EFFECT OF MELTING ON REDISTRIBUTION AND RELEASE OF PCBs FROM ALPINE GLACIERS

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Introduction

In glacial systems the inventory of contaminants depends on the atmospheric input, the accumulation and ablation (mass balance) of the ice, but also on transport processes in the glacier itself. Partitioning of the substances between the different phases (ice, pore space and aerosol particles) occurs according to their physicochemical properties. So far only few datasets on legacy persistent organic pollutants (POPs) in glacier ice have been published, which cover the entire time period from their introduction in the environment until today.[1,2] Data from the Alps are even more scarce.[3] In addition a major knowledge gap remains for temperate Alpine glaciers, which represent the majority of glaciers in the Alps. This type of glacier is characterized by ice temperatures around 0º C and the presence of liquid water within the ice matrix. We have analyzed polychlorinated biphenyls (PCBs) in glacier ice in order to confirm the “glacier hypothesis”, which proposes that POPs previously deposited to and incorporated into glaciers are now released back to the environment due to the accelerated melting induced by global warming.[4] In particular we are interested in the effect of surface melt water percolating in the pore space and washing away substances. Furthermore, in a parallel study, those processes are modelled and quantified[5].

Materials and methods

Sites and study set up

In order to obtain a quantitative inventory of PCBs input into Alpine glaciers, we analyzed PCBs in two ice cores from a cold and a temperate glacier. The ice core from Fiescherhorn glacier in the central Swiss Alps , with a drilling site located at around 3900 m above sea level (a.s.l.), is characterized by almost no summer melt and percolating water, which ensures the conservation of the deposited atmospheric pollutants in the ice. The age-depth relationship was established with a multiproxy approach using annual layer counting of seasonal varying parameters like NH_4^+, identification of well-known Saharan dust reference horizons and an annual layer thinning ice flow model.[6] Furthermore, to examine the effect of melting on the distribution of the contaminants in the glacier, we analyzed an ice core from Silvretta glacier, located in eastern Swiss Alps. This glacier stretches between 2500 and ca. 3000 m a.s.l. and is affected by extensive summer melt. Overall Silvretta glacier is continuously loosing mass and even in the accumulation area the mass balance has been negative in recent years (Figure 1). Since there was no continuous accumulation of ice on this glacier, the measured concentrations of PCBs are assigned only to the positive mass balance years of the record.

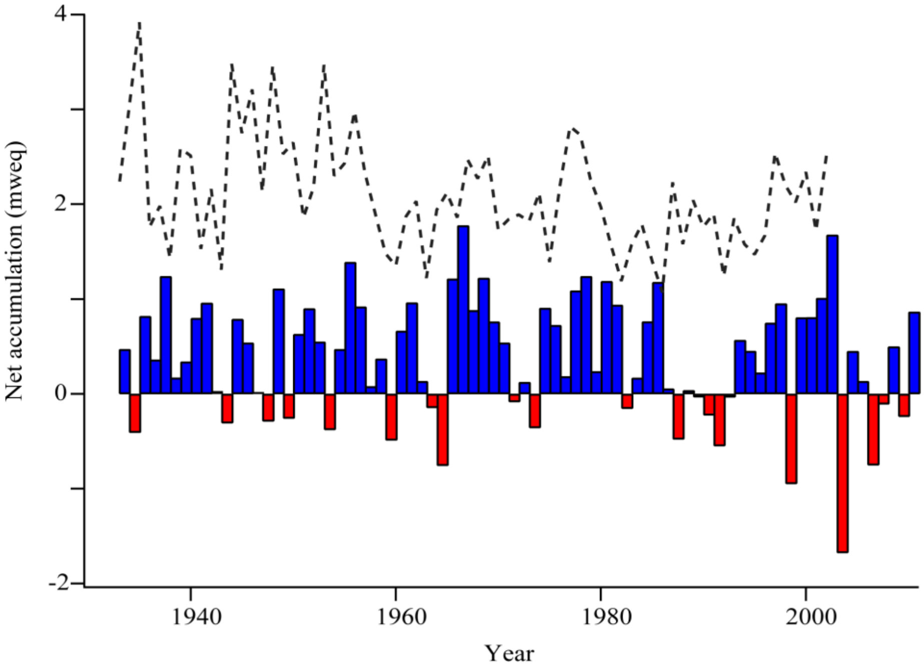

Figure 1: Net accumulation of snow on the Silvretta glacier close to the drilling site in m water equivalent (mweq) (blue - positive, red - negative) and reconstructed annual accumulation from Fiescherhorn ice core[5] (black dashed line).

Analysis of organic compounds

Six PCB congeners, the so-called indicator PCBs (iPCBs), PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180, were selected for this study. Special measures were taken to reduce background contamination. These include baking out in addition to solvent rinsing of the glassware and removing the outer part of the ice core, which was in contact with the drill and the packing material. For the extraction of the organic compounds from the ice, we use a novel method, developed in house. Briefly, our method is based on partitioning of the analytes from the melted sample into the polydimethylsiloxane (PDMS) coating of an open tubular fused silica capillary, followed by solvent elution and analysis with gas chromatography coupled to electron ionization high-resolution mass spectrometry (GC/EI-HRMS).[7] In order to capture the particle bound fraction of iPCBs in the ice core, a silver membrane filter was installed after the capillary. The filter was also preheated and washed with solvent mixture (acetone, *n*-hexane, methanol 1:1:1 v:v:v). After trapping, the filter was Soxhlet extracted with toluene and the extract was analyzed with GC/EI-HRMS. Thus, in this study we differentiate between dissolved and particulate fraction.

Results and discussion

Hereby we present two independent iPCB records from glaciers in the Alps (Figure 2). The cold Fiescherhorn glacier, serves as a measure of the atmospheric input in high mountain areas in Europe. Contrastingly, the ice core record from the temperate Silvretta glacier is used to examine the transport and release of contaminants.

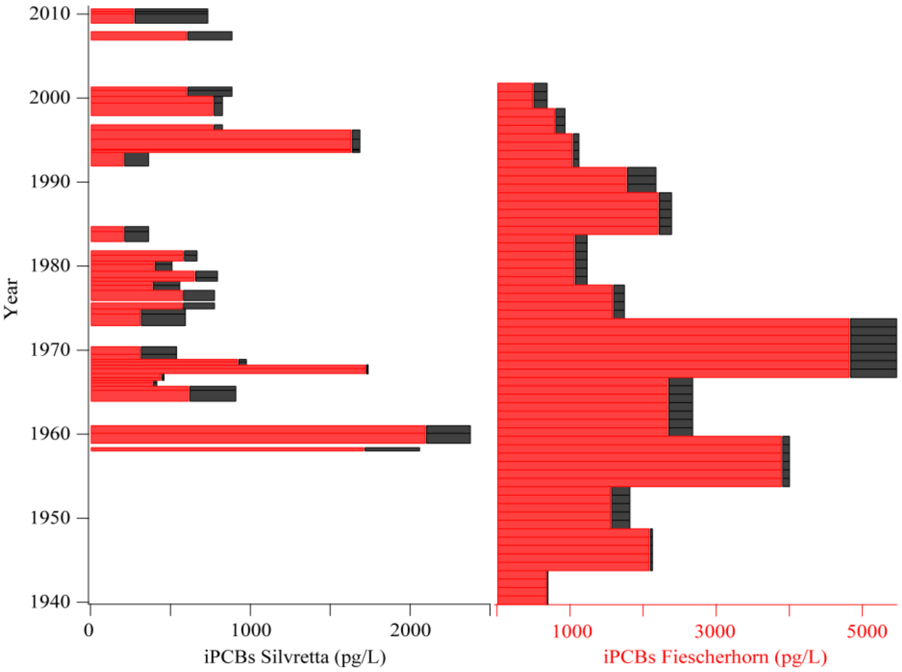

Figure 2: Total annual iPCB concentrations in ice cores core (dissolved fraction – red, particulate - black): on the left, black axis: the Silvretta ice core; and right, red axis: the Fiescherhorn ice core (red line)

The iPCB time trend in the Fiescherhorn ice core reveals a sharp increase around 1970s, followed by a decrease, which is in agreement with estimated emissions of the six compounds in Switzerland.[8] In contrast to the emission data, the PCB concentration shows a second peak in the 1980s before further decreasing, although PCBs are expected to have been phased-out globally in that decade. . We hypothesize the secondary peak to be related to increasing air temperature, leading to stronger convective mixing and transport of pollutants from the valley.[9] On the Silvretta glacier, iPCB concentrations shown in Figure 2 are only presented for the years with positive net mass balance. Although it is located at a lower altitude, mainly exposed to the more polluted atmospheric planetary boundary layer, the iPCB concentrations in this ice core are a factor of two lower than in Fiescherhorn ice core. We assume a fraction of PCBs was removed with melt water. Contrastingly to the cold glacier record the concentrations of the 1980s and 1970s are lower than those closer to the surface, corresponding to 1990s. We measured the highest loads of PCBs in this record in the samples from 1958 and 1960, which may be a result of relocation with depth. In order to examine this effect, we study the partitioning of the PCBs between dissolved and particulate phase in our dataset. As seen in Figure 2 the dissolved fraction is larger than the particulate one. Still, there are some samples where the particle fraction is enriched, particularly in the layers following negative net accumulation years (1970, 1985, 2001). We therefore suppose partial elution of iPCBs from the snow and preservation in the particle bound fraction. The effect has already been observed in smaller extent for Fiescherhorn glacier.[9] However, the underlying layers are not characterized with higher total loads, suggesting that there is no enrichment of contaminants in layers, which are not subject to melting. We assume that the chemicals are transported further away with the melt water and, thus, indicating that glaciers represent a secondary source of POPs. The overall load of iPCBs for the Fiescherhorn site of 26 µg/cm^2, compared to 2 µg/cm^2 for Silvretta, confirms this assumption. We measure contaminant profiles in ice cores to reconstruct past atmospheric pollution. Furthermore, depending on the chemical properties of the analyzed substances and due to changing climate, we detect secondary processes like transport and elution. Hence, ice cores might serve as a basis for predictions on the future release of legacy environmental burden.

Acknowledgements

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References

1. Garmash, O.; Hermanson, M. H.; Isaksson, E.; Schwikowski, M.; Divine, D.; Teixeira, C.; Muir, D. C. G (2013). *Environ. Sci. Technol*. 47, 12064–12072.
2. Wang, X.; Yao, T.; Wang, P.; Wei-Yang; Tian, L.(2008) *Sci. Total Environ*. 394, 134–143.
3. Villa, S.; Maggi, V.; Negrelli, C.; Finizio, A.; Bolzacchini, E.; Vighi, M. (2001) *Fresenius Environ. Bull.* 10, 711–716.
4. Bogdal, C.; Schmid, P.; Zennegg, M.; Anselmetti, F. S.; Scheringer, M.; Hungerbühler, K. (2009) *Environ. Sci. Technol*. 2009, 43, 8173–8177.
5. Steinlin, C.; Bogdal, C.; Lüthi, M. P.; Scheringer, M.; Pavlova, P. A.; Schwikowski, M.; Schmid, P.; Hungerbühler, K. 2014, *Organohalogen Comp.* Submitted, this issue
6. Jenk, T. M., (2006) *Universtiy of Bern*
7. Pavlova, P. A.; Schmid, P.; Zennegg, M.; Bogdal, C.; Schwikowski, M. (2014) *Chemosphere* 2014, 106, 51–56.
8. Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C.(2007) *Sci. Total Environ*. 377, 296–307.
9. Pavlova, P. A.; Schmid, P.; Bogdal, C.; Steinlin, C.; Schwikowski, M.(2014) *Env. Sci Technol* 2014, submitted.