposphere. In winter, Silvretta glacier is exposed to air from the free troposphere due to atmospheric stratification. This seasonal decoupling from the planetary boundary layer is well known for high-alpine areas [Baltensperger et al., 1997; Gaggeler et al., 1995; Gabbi et al., 2015]. In summer, Silvretta glacier is exposed to 80% tropospheric and 20% boundary layer air. This mixing ratio was estimated from sulfate concentrations in aerosol particles, which show a seasonal pattern at Jungfraujoch with high values during summer (contribution from polluted boundary layer air) and low values during winter (clean tropospheric air) [NABEL, 2014]. More information is provided in Appendix A (Section A.2).

Chemical property data used in the model are provided in Appendix B, Table B.2. We included temperature dependence of partition coefficients and estimate adsorption to ice using the polyparameter linear free-energy relationship presented by Roth et al. [2004].

### 3.2.5 Chemical Fate Processes

In the atmosphere, advective in- and outflow by wind, snow–air (winter), raindrop–air (summer), and aerosol particle–air partitioning, and degradation of PCBs by hydroxyl
radicals are included in the model (Figure 3.1). The concentration of hydroxyl radicals is seasonally resolved, with a higher concentration during summer and lower values during winter [Spivakovsky et al., 2000]. Wet deposition occurs by snow during winter and by rain during summer. More particles are deposited by dry particle deposition in summer than in winter. Exchange of PCBs between the atmosphere and the pore air of the glacier compartment at the surface, as well as between the top and the second glacier compartments is described by advection (wind pumping), where the mass-transfer coefficient depends on the surface roughness, wind speed, and firn permeability [Meyer and Wania, 2010]. Between the other glacier compartments, chemical exchange occurs by molecular diffusion in pore air.

Postdepositional processes such as ice–pore air and particle–pore air partitioning, and photochemical degradation of PCBs at the glacier surface are described as in Chapter 2. Photochemical degradation is higher during summer and low during winter, according to the seasonal variation in radiation at Weissfluhjoch [MeteoSwiss, 2014a]. When chemicals are associated with meltwater or particles, they are transported downward in the glacier column by meltwater percolation and particle relocation, and can be lost from the glacier column by meltwater and particle runoff. Details of the model parametrization are provided in Appendix B (Sections B.6 and B.7).

### 3.2.6 Model Application

To understand spatial differences of the fate of PCBs at the glacier surface, we applied the model to two additional sites. These sites are both located in the accumulation area, but closer to the equilibrium line than the ice core site. Site A is located 250 m down the glacier from the ice core drilling site (at a 40 m lower elevation), and site B is located 500 m down the glacier (80 m lower) (Appendix B, Figure B.1). The air temperature was corrected for elevation differences. Snow accumulation is taken from the mass balance model of Silvretta glacier, which is spatially resolved on a 25 x 25 m grid [Huss et al., 2008a; Huss and Bauder, 2009]. As described above, the specific snow accumulation for every site leads to a specific compartment setup and properties in the model. The maximum number of glacier compartments formed in the model is 395 and 272 for sites A and B, respectively. This difference is caused by lower snow accumulation and more snowmelt further down the glacier compared to the ice core site (Appendix B, Figures B.4 and B.6). Density and particle depth profiles of sites A and B are shown in Appendix B (Figures B.9 and B.11).
3.2.7 Sensitivity and Uncertainty Analysis

A parameter sensitivity and uncertainty analysis was performed to identify the most influential parameters, the variance of the output, and the contribution of the parameters to variance of the output. For this analysis, the value of each parameter was increased independently by 5%, and the effect on the amount of chemicals stored in the glacier column in December 2010 was calculated. The main assumptions of this method are linear relationships between input and output parameters, as well as independence and log-normal distributions of input variables [MacLeod et al., 2002]. We included 56 parameters in the sensitivity analysis, three PCB congeners (28, 101, and 180), and the three sites (ice core site, site A, and site B). A list of the 56 parameters as well as their confidence factors is provided in Appendix B (Section B.8).

3.3 Results

3.3.1 Concentration Profiles in the Ice Core

The modeled and measured [Pavlova et al., 2015a] concentration depth profiles of all PCB congeners peak at a depth of 20–40 m (Figure 3.2). In addition to this main peak, modeled and measured concentrations of the higher-chlorinated congeners (PCB 138, 153, and 180) show local maxima at various depths (5–10 and 50–60 m). For the lower-chlorinated congeners (PCB 28, 52, and 101), local maxima exist in the measured concentrations, but not in the modeled profiles. The average modeled concentrations of PCB 138, 153, and 180 between 0 and 60 m depth are 153, 233, and 167 pg L$^{-1}$, respectively. Over the same depth range, the average measured concentrations of these congeners are similar, namely 329, 278, and 184 pg L$^{-1}$. For the lower-chlorinated congeners, the average modeled concentrations of PCB 28, 52, and 101 are 26.7, 22.9, and 43.8 pg L$^{-1}$, which is lower than the average measured concentrations of 90.9, 181, and 208 pg L$^{-1}$, respectively.

3.3.2 Fate of PCBs at the Ice Core Site

Air-to-glacier transfer of PCBs, consisting of wet particle, wet gaseous, dry particle, and dry gaseous deposition, increases between 1940 and 1970 (Figure 3.3, Appendix B, Figures B.17–B.20), following the estimated global emissions [Breivik et al., 2007]. During the peak years (1960–1980), air-to-glacier transfer reaches 1–2 ng m$^{-2}$ d$^{-1}$ for the individual PCB congeners, but interannual variability is high. Dry gaseous deposition is the main air-to-glacier transfer pathway for lower-chlorinated congeners such as PCB 28, whereas wet particle deposition is the most important transfer flux for higher-
chlorinated congeners such as PCB 180. For PCB 101, dry gaseous, wet particle, and wet gaseous deposition are equally important.

Loss processes follow the temporal trend of the input processes for the lower-chlorinated congeners, but they are temporally delayed for the higher-chlorinated congeners. Revolatilization is the most important loss process for the lower-chlorinated congeners, accounting for the loss of 86% of PCB 28, and 77% of PCB 52. With increasing chlorination, loss by particle runoff is more important (33% and 31% for the two hexachlorinated PCB congeners 138 and 153, and 36% for the heptachlorinated PCB congener 180). Meltwater runoff as well as photochemical degradation are of minor importance for all PCB congeners.

The net accumulation of PCBs (deposition minus loss) is positive until the 1990s and negative thereafter (Appendix B, Figure B.21). Between 1970 and 1979, the modeled average net accumulation of PCB 28, 101, and 180 is 0.18, 0.23, and 0.76 ng m$^{-2}$ d$^{-1}$, respectively. Except for PCB 101, these values are close to the net accumulation of 0.35, 0.81, and 0.57 ng m$^{-2}$ d$^{-1}$ determined by the ice core inventory in Pavlova et al.
Figure 3.3: Fate of PCB 28, 101, and 180 at the ice core site of the Silvretta glacier between 1930 and 2010. Air-to-glacier transfer by dry gaseous, dry particle, wet particle, and wet gaseous deposition (left side, left axis), and loss by particle runoff, meltwater runoff, photochemical degradation, and revolatilization (right side, left axis). The black line indicates the cumulative storage in the glacier column (right side, right axis). Results for PCB 52, 138, and 153, as well as seasonal fluxes of PCB 28, 101, and 180 are provided in Appendix B, Figures B.18–B.20.

[2015a] for the same congeners in the same time period. As a consequence of the net accumulation, the total storage of chemicals increases until the 1990s, when loss processes become more important than input processes and the stored amounts of all PCB congeners start to decrease. In 2010, only a minor part of the lower-chlorinated congeners deposited to the glacier surface between 1930 and 2010 is stored in the glacier (7.0% of PCB 28, and 12% of PCB 52), while storage is more important for the higher-chlorinated congeners (52–59% for PCB 138, 153, and 180). The total quantity of PCB 28, 52, 101, 138, 153, and 180 stored at the Silvretta ice core site in 2010 is 33 µg m$^{-2}$, of which the higher-chlorinated congeners PCB 138, 153, and 180 account for 86%.
3.3 Results

3.3.3 Model Application

The concentration depth profiles of iPCB (summed up from Figure 3.2) and the postdepositional fate (averaged over time from Figure 3.3) at the ice core site are shown in Figure 3.4. In contrast to the ice core site, at site A (250 m downward from the ice core site), modeled concentration depth profiles of the sum of the PCB congeners 28, 52, 101, 138, 153, and 180 (iPCB) are highest in the top 5 m, as well as at a depth of 20 m (Figure 3.4 A). At site A, the layers in 20 m depth were formed in the late 1970s (Appendix B, Figure B.7). At site B (500 m downward from the ice core site), the modeled concentration is highest at the glacier surface.

Similar to the ice core site, revolatilization is the most important postdepositional process for the lower-chlorinated congeners at sites A and B (Figure 3.4 B). Storage in glacier ice is even less important at sites A and B. The main postdepositional processes affecting higher-chlorinated congeners are particle runoff and storage in glacier ice. In contrast to the ice core site, storage in glacier ice is smaller at sites A and B, while

Figure 3.4: A) Modeled (red line) and measured [Pavlova et al., 2015a] (gray bars) concentration depth profiles of iPCB at the ice core site, site A, and site B. Model results are averaged over the sample depth. B) Postdepositional fate of PCB 28, 52, 101, 138, 153, and 180 at the ice core site, site A, and site B. The values are in percent of the air-to-glacier transfer and indicate the total fate of the chemicals deposited between 1930 and 2010.
more chemical is lost by particle runoff.

### 3.3.4 Sensitivity and Uncertainty Analysis

Of the 56 tested parameters, 13 parameters have a strong influence (sensitivity over 0.5) on the total amount of PCBs stored in the glacier in 2010 (Appendix B, Figure B.12). This means that an increase in the input parameter by 5% leads to an increase (positive sensitivity) or decrease (negative sensitivity) of more than 2.5%. At all sites (ice core site, site A, and site B), the two most influential parameters are the energy of phase change between octanol and air, and the annual snow accumulation. A high energy of phase change increases partitioning to organic matter at low temperatures, and, therefore, strengthens aerosol particle–air and particle–pore air partitioning, leading to stronger particle deposition and less revolatilization. The higher the annual snow accumulation, the higher the amounts of chemicals incorporated. This effect is stronger for PCB 180 than for PCB 28, as the latter is mainly revolatilized to the atmosphere, independently of glacier properties.

The parameter uncertainty analysis quantifies the uncertainty of the amount of chemicals stored in the glacier column in December 2010. The stored amount varies by a factor of 12, 20, and 19, for the PCB congeners 28, 101, and 180, respectively. The parameters with high contributions to variance of the output are the PCB concentration in the free troposphere, the scavenging factor of snow, and the octanol–air partition coefficient (Appendix B, Figure B.13).

### 3.4 Discussion

#### 3.4.1 Concentration Profiles in the Ice Core

The concentration peak at 20–40 m depth in the modeled and measured profiles corresponds to the years 1960–1980, a period of high PCB input [Breivik et al., 2007]. In contrast, the high modeled concentrations of the higher-chlorinated PCB congeners (PCB 138, 153, and 180) at 5–10 and 50–60 m depth were formed after 1990 and in the 1950s, respectively (Appendix B, Figure B.7). These peaks can be related to the strong melt and the low snow accumulation in the periods when these layers were formed (Appendix B, Figures B.4 and B.7). Snow melt causes loss of water-soluble species (such as ions) [Eichler et al., 2001], but it leads to an enrichment of particles and water-insoluble substances (such as PCBs). This happens because meltwater runs off from the glacier surface, and chemicals and particles that are not eluted by meltwater accumulate in the surface layer. This is also evident from the modeled and measured profiles of particles
in the glacier ice, which also show concentration peaks at 5–10 and 50–60 m depth (Appendix B, Figure B.10). The concentration peak between 5.5 and 7.8 m depth covers the years 1985–1992. In these years, 77% of the snow deposited onto the glacier surface is lost as meltwater, while only 47% of the particles are lost from the surface. In total (1900–2010), 45% of the snow and 33% of the particles are lost from the ice core.

The modeled concentrations of the lower-chlorinated congeners (PCB 28, 52, and 101) are lower than measured levels. Emissions, global distribution, transport, and air-to-glacier transfer cannot be responsible for this discrepancy, because modeled and measured [Offenthaler et al., 2009a] air concentrations and air-to-glacier transfer fluxes of the lower-chlorinated congeners agree well (Appendix B, Figures B.16–B.17). The mismatch might be due to an overestimation of loss processes in the model. The main loss process for lower-chlorinated congeners is revolatilization, whereas photochemical degradation, meltwater and particle runoff are less relevant (Figure 3.3). Revolatilization might be overestimated due to underestimated sorption to ice or particles. A comparison of snow/ice–air partition coefficients estimated using the method described by Roth et al. [2004] with measured partition coefficients reported in literature shows that for lower-chlorinated congeners, sorption to ice is probably underestimated by this method (Appendix B, Figure B.14). If the snow/ice–air partition coefficient is increased by a factor of 10, the modeled concentrations in the ice core are clearly higher (Appendix B, Figure B.24). In Silvretta glacier, sorption to particles is important, due to the high particle concentration. Particle sorption models based on octanol–air partitioning (included in our model) have been found to be appropriate for nonpolar chemicals [Götz et al., 2007]. Besides sorption to amorphous organic matter, sorption to carbonaceous particles such as black carbon (not included in our model) might be relevant for hydrophobic organic contaminants such as PCBs [Cornelissen et al., 2005]. Another possible reason for overestimated revolatilization might be the thin ice layers formed during short periods of strong melt (e.g. one week), hence sealing off the underlying layers and retaining the lower-chlorinated congeners underneath. However, as the model is monthly resolved, such small-scale snow processes cannot be accounted for in the model.

According to our model, the partitioning of PCBs between the particles and the solid ice matrix is considerably shifted toward the particles. This is in contrast to the profiles presented in our accompanying publication, where the concentration of PCBs in the experimentally derived dissolved phase is higher than in the particulate phase [Pavlova et al., 2015a]. A possible explanation for this difference could be the general assumption of chemical fate models that an instantaneous thermodynamic equilibrium is reached between the phases in a compartment. However, this equilibrium might not be reached, due to kinetic limitations, when particles are only in direct contact with parts of the solid ice matrix. To test this hypothesis, we decreased the ratio between
sorption to particles and sorption to ice by a factor of 100 in the model and compared the fate of PCB 180 to the original model version. Even with a decreased sorption to particles, particle runoff remains the most important loss process for PCB 180. The average modeled concentration of PCB 180 between 0 and 60 m depth is higher (by 23%) than in the original version but it is still in the same order of magnitude as the measured concentration. Therefore, the importance of the dissolved phase in Pavlova et al. [2015a] can only be reasoned by the explanation provided by the authors that the PCB fraction sorbed to small particles is included in the dissolved phase in their experimental setup. The fraction of PCBs sorbed to particles reported in Pavlova et al. [2015a] has, thus, to be considered as an operationally defined particulate phase, and a comparison between modeled and measured PCB concentrations needs to be based on the total bulk concentrations (sum of dissolved and particulate phase).

### 3.4.2 Fate of PCBs at the Ice Core Site

The modeled air-to-glacier transfer of all PCB congeners strongly follows global PCB emissions (Figure 3.3, Appendix B, Figure B.18). Besides this general trend, short-term variability in transfer rates occurs. For example, the transfer rate of PCB 28 shows a sudden dip in 1982, caused by a decrease in dry gaseous deposition that originates from low monthly wind speed during this period (Appendix B, Figure B.2). In contrast, as wet particle deposition is the main transfer pathway of the higher-chlorinated congeners, short-term variation of transfer rates is mainly connected to snow accumulation, with strong air-to-glacier transfer when snow accumulation is high. However, periods of high or low input fluxes do not necessarily lead to the same variability in concentrations within the glacier. Years with low input fluxes might be followed by years of strong melt, leading to high concentrations in the glacier as the snow melts and chemicals are enriched in the surface layer.

The importance of revolatilization for the lower-chlorinated congeners (PCB 28 and 52) is in line with the volatile character of these congeners, and has been observed before (Chapter 2) [Stocker et al., 2007]. Even if we decrease the modeled revolatilization to reach measured levels in the ice core, revolatilization is still the dominant process, accounting for the loss of almost 60% of PCB 28. The loss of higher-chlorinated congeners (PCB 138, 153, and 180) from the glacier by particle runoff is relevant because these congeners sorb strongly to particles. Runoff with meltwater is of minor importance, however, the higher-chlorinated congeners are affected by the indirect effect of the meltwater flow on particle elution. In summer, PCBs can be redistributed through the glacier column by meltwater and particle percolation (Appendix B, Figures B.22 and B.23). However, in the model, the effect of chemical enrichment at the glacier surface, due to the melting of overlying compartments, is more important than the
3.4 Discussion

Redistribution by meltwater and particle percolation. This can clearly be seen in the high input flux and accumulation of chemicals in the summer months compared to the smaller loss and downward fluxes (Appendix B, Figure B.23). Photochemical degradation is negligible for all PCB congeners; however, the degradation rate constant is highly uncertain, as it has so far only been measured for PCB 153 under laboratory conditions [Matykiewiczová et al., 2007].

Higher-chlorinated congeners are more likely to be incorporated into the glacier ice than lower-chlorinated congeners, a behavior that was also observed and discussed before (Chapter 2) [Stocker et al., 2007; Meyer et al., 2009a]. In a previous study, up to 98% of the deposited PCB 180 was shown to be incorporated into the cold Fiescherhorn glacier (Chapter 2). Here, the incorporated percentage of PCB 180 is 59%, a difference which can be explained by the lower snow accumulation and the occurrence of melt processes on the Silvretta glacier compared to the Fiescherhorn glacier. Storage of lower-chlorinated chemicals in a temperate glacier is of minor importance (7–12% for PCB 28 and 52, respectively, compared to 14–22% on the Fiescherhorn glacier).

3.4.3 Model Application

The use of the local snow accumulation in the incorporation model makes it possible to investigate spatial differences in compartment setup and properties (Appendix B, Figures B.4, B.6, B.7, B.9, and B.11). At sites A and B, the net mass balance is lower compared to the ice core site, and as a consequence, the particle concentration is higher (Appendix B, Figure B.11). Input and loss fluxes of the lower-chlorinated congeners at sites A and B are similar to the ice core site, with more than 87% of PCB 28 volatilizing to the atmosphere (Figure 3.4, Appendix B, Figure B.19). Input fluxes of the higher-chlorinated congeners are lower at site B than at the ice core site, while loss fluxes are more important. This difference can be explained by the lower snow accumulation at sites A and B, inducing stronger loss by particle runoff and lower storage in glacier ice. This is in line with higher air-to-glacier transfer fluxes on the cold Fiescherhorn glacier, where snow accumulation is clearly higher than on the Silvretta glacier (Chapter 2).

Storage in glacier ice occurs when snow is buried beneath new snow, conserving the chemicals contained within the snow. This occurs at all three sites when snow accumulation is positive. However, since 1980, the local mass balance has been around zero at the ice core site and site A, while it is negative at site B (Appendix B, Figure B.4). This leads to strong loss of previously incorporated chemicals at site B, visible as a decrease in the cumulative storage of chemicals (Appendix B, Figure B.19). Strong melt at sites A and B also explains the high PCB concentration in the top part of the concentration profiles of these sites, due to enrichment of chemicals in the surface layers (Figure 3.4).
The total amount of chemicals incorporated at sites A and B in 2010 is smaller than at the ice core site, with respective values of $29 \mu g \, m^{-2}$ and $20 \mu g \, m^{-2}$, compared to $33 \mu g \, m^{-2}$ ($3.3 \, ng \, cm^{-2}$) at the ice core site. At the ice core site, this amount agrees well with the total environmental burden of $5.3 \, ng \, cm^{-2}$ determined by Pavlova et al. [2015a]. In contrast, no validation is available for sites A and B, and therefore, these values are uncertain.

In this work, we have provided explanations of empirical observations reported in the accompanying article about the ice core profile from Silvretta glacier [Pavlova et al., 2015a]. This study quantifies PCB incorporation into a temperate Alpine glacier, which is only possible due to the combination of chemical fate modeling, glacier mass balance modeling, and ice core analytics. The model is able to reconstruct measured PCB concentrations in the Silvretta glacier, but some uncertainties remain and provide relevant input for future research directions. The model shows that particles have an important effect on the fate of chemicals in a temperate glacier. However, no information is available about the composition of particles in the Silvretta glacier. In addition, the effect of meltwater flow on the fate of particles is unclear, even though this process could be included in the model in an approximate way. Further, the role of thin ice layers, probably preventing revolatilization of the lower-chlorinated congeners, is still uncertain. Further research might focus on the release of chemicals to proglacial lakes and sensitive Alpine ecosystems, or on incorporation differences between glaciers.

Supporting Information

Further information on input parameters, compartment setup, processes, chemical fate modeling, as well as additional results are available in Appendix B.

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Chapter 4

A Temperate Alpine Glacier as a Reservoir of Polychlorinated Biphenyls: Model Results of Incorporation, Transport, and Release

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Abstract

In previous studies, the incorporation of polychlorinated biphenyls (PCBs) has been quantified in the accumulation areas of Alpine glaciers. Here, we introduce a model framework that quantifies mass fluxes of PCBs in glaciers and apply it to the Silvretta glacier (Switzerland). The models include PCB incorporation into the entire surface of the glacier, downhill transport with the flow of the glacier ice, and chemical fate in the glacial lake. The models are run for the years 1900–2100 and validated by comparing modeled and measured PCB concentrations in an ice core, a lake sediment core, and the glacial stream water. The incorporation and release fluxes, as well as the storage of PCBs in the glacier increase until the 1980s and decrease thereafter. After a temporary increase in the 2000s, the future PCB release and the PCB concentrations in the glacial stream are estimated to be small but persistent during the 21st century. This study quantifies all relevant PCB fluxes in and from a temperate Alpine glacier over two centuries, and concludes that Alpine glaciers are a small secondary source of PCBs, but that the aftermath of environmental pollution by persistent and toxic chemicals can endure for decades.

4.1 Introduction

In a previous study, we investigated the fate of PCBs in the accumulation area of a cold glacier (Fiescherhorn glacier, Switzerland) (Chapter 2) [Pavlova et al., 2014a]. A cold glacier consists of ice at a temperature below 0°C and seasonal melt processes are negligible in the accumulation area. We showed that the postdepositional fate of individual PCB congeners depends on their physico-chemical properties. The higher-chlorinated PCB congeners (e.g. PCB 180), characterized by stronger sorption to surfaces, were mainly incorporated into the glacier ice. In contrast, the more volatile lower-chlorinated congeners (e.g. PCB 28) were lost from the glacier by revolatilization to the atmosphere (Chapter 2). In a follow-up study, we quantified the incorporation of PCBs into the accumulation area of a temperate glacier (Silvretta glacier, Switzerland) (Chapter 3) [Pavlova et al., 2015a]. In contrast to a cold glacier, the ice of a temperate glacier is at the pressure melting point, and seasonal melt processes are important. As a consequence, processes such as meltwater percolation or elution of particles by meltwater flow influence the fate of semivolatile chemicals. We found that the incorporated amount of chemicals is smaller than on the cold glacier, and revolatilization and particle washout are the most important loss processes of PCBs.

Both previous studies compared modeled (Chapters 2 and 3) and measured [Pavlova et al., 2014a, 2015a] PCB levels in ice cores. Therefore, these studies focused on one
specific site in the accumulation area of the glacier, but they could not quantify the total amount of PCBs stored in a glacier, nor the storage duration, or the release of chemicals from a glacier. However, investigating the potential release of toxic pollutants to sensitive freshwater systems is another component of high importance.

While the previous studies focused on fate processes of chemicals in glaciers, in this study, we investigate mass fluxes. Starting with a parametrization for the Silvretta glacier, a general model framework for glaciers was developed, with the important advantage that it is applicable to any glacier, if data of locally resolved glacier mass balance, glacier flow, and meteorology are available. This model can be applied to accumulation areas (where glacier ice is formed) as well as to ablation areas (where seasonal snow accumulates and melts, and no glacier ice is formed), and operates for any glacier mass balance input data. The new model framework describes the entire system of the Silvretta glacier, including the glacier surface, glacier flow, and the proglacial lake. This study provides knowledge about the incorporation of PCBs into the glacier, storage amount and duration, and temporally resolved release of PCBs to the freshwater system over two centuries (1900–2100).

First, we quantify the incorporation of PCBs into the entire Silvretta glacier, followed by downhill transport of chemicals with the flow of the glacier ice. Then, we quantify the release of chemicals from the glacier to the glacial lake, deposition to the lake sediment, and runoff to the glacial stream. The model framework is validated by comparing modeled PCB levels to a unique set of PCB measurements in three different matrices: (i) an ice core from the accumulation area of the Silvretta glacier [Pavlova et al., 2015a], (ii) a sediment core from the glacial lake fed by glacial meltwater [Pavlova et al., 2015b], and (iii) the stream water downstream of the glacial lake [Pavlova et al., 2015b]. This field data are used as an independent model validation, which means that the model results were not fitted to the measurements. The future climate predictions of strong glacier melt are described by the A2 emission scenario of the third IPCC report [IPCC, 2001]. As representative persistent hydrophobic and semivolatile organic chemicals, we use the six indicator PCB congeners (iPCBs) 28, 52, 101, 138, 153, and 180, as they cover a wide range of physico-chemical properties. To understand the importance of Alpine glaciers as secondary sources of PCBs, we study 1) the amount of PCBs stored in the Silvretta glacier, 2) the amount and timing of the PCB release to the freshwater system, and 3) the past and future PCB concentrations in the glacial stream water.
4.2 Methods

4.2.1 Site Description and Sampling

Silvretta glacier is located in Eastern Switzerland (46.85° N, 10.08° E). It lies at an elevation of 2500–3000 m above sea level (a.s.l.) and has an area of approximately 3 km² (Appendix C, Figure C.1). Silvretta glacier is included in the Swiss Glacier Monitoring Network [VAW, 2014], and has a long record of glacier mass balance measurements, starting in 1915. A considerable mass loss since 1900 was reported, with strong melt in the 1950s and the 1990s [Huss et al., 2008b; Huss and Bauder, 2009]. An ice core was drilled from the accumulation area of Silvretta glacier (2950 m a.s.l.) in April 2011, dated, and analyzed for PCBs and black carbon [Pavlova et al., 2014b, 2015a; Pavlova, 2014]. The ice core samples cover the period 1930–2010.

The glacial lake is located 300 m downstream of the glacier terminus, at an elevation of 2440 m a.s.l. The lake has a surface area of 10,000 m², a depth of 1–2 m, and a temperature of approximately 1°C. The glacial lake was formed around 1950 due to the retreat of the glacier [Pavlova et al., 2015b]. The lake is solely fed with glacial meltwater from the Silvretta glacier. Between the glacier and the lake, the meltwater flows at a very fast flow over a rocky area. There is limited biological activity, and the lake is entirely frozen in winter. The small dimensions of the lake, combined with a strong flow-through of water in summer lead to a short residence time of water in the lake, and therefore to a very dynamic system. A sediment core was extracted from the glacial lake in August 2010, dated, and analyzed for PCBs [Pavlova et al., 2015b]. The sediment core includes the years 1950–2010. Levels of PCBs in the stream water downstream the lake were determined in the summers 2012, 2013, and 2015 by passive water sampling, a method that integrates the amount of PCBs in the dissolved phase during a four week sampling period, and by active bulk water sampling, providing a snapshot of the PCB concentration in the stream water [Pavlova et al., 2015b].

4.2.2 Model Setup

The model framework includes three connected models that describe the Silvretta glacier and its glacial lake (Figure 4.1). The first model (Gla–surf) quantifies the incorporation of PCBs into the glacier. Gla–surf is a dynamic multimedia chemical fate model. In this type of models, an environmental system is divided into internally well-mixed compartments, and fluxes of the chemical between the compartments are described by first-order differential equations. A mass balance equation of the chemical is then solved numerically for every compartment. The second model (Gla–flow) describes the downhill flow of glacier ice and calculates the storage duration of chemi-
4.2 Methods

4.2.3 Input of Chemicals to the Alpine Area

Global PCB emissions were taken from the maximum inventory of Breivik et al. [2007]. A global multimedia chemical fate model (BETR Research) was used to calculate the global distribution of PCBs [Macleod et al., 2011]. BETR Research consists of 288 regions, with each region including seven environmental compartments. Two atmospheric compartments describe the planetary boundary layer and the free troposphere. Chemicals reach Gla–surf and Gla–lake by atmospheric transport from the region of
the BETR Research model representing western Europe. In winter, 80% of the air originates from the free troposphere, due to atmospheric stratification frequently observed in the Alps [Gäggeler et al., 1995; Baltensperger et al., 1997; Gabbi et al., 2015]. In summer, a mixture of 80% boundary layer air and 20% tropospheric air reaches the Silvretta glacier area. These mixing ratios were estimated by long-term aerosol measurements from Jungfraujoch (3450 m a.s.l., 120 km from Silvretta glacier) [Herrmann et al., 2015]. A comparison between modeled and measured PCB concentrations in air and PCB deposition at the Silvretta ice core drilling site is available in Appendix B.

4.2.4 The Glacier Surface Model (Gla–surf)

Gla–surf consists of an atmospheric compartment and a set of connected glacier compartments (Figure 4.1). Chemical-loaded air reaches the atmosphere, where the chemicals partition between air and aerosol particles, and can be degraded by hydroxyl radicals, or leave the area by advective outflow by wind. Deposition to the glacier occurs by dry and wet gaseous and particle deposition, where wet deposition is initiated by snowfall in winter and by rainfall in summer. Summer rain is assumed to run off without interaction with the glacier surface. This assumption is discussed in Chapter 3. After deposition to the glacier surface, chemicals can degrade photochemically, revolatilize to the atmosphere by wind ventilation, or be relocated by molecular diffusion in pore air or by meltwater and particle flows.

The setup of the glacier compartments is based on the glacier mass balance, which quantifies the amount of snow that accumulates on the glacier surface. In winter, when the air temperature is negative, the mass balance is positive and snow is accumulated by snowfall. In Gla–surf, this means that a new glacier compartment is formed on the glacier surface every month. In summer, when the glacier mass balance is negative, the compartments on the glacier surface melt and meltwater percolates down through the glacier column, leaches out particles from the glacier compartments, and leaves the glacier as runoff. Temporally and spatially resolved glacier mass balance data were taken from a glacier mass balance model of the Silvretta glacier that was calibrated with point-based mass balance measurements, ice volume changes from high-resolution digital elevation models, and discharge records [Huss et al., 2008b; Huss and Bauder, 2009]. The glacier mass balance model is described elsewhere [Huss et al., 2008b; Huss and Bauder, 2009], while the input data used in this study are explained in Appendix C (Section C.2). Where available, regional meteorological data were used as model input. For future climate conditions, we used the Swiss Climate Change Scenarios (CH2011) [Appenzeller et al., 2011], based on the A2 emission scenario of the third IPCC Assessment Report [IPCC, 2001].

Gla–surf was previously applied to the ice core site of Silvretta glacier and validated by
comparing modeled concentration depth profiles of PCBs to measurements (Chapter 3) [Pavlova et al., 2015a]. Here, we apply Gla–surf to 71 sections of the Silvretta glacier (Figure 4.1, Appendix C, Figure C.1). In contrast to the previous version of Gla–surf, here, after five years of chemical exchange with the atmosphere or the overlying compartments, the glacier compartments are disconnected from the site where they were formed. This disconnection is due to lateral glacier flow caused by ice deformation under gravitational stresses. In the previous study, the ice was assumed to be transported solely in the vertical direction, which is reasonable for the ice core site, which was selected for negligible horizontal flow. Concentration depth profiles of PCBs in the ice core determined in this model version (Appendix C, Figure C.7) are similar to the profiles shown in Chapter 3, and therefore demonstrate the validity of the five years of interaction assumption.

Gla–surf quantifies the incorporation of chemicals into the entire glacier. Chemicals are assumed to be incorporated when the glacier compartment they are contained in is older than five years. The incorporated chemicals are transferred to Gla–flow, while the amount of chemicals lost from the system is transferred to Gla–lake (Figure 4.1). More details of Gla–surf can be found in Appendix C (Section C.2) and in Chapter 3.

### 4.2.5 The Glacier Flow Model (Gla–flow)

Gla–flow solves the incompressible Stokes equation for ice flow with the finite element method [Lüthi, 2009]. Similar to Gla-surf, the model is based on temporally and spatially resolved glacier mass balance data [Huss et al., 2008b; Huss and Bauder, 2009] and future climate conditions [Appenzeller et al., 2011]. Gla–flow provides a data set of glacier flow information, including the starting point (e.g. year 1955, section 5) and the arriving point of ice moving along a flowline (e.g. year 1975, section 40) (Figure 4.4, Appendix C, Figure C.4). Model details are given elsewhere [Lüthi, 2009] and in Appendix C (Section C.3). After chemicals are incorporated into the glacier ice (calculated by Gla–surf) they are stored in the glacier and transported along the flowlines. During this time, the chemicals are assumed to stay inert. When the ice reaches the glacier surface, the chemicals contained within the ice are released and reach the glacial lake (Gla–lake) (Figure 4.1). Gla–flow is yearly resolved, but the release of chemicals from Gla–flow to Gla–lake is transformed to a monthly resolution, according to the seasonality of the particle runoff of Gla–surf.

### 4.2.6 The Glacial Lake Model (Gla–lake)

Gla–lake consists of compartments for the atmosphere (height 400 m), lake water (depth 2 m), and sediment (layers of variable depth dependent on particle sedimentation).
Chemicals can reach the atmospheric compartment by advective inflow of air, or they can be imported to the water compartment from the glacier (output of Gla–surf and Gla–flow). This import of chemicals includes summer rain, meltwater and particle flows, and release from the glacier. Gla–lake includes air and water advection, wet and dry particle and gaseous deposition, degradation by hydroxyl radicals in the atmosphere, diffusion between air and water, and between water and sediment, and particle sedimentation and resuspension to and from the lake sediment. In winter, the glacial lake is frozen, and no meltwater from the glacier is released to the lake. During this period, an ice cover disrupts the exchange between air and water, and chemicals deposited to the ice cover are transferred to the lake in spring. Additional model details are presented in Appendix C (Section C.4).

4.2.7 Partitioning of Chemicals

Chemical fate processes are described using congener-specific chemical property data of the six indicator PCB congeners. We include temperature-specific partitioning between aerosol particles and air, raindrops and air, snowflakes and air (in the atmosphere), ice matrix and pore air, particles and pore air, liquid water and pore air (in the glacier), particles and lake water (in the lake), and between sediment solids and sediment pore water (in the sediment). A detailed parametrization of all processes is provided in Appendix C (Sections C.2–C.4).

4.3 Results

4.3.1 Model Validation

Gla–surf was validated for the ice core drilling site in a previous study (Chapter 3). As in the previous study, PCB concentration depth profiles in the ice core modeled by the slightly modified version of Gla–surf used here are in agreement with the measurements for the higher-chlorinated congeners, but lower than the measurements for the lower-chlorinated congeners (Appendix C, Figure C.7).

Gla–surf and its coupling to Gla–flow and Gla–lake is validated by comparing modeled and measured [Pavlova et al., 2015b] concentration depth profiles in the glacial lake sediment. Concentrations peak at a depth of 1–2 m, in layers that were formed between 1966 and 1987 (Figure 4.2 for PCB 52 and 153, Appendix C, Figure C.8 for the other congeners). After 1987, modeled and measured concentrations decrease; then they rise again in the 2000s. In the 1990s, major short-lived runoff pulses can be identified in the sediment core as layers of coarse material (blue shading in Figure 4.2) [Pavlova
Figure 4.2: Modeled (red line) and measured [Pavlova et al., 2015b] (gray bars) concentrations of the PCB congeners 52 and 153 in the glacial lake sediment. Model results are yearly averages and shown on different x-axes than the measurements. The sediment core was drilled in August 2010. The blue shading indicates periods of short-lived runoff pulses, identified as layers of coarse material in the sediment core. Results from before 2010 and predictions after 2010 are separated by a black line. Modeled and measured net sedimentation fluxes are shown in Appendix C (Figure C.9).

et al., 2015b]. These events delivered large amounts of sedimentary material to the glacial lake. Modeled concentrations of the lower-chlorinated congeners are lower than measured concentrations, with average modeled values between 0 and 2 m depth of 4.0, 5.2, and 14.0 pg g\(^{-1}\) dry weight, and measured concentrations of 41, 110, and 120 pg g\(^{-1}\), for PCB congeners 28, 52, and 101, respectively. In contrast, average modeled levels of the higher-chlorinated PCB congeners 138, 153, and 180 (150, 150, and 170 pg g\(^{-1}\)) are higher than the measured concentrations of 83, 89, and 40 pg g\(^{-1}\), respectively.

Modeled bulk concentrations in the glacial stream water are similar for the three summers 2012, 2013, and 2015, with iPCB concentrations between 120 and 130 pg L\(^{-1}\) (Appendix C, Figure C.10). The modeled iPCB concentrations are higher than the concentrations determined by passive water sampling, but in the same range as the concentrations from bulk water sampling. The modeled concentrations are dominated by higher-chlorinated PCB congeners. In contrast, an equal importance of all PCB congeners was determined by passive water sampling, while the lower-chlorinated congeners dominate the bulk water samples.
4.3.2 Incorporation into the Glacier

In the following, we focus on model results for PCB 153, because modeled and measured concentrations of this congener were in good agreement for ice, sediment and stream water. Results of the other iPCB congeners are provided in Appendix C. Chemical fluxes are shown for the period from 1930 (start of PCB emissions) to 2070 (disappearance of the Silvretta glacier). The net PCB accumulation, that is, deposition minus loss processes to and from the glacier compartments is positive until the 1980s, with maximum values between 1960 and 1980 (Figure 4.3 A for PCB 153, Appendix C, Figure C.11 A for the other congeners). After 1980, the negative net accumulation indicates a loss of chemicals from the Silvretta glacier, especially in the period 1980–2010. The yearly PCB incorporation (chemicals contained in glacier compartments that are older than five years) is temporally delayed to the net accumulation. The incorporation increases until the 1980s, followed by a decrease (Figure 4.3 A, Appendix C, Figure C.11 B).

4.3.3 Transport and Storage in the Silvretta Glacier

The total amount of PCBs stored in the Silvretta glacier strongly increases between 1960 and 1980, and reaches a maximum of 25 g PCB 153 and of 71 g iPCBs in 1982, respectively (Figure 4.3 B, Appendix C, Figure C.11 C). This amount corresponds to 350 g for the sum of all PCB congeners ($\sum$PCBs), when an extrapolation factor of five is used [FOEN, 1997]. After the 1980s, the storage continuously decreases, with strong drops in the 1990s and the 2000s, which were periods of strong melt. In 2060, no chemicals remain in the Silvretta glacier, as the glacier is expected to be completely melted.

The number of flowlines that start from the Silvretta glacier accumulation area is high in the 1940s and the 1970–80s (Figure 4.4). In contrast, after 1990, only a small number of flowlines start, as the Silvretta glacier experiences strong melt during this period, and negative glacier mass balances dominate on the entire glacier area.
Figure 4.3: A) Net accumulation (deposition minus losses) and incorporation (chemicals contained in glacier compartments older than five years) of PCB 153 between 1930 and 2070. B) Total storage of PCB 153 in the Silvretta glacier. C) Modeled release of PCB 153 from Gla–surf (black line) and Gla–flow (red shading). Modeled summer concentration of PCB 153 in the glacial stream water (blue line). Results of the PCB congeners 28, 52, 101, 138, and 180 are shown in Appendix C (Figures C.11–C.12).

Figure 4.4: The number of flowlines starting and arriving in specific years.
4.3.4 Release from the Silvretta Glacier

Between 1940 and 1980, the release of PCB 153 from the Silvretta glacier follows the temporal trend of the PCB emissions, and reaches a maximum of 3.7 g yr\(^{-1}\) in 1971 (Figure 4.3 C, Appendix C, Figure C.12 A). The maximum release of iPCBs and \(\sum\)PCBs is 11.2 and 56 g yr\(^{-1}\), respectively. After the 1970s, the PCB release from Gla–surf decreases. In the 1990s and the 2000s, the release from Gla–flow becomes important, and causes the total release to increase temporarily. After 2010, the PCB release from Gla–flow is the only release pathway, and leads to a constant release of approximately 0.3 g PCB 153, 1.0 g iPCBs, and 5.1 g \(\sum\)PCBs per year.

The concentration of PCB 153 in the glacial stream water closely follows the release from the Silvretta glacier (Figure 4.3 C, Appendix C, Figure C.12 B). A maximum concentration of 570 pg L\(^{-1}\) is reached in 1974, followed by a decrease. In 2004, the modeled concentration of PCB 153 reaches again 210 pg L\(^{-1}\), before it remains on a low level of approximately 40 pg L\(^{-1}\) until the complete deliquescence of the glacier. The expected iPCBs and \(\sum\)PCBs concentrations between 2020 and 2060 are 110 and 530 pg L\(^{-1}\), respectively. The seasonal concentrations in the glacier stream vary from year to year, depending on the dynamics in the glacial lake, such as chemical, meltwater, and particle inflow (Appendix C, Figures C.13–C.14).

4.4 Discussion

4.4.1 Model Validation

4.4.1.1 Model Validation with Ice Core Data

Gla–surf describes the chemical fate processes of the higher-chlorinated PCB congeners (PCB 138, 153, and 180) at the ice core site well, with modeled concentration depth profiles corresponding to measured concentrations (Appendix C, Figure C.7). In contrast, the model underestimates the concentrations of the lower-chlorinated PCB congeners (PCB 28, 52, and 101), a deviation that could be explained by the underestimated sorption of these congeners to the snow/ice surface as discussed before (Chapter 3). The underestimation of these concentrations is smaller than in the previous study because here the exchange between a glacier compartment and the atmosphere or neighboring compartments is restricted to five years, which reduces revolatilization. A better fit between model and measurements could be obtained by adapting the ice sorption parameter of the lower-chlorinated congeners (Appendix C, Figure C.15). However, while it is reasonable that this parameter should be higher, empirical data on sorption to ice are limited and the choice of a higher partition coefficient would be arbitrary.
The ice core site is the only glacier section where field data are available to perform an independent model validation. The application of Gla–surf to sections similar to the ice core site is reasonable, as the compartment setup functions in a similar way than at the ice core site (Chapter 3). In contrast, the sections in the ablation area have very different properties. There, no perennial ice is formed because the glacier mass balance is negative and there is a net mass loss. As a consequence, seasonal snow is deposited onto older ice that was transported to the section by glacier flow. This old ice melts and forms a porous ice layer with a complex hydrology. Chemicals and particles can percolate through this layer, be trapped within, or run off with meltwater. Currently, the porous ice layer is poorly characterized, and the fate of hydrophobic chemicals in this layer is unknown.

4.4.1.2 Model Validation with Lake Sediment Data

Modeled and measured concentrations in the glacial lake sediment agree for the higher-chlorinated PCB congeners, but differ for the lower-chlorinated congeners by up to a factor of 20. On the one hand, this divergence can be explained by the underestimated sorption of the lower-chlorinated congeners in Gla–surf. At sites with a lower glacier mass balance than the ice core site, the loss by revolatilization is even larger, as the chemicals are enriched at the glacier surface (Figure 3.4 in Chapter 3). By increasing the sorption to ice of the lower-chlorinated congeners by a factor of 10, the modeled concentrations in the sediment core are still lower than the measurements (Appendix C, Figure C.16). Therefore, in the ablation area, additional processes that are not included in the model might be important, such as percolation through and temporary storage in the porous ice layer.

On the other hand, the discrepancy might also be explained by the sedimentation processes in Gla–lake. Several model parameters are poorly known, such as the volume fraction of particles in the lake water or the settling velocity of these particles. The highly dynamic glacial lake system might not be well captured by a monthly resolved model, as lake properties vary strongly on a day-night scale with melting during the day and low runoff in the night. In addition, short-lived runoff pulses were identified in the sediment core as layers of coarse material that was deposited in the 1990s (Figure 4.2).

In the lake sediment, the peak of PCB input in the 1970s, when emissions were highest, is captured by both the modeled and measured sediment profiles. In the 2000s, the modeled concentrations show a smaller increase than the measurements, especially for the higher-chlorinated congeners. In contrast, the modeled concentrations increase in the 1990s, when measured levels are low. While the divergence in the 1990s can be explained by the complex hydrological regime of the glacial lake in this period, the
different levels in the 2000s might originate from the glacier flow and surface storage in the ablation area (see below).

4.4.1.3 Model Validation in the Glacial Stream Water

Compared to passive water sampling, the model predicts similar concentrations for the lower-chlorinated congeners, but higher levels for the higher-chlorinated congeners. This discrepancy is probably related to the passive water sampling technique, which excludes the particulate phase [Pavlova et al., 2015b]. The strong partitioning of PCBs to the particulate phase is evident from the physical properties (octanol–water partitioning) of these chemicals. In an Alpine glacial lake, the particulate phase has been determined to contain 84% of the PCB reservoir [Nellier et al., 2015b].

Compared to bulk water sampling, the model predicts lower concentrations for the lower-chlorinated congeners, which is in agreement with the divergence in the ice and sediment cores discussed above. For the higher-chlorinated congeners PCB 138, 153, and 180, the average modeled concentrations of 30, 41, and 32 pg L$^{-1}$ are higher than the levels of 14, 16, and 10 pg L$^{-1}$ determined by bulk water sampling, respectively. However, bulk water samples only show an instantaneous concentration, as the samples are not averaged over time. Also, the congener pattern in the bulk water samples is not consistent in the two years. In multimedia chemical fate models, we assume equilibrium between the particles and the water phase, which might not be entirely valid in the summer months [Nellier et al., 2015b]. As a result, the partitioning of PCBs to the particulate phase might generally be overestimated in the glacial runoff, which may explain the high modeled concentration of the higher-chlorinated congeners in the lake sediment.

4.4.2 Incorporation into the Glacier

The net accumulation (input minus loss) strongly follows the estimated PCB emissions [Breivik et al., 2007], and is higher in years when the glacier mass balance is high. This is consistent with the finding that the PCB incorporation at the ice core site of the Fiescherhorn glacier (Chapter 2) (higher mass balance) is higher than at the ice core site of the Silvretta glacier (Chapter 3) (lower mass balance). The effect of the glacier mass balance is also visible when comparing the different sections of the Silvretta glacier. Low section numbers (accumulation area, high mass balance) have smaller losses than high section numbers (ablation area, low mass balance), and the incorporation is higher in the accumulation area than in the ablation area (Appendix C, Figure C.5–C.6). The loss flux of the lower-chlorinated congeners closely follows the input flux, which means that the major part of these chemicals is immediately lost
from the glacier after deposition. In contrast, higher-chlorinated congeners remain in the glacier ice to a higher extent.

4.4.3 Transport and Storage in the Silvretta Glacier

The higher incorporation of the higher-chlorinated congeners leads to a modeled PCB storage that is dominated by the PCB congeners 138, 153, and 180. The lower-chlorinated congeners PCB 28, 52, and 101 account for the minor part of stored pollutants, although their incorporation may be underestimated. In 2015, 14 g of PCB 153 (41 g iPCBs, 200 g $\sum$PCBs) are stored in the Silvretta glacier (Figure 4.3 B).

In the 1990s and the 2000s, an increased number of flowlines arrives at the glacier surface (Figure 4.4), due to strong melt in these periods. However, more flowlines that started in the 1970s, when most PCBs were incorporated into the glacier, arrive in the 1990s (31 flowlines) than in the 2000s (23 flowlines) (Appendix C, Figure C.4 B). Also, the flowlines arriving in the 1990s have a higher load of PCB 153 (Appendix C, Figure C.4 C). As a consequence, the flowlines explain the high modeled concentrations in the sediment in the 1990s and the low modeled values in the 2000s (Figure 4.2).

However, these concentrations do not agree with the high measured concentrations in the sediment in the 2000s, a discrepancy that has to be explained by processes in the ablation area. In the model, when a flowline arrives at the glacier surface of the ablation area, the chemicals stored within the ice are instantaneously released to the glacial lake. Instantaneous release might be realistic when the ice melts on top of bare rock, which has a low affinity for organic pollutants. However, when the ice melts on top of older ice that was formed before 1900 (not included in the model), the chemicals can be transferred to and stored in the porous ice layer instead of being released to the lake. To test the importance of such a process in the model, we added a temporary storage of 10 years for chemicals and particles that were released by flowlines. As expected, the concentration of PCB 153 in the lake sediment in the 2000s (between 0 and 0.3 m depth) is increased (Appendix C, Figure C.17). Thus, including additional processes in the ablation area could improve our model. A small vertical meltwater percolation within the glacier (not included in the model) could relocate chemicals and particles from the flowline they are transported along to flowlines deeper in the glacier. This would lead to a delayed release of these chemicals. However, information about this water percolation is missing.

4.4.4 Release from the Silvretta Glacier

In the future, modeled PCB release from the glacier is more important than atmospheric deposition. In contrast, Nellier et al. [2015a] found glacial runoff from the
Muzelle glacier to be a negligible source of PCBs relative to atmospheric deposition. The relationship between glacial runoff and atmospheric deposition depends on the characteristics of the catchment. The Muzelle glacier is surrounded by a large catchment area, with only 6% of the catchment covered by the glacier. In contrast, the Silvretta glacier covers almost the whole catchment, and therefore the area available for the accumulation of seasonal snow is small compared to the glacier surface.

However, determining the influence of a glacier on contaminant levels in a complex environmental system (water, sediment, biota) is not straightforward. At a first glance, a large glacier coverage in a catchment or a period of strong melting leads to a high relevance of the glacier compared to seasonal snow for the release of PCBs. However, it is important to understand that in the context of PCBs, the age of the melting ice is crucial to understand the importance of the glacier. Glacier ice that was formed between the 1950s and the 1970s contains high PCB levels, while ice formed earlier or later than this period contains lower levels. Therefore, only the melting of ice from the PCB input period, leads to high pollutant levels. This melting strongly depends on the glaciers dynamics of melting and runoff, as pointed out by Elliott et al. [2012]. For example, a long glacier leads to a long storage of ice, which means that the ice from the PCB input period in the 1970s has not yet been released. In contrast, a small glacier such as the Silvretta glacier leads to a rather short storage, which means that the ice from the 1970s has already been released.

Between 2012 and 2015, the modeled stream water concentration of iPCBs is between 120 and 130 pg L$^{-1}$. This level is higher than the iPCB concentration of 15–20 pg L$^{-1}$ measured by Nellier et al. [2015a], but lower than the PCB 101 concentration of 1000 pg L$^{-1}$ determined by Bizzotto et al. [2009] [Morselli et al., 2014] and in the same range as the iPCB (including PCB 118) concentration of 110 pg L$^{-1}$ measured by Vilanova et al. [2001] in the Austrian Alps. The model predicts a constant iPCB concentration of approximately 100 pg L$^{-1}$ in the glacial stream during the next decades, corresponding to 500 pg L$^{-1}$ $\sum$PCBs. This concentration is three orders of magnitude lower than the concentration of a few $\mu$g L$^{-1}$ that was determined to be chronically toxic for fish [Stalling and Meyer, 1972; Hansen et al., 1971; Fent, 1998]. However, the effects on long-living predators and mammals remain unknown.

### 4.4.5 Implications of this Study

In this study, a general model framework that quantifies mass fluxes of semivolatile chemicals in glaciers was developed and applied to Silvretta glacier. It is the first study that provides a consistent overall picture of PCB fate and dynamics in an entire glacier system. For Silvretta glacier, the models show that the peak in PCB concentrations was reached in the past and that future concentrations are predicted to be low. However,
it is not possible to generalize these results for other glaciers. Silvretta is a rather small glacier, chosen for our study because of its simple geometry used for glacier flow calculations, and its record of glacier mass balance data covering the past 100 years. However, many Alpine glaciers have a higher glacier mass balance, and are larger than the Silvretta glacier, and the ice from the PCB input period has not melted yet. For estimating when and how much POPs will be released from Alpine glaciers, the model framework presented here could be applied to other glaciers, under the condition that glacier mass balance and glacier flow data is available. Alpine glaciers that are larger and at higher elevations than the Silvretta glacier might potentially release POPs in the next decades. With a warming climate, the glaciers in the European Alps retreat, and all pollutants that were previously incorporated into the glacier ice, and that are still stored in glaciers, are released simultaneously. This mixture, especially with chemicals that are emitted currently might be a challenge for sensitive species, such as long-living predators and mammals, in the unique Alpine ecosystem.

Supporting Information

Details on model setup, input parameters, and results are provided in Appendix C.

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Chapter 5

Conclusions and Future Research

5.1 Conclusions

The scope of this thesis was to investigate the fate of PCBs in a glacial system, including the glacier and the glacial lake. To this end, a multicompartment chemical fate model that quantifies the incorporation of semivolatile chemicals into the snow-firn-glacier ice system was developed in this thesis. The model framework also investigates the downhill transport of pollutants with the flow of glacier ice, and describes the fate of the chemicals in the glacial lake. The three studies provide knowledge about PCB fate and dynamics in glaciers and about the importance of glaciers as a secondary source of persistent organic pollutants.

In a first step, the incorporation model developed in this thesis was applied to the accumulation areas of three glaciers: the Fiescherhorn and Silvretta glaciers in the Swiss Alps, and the Lomonosovfonna glacier in the Arctic. The model was able to reproduce and explain measured PCB levels in the ice cores. The concentrations of the six PCB congeners in the ice cores from the Alpine glaciers Fiescherhorn and Silvretta peak between 200 and 1000 pg L\(^{-1}\). In the Arctic Lomonosovfonna glacier, the levels are roughly one order of magnitude lower.

On all investigated glaciers, the dominant pathway for the air-to-glacier transfer of the higher-chlorinated PCB congeners is wet particle deposition. In the accumulation areas of the cold Fiescherhorn and Lomonosovfonna glaciers, the majority of the deposited chemicals is incorporated into the glacier ice. The incorporation into the Fiescherhorn glacier, where more snow is accumulated, is higher than into the Lomonosovfonna glacier, where a larger percentage of the chemicals is lost by revolatilization. In contrast to the cold glaciers, the incorporation of the higher-chlorinated congeners into the temperate Silvretta glacier is smaller, while loss by particle runoff is important. According to the model, particle dynamics are crucial for the PCB fate in a temperate glacier, and their fate and influence on the behavior of semivolatile chemicals deserves
Conclusions and Future Research

In the incorporation model, the lower-chlorinated PCB congeners are mainly deposited by dry gaseous deposition, and the most important postdepositional process is revolatilization from the glacier to the atmosphere. The fate of these congeners is similar in the accumulation areas of cold and temperate glaciers. However, dry gaseous deposition and revolatilization are probably overestimated in the incorporation model, due to underestimated sorption of the lower-chlorinated congeners to snow and ice. This implies that the importance of other processes, such as wet gaseous deposition and loss by meltwater runoff might in reality be higher than they appear in the model.

In a temperate glacier, a period of strong melt leads to increased loss of chemicals by meltwater runoff, particle runoff, and revolatilization. However, the effect of these losses is smaller than the enrichment effect of simultaneous meltwater runoff and accumulation of particles and associated chemicals in the surface layer. Also, the enrichment in melt layers is more important than redistribution of chemicals by meltwater and particle percolation. This leads to increased concentrations in layers of strong melt, a feature that is visible in the modeled and measured concentration profiles of the Silvretta ice core. These melt layers cause disturbed concentration profiles in temperate glaciers. As a consequence, the direct use of ice core concentrations as archives of past atmospheric levels and emissions is problematic. For the interpretation of ice core concentration profiles, postdepositional processes have to be taken into account, a challenge that is getting more important with increasing melting in Alpine glaciers due to climate change.

The incorporation model, validated for the accumulation area, was also applied to the ablation area, where no validation is available. In the ablation area, seasonal snow is deposited onto old ice, and is completely melted in the following summer. While the seasonal snow is included in the model, not enough data was available to include the old ice. However, the porous ice layer might play a role in PCB dynamics, and could explain the two inconsistencies in the model: First, the modeled concentrations of the lower-chlorinated congeners in the lake sediment are lower than the measured levels, even if the sorption of these congeners to snow/ice is increased. In the model, the lower-chlorinated congeners are completely lost by revolatilization from the ablation area, because no transfer process from the seasonal snow to the old ice is included. Second, the higher-chlorinated congeners are released from the glacier flowlines in the 1990s, leading to a concentration increase in the lake sediment in this period, which is in contrast to the measured levels. In the model, chemicals released from the glacier flowlines instantaneously reach the glacial lake, however, in reality, they might be temporarily stored on the surface of the ablation area.

The total amount of PCBs stored in the Silvretta glacier is decreasing in the present days. Today (in 2015), 41 g of iPCBs and 200 g of the sum of PCBs are stored in the
Silvretta glacier. When extrapolating this amount from the Silvretta glacier (3 km$^2$) to the entire glacier area in the European Alps (2800 km$^2$), simply based on the surface area, the reservoir of iPCBs in European glaciers can be estimated to 40 kg (200 kg sum of PCBs). However, as for the Silvretta glacier, the documented ice mass loss is stronger and the ice storage duration is shorter than for other glaciers, the pool of PCBs stored in the Alpine glaciers is probably higher.

The decrease in storage leads to a release of chemicals from the glacier to the freshwater system. The PCB release from Alpine glaciers is small compared to emissions from contemporary sources, and the subsequent glacial stream concentration is below toxic levels. However, the effects on long-living predators and mammals remain unknown. In the next decades, besides releasing legacy pollutants, Alpine glaciers will also release other chemicals previously or presently incorporated into the glacier ice. Concurrent to a changing water regime caused by climate change, the release of potentially toxic chemicals by Alpine glaciers might be an additional stressor for sensitive organisms.

5.2 Future Research

To improve the incorporation model, several processes deserve further investigations. First, the meltwater and particle flows in the glacier ice are still not well known and had to be described in the model in a simplified way. Their parametrization might be improved by including a dense layer, overlaid by a percolation layer, that is temporally water-saturated. Water flow and particle washout experiments in combination with a characterization of particle properties, such as their organic carbon content or their location within the ice matrix could possibly further improve the model. Second, revolatilization is a key process for the fate of the lower-chlorinated congeners, but it is still overestimated by the current model version. Laboratory studies quantifying the sorption of the lower-chlorinated congeners to snow or ice, or field studies including measurements of PCB concentration gradients in the glacier surface could be used to calculate the fluxes of the different PCB congeners to the atmosphere. Third, photochemical degradation at the glacier surface was included in the model, but its description is based on the only experimental study existing so far and therefore, the degradation rate constant used in the model is uncertain. Additional laboratory or even field studies could provide more information about this process. Biotic degradation at the glacier surface might be important in the ablation area, where particles and chemicals are not covered with new glacier layers. Biotic degradation or transformation might occur in cryoconites, biologically active deposits of organic and inorganic material. Field studies investigating PCB levels at the surface of the ablation area might be worthwhile in future studies. Finally, the inflow of POPs to the high-Alpine area may be improved in the model by including processes such as local winds or gradual
It was shown that the porous ice layer in the ablation area might be important for chemical fate. Chemicals might percolate through the layer, or be trapped and temporally stored within. Information about this system could be gained by analyzing POP levels in a horizontal ice core from the ablation area. Also, the fate of particles and meltwater in the porous ice layer could be studied by field measurements, including an investigation of properties of meltwater and particle percolation, refreezing, or trapping.

Besides PCBs, the models developed in this thesis could be applied to other chemicals. This would especially be of interest for current-use chemicals, that are emitted in large amounts. The release of chemicals that are incorporated into glacier ice today will depend on future climate developments. For such chemicals, climate-dependent release scenarios could be studied by including different climate scenarios in the model. In addition, by comparing exposure and effect levels, the risk of pollutants in a glacial stream could be assessed. For this, the models might be combined with models including stream biology.

In a different context, POPs could be used as tracers in hydrology. The persistence of POPs, together with broad knowledge of their emission history, properties, and environmental fate gives a unique opportunity to track their past distribution. For example, the levels of legacy POPs in a groundwater reservoir might provide information about whether this reservoir was fed with ancient or recent water, with glacial runoff or fresh rainwater.

In this thesis, the incorporation model was applied to the accumulation areas of three different glaciers, but the model combining the glacier surface, the glacier flow, and the glacial lake was applied uniquely to Silvretta glacier. However, this model combination is required to quantify the total amount of PCBs stored in a glacier. The models developed in this thesis can be applied to other glaciers, if data of locally resolved glacier mass balance, glacier flow, and meteorology is available. Comparing the model results of different glaciers could also provide knowledge on the influence of general glacier properties on chemical fate. For example, in this thesis, it could be demonstrated that a high elevation and a high glacier mass balance increase the incorporation of semivolatile chemicals into the glacier ice. Additional studies could show that the longer transport duration in a long glacier might lead to a later release of chemicals. In contrast, a steeper inclination of a glacier might induce shorter transport and earlier release. In addition, the distance to industrial or agricultural areas cause higher or lower POP concentrations in glaciers, as it was shown for the ice cores from Fiescherhorn and Lomonosovfonna glaciers. Such studies could be used to extrapolate the results of this thesis to other glacial systems and to entirely quantify the importance of glaciers as a secondary source of persistent organic pollutants.
Appendix A

Supporting Information for Chapter 2: Polychlorinated Biphenyls in Glaciers. Model Results of Deposition and Incorporation Processes

A.1 Environmental Parameters

A.1.1 Time-resolved Parameters

Time-resolved parameters include air temperature, ice accumulation, precipitation rate and aerosol particle concentration (Figure A.1). Air temperature on the Fiescherhorn glacier is estimated from air temperature at the high-Alpine research station Jungfraujoch [MeteoSwiss, 2014b], which is located approximately 6 km west of the drilling site. This air temperature is corrected for the higher altitude of the Fiescherhorn drilling site using a temperature gradient of 0.83°C/100 m. This gradient is estimated using a dry adiabatic temperature gradient of 1°C/100 m and a saturated adiabatic temperature gradient of 0.65°C/100 m, a value that is valid in the middle troposphere [Wallace and Hobbs, 2006]. The number of rain days with precipitation > 0.1 mm was 182 days per year between 1961 and 2002, which is 50% on Kleine Scheidegg (Switzerland) [MeteoSwiss, 2014b].

Air temperature on the Lomonosovfonna glacier is estimated from air temperature at Svalbard airport [MET, 2013], which is located approximately 80 km west of the drilling site. This air temperature is corrected for the higher altitude of the drilling site using a temperature gradient of 0.44°C/100 m [Pohjola et al., 2002].

Ice accumulation of both drilling sites was estimated by dating the ice cores [Jenk et al., 2006; Wendl, 2014]. The Lomonosovfonna ice core was dated with a combination of reference horizons, annual layer counting and 210Pb decay [Wendl, 2014; Garmash et al., 2013]. The accumulation was corrected for layer thinning and plastic deformation as
Figure A.1: Air temperature, ice accumulation rate and aerosol particle concentration at A) the Fiescherhorn drilling site and B) the Lomonosovfonna drilling site.

described in Mariani et al. [2012] following the approach of Henderson et al. [2006]. To maintain conservation of mass, precipitation is set equal to the ice accumulation. Measured aerosol particle concentration (PM10) at Jungfraujoch is used for Fiescherhorn glacier [EMEP, 2014] while measurements from Zeppelin are used for Lomonosovfonna glacier [Tunved et al., 2013]. In the model, the concentrations are averaged over the winter and summer seasons.

### A.1.2 Depth-resolved Parameters

The density profiles used in the model were determined by fitting a saturation function to the measured profiles (Figure A.2, Equation (A.1)). The parameters $X_1$, $X_2$ and $X_3$ as determined by curve fitting are 475, 19 and 444 for Fiescherhorn and 512, 5 and 327 for Lomonosovfonna. The units of density $\rho$ and depth $d$ are kg m$^{-3}$ and m weq, respectively.

\[
\rho = X_1 \ast (1 - \exp(-\frac{1}{X_2} \ast d)) + X_3
\]  

(A.1)
A.1 Environmental Parameters

Figure A.2: Measured (black points) and fitted (red line) density profiles for the Fiescherhorn ice core [Jenk et al., 2006] and the Lomonosovfonna ice core [Wendl, 2014].

A.1.3 Constant Parameters

Constant input parameters used in the Fiescherhorn and Lomonosovfonna model versions are summarized in Tables A.1 and A.2.

Fraction of organic matter in aerosol particles: Aerosol measurements at the Sevettijarvi monitoring station in northern Finland showed a background volume fraction of organic matter in aerosol particles of 0.16, when averaging the values reported for fall, winter and spring, without accounting for values during summer, as they were reported to be linked with local conditions, and assuming the same density for organic matter than for the aerosol particle [Ricard et al., 2002]. However, the ice core drilling site on Lomonosovfonna glacier is at a higher latitude (79°N, compared to 69°N) and at a higher altitude (1200 m a.s.l. compared to 130 m a.s.l.) than the study site in northern Finland, and is therefore more distant from vegetation. As a consequence, in our model, we use a volume fraction of organic matter in aerosol particles of 0.1.

Specific surface area of snowflakes: The specific surface area of snowflakes is set to a constant value of 96 m² kg⁻¹. However, this value is valid for freshly fallen snow on the ground and is highly variable [Legagneux et al., 2002].
Table A.1: Constant input parameters used in the Fiescherhorn model version: wind speed [MeteoSwiss, 2014a], density of ice [Cuffey and Paterson, 2010], density of aerosol particles [FCAH, 2007], density of particles in ice (set equal to aerosols), volume fraction of organic matter in aerosol particles [FCAH, 2007], volume fraction of organic matter in particles (set equal to aerosols), volume fraction of aerosols in air [EMEP, 2014], dry deposition velocity of aerosols [Daly and Wania, 2004], scavenging factor for snow [Franz and Eisenreich, 1998], specific surface area of snowflakes [Legagneux et al., 2002], wind factor [Daly and Wania, 2004], mass transfer coefficient air–snow [Mackay and Paterson, 1991] (value for soil), degradation depth [Grannas et al., 2007], molecular diffusivity in air [Mackay, 2001], temperature gradient [Wallace and Hobbs, 2006], radiation factor (estimated from radiation data) [MeteoSwiss, 2014a], glacier temperature [Schwerzmann et al., 2006]. The confidence factors \( C_f \) used in the uncertainty analysis are also reported.

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<td>Density of particles in ice</td>
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<tr>
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</tr>
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<tr>
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</table>

\(^a\)Wind factor: influence of wind pumping in diffusive exchange between air and the snow surface. The wind factor is selected so that the air to snow mass transfer coefficient and the snow to air mass transfer coefficient are of similar magnitude [Daly and Wania, 2004].

\(^b\)Depth of glacier surface influenced by photochemical degradation.

\(^c\)Temperature gradient for correcting the air temperature to the higher altitude.

\(^d\)The radiation factor is used to adapt the photochemical degradation rate to seasonal changes in solar radiation.
Table A.2: Constant input parameters used in the Lomonosovfonna model version: wind speed (see Section A.4), density of ice [Cuffey and Paterson, 2010], density of aerosol particles (set equal to Fiescherhorn value), density of particles in ice (set equal to aerosols), volume fraction of organic matter in aerosol particles [Ricard et al., 2002], volume fraction of organic matter in particles (set equal to aerosols), volume fraction of aerosols in air [Tunved et al., 2013], dry deposition velocity of aerosols [Daly and Wania, 2004], scavenging factor for snow [Franz and Eisenreich, 1998], specific surface area of snowflakes [Legagneux et al., 2002], wind factor [Daly and Wania, 2004], mass transfer coefficient air–snow [Mackay and Paterson, 1991] (value for soil), degradation depth [Grannas et al., 2007], molecular diffusivity in air [Mackay, 2001], temperature gradient [Pohjola et al., 2002], radiation factor (set higher than Fiescherhorn value) The confidence factors ($C_f$) used in the uncertainty analysis are also reported.

<table>
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<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>$C_f$</th>
</tr>
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<tr>
<td>Area</td>
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</tr>
<tr>
<td>Wind speed</td>
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<td>1.5</td>
</tr>
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<td>Density of ice</td>
<td>kg m$^{-3}$</td>
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<td>1.05</td>
</tr>
<tr>
<td>Density of aerosol particles</td>
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<td>1.5</td>
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<tr>
<td>Density of particles in ice</td>
<td>kg m$^{-3}$</td>
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<td>Scavenging factor for snow</td>
<td>–</td>
<td>3.2 $10^5$</td>
<td>5</td>
</tr>
<tr>
<td>Specific surface area of snowflakes</td>
<td>m$^2$ kg$^{-1}$</td>
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<td>Wind factor$^a$</td>
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$^a$Wind factor: influence of wind pumping in diffusive exchange between air and the snow surface. The wind factor is selected so that the air to snow mass transfer coefficient and the snow to air mass transfer coefficient are of similar magnitude [Daly and Wania, 2004].

$^b$Depth of glacier surface influenced by photochemical degradation.

$^c$Temperature gradient for correcting the air temperature to the higher altitude.

$^d$The radiation factor is used to adapt the photochemical degradation rate to seasonal changes in solar radiation.
A.1.4 Dependent Parameters

Specific surface area of firn: The specific surface area of firn ($A_f$) was estimated from density of ice ($\rho_{\text{ice}}$) using a relationship presented by Dominé et al. [2007] for seasonal snow (Equation (A.2)). This equation is valid for aged snow, and used for compartments with densities below 500 kg m$^{-3}$. The $A_f$ in compartments with higher densities is set to 10 m$^2$ kg$^{-1}$, a value that is in the range of the lowest values reported in Legagneux et al. [2002] for aged snow where particles are no more recognizable. The units of density and SSA in Equation (A.2) are g cm$^{-3}$ and cm$^2$ g$^{-1}$.

$$A_f = -313.17 \times \ln \rho_{\text{ice}} + 160.1$$ (A.2)

Fraction of particles in the glacier: The volume fraction of particles in the glacier is a function of the deposition of aerosol particles by dry and wet deposition, the amount of snowfall and the glacier compartment density. These particles have the same properties (density and organic matter content) as the aerosol particles.

Air height: The air height is a function of the area according to the relationship used in Bogdal et al. [2010].

A.2 Emissions and Global Distribution

Global distribution of PCBs was calculated using the BETR Research model [Wöhrnschimmel et al., 2013]. In BETR Research, the upper air compartment represents the free troposphere, whereas the lower air compartment corresponds to the planetary boundary layer. To calculate the amount of chemical emitted to the air compartment of the glacier system we need to determine to which air compartment of the BETR Research model the glacier surface is exposed. The Lomonosovfonna glacier is constantly exposed to the free troposphere [Garmash et al., 2013]. The Fiescherhorn glacier is exposed to the free troposphere during winter due to atmospheric stratification. During summer, the planetary boundary layer can increase to high altitudes, which was shown by seasonal monitoring of various environmental parameters at Jungfraujoch and other Alpine mountain stations, e.g. radon [Griffiths et al., 2014; Gäggeler et al., 1995], aerosol particle concentration [Baltensperger et al., 1997], or aerosol particle components [Henning et al., 2003; Kasper and Puxbaum, 1998]. We estimate the frequency of exposure of Fiescherhorn glacier to the planetary boundary layer by comparing the sulfate concentration in aerosol particles at Jungfraujoch to the sulfate concentration measured in a remote area within the planetary boundary layer (Payerne) [NABEL, 2014]. The main precursor of sulfate in aerosol particles is sulfur dioxide, which is produced by incineration of fossil fuels and therefore an indicator of air from the planetary boundary layer. On Jungfraujoch, the sulfate concentration in aerosol particles shows
a clear seasonal trend with low concentrations during winter and increased concentrations during the summer months (Figure A.3). In Payerne, the sulfate concentration is high during winter and lower during summer with an average of 1.64 $\mu$g m$^{-3}$. We estimate the fraction of planetary boundary layer air needed to lift the concentration at Jungfraujoch from 0.16 $\mu$g m$^{-3}$ (December and January) to 0.42 $\mu$g m$^{-3}$ (July and August) to approximately 20%. Therefore, we use a ratio of 80% free troposphere air and 20% planetary boundary layer air as input in our model during the six summer months. The ratio of 20% planetary boundary layer air is comparable to a value of 15% determined by Seibert et al. when investigating the frequency of transport of air from lower layers of the Po valley to mountain peak stations [Seibert et al., 1998]. However, the ratio of 20% is uncertain as processes such as local winds along the earth surface or gradual mixing (mixing of air layers without the planetary boundary layer reaching an altitude of 3900 m a.s.l.) could not be quantified.

Finally, the amount of chemical emitted into the area is determined by the air concentration (mol m$^{-3}$), the average wind speed in the area (m h$^{-1}$), and the vertical area of the air compartment (m$^2$). The same quantity of air entering the system leaves the system by air advection.

![Figure A.3: Sulfate concentration in aerosol particles as reported by the National Air Pollution Monitoring Network (NABEL) [NABEL, 2014]. The concentration is reported in $\mu$g S m$^{-3}$, in a monthly resolution for the years 1981–2012 for the measurement stations Jungfraujoch (green dots) and Payerne (blue dots).](image)

### A.3 Chemical Parameters

Chemical parameters used in the model are shown in Table A.3. The partition coefficients are adjusted to the colder temperatures using the van’t Hoff equation (Equation...
Table A.3: Chemical specific input parameters for PCB 28 (2,4,4'-trichloro-biphenyl), PCB 52 (2,2',5,5'-tetrachloro-biphenyl), PCB 101 (2,2',3,4,4',5-hexachloro-biphenyl), PCB 138 (2,2',3,4,4',5-hexachloro-biphenyl), PCB 153 (2,2',4,4',5,5'-hexachloro-biphenyl) and PCB 180 (2,2',3,4,4',5,5'-heptachloro-biphenyl). Confidence factors and their references (if available) are reported. Cf of molar mass [MacLeod et al., 2002], Partition coefficients [Schenker et al., 2005], Energies of phase change [Schenker et al., 2005], Electron donor and acceptor properties [van Noort et al., 2010], Partition coefficient hexadecane–air [Abraham and Al-Hussaini, 2005], OH-radical degradation rate [Anderson and Hites, 1996], Photochemical degradation rate [Matykiewiczová et al., 2007], Activation energy of \( k_{\text{air}} \) [Bogdal et al., 2010], Electronic acceptor properties [Gasic et al., 2009].

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<td>15000</td>
</tr>
</tbody>
</table>
where $K$ is the partition coefficient, $dU$ the energy of phase change, $R$ the gas constant, $T_c$ the temperature of the property data and $T$ the temperature in a specific compartment.

$$K(T) = K(T_c) \times \exp\left(\frac{dU}{R} \times \left(\frac{1}{T_c} - \frac{1}{T}\right)\right)$$ (A.3)

The degradation rate constant in air is adjusted to temperature using the two-point Arrhenius equation (Equation (A.4)), where $E_a,\text{air}$ is the activation energy of the rate constant in air.

$$k_{\text{air}}(T) = k_{\text{air}}(T_c) \times \exp\left(-\frac{E_a,\text{air}}{R} \times \left(1 - \frac{T}{T_c}\right)\right)$$ (A.4)

The photochemical degradation rate in the glacier surface is adapted to seasonal changes using a radiation factor, increasing the average rate constant during the summer months (high radiation) and decreasing the rate during the winter months (low radiation). This factor is set to 1.5 on Fiescherhorn, according to the variation in solar radiation measured at Jungfraujoch [MeteoSwiss, 2014b]. Assuming a higher seasonal difference in solar radiation, the factor is set higher on Lomonosovfonna than on Fiescherhorn glacier (factor=2) (Tables A.1 and A.2).

## A.4 Chemical Fate Processes

### A.4.1 Air Advection

Air is advected out of the system according to the average wind speed and the surface geometry which is defined as a square. Wind speed on Fiescherhorn glacier is set equal to wind speed on Jungfraujoch which has an average of 7.5 m s$^{-1}$ MeteoSwiss [2014a]. Wind speed has been measured at several stations on Svalbard (Norway) with average values between 2.2 and 5.4 m s$^{-1}$ [MET, 2013] (data for Pyramiden, Edgeoya, Svalbard airport and Ny-Ålesund). However, all these stations are located close to sea level. As we expect wind speed on 1200 m a.s.l. to be higher than wind speed at sea level, we set the wind speed on Lomonosovfonna equal to the wind speed on Fiescherhorn.

### A.4.2 Deposition

Dry particle deposition, wet particle deposition and wet gaseous deposition are modeled according to Mackay [2001]. The calculation of deposition D-values is shown in Equations (A.5)–(A.7), where $D_{\text{dep,wp}}$ is the D-value of wet particle deposition, $A$ is the surface area, $U_{\text{snow}}$ is the precipitation falling as snow, $f_{\text{aer}}$ is the fraction of
aerosol particles in air, $Z_{\text{aer}}$ is the fugacity capacity of aerosol particles, and $Q_{\text{snow}}$ is the particle scavenging factor of snow, which is set to $3.2 \times 10^5$ [Franz and Eisenreich, 1998]. $D_{\text{dep, wg}}$ is the D-value of wet gaseous deposition, and $Z_{sf}$ the fugacity capacity of snowflakes. Finally, $D_{\text{dep, dg}}$ is the D-value of dry gaseous deposition, and $U_{\text{aer}}$ is the particle deposition rate.

\begin{align*}
D_{\text{dep, wp}} & = U_{\text{snow}} \ast A \ast Q_{\text{snow}} \ast f_{\text{aer}} \ast Z_{\text{aer}} & \text{(A.5)} \\
D_{\text{dep, wg}} & = U_{\text{snow}} \ast A \ast Z_{sf} & \text{(A.6)} \\
D_{\text{dep, dg}} & = U_{\text{aer}} \ast A \ast f_{\text{aer}} \ast Z_{\text{aer}} & \text{(A.7)}
\end{align*}

### A.4.3 Diffusion (Dry Gaseous Deposition and Revolatilization)

Diffusion is modeled between air and firn as well as between the firn boxes. Diffusion between air and the glacier surface ($D_{\text{diff, air-gla}}$) is described by a two-resistance model, consisting of an air-side and a glacier-side resistance. These resistances are described using a mass transfer coefficient from air to firn ($U_{\text{air-gla}}$) of $5 \text{ m h}^{-1}$ [Mackay and Paterson, 1991] and a mass transfer coefficient from firn to air ($U_{\text{gla-air}}$) determined by Equation (A.11), where the wind factor ($W_f$) accounts for an increased air exchange between firn and air due to wind pumping. The wind factor is chosen in order to set the mass transfer coefficient from firn to air to a similar magnitude as the mass transfer coefficient from air to firn [Daly and Wania, 2004] and has therefore a value of 181 on Fiescherhorn and a value of 47 on Lomonosovfonna glacier. $L_m$ is the size of the compartment. The effective diffusivity in firn ($d_{\text{diff, eff}}$) is estimated according to Millington [1959] and depends on the diffusivity in air ($d_{\text{diff, air}}$) and the fraction of air in the glacier ($f_{\text{pore-air}}$).

Diffusion between the firn compartments is also modeled using a two-resistance model and mass transfer coefficients are calculated similar to the air-firn transfer, however, no wind factor is included.

\begin{align*}
D_{\text{diff, air-gla}} & = \frac{1}{D_{\text{diff, air-side}}} + \frac{1}{D_{\text{diff, gla-side}}} & \text{(A.8)} \\
D_{\text{diff, air-side}} & = U_{\text{air-gla}} \ast A \ast Z_a & \text{(A.9)} \\
D_{\text{diff, gla-side}} & = U_{\text{gla-air}} \ast A \ast Z_{\text{pore-air}} & \text{(A.10)} \\
U_{\text{gla-air}} & = \frac{d_{\text{diff, eff}}}{0.5 \ast L_m} \ast W_f & \text{(A.11)} \\
d_{\text{diff, eff}} & = d_{\text{diff, air}} \ast f_{\text{pore-air}}^{1/3} & \text{(A.12)}
\end{align*}
A.4.4 Sorption to Aerosol Particles and Particles

The aerosol particle–air (in the atmosphere, $K_{pa,air}$) and the particle–pore air (in the glacier, $K_{pa,gla}$) partition coefficients are estimated from the octanol–air partition coefficient ($K_{oa}$) and the fraction of organic matter in aerosol particles ($f_{om,aer}$) and particles ($f_{om,gla}$) (Equations (A.13)–(A.15)) [Harner and Bidleman, 1998].

\[
K_{pa,\text{dim}} = 10^9 \times 10^{(\log K_{oa} - \log f_{om} - 11.91)} \\
K_{pa,air} = K_{pa,\text{dim}} \times \rho_{aer} \\
K_{pa,gla} = K_{pa,\text{dim}} \times \rho_{par}
\]  

(A.13)  
(A.14)  
(A.15)

A.4.5 Sorption to Ice

The snow surface-air partition coefficient ($K_{ca}$) is estimated using the poly-parameter linear free energy relationship introduced by Roth et al. [2004] (Equation (A.16)), where $\log K_{ca,\text{dim, c}}$ is valid for a temperature of -6.8°C and has units of m$^3$m$^{-2}$. We adjust this coefficient to the glacier temperature assuming a constant enthalpy of adsorption over the considered temperature range and derive the unitless snow surface-air partition coefficient using Equation (A.17) (Equation 4 in Lei et al. [Lei and Wania, 2004]) where $K_{ca,\text{dim}}$ is in m$^3$m$^{-2}$, the snow surface area ($A_{\text{ice}}$) in m$^2$kg$^{-1}$ and the density of ice ($\rho_{\text{ice}}$) in kg m$^{-3}$.

\[
\log K_{ca,\text{dim, c}} = 0.639 \times \log K_{ha} + 3.38 \times B + 3.53 \times A \\
K_{sa} = K_{ca,\text{dim}} \times A_{\text{ice}} \times \rho_{\text{ice}}
\]  

(A.16)  
(A.17)

A.4.6 Photochemical degradation in the glacier surface

The degradation rate constant for photochemical degradation in the ice surface was determined in a laboratory study by Matykiewiczová et al. [2007]. The authors irradiated snow samples using multiwavelength UV light passing through Pyrex to simulate solar radiation. Here we use an average half-life time of 1 year, as determined for PCB 153. We assume this rate constant to not be temperature dependent but rather dependent on solar radiation and therefore set it higher during summer and lower during winter (see radiation factor in Tables A.1 and A.2). Photochemical degradation is limited to the uppermost 15 cm of the glacier surface [Grannas et al., 2007].
A.5  Concentrations in Air, Air-to-Glacier Transfer and Concentrations in Glacier Ice

Table A.4 summarizes model results of PCB concentrations in air, air-to-glacier transfer and concentrations in glacier ice and available measurements at reference sites.

Table A.4: PCB concentrations in air, air-to-glacier transfer fluxes, and concentrations in glacier ice over the peak period.

<table>
<thead>
<tr>
<th></th>
<th>Concentrations in air (pg m$^{-3}$)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>4.9</td>
<td>2.7–29</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>1.3</td>
<td>1.5–8.2</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>0.5</td>
<td>0.5–1.9</td>
<td></td>
</tr>
<tr>
<td>PCB 28</td>
<td>2.6</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>0.6</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>0.2</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Air-to-glacier-transfer (pg m$^{-2}$d$^{-1}$)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>369</td>
<td>144–175</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>210</td>
<td>258–572</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>752</td>
<td>373–1060</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lomonosovfonna</td>
<td>Modeled (in 2002)</td>
<td></td>
</tr>
<tr>
<td>PCB 28</td>
<td>182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Concentrations in glacier ice (pg L$^{-1}$)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>65</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>120</td>
<td>543</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>482</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>PCB 28</td>
<td>17</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>12</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>70</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>
A.6 Air-to-Glacier Transfer Processes

Figure A.4 shows the modeled ratios of dry particle, wet gaseous, wet particle and dry gaseous deposition (diffusion) in percent of the total air-to-glacier transfer.

Figure A.4: Modeled wet particle deposition, wet gaseous deposition, dry particle deposition and dry gaseous deposition in percent of the total air-to-glacier transfer of PCB 28, PCB 101 and PCB 180 for (A) Fiescherhorn glacier and (B) Lomonosovfonna glacier.

A.7 Congener Profiles

Figure A.5 summarizes the modeled PCB congener profiles of PCB concentrations in air, air-to-glacier transfer fluxes and PCB concentrations in the glaciers. All congener profiles are in weight.

Figure A.5: Modeled congener profiles (PCB 28, PCB 101, PCB 180) of PCB concentrations in air above the glacier surface, air-to-glacier transfer fluxes and PCB concentrations in the glaciers. (A) Fiescherhorn glacier and (B) Lomonosovfonna glacier.
A.8 Sensitivity and Uncertainty Analysis

Analysis of model sensitivity and uncertainty was performed based on the error propagation method of MacLeod et al. [2002]. The main assumptions of this method are linear relationships between inputs and outputs, log-normal distributions of input variables and independence of input variables. This one-factor-at-a-time method has important drawbacks [Saltelli and Annoni, 2010], therefore we keep in mind that this uncertainty analysis provides a qualitative rather than a quantitative picture of the parameter uncertainty. In addition, even though model uncertainty (e.g. a missing process) is discussed in the main text, it is not analyzed in a quantitative way.

The sensitivity and uncertainty analysis is done for the concentration in every glacier compartment in the last year of the model run (as shown in the depth concentration profiles). No sensitivity and uncertainty analysis is done for the net ice accumulation, as this parameter changes the entire model setup by defining the dimensions of the compartments. In addition, the mixing ratio of free troposphere and planetary boundary layer air on Fiescherhorn is not included in the sensitivity and uncertainty analysis, however, the uncertainties of the PCB concentrations in these two air compartments are included.

The sensitivity analysis is run by changing every input parameter by 5% and calculating the output. The sensitivity S of every input parameter is then calculated by Equation (A.18), where I is the input parameter and O is the output. A sensitivity of 2 thereby indicates a 10% change of the PCB concentration in the glacier when changing the input parameter by 5%. A positive sensitivity increases the concentration while a negative sensitivity leads to a concentration decrease.

\[ S = \frac{\Delta O}{\Delta I} \]  
(A.18)

In the uncertainty analysis, a confidence factor \((C_I)\) is set for every input parameter as reported in Tables A.1–A.3. This confidence factor means that with a probability of 95%, the parameter lies within \(1/C_I\) and \(C_I\) times the median of the parameter [MacLeod et al., 2002]. The variance in the output \((C_{f,\text{out}})\) is then calculated by weighting the sensitivities and the confidence factors of every input parameter using Equation (A.19) (Equation 12 in MacLeod et al. [2002]).

\[ C_{f,\text{out}} = \exp \sqrt{\sum S_i^2 \ast (\ln C_{I,I})^2} \]  
(A.19)

Figure A.6 shows the sensitivities of all input parameters included in the sensitivity analysis, while Figure A.7 shows the contribution of the individual parameters to variance in output. The results are discussed in the main text. The molar mass has a
high negative sensitivity, as it directly influences the amount of chemical entering the system. However, the molar mass has no uncertainty.

Figure A.6: Sensitivities of all input parameters included in the sensitivity and uncertainty analysis.
Figure A.7: Contribution of the individual input parameters to variance in output. Parameters with a contribution below 0.5% are not shown.
A.9 Depth Profiles with Uncertainty Factors

Figure A.8 shows the modeled concentration profiles of PCB 28, PCB 101 and PCB 180 in the ice cores from Fiescherhorn (A) and Lomonosovfonna (B) glaciers with corresponding uncertainty factors. In total, average confidence factors of the concentrations in the glacier compartments are 11, 17, 12 on Fiescherhorn glacier and 8, 9 and 11 on Lomonosovfonna glacier, for PCB 28, PCB 101 and PCB 180, respectively. This means that with a 95% probability, concentrations lie within two orders of magnitudes (Figure A.8).

Figure A.8: Modeled concentration profiles with uncertainty factors.
A.10 Depth Profiles of PCB 52, 138 and 153

Figure A.9 shows the concentration profiles of the PCB congeners 52, 138 and 153 in the Fiescherhorn and Lomonosovfonna ice cores.

Figure A.9: Depth concentration profiles of PCB 52, PCB 138 and PCB 153.
Appendix B

Supporting Information for Chapter 3: Polychlorinated Biphenyls in a Temperate Alpine Glacier. Model Results of Chemical Fate Processes

B.1 Chemical Fate Modeling

The model is a dynamic multimedia chemical fate model, describing the fate of a chemical in a specific system. For this, the system is divided into well-mixed compartments each one having specific properties. All processes, such as losses from the system or inter-compartmental transfer are described by first-order differential equations. The processes are variable in time and specific for each compartment. A differential equation describing the amount of chemical in a compartment is set up for every compartment (Equation (B.1)), where $N$ is the amount of chemical in the compartment (mol), $I$ is the inflow into the compartment from outside the system (mol month$^{-1}$), $D$ is the sum of all loss and transfer processes from and to the other compartments as well as leaving the system (mol Pa$^{-1}$ h$^{-1}$), $V$ is the volume of the compartments (m$^3$), and $Z$ is the fugacity capacity of the compartments (mol Pa$^{-1}$ m$^{-3}$). While $N$, $I$, $V$, and $Z$ are vectors with a length equal to the number of compartments, $D$ is a matrix with a size equal to the number of compartments in two dimensions. $N$, $I$, $V$, $Z$, and $D$ change with time, in this model in a monthly resolution from January 1900 to December 2010.

$$
\frac{dN}{dt} = I + D \ast \frac{N}{V \ast Z} \quad (B.1)
$$

The model is fugacity-based, a concept that was used numerous times before and is described in detail by Mackay [2001]. In this concept, concentration ($C$, mol m$^{-3}$), fugacity ($f$, Pa), and fugacity capacity ($Z$, mol Pa$^{-1}$ m$^{-3}$) are connected by Equation
$C = Z \ast f$ \hspace{1cm} \text{(B.2)}$

D-values of advection ($D_{\text{adv}}$) are calculated from the amount of medium advected out of the system during a period of time ($G$, m$^3$ month$^{-1}$), D-values of degradation ($D_{\text{deg}}$) are calculated from rate constants ($k$, month$^{-1}$) and the volume ($V$, m$^3$), and D-values of mass transfer ($D_{\text{mtr}}$) are calculated from mass transfer coefficients ($k_m$, m$^3$ m$^{-2}$ month$^{-1}$) and the area ($A$, m$^2$) (Equations (B.3)–(B.5)).

$$D_{\text{adv}} = G \ast Z \hspace{1cm} \text{(B.3)}$$
$$D_{\text{deg}} = k \ast V \ast Z \hspace{1cm} \text{(B.4)}$$
$$D_{\text{mtr}} = k_m \ast A \ast Z \hspace{1cm} \text{(B.5)}$$

### B.2 Solving the System of Chemical Mass Balance Equations

The system of mass balance equations is solved numerically using the Matlab built-in solver ode15s. In order to track all fluxes (losses and transfers) in the system and to close the mass balance of the chemical for every time unit and compartment, we expand the system in Equation (B.1) by adding a copy of every compartment to the system. If there are four compartments, the vectors $I$, $V$ and $Z$ in Equation (B.1) are expanded from 4x1 to 8x1, while the $D$-matrix is expanded from 4x4 to 8x8. For the copied compartments, the input $I$ is zero, and $V$ and $Z$ can be set to any number (e.g. the same as the original compartment) as no fluxes are leaving these compartments.

The upper left part of the $D$-matrix (4x4) stays the same (original $D$-matrix). In the diagonal of this part, the $D$-values of all processes leaving the compartments can be found, loss processes as well as transfer processes. These values are used as input to the copied compartments (as positive values). This means that now, the mass leaving a specific compartment is still transferred to the original destination (defined by the original part of the $D$-matrix), but at the same time, a copy of this mass is passed on to the copied compartments. In these compartments, the mass accumulates until we set it back to zero (e.g. at the end of the month or the time unit we are interested in).

Here is an example for four compartments.

Original $D$-matrix:

$$
\begin{bmatrix}
-D & + & + & + \\
+ & -D & + & + \\
+ & + & -D & + \\
+ & + & + & -D
\end{bmatrix}
$$
D-matrix including copied compartments:

\[
\begin{bmatrix}
-D & + & + & 0 & 0 & 0 & 0 \\
+ & -D & + & 0 & 0 & 0 & 0 \\
+ & + & -D & 0 & 0 & 0 & 0 \\
+ & + & + & -D & 0 & 0 & 0 \\
+D & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & +D & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & +D & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & +D & 0 & 0 & 0 \\
\end{bmatrix}
\]

In addition to knowing the mass that has left a specific compartment, we also want to know which process is responsible for which amount of the transferred mass. For this, we can benefit from the additivity of the $D$-values (Equation (B.6)), where $F_i$ is the amount of chemical transferred by process $i$ (mol month$^{-1}$), $F_{tot}$ is the total amount of chemical leaving a specific compartment (mol month$^{-1}$), $D_i$ is the $D$-value of process $i$ (mol Pa$^{-1}$ h$^{-1}$), and $D_{tot}$ is the sum of the total $D$-values found in the diagonal of the original $D$-matrix (mol Pa$^{-1}$ h$^{-1}$).

\[
F_i = F_{tot} \times \frac{D_i}{D_{tot}} \tag{B.6}
\]

This approach enables us to keep track of all fluxes in the system, losses and transfer fluxes from all compartments in all time units, and we can verify the model by closing the mass balance of the chemical in our system for every compartment and time unit.

### B.3 Study sites of the Silvretta glacier

Silvretta glacier and the three study sites are shown in Figure B.1. The accumulation area is located in the eastern part of the glacier, the ablation area is located in the western part. The glacier flows from east to west.

### B.4 Environmental System

#### B.4.1 Input Parameters

Air temperature on Silvretta glacier (2500–3000 m a.s.l., Figure B.2) is calculated from measured monthly air temperatures from Weissfluhjoch (2700 m a.s.l., 1959–2010) and Säntis (2500 m a.s.l., 1900–1959), two meteorological stations in Eastern Switzerland. All stations are indicated on Figure B.3. Air temperature is corrected for elevation differences using a temperature gradient of 0.83°C/100 m. This gradient was calculated using a dry adiabatic gradient of 1°C/100 m and a saturated adiabatic temperature
gradient of 0.65°C/100 m (valid in the middle troposphere) [Wallace and Hobbs, 2006]. The average of these two gradients corresponds to the 0.83°C/100 m used in the model, as the ratio of rain days in the Swiss Alps was 50% between 1961 and 2002 (days with precipitation higher than 0.1 mm, data for Kleine Scheidegg, a station close to Jungfraujoch) [MeteoSwiss, 2014b].

The first glacier snow accumulation (mass balance) measurements on Silvretta glacier were done in 1915, resulting in one of the longest mass balance measurement series existing [Huss et al., 2008a; Huss and Bauder, 2009; VAW, 2014]. Snow accumulation is measured by placing stakes on the glacier surface and determining the change in snow mass after a specific period of time. Spatially distributed winter and summer mass balances were determined by calibrating a mass balance model of Silvretta glacier with ice volume changes from high-resolution digital elevation models, point-based mass balance measurements and discharge records, using air temperature and precipitation data from two high-altitude meteorological stations [Huss et al., 2008a; Huss and Bauder, 2009]. The resulting mass balance grid data was then combined for 71 glacier sections located perpendicular to the main flowline of the glacier. The local snow accumulation for the ice core site, site A, and site B is shown in Figure B.4. While the winter balance is in the same range for all sections, the annual balance is higher on the ice core site, located at a higher elevation than sites A and B. After 1990, the annual mass balance decreases markedly.

Wind speed, precipitation, and the volume fraction of aerosol particles in the atmo-
sphere are temporally resolved, but equal for all sites of the glacier. Monthly wind speed measurements from Weissfluhjoch are available from 1959 to 2010 [MeteoSwiss, 2014b]. Between 1900 and 1958, the wind speed of the period 1959-1987 is used. Monthly precipitation measurements from Weissfluhjoch (1959–2010) and Davos (1900–1958) are normalized to the average annual precipitation measured on the Silvretta glacier forefield [MeteoSwiss, 2014b]. Precipitation is set equal to the snow accumulation during winter. Precipitation occurs as rain during summer and as snow during winter. During winter, precipitation induces wet gaseous and particle deposition to the glacier surface. During summer, wet gaseous and particle deposition is described as a loss process from the system, assuming the rain to run off from the glacier before interacting with the glacier surface. Refreezing of rainwater in the glacier is neglected. Monthly measurements of particulate matter (PM10) from Jungfraujoch (1973–2010, 3600 m a.s.l., 130 km from Silvretta glacier) are used to describe the fraction of aerosol particles in the model [NABEL, 2014]. These measurements are available between 1973 and 2010. Between 1900 and 1972, monthly resolved PM10 values are estimated from the monthly measurements between 1973 and 2010, normalized to black carbon emissions in early and late decades in the 20th century, as estimated by Bond et al. [Bond et al., 2007].

The density of the glacier compartments ($\rho$) increases with depth ($d$) (Equation (B.7)). The fitting parameters $X_1$, $X_2$, and $X_3$ are set to 567, 10, and 350, in the same range as parameters determined for Fiescherhorn glacier in Steinlin et al. [2014]. The units of density and depth are kg m$^{-3}$ and m weq, respectively. In addition to the increase of density with depth, the density can increase due to refreezing (see Compartment Setup as well as Meltwater Percolation and Runoff).

$$\rho = X_1 \ast (1 - \exp(-\frac{1}{X_2} \ast d)) + X_3 \tag{B.7}$$

The porosity ($\phi$) of the glacier compartments is calculated as a function of the density of the compartment ($\rho$, kg m$^{-3}$) and the density of ice ($\rho_{\text{ice}}$, kg m$^{-3}$) (Equation (B.8)).

$$\phi = 1 - \frac{\rho}{\rho_{\text{ice}}} \tag{B.8}$$

The volume fraction of pore air in the compartment is set equal to the porosity. The volume fraction of particles in the compartment depends on the amount of aerosol particles deposited by wet and dry particle deposition during a specific month and the volume of the compartment, which depends on the amount of snow accumulated on the surface and the compartment density. The volume fraction of liquid water is set to 0.09 during summer [Fountain and Walder, 1998], and zero during winter. The volume fraction of solid ice is then calculated from the volume fractions of the other subcompartments, decreasing during summer due to the increase of the liquid water phase.
The ice temperature in the glacier surface $T_{\text{firn}}$ is monthly resolved as a function of depth (Equation (B.9)). The temperature in the deep glacier ($T_0$) is set to 273 K, the amplitude of the temperature ($A_T$) to 10 K, the cycle per time unit ($\omega$) is 1 per 12 months, the thermal diffusivity ($\alpha_T$) is $10^{-6}$ m$^2$s$^{-1}$. $z$ indicates the depth of the glacier compartment, while $t$ indicates the time.

$$T_{\text{firn}} = T_0 + A_T \exp(-z \sqrt{\frac{\pi \omega}{\alpha_T}}) \sin(2 \pi \omega t - z \sqrt{\frac{\pi \omega}{\alpha_T}})$$  \hspace{1cm} (B.9)$$

Other environmental parameters are constant and reported in Table B.1. The air height is set to 400 m, a value which is uncertain, but not influential (see Figure B.12).
Figure B.3: Map of Switzerland with the Silvretta glacier (red dot) and the meteorological stations Weissfluhjoch, Davos, Säntis, and Jungfraujoch (blue dots).

Figure B.4: Annual and winter snow accumulation at the ice core site (red line), site A (orange line), and site B (blue line) of the Silvretta glacier in meter water equivalent (m weq) per year. A negative snow accumulation indicates snowmelt. The solid black line is the simple moving average of the snow accumulation at the ice core site, with a lag of 5 years. The annual balance is reached in the last summer month; the winter balance in the last winter month. The snow accumulation of the remaining months is calculated by linear interpolation.
Figure B.5: Modeled firn temperature of the Silvretta ice core for the twelve months of the year, including the surface freezing during winter.
Table B.1: Constant environmental input parameters used in the model. Air height (estimated), volume fraction of organic matter in aerosol particles [FCAH, 2007], density of aerosol particles [FCAH, 2007], dry deposition velocity of aerosols [Daly and Wania, 2004], scavenging factor of snow [Franz and Eisenreich, 1998], scavenging factor of rain [Mackay, 2001], specific surface area of snowflakes [Legagneux et al., 2002], temperature gradient for elevation correction [Wallace and Hobbs, 2006], volume fraction of liquid water in glacier compartments [Fountain and Walder, 1998], volume fraction of organic matter in particles (set equal to aerosols), density of ice [Cuffey and Paterson, 2010], density of particles in ice (set equal to aerosols).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air compartment</strong></td>
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<td></td>
</tr>
<tr>
<td>Air height</td>
<td>m</td>
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</tr>
<tr>
<td>Volume fraction of organic matter in aerosol particles</td>
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</tr>
<tr>
<td>Density of aerosol particles</td>
<td>kg m$^{-3}$</td>
<td>1000</td>
</tr>
<tr>
<td>Dry deposition velocity of aerosols</td>
<td>m h$^{-1}$</td>
<td>1.8</td>
</tr>
<tr>
<td>Scavenging factor of snow</td>
<td>-</td>
<td>3.2 $10^5$</td>
</tr>
<tr>
<td>Scavenging factor of rain</td>
<td>-</td>
<td>2 $10^5$</td>
</tr>
<tr>
<td>Specific surface area of snowflakes</td>
<td>m$^2$ kg$^{-1}$</td>
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</tr>
<tr>
<td>Temperature gradient for elevation correction</td>
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<td><strong>Glacier compartments</strong></td>
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<td></td>
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<tr>
<td>Volume fraction of liquid water in glacier compartments (summer)</td>
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<td>0.09</td>
</tr>
<tr>
<td>Volume fraction of organic matter in particles</td>
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</tr>
<tr>
<td>Density of ice</td>
<td>kg m$^{-3}$</td>
<td>917</td>
</tr>
<tr>
<td>Density of particles in ice</td>
<td>kg m$^{-3}$</td>
<td>1000</td>
</tr>
</tbody>
</table>
B.4.2 Compartment Setup

The monthly accumulated or melted snow (=change in the local glacier mass balance) \((dM_{\text{ice}})\) dictates the compartment setup. The compartment setup is different for every site and every month, according to the specific mass balance. During winter, when the mass balance is positive, new compartments are formed on the glacier surface, with dimensions dictated by the mass balance. Let’s assume four winter months (months 1–4), with a mass balance \(dM_{\text{ice}} = 0.2\, \text{m weq month}^{-1}\). During the four months, four compartments are formed on the glacier surface, each one with dimensions of 0.2 m weq. This unit describes the vertical dimension and is, after being transformed to meters, multiplied with the surface area of the site to calculate the volume of the compartment.

\[
\begin{array}{cccc}
\text{(month 1)} & (2) & (3) & (4) \\
\begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} \\
\end{array}
\]

Following the function in Equation (B.7), the density of these four compartments increases with depth. The top compartments have the lowest density \((356\, \text{kg m}^{-3})\), which is the density in an average depth of 0.1 m weq.

\[
\begin{array}{cccc}
\text{(month 1)} & (2) & (3) & (4) \\
\begin{bmatrix} 356 \\ 356 \\ 356 \\ 356 \end{bmatrix} & \begin{bmatrix} 367 \\ 367 \\ 367 \\ 367 \end{bmatrix} & \begin{bmatrix} 378 \\ 378 \\ 378 \\ 378 \end{bmatrix} & \begin{bmatrix} 388 \\ 388 \\ 388 \\ 388 \end{bmatrix} \\
\end{array}
\]

During summer, the mass balance is negative. This means, material according to the mass balance is lost from the glacier surface, transforms to meltwater, percolates down, and is lost from the glacier column. Therefore, compartments on the surface shrink and are inactivated. Let’s assume three summer months, where the mass balance is \(-0.1\, \text{m weq month}^{-1}\). Every month, 0.1 m weq are lost from the glacier surface. Here are the dimensions of the compartments for the four winter and three summer months.

\[
\begin{array}{cccccc}
\text{(month 1)} & (2) & (3) & (4) & (5) & (6) & (7) \\
\begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.1 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} & \begin{bmatrix} 0.2 \\ 0.2 \end{bmatrix} \\
\end{array}
\]
The densities of the compartments do not decrease when approaching the surface, leading to a higher compartment density on the glacier surface during summer than during winter.

Once the dimensions of the compartments in m weq and the densities are defined, we can calculate the dimension of the compartment in meter using Equation (B.10), where $L_m$ is the dimension of the compartment in meter, and $L_{m\text{weq}}$ is the dimension of the compartment in meter water equivalent, $\rho_{\text{wat}}$ is the density of water, and $\rho$ the density of the compartment.

$$L_m = L_{m\text{weq}} \cdot \frac{\rho_{\text{wat}}}{\rho}$$ (B.10)

In addition to the mass lost from the surface by the negative mass balance (snowmelt), additional mass is lost from the surface to refreeze in lower compartments. This amount is set to 20% of the mass balance (see Meltwater Percolation and Runoff for more information). Therefore, in our example, additional 0.02 m weq are lost from the surface per month. As a consequence, in total, 0.12 m weq are melt on the surface, and percolate down; 0.02 m weq are added to underlying compartments; 0.1 m weq run off as meltwater runoff. In this example, we assume the refreezing to happen uniformly in all compartments, however, in the model, the refreezing meltwater is distributed to the compartments as a function of depth and density (see main text and Meltwater Percolation and Runoff). The dimensions of the compartments (m weq) are then the following.
The dimension of the compartment on the glacier surface in the last month (0.047 m weq) is below the cutoff size of 5 cm weq. In order to minimize the number of compartments in the model, a compartment below the cutoff size is inactivated, and its mass is transferred to the underlying compartment, which increases from 0.227 to 0.274 m weq.

\[
\begin{bmatrix}
0.2 \\
0.2 \\
0.2
\end{bmatrix}
\]

\[
\begin{bmatrix}
0.08 \\
0.207 \\
0.207
\end{bmatrix}
\]

\[
\begin{bmatrix}
0.167 \\
0.217 \\
0.217
\end{bmatrix}
\]

\[
\begin{bmatrix}
0.274 \\
0.227
\end{bmatrix}
\]

Except for the compartments on the surface, from where the refreezing meltwater is lost, the refreezing does not change the size of the compartments in meter, as the compartments within the glacier can not increase or decrease in size. However, the refreezing increases the density of the compartments where the meltwater refreezes. We can calculate the new densities using Equation (B.11), where \( L_{\text{mweq}} \) is the compartment dimension in m weq, \( L_m \) is the compartment dimension in m, and \( \rho_{\text{wat}} \) is the density of water (1000 kg m\(^{-3}\), or here unit-wise more correct: kg m\(^{-2}\) m weq\(^{-1}\)). In addition, due to solar radiation, the density of the surface compartment increases by 20% in each summer month (not shown here).

\[
\rho = L_{\text{mweq}} \times \rho_{\text{wat}} / L_m
\]  

(B.11)

\[
\begin{bmatrix}
356 \\
367 \\
378
\end{bmatrix}
\]

\[
\begin{bmatrix}
356 \\
380 \\
401
\end{bmatrix}
\]

\[
\begin{bmatrix}
380 \\
410 \\
421
\end{bmatrix}
\]

\[
\begin{bmatrix}
429 \\
440
\end{bmatrix}
\]

This compartment setup leads to a monthly varying number of compartments in the system. As the setup depends on the local mass balance, the number of compartments is individual for every site on the glacier surface. Figure B.6 illustrates the number of compartments between 1900 and 2010 (1332 months) on the ice core site, site A, and site B.
Figure B.6: Number of compartments in the system between 1900 and 2010 at the ice core site, site A, and site B of the Silvretta glacier. On all sites, the number of compartments increases until the 1980s, when ice accumulation decreases. As a consequence, the number of compartments remains constant (ice core site, site A) or decreases (site B).

Figure B.7: Modeled age-depth relationship as calculated from the snow accumulation and meltwater refreezing at the ice core site (red line), site A (yellow line), and site B (blue line). Age-depth relationship derived by isotopic tritium (³H) dating (red dot) [Pavlova et al., 2015a; Pavlova, 2014]. The smaller snow accumulation on site B leads to an older age of compartments at a smaller depth. The ice formed in the 1970s is located at 30–40 m depth (ice core), 30 m depth (site A), and 10 m depth (site B).
B.4.3 Meltwater Percolation and Runoff

Functions and parameters of meltwater processes are selected in a way that modeled and measured [Pavlova et al., 2015a] density profiles in the ice core are similar (Figure B.8). As described in the main text and above, the amount of snow melt at the glacier surface and lost from the glacier as runoff is equal to the total change in local mass balance ($dM_{\text{ice}}$, m weq month$^{-1}$). Snowmelt only occurs during summer when $dM_{\text{ice}}$ is negative. Snowmelt processes are active down to a depth of 15 m weq ($d_{\text{max}}$).

The amount of meltwater lost from individual glacier compartments as runoff ($U_{w,\text{run}}$) is inversely correlated to depth ($d$) (Equation (B.12)). The distribution of meltwater runoff to the glacier compartments ($U_{w,\text{run, key}}$, a value between 0 and 1) is first calculated as a function of depth, relative to the maximum depth where the process is active ($d_{\text{max}}$). Then, $U_{w,\text{run, key}}$ is multiplied by $dM_{\text{ice}}$ and divided by its sum, so that the sum of meltwater lost from the glacier compartments corresponds to $dM_{\text{ice}}$ (Equation (B.13)). The unit of $U_{w,\text{run}}$ is m weq month$^{-1}$.

$$U_{w,\text{run, key}} = 1 - \frac{d}{d_{\text{max}}} \quad \text{(B.12)}$$

$$U_{w,\text{run}} = U_{w,\text{run, key}} \cdot \frac{-dM_{\text{ice}}}{\sum U_{w,\text{run, key}}} \quad \text{(B.13)}$$

The amount of snow melt at the glacier surface for refreezing in the glacier compartments is set to 20% of $dM_{\text{ice}}$. The amount of meltwater refreezing in individual glacier compartments ($U_{w,\text{freez}}$) is a function of compartment density ($\rho$) and depth ($d$) (Equation (B.14)), where depth is weighted to be twice as important as density. The distribution-parameter ($U_{w,\text{freez, key}}$) is then multiplied by $0.2 \cdot -dM_{\text{ice}}$ and divided by its sum, so that the total amount of refreezing meltwater is 20% of $dM_{\text{ice}}$ (Equation (B.15)). The unit of $U_{w,\text{freez}}$ is m weq month$^{-1}$.

$$U_{w,\text{freez, key}} = \frac{\rho}{\rho_{\text{max}}} + 2 \cdot (1 - \frac{d}{d_{\text{max}}}) \quad \text{(B.14)}$$

$$U_{w,\text{freez}} = U_{w,\text{freez, key}} \cdot \frac{0.2 \cdot -dM_{\text{ice}}}{\sum U_{w,\text{freez, key}}} \quad \text{(B.15)}$$
B.4 Environmental System

Figure B.8: Modeled (red line) and measured (black line [Pavlova et al., 2015a]) density profiles in the Silvretta ice core. The modeled density profile is averaged over the sample depth.

Figure B.9: Modeled density profiles on the ice core site (red line, left plot), site A (orange line, middle plot), and site B (blue line, right plot). In contrast to Figure B.8, the density profiles are not averaged over the sample depth. The stronger melt on sites A and B leads to strong melt layers (high densities) in the upper 20 m.
B.4.4 Particle Percolation and Runoff

Similar to the meltwater processes, we select functions and parameters of particle processes by comparing the modeled black carbon profile with the black carbon profile measured in the ice core [Pavlova et al., 2015a] (Figure B.10). For this, we assume a black carbon content of the aerosol particles in the model of 2.4%, according to PM10 and black carbon measurements from Jungfraujoch [EMEP, 2014]. Modeled and measured black carbon profiles are similar.

The fraction of particles washed out from a glacier compartment and leaving the glacier as particle runoff ($f_{p,\text{run}}$) is a function of compartment density ($\rho$) and depth ($d$), with increasing runoff when density and depth are low (Equation (B.16)). Again, depth is weighted to be twice as important as density. The parameter $f_{p,\text{run}}$ is unitless, as this is a fraction of the particles that are present in a specific glacier compartment. This fraction is set to reach a maximum of 0.02, therefore, $f_{p,\text{run,\text{key}}}$ is multiplied by 0.02 and divided by its maximum value ($f_{p,\text{run,\text{key,\text{max}}}}$) (Equation (B.17)). In the model, particles are washed out from a glacier compartment to leave the glacier as particle runoff down to a depth of 10 m weq.

\[
f_{p,\text{run,\text{key}}} = (1 - \frac{\rho}{\rho_{\text{max}}}) + 2 \times (1 - \frac{d}{d_{\text{max}}}) \quad \text{(B.16)}
\]

\[
f_{p,\text{run}} = f_{p,\text{run,\text{key}}} \times \frac{0.02}{f_{p,\text{run,\text{key,\text{max}}}}} \quad \text{(B.17)}
\]

The fraction of particles washed out from a glacier compartment and being relocated with percolating meltwater ($f_{p,\text{perc}}$) is also a function of compartment density and depth (Equation (B.18)). Again, this parameter is unitless, as it describes a fraction of the particles in the glacier compartment, and its maximum value is set to 0.01 (Equation (B.19)). In the model, particles are washed out from a glacier compartment to be relocated down to a depth of 10 m weq.

\[
f_{p,\text{perc,\text{key}}} = (1 - \frac{\rho}{\rho_{\text{max}}}) + 2 \times (1 - \frac{d}{d_{\text{max}}}) \quad \text{(B.18)}
\]

\[
f_{p,\text{perc}} = f_{p,\text{perc,\text{key}}} \times \frac{0.01}{f_{p,\text{perc,\text{key,\text{max}}}}} \quad \text{(B.19)}
\]
Figure B.10: Modeled (red line) and measured (black line [Pavlova et al., 2015a]) black carbon profile in the Silvretta ice core, using a black carbon content of aerosols of 2.4% (red line). Modeled and measured profiles are averaged over the sample depth.

Figure B.11: Modeled black carbon profiles on the ice core site (red line, left plot), site A (orange line, middle plot), and site B (blue line, right plot). In contrast to Figure B.10, the profiles are not averaged over depth, but correspond to the individual compartments. The stronger melt on sites A and B leads to stronger enrichment of particles (higher concentrations) in the surface layers.
B.5 Input of Chemicals into the System

The maximum PCB emission scenario by Breivik et al. [2007] was used as input to the global chemical fate model BETR Research [Wöhnschimmel et al., 2013]. BETR Research includes 288 regions on a $15^\circ \times 15^\circ$ resolution, with each region containing seven compartments: upper air, lower air, vegetation, fresh water, ocean water, soil, and freshwater sediment. The upper air compartment describes the free troposphere, while the lower air compartment represents the planetary boundary layer. We assume an air mix of 20% tropospheric air and 80% boundary layer air reaching Silvretta glacier during summer, and pure tropospheric air reaching Silvretta glacier during winter. The mixing ratio during summer was estimated from seasonal variations in sulfate concentration in aerosol particles at Jungfraujoch, compared to sulfate concentrations in the Swiss lowlands. For more information please refer to the Supporting Information of Steinlin et al. [2014].

B.6 Physicochemical and Kinetic Properties of PCBs

Physicochemical properties of the six indicator PCBs are shown in Table B.2.

B.6.1 Basic Partition Coefficients

The partition coefficients octanol–water ($K_{ow}$), air–water ($K_{aw}$), and octanol–air ($K_{oa}$) are adjusted to temperature using the van’t Hoff equation (Equations (B.20)–(B.22)), where $dU$ is the energy of phase change (J mol$^{-1}$), $R$ the gas constant (8.31 J mol$^{-1}$ K$^{-1}$), $T_c$ the temperature of the property data (K), and $T$ the temperature in a specific compartment (K).

$$K_{ow}(T) = K_{ow}(T_c) \times \exp\left(\frac{dU_{ow}}{R} \times \left(\frac{1}{T_c} - \frac{1}{T}\right)\right)$$

(B.20)

$$K_{aw}(T) = K_{aw}(T_c) \times \exp\left(\frac{dU_{aw}}{R} \times \left(\frac{1}{T_c} - \frac{1}{T}\right)\right)$$

(B.21)

$$K_{oa}(T) = K_{oa}(T_c) \times \exp\left(\frac{dU_{oa}}{R} \times \left(\frac{1}{T_c} - \frac{1}{T}\right)\right)$$

(B.22)

B.6.2 Particle–Air Partitioning

The aerosol particle–air (in the atmosphere, $K_{pa,air}$) and particle–pore air (in the glacier, $K_{pa,gla}$) partition coefficients are calculated from the temperature-adjusted $K_{oa}$ and the fraction of organic matter in the particle ($f_{om}$) as described by Harner and Bidleman
Table B.2: Physicochemical and kinetic properties of the PCB congeners 28, 52, 101, 138, 153, and 180. Molar mass, octanol–water, air–water, and octanol–air partition coefficients [Schenker et al., 2005], energy of phase changes octanol–water, air–water, and octanol–air [Schenker et al., 2005], electron acceptor (A) and electron donor (B) properties [van Noort et al., 2010], hexadecane–air partition coefficient [Abraham and Al-Hussaini, 2005], degradation rate constants in air [Anderson and Hites, 1996] and in ice [Matykiewiczová et al., 2007], activation energy of the rate constant in air [Bogdal et al., 2010].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>PCB 28</th>
<th>PCB 52</th>
<th>PCB 101</th>
<th>PCB 138</th>
<th>PCB 153</th>
<th>PCB 180</th>
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<tbody>
<tr>
<td>molar mass</td>
<td>g/mol</td>
<td>257.5</td>
<td>292.0</td>
<td>326.4</td>
<td>360.9</td>
<td>360.9</td>
<td>395.3</td>
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<td>7.19</td>
<td>6.86</td>
<td>7.15</td>
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<td>-1.96</td>
<td>-2.08</td>
<td>-1.97</td>
<td>-2.13</td>
<td>-2.51</td>
</tr>
<tr>
<td>log $K_{oa}$</td>
<td>[-]</td>
<td>7.86</td>
<td>8.22</td>
<td>8.83</td>
<td>9.67</td>
<td>9.45</td>
<td>10.17</td>
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<td>$dU_{ow}$</td>
<td>kJ/mol</td>
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<td>-27.5</td>
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<td>-26.6</td>
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<td>$dU_{aw}$</td>
<td>kJ/mol</td>
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<td>53.8</td>
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<tr>
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<td>-81.3</td>
<td>-84.4</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
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<td>9.78</td>
<td>9.59</td>
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<td>$10^{-12}$ cm$^3$/molecule$^{-1}$ s$^{-1}$</td>
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<td>0.74</td>
<td>0.45</td>
<td>0.27</td>
<td>0.27</td>
<td>0.16</td>
</tr>
<tr>
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<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
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</tr>
<tr>
<td>$E_{a, air}$</td>
<td>kJ/mol</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

$^a_{wet}K_{ow}$.

[1998] (Equation (B.23)). The factor $10^9$ transforms the units of $K_{pa, dim}$ from m$^3$ µg$^{-1}$ to m$^3$kg$^{-1}$. The partition coefficient with dimensions ($K_{pa, dim}$) is then transformed to the unitless partition coefficients using the density of aerosols ($\rho_{aer}$, kg m$^{-3}$) and particles ($\rho_{par}$, kg m$^{-3}$) (Equations (B.24)–(B.25), Table B.2).

\[
K_{pa, dim} = 10^9 \times 10^{(\log K_{oa} + \log f_{om} - 11.91)} \tag{B.23}
\]
\[
K_{pa, air} = K_{pa, dim} \times \rho_{aer} \tag{B.24}
\]
\[
K_{pa, gla} = K_{pa, dim} \times \rho_{par} \tag{B.25}
\]

### B.6.3 Snow Surface–Air Partitioning

The snow surface–air partition coefficient is calculated from the hexadecane–air partition coefficient ($K_{ha}$), electron acceptor property (A), and electron donor property (B)
according to Roth et al. [2004] (Equation (B.26)). $K_{ca, dim,c}$ has units of m³ m⁻² and is valid for −6.8 °C.

$$\log K_{ca, dim,c} = 0.639 \times \log K_{ha} + 3.53 \times A + 3.38 \times B - 6.85 \quad (B.26)$$

Temperature dependence is calculated using Equation (4) in Goss and Schwarzenbach [Goss and Schwarzenbach, 1999] (Equation (B.27)), where $T_{cc}$ is −6.8 °C, $T_{av}$ is the average temperature in the considered temperature range, $T$ is the actual temperature in a glacier compartment, and $\Delta H$ the enthalpy of sorption.

$$K_{ca, dim} = K_{ca, dim,c} \times \exp\left(\frac{-\Delta H + R \times T_{av} \times \left(\frac{1}{T} - \frac{1}{T_{cc}}\right)}{R}\right) \quad (B.27)$$

The enthalpy of sorption ($\Delta H$) is assumed to be constant, and is calculated as a function of $K_{ca, dim,c}$, similar to Equation (11) in Goss and Schwarzenbach [1999] (Equation (B.28)). In Equation (B.28), $K_{ca, dim,c}$ is valid at 20 °C, therefore, we adapted this equation for the use of $K_{ca, dim,c}$ at −6.8 °C (Equation (B.29)).

$$\Delta H = -5.26 \times \ln K_{ca, dim,c} - 112 \quad (B.28)$$

$$\Delta H = -4.32 \times \ln K_{ca, dim,c} - 92.4 \quad (B.29)$$

The unitless partition coefficients snowflake–air ($K_{sa}$, in the atmosphere) and glacier ice–pore air ($K_{ga}$, in the glacier) are then calculated using the snow surface area of snowflakes ($A_{sf}$) and ice ($A_{ice}$) in the specific compartment and the density of ice ($\rho_{ice}$) (Equations (B.30)–(B.31)). While $A_{sf}$ has a constant value of 96 m² kg⁻¹ (Table B.1), $A_{ice}$ is a function of density up to compartment densities of 500 kg m⁻³ (Equation (B.32), [Dominé et al., 2007]), and set to a constant value of 10 m² kg⁻¹ in compartments with densities above 500 kg m⁻³.

$$K_{sa} = K_{ca, dim} \times A_{sf} \times \rho_{ice} \quad (B.30)$$

$$K_{ga} = K_{ca, dim} \times A_{ice} \times \rho_{ice} \quad (B.31)$$

$$A_{gla} = -313.17 \times \ln \rho + 160.1 \quad (B.32)$$

### B.6.4 Degradation Rate Constants

The degradation rate constant in air ($k_{air}$) is calculated from the second-order rate constant for the degradation with hydroxyl radicals ($k_{air, sec}$, cm³ molecule⁻¹ s⁻¹, Table B.2) and the concentration of hydroxyl radicals in the atmosphere ($C_{OH}$, molecules cm⁻³) (Equation (B.33)). The second-order rate constant is calculated from the degree of chlorination ($N_{Cl}$) of the PCB congeners using a regression presented in Anderson and Hites [1996] (Equation (B.34)). The concentration of hydroxyl radicals is seasonally resolved, varying between $1.4 \times 10^5$ and $25.1 \times 10^5$ molecules cm⁻³, and is valid for a latitude
of 44°N and a pressure of 700 hPa [Spivakovsky et al., 2000]. The degradation rate constant is adjusted to temperature using the two-point Arrhenius equation (Equation (B.35)), where $E_{a,\text{air}}$ is the activation energy of the rate constant in air (J mol$^{-1}$, Table B.1), $R$ is the gas constant (8.31 J mol$^{-1}$ K$^{-1}$), $T_c$ the temperature of the property data (K), and $T$ the air temperature (K).

$$k_{\text{air}}(T) = k_{\text{air}}(T_c) \times \exp\left(-\frac{E_{a,\text{air}}}{R} \times \left(\frac{1}{T} - \frac{1}{T_c}\right)\right)$$  \hfill (B.35)

The photochemical degradation rate constant reported in Table B.2 corresponds to a halflife of approximately one year [Matykiewiczová et al., 2007]. We assume this rate constant to be the average rate constant in the model, and adapt it to seasonal changes in radiation using a factor of 1.5, according to the seasonal variation in radiation at Weissfluhjoch [MeteoSwiss, 2014a]. This factor increases the rate constant during the summer months and decreases the rate constant during the winter months. Photochemical degradation is occurring only in the top glacier compartment, and only in the top 15 cm of the compartment [Grannas et al., 2007]. This means, the degradation rate constant is decreased if the surface compartment is higher than 15 cm. We assume that only the fraction of chemicals in the solid ice subcompartment can be degraded photochemically.

### B.6.5 Molecular Diffusivity

Molecular diffusivity in air ($d_{\text{diff,air}}$, m$^2$ s$^{-1}$) is a function of the molar mass ($M$, g mol$^{-1}$) according to Schwarzenbach et al. [2003] (Equation (B.36)).

$$d_{\text{diff,air}} = \frac{1.55}{M^{0.65}} / 10000$$  \hfill (B.36)

### B.6.6 Fugacity Capacities

The fugacity capacities of the pure phases (Z-values) are calculated as a function of the partition coefficients [Mackay, 2001]. Equations (B.37)–(B.38) illustrate the calculation of the fugacity capacities in pure air ($Z_a$) and pure water ($Z_w$). The fugacity capacities of the compartments are then calculated as a function of the fugacity capacities of the subcompartments (pure phases) and the volume fractions of the subcompartments in the compartment. For more information on fugacity capacities we refer to Mackay
$Z_a = \frac{1}{R * T}$ \hspace{1cm} (B.37)

$Z_w = \frac{Z_a}{K_{aw}}$ \hspace{1cm} (B.38)

## B.7 Chemical Fate Processes

The D-values used in the system of differential equations in Equation (B.1) are calculated by combining the D-values of every single process accounted for in the model.

### B.7.1 Air Advection

The D-value of air advection ($D_{\text{adv,air}}$) is calculated by multiplying the amount of air flowing in and out of the system ($G_{\text{air}}$, m$^3$ month$^{-1}$) and the fugacity capacity of the air compartment ($Z_{\text{air}}$, mol Pa$^{-1}$ m$^{-3}$) (Equation (B.39)).

$$D_{\text{adv,air}} = G_{\text{air}} * Z_{\text{air}}$$ \hspace{1cm} (B.39)

### B.7.2 Degradation

The D-values of degradation by OH-radicals in air ($D_{\text{deg,air}}$) and photochemical degradation in the glacier surface ($D_{\text{deg,gla}}$) are shown in Equations (B.40)–(B.41). The following parameters are used in the equations: degradation rate constant in air ($k_{\text{air}}$, month$^{-1}$), degradation rate constant in the glacier surface ($k_{\text{pho}}$, month$^{-1}$), volumes of air and glacier surface active for photochemical degradation ($V_{\text{air}}$ and $V_{\text{pho}}$, m$^3$), and the fugacity capacities of the subcompartments air and ice ($Z_a$, $Z_{\text{ice}}$, mol Pa$^{-1}$ m$^{-3}$). The use of $Z_{\text{ice}}$ here means that only the fraction of chemicals in the solid ice subcompartment is transformed by photochemical degradation.

$$D_{\text{deg,air}} = k_{\text{air}} * V_{\text{air}} * Z_a$$ \hspace{1cm} (B.40)

$$D_{\text{deg,gla}} = k_{\text{pho}} * V_{\text{pho}} * Z_{\text{ice}}$$ \hspace{1cm} (B.41)

### B.7.3 Deposition

The D-values of deposition from the atmosphere to the glacier surface are shown in Equations (B.42)–(B.46). Dry particle deposition (dp), wet particle deposition (wp), and wet gaseous deposition (wg). While $D_{\text{dep,wp,loss}}$ and $D_{\text{dep,wg,loss}}$ are losses from the system, occurring during summer, $D_{\text{dep,dp}}$, $D_{\text{dep(wp)}}$, and $D_{\text{dep,wg}}$ transfer chemical from
the atmosphere to the glacier, with $D_{\text{dep,dp}}$ being active during winter and summer, and $D_{\text{dep,wp}}$ and $D_{\text{dep,wg}}$ being active only during winter. The following parameters are used in the equations: particle deposition rate ($U_{\text{aer}}$, m month$^{-1}$), surface area of glacier sections ($A_{\text{gla}}$, m$^2$), fugacity capacities of the subcompartments aerosol particles, snowflakes, and raindrops ($Z_{\text{aer}}$, $Z_{\text{sf}}$, $Z_{\text{w}}$, mol Pa$^{-1}$ m$^{-3}$), precipitation to the glacier surface (winter) ($U_{\text{snow}}$, m weq month$^{-1}$), precipitation as direct runoff (summer) ($U_{\text{rain}}$, m weq month$^{-1}$), scavenging factor of snow (winter) or rain (summer) ($Q_{\text{snow}}$ and $Q_{\text{rain}}$, unitless), and the volume fraction of aerosol particles in the atmosphere ($f_{\text{aer}}$, unitless).

\[
D_{\text{dep,dp}} = U_{\text{aer}} \times A_{\text{gla}} \times f_{\text{aer}} \times Z_{\text{aer}} \quad (B.42)
\]

\[
D_{\text{dep,wp}} = U_{\text{snow}} \times Q_{\text{snow}} \times A_{\text{gla}} \times f_{\text{aer}} \times Z_{\text{aer}} \quad (B.43)
\]

\[
D_{\text{dep,wp,loss}} = U_{\text{rain}} \times Q_{\text{rain}} \times A_{\text{gla}} \times f_{\text{aer}} \times Z_{\text{aer}} \quad (B.44)
\]

\[
D_{\text{dep,wg}} = U_{\text{snow}} \times A_{\text{gla}} \times Z_{\text{sf}} \quad (B.45)
\]

\[
D_{\text{dep,wg,loss}} = U_{\text{snow}} \times A_{\text{gla}} \times Z_{\text{w}} \quad (B.46)
\]

### B.7.4 Wind Pumping

Dry gaseous deposition and revolatilization between the atmosphere and the glacier surface as well as between the top and the second glacier compartments are described as advection due to wind-pumping [Meyer and Wania, 2010]. The D-value of this exchange ($D_{\text{adv,airgla}}$) is a function of the mass transfer coefficient from the atmosphere to the glacier ($U_{\text{airgla}}$) and the mass transfer coefficient from the glacier to the atmosphere ($U_{\text{glaair}}$), as well as the area of the glacier section ($A_{\text{gla}}$), and the fugacity capacity of the air ($Z_{a}$) and the pore air ($Z_{\text{poreair}}$) (Equation (B.47)).

\[
D_{\text{adv,airgla}} = \frac{1}{U_{\text{airgla}} \times A_{\text{gla}} \times Z_{a}} + \frac{1}{U_{\text{glaair}} \times A_{\text{gla}} \times Z_{\text{poreair}}} \quad (B.47)
\]

The mass transfer coefficient from the atmosphere to the glacier ($U_{\text{airgla}}$) is a function of wind speed ($U_{\text{wind}}$, m month$^{-1}$) and the aerodynamic roughness length on the glacier ($z_0$, m), which is set to 0.023 m, an average between values reported for snow and ice [Gerbaux et al., 2005] (Equation (B.48)).

\[
U_{\text{airgla}} = 0.42 \times U_{\text{wind}} \times \frac{1}{\ln\left(\frac{10}{z_0}\right) \times \ln\left(\frac{2}{z_0}\right)} \quad (B.48)
\]

The mass transfer coefficient from the glacier to the atmosphere ($U_{\text{glaair}}$) is a function of permeability ($P$, m$^2$), the air viscosity ($\mu$, Pa s), the pressure amplitude ($p_0$, Pa), and the depth of the compartment ($d$, m) (Equation (B.49)).

\[
U_{\text{glaair}} = \frac{P}{\mu} \times \frac{p_0}{\ln 2 \times d} \quad (B.49)
\]
Permeability is calculated from open porosity ($\phi_{\text{open}}$) (Equation (B.50)), which is calculated from total porosity ($\phi_{\text{tot}}$) and closed porosity ($\phi_{\text{closed}}$) (Equation (B.51)), where the latter is estimated from the total porosity using the Schwander relationship [Schwander, 1989; Adolph and Albert, 2014] (Equation (B.52)), using a pore close off density of 830 kg m$^{-3}$ [Cuffey and Paterson, 2010].

$$P = 10^{7.7} \bullet \phi_{\text{open}}^{3.4} \quad \text{(B.50)}$$

$$\phi_{\text{open}} = \phi_{\text{tot}} - \phi_{\text{closed}} \quad \text{(B.51)}$$

$$\phi_{\text{closed}} = \begin{cases} 
\phi_{\text{tot}} \times \exp(75 \bullet (\frac{\rho}{830} - 1)) & \text{if } \rho < 830, \\
\phi_{\text{tot}} & \text{if } \rho \geq 830.
\end{cases} \quad \text{(B.52)}$$

The pressure amplitude ($p_0$) is calculated as a function of the density of air ($\rho_{\text{air}}$, kg m$^{-3}$), the wind speed ($U_{\text{wind}}$, m month$^{-1}$), the surface roughness amplitude ($A_{\text{sr}}$, m), and the surface roughness wavelength ($\lambda$, m) (Equation (B.53)). The surface roughness amplitude is calculated from the aerodynamic roughness length ($z_0$) [Meyer and Wania, 2010; Seinfeld and Pandis, 1998] (Equation (B.54)), while the surface roughness wavelength is set to 10 m.

$$p_0 = 3 \bullet \rho_{\text{air}} \bullet U_{\text{wind}}^2 \bullet A_{\text{sr}} \over \lambda \quad \text{(B.53)}$$

$$A_{\text{sr}} = z_0 \bullet 30 \quad \text{(B.54)}$$

### B.7.5 Molecular Diffusion

Exchange between the second and all the lower glacier compartments is described by molecular diffusion ($D_{\text{diff}}$) (Equation (B.55)), where diffusion between compartment $i$ and compartment $j$ is a function of the mass transfer coefficient ($U_{\text{gla}}$, m month$^{-1}$), the area of the glacier section ($A_{\text{gla}}$, m$^2$) and the fugacity capacity of the pore air ($Z_{\text{poreair}}$, mol Pa$^{-1}$ m$^{-3}$). The mass transfer coefficient is calculated from the effective diffusivity in pore air ($d_{\text{diff,eff}}$, m$^2$ month$^{-1}$) and the size of the compartment ($L_m$, m) (Equation (B.56)). The effective diffusivity is a function of the diffusivity in air and the volume fraction of pore air in the compartment ($f_{\text{poreair}}$, unitless) (Equation (B.57)) [Millington, 1959].
B.8 Sensitivity and Uncertainty Analysis

The following parameters were included in the sensitivity and uncertainty analysis:

1. octanol–water partition coefficient (confidence factor (cf) = 1.1 on log value)
2. air–water partition coefficient (cf = 1.1 on log value)
3. octanol–air partition coefficient (cf = 1.1 on log value)
4. energy of phase change octanol–water (cf = 1.2)
5. energy of phase change air–water (cf = 1.2)

\[ D_{\text{diff}} = \frac{1}{U_{\text{gla},i} * A_{\text{gla}} * Z_{\text{poreair},j} * U_{\text{gla},j} * A_{\text{gla}} * Z_{\text{poreair},j}} \quad (B.55) \]

\[ U_{\text{gla}} = \frac{d_{\text{diff,eff}}}{0.5 * L_m} \quad (B.56) \]

\[ d_{\text{diff,eff}} = d_{\text{diff,air}} * j_{\text{poreair}}^{4/3} \quad (B.57) \]

B.7.6 Meltwater Processes

Chemicals can percolate through the glacier column or leave the glacier with meltwater. The D-values of percolating meltwater \((D_{\text{meltflux}})\) and meltwater runoff \((D_{\text{meltrunoff}})\) are calculated from the meltwater flux \((U_{\text{meltflux}} \text{ and } U_{\text{meltrunoff}}, \text{ m month}^{-1})\), the area of the glacier section \((A_{\text{gla}}, \text{ m}^2)\), and the fugacity capacity of the pore water \((Z_w, \text{ mol Pa}^{-1} \text{ m}^{-3})\) (Equations (B.58)–(B.59)).

\[ D_{\text{meltflux}} = U_{\text{meltflux}} * A_{\text{gla}} * Z_w \quad (B.58) \]

\[ D_{\text{meltrunoff}} = U_{\text{meltrunoff}} * A_{\text{gla}} * Z_w \quad (B.59) \]

B.7.7 Particle Processes

The D-values of percolating particles \((D_{\text{partflux}})\) and particle runoff \((D_{\text{partrunoff}})\) are calculated as a function of the particle flux \((U_{\text{partflux}} \text{ and } U_{\text{partrunoff}}, \text{ m month}^{-1})\), the area of the glacier section \((A_{\text{gla}}, \text{ m}^2)\), and the fugacity capacity of the particles \((Z_{\text{par}}, \text{ mol Pa}^{-1} \text{ m}^{-3})\) (Equations (B.60)–(B.61)).

\[ D_{\text{partflux}} = U_{\text{partflux}} * A_{\text{gla}} * Z_{\text{par}} \quad (B.60) \]

\[ D_{\text{partrunoff}} = U_{\text{partrunoff}} * A_{\text{gla}} * Z_{\text{par}} \quad (B.61) \]
6. energy of phase change octanol–air (cf= 1.2)
7. hexadecane–air partition coefficient (cf= 1.1 on log value)
8. electron acceptor properties (cf= 1.5)
9. electron donor properties (cf= 1.5)
10. degradation rate constant in air (cf= 3)
11. OH radical concentration in air (cf= 1.5)
12. degradation rate constant in water (not used in this model version)
13. degradation rate constant in glacier surface (cf= 10)
14. activation energy of degradation rate constant in air (cf= 1.2)
15. activation energy of degradation rate constant in water (not used in this model version)
16. factor to adjust the photochemical degradation rate to seasonal changes in radiation (cf= 1.5)
17. depth to which photochemical degradation is active (cf= 3)
18. surface area of glacier site (cf= 2)
19. height of air compartment (cf= 3)
20. volume fraction of aerosol particles in the atmosphere (cf= 1.5)
21. volume fraction of liquid water in glacier compartments (cf= 2)
22. volume fraction of organic matter in aerosol particles (cf= 1.5)
23. volume fraction of organic matter in particles in glacier (cf= 1.5)
24. density of aerosol particles (cf= 1.5)
25. density of particles in glacier (cf= 1.5)
26. specific surface area of snowflakes (cf= 1.2)
27. specific surface area of snow/ice in glacier (cf= 2)
28. particle deposition rate (cf= 3)
29. scavenging factor of rain (cf= 5)
30. scavenging factor of snow (cf= 5)
31. air temperature (cf= 1.02)
32. glacier temperature (cf= 1.2)
33. temperature gradient for elevation correction (cf= 1.2)
34. monthly precipitation (cf= 1.5)
35. wind speed (cf= 1.5)
36. annual local glacier mass balance (snow accumulation) (cf= 1.5)
37. winter local glacier mass balance (snow accumulation) (cf= 1.5)
38. cutoff size of compartments below which compartments are added to the underlying compartment (cf= 2)
39. factor $X_2$ in density function (Equation (B.7)) (cf= 1.5)
40. factor $X_3$ in density function (Equation (B.7)) (cf= 1.2)
41. aerodynamic roughness length on the glacier (cf= 1.2)
42. pore close off density (cf= 1.05)
43. surface roughness wavelength (cf= 2)
44. molecular diffusivity in the atmosphere (cf= 1.05)
45. factor by how much the density of the surface compartment increases in summer (cf= 1.5)
46. factor for refreezing (fraction of $dM_{\text{ice}}$ for additional melt on the glacier surface and refreezing) (cf= 2)
47. depth to which refreezing is active (cf= 1.5)
48. depth to which meltwater runoff is active (cf= 1.5)
49. depth to which particle runoff is active (cf= 1.5)
50. depth to which particle relocation is active (cf= 1.5)
51. maximum fraction of particles washed out from glacier for runoff (cf= 10)
52. maximum fraction of particles washed out from glacier for relocation (cf= 10)
53. fraction of particles in the particle layer that are washed off (not used in this model version)
54. size of particle layer (not used in this model version)
55. PCB concentration in the free troposphere used for chemical input to the model
56. PCB concentration in the planetary boundary layer used for chemical input to the model
Figure B.12: Results of the sensitivity analysis for PCB 28 (blue bars), 101 (green bars), and 180 (yellow bars), at the ice core site, site A, and site B of the Silvretta glacier. Sensitivity is calculated for the total amount of chemicals stored in the glacier in 2010. Only parameters with a sensitivity of more than 0.5, or less than -0.5 are shown.
Figure B.13: Parameter uncertainty analysis on the amount of chemicals stored in the glacier column in December 2010 at the ice core site of the Silvretta glacier. The contribution to variance of the output is shown for the 56 parameters included in the sensitivity and uncertainty analysis. Only the names of parameters having a contribution of more than 0.5% are shown in the Figure.
B.9 Model Validation

Figure B.14: Snow/ice-air partition coefficients estimated using the Roth et al. [2004] method (Silvretta model), and calculated from air and snowfall concentrations [Franz and Eisenreich, 1998; Agrell et al., 2002], or from air concentrations and concentrations in freshly fallen snow on the ground [Herbert et al., 2005; Finizio et al., 2006] reported in the literature. All partition coefficients are corrected for a temperature of 0°C. The values from Franz and Eisenreich [1998] and Herbert et al. [2005] are corrected for the particle fraction, the values from Agrell et al. [2002] and Finizio et al. [2006] are not particle corrected. The data is shown for tri- (PCB 28), tetra- (PCB 52), penta- (PCB 101), hexa- (PCB 138, PCB 153), and hepta- (PCB 180) chlorobiphenyl. The data of Agrell et al. is valid for individual congeners, the other studies report data for tri-, tetra-, penta-, hexa-, and heptachlorobiphenyl. The measured partition coefficients have a large variability. However, for the lower-chlorinated congeners, the Roth et al. method clearly underestimates the sorption to the ice/snow surface.
Figure B.15: Modeled and measured snow/ice–water partition coefficients. In the Silvretta model, snow/ice-water partitioning is calculated using the Roth et al. method [Roth et al., 2004] and air-water partition coefficients from Schenker et al. [2005] (snow–water partition coefficient = snow–air partition coefficient / water–air partition coefficient). Similarly, the literature values are calculated from measured PCB concentrations in air, rain, and snow [Franz and Eisenreich, 1998; Agrell et al., 2002]. All partition coefficients are corrected for a temperature of 0°C, and shown for tri- (PCB 28), tetra- (PCB 52), penta- (PCB 101), hexa- (PCB 138, PCB 153), and hepta- (PCB 180) chlorobiphenyl.
B.10 Results

Figure B.16: Modeled (red line, Silvretta glacier) and measured (black markers, [Offenthaler et al., 2009a]) PCB concentrations in the atmosphere for the years 2005, 2006, and 2007. The measurements were done on Sonnblick (squares, 3100 m a.s.l., 250 km from Silvretta glacier), Weissfluhjoch (diamonds, 2660 m a.s.l., 20 km from Silvretta glacier), and Zugspitze (triangles, 2650 m a.s.l., 100 km from Silvretta glacier).
Figure B.17: Modeled (red and blue lines, Silvretta glacier) and measured (black markers, [Offenthaler et al., 2009a]) PCB deposition fluxes for the years 2005, 2006, and 2007. The red line corresponds to the sum of wet gaseous, wet particle, and dry particle deposition. The blue line includes the dry gaseous deposition in addition to the other three air-to-glacier transfer processes. The markers indicate measured deposition on Sonnblick (squares), Weissfluhjoch (diamonds), and Zugspitze (triangles). In contrast to the modeled transfer in Figure 3, the modeled transfer here includes deposited chemicals lost by runoff during summer rain.
Figure B.18: Fate of PCB 52, 138, and 153 at the ice core site of the Silvretta glacier between 1930 and 2010. Air-to-glacier transfer by dry gaseous, dry particle, wet particle, and wet gaseous deposition (left side, left axis), and loss by particle runoff, meltwater runoff, photochemical degradation, and revolatilization (right side, left axis). The black line indicates the cumulative storage in the glacier column (right side, right axis).
Figure B.19: Fate of PCB 28, 101, and 180 at site B of the Silvretta glacier between 1930 and 2010. Air-to-glacier transfer by dry gaseous, dry particle, wet particle, and wet gaseous deposition (left side, left axis), and loss by particle runoff, meltwater runoff, photochemical degradation, and revolatilization (right side, left axis). The black line indicates the cumulative storage in the glacier column (right side, right axis).
Figure B.20: Seasonal fluxes of dry gaseous deposition, dry particle deposition, wet particle deposition, wet gaseous deposition, particle runoff, meltwater runoff, photochemical degradation, and revolatilization of PCB 28, 101, and 180 at the ice core site of the Silvretta glacier between 1980 and 1984. The summer months are indicated by a gray background. Dry gaseous deposition transfers chemicals from the air to the glacier surface in summer, the other deposition processes are modeled as loss processes during summer. Loss processes by particle runoff and meltwater runoff are only active in summer. The different processes active during winter and summer lead to different fate of chemicals depending on the season. The variations during the summer months depend on meteorological parameters, such as precipitation, temperature, etc.
Figure B.21: Net accumulation (deposition fluxes minus loss fluxes) of PCB 28, 101, and 180 at the ice core site of the Silvretta glacier between 1930 and 2010.
Figure B.22: Input and loss fluxes to and from the surface glacier compartment at the ice core site of the Silvretta glacier during the summer 1991 (July, August, and September). The fluxes of PCB 28 (green), PCB 101 (blue), and PCB 180 (red) are in ng m$^{-2}$ d$^{-1}$. Input fluxes (deposition, advection, transfer from over-lying compartments that melt in the specific month, and upwards air advection/diffusion) are shown in bold font. Loss fluxes from the compartment include revolatilization, degradation, particle runoff, meltwater runoff, particle percolation, meltwater percolation, and downwards air advection/diffusion. The change in storage corresponds to the change in the amount of chemical stored in the surface glacier compartment. All values in percent correspond to 100% of the sum of all the input fluxes. The glacier mass balance during the three summer months was -0.51 m weq month$^{-1}$, indicating a strong mass loss. As a consequence, the number of compartments in the model decreases from 428 to 421 in July, from 421 to 416 in August, and from 416 to 412 in September. The fluxes shown here are valid for the surface compartment, this means compartment 421 in July, 416 in August, and 412 in September.
Figure B.23: Input and loss fluxes to and from the surface glacier compartment at the ice core site of the Silvretta glacier in the year 1991, for PCB 28, PCB 101, and PCB 180, in ng m$^{-2}$ d$^{-1}$. The input fluxes include deposition, advection, transfer from melting over-lying compartments, and upwards air advection/diffusion. The loss fluxes include revolatilization, degradation, particle and meltwater runoff, particle and meltwater percolation, and downwards air advection/diffusion. The change in mass corresponds to the change in the amount of chemical stored in the surface glacier compartment. The importance of chemical enrichment at the glacier surface in summer can be seen by the high values of input and change in mass during the summer months, compared to the low values of loss and downward fluxes in the same season, especially for the higher-chlorinated congeners.
Figure B.24: Concentration depth profiles of PCB 28 and PCB 52 in the Silvretta ice core when the snow–air partition coefficient is increased by a factor of 10 (red), compared to the original version (Figure 3.2, green).
Appendix C

Supporting Information for Chapter 4: A Temperate Alpine Glacier as a Reservoir of Polychlorinated Biphenyls: Model Results of Incorporation, Transport, and Release

C.1 Silvretta Glacier

The Silvretta glacier consisting of 71 sections is shown in Figure C.1. The accumulation area is located in the eastern part of the glacier, the ablation area is located in the western part. The glacier flows from east to west.

C.2 The Glacier Surface Model (Gla–surf)

The following information about input parameters and model parametrization of Gla–surf is provided in Appendix B: General basics of multimedia chemical fate modeling, such as a short introduction to chemical fate modeling, the fugacity concept, and how to solve the system of chemical mass balance equations. Air temperature, glacier mass balance, wind speed, volume fraction of aerosol particles, density of the glacier compartments, porosity, volume fractions of pore air, particles, liquid water, and solid ice in the glacier compartments, as well as the glacier ice temperature, and other environmental input data. The glacier compartment setup as a function of the glacier mass balance. Meltwater and particle percolation and runoff, and density and particle concentration depth profiles. Information about the input of chemicals into the system, such as global emissions and global distribution, and seasonal input from the planetary boundary layer and the free troposphere. Physicochemical properties of the PCB congeners, temperature-dependence of the partition coefficients, particle–air,
snow surface–air partitioning, and degradation rate constants. The model parametrization of the chemical fate processes air advection, degradation, air-to-glacier transfer, wind pumping, molecular diffusion, meltwater and particle processes.

C.2.1 Novelties included in the Gla–surf model version used in this study

C.2.1.1 Environmental input parameters for 2011–2100

For future climate conditions, we used the Swiss Climate Change Scenarios (CH2011) [Appenzeller et al., 2011], which are based on the A2 emission scenario of the third
The Glacier Surface Model (Gla–surf) in the IPCC Assessment Report, which is a scenario considering a heterogeneous world with strong greenhouse gas emissions until 2100 [IPCC, 2001]. The CH2011 report predicts time-resolved changes in a seasonal resolution (4 seasons per year) for three representative regions in Switzerland: northeastern Switzerland, western Switzerland, and Switzerland south of the Alps. Here we use the results of northeastern Switzerland, where the Silvretta glacier is located. Future air temperature (2015–2100) was determined by correcting the average monthly temperature calculated for the glacial lake between 1980 and 2009 with the temperature increase predicted by the medium A2 emission scenario. Temperature changes are predicted for the four seasons of the year, and for the years 2035, 2060, and 2085. For the remaining years, these predictions were linearly interpolated. The air temperature from the glacial lake was then used to calculate the air temperatures of all 71 glacier sections. From the glacial lake, temperature decreases with a gradient of 0.83°C per 100 m of elevation (Chapter 3). To estimate the elevation of the 71 glacier sections we linearly interpolate the elevation of the lowest (glacial lake) and the highest point of the glacier. This linear interpolation is a good approximation, as the Silvretta glacier surface is flat and the elevation increases constantly. This can be seen in the topographic map in Figure C.1.

Future precipitation (2015–2100) was estimated in the same way as air temperature. In summer, the precipitation onto the Silvretta glacier is assumed to be constant. In contrast, in winter, precipitation is set equal to the snow accumulation, in order to consider the conservation of mass. As the snow accumulation differs for the 71 glacier sections, precipitation is different for the sections, and increases with elevation. This corresponds to the general increase of precipitation with elevation that is shown by meteorological data [MeteoSwiss, 2014b].

For future aerosol particle concentrations (2014–2100), we used predictions of future black carbon emissions of the Representative Concentration Pathways (RCP) database [Moss et al., 2010]. For the A2 scenario, we use RCP 8.5, which was developed by the MESSAGE modeling team. The database provides black carbon emissions estimates for the years 2000, 2005, and 2010–2100 in 10 years intervals. We interpolated these predictions linearly and used the measurements of particulate matter (PM10) from Jungfraujoch between 2001 and 2010, relative to past and future black carbon emissions. Aerosol particles are related to black carbon emissions based on the assumption that combustion is a suitable indicator of the total aerosol particle emissions.

For future wind speed (2014–2100) we used the average monthly wind speed values of the period 1959–2013. In the model, wind speed was kept constant for the entire Silvretta glacier. In reality, the complex topography of the area might lead to spatial differences in wind speed and, thus, to snow relocation. However, the Silvretta glacier has a simple geometry with a constant change in elevation and a flat surface, which was one of the reasons to study this glacier. In addition, the spatially resolved snow
accumulation data was calculated from measurements done on several locations on the Silvretta glacier since 1915. In these measurements, and consequently also in the snow accumulation data, snow relocation by wind is included.

### C.2.1.2 Glacier mass balance data

The Silvretta glacier has one of the longest mass balance measurement series existing, with mass balance/snow accumulation measurements available from 1915 [Huss et al., 2008a; Huss and Bauder, 2009; VAW, 2014]. Snow accumulation is measured by placing stakes on the glacier surface and quantifying the snow mass accumulated or lost after a specific period of time. Mass balance grid data is determined by calibrating a mass balance model of Silvretta glacier with ice volume changes from high-resolution digital elevation models, point-based mass balance measurements and discharge records, using air temperature and precipitation data from two high-altitude meteorological stations [Huss et al., 2008a; Huss and Bauder, 2009].

The mass balance grid data is available on a 25x25 m grid of the entire Silvretta glacier. Seasonal data is available for the period between 1900 and 2014, including a winter balance, quantifying the amount of snow deposited onto the glacier surface between October and April, and a yearly balance, describing the amount of snow deposited onto (or lost from) the glacier between October and September. We interpolated this data set by setting the yearly balance to the last month of the year with air temperature above 0°C, and the winter balance to the last month before the first month with air temperature above 0°C, followed by linear interpolation of the mass balance to the remaining months.

Monthly resolved mass balance grid data is available for the period between 2015–2100. The future mass balance is calculated in the Silvretta glacier mass balance model, [Huss et al., 2008a; Huss and Bauder, 2009] using the Swiss Climate Change Scenarios (CH2011) [Appenzeller et al., 2011], based on the A2 emission scenario of the third IPCC Assessment Report [IPCC, 2001]. For the 71 glacier sections, the mass balance data of all the grid cells contained in the section in a specific year are used to determine the mass balance of the section. An example of the mass balance (snow accumulation) for three sections is shown in Figure C.2.

### C.2.1.3 Inactivation of the glacier compartments with compartment age

In the previous model version of Gla–surf [Steinlin et al., 2015], the glacier compartments were assumed to move only in the vertical direction and to stay in contact with the overlying compartments for the whole time period included in the model. In contrast, here, the glacier compartments are disconnected from the overlying com-
Figure C.2: A) Yearly snow accumulation (glacier mass balance) of the sections 7, 25, and 50 of the Silvretta glacier between 1900 and 2100. The dashed line indicates a mass balance of zero. B) Monthly snow accumulation of section 7 between 1900 and 2100. C) Monthly snow accumulation of section 7 between 1980 and 2040. Until 2014, the monthly mass balance data is interpolated from the seasonal (winter and yearly) mass balance. After 2014, the monthly mass balance is calculated by the Silvretta glacier mass balance model.

Partments after five years, and the chemicals contained within the compartments are defined as incorporated into the glacier, and can be transported away along a flowline starting in this specific section. This incorporation is only active in years with a positive glacier mass balance in the section. If the mass balance is negative in the specific year, the chemicals are stored until the next year with a positive balance, and then passed on to the flowline.

The disconnection between an old glacier compartment and the above-lying compartments is caused by horizontal flow, inducing ice deformation and density increase. As a consequence, the amount of meltwater refreezing (formerly set to 20%) is lowered to 15%, as the refreezing occurs distributed on a smaller number of compartments. Consequently, the density profile as well as the PCB concentration depth profiles are slightly different than in Steinlin et al. [2015]. The new density profile is shown in Figure C.3,
the new PCB concentration profiles in Figure C.7. PCB concentrations calculated with our model are similar to the measured concentrations. The lower-chlorinated congeners that were found to be underestimated by the model in Steinlin et al. [2015] have higher concentrations here. This difference can be explained by the inactivation of the re-volatilization process after five year, the process, that was suspected to be overestimated before. This shows that the interaction with the overlying compartments for more than five years (used in the previous model version) is problematic, and that horizontal flow is important.

C.2.1.4 Input of chemicals into the system

PCB concentrations calculated by BETR Research for Western Europe were used as input to the Silvretta model. Air with the specific PCB concentration reaches the Silvretta region. The amount of air flowing into the region is defined by wind speed and the geometry of the atmospheric compartment (vertical area) of the Silvretta model. BETR Research includes two atmospheric compartments, the free troposphere and the planetary boundary layer. There is a seasonal difference in exposure of the high-alpine area to these two air layers, which is taken from a recent study by Herrmann et al. [2015]. The authors analyzed six years of aerosol size distribution data from Jungfraujoch. They concluded that at Jungfraujoch, the free troposphere is prevalent for more than 60% of the time in winter and for less than 20% during summer. This is a lower prevalence than it has been assumed before, and can be explained by fast horizontal air transport in mountainous areas. In the model we use an inflow of tropospheric air of 80% in winter and 20% in summer, while the inflow of air from the planetary boundary layer accounts for 20% in winter and 80% in summer.
C.3 The Glacier Flow Model (Gla–flow)

The glacier flow model is implemented with the Finite Element method with the Libmesh code base [Kirk et al., 2006]. The model solves the incompressible Stokes equations for ice flow along a vertical section along a flow line (2D, plane strain) [Lüthi, 2009]. For each time step (one year) a velocity field is calculated on the current geometry. The glacier geometry is then updated by motion of the surface according to the flow field and the surface mass balance (i.e. vertical motion due to accretion or melting of ice). This mass balance data is taken from the reconstructions and future projections [Huss and Bauder, 2009; Huss et al., 2008a], which are resampled onto the considered glacier flow line.

The flowlines are calculated from the velocity fields of each time step (year). These

![Figure C.4: Characteristics of the Silvretta glacier flowlines starting in the 1970s. A) Number of flowlines starting in and arriving to a specific glacier section. B) Number of flowlines arriving to the glacier surface in a specific year. C) Amount of PCB 101 arriving to the glacier surface in a specific year.](image-url)
velocity fields are interpolated with the same Finite Element shape functions used to solve for the velocity field. Each year, tracers are put on the glacier surface in intervals of 50 m and advected through the velocity field with a forward Euler method (10 steps per time step). All of these markers are tracked through the changing velocity fields (one per year) until they reach the surface.

The glacier flow model provides the starting year and section of a flowlines, as well as the year and the section where a flowline ends. This information is then combined with Gla–surf, which provides the amount of chemicals incorporated into the glacier surface in a specific year and section. These chemicals are transported along the flowline starting in the same year and section. During the transport, the chemicals are assumed to stay inert, and their amount does not change. Figure C.4 shows the flowlines starting in the 1970s. Most flowlines arrive to the surface in the 1990s, the 2000s, as well as after the year 2050. The release of PCB 153 from flowlines starting in the 1970s is especially high in the 1990s and the 2000s. Eventually, when the flowline arrives at the surface in its arrival year and section, the ice melts and the chemicals and the particles contained within the ice are transferred to the glacial lake.

C.4 The Glacial Lake Model (Gla–lake)

C.4.1 Environmental system

C.4.1.1 Input parameters

Meteorological parameters such as the aerosol concentration, the air temperature (corrected for the elevation of the glacial lake), precipitation, and wind speed, as well as the definition of summer and winter seasons are the same as in Gla–surf. Constant input parameters used in Gla–lake are reported in Table C.1.

The air height is the annual average of the height of the nocturnal boundary layer and the planetary boundary layer in the Engadin Mountains, where the Silvretta glacier is located. The value originates from the weather forecast COSMO-2 model of MeteoSwiss and has been calculated in Glüge et al. [2016]. More information, including layer heights of the months January and July can be found in Glüge et al. [2016].

C.4.1.2 Input of water to the lake

In the model, the inflow of water into the Silvretta lake (\(G_{\text{wat}}\), m\(^3\) water month\(^{-1}\)) is defined by the runoff of meltwater and rainwater from Gla–surf, and by the amount of precipitation onto the lake surface. The same amount of water entering the lake also
Table C.1: Constant environmental input parameters used in Gla–lake. Surface area (estimated by GIS from Google maps [Google, 2015]), air height [Glüge et al., 2016], water depth (estimated by field visits), volume fraction of solids in sediment [Bogdal et al., 2010], volume fraction of organic matter in aerosol particles [FCAH, 2007], volume fraction of organic matter in particles in the water [Bogdal et al., 2010; Morselli et al., 2014]b, volume fraction of organic carbon in sediment solids (set equal to water), density of aerosol particles [FCAH, 2007], density of particles in the water and of sediment solids [Bogdal et al., 2010], dry deposition velocity of aerosols [Daly and Wania, 2004], specific surface area of snowflakes [Legagneux et al., 2002], scavenging factor of snow [Franz and Eisenreich, 1998], scavenging factor of rain [Mackay, 2001], temperature gradient for elevation correction [Wallace and Hobbs, 2006], mass transfer coefficients air–water, water–air, and water–sediment [Mackay, 2001], lake water temperature (measured), sediment temperature (set equal to lake water).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
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</tr>
<tr>
<td>Air height</td>
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<td>400</td>
</tr>
<tr>
<td>Water depth</td>
<td>m</td>
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</tr>
<tr>
<td>Volume fraction of solids in sediment(^a)</td>
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</tr>
<tr>
<td>Volume fraction of organic matter in aerosol particles</td>
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</tr>
<tr>
<td>Volume fraction of organic carbon in particles in the water(^b)</td>
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<td>0.002</td>
</tr>
<tr>
<td>Volume fraction of organic carbon in sediment solids</td>
<td>[-]</td>
<td>0.002</td>
</tr>
<tr>
<td>Density of aerosol particles</td>
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<tr>
<td>Density of particles in the water</td>
<td>kg m(^{-3})</td>
<td>2600</td>
</tr>
<tr>
<td>Density of sediment solids</td>
<td>kg m(^{-3})</td>
<td>2600</td>
</tr>
<tr>
<td>Dry deposition velocity of aerosols</td>
<td>m h(^{-1})</td>
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<tr>
<td>Specific surface area of snowflakes</td>
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<td>96</td>
</tr>
<tr>
<td>Scavenging factor of snow</td>
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<td>3.2 (10^5)</td>
</tr>
<tr>
<td>Scavenging factor of rain</td>
<td>[-]</td>
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<td>Temperature gradient for elevation correction</td>
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</tr>
<tr>
<td>Mass transfer coefficient air–water</td>
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<tr>
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</tr>
<tr>
<td>Sediment temperature</td>
<td>°C</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) The volume fraction of solids in sediment in combination with the density of sediment solids result in a bulk sediment density of around 2000 kg m\(^{-3}\), corresponding to the measured sediment density in the Silvretta lake sediment core.

\(^b\) Bogdal et al. [2010] used a value of 0.005, and Morselli et al. [2014] measured 0.0056. Here we use an even lower value, as the Silvretta lake has a very low biological activity, compared to the bigger lakes studies by these authors.
leaves the lake in the same month.

### C.4.1.3 Input of particles to the lake

Similar to the water input, the amount of particles reaching the Silvretta lake from the glacier surface ($G_{p,\text{in,surf}}$, m$^3$ water month$^{-1}$) is calculated in Gla–surf. These particles can originate from wet particle deposition by rainfall (assumed not to interact with the glacier), from particle runoff from the glacier surface, or from flowlines storage. The latter is yearly resolved, as the model Gla–flow is in a yearly resolution. Therefore, we assume a seasonality similar to the seasonality of the particle runoff from the glacier surface. Particles can also reach the lake by wet and dry particle deposition from the atmosphere to the lake surface.

In reality, the amount of particles reaching the glacial lake is much higher than $G_{p,\text{in,surf}}$. This is because $G_{p,\text{in,surf}}$ only includes particles that were originally deposited from the atmosphere to the glacier surface, have an organic carbon content of 20% and a density of 1000 kg m$^{-3}$. However, in a glacial lake, the largest amount of particles originates from the glacier bed, produced by grinding of the ice mass on the bedrock. These particles have a very low organic carbon content, and a high density. Most importantly, these particles are not contaminated with PCBs, as they originate from the glacier base, and were not in contact with the atmosphere during the time of PCB emissions. Also, particles can be deposited to the glacier surface from surrounding rocks, or organic material can be produced by biological activity on the glacier surface (e.g. in cryoconites [Hodson, 2014]). However, these processes are not included in Gla–surf. For this reason, we determine the volume fraction of particles in the lake by closing the mass balance of the total volume of particles in the lake (see below).

### C.4.1.4 Particle mass balance in the lake

The change in total volume of particles in the lake ($dV_{\text{par}}$) is a function of the monthly inflow of particles ($G_{p,\text{in}}$), the particle sedimentation ($G_{p,\text{sed}}$), the particle resuspension ($G_{p,\text{res}}$), and the particles lost by water advection ($G_{p,\text{adv}}$) (Equation (C.1)) (all values in m$^3$ particles month$^{-1}$).

$$\frac{dV_{\text{par}}}{dt} = G_{p,\text{in}} - G_{p,\text{sed}} + G_{p,\text{res}} - G_{p,\text{adv}}$$  \hspace{1cm} (C.1)$$

$G_{p,\text{in}}$ corresponds to $G_{p,\text{in,surf}}$, corrected by an unknown factor $f_{\text{part}}$, taking into account the higher amount of particles entering the lake compared to the amount of particles release from the glacier surface (Equation (C.2)). $G_{p,\text{sed}}$ is a function of the particle settling velocity ($U_{\text{p,sed}}$, m month$^{-1}$), the lake area ($A_{\text{lake}}$, m$^2$), and the volume fraction of particles in the lake ($V_{\text{par}}/V_{\text{lake}}$, m$^3$ particles m$^{-3}$ water) (Equation (C.3)). $G_{p,\text{res}}$ is set
to 10% of the deposited particles (Equation (C.4)). This corresponds to a resuspension of 10% of the sediment layer mass per year, as proposed by Schwarzenbach et al. [2003], as here, the density of the particles in the water is assumed to be similar to the density of the sediment solids. $G_{p,\text{adv}}$ is a function of the advective outflow of water ($G_{\text{wat}}$) and $V_{\text{par}}/V_{\text{lake}}$ (Equation (C.5)).

\[
G_{p,\text{in}} = f_{\text{part}} \cdot G_{p,\text{in,surf}} \quad \text{(C.2)} \\
G_{p,\text{sed}} = U_{p,\text{sed}} \cdot A_{\text{lake}} \cdot V_{\text{par}}/V_{\text{lake}} \quad \text{(C.3)} \\
G_{p,\text{res}} = 0.1 \cdot U_{p,\text{sed}} \cdot A_{\text{lake}} \cdot V_{\text{par}}/V_{\text{lake}} \quad \text{(C.4)} \\
G_{p,\text{adv}} = G_{\text{wat}} \cdot V_{\text{par}}/V_{\text{lake}} \quad \text{(C.5)}
\]

In these equations, we have three unknowns: $V_{\text{par}}$, $f_{\text{part}}$, and $U_{p,\text{sed}}$. To define these unknowns, we use the following information available about the system: 1) In summer 2015, we measured a particle concentration in the glacial stream of 460 mg L$^{-1}$. 2) From the glacial lake sediment core, we know that the average sediment formation in the Silvretta lake is 4.8 cm yr$^{-1}$ [Pavlova et al., 2015b], which with a volume fraction of solids of 0.65 [Bogdal et al., 2010], corresponds to an average accumulation of sediment solids of 3.12 cm yr$^{-1}$. This sediment accumulation leads to more sediment accumulating than in Pavlova et al. [2015b], as it is valid for the sediment surface layers. However, we use this value for the sediment accumulation, as no densification of the sediment in deeper layers is included in the model. In the model, all these parameters are monthly resolved, and vary over the years (1900–2100). In addition, these processes are only active during summer, and in winter, when the lake is frozen, the volume of particles in the glacial lake remains constant.

We define the two unknown parameters in a way that the average particle concentration and the average sediment accumulation correspond to the measurements: this leads to $f_{\text{part}} = 640$, and $U_{p,\text{sed}} = 0.047$ m h$^{-1}$. For $f_{\text{part}}$, no data is available, as this factor is specific for every glacier, and depends on the bedrock, inclination, glacier dimensions, etc. $U_{p,\text{sed}}$ is in the same range as the value of 0.02 m h$^{-1}$ used by Morselli et al. [2014]. We solve the differential equation numerically using Euler timesteps, and get an average particle concentration of 460 mg L$^{-1}$. This value is between the 62 mg L$^{-1}$ used by Bogdal et al. [2010], and the suspended solid concentration of 1000–2000 mg L$^{-1}$ measured by Morselli et al. [2014]. The value corresponds to our measurement from the Silvretta stream.

### C.4.2 Input of chemicals into the system

Chemicals can be imported into the atmospheric compartment of Gla–lake by long-range atmospheric transport from the planetary boundary layer or the free troposphere of the air compartments in the global model BETR Research. This import is modeled
in the same way as the import into the air of Gla–surf, and was described in detail before [Steinlin et al., 2014, 2015].

Besides the inflow by air, chemicals can reach the glacial lake by runoff from the glacier. This includes runoff with meltwater and runoff with particles. These fluxes are quantified in Gla–surf, in a monthly resolution. Chemicals can also directly reach the glacial lake by wet particle and gaseous deposition to the glacier surface initiated by rainfall. The release of chemicals from flowlines arriving to the glacier surface is modeled in a yearly resolution. To estimate a monthly resolution, the seasonality of particle runoff is used to calculate the seasonality of the flowlines release.

C.4.3 Physicochemical and kinetic properties of PCBs

Physicochemical and kinetic properties of PCBs are the same as in Gla–surf. In addition, in Gla–surf, partitioning between particles and water, and between sediment particles and pore water is included. Particle–water partitioning is based the organic carbon–water partition coefficient \( K_{oc} \), which can be related to the octanol–water partition coefficient \( K_{ow} \). We use the relation presented by Schwarzenbach et al. [2003], which is specific for PCBs (Equation (C.6)).

\[
\log K_{oc} = 0.74 \times \log K_{ow} + 0.15
\]  

(C.6)

C.4.4 Chemical fate processes

In addition to the chemical fate processes included in Gla–surf, the following processes are included in Gla–lake.

C.4.4.1 Water advection

The D-value of water advection \( D_{adv,\text{wat}} \) is calculated by multiplying the amount of water leaving the lake \( G_{\text{wat}, \text{m}^3 \text{month}^{-1}} \) and the fugacity capacity of the lake water bulk compartment \( Z_{\text{wat}, \text{mol Pa}^{-1} \text{m}^{-3}} \) (Equation (C.7)).

\[
D_{adv,\text{wat}} = G_{\text{wat}} * Z_{\text{wat}}
\]  

(C.7)

C.4.4.2 Deposition from air to the lake

Wet particle and gaseous deposition and dry particle deposition are modeled in the same way as in Gla–surf, induced by snowfall in winter, and by rainfall in summer. In summer, deposition occurs from air to the lake water. In winter, the lake is covered by an ice cover, and the air–water interaction is interrupted. As a consequence, deposition
occurs from air to the ice cover during winter. The amount of water, particles, and chemicals deposited to the ice cover is then stored (no interaction or transformation is included), until the first month having a positive air temperature, when the ice cover melts, and water, particles, and chemicals are transferred to the lake.

C.4.4.3 Air–water and water–sediment diffusion

Diffusion between phases is modeled using the Whitman two-film resistance approach described before [Whitman, 1923; Mackay, 2001; Schwarzenbach et al., 2003]. In this approach, two layers are set in series, and the D-value for diffusion between air and water \( (D_{\text{diff,airwat}}) \) and between water and sediment \( (D_{\text{diff,watsed}}) \) are a function of the mass transfer coefficients \( (U, \text{ m month}^{-1}) \), the surface area of the lake \( (A_{\text{lake}}, \text{ m}^2) \), and the fugacity capacities of air, water, and pore water \( (Z_a, Z_w, Z_{\text{porewat}}, \text{ mol Pa}^{-1} \text{ m}^{-3}) \) (Equations (C.8)–(C.9)). The mass transfer coefficients air–water \( (U_{\text{airwat}}) \), water–air \( (U_{\text{watair}}) \), and water–sediment \( (U_{\text{airwat}}) \) are taken from literature and are reported in Table C.1. The mass transfer coefficient sediment–water \( (U_{\text{sedwat}}) \) is a function of the effective diffusivity in the sediment pore water \( (d_{\text{diff,eff}}) \) and the diffusion path length in sediment \( (y_{\text{sed}}) \). \( y_{\text{sed}} \) is set to half of the monthly sediment layer height (Equation (C.10)). The effective diffusivity in sediment pore water is estimated from the diffusivity in water \( (d_{\text{diff,wat}}) \) and the fraction of water in the sediment \( (f_{\text{porewat}}) \) using the Satterfield relationship Satterfield [1970]; Mackay [2001] (Equation (C.11)).

\[
D_{\text{diff,airwat}} = \frac{1}{U_{\text{airwat}} * A_{\text{lake}} * Z_a + U_{\text{watair}} * A_{\text{lake}} * Z_w} \tag{C.8}
\]

\[
D_{\text{diff,watsed}} = \frac{1}{U_{\text{watsed}} * A_{\text{lake}} * Z_w + U_{\text{sedwat}} * A_{\text{lake}} * Z_{\text{porewat}}} \tag{C.9}
\]

\[
U_{\text{sedwat}} = d_{\text{diff,eff}} / y_{\text{sed}} \tag{C.10}
\]

\[
d_{\text{diff,eff}} = d_{\text{diff,wat}} * f_{\text{porewat}}^{1.5} \tag{C.11}
\]

In winter, the diffusion between the atmosphere and the lake is disrupted by the ice covering the lake. The diffusion between water and sediment is set to zero in months when there is no sedimentation (corresponding to winter months when no water is flowing through the lake).

C.4.4.4 Lake–Sediment Sedimentation and Resuspension

The D-values for sedimentation and resuspension \( (D_{\text{sed}} \text{ and } D_{\text{res}}, \text{ mol Pa}^{-1} \text{ h}^{-1}) \) are a function of the particle sedimentation and resuspension fluxes \( (G_{\text{p,sed}}, G_{\text{p,res}}, \text{ m}^3 \text{ month}^{-1}) \)
and the fugacity capacities of particles in the lake water and sediment particles \((Z_{\text{par}}, Z_{\text{sol}}, \text{mol Pa}^{-1} \text{ m}^3)\) (Equations (C.12)–(C.13)).

\[
D_{\text{sed}} = G_{p,\text{sed}} * Z_{\text{par}} \quad (\text{C.12})
\]

\[
D_{\text{res}} = G_{p,\text{res}} * Z_{\text{sol}} \quad (\text{C.13})
\]

### C.5 Results

#### C.5.1 Fate of PCBs on the glacier surface

![Figure C.5: Fluxes of the PCB congeners 28 and 180 in the 71 sections of the Silvretta glacier, summed up over the years 1900–2100. Input by dry and wet gaseous and particle deposition (blue line), revolatilization to the atmosphere (red line), and runoff by meltwater and particle flows and by runoff from the particle layer (yellow line). The major part of PCB 28 is lost to the atmosphere by revolatilization, while a large part of PCB 180 is incorporated in the accumulation area (small section numbers), and lost by runoff in the ablation area (large section numbers).](image-url)
Figure C.6: Spatially resolved incorporation of PCB 153 into the 71 sections of the Silvretta glacier summed up between 1960 and 1999 (40 years). The incorporation is high the accumulation area (high glacier mass balance, eastern part of the glacier), and it is zero in the ablation area (negative glacier mass balance, western part of the glacier).
C.5.2 Concentration profiles in the ice core

Figure C.7: Modeled (red line) and measured (gray bars) [Pavlova et al., 2015a] concentration depth profiles of the PCB congeners 28, 52, 101, 138, 153, and 180 in the Silvretta ice core when using the model version of Gla–surf of this study. For comparison, please refer to the concentration depth profiles in Steinlin et al. [2015].
C.5.3 Concentration profiles in the lake sediment

![Graph showing modeled and measured concentration profiles of six indicator PCB congeners in glacial lake sediment.]

**Figure C.8:** Modeled (red line) and measured (gray bars) [Pavlova et al., 2015b] concentration depth profiles of the six indicator PCB congeners in the glacial lake sediment.
C.5.4 Net sedimentation fluxes from the glacial lake to the lake sediment

Figure C.9: Modeled (red line) and measured (gray line) net sedimentation fluxes from the glacial lake to the lake sediment for the six indicator PCB congeners.
C.5.5 Concentrations in the glacial stream

![Bar chart showing PCB concentrations in the glacial stream over 2012, 2013, and 2015. The chart includes modeled and measured values for different PCB congeners.]

Figure C.10: Modeled and measured [Pavlova et al., 2015b] PCB concentrations in the glacial stream, in the summers 2012, 2013, and 2015. The modeled values are averaged over all summer months in the specific year. Passive water sampling was done over two months with duplicates in 2015. Bulk water sampling was done three times per summer with duplicates in one of the samplings. Details on sampling and analysis are provided in Pavlova et al. [2015b].
C.5.6 Net accumulation, incorporation, and storage

Figure C.11: Net accumulation, incorporation, and storage of the six indicator PCB congeners in the Silvretta glacier system.
C.5.7 Release and stream concentration

Figure C.12: Release to the glacial lake and concentration in the glacial stream of the six indicator PCB congeners.
C.5.8 Seasonal trend of stream concentrations

Figure C.13: Seasonal trend of the PCB concentrations in the glacial stream.
C.5.9 Factors determining seasonal stream concentrations

Figure C.14: Factors determining the seasonal trend of the stream concentrations: inflow of PCB 101 from the Silvretta glacier to the lake water compartment, inflow of water to the lake, inflow of particles to the lake, and volume fraction of particles in the lake.
C.5.10 Ice core and sediment concentration profiles when the sorption to ice is increased

Figure C.15: Concentration profiles of the PCB congeners 28, 52, and 101 in the Silvretta ice core when the sorption to snow/ice is increased by a factor of 10.

Figure C.16: Sediment concentration profiles of the PCB congeners 28, 52, and 101 when the sorption to snow/ice is increased by a factor of 10. Mind the different x-axis compared to Figure C.8.
C.5.11 Sediment concentration profile of PCB 153 with storage in the ablation area

Figure C.17: Sediment concentration profile of PCB 153 without surface storage (black line), and when particles and chemicals released from flowlines are stored in the ablation area for a period of 10 years (red line).
Bibliography


