Environmental signiﬁcance

Glaciers provide water to populations in many regions of the world, but atmospheric warming and rapid glacier melt are causing changes in seasonal discharge quantity and timing. Contamination from legacy pollution stored within and subsequently released from glaciers may further limit clean glacial water availability in some watersheds. Identifying glaciers that may act as OCPs reservoirs requires an understanding of the spatial and temporal glacial processes that control the deposition, storage, and release of pollutants. Planning for long-term impacts to downstream ecosystems is critical as the reemergence of OCPs from meltwater can have impacts on communities reliant on glaciers.19 Here we summarize existing work in order to help prioritize future study areas and chemical compounds.

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.12 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.1–9 In addition to landscape modiﬁcation, glacier ice can serve as a record of atmospheric processes and human use of metals, chemicals and carbon.8–10

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.11–12 OCPs species include, but are not limited to; DDT, lindane, chlordane, dieldrin, and hexachlorobenzene. OCPs 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.13 Subsequent studies have shown that glaciers near areas of OCPs use maintain reservoirs of OCPs chemicals in their ﬁrm and ice layers.14 As glacial melt continues, the release of compounds...
stored in glacial ice, including banned OCPs, is an increasingly critical issue.

Glaciers house about 75% of Earth’s freshwater, making them a valuable resource and vital part of proglacial ecosystems. However, meltwater from glaciers not only transports important freshwater, but also dissolved organic carbon, black carbon, heavy metals, and legacy chemicals downstream (Fig. 1). 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. The rapid reintroduction 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.

2. Relevant background on OCPs dispersal and glaciology

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. 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. 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 environmental pollutants on natural systems. His main emphasis is on the sources, pathways and fate of persistent pollutants in aquatic environments.
lindane, 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.\(^{12,22,23}\) Major DDT use spanned 1940–1986, but aerial distribution to utilize its anti-malarial properties continues presently in areas of high disease incidence.\(^{2,23,24}\) OCPs were used largely by industrialized nations, with the level of volatility and proximity to use reflected in subsequent environmental concentrations.\(^{12}\) 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.\(^{20,25–31}\) 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.\(^{20,32,33}\) Even at background levels OCPs may cause health problems in human populations after prolonged exposure or consumption.\(^{2,20,24–42}\)

### 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.\(^{27,43,44}\) When OCPs are released into the atmosphere they can be transported as a gas or adsorbed to particles.\(^{45}\) 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’.\(^{46–47}\) 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.\(^{51,14,45,48}\)

Though movement of more persistent chemicals may decrease with distance from source, more volatile OCPs have greater traveling potential and broader distribution ranges.\(^{49–52}\)

To our knowledge, the first research to discuss the distribution and concentration of persistent pollutants in northern latitudes was published in 1973.\(^{43}\) 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.\(^{43}\) 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.\(^{44,45,53,54}\) The literature focusing on legacy pollutant transport and re-emergence increased rapidly, with a review covering the state of the science published in 1995.\(^{44}\) That same year, researchers showed that more volatile compounds have the greatest atmospheric latitudinal range due to their lower molar mass.\(^{13}\) 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.\(^{13}\) 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.\(^{55}\) Blending atmospheric transport and compartmental modeling with chemical flux, volatility and fugacity data, researchers moved towards a more complete understanding of organochlorine transport.\(^{46,55–57}\)

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. 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.  

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. 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.  

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. 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. 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 (Fig. 1). 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.  

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. 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. In such a glacier, the time that it takes for a specific layer of ice to remerge at the terminus is a function of ablation and the geometry of the glacier. 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.  

The primary driver for glacier movement is the budget gradient – the angle of the surface slope with respect to accumulation and aspect. The pressure exerted by overlying 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. Multiple frictional forces add drag to this forward, downslope movement and create a slowly moving system. 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. 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. Whereas temperatures below 0 °C greatly limit revolatilization, increased temperatures and wind speeds above a glacier can lead to greater mobility. 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. Diurnal mountain winds that travel upslope in the day and downslope with cooler temperatures in the evening also prevent revolatilization at night. 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.  

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. 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. 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 °C. 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 scavengen semi-volatile compounds of varying molar masses, with increasing efficiency for molecules of higher weight. The scavenging ratios for snow suggest that up to 88% of chemicals present in the 2 km of atmosphere of a model environment are scavenged by snow during the period of one year.  

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. 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. 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.

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. 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.\textsuperscript{18,19,67} 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.\textsuperscript{19,85} These percentages represent a wide range of melt regimes, but both individual and aggregate glacial ice loss corresponds with global temperature increase.\textsuperscript{86} 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.\textsuperscript{85} Recent warming trends leading to glacier mass loss will greatly reduce the storage of water available for the future.\textsuperscript{18,19,85} 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. 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 (Fig. 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.\textsuperscript{18,16,61,87}

Ice cores are often used to understand climatological trends and human activities including the global use of OCPs.\textsuperscript{8,19,60,71,72,88–91} In order to analyze glacier ice cores there must be a complete understanding of glacier dynamics and the overall mass balance of the glacier.\textsuperscript{71,90} Studies show that ice core concentrations reflect glacial proximity to greatest OCPs use around 45° N, leading to significantly higher concentrations in European than in Arctic nations (Fig. 3). Crevasse samples from Donald \textit{et al.} in Canada indicated that glaciers may be acting as a reservoir for OCPs, which was later confirmed with European ice core sampling.\textsuperscript{88} Data from the first full length ice cores documenting OCPs deposition were published in 2001 and 2003 by Villa \textit{et al.} in the Italian Alps.\textsuperscript{10,92} The Italian samples suggested that proximity to Italian factories and agriculture increased deposition of chemicals in the ice. In Switzerland, work from Pavlova \textit{et al.} and Steinlin \textit{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.\textsuperscript{24,65,71,72,93,94} 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

![Fig. 2](Fig_2.png) Locations of glacial meltwater, ice and sediment core OCPs sample studies globally, overlain on the GLIMS glacier database web map.\textsuperscript{2} White dots indicate ice core sampling studies, blue dots indicate meltwater and sediment sampling studies.
studied than in the Italian ice core, concentrations were similar to studies from the Italian Alps (Fig. 4). 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 (Fig. 5). 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. 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. In 2008 Wang et al. published the first ice core results from Asia, after their expedition to the Mt. Everest East Rongbuk Glacier. 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 modeling. 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 (Fig. 6). Beginning in 2001, water samples in the Canadian Rocky Mountains,59 showed higher concentrations of banned OCPs in glacial meltwater than in non-glacial streams.79,61 This study confirmed that some Canadian glaciers may be harboring legacy pollutants, and was followed with crevasse sampling at Snow Dome.79,60 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.92,97,98 Subsequently, Swiss researchers developed a model of glacial entrainment and particle flow, complimented with proglacial water sampling.89,91 Proglacial sampling showed a concentration decrease from the glacier terminus to the immediate proglacial environment, with subsequent concentration steady throughout the lower watershed.10,12,60,61 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.67 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.99

Proglacial lake sediment cores (Fig. 7) provide a corresponding temporally constrained signal, as particles scavenging OCPs from glacial meltwater partition in the water column and are deposited.10,12,60,61 These layers provide a clear record of glacial pollutant melt and reemergence over time.10,12 Swiss researchers were the first group to take proglacial lake sediment cores looking for a signal of OCPs in 2009.16 Their study identified OCPs sorption onto dissolved organic carbon and deposition onto the lake bed following seasonal settling.10,12,56 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.16,101

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.16,101 To develop a full-system perspective, researchers utilized the capabilities of an interdisciplinary team, which included glacial flow modelers, glaciologists and analytical chemists.87,94 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.16,32,65,67 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.

### 3.1 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.10,24,60,61 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 (Fig. 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.10,12,16,24,60,61

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.10,12,16,24,61 Regional differences in sampling studies show higher transport and deposition rates for OCPs with a higher molar mass and chlorination.10,12,60. 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.10

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 dynamics. 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.

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, but targeted studies of downstream human communities are few, and do not incorporate direct glacial water uptake. As studies continue to expand on the minimum OCPs dose necessary to cause human harm, 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. Pathways for OCPs bioaccumulation in proglacial flora and fauna is relatively well understood, but human uptake patterns have yet to be quantified.

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.

Conflicts of interest
We have no conflicts of interest to declare.

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