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Developing a Risk Assessment Protocol to Quantify Distribution and Uptake of Persistent Organic Pollutants in Glacial Outflows

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DEVELOPING A RISK ASSESSMENT PROTOCOL TO QUANTIFY DISTRIBUTION AND UPTAKE OF PERSISTENT ORGANIC POLLUTANTS IN GLACIAL OUTFLOWS

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A DISSERTATION
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
(in Earth and Climate Sciences)

The Graduate School
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May 2018

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Dissertation Advisor: Dr. Karl Kreutz

An Abstract of the Dissertation Presented
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Pollutants released by industrialized nations between 1960 and 2004 have been transported northward through atmospheric processes and deposited into glaciated alpine ecosystems. Many of these chemicals retain their original structure and are absorbed into the biota thousands of miles away from where they were originally utilized. With a warming climate increasing the melt of alpine glaciers, these glaciers may be introducing growing amounts of toxins into the watershed. While studies have demonstrated the existence of resident pollutants within glaciated ecosystems, no one has developed a risk assessment to identify sources and quantity of risk posed by these compounds when released in glacial outflows. Therefore, the goal of this study is to develop a framework to assess the conditions under which glacial release of persistent organic pollutants are a risk to the health of downstream communities.

The first section of our study utilizes ice core and meltwater records we measured at Jarvis Glacier, in the Interior of Alaska. Within interior Alaskan glaciers, our study was the first to identify pollutants, including DDT, DDE, DDD, α-HCH and ϒ-HCH concentrations using Solid-Phase Extraction (SPE) and Semi-Permeable Membrane Devices (SPMD). Subsequently, we developed a screening-level risk assessment model for pollution in glacial watersheds based upon the US Environmental Protection Agency (EPA) methodology which we apply to three unique case studies. With collaborators in Italy, Switzerland, and our own research in Alaska, we analyze varying chemicals, glacial regimes and uptake rates characteristic of each watershed to determine the potential risk to humans. We find that within all glacial systems studied potential human risk is determined by quantity of fish consumption and chemical toxicity based on species. Chemicals with higher human toxicity and bioaccumulation rates, such as DDT and PCBs, are identified to have a greater long-term risk even at low levels. Our results imply that further investigation of an Organochlorine Pollutant (OCP) signal in glacial meltwater and fish throughout the North American Arctic and European Alps is warranted. Other glacial watersheds of a similar size and latitude may see similar risk, and our model can be applied broadly to other glaciated ecosystems.

DEDICATION

This Dissertation is dedicated to Warren “Buddy” Wolff, Sherrie Wolff and

my Father and Mother.

Their compassion for others and dedication to kindness taught me to be tireless in my work for equity.

“We are explorers reading every sign, we tell the stories of our elders in a never-ending chain.”

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In my undergraduate studies I had two mentors who changed the way I saw the world and made me who I am. Steve Gliessman taught me how to recognize system dynamics and interconnections in all things, and Frank Andrews taught me to infuse my science, and my life, with passion and meaning. During Freshman year when I was in a wheelchair and very ill, my Oma and Opa sent me motivational cards every week.

I miss them, but I hope to be a source of strength for someone the way that they were for me, someday.

In Maine the Belknap/Hashey family have been my home away from home, warming cold winter nights, dancing and singing, and growing up together. My family, though far away, you give me strength and inspiration every day, and I am blessed to have you in my life.

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I felt it shelter, to speak to you.

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CHAPTER 1.

RESEARCH APPROACH AND SUMMARY OF FINDINGS

For centuries anthropogenic chemicals released into the atmosphere by humans have been deposited on glaciers worldwide, detailing within the glaciated ecosystems the breadth and range of human civilization.(Xiao ping Wang, Xu, Kang, Cong, & Yao, 2008; Wania, Frank; Mackay, 1996) Typically, snow and ice core records of these chemicals are used to interpret past emission strength, usage patterns or efficacy of mitigation policies.(Erich C. Osterberg et al., 2008) The timing of deposition and entrainment of chemicals into alpine glaciers aligns with the introduction, usage and regulation of compounds providing an understanding of use and atmospheric distribution.(Daly & Wania, 2004; Donald et al., 1999; Shen et al., 2005; Wania, Frank; Mackay, 1996) Organochlorine pollutant (OCP) species including DDT, Lindane, dioxins and PCBs were utilized and released by developed nations beginning in the 1940s, with international regulations mandating phase out in 2001.(P. Pavlova, 2014; B. van Drooge et al., 2014) Secondary emission of these persistent organic pollutants from glacial sources have been detected in glaciated watersheds of the Canadian Rockies, the Norwegian Arctic, the Swiss and Italian Alps, and the Tibetan Plateau, with quantities and locations englacier mirroring spatiotemporal human use.(Roberta Bettinetti et al., 2008; J M Blais et al., 1998; Bogdal et al., 2009; Garmash et al., 2013; Hermanson et al., 2005; P. Pavlova, 2014; P. A. Pavlova et al., 2016; C. Steinlin et al., 2015; S. Villa et al., 2001; Sara Villa, Vighi, Maggi, Finizio, & Bolzacchini, 2003; Xiao ping Wang, Xu, et al., 2008)

One of the characteristics of organochlorine pollutants is that they are hydrophobic, and bind easily with lipids.(F. Wania, Hoff, Jia, & MacKay, 1998) This property allows for ready absorption by regional biota as contributes significant bioaccumulation potential. Studies completed at both the regional and local scales have verified that organochlorine pollutants have long environmental residence times and high mobility within ecosystems through predator-prey chains.(Bizzotto, Villa, & Vighi, 2009; J M Blais et al., 2003; Elliott et al., 2012) In addition, the low organic matter content typical within glaciated ecosystems may prohibit the adherence of these pollutants to suspended particles below the glaciers.(Jones & de Voogt, 1999; Frank Wania, Westgate, Technol, & Asap, 2008) This increases dispersal potential within downstream watersheds and alpine ecosystems, making alpine glaciers a secondary emission source of significant interest. Within a glaciated ecosystem, exposure pathways to humans can be through the consumption of animal fat, uptake in the environment, or transference from mother to child.(E Dewailly, 2006; Matsuura et al., 2001) The side effects of human uptake of OCPs in even small doses are severe and can include birth defects, obesity, diabetes and cancer.(Bergonzi et al., 2009; Dassanayake, 2014; Gaspar et al., 2015; Patandin, 1999; Vizcaino, Grimalt, Fernandez-Somoano, & Tardon, 2014; S.-L. Wang et al., 2005) While studies have demonstrated the prevalence of OCPs within glaciated ecosystems, no one has used standard toxicological risk assessment methods to assess the threat posed to humans by glacial outflows of these compounds.

The goal of this thesis is to develop a framework to identify spatiotemporal trends across existing OCP studies and assess the possibility that secondary release of OCPs from glaciers could be a risk to the health of downstream communities. This work integrates non-linear change and systems dynamics to identify risks that were previously unrecognized. The application of this risk assessment methodology provides a snapshot of different types of glacial watersheds while also working to capture many facets of the population’s life. By blending an understanding of chemical toxicology with human consumption habits in three case studies, I identify that glacial release of pollutants can be amplified within specific glacial systems, allowing for the prioritization of similar watersheds for future work. To create an interdisciplinary protocol that captures a full system perspective of the current and future risks I integrate glaciological, hydrological, toxicologic and policy with a field-based understanding of the state of the system.

The first step in protocol development was compiling a comprehensive review of the current state of the science. This review elucidated a concentration gradient in glacial OCP storage that was greatest in the Alps and decreased towards the Arctic. In addition to these existing data, I add results from an ice core and water sampling campaign at Jarvis Glacier, Alaska. This is the first North American data taken since 1999 and the highest latitude study outside of Europe.

For the development and testing of a risk assessment protocol, this thesis utilizes published field sampling data from two European research groups in conjunction with risk assessment methodology developed by the Environmental Protection Agency. I adapted this risk assessment methodology to capture the exposure routes and uptake potential for glacial watersheds, to develop the most comprehensive understanding of the potential for human health risk from distribution of OCPs. I applied this risk screening methodology to three case studies, two in the European Alps but with different chemicals studied, and one in the Interior of Alaska.

Developing risk assessments for these three case studies allowed me to determine the possibility and the conditions under which risk from secondary emission of OCPs in glacial meltwater is increased. Amplification of pollutants was found to be a function of the toxicity of the chemical and the potential for bioaccumulation within the watershed. Downstream communities that consume large quantities of high-lipid fish from a glacial watershed are indicated for future study. In addition, chemicals with significant bioaccumulation potential and toxicity pose more risk to consumers, particularly within the context of lifetime exposure. Identifying routes of exposure, chemical bioaccumulation and toxicity and human consumption habits specific to glacial ecosystems allow for the development of a risk assessment model that can be applied to multiple systems. Ultimately, a better understanding of the pollutants stored in glacier watersheds will allow refinement of risk management strategies.

CHAPTER 2.

DEVELOPING CRITERIA FOR CHARACTERIZING GLACIAL ENTRAINMENT OF ORGANOCHLORINE POLLUTANTS

Research that characteristically identifies mountain glaciers as reservoirs for legacy organochlorine pollutants (OCPs) has been ongoing since the late 1990’s.(Jules M Blais et al., 2001; Bogdal et al., 2009; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; C. Steinlin et al., 2015) However, criteria for identifying glaciers with high reservoir and release potential in the Northern Hemisphere have not been developed. We identify glacial typological trends based on atmospheric distribution and deposition models, glacial flow and OCP loss pathway modeling to determine that high altitude, high accumulation, mid to northern latitude glaciers with a medium to steep aspect and relatively short response rate, near a OCP use location accumulate and disperse legacy pollutants at the highest rates.

Glacial OCP concentration varies across latitudes and altitudes, with proximity to areas of high usage significantly impacting glacial concentrations.(P. A. Pavlova et al., 2016; Sara Villa, Negrelli, Finizio, Flora, & Vighi, 2006; Frank Wania et al., 2008) While identifying OCP concentrations of individual glaciers requires field analysis, defining the global range of glaciers that may store OCPs is possible. Based on data from available literature, high-latitude, high altitude alpine glaciers on a steep slope are most susceptible to rapid and frequent OCP deposition and distribution. Our conclusions characterize these alpine glaciers as secondary distribution sources to downstream ecosystems.(Bogdal et al., 2009) With continued 21st century atmospheric warming, unprecedented glacier mass loss worldwide may lead to increased pollutant exposure from glacial meltwater. Criteria to determine glaciers with the highest potential for concentrated OCP storage are necessary to prioritize future OCP glacier studies worldwide. This review seeks to elucidate specific glaciological properties that are of significance in determining which glaciers may contain legacy OCPs, as well as necessary steps in assessing risk to humans downstream.

2.1 Glacier altitude

Geographic location of a glacier is a significant consideration in determining the potential for deposition of pollutants into a glaciated system. Temperatures regularly below 0^{o}C increase success of chemicals snow scavenging and limit revolitilization, making it possible for glaciers to trap less volatile chemicals for long term storage. (Beyer, Mackay, Matthies, Wania, & Webster, 2000; Frank Wania et al., 2008) A high lapse rate between valley and summit increases likelihood of pollutant partitioning, scavenging and subsequent glacial trapping. Adiabatic lapse predicts a -1 degree Celsius decrease in temperature each 100 meters of elevation gained,(Davidson et al., 2003; Mountain Research Initiative E D W Working, 2015) with highest snowfall occurring where the lifting air masses cool rapidly with elevation, simultaneously increasing density in the cloud and leading to precipitation.(Cuffey & Patterson, 2010) At low temperatures, snowfall is limited by the water content of the surrounding air, so that snowfall is highest in high altitude, moderate temperature locations with maritime air influx.(Cuffey & Patterson, 2010) These are also the regions with highest OCP snow scavenging, a process described in the accumulation section. Thus, in high altitude, maritime alpine systems the combination of rapid cooling and reduced temperature gradients combine to produce colder snow of higher densities, high specific surface area, and low vapor pressure able to easily bind

OCPs.(Benn & Evans, 2010; J M Blais et al., 2003; Grannas et al., 2013a) Where gradients in precipitation generally mirror gradients in elevation, higher elevation locations (glaciers above 1000 m a.s.l.) can expect to see more snow, increasing the opportunities for snow scavenging and decreasing temperatures.(Daly & Wania, 2005b; Grimalt et al., 2001) The convergence of factors that aggregate chemicals and allow for the development of glaciers suggests that a large number of mid-latitude, alpine glaciers located at elevations above 1000m may contain legacy pollutants.(Frank Wania et al., 2008)

The preferential deposition of OCPs in high altitude, cold, alpine ecosystems coincides with a significant number of glaciers globally. According to data from the World Glacier Monitoring Service, of the 40 ‘reference’ glaciers with continual mass balance data for over 30 years, 32% are at or below 1000 m a.s.l., with 90% at or below 5000 m a.s.l..(M. Zemp, Hoelzle, & Haeberli, 2009) This combination of factors elucidates the possibility that the 90% of the 40 glaciers resident at or between 5000 m a.s.l. and 1000 m.a.s.l may contain legacy pollutants within their ice layers.

2.2 Accumulation and mass balance

Atmospheric transport drives movement of pollutants globally, with precipitation type and rate directly impacting glacial deposition and concentration.(Carey L. Friedman & Selin, 2012; Lei & Wania, 2004; Sara Villa, Vighi, & Finizio, 2014) High seasonal snow deposition and low mean temperature are essential to the formation and preservation of glaciers,(Cuffey & Patterson, 2010) but these processes also act to trap atmospherically transported OCPs.(Arellano et al., 2015; C. L. Friedman & Selin, 2016; Jiménez, Dachs, & Eisenreich, 2015; Shen et al., 2005) In order for a glacier to grow, or have positive mass balance, it must have greater snow accumulation than loss, with frequent snow deposition increasing the opportunity for scavenging.(Cuffey & Patterson, 2010) Snow's high specific surface area and sorption coefficient combined with low temperatures also makes it the most effective OCP atmospheric scavenger, increasing chance of glacial entrainment.(Bizzotto, Villa, Vaj, & Vighi, 2009; Daly & Wania, 2004; Lei & Wania, 2004; Frank Wania, 1998; Frank Wania et al., 2008)

Compared to rain, snow offers an increased opportunity for chemicals to sorb through the crystalline snow matrix, removing pollutants from the air column above glaciers.(Frank Wania et al., 2008) Uptake through the crystal-air interface and incorporation into the solid ice nucleus increase scavenging potential of snow.(Grannas et al., 2013a) Efficacy of snow particle sorbtion at higher elevations positively correlates with higher mass in chemicals, allowing for greater deposition of chemicals with higher mass and volatility at locations near use.(Lei & Wania, 2004) The high efficiency of snow as a OCP scavenger over rain was characterized in a model by Lei et al. in 2004 by comparing the quotient of the sorption coefficients relative to temperatures and kinetic parameters.(Lei & Wania, 2004) As they describe, the value for the sorption coefficient of snow as it relates to the surface area can be described through the equation:

$$K_{Snow/Air} = A_I \rho_W K_{SA}. \tag{2}$$

Where A_I is the surface area of the particle measured in $m^2\ g^{-1}$, K_{SA} as the quotient of particle surface concentration by concentration in the gas phase, and ρ_W is the water density which is known at $10^6 g\ m^{-3}$(Lei & Wania, 2004). In essence, the greater surface area and density of snow particles combined with aerosols in particle phase in colder temperatures increases the opportunity for sorption.(Lei & Wania, 2004) This equation describes the potential uptake of atmospheric chemicals by snow at temperatures below freezing in atmospheric equilibrium. Molecules of higher weight, such as some of the PCB congeners, may be more efficiently scavenged by snow than lighter molecules due to their increased area and mass.(Daly & Wania, 2004; Lei & Wania, 2004; Frank Wania et al., 2008) Scavenging ratios for snow (Daly & Wania, 2004) show that up to 88% of chemicals present in the atmosphere of a model environment are scavenged by the snow during the period of one year, making glaciers with high rates of snow deposition and proximity to OCP usage areas significantly more probable to act as reservoirs.(Daly & Wania, 2004)

2.3 Glacier latitude

In the late 1980's Dewailly et al.(E Dewailly, 2006) drew significant attention to the transport and deposition of OCPs into the arctic with their study on PCBs in breast milk of isolated Nunavik mothers.(E Dewailly, 2006) This result was a surprise to many who did not realize the significant range available to OCPs through atmospheric or oceanic transport. Medium to high volatility, low polarity and high octanol-air partition coefficient (KoA) of the organochlorine species make both direct deposition and revolitilization of OCPs possible.(Daly & Wania, 2004; Herbert, Villa, & Halsall, 2006) In the years following the Nunavik research, OCP studies expanded across the Arctic to include Northern Europe and Asia, mapping both atmospheric distribution and depositional factors.(Anttila, Brorström-Lundén, Hansson, Hakola, & Vestenius, 2016; Arellano et al., 2015; Grannas et al., 2013b; Donald Mackay & Wania, 1995) Using both empirical and modeling approaches, numerous studies have confirmed that the variability in distance traveled by OCPs corresponds strongly to chemical weight and volatility.(Anttila et al., 2016; Carey L. Friedman & Selin, 2012; Hung et al., 2016; Jiménez et al., 2015; Shen et al., 2005; Sara Villa, Vighi, & Finizio, 2014) Identifying chemicals that revolatilize from atmosphere to earth once or multiple times add specificity to the range of chemicals based upon their structure.(Wöhrnschimmel, MacLeod, & Hungerbühler, 2013) Chemicals with greater mass often have significantly decreased range compared to more volatile chemicals, which limits the depositional rates at high latitude locations.(Macdonald et al., 2000; Don Mackay et al., 2001; Frank Wania, 2003) Additionally, the "cold wall" effect in the atmosphere concentrates low mass, semi-volatile chemicals in colder high altitude and latitude regions, increasing opportunity for snow sorbtion and glacial entrainment.(Daly & Wania, 2005a; Dunbar, 1973; Donald Mackay & Wania, 1995; Frank Wania et al., 2008)

Though OCPs are found throughout the northern latitudes, proximity to source significantly increases glacial chemical deposition rate.(Sara Villa, Vighi, & Finizio, 2014; Sara Villa et al., 2003)

The predominant usage areas for OCP pesticides and industrial additives in the northern hemisphere correspond with agricultural and industrial development during peak usage periods of 1940-2000(P. Pavlova, 2014), between 30-50 ^{o}N. Ice core and meltwater studies corresponding with these latitudes consistently show greater concentration of OCPs in studies near the 45th parallel, due to the combination of colder temperatures and proximity to usage areas.(Bizzotto, Villa, Vaj, et al., 2009; Jules M Blais et al., 2001; Ferrario, Finizio, & Villa, 2017; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014) Though global atmospheric transport of OCPs has been described as 'ubiquitous,'(Simonich & Hites, 1995) mid-latitude glaciated ranges show significantly higher concentrations of OCPs in ice and water samples than more northern sample studies, suggesting that latitude greatly impacts OCP concentration of a glacier.(Garmash et al., 2013; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Sara Villa et al., 2003)

2.4 Glacial flow and response time

Understanding of morphology and thermal regime is critical to determining glaciers that have the highest probability of storing and releasing pollutants. Once a molecule of snow is deposited onto a glacier, the length of time that it takes to move through and be lost from the glacier is the "residence time."(Patterson, 2013) Accumulation rate, aspect, slope and glacier length can either increase or decrease the residence time of an englacial snow particle, determining response rate and movement velocity.(Cuffey & Patterson, 2010) Globally, glaciers are divided into temperature categories with correspondingly different residence times. Cold or polar glaciers and many ice sheets maintain a temperature below pressure melting point throughout the glacier, with melt possible at the high pressure ice bed.(Hock, 2005) This temperature regime may be found in polar regions, with very few in the mid-latitude regions close to large human populations.(Donald et al., 1999; Pavlina Aneva Pavlova et al., 2015) Polar ice fields can have an area up 50,000 km^2, with ice sheets larger still, covering an area greater than 50,000 km^2 or in some cases, entire continents.(Farinotti, Huss, Bauder, Funk, & Truffer, 2009) The size and length of ice sheets and ice fields limit their capacity to rapidly disperse recently deposited contaminants. For this reason, glaciers of this size are not prioritized in development of glacial criteria for OCP dispersal.

In contrast to cold, slow moving glaciers, temperate glaciers are entirely at or above pressure melting point, with melt at the base increasing bedrock or sediment lubrication and leading to faster flow and melt rates.(Hubbard & Nienow, 1997; C. Steinlin et al., 2015) Often within this thermal regime, mountain, or alpine, glaciers are irregularly shaped glaciers smaller than ice fields with local topography adding frictional stress.(Cogley, J.G., R. Hock, L.A. Rasmussen, A.A. Arendt, A. Bauder, R.J. Braithwaite, P. Jansson, G. Kaser, M. Möller, 2011) Alpine glaciers may be found close to human settlements, where they contribute to the proglacial watershed seasonally. Smaller alpine glaciers subject to medium to high deposition and temperate thermal regimes have lower residence times from particle deposition to emergence and are often valuable water sources for proglacial human systems. However, high deposition and melt rates combined with proximity to human use areas also characterize them as the largest sinks for local OCP deposition and make them the main glacial focus for this study.(Hock, 2005; Hooke, 2005; Jansson, Hock, & Schneider, 2003)

The primary driver for glacier movement is the angle of the surface slope, or budget gradient, based upon accumulation and aspect.(Patterson, 2013) Pressure exerted by overlaying snow is a result of deposition in the accumulation zone, forcing the downward and forward movement of the glacier and compression from snow to firn and ice.(Hooke, 2005) Multiple frictional forces add drag to this forward, downslope movement.(Hooke, 2005) Depending on which stresses are strongest, layers, or isoclines, within the glacier may orient differently to the surrounding isoclines.(Patterson, 2013) The combination of medium to high accumulation, small to moderate length and a steep slope contribute to low residence times and high glacial flow rates which increase the chance of emergence of recently deposited OCPs.(Cuffey & Patterson, 2010;

Patterson, 2013) Therefore temperate or alpine glaciers categorically pose the greatest risk for increased distribution of OCPs to downstream ecosystems.

Data from the WGMS has determined that a large proportion of the world's high alpine glaciers are in a state of negative mass balance.(WGMS, 2015; Michael Zemp et al., 2015) This increased water loss can lead to rapidly release of pollutants trapped in glacial ice deposited from the early 1950s to the 1990s.(Donald et al., 1999; P. Pavlova, 2014) Glaciers responding to an increasingly longer and warmer melt season may be subject to supraglacial melt of recent deposition as well as legacy deposition in firn and ice. This is particularly true of smaller alpine, temperate, glaciers subject to heating from both climate, friction and meltwater infiltration. The current climatological warming trend suggests melt rates will continue or increase, releasing stored OCPs, according to specific glacial melt regimes.(Cuffey & Patterson, 2010; C. Steinlin et al., 2015) Peak ice melt coincides with peak OCP emergence during June, July, August and September, with concentrations increasing as greater mass loss is observed. This period is also the dry season for many climates, increasing the need for populations to consume glacial meltwater and subsequent pollutant uptake risk.

2.5 Proglacial biota

OCP concentrations within glaciers are documented in land-based ice formations,(Sara Villa et al., 2003) water-based icebergs(Geisz, Dickhut, Cochran, Fraser, & Ducklow, 2008) and tidewater glaciers.(Bogdal et al., 2009; Geisz et al., 2008; Kwok et al., 2013; C. Steinlin et al., 2015) The risk to organisms from mobilized OCPs varies based upon the uptake routes within the proglacial ecosystem. Bioaccumulation of OCPs is documented in Antarctic animals,(Geisz et al., 2008) high arctic human communities,(E Dewailly, 2006) and throughout proglacial alpine ecosystems.(J M Blais et al., 1998, 2003) The low organic matter content in some glaciated ecosystems may increase dispersal of OCPs away from the glacier terminus while also increasing the bioavailability and mobility of these chemicals through the food web(Frank Wania et al., 2008) while systems with high dissolved organic carbon (DOC) and subsequent near-glacier deposition provide a route for trapping pollutants in sediment basins.(Jules M Blais et al., 2007; Bogdal et al., 2009; Davidson et al., 2003; P. A. Pavlova et al., 2016) Without entrainment onto particles or into sediment basins, chemicals may travel through downstream in constant concentrations throughout the proglacial watershed.(R. Bettinetti, Quadroni, Boggio, & Galassi, 2016; Roberta Bettinetti, Galassi, Guilizzoni, & Quadroni, 2011; Bidleman, 1988; Bogdal et al., 2008; Cheng et al., 2014; Grannas et al., 2013b; P. A. Pavlova et al., 2016; Peter Schmid, Bogdal, Blüthgen, & Anselmetti, 2012)

In high alpine ecosystems the combination of low proglacial organic content and secondary emission of OCPs directly impacts downstream organisms.(Birnbaum, 2013; Bizzotto, Villa, & Vighi, 2009; J M Blais et al., 2003; Campbell, Schindler, Muir, Donald, & Kidd, 2000; Davidson et al., 2003; Li & Macdonald, 2005; Peter Schmid, Kohler, Gujer, Zennegg, & Lanfranchi, 2007) Once OCPs have melted from a glacier, bioaccumulation becomes a major pathway for movement, with uptake by fish and local insects primary pathways for continued transfer.(Bizzotto, Villa, & Vighi, 2009; Jules M Blais et al., 2006; Davidson et al., 2003) Proglacial environments that contain a variety of aquatic and terrestrial flora able to live in stressful alpine environments may serve as a biotic limiter for further pollutant distribution.(Daly & Wania, 2005b) Work on bioaccumulation routes within glaciated ecosystem has focused on uptake by animals, insects and plants including research on macro invertebrates, fish, birds and regional plant life.(Bizzotto, Villa, & Vighi, 2009; Jules M Blais et al., 2007; Campbell et al., 2000; G. Czub & McLachlan, 2004; Davidson et al., 2003; Lignell, Aune, Glynn, Cantillana, & Fridén, 2012) Organisms adapted to alpine environments often have higher percentages of lipid than valley organisms, making them more susceptible to bioaccumulation in fatty tissues.(Adetona et al., 2013; Bizzotto, Villa, & Vighi, 2009; J M Blais et al., 2003; Calamari et al., 1991; Campbell et al., 2000) This property allows them to be easily absorbed by biota, and bioaccumulation can lead to an increased concentration within local plants and animals.(Jules M Blais et al., 2007; Davidson et al., 2003) Downstream melt water output modeling must incorporate representative scavenging rates by downstream organisms where necessitated, with proglacial ecosystems with low DOC and biotic content prioritized for this study. (Bizzotto, Villa, & Vighi, 2009; Jules M Blais et al., 2007; Davidson et al., 2003)

2.6 Conclusions and future work

Utilizing the above criteria as applied to the WGMS glaciers with a record of mass-balance observations(WGMS, 2015) we are able to begin to quantify the possibility of legacy pollutant deposition into glaciers globally. Of the 698 glaciers with either mass balance data, glacial front data, changes in area measurements or some combination of the three, listed in the first Global Glacier Change Bulletin, 374, or 54% of the glaciers reside above a latitude of 30 N and an elevation above 1000m, making them susceptible to high snow deposition and potential northern atmospheric cold trapping. From these 345 glaciers, 175, or 46% of previous have been in a state of continuous negative mass balance since 2005, resulting in the greatest volume loss of monitored glaciers (WGMS, 2015). Utilizing the recently released “Fluctuations of Glaciers” browser map (http://wgms.ch/fogbrowser/) published by the WGMS, it is possible to determine the location of these glaciers relative to human centers. Understanding that there are differences in size, population, and traditional use between rural and urban locations in northern latitudes, 90 glaciers, or 51% of previous are in proximity (< 500 miles) to centers of human population. This represents 13% of known glaciers with a high likelihood of contamination which reside near human centers.

Though this percentage of glaciers appears small on a global scale, these individual glaciers must be prioritized for research into OCP reservoir concentrations and human consumption risk. Natural variation in glacial flow and melt rates may change the concentration of OCPs below glacier. For example, abbreviated melt periods seen with a warming climate may lead to intensified melt pulses and subsequent OCP concentration increases, whereas long-term releases of OCPs may increase the concentration throughout the system to above background noise, but more gradually.(Jansson et al., 2003) Timely study into quantities and loss rates is necessitated.

CHAPTER 3.

LEGACY ORGANOCHLORINE POLLUTANTS IN GLACIAL WATERSHEDS: A REVIEW

3.1 Introduction

The cryosphere is a fundamental component of the global climate system. Over the past several decades, increasing atmospheric temperatures have led to a significant loss of glacier ice worldwide.(Moon, 2017; M. Zemp et al., 2009) As long-term reservoirs of terrestrial freshwater, the impacts of significant glacial melt include sea level rise, changes in atmospheric and oceanic circulation, and changes in the quantity and quality of fresh water available to local human and natural ecosystems.(Baraer et al., 2012; Hock, 2003; Hood, Battin, Fellman, O’Neel, & Spencer, 2015; Erich C. Osterberg et al., 2008; Slemmons, Saros, & Simon, 2013) In addition to landscape modification, glacier ice can serve as a record of atmospheric processes and human use of metals, chemicals and carbon.(Hood et al., 2015; Erich C. Osterberg et al., 2008; Sara Villa et al., 2003)

The green revolution in agriculture, which began in the early 1950’s, was predicated on the widespread use of a class of pesticides and industrial additives manufactured by replacing the carbon molecules of hydrocarbon structures with chlorines, so that they easily bind to lipids.(Nadal, Marquès, Mari, & Domingo, 2015; P. Pavlova, 2014) OCPs species include, but are not limited to; DDT, Lindane, chlordane, dieldrin, and hexachlorabenzene. OCP’s were banned internationally by the multinational Stockholm Convention in 2004 due to their toxicity and cascading ecosystem impacts. However, during widespread use, OCPs were transported atmospherically and were deposited with fresh snow onto glaciers worldwide.(Simonich & Hites, 1995) Subsequent studies have shown that glaciers near areas of OCPs use maintain relatively higher concentrations of OCPs chemicals in their firn and ice layers.(Sara Villa, Vighi, Maggi, Finizio, & Bolzacchini, 2014) As glacial melt continues, the release of compounds stored in glacial ice, including banned OCPs, is an increasingly pertinent issue.

Glaciers house about 75% of Earth's freshwater, making them a valuable resource and vital part of proglacial ecosystems.(Jansson et al., 2003) However, meltwater from glaciers not only transports important freshwater, but also dissolved organic carbon, black carbon, heavy metals, and legacy chemicals downstream (Figure 3.1).

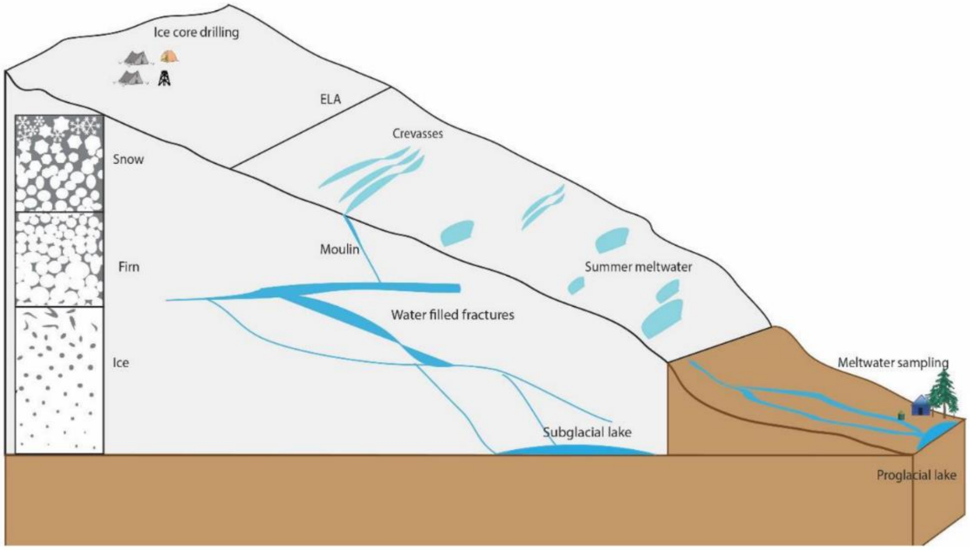

Figure 3.1 Schematic diagram of a glacier system with meltwater to illustrate potential routes of particle and water-driven OCPs movement. Deformation processes from snow to firn and ice included for reference. Ice core drilling sites are in accumulation area above the equilibrium-line altitude, and meltwater sampling in proglacial locations at the base of the glacier. Lake sediment core sampling locations can be in proglacial reservoirs at varying distances.(Bogdal et al., 2009; Cuffey & Patterson, 2010; Hock, 2005; Jansson et al., 2003; P. A. Pavlova et al., 2016; P Schmid et al., 2011)

Significant glacier loss is already impacting alpine ecosystems such as Glacier National Park in North America. This park has lost 134 glaciers in the last decade, reflecting the consistent global trend towards negative mass balance seen in 16 alpine glacial regions for almost 40 years.(Blunden, Arndt, Blunden, & Arndt, 2016; Moon, 2017; Michael Zemp et al., 2015) The rapid re-introduction of glacially stored chemical compounds can lead to ecosystem changes and directly impact downstream human communities.

The purpose of this tutorial review is to synthesize data on OCPs in glacial systems, evaluate competing interpretations and methodologies, and to identify critical research needs. Existing data, which identifies glaciers as melting reservoirs of OCPs indicates the immediate need for interdisciplinary collaboration among atmospheric scientists, glaciologists, hydrologists, glacial geologists, ecologists and toxicologists. With an inclusive analysis of full system dynamics, researchers may be able to forecast downstream OCPs distribution pathways in order to minimize the potential for human impacts.(Nadal et al., 2015)

3.2 Relevant background on OCPs dispersal and glaciology

3.2.1 History of organochlorine use

OCPs were developed for agricultural and industrial use in the 1930s and 1940s with a number of them decommissioned by the 2004 Stockholm Convention after their toxicity was established.(Gertje Czub & McLachlan, 2004; P. Pavlova, 2014; B. van Drooge et al., 2014) Usage timelines vary by pollutant species. Polychlorinated biphenyls’ (PCB) 209 congeners were used as insulating liquids in electronic equipment, plasticizers in building sealants and paints, with a few further minor applications from the 1930-1970s, with Monsanto Corporation in the United States leading production until they were decommissioned in 1977.(P. Pavlova, 2014)

Hexachlorobenzene (HCB) was used agriculturally as a fungicide and wood preservative largely in the industrialized countries of Europe from 1945-1986, with use peaking in the 1970s. Gamma-HCH is the main ingredient in Lindane and Technical HCH, with alpha-HCH as a byproduct, used from 1942-1983 and manufactured in North America, Europe and China, with global phase out beginning with North America in 1971 and ending with China in 1983.(Barrie et al., 1992; Cheng et al., 2014; P. Pavlova, 2014) Major DDT use spanned 1940-1986, but aerial distribution to utilize its anti-malarial properties continues presently in areas of high disease incidence.(Cheng et al., 2014; Jaacks & Staimez, 2015; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014)

OCPs were used largely by industrialized nations, with the level of volatility and proximity to use reflected in subsequent environmental concentrations.(P. Pavlova, 2014) Individual OCPs species move differently through environmental compartments, but wide distribution increases the opportunity to affect non-target species including local vegetation, insect life, birds of prey and polar bears.(Bizzotto, Villa, & Vighi, 2009; Gertje Czub & McLachlan, 2004; Daly & Wania, 2005a; Davidson et al., 2003; Elliott et al., 2012; Ren et al., 2016; Sara Villa, Migliorati, Monti, Holoubek, & Vighi, 2017; Frank Wania, 2003) Both decommissioned and newer classes of industrial chemicals may drive impacts for non-target species, making both industrial and pesticide compounds potential sources of toxicity.(Ferrario et al., 2017; Guzzella et al., 2016; Sara Villa et al., 2017) Even at background levels OCPs may cause health problems in human populations after prolonged exposure or consumption.(Bergonzi et al., 2011a; Birnbaum, 2013; Gertje Czub & McLachlan, 2004; Dassanayake, 2014; El-Shahawi, Hamza, Bashammakh, & Al-Saggaf, 2010; Jaacks & Staimez, 2015; K.-S. Kim et al., 2014; Lignell et al., 2012; Matsuura et al., 2001; Ngwa, Kengne, Tiedeu-Atogho, Mofo-Mato, & Sobngwi, 2015; S.-L. Wang et al., 2005)

3.2.2 Tracking movement to the Arctic

For the last 40 years, investigation into the drivers behind OCPs atmospheric transport and deposition has traced the chemicals to both high alpine mountain ranges and the Arctic.(Daly & Wania, 2005a; Dunbar, 1973; Donald Mackay & Wania, 1995) When OCPs are released into the atmosphere they can be transported as either a gas or adsorbed to particles.(Anttila et al., 2016) This characteristic makes it possible for the chemicals to attach to dust and snow to be deposited and revolatilized multiple times – a process known as the ‘grasshopper effect’.(Octaviani, Stemmler, Lammel, & Graf, 2015; Wania, Frank; Mackay, 1996) The grasshopper effect allows compounds to mobilize through recurrent deposition and revolatilization, transporting chemicals poleward in the atmosphere where they become trapped in cold regions.(Anttila et al., 2016; Davidson et al., 2003; El-Shahawi et al., 2010; B. L. van Drooge, Grimalt, & Stuchlík, 2013) Though movement of more persistent chemicals may decrease with distance from source, more volatile OCPs have greater traveling potential and broader distribution ranges.(Bidleman, 1988; C. L. Friedman & Selin, 2016; Carey L. Friedman & Selin, 2012; Frank Wania et al., 2008)

To our knowledge, the first research to discuss the distribution and concentration of persistent pollutants in northern latitudes was published in 1973.(Dunbar, 1973) This work addressed the concept of a “cold wall” in the northern latitudes where colder temperatures allowed for the concentration of semi-volatile chemicals with low mass.(Dunbar, 1973) Subsequent studies confirmed OCPs transport, regionally expanding from the North American Arctic to include Northern Europe and Asia, while mapping both atmospheric distribution and depositional factors.(Anttila et al., 2016; Arellano et al., 2015; Grannas et al., 2013b; Donald Mackay & Wania, 1995) The literature focusing on legacy pollutant transport and re-emergence increased rapidly, with a review covering the state of the science published in 1995.(Donald Mackay & Wania, 1995) That same year, researchers showed that more volatile compounds have the greatest atmospheric latitudinal range due to their lower molar mass.(Simonich & Hites, 1995) This was also one of the first large-scale studies to confirm through field observations that OCPs had been transported globally into polar and high-alpine regions.(Simonich & Hites, 1995) Subsequent modeling of OCPs atmospheric transport traced the movement of organochlorines toward the Arctic utilizing multi-compartmental models, numerical flow modeling and field sampling campaigns.(Macdonald et al., 2000) Blending atmospheric transport and compartmental modeling with chemical flux, volatility and fugacity data, researchers moved towards a more complete understanding of organochlorine transport.(Macdonald et al., 2000; D Mackay & Patterson, 1990; Wania, Frank; Mackay, 1996; Frank Wania, 1998)

Though direct atmospheric deposition was considered to be the primary pathway for OCPs into high alpine ecosystems, the reemergence of banned chemicals in these environments suggested inputs from an unknown source.(Daly & Wania, 2005b; Macdonald et al., 2000) Researchers, aware of the concentrating effect of cold temperatures and the high OCPs sorption rates to snow crystals, identified glaciers as the route for secondary OCPs release.(J M Blais et al., 1998; Donald et al., 1999)

3.2.3 Glaciological considerations and chemical entrainment

The secondary emergence of OCPs from alpine glaciers became an area of research interest in the mid-1990s, as compounds were detected at increasing concentrations and deposition rates in alpine ecosystems.(J M Blais et al., 1998) The possibility that glaciers were acting as reservoirs for harmful compounds was initially confirmed by researchers who contrasted glacially and non-glacially derived water, finding increased concentrations in glacial melt water streams.(J M Blais et al., 1998; Jules M Blais et al., 2001; Donald et al., 1999)

Glaciers are often described as rivers of ice but are in reality closer to metamorphic rock, with density increasing with depth as snow crystals are deformed into firn and ice.(Cuffey & Patterson, 2010) In cold glaciers, annual snow deposition has the lowest density at around 0.4 g/cm^3. Firn represents the prior years' accumulation, slightly deformed with an increased density, occurring in layers below the annual snow layer.(Cuffey & Patterson, 2010) As firn grains continue to be deformed through driving pressure from the overlaying layers and local and glacier-wide stresses, permeability and porosity decrease while density increases to around 0.9 g/cm^3 to form glacier ice (Figure 3.1).(Cuffey & Patterson, 2010; Faria, Weikusat, & Azuma, 2014a, 2014b) This densification process traps pollutants sorbed to the snow nucleus as the decreased porosity of the glacier ice reduces opportunities for revolatilization and water-driven transport.(Christine Steinlin et al., 2014)

Within a glacier, the highest water storage capacity is in the glacial ice, while snow and firn contribute the most to discharge in a melt season through both supraglacial melt and percolation.(Hock, 2005; Jansson et al., 2003) For a glacier in a steady state, the mass loss in water equivalence in the ablation zone is equal to the mass gained in water equivalence in the accumulation zone.(Cuffey & Patterson, 2010; Mountain Research Initiative E D W Working, 2015; Michael Zemp et al., 2015) In such a glacier, the time that it takes for a specific layer of ice to reemerge at the terminus is a function of ablation and the geometry of the glacier.(Cuffey & Patterson, 2010) However, glacial melt often increases as the atmosphere warms, leading to negative mass balance where the glacier loses proportionally more water, snow, ice and reservoir OCPs.(Hock, 2005; Roe, Baker, & Herla, 2017)

The primary driver for glacier movement is the budget gradient – the angle of the surface slope with respect to accumulation and aspect.(Patterson, 2013) The pressure exerted by overlaying snow is a result of deposition in the accumulation zone, forcing the downward and forward movement of the glacier and compressing snow to form firn, and subsequently, glacial ice.(Hooke, 2005) Multiple frictional forces add drag to this forward, downslope movement and create a slowly moving system.(Faria et al., 2014a; Hooke, 2005) Glaciers of different sizes and densities see varying rates of flux depending on frequency of precipitation and climate. For example, smaller glaciers in maritime climates may have greater system flux, linking an increase in snow deposition with the potential for faster distribution of OCPs from the glacier terminus.(Hock, 2005; Pavlina Aneva Pavlova et al., 2015) Even at a steady state, glaciers will release all reservoir compounds eventually, however increased warming and mass loss shortens the time frame.

Another route for OCPs loss from a glacier is through revolatilization from the supraglacial surface, which allows compounds to re-enter the overlying atmosphere in vapor phase.(C. Steinlin et al., 2015) Whereas temperatures below 0^{o}C greatly limit revolatilization, increased temperatures and wind speeds above a glacier can lead to greater mobility.(Davidson et al., 2003; Shen et al., 2005; Frank Wania, 2003; Frank Wania et al., 2008) A number of studies have shown the importance of revolatilization as a pathway for pollutant distribution within an ecosystem, allowing up to 60% of lower-chlorinated compounds to be deposited multiple times.(Daly & Wania, 2005b; Lei & Wania, 2004; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Shen et al., 2004; C. Steinlin et al., 2015) Diurnal mountain winds that travel upslope in the day and downslope with cooler temperatures in the evening also prevent revolatilization at night.(Daly & Wania, 2005a; Frank Wania et al., 2008) The revolatilization of these compounds increases OCPs concentrations in the above-glacier air, from which chemicals can be scavenged and redeposited during subsequent precipitation events.(Li & Macdonald, 2005; Macdonald et al., 2000; C. Steinlin et al., 2015)

Processes that allow OCPs to be deposited with snow onto the glacier surface at higher elevations correlate with the mass and structure of the chemical as well as the snow surface area.(Lei & Wania, 2004)

In high alpine glaciated systems, the winter period can have high snow accumulation and lower temperatures, which will lead to efficient scavenging of any OCPs particles in the above glacier atmosphere.(Helm et al., 2002; Lei & Wania, 2004; Morselli, Semplice, Villa, & Di Guardo, 2014) At lower temperatures a majority of OCPs are found in the particle phase, with highly chlorinated chemicals attaching most strongly to snow surfaces at temperatures at or below 0^{o}C.(Grannas et al., 2013a; Herbert et al., 2006; D Mackay & Patterson, 1990; Don Mackay et al., 2001; Donald Mackay & Wania, 1995; F. Wania et al., 1998; Frank Wania, 2003; Frank Wania et al., 2008) Uptake through the crystal-air interface of the disordered snow surface and incorporation into a snowflake’s solid ice nucleus make it possible for snow to scavenge semi-volatile compounds of varying molar masses, with increasing efficiency for molecules of higher weight.(Daly & Wania, 2004; Grannas et al., 2013b; Lei & Wania, 2004; Frank Wania et al., 2008) The scavenging ratios for snow suggest that up to 88% of chemicals present in the 2km of atmosphere of a model environment are scavenged by snow during the period of one year.(Daly & Wania, 2004)

Thus, even chemicals in the vapor phase resident in the atmosphere at lower valley elevations are subject to particle snow scavenging at higher, colder elevations due to temperature-driven revolatilization, condensation, and magnification.(Frank Wania et al., 2008) Chemicals are concentrated in low temperature, high altitude areas that limit revolatilization in a process referred to as “mountain-cold trapping” where the mountains act as physical barriers to chemical remixing in the atmosphere.(Beyer et al., 2000; Daly & Wania, 2005b; Frank Wania, 1998; Frank Wania et al., 2008) These dynamics, inherent to the glacier system, mean that the periods of greatest snow accumulation and glacier growth are also the periods of greatest OCPs deposition, with glaciers becoming OCPs reservoirs over time.

3.2.4 Global glacier mass loss

The preferential deposition of OCPs in high altitude, mid-latitude, alpine ecosystems coincides with a significant number of glaciers globally. The World Glacial Monitoring Service (WGMS) uses 40 ‘reference’ glaciers with more than 30 years of consecutive mass balance data as a representation of global glacier dynamics. (WGMS, 2015; M. Zemp et al., 2009; Michael Zemp et al., 2015) Although these reference glaciers are of different thermal regimes and sizes, the WGMS has determined that average annual mass loss and retreat of all sample glaciers is increasing exponentially.(Blunden et al., 2016; Mountain Research Initiative E D W Working, 2015; Michael Zemp et al., 2015) The last decade (2001-2010) shows the greatest global mass loss ever recorded in all WGMS reference glaciers, in agreement with the extensive Randolph Glacier Inventory, which showed 11 out of 13 alpine regions are experiencing less runoff as glacier size decreases.(Blunden et al., 2016; WGMS, 2015) These percentages represent a wide range of melt regimes, but both individual and aggregate glacial ice loss corresponds with global temperature increase.(Roe, Baker, & Herla, 2016) Although the variation in glacial melt rates and regimes is governed by morphology of the glacier, local topography, climate and radiative forcing, the trend of significant mass loss can be seen worldwide.(WGMS, 2015) Recent warming trends leading to glacier mass loss will greatly reduce the storage of water available for the future.(Blunden et al., 2016; WGMS, 2015; Michael Zemp et al., 2015) In addition to this water strain, if legacy compounds carried within glacial outflow enter the below-glacier ecosystem, the risk of biological impacts arise.

3.3 Current state of the field

Since the early 2000s several research groups have pioneered research into glacial entrainment and reemergence of OCPs, using glacial ice cores, meltwater samples, proglacial lake sediment cores, and glacial flow modeling to identify pollutant reemergence in glaciated watersheds at sites throughout the Northern Hemisphere (Figure 3.2). These groups have developed field sampling of glacial meltwater, ice cores and lake sediments that incorporate environmental chemistry protocols with a systems perspective of the glaciated ecosystem and watershed.(Jules M Blais et al., 2001; Bogdal et al., 2009; P. A. Pavlova et al., 2016; Sara Villa et al., 2003)

Figure 3.2 Locations of glacial meltwater, ice and sediment core OCPs sample studies globally, overlain on the GLIMS glacier database web map.(M. Zemp et al., 2009) White dots indicate ice core sampling studies, blue dots indicate meltwater and sediment sampling studies.

Ice cores are often used to understand climatological trends and human activities including the global use of OCPs.(Donald et al., 1999; Eichler, Schwikowski, & Gäggeler, 2001; Garmash et al., 2013; Erich C. Osterberg et al., 2008; Pavlina Aneva Pavlova et al., 2015; C. Steinlin et al., 2015; S. Villa et al., 2001; Sara Villa et al., 2003; Xiao ping Wang, Yao, Wang, Wei-Yang, & Tian, 2008) In order to analyze glacier ice cores there must be a complete understanding of glacier dynamics and the overall mass balance of the glacier.(Eichler et al., 2001; Pavlina Aneva Pavlova et al., 2015) Studies show that ice core concentrations reflect glacial proximity to greatest OCPs use around 45 ^{o}N, leading to significantly higher concentrations in European than in Arctic nations (Figure 3.3).

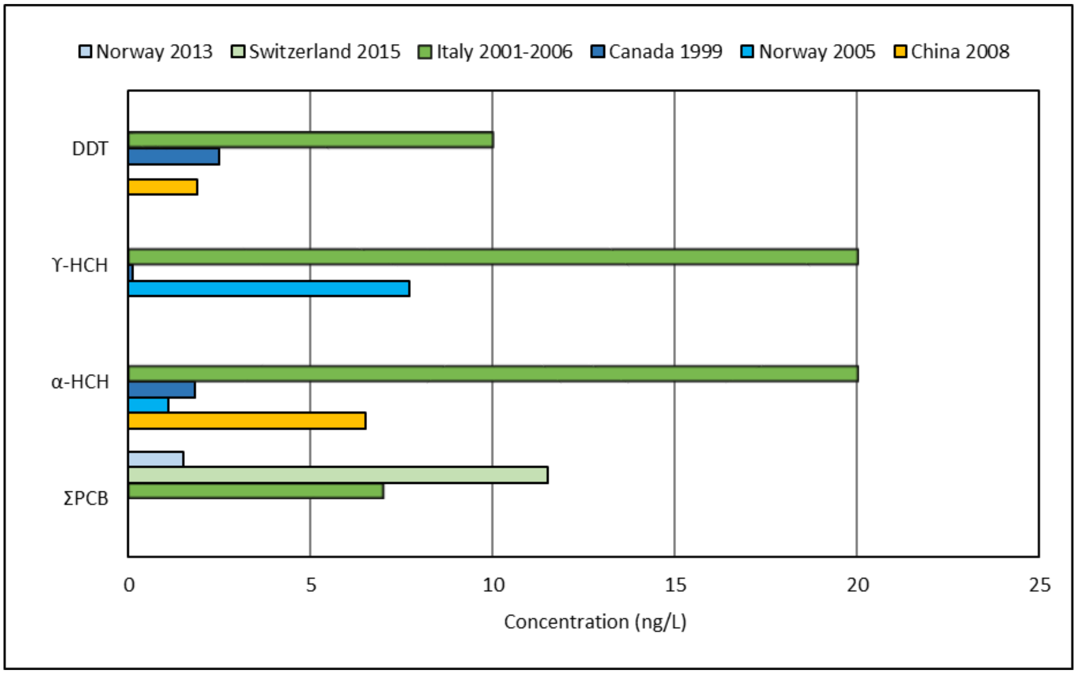

Figure 3.3 Peak concentrations of OCPs in ice cores, not temporally constrained, by country. Blue indicates studies from the Arctic, green indicates European studies and yellow indicates studies from Asia. Concentrations from Europe are higher than Arctic concentrations due to proximity of the glaciers to usage locations. ΣPCB concentrations have been standardized to 30 congeners.(Donald et al., 1999; Garmash et al., 2013; Hermanson et al., 2005; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; S. Villa et al., 2001; Sara Villa, Negrelli, Maggi, Finizio, & Vighi, 2006; Sara Villa et al., 2003; Xiao ping Wang, Xu, et al., 2008)

Crevasse samples from Donald et al. in Canada indicated that glaciers may be acting as a reservoir for OCPs, which was later confirmed with European ice core sampling.(Donald et al., 1999) Data from the first full length ice cores documenting OCPs deposition were published in 2001 and 2003 by Villa et al. in the Italian Alps.(Sara Villa, Negrelli, Maggi, et al., 2006; Sara Villa et al., 2003) The Italian samples suggested that proximity to Italian factories and agriculture increased deposition of chemicals in the ice. In Switzerland, work from Pavlova et al. and Steinlin et al. looked at temperate and cold glacier ice cores, water samples, and flow modeling to track the distribution and flow of OCPs through glaciers in the Swiss Alps.(Pavlina Aneva Pavlova et al., 2015; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Pavlina Aneva

Pavlova, Schmid, Zennegg, Bogdal, & Schwikowski, 2014; C. Steinlin et al., 2015; Christine Steinlin et al., 2014, 2016) For the first time, this combination of ice coring, glacier modeling, and water sampling elucidated the full system of deposition, entrainment and reemergence of OCPs both within the glacier and through the glacial ecosystem. Though fewer OCPs compounds were studied than in the Italian ice core, concentrations were similar to studies from the Italian Alps (Figure 3.4).

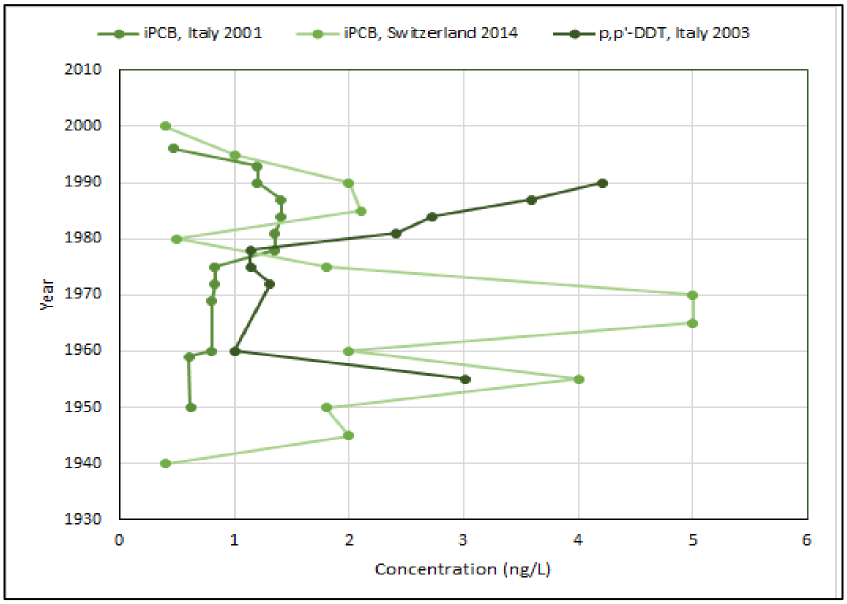

Figure 3.4 Selected ice core deposition trends in Europe highlighting chemicals with greatest human toxicity potential from the Swiss Silvretta glacier and the Italian Lys glacier. The initial deposition peak in the 1950s can be seen in two cores, with increased deposition in the 1970-1990s from local and distal sources.(Donald et al., 1999; Macdonald et al., 2000; Sara Villa et al., 2003) Proximity to usage locations allows for deposition of higher concentrations into the European Alps.(Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; S. Villa et al., 2001; Sara Villa et al., 2003)

In regions North of 45° N, researchers found decreased concentration of OCPs in ice cores, suggesting a latitudinal concentration gradient with deposition delayed at distal sources, due to time required for atmospheric transport (Figure 3.5).

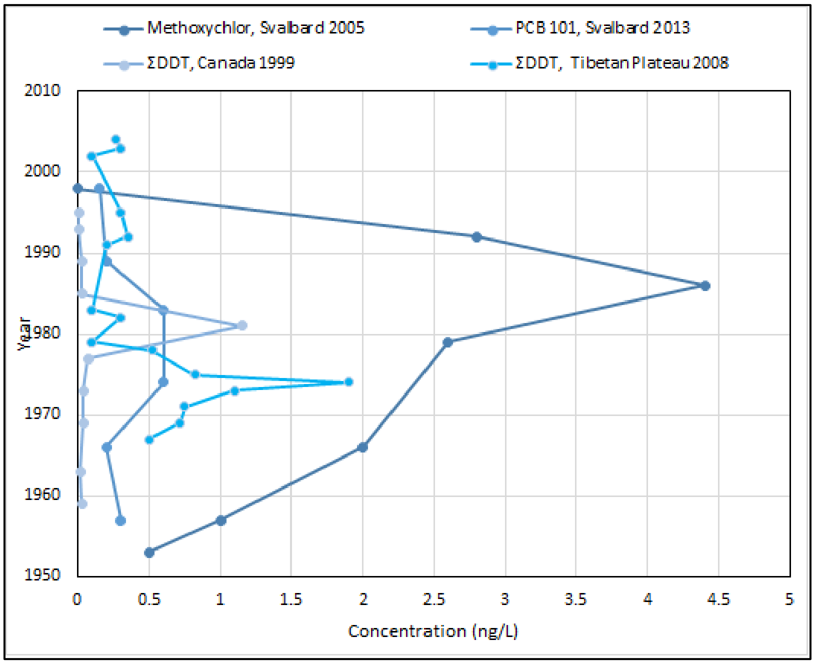

Figure 3.5 Selected ice core deposition trends from the Arctic Snow Dome in Canada, the Lomonosovfonna and Austfonna glaciers in Svalbard, and the Rongbuk glacier on the Tibetan Plateau highlighting OCPs with greatest toxicity potential. Though concentration varies, peak deposition from late 1975-1990 is seen in all data sets. (Donald et al., 1999; Garmash et al., 2013; Hermanson et al., 2005; Xiao ping Wang, Xu, et al., 2008)

In 2005, Hermanson et al. collected a 40 m shallow ice core from Svalbard's Austfonna ice cap, finding concentrations lower than the European cores, and similar to concentrations from the Canadian Rocky Mountains.(Donald et al., 1999; Hermanson et al., 2005) This work was followed by ice core samples taken a few years later in 2013 by Garmash et al., with concentrations reflecting the latitudinal gradient seen in the Austfonna ice core.(Garmash et al., 2013) In 2008 Wang et al. published the first ice core results from Asia, after their expedition to the Mt. Everest East Rongbuk Glacier.(Xiao ping Wang, Xu, et al., 2008) This was the first ice core study from the Tibetan Plateau and the highest altitude sample taken to date. The core showed concentrations similar to the Arctic nations, suggesting an altitudinal as well as latitudinal gradient in OCPs movement and deposition. OCPs concentrations on Mt. Everest were traced to DDT and Lindane usage in India through atmospheric modelling.(Xiao ping Wang, Xu, et al., 2008) This study reaffirmed the decreased, yet clear, signal of OCPs at locations distant from use, echoing the conclusion that OCPs have been distributed globally. Sampling of glacial water and ice began concurrently on opposite sides of the Atlantic Ocean (Figure 3.6).

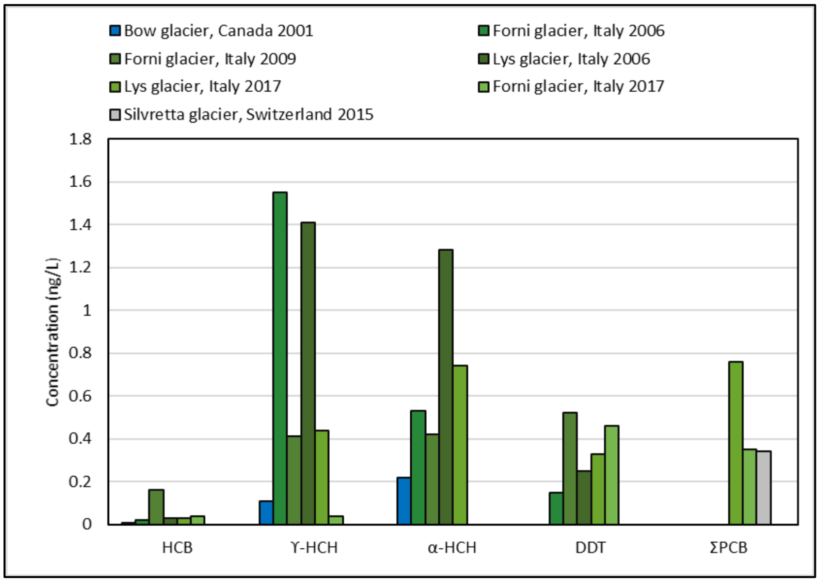

Figure 3.6 Peak OCPs meltwater concentrations by glacier from published sampling studies in Europe and Canada. Glaciers from Italy are indicated in green, blue indicates Canada and grey is Switzerland. Concentrations from continental Europe are higher than those in Canada due to source proximity. ΣPCB concentrations have been standardized to 30 congeners.(Bizzotto, Villa, Vaj, et al., 2009; Jules M Blais et al., 2001; Ferrario et al., 2017; P. A. Pavlova et al., 2016; Sara Villa, Negrelli, Finizio, et al., 2006)

Beginning in 2001, water samples in the Canadian Rocky Mountains.(Jules M Blais et al., 2001) showed higher concentrations of banned OCPs in glacial meltwater than in non-glacial streams.(J M Blais et al., 1998; Jules M Blais et al., 2001) This study confirmed that some Canadian glaciers may be harboring legacy pollutants, and was followed with crevasse sampling at Snow

Dome.(J M Blais et al., 1998; Donald et al., 1999) Researchers in Italy continued to trace the flow of OCPs in glacial systems in glacial streams, sampling multiple proglacial watershed correspondent with sampled glaciers, confirming the presence of a strong yet slightly less concentrated, OCPs signal.(Bizzotto, Villa, Vaj, et al., 2009; Finizio, Villa, Raffaele, & Vighi, 2006; Sara Villa, Negrelli, Maggi, et al., 2006) Subsequently, Swiss researchers developed a model of glacial entrainment and particle flow, complimented with proglacial water sampling.(P. A. Pavlova et al., 2016; Pavlina Aneva Pavlova, Schmid, Zennegg, et al., 2014) Proglacial sampling showed a concentration decrease from the glacier terminus to the immediate proglacial environment, with subsequent concentration steady throughout the lower watershed.(Bogdal et al., 2009; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2014) This research was the first to illustrate that OCPs released by melting glaciers can affect the entire proglacial watershed at increasing distance from the glacier.(P. A. Pavlova et al., 2016) This finding elucidates that despite a minimal, immediate concentration decrease at the terminus, OCPs released by the glacier are found throughout the proglacial watershed. Recent water sampling from the Gangotri glacier at the head of the Ganges River found similar PCB signal from the glacier terminus through the proglacial watershed, with minimal dilution and additional inputs downstream.(Sharma et al., 2015)

Proglacial lake sediment cores (Figure 3.7) provide a corresponding temporally constrained signal, as particles scavenging OCPs from glacial meltwater partition in the water column and are deposited.(Bogdal et al., 2008; P Schmid et al., 2011)

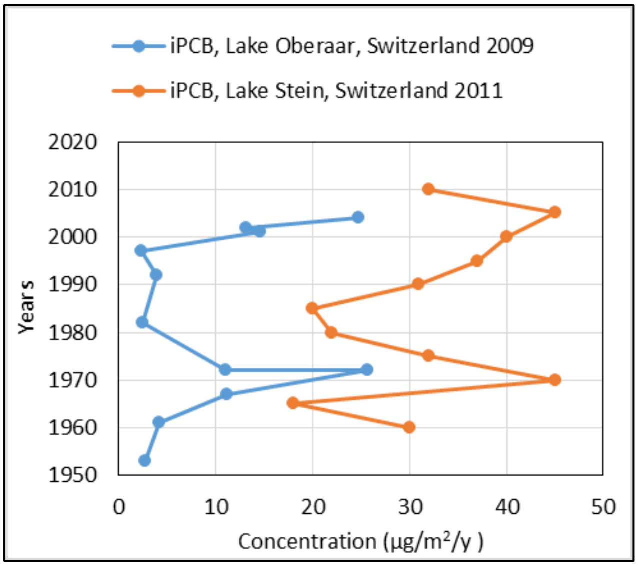

Figure 3.7 Sediment core concentrations from two lake studies in the Swiss Alps. The initial deposition peak from direct atmospheric deposition and the secondary peak from meltwater particulate deposition can be seen in both data sets.(Bogdal et al., 2009; P Schmid et al., 2011)

These layers provide a clear record of glacial pollutant melt and reemergence over time.(Bogdal et al., 2009; P Schmid et al., 2011) Swiss researchers were the first group to take proglacial lake sediment cores looking for a signal of OCPs in 2009.(Bogdal et al., 2009) Their study identified OCPs sorption onto dissolved organic carbon and deposition onto the lake bed following seasonal settling.(Bogdal et al., 2009; D Mackay & Patterson, 1990) Lake cores showed OCPs concentration peaks corresponding with the ice cores, with a primary concentration spike from direct deposition during peak chemical usage, and a secondary concentration spike indicating re-emergence in glacial meltwater. In 2011, these cores were complemented by a study from nearby Lake Oberaar, which showed the same pattern of a primary concentration spike during usage and secondary concentration spike.(Bogdal et al., 2009; P Schmid et al., 2011)

To date, only one research group from the Italian Alps and one research group from the Swiss Alps have sampled both ice cores and water samples from the same glacier.(P. Pavlova, 2014; Sara Villa, Negrelli, Finizio, et al., 2006) To develop a full-system perspective, researchers utilized the capabilities of an interdisciplinary team, which included glacial flow modelers, glaciologists and analytical chemists.(P. A. Pavlova et al., 2016; Christine Steinlin et al., 2016) The study of the cold Lys glacier in Italy, and the temperate Silvretta glacier in Switzerland offer the best understanding of OCPs glacial dynamics by providing the most complete flow model within a glacial ecosystem.(Ferrario et al., 2017; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2014; Sara Villa et al., 2003) It is critical that studies in the future incorporate both interdisciplinary research as well as sampling of multiple substrates to understand the deposition and flow of OCPs within glaciers.

3.3.1 Global trends

Globally, all studies to date have found legacy organochlorine pollutants within high-alpine glaciers. Ice core concentration profiles show peak deposition from 1970-1990 with some variation for local inputs as well as complications with surface melting.(Donald et al., 1999; Garmash et al., 2013; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Sara Villa et al., 2003) All water sampling showed lower quantities of OCPs than were found in the ice core samples, which may be due to loss through revolatilization, transportation to other media, uptake, or dilution with melt from multiple ice layers (Figure 3.7). Similarities in OCPs concentration appear on a regional scale, with variation governed by thermal regime of the glacier and dynamics of the glacial ecosystem.(Jules M Blais et al., 2001; Bogdal et al., 2009; P. Pavlova, 2014; Sara Villa et al., 2003) (Donald et al., 1999; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Sara Villa et al., 2003)

Within the mid latitudes of the northern hemisphere, the relationship between high OCPs glacial concentrations and proximal urban centers is clear, but additional ice cores from southern hemisphere glaciers will be required for a global perspective.(Arellano et al., 2015; Finizio et al., 2006; S. Villa et al., 2001; Sara Villa, Negrelli, Maggi, et al., 2006; Sara Villa, Vighi, & Finizio, 2014) Regional differences in sampling studies show higher transport and deposition rates for OCPs with a higher molar mass and chlorination.(Donald et al., 1999; P. Pavlova, 2014; Sara Villa et al., 2003) While ice cores from the European Alps show significantly greater deposition and storage rates than Canadian and Icelandic cores, corroborating data from North America is needed to determine the extent to which atmospheric circulation patterns affect deposition rates.(Sara Villa et al., 2003)

While significant progress on understanding OCPs distribution, glacial entrainment, and reemergence has been accomplished, continued research is still needed. An interdisciplinary, full system perspective is necessary to understand the implications of observed chemical flow. The most robust research accomplished to this point has incorporated multidisciplinary teams to gain a more complete picture of ecosystem dynamics. For example, while new sampling approaches, such as coring an alluvial fan, may be interesting, lake sediment cores provide a more accurate representation of concentrations due to DOC adhesion and limited revolatilization. Future research must incorporate interdisciplinary teams that include glacial geologists, glaciologists, hydrologists and toxicologists to eliminate sample bias and increase knowledge of systems fluxes. The movement of OCPs through a glaciated watershed is a system dynamics problem most clearly addressed by diverse research teams that can provide accurate information as the field moves forward.

3.4 Future research

The implications of human OCPs exposure in high alpine, glaciated ecosystems have yet to be assessed. Smaller glaciers in rapidly warming environments may be more susceptible to rapid OCPs release, making it necessary to analyze health risks for humans utilizing glacier water resources in near source, high-latitude, and high-altitude alpine systems. The need to assess human exposure to OCPs is published in the literature,(Dassanayake, 2014; El-Shahawi et al., 2010; Lignell et al., 2012) but targeted studies of downstream human communities are few, and do not incorporate direct glacial water uptake.(Byrne et al., 2015; Quadroni & Bettinetti, 2017) As studies continue to expand on the minimum OCPs dose necessary to cause human harm,(Jaacks & Staimez, 2015; K.-S. Kim et al., 2014; Ngwa et al., 2015) an understanding of future glacial release and uptake of compounds will be critical. Research on screening and risk profile development for downstream communities must be prioritized, with new work forthcoming.(Quadroni & Bettinetti, 2017) Pathways for OCPs bioaccumulation in proglacial flora and fauna is relatively well understood, but human uptake patterns have yet to be quantified.(Bizzotto, Villa, & Vighi, 2009; G. Czub & McLachlan, 2004; Davidson et al., 2003; Geisz et al., 2008)

Human communities that are solely dependent upon glacier meltwater could have a higher potential for risk than those that are dependent on a variety of precipitation and glacially fed sources. The prevalence of these dynamics in some South American communities necessitates immediate study. Additionally, watersheds with high glacier meltwater contribution to lakes and rivers providing animal food sources may have the highest potential for bioaccumulation through tissue consumption. To determine if there is any risk to downstream populations, a survey of chemical fluxes through the melt season and subsequent routes and rates human uptake must be determined. The introduction of additional, modern chemicals may increase the overall toxicological risk when added to the OCPs concentration. Further research into this possibility is necessary and timely, as glacial melt increases proportional to the climate forcing.

Meaningful work to understand the variety of human impacts upon glaciers has been accomplished throughout the 20th century as researchers develop a greater understanding of how glaciers continue to be a record of the interactions between humans and nature. The discovery that products used to accomplish short-term goals, such as DDT, can emerge in ecosystems throughout the world for generations has been an alarming and critical step towards understanding humanity's place within whole earth system dynamics. The implications of our interactions with the natural world have yet to be fully realized, as changes outpace forecasting tools. It is only through constant research and evaluation of our own knowledge that we will understand the large-scale impacts of our actions.

CHAPTER 4.

ORGANOCHLORINE POLLUTANTS WITHIN A POLYTHERMAL GLACIER IN THE INTERIOR EASTERN ALASKA RANGE

4.1 Introduction

Glaciers act as a reservoir for atmospherically deposited chemical compounds and provide a temporally constrained record of global anthropogenic chemical development and use .(Jules M Blais et al., 2001; Bogdal et al., 2009; Sara Villa et al., 2003) The organochlorine pollutants (OCPs), manufactured as industrial additives and pesticides starting in the late 1800s and ending with the enforcement of the Stockholm Convention in 2004, are a group of highly mobile toxic chemicals that have been found in alpine glaciers throughout the northern hemisphere.(Grannas et al., 2013b; S. Villa et al., 2001) Risks from direct human uptake of OCPs include cancer, immune system and organ damage, and bioaccumulation from one generation to the next.(Denise K. Reaves, Erika Ginsburg, John J. Bang, 2015; E Dewailly, 2006; Eric Dewailly, Nantel, Weber, & Meyer, 1989; Rubin et al., 2006)

Studies from Europe, Svalbard and western Canada have identified an OCP latitudinal gradient with highest concentrations found in glaciers near 45 ºN, leading researchers to believe that atmospheric transport of OCPs is ubiquitous, but that concentrations vary.(J M Blais et al., 1998; Garmash et al., 2013; K. R. Miner et al., 2017; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014) The highest OCP concentrations measured englacially, to date, were found in the Italian Alps in 2001(S. Villa et al., 2001) (20 ng/L) of chemicals ϒ-,α-HCH. Subsequent studies found the same magnitude concentrations in the Swiss Alps were (PCB-12.5 ng/L)(Pavlina Aneva

Pavlova, Schmid, Bogdal, et al., 2014), but lower concentrations of all chemicals in Svalbard (PCB- 1.5 ng/L)(Garmash et al., 2013) and Canada (DDT- 2.5 ng/L).(Donald et al., 1999; K. R. Miner et al., 2017) The atmospheric range of each compound is determined by distance from source, weight and volatility, with some pesticides redepositing multiple times.(Burkow & Kallenborn, 2000; Donald et al., 1999; C. L. Friedman & Selin, 2016; Carey L. Friedman & Selin, 2012; Garmash et al., 2013; Hauptmann et al., 2017; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014) ΣHCH has the greatest atmospheric range of all OCPs, due in part to its high volatility and low reactivity, thus increasing the probability of Arctic deposition.(Daly & Wania, 2005a; Hansen, Christensen, Geels, Silver, & Brandt, 2015; Helm et al., 2002; Octaviani et al., 2015; Shen et al., 2004) Based upon this previous work, we hypothesized that it would be possible to identify an OCP signal within glaciers of the Interior Alaskan Arctic. Though Arctic OCP studies have been accomplished at Svalbard and Canada, no sampling studies from the Alaska subarctic region have been conducted.

Our recent assessment of screening level risk from glacially mobilized OCPs in the Swiss Alps identified potential cancer and disease risk from fish consumption in the proglacial watershed.(K. R. Miner, Bogdal, Pavlova, Steinlin, & Kreutz, 2018) Human consumption of local fish put health risk in the Swiss Alps just above screening level thresholds, even though the region is characterized by low levels of fish consumption.(K. R. Miner et al., 2018; Statistical Office, 2017) The elevated fish consumption in subsistence groups of the Alaskan Arctic(Ballew, Ross, Wells, & Hiratsuka, 2004; Conservation, 2017; Fall et al., 2013) indicates the need to identify the potential presence of OCPs in Alaskan glaciers and meltwater to identify possible human health risks. Furthermore, Alaskan glaciers are losing mass at an increasing rate,(Hock, 2010; Mountain

Research Initiative E D W Working, 2015; Michael Zemp et al., 2015) necessitating prompt study of OCP glacial entrainment to determine if pollutants are entering the glacier watershed below.

Jarvis Glacier in Interior Alaska represents one of the most well studied glacial systems in Eastern Alaska (Figure 4.1).(Fall et al., 2013; Gatesman, 2017; Liljedahl, Gädeke, O’Neel, Gatesman, & Douglas, 2017; Wada, Chikita, Kim, & Kudo, 2011) Research into the connections between watershed dynamics,(Gatesman, 2017; Liljedahl et al., 2017) permafrost(Liljedahl et al., 2017) and ice dynamics allow for a systems perspective of the region. Ice cores collected for investigation into Jarvis Glacier’s ice dynamics allowed for the opportunity to conduct the first study of OCPs entrained within a glacier of Interior Alaska. The primary goal of the work presented here is to assess the presence or absence of OCPs in an Alaskan glacier for the first time.

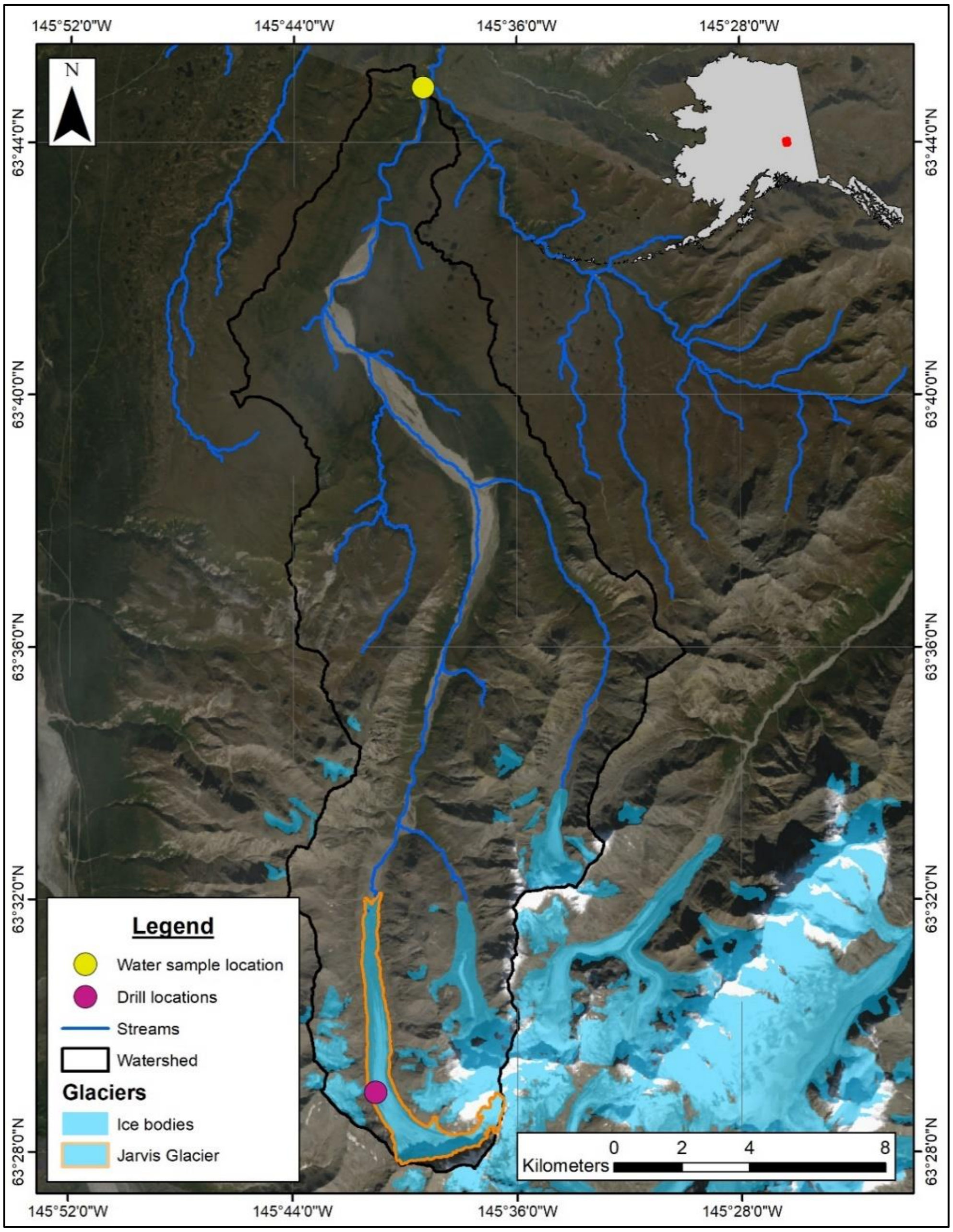

Figure 4.1 Map of Jarvis Glacier in the Interior of Alaska. The bulk water and SPMD sampling location in Jarvis Creek is indicated in yellow, an entirely glacier-fed tributary upstream of McCumber creek. Ice core drilling site is indicated in purple and is located on the left lateral ice stream of the glacier.

There are relatively few historical and/or present uses of OCPs within Alaska, suggesting that any glacier-stored OCPs must be transported from distant locations. The use of DDT has been recorded within the last decade in China, India and DPR Korea,(van den Berg, Manuweera, & Konradsen, 2017; Xiao ping Wang, Xu, et al., 2008) with atmospheric transport across the Pacific(Octaviani et al., 2015; Stein et al., 2015; Toose, Woodfine, MacLeod, MacKay, & Gouin, 2004) and preferential OCP snow scavenging(Carey L. Friedman & Selin, 2012; Lei & Wania, 2004) suggesting the possibility of deposition onto Alaskan glaciers.(E. C. Osterberg et al., 2017; Erich C. Osterberg et al., 2008; Yasunari & Yamazaki, 2009) Recent ice core records from Interior Alaska indicate that the strengthening Aleutian low has resulted in the doubling of snow deposition in the Alaska Range since 1840.(Winski et al., 2017) This increase of precipitation may allow for the greater success of OCP atmospheric scavenging and glacial deposition,(Lei & Wania, 2004; Morselli et al., 2014) with variation in deposition dependent on the above-glacier OCP concentration.(Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Christine Steinlin et al., 2014) The potential for OCP deposition in Alaskan glaciers combined with recent elevated glacial mass loss in the Eastern Alaska Range (WGMS, 2015; Michael Zemp et al., 2015) makes Jarvis Glacier relevant from the perspective of glacial chemistry and the potential for human risk. This study therefore serves as an initial investigation into the presence of glacially entrained OCPs in interior Alaska glaciers as a first effort to characterize species and concentrations. Here, we identify the presence and concentration of OCPs pollutants in Jarvis Glacier watershed to add an understanding of glacially entrained pollutants to ongoing research on system dynamics. We identify meltwater and ice core concentrations above background levels of pesticides DDT, p,p'-DDD, p,p'-DDE (ΣDDT), and α-HCH and ϒ-HCH (ΣHCH).

4.2 Methods

4.2.1 Study site: glaciology and hydrology

Jarvis Glacier (~6 km^2) is a north facing, polythermal valley glacier in the Eastern Alaska Range of interior Alaska at latitude 63.74, longitude 145.65 (Figure 4.1). The region is characterized by the semi-arid precipitation of a subarctic continental climate regime with a mean annual lowland precipitation accumulation of 303 mm and temperature of -0.5 ^{o}C.(Gatesman, 2017) The glacier at present is in a state of overall mass loss characterized by negligible accumulation area and significant yearly glacial discharge from April-November.(Gatesman, 2017)

Summer warming in Interior Alaska of 0.1 ^{o}C yr^{-1} has resulted in a 12% glacier cover reduction and a continuously negative glacier mass balance for the last five decades,(Liljedahl et al., 2017; O'Neel, Hood, Arendt, & Sass, 2014) where glacial meltwater contribution to the Tanana River is already up to 60% annual stream flow.(Wada et al., 2011) For Jarvis Glacier, the seasonal warming and an absent compensation in solid precipitation have resulted in a ~1600 m bare-ice retreat in the past 5 years, with an average of -3.0 mwe yearly loss.(Liljedahl et al., 2017) Seasonal terminus discharge contribution from the Glacier varies from 2% in May to 80% in September with a seasonal average of 35%.(Gatesman, 2017) Jarvis Glacier feeds Jarvis Creek (634 km^2), which flows year-round and with a late winter discharge of approximately 3 m^3 s^{-1}.(Liljedahl et al., 2017) Glacial meltwater from Jarvis Glacier contributes 15% to 28% (in 2015 and 2016, respectively) of the annual runoff to Jarvis Creek, which in turn feeds the Delta, Tanana and Yukon Rivers.(Liljedahl et al., 2017) Glacial contributions to stream flow have been found to increase in June and July, concurrent with a yearly precipitation decrease from 26-12%, during the past 6 years.(Gatesman, 2017) This makes summer streamflow the period of greatest glacial discharge, and therefore presents the best opportunity to capture a glacial OCP signal.

Records identify that winter runoff increased in the Tanana River beginning in 1970's(Brabets & Walvoord, 2009) in alignment with shrinking glaciers and aquifer recharge via glacierized headwater stream corridors, but without subsequent increase in precipitation.(Liljedahl et al., 2017) With internal temperatures fluctuating from -10 – 0 ^{o}C,(Ian Lee, 2017) Jarvis lies within a system in a state of negative mass balance.

4.2.2 Ice core

In April 2017, a surface-to-bed (0-79 m) ice core was recovered from Jarvis Glacier. The ice core was retrieved using a 3 in. (8.2 cm) diameter Badger-Eclipse drill. The ice core drilling site was at the left lateral glacier margin in an area with folding, faulting and conjugate fractures (Figure 4.1). While the core was initially drilled to satisfy the objectives of a concurrent ice dynamics research study, drilling near the lateral margin provides a more direct comparison with stream samples. The ice core had alternating debris and melt layers, characteristic of a polythermal glacier, with clear layers containing bubble planes. Significant debris, englacial, and basal water was discovered during drilling, which was verified by ground penetrating radar profiles that showed laterally extensive debris bands, water tables, and pockets of water (Figure 4.2). The combination of high water content that diffuses annual chemical layering, faulting and fracturing, glacial thermal regime and position near the lateral margin, make it impossible to determine chemical chronology of the core (Figure 4.1, 4.2).[76]

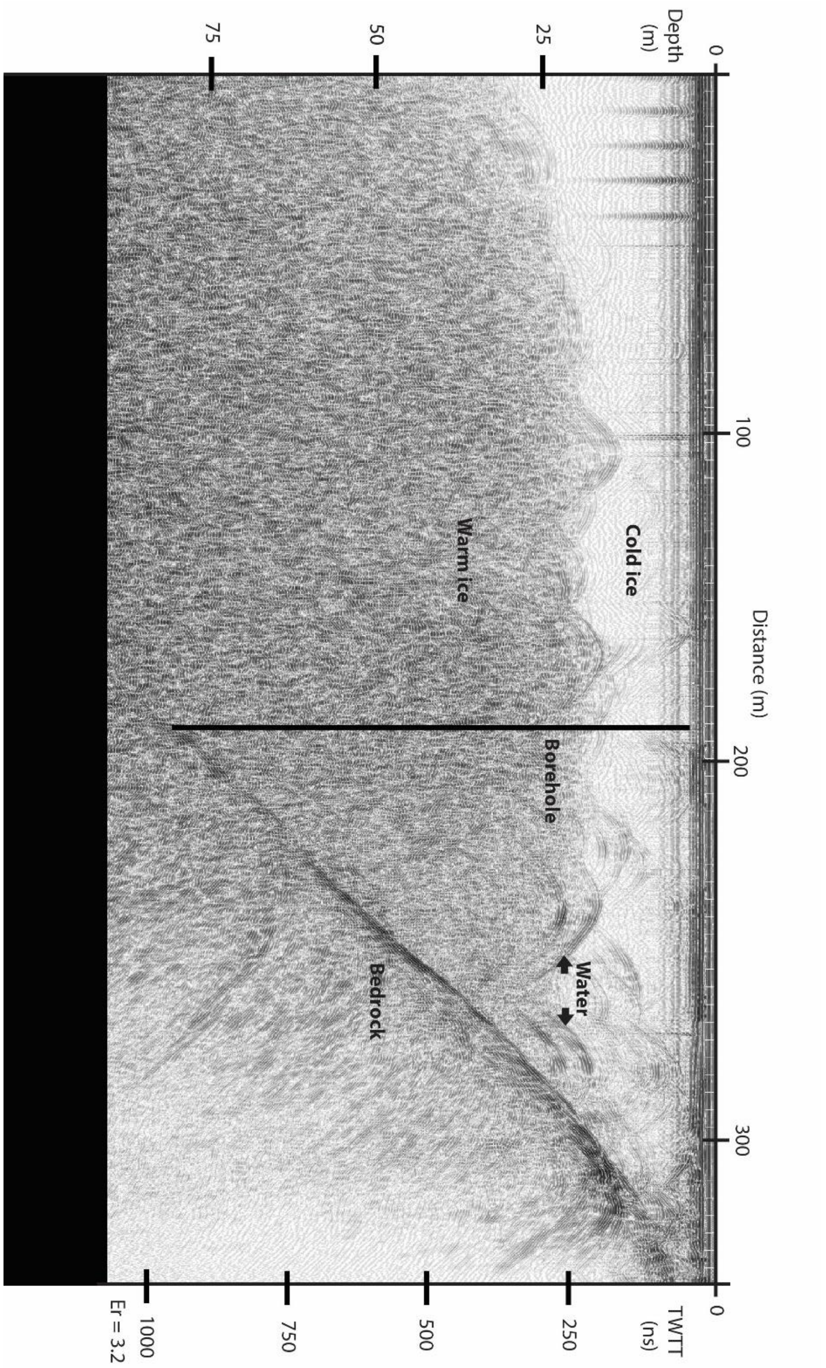

Figure 4.2 Radar profile for Jarvis Glacier 80m borehole. Warm ice, cold ice and water in the transition between them are identified. Two-way travel time (TWTT) is indicated on the right y-axis. Depth is indicated on the left y-axis with distance across glacier indicated on the x-axis.

Once removed, the core was stored in a freezer on site at temperatures between -18 to -20 ^{o} C. Ice core sections were transported in 3-5-day intervals by helicopter to the Cold Regions Research and Engineering Laboratory (CRREL) in Fairbanks, Alaska, where they were stored at -18 ^{o} C. At CRREL, we retrieved 2L of water equivalent from 7 m long segments of ice core, using a table saw cleaned with ethanol and methanol, then kept in a room at a constant temperature of -18 ^{o}C. The segments were melted in sealed and cleaned one-gallon glass jars to prevent loss due to revolitilization. Once each section was melted, samples were filtered and extracted with C-18 Solid Phase Extraction (SPE) cartridges (Oasis HLB, 6 cm^3/500 mg, LP Extraction Cartridge, 60 µm; Water Corporation, Milford, Massachusetts, USA) to separate OCP particles from polar organic material.((EPA), 2007; Ferrario et al., 2017; Fortuny, Pineda, Rúbies, Centrich, & Companyó, 2013) The cartridges were pre-cleaned with 5 ml hexane and 5 ml ethyl acetate followed by 5 ml methanol and 5 ml deionized water (Milli-Q). A tracing spike of 10 µl of 100 ppm organochlorine pesticides (Absolute standards, Hamden, CT) was added to one sample before filtration to verify the efficacy of the method, and 50 µl of the recovery standard was added to all samples (PCB 40 -10 ppm in acetone). Samples were then drawn through cartridges using a vacuum manifold at a flow rate of approximately 10 ml/min. After the extraction, the cartridges were dried under full vacuum pressure for 5 min. and subsequently eluted with 3 ml ethyl acetate and 5 ml of hexane followed by a repeat elution of 5 ml hexane. Samples were then blown down to a concentration of 1 ml for injection into the gas chromatography tandem mass spectrometer (GC-MS/MS). In the final extract 20 µl of 100 ppm internal standard TCX was added for continuity. After elution, 1ml analytes were sealed and shipped directly to Anatek labs in Moscow, Idaho, for processing using triple quadrupole imaging GC-MS/MS with the limit of detection at 0.1 ng/L.

4.2.3 Stream water samples

Sampling of Jarvis Creek was accomplished using both solid phase extraction (SPE)((EPA), 2007; Fortuny et al., 2013) and semi-permeable membrane devices (SPMD).(Alvarez, 2010; Itrc, 2006; U.-J. Kim, Kim, Alvarez, Lee, & Oh, 2014) Small SPMD filters were installed monthly 1 km above the confluence of Jarvis Creek and Delta River, 10 m downstream of Jarvis Glacier terminus (Figure 4.1) during the summer 2016 field season (June-September). Two SPMD canisters containing 2 filters each (4 total), were placed and/or recovered during three trips in June, July and August. The 4 filters were combined into 2 analytes for the greatest opportunity of OCP identification. SPMDs were spiked using a spiking suite of three deuterated PAHs: Anthracene-d10, Fluoranthene-d10, and a photolysis marker of Dibenz[a,h], Anthracene-d14 – all at 1ug/SPMD. Three PCBs not found in the ecosystem were also added as standards: PCB #14 (3,5-Dichlorobiphenyl), PCB #29 (2,3,5-Trichlorobiphenyl) and PCB #50 (2,2',4,4'-Tetrachlorobiphenyl), each at 0.200ug/SPMD. SPMD filters were cleaned and processed at EST labs in St. Joseph, Missouri, in accordance with previously published methodology.(Alvarez, 2010) All stream samples were processed at Anatek labs in Moscow, Idaho, using triple quadrupole gas chromatography tandem mass spectrometry (GC-MS/MS) imaging with the limit of detection at 0.1 ng/L. In addition, 2 bulk water samples of 4 L each were taken to sample for particulates during the monthly sampling trips in 2016. We sampled 1 L using SPE cartridges (Sigma-Aldrich lab in St. Louis, MO) and processed samples following the previously described SPE methodology. Stream water samples were processed at the University of Maine following SPE protocol.(Ferrario et al., 2017) All SPE samples were processed at Anatek labs using GC-MS/MS imaging.

4.3 Results

4.3.1 Quality control

The recoveries of all samples averaged 90% of blank values. SPE blanks and spikes were generated using 1 L of milli-Q water per filter, with milli-Q water treated like a meltwater sample. Low level concentrations of ΣDDT and ΣHCH were present in the blanks, at 1-2 orders of magnitude less than samples. Reported sample values were not normalized for blanks. Bulk stream water samples from August 2016 contained significantly higher sediment quantities, leading to low recoveries and incomplete data, hence these samples were not reported here. GC-MS/MS error is determined after an initial demonstration of capability from the extraction and analysis of four spiked samples. Uncertainty is then calculated based on the variability of the 4 spiked samples after performing a calibration and contributes ± 10% to reported concentrations.

4.3.2 Patterns of OCPs in the ice core

Out of the 18 pesticide compounds tested under the Environmental Protection Agency method 8270A, we found 3 DDT compounds and 2 HCH compounds in both the Jarvis ice core and meltwater (Figure 4.3-4.4).((EPA), 1998) Though ice core chronology is not clear, we are able to determine the presence of OCPs in the surface to bed ice core. Throughout the ice core we found greater quantities of ΣDDT than ΣHCH, with highest concentrations of all OCPs in ice core sections near the surface and peaking in the 7-14m segment (Figure 4.3). Subsequent depths trended towards lower concentrations of all OCPs with ΣDDT remaining highest in all layers.

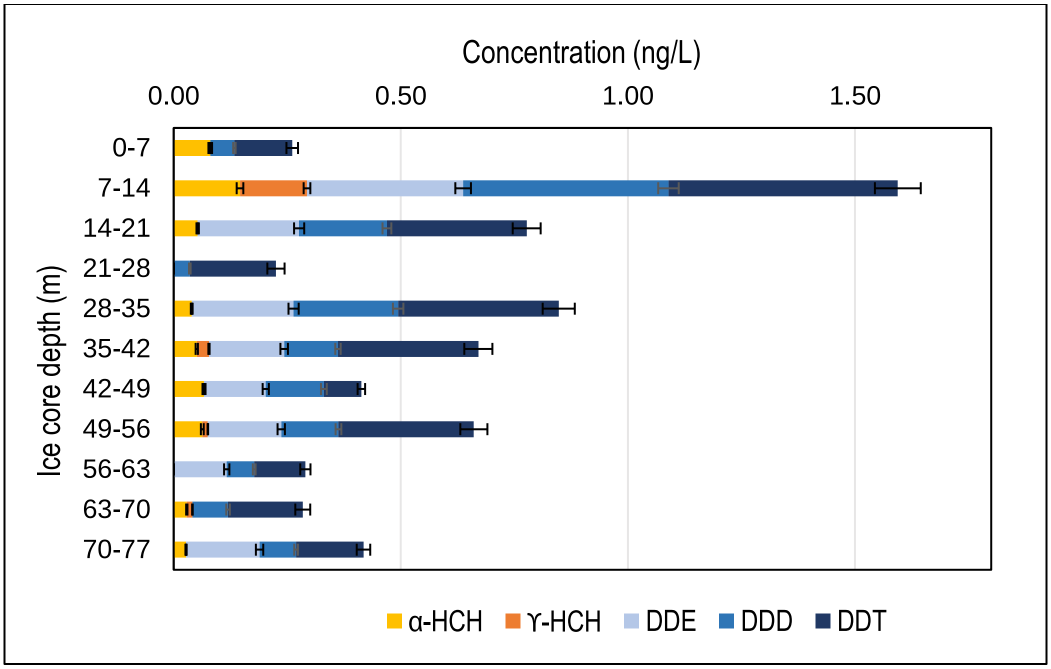

Figure 4.3 Stacked bar plot of ice core OCP concentrations by depth from 0 m to 77m. ΣDDT contributes the greatest quantity of OCPs to the core, with greatest concentrations accumulated at 7-14m.

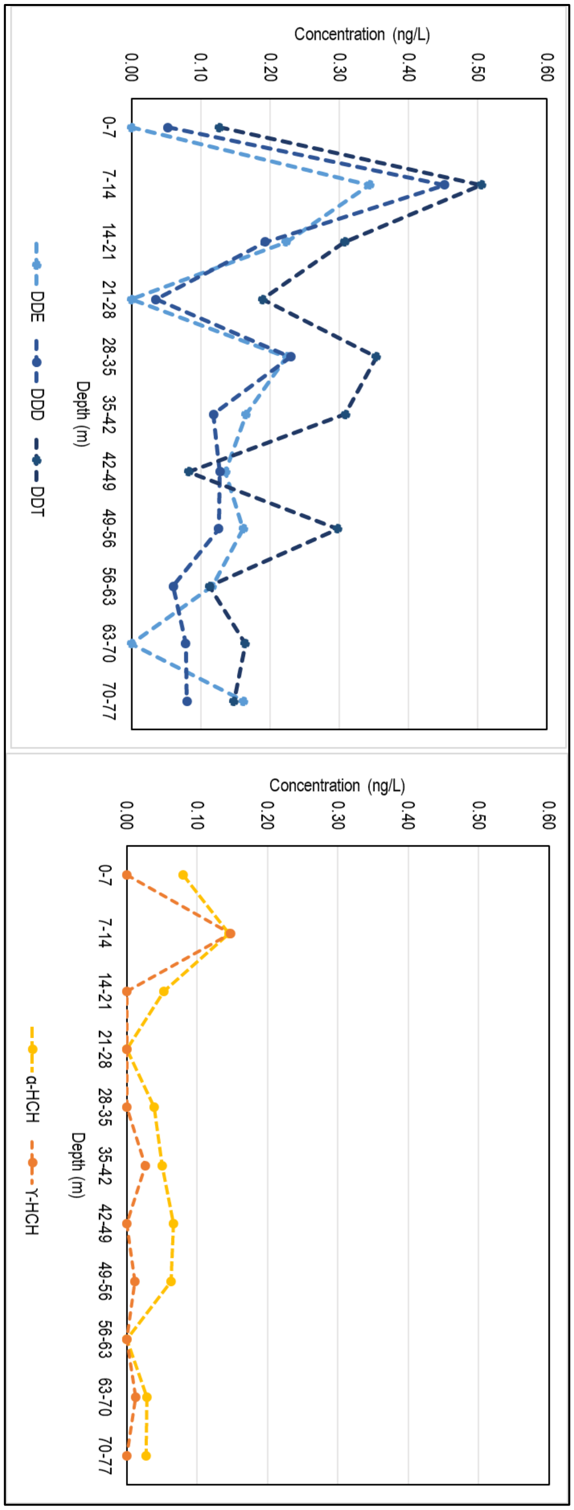

Figure 4.4 Ice core OCP concentration trends by depth with DDT and metabolites on the left and HCH on the right. Depth profiles are similar across species, but the concentration magnitude of all DDT components is higher. Concentrations seen throughout the ice core profile may be a result of chemical movement due to melt and refreezing.

Overall DDT was the OCP found at greatest quantities throughout the ice core (total: 2.47, 7-14m peak: 0.51 ng/L), followed by p, p’-DDE (total: 1.53, 7-14m peak: 0.34 ng/L) and p,p’-DDD (total: 1.50, 7-14m peak: 0.45 ng/L). Both α-HCH (total: 0.48, 7-14m peak: 0.15 ng/L) and ϒ-HCH were found at much lower concentrations throughout all layers (total: 0.20, 7-14m peak: 0.15 ng/L). Concentrations in the ice core samples of both chemical groups were lower than concentrations found in the meltwater, potentially a result of chemical loss from a large section of the glacier.

4.3.3 Patterns of OCP in meltwater

Bulk meltwater samples showed greater concentrations of ΣDDT than of ΣHCH, consistent with the results from ice core samples (Figure 4.5). For both June and July, p,p’-DDE was found in the greatest concentration (Average June: 0.69, July: 0.73 ng/L) throughout the bulk water samples, followed by p,p’-DDD (Average June: 0.60, July:0.56 ng/L) and DDT (Average June:0.58, July:0.47). Bulk water concentrations of α-HCH and ϒ-HCH were again in slightly lower concentrations while ϒ-HCH concentrations (Average June: 0.36, July:0.32 ng/L) were slightly above α-HCH (Average June: 0.27, July: 0.19 ng/L).

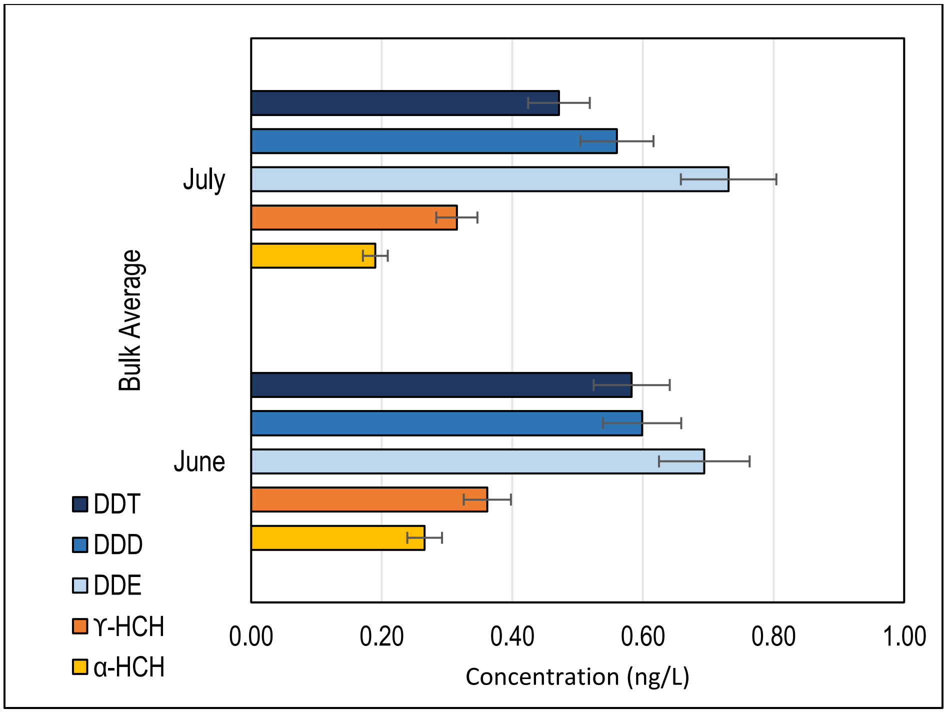

Figure 4.5 Bulk meltwater concentrations by month sampled. Higher sediment loads captured in the bulk samples are reflected in higher concentrations measured, with chemical species the same across ice core and meltwater samples.

	Bulk Average	
	June	July
α-HCH	0.27	0.19
ϒ-HCH	0.36	0.32
DDE	0.69	0.73
DDD	0.60	0.56
DDT	0.58	0.47

Table 4.1 Meltwater concentrations in ng/L for bulk water samples. SPMD sample concentrations are included in *Supplementary information*. All concentrations are above 0.1 ng/L, or the limit of detection.

The SPMD samples showed concentrations an order of magnitude lower but reflected highest concentration during peak glacial melt in June and July. The natural variation of the glacial meltwater stream left SPMD filters exposed to the air for a period of up to 10 days, significantly increasing uncertainty. This is an ongoing issue when utilizing SPMDs in glacial watersheds, and subsequently the results have been added in supplementary information.

4.4 Discussion

4.4.1 Ice core OCP concentrations

Ice core concentrations indicate that deposition of ΣDDT is the greatest contributor to OCPs within Jarvis Glacier. Throughout the meltwater and ice core samples we found the same chemical species, with ΣDDT concentrations higher than ΣHCH concentrations. Influx of ΣDDT may be from atmospheric deposition from use prior to the Stockholm Convention ban, however, recent use in Asia may explain why comparatively elevated rates of ΣDDT occur in samples proximal to the surface.(Stein et al., 2015; van den Berg et al., 2017; Xiao ping Wang, Xu, et al., 2008; Yasunari & Yamazaki, 2009)

Jarvis is a polythermal glacier where supraglacial water flowing into the ice can mobilize particulates, including OCPs, to the sub-glacier environment.(P. A. Pavlova et al., 2016) The Jarvis Glacier polythermal regime combined with recent warming trends result in high water mobility between ice layers and below glacier, increasing basal lubrication. There was significant meltwater and geological debris found at the bottom of the bore hole and throughout the ice layers within Jarvis Glacier. This may account for lower concentrations of OCPs in ice as compared to meltwater, as englacial and basal meltwater flow into basal sediment ultimately drains to the terminal ice margin stream. In addition to basal meltwater transport and debris at the bed increases basal porosity can act as a deep-water storage, influencing OCP entrainment and transport. Particle sorbtion within Jarvis' high sediment ice layers may increase the mobility of OCPs during melt events as chemicals sorbed to particles are released.(Pavlina Aneva Pavlova et al., 2015; C. Steinlin et al., 2015; Christine Steinlin et al., 2016)

4.4.2 Meltwater transport and OCP dynamics downstream

Jarvis' polythermal structure raises the possibility of supraglacial water flowing into the ice and moving OCPs englacially to the sub-glacier environment.(P. A. Pavlova et al., 2016) Resultant subglacial storage may increase flux in subsequent years as summer surface melt and englacial transport to the base increases. Subglacial transport may be a predominant driver of OCP movement, increasing the possibility of OCP transport and pooling. The higher quantities of ΣDDT and ΣHCH found in the glacial meltwater as compared to the ice core may indicate that the glacier has lost a majority of reservoir OCPs through meltwater flux or pooling and storage at the base.(Ferrario et al., 2017; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2016) Additionally, sediment inputs from the glacier bed or walls may increase OCP sorbtion and transport out of the glacier, preferentially scavenging OCPs.

Debris at the bed increases basal porosity and deep-water flow, thus increasing the potential for OCP entrainment and transport. Subglacial till or basal sediments may allow for OCP movement, increasing the possibility of OCP transport and pooling as summer basal meltwater flow increases. Additionally, sediment inputs from the glacier bed or walls may increase OCP sorbtion and transport out of the glacier, preferentially scavenging OCPs. Higher quantities of ΣDDT and ΣHCH in meltwater as compared to ice core samples may therefore be the result of this preferential adhesion to particulates present in the water column.

SPMD methodology presents challenges when used in remote streams with highly variable flow rates that may impair the device's functioning. Due to significant variation within the glacial stream, SPMD filters were exposed to or inundated with silt during July-September, making it impossible for them to filter OCPs from the glacial meltwater during this time. A high rainfall event on August 27th inundated the filters with silt, but they were exposed to the air for at least one day prior to September retrieval. Due to the inaccessibility of the sample location and the inherent variation in glacial stream flow, SPMD filters may not provide the best approximation of OCP concentration. Our research mirrors previous findings that bulk water samples allow a better understanding of both particulate and meltwater concentrations, providing the best representation of overall OCP meltwater data.(P. A. Pavlova et al., 2016)

The permafrost-rich environment below Jarvis Glacier may pose additional routes for storage and release of OCPs from meltwater over time. Pooling within the proglacial permafrost may temporarily stall the movement of OCPs from flowing into the larger watershed, yet as temperatures warm, permafrost thaw may increase tertiary OCP release.(Ma, Hung, Tian, & Kallenborn, 2011) Sediments below the glacier can also act as short-term storage with release dependent on water transport, bioturbation, or direct sediment transport.(P Schmid et al., 2011; B. van Drooge et al., 2014) An understanding of the chemical species found throughout alpine environments may be critical to protecting the surrounding biota from abbreviated pollutant influx. Though the secondary and tertiary emergence of these chemicals will not reflect the pollution problems of industrial watersheds, OCP bioaccumulation in the ecosystem may cause long-term health impacts in certain populations.

4.4.3 Patterns of atmospheric deposition

Though the Arctic is geographically distant from a majority of OCP use areas, the interconnected atmosphere-cryosphere system reflects the transport of human-use chemicals globally. Influx of ΣDDT from recent use in Asia (Stein et al., 2015; van den Berg et al., 2017; Xiao ping Wang, Xu, et al., 2008; Yasunari & Yamazaki, 2009) may explain why comparatively elevated rates of ΣDDT occur in our samples. DDT is currently used for fighting Malaria throughout Asia and this use is unique in Eurasia and the Americas.(van den Berg et al., 2017; Xiao ping Wang, Xu, et al., 2008) Research into the pollution and dust deposition trends in Alaskan ice cores using satellite images and back trajectories highlight the Asia to North Pacific atmospheric transport route as a source of particulates to Alaska.(E. C. Osterberg et al., 2017; Erich C. Osterberg et al., 2008; Stein et al., 2015) Back trajectories have identified that a 10-day period is sufficient to track air masses containing pollution from use sources in Asia to the North Pacific and Alaska, especially in the late spring.(Yasunari et al., 2007; Yasunari & Yamazaki, 2009) The potential for an increase of OCP deposition in the late spring snow may mean an influx into the snowpack either melting supraglacially (C. Steinlin et al., 2015; Christine Steinlin et al., 2014) during the beginning of melt season in April if the glacier is losing mass,(Gatesman, 2017) or becoming entrained within the glacier during a period of mass gain. Supraglacial melt in the spring may introduce pollutants immediately into the downstream watershed. We speculate, based upon transport analysis, that OCP deposition in Interior Alaska is not limited to Jarvis Glacier, but is reflected throughout the Eastern Alaska Range.

The ice core samples show concentrations lower than those recorded in other Arctic studies,(Hermanson et al., 2005; Christine Steinlin et al., 2016) which may result from loss due to melt, or the distant location of Jarvis Glacier from regions of greatest use.(Hermanson et al., 2005; Christine Steinlin et al., 2016) This is in line with a latitudinal OCP concentration gradient noted by previous studies that identifies lower concentration within glaciers north of 65 ^{o}N.(Daly & Wania, 2005b; K. R. Miner et al., 2017) The Alaskan Interior is even more distal from use areas than Svalbard, for example, which may explain the difference in concentrations.(Garmash et al., 2013; Hermanson et al., 2005) The higher quantities of ΣDDT and ΣHCH found in the glacial meltwater as compared to the ice core may correlate with increased atmospheric warming and subsequent melt over the last 6 years.(Ferrario et al., 2017; Gatesman, 2017; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2016)

4.4.4 Implications for Arctic populations and ecosystems

Presence of OCPs within Jarvis Glacier and remote Interior Alaska reaffirms the transport and deposition of organochlorine compounds within the high Northern latitudes. Though the concentrations of ΣDDT and ΣHCH found within Jarvis Glacier ice and meltwater are low, the potential for bioaccumulation within the proglacial food chain(J M Blais et al., 2003; Daly & Wania, 2005a; Davidson et al., 2003) and within human consumers(Gertje Czub & McLachlan, 2004; Dassanayake, 2014) may increase their impact.

Within the Tanana River, glacial meltwater currently accounts for over 50% of annual stream flow.(Wada et al., 2011) We assume that as glacial melt seasons increase in length, the rate of OCP loss may also increase until much of the glacial reservoir of these chemicals has entered the proglacial watershed.(Liljedahl et al., 2017; C. Steinlin et al., 2015; Christine Steinlin et al., 2016) This may also be true for other ablating glaciers of interior Alaska, raising the possibility that OCP concentration in the Yukon watershed has been increasing for decades. As these glaciers collocated with human populations in the Arctic continue to melt, the small but impactful OCP concentrations may increase within the watershed and bioaccumulate within the local ecosystem.(Bizzotto, Villa, & Vighi, 2009; J M Blais et al., 2003; K. R. Miner et al., 2017)

It is likely that Jarvis Glacier is not an isolated case and that numerous glaciers in the Eastern Alaska Range house legacy OCPs. Concurrent with glacial melt contribution to the watershed,(Wada et al., 2011) multiple glaciers releasing stored legacy chemicals into the ecosystem may raise the concentration of OCPs above background levels throughout the watershed. Ice core studies in Svalbard have also identified glacially entrained OCPs,(Garmash et al., 2013) but the North American Arctic contains a much larger human population. This resident Arctic population raises the potential for consumption of glacial meltwater and/or fish to have human health impacts.(K. R. Miner et al., 2018)

Dispersion throughout the watershed in concentrations above background level may have the potential to increase if OCP loss from numerous glaciers occurs. Human uptake of these chemicals even at background levels can effect multiple generations and lead to significant health problems.(Iszatt et al., 2015; Jaacks & Staimez, 2015; Vizcaino et al., 2014) Thus, investigations into the reemergence and distribution of OCPs in Arctic glaciers should be prioritized. With the elevated fish consumption of many Arctic subsistence groups,(Ballew et al., 2004) the risk of toxicity from OCP bioaccumulation is higher than other alpine regions.

4.5 Conclusions

Our work adds a new North American data set to the research of OCPs in glaciers, while reaffirming existing knowledge on the deposition of OCPs into ecosystems in the Arctic.(Burkow & Kallenborn, 2000; Octaviani et al., 2015; Shen et al., 2004; Simonich & Hites, 1995) The Eastern Alaska Range is geographically isolated from areas of high DDT and HCH use, but the existence of these compounds in glacial ice and meltwater indicates sources outside of the Interior Alaska region. The entrainment of chemicals in a remote Interior Alaskan glacier reiterates the transport and deposition of organochlorine compounds globally and the increasing need to assess human health risks from glacial meltwater. Though these chemicals are found in trace quantities within Jarvis Glacier, they introduce OCPs into the watershed at levels higher than direct atmospheric deposition, suggesting that glaciers act as a reservoir for OCPs.

As atmospherically deposited pollutants emerge from glacial environments under a warming climate, the health risks to surrounding populations from bioaccumulation in the food chain may be compounding. Detailed risk assessment modeling that incorporates bioaccumulation would help elucidate the potential for concentration increase and uptake. Emergent pollution from melting glaciers is one of the implications of climate change that requires further exploration and represents an area of critical research importance. Though OCPs are only one contributor to emergent pollution within glacial ecosystems, they form part of a greater picture of the long-term fingerprint humans have left on even the most remote locations.

CHAPTER 5.

QUANTITATIVE SCREENING LEVEL ASSESSMENT OF HUMAN RISK FROM PCBS IN GLACIAL MELTWATER: SILVRETTA GLACIER, SWISS ALPS

5.1 Introduction

Despite being banned by the multinational Stockholm Convention agreement in 2004, long-range atmospheric transport has made some organochlorine pollutants (OCPs) ubiquitous in the environment.(Jules M Blais et al., 2001; Bogdal et al., 2009; Simonich & Hites, 1995; S. Villa et al., 2001) In Arctic and high alpine environments, OCP sorption to snow crystals leads to deposition and entrainment in glaciers, resulting in the long term storage of legacy chemicals in glacial ice.(Jules M Blais et al., 2001; Daly & Wania, 2004; Lei & Wania, 2004; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2014; Xiao ping Wang, Yao, et al., 2008) OCPs accumulate at enhanced rates in high-altitude alpine environments with high snow fall and proximal areas of use.(Daly & Wania, 2004; P. A. Pavlova et al., 2016; Christine Steinlin et al., 2014) Glacial entrainment of OCPs has been documented in mountain ranges within China, Svalbard, Canada, Switzerland and Italy, with the highest concentrations found in the European Alps.(Roberta Bettinetti et al., 2008; J M Blais et al., 1998; Hermanson et al., 2005; Lafrenière, Blais, Sharp, & Schindler, 2006; K. R. Miner et al., 2017; Christine Steinlin et al., 2014; S. Villa et al., 2001; Xiao ping Wang, Xu, et al., 2008) The central location and high altitude of the Alps range concentrates pollution input from both local and distal sources making glacial OCP concentrations the highest of any sampled, including PCBs.(Ferrario et al., 2017; K. R. Miner et al., 2017; P. Pavlova, 2014) Though OCPs have been identified in glacial meltwater, long-term human risk from water or fish consumption is unknown. Assessing exposure to OCPs in glacial meltwater from the Alps allows for a preliminary characterization of the highest risk to humans. The combination of ice cores, water samples and glacial flow models from the Silvretta glacier in the Swiss Alps (Figure 5.1) represents one of the most complete data sets of OCP movement over time, providing the best baseline for hazard identification.(P. A. Pavlova et al., 2016; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; S. Villa et al., 2001; Sara Villa, Negrelli, Finizio, et al., 2006)

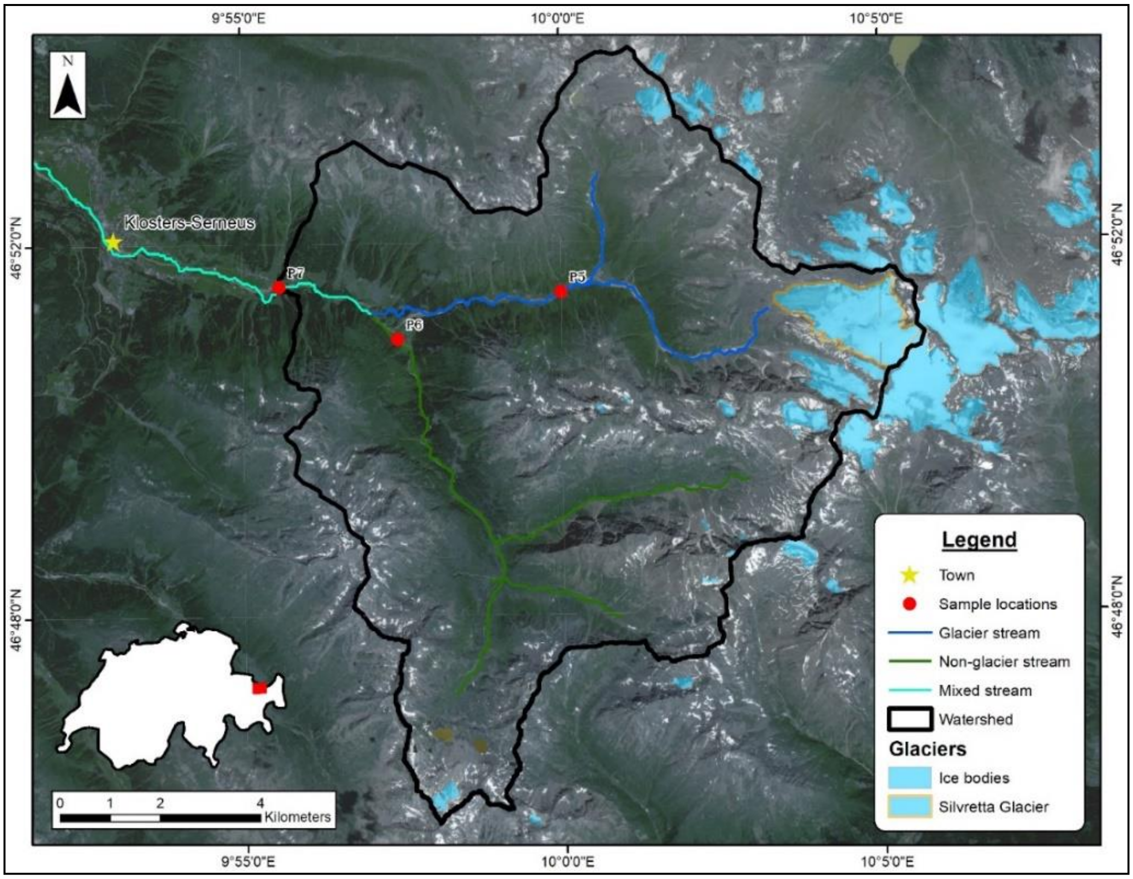

Figure 5.1 Map of Silvretta Glacier watershed where Silvretta Glacier is outlined in orange. P5 is the sample location fed directly by glacial meltwater, P6 is the sample location for non-glacial samples and P7 is the sample location for the mixed stream. Klosters-Serneus is the closest town to the Silvretta Glacier and is indicated by a yellow star.

Since 1975 the U.S. Environmental Protection Agency (EPA) has developed protocols for understanding human cancer and non-cancer risk from chemicals.((EPA), 1989, 1992, 1999, 2001b, 2003) Applying a well-tested multi-stage linear screening level tool that utilizes both a conceptual and quantitative modeling approach allows us to screen for human risk in the glacial ecosystem. Even at the low concentrations found in glacial meltwater, OCPs have the potential to create health problems in downstream populations with long term exposure.(Bergonzi et al., 2011a; Birnbaum, 2013; Gertje Czub & McLachlan, 2004; Dassanayake, 2014; El-Shahawi et al., 2010; Gaspar et al., 2015; Gauthier et al., 2014; Iszatt et al., 2015; Jaacks & Staimez, 2015; K.-S. Kim et al., 2014; Lignell et al., 2012; Matsuura et al., 2001; Ngwa et al., 2015; S.-L. Wang et al., 2005; Xiaoping Wang, Xue, Gong, & Yao, 2014)

Therefore, the goal of this study is to determine population-level human risk from secondary emission of pollutants in glacial meltwater. This is the first human risk assessment of glacial meltwater, and we utilize observed PCB concentrations from the Silvretta Glacier in the Swiss Alps to represent the upper bound risk from glacial release of OCPs. While this study is site specific, the need to understand risk from pollutants in glacial meltwater is broadly applicable to numerous glaciated ranges.

5.2 Materials and Methods

5.2.1 Silvretta data and conceptual model

Silvretta glacier (3 km^2) is a temperate alpine glacier located in the Central Eastern Range of the Swiss Alps where yearly ice melt begins in April and ends in December.(Pellicciotti, Bauder, & Parola, 2010) Glacial mass gained in the 1960-70s, was subsequently lost at a logarithmic rate in alignment with climate warming, leading to increased runoff.(Pellicciotti et al., 2010; Christine

Steinlin et al., 2014)(P. Pavlova, 2014; Christine Steinlin et al., 2014) The closest town is Klosters-Serneus, which receives water from the entire Silvretta watershed. Fish from the Salmonidae family with a 4 % normalized lipid content were utilized by this case study and are of the species found in this region.(Froese, 2017) Researchers have found no difference in OCP concentration in meltwater streams below the terminus lake, characterizing the watershed as a region of PCB distribution and uptake.(Bizzotto, Villa, Vaj, et al., 2009) Silvretta glacial meltwater reaches the Rhine River after 20 km and deposits into Lake Constance after 100 km. This lake is Europe’s third largest lake and is used for both local and commercial fishing.

Fourteen meltwater samples taken at three locations (P5,P6,P7-Figure 5.1) in the glacial watershed during the summer months of two years were analyzed for 6 representative PCB congeners and characterize the peak glacial meltwater contribution to the watershed.(P. A. Pavlova et al., 2016) While the bulk water sample data for the proglacial stream (P5: 73 pg/L-Sept. 2013; 52 pg/L-Oct. 2013) and non-glacial stream (P6: 51 pg/L-Sept. 2013; 55 pg/L-Oct. 2013) are similar, samples from the mixed stream where glacial and non-glacial water sources combine (P7: 100 pg/L-Sept. 2013; 100 pg/L-Oct. 2013) show an elevated PCB concentration.(P. A. Pavlova et al., 2016; Christine Steinlin et al., 2016) Though these details are specific to the Silvretta watershed, data are within the observed range for PCB throughout the Alps.(Bogdal et al., 2010; Quadroni & Bettinetti, 2017; P Schmid et al., 2011; S. Villa et al., 2001)

The below glacier watershed encompasses a variety of potential PCB exposure routes including the consumption of water or fish, direct contact with the skin, inhalation, or through hereditary bioaccumulation (Figure 5.2, 5.3).((EPA), 1999; Adetona et al., 2013; Bergonzi et al., 2011a; G. Czub & McLachlan, 2004; Gertje Czub & McLachlan, 2004; Koopman-esseboom et al., 1994; Lignell et al., 2012; Matsuura et al., 2001; Vizcaino et al., 2014)

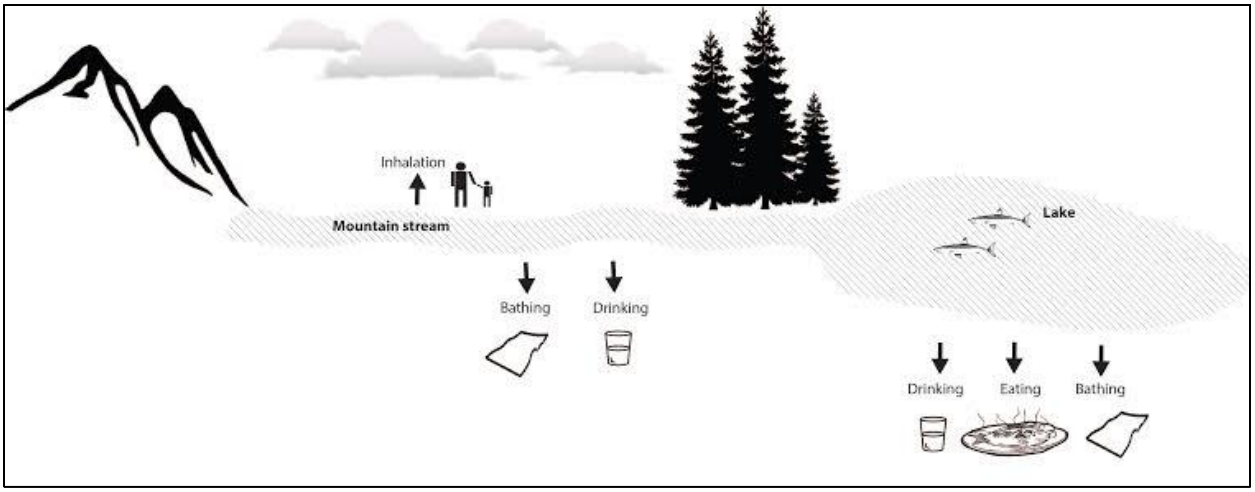

Figure 5.2 Conceptual model of potential PCB human uptake routes from glacial meltwater in the Silvretta proglacial watershed.

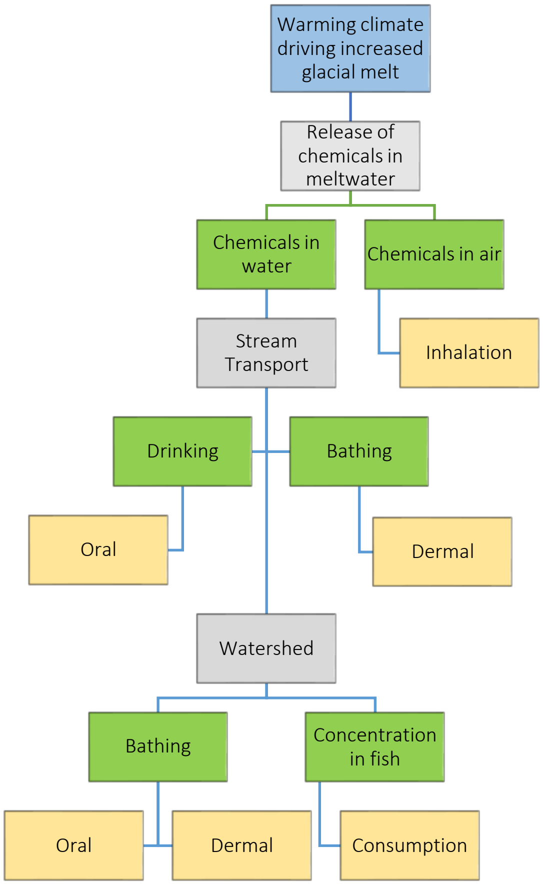

Figure 5.3 Conceptual model of potential PCB human uptake routes in the Silvretta proglacial watershed. Grey represents ecosystem transport routes of PCB, green represents human exposure sources and yellow represents the type of human exposure.

Compared to some industrial waterways such as the Hudson River, Silvretta Glacier meltwater exhibits relatively low concentrations of PCBs.((EPA), 2001a) Therefore, exposure through skin contact and inhalation posed extremely low risk in the conceptual model and was thus eliminated from the quantitative screening model. Within the Swiss Alps, high altitude, proglacial lakes immediately below the glacial terminus often contain fish, increasing the potential for bioaccumulation from surrounding media.((EPA), 2015; D Mackay & Patterson, 1990; Don Mackay et al., 2001; Ren et al., 2016; Peter Schmid et al., 2007) Such bioaccumulation in fish can increase PCB concentrations by up to 6 orders of magnitude that of the surrounding water.(Roberta Bettinetti et al., 2008; Kallenborn, 2006; Quadroni & Bettinetti, 2017; Peter Schmid et al., 2007) This magnification makes fish the greatest contributor of risk in the local environment.((EPA), 1999; E Dewailly, 2006) However, the Silvretta Glacier proglacial lake is frozen through in the winter and no fish reside there. Therefore, to best represent the high-risk scenario integrating fish consumption, we utilized concentration data from the lower watershed mixed stream (P7) that contains endemic Salmonidae fish and is fed by both glacial and non-glacial sources (Figure 5.1). We incorporated bioaccumulation factors developed for PCB uptake in salmonid species to estimate subsequent bioaccumulation rates.

To address potential fluctuation in yearly PCB meltwater concentrations, we took the average and upper limit values from sampled data. This allows for an understanding of the range of risk that may occur under a variety of glacial release scenarios. For this risk assessment, the upper limit PCB water concentration data was derived from the highest concentrations in the mixed stream bulk samples (100 pg/L) with the average concentrations determined using the mean of all mixed stream data (57 pg/L, averaged from 4 samples from 2012 and 2013). These concentrations were multiplied by a factor of 5 to account for the 30 representative congeners frequently found in the environment, and then extended to the entire year.(Glüge et al., 2017; P. A. Pavlova et al., 2016; Pavlina Aneva Pavlova et al., 2015; C. Steinlin et al., 2015)

5.2.2 Quantitative screening model

Our baseline multi-phase, linear screening level model determines if human risk from consumption of glacial meltwater or fish is high enough to necessitate analysis on an individual scale.((EPA), 1999, 2001c, 2003) Initial steps are predicated on retrieving PCB concentration data, determining human uptake pathways, doses and duration (Figure 5.4).((EPA), 1999)

We use the EPA Guidelines for Exposure Assessment and Framework for Cumulative Risk Assessment ((EPA), 1999, 2003, 2015) in combination with fish consumption data from the Switzerland Federal Statistical Office (SFSO) (Statistical Office, 2016, 2017) and bioaccumulation factors from the California Office on Environmental and Health Hazard Assessment (OEHHA). These bioaccumulation factors calibrate chemical uptake in fish utilizing the mean percentage of muscle lipid tissue, chemical species and characterization of surrounding media (see Supplemental Information: Risk assessment model layout for additional model parameters).((EPA), 2016a; D Mackay & Patterson, 1990; Office of Environmental Health Hazard Assessment, 2012) Fish species native and endemic to Switzerland include numerous members of the Salmonidae family, a fish frequently used for consumption and also utilized by the OEHHA for calibration.(Froese, 2017) SFSO statistics indicate that the mean domestic fish consumption for Swiss residents is 6% (0.0013kg/day) of total annual fish consumption (0.022 kg/day).(Statistical Office, 2017) Domestic fish are generally found in river and lakes with inputs of a mixture of snow, rain and glacial meltwater, similar to the mixed stream from which we derive concentration data. This allows us to use the Silvretta watershed as an initial case study for a model that can be applied to similar sized glaciers.

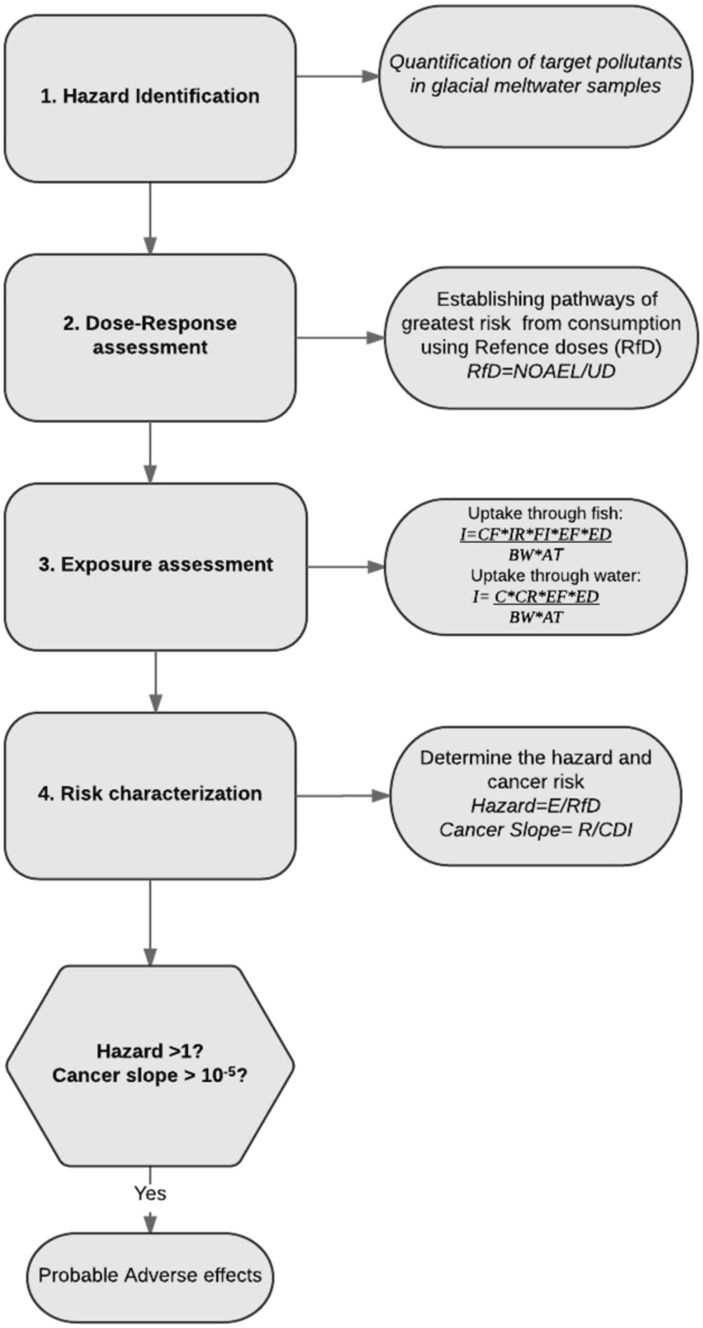

Figure 5.4 Flow diagram of EPA quantitative screening model risk assessment methodology adapted from Zhai et al. 2017.

Human population residence time, water consumption and body weight are standardized in the EPA methodology based upon population averages.((EPA), n.d., 1999, 2005; Phillips & Moya, 2013) The EPA Integrated Risk Information System (IRIS) is used to determine the cancer and non-cancer risk.((EPA), 2017) For children, the model assumes lifetime (70 year) consumption of glacial meltwater and domestic fish, whereas for adults, a 30-year timeframe is standard.

5.2.3 System uncertainty

Uncertainty in the screening model is predominantly based upon the model reliance on population level consumption rates and the extrapolation of PCB concentration data across multiple months. Uncertainty is both natural and inherent to the fluctuations in glacial melt and local hydrology, as well as specific to model parameters and variables.

Glacial meltwater concentration data is based upon published concentrations at peak summer glacial melt for multiple years, but then all known concentrations have been averaged to gain a representative understanding of standardized concentration, such as might be found in a downstream lake, over time. Peak concentration rates are also considered, to represent the potential for an increased or tertiary chemical release under continuing climate warming scenarios. Inherent natural uncertainty exists both within the seasonal fluctuations of glacial melt as well as the spatial distribution of pollutants within the glacier. We attempt to offset some of this uncertainty by utilizing available concentrations that most closely mirror watershed input from glacial and non-glacial sources that could be found in local lakes and streams. In addition, the inherent variability of the linked glacial-atmospheric system leads to the possibility of non-linear melt over an abbreviated period that could increase variability of chemical concentration within the watershed.

In addition to the complications of modeling glacial OCP distribution, the application of a screening-level model that does not utilize individual consumption, body weight or lifetime data but instead uses the population mean requires certain assumptions. For this linear model we utilize consumption, body weight and exposure duration data that take the population mean, in line with the established EPA methodology.((EPA), n.d., 2001b) Though not specific to individuals, standardized consumption rates for fish and water are considered typical for screening level risk assessments, and are put forward by the EPA and refined by country statistics.((EPA), 1999, 2001b) These values may not adequately represent the natural biological variation in individuals, or represent vulnerable populations with greater susceptibility.(Frey, 1992; Gallagher et al., 2015) To this end, it is appropriate that the results of this screening model be viewed as an indication of the need for further study if standard thresholds are breached. Fluctuations in fish and water consumption can occur on a generational timescale and indicate the need for additional screening. Recent studies of PCBs in glacially derived water sources from the Italian Alps have identified bioaccumulation in fish with potential health risks from subsequent consumption in local populations.(R. Bettinetti et al., 2016) Our study mirrors these findings while integrating human consumption dynamics on a population scale.

5.3. Results

5.3.1 Drinking water

In all iterations of the model, the risk from oral uptake of glacial water, even with lifetime consumption, is low (Table 5.1). Risk from consumption of meltwater is up to 4 orders of magnitude below screening level, suggesting insignificant risk within any timeframe. While the risk to children is marginally higher than the risk to adults, it is still below the screening level.

This suggests that risk from ingestion of PCBs in glacial meltwater is negligible across uptake periods and body sizes.

Point Estimate Cancer Risk Summary, median fish consumption				
Pathway	**Cancer Median Risk**	**Cancer Highest Risk**	**NC Median Risk**	**NC Highest Risk**
Fish Consumption				
Adult	**2.1×10^{-5}**	**3.7×10^{-5}**	0.23	0.41
Child	**7.3×10^{-5}**	**1.3×10^{-4}**	0.8	**1.4**
Water Consumption				
Adult	6.9×10^{-9}	1.2×10^{-8}	7.6×10^{-5}	1.3×10^{-4}
Child	3.9×10^{-8}	7.0×10^{-8}	4.3×10^{-4}	7.7×10^{-4}
Both Pathways				
Adult	**2.1×10^{-5}**	**3.7×10^{-5}**	0.23	0.41
Child	**7.3×10^{-5}**	**1.3×10^{-4}**	0.8	**1.5**

Table 5.1 Cancer and Non-Cancer Risk Summary for 6% annual domestic Swiss fish consumption (population average- 0.0013 kg/day). Mixed stream (P7) data is for both the average (2.8×10^{-7} ng/L) and upper limit (5.0×10^{-7} ng/L) PCB concentration. Threshold for risk is 1 in non-cancer (NC) screening and 1×10^{-5} in cancer screening, with numbers over threshold indicated in bold

5.3.2 Fish consumption

Fish consumption is the main driver of risk for both children and adults. It contributes the greatest risk for long term cancer and non-cancer risk, assuming continued consumption over time. For children consuming domestic fish as 6% of their yearly fish consumption, or 0.0013 kg/day,(Statistical Office, 2017) out of water with a mean adjusted PCB concentration of 286 pg/L, cancer risks are just above acceptable cancer screening level, indicating potential risk and the need for further assessment at an individual level. Increasing the PCB concentration to the upper limit concentration of 500 pg/L, and holding fish consumption steady, cancer risk is above the screening level, with hazard risk also indicated (Table 5.1).

For adults with the mean fish consumption rate of 0.0013 kg/day and mean adjusted PCB concentration in meltwater of 285 pg/L, cancer risk is just above acceptable screening level for cancer, and below the non-cancer screening level, indicating minimal risk and that further study may not be necessary. Increasing PCB concentration values to 500 pg/L, adults remain slightly above the cancer screening level and below non-cancer values (Table 1).

The model shows that even within a population level analysis of glacial meltwater risk, secondary emission of PCBs from glacial sources, even with the addition of non-glacial sources, may lead to previously unexplored risks to human health. While the thresholds used by the EPA model are not indicative of direct cancer rates, they indicate the need for individual-level data analysis on uptake routes, quantities of fish consumption and lifetime risk factors.

5.4. Discussion

5.4.1 Drinking water

Due to its proximity to pollution sources and high concentration of toxic PCBs, Silvretta Glacier represents a near endmember scenario for OCP reemission in glacial meltwater, representing the highest potential for risk to humans. However, we show that the human risk from consumption of only water from the glaciated watershed is negligible in both adults and children. Locations with very low glacial OCP concentrations such as the Arctic could be expected to have even less risk from drinking glacial meltwater. Therefore, both our exposure and screening level model suggests that in the northern hemisphere the impact of drinking glacial meltwater containing OCPs is insignificant in any timeframe. Future work on OCP concentrations should focus on Southern Hemisphere glaciers in a state of ablation and in regions proximal to pollution sources.

5.4.2 Fish consumption

While fish consumption rates are low in Switzerland, our model suggests caution must be exercised by populations that frequently consume fish from glacial watersheds, due to the high potential for bioaccumulation. The toxicity and bioaccumulation potential of PCBs make the chemical class a specific concern for biomagnification in large and long lived species.(G. Czub & McLachlan, 2004; Office of Environmental Health Hazard Assessment, 2012) While these concentrations are significantly lower than those seen in industrial watersheds, the addition of glacially derived chemicals to the system may increase the risk of cancer and non-cancer impacts in resident populations. Populations that rely on fish consumption from glaciated watersheds to meet their energy needs, including indigenous populations in Arctic, may have proportionally higher risk and should be assessed individually. With increasing glacial ice melt, the release of OCPs may fluctuate or increase within glacial meltwater. Risk can be minimized on a local level in some situations by decreasing fish consumption from watersheds of concern.

5.4.3 Glacial modeling assumptions

Application of the risk assessment methodology to a glacial system requires an understanding of glacial morphology, watershed structure, and human uptake rates and routes.(Bogdal et al., 2010; Grannas et al., 2013a) Glacial ice, firn and snow all represent water contained in reservoirs with respectively decreasing residence and melt timeframes with OCP storage capacity. (Cuffey & Patterson, 2010; Davidson et al., 2003; Jansson et al., 2003) Warming temperatures and changes in precipitation type can increase glacial melt and opportunities for downstream OCP distribution.(Cuffey & Patterson, 2010; Hock, 2003; Hooke, 2005; Jansson et al., 2003) The length, thickness and response rate of a glacier directly impacts when pollutant release will occur. Complications in modeling future release of pollutants from glaciers emerge from unknown rates of glacier melt, making it difficult to temporally constrain anticipated chemical release.(Farinotti et al., 2009; McNeill et al., 2012; Christine Steinlin et al., 2016) Therefore, variability in glacial melt over time limits the ability to predict future OCP concentrations accurately across all glaciers. This increases uncertainty within the models and presents challenges in developing risk assessments that anticipate future concentrations.

We minimized the uncertainty within this variability by utilizing both the highest sampled concentrations and average PCB concentrations from 2 different sampling techniques taken over two years. This allowed us to identify the median and end member pollution scenarios that may be developing within glaciated systems. These values reflect the magnitude of all PCB concentration data taken across the Alps range that integrate numerous sampling months and years. While glacial melt may not occur year-round in some ecosystems, bioaccumulation in fish will reflect long term concentrations, which are growing steadily in some glacial watersheds. The possibility of non-linear glacial melt, not represented by this model, is a consideration that may require further research.(Jansson et al., 2003)

While this risk assessment incorporates PCB uptake, additional chemicals not investigated here, but resident in glacial meltwater from similar watersheds, may increase risk. For example, samples taken from glaciers in the Italian Alps have identified the presence of hexachlorobenzene (HCB), hexachlorahexene (HCH), dichlorodiphenyltrichloroethane (DDT) and current use pesticides.(Ferrario et al., 2017; Sara Villa, Negrelli, Finizio, et al., 2006; Sara Villa et al., 2003; Wu et al., 2017) Adding multiple chemicals to a risk assessment model may increase the risk above screening level. The combination of variable glacial flow rates and unprecedented warming may continue to add unforeseen variables that will need to be monitored. Although the cancer risk from consumption of OCPs released during glacial melt is not comparable to more heavily polluted industrial waterways, long-term risk may exist. Further monitoring of new inputs and residual concentrations will ensure the health of residents and visitors to these systems.

Since the passage of the Stockholm Convention in 2004, environmental levels of PCBs (and many OCPs) are decreasing in the environment. The efficacy of this convention agreement is clear and human exposure can be expected to decrease. In selected glacial watersheds, the release of OCPs from melting glaciers may however counteract the overall trend towards OCP reduction in the environment and must be investigated further.

CHAPTER 6.

APPLYING A QUANTITATIVE SCREENING LEVEL ASSESSMENT OF HUMAN RISK FROM PERSISTENT ORGANIC POLLUTANTS IN GLACIAL MELTWATER: LYS GLACIER, ITALY

6.1 Introduction

Beginning in the 1940’s the use of organochlorine pollutants (OCPs) in industry and agriculture expanded globally.(Programme, Environment, 2004) Expansion through the environment and high bioaccumulation rates have made OCPs ubiquitous in ecosystems.(Shen et al., 2005; Simonich & Hites, 1995) OCPs have been found in glacial ice core and meltwater samples across the northern hemisphere, with the greatest concentrations in the Swiss and Italian Alps.(Jules M Blais et al., 2001; Ferrario et al., 2017; P. A. Pavlova et al., 2016; Sara Villa et al., 2003; Xiao ping Wang, Xu, et al., 2008) These toxic compounds can be a health risk to humans at low levels, necessitating a risk assessment of secondary emission from glaciers.(Birnbaum, 2013; Lee et al., 2014; Vizcaino et al., 2014) Risk to humans from OCPs is significant due to their lipid-binding preference, potential for direct uptake from surrounding media, high residence time and bioaccumulation rates.((EPA), 2002; Gertje Czub & McLachlan, 2004) A small dose of these OCPs can be detrimental, and the threshold for safe uptake in humans is higher for adults than for children.((EPA), 2016b; Birnbaum, 2013) Dose thresholds also decrease with bioaccumulation via tissue ingestion or placental transfer, increasing potential for exposure in the second generation.(Adetona et al., 2013; Bergonzi et al., 2011b; Dassanayake, 2014) Applying an established risk assessment model to multiple glaciated watersheds will determine whether pollutants contained within glacial meltwater are above the risk screening level for humans.

Previous research (K. R. Miner et al., 2018) has assessed screening level risk from polychlorinated biphenyls (PCBs) in the Swiss Silvretta Glacier, providing an indication of a 95% risk scenario for this chemical. Here, we seek to expand our risk assessment profile of glacial meltwater samples taken in the Italian Alps that identified the presence of organochlorine pesticides Dichlorodiphenyltrichloroethane (DDT) and Hexachlorobenzene (HCB). Utilizing known concentrations in glacial meltwater from multiple years of sampling studies at the Lys Glacier in Italy, we apply the US Environmental Protection Agency screening assessment to identify the cancer and non-cancer impacts of consuming glacial meltwater and local fish over lifetime exposure for both children and adults.((EPA), 1999, 2001b, 2003; Bizzotto, Villa, Vaj, et al., 2009; Ferrario et al., 2017; Sara Villa, Negrelli, Finizio, et al., 2006)

6.2 Methods

6.2.1 Lys Glacier

Lys glacier is a cold glacier in the Monte Rosa Massif in the Western Alps of Italy (Figure 6.1). It is debris-covered, with an area of 9 km^2 and an altitude of 4250m a.s.l. and is emergent from the larger Monte Rosa group.(Smiraglia et al., 2006; Sara Villa, Negrelli, Finizio, et al., 2006; Sara Villa, Negrelli, Maggi, et al., 2006; WGMS, 2015) It is the 4th largest Italian glacier and has mass balance records detailing volume and thickness changes for the past 30 years.(Smiraglia et al., 2006) During that time, over 10% of ice area was lost and significant retreat is ongoing with increasing rapidity.(Smiraglia et al., 2006) Consistent ablation may result in loss of reservoir OCPs over time.(Christine Steinlin et al., 2014) Mountain huts are located alongside the glacier and are staffed up to 9 months of the year with cable car access driving tourist influx. Below the glacier, the Lys stream converges with the larger Dora Baltea River watershed. There are four towns immediately below glacier, Staffal, Tache, Tschemenoal and Gressony-Saint-Jean, and numerous resorts with populations fluctuating seasonally.

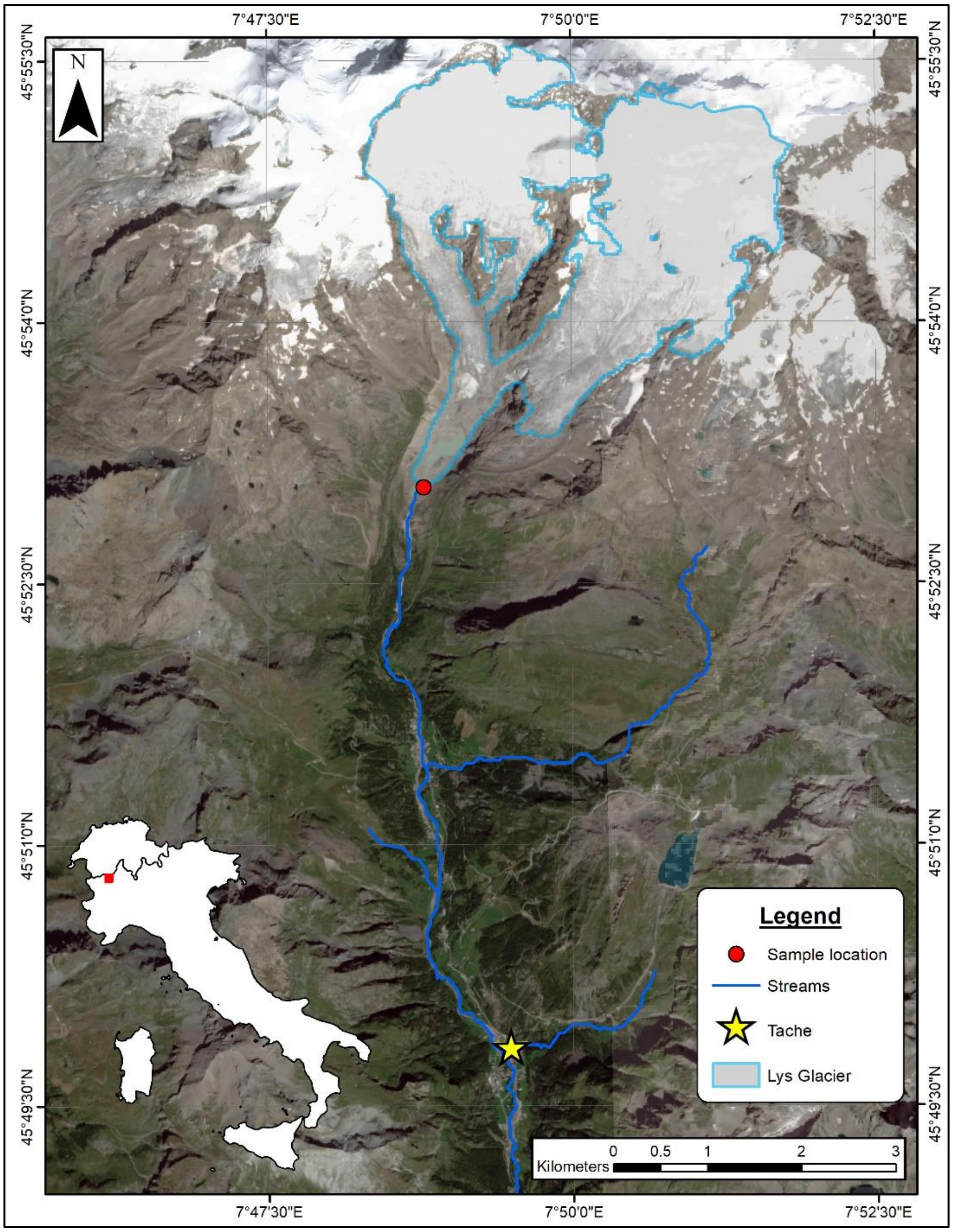

Figure 6.1 Map of Lys glacier in the Italian Alps including proglacial watershed. Sampling location indicated in red and the town of Tache indicated in yellow.

Researchers at the University Milan have analyzed meltwater and ice cores from the Lys glacier for over 15 years, representing the longest analysis of glacial OCP concentrations available.(Bizzotto, Villa, Vaj, et al., 2009; Ferrario et al., 2017; S. Villa et al., 2001; Sara Villa, Negrelli, Maggi, et al., 2006; Sara Villa et al., 2003) Numerous compounds were studied by this research group including both DDT and HCB.(Sara Villa, Vighi, & Finizio, 2014) Areas of pesticide use are relatively proximal to glacier sites in the Alps, with inputs thought to be sourced from Northern Italy.(Bergonzi et al., 2011b; Roberta Bettinetti et al., 2011; Sara Villa, Vighi, & Finizio, 2014)

Beginning in 2000, meltwater concentration data was collected monthly during summer peak glacial melt.(Ferrario et al., 2017; Sara Villa, Negrelli, Finizio, et al., 2006) Additional samples were added most recently in 2014.(Ferrario et al., 2017) For this assessment, peak sample concentrations established the upper concentration limit (DDT- 0.33 ng/L; HCB- 0.03 ng/L), and average concentrations were developed by taking the mean of all data (DDT- 0.16ng/L; HCB- 0.028 ng/L). While these concentrations are relatively low compared to industrial waterways, they represent some of the highest chemicals concentrations found in glacial meltwater. (Miner et al., 2017)

The model background has been previously described in Miner et al., and utilizes the EPA Guidelines for Exposure Assessment and Framework for Cumulative Risk Assessment (Figure 6.2).((EPA), 1999, 2001b, 2003) Toxicant cancer slope and non-cancer hazard rates were taken from published EPA Integrated Risk Information System (IRIS) data and applied to the known OCP concentration data.(Ferrario et al., 2017) Fish consumption rates were taken from the European Union’s Expofacts database, which regularly completes census analysis of fish consumption on a national level, and was updated in 2016.(Joint Research Centre, 2016) Fish bioaccumulation data for DDT was taken from the EPA database of bioaccumulation factors, and from the California Office of Environmental Health Hazard Assessment (OEHHA) for HCB.((EPA), 2015; Office of Environmental Health Hazard Assessment, 2012) All bioaccumulation factors incorporate similar data for fish size and chemical uptake rates.

6.3 Results

6.3.1 Drinking water

Drinking water contamination from DDT and HCB released by Lys glacier is not a risk to children or adults. Modeled cancer risk is significantly below the threshold for both adults and children. A slightly higher risk is indicated for children due to smaller body size and lifetime exposure. The non-cancer impacts are also below threshold level for both children and adults, indicating no disease risk from secondary uptake of DDT or HCB. The greatest risk observed is 4 orders of magnitude below screening level, suggesting that drinking glacial meltwater will not be a risk under any scenario. While additional output of chemicals from Lys glacier may increase the concentration downstream, a significant concentration increase would be necessary to move either the child or adult population over the screening level threshold. This finding is in line with our results from the Silvretta Glacier in Switzerland, another example of a high-risk watershed in the Alps.

6.3.2 Fish consumption

Bioaccumulation can concentrate OCPs in fish by up to 6 orders of magnitude. (cite EPA) As a result, these concentrations make fish consumption the most significant contributor to human risk. For children with a lifetime consumption (70 years) of 0.0043 kg/day domestic fish at both the mean and upper limit concentration for DDT, cancer and non-cancer risk are up to 4 orders of magnitude below thresholds (Table 6.1). HCB risk is lower, with risk up to 7 orders of magnitude below cancer screening level.

Screening Level Cancer Risk Summary- Sum

Pathway	Cancer Median Risk	Cancer Highest Risk	NC Median Risk	NC Highest Risk
Fish Consumption				
Adult	2.5×10^{-7}	1.4×10^{-6}	1.6×10^{-2}	8.4×10^{-2}
Child	5.5×10^{-6}	7.0×10^{-6}	0.5	0.61
Water Consumption				
Adult	6.2×10^{-10}	7.3×10^{-10}	6.9×10^{-6}	1.4×10^{-5}
Child	2.3×10^{-9}	2.8×10^{-9}	2.7×10^{-5}	5.3×10^{-5}
Both Pathways				
Adult	2.5×10^{-7}	4.3×10^{-7}	1.6×10^{-2}	3.2×10^{-2}
Child	1.4×10^{-6}	2.3×10^{-6}	8.5×10^{-2}	0.17

Table 6.1 Cancer and Non-Cancer Risk for fish and glacial water with the sum of all OCP concentrations studied, at both the average chemical concentration and greatest observed concentration. Threshold for risk is 1 in non-cancer screening and 1×10^{-5} in cancer screening

For adults who have consumed fish for 30-years at the average rate of 0.0043 kg/day, under both the upper limit and mean DDT concentration, cancer and non-cancer risk is up to 5 orders of magnitude below screening level (Table 6.1). HCB cancer risk is again lower, with risk 8 orders of magnitude below screening level.

Therefore, the impact of DDT and HCB in glacial meltwater from Lys Glacier is negligible for populations either drinking meltwater or eating local fish. Of these two pesticides, DDT concentrations are greater than HCB, leading to relatively higher, but still minimal, risk. Adding the cumulative impact of both compounds does not increase uptake above screening levels, suggesting that these OCPs do not pose a health risk, even to the 95th percentile, or high-risk, consumer (Table 6.1-6.3).

Screening Level Cancer Risk Summary- DDT				
Pathway	**Cancer Median Risk**	**Cancer Highest Risk**	**NC Median Risk**	**NC Highest Risk**
Fish Consumption				
Adult	1.6×10^{-7}	3.2×10^{-7}	1.5×10^{-2}	3.2×10^{-2}
Child	8.6×10^{-7}	1.8×10^{-6}	8.4×10^{-2}	0.17
Water Consumption				
Adult	6.7×10^{-11}	1.4×10^{-10}	6.5×10^{-6}	1.3×10^{-5}
Child	2.5×10^{-10}	5.2×10^{-10}	2.5×10^{-5}	5.1×10^{-5}
Both Pathways				
Adult	1.6×10^{-7}	3.3×10^{-7}	1.5×10^{-2}	3.2×10^{-2}
Child	8.6×10^{-7}	1.8×10^{-6}	8.4×10^{-2}	0.17

Table 6.2 Cancer and Non-Cancer Risk for fish and glacial water for ΣDDT concentrations studied, at both the average chemical concentration and greatest observed concentration. Threshold for risk is 1 in non-cancer screening and 1×10^{-5} in cancer screening.

Screening Level Cancer Risk Summary- HCB				
Pathway	**Cancer Median Risk**	**Cancer Highest Risk**	**NC Median Risk**	**NC Highest Risk**
Fish Consumption				
Adult	9.4×10^{-8}	1.0×10^{-7}	7.4×10^{-5}	7.9×10^{-5}
Child	5.1×10^{-7}	5.5×10^{-7}	4.0×10^{-4}	4.3×10^{-4}
Water Consumption				
Adult	5.5×10^{-10}	5.9×10^{-10}	4.3×10^{-7}	4.6×10^{-7}
Child	2.1×10^{-9}	2.2×10^{-9}	1.6×10^{-6}	1.8×10^{-6}
Both Pathways				
Adult	9.5×10^{-8}	1.0×10^{-7}	7.4×10^{-5}	7.9×10^{-5}
Child	5.2×10^{-7}	5.5×10^{-7}	4.0×10^{-4}	4.3×10^{-4}

Table 6.3 Cancer and Non-Cancer Risk for fish and glacial water for HCB concentrations studied, at both the average chemical concentration and greatest observed concentration. Threshold for risk is 1 in non-cancer screening and 1×10^{-5} in cancer screening.

6.4 Discussion

Our assessment indicates minimal risk to populations from glacial dispersal of DDT and HCB pollution in the Lys watershed. These results contrast with earlier application of the risk assessment model analyzing PCB uptake in Switzerland (K.R. Miner, 2018) that identified risk from PCBs to children with long term local fish consumption. While all available data was utilized by our study, the lower toxicity and bioaccumulation rates of DDT and HCB as compared with PCB results in reduced risk with similar consumption patterns.((EPA), 2001a, 2015, 2016a) Recent meltwater sampling completed at the Lys Glacier included two PCB samples but additional data will be needed to complete a risk assessment of this compound.(Ferrario et al., 2017) Preliminary sampling at Lys glacier suggests potentially high concentrations of PCBs, much like other Alpen glaciers. When added to the other OCPs assessed in this model, PCBs may increase risk above the acceptable screening level. For this reason, further sampling is necessary before a comprehensive analysis of risk from polluted glacial meltwater can be fully assessed.

Such additional sampling of PCB and current use chemicals over multiple years will give a better understanding of cumulative human health risk.

Sources of PCBs and ΣDDT in these watersheds are not exclusively glacial, but the addition of reemitted glacially derived compounds may increase risk to residents. Recent studies assessing the concentration of both PCB and ΣDDT in fish from the Lago di Como Agone in Italy, 220 km away, suggest that the addition of PCB may increase human risk from fish consumption past the screening level threshold. (Quadroni & Bettinetti, 2017) Though lakes have the potential for dilution effect, concentrations in sampled fish tissue were found to be of potential risk to humans within certain consumption frequencies.(Quadroni & Bettinetti, 2017) These results suggest that not only that OCPs are ubiquitous in glacial watersheds, but that the addition of PCBs to an assessment model may significantly increase risk.

6.5 Conclusions

We found that the concentrations of DDT and HCB emitted from the Lys Glacier in Italy would not have a detrimental effect on human populations eating local fish or drinking glacial meltwater. While these compounds are two of the OCPs found in glacial meltwater, there may be additional legacy or current use compounds that need to be incorporated into future risk assessments. It is also possible that increased fish consumption would make the concentrations in Lys Glacier a risk for human consumption. Identifying all sources and concentrations of OCPs in glacial meltwater would provide a more comprehensive risk profile and should be accomplished at the regional level.

CHAPTER 7.

A SCREENING LEVEL APROACH TO QUANTIFYING RISK FROM GLACIAL RELEASE OF ORGANOCHLORINE POLLUTANTS IN THE ALASKAN ARCTIC

7. 1 Introduction

Atmospheric mobility and compound volatility has made organochlorine pollutants (OCPs) ubiquitous in the environment.(Jiménez et al., 2015; Shen et al., 2005; Simonich & Hites, 1995) Sorbed to snow and rain, OCPs have been directly deposited onto and entrained into glaciers where they have been stored for the last 60-70 years. (Bogdal et al., 2009; Lei & Wania, 2004; C. Steinlin et al., 2015; Christine Steinlin et al., 2016) Subsequent secondary emission of OCPs from melting glaciers can impact the downstream human populations who consume glacial meltwater and local fish.(Jules M Blais et al., 2001; K. R. Miner et al., 2018; Quadroni & Bettinetti, 2017) Within Arctic regions that include Canada, Norway and Alaska, OCPs have been found in glacial ice cores, firn and snow samples, and in meltwater, yet no assessment of glacial meltwater pollution risk has been completed for Interior Arctic communities. (C. L. Friedman & Selin, 2016; Garmash et al., 2013; Hauptmann et al., 2017; Helm et al., 2002; Hermanson et al., 2005; Kwok et al., 2013; K. R. Miner et al., 2018) Potential implications of OCP exposure include developmental, neurologic, and physiological impacts in the primary and secondary generation.(Birnbaum, 2013; Gauthier et al., 2014; Lee et al., 2014; Rubin et al., 2006; Ruzzin, 2012; Vizcaino et al., 2014)

Our goal is to produce the first risk assessment of organochlorine pollution from glacial meltwater in the Arctic. We utilize OCP data from recent ice core and meltwater sampling campaigns at the Jarvis Glacier in the Interior Alaskan Range, and Tanana watershed dynamics(Liljedahl et al., 2017) integrated with self-reported fish consumption from local subsistence communities.(Ballew et al., 2004) Our risk assessment has been applied in the Swiss Alps, however, the elevated fishing consumption rates may put subsistence communities in Alaska at greater risk from glacial meltwater pollution. Therefore, the purpose of this research is to accomplish a first order analysis of the potential for human impacts from OCPs in glacial meltwater within the Tanana watershed as glacier melt continues. This case study is intended to serve as a screening level assessment of the potential for increased bioaccumulation and toxicity from the glacial reemission of OCPs over time. Ultimately, we aim to provide guidance on whether further human risk assessment is warranted.

7.2 Methods

7.2.1 Jarvis Creek and watershed hydrology

Jarvis Glacier (6 km^2) is a temperate glacier in Alaska's Eastern Range. The glacier is in a state of negative mass balance with an average yearly loss of -3.0 mwe.(Liljedahl et al., 2017) Jarvis Creek is a small tributary to the Tanana River (113,960 km^2), which subsequently flows into the much larger Yukon watershed (Figure 7.1).(Flowers & Clarke, 2002; Liljedahl et al., 2017) The Jarvis glacier is one of multiple potential sources of OCP input to the system, which includes numerous glaciers, direct snow, and rain deposition. However, glacial melt is an increasing contributor and water table records beginning in 1907 identify an increase in Tanana River runoff, with growing input over the last 5 years.(Liljedahl et al., 2017) The Tanana River sources up to 60% of its annual streamflow from glacial melt, with melt continually increasing in glaciers throughout due to atmospheric warming.(Gatesman, 2017; Michael Zemp et al., 2015)

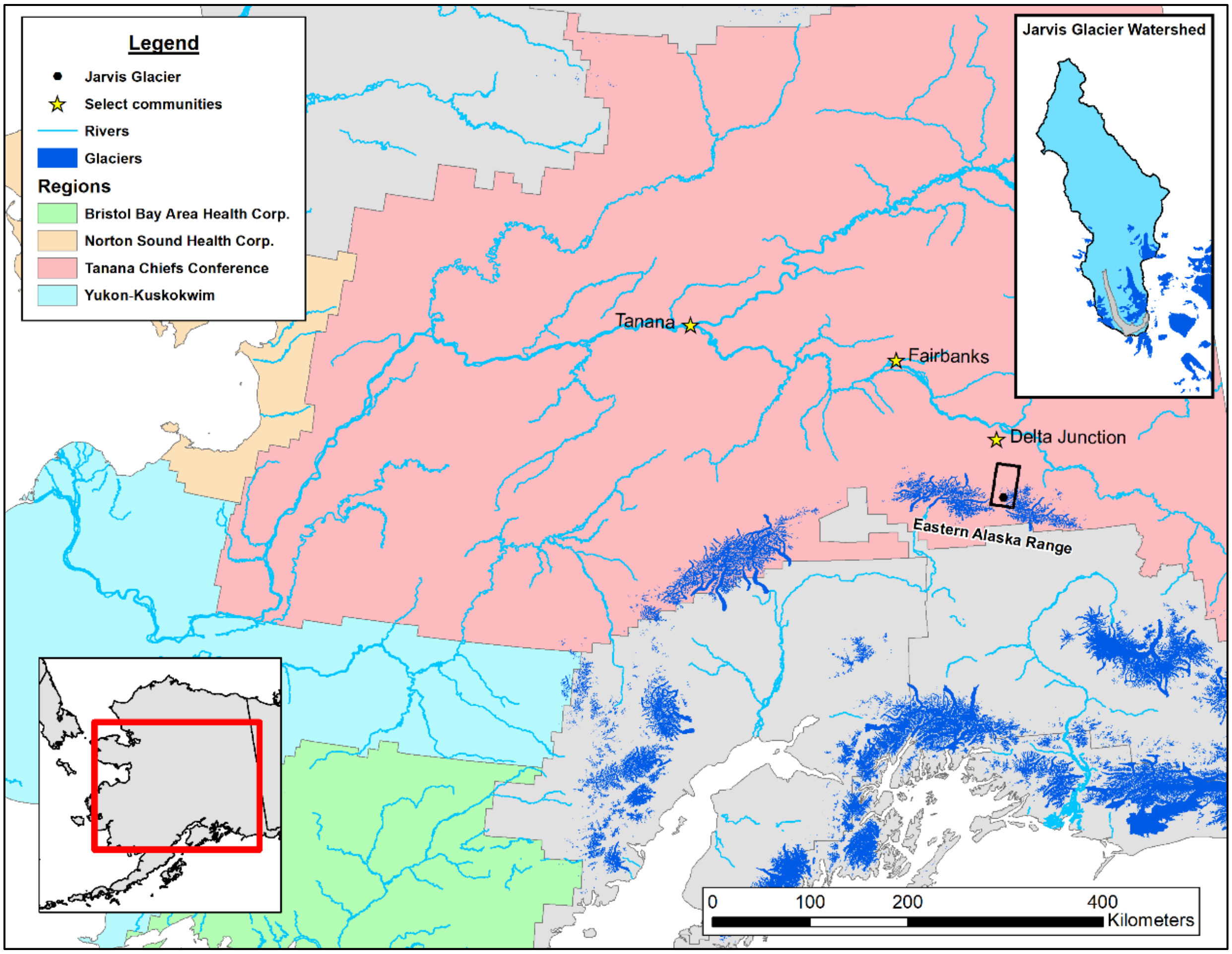

Figure 7.1 Tanana Chiefs Conference Region with the Eastern Alaska Range and Jarvis Glacier Watershed identified. The Tanana Chiefs region is identified in pink, with neighboring subsistence corporation boundaries also identified for reference. The watershed emerging from the Eastern Alaska Range flows east to west.

7.2.2 Tanana River watershed demographics

In the watershed directly below Jarvis Glacier there is minimal fish harvesting and no subsistence-based groups. However, 1,655 subsistence families reside in the larger Yukon interior region and 508 families live within the Tanana River watershed (Figure 7.1).(Ballew et al., 2004; Fall et al., 2013) The Tanana Chiefs Conference Region is the nearest subsistence region with fish consumption data available,(Ballew et al., 2004) though consumption rates are some of the lowest in the region (Table 1,2). As this region is also downstream of Jarvis Glacier, it provides the most applicable screening level consumption data for the Jarvis Glacier watershed. While inputs from multiple glaciers, direct snow, and rain deposition may change the OCP glacial signal, we make the assumption that increased glacial melt throughout the region over time may raise the overall OCP concentration in the watershed.(R. Bettinetti et al., 2016; Quadroni & Bettinetti, 2017)

7.2.3 Jarvis watershed OCP data

Glacial ice core and meltwater samples were collected at Jarvis Glacier over the summer of 2016 and spring of 2017 by joint teams from the University of Maine and the University of Alaska at Fairbanks. Jarvis Creek is predominantly glacier fed and contributes to the Tanana River watershed below. Testing identified the presence of the pesticides DDT, ‘p,’p-DDE, ‘p,’p-DDD, α-HCH and ϒ-HCH, (heretofore referred to as ΣDDT and ΣHCH). ΣDDT had the highest concentration and was present in glacial meltwater throughout peak summer glacial melt in June-September (CITE self). These values are the first record of OCPs entrained within glaciers in the interior of Alaska and serve as an index for this study

7.2.4 Quantitative screening model

For this study, we utilized the upper limit and average sample concentrations of DDT (upper limit:1.12 ng/L, average:0.61 ng/L*)* α-HCH (upper limit:0.34 ng/L, average:0.23 ng/L) and ϒ-HCH (upper limit:0.53 ng/L, average:0.34 ng/L) taken from Jarvis Creek (Figure 7.1). We utilize Jarvis Glacier OCP concentrations to gain an idea of the potential watershed input, integrating the average and upper limit concentrations to account for variability. We utilized the conceptual model and quantitative screening level risk assessment developed previously, with adjusted inputs for the Jarvis Creek and Tanana River watersheds.(K. R. Miner et al., 2018)

The risk assessment is based on the Environmental Protection Agency (EPA) Guidelines for Exposure Assessment and Framework for cumulative risk assessment ((EPA), 1999, 2015) and fish consumption data from the Traditional Diet Survey(Hamade & Consumption, 2014) conducted by the Alaskan Department of Health and Human Services for the Tanana Region. This region was noted to have one of the lowest fish consumption levels in Interior Alaska, but it is still above the national average making their potential risk, 1-2 orders of magnitude lower than surrounding subsistence communities (Table 7.1). (Ballew et al., 2004; Epidemiology, 2014; Fall et al., 2013; Hamade & Consumption, 2014) Therefore these consumption numbers are applied to the risk assessment as an indicator of moderate risk for subsistence communities in the Eastern Alaskan region. While the Tanana Chiefs community does not reside directly below glacier, we utilize this data in this screening study as a representative consumption measurement based on available data and the assumption that similar OCP concentrations are likely to be found in glaciers throughout the range.

Population Reporting	**Participants**	**Median Consumption (lb/yr)**	**Maximum Consumption (lb/yr)**	**Median (g/day)**
Norton Sound Health Corp.	151	63	1886	47
Yukon-Kuskokwim Health Corp.	224	55	2814	68
Bristol Bay Area Health Corp.	134	61	3420	76
Tanana Chiefs Conference Region	**33**	**26**	**195**	**32**
SE Alaska Health Corp. Region	125	39	1100	49

Table 7.1 Subsistence Fish Consumption by Alaskan region. Tanana Chiefs Conference Region has the lowest median fish consumption from the groups sampled. All data is self-reported by tribal corporation members. Full data including species consumed included in supplemental information.(Ballew et al., 2004)

Bioaccumulation factors were taken from the EPA database for DDT and from the California Office on Environmental and Health Hazard Assessment (OEHHA) for HCH.((EPA), 2016a; Office of Environmental Health Hazard Assessment, 2012) These bioaccumulation factors calibrate fish data in accordance with environmental fate models by specific chemical concentrations, chemical type and fish species.((EPA), 2016a; D Mackay & Patterson, 1990; Donald Mackay, 2001; Office of Environmental Health Hazard Assessment, 2012) For this assessment, we utilized bioaccumulation models for Salmonid species interacting with DDT as it is the species most commonly utilized by the interior communities. Cancer slope factors and non-cancer reference doses are calculated by the EPA's Integrated Risk Information System (IRIS).((EPA), 2017) Residence time, water consumption, and body weight are standardized based upon population averages in the EPA methodology.((EPA), n.d., 1999, 2005; Phillips & Moya, 2013) Timeframe for uptake under the model assumes a consistent lifetime (70 years) consumption rate for children, and an abbreviated period for adults (30 years). Body weight for children in this study was standardized at 30 kg and adult weight at 70 kg in accordance with EPA standards.((EPA), 1999, 2001b)

7.2.5 Uncertainty analysis

Uncertainty as natural variability exists in the model in the form of glacier interaction with the atmosphere and subsequent melt patterns, spatiotemporal location and release of DDT, and watershed fluctuations in concentration. As the meltwater sampled from below Jarvis Glacier(K. Miner et al., 2018) gives a representative profile of peak melt in one year, it does not account for the overall release of Jarvis and other glaciers in the range. In addition, natural processes throughout the watershed such as sedimentation and volatilization may vary the concentration over a distance. Another source of variability lies within the individual fish consumption rates. While this study utilizes the median consumption rates of the closest subsistence community, individuals within that group may show significant variability (Table 7.2).(Ballew et al., 2004)

In addition to natural variability, within the risk assessment model structure there is the challenge that taking mean uptake concentrations and average water concentrations do not perfectly describe the system.(Risk et al., 2009) Unfortunately, we are constrained by a dearth of data in glacial meltwater OCP studies across the globe,(K. R. Miner et al., 2017) limiting the precision of a screening level model. Finally, population variability in body weight and length of life or residency varies person to person.(Frey, 1992) While this risk assessment model is intended to be conservatively protective, the risk to vulnerable populations may be underreported.(Bogen, 2014; Finkel, 2014)

Population Reporting	Participants	Species	Median Consumption (lb/yr)	Maximum Consumption (lb/yr)
Norton Sound Health Corporation	151	King Salmon	1	61
		King Salmon	2	92
		Chum Salmon	7	223
		Silver Salmon	5	679
		King Salmon	2	102
		Pink Salmon	7	679
		Red salmon	7	679
		Red salmon	2	245
		Pink salmon	3	113
		Chum Salmon	2	81
Total			**38**	**2954**
Yukon-Kuskokwim Health Corporation	224	King Salmon	19	611
		King Salmon	7	196
		Chum Salmon	13	543
		Chum Salmon	3	589
		Silver Salmon	10	679
		Silver Salmon	3	196
Total			**55**	**2814**
Bristol Bay Area Health Corporation	134	King Salmon	9	272
		Red Salmon	7	1472
		King Salmon	5	196
		Red Salmon	10	272
		Silver Salmon	4	196
		Silver Salmon	8	272
		Chum Salmon	4	196
		Chum Salmon	7	272
		Pink Salmon	7	272
Total			**61**	**3420**
Tanana Chiefs Conference region	33	King Salmon	7	49
		King Salmon	8	68
		Silver Salmon	3	19
		Silver Salmon	8	59
Total			**26**	**195**
SouthEast Alaska Health Corporation	125	King Salmon	3	74
	126	King Salmon	3	74
		Red Salmon	14	140
		Silver Salmon	3	295
		King Salmon	6	272
		Silver Salmon	4	125
Total			**33**	**980**

Table 7.2 Species of salmon consumed by Alaskan subsistence community. Median and maximum consumption of participants surveyed are listed for all regions.(Ballew et al., 2004)

7.3 Results

7.3.1 Drinking water

Risk from direct consumption of glacial water is negligible in both adults and children (Table 7.3, 7.4). Cancer risk from uptake of ΣDDT is 10 orders of magnitude below screening level for adults and 9 orders of magnitude for children. Non-cancer risk is up to 5 orders of magnitude below screening level risk for both ΣHCH and ΣDDT. Results indicate that no risk exists from drinking ΣDDT and ΣHCH in Jarvis meltwater under any timeframe, regardless of body weight.

Screening Level Cancer Risk Summary- DDT				
Pathway	**Cancer Median Risk**	**Cancer Highest Risk**	**NC Median Risk**	**NC Highest Risk**
Fish Consumption				
Adult	4.7×10^{-6}	8.7×10^{-6}	0.47	0.85
Child	**2.6×10^{-5}**	**4.7×10^{-5}**	**2.5**	**4.7**
Water Consumption				
Adult	2.5×10^{-10}	4.7×10^{-10}	2.5×10^{-5}	4.6×10^{-5}
Child	9.7×10^{-10}	1.8×10^{-9}	9.5×10^{-5}	1.7×10^{-4}
Both Pathways				
Adult	4.7×10^{-6}	8.7×10^{-6}	0.47	0.85
Child	**2.6×10^{-5}**	**4.7×10^{-5}**	**2.5**	**4.7**

Table 7.3 Cancer and Non-Cancer Risk Summary for DDT in Jarvis Glacier watershed. Fish consumption is 0.034 kg/day for both the average chemical concentration (.61 ng/L) and greatest observed concentration (1.12 ng/L). Threshold for risk is 1 in non-cancer (NC) screening and 1 x 10^{-5} in cancer screening, with numbers over threshold indicated in bold.

Screening Level Cancer Risk Summary- αHCH		
Pathway	**NC Median Risk**	**NC Highest Risk**
Fish Consumption		
Adult	4.8 x 10^{-4}	7.1 x 10^{-4}
Child	2.6 x 10^{-3}	3.9 x 10^{-3}
Water Consumption		
Adult	9.4 x 10^{-6}	1.4 x 10^{-5}
Child	3.6 x 10^{-5}	5.3 x 10^{-5}
Both Pathways		
Adult	4.9 x 10^{-4}	7.2 x 10^{-4}
Child	2.6 x 10^{-3}	3.9 x 10^{-3}

Screening Level Cancer Risk Summary- ϒHCH		
Pathway	**NC Median Risk**	**NC Highest Risk**
Fish Consumption		
Adult	7.1 x 10^{-4}	1.1 x 10^{-3}
Child	3.9 x 10^{-3}	6.0 x 10^{-3}
Water Consumption		
Adult	1.4 x 10^{-5}	2.2 x 10^{-5}
Child	5.3 x 10^{-5}	8.2 x 10^{-5}
Both Pathways		
Adult	7.2 x 10^{-4}	1.1 x 10^{-3}
Child	3.9 x 10^{-3}	6.1 x 10^{-3}

Table 7.4 Non-Cancer Risk Summary for α,ϒ-HCH in Jarvis Glacier watershed. Fish consumption is 0.034 kg/day for the average chemical concentration and greatest observed concentration of α-HCH (0.34ng/L,0.23ng/L) and ϒ-HCH (0.53ng/L, 0.34ng/L). Threshold for risk is 1 x 10^{-5} in cancer screening.

7.3.2 Fish consumption

Consumption of fish resident in glacial meltwater is the main driver of risk for both children and adults. For children with lifetime fish consumption of 0.034 kg/day with exposure to both the upper limit (1.12 ng/L) and average (0.61 ng/L) concentrations of DDT, cancer risk was just above the acceptable screening level (Table 3). This finding indicates the possibility of long term cancer risk. The risk of non-cancer impacts at both the upper limit and average concentrations of DDT are also above the screening level for lifetime exposure, indicating a potential for disease impacts from the lifetime consumption of local fish.

For both cancer and non-cancer, the risk to adults with an abbreviated 30-year consumption timeframe was below screening level for both chemicals due to the shortened exposure time and higher body weight. DDT cancer risk was one order of magnitude higher than the screening level.

As cancer risks from exposure to α-HCH and ϒ-HCH are considered negligible, the EPA only provides risk assessment factors for non-cancer risk.((EPA), 2016a, 2017) Non-cancer risk from α-HCH and ϒ-HCH are 3-5 orders of magnitude below screening level in adults and children, indicating no impact from uptake (Table 4). Risk from ϒ-HCH was relatively higher, though still significantly below screening level.

7.4 Discussion

7.4.1 Drinking water

Similar to the null risk result from our assessment of the high risk Silvretta watershed in Switzerland,(K. R. Miner et al., 2018) we hypothesized correctly that the more distal Arctic watersheds see minimal human risk from water consumption. Risk in the Jarvis Creek watershed was identified to be 9 orders of magnitude below screening level and indicates negligible risk within any timeframe from intake of DDT and ΣHCH in Jarvis Creek glacial meltwater.

7.4.2 Fish Consumption

Risk to children from exposure to DDT in fish was significantly higher than adult exposure due to smaller body size and lifetime exposure, indicating the need for future study at an individual level. Populations in Arctic nations consume significantly more fish than the US national average that increases the potential for human uptake of bioaccumulated watershed pollutants (Table 1,2).(Arnot & Gobas, 2006; Birnbaum, 2013) As Alaskan glaciers continue to melt, the gradual release of OCPs may continue to elevate watershed concentrations above the background level. Which, when combined with high fish consumption rates, necessitates an understanding of human impacts to individuals or communities.

Our study found OCP concentrations in fish similar to those found in a sampling study of the Fairbanks region in 1998,(Mueller & Matz, 2000) but higher than those found by the Office of the Veterinarian in an Alaska-wide sampling study.(Conservation, 2017) Within the Alaska-wide study, both coastal and interior fish were sampled, with coastal sites outnumbering interior sampling sites, and reporting variation in concentration between 1-3 orders of magnitude.(Conservation, 2017; Mueller & Matz, 2000) This variation within fish species from all sample sites was averaged to represent overall OCP concentration throughout Alaska, and may not provide a complete picture of emerging contaminants in the interior's glaciated watersheds. Samples taken in coastal Alaska may reflect an ocean-based OCP signal that is not indicative of the concentrations being released from glaciers in the interior. In addition, the wide variation of OCP uptake within fish species and sample locations within the Interior, may provide an incomplete picture of the OCP bioaccumulation of fish within Alaska's interior where OCP data from individual samples is not available by region but focuses on species within ocean ecosystems.(Lance, 2017)

In our model, we utilize salmon bioaccumulation factors, which reflect high lipid percentage and long lifespan, to capture the highest bioaccumulation potential. This trend towards greater bioaccumulation in older and larger fish species can also be seen in the fish sampling data, where the larger species show a mean DDT accumulation 1-2 orders of magnitude higher than smaller species.(Conservation, 2017) Additionally, our research utilized data from the immediate proglacial area of Jarvis Glacier where an undiluted OCP signal may be currently higher than that found throughout the larger watershed, but may reflect the broader, regional concentration patterns with continued increases in glacial release.

The fish consumption advice put forward by the Alaska State Epidemiology Department presents conservative suggestions for dietary fish intake in a subsistence lifestyle.(Epidemiology, 2014; Hamade & Consumption, 2014) Interior communities relying on fish consumption will eat different species and quantities of fish than coastal populations, changing the risk profile for each community and further increasing variability in exposure. Species dependent uptake of OCPs correlates with animal fat content, lifespan and habitat, making some older, larger fish (such as salmon) more susceptible to bioaccumulation.((EPA), 2016a; Bizzotto, Villa, & Vighi, 2009; Office of Environmental Health Hazard Assessment, 2012) Higher fish consumption rates in communities adjoining the Tanana Chiefs Conference region suggest that a greater risk to subsistence populations is possible and has not been assessed (Table 1,2). High risk consumers within these communities may eat 3-4 orders of magnitude more salmon than the local median values, making risk within the community variable, but significant.(Ballew et al., 2004) In order to complete this analysis, concentration profiles in the watershed of each community must be understood, so that bioaccumulation can be assessed correctly. Within the screening level model, fish consumption is the greatest contributor to risk, with an increase in consumption directly reflecting

This elevates the challenges for governmental groups interested in protecting the population from OCP uptake. Adopting a precautionary approach for consumption incorporates variation in spatiotemporal intake patterns in order to safeguard public health. (Epidemiology, 2014; Hamade & Consumption, 2014)

7.4.3 Potential Alaska and Arctic-wide implications

Studies in Europe have shown that the presence of OCPs in one glacier reflects the presence of OCPs throughout the mountain range.(Ferrario et al., 2017; P. A. Pavlova et al., 2016) We expect, therefore, that multiple glaciers in the Interior of Alaska store legacy OCPs, elevating their concentrations throughout the watershed over time. Glaciers located near the ocean may see higher rates of OCPs, as they are the first physical barrier for accumulation of OCPs transported across the Pacific. While atmospheric OCP inputs into the Arctic were identified decades ago, our model quantifies the unexplored risk or glacial redistribution of pollutants.(E Dewailly, 2006; Eric Dewailly et al., 1989) Though this is the first human risk assessment of glacial meltwater that has been accomplished in the Arctic, this study, as well as our previous study site in the Swiss Alps, suggest that the risk of cancer and non-cancer impacts is driven by fish consumption.(K. R. Miner et al., 2018) The risk to populations from glacial meltwater consumption is negligible in both studies, however, risk increases proportionally with greater fish consumption — even with meltwater pollutants at extremely low levels.

With glacial mass loss increasing on average by 200 mm w.e. per decade in Alaska over the past 50 years, the contribution of OCPs released from glacial meltwater may gradually elevate concentrations throughout the watershed.(Bogdal et al., 2008; P Schmid et al., 2011) Further research into the watershed contribution of OCPs from melting glaciers will require water sampling throughout the watershed and within subsistence communities. As the release of OCPs from glaciers is an emergent source of OCP pollution, a bioaccumulation leading to generational transference may not have impacted current generations.(Programme, 2009) It is therefore necessary to assess OCP release over time in Alaska's interior to determine potential intergenerational impacts.

7.5 Conclusions

We find that with an increased consumption of fish, OCPs, even at the low concentrations found in the arctic, can create human health risk. This screening-level model indicates the need for an in-depth and individualized study of uptake in children who live within and below glacier ecosystems of Interior Alaska. Previous fish sampling studies within Alaska's Interior regions have not accounted for the possibility of glacial emission of OCPs and will need to be updated as glacier melt continues. The potential for increased release of OCPs through glacial melt indicates the need for additional studies of proglacial systems that provide fish to local subsistence communities. Therefore, Arctic subsistence populations that consume large amounts of fish collocated with melting glaciers should be prioritized for future research into human risk from the distribution of glacial meltwater pollution. Subsequent research could include the use of Geographic Information System technologies to identify regions where high fish consumption and inputs of glacial meltwater overlap throughout the Arctic. Overall, the need for monitoring and further assessment of the ongoing input of reemergent OCPs in Alaska is clear and utilizing risk assessment tools can help to protect the health of subsistence populations in the Arctic.

CHAPTER 8.

CONCLUSION

This thesis developed a protocol to identify spatiotemporal trends in existing glacial OCP studies and characterize systems of greatest risk for secondary dispersal of organochlorine pollutants. In addition, we introduce new results from the Jarvis Glacier in Alaska, presenting the first risk assessment of glacially distributed Arctic pollutants. To complete the protocol objectives, I developed an understanding of global trends in a review of previous OCP studies, completed a sampling campaign at Jarvis Glacier in Alaska to add to the understating of Arctic glacial OCP release and utilized three case studies to build a risk assessment model that was used to gain a more comprehensive understanding of augmentation of pollutants through the watershed.

Compiling all relevant literature on OCP glacial ice and meltwater sampling campaigns was crucial to developing an understanding of the trends across glacial systems in the Northern Hemisphere. This review found that medium size glaciers with rapid flow and low residence time and near to urban or industrialized areas can be expected to store the greatest quantity of OCPs. Latitudinal trends are also clear. Glaciers in Arctic nations see significantly lower concentrations of OCPs than glaciers near to 45 N. This movement trend is driven by chemical molar mass and subsequent atmospheric transport with compounds of a greater weight collocated with distribution sites.

From this data we identified a lack of field sampling at glaciers in North America, and specifically in interior Alaska. While distant from industrial sites, early work discovered that coastal Alaskan Nunavik communities were exposed to OCPs through their traditional diets.(E

Dewailly, 2006) While the routes of transport were expected to be dry and wet direct deposition, the potential of secondary emission from the glaciers in interior Alaska had never been explored. To this end, ice core and water samples were collected from Jarvis Glacier in the Eastern Alaskan Range, south of Fairbanks. The concentrations of DDT, DDE, DDD, ϒ-HCH and α-HCH found in both ice cores and water samples were consistent with other Arctic studies. Elevated rates of ΣDDT deposition may indicate transport from regions in Asia currently utilizing DDT to fight malaria. HCH also has great atmospheric mobility, which allows for increased range and deposition into interior Alaska. From the organochlorine pesticide compounds, ΣDDT and ΣHCH were the only two identified above the limit of detection, which could be potentially due to the remote nature of the Jarvis Glacier.

Finally, the risk assessment model described in this thesis utilizes the Environmental Protection Agency’s human risk screening level model framework that has been applied across the United States and adapted worldwide. This study was the first application of this model to secondary chemical emissions from glaciers, but it incorporates methodology for identifying risk from OCPs that have been applied to numerous urban water sources.((EPA), 2001c, 2003) Calibrating the risk assessment model to glacial watersheds required a comprehensive qualitative understanding of system dynamics, and elucidated the opportunities for amplification of risk in the local population. Within the risk assessments we prioritized quantifying the risk from DDT due to the ubiquity of the compound and range of transport, as well as PCBs due to their elevated toxicity. To contrast the impact of these chemicals within two glacial systems, I developed case studies in Italy and Switzerland, which provided an opportunity to compare the toxicity of DDT with PCBs at similar magnitudes within similar watershed systems. To accomplish this, we utilized existing data from sampling studies of DDT from the Italian Alps, and PCB from the

Swiss Alps while developing a conceptual model to identify likely routes of human uptake in a glaciated system. After modeling these comparable watersheds with different OCP compounds, PCBs were identified as a driver of risk at a much greater rate than DDT due to PCB's elevated toxicity and bioaccumulation potential. Within our framework, potential risk from a lifetime of domestic fish consumption from fish that reside in glacial meltwater from Silvretta Glacier was identified. Concentrations of PCBs in the Silvretta Glacier are well studied, but larger glaciers in the Alps may house more PCBs and the rates of release may vary. While PCBs are found in numerous watersheds globally, they have a small range of travel atmospherically, such that areas of industry near glaciated mountain ranges should be prioritized for further study. The risk from PCBs indicates that future studies focused on the human impacts of secondary emission of OCPs from glaciers should prioritize PCB congeners in their sampling campaigns. Additional research into the potential for human health risks from secondary release of PCBs is indicated.

The third risk assessment case study completed was in the Arctic at Jarvis Glacier, in the Interior Eastern Alaska Range. We found that though our previous case studies indicated that DDT was a lower risk than PCBs, the risk from consumption of DDT in elevated fish consumption increased the overall risk to vulnerable populations. This result elucidated that augmentation of glacial pollution can impact risk in the system due to the high toxicity of a chemical or through elevated bioaccumulation in the form of fish consumption. This information will help to inform the design of sampling and monitoring studies in the future, as researchers seek to identify other communities within glacial systems who may be at risk from glacial meltwater pollution. There also is an indication of a two-way tug between the levels of contaminants and consumption habits where risk and vulnerability may be predicated by lifestyle, particularly in the form of high fish consumption.

8.1 Future Work

Sampling studies that quantify the risk from legacy pollutants stored within glaciers have greatly illuminated trends in OCP concentration throughout northern hemisphere glaciers. Regions close to areas of OCP use have been identified as reservoirs of a greater quantity and diversity of OCP chemicals. While OCPs are useful in identifying trends in deposition, they do not give a complete picture of all the chemical species that could be currently contained in glaciers. To identify and classify all chemicals resident within glacial meltwater, studies seeking to identify the potential for human health risk must be expanded to incorporate current use compounds, metalloids and chemically altered carbon. Though patterns of change within glacial systems under a warming climate act as an uncertainty, the overlap of glacial melt and proximity to chemical use areas are also as a measure of where we can expect potential risk, and which regions should be proactively monitored.

When we began our research, no risk assessment for glacial meltwater had been accomplished, largely under the assumption that the concentrations of OCPs were so low that there would be no significant risk to humans. In the case of the three chemical compounds compared in our risk model, significant variation was found in risk posed by different chemicals at similar magnitude. The inherent toxicity and bioaccumulation potential of PCBs increased human risk in our screening level model at a much greater rate than ΣDDT. Where human risk is a concern, future studies should prioritize compounds with higher known toxicity and bioaccumulation potential, such as PCB. Additional work towards identifying current use compounds in addition to metalloid and carbon compounds should also be considered, though labor intensive and expensive.

When the idea of glaciers acting as a reservoir for pollutants was proposed, glaciers were considered the ‘cleanest’ source of water on earth. Millennia old, these ice forms have existed on the planet since the beginning of stories – their ebb and flow has continually shaped the face of the earth. Questioning this assumed purity meant that the human impacts on our ecosystems are much greater than we have ever imagined, the implications of which the world is still seeking to fully understand. So often humans see themselves as small creatures, and we assume our ability to affect change is similarly insignificant. Yet as we are increasingly overtaken by the effects our actions have wrought, coming to terms with the grand scale of our impact on the earth must be an immediate priority.

The continued use of toxic compounds for industrial and agricultural processes and their presence in distant areas suggests a growing impact of these chemicals. While this study identified the 209 PCB congeners as compounds of significant concern, newer chemicals such as brominated flame retardants and PAHs can accumulate in glaciated watersheds, increasing the toxicity of glacial meltwater now and into the future. The earth is a closed system. All compounds that are manufactured and distributed can affect secondary ecosystems, including the people who live there. The release of toxins from melting glaciers is but one of the numerous unfolding threats of a warming world – many of which are not categorized or understood. It is, therefore, the job of researchers to anticipate and understand worst case scenarios and cascading impacts. In glaciated ecosystems, where increasing variation of yearly precipitation is coupled with the melting of the glaciated water reservoir, the added complication of toxicity can pose significant health risks. There are currently unsampled regions in the southern hemisphere, such as the Peruvian Highlands, that are heavily dependent on glacier melt for human wellbeing.

These areas must be prioritized for future studies to protect the populations living in the watershed.

The impacts of the planet-altering loss of glaciers in response to atmospheric warming are not yet fully known and the complicating factors of meltwater toxicity may make the watersheds untenable. These are unknown, under studied risks that exist across disciplines and while we may not be able to immediately identify all the hazards, it is the job of forward thinking scientists, policy makers and regional managers to protect their populations with the best science available. Exploratory research can be the most crucial, opening the door for further breakthroughs.

Denying the effects of climate change may help with the feelings of fear and insecurity in the short term, yet the winds are still changing, and the glaciers are melting into a warming sea. As a species we have the opportunity to be extraordinary as ambassadors to other species, explorers of hidden worlds and caretakers outside the hierarchy of predators and prey.

The time to make a choice has come, we can bravely face the consequences of our folly and become the bold explorers we inherently are, or we can watch the world change into something unrecognizable. It is our duty and our privilege to follow in the footsteps of all the scientists who came before and prepare the world for the irrevocable – yet inevitable – changes we are facing.

“The Earth is a very small stage in a vast cosmic arena…. Our posturing, our imagined self-importance, the delusion that we have some privileged position in the universe, are challenged by this point of pale light. To me, it underscores our responsibility to deal more kindly with one another, and to preserve and cherish the pale blue dot, the only home we have ever known.” October 13, 1994, Dr. Carl Sagan.

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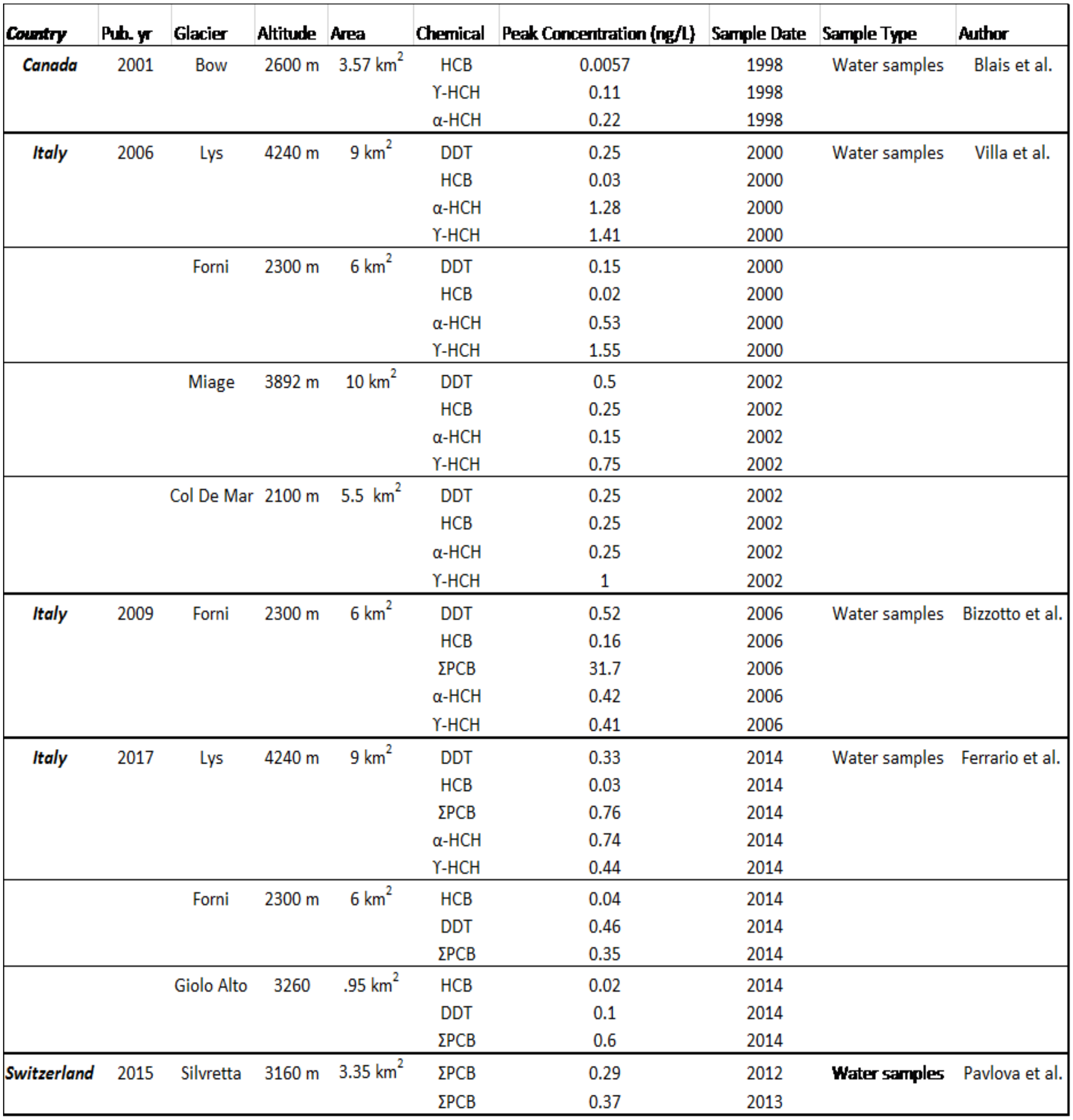
APPENDIX A. SUPPLEMENTARY MATERIAL FOR CHAPTER 1



Country	**Pub. yr**	**Glacier**	**Altitude**	**Area**	**Chemical**	**Peak Concentration (ng/L)**	**Sample Date**	**Sample Type**	**Author**
Canada	2001	Bow	2600 m	3.57 km^2	HCB	0.0057	1998	Water samples	Blais et al.
					Υ-HCH	0.11	1998		
					α-HCH	0.22	1998		
Italy	2006	Lys	4240 m	9 km^2	DDT	0.25	2000	Water samples	Villa et al.
					HCB	0.03	2000		
					α-HCH	1.28	2000		
					Υ-HCH	1.41	2000		
		Forni	2300 m	6 km^2	DDT	0.15	2000		
					HCB	0.02	2000		
					α-HCH	0.53	2000		
					Υ-HCH	1.55	2000		
		Miage	3892 m	10 km^2	DDT	0.5	2002		
					HCB	0.25	2002		
					α-HCH	0.15	2002		
					Υ-HCH	0.75	2002		
		Col De Mar	2100 m	5.5 km^2	DDT	0.25	2002		
					HCB	0.25	2002		
					α-HCH	0.25	2002		
					Υ-HCH	1	2002		
Italy	2009	Forni	2300 m	6 km^2	DDT	0.52	2006	Water samples	Bizzotto et al.
					HCB	0.16	2006		
					ΣPCB	31.7	2006		
					α-HCH	0.42	2006		
					Υ-HCH	0.41	2006		
Italy	2017	Lys	4240 m	9 km^2	DDT	0.33	2014	Water samples	Ferrario et al.
					HCB	0.03	2014		
					ΣPCB	0.76	2014		
					α-HCH	0.74	2014		
					Υ-HCH	0.44	2014		
		Forni	2300 m	6 km^2	HCB	0.04	2014		
					DDT	0.46	2014		
					ΣPCB	0.35	2014		
		Giolo Alto	3260	.95 km^2	HCB	0.02	2014		
					DDT	0.1	2014		
					ΣPCB	0.6	2014		
Switzerland	2015	Silvretta	3160 m	3.35 km^2	ΣPCB	0.29	2012	**Water samples**	Pavlova et al.
					ΣPCB	0.37	2013		

Table A.1. Glacial meltwater samples with peak OCP concentrations. The source glacier, years sampled and publication are referenced.(Bizzotto, Villa, Vaj, et al., 2009; J M Blais et al., 1998; Ferrario et al., 2017; P. A. Pavlova et al., 2016; Sara Villa, Negrelli, Finizio, et al., 2006)

Country	Pub. Yr	Glacier	Altitude	Area	Chemical	Peak Concentration (ng/L)	Sample Layer	Sample Type	Author
Svalbard	1998	Austfonna	740 m		α-HCH	1.1	1957-1972	Ice core	ermanson et al
					ϒ-HCH	7.7	1979-1986		
	2013	Lomonosovfonna	1202 m	600 km^2	ΣPCB	1.525	1998-2009	Ice core	Garmash et al.
Canada	1999	Snow Dome	3456 m	325 km^2	DDT	2.5	1983	Crevasse ice	Donald et al.
					HCB	0.05	1961		
					ϒ-HCH	0.12	1961		
					α-HCH	1.82	1994		
Italy	2003	Lys	4240 m	9 km^2	DDT	10	1994-1996	Ice core	Villa et al.
					HCB	0.7	1985-1987		
					α-HCH	20	1964-1972		
					ϒ-HCH	20	1964-1972		
	2001				ΣPCB	7	1984-1987		
China	2008	East Rongbuk	6518 m		DDT	1.9	1973	Ice core	Wang et al.
					α-HCH	6.5	1971		
Italy	2006	Lys	4240 m	9 km^2	DDT	0.646	1998	Firn Core	Villa et al.
					HCB	0.168	1998		
					ΣPCB	9.95	1998		
					ϒ-HCH	2.43	1999		
Switzerland	2014	Fiescherhorn	3900 m	3 km^2	ΣPCB	6	1971-1975	Ice core	Pavlova et al.
Switzerland	2015	Grenz	4200 m	50 km^2	ΣPCB	15	1970-1975	Ice core	Pavlova eta al.
Switzerland	2015	Silvretta	2927 m	3 km^2	ΣPCB	12.5	1970-1971	Ice core	Pavlova et al.

Table A.2. Selection of ice cores from alpine glaciers taken to study the OCP concentration by depth and time. Peak OCP concentrations found in specific sample layers, representing the years of greatest OCP deposition. Peak deposition in samples correlated with global usage peaks.(Donald et al., 1999; Garmash et al., 2013; Hermanson et al., 2005; Pavlina Aneva Pavlova, Schmid, Bogdal, et al., 2014; Sara Villa, Negrelli, Maggi, et al., 2006; Sara Villa et al., 2003; Xiao ping Wang, Yao, et al., 2008)

Country	Pub. yr	Glacier	Altitude	Area	Chemical	Peak Concentration (ng/L)	Sample Date	Sample Type	Author
Switzerland	2009	Oberaar F	3200 m	5.82 sq km	DDT	13 µg/m2/y	1960-1970	Sediment Cores	Bogdal et al.
					Dieldrin	1.4 µg/m2/y	1960-1970		
					HCB	24 µg/m2/y	1960-1970		
					ΣPCB	75 µg/m2/y	1960-1970		
					ϒ-HCH	.6 µg/m2/y	1960-1970		
					DDT	65 µg/m2/y	1995-2005		
					Dieldrin	.5 µg/m2/y	1995-2005		
					HCB	40 µg/m2/y	1995-2005		
					ΣPCB	75 µg/m2/y	1995-2005		
					ϒ-HCH	2.1 µg/m2/y	1995-2005		
Switzerland	2011	Stein Gla	2900 m	6.06 sq km	DDT	44 µg/m2/y	1975	Sediment Cores	Schmid et al.
					ΣPCB	225 µg/m2/y	1973		
					DDT	28 µg/m2/y	2006		
					ΣPCB	245 µg/m2/y	2006		

Table A.3. Selection of sediment cores from remote, alpine glacier lakes taken to study the OCP concentration by depth and time. Table presents peak OCP concentrations found in specific sample layers, representing the years of greatest OCP deposition. Peak deposition in samples correlated with direct deposition during global usage peaks and subsequent delayed release from glaciers.(Bogdal et al., 2009; P Schmid et al., 2011)

APPENDIX B. SUPPLEMENTARY MATERIAL FOR CHAPTER 4

B.1. SPMD and Ice core results

For the SPMDs, α-HCH was found in greatest concentration by the SPMDs (June-July: 0.07 August-September: 0.15 ng/L) followed by DDT (June-July: 0.14, August-September:0.01 ng/L), p,p'-DDE (June-July: 0.10 August-September: 0.04 ng/L), ϒ-HCH (June-July: 0.03, August-September: 0.06 ng/L) and p,p'-DDD (June-July: 0.01, August-September: 0.01), which was found at trace levels.

	SPMD calculated	
	June-July	August-September
α-HCH	0.21	0.31
ϒ-HCH	0.08	0.00
DDE	0.07	0.07
DDD	0.02	0.02
DDT	0.15	0.02

Table B.1. Alaska SPMD results by two-month period. Concentrations below 0.1 ng/L are below the limit of detection and should be taken as approximations.

Depth (m)	0-7	7-14	14-21	21-28	28-35	35-42	42-49	49-56	56-63	63-70	70-77
α-HCH	*0.08*	**0.15**	*0.05*	*0*	*0.04*	*0.05*	*0.07*	*0.06*	*0*	*0.03*	*0.03*
ϒ-HCH	*0*	**0.15**	*0*	*0*	*0*	*0.03*	*0*	*0.01*	*0*	*0.01*	*0*
DDE	*0*	**0.34**	**0.22**	*0*	**0.22**	**0.17**	**0.14**	**0.16**	**0.12**	*0*	**0.16**
DDD	*0.05*	**0.45**	**0.19**	*0.04*	**0.23**	**0.12**	**0.13**	**0.13**	*0.06*	*0.08*	*0.08*
DDT	**0.13**	**0.51**	**0.31**	**0.19**	**0.35**	**0.31**	*0.08*	**0.30**	**0.11**	**0.16**	**0.15**

Table B.2. Alaska ice core OCP concentration by depth. Concentrations below 0.1 ng/L are below the limit of detection and should be taken as approximations

APPENDIX C. SUPPLEMENTARY MATERIAL FOR CHAPTER 5-7

Risk assessment model framework

C.1 Bioaccumulation Factors

To establish bioaccumulation factors, EPA bioaccumulation values were adjusted by the California Office on Environmental and Health Hazard Assessment (OEHHA) based on fish species.(Office of Environmental Health Hazard Assessment, 2012) These values are applied to fish found in the study area with increased adipose tissue percentages allowing them to withstand temperatures in glaciated watersheds. These fish are often larger and have the capacity for increased uptake and bioaccumulation of chemicals found in the surrounding media.

The bioaccumulation factor (BAF) is calculated as:

$$BAF= C_t/C_w \qquad (1)$$

Where C_t is the concentration of the chemical in wet tissue, and C_w is the concentration of the chemical in water. The BAF reflects the potential uptake from all media within the limits of a steady-state. It is often described as the ratio of concentration in tissue to that of the surrounding water and can be unitless.

C.2 Risk Assessment Model layout

Utilizing risk assessment framework guidelines from the EPA we have incorporated average consumption data into published model framework.((EPA), 2001b) Oral intake of polluted meltwater or impacted fish species utilize the same equation:

$$CDI= C*CR*EF*ED/BW*AT \qquad (2)$$

Where CDI represents chronic daily intake, C is concentration of the pollutant, CR is the rate of contact through consumption, EF is how many days in a year this contact is made, and ED is the number of years contact is made. BW represents body weight, which also demarcates age and follows the average weights published by the EPA,((EPA), 1999) AT is the averaging time, which represents years in terms of

days. The equation gives the result in terms of mg/kg/day (CDI). This number is then multiplied times the laboratory derived slope factor for cancer (SL) or upper bound limit, to find risk, or R, representing the 95% confidence level that cancer will result at the concentration level modeled.((EPA), 1999, 2017)

$$R=CDI*SL \qquad (3)$$

Here, risk is set equal to chronic daily intake or CDI times the slope factor, SL. The slope factor is derived from laboratory experiments on human-chemical interactions and integrates relatively high administered doses of a chemical with expected low doses in the environment. The second assessment of human risk over time is the non-cancer reference dose, which determines the risk from non-cancer diseases. The CDI is divided by the concentration (RfD) above which there is considered to be toxicological risk to humans.

$$E/RfD \qquad (4)$$

Where E is the actual exposure level developed in the model (also referred to as CDI) and RfD is the reference dose from peer reviewed studies. For this measurement, any number over 1 represents a risk of disease due to pollutant uptake over time.((EPA), 1999) The diseases represented by the non-cancer slope factor are specific to the chemical compound. ((EPA), 1999, 2016b)

C.3 Values for Silvretta Glacier Risk Assessment

- Cancer slope factor((EPA), 2017) (SL): 2 mg/kg/day
- Non-Cancer Reference Dose (RfD)((EPA), 2017): 0.000045 mg/kg/day
- Bioaccumulation Factor(Office of Environmental Health Hazard Assessment, 2012): 2000000
- Fish Consumption Rate(Statistical Office, 2017): 0.0013 kg/day (6% domestic); 0.011 kg/day (50% domestic)
- Concentration in fish((EPA), 2001b) (CF): 1 mg/kg
- Fraction ingested((EPA), 2001b) (FI): 1
- Exposure frequency((EPA), 2001b) (EF): 365 days of meals
- Averaging Time((EPA), 2001b) (AT): 25,550 days

C.4 Values for Lys Glacier Risk Assessment

- Cancer slope factor[69] (SL): 0.034 mg/kg/day
- Non-Cancer Reference Dose (RfD)[69]: 0.0005 mg/kg/day
- Bioaccumulation Factor[63]: 1,100,000
- Fish Consumption Rate[62]: 0.0043 kg/day
- Concentration in fish[20] (CF): 1 mg/kg
- Fraction ingested[20] (FI): 1
- Exposure frequency[20] (EF): 365 days of meals
- Averaging Time[20] (AT): 25,550 days

C.5 Values for Jarvis Glacier Risk Assessment

- Cancer slope factor[69] (SL): 0.034 mg/kg/day
- Non-Cancer Reference Dose (RfD)[69]: 0.0005 mg/kg/day
- Bioaccumulation Factor[63]: 1,100,000
- Fish Consumption Rate[62]: 0.034 kg/day
- Concentration in fish[20] (CF): 1 mg/kg
- Fraction ingested[20] (FI): 1
- Exposure frequency[20] (EF): 365 days of meals
- Averaging Time[20] (AT): 25,550 days

BIOGRAPHY OF THE AUTHOR

Kimberley R.N.E. Miner was born in Boulder, Colorado in 1985, at the base of the Rocky Mountains. An early problem solver dedicated to helping others, she became a First Responder during High School at Fairview High, where she graduated in 2003. She went on to work for the National Park Service in Arkansas and Bureau of Land Management in California where she received her Firefighting Red Card and Wilderness First Responder training. In college at the University of California at Santa Cruz she studied Ecology and Agriculture while working and teaching children on the Center for Agroecology & Sustainable Food Systems Farm until she graduated with a Bachelor of Arts in 2004. Upon graduating she worked at a draft horse farm in Oregon, and at the Heifer International Headquarters farm in Massachusetts.

Before she returned to school to complete her Master of Public Administration at Columbia University in 2012, she taught karate in Los Angeles and excelled at sales in Silicon Valley. After graduating from Columbia in 2013 she worked at Lamont-Doherty Earth Observatory in the Development Office and the Office of Emergency Management where she had the opportunity to combine her communication background and dedication to science and policy. During this time, she also earned her Black Belt in Kenpo Karate under the tutelage of Grand Master Larry Tatum.

She returned to school to work on her PhD at the University of Maine, where she traveled to Antarctica, Alaska, Canada, Switzerland and The Netherlands for research. While at the University of Maine she served on the University of Maine System Board of Trustees for almost 3 years where she led efforts to increase inclusivity, diversity and graduate student rights. During her PhD she was awarded a National Science Foundation Fellowship, Fulbright Fellowship, Department of Defense Fellowship, Switzer Foundation Fellowship, Dan and Betty Churchill Exploration Grant, Outstanding Service Award and Edith M. Patch Outstanding PhD Award in the College of Natural Science, Forestry and Agriculture, and the Outstanding Service Award in the Climate Change Institute. After graduation Kimberley will be working for the Army as a physical scientist in the Army Corps of Engineers in Alexandria, Virginia.

Kimberley is a candidate for the Doctor of Philosophy degree in Earth and Climate Sciences from the University of Maine in May 2018.