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**The global
cryosphere in the fate
of organic
contaminants**

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The role of the global cryosphere in the fate of organic contaminants

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Received: 26 June 2012 – Accepted: 29 June 2012 – Published: 10 July 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The cryosphere is an important component of global organic contaminant cycles. Snow is an efficient scavenger of atmospheric organic pollutants while a seasonal snowpack, sea ice, glaciers and ice caps are contaminant reservoirs on time scales ranging from days to millennia. Important physical and chemical processes occurring in the various cryospheric compartments impact contaminant cycling and fate. A variety of interactions and feedbacks also occur within the cryospheric system, most of which are susceptible to perturbations due to climate change. In this article, we review the current state of knowledge regarding the transport and processing of organic contaminants in the global cryosphere with an emphasis on the role of a changing climate.

1 Introduction

It is now widely recognized that organic contaminants are globally distributed and may pose severe risk to wildlife and human health (AMAP, 2009a). The global transport of contaminants has been well documented and characterized (Wania et al., 1998a; Finizio et al., 1998; Bard, 1999; Wania, 2003; Gouin et al., 2004; Harner et al., 2006; Scheringer, 2009). Accumulation of contaminants in Polar regions and mountains, due to global and local cold-trapping, is of particular concern (Wania and Mackay, 1993; Blais et al., 1998; Daly and Wania, 2005; Wania and Westgate, 2008). The observation of elevated concentrations of organic contaminants in polar and mountain areas far from contaminant source regions has led to much work aimed at characterizing the role of snow and ice in contaminant transport and fate during the last decade. A number of reviews discuss various aspects of the cryosphere in contaminant cycling (Wania et al., 1998b; Herbert et al., 2006), including contaminant interaction with seasonal snowpack (Halsall, 2004), photochemistry in snow (Domine and Shepson, 2002; Grannas et al., 2007), contaminant fate during snowmelt (Meyer and Wania, 2008), and changing contaminant-environment interactions with climate change (Couillard et

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al., 2008). While much recent work has been on individual compartments within Polar and mountain regions (e.g. snow, sea ice, glaciers) or the impact of contaminants on ecosystem health, this work has not yet been placed in the context of understanding the role of the global cryosphere in contaminant fate. Here we seek to synthesize the information available about specific elements of the cryosphere into a global picture of contaminant fate in cold environments.

The global cryosphere is defined as the part of the Earth's surface where water is present in solid form. It thus includes sea ice, lake ice, river ice, snowpack, glaciers, ice caps, ice sheets, and the frozen geosphere (permafrost). The cryosphere is a crucial component of the Earth system for several key reasons. It is important in the energy balance of the Earth due to sensible and latent heat involved in the transport of moisture from warm locations to cold locations, and the high albedo of snow and ice surfaces. Snow and ice play important roles in decoupling the surface-air interface with respect to heat, moisture and contaminant fluxes. In the case of snow, the quantitative nature of these effects is highly dependent on snowpack physical properties such as density, specific surface area, air permeability and thermal conductivity (Dominé et al., 2008, 2012). The cryosphere is also a critical component of the global water cycle. Ice sheets hold nearly 80 % of the world's freshwater. It has been shown that snow and ice can play an important role in surface atmospheric chemistry processes (Grannas et al., 2007). The cryospheric environments in Polar regions on Earth are considered vital parts of regional ecosystems (McConnell, 2006; Slaymaker and Kelly, 2007). The cryosphere is also present in high altitude, boreal and mid-latitude (including urban) regions. Each component of the cryosphere plays a unique role in the global transport and fate of contaminants and is discussed in turn in Sect. 3.

Climate change may significantly impact the nature and extent of the cryosphere, thus affecting cryospheric processes and properties. Arctic sea ice extent is decreasing at an alarming rate (Perovich, 2011; AMAP, 2011a), and glaciers, also now undergoing rapid wastage (Sharp et al., 2011; Hanna et al., 2011), may deliver previously stored contaminants to surrounding ecosystems (Blais et al., 2001a; Bogdal et al., 2010).

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Predicting the impact of climate change on contaminant fate within the cryosphere presents a great challenge. Not only are these fate processes controlled by a wide range of physical and chemical properties of contaminants that are strongly temperature dependent, but the cryosphere itself is highly variable under climate change scenarios. As discussed in a recent detailed review (AMAP, 2011a), there are three major feedback systems in complex cold ecosystems that have relevance to contaminant transport and cycling: the hydrologic cycle, the cryospheric cycle, and the organic carbon cycle. Cryosphere-dominated environments are thus exceptionally vulnerable to change of the physical environment because such change may influence all three feedback mechanisms. Contaminant cycles, as integrated parts of this complex environmental system of cold regions, are similarly prone to change as a result of expected climate-related environmental change (Macdonald et al., 2000, 2003a, b, 2005; Hoffmann et al., 2012; Guglielmo et al., 2012). This review offers a perspective on the interactions between contaminants and the various cryospheric compartments at a range of latitudes and considers the potential impacts of climate-change in each compartment.

2 Current policy and monitoring efforts

The importance of the cryosphere in the context of organic contaminants and other hazardous chemicals is addressed at the international level through various treaties, agreements and programs. In many cases these policies recognize the uniqueness of polar and/or alpine regions where the cryosphere plays a key role in the cycling and fate of toxic chemicals and ultimately their delivery to the food chain, including humans. As new contaminants are included in reduction efforts, changing policies and monitoring priorities will in part dictate the measurement and process studies undertaken by the scientific community. Looking to the future, we can foresee the need for political engagement to address changes to these once pristine regions that are associated with climate change and increased human activity including transport/shipping, industrial development, and mining of resources.

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The Stockholm Convention on persistent organic pollutants (POPs) came into force in 2004 and is the largest international Convention on POPs. A key component of the Stockholm Convention is the Global Monitoring Plan (GMP) which addresses the needs of Article 16 of the Convention, dealing with measuring its effectiveness. The first global monitoring report targeting POPs in air and human milk/blood was completed in 2009 and recognized the importance of the cryosphere on levels and trends of POPs in air, their cycling between the cryosphere and air, and re-release (from ice/snow) of previously trapped POPs due to climate change. The report also emphasized that monitoring data need to be integrated with multi-media models and emissions information to distinguish changes that are due to regulatory actions from changes associated with historical releases and chemical cycling (UNEP, 2009).

The POPs Protocol of the Convention on Long-Range Transboundary Air Pollution (CLRTAP), established in 1998 (UNECE, 1998), is complementary to the Stockholm Convention but addresses the concerns of countries within the United Nations Economic Commission for Europe region. Under the CLRTAP, monitoring is carried out through the European Monitoring and Evaluation Programme and work on emissions and transport and fate modeling is carried out through The Meteorological Synthesizing Centre – East and several working groups, namely the Task Force on Measurements and Modelling, the Task Force on Integrated Assessment and Modelling and the Task Force on Hemispheric Transport of Air Pollutants. The 2010 POPs Assessment Report of the Task Force on Hemispheric Transport of Air Pollutants included monitoring results for POPs in the cryosphere and the important role of this compartment in modeling the fate and transport of POPs, including the delivery of POPs to the food chain (UNECE, 2010).

The Arctic Monitoring and Assessment Programme (AMAP) is an international organization of circumpolar countries established in 1991. POPs are one of several priority issues of AMAP. Results of Arctic monitoring and research are integrated in assessment reports to inform on the status of the Arctic environment. The latest assessment on POPs was published in 2009 (AMAP, 2009a) and a special report on “The Greenland

Ice Sheet in a Changing Climate” (AMAP, 2009b) was prepared. The Canadian Northern Contaminants Program (NCP), which reports through AMAP, has been operating since the late 1980s. Some of the early work under NCP synthesized a wide variety of data collected by various Arctic programs into five reviews dealing with sources, occurrence, and pathways of contaminants (Barrie et al., 1992); marine ecosystem contamination (Muir et al., 1992); terrestrial ecosystem contamination (Thomas et al., 1992); freshwater contamination (Lockhart et al., 1992), and risks/ benefits of northern diets (Kinloch et al., 1992).

The Antarctic Treaty entered into force in 1961. The purpose of the treaty is to protect the Antarctic environment from negative anthropogenic influence. Among other protective measures that have been adopted under this treaty, the Protocol on Environmental Protection, adopted in 1991, commits Parties to the comprehensive protection of the Antarctic environment and prohibits all activities relating to Antarctic mineral resources, except for scientific research. The Scientific Committee on Antarctic Research has recently published a thorough report on Antarctic Climate Change (ATME, 2010), which highlights changes to the cryosphere of this continent.

The sensitivity of alpine regions to organic contaminants is dealt with through a variety of regional and multinational programs, including the International Commission for the Protection of the Alps and the Alpine Convention and the International Scientific Committee for Alpine Research.

A number of global and regional long-term monitoring efforts have been established within the above mentioned treaties, agreements and programs to measure long-term records of contaminant levels. With the list of contaminants expanding, future research and monitoring efforts will need to consider the cycling and fate of chemically diverse analytes. This will present sampling and analytical challenges. Process studies are critical to understanding the local, regional and global fate of historic and emerging contaminants. In Sect. 3, we discuss in more specific terms these processes and the role of the global cryosphere in contaminant transport, dynamics and variability.

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3 Impacts of the cryosphere on contaminant fate

Once emitted to the atmosphere, organic contaminants can undergo a variety of physical, chemical and biological processes that in combination make up their fate in the environment. Long-range atmospheric transport is the main mechanism that results in the observed global distribution of contaminants (Peterle, 1969; Peel, 1975; Risebrough et al., 1976; Tanabe et al., 1983; Oehme and Mano, 1983; Oehme, 1991, Barrie et al., 1992, 1997, 1998) and numerous partitioning processes can occur along these transport routes. Long-term atmospheric monitoring provides a critical activity to estimate spatial and temporal trends, and also to identify the manner in which climate change may affect atmospheric transport. In both Arctic and Antarctic regions long-term atmospheric monitoring programs are presently established (Su et al., 2008; Hung et al., 2010; Ma et al., 2011; Kallenborn et al., 2012). Specifically, in the Arctic, legacy POPs have been monitored for the past two decades, whereas in the Antarctic similar monitoring has been initiated more recently, commencing in 2007 (Kallenborn et al., 2012). Incorporation in snowpack and ice creates temporary reservoirs of contaminants, but as melting of the reservoirs progresses, redistribution occurs. The wide variety of processes that contribute to contaminant cycling and fate are summarized in Fig. 1, and discussed in further detail in Sect. 3.1–3.9.

3.1 The role of snowfall in contaminant delivery to surfaces

Falling snow plays an important role in the transport and ultimate distribution of organic contaminants in cold environments. The enhanced partitioning of gas-phase chemicals to surfaces at cold temperatures, combined with the large surface areas of snowflakes, results in snow being an excellent scavenger of semi-volatile organic chemicals from the atmosphere (Lei and Wania, 2004). Chemicals that reach the Earth's surface with falling snow are then subject to several different possible fates, which will be discussed in the following sub-sections. However, here we discuss the transport of chemicals from the atmosphere to the Earth's surface via snowfall.

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Organic contaminants have been measured in freshly fallen snow collected in different parts of the world, including at an urban site in Europe (Czucwa et al., 1988), in mid-latitude mountains (McConnell et al., 1998; Zabik and Seiber, 1993), in the Arctic (Herbert et al., 2005a, b), and in Antarctica (Cincinelli et al., 2005). Lab-based studies have measured the sorption of organic contaminants to snow and ice (Hoff et al., 1995; Roth et al., 2004; Dominé et al., 2007a), models have been developed for estimating snow-air partition coefficients (Roth et al., 2004), and scavenging ratios have been determined for a number of volatile and semi-volatile organic compounds (Franz and Eisenreich, 1998; Starokozhev et al., 2009).

Snowfall scavenges a wide array of contaminants with different physicochemical properties. This occurs because (a) relatively volatile contaminants that reside predominantly in the atmospheric gas phase can partition into or onto snowflake surfaces and (b) contaminants with lower volatility sorb to atmospheric particulate matter that is trapped by falling snow. The degree of scavenging, and its mechanism, varies for different chemicals and at different temperatures, as shown for polycyclic aromatic hydrocarbons (PAHs) and PCBs via calculations for vapor and particle scavenging ratios (Wania et al., 1999a; Lei and Wania, 2004). Because chemicals redistribute between phases when snow is melted for analysis, measurements in melted snow cannot be used to directly determine how snowpack-entrapped chemicals were distributed in the atmosphere before deposition (Wania et al., 1999a). However, Carrera et al. (2001) detected in snowpack both low- and high-molecular weight PAHs, which reside in the vapor- and particle-bound phases in the atmosphere, respectively. Likewise, Schrlau et al. (2011) observed a wide range of particle-bound fractions of chemicals in snow melt water.

The pathways via which organic contaminants enter snowpack include vapor scavenging by snow, particle scavenging by snow, dry gaseous deposition, dry particle deposition, and scavenging by spring rain. The relative importance of these different pathways has been investigated via modeling (Daly and Wania, 2004; Stocker et al., 2007) and varies significantly between specific contaminants, depending on their

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physicochemical properties. Carrera et al. (2001) used field data to show that the importance of snowfall in delivering contaminants to remote alpine regions varied significantly between mountain regions in Europe. More than two thirds of the total deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) to a Northern Swedish watershed occurred during months with average temperatures below freezing, with the highest values observed during months with snowfall (Bergknut et al., 2011). By measuring pesticides in both summer rain and winter snowfall, Mast et al. (2007) showed that the total annual wet deposition of the relatively water-soluble pesticides, atrazine, carbaryl, and dacthal in the Rocky Mountains was > 85% from rain. Snow is actually less efficient than rain in scavenging water soluble organic species (Lei and Wania, 2004). Thus, both modeling and measurement studies indicate that the importance of snowfall in affecting the transport behavior and distribution of organic contaminants in the environment depends heavily on chemical properties and the location.

Due to the temperature-dependence of snow-air partition coefficients, temperature plays an important role in determining the degree to which snow scavenging occurs. This effect is apparent when sampling snowpack along elevational gradients in mountains (Blais et al., 1998; Arellano et al., 2011). Wania and Westgate (2008) used calculated vapor and particle scavenging ratios for both snow and rain at different temperatures to demonstrate why increasing contaminant concentrations along elevational gradients in mountains are sometimes, but not always, found. Hageman et al. (2010) found that the geographic distribution of contaminants in snowpack in eight alpine and Arctic national parks in North America could be explained by local contaminant sources but only if the effect of temperature on snow-air partitioning was considered as well (i.e. the concentrations at the much colder arctic sites were higher than expected based on source contribution alone).

The degree to which contaminants are delivered from the atmosphere to the Earth's surfaces by falling snow depends on both the contaminant concentrations in snow as well as the amount of snow that falls. Blais et al. (1998) showed that the increasing amounts of contaminant deposition along an elevational gradient in western Canada

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was due to both increasing contaminant concentrations in snow with elevation (due to the temperature effect) and increasing amounts of snowfall with elevation. Annual precipitation trends along elevational gradients vary significantly in different mountain systems (Wania and Westgate, 2008), which partly explains why contaminant concentration trends in mountains vary. In a different type of spatial comparison, Usenko et al. (2007) showed that increased snowfall on the east side of the Rocky Mountains contributed significantly to the higher relative contaminant concentrations in lake sediments on that side of the divide.

Because snow can serve as an efficient transport medium for semi-volatile organic contaminants, this mechanism of contaminant delivery to the surface is susceptible to changes due to climate change. A change in the extent of snow cover brought about by a changing climate may affect the global fate of organic contaminants (Macdonald et al., 2003a, b; Stocker et al., 2007). The Intergovernmental Panel on Climate Change (IPCC, 2007) projected that precipitation in a changing climate will differ considerably around the globe with increasing (e.g. 40% increase from mean) and decreasing (e.g. 20% reduction from mean) trends occurring in different regions. In regions with increased snow precipitation, deposition of organic contaminants from air to surface media would increase; and in regions with and during times of low or no precipitation, organic contaminants can be atmospherically transported more effectively (UNEP/AMAP, 2011). However, there is a lack of direct observed evidence of the effect of changing snow in terms of both quality, e.g. changing specific surface area or timing of aging and compaction etc., and quantity due to climate change on organic contaminant transport and fate. This is certainly an area for future research and monitoring endeavors.

3.2 Preservation of contaminant deposition records in ice cores

In geographic locations where snow is converted to firn, and eventual permanent ice, it is possible to examine contaminant records preserved in ice cores. Anthropogenic organic contaminants have been measured in ice cores collected in a variety of locations

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including Svalbard, Norway (Isaksson et al., 2003; Ruggirello et al., 2010; Hermanson et al., 2010); Colle Gnifetti in the Swiss/Italian Alps (Gabrieli et al., 2010); Mt. Everest (Wang et al., 2008); Lys Glacier, Italy (Villa et al., 2006) and Ellesmere Island, Canada (Gregor et al., 1995). Using literature-reported data, Wang et al. (2010b) found correlations between climate variation patterns (including the El Niño-Southern Oscillation, the Siberia High pattern and the North Atlantic Oscillation) and deposition of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) in ice cores from Mt. Everest (the Tibetan Plateau), Mt. Muztagata (in the eastern Pamirs) and the Rocky Mountains in North America. These associations suggest linkages between climate variations and organic contaminant distribution. It is difficult to segregate the relative extent of the influence of climate variation/change from emission changes on the deposition of contaminants to ice and snow cores, but the records clearly show that deposition at given sites is a product of both the strength of emissions and other factors (winds, temperatures, secondary sources) that are strongly affected by climate variability and climate change. As emissions decrease, the secondary sources grow in relative importance and these are strongly controlled by climate.

Utilization of firn and ice cores in the Arctic is providing insight into the recent (< decade) and longer-term (multi-decadal) accumulation history of POPs and other organic contaminants (e.g. currently used pesticides, brominated flame retardants, perfluorinated alkylated acids) (Young et al., 2007; Hermanson et al., 2005, 2010; Ruggirello et al., 2010; Meyer et al., 2012). Contaminant accumulation in ice is unlikely to provide accurate depositional fluxes for a given year due to the post-depositional processes that can occur. In order to reconstruct past atmospheric pollution and climate from Alpine ice cores, glaciers having negligible influence by percolating meltwater were selected, because meltwater disturbs the annual layer structure. However, due to recent climate warming it becomes more and more difficult to find unaffected cold glaciers, particularly in temperate mountain regions. Eichler et al. (2001) drilled an ice core from the accumulation area of the glacier Grenzgletscher (Swiss Alps) at 4200 m.a.s.l. and analyzed inorganic tracers. A significant deviation of the

5 Cl^- -to- Na^+ -ratio from the expected seawater ratio of 1.16 provided evidence for the transport of soluble chemical species with the percolating meltwater moving within this glacier. Today, the relevance of percolating meltwater for the conservation of organic contaminants within temperate ice is hardly known. Nonetheless, the few existing studies do provide an excellent assessment of relative contaminant accumulation history. Ice/firn cores taken in the Norwegian and Canadian Arctic provide information on geographical differences in sources and contaminant transport patterns. The valuable time-series provided by firn and ice cores could complement air monitoring efforts in the Arctic and elsewhere, particularly with respect to newer, emerging contaminants for which longer term measurements in air are lacking. Coordination of coring efforts and the tying together of different field programs (polar regions and alpine) may provide a useful endeavor for global monitoring efforts under UNEP.

3.3 The exchange of organic chemicals between snow and the atmosphere by wind ventilation

15 The porous nature of snow as well as the extent of the global area that is permanently or seasonally covered by snow provides for a substantial exchange of organic chemicals between snow and the overlying atmosphere (Wania et al., 1998b; Halsall, 2004), which may even affect global atmospheric chemistry (Dominé and Shepson, 2002; Grannas et al., 2007). Losses of chemicals from the snowpack may be driven thermodynamically by a loss of storage capacity in ageing snow with diminishing surface area (Cabanés et al., 2003) and possibly higher temperature, and kinetically by wind ventilation (Colbeck, 1989; Albert and Shultz, 2002; Albert et al., 2002). Such loss has been observed empirically in the field (Herbert et al., 2005b; Finizio et al., 2006; Burniston et al., 2007) and also reproduced by simulation models (Daly and Wania, 2004; Hansen et al., 2006; Stocker et al., 2007). Even semi-volatile organic contaminants such as tri- and tetrachlorinated PCBs as well as three- and four-ring PAHs can volatilize from the snow in notable amounts (Meyer and Wania, 2011b). In such cases wind ventilation efficiently removes gaseous substance from the snowpack, while the

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associated chemical loss in the snow pore space is rapidly compensated for by desorption from snow grain surfaces, in order to maintain partitioning equilibrium (Meyer and Wania, 2011b).

The gaseous mass transfer between snow and the atmosphere is in most cases limited by chemical transport within the snow pore space (interstitial air). The more a chemical partitions into the pore space, the larger is its potential for exchange with the atmosphere (Meyer and Wania, 2011b). Chemicals in dry snow are either present as gases in the pore space, or sorbed to snow grain surfaces and particulate matter. In dry and clean snow, prevalent in subarctic and arctic regions during winter, only the pore space and snow grain surfaces are important for mass transport (Meyer and Wania, 2011b). The distribution between those two phases depends on the chemical's partitioning properties, snowpack properties and temperature. The temperature-dependent equilibrium sorption coefficient to the snow grain surface from the gas phase K_{IA} [m] can be expressed as:

$$K_{IA} = C_I / C_A \quad (1)$$

where C_I [mol m^{-2}] is the chemical concentration at the snow grain surface and C_A [mol m^{-3}] is the snow pore vapor concentration. The dimensionless bulk snow/air partition coefficient K_{SA} can be calculated using:

$$K_{SA} = K_{IA} \cdot SSA \cdot \rho \cdot 100 \quad (2)$$

where SSA and ρ are the specific surface area, and density of the snow. Roth et al. (2004) measured K_{IA} values for numerous organic chemicals and provided a linear free energy relationship that can be used to estimate the chemical partitioning into the gas phase for numerous organics.

In previous studies that describe snow-atmosphere exchange, the chemical flux has been calculated as the product of the concentration difference between the air above the snow and the snow pore space, and an overall mass transfer coefficient (MTC).

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The latter parameter is associated with relatively high uncertainty. In some studies the MTC was set as a constant (Wania, 1997; Halsall, 2004; Herbert et al., 2006; Stocker et al., 2007), whereas in other studies it was treated as a wind speed dependent variable (Daly and Wania, 2004; Hansen et al., 2006). Such parameterizations of the MTC should be appropriate when investigating chemical exchange processes over time periods of weeks or months. However, the description of processes occurring on shorter time scales, such as the diurnal chemical exchange induced by photolytic reactions, requires a more precise MTC parameterization. Albert and Shultz (2002), Albert and Hawley (2002) and Albert et al. (2002) filled some of the associated knowledge gap by investigating chemical transport within snow induced by wind ventilation. Wind ventilation was found to substantially enhance the snow-atmosphere exchange and can cause advective chemical transport even at snow depths of several meters (Albert et al., 2002). The intensity of wind ventilation depends on the wind speed, snow permeability and snow surface roughness features. Wind ventilation in snow is caused by pressure variations induced by wind turbulence and “form drag” pressure around snow surface roughness features (Albert and Hawley, 2002). At Summit, Greenland, snow surface roughness features that are more pronounced in winter than summer can notably increase the rate of chemical transport in snow, assuming similar wind conditions (Albert and Hawley, 2002).

It is also important to note that artificial ventilation of snowpack can be induced by certain chemical measurement techniques. Measurement methods that rely on pumping of interstitial air from the snowpack for chemical analysis/detection often require flow rates on the order of liters per minute, which causes advection-dominated flow and mixing of concentrations of analyte from various depths in the snowpack (Albert et al., 2002). As such, measured interstitial air chemical concentrations may not represent the true, local concentration at a given point in a snowpack.

Snow permeability strongly influences snow-atmosphere exchange, and depends mainly on snow layering and snow microstructure. Although snow density has been commonly applied in the past to estimate permeability, it only correlates poorly in terms

of air transmissibility (Albert et al., 2000). Adopting Darcy's Law, we can describe the permeability in snow as the proportionality factor between the bulk snow pressure gradient and the flow velocity (Albert and Perron, 2000). Permeability in a seasonal snowpack can change by two orders of magnitude over the course of the winter (Dominé et al., 2008). Snow permeability can also vary by almost one order of magnitude between different snow layers within one snowpack (Albert et al., 2000).

Polar and subarctic snow covers have the largest spatial and temporal extension. Compared to subarctic snow, arctic snow usually exhibits higher densities and specific surface areas (Dominé et al., 2007b), shallower depths (Sturm et al., 1995), and lower permeability (Albert and Shultz, 2002), and is exposed to higher wind speeds (Canadian Wind Energy Atlas, 2003) as well as lower temperatures (Taillandier et al., 2006). The latter results in a generally much higher K_{SA} in the Arctic. A case study by Meyer and Wania (2011b) revealed that by assuming snowpack properties and environmental conditions typical for subarctic and arctic regions, PCB-28 would experience a net release from a subarctic snowpack, whereas in the Arctic net deposition would occur. By combining the effects of chemical partitioning and snow properties, the MTCs are two to three orders of magnitudes larger under the influence of moderately strong winds than under still wind conditions.

3.4 The role of seasonal snowmelt in modifying organic contaminant behavior in watersheds

Snow (and associated contaminants) can experience various processes once deposited to the surface. In persistently cold climates, snow will continue to accumulate and at higher depths form firn as it is compressed by the snow above. During this time, interstitial air between snow grains can be exchanged with the atmosphere above the snowpack, until the pores eventually close off and air is trapped. As pressure increases, firn is eventually compressed into ice, and this ice (and the air trapped within) can serve as an invaluable record of past atmospheric composition. In all but the most extreme environments, seasonal snowmelt occurs, and this can significantly impact

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the local and regional hydrology, nutrient cycles and contaminant fate. For much of the Arctic and at lower elevations in alpine regions, the snow melts completely by the end of summer (e.g. Armstrong, 2001), but warming is leading to a shortening of the snow season (Olsen et al., 2011 and references therein). Here we discuss the fate of contaminants in the context of seasonal snowmelt cycles.

3.4.1 The role of seasonal snow in contaminant amplification

In high latitudes or altitudes, snow influences both watershed input and retention of contaminants. Seasonal snow can act as a temporary reservoir for contaminants and as a contaminant source to a watershed during the snowmelt period. The likelihood of detrimental effects of contaminants on aquatic species depends on the contaminants' toxicity, its concentration, and the period of exposure. Not only is the long-term average concentration in water relevant in this context, but also the short-term concentration variability, especially as it relates to seasonal biological cycles. Specifically, fluctuating concentrations can be more toxic than average concentrations (Ashauer et al., 2011). The specific timing of concentration peaks is crucial, namely whether they coincide with time periods of particular organism susceptibility or food uptake. Water concentrations strongly depend on a contaminant's input to a watershed, i.e. either the use and emission of the contaminant within the watershed or the rate of atmospheric deposition to watershed surfaces. However, water concentrations will also depend on the retention capacity of the watershed, namely the fraction of the contaminant input that finds its way into the water compartment (Bergknut et al., 2011). In addition to contaminant properties, such as partitioning behavior and degradability, many watershed properties will influence this retention capacity, including relief, soil properties, and meteorological and hydrological characteristics. Watershed retention will almost certainly be subject to high temporal variability on a number of time scales, and thus will impact the extent and timing of concentration peaks and thereby also toxicity.

Falling snow can influence contaminant input to a watershed by modifying the rate of atmospheric deposition, as discussed in Sect. 3.1. A seasonal snow cover is of interest

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partly because it may influence the long-term average retention of contaminants in a watershed, but mostly by modifying the extent and timing of concentration peaks in the water. This is because:

- A seasonal snow cover functions as a recipient and temporary storage reservoir for atmospherically deposited contaminants (for periods ranging up to 10 months), which disappears during melt and therefore releases the stored contaminants in a relatively short period of time.
- The high run-off associated with the spring freshet during snowmelt can result in the mobilization of particle-bound contaminants in soils and sediments.
- Contaminants are typically not released from snow packs with temporally uniform melt water concentrations, but they can be enriched in early or late melt water fractions.

These features of a seasonally snow covered watershed can essentially contribute to contaminant amplification, i.e. result in long-term average and/or peak concentrations of contaminants in water that are higher than they would be in the absence of snow (Meyer and Wania, 2008). Furthermore, the melt of a seasonal snow cover causes highest contaminant loads to occur in early spring, when organisms are at a particularly vulnerable stage of development. One particular motivation for seeking to understand the role of a seasonal snow cover in contaminant amplification is to achieve the ability to anticipate how climate change may impact aquatic organism exposure to contaminants (Macdonald et al., 2003a). Whereas rising temperatures may only slightly modify contaminant behavior in a watershed, small temperature changes can precipitate large changes in the characteristics of a seasonal snow cover (e.g. duration, depth, surface ice cover) and its melt (e.g. rate of melting). In other words, changes in contaminant pathways consequent to the melting of seasonal snow cover create a greater vulnerability to change than is the case in warmer regions.

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3.4.2 Snow cover as a recipient and temporary storage reservoir for atmospherically deposited contaminants

Organic contaminant deposition with and to snow is enhanced mostly because of the low temperatures, which cause semi-volatile chemicals to transition from the gas phase to atmospheric particles and ice surfaces (Lei and Wania, 2004). Snow cover is not an efficient storage reservoir for all organic species. As discussed in Sect. 3.3, more volatile substances are readily lost by evaporation back to the atmosphere. Some contaminants may also be degraded within the snow, as discussed in Sect. 3.9. Despite high thermodynamic forcing, contaminants may not be able to escape the snowpack in locations where freezing rain has sealed the surface, an occurrence which appears more frequently in a warming climate (e.g. Post et al., 2009), and in these special cases a higher proportion of the contaminant may enter the water cycle during the freshet.

Generally, only the photochemically stable and less volatile organic contaminants will still be present to a large extent in a seasonal snow cover at the onset of melt. Empirically, it has not yet been established whether the annually averaged watershed retention of these organic contaminants is enhanced or diminished through the presence of a seasonal snow cover. However, we may surmise that contaminant retention in a watershed experiencing highly episodic run-off with very high, albeit short run-off rate maxima is lower than in a watershed where run-off occurs more uniformly. There are two reasons for this: (i) Whereas run-off conditions that favor infiltration to soils are expected to increase contaminant retention within the watershed, in particular for compounds sorbing to soil organic matter, overland flow is less likely to be “filtered” by passage through the ground. Snowmelt generates high run-off during time periods when the ground is often still frozen and thus largely impermeable, resulting in a higher portion of run-off occurring on the surface than below the ground. (ii) Very high run-off rates as may occur during snowmelt result in greatly enhanced potential for solid phase transport and thus in the mobility of particle-sorbed substances. Overall, we may therefore expect that not only are the maximum water concentrations higher in the presence

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of a seasonal snowpack, but so are the annually averaged water concentrations. Exceptions may be urban watersheds that experience intense rain events that resemble those during the spring freshet (Zhao and Gray, 1999).

There is field evidence of the contaminant amplification potential of a seasonal snow cover. Lafrenière et al. (2006) noted that organic contaminant concentrations in early melt water from a remote alpine area were much higher than in the snowpack, and even the more hydrophobic compounds were highly concentrated in melt water. Bergknut et al. (2011) noted that as much as 71 % of the annual export of PCBs and 79 % of that of the PCDD/Fs from a Boreal catchment in Northern Sweden occurred during the snowmelt induced spring flood, a percentage exceeding considerably the contribution that the spring freshet makes to the annual flow of water (52 % to 66 %). The higher percentage for the contaminant export was attributed to significant amounts of melt water reaching streams through overland flow. Comparing snowmelt run-off in an urban area during two subsequent years, Meyer et al. (2011a) observed higher peak concentrations of the pesticides chlorothalonil and γ -HCH in stream water in the year when the snowpack was thicker and when a higher proportion of run-off occurred by overland flow rather than subsurface flow. PAH transport in this urban watershed during snowmelt was found to correlate strongly with run-off rates, which in turn were controlled by the intensity of melting (Meyer et al., 2011a). Concentrations of PAHs during high flow conditions were as much as two orders of magnitude higher than during low flow. Because of the 10 times higher run-off, PAH transport in the river during the spring freshet was three orders of magnitude higher than during normal flow (Meyer et al., 2011a). Also the flow of long chain perfluoroalkyl acids, believed to be largely particle-bound, had peak concentrations during the period of maximum snowmelt run-off, likely due to the mobilization of contaminated particles under high flow conditions (Meyer et al., 2011b).

Incidentally, dilution of compounds by the high run-off occurring during snowmelt is also possible, namely for compounds that do not have primarily atmospheric origin. Non-atmospheric watershed sources may become diluted by melt water containing

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low concentrations of such contaminants, at least as long as these are not particle bound and the remobilization of solids counteracts this dilution effect. An example of this phenomenon is the concentrations of short chain perfluoroalkyl acids in an urban creek, which dipped during the spring freshet (Meyer et al., 2011b), in contrast to the behavior of long chain perfluoroalkyl acids mentioned above.

3.4.3 Fractionated release of contaminants from melting snow

Snow can contribute to contaminant amplification not only at the watershed scale, but also on the scale of the snowpack itself (Meyer and Wania, 2008). It had been established for quite some time that early melt water fractions are enriched in inorganic ions (Johannessen and Henriksen, 1978; Tsiouris et al., 1985). Mechanistically, this is explained by a melt water front percolating down a snowpack and dissolving the ions that have been excluded from the ice matrix and are, thus, present within a liquid-like layer at the snow grain surface. When late melt water forms and percolates through the snowpack, most of the ions have already been eluted. A mechanistically similar phenomenon of early elution (type 1 in Table 1) was observed for water soluble organic contaminants during studies involving artificially generated and contaminated homogeneous snow that was subjected to controlled melt conditions (Schöndorf and Herrmann, 1987; Meyer et al., 2006, 2009a). In fact, elution curves of water soluble organics, which are estimated to partition predominantly (> 90 %) to the liquid water phase present in a melting snowpack, closely resembled electrical conductivity measurements in the melt water (Meyer et al., 2009a, b). Because of the larger molecular size of organic contaminants, exclusion from the ice matrix can be assumed to be even more complete than that of inorganic ions (Kammerer and Lee, 1969). In laboratory experiments, the first quarter of the melt water contained as much as three quarters of the total load of water soluble chemicals, such as the pesticide atrazine. The first melt water fraction had concentrations in excess of five times the average snow concentration (Meyer et al., 2009a). Preferential enrichment of water soluble organic contaminants

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was also observed in the field: Lafrenière et al. (2006) noted the strongest enrichment in early melt water samples for HCHs.

The opposite behavior was observed for particle bound organic substances in the controlled melting experiments. Because snow, in particular if it has undergone repeated freeze-thaw cycles, often acts as a particle filter, particle-sorbed substances are retained in the melting snowpack to be released only at the very end of the melt (type 2, Table 1). Examples of contaminants behaving this way are the larger PAHs (Meyer et al., 2009a), the longer chain semifluorinated alkanes used in skiwaxes (Plassmann et al., 2010), and mercury (Mann et al., 2011).

Some substances' sorption behavior is such that they are only partially particle-sorbed in snow. Their release from melting snow is then characterized by an early elution of the fraction dissolved in water and a second late peak associated with the release of particles from the snowpack (type 4, Table 1). Which one of these peaks dominates not only depends on the contaminant's partitioning properties, but is also strongly dependent on snowpack properties, such as the particle content (Meyer et al., 2009a, b; Meyer and Wania, 2011a). For example, in snow with very low particle content, even quite hydrophobic contaminants are enriched in early melt water fractions (Lafrenière et al., 2006).

Particle sorption is not the only reason for contaminant enrichment in late melt water fractions. A late release is also observed for somewhat water soluble substances that sorb strongly to the snow grain surface, but instead of being released only at the very end of the melt period, concentrations in the melt water tend to gradually increase in a late stage of melting when the snow surface area and thus the snow's sorptive capacity is diminishing and disappearing (type 3, Table 1). Such behavior was observed for long chain perfluoroalkyl acids (Plassmann et al., 2011) and predicted for pesticides such as chlorpyrifos (Meyer and Wania, 2011a).

A peculiar release behavior with maximum melt water concentration in the middle of the melt period (type 5, Table 1) was observed for intermediate chain length perfluoroalkyl acids (Plassmann et al., 2011). This release profile could only be explained by

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assuming that the strength of sorption of the compounds to the snow grain surface is declining during the snowmelt period, for reasons that are currently still unclear, but may be related to the changing ionic composition of the melt water (Plassmann et al., 2011). Also the release of mercury from a melting snowpack was found to be influenced by the ionic strength of the water used to make the artificial snow (Mann et al., 2011).

All five types of elution behavior in Table 1 could be reproduced with, and thereby mechanistically explained by, a snowpack melt model that simulates the sequential melting of several horizontal snow layers and the resulting downward percolation of melt water (Meyer and Wania, 2011a; Plassmann et al., 2011). The model assumes equilibrium partitioning between the various snowpack phases (snow grain surface, particulate matter, melt water, air-filled pore space), suggesting that thermodynamic considerations are sufficient to explain the differences in the elution behavior of different chemicals (Meyer and Wania, 2011a).

Both laboratory experiments and model calculations have been used to explore what snowpack and melt characteristics have the largest influence on the contaminant enrichment in melt water (Meyer et al., 2009b; Meyer and Wania, 2011a). The early elution of water soluble compounds (type 1, Table 1) was found to be most pronounced in deep and aged snowpack that is melting rapidly, while it is attenuated in layered snow with hydraulic barriers and in snowpacks that are subject to bottom melt (Meyer et al., 2009b; Meyer and Wania, 2011a). The filtering of particles by the snow, and therefore enrichment of type 2 (Table 1) was enhanced in dense snow consisting of fine and faceted snow grains as well as by the formation of dirt cones (Meyer et al., 2009b).

The contaminant enrichment in melt water observed at the base of the snowpack may be reflected to different extents in the timing of concentration peaks in the receiving water bodies. In the case of the water soluble contaminants that peak early during snowmelt the concentration observed in receiving waters depends on the extent of ground infiltration and surface run-off, as was illustrated by the case of the pesticide chlorothalonil in an urban stream discussed earlier (Meyer et al., 2011a).

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The enrichment of particle-bound substances in the late melt water fractions is likely of little relevance for the timing of concentration peaks of such substances in the receiving rivers, because it is overwhelmed by the high particle loads caused by high run-off rates during snowmelt. In other words, highest water concentrations for such substances would likely occur during the period of highest run-off. In cases where melt water directly enters water bodies, such as occurs during glacial melt or when snow on ice covered lakes and oceans is melting, the timing of release from the snowpack base may be more relevant in understanding the timing of concentration peaks in the water.

3.5 Fate of contaminants in melting glaciers

Similar to Arctic environments, the scavenging and deposition of atmospherically transported POPs by snow plays an important role delivering POPs to alpine environments (Finizio et al., 2006; Vighi, 2006; Thies et al., 2007; Kang et al., 2009; Wang et al., 2010b; Bogdal et al., 2010). High altitude environments, which are believed to be particularly susceptible to rapid climate change, provide cryospheric reservoirs of POPs (Blais et al., 2001b; Batterbee et al., 2009; Schmid et al., 2011). Blais et al. (2001a) have shown that a glacier-fed tributary was the dominant source of most POPs to a sub-alpine lake in the Canadian Rocky Mountains. They have also found that at least 10 % of the glacier melt discharging into this lake originated from the ice that was deposited during 1950–1970, a period with greater contamination by organochlorines (Blais et al., 2001b). The authors warned that enhanced glacial melt due to climate change may increase the release of contaminants to freshwater. Melting mountain glaciers have become a local secondary source for POPs (Blais et al., 1998; AMAP, 2005; Bogdal et al., 2009); measurements of a large range of POPs, including PCBs, PCDD/Fs and organochlorine pesticides, revealed a remarkable re-increase of sediment concentrations in pro-glacial lakes directly fed by melt water from rapidly melting adjacent glaciers (Fig. 2). A comparison between sediment trends in vicinal Swiss Alpine lakes confirmed that sediment concentrations are increasing in glacier-fed lakes closely following the movement of the glacier (Fig. 2a and b), while in non-glacial lakes concentrations are

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following a decreasing trend expected by emission reduction measures taken a few decades ago (Fig. 2c; Schmid et al., 2011).

Coupling of a dynamic chemical fate model for PCBs, DDTs, and PCDD/Fs based on historical use and emission scenarios for these POPs with a transient glacial ice flow model enabled further confirmation of this glacier hypothesis and provided insight into the interconnection between contaminant-, glacier-, and climate-dynamics (Bogdal et al., 2010). It could be shown that since the 1990s, climate change has resulted in an acceleration of the release of POPs stored in Alpine glaciers. A steady-state climate would also have resulted in a release of contaminants but at a much slower rate. Due to climate warming, POPs are released earlier and more concentrated by glacial melt water. The release of chemicals may be further boosted if glacier melting continues to accelerate at the same rate in the future. Between 1999 and 2008, the Swiss glaciers lost about 12 % of their ice volume, whereas the extraordinarily warm summer of 2003 caused a volume loss of 3.5 % (Farinotti et al., 2009).

Locally the release of POPs during the glacial melting season may represent a relevant source of toxic compounds to sensitive mountain ecosystems and may affect biota. Melting glaciers have also been hypothesized as a source for the continuing exposure to DDT of Adélie penguins from the Western Antarctic Peninsula (Geisz et al., 2008).

3.6 Contaminant occurrence and processing in the sea-ice snowpack and sea-ice

The year-round ice cover of the Polar oceans (central Arctic Ocean and the southern margin of the Southern Ocean) is an effective barrier to evaporation of POPs from sea-water to the atmosphere. Sea ice cover responds directly to average ambient temperature (i.e. thermodynamic processes of freezing and melting) and is strongly affected by winds (i.e. dynamic forcing, Screen and Simmonds, 2010). Sea ice cover itself is a transient reservoir and transporting mechanism for anthropogenic contaminants (e.g. MacDonald et al., 2005). In addition, significantly reduced ice cover in late summer, as

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observed over the western Arctic Ocean in recent years, will lead to increased evaporation of semi-volatile contaminants formerly trapped below the sea ice. α -HCH and other volatile POPs (e.g. hexachlorobenzene, HCB) are sensitive to this temperature effect (e.g. Li et al., 2004). Measurements made as early as 1993 (Jantunen and Bidleman, 1996) showed that atmospheric declines in α -HCH, due to abandonment of use by China and India (e.g. Li and Macdonald, 2005), resulted in a reversal of the air-sea flux direction of HCHs from net deposition in the 1980s to net volatilization in the 1990s. Measurements of the enantiomer compositions of α -HCH (the only chiral HCH) in air and surface seawater in Arctic Canada (Jantunen et al., 2008; Wong et al., 2011) show that more open water is allowing for more volatilization from the ocean reservoir. Both Jantunen et al. (2008) and Wong et al. (2011) showed that during winter/spring ice coverage, α -HCH in the air had racemic enantiomeric composition (EF = E1 / E1 + E2; racemic mixture = even distribution for both enantiomers where EF = 0.5) but with the loss of ice cover in spring, the concentrations in the air rose considerably from the winter values, and the EF changed towards the signature of the surrounding waters (Fig. 3). Changes in EF upon ice breakup allow non-racemic α -HCH in sea water to volatilize and mix with nearly racemic atmospheric α -HCH advected by long-range transport, resulting in the potential to use chiral signatures to track changes in air-water gas exchange due to loss of ice cover in the ocean.

Pučko et al. (2012) evaluated the evolution of the α -HCH inventory in the Beaufort Sea and found that between 1986 and 1993, the inventories increased due to loading via ocean currents, while gas exchange, river inflow and ice export were negligible α -HCH input/output routes. Degradation processes could explain the decrease in observed α -HCH concentrations between 1993 and 2007 and they anticipate that the majority of α -HCH could be degraded in the Beaufort Sea by 2020.

Concentrations of POPs in the Arctic atmosphere during the past ten years have varied regionally but are generally trending downward (Hung et al., 2010). An exception to this is hexachlorobenzene (HCB), a former pesticide and still an unintended by-product of various industrial chemical processes. Atmospheric increases of HCB are

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observed since 2003 at the Zeppelin (Svalbard) mountain research station (Fig. 4). A similar increasing trend in HCB was also observed at the Canadian High Arctic station of Alert (Wang et al., 2010a).

Overall, the downward trends of organochlorine air concentrations are due to the reduction of use/production of these compounds. It is currently unclear what has caused the change in the downward trend of HCB atmospheric concentrations since 2003 near Zeppelin. Becker et al. (2012) discuss the recent upturn in HCB concentrations and consider several hypotheses for this behavior. Revolatilization from previously contaminated soils and vegetation may influence atmospheric concentrations (Bailey, 2001; Barber et al., 2005), as well as the presence of HCB impurities in currently used pesticides. The fungicides, chlorothalonil and quintozene, and the arachnicide, tetradifon, have been shown to contain HCB as impurities (Gouin et al., 2008). Besides the possible use of HCB-contaminated pesticides, these increases may be related to a reduction in sea ice cover on the west coast of Spitsbergen, where Zeppelin is located, which has become ice free in the past 6–7 yr. The reduced ice cover in Fram Strait is a consequence of the significantly increased inflow of warm, surface North-Atlantic water (Slubowska-Wodengen, 2007; Nilsen et al., 2008). Although dramatic ice retreat has been observed in other parts of the Arctic, a permanently ice-free state at 80° N is unique. Ma et al. (2011) further analyzed the time series of POPs in Arctic air measured at Zeppelin and Alert to reveal evidence of remobilization of POPs trapped in Arctic environmental sinks (ice/snow, land and water) due to Arctic warming and sea ice retreat. They hypothesized that the overall downward trends observed in measured atmospheric POPs caused by decreasing emissions, changing locations of sources and environmental degradation may have masked any climate change influence on atmospheric POPs. By statistically removing the declining time trends, the underlying residuals showed increasing tendencies when Arctic sea-ice retreat sped up (Stroeve et al., 2007). The statistical detrending and correlation analysis of Ma et al. (2011) were almost entirely performed using summertime datasets in order to minimize the effects of low-latitude emissions and seasonality in the data (since Arctic ice melt is

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most significant and POPs input from southerly sources is lowest in summer). They found that concentrations of most POPs were positively correlated with summer surface air temperatures and negatively correlated with sea-ice extent from 2000 to 2009, at significance levels of 90 % or more.

5 Relatively few studies have examined the occurrence of organic contaminants in the sea ice system, largely due to logistical difficulties such as gaining access at the right time of the year. However, given the extensive areas covered by sea-ice and the dynamic nature by which organic contaminants can associate with and accumulate in snow and be transported and/or released during periods of melt, sea ice studies
10 are warranted. The transport of sea ice across the Arctic Ocean is an important process within the global cryosphere, as part of the freshwater cycle and possibly for the movement of contaminants contained within or deposited upon the ice (Pfirman et al., 1995; Lange and Pfirman, 1998). Simulations of contaminant transport by ice (Pavlov, 2007) have specifically investigated the potential for contaminants located in the vicinity of river-mouths of major rivers flowing into the Arctic Ocean, the Bering Strait, the White Sea on the northwest coast of Russia, and in the Faroe-Shetland Channel to transport elsewhere over a period of 15 yr. The model results support the concept that contaminated sediments from the East Siberian rivers (Melnikov et al., 2003) may be transported with the ice into the Central Arctic Ocean over a period of several years,
15 eventually reaching the marginal ice zones (MIZ) of the Western Arctic and the Barents Sea (Gustafsson et al., 2005) where they are released when the ice melts. Changes in the locations of ice formation and melting, and in the types and amounts of ice induced by climate change, therefore, may have the capacity to alter the export of contaminants from the Arctic. Although we have reasonable estimates of the volumetric transport of sea ice, the transport of particulates contained within sea ice, and some contaminant loads carried by that ice (Macdonald et al., 2005), the magnitude of this transport pathway for most POPs remains poorly quantified.

25 An additional concern is that contaminants stored in the winter snowpack over ice will in turn yield relatively contaminated melt water (see Sect. 3.4) which will collect in

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melt ponds and accumulate as a buoyant layer under melting ice resulting in exposure for ice-associated biota at a biologically-important time of the year. Furthermore, the entrainment of waterborne contaminants within seasonal sea-ice and their subsequent possible enrichment in ice-brine provides a mechanism resulting in the concentrated re-release of contaminants to marine waters. A notable summer field investigation in the MIZ of the Barents Sea examined PCBs in ice, snow and beneath-ice seawater as well as the micro-environments of ice-interstitial water and ice-rafted particulate matter (Gustafsson et al., 2005; Sobek et al., 2006). PCB concentrations, however, were found to be relatively low (e.g. PCB-52 in snow and seawater was observed in the range of 0.1–0.3 pg l⁻¹), with little evidence of contaminant enrichment in the various sea-ice sub-compartments, like the ice-melt water ponds. However, this field campaign was conducted during the warmer months of July–August when substantial freeze-thaw activity and melting had occurred, and when considerable time had elapsed to allow atmosphere-surface water gas exchange.

More recently, winter-based studies, as part of the Canadian Circumpolar Flaw Lead (CFL) system study, examined the entrapment and dynamics of POPs in the sea ice system of the eastern Beaufort Sea and Amundsen Gulf, including a detailed examination of the behavior of α - and γ -HCH in sea ice (Pućko et al., 2010a, b, 2011). Significant inverse relationships were evident between chemical concentrations in snow samples (i.e. melt water derived from well mixed snowpack samples) and snowpack density for HCB and the lower chlorinated PCB congeners, with a weaker relationship apparent for α - and γ -HCH and *cis*- and *trans*-chlordane, and no relationship apparent for PBDEs (congeners 47, 99 and 100) and C₄–C₁₀ perfluorocarboxylic acids (PFCAs). In this case, snow density was used as a surrogate for SSA, where samples of snow with higher density are assumed to have lower SSA (see Legagneux et al., 2002) based on the observations of the different snow types encountered during the CFL campaign. Interestingly, for the longer chain PFCAs (C₁₁–C₁₄) a significant positive relationship was apparent with snow density ($r^2 = 0.3$ – 0.7 , $n = 5$ – 10 , $p < 0.05$) indicating their accumulation or enrichment within higher density snow (with presumably lower

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SSA). However, the particle-bound fraction of these chemicals is likely to be significant (although this fraction was not analyzed separately) and the older, higher density snow may also effectively retain particulate matter, particularly following partial melt and water loss, which may account for the increase in concentrations. Conversely, a significant loss of α - and γ -HCH (by $\sim 40\%$) from fresh snowfall via re-volatilization was observed when windy conditions were encountered on the sea-ice, again attributed to the rapid increase in snow density and reduction in the SSA over a relatively short time period (< 24 h) following fresh snowfall (Pućko et al., 2011). These relationships with density and hence SSA indicate the degree to which a chemical is likely to be vapor-sorbed to the snow crystals, hence reductions in SSA are likely to result in evaporative loss of the more volatile chemicals, whereas lower volatile chemicals (e.g. PBDEs and PFCAs – the latter present in the snow in their anionic form) will be retained within the snowpack, especially if the compound has a significant particle-bound fraction.

Figure 5 presents a time-series of contaminant concentrations (HCB, α - and γ -HCH) measured in the ice snowpack of the Amundsen Gulf of the Canadian Arctic during CFL from late April to early June. The average daily air temperature fluctuated around 0°C from mid-May onwards, resulting in a notable reduction in the snowpack depth and cover, with the occurrence of melt-ponds on the sea-ice surface by late May. By early June, ice-cover in the Amundsen Gulf had decreased to $< 40\%$, compared to $\sim 98\%$ prior to May. Concentrations of HCB and HCHs in the snow appeared to decline from mid-May onwards accompanied by increasing concentrations in air. For α -HCH, increasing concentrations in overlying air as the melt season progresses are shown to be driven by increased volatilization from surfaces, particularly open seawater. Evidence for this comes from the signal of the enantiomeric fractions (EF) of α -HCH, which in air increasingly reflect the EF signal (< 0.5) of α -HCH observed in surface seawater during this period (Wong et al., 2011). The fraction of contaminants retained in the aged, melting snowpack are therefore likely to be released to surface marine waters during ice-floe breakup, although percolation into the ice matrix may occur first as the brine content exceeds 5% (volume fraction) during the onset of melting.

Multi-year or “old” sea ice was sampled in the Arctic Ocean and the MIZ of the Bar-
ents Sea during July–August, and showed low levels of PCBs ($\sum_{15}\text{PCBs}$, 9–48 pg l^{-1}
of ice melt water) that had significant particle-bound fractions (0.20–0.83) (Gustaf-
son et al., 2005). The particulate organic carbon content in ice (and snowpack) had a
notable role in dictating particle-bound PCB concentrations, with evidence of near equi-
librium partitioning conditions (i.e. empirically derived organic carbon/water partitioning
coefficients, K_{OC} , for PCBs showed strong linear correlations with corresponding K_{OW}
values). In this older ice there was little evidence of PCB enrichment in ice-associated
water, including ice-brine. However, at one site where seasonal melting had progressed
the least elevated PCB concentrations were observed relative to the other sample sites
(by factors of 5–10) (Gustafsson et al., 2005).

More recently, Pućko et al. (2010a, b) examined the behavior of α - and γ -HCH in
seasonal and first year ice in the CFL campaign and found HCH concentrations to be
higher in younger ice that contained brine (brine salinity $\gg 50$). The concentrations of
both HCH isomers and their vertical distributions in the ice were highly dependent on
the initial entrapment of brine in young ice and the subsequent desalination process. α -
HCH and γ -HCH levels decreased exponentially with increasing sea ice thickness fol-
lowing the sea ice desalination curve (Fig. 6). The correlations observed between HCH
concentrations, salinity and ice thickness imply that brine rejection is also accompanied
by HCH rejection which, in turn, will yield elevated concentrations in the brine-channels
within the ice and in the beneath-ice seawater during periods when brine exits the sea-
ice. HCH levels in the brine in the winter were approximately 13 times higher than in
bulk ice due to the freezing out effect as new ice forms, reaching $4.0 \pm 0.3 \text{ ng l}^{-1}$ for
 α -HCH, and $0.42 \pm 0.01 \text{ ng l}^{-1}$ for γ -HCH. At this time, these concentrations represent
the highest HCH concentrations in the Arctic marine environment, exceeding under-ice
water concentrations by a factor of ~ 3 in the spring (April–May) (Pućko et al., 2010a,
b). In spring, (i.e. from mid-April to mid-May) HCH concentrations in ice brine were
found to decrease gradually with time as the brine volume fraction increased (due to
melting of the ice crystal matrix) and the brine salinity decreased (Pućko et al., 2010b).

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Figure 7 summarizes the behavior of α - and γ -HCH in the sea-ice system of the Canadian Arctic and illustrates the physical processes which affect chemical behavior including the growth of sea-ice during fall/winter and the desalination of sea-ice as a likely source of organic contaminants to the beneath ice environment. HCH concentrations in newly-forming sea ice depend primarily on the initial sea water concentration, the rate of ice formation (HCH accumulation) and desalination (concurrent HCH rejection) until the combination of declining atmospheric temperature and increasing insulation by a thickening ice cover permit the ice to cool sufficiently for its brine volume fraction to drop below 5% (the fraction below which there is little brine movement within the ice). In the winter, most of the ice column exhibits a brine volume fraction below 5%; throughout this time the accumulating HCH concentrations at the bottom of the ice will become locked as the ice grows, thereby initially reflecting the HCH concentration of the water beneath the ice. After the first snow deposition, upward migration of brine from the surface of the ice will affect levels of salt and HCHs in the snow by diffusion out of the shallow 'slush' layer, which maintains a brine volume fraction > 5% (see Pućko et al., 2011). In contrast, and as stated above, ventilation under windy conditions will lead to a decrease in HCH concentrations in the pore spaces of the snowpack due to the loss of snow surface area. The extent to which snow can affect HCH levels in sea ice (and presumably other contaminants that possess similar physicochemical properties) is significantly smaller, and restricted to a short period in spring when the ice warms enough for its brine volume fraction to exceed 5%. Further research is needed to determine whether this behavior applies to other contaminants, particularly some of the newer POPs like the perfluoroalkyl acids, which are present in seawater and hence will be entrained in newly forming sea ice and deposited to the surface of the ice with snowfall.

In a warming Arctic, summer sea ice has experienced significant retreat in the past three decades with decreasing area coverage, reduced growth after summer, delayed fall freeze-up with a lengthened melt season, decrease in ice thickness over the central Arctic Ocean and a shift from a multi-year ice cover to ice less than a year old (Stroeve

et al., 2007; Steele et al., 2008; Lindsay et al., 2009; Perovich, 2011). More open water enhances solar heat input resulting in a warming upper ocean with greater ice melt (Perovich, 2011). Changes in ice coverage and temperature increase in the upper ocean have significant implications for the exchange of POPs between air and ocean.

5 POPs that have accumulated in the sea ice may be released during melt, and those stored in sea water may volatilize to the atmosphere when the Arctic Ocean opens. On the other hand, open water may receive more input of POPs via atmospheric deposition. The net amount and direction of flux between air and water depends on the fugacity gradient between air and water and the partitioning properties of the compound,
10 which are temperature dependent. Studies have shown that sea ice is an effective barrier for air-ocean exchange of contaminants (Jantunen and Bidleman, 1996). During an expedition in June–August 2004, Gioia et al. (2008) performed coupled air and water concentration measurements from which they inferred that deposition dominates over volatilization for PCBs in the Arctic region. However, near the MIZ (78–79° N), their
15 calculations show higher net deposition of PCBs because of higher PCB air concentrations. It is uncertain whether this was because melting ice margins were a source of PCBs to the atmosphere or whether more complex ice-water-atmosphere interactions were occurring (e.g. coupled to phytoplankton activity). Note that not all chemicals show net volatilization; recent studies have predicted net deposition of HCB into the Arctic
20 Ocean (Su et al., 2006; Lohmann et al., 2009; Wong et al., 2011) and exchange directions varied for α - and γ -HCH, 2,4-dibromoanisole (DBA) and 2,4,6-tribromoanisole (TBA) by season and locations (Wong et al., 2011).

25 In the last decade the proportion of older, multiyear ice (> 2 yr old) in the Arctic Ocean has diminished markedly (e.g. > 4 % decrease from 2005 to 2008) with a corresponding increase in younger ice (< 1 yr old) (Kwok et al., 2009). Diminishing perennial sea ice in favor of annual ice will affect the dynamics of organic contaminants in the sea-ice system, with a widespread predominance of the ice-brine enrichment pathway affecting the exposure of ice-associated organisms such as ice algae in the spring. The presence of ice-brine in younger ice also allows greater interaction of contaminants

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between the snowpack and the ice, with potential for downward migration or percolation from the snowpack into the ice, once brine levels increase with the onset of spring; again, providing a direct contaminant pathway to ice-associated organisms, which sit at the base of the marine food web.

As part of a critical review on the implication of global climate change for human exposure to organic contaminants in the Arctic, Armitage et al. (2011) examined the sensitivity of the accumulation of organic contaminants in the Arctic as a result of sea-ice cover reduction/elimination. An increase in primary productivity in aquatic systems, related to changes in sea-ice cover and nutrient availability, would affect the distribution of organic contaminants between the freely dissolved phase and the particle-bound fraction. While the former drives pelagic food web exposure and is available for volatilization to the atmosphere, the latter would enhance deposition to the sediments and deep ocean. Their calculations showed that the freely dissolved fraction would only increase for very hydrophobic contaminants with unrealistic temperature-dependencies and temperature increases in the water column. However, the magnitude of change is uncertain. Although salinity would affect organic chemical solubility and partitioning properties, the magnitude of changes in salinity linked to climate change (e.g. melting ice/snow) are unlikely to affect such properties to a great extent as compared to other changes. Their study concluded that human behavioral change could be potentially more influential to exposure than changes to the physical environment.

3.7 Transport of contaminants by biota (biovectors)

Biota that undergo seasonal migrations into the cryosphere have the capacity to provide a transport route for contaminants that bioaccumulate or biomagnify (Wania, 1998; Blais et al., 2007). Although this route is quantitatively small in comparison to mass transport by air or water, it is focused within biological compartments, and where population densities become large due to small breeding areas this pathway can dominate all others and be of far greater significance to the populations themselves (Krümmel et al., 2003). Species with forage behaviors will accumulate

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contaminants from distributed sources and bring these contaminants to localized accumulation points. Leading species engaging in migratory behavior include fish, marine mammals, and birds with the latter providing the best-known examples for the Arctic (Evenset et al., 2004, 2007a, b; Michelutti et al., 2008, 2009; Foster et al., 2011). In these studies, the birds feed from surrounding productive ocean areas (e.g. polynyas), and rear their young in colonies that may include over 20 000 birds. The ponds or lakes associated with these bird colonies are on one hand provided with enhanced nutrients making them Arctic oases, while on the other hand they are contaminated with biomagnifying industrial organochlorine compounds. In Antarctica, penguins clearly provide a similar set of circumstances to transport contaminants and enrich them in select locations, but in some cases non-migratory populations may produce similar results simply by harvesting over a wide ocean area and concentrating contaminants into local rearing areas and associated ecosystems (e.g. Roosens et al., 2007; Corsolini et al., 2007). Climate change presents many opportunities to alter migratory behavior in all regions, but it seems likely that animals that time their migrations and choose specific foraging locations that are controlled seasonally by ice cover stand to be among the most impacted by loss of ice in a warming climate. These changes in migratory behavior could thus have a subsequent impact on the delivery of contaminants to these localized (but biologically important) breeding areas.

3.8 Contaminants in thawing permafrost

Human activities in remote cold regions lead to the production of waste and the release of anthropogenic contaminants into surrounding ecosystems. The Arctic regions are more vulnerable than those in Antarctica to such sources given the resident populations and the location of industry, especially in the Eurasian north (AMAP, 1998), and in terms of extraction of resources from the continental shelves (e.g. oil and gas recovery). Given the lack of these sorts of sources in Antarctica, and that most industrial/agricultural sources are in the Northern Hemisphere, Antarctic biosystems are considered minimally impacted by primary sources of contaminants. Today, regulations

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under the Antarctic Treaty prevent industrial and some tourist-related activities on the continent.

For many Arctic settlements in regions of permafrost, historical containment of wastes has depended in one way or another on the advantage of containment by permafrost (ACIA, 2005). Waste handling in the form of sewage lagoons, dumpsites at military installations and solid waste dumps in small communities and industrial installations (i.e. oil-drilling sumps) continues to the present (Macdonald et al., 2005). Waste disposal in landfills and dumpsites is a potential local source of POPs and has received significant attention in the case of PCBs associated with the distant early warning sites (“DEW-line”) across Arctic Canada (e.g. Brown et al., 2009). Recently, PBDEs have been measured in soils around dumpsites in Cambridge Bay and Iqaluit in Arctic Canada. Concentrations in landfill soils were, in some cases, over 100-fold higher than concentrations measured in background soils, thereby presenting a significant local source of these persistent chemicals (Danon-Schaffer et al., 2008). Permafrost thawing would result in enhanced transport of leachates and associated contaminants away from these sites, promoting input to aquatic systems in close proximity to major Arctic communities. In Canada, climate change has been considered during the development/approval of waste-containment infrastructures for the past ten years (AMAP, 2011).

Although far more remote from highly-industrialized temperate countries than Arctic regions, the Antarctic also receives POPs (Tanabe et al., 1983; Bargagli, 2008). Large international research stations along the Antarctic coast have been identified as significant local POP contamination sources (Risebrough et al., 1990; Choi et al., 2008), but strict handling protocols for waste in Antarctica minimize this source. As in the case of the Arctic, potential challenges may be expected from contaminant reservoirs contained in or by ice and snow (secondary sources) and the release of these contaminants due to permafrost and ice cover reduction (Curtosi et al., 2007; Mayewski et al., 2009; Aronson et al., 2011).

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3.9 Photodegradation of contaminants in ice and snow

While the physical processing of contaminants in ice/snow is critical in determining their cyrospheric fate, field and laboratory investigations have unambiguously demonstrated that organic compounds can undergo chemical changes in ice or snow (Klán and Holoubek, 2002; Grannas et al., 2007; McNeill et al., 2012). Subsequent release of the products may significantly impact the composition and chemistry of the overlying atmosphere or the aquatic environment. The primary chemical transformations can either be photochemically or thermally initiated. If the compounds do not absorb solar radiation they may still react with other species present in snow and ice. However, only chemically reactive substances, for example, organic radicals, carbanions, or oxygen, can undergo dark reactions at low temperatures, that is, only reactions which have sufficiently low activation energies can occur. The course of a photochemical reaction depends on many factors, including the optical, photophysical, and chemical properties of the chromophores (light-absorbing species). However, the optical and phase properties of the host matrix (snow/ice), the presence of other reactive species, and temperature also play important roles (Grannas et al., 2007 and references therein; Kahan and Donaldson, 2007; Ram and Anastasio, 2009; Kahan and Donaldson, 2010; Kahan et al., 2010).

Freezing of aqueous solutions of organic compounds results in substantial increased local concentrations at the ice/air interface (Klánová et al., 2003b; Heger et al., 2005; Ruzicka et al., 2005; McNeill et al., 2012) and their deposition on an ice surface from the gas phase leads gradually to the formation of a monomolecular layer (Heger et al., 2011; Kurkova et al., 2011; Ray et al., 2011). The absorption spectra of chromophores in liquid water do not necessarily coincide with those of the same substances in/on ice because of the specific substance-ice or substance-substance interactions (Heger and Klán, 2007) or altered acid/base concentrations caused by the freezing process (Heger et al., 2006). For example, the spectra of simple aromatic compounds, such as phenol derivatives (Matykiewiczova et al., 2007b) or benzene (Kahan and Donaldson, 2010),

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exhibit bathochromic shifts to wavelengths that overlap with those of solar radiation reaching the Earth's surface, making the likelihood of photochemical degradation in environmentally relevant matrices greater.

Laboratory studies have raised the question of whether potential chromophoric organic contaminants, deposited in polar snowpacks or adsorbed on ice crystals in the atmosphere and exposed to solar irradiation, can produce environmentally hazardous photoproducts, which can later be introduced into the environment via melting or evaporation processes. Studies have been reported for species such as halogenated aromatic compounds (e.g. chlorobenzenes, chlorophenols, PCBs) (Klán et al., 2001, 2000a, b; Klánová et al., 2003b; Literak et al., 2003; Dolinova et al., 2006; Matykiewiczova et al., 2007b), nitroaromatic compounds (Dubowski and Hoffmann, 2000), or organophosphorus compounds (Weber et al., 2009). However, these experiments employed frozen aqueous solutions with relatively high initial reactant concentrations ($> 10 \mu\text{g kg}^{-1}$); contaminant concentrations in natural snow are considerably lower – on the order of 10 ng kg^{-1} or less (Grannas et al., 2007). Photolysis of frozen solutions of, for example, haloarenes at or below -7°C gave predominately reductive dehalogenation and coupling products, instead of photosolvolysis products, which are formed in irradiated liquid aqueous solutions (Klán et al., 2000a, 2001; Klánová et al., 2003b) (Fig. 8). Predominant formation of the coupling products has been shown to be related to a substantial concentration effect (Heger et al., 2005) and efficient diffusion of reactive intermediates (Ruzicka et al., 2005). The specific course of the reaction is then related to the fact that water molecules of ice do not act as nucleophiles (Klánová et al., 2003b). When chlorophenols and hydrogen peroxide (as a source of the OH radicals upon photolysis) or inorganic nitrates (a source of NO_x and OH radicals) are irradiated in frozen aqueous solutions, oxidation/nitration reactions compete with the photolysis (Klánová et al., 2003a; Matykiewiczova et al., 2007b). In contrast, some compounds, such as 4-nitrophenol (Dubowski and Hoffmann, 2000), were found to give the same photoproducts in both liquid and frozen samples. In cases where different products are produced due to chemistry in snow/ice, it will be important to assess their toxicity and

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bioaccumulation potentials, as these may be quite different than the products formed from gas phase or aqueous (liquid) chemistry.

Specific photoproduct formation in frozen solution is of considerable environmental interest. Indeed, the toxic effects of chlorobiphenyldiols formed upon the photolysis of 2- and 4-chlorophenol in frozen aqueous solutions were evaluated using a bacterial luminescence test and in vitro biomarker assay for dioxin-like effects, and compared to those manifested by product (dihydroxybenzenes) formation in the liquid aqueous solutions (Blaha et al., 2004). Contrary to the aqueous solutions, the irradiated ice samples elicited significant inductions of dioxin-like effects. The authors concluded that the photochemistry can have an unexpected impact to pristine polar regions, when organic contaminants are present in ice/snow as trace constituents.

The porous nature of ice surfaces, especially of snow crystals, allows for adsorption of volatile and semi-volatile organic compounds, such as persistent organic pollutants (Wania et al., 1998b, 1999a; Dominé and Shepson, 2002; Dominé et al., 2008). Their concentrations are then directly proportional to their partial pressure and the snow specific surface area, and inversely proportional to the snow sorption constant K_{IA} at low surface coverages (Dominé et al., 2008). Low concentrations of snow contaminants and the complexity of the system are great challenges to those who want to study the physical and chemical processes occurring in natural snow. Therefore, investigations of ice surface/air exchange and photochemical processes of hydrophobic organic compounds have been carried out using artificial snow (Matykiewiczova et al., 2007a; Heger et al., 2011; Kurkova et al., 2011; Ray et al., 2011). It is produced by a shock-freezing preparation technique either as pure snow (which is then exposed to vapors of an organic compound), or as contaminated snow prepared directly from the corresponding aqueous solutions (Jacobi et al., 2004, 2006; Jacobi and Hilker, 2007; Matykiewiczova et al., 2007a; Bock and Jacobi, 2010; Heger et al., 2011; Kurkova et al., 2011; Ray et al., 2011). The specific surface coverage of artificial snow grains by hydrophobic organic compounds has been estimated with the help of a photofragmentation process (Heger et al., 2011; Kurkova et al., 2011) or ozonation

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reaction (Ray et al., 2011). Even in the case of ice surface loadings which correspond to sub-monolayer coverages, some organic compounds tend to self-associate on the ice/snow surface (Kahan and Donaldson, 2007, 2010; Heger et al., 2011; Kurkova et al., 2011). Therefore, intramolecular as well as intermolecular (substance-substance or substance-gaseous reactant) chemical processes are likely to occur on the ice surfaces.

A laboratory study of the photochemical behavior of POPs, such as PCBs, in artificial snow at environmentally relevant concentrations enabled simultaneous monitoring of their photochemical changes and volatilization fluxes from the solid matrix (Matykiewicz-zova et al., 2007a). Reductive dehalogenation (Fig. 8), as the major degradation pathway, competed with a desorption process responsible for the contaminant loss from snow. It has been estimated that the lifetime of PCBs in snow under solar radiation at -25°C , connected exclusively to this process, is 1–2 orders of magnitude longer than that in surface water. However, in cases where sufficient amounts of hydrogen peroxide (a photochemical OH radical source) are present in snow, photoinduced oxidation processes could surpass both photoreductive dechlorination and evaporative losses of PCBs as the major sink in a sunlit snowpack (Matykiewicz-zova et al., 2007a).

The kinetics of ozonation reaction of 1,1-diphenylethylene in artificial snow has been measured in order to evaluate the impact of the presence of ozone in the polar areas (Ray et al., 2011). For typical atmospheric ozone concentrations in polar regions (20 ppbv), it has been estimated that the half-life of an alkene deposited on the surface of snow grains is ~ 5 days at sub-monolayer coverages and -15°C .

While the majority of studies have been conducted in laboratory settings, several studies conducted in the field point to the potential importance of photochemical degradation of contaminants in/on snow and ice surfaces. Klán et al. (2003) demonstrated that several aromatic carbonyl, chloro, nitro and hydroxyl compounds underwent very efficient sunlight-induced chemical reaction in experiments conducted using ice samples prepared from clean water, but irradiated in natural sunlight in Svalbard, Arctic Norway. The observed photoproducts could pose a high toxicological risk to biota if they

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entered the environment. Rowland et al. (2011) studied the photochemical degradation of several organochlorine compounds via both direct photodegradation as well as photo-oxidant induced reaction during field experiments conducted in Barrow, Alaska. Interestingly, samples made using snow collected from the Barrow area showed the greatest reactivity (when compared to several control experiments), and the authors hypothesized that natural organic matter present in the snowpack could be an important photosensitizer for environmental photochemical reactions in snow/ice. Given the chemical complexity of snow/ice in the environment, and the various ways in which species may be incorporated into the snow/ice matrix, it will be a challenging, but important, effort to elucidate the various chemical mechanisms at play at the molecular level.

3.10 Comparison of contaminant/cryosphere interactions in different environments

Various interactions between contaminants and the cryosphere have been described in Sect. 3.1–3.9. Each cryospheric compartment plays a unique role in influencing contaminant transport and fate. It should be noted that these interactions may be very different depending on the environment. For example, as discussed in Halsall (2004), snow-atmosphere chemical exchange will in large part be controlled by the evolution of SSA. The physical processes controlling SSA will be quite different in, for example, the high Arctic as compared to warmer sub-arctic areas. In the Arctic, low precipitation amounts and frequent windstorms during winter result in the surface snow being shaped by repeated wind events, rather than numerous fresh snowfall events. This results in a hard wind-packed snow, with the surface dominated by sastrugi, with relatively shallow depth. In contrast, sub-arctic snow tends to exhibit lower density and SSA, higher depths, higher permeability and is exposed to lower wind speeds and higher temperatures. These variables will certainly affect snow-atmosphere transfer, as discussed in Sect. 3.3.

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An additional factor influenced by the local environment is the snowmelt process. As discussed in Sect. 3.4, the springtime contaminant “pulse” observed in receiving waters depends in part on the extent of ground infiltration and surface run-off. Additionally, the early elution of water soluble compounds was found to be most pronounced in deep and aged snowpack that is melting rapidly, while it is attenuated in layered snow with hydraulic barriers and in snowpacks that are subject to bottom melt. Thus, it is crucial that lab or field-based studies investigating contaminant fate consider not only the physicochemical properties of the contaminants, but also the physical nature and evolution of a snowpack over the timescale of the process being studied.

Another comparison can be made at the large scale between sea ice produced in the Arctic Ocean and in the Southern Ocean. For the former, the ice generally accretes by freezing at the bottom while a relatively small snow load is accumulated at the top of the ice due to the desert-like conditions of the Arctic (e.g. Serreze et al., 2006). For much of the Arctic’s ice these large-scale circumstances allow us to infer generality from the relatively few detailed studies of contaminants in ice reviewed above. In the Southern Ocean, sea ice initially forms in much the same way, accreting new ice at the bottom. However, a substantially larger snow loading favors flooding of the sea ice with seawater, which then freezes together with the snowpack to form layers at the top of the ice (Lange et al., 1990). We know nothing about how the flooding of snow-covered ice affects contaminant distributions and the subsequent entry of these contaminants into marine ecosystems. It is, however, clear that general conclusions based on studies of un-flooded sea ice cannot be extended to ice that has been flooded. Within the Arctic Ocean itself, sea-ice flooding is known to occur in coastal regions prone to storm surges (Carmack and Macdonald, 2008).

4 Knowledge gaps and research needs

There are currently several knowledge gaps and research needs that limit our understanding of contaminant fate and the potential impact of climate change on contaminant

transport and processing. These include challenges related to field, laboratory and modeling studies. Adequate consideration of these issues will require interdisciplinary studies at a variety of scales, from molecular level processes to global transport studies.

5 4.1 Experimental challenges

One of the great challenges of studying contaminant fate in the cryosphere is the very large heterogeneity of snow and ice on both a spatial and temporal scale and how this may impact contaminant fate. Laboratory experiments on contaminant behavior in melting snow have proven useful in gaining important mechanistic insights and in facilitating a quantitative description of contaminant fate during snowmelt. Other contaminant fate processes related to the cryosphere may be amenable to similar approaches relying on a set of highly controlled and reproducible experimental conditions within a cold room. Examples include:

- 15 – Contaminant fate during sea ice formation, growth and melting, including the fate of contaminants from snowpacks accumulating and melting on top of ice,
- Air-snow exchange of contaminants and its dependence on snow permeability and wind conditions,
- Mobility, reactivity, and potential for redistribution of contaminants in firn and glacier ice, in particular during time periods of seasonal melting,
- 20 – Photochemical, microbial and other transformation processes of contaminants in snow.

Ultimately, comprehensive experiments may be feasible that look at all of the fate processes affecting contaminants in a snowpack or in sea ice simultaneously, i.e. experiments that investigate the interaction between contaminant reactions, redistribution and loss by melt water or brine, and in the vapor phase, and how these interactions

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are governed by snowpack/ice characteristics, chemical properties, and meteorological conditions. Another possibility is a hybrid approach, where environmental snow/ice samples are transferred to a cold-room to conduct experiments under controlled and reproducible conditions, thereby avoiding the question to what extent artificial snow/ice samples are representative of the real environment.

Assessment of spatial and temporal trends of contaminants in snow and ice is complicated by post-depositional changes in the snow concentrations, sampling access, and analytical challenges. It has been suggested that the wide range of reported concentrations of organic contaminants in snow can be partly attributed to post-depositional processes. Revolatilization of organochlorines has been shown to take place in response to increases in snow density and decreases in snow surface area (Blais et al., 1998; Herbert et al., 2005b; Finizio et al., 2006, Burniston et al., 2007). Seasonal snowmelt (Gustafsson et al., 2005) and chemical degradation (Hoyau et al., 1996) are also important factors contributing to within-region variability. Gas-particle partitioning is an additional factor affecting the behavior of organic compounds in cold environments. Assessment of snow/ice concentrations of contaminants and their association with the particle phase is difficult. Snow and ice samples must be melted prior to analysis, and this will likely result in a redistribution of dissolved and particle-phase contaminants (Wania et al., 1999b). As such, quantitative assessments of dissolved and particle-phase contaminants in snow and ice should be interpreted with caution. The best way to assess the various sources of both spatial and temporal variability is through long term and high resolution sample analysis. Unfortunately, the ability to conduct such large scale monitoring efforts is hampered by the large sample sizes typically required for snow/ice analysis and the careful and time-consuming sample preparation and analysis process. Thus, the development of analytical techniques that can increase sensitivity and decrease interferences would allow for smaller sample sizes and open the door to higher spatial and temporal resolution studies.

4.2 Validation and improvement of models

Although contaminant pulses resulting from spring snowmelt have been predicted from modeling and lab studies (reviewed in Meyer and Wania, 2008) and observed in the field in a few cases (LaFrenière et al., 2006; Bizzotto et al., 2009a, Meyer et al., 2011a, b), more field studies are needed to determine how common and how important this phenomenon is. For example, we need to better understand how different environmental conditions affect snowmelt-induced contaminant pulses, especially by comparing field and modeling results. We also need to identify the types of mountain and polar systems and locations in the world that might be most prone to snowmelt-induced contaminant pulses. Moreover, more studies need to be conducted to determine the likelihood and degree to which snowmelt-induced contaminant pulses are causing biological impacts (i.e. extension of the work by Bizzotto et al., 2009b) and to identify which aquatic organisms might be most affected. These types of studies will require increasing collaboration between chemists and ecologists/ecotoxicologists. Additionally, the importance of contaminant exposure via snowmelt should be compared to that arising from other sources of contaminant exposure. Similarly, more field and modeling studies need to be conducted to determine the degree to which the release of contaminants from melting glaciers may cause biological impacts. It will be important to differentiate contaminant releases due to the melting of seasonal snowpack versus those due to climate change induced glacier melt. Likewise, it will be important to understand if contaminants in polar marine systems predominantly come from melting glaciers, sea ice, sea snowpack or directly from the atmosphere.

One advance that will aid in modeling efforts is the European Space Agency Cryosat-2 mission. Cryosat-2 was launched in 2010 with the goal of monitoring changes in the thickness and extent of polar ice. Recent reports indicate that Cryosat is delivering an unprecedented view of the seasonal growth and retreat of sea ice across the Arctic, as well as information on the thickness of the Greenland ice sheet, accurate to within

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10–20 cm (Parrinello et al., 2012). This information will be a critical component in models that attempt to quantify the role of melting sea ice/glaciers on contaminant fate.

While modeling should continue and increasingly be used to understand the role of the cryosphere in contaminant fate processes, input values still need improvement. In particular, snow-air and snow-ice partition coefficients need to be measured for a larger set of chemicals than currently available (Hoff et al., 1995; Roth et al., 2004). Although estimation methods for these partition coefficients exist (Roth et al., 2004), they may not be appropriate for more complicated chemicals such as current-use pesticides and some of the semi-volatile emerging contaminants.

4.3 Logistics and community coordination

For many of the POPs, we have few or no reliable ocean data collected as depth profiles or along transects from shelf to basin interior locations. These sorts of profiles are crucial to obtain an accurate assessment of contaminant distribution, storage by the upper ocean and the state of equilibrium between ocean and atmosphere. Presently, there are few ice-breakers capable of doing such work (requirements include ice capability plus clean laboratory and sampling facilities plus ancillary geochemical/instrumental profiling). Some Arctic countries (USA, Canada) face the issue of aging ice-breakers that will require years to bring replacements on line (NRC, 2011). Recently there have been opportunities to collect appropriate, year-round data at field camps from which contaminant processes can be inferred. For example, the CFL project overwintered the Canadian Coast Guard icebreaker *Amundsen* in the Beaufort Sea providing facilities and time to conduct a variety of contaminant measurements on snow, ice, water and biota (e.g. Pučko et al., 2010a, b; Codling et al., 2012). However, these opportunities are rare and require expensive commitments in logistics. Because the scientific community currently faces increasingly limited resources, it is crucial that we effectively communicate key research priorities and work collaboratively to make efficient use of the available opportunities and field research platforms. Additionally, the contaminant research community does work at a variety of scales, from experiments aimed at

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a molecular-level understanding of chemical degradation to modeling of atmospheric transport at the global scale. Interdisciplinary collaboration and communication is critical to link the various individual studies done at multiple scales in a meaningful and accurate manner.

5 Finally, opportunities should be sought to extend collaboration between the science community and the people who live in cold regions. One immediate benefit is the potential to engage local communities in monitoring activities, which otherwise could be prohibitively expensive. Collaboration then leads to better monitoring design by incorporating local knowledge, and better communication between scientists and local communities.

5 Conclusions

The cryosphere has the capacity to significantly impact the local, regional and global cycling of contaminants. Field, laboratory, and modeling studies have shown that snow and ice are crucial components of the Earth system that can influence the fate of contaminants, through both uptake and release mechanisms. Chemical processes occurring in snow and ice may also impact contaminant fate, in some cases generating products potentially more toxic or more bioaccumulative than the original contaminant. The scientific community has made much progress in elucidating the mechanisms of contaminant transport and redistribution within the cryosphere, and how these may be impacted by a changing climate.

The effects of climate change are becoming more pronounced in the cryosphere, evidenced for example by unprecedented declines in sea ice extent. Climate-induced changes to the cryosphere will certainly impact the fate of contaminants, altering atmospheric and oceanic transport and releasing previously trapped contaminants from melting ice and glaciers. There remain many unanswered questions regarding the impact of climate change on cryospheric contaminant cycles. For example, recent winter warming anomalies in the Arctic are resulting in rapid temporary thawing events

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resulting in partial melt of the winter snowpack and the exposure of the underlying tundra vegetation (e.g. Olsen et al., 2011; Callaghan et al., 2011). This is often followed by the subsequent formation of sheet-ice once temperatures decline again. The ecological implications of these events on terrestrial flora and fauna are the subject of ecological research (e.g. Bokhurst et al., 2011) but the release and fate of contaminants from the seasonal snowpack and their potential impact as additional stressors during these types of events are currently unknown.

The greening of the Arctic will likely impact air/surface exchanges, may increase forest/tundra fire frequency, and could lead to remobilization of contaminants associated with plant and soil carbon. In addition to climate change impacts, the expanding development of the Arctic may have a large future impact on organic contaminant levels and trends within the region, as energy resource exploration expands and waterways open to shipping traffic. Contaminants interact with the cryosphere in varied and complex ways, involving the interplay of biological, chemical, and physical processes. Although these are often studied as isolated processes, it is crucial to develop an interdisciplinary picture of contaminant cycling, which will require effective communication across multiple disciplines.

Acknowledgements. This manuscript arose from discussions during and following the 3rd Workshop on Air-Ice Chemical Interactions (AICI) in June 2011, in New York, NY. This workshop was sponsored in part by IGAC and the Columbia University School of Engineering and Applied Sciences. We wish to acknowledge IGAC for financial support for publication costs. A.M.G. wishes to acknowledge support from the NSF CAREER award (ATM-0547435). P.K. wishes to acknowledge support from the Grant Agency of the Czech Republic (P503/10/0947), and the project CETOCOEN (CZ.1.05/2.1.00/01.0001) granted by the European Regional Development Fund.

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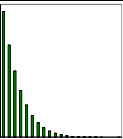
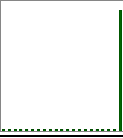
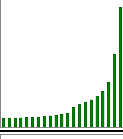
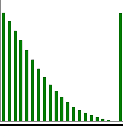
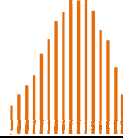


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Table 1. Types of snowpack elution behavior observed in the laboratory.

Type	Timing of release	Release profile	Contaminant characteristics	Examples
1	early during melt		water soluble	atrazine, chlorothalonil, short chain perfluoroalkyl acids
2	at the end of melt		strongly sorbing to particulate matter (PM) or snow grain surfaces	4 to 5 ring PAHs, PCBs, semifluorinated alkanes
3	late during melt		somewhat water soluble and at the same time high affinity for snow grain surfaces	long chain perfluoroalkyl acids, chlorpyrifos
4	early during melt and at the end of melting		partially dissolved in the aqueous melt water phase and partially sorbed to PM	lindane, fluorene
5	in the middle of the melt		sorption to snow grain surface decreasing during the melt	intermediate chain perfluoroalkyl acids



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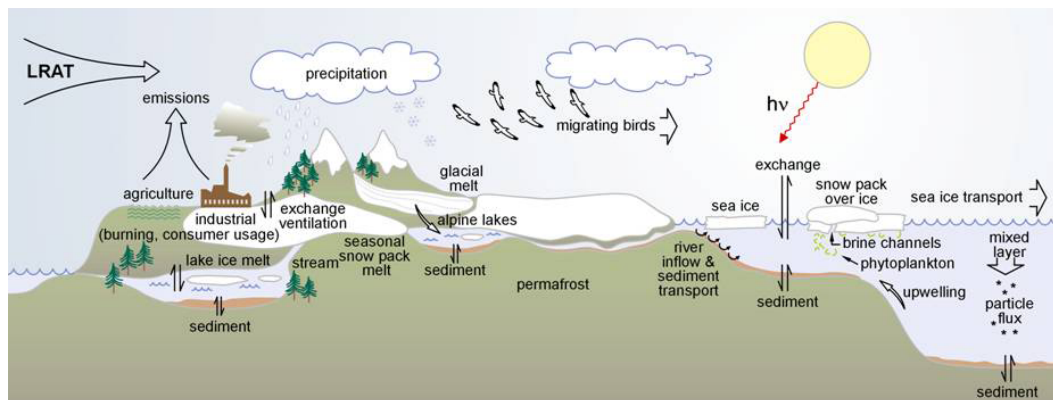


Fig. 1. Schematic diagram illustrating the various elements of and interactions occurring in the cryosphere that impact contaminant cycling and fate.

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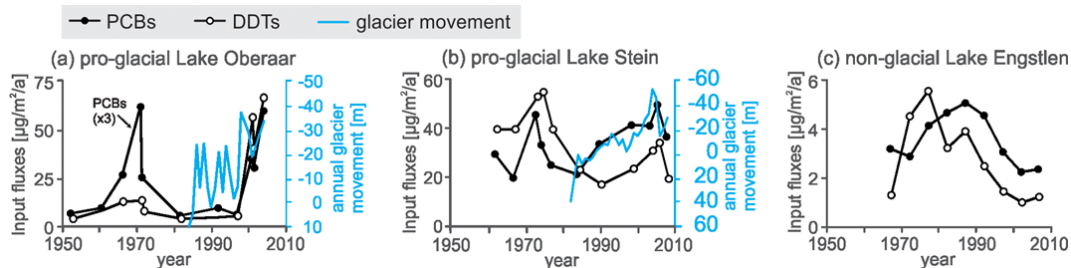


Fig. 2. Annual input fluxes of PCBs and DDTs (left y-axes) into sediment in three Swiss Alpine lakes including (a) the pro-glacial Lake Oberaar, (b) the pro-glacial Lake Stein, and (c) the non-glacial Lake Engstlen. For pro-glacial lakes, the annual movement of the adjacent glacier is provided (right y-axes) with a positive value corresponding to a glacier growth and a negative value to a glacier retreat. Note that the values for PCBs in Lake Oberaar have been multiplied by three to fit to the y-axis scale. Figure adapted from Bogdal et al. (2009) and Schmid et al. (2011).

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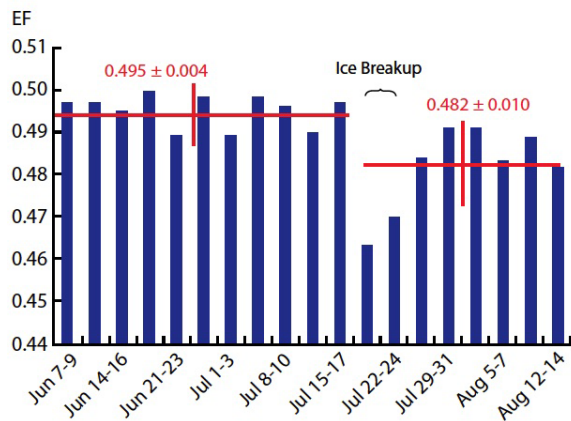
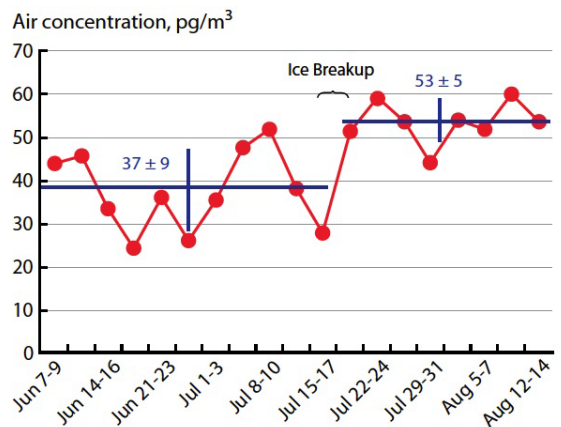


Fig. 3. Average air levels (top) and enantiomer fractions (bottom) at Resolute Bay before and after the seasonal ice melt (Jantunen et al., 2008). Picture modified according to AMAP (2011b). Reported errors represent 1 standard deviation based on method uncertainties.

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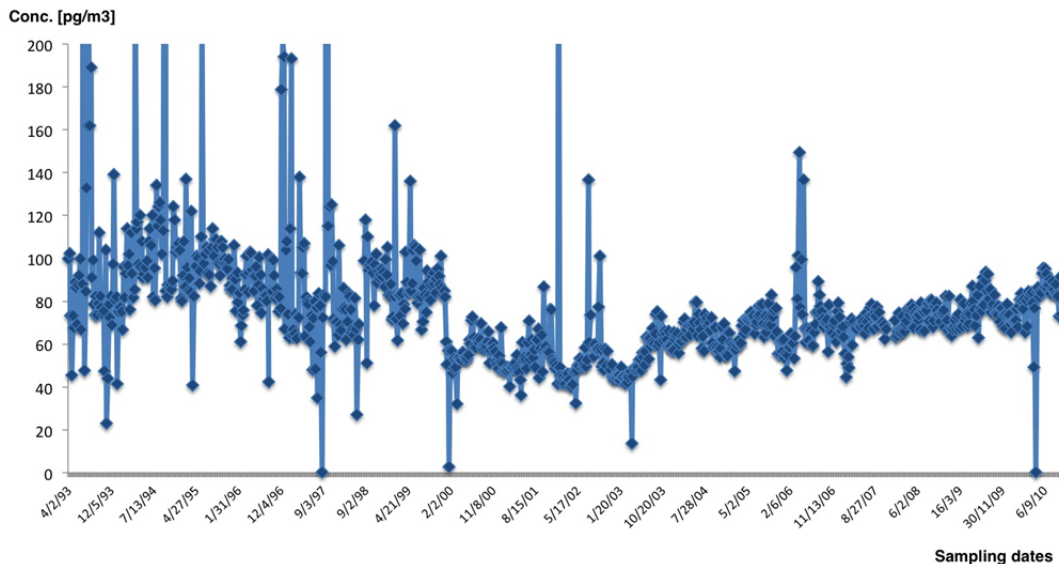


Fig. 4. Temporal trend for hexachlorobenzene (HCB) in air at Zeppelin, Norway during the monitoring period 1993–2010.

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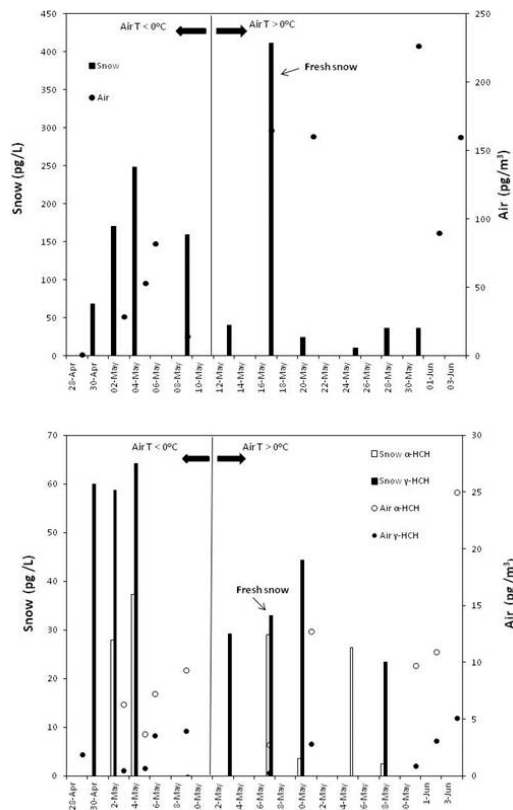


Fig. 5. Time-series of HCB (top) and α - and γ -HCH (bottom) concentrations in snow and air measured in the Amundsen Gulf, Canadian Arctic (April–June 2008). The vertical lines approximately denote the period when average air temperatures were at or above 0 °C. HCB and HCH concentrations in air are shown on the secondary y-axes. Data from Codling et al. (2012).

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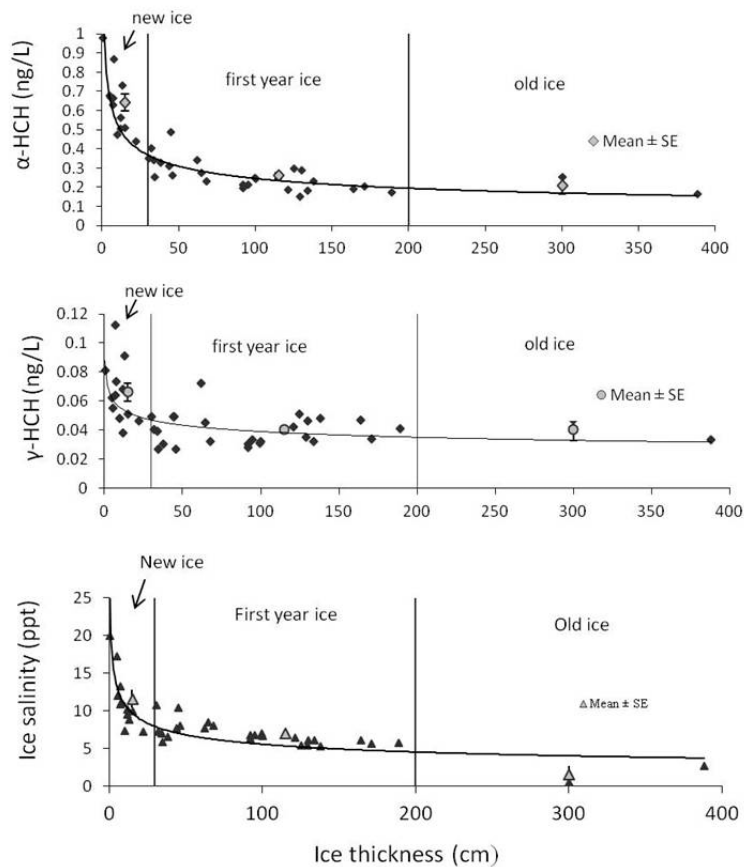


Fig. 6. Dependence of α -HCH (top) and γ -HCH (middle) concentrations and ice salinity (bottom) on sea ice thickness (adapted from Pućko et al., 2010a).

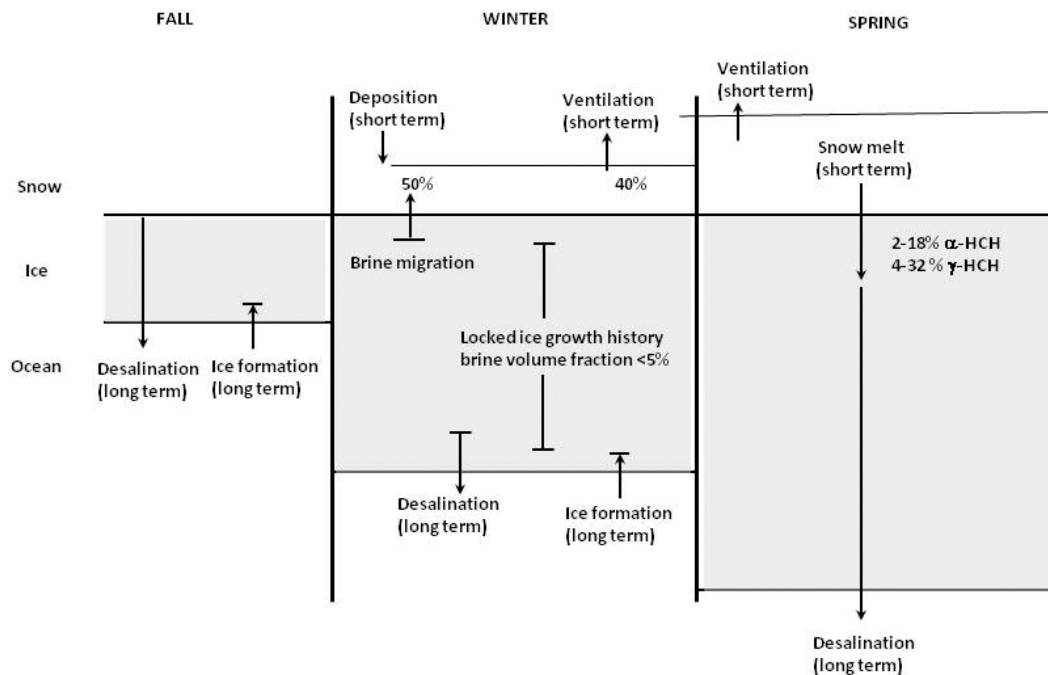


Fig. 7. Schematic diagram of atmosphere-snow-sea ice-ocean processes affecting HCH concentrations in various compartments of the Arctic environment in various seasons (adapted from Pućko et al., 2011).

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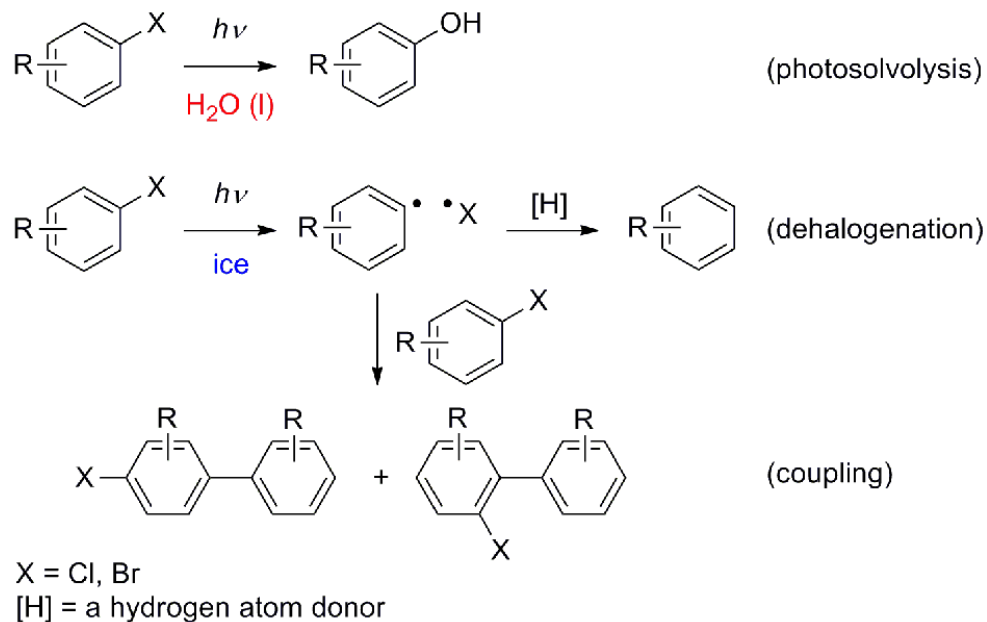


Fig. 8. Comparison of photochemistry of haloarenes in water and frozen aqueous solutions, illustrating the different mechanisms and products that occur in liquid water and ice.

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