ACCELERATED RELEASE OF PERSISTENT ORGANIC POLLUTANTS FROM ALPINE GLACIERS

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SUMMARY

Persistent organic pollutants (POPs) represent a group of anthropogenic compounds, including industrial chemicals, pesticides, as well as unintentional by-products of combustion processes and chemical reactions, which were released in the environment in the 20th century. Because of their toxicity and bioaccumulation potential, production and use of POPs was regulated with the Stockholm convention in 2004. These organic chemicals are characterized with persistence, volatility and lipophilicity, which determine their distribution in the environment. Substances of interest for the current study include polychlorinated biphenyls (PCBs; plasticizers, insulating and cooling liquid, etc.), dichlorodiphenyltrichloroethane and by-products (DDTs; insecticide for malaria control) and hexachlorocyclohexane (HCH; pesticide) and hexachlorobenzene (HCB; fungicide and combustion by-product). Although, POPs are no longer produced, they are still present in remote areas, far away from their initial sources. Because of the specific meteorology in mountains including low temperatures, high wind speed and high precipitation rates, POPs are enriched in high altitudes, despite of the remoteness.

Glaciers represent climate and atmospheric composition archives in mountain ranges. When meteorology and topographic characteristics allow annual snow to accumulate over several years it transforms gradually to firn and finally to glacier ice. Under the force of gravity, the ice flows downwards to elevations with higher temperatures, where loss due to melting dominates over accumulation. The net gain or loss of ice mass on a glacier defines its mass balance. Since glaciers accumulate impurities together with snow, they represent not only archives, but also sinks of pollutants in the environment. Recent studies have shown, that accelerated melting of glaciers results in increased release rates of legacy pollutants into proglacial lakes.

In the present project we investigate POPs regarding their deposition on, incorporation into, transport within, and release from temperate Alpine glaciers. To do so, we were challenged by the development of novel methods for dating temperate ice cores and the analysis of POPs in ice.

Silvretta glacier in the Swiss Alps was chosen as a study site, because of the relatively simple glacier form and structure, the connected proglacial lakes and the available comprehensive mass balance dataset. Silvretta, as most of the glaciers in the Alps, is a temperate glacier, with ice temperatures around 0 °C and high liquid water content. Two additional ice cores were considered in the frame of this project. Fiescherhorn is a cold glacier in central Swiss Alps, where an ice core was extracted at around 3900 m a.s.l.. Samples covering 1940-2002 were analysed and used as a measure for atmospheric input in high-Alpine regions. In addition, samples covering 1941-1993 from another ice core drilled at 4200 m a.s.l. from Grenzgletscher, located in the Monte Rosa Massif were prepared. Grenzgletscher is a cold glacier with a well described melt event in the period 1985-1989. The record is used to study the differences between undisturbed und affected by melting ice.

An important step in the development of the project was to date the ice core from the Silvretta glacier. Since it is strongly affected by melting, annual layer counting of

seasonal cycles in the concentrations of major ions and stable water isotopes was not suitable. Hence, we used model gridded local mass balance calculation for our drilling site as a basis for the age-depth relationship. In addition, we analysed tritium - a radioactive isotope of hydrogen, which was emitted during nuclear bomb tests until 1963 and is characterized with a distinct peak in this year. Since tritium is incorporated in the ice crystals, it was not eluted with melt water and the signal is preserved in the Silvretta ice core. The results from the local mass balance calculation correspond very well to the depth obtained for the tritium peak, providing a reliable age-depth model for the temperate Silvretta ice core. Further, we attempt the use of seasonal variation of black carbon in the ice core to constrain single years in the record. With the assumption that the input of black carbon peaks in summer due to convective transport, we identified 35 years in the uppermost 20 m water equivalent (mweq) of the Silvretta record, pointing out the method as promising for dating temperate ice.

Since conventional analysis of hydrophobic pollutants at ultra-trace levels in ice requires high sample volumes and possesses the risk of contamination, we developed a novel extraction method to fit our particular requirements. It is based on polydimethyl siloxane (PDMS) coated capillary traps, where POPs partition while the melted ice flowing through. The contact of the sample with surface and thus background contamination and analyte loss was minimized. Samples from the three ice cores were analysed using the novel method and the results were compared. Whereas PCBs were detected in all samples, DDTs were not detected in glacier ice. The PCB ice core records from the three glaciers corresponded well with loads in the range of ng/L and concentration trends peaking in 1970 in agreement with emission data.

Fiescherhorn record serves as an inventory of the atmospheric input into glacier ice and is characterised with the highest concentrations of all three ice cores. However, measured loads correspond to available records from the Alps, but are higher than concentrations measured in the Arctic. Fluctuations in the record can be explained with change of environmental parameters like ambient temperature and occurrence of surface melting. Wet or dry deposition is responsible for the transport of pollutants to the glacier ice. During snow aging more volatile compounds are lost back to the atmosphere. Thus, we observe fractionation towards heavier, less volatile compounds in Fiescherhorn ice.

Grenzgletscher, although it is located closer to additional suspected pollutant sources in the Po plain, exhibits lower concentrations of PCBs than Fiescherhorn. Here we also observed partial redistribution of PCBs as a result of melting. In the temperate Silvretta glacier, where surface melting occurs every year and liquid water is percolating in depth, the measured loads are slightly lower than in Grenzgletscher. Since Silvretta glacier is located at lower altitude, we assume even higher atmospheric input of pollutants. Thus, partial elution occurred in Silvretta glacier and was more prominent in periods with negative glacier mass balances. In case of refreezing of the melt water, layers with compact air-free ice were formed, which were often enriched in particle bound organic pollutants.

Finally, the release of POPs in glacier streams and proglacial lakes was quantified. In order to obtain a spatial and temporal distribution of pollutants in glacier melt, we combined two different sampling techniques – sediment records as archives of past release and passive PDMS water samples to capture current release loads. We sampled the Silvretta proglacial lakes, a glacier meltwater fed stream and a reference non glacier meltwater fed stream. Due to visual assessment and pollutant profiles, only one of the Silvretta proglacial lakes currently receives glacier meltwater. The PCBs in the sediment record from this lake follows emission trends and is characterized with elevated concentrations at the surface, because of accelerated melting. Whereas PCBs are released at higher rates in recent years due to glacier retreat, the same effect is not observed for DDTs. The passive sampler data from the proglacial lakes is comparable with sediments records, with notable fractionation towards heavier congeners. In the catchment area, we observed decreased concentrations in PDMS samples owing to decreasing ambient temperatures and increasing precipitation. However, no important decrease with distance from the glacier was noted, which leads to the conclusion that surface runoff contribution is important for the distribution of pollutants in the catchment.

The obtained ice core and sediment data is robust and reliable and will be used for the validation of a multimedia environmental fate model for the deposition, transport and redistribution of POPs in glaciers. Thus, at a further stage, the obtained results, combined with climate and aerosol models can be used to map the current sources of legacy pollutants in the air and to assess the importance of long range atmospheric transport, versus local sources in pristine environments.

ZUSAMMENFASSUNG

Persistente organische Schadstoffe (persistent organic pollutants, POPs) sind chemische Verbindungen, die seit Mitte des 20. Jahrhunderts als Pestizide und Industriechemikalien verwendet wurden auch als Nebenprodukte bei Verbrennungsprozessen und chemischen Reaktionen entstehen können. Aufgrund ihrer Toxizität und der Gefahr der Bioakkumulation wurden Herstellung und Verwendung von POPs mit der Stockholm-Konvention von 2004 reguliert. POPs zeichnen sich durch ihre Persistenz, Flüchtigkeit und Fettlöslichkeit aus – diese Eigenschaften beeinflussen ihre Verteilung in der Umwelt. In dieser Studie wurden folgende Substanzen untersucht: polychlorierte Biphenyle (PCBs, Weichmacher, Insolier- und Kühlflüssigkeit etc.), Dichlordiphenyltrichlorethan (DDT, Insektizid), Hexachlorcyclohexan (HCH, Insektizid), Hexachlorbenzol (HCB, Fungizid, Verbrennungsnebenprodukt). Trotz Einstellung von Produktion und Verwendung sind diese Chemikalien immer noch selbst in abgelegenen Gebieten weit entfernt von den ursprünglichen Quellen zu finden. Speziel in hochalpinen Regionen sorgen die klimatischen Bedingungen wie tiefe Temperaturen, hohe Windgeschwindigkeiten und hohe Niederschlagsraten für eine verstärkte Anreicherung dieser Substanzen.

Im Gletschereis werden klimatische und atmosphärische Informationen von Gebirgsregionen gespeichert. Wenn Schnee dank günstiger Wetterbedingungen und Topographie über mehrere Jahre akkumuliert, wird er allmählich zu Firn und schliesslich zu Gletschereis transformiert. Durch die Schwerkraft bewegt sich das Eis abwärts, wobei der Temperaturgradient Abschmelzen und somit einen Massenverlust bewirkt. Die Massenbilanz eines Gletschers wird durch Zuwachs oder Verlust der Eismasse definiert. Da mit dem Schnee auch atmosphärische Begleitstoffe abgelagert werden, repräsentieren Gletscher nicht nur ein Klimaarchiv, sondern sind gleichzeitig Speicher für Schadstoffe. Kürzlich publizierte Studien haben gezeigt, dass beschleunigtes Schmelzen von Gletschereis zu erhöhter Freisetzung von Altlasten in Gletscherseen führt.

In dieser Arbeit beschäftigen wir uns mit Deposition, Inkorporation, Transport und Freisetzung von POPs eines temperierten Gletschers. Die grössten Herausforderungen dabei waren die Datierung der temperierten Eisbohrkerne sowie die Analyse der Schadstoffe im Eis.

Studienobjekt war der Silvrettagletscher in den Schweizer Alpen, welcher sich durch eine relativ einfache Form und Struktur auszeichnet und mit zwei proglazialen Seen verbunden ist. Aufgrund der Höhenlage handelt es sich um einen temperierten Gletscher mit Eistemperaturen um 0 °C und einem relativ hohen Flüssigwassergehalt. Für diesen Gletscher existiert eine lange Zeitreihe der Massenbilanzen. Im April 2011 wurde auf 2900 m Höhe ein Eisbohrkern von 101 m Länge entnommen. Im Rahmen unserer Studie wurden zudem weitere Eisbohrkerne von dem Fiescherhorn- und dem Grenzgletscher untersucht. Der in den Schweizer Zentralalpen gelegene Fiescherhorngletscher ist ein kalter Gletscher; der Eisbohrkern wurde auf 3900 m Höhe gebohrt. Proben von 1940-

2002 wurden analysiert und dienten als Referenz für den atmosphärischen Eintrag in hochalpine Regionen. Aus dem Eisbohrkern vom Grenzgletscher (4200 m) im Monte Rosa-Massiv haben wir die Proben aus den Jahren 1941-1993 analysiert. Der Grenzgletscher ist ebenfalls ein kalter Gletscher mit einem gut dokumentierten Schmelzereignis zwischen 1985 und 1989. Die entsprechenden Daten wurden zum Vergleich von ungestörtem mit geschmolzenem Eis verwendet.

Ein wichtiger Schritt im Projekt war die Datierung des Eisbohrkerns aus dem temperierten Silvrettagletscher. Da dieser stark durch Schmelzen beeinflusst ist, war die Zählung von Jahresschichten anhand von saisonalen Konzentrationsunterschieden von Ionen und stabilen Wasserisotopen als Datierungsmethode nicht geeignet. Deshalb haben wir modellierte Massenbilanzen für unsere Bohrstelle als Basis für eine Alters-/Tiefenskala benutzt. Zusätzlich haben wir den Gehalt des Tritiums – ein radioaktives Wasserstoffisotop, welches bei Atomwaffentests bis 1963 emittiert wurde – bestimmt. Tritium ist in den Eiskristallen eingeschlossen und wurde deshalb nicht mit Schmelzwasser ausgewaschen. Ausserdem haben wir die Schwankungen in der Konzentration von Russpartikeln im Eis zur Identifikation der Jahresschichten genutzt. Aufgrund des konvektiven Transportes von Luftmassen aus dem Tal nach oben dürfte der Russeintrag im Sommer am höchsten liegen. Diese Annahme ermöglichte es, 35 Jahre in den obersten 20 m weq (Wasseräquivalent) des Bohrkerns vom Silvrettagletscher zu zählen, was zeigt, dass diese Methode für die Datierung temperierter Eisbohrkerne geeignet ist.

Die konventionelle Analyse von hydrophoben Chemikalien im Ultraspurenbereich in Gletschereis erfordert grosse Probenvolumina und ist daher mit einem beträchtlichen Risiko für störende Kontamination der Probe durch auf den Gefässwandungen vorhandene Spurenchemikalien verbunden. Deshalb haben wir eine neue Methode nach unseren Ansprüchen entwickelt. Sie ist basiert auf einer mit Polydimethylsiloxan (PDMS) beschichteten Kapillaren, durch welche das Wasser gedrückt wird. Der Kontakt der Probe mit Oberflächen und somit Verluste und Kontamination werden so minimiert. Wir haben die drei Eisbohrkerne mit dieser neuen Methode analysiert und die Resultate verglichen. PCBs konnten in allen Proben nachgewiesen werden, hingegen wurden in keiner der Proben DDTs gefunden. Die PCB-Gehalte von einigen ng/L von allen Gletschern stimmen gut überein und die Höchstwerte liegen in den in den 1970er Jahren. Dieser Befund deckt sich mit dem zeitlichen Verlauf der Emission dieser Stoffe in die Umwelt.

Der Fiescherhorn-Eisbohrkern dient als Beispiel für atmosphärischen Eintrag in Gletschereis und weist die höchsten Schadstoffkonzentrationen aller drei Kerne auf. Die gemessenen Gehalte vom Fiescherhorngletscher sind vergleichbar mit anderen Studien aus den Alpen, aber höher als die Konzentrationen in der Arktis. Zeitliche Konzentrationsschwankungen können mit der Änderung von Umweltparametern (Lufttemperatur und Schmelzen an der Oberfläche) erklärt werden. Nasse oder trockene Ablagerung auf dem Gletscher ist verantwortlich für den Transport von Schadstoffen in das Gletschereis. Im Rahmen der Schneealterung werden flüchtige und wasserlöslichere

Chemikalien teilweise wieder in die Atmosphäre emittiert bzw. mit Schmelzwasser ausgewaschen. Aus diesem Grund wurde eine bevorzugte Anreicherung der weniger flüchtigen und weniger wasserlöslichen, höherchlorierten PCBs beobachtet.

Im Vergleich zu den beiden übrigen Gletschern liegt der Grenzgletscher näher an zusätzlichen Schadstoffquellen in der Poebene. Trotzdem ist sein Eis durch tiefere Konzentrationen als dasjenige aus dem Fiescherhorngletschern charakterisiert. Wir beobachteten teilweise eine Umlagerung der PCBs durch Schmelzen. Im temperierten Silvrettagletscher, wo das Eis jedes Jahr an der Oberfläche schmilzt und flüssiges Wasser in der Tiefe sickert, sind die gemessenen Konzentrationen viel tiefer als im Grenzgletscher. Aufgrund der geringeren Höhenlage des Silvrettagletschers ist der atmosphärische Eintrag aber vermutlich grösser als am Grenzgletscher. Jedoch wurden vor allem in Jahren mit negativen Massenbilanzen die Substanzen teilweise von Schmelzwasser ausgewaschen. Zugleich entstehen beim erneuten Gefrieren von Wasser Schichten von luftblasenfreiem Kompakteis, welche oft mit partikelgebundenen organischen Schadstoffen angereichert sind.

Zum Schluss haben wir die Freisetzung von POPs in Gletscherbächen und -seen quantifiziert. Wir haben zwei Methoden kombiniert, um die räumliche und zeitliche Auflösung der Schadstoffschwankungen zu verbessern. Seesedimente und Passivsammler aus PDMS wurden zur Erfassung von historischer und aktueller Freisetzung verwendet.

Wir haben die proglazialen Silvrettaseen, einen Bach mit Schmelzwasser vom Gletscher sowie einen Bach mit gletscherfreiem Einzugsgebiet analysiert. Visuelle Untersuchung der Seesedimente sowie die Kontaminationsprofile und zeigen, dass seit einigen Jahren nur noch einer der Silvrettaseen Schmelzwasser aus dem Gletscher erhält. Die PCB-Konzentrationen im Sediment aus diesem See sind vergleichbar mit Emissionsdaten, wobei die obersten Lagen aufgrund von schnellerem Schmelzen erhöhte Werte aufweisen. PCBs werden im Gegensatz zu DDTs in jüngster Vergangenheit durch starken Gletscherrückzug in höheren Raten freigesetzt. Die Passivsammler-Daten von den proglazialen Seen sind vergleichbar mit Sedimentdaten, mit einer Bevorzugung von höher chlorierter Verbindungen. Im Einzugsgebiet beobachteten wir abnehmende Konzentrationen in den Passivsammlern; vermutlich als Folge abnehmender Umgebungstemperaturen und höherer Niederschlagsraten. Hingegen wurde mit zunehmender Entfernung von der Gletscherzunge keine Abnahme des Schadstoffgehalts beobachtet. Deshalb spielt den Oberflächenabfluss für die Verbreitung von Schadstoffen im Einzugsgebiet eine wichtige Rolle.

Wir konnten robuste und zuverlässige Daten von Sedimenten und Eiskernen für die Validierung eines Modells des Umweltverhaltens von POPs liefern, welches Deposition, Transport und Freisetzung von Chemikalien in Gletschern umfasst. Daraus können in Zukunft Messergebnisse mit Klima- und Aerosolmodellen kombiniert werden und damit derzeitige Quellen von Altlasten in der Atmosphäre und die Bedeutung von Transportprozessen im Vergleich zu lokalen Quellen in der Umwelt charakterisiert werden.

LIST OF ABBREVIATIONS

ABL	Atmospheric Boundary Layer
DDTs	Dichlorodiphenyltrichloroethane
ELA	Equilibrium Line Altitude
Empa	Swiss Federal Laboratories for Materials Science and Technology
EPA	Environmental Protection Agency
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IPPC	Intergovermental Panel on Climate Change
LRAT	Long Range Athmospheric Transport
NTP	United States National Toxicology Program
PCBs	Polychlorinated Biphenyls
PDMS	Polydimethyl siloxane
POPs	Persistent organic pollutants
PSI	Paul Scherrer Institute
PVDF	Polyvinylidene fluoride
UNEP	United Nations Environmental Program
WHO	World Health Organization

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1 INTRODUCTION

Persistent organic pollutants (POPs) represent a group of anthropogenic organic substances, including industrial chemicals, pesticides, as well as unintentional by-products of combustion processes and chemical reactions. During the phase of application in the 20th century, they were released to the environment and distributed mainly by atmospheric transport. Today, these hazardous chemicals are banned worldwide by the Stockholm Convention (UNEP, 2004). Nevertheless, because of their persistence and volatility, they are still found and even enriched in remote polar and mountain areas, far away from their initial emission sources (Hung et al., 2010). In high-alpine regions snow is accumulated on glaciers and with time is transformed to firn and ice. Because atmospheric pollutants are deposited with precipitation, glacier ice represents an archive for the air quality above the site. However, secondary processes of redistribution of pollutants occur in the ice matrix and may affect its composition. Therefore, further knowledge of these processes is essential for the interpretation of ice core records.

Organic contaminants in glacier environments might have direct impact on humans by effecting drinking water resources, as well as an indirect effect on quality of agricultural production and contamination in dairy, meat and fish. Since glaciers are located in pristine mountain areas, pollution in glacier ice has a potentially more important effect on sensitive ecosystems, which can be further amplified by bioaccumulation. Moreover, since the cryosphere is influenced by global climate change more dramatically than other areas (IPCC, 2013), the accelerated melting of glaciers can be responsible for enhanced release of previously deposited environmental pollutants.

1.1 Substances of interest

1.1.1 *Polychlorinated biphenyls (PCBs)*

Polychlorinated biphenyls represent a group of 209 congeners, with the general formula $C_{12}H_{10-n}Cl_n$ (n = 1 to 10), differing only in number or position of the Cl atoms (Figure 1). The unique numbering of the single congeners was proposed by Ballschmiter & Zell (1980) and was adapted by IUPAC. PCBs were used in insulating liquids, coolants, in electrical transformers and capacitors, additives in paint, plastics and carbonless printing paper (Safe and Hutzinger, 1987). The biggest producer of PCBs was Monsanto with more than 600 Kt produced in USA for the period 1930-1977 (EPA, 2010). Globally, more than 1500 Kt PCBs have been produced since 1930 (Breivik et al., 2007). Today although PCBs are no longer produced, primary emissions from use and disposal represent important sources.

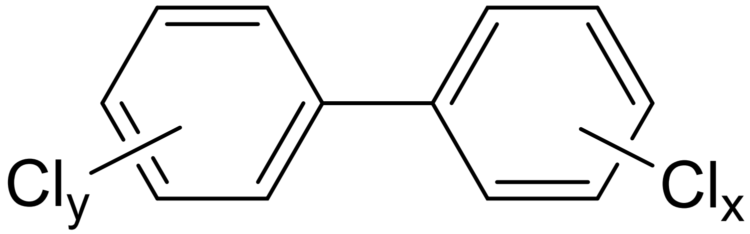


Figure 1: **Structural formula of PCBs**

Bioaccumulation of PCBs was reported for the first time by Jensen (1966), who detected PCBs in pike from Sweden (Atlas et al., 1993). Since then multiple studies have reported PCB concentrations in remote areas, various matrixes and biota (Bogdal et al., 2009a; Grimalt et al., 2004; Nizzetto et al., 2006; Offenthaler et al., 2009). Today, concentrations of PCBs in tropospheric air are highest over the northern industrialized belt between 30º N and 60° N ranging from 2 to 20 ng/m^3 in urban air, and 0.02 to 5.4 ng/m^3 in rural air. Because of their chemical properties, PCBs are also characterized with very strong seasonal cycle, showing maximum concentrations during the warmest season (Atlas et al., 1993).

1.1.2 *Hexachlorobenzene (HCB)*

Hexachlorobenzene (HCB, see Figure 2) – has the general formula C_6Cl_6 and was introduced as a fungicide for crop seeds in 1945. Later it has also been used as a wood-preserving agent, and in industry as a porosity-control agent, in the manufacture of graphite anodes, as a peptizing agent in the production of nitroso and styrene rubber for tires (Barber et al., 2005). Substantial quantities of HCB are contained in the wastes generated through the manufacture of chlorinated solvents. In addition, many combustion and metallurgical processes emit small amounts of HCB (EPA, 2010). Therefore, incineration is an important source of HCB in the environment. HCB has been detected in emissions from the combustion of coal and hazardous waste, cement production as well as leaks from landfills. Technical HCB was produced mainly in Europe (around 80%) (Rippen and Frank, 1986) in industrialized regions of countries such as Germany, Spain, and the Czech Republic. Peak annual worldwide HCB production was in the late 1970s and early 1980s with around 10 Kt. It was banned from use in the USA in 1966 and in Switzerland in 1986 (Barber et al., 2005)

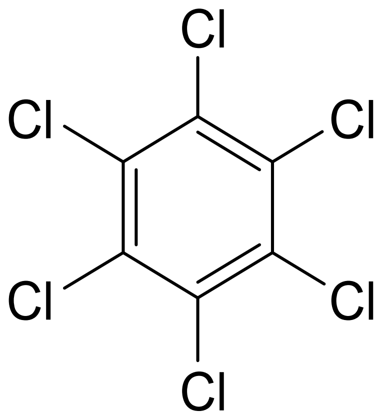


Figure 2: Structural formula of HCB

Today, as emissions of HCB from point sources have decreased, the variability in HCB air concentrations has been reduced. Regionally, levels of HCB in the atmosphere are very uniform (Barber et al., 2005). The half-life of HCB in air with respect to photo-oxidation ranges from 156 days to 4.2 years. The half-life of residence of HCB in soil has been estimated to be 970-2100 days (Griffin and Chou, 1981), with the major loss process from soil at the surface being volatilization. HCB is also prone to anaerobic degradation. Kaupp et al. (1996) observed a clear annual cycle in HCB air concentrations in Germany, with the mean urban concentration in summer being three times higher than in winter. HCB is very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment. Ecological investigations have found that biomagnification up the food chain does occur.

1.1.3 Hexachlorocyclohexane (HCH)

Hexachlorocyclohexane ($C_6H_6Cl_6$, Figure 3) was first synthesised in 1825 by Faraday, but its pesticidal effect was discovered in 1942, after which lindane (γ-HCH) production and use started up in the United Kingdom (UNEP, 2007). A total of nine HCH isomers have been identified in technical HCH. However, only the α-, β-, γ-, δ- and ε-isomers are stable and these are the ones commonly identified in technical HCH. α-HCH is the most abundant with share of 60-70% (Li and Macdonald, 2005). Lindane contains more than 90% of γ-HCH which posseses significant insecticidal properties. It has been used to treat food crops and forestry products, as a seed treatment, a soil treatment, and to treat livestock and pets (CEC, 2006). It was estimated that between 1948 and 1997, around 10 000 Kt of technical HCH were released to the environment, and whereof the vast majority was used in agriculture (Li, 1999). Lindane has been manufactured by several countries, including USA, China, and several European countries. Two significant drops in global technical HCH usage were identified: the first one in 1971, when Canada, USA and some European countries banned the use of technical HCH, and the second one in 1983 when China banned the use of technical HCH in agriculture (Li and Macdonald, 2005). The Environmental Protection Agency (EPA) and World Health Organization

(WHO) both classify lindane as "moderately" acutely toxic.Most of the adverse human health effects reported for lindane have been related to agricultural uses and chronic, occupational exposure of seed-treatment workers. (WHO, 2012)

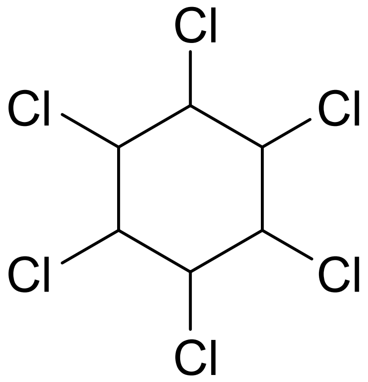
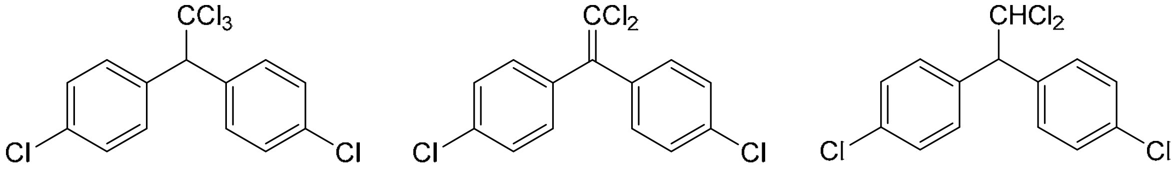


Figure 3: Chemical formula HCH

1.1.4 Dichlorodiphenyltrichloroethane (DDT) and by-products

Dichlorodiphenyltrichloroethane (DDT) was discovered as a pesticide in 1940 by Paul H. Müller, who was awarded Nobel Prize in Physiology and Medicine in 1948 for this discovery (Kenneth, 1992). DDT was extensively used in agriculture but also worldwide for medical and public health issues. From 1950 to the mid-1990s more than 35 Kt were used each year worldwide and it has been estimated that a total of 4500 Kt have been produced globally since the 1940s (Li and Macdonald, 2005). After 1960 a number of reports revealed negative effects on non-target species like wildlife and humans. Bird species, especially fish eating, showed a decline in population due to egg shell thinning. In 1970, DDT was banned in USA and in Europe in 1986 (Kenneth, 1992). Nevertheless, DDT is still being used against malaria mainly in developing countries (nowadays used as much as in Europe 1960) (Atlas et al., 1993). DDT has two isomers: 2,4′-DDT (25% share by production) and 4,4′-DDT (75%). In the environment, 4,4’-DDT is degraded to 4,4’-DDE (dichlorodiphenyldichloroethylene), which is more persistent than the parent compound and 4,4’-DDD (dichlorodiphenyldichloroethane) (Figure 4). The physicochemical properties of DDT and its major metabolites enable these compounds to accumulate readily in organisms via the surrounding medium and food. Today, tropospheric concentration ranges from 70 to160 pg/m^3. DDT is classified as "moderately toxic" by the United States National Toxicology Program (NTP) and "moderately hazardous" by the WHO (WHO, 2012).



4,4’-DDT 4,4’-DDE 4,4’-DDD

Figure 4: DDT and its metabolites

1.1.5 Emission pattern of POPs

Most of the legacy POPs were introduced in in the 20th century and were banned after the Stockholm Convention (UNEP, 2004). For this reason, most of them are characterized with a comparable emission pattern. However, depending on the use and the chemical properites of the substances, their distribution and dynamics in the environment is different. There is no single dataset summarizing POPs emissions worldwide. We compiled a comparison of production, usage and emission data on a global scale for three different chemicals (Figure 5). Since DDT was introduced to the market earlier than the other chemicals, its emission peaked already in the 1950s. The broad peak of DDT emissions is due to the open application in agriculture. The use of technical HCH was regulated later than other POPs, which also reflects its global emissions. In addition, because of differences in the market development, it is also characterized with two peaks (see chapter 1.1.3, HCH). In contrast to the other two pollutant groups, PCBs shows a well pronounced global production peak in 1970s, followed by a gradual decline.The described patterns for the different pollutants are also detected in the environment (Meijer et al., 2003; Wang et al., 2008).

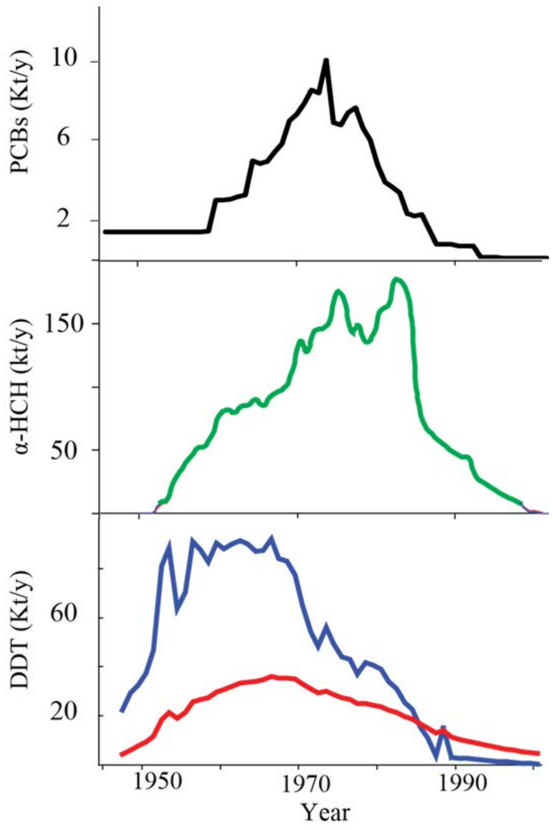


Figure 5: Emission and usage trends of POPs: global production of PCBs (Breivik et al., 2007, black line), global α-HCH emissions (greed line); global DDT emissions (red line), usage (blue line). Figure adapted from Li and Macdonald, 2005

1.2 Organic contaminants in high-Alpine regions

1.2.1 Environmental properties of POPs

The behavior and fate of POPs is determined by their chemical and physical properties, which depend on their molecular structure. The most important properties for the distribution of POPs in the environment include persistence, lipophilicity, and semi-volatility (Schwarzenbach et al., 2003). Persistence is defined by the time a compound remains unaffected in the environment before is degraded to a less hazardous one. The semi-volatility represents the degree of mobility, which allows compounds to enter the atmosphere and be transported with air masses at long distances (Ritter et al., 1996). The mobilty occurs to a moderate extent, therefore the term “semi”, which also determines the deposition back to the Earth’s surface. Whereas the persistence increases with degree of chlorination, the volatility decreases, i.e. pollutants with less chlorine atoms easily partition to air and are transported to greater distances, but at the same time degradation in air is higher. The property responsible for the toxicity and the bioaccumulation of POPs in living organisms is lipophilicity or their tendency to preferentially dissolve in fats and lipids. It is inversely proportional to water solubility and also increases with chlorination degree. The distribution of organic pollutants between environmental media can be described by three solubilities: solubility in air, solubility in water, and solubility in octanol, assuming partitioning into soil is dominated by organic matter, which can be represented by octanol (Schwarzenbach et al., 2003). Thus, the ratios of these solubilities are defined as partitioning coefficients K_{OW} (ocatnol-water), K_{OA} (octanol-air), K_{AW} (air-water). The chemical properties of POPs are summarized in Table 1.

Table 1: Chemical properties of POPs.

Substance group	**Molar mass**	**Log Kow**	**Log Kaw**	**Log Koa**	**Aqueous solubility**	**Vapour pressure**
	g/mol					**$*10^{-5}$mmHg**
PCBs[1,2]	188-498	4.61÷7.76	-2.2÷-1.99	6.77÷11.13	$10^{-2}÷10^{-3}$	≤ 4
DDTs[1,3]	283.56 -354.49	6.45÷6.73	-3.22÷-2.88	9.33÷9.95	10^{-2}	2.3
HCHs[1,3]	290.83	3.69÷3.79	-4.07÷-3.59	7.38÷7.76	10^{-3}	≤ 4
HCB[3]	284.8	5.31	-1.64	6.88	10^{-3}	1.1

[1]Schenker et al., 2005; [2]Shiu and Mackay, 1986b; [3]EPA, 2010

1.2.2 *Scavenging of POPs in the atmosphere*

The main distribution path for organic pollutants to remote regions is atmospheric transport, which is caused by persistence and volatility. The exchange between atmosphere and the Earth's surface (soil, water, snow) depends on a number of processes including vapour and particle scavenging, vapour sorption/desorption onto the surface and diffusion of chemicals bewteen air and surface. Vapour pressure is the main characteristic of the chemicals, which controls partitioning between gas and particle phase. It depends on the number of chlorine atoms and temperature. Further, Henry's law constant, which decribes the ratio of the vapour pressure to the amount dissolved in water under equilibrium, controls partitioning between vapour and dissolved liquid phase (water or rain). Based on the ratio of the concentrations, for every chemical and environmental compartment, a scavenging ratio is defined. Whereas the scavenging ratio of the vapour phase increases with decreasing vapour pressure and higher specific surface area (SSA) of the environmental matrix, the total scavenging depends mainly on decreasing temperature (Herbert et al., 2006). The effect of the shift in partitioning of the pollutants from vapour to liquid/solid phase is called "cold trapping" or "cold condensation" and is interpreted as the driving process for the enrichment of POPs in high latitude and altitudes (Bidleman, 1988).

1.2.3 Deposition and revolatilization

The main process of removal of organic pollutants from the atmosphere to the underlying surface is wet or dry deposition. Wet deposition is more efficient for water soluble POPs (gas scavenging of HCHs) or low volatility compounds (particle-bound heavy PCBs). Dry deposition is in general less important than wet deposition and depends mainly on temperatures and wind speed. Whereas wet deposition is relatively independent on the underlying surface, dry deposition is strongly influenced by the surface type and composition.

Elevated concentrations, transport and distribution of organic chemicals in the environment can be explained also in the framework of fugacity i.e. the chemical behaviour of substances to strive for equilibrium distribution between phases (Wania et al., 1999). Moreover, the difference in fugacities between two phases is a measure of degree of disequilibrium and results from three main effects. First, pollutant transport is mainly triggered by partitioning between phases – the higher the fugacity capacity of a compound, the higher the concentration in a certain media. The effect depends on type of phase, the chemical composition of that phase and temperature. For example, higher organic content in the accepting media as well as lower temperature, leads to increased fugacity capacity of POPs in mountain sites and provides the main explanation for the "cold trapping". Second, as a result of change in phase composition, structure, temperature, volume, etc., the potential of a compartment to hold a chemical decreases faster than loss of chemical from the phase, which leads to increased fugacity and respectively in the case of decreasing volumes, increased concentrations in the selected media. Last, in case of difference in the in- and outflux, the difference in concentration is maintained dynamically against the concentration gradient. Such kinetic effects include for example funelling, filtering, pumping, trapping, etc. (Wania et al., 1999).

1.3 Glaciers as pollutant archives

1.3.1 High-alpine climate archives

High alpine glaciers form by continuous accumulation of annual snow and thus represent the perennial surface land ice masses. When climate conditions and topographic characteristics allow snow to accumulate over several years it transforms gradually to firn and finally to glacier ice. Snow-to-ice metamorphosis is mainly driven by pressure change due to weight of the overlaying snow. As a result snow grains grow larger, the air space between them is reduced and the density is increased. When the density reaches 0.83 g/m^3, the pore space between the crystals is closed and the firn is transformed into glacier ice. Further slow increase of density results in compression of air bubbles (Cuffey and Paterson, 2010). The section, where the glacier is gaining mass, is called accumulation area. Under the force of gravity, this ice flows downwards to elevations with higher temperatures, where loss of ice due to melting dominates over accumulation.

This area is defined as the ablation area of the glacier (Figure 6). The calculated net change of ice mass resulting from the accumulation and the ablation for a glacier is called mass balance. The boundary between accumulation and ablation area is the defined by the equilibrium line (Cuffey and Paterson, 2010). The equilibrium line altitude (ELA) change is representative for the net mass balance of the glacier i.e. glaciers with increasing ELA are shrinking. Depending on the temperature of the ice, cold and temperate glaciers are distinguished. In cold glaciers the ice temperature is well below the pressure melting point throughout the ice and they are often frozen to the bedrock. In temperate glaciers, which represent the majority of the glaciers in mid latitudes and altitudes, the temperature of ice is at the pressure melting point. Therefore, up to 9 % bulk liquid water is present within the ice matrix, in ice lenses between the ice grains, in veins, in triple grain intersections and in nodes, where veins intersect (Pettersson, 2004).

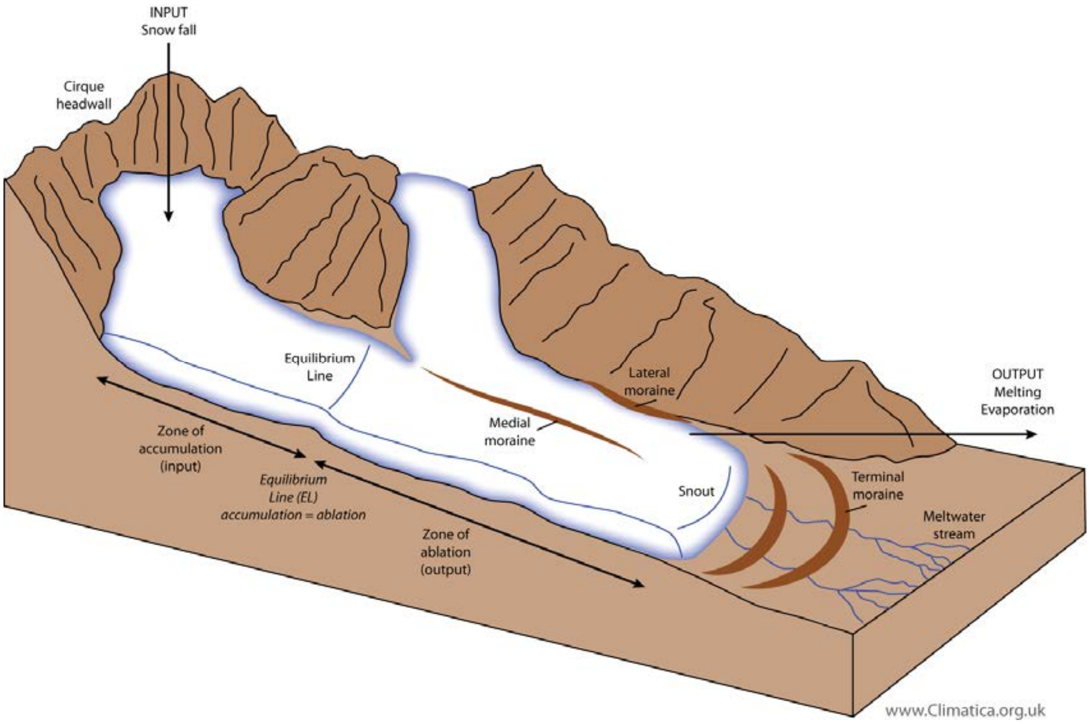


Figure 6: Schematic structure of mountain glacier (www climatica.org.uk)

1.3.2 Pollutant transport to glaciers

Because snowfall scavenges impurities present in the atmosphere, glaciers provide time resolved information about composition of the impurities in the atmosphere. Hence, glaciers represent an archive for aerosol related species. Some specific climatic properties like low temperatures, high precipitation rates, high wind speed and low atmospheric pressure enhance the deposition and preservation of organic pollutants in glaciers (Daly and Wania, 2005). Synoptic scale (in the range of 1000 km) weather systems transport pollutants over long distances, being the most important factor in long range atmospheric transport. In addition, temperature driven diurnal mountain/valley wind systems bring contaminated air masses uphill during the day, which is reversed to down-slope conditions during the night. Further, the air-surface exchange is enhanced by low temperatures, high precipitation and rough surface, whereas evaporation is being favored by high temperatures and low capacity of the surface (high fugacity) (Daly and Wania, 2005). The deposition is also dependent on the type of precipitation, i.e. snow is a much more efficient scavenger than rain, especially for the less volatile compounds.

Many studies have reported increased concentration of POPs with increasing altitude (Blais et al., 1998; Quiroz et al., 2009). Apart from the listed favorable conditions in mountains, "cold trapping" might be also responsible for the enrichment along the altitudinal gradient, which is more pronounced for the more volatile compounds. Still, the location of the sampling sites relative to the sources plays an important role, because deposition rates are generally higher in proximity of sources (Daly and Wania, 2005). When contaminant sources are within or in the vicinity of the mountains, the concentrations are a consequence of a dynamic process of prevailing high deposition than volatilization (Gong et al., 2014). Deposition depends on a number of environmental factors, many of which undergo a strong seasonal cycle. Thus, lack of clear patterns in POPs load datasets is not surprising (Daly and Wania, 2005).

1.3.3 Snow aging and metamorphosis

Fresh fallen snow consists of ice crystals, pore air, liquid water and particles, where, depending on their chemical properties, organic pollutants partition between phases. During metamorphosis snow changes in grain size and shape, which is defined by increase in density (0.3-0.9 g/cm^3) and a decrease in the specific surface area (SSA – 100-1500 cm^2/g) (Herbert et al., 2006). Decreasing SSA reduces the capacity of the snow layer to retain molecules adsorbed at the surface and the chemicals are released from the ice crystals back to pore space. Snow aging is accelerated with rising temperature and wind speed because of the rounding of snow crystal edges, sublimation of microstructures and dilution by surface hoar (Cabanes et al., 2002). Diffusion/wind pumping defines the exchange of air between the atmospheric boundary layer (ABL) and the pore spaces in snow and strongly depends on the concentration gradient. Thus, aging of the snow cover results in redistribution of the POPs between different compartments present in the snow and, respectively, their loss through revolatilization or degradation. Significant loss of volatile compounds has been reported by Herbert et al. (2006): 75% of PCB lost in 96 hours, followed by stable concentrations up to 240 h and an additional increase in the underlying layer load after a new snow event. This is a sign of exchange of pollutants stored most likely in the pore air. In addition, aging causes more chemicals to be bound to particles. As a result, fractionation towards heavier, less volatile compounds in the snowpack takes place (Gregor and Gummer, 1989).

In glacier environments apart from revolatilization POPs can be lost by photodegration. Although at very slow rates, below -10°C exclusively dehalogenation, coupling, or rearrangement reactions may take place. Nevertheless, organic contaminants have minimal absorption in the region of the tropospheric solar spectrum and, therefore, their direct photochemical degradation is relatively inefficient (Matykiewiczová et al., 2007).

1.3.4 Melting and release

Glaciers adjust their size in response to changes in climate and therefore are sensitive climate indicators. The 5th IPCC Assessment on Climate Change provides robust evidences that glaciers are shrinking globally, and in some regions even with accelerating rates (IPCC, 2013). In the Alps, glaciers are constantly loosing mass since mid-1980s. (Figure 7). Furthermore, depending on the future emissions, the loss due to melting might be even higher. Huss (2012) examine glacier mass balance change in the Alps for the period 2011-2100 as a subject to different CO_2 emission scenarios and shows that no big changes in mass and volume of glaciers is expected until 2050. In contrast, after that period depending on the emissions and the size of the glaciers from 4% to 80 % of the glacier mass (relatively to 2003) in the Alps can be lost.

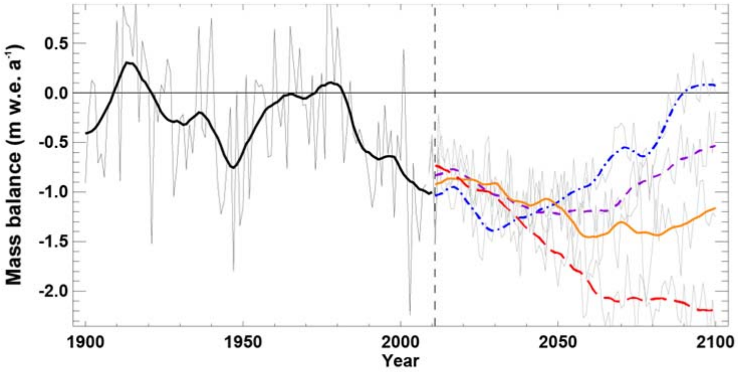


Figure 7: Mass balance change series extrapolated to all glaciers in the European Alps for 1900–2100. The dashed line indicates the onset of future modelling results (2011). Four different climate scenarious according to IPCC are considered: high emission scenario (RCP8.5 - red dotted line), medium mitigation scenario(RCP4.5-purple dotted line), a peak-decline scenario with a rapid stabilization of CO_2 concentrations (RCP2.6-purple-dotted line), and an intermediate scenario (RCP6.0-yellow dotted line). Figure is adapted from Huss (2012).

In a warming climate, substances stored in the glacier ice are released at higher rates. However, melting is triggered not only by higher air temperatures but also by decreased albedo due to the presence of impurities on the glacier surface. Overall, seasonal snowmelt results in re-emission of volatile compounds back to the atmosphere or release with meltwater to the freshwater systems. In case of refreezing of meltwater formed at the surface in deeper and colder areas of the glacier, layers of compact ice, called ice lenses are formed below the glacier surface. These layers might be enriched in particles and thus accumulate particle bound chemicals. In addition, ice lenses seal the surface of the glacier and isolate the underlying layers from contact with the atmosphere. During melt events, fractionation of organic pollutants which depends on solubility and partition coefficients (K_{OA} and K_{OW}) takes place. Meyer and Wania (2011) proposed two types of enrichment of the meltwater with organics during melt event. The "first flush" mimics the behaviour of inorganic ions and is important for chemicals and small particles, located at the ice lattice on the onset of the melt event. As a result, the pollutants are transported downwards from the grain boundaries with gravimetrically percolating meltwater, which becomes enriched. Thus, difference in the first flush behaviour arises from the snow metamorphism process prior to melt or due to diverse meltwater hydraulics. On the contrary, the second type enrichment is essential for the particle bound fraction and occurs late in the melt event. It is generally attributed to the filtering of particles by the snowpack, where coagulation of particles enhances retention of the particulate fraction. Due to the rapid snow densification, large particle coagulates can clog the pore spaces and are accumulated at the surface. Thus, relatively small differences in the affinity of the chemicals for interface and organic matter could result in diverse phase distribution in snow. In addition, melt and refreeze cycles lead to a denser snowpack and even more efficient filtering of particles.

2 MOTIVATION OF THE STUDY

This thesis is part of a multidisciplinary project: “Accelerated release of POPs from Alpine glaciers” dedicated to the investigation of the fate of legacy persistent organic pollutants (POPs) in glacier environments. Several studies have shown that organic contaminants previously deposited to and incorporated into ice and are now released at historically high rates to the environment due to the rapid melting of glaciers (Bettinetti et al., 2011; Bizzotto et al., 2009; Blais et al., 1998; Bogdal et al., 2009b). However, none of the previous studies provided enough data to enable a comprehensive physical understanding of the involved glacial processes. In the present project, we investigate the selected anthropogenic organic chemicals regarding their deposition on, incorporation into, transport within, and release from temperate Alpine glaciers. Silvretta glacier in the Swiss Alps was chosen as a study site, because, as part of the Swiss Glacier Monitoring Network, it has been studied since the early 20th century and there are available local mass balance data, reaching back to 1915 (Huss et al., 2009). Known from ground-penetrating radar soundings, the Silvretta glacier has a relatively simple geometry and bed topography, which allows modelling of the glacier flow. Furthermore, it has retreated more than 300 m since the 1950s, resulting in the formation of two proglacial lakes.

Initially, sediment cores from the Silvretta lakes were analysed using conventional methods and proved the site suitable for the project. In addition, to quantify current release of contaminants in the Silvretta catchment area, PDMS passive samplers were employed. Since POPs are unambiguous in our environment and, at the same time, present in very low concentrations in glacier ice, we developed an extraction method for glacier ice samples, which minimizes blank contribution. Using the novel method we provided a comprehensive PCB record from the Alps: Fiescherhorn glacier, a cold glacier with negligible surface melting, which was further used as atmospheric input function. Since most of the glaciers in the Alps are affected by melting, we are interested particularly in the transport and redistribution of POPs with percolating meltwater. Therefore, an ice core from Grenzgletscher - another cold glacier, which has one distinct melt feature, was analysed. Finally, the ice core from the Silvretta glacier was analysed for PCBs and was used to examine the effect of annual melting on the release of organic pollutants in the einvironment. Further the obtained record will be used for validation of an environmental fate model of the Silvretta glacier and proglacial lakes system.

This thesis is subdivided into 8 parts. In Chapter 1, the chemical-physical properties of the substances of interest and their importance for the distribution in the environment are summarized, followed by a brief motivation for the current resreach interest (Chapter 2). In Chapter 3, the study sites, the field campaigns and the obtained ice cores are described. In Chapter 4, we discuss the analytical methods and focus on the dating of the temperate Silvretta ice core. In Chapter 5, a novel method for analysis of POPs in ice cores is presented in detail. In Chapter 6, we examine the inventory of PCBs in the Alps in the cold Fiescherhorn glacier. In Chapter 7, we further extend our study to two other ice cores, which are affected by melting and in Chapter 8, we evaluate the release of legacy pollutants from melting glaciers. The work is finalized with a conclusion and outlook part in Chapter 9.

3 STUDY SITES AND FIELD WORK

3.1 Fiescherhorn

The Fiescherhorn glacier is located in the central Swiss Alps, 6 km away from the Jungfraujoch research station. In a glaciological pre-study, radar sounding and water drilling were performed to map the bedrock topography and determine thermal conditions (Schwerzmann et al., 2006). The drilling site was chosen on a plateau at approximately 3900 m a.s.l between the summits of Gross Fiescherhorn (4049 m a.s.l.), Hinter Fiescherhorn (4025 m a.s.l.), and Ochs (3895 m a.s.l.) (Figure 8). Two ice cores were extracted from this location: a 77 m long ice core in 1989 (Schwikowski, 1999) and a 151 m long ice core in 2002 (Jenk, 2006; Schwerzmann et al., 2006). Both have been extensively studied and used as paleoclimate records (Cao, 2013; Jenk, 2006; Schotterer et al., 1999, 1998) and proved that Fiescherhorn glacier is a cold glacier with almost no percolating water. In this thesis we focus on the 2002 ice core. The age-depth relationship for this ice core was established using a multiproxy method including: (1) annual layer counting of the seasonally varying stable isotope ratio $\delta^{18}O$ and the concentration of NH_4^+, (2) identification of well-documented Saharan dust events, (3) investigation of the ^{3}H maximum from thermonuclear bomb tests in 1963, and (4) detection of the ^{137}Cs peak from the Chernobyl accident in 1986 (Mariani et al., 2012). The dating uncertainty is ±1 year for the time period considered in this study. The average accumulation rate for the Fiescherhorn drilling site has been estimated 1.7 m weq, homogeneously distributed over all seasons. Thus, in the frame of this project, we analysed samples covering 1940-2002 contained in the upper 107 m weq of the ice core (see section 6.2).

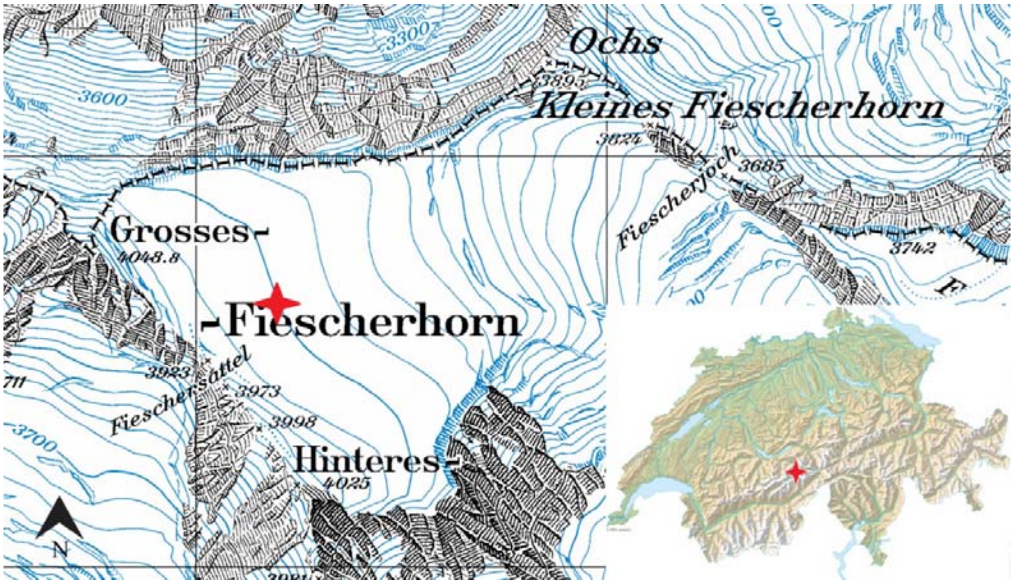


Figure 8: Map of the Fiescherhorn glacier with the 2002 drilling site (© 2014 swisstopo JD100043). The grid represents 1 km. In the bottom right an overview map of Switzerland is showing the location of the study site.

3.2 Grenzgletscher

Grenzgletscher is a tributary to the Gornergletscher, the second largest glacier in the Alps, located in the Monte Rosa Massif, Swiss Alps (Figure 9). The 125 m long ice core was drilled at 4200 m a.s.l.in October 1994 in the accumulation area of the glacier, downstream of the Colle Gnifetti saddle, which has been extensively studied (Gäggeler, 1977; Luethi and Funk, 2001; Sigl et al., 2009; Wagenbach and Geis, 1989). The dating of the ice core is based on the radioactive decay of the isotope ^{210}Pb, and confirmed by combined evaluation of the NH_4^+ and $\delta^{18}O$ and location of stratigraphic markers from Saharan dust falls, atmospheric nuclear weapon tests, and the reactor accident in Chernobyl (Eichler et al., 2000). The resulting dating uncertainty is ± 1 year for the period 1970-1993 and ± 3 years for the period 1941-1969. A mean precipitation rate of 2.7 ± 0.4 m weq at Grenzgletscher, compared to 2.4 ± 0.3 m water at the closest meteorological station Col du Grand Saint Bernard, suggests that the accumulated precipitation at the Grenzgletscher corresponds roughly to the actually fallen precipitation. The borehole temperature was 0 º C to - 3º C in the upper 18 m and reaching - 9º C at 80 m depth (Eichler et al., 2000), which ensures the preservation of the climate signal in the ice core. However, in a 13 m firn section a drastic disturbance of the concentration records of certain ionic species was noted (Eichler et al., 2001). Depending on their properties, the species were eluted with different efficiencies, which provided the possibility to investigate the effects of leaching processes on the chemical composition of a natural firn layer. The effect was attributed to the lateral inflow of meltwater. For the scope of the current project, we have analysed the samples covering 1941-1993, including samples from the section affected by melt (1985-1989).

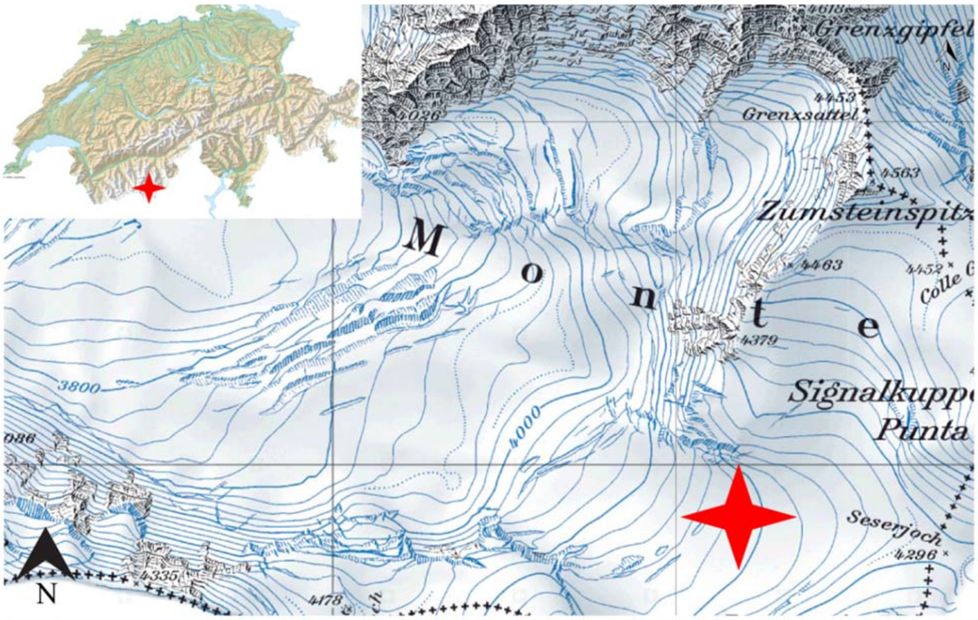


Figure 9: Grenzgletscher drilling site (red star). The grid represents 1 km (© 2014 swisstopo JD100043). In the upper left an overview map of Switzerland is showing the location of the study site.

3.3 Silvretta glacier

Silvretta glacier is a temperate glacier in the Eastern Swiss Alps. Located between between Silvrettahorn and Gletscherchamm, it has a surface area of around 3 km^2 and expands between 2500 and 3000 m a.s.l. (Figure 10). Silvretta is a temperate glacier with ice temperatures near the pressure melting point from 10 m below surface down to the bedrock and thus is strongly affected by melting. In April 2011 a 101 meter long surface-to-bedrock ice core was extracted from Silvretta glacier (46°50’47’’ N, 10°05’79’’ E, 2927 m a.s.l.). We used a combined electromechanical-thermal drill system whereby the first 12 m were drilled by electromechanical drill (Schwikowski et al., 2014). Power supply for the energy-consuming thermal drilling was ensured by two gasoline generators with a capacity of 2 kW each. The Silvretta ice core consists of alternating layers of superimposed ice and normal glacier ice containing air bubbles. The superimposed ice layers are up to 1 meter thick, containing deposits. After drilling, 70-cm-segments were packed separately in polyethylene tubes and stored in insolating boxes on the glacier. Because of the unusually high temperatures during daytime, the insulating boxes were covered with snow to assure a temperature below -1° C. Finally, the ice core was additionally cooled with dry ice during transport to PSI. The uppermost 44.3 m (34 m weq) of the Silvretta ice core, contained in 67 segments were analysed for major ions, black carbon (BC), radioactive isotopes and for selected POPs.

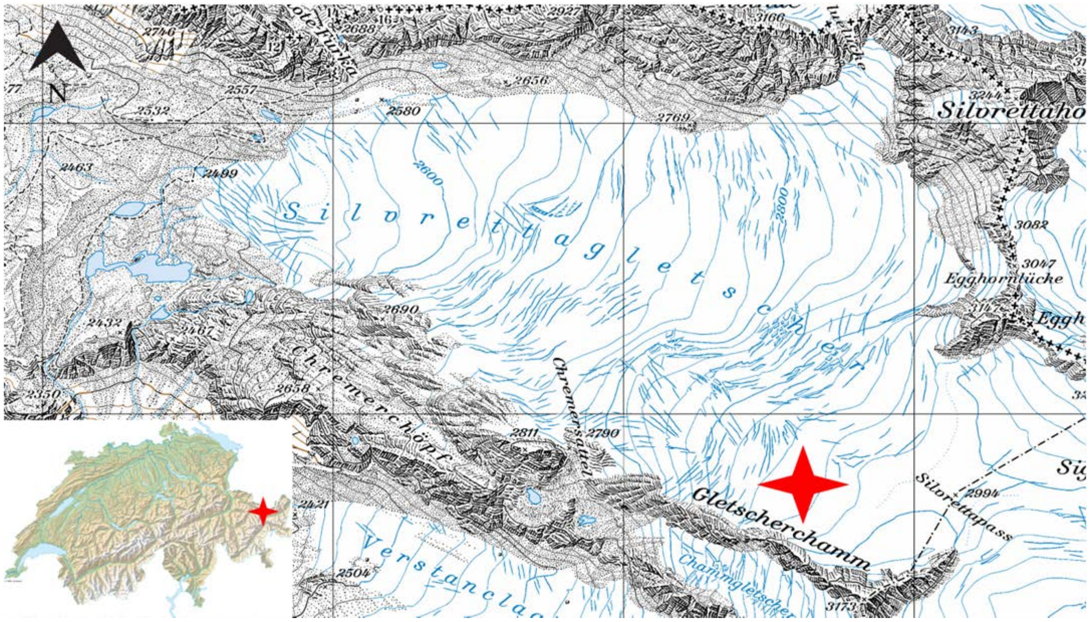


Figure 10: Silvretta glacier and proglacial lakes; drilling site Silvretta (red star). The grid represents 1 km (© 2014 swisstopo JD100043). In the bottom left an overview map of Switzerland is showing the location of the study site.

4 METHODS

4.1 Ice core sample preparation

Ice core segments with a length of approximately 70 cm and a diameter of around 7 cm were transported to PSI. Each segment was photographed on a light table in a - 20 °C cold room and stratigraphic features like dark particle or bubble free layers were carefully described. Subsequently, the samples were prepared using an electrical band saw, equipped with a stainless steel blade and a polyvinylidene fluoride (PVDF) covered table as described by Eichler et al.(2000). Whereas, the outer part of the ice core was used for species, which are less susceptive to contamination, e.g. radioactive isotopes, the inner part was used for major ions, black carbon and POPs (Figure 11). In addition, the volume of the POPs samples was calculated and used for density determination. The density of the segments was determined and varies between 0.4-0.9 g/cm^3. In contrast to cold glaciers, where density increases gradually down to 50 m, in the temperate Silvretta glacier, the density reaches 0.8 g/cm^3 at 3 m. The calculated density was used to obtain depths in m weq. The samples for POPs, analysed in Empa, were transported in an insulating box in frozen state. All samples were melted immediately prior to analysis to minimize losses.

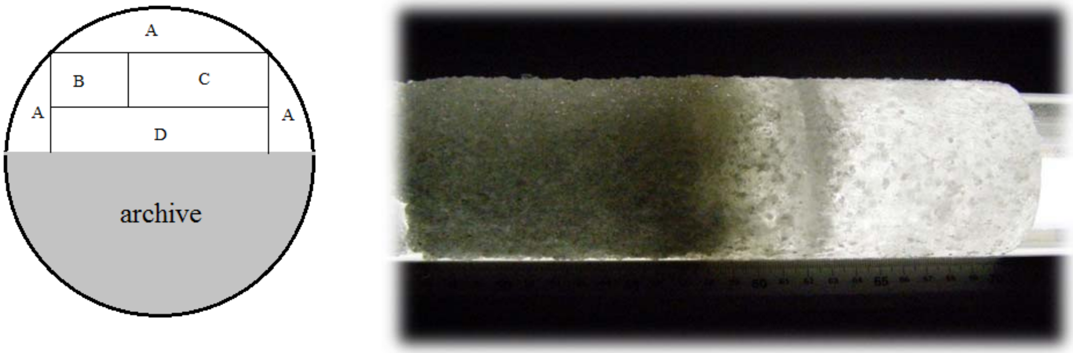


Figure 11: Ice core sample preparation: ice cutting scheme (left): A) ^{3}H and ^{210}Pb samples, B) major ions and black carbon, C) particulate carbon (measurement not conducted), D) POPs and density. Stratigraphic features under backlight (right)

4.2 Ice core dating of the Silvretta ice core

Age-depth scales for ice cores are constructed by applying a multiparameter approach. Annual layer counting of major contaminants or stable water isotopes is applied to constrain single years in the ice core record (Schwikowski et al., 1999). In addition, stratygraphic horizons e.g. nuclear weapon tests, volcanic events, Saharan dust falls (Eichler et al., 2000), ^{210}Pb decay (Gäggeler et al., 1983) and ^{14}C ages (Sigl et al., 2009) are used to fortify the dating. Obtaining a reliable age-depth relationship of the temperate Silvretta ice core represents a particular challenge, since meltwater percolation affects the annual layers (Schotterer et al., 1977).

4.2.1 Annual layer counting

Seasonal variations of the concentration of water soluble ions in snow represent the basis for identification of distinct annual layers, when they are preserved in the ice under favourable conditions. In Alpine glaciers concentrations of major ions are highest in summer, when there is more convective transport from the source areas located in the lowlands (Eichler et al., 2000; Henderson et al., 2006). The quality of the ion records depends on the accumulation rate at a given site and the temperature of the ice. Because of their solubility, major ions are eluted from the ice with percolating water. Also other aerosol related species, such as Black carbon (BC) might experience pronounced seasonality (Ginot et al., 2013). In contrast to ions, BC particles are less eluted during melt events and are accumulated in layers, which might also represent an annual signal (Doherty et al., 2013). Therefore, we investigate the concentration records of ammonium and BC in the Silvretta ice core to assess the potential of use annual layer counting as a dating technique for this glacier (Figure 12). Major ion concentrations were analysed in 10 cm samples of the upper 8 m weq of the Silvretta ice core, using ion chromatography (*850 Professional IC* combined with 872 Extension module, Metrohm) (Herren et al., 2013). The ammonium record experiences some variations in the uppermost 1 m weq of the ice core, which might reflect seasonal variations. Thus, we assume the first double peak (200 ppb) at around 0.7 m weq to correspond to the summer 2010, which is also in agreement with net mass-balance data. Ammonium concentrations obtained from Findelen glacier provide similar values for the year 2010 and further support our assumption (Sold et al., 2014). Below 1m weq the concentrations of ammonium are always lower than 50 ppb and experience almost no fluctuations, indicating removal by meltwater percolation. BC was analysed in the uppermost 21 m weq of the core with 10 cm resolution, using a Single Particle Soot Photometer (SP2, Droplet Measurement Technology, Inc.) (Wendl et al., 2014). BC shows a reverse behaviour compared to ammonium with values varying between 10 and 200 ppb and some layers with exceptionally high concentrations up to 1000 ppb. An attempt for identification of annual cycles is hereby presented (Figure 12). If we interpret every peak in BC concentration as an annual layer, according to the attribution shown in Figure 12, at 20 m weq 35 layers were identified and this depth corresponds to the year 1975. This is in good agreement with the dating obtained from mass balance and tritium data (see 1.2.5). However, the assigning the peaks in BC concentration to particular years implies analytical errors and requires further understanding of the transport processes of BC in temperate ice.

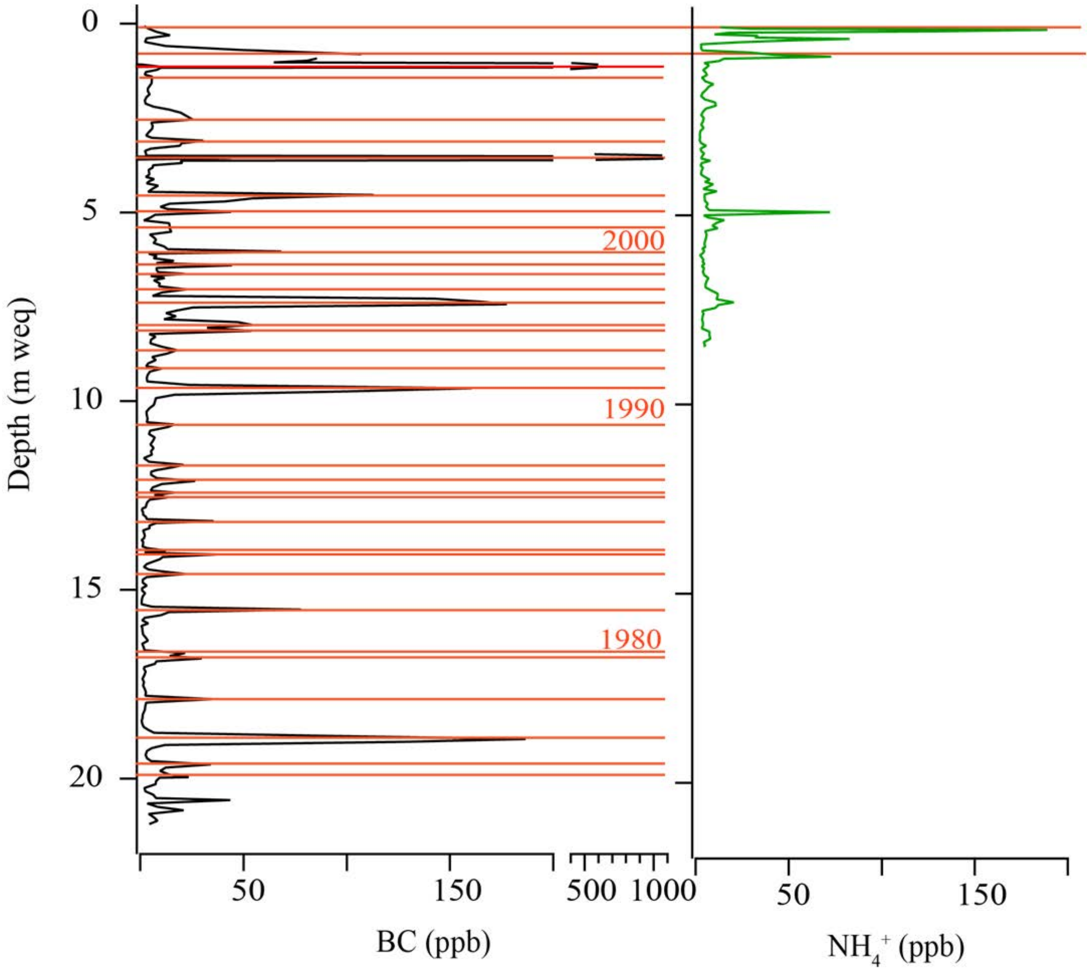


Figure 12: Concentration record the Silvretta ice core: BC (black line left) and NH_4^+ record (green line, right) with assigned annual layers (red).

4.2.2 ^3H

The isotope tritium (^3H) is a radioactive β-emitter with a half-life of 12.3 years. It is the third frequent isotope of hydrogen in nature, produced from interaction of cosmic rays and atmospheric gases.

$^{14}N + n = {}^{12}C + {}^3H$

In addition to this production pathway, there was a significant direct anthropogenic input of tritium in the stratosphere as a result of thermonuclear weapon tests starting around 1950. Emitted tritium is rapidly oxidized and enters the hydrological cycle. After 1963, the year of the US-Soviet Test Ban Treaty, atmospheric concentration of tritium decreased with the rate of the radioactive decay: The maximum activity in 1963 can be used as a marker horizon for dating. Tritium is characterized with a pronounced seasonal cycle, with peaking values in spring, depending on the mixing between troposphere and the stratosphere. The ^3H measurements of the Silvretta ice samples were conducted by

Max Rüthi in the Radioanalytic laboratory at PSI, using liquid scintillation counting (TriCarb 2770 SLL/BGO, Packard SA, Meriden; II; USA). For the measurements, 10 g of melted ice sample was mixed into scintillation liquid, which is excited by interaction with β-radiation. This is followed by emission of light, detected with a photomultiplier tube, which is producing an electrical pulse proportional to the number of photons. The counting time was 1200 min, with blank value of 0.69 counts per minute (cpm) and limit of detection of around 15 Bq/kg. The presented results are corrected for radioactive decay between the year of the drilling (2010) and 1963. This implies an overestimated activity for the recent years.

4.2.3 ^{210}Pb

In contrast to tritium, the radioactive isotope ^{210}Pb is formed in the decay chain of naturally occurring ^{238}U, and is produced in the atmosphere by the decay of ^{222}Rn. On the glacier surface ^{210}Pb is deposited bound to aerosol particles through wet and dry deposition. It has a half-life of 22.3 years and the age of the ice layer is calculated based on the assumption of constant accumulation and an estimated surface activity (Gäggeler et al., 1983). For the analysis of ^{210}Pb in ice samples, the activity of a decay product ^{210}Po, which is an α-emitter, is measured after chemical enrichment. Between 100 and 200 g of melted ice were used for the measurements after acidifying with HCl and adding ^{209}Po as internal standard. The ^{210}Po was deposited on a silver plate by stirring the solution for 7 hours at 90-93 ºC. Analysis was obtained by α-spectroscopy with energies of the alpha lines 4.9 MeV for ^{209}Po and 5.3 MeV for ^{210}Po. The background activity per kg of ice is around 3 mBq. The chemical enrichment was conducted by Edith Vogel at the University of Bern and the α-spectroscopy by Theo Jenk at PSI.

4.2.4 Glacier mass balance

Modelled gridded local mass balance data for the location of the drilling site covering the period 1915-2011 was used to support the dating of the Silvretta ice core (Huss and Bauder, 2009; Luethi, 2014). The ice core record is not continuous but some annual layers were removed by melt. (Figure 13). By subtracting the cumulative local mass balance (LMB) at year x from the cumulative LMB at the date of drilling (i.e. surface) each annual measurement of the mass balance could be associated with a certain ice core depth (no layer thinning considered). According to this dating, the ice at 33.5 mweq originates from 1961 (Figure 14)

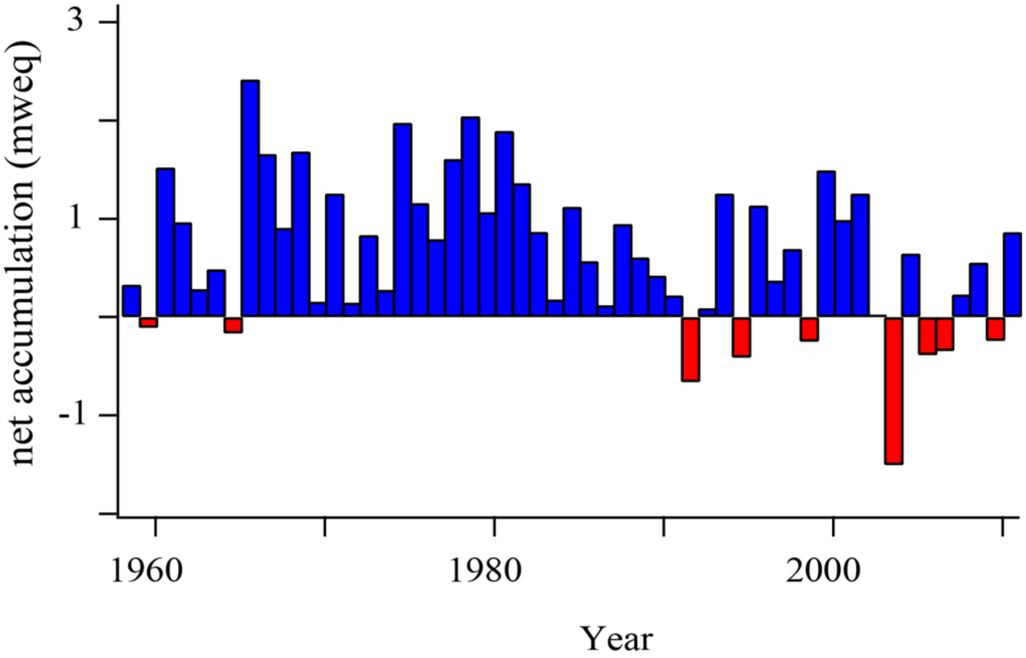


Figure 13: Net annual accumulation of snow on the Silvretta glacier at the drilling site in m water equivalent (mweq) (blue - positive, red - negative).

4.2.5 *Time scale*

Tritium is present in the water molecule and is thuspart of the ice matrix. Therefore, tritium is an ideal tracer for the percolation of meltwater within temperate glaciers A conserved profile of ^{3}H with a clear single peak points out that exchange between percolating meltwater and ice has been insignificant over time. In contrast, in case of redistribution of ^{3}H in the ice, no clear maximum would be visible. Elevated tritium activities in the Silvretta ice core spread over 6 m weq, between 25 and 31 m weq (Figure 14), which is comparable to the tritium activity measured in the Fiescherhorn glacier (5 m weq, Schwikowski et al., 1999a).The peak at 29.5 m weq corresponds to the year 1963 and fits to the age derived from LMB data. The peak value of 87 Bq/kg in Silvretta is lower than the 650 Bq/kg measured in Fiescherhorn and 550 Bq/kg in Grenzgletscher. All data is decay-corrected to the initial input year 1963. The total activity per cm^{2} integrated over the segment in the core containing peak values is comparable for Grenzgletscher and Fiescherhorn ice cores (Grenzgletscher 1448 Bq/cm^{2}, Fiescherhorn 1331 Bq/cm^{2}) and a factor of 50 lower in Silvretta (26 Bq/cm^{2}), pointing out that partial elution of tritium occurred in Silvretta ice core. Nevertheless, according to our results, tritium represents a reliable proxy for dating temperate ice.

In contrast to tritium, ^{210}Pb is enriched in particle layers. Therefore, the ^{210}Pb activity concentration in snow experience larger variations than what has been observed in cold glaciers (Gäggeler et al., 1983). This might be explained by removal/redistribution of particles with meltwater. The ^{210}Pb dating suggests an age of 90 ± 10 years (1920 AD) at

33 m weq (Figure 15), which is sligtly older than the age obtained by LMB and tritium dating (Figure 14). However since the background value of about 3 mBq/kg was not yet reached, this dating fit is considered preliminary. Surface activity concentrations are in agreement with other values in the Alps (Eichler et al., 2000).

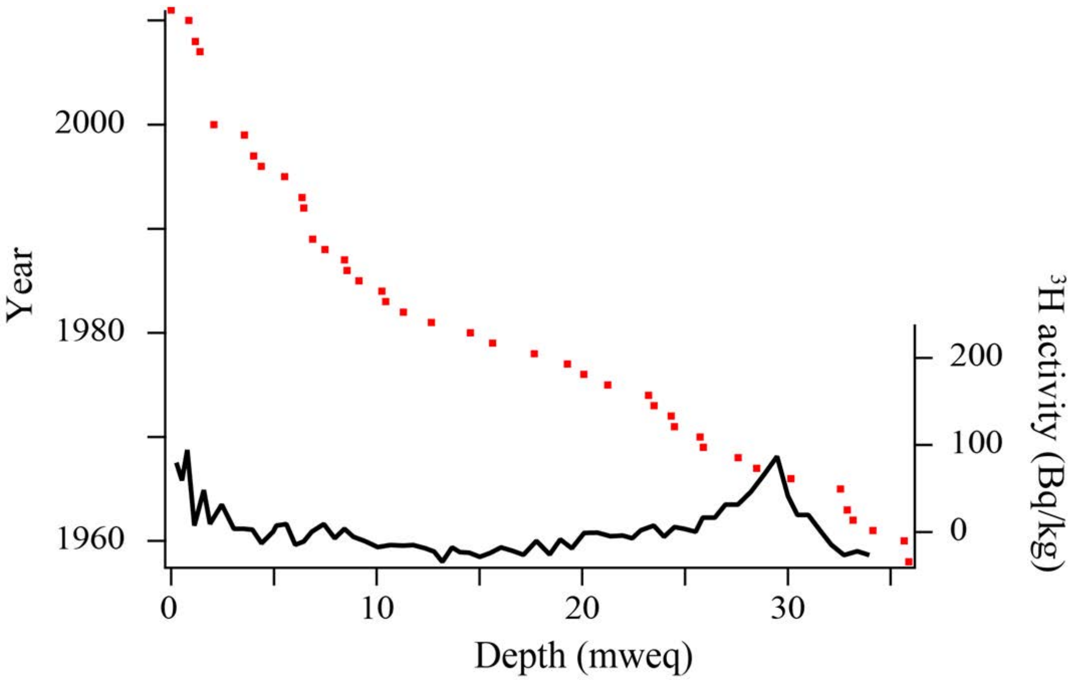


Figure 14: Age-depth relationship for Silvretta ice core: positive LMB (red), ^{3}H activity, decay corrected for 1963 (black line).

In addition, we attempted using methane concentrations in gas bubbles in the ice as a potential proxy for dating of temperate ice. As a result of anthropogenic activity, CH_4 concentrations in the atmosphere have increased more than 150% since 1750 to levels of 1800 ppb (IPCC, 2013). Thus, we assumed that with identifying methane concentrations of air content in ice, we can attribute the layers to certain years. For the methane measurements three 10 cm x 10 cm sections (depths 8.4 to 11.8 mweq) with high gas bubles content were chosen from the core. However, the total air content was lower than in polar ice cores (Spahni, 2006). The measurements were held by M. Baumgarten and O.Eicher at the Climate and Environmental Physics of the University of Bern using gas chromatography and flame ionization detector for CH_4 (Baumgartner et al., 2014). Mean value of 1784 ± 15 ppb was obtained from the three samples. This value corresponds to the atmospheric methane levels today. Since CH_4 is water soluble, we assume percolating water from the surface is transporting dissolved methane to deeper layers. Therefore, methane cannot be used for dating of temperate Silvretta glacier. For further interpretation of the POPs record, the age scale obtained by LMB is used.

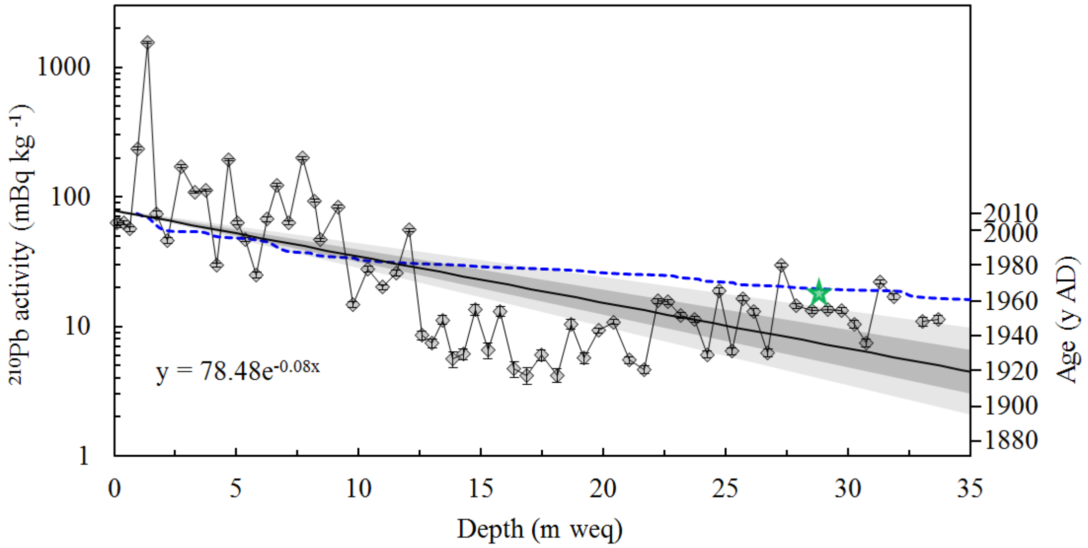


Figure 15: ^{210}Pb record from the Silvretta ice core: ^{210}Pb in ice core samples with associated errors (black diamonds), ^{210}Pb dating fit (black line and equation), uncertainty in dating (grey shaded area), mass balance age-depth relationship (blue dashed line), ^{3}H activity peak in 1963 horizon (green star)

4.3 Gas chromatography coupled to high resolution mass spectrometry

All organic compounds were analysed by gas chromatography coupled to electron ionization high resolution mass spectrometry (GC/EI-HRMS). Gas chromatography was applied as a separation technique using hydrogen as a carrier gas. Separation was effected on capillary columns coated with polysiloxanes PS086 (85% dimethyl-/15% diphenylpolysiloxane; Fluka, Buchs, Switzerland) and Rtx-5 (95% dimethyl-/5% diphenylpolysiloxane; Restek). Samples were injected in splitless mode (split valve closed for 20 s) at an injector temperature of 260 ºC. Depending on the solvent and column dimensions, different temperature programs were used. GC/EI-HRMS analysis was carried out on a high resolution double-focusing magnetic sector field mass spectrometer MAT 95 (Thermo Finnigan MAT, Bremen, Germany), coupled to a gas chromatograph HRGC Mega 2 series (Fisons Instruments, Rodano, Italy) equipped with an A200S autosampler (CTC Analytics, Zwingen, Switzerland). The ion source was operated at 220 °C, the electron energy was 70 eV. The two most abundant signals of the molecular ion clusters of the analytes were recorded using single ion monitoring (SIM). Typical mass resolution was set to 8000 enabling mass spectrometric fading out of interfering ions with similar nominal masses. Perfluorkerosene (PFK, high boiling, for mass spectrometry, Fluka, Buchs, Switzerland) was used as a calibration compound

5 CAPILLARY TRAPS FOR ORGANIC POLLUTANTS

Trace analysis of hydrophobic micropollutants in aqueous samples using capillary traps

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PDMS, micropollutants, POPs, aqueous samples, GC-MS

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Abstract

Studying the fate of persistent organic pollutants (POPs) in glacier environments scientist face the challenge of snow and ice samples, in which concentrations of these pollutants are at the ultra-trace level and the amount of sample available is often very limited. We have improved an extraction method for hydrophobic organic pollutants such as polychlorinated biphenyls (PCBs) in aqueous media to meet the requirements of these challenging samples. It is based on partitioning of the analytes from the water into the polydimethylsiloxane (PDMS) coating of an open tubular-fused-silica capillary. By comparison with conventional liquid-liquid extraction, we validated the method for six indicator PCBs, covering a wide range of polarity. The new method has very low detection limits of 10–20 pg/L for the investigated PCBs, a small uncertainty between 9% and 37%, depending on concentration, and requires a small sample volume of less than one liter. Further, it is characterized by easy handling and reduced organic solvents consumption. The method is comparatively insensitive to contamination, reproducible, and suitable for a wide range of applications.

5.1 Introduction

Persistent organic pollutants (POPs) represent a group of anthropogenic organic substances, including industrial chemicals, pesticides, as well as unintentional by-products of combustion processes and chemical reactions, which have been regulated by the UN Stockholm Convention since 2004 (UNEP, 2004). Due to their widespread use in the past, their resistance to environmental degradation, and potential for bioaccumulation, POPs became ubiquitous in the environment, even far away from their initial emission sources. Remobilization processes such as volatilization, erosion and leaching into water bodies lead to widespread distribution in the environment. Depending on the environmental compartment detection of these compounds may pose considerable analytical challenges. Whereas for certain matrices such as soil, sediment, and biological tissue extraction methods of hydrophobic compounds such as polychlorinated biphenyls (PCBs) are well established, determination in water is still a demanding task. Due to extremely low concentrations ultra-trace analytical methods require enrichment steps, which are prone to interferences of these compounds ubiquitous also in the laboratory environment.

The existing methodical approaches can be divided into liquid and solid phase extraction methods. The laborious liquid-liquid extraction (LLE), being the classical method for analysis of POPs in aqueous samples, usually requires large sample volumes (up to dozens of liters) and high amounts of organic solvents, leading to relatively high blank values, because of the extensive glass surfaces in contact with the sample. Still, LLE is appreciated for its robustness, wide range of application, and the relatively high analyte recovery rates, as well as the fact that both dissolved and particulate analytes are covered (Barra et al., 2005; Finizio et al., 2006; Gregor and Gummer, 1989). Solid phase extraction (SPE) is the alternative approach consisting in enrichment of the analytes on or in a solid extraction medium, from which they are subsequently released. The solid extraction phase may be a chromatographic packing material or a coating absorbing the analytes. SPE using packed cartridges is easy to perform, although, because of the vast surface of the adsorbent, it implies risks of adsorption losses and contamination (Carrera et al., 2001; Hermanson et al., 2005; Zhang et al., 2011).

Other SPE techniques are based on supports of different geometry coated with a stationary extraction phase such as polydimethyl siloxane (PDMS), which absorbs the analytes from the aqueous sample. The most common techniques used are solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE). SPME is based on partitioning of analytes between a coated fused silica fiber and the sample, following thermal desorption in the injector of a gas chromatograph (GC) (Pawliszyn, 1997). In SBSE, a magnetic stir bar with a PDMS coating adsorbs the analytes from an aqueous sample (Baltussen et al., 1999; Nogueira, 2012). However, this technique requires specific instrumentation and, as reported by Lung et al., intensive continuous stirring enhances contact of the aqueous phase with the container walls, which may result in unaccounted adsorptive losses of the analytes (Lung et al., 2000).

Trap columns are short open tubular columns coated with immobilized PDMS, which absorbs hydrophobic analytes while purging the aqueous samples. Thermal desorption and detection of the analytes is conducted by mounting the trap in a GC as a pre-column to the analytical column and applying a chromatographic temperature program (Grob Jr. and Schilling, 1985; Russo et al., 2001; Nardi, 2003) (Grob Jr. and Schilling, 1985; Nardi, 2003; Words et al., 2001). In solid phase dynamic extraction (SPDE), which is based on the same principle, the aqueous sample is drawn into a syringe and expelled through a syringe needle coated with PDMS. The analytes are subsequently desorbed by injection of a flush gas at reduced pressure from the sampling syringe into the hot GC injector (Lipinski, 2001). All the above mentioned techniques are practicable for samples volumes up to 100 mL.

In an ongoing project on the behaviour of POPs in glacier environments, selected POPs are to be determined in ice samples (Bogdal et al., 2009b; Schmid et al., 2011). This calls for extraction methods suitable for limited sample volumes in the range of 1 L for which the above mentioned techniques are inadequate. Furthermore, many environmental contaminants are characterized by their ubiquitous occurrence, which is a pitfall also for the sample handling in the laboratory. Thus, an optimal enrichment method should feature (i) low susceptibility to background contamination, (ii) minimal contact of aqueous samples with surfaces, (iii) capacity for sample volumes in the range of one liter, (iv) easy handling, and (v) minimized consumption of resources in compliance with green analytical chemistry.

To meet these requirements, a new approach based on capillary traps was developed. Extraction was directly performed from the sample container, i.e., no sample transfer was necessary. In contrast to previously applied thermal desorption, target analytes are eluted by a suitable solvent directly into a GC sample vial avoiding any additional contact with potentially contaminated surfaces and enabling multiple analyses of the same sample by injection of aliquots.

5.2 Materials and methods

5.2.1 Chemicals and reference materials

All solvents used were of pesticide residue analysis grade. Reference indicator PCBs (i-PCBs, mixture of PCB 28, 52, 101, 138, 153, and 180) were purchased from AccuStandard Inc., New Haven, CT, USA. 13C12-labeled i-PCBs and 13C12-labeled PCBs 70 and 111 were from Cambridge Isotope Laboratories, Andover, MA, USA. The recovery standard mixture PCB ISS-H, Wellington Laboratories, contains 13C12-labeled PCB 37, 79, 111and 162.

5.2.2 Preparation of trap capillaries

Fused silica tubing of 0.32 mm inner diameter (BGB, Boeckten, Switzerland) was coated with a film of vinyl terminated PDMS PS-255 (Fluka, Buchs, Switzerland). Coating of the capillary tubing and immobilization of the stationary phase using dicumyl peroxide as a cross-linker was based on methods described by Grob (1986). The degree of immobilization was measured gravimetrically in the eluate after rinsing the coated capillary with diethyl ether and dichloromethane. Starting from a target value of 2.5 µm an extractable loss of 18% of the phase resulted in a remaining film thickness of 2.1 µm.

Commercially available capillary fused silica GC columns coated with an immobilized PDMS stationary phase may be used as well. Based on the following considerations in section 4.2.4. (calculation of PCB retention volumes in the capillaries), the thickness of the coating should be in the range of 2 µm and sufficient immobilization should previously be tested by rinsing as described above.

5.2.3 Preparation of glassware

Glassware was immersed in an alkaline bath (RBS35 5% Fluka, Buchs, Switzerland) for 12 h, subsequently washed in a glassware washer with RBS50 (Fluka, Buchs, Switzerland) and baked out at 450 °C in a muffle furnace overnight. Glass containers were rinsed with a solvent mixture (acetone, n-hexane, methanol 1:1:1 v/v) immediately before use.

5.2.4 Extraction of water samples

Hydrophobic analytes in a water sample partition into the PDMS coating (stationary phase) of a short open tubular column. Based on the assumption that the mobile phase (water sample) and the stationary phase are in equilibrium, retention can be described by the partition coefficient K_{sm} between the two phases which represents the ratio of the analyte concentrations in both phases (equation 1).

$$K_{sm} = c_s/c_m \qquad (1)$$

cs and cm are the concentrations of the analyte in the stationary and mobile phase, respectively. The retention of extracted analytes depends on the volumetric phase ratio β (equation 2).

$$\beta = V_m/V_s \qquad (2)$$

V_s and V_m are the volumes of the stationary and mobile phase in the capillary, respectively. The phase ratio β is inversely proportional to the capacity ratio k’ as shown in equation 3.

$$k' = K_{sm} \cdot V_s/V_m = K_{sm}/\beta \quad (3)$$

Equation 3 reveals that a high phase ratio β is compensated by a high partition coefficient K_{sm}. The retention limit of an analyte in the trap column is defined as the retention volume of the analyte V_r after deposition in the stationary phase at the beginning of the trap capillary column (equation 4).

$$V_r = V_m \cdot (k' + 1) \qquad (4)$$

The partition coefficient K_{sm} can be approximated by the *n*-octanol/water partition coefficient K_{OW} (DiFilippo and Eganhouse, 2010). Partition coefficients of POPs such as PCBs are higher than 105 (corresponding log $K_{OW} > 5$) indicating strong retention in the stationary phase. Table 2 shows that PCB 28 in a water sample volume of <900 mL is completely retained in a CT of the selected dimensions and PCB 180 is even retained in a water volume of 30 L.

Table 2: Estimated chromatographic equilibrium constants K_{sm}, calculated capacity ratios k' and retention volumes V_r of PCBs for CT of 1 m × 0.32 mm coated with a 2.1 µm PMDS film resulting in Vs = 2 µL and V_m = 80 µL. K_{OW} are adopted from. Schenker et al., 2005.

Analyte	log K_{sm} ≈ log K_{OW}	k′	V_r [mL]
PCB 28	5.66	11999	965
PCB 52	5.95	23395	1882
PCB 101	6.38	62969	5064
PCB 138	7.19	406564	32698
PCB 153	6.86	190164	15294
PCB 180	7.15	370791	29821

The setup used for the extraction of water samples is shown in Figure 1. In order to avoid possible additional contamination and adsorptive loss of analytes, the trap capillary is mounted directly in the sampling container (2 L Schott Duran glass bottles). Before extraction, the water sample is spiked with an ethanolic solution of the internal standard using a microliter syringe. The bottle is closed with a cap equipped with a port for the trap capillary, an inlet for compressed air and a manometer. Filtered air with a pressure of approximately 100 kPa is applied to the bottle resulting in a flow rate through a 1 m capillary of around 1 mL/min. Following extraction of the sample and displacement of the water by air, the capillary still contains residues of water. In order to prevent the formation of emulsions in the eluate a water soluble solvent such as ethanol is recommended. Assuming that the solubility of the analytes in the rinsing solvent (mobile phase) and the PDMS coating (stationary phase) is similar ($K_{sm} = 1$), the minimal elution volume V_r is 80 µL, which corresponds to the inner volume of 1m capillary. Thus, the trap capillary is rinsed with 130 µL ethanol (inner volume of the capillary (80 µL) plus volume of the eluate (50 µL)). The eluate is collected in a 0.7 mL vial and is directly used for subsequent injection into the GC. For determination of the recovery of the analytes, a set of $^{13}C_{12}$-labeled PCB congeners was used, which was added immediately prior to analysis.

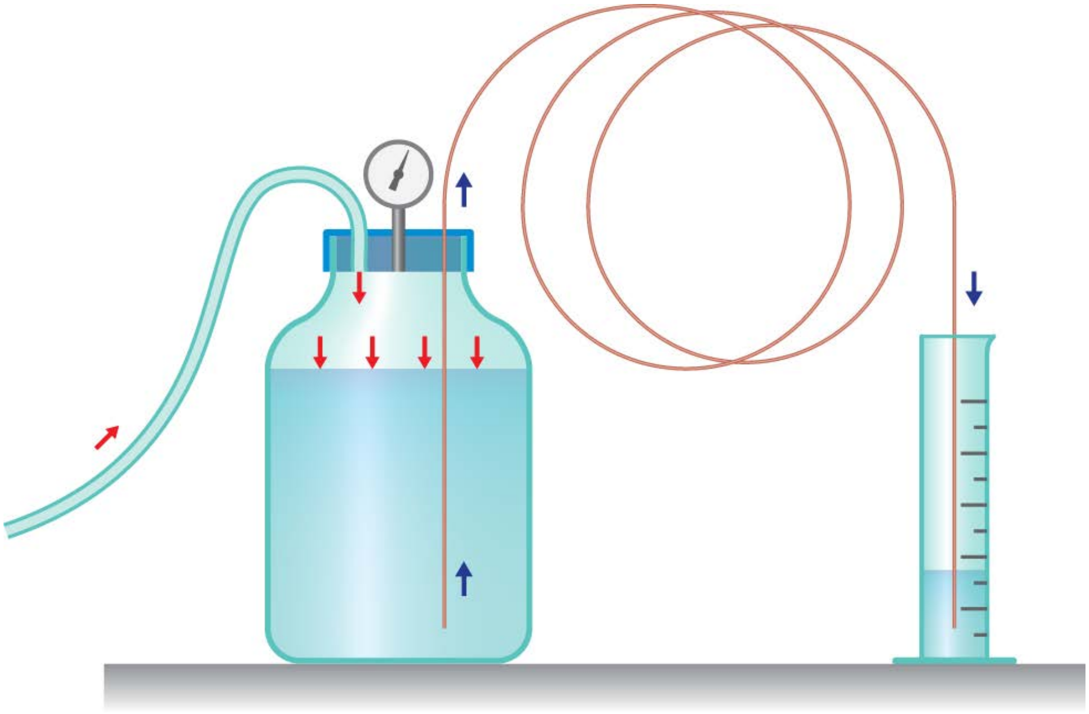

Figure 16: Setup of the capillary trap (CT) extraction method showing the sample container with sealed cap equipped with trap capillary, a gas inlet for pressure build-up (red arrows) and a manometer. Blue arrows indicate flow directions.

5.2.5 *Retention characteristics*

Retention characteristics of CT were tested using a segmented capillary of 2 m total length consisting of four 50 cm pieces connected with press-fit connectors. 5 µL n-hexane, containing 0.5 ng $^{13}C_{12}$-PCB 111 were spiked directly into the start of the trap, and the solvent was evaporated by application of vacuum. 250 mL water spiked with 1 ng 13C12-labeled i-PCB mixture was passed through the capillary at a flow rate of 1 mL/min. Subsequently, the 4 segments were disconnected and individually eluted with ethanol. Two 50 µl fractions were collected after feeding 140 µl (50 cm capillary volume: 40 µL).

5.2.6 *Detection and quantification*

All compounds were analysed by gas chromatography coupled to electron ionization high resolution mass spectrometry (GC/EI-HRMS). GC/EI-HRMS analysis was carried out on a MAT 95 mass spectrometer (Thermo Finnigan MAT, Bremen, Germany) coupled to a gas chromatograph HRGC Mega 2 series (Fisons Instruments, Rodano, Italy) equipped with an A200S autosampler (CTC Analytics, Zwingen, Switzerland).

Samples were injected in splitless mode (split valve closed for 20 s) at an injector temperature of 260 °C. For GC separation, a glass capillary column 20 m × 0.28 mm coated with a 85% dimethyl-/15% diphenylpolysiloxane stationary phase (PS 086, Fluka, Buchs, Switzerland) with a film thickness of 0.15 µm was used with hydrogen at 50 kPa as carrier gas. The temperature program was started at 80°C, held for 1 min, increased to 160 °C at 20 °C/min, then increased to 260 °C at 5 °C/min and held for 5 min. The ion source was operated at 180 °C, the electron energy was 70 eV, and the mass spectrometer was tuned to a mass resolution of at least 8000. Using single ion monitoring (SIM), the two most abundant signals of the molecular ion clusters of the analytes were recorded.

5.2.7 Method performance

Precision and accuracy of the method were tested by comparison of parallel extraction series using both classical LLE and CT (length 1 m). The aqueous test solution was prepared by spiking 1 L analytical grade water (LiChrosolv®, Merck, Darmstadt, Germany) with each of the six i-PCBs at 10 ng/L together with their $^{13}C_{12}$-labeled analogue at the same concentration as internal standards. This concentration was selected in order to significantly exceed the observed traces of PCBs in the analytical grade water used. CT extractions and taking of aliquots for LLE were performed alternatingly using *ca*. 100 mL per sample. After elution from the CT and volume reduction of the LLE extracts, a recovery spike containing $^{13}C_{12}$-labeled PCB 37, 79, 111, and 162 at 0.5 ng per sample was added enabling determination of the recoveries of the $^{13}C_{12}$-labeled internal standard i-PCB.

5.3 Results and Discussion

5.3.1 Retention characteristics of the capillary trap

Retention characteristics of the trap capillary were tested using separate elution of four 50 cm capillary segments as described above, which were eluted twice (first and second fraction). Inspection of the recoveries of $^{13}C_{12}$-labeled PCB 111, which had been directly spiked to the start of the capillary before elution of the water sample does not reveal significant chromatographic migration: 96% of the total recovered amount remained in the first segment of the trap. Similarly, the relative recoveries of the $^{13}C_{12}$-labeled i-PCBs spiked to the water are highest in the first segment of the trap. Hence, a significant transport by elution within the capillary can be excluded, even for PCB 28, which is most susceptible to chromatographic elution due to its low chromatographic equilibrium constant K_{sm} (Table 3). The observed retarded partitioning of the analytes in the following segments is therefore due to the partition dynamics. Alternatively, elution of the analytes from the trap with a total of 90 µL ethanol (40 + 50 µL) is almost complete: around 90%

of the total recovered analytes was present in the first fraction, and less than 10% were recovered in the second fraction eluted with additional 50 µL ethanol

Capillary traps can be reused after rinsing with 3-4 ml of ethanol i.e. the same solvent as for extraction. Since there is no washing out of the PDMS coating, its properties remain constant over time. The limitation could originate from clocking with particle rich samples, which is irreversible.

The optimal length of the capillary was also evaluated: A longer trap provides higher yields but results in reduced elution speed, as well as more residual water in the capillary after extraction, which may hamper the GC separation. In contrast, a short trap might not provide sufficient retention capacity. Therefore, a capillary length of 1 m proved to be optimal for the required purposes. Figure 17 shows the cumulated recoveries of the $^{13}C_{12}$-labeled PCBs for the four segments. Assuming partitioning of the analytes between the mobile and stationary phase to follow a first-order process, the fraction of amount retained f_c as a function of the length l of the capillary is defined by equation 5.

$$f_c = f_{tot} \cdot (1 - e^{-k \cdot l}) \qquad (5)$$

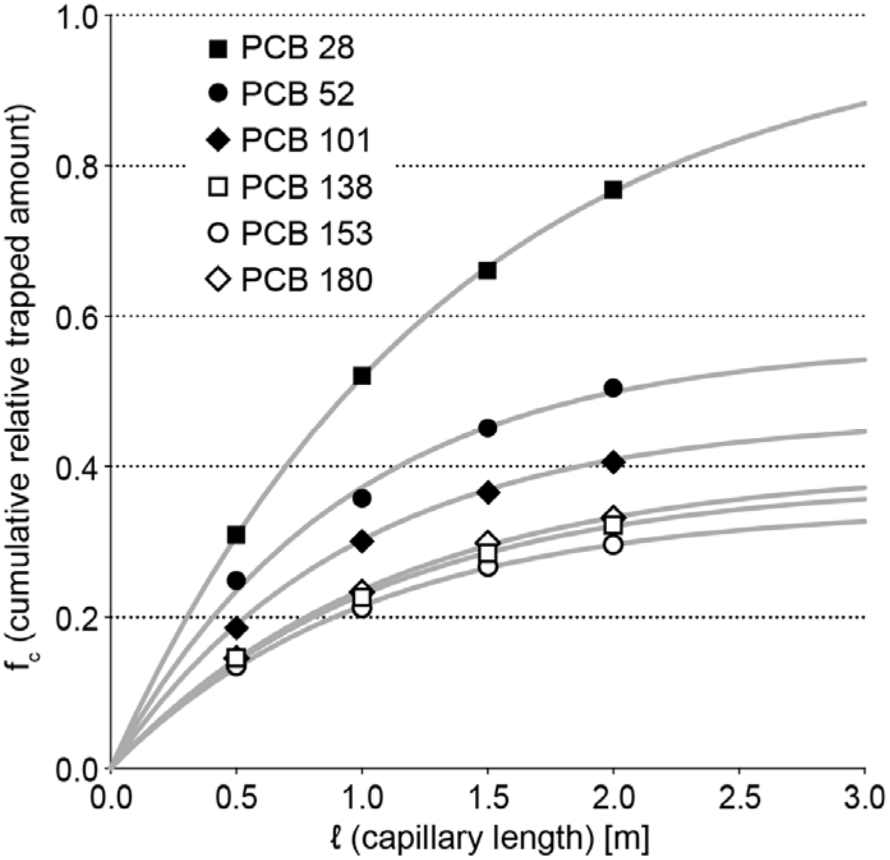

Figure 17 **Cumulated relative trapped amounts of $^{13}C_{12}$-labeled i-PCB congeners in capillary segments relative to the preset concentrations in the water sample together with fitted curves (equation 5).**

f_{tot} is the fraction of the total amount retained in a capillary of infinite length corresponding to the amount entering the trap and k is the kinetic rate constant of the partitioning of the analytes into the stationary phase at the selected elution conditions. These parameters were determined by a least squares curve fitting. According to this, f_{tot} is between 35% and 99%, and the full length at half maximum $l_{½}$ (corresponding to retention of 50% of the PCBs entering the capillary) is below 1 m at the applied flow rate of 1 mL/min. The similarity of the $l_{1/2}$ values for PCB 52, 101, 138, 175, and 180 suggests that partitioning kinetics of these congeners into the stationary phase is determined by flow dynamics in the capillary rather than by molecular properties of the analytes. The slightly increased $l_{1/2}$ of PCB 28 can be explained by chromatographic migration of this congener, which is in agreement with the theoretical retention volume V_r of 965 mL (see equation 4 and Table 3).

5.3.2 *Adsorptive properties of the analytes*

The variation f_{tot} distinctly below 1 (Figure 17) indicates substantial losses depending on the molecular weight and/or the chlorination degree of the PCBs. As these losses cannot be explained by incomplete retention this finding suggests that part of the PCBs spiked into the water sample has been lost before entering the trap capillary, likely by adsorption to the walls of the sample container. Rawa-Adkonis *et al.* reported adsorption losses of PCBs of up to 62% to the surface of glass bottles, in which spiked aqueous solutions of the analytes had been stored for 0-30 days (Rawa-Adkonis et al., 2006). Hsieh et al., (2011) showed that glass-water distribution coefficients (K_{GW}) of PCBs correlate well with the octanol-water partition coefficients (K_{OW}) of the different congeners (Table 3). This correlation corresponds to the variable losses observed. However, adsorptive losses are difficult to control and represent probably the major error source in trace analysis of hydrophobic compounds in water.

5.3.3 *Quality assurance and performance indicators of the method*

Limit of detection (LOD) and method blank: Determination of the LOD of the method is impeded by the lack of blank sample material, i.e. sufficiently PCB-free water. In fact, even analytical grade water contains traces of PCBs at about 1 ng/L (sum of the six i-PCBs) (Table 3). In this situation, the LOD was defined as the mean blank plus three standard deviations (SD) measured in the eluate of a CT capillary without previous passage of a water sample. The instrument LOD of the GC/EI-HRMS method is 0.1 - 0.2 pg for single PCB congeners (signal to noise ratio = 3). Starting from a hypothetical water sample of 0.5 L and an injected 1:20 aliquot of the CT extract the calculated LOD is 4 - 8 pg/L (SD = 50%). The resulting LOD of the method as defined above is thus 10 - 20 pg/L for single PCB congeners.

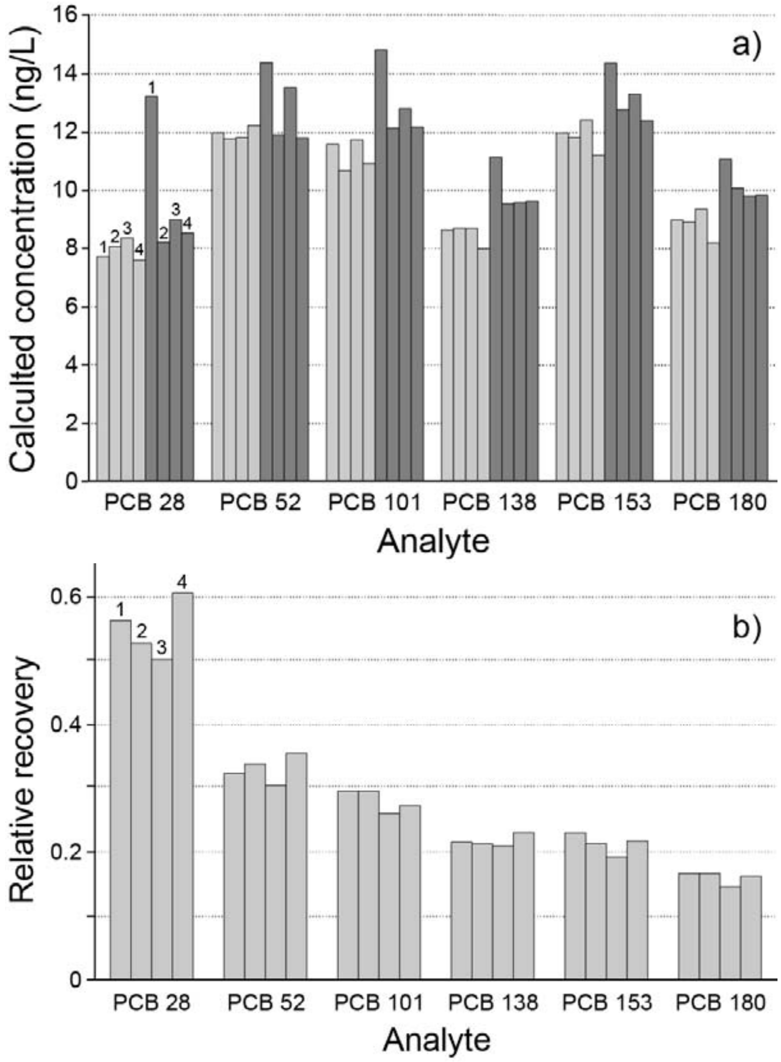

Figure 18: a) Measured concentrations of i-PCBs in CT (light gray) and LLE (dark gray) extracts of 100 mL subsamples of a test solution spiked at 10 ng/L per analyte; b) Measured recoveries of $^{13}C_{12}$-labeled i-PCB internal standards in CT extracts of 100 mL subsamples of a test solution spiked at 10 ng/L.

Precision and accuracy: The method performance was compared to classical LLE by multiple extractions of subsamples of the same sample using both LLE and CT. In Figure 3a the concentrations of the spiked i-PCBs quantified using the spiked $^{13}C_{12}$-labeled analogues as internals standards are given. Apart from the first LLE sample, the data reveals good comparability as well as good reproducibility. The slightly higher values obtained using LLE may be due to the method blank in the order of 2.3 ± 0.8 ng/L observed in LLE, where the sample has contact with potentially contaminated glass surfaces of e.g. separating funnels and flasks. Recoveries of the $^{13}C_{12}$-labeled surrogates are consistent with the recoveries already observed in the experiment for the characterization of the retention of the CT where adsorption loss up to 60% has been observed (see Figure 18b and Tables 3 and 4).

5.3.4 Environmental samples

In order to test the applicability of the method real aqueous samples of different origin and contaminant load were analysed.

River Saane: As an example of a considerably contaminated environmental sample surface water from the river Saane in Western Switzerland was studied. The sampling site is located close to a former landfill releasing PCBs from electrical waste. An investigation of fish catched in the river in the vicinity of this landfill revealed extraordinary high PCB concentrations (Zennegg and Schmid, 2011). In July 2012, surface water from river Saane was collected in pre-cleaned glass containers and immediately analysed. Four subsamples of around 800 mL each were analysed using CT as described before. For comparison, 4.5 L of the same sample were pre-filtered and analysed using conventional LLE. The results are listed in Table 3.

Table 3: Concentrations of i-PCBs in surface water from river Saane, snow from Jungfraujoch and analytical grade water determined using the capillary trap technique (CT) and liquid-liquid extraction (LLE). Errors represent the standard deviation of the mean value after multiple GC injections of the same extract, average refers to subsamples.

Sample	Sample volume (L)	Σ 6 i-PCBs (ng/L)
Saane CT 1	0.8	27.4 ± 4.7
Saane CT 2	0.8	30.6 ± 10.8
Saane CT 3	0.8	31.8 ± 4.4
Saane CT 4	0.8	26.6 ± 4.1
Saane CT average		29 ± 2.7 (9%)
Saane LLE	4.5	28.1
Jungfraujoch CT 1	0.8	1.1 ± 0.1
Jungfraujoch CT 2	0.7	1.3 ± 0.0
Jungfraujoch CT 3	0.6	0.9 ± 0.1
Jungfraujoch CT average		1.1 ± 0.2 (21%)
Jungfraujoch LLE	3.5	0.4
Analytical grade water CT	0.5	1.2 ± 0.2 (22%)

Jungfraujoch: Since the method development was particularly customized to an extraction technique suitable for analysis of ice and snow samples, fresh fallen snow, collected at approximately 3500 m a.s.l. close to the Jungfraujoch high-alpine research station in the Bernese Alps (Switzerland) was analysed. The sampling was done in April 2012 in a plastic bag, which was afterwards transported frozen to the laboratory. Three distinct snow samples were analysed for PCBs using the CT technique. The results are listed in Table 2.

In all CT samples the six i-PCBs were detected above the LOD, which confirms that a sample volume of around one liter was sufficient for these analyses. As expected, the concentrations in snow from Jungfraujoch are considerably lower than those in the contaminated water sample from river Saane. PCB concentrations in the Jungfraujoch snow samples show higher variability due to the increased analytical uncertainty near the detection limit and higher susceptibility to contamination. Whereas the CT and LLE data of the Saane samples are in good agreement, the LLE concentration of the Jungfraujoch snow sample is distinctly lower than the corresponding CT values. This can be possibly explained with wall adsorption of the analytes in the melt container, which becomes more manifest at very low concentrations. Nevertheless, the measured concentrations in the CT extracts are in good agreement among each other, confirming the CT method being a reliable and robust technique for analysis of hydrophobic compounds in water.

5.4 Conclusions

The CT method developed for extraction of hydrophobic trace contaminants such as PCBs excels by a sample volume tolerance up to 1 liter, low solvent consumption, and easy handling. Adsorptive loss of hydrophobic analytes to the surfaces of glass containers and chemical interferences deposited on surfaces of laboratory glassware are inherent in trace analysis of ubiquitous hydrophobic chemicals in aqueous samples. As the water sample has no contact to any surface except the polysiloxane coating of the CT these two confounding factors are reduced to a minimum using the described technique. However, as aqueous samples are preferably collected and stored in glass containers adsorptive loss of hydrophobic analytes to the glass surface is unavoidable and thus an intrinsic problem of such investigations. Otherwise, the only serious limitation for the detection of the analytes is given by the instrumental detection limit, which is in the range of pg/L, and control of the blank.

5.5 Acknowledgements

We are indebted to André Niederer for the preparation of the method set-up sketch (Figure 16). This study was partly supported by the Swiss National Science Foundation (grant number 20021_130083).

6 INVENTORY OF POPS IN COLD GLACIERS

Polychlorinated biphenyls in glaciers: 1. Deposition history from an Alpine ice core

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Abstract

In this study, we present a highly time-resolved historical record of polychlorinated biphenyls (PCBs) from an Alpine ice core (Fiescherhorn glacier, Switzerland). Introduced in the 1940ies, PCBs were widely used industrial chemicals. Because of their persistence they are still found in the environment, long after their production phase-out. The Fiescherhorn ice core record covers the entire time period of industrial use of PCBs, i.e. 1940 – 2002. The total concentration of six PCBs varies from 0.5 to 5 ng/L and reveals a temporal trend, with an 8-fold increase from the early 1940s to the peak value in the 1970s. The level in 2002 is comparable to the concentration in the 1940s, when PCBs were introduced into the market. The time trend of PCBs associated with the particulate fraction closely follows the trend found in the dissolved fraction, but the absolute values are a factor of 10 lower. In addition to changing emissions, fluctuations in the PCB record were explained by variabilty in convective transport and post-depositional processes such as surface melting. Concentrations of PCBs are in agreement with data from seasonal snow samples in the Alps, but are a factor of 100 higher than concentrations measured in the Arctic. Contrasting time trends and congener patterns between the Alpine and Arctic region indicate the importance of atmospheric transport and post-depositional effects.

6.1 Introduction:

Polychlorinated biphenyls (PCBs) represent a group of persistent, bioaccumulative, and toxic compounds, which were used as dielectric and hydraulic fluids and as plasticizers in sealing materials and coatings. Because of their toxic properties they were banned internationally in 2004 with the Stockholm Convention on POPs. (UNEP, 2004) Nowadays, although declining, primary emissions e.g. from sealing materials, coatings, cable insulations, transformers and capacitors, still exceed secondary emission sources such as revolatilization from inadequate disposal on landfills, from soils and water bodies (Weber et al., 2008; Zennegg et al., 2013). Due to their persistence, PCBs are still found in most compartments of the environment (Li et al., 2010; Schmid et al., 2010; Simonich and Hites, 1995). In remote high mountain areas, organic chemicals can even be enriched by cold trapping due to low ambient temperatures and increased precipitation (Wania and Westgate, 2008). Particularly in the Alps, which are close to the most densely populated areas in Central Europe, PCB emissions are still considerable today(Bogdal et al., 2014).

Even though there are a few continuous datasets documenting current PCB pollution, (Halse et al., 2011; Meijer et al., 2003; Pozo et al., 2006; Ramu et al., 2007) continuous long term monitoring data is missing. In order to examine the history of PCB pollution, natural archives like annually laminated (varved) lake sediments are investigated (Schmid et al., 2011). Because of their hydrophobic properties, aquatic PCBs preferentially sorb to the sediment. Nevertheless, annual layers are composed of sediments from the whole catchment area, comprising different runoff time scales. In high mountain regions glacier ice represents the most direct natural archive of atmospheric contamination. Additionally, glaciers form a secondary source of previously deposited legacy pollutants when these contaminants are released with meltwater (Bogdal et al., 2009b). Due to high snow accumulation rates in the Alps ice cores allow sampling with fine temporal resolution. However, the analysis of PCBs in glacier ice is challenging because of the ultra-trace concentrations and the demanding sample preparation, prone to contamination and/or losses. Therefore, only a few datasets of PCB concentrations in annual snow accumulation have been published (Blais et al., 1998; Gregor et al., 1995; Lacorte et al., 2009; Quiroz et al., 2009). To our knowledge, there is only one ice record from a mountain glacier documenting the entire time period of industrial use of PCBs, and this record is from Svalbard in the Arctic (Garmash et al., 2013).

Here, we present the inventory of PCBs from an Alpine glacier ice core, covering the entire time period from introduction of the chemicals in the 1930s to the year 2002. We compare our results with the ice core record from the Arctic (Garmash et al., 2013) and with available data from the Alps (Carrera et al., 2001; Villa et al., 2006b). PCB concentrations in glaciers not only depend on emissions, atmospheric transport and deposition rates, but also on local processes such as, revolatilization, elution with meltwater etc.. Therefore, in a companion paper, we present a second study where a chemical fate model is developed and applied to investigate the effects of these processes on the selected compounds (Steinlin et al., 2014).

6.2 Materials and methods

6.2.1 *Ice core sampling and dating*

A 151 m surface-to-bedrock ice core was extracted from Fiescherhorn glacier at 3900 m above sea level (a.s.l.) in December 2002 (46.55°N; 8.07°E) (Schwerzmann et al., 2006). The extended glacier plateau is located in the Swiss Alps, between the summits of Gross Fiescherhorn (4049 m a.s.l.), Hinter Fiescherhorn (4025 m a.s.l.), and Ochs (3895 m a.s.l.), approximately 6 km east of the high-Alpine research station Jungfraujoch (JFJ, 3450 m a.s.l.) (Figure 19) (Schwikowski et al., 1999).

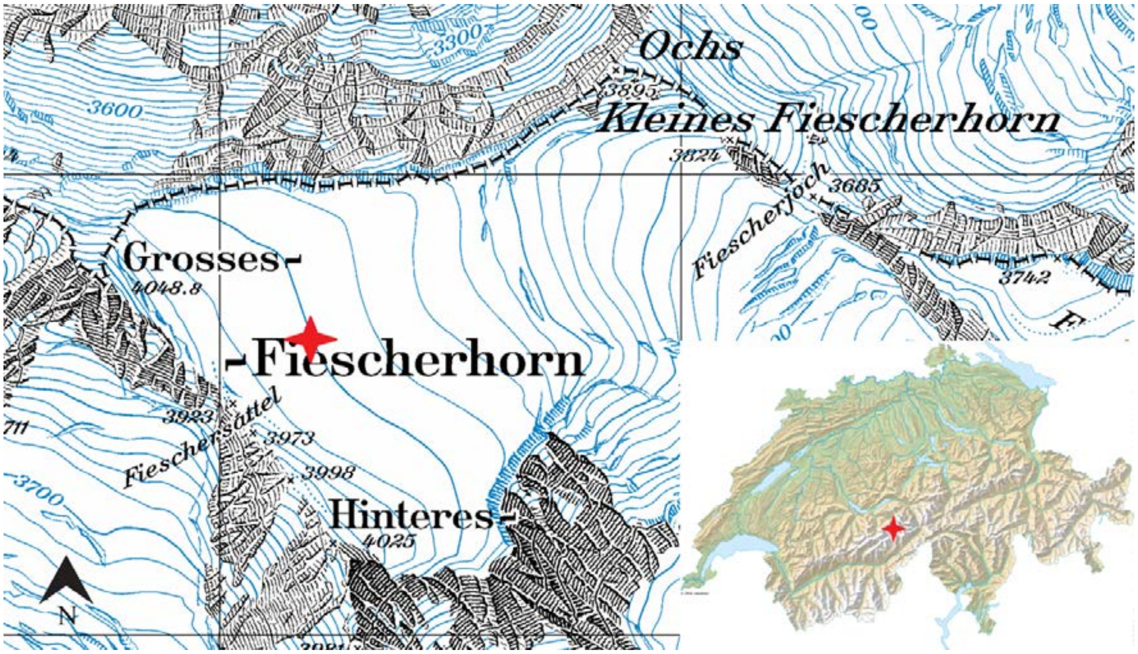

Figure 19: A detailed map of the Fiescherhorn glacier with the drilling site (© 2014 swisstopo JD100043). The grid represents 1km. In the bottom right an overview map of Switzerland showing the location of the study site.

Temperature between -6 and -2 °C measured in the borehole confirmed the presence of cold ice (Schwerzmann et al., 2006), which ensures preservation of concentration profiles of chemical species. Surface melting occasionally occurred in summer, as indicated by the presence of melt features formed by refreezing of the percolating melt water. Meltwater-infiltrated layers appear bright and bubble-free when the ice core is backlit in a darkened room and were quantified by visual evaluation. The corresponding numerical parameter is the stratigraphic melt index, which we define as the percentage of the length of the melt layer, compared to the total length of an annual layer (both in m weq). Because of the high net accumulation rate of 1.7 m water equivalent (m weq) per year (Mariani et al., 2012) , meltwater and the contained impurities are assumed to refreeze within the same annual layer in most cases.

The age-depth relationship for the Fiescherhorn ice core was established using a multiproxy method including: (1) annual layer counting of the seasonally varying stable isotope ratio $\delta^{18}O$ and the concentration of NH_4^+ (S1), (2) identification of well-documented Saharan dust events, (3) investigation of the ^3H maximum from thermonuclear bomb tests in 1963, and (4) detection of the ^{137}Cs peak from the Chernobyl accident in 1986(Mariani et al., 2012). The dating uncertainty is ±1 year for the time period considered in this study.

6.2.2 *Sample preparation and PCB analysis*

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. They represent a variety of chlorination degrees and are thus characterized by different physicochemical properties. Since iPCBs are major components in most industrial mixtures, they are also the most abundant in the environment. We focused on the time period 1940-2002 contained in the upper 107 m weq of the ice core. Samples were prepared in the -20 °C cold room at Paul Scherrer Institut, using a modified electrical band saw equipped with a stainless steel blade and a Polyvenylidene fluoride (PVDF) covered table as described by Eichler et al. (2000). After removing 5 mm outer surface of the ice, which was potentially contaminated during drilling or ice core storage, a stick with a cross-sectional area of 1.5 cm × 1.5 cm was cut out from every core segment with an average length of 0.6 m. In order to obtain a sample size of not less than 0.5 L, 2 to 7 ice core segments, representing 3 to 6 years were combined in one sample

We analysed PCBs in the glacier ice samples using a novel method, developed in house (Pavlova et al., 2014). In short, the ice was stored at -20 ºC in a pre-cleaned container after cutting and transported in an insulated box to the laboratories, where it was melted at room temperature immediately prior to extraction. The extraction 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). Because of the hydrophobic properties of the PCBs and the inhomogeneous distribution of the particles in glacier ice, particle-bound pollutants may represent an important fraction in the record. Therefore, a silver membrane filter was installed after the capillary to collect particles, which entered the capillary (i.e. smaller than 0.32 mm), but were not retained. The filter was preheated at 300 ºC and washed with solvent mixture (acetone, *n*-hexane, methanol 1:1:1 v:v:v) in order to minimize background contamination. After trapping, the filter was Soxhlet extracted in toluene and the extract was analysed with GC/EI-HRMS.

6.2.3 *Quality assurance*

As observed in earlier work, (Pavlova et al., 2014) the preparation of a method blank for the extraction is hampered by the occurrence of PCB traces of around 1 ng L^{-1} even in analytical grade water, being in the range of the concentrations measured in glacier ice. Therefore, we estimated an instrumental blank for liquid samples, based on the signal-to-noise ratio of the GC/EI-HRMS method of 0.1 to 0.2 pg for single congeners or around 1 pg for the sum of the six iPCBs considered here. This blank is low compared to the concentrations in the analysed ice samples and was thus neglected. In order to assess the filter extraction blank contribution, we performed a series of six second extractions of already extracted filters. The obtained amounts range between 70 and 112 pg independent of the initial load from 160 to 470 pg iPCBs. Therefore, the average value (±standard deviation of 6 replicates) of 88±15 pg iPCBs is defined as the maximum blank. The measured values presented were not corrected for blank contribution and recovery, but only samples with particulate iPCB loads exceeding the blank value were interpreted (i.e. 10 from 13 samples). We estimate precision and accuracy of the method with fortified analytical grade water and snow. Replicate measurements (n=3) resulted in overall uncertainty of 10-20% for the analytical method(Pavlova et al., 2014).

6.3 Results

The multiannual record of PCBs in an Alpine glacier, covering the time of maximum use and production and reaching back to their introduction phase is presented in Figure 2. The concentrations expressed as the sum of six PCBs in the Fiescherhorn ice core vary from 0.5 to 5 ng/L, which considerably exceeds the instrumental blank. The record reveals a temporal concentration trend, with an 8-fold increase from the early 1940s to the peak value in the 1970s. After the maximum, concentrations decrease gradually to a value below 1 ng/L at glacier surface, representing the year 2002. This level of sum iPCBs in 2002 is comparable to the concentration in the 1940s, before the introduction of PCBs. The time trend of the particulate fraction (tot iPCBs part.) follows the trend observed for the dissolved fraction (tot iPCBs diss.), but the absolute values (average 0.2 ng/L) are lower by a factor of 10 (average 2.1 ng/L). This is not explained by the chemical properties of the PCBs, but by the low particle content in the ice, limiting the sorption process (carbonaceous particles 72.5±4.2 μg/kg ice(Cao, 2013)).

The records of both tot iPCBs fractions show sample-to-sample fluctuations, which cannot be explained exclusively by changing emissions. This phenomenon is known for other chemical traces in ice cores and is related to variations in atmospheric transport and precipitation amount as well as post-depositional effects such as surface melting (Schwikowski et al., 2004). These processes will be discussed in the following sections.

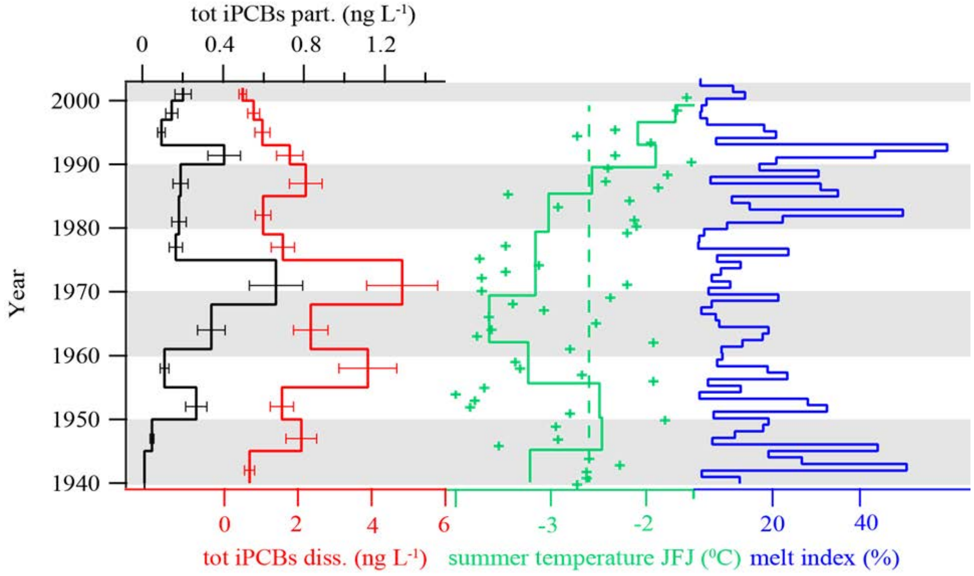

Figure 20: Concentration trends of the sum of six PCBs in the dissolved (red, bottom axis) and particle-bound (black, top axis) fraction in the Fiescherhorn ice core in ng L^{-1}. The error bars represent the calculated maximum uncertainty for the analytical method (±20%), see Quality assurance. The middle graphic represents summer temperatures (May-August) at Jungfraujoch (JFJ) (green crosses) averaged over the same period as the samples (green line) as well as the mean temperature from 1940-2000 (dashed green line). On the right side (blue line) the annual ice core melt index is shown.

6.4 Discussion

6.4.1 Temperature dependent air mass transport

Pronounced seasonality with concentration peaks in summer for species such as NH_4^+, SO_4^{2-}, and NO_3^- and heavy metals (e.g. Pb) in ice cores from high-alpine glaciers was previously attributed to the prevailing meteorological conditions (Schwikowski et al., 2004) Warm summer temperatures trigger strong convective mixing of air masses, which increases the height of the planetary boundary layer. This enables transport of pollutants from the valley, where the sources are located, to high mountain areas. On the contrary, in cold winter conditions, stable atmospheric stratification leads to a decoupling from the emission sources, and the glacier is exposed to free tropospheric air. Convective mixing varies due to changing meteorological conditions (Baltensperger et al., 1997). To examine this effect on the PCB record, we used summer air temperature (May-August) at the closely located JFJ research station as a proxy for convective transport (Figure 20). Summers of the 1960s to the 1980s are characterized by temperatures lower than the average over the entire period (1940-2002), which is -2.6 °C. Especially, in the years from 1961 to 1966 (-3.6 °C), reduced convective transport potentially explains the low iPCB concentrations. A similar but less pronounced effect is observed for the time period 1975-1984. The period 1968-1974 with the highest iPCB concentrations in the ice record is also characterized by temperatures that were below average of the last 60 years, suggesting that, based on concentrations in the ice, the input of iPCBs is underestimated. In contrast, the last twelve years of the record were much warmer than the average, probably resulting in a positive anomaly of the iPCB concentration. The effect of temperature on PCB concentration is further supported by multivariance regression analysis (see Congener profiles section).

6.4.2 *Relocation of PCBs due to surface melting*

Surface melting and related percolation and refreezing of meltwater can result in relocation of chemical impurities in the firn layer. However, melting is triggered not only by high air temperatures but also by decreased albedo due to the presence of impurities on the glacier surface. Therefore, the melt index does not strictly follow the temperature profile at the JFJ station (Figure 20). The Fiescherhorn ice core shows a relatively low average melt index of 9% compared to a melt index of 31% at Lomonosovfonna in Svalbard (Luethi, 2014). A few high values exceeding 20% are observed in the early 1940s and 1990s, probably related to the warm summers 1945-1955 and 1990-2000, whereas relatively low melt occurred during the cold summers 1960-1984. For the sample corresponding to the 1990-1992 period when the melt index reaches 48%, a shift in partitioning of iPCBs from the dissolved to the particulate phase is prominent. We attribute this effect to partial elution of iPCBs from the snow and preservation in the particle bound fraction. The underlying layer (1986-1991) shows increased concentrations, probably due to relocation of PCBs from overlaying strata. An analogous effect of elution is observed in the 1950-1954 as well as in the 1940-1944 samples. However, in 1940-1944 the total iPCB concentration was too low to identify a shift in partitioning. Compared to other water soluble traces, such as SO_4^{2-} (Eichler et al., 2001) , melting has a limited influence on the hydrophobic iPCB record.

6.4.3 *Pollutant fluxes*

In order to account for changes in the annual precipitation amount, we calculate annual pollutant deposition fluxes. First we obtained the annual accumulation rate from the annual layer thickness corrected for layer thinning according to Nye (1963) using the approach suggested by Henderson et al. (2006) and described in detail for the Fiescherhorn ice core in Mariani et al. (2012) Subsequently, by multiplying total concentrations of PCBs (dissolved and particle-bound) with the mean annual accumulation rate for the time period covered by the individual samples, annual deposition fluxes of iPCBs onto the Fiescherhorn glacier were calculated (Figure 21, b). The total flux of iPCBs shows a temporal trend comparable to the concentration of iPCBs, indicating that the effect of changing precipitation is negligible. In relation to emission estimates for Switzerland (Breivik et al., 2002) three emission periods can be distinguished: i) the initial production period of PCBs (market expansion) from 1940 to 1965 is characterized by increasing emissions of 0-1 t/a and moderate PCB fluxes in the range of 2-8 ng/cm^{2}a, ii) the peak use phase of PCBs from 1970 to 1980 shows a sharp 2-fold increase of the emissions up to 3/a, which is reflected in our record, by a maximum value of 12 ng/cm^{2}a in the 1968-1974 sample and iii) the phase-out period of PCBs from 1980 to 2000, is characterized by gradually decreasing emissions and reduced fluxes of PCBs.

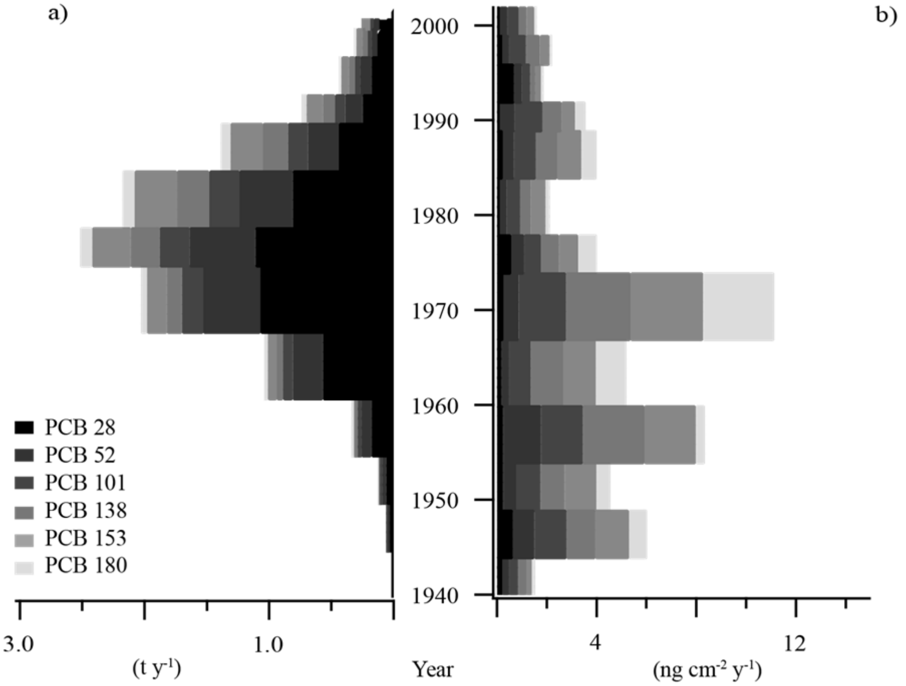

Figure 21: Emission data from Switzerland (maximum emission scenario) from Breivik et al (a), compared to annual tot iPCB flux at Fiescherhorn glacier (b).

6.4.4 Congener profiles

Despite similar temporal trends of global PCB emissions and fluxes into Fiescherhorn glacier, the trends of the congener patterns are noticeably different. Whereas the emission is dominated by the more volatile congeners, mainly light iPCBs (e.g. PCB 28 with three chlorine substituents), the most abundant congeners in glacier ice are hexachloro biphenyls PCB 138 and PCB 153 (Figure 3). We performed congener specific multivariance regression analysis to identify the dependence of the obtained fluxes from emissions in Switzerland, the summer temperature and the melt index, which revealed significant correlation for PCB 138, PCB 153 and PCB 180 (S3). According to the regression, 6-30% of the variation of the fluxes can be explained by the listed factors.

This underlines the previous findings that post-emission alteration can be attributed to processes involved in transport and deposition as well as post-depositional processes. Principally, the chlorine content of PCBs affects volatility and water solubility (both decreasing with increasing chlorine content). This makes the lighter PCBs more mobile, which may manifest in increased revolatilization and elution with meltwater. In the overall PCB congener pattern of the Fiescherhorn ice core the higher chlorinated (hexa- and heptachloro-) PCBs are overrepresented by a factor of 1.5 compared to lighter ones (tri to pentachloro-) (Figure 21) (Steinlin et al., 2014). This is not the case for layers underlying strong melt features, which seal off the surface from exchange with the atmosphere Thus, revolatilization is hindered and the initial proportion of lighter to heavier PCBs is preserved. This effect is particularly distinct for PCB 28 in the time periods 1993-1996, 1975–1978, and 1945-1949 (Figure 22). Such post-depositional processes, responsible for the fractionation of PCBs are discussed in detail in our companion paper (Steinlin et al., 2014).

6.4.5 *PCB concentrations in Alpine snow*

To our knowledge, there are two available studies on PCBs in Alpine snow: i) PCBs were determined in firn cores from the Lys glacier in the Monte Rosa Massif (4250 m a.s.l.,located 60 km from Fiescherhorn glacier) covering the period from winter 1997/1998 to spring 2000 (Figure 22) (Villa et al., 2006b); ii) PCBs were measured in winter snow 1997-1998 at lake Gossenkölle (2417 m a.s.l, located 230 km from Fiescherhorn glacier) and lake Jöri (2519 m a.s.l., located 150 km km from Fiescherhorn glacier) (Carrera et al., 2001). Considering these literature references to be all based on different analytical methods and not providing long-time data sets, very good agreement with the Fiescherhorn data, was found (Figure 22). Thus, we confirm homogenous distribution of PCBs in the Alpine region.

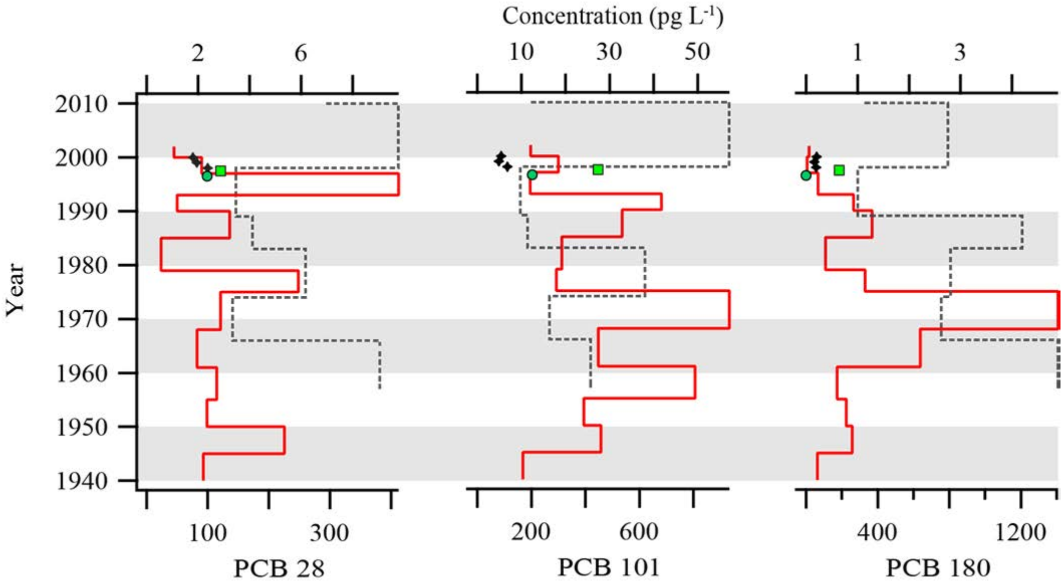

Figure 22: PCB concentration profiles in the Fiescherhorn ice core (bottom axis, red line), compared to other available data from the Alps (Carrera et al., 2001; Villa et al., 2006b)(bottom axis; black diamonds – Col de Lys, green circle – lake Gossenkölle, green squares – lake Jöri) and the Arctic (Lomonosovfonna, top axis, gray dashed line). Data from Lomonosovfonna glacier are from Garmash et al(Garmash et al., 2013).

6.4.6 PCB concentrations in Arctic snow

The only other deposition record of PCBs that covers a long time period, was available from Lomonosovfonna glacier in the Artic (Svalbard, 78.82°N; 17.43°E) (Garmash et al., 2013). Although the characteristics of the glacier, the meteorology of the region, as well as the sources and the transport pathways of PCBs are different, annual average air temperatures are similar at both sites with -10 °C (average in winter -14 °C, summer -7 °C) at Fiescherhorn glacier and -11°C (winter: -17 °C, summer: -5 °C) at Lomonosovfonna glacier (Steinlin et al., 2014). Generally, PCB concentrations in the Arctic are approximately by a factor of 100 lower than in the Alps (Figure 22). The substantial difference of PCB concentrations is most likely explained with the longer distance from the sources of PCBs. The Alpine-to-Arctic concentration ratio is about 30 for the lower chlorinated PCBs, compared to 130 for the higher chlorinated ones, which cannot be explained with secondary processes on the glaciers (e.g. degradation, revolatilization in the atmosphere or elution with meltwater) (Steinlin et al., 2014). We, therefore, assume that long-range atmospheric transport to the Arctic results in preferential loss of heavier congeners, which are more susceptible to dry and wet particle deposition. The Lomonosovfonna record shows high PCBs levels for the period 1998-2009, which is explained with a decline in the PCB content as the snow is converted to firn during the summer and with increasing importance of secondary sources (Garmash et al., 2013). A similar effect is not observed in the Fiescherhorn record.

In this study, we present a highly-time resolved deposition record of PCBs from an Alpine ice core. Since most glaciers in the Alps are retreating, a quantitative inventory of the amounts of PCBs stored in glacier ice is important for understanding and anticipating possible future effects on pristine Alpine ecosystems.

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7 EFFECT OF MELTING ON POPS IN ALPINE GLACIER ICE CORES

In glacial systems the inventory and localization of contaminants depends on the atmospheric input, the accumulation and ablation of the ice (mass balance), but also on transport processes within the glacier ice. Partitioning of the substances between the different phases (ice, pore space and deposited aerosol particles) occurs according to their physicochemical properties. We analysed an ice core, taken at 3900 m.a.s.l. from the cold Fiescherhorn glacier, where almost no melting in summer occurs, and therefore the atmospheric input is preserved (Chapter 6). Being particularly interested in the effect of surface meltwater percolating through the pore space and the related leaching of POPs, we measured PCBs in two additional ice cores from glaciers affected by surface melting. Grenzgletscher is a cold glacier, located in the Monte Rosa Massif, where an ice core was collected at 4200 a.s.l. The signal of major ions in this ice core is well preserved apart from a 10 mweq segment covering 1985-89. Presumably, the signal in this section is disturbed by a horizontal meltwater flow, originating from a closely located crevasse (Eichler et al., 2001). The second ice core was obtained from Silvretta glacier, a temperate glacier with surface melting occurring regularly every year. The results from this ice core (see Sampling sites, section 3.3), combined with sediment records are further used to describe and quantify the release of organic pollutants as a consequence of extensive melting of high alpine glaciers.

7.1 Concentration of iPCBs in Grenzgletscher and Silvretta glaciers

7.1.1 Profiles

We analysed the iPCB concentrations in the three ice cores, using the method described in Chapter 5 (Capillary traps for organic pollutants). Depending on the availability and the condition of ice, the resolution was between 1 and 5 years. In Figure 23 we present ice core concentration profiles of iPCBs from the glaciers Grenzgletscher (Figure 23B) and Silvretta (23C), compared to the concentrations measured in Fiescherhorn glacier, which is not affected by melting (Chapter 6, Figure 23A). Samples from the Grenzgletscher ice core cover the period between 1941 and 1993. The concentration of iPCBs varies between 0.5 and 3 ng/L, peaking in 1971. Although the dissolved fraction dominates, we observed relatively high particulate loads. The concentration trend in the ice core is in agreement with the PCB emission history (Breivik et al., 2007) and corresponds to the record from Fiescherhorn glacier (Table 4). However, there are some fluctuations of the concentration, which may origin from transport or deposition processes. High precipitation rates lead to dilution of the pollutants in the record and may explain the low iPCBs concentration in the 1960s and late 1970s. However, high precipitation rates cannot serve as an explanation of the low pollutant levels during the 1980s (Figure 24).

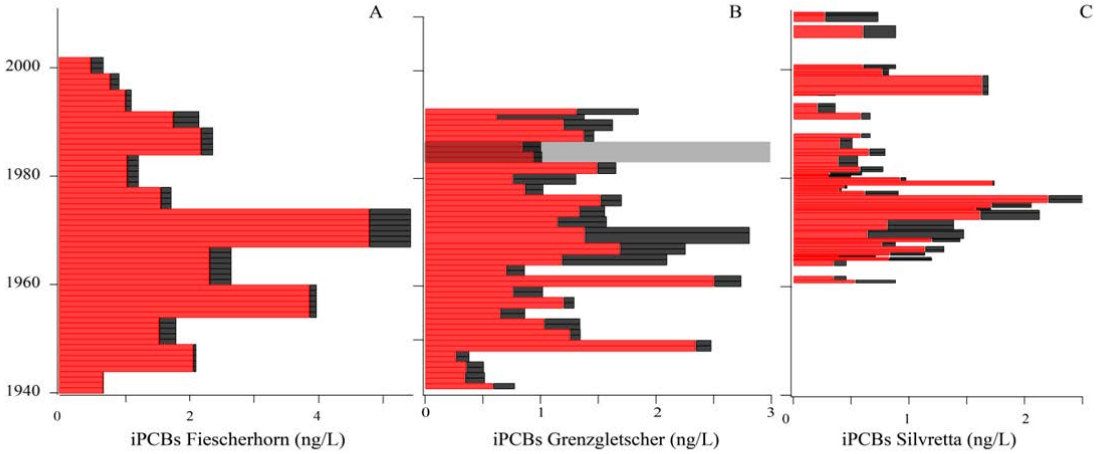

Figure 23: Historical record of iPCBs in three ice cores: Fiescherhorn (no melting), Grenzgletscher (melting 1985-1989, marked with grey shaded area) and Silvretta (temperate - melting most of the years) - dissolved (red) and particulate phase (black); missing values represent years with negative mass balance.

Table 4: PCBs in ice cores.

Ice core	average iPCBs dissolved (ng/L)	average iPCBs particulate (ng/L)	accumulation rate (m weq)	time period covered by ice core years	total burden µg/cm^2
Silvretta	0.8	0.2	0.9	1960-2010	4
Grengletscher	1.1	0.3	2.7	1942-1993	19
Fiescherhorn	1.9	0.2	1.7	1940-2002	26

In Figure 23C, years with positive net mass balance (1925-2010) of the Silvretta glacier are presented with corresponding pollutant loads (see Silvretta dating, section 4.2). The iPCBs concentration peak in the 1970s, which is in agreement with the other ice cores (Figure 23). In the 1980s we observe a rapid decrease of iPCBs loads (to 0.5 ng/L), which is associated with years with negative mass balances and may indicate elution of pollutants with meltwater. The high concentrations of PCBs in the ice from the late 1990s, might represent preserved atmospheric deposition signal Due to cold trapping, an altitudinal gradient can lead to enrichment, but sites located at higher altitudes are more distant from the sources. However, the concentrations of up to 3 ng/L in Silvretta are in the range of Grenzgletscher and Fiescherhorn, which are located at a higher altitude. In the ice core from the temperate Silvretta glacier, the dissolved fraction prevails, although its relative importance decreases with depth. Therefore, we assume a strong effect of percolating meltwater and corresponding transport and redistribution of PCB species, which is discussed in the following.

In addition we analysed HCB and HCHs in the Silvretta ice core. Since the data is preliminary and needs further corroboration is included in Appendix 1.

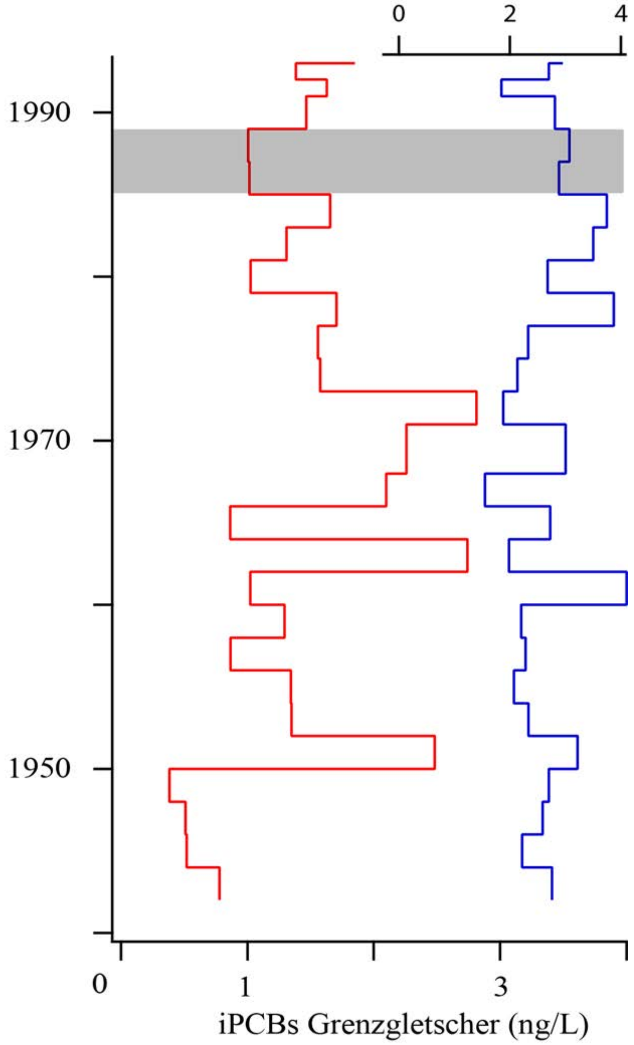

Figure 24: Precipitation amount effect in Grenzgletscher ice core: total iPCBs (red), annual accumulation (blue) and segment affected my melt (shaded grey area)

7.2 Effect of melting

7.2.1 *Elution and transport*

Surface melting on the glacier effects the fractionation of organic contaminants between ice, liquid water, particulate phase and gas phase, which results in spatial redistribution of pollutants. Compounds dissolved in the percolating water are transported through the pore system in the firn to deeper layers, where meltwater might refreeze or be discharged from the ice. In the Grenzgletscher ice core the segment 11-24 m weq, corresponding to the years 1985-1989 is strongly affected by melting as shown by ion records (Eichler et al., 2001), which in contrast to POPs are highly water soluble. Nevertheless, PCBs are also eluted from this layer, regardless of their hydrophobicity and are presumably retained in the underlying layers (1980-1982) as a result of refreezing. In contrast to percolating water, particles filtered through the snowpack coagulate (Herbert et al., 2006) and are accumulated, which leads to enrichment of particle bound analytes. Thus, the slightly higher particle loads in the 1980 to1982 samples compared to the samples above support the elution of PCBs with meltwater.

Available net mass balance data and visual observations of the Silvretta ice core indicate numerous melt events throughout the whole glacier. Therefore, we assume that widespread downward redistribution of pollutants in the dissolved and the particulate phase is responsible for the low levels in the samples originating from 1980s. However, total concentrations measured in the ice core that are in the range of those measured in cold glaciers, emphasis that although POPs are partly eluted with melting water, a significant amount is conserved in the ice and thus also temperate glaciers represent reservoirs for organic pollutants.

7.2.2 Total environmental burden

Total loads per cm^2 for Silvretta, Fiescherhorn and Grenzgletscher were calculated by summing-up the deposition fluxes with depth. Since the three glaciers are located in the Alps, where the sources are similar (Offenthaler et al., 2009), we assume a comparable input of pollutants to the three glaciers. Therefore, significant differences in the calculated burden most probably origin from post-depositional processes like melting and release of contaminants. In all three studied glaciers the total loads of iPCBs are in the range of µg/cm^2 (Table 4). Fiescherhorn, considered to preserve the entire inventory, has a load of 26 µg/cm^2. Grenzgletscher, although located closer to additional sources in the Po plain (Kaiser, 2009), is characterized with a burden of 19 µg/cm^2,which corresponds to the load in Fiescherhorn for the same period (1941-1993 - 20 µg/cm^2). Remarkably, the contaminant load of Silvretta glacier is a factor of 10 lower than the other two (4 µg/cm^2), supporting that melting results in partial loss of organic pollutants from temperate glaciers in the Alps. Still this results should be interpreted carefully, because certain loads of PCBs might be stored in deeper layers of the Silvretta glacier, in ice originating from the years 1940 to 1960.

In order to further corroborate our findings we compare iPCBs in sediments from the Silvretta proglacial lake (see Chapter 8), with the ice core data (Figure 25). Peaking PCBs concentrations in the sediment record correspond to the periods with negative net mass balance on the glacier (i.e. 1990, 2003), indicating that Silvretta glacier represents a secondary source for POPs in the proglacial lake.

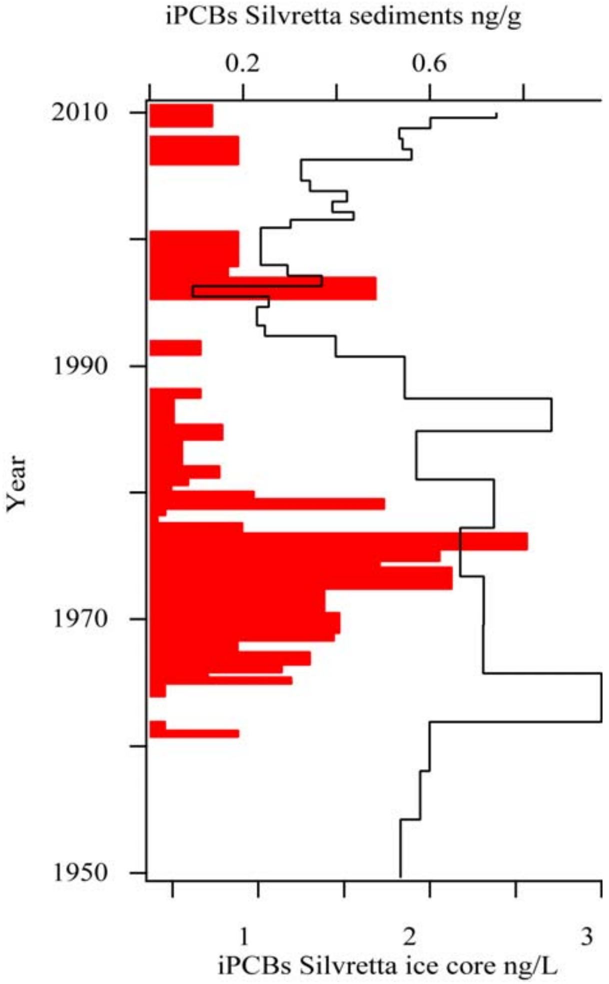

Figure 25: PCBs in Silvretta glacier system: sediment (black line) and ice core (red bars)

7.3 Conclusions

Here we present the first comparison of iPCBs concentration records in ice cores from Alpine glaciers, which are to a different extent affected by melting. Despite the hydrophobic properties, PCBs are partly eluted and transported with meltwater in glacier ice. Depending on the physicochemical properties of the pollutants, fractionation between phases in the glacier ice occurs and transport processes result in enrichment of the particulate phase within melt layers and deeper parts of the glacier. Nevertheless, considerable losses of glacial burden, which is attributed to melting, are observed in temperate Silvretta glacier, confirming the hypothesis that glaciers represent a source of legacy pollutants for the proglacial environment

8 RELEASE OF POPs FROM MELTING GLACIERS

Release of legacy pollutants from Alpine glaciers: a multiproxy approach based on analyses of meltwater and sediments

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To be submitted

8.1 Introduction

Persistent organic pollutants (POPs) represent a group of anthropogenic compounds, which were extensively used in 20th century and, because of their persistence, are still recirculating in the environment. The main pathway of the organic contaminants to the glacial ecosystems including glacier ice, proglacial lakes, glacier streams and their catchment areas are atmospheric wet and dry deposition. Because of their sorption affinity, POPs in water are preferably bound to suspended particles. Hence, sediments represent a useful tool for monitoring standing or flowing water bodies. Sediment records are commonly used to examine historical records of pollution, ideally with annual resolution (Bogdal et al., 2008; Thevenon et al., 2013). Type, rate and area of sedimentation strongly depend on particle nature, amount and size, and variability in runoff, which can lead to difficulties in interpretation, especially in high mountain areas, where hydrological data is scarce. In addition, POPs partly also occur in the dissolved phase, which eventually leaves the lake system and thus is not captured in sediment records. Contrastingly, passive water sampling provides bulk pollutant loads data for larger area and shorter time scales.

Several studies have reported that revolatilization and runoff of glacier meltwater results in redistribution of legacy substances and, therefore, glaciers represent a secondary source of pollutants (Blais et al., 2001; Bogdal et al., 2009b; Morselli et al., 2014). Bizzotto et al., (2009) compare data from glacier streams obtained on varying distances from the terminus, and oppose it to a non-glacier fed stream located in the vicinity. Bettinetti et al., (2008) used pollutant concentrations in mussels and were able to capture the prominent melting resulted from the warm summer in 2003. Bogdal et al., (2009b) and Schmid et al., (2011) demonstrated elevated concentrations of different POPs in the surface sediments in lakes in the Alps. However, data regarding release of organic pollutants from melting glaciers is still scares and not well understood (Villa et al., 2006a).

Hereby, we combine sediment records from proglacial lakes, located just below the glacial terminus, with passive water sampling data from the catchment area of the glacier stream. Thus, this attempt to combine the two different techniques enables an improved spatial and temporal resolution for the understanding the processes of redistribution and release of pollutants from the melting glaciers. The sediment records are used to represent historical data, reaching back to the application phase of POPs. Further, passive samplers provide monthly to seasonally resolved load data of a broader area, which is however strongly influenced by changes in the environmental parameters during sampling. Silvretta glacier in the Swiss Alps and the corresponding two proglacial lakes were chosen as a study site.

8.2 Methods

8.2.1 *Lake sediments*

To study the historical trends of POPs in glacier runoff, we analysed varved lake sediments from Upper Silvretta (SIO) and Lower Silvretta Lakes (SIU), located just below the Silvretta glacier terminus (Figure 26). These lakes were formed in the 1950s due to the retreat of the glacier. The lacustrine sediments in these proglacial settings consist of clastic varves (Anselmetti et al., 2007; Leemann and Niessen, 1994).

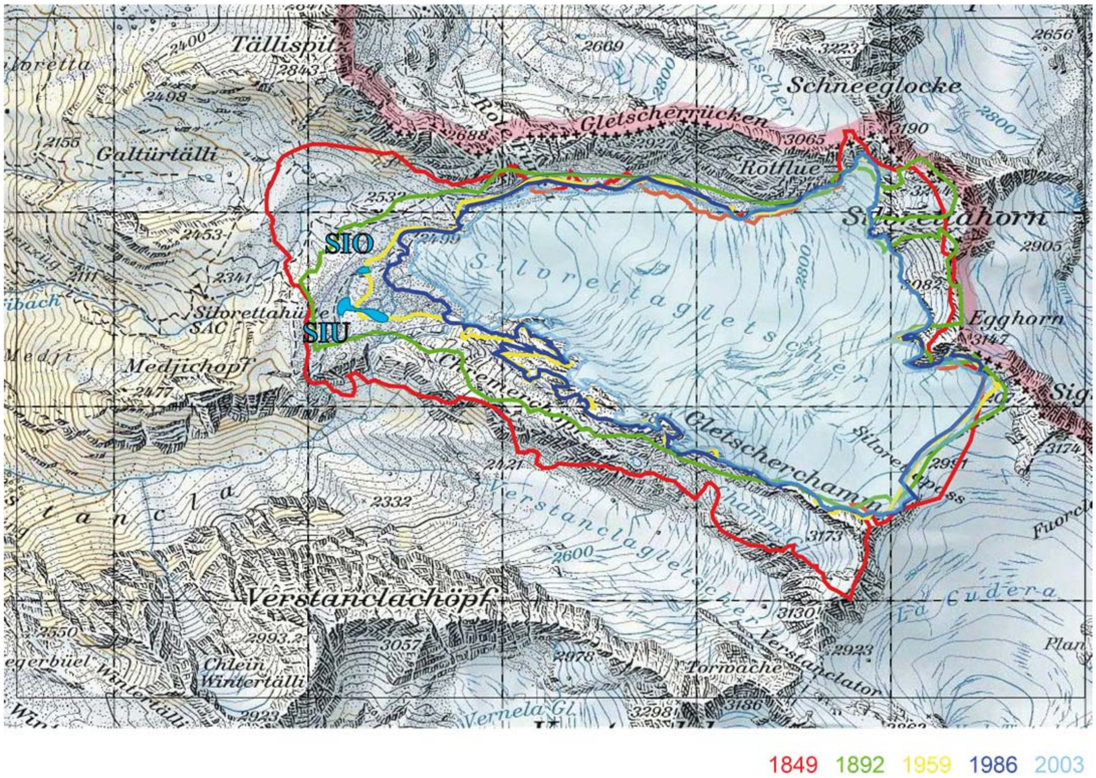

Figure 26: Map of Silvretta glacier and the two proglacial lakes, which are highlighted in light blue. Coloured lines show the glacier's extent in 1849 (red), 1892 (green), 1959 (yellow), 1983 (dark blue) and 2003 (light blue); adapted from A. Bauder (ETHZ)(Huss and Bauder, 2009).

Drilling and sampling of the sediments. Two sediment coring campaigns were conducted in the two proglacial Silvretta lakes. In August 2010, three sediment cores (each ~1 m in length) per lake were taken from an inflatable boat using a gravity short corer. In addition, surface cores (30 cm in length) were retrieved at the same locations with less weight to obtain undisturbed surface sediment. In order to extend the record, a longer core was recovered in February 2012 from the SIU. This second coring campaign was conducted from the surface of the frozen lake after removing the overlaying snow. A manual percussion piston corer (Uwitec) was used to recover a 2.5 m-long sediment core that reached the underlying moraine, i.e. covering the time back to the formation of the lakes of around 1950 (Figure 26).

The sediment cores were collected in a PVC tube with an inner diameter of 5.9 cm. In the laboratory, they were split lengthwise into two halves. After drying at room temperature and removing the surface layer, the varved structure of the cores was inspected. Based on core-to-core correlation, two composite sections (one for each lake), which contained the best preserved sediment, were defined. For the SIO the composite section consists of cores SIO_2B and SIO_5. For the SIU, SIU_1 and SIU_2A were used and complemented by the deeper 1.5 m of the long core from 2012 (SIU12). The sampling resolution of SIU for the surface section (0-100 cm) is 2 cm and 10 cm for the segment the 110-210 cm.

Organic pollutant analysis. Freeze-dried, pulverized lake sediments (5 gr per sample) were Soxhlet-extracted with *n*-hexane/dichloromethane (1:1) for around 12 hours. Once enriched, the extracts were subject to chromatographic separation using chromatographic columns, packed with silica gel and Na_2SO_4 (Bogdal et al., 2009b). The obtained fractions were analysed for PCBs and DDT content through gas chromatography coupled to high-resolution mass spectrometry (GC/EI–HRMS). For quantification, isotope-labeled internal standards were used. All the glassware is preheated and rinsed with acetone and dichloromethane immediately before use. The analytical procedure included preparation of blank samples with average load of 176 ± 67 pg (n=6) and an average recovery of the internal standard of more than 80% in total.

8.2.2 Passive water samples

Polydimethylsiloxane (PDMS) passive samplers were employed to monitor current levels of target analytes in meltwater.

Uptake efficiency. POPs partition between the water phase and the passive sampler phase (in this case PDMS) until equilibrium between the concentration in the two phases is reached, defined by the partition coefficient K:

$$K = C_{PDMS}/C_{water}$$

Uptake depends not only on the kinetics but also on environmental parameters like water temperature, flow velocity, organic carbon content and possible formation of biofilm. Higher temperature increases diffusion and accelerates the uptake rate (Huckins et al., 1990), but this effect is assumed to be negligible for temperatures below 20 °C and especially for water bodies where the difference in temperature between different sampling locations is very small. The uptake rate increases with increasing flow velocity. In the case of glacier fed streams, there is a strong variation in diurnal flow rate. Therefore, we assume an average comparable flow velocity between all flowing water bodies. This assumption implies that concentrations in standing waters might be underestimated compared to fast flowing waters. Both the availability of dissolved organic carbon in the water and of a biofilm on the passive sampler is associated with bioactivity and reduces the sorption capacity of the PDMS. However, for most of our sampling sites, those can be neglected, since due to reduced bioactivity, the organic carbon content is low.

PDMS preparation, sampling and analysis. For the preparation of the samplers, PDMS foil (0.040“ Ultra-Thin Silicone Membrane SSPM823 12“× 20 ft) with white 1 mm thick virgin Teflon liner (J-Flex Rubber Products http://www.J-Flex.com) was used. Pieces of 10 × 40 mm were cut and weighted. The foil was washed and Sohxlet extracted with ethyl acetate for 96 hours and with methanol for 48 hours. Until use, clean PDMS foils were stored in methanol in sealed glass bottles. Foils were taken out in the field and fixed with screws on a concrete-based sampling apparatus. In the proglacial lakes, the PDMS samplers were fixed on heavy stones. Exposure time for the passive samplers was four weeks. Flow velocity and temperature were measured at every site during setting up and collecting. After exposure PDMS foils were cut off and cleaned from any precipitate, and biofilm. Packed in pre-cleaned glass bottles, they were analysed immediately upon arrival in the laboratory or stored at -20°C until analysis. Sohxlet extraction of the internal standard spiked samplers was conducted in methanol for 24 hours. The extracts were concentrated and treated with concentrated H_2SO_4, followed by clean-up with silica gel chromatography. All compounds were analysed by gas chromatography coupled to electron ionization high resolution mass spectrometry (GC/EI-HRMS).

We conducted PDMS sampling in two consecutive years. Sampling during early summer was omitted, because due to the melting of the seasonal snow, the legacy organic pollutant signal is diluted. In August 2012 passive samplers were exposed for four weeks in the two proglacial lakes and the runoff stream from SIO to SIU (Figure 28). In order to evaluate the loads of POPs delivered to the ecosystems further down the valley, we installed PDMS samples in Verstanclabach, receiving the meltwater from Silvretta glacier and from Verstancla Glacier, located 0.5 km south from Silvretta glacier (see Study sites, section 3.3). Since both glaciers are located at the approximately same elevations, we assume similar environmental conditions. However, Verstancla glacier has a smaller surface area and, therefore, is contributing less to the glacier melt runoff in the river. In the catchment area, we conducted a series of PDMS sampling campaigns – August-October in 2012 and in 2013, respectively. In 2012 we sampled only the Verstanclabach for two four-week-periods. In 2013 the study was extended and the PDMS sampling campaign in the catchment area of Silvretta und Verstancla glaciers covered three sampling sites over the three periods: the glacier fed Verstanclabach (V3), the non-glacier fed Vereinabach (V2) and another location in the Verstanclabach after confluence with Vereinabach (V1) (Figure 27). During the sampling campaign in 2012 we analysed merely PCBs, and in 2013 we also included analysis of DDTs.

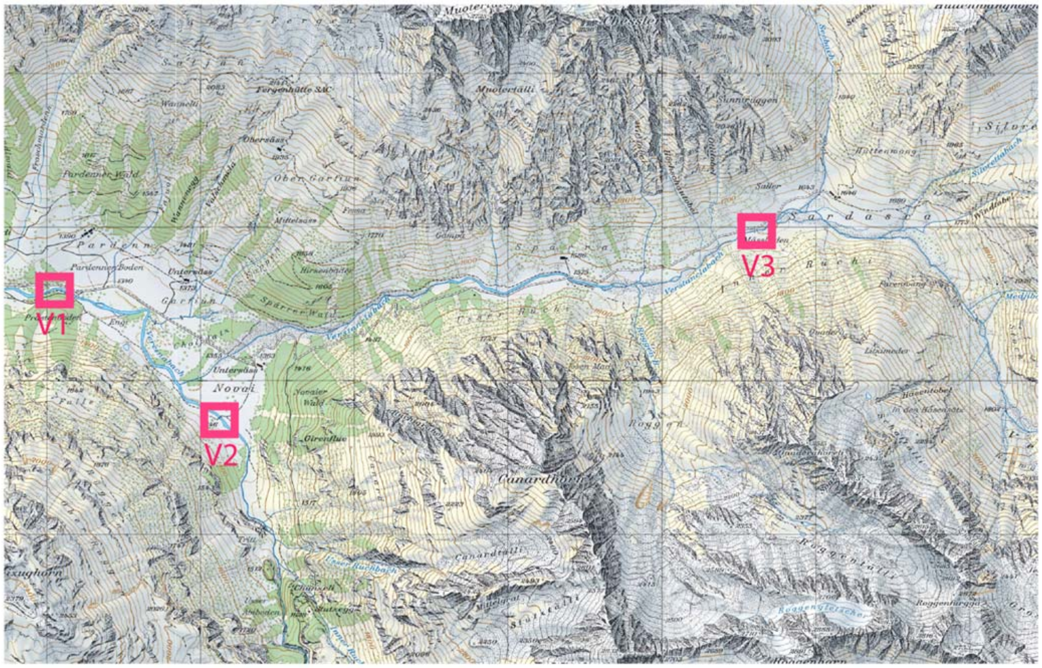

Figure 27: Map of the catchment area of Silvretta and Verstancla glaciers with the location of the PDMS sampling sites

Substances of interest

We analyze different groups of POPs:

- Indicator PCBs (iPCBs) - PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180, were selected for this study. Due to the range of chlorination degrees - from 3 to 7 chlorine atoms, indicator PCBs are representative for the whole class of PCB congeners covering a wide range of volatilities and water solubilities (log K_{ow} 5.66-7.15 (Schenker et al., 2005)
- DDT isomers (2,4′-DDT and 4,4′-DDT) and their main transformation products (2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE and DDMU), the sum is presented as DDTs (log K_{ow} 4.3-7).

8.3 Results and discussion

8.3.1 *Age model for the Lower Silvretta lake*

Visual inspection of the upper Silvretta lake throughout the melt season revealed particle-poor water indicating that this lake no longer receives meltwater from the glacier (Figure 28). Therefore, we focused on the lower Silvretta lake for further discussion. In contrast to the upper lake, the SIU is turbid and experiences a prominent strong diurnal cycle of the runoff volume, confirming the fact that it is fed mainly by glacier meltwater during summer.

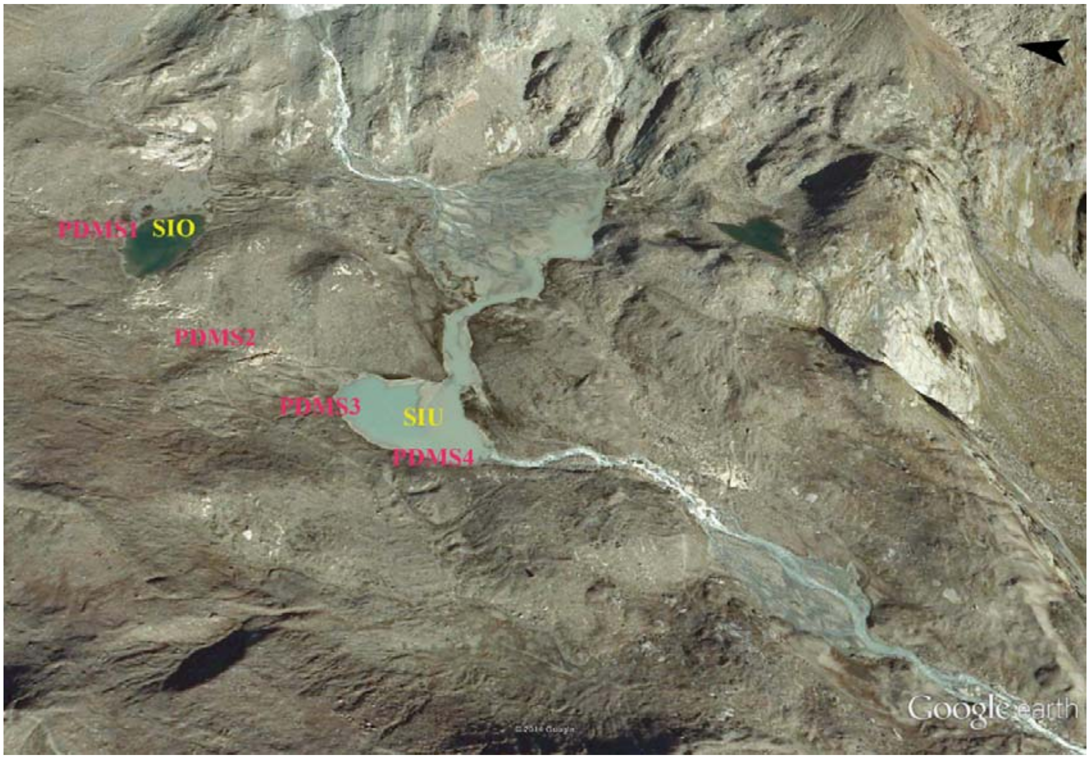

Figure 28: Location of the PDMS samplers in the Silvretta lake area

Dating of lake sediment is achieved conventionally by counting annual varves and by measuring gammaspectroscopically radioactive isotopes (^{137}Cs, ^{239}Pu and ^{241}Am). Annual varves are formed through the difference in particle-size-dependent seasonal variations in the deposition processes. In summer, coarse particles from the glacier are transported with melt or rain water directly to the lake. On the contrary, in winter, when the lake surface is frozen, no new sediment is entering the water column so that a layer is formed by the fine particles that settled down in the quiet water column. The Silvretta proglacial lakes are characterized by a rather complex structure so that seasonal varves often cannot be differentiated uneqiovocally. In addition, some prominent coarse sediment events are noticeable and were excluded from the analysis.

The age model of SIU was compiled using radioactive isotopes of anthropogenic origin. 10-gram samples for ^{137}Cs, which is known to have two distinct activity peaks (Appleby et al., 2001), corresponding to the peak fallout of nuclear bomb testing (1963) and the Chernobyl power plant accident (1986), were measured gammaspectroscopically (662 keV) at Eawag Dübendorf using low background, High Purity Germanium (HPGe) well detectors (Canberra) (Elbert et al., 2011). The age-depth relationship for the core was obtained through linear interpolation between the two identified horizons and the time of formation of the lakes (year 1950). An independent confirmation of the dating was provided by activity measurements of actinides ^{239}Pu and ^{241}Am, which are part of the Pu radioactive decay chain series and were emitted during nuclear bomb testing but not during the Chernobyl accident. Thus, the activity of the selected isotopes increases with depth. In addition, the measured isotope ratio of around 0.4 is characteristic for the bomb tests signal (Röllin et al., 2013). Based on the age model (Figure 29), the average annual sedimentation rate for the lower lake is ~4.8 cm/yr.

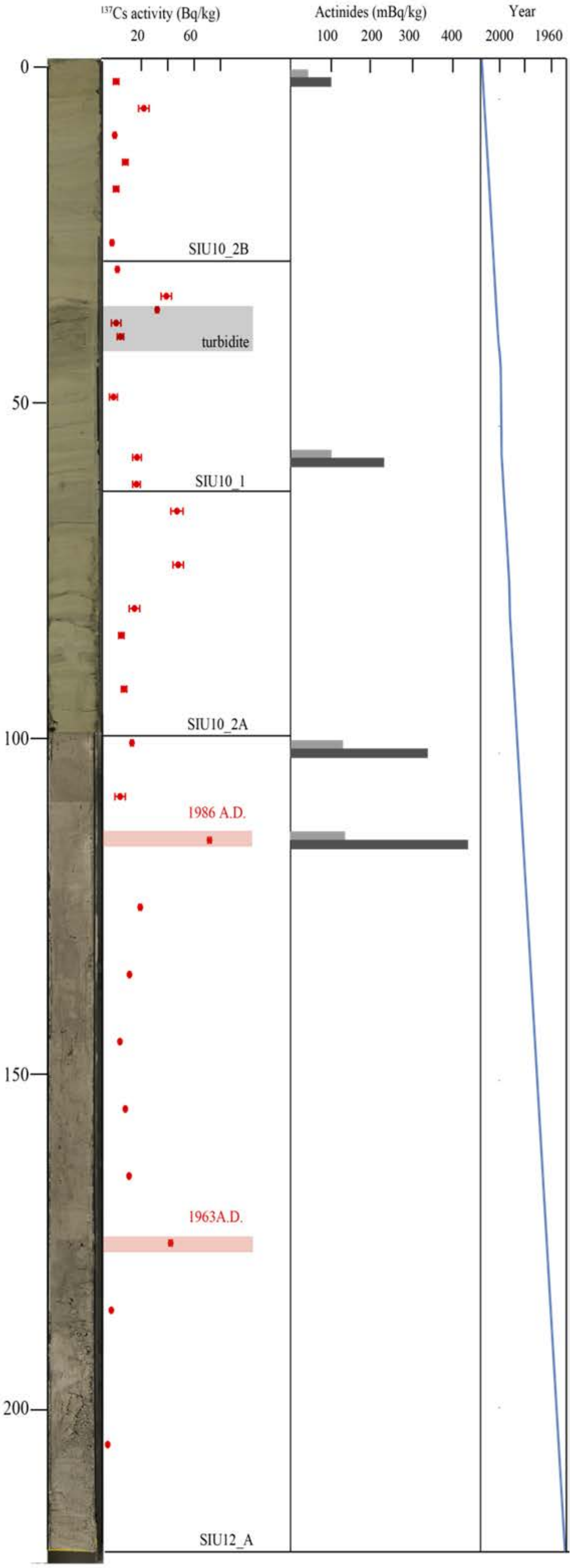

Figure 29: Age-depth model of the Silvretta lake including composite photo, ^{137}Cs activity (red dots + standard error), actinides activities (light grey ^{241}Am and dark grey ^{239}Pu)

8.3.2 Historical trends of primary vs secondary emissions in PCB-homolog composition data from lake sediments

The sum of iPCBs concentrations measured in sediments from the SIU varies between 100-800 pg/g (see Figure 5). These loads correspond to the values reported in other proglacial lakes in the Alps: lake Stein (Schmid et al., 2011) (300-900 pg/g sum iPCBs) and lake Oberaar (Bogdal et al., 2009b) (500-1000 pg/g sum iPCBs). We observe the highest concentrations (>700 pg/g) during the period 1960-1980, which is in good agreement with other studies and the temporal emission trends (Breivik et al., 2007). The following decrease in concentrations down to a background level of 20 pg/g is attributed to PCB production and disposal restrictions in the end of the 20th century. Increasing concentrations in the sediments from the most recent 10 years was interpreted as secondary release from the melting ice, an effect observed for other sites in the Alps and the Arctic (Bettinetti et al., 2011; Bizzotto et al., 2009; Blais et al., 2001). Depending on their physical-chemical properties (i.e. water solubility, sorption affinity, vapour pressure, etc.), PCBs experience congener-specific behaviour in glacier ice, which results in fractionation of homologues along the pathway from primary emission sources to the meltwater. Less chlorinated and thus more volatile congeners (PCB 52 and PCB 101) are readily scavenged from the atmosphere, and are deposited with precipitation through runoff in the lakes, where they remained trapped in the sediments. On the contrary, when deposited on the glacier ice, because of the high volatility, they preferentially are re-emitted back to the atmosphere or are eluted right after deposition with surface meltwater. As a consequence, sediments influenced by melting glacier ice might be enriched in heavier, high-Cl containing compounds like PCB 138 and PCB 180 (Figure 30).

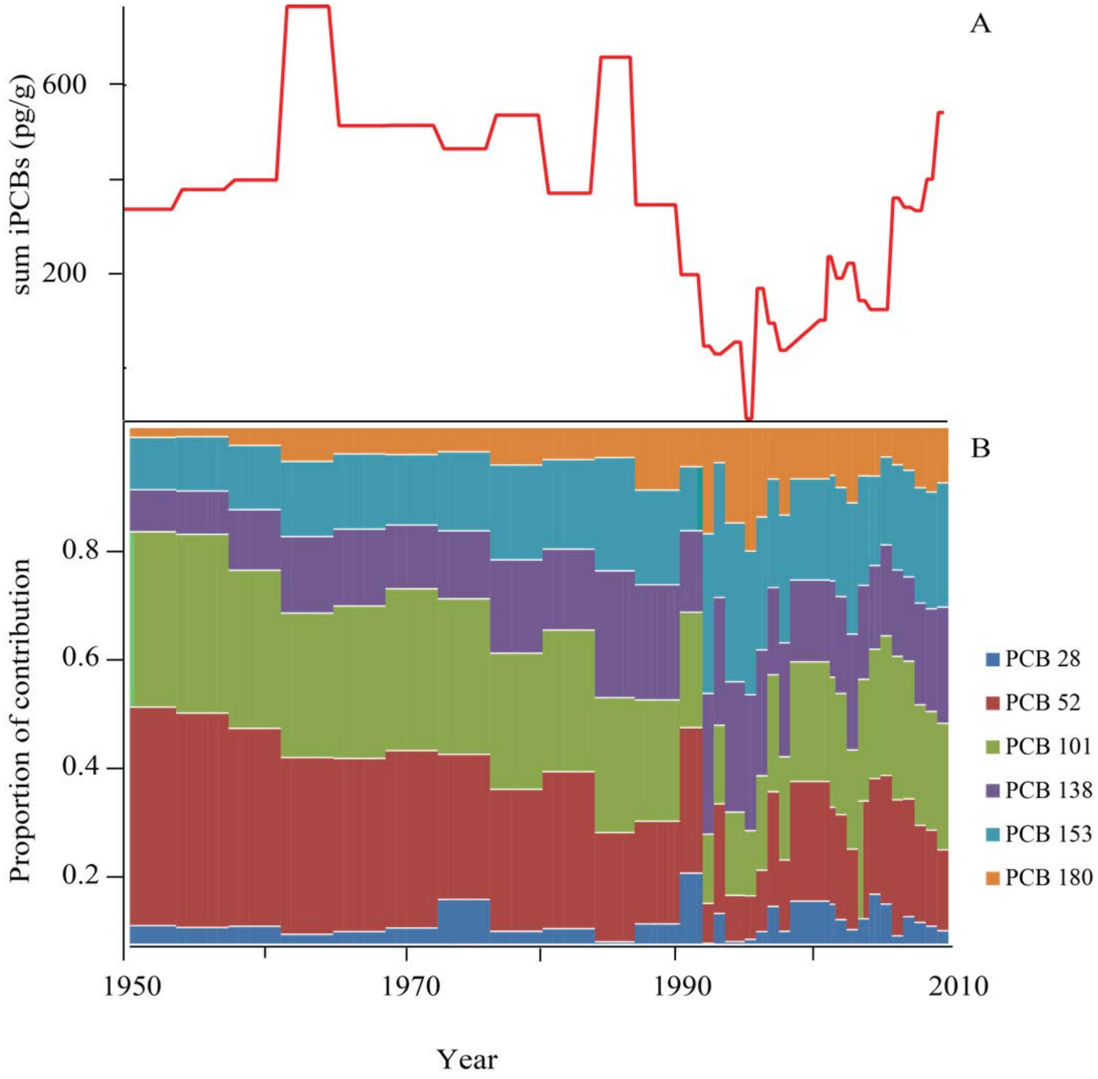

Figure 30: PCBs in the lower lake (SIU): A)total iPCBs; B)homolog pattern

8.3.3 *Effect of surface melting on DDT metabolite composition*

The sum of DDTs in Silvretta sediments varies between 50 and 3000 pg/g. DDT was extensively used and released to the environment in Europe between 1960 and 1970, until first restrictions were introduced. The peak load of sum DDTs in the sediment record, covering the 1960s until early 1970s coincides well with historic data (Li and Macdonald, 2005). However, the measured concentrations are higher than the concentrations measured in lake Oberaar for the period 1950-1990 (500-1000 pg/g sediment) (Bogdal et al., 2009b), but by a factor 100 lower than the loads in lake Iseo sediment in Northern Italy (Bettinetti et al., 2011). The DDT load in SIU remains relatively constant around 50 pg/g during the period 1975 to 2010. Surprisingly, in contrast to PCBs, we do not observe an increase of the concentrations of the DDTs towards the surface of the sediment. A similar discrepancy in the concentration trends between the two substance groups was reported by Bettinetti et al. (2011a) in lake Iseo. PCBs do not show an increase in the surface layers and this was attributed to differences between local and long range atmospheric transport. In Silvretta, analogically to the atmospheric input in the sediment record, the high levels of DDT in the glacier ice are concentrated in a layer covering around ten years. Thus, the melting of this layer will result in release of high levels of pollutants in short time, which we did not detect yet. Therefore, we assume that due to glacier flow patterns, the main load of DDT is not released yet and, therefore, the Silvretta glacier represents a reservoir for DDTs. Future monitoring of the proglacial lake is needed in order to confirm this hypothesis.

Then, we examine ratios of substances in the lake sediments, which might be affected by secondary processes like transport, elution, and transformation (Figure 28). For example, abiotic (photolysis) and biotic transformation of the parent compound 4,4´-DDT into the more stable 4,4´-DDE which has been extensively studied can be used for identifying environmental circulation time (Bettinetti et al., 2011). The higher ratio (>>1) between metabolite and parent compound suggests occurrence of transformation processes and is associated with longer residence time in the environment. On the contrary, ratios of ~1 correspond to combined contemporary use of DDT with legacy pollution as a source (Gong et al., 2014). 4,4-DDE/4,4-DDT in sediments from the lower Silvretta lake varies between 0.05 and 5, with lowest values corresponding to the highest concentrations in the record 1961-1971, which can be explained with the primary emissions of DDT. More recently, the fraction of DDE is fluctuating around 1, with peak values of 2 and higher (Figure 28). Since nowadays DDT is still used only in developing countries to fight malaria, the obtained ratio suggests atmospheric transport as an important source in the recent years. High 4,4-DDE/4,4-DDT ratios were also measured in lake Iseo and were attributed to indirect i.e. glacier input (Bettinetti et al., 2011). Therefore, we assume that in the recent 40 years, input of DDTs into Silvretta lake alternated between direct atmospheric and surface meltwater from the glacier.

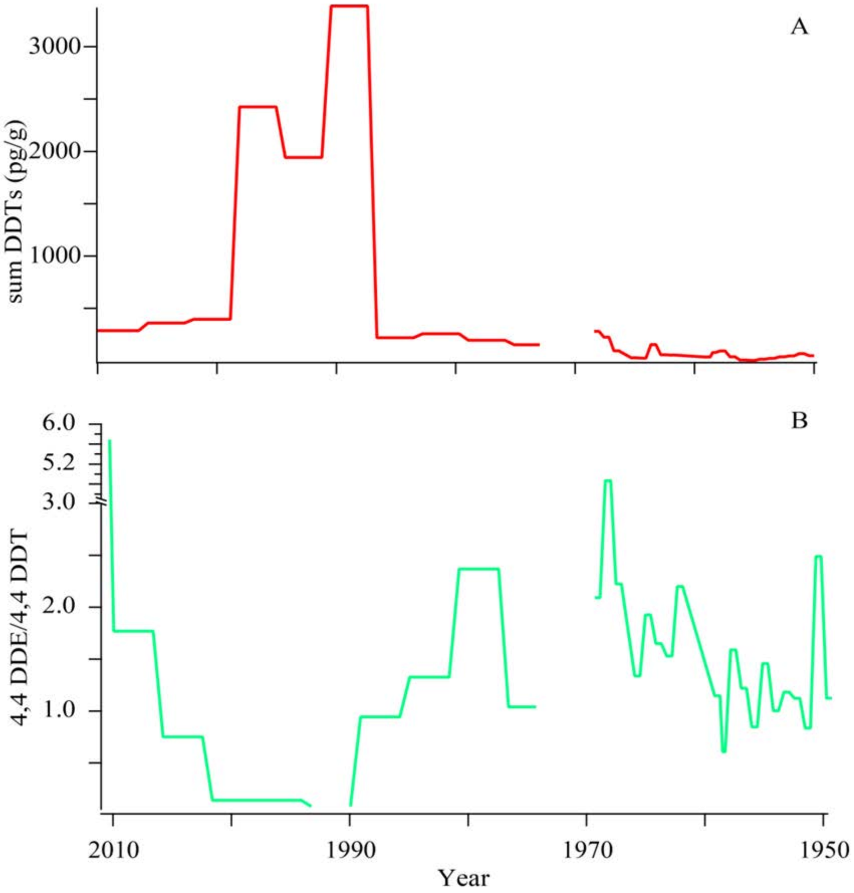

Figure 31: DDTs in the lower Silvretta lake: A) sum DDTs concentration profile – red line; B) metabolite to parent compound ratio 2,4-DDE/4,4-DDT – green line

8.3.4 *Recent concentration of legacy organic pollutants in Silvretta proglacial lakes*

PDMS samplers were located in the Silvretta proglacial lakes and a connecting stream. Exposure time for the passive samplers was four weeks and data is provided in pg/g PDMS, which is in the range of the loads obtained from the surface samples in the sediment cores (Figure 32). Samplers at sites PDMS 2-4, located in the stream and the lower Silvretta lake revealed very similar loads of iPCBs of 330-530 pg/g. The measured concentration in the surface sediment sample from the lower lake is 743 pg/g and thus slightly higher. The sampling site PDMS1 (SIO) is characterized with the lowest concentrations of 78 pg/g PDMS, which confirms the assumption, that the main transport pathway of pollutants to this lake currently is atmospheric transport. In addition, higher temperatures and almost no water flow in the lake resulted in biotic activity, which might hinder the uptake. The overall homolog pattern composition of sediments and PDMS samplers appears very similar. The dominance of more hydrophobic PCBs with 4 and 5

Cl atoms - PCB 101, PCB 138, PCB 180 - is explained with the hydrophobicity and the sorption affinity of these congeners.

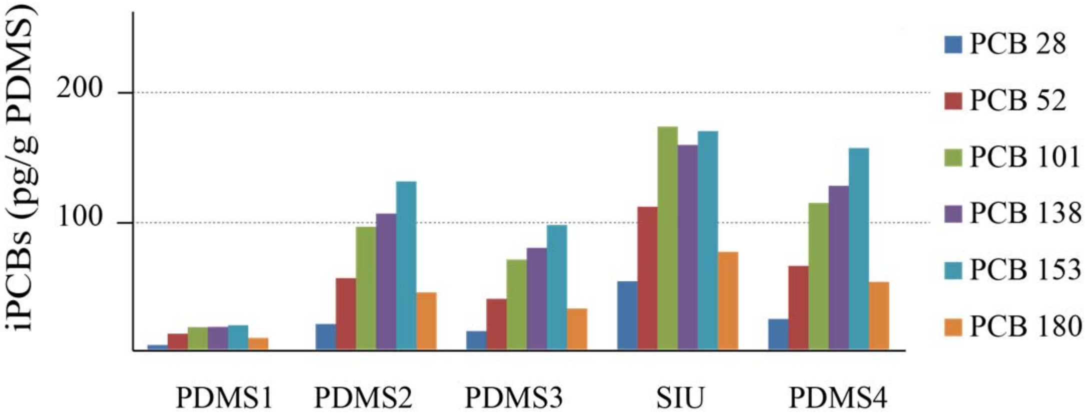

Figure 32: PCBs in Silvretta lakes area compared to SIU surface sediment data

8.3.5 *Differences in the pollutant profile and the total loads of POPs between glacier-fed and non-glacier fed streams*

The loads of the PDMS samplers in the catchment area at the different sites and the different sampling periods are quite uniform with values ranging between 300 to 450 pg/g iPCBs (Figure 33). In general the iPCBs concentrations measured in October are lower than those in September, because of the lower temperatures, respectively less melting, and higher precipitation rates (Meteoswiss, 2014). Moreover, according to meteorological data for the closely located Davos station, the summer of 2013 was characterized with higher diurnal temperatures, which foster melting and would explain the slightly higher concentrations of around 10 pg/g per single compound in 2013. Sampling site V2 (Vereinabach) exhibits different behaviour. It is not directly connected to a glacier and, therefore, the concentrations in September and October are similar. Here we also observed biotic activity and formation of biofilm, which depending on the volatility of the analytes, can reduce up to 50% of the uptake. However, the comparison between the different sites does not reveal significant differences, possibly due to the large distance from the glacier terminus and possible additional inflow of surface waters in Verstanclabach (V1 and V3). Bizzotto et al., 2009 got similar results, showing that the PCBs concentration do not increase with decreasing distance from the glacier terminus and that there is no significant variance of the PCBs loads between glacier-fed and non-glacier fed streams. Thus, in the present years the runoff and the revolatilization from soils is contributing more to the total loads than glacial meltwater.

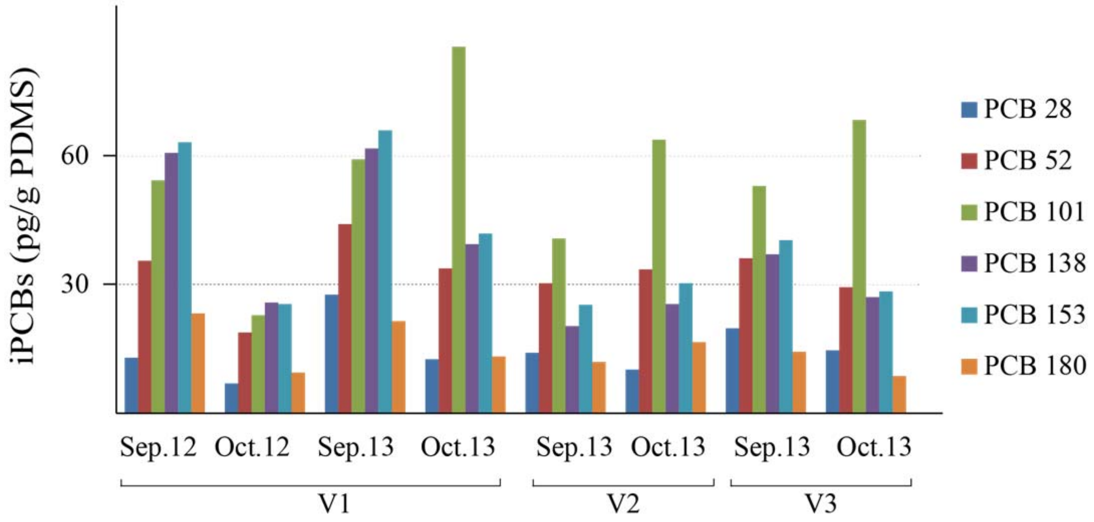

Figure 33: PCBs in the catchment area of Silvretta and Vestancla glaciers

In contrast to the iPCBs measured in PDMS in the catchment area of Silvretta and Verstancla glaciers, the concentrations of the DDTs do not decrease with decreasing ambient temperature and glacier meltwater runoff i.e. in October (Figure 34). Sampling site V3 (Verstanclabach) has the highest loads of DDTs. Since the sampling site V2 has the lowest DDT loads, the concentrations measured in sampling site V1 in Verstanclabach, after the inflow of Vereinabach are slightly lower due to dilution. Unlike in lake sediments, 4,4-DDT is the most abundant compound in all samples, suggesting increasing importance of direct input of DDT to the studied streams. In addition, we also observe very low ratio of 4,4-DDE/4,4-DDT as a proxy for environmental degradation, confirming atmospheric origin. The higher 4,4-DDE/4,4-DDT ratios in V2 might be explained by bioactivity in the stream.

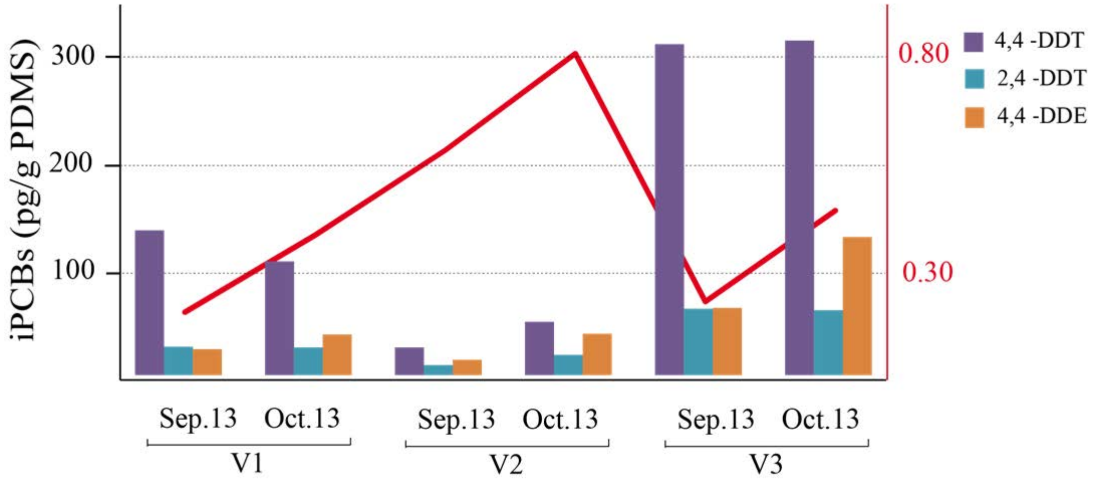

Figure 34: DDTs in the catchment area of Silvretta and Vestancla glaciers: concentration in bars, 4,4-DDE to 4,4-DDT ratio (red line)

8.4 Conclusions

We present a quantification of the accelerated release of legacy POPs from glaciers using two different sampling techniques. First we analysed lake sediments, to study the meltwater release history at the study site. Second, we use passive PDMS samplers to assess current contaminant levels in meltwater. PCBs in Silvretta glacier system currently originate mainly from glacier surface runoff and are, therefore, relative homogeneously distributed. In contrast, DDTs are currently not being released from the glacier and their prevailing sources is long range atmospheric transport. The delivered results confirm that the multiproxy approach is very promising and can be even extended to qualitative and quantitative prediction of future release of contaminants from glaciers.

9 CONCLUSION AND OUTLOOK

The goal of this study was to obtain a complete inventory of POPs in glacier ecosystems including glacier ice, sediment from proglacial lakes and meltwater. We aimed at improving the understanding of transport and redistribution processes of the selected pollutants in such systems. Therefore, we have employed different techniques and analysed an array of compounds with different characteristics. In the frame of this project we conducted a number of successful field campaigns, including collection of sediment cores and PDMS passive water sampling. A central accomplishment was the drilling of the first temperate ice core in the Alps from the Silvretta glacier, using a combined system of electromechanical-thermal drill. For sediments and passive water samples, we used conventional extraction techniques, which produced comparable and reliable results. The ice core samples represented a certain analytical challenge because of the ultra-trace concentrations and possible losses to container walls. Hence, we developed a novel capillary trap extraction method, which by minimizing the contact of the samples with surfaces, reduces adsorption losses and background contamination. Further advantages of the trap method include small sample volumes, easy handling, and minimized consumption of resources in compliance with green analytical chemistry. As we analysed and interpreted three ice cores, the method proofed to be robust and reproducible. In addition, we implemented a filter for the particulate bound fraction, which showed to be very useful for capturing the enrichment of the particle fraction as a result of melting. We concentrated on two different groups of substances: industrial chemicals, represented by PCBs and pesticides, including DDTs, HCB and HCH. PCBs were detected in all media at very low detection limits. In contrast, DDTs were not detected in ice, possibly due to the higher detection limit and the very low concentration. HCB and HCH were not measured in sediments, but were detected sporadically in ice. However, it is not clear if this is a result of their environmental behaviour influenced by higher volatility and different sources.

It was further confirmed that glaciers represent reservoirs of legacy organic pollutants. Another task of this work was to examine the effect of changing climate and accelerated glacier melting to the redistribution of these substances in the environment. We showed that an essential part of the pollutants are removed with percolating meltwater despite of their hydrophobic properties. With the assumption that with increasing temperatures, POPs will be further re-volatilized, the problem with organic pollutants in pristine areas will persist. However, the bulk loads in the glaciers in the Alps are relatively low.

In context of the presented results, further monitoring of POPs in Alpine glacier environments should include more profound studies of the behaviour of more soluble compounds, such as HCH, which are also readily scavenged from the atmosphere. Further sampling of the ablation area of the glacier could corroborate the time scale of the release of legacy pollutants from the glacier ice. The processes controlling enrichment of particulate organic carbon and black carbon in layers appear to be very important and should be better investigated. The fractionation of organic contaminants between inert and organic particles plays an important role and is still poorly studied. Further understanding of the seasonality in the particulate deposition processes on Alpine sites could provide a useful tool for dating temperate glaciers. Last but not least, new “emerging” POPs like flame retardants, cosmetic by-products, impregnating agents should be included in the data, which represents analytical and interpretational challenge. The presented data will be used for the validation of an environmental fate model regarding the distribution of POPs in glacier environments. Thus, at a further stage, the obtained results can be combined with climatic and aerosol models in order to better quantify the current sources of legacy pollutants in the air and to evaluate the importance of long range atmospheric transport versus local sources in pristine environments.

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LIST OF FIGURES

APPENDIX

Time concentration trends of HCB and HCH in Silvretta ice core

Parallel to the iPCBs we analysed HCB and HCHs in the Silvretta ice core. Since the measred concentrations are very close to LOD, we optimized the GC/MS measrement procedure in the course of the analysis. Therefore, the presented results are prelimited and are not discussed. Additional repetition of the analysis is needed in ordert o obtain reliable data.

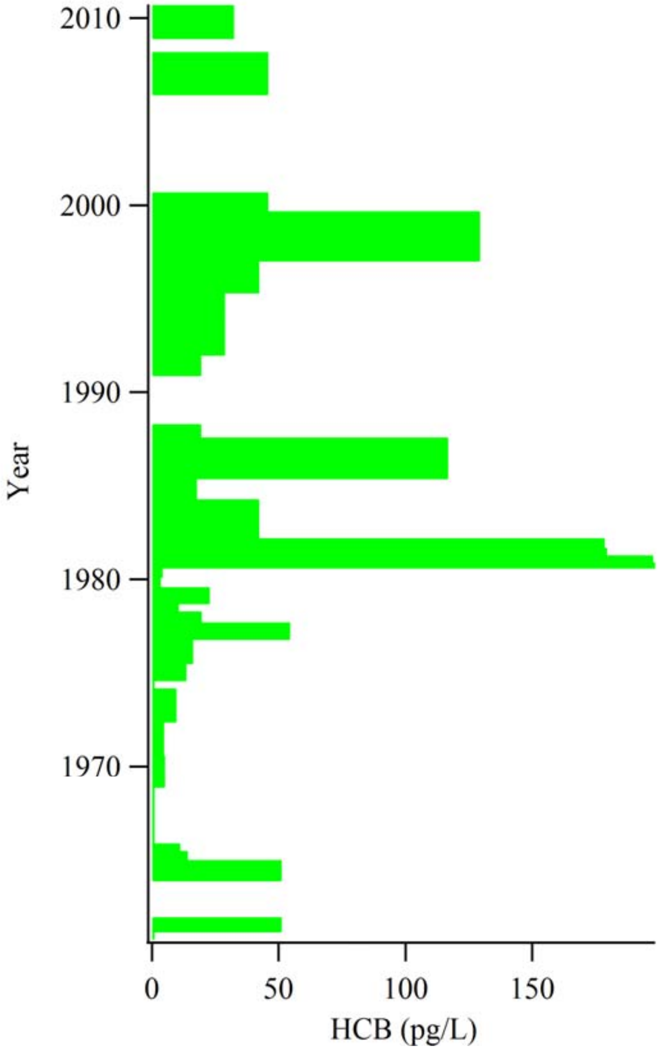

Figure 1: HCB in Silvretta ice core.

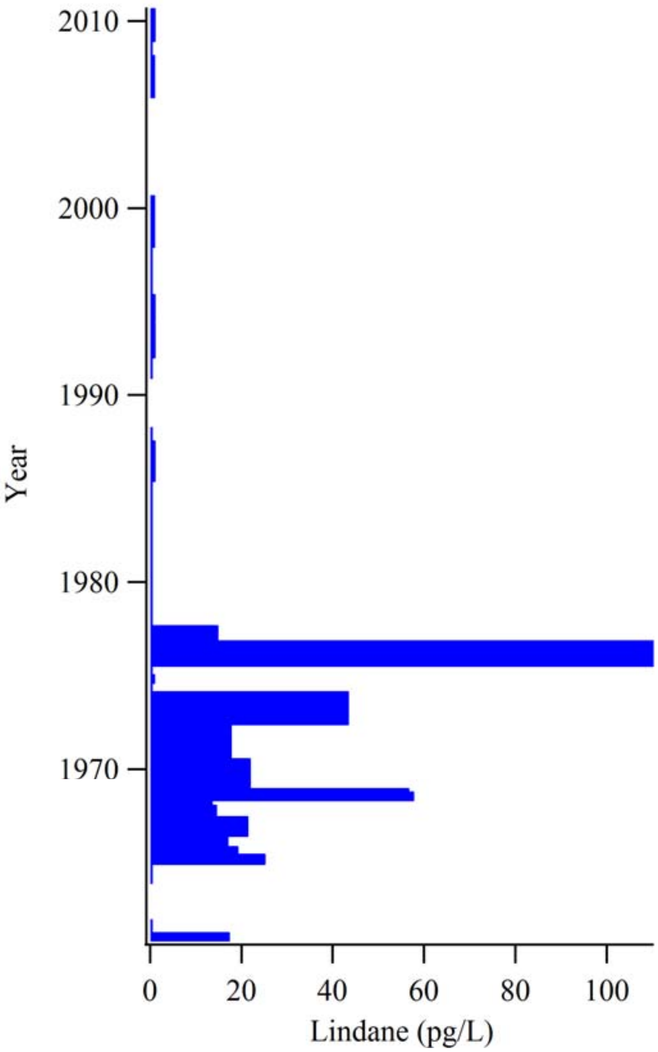

Figure 2: Lindane in Silvretta ice core

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