Organic Contaminant Release from Melting Snow

By

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ABSTRACT

Snow efficiently scavenges organic contaminants from the atmosphere. Those chemicals can be released in short, concentrated pulses during spring snowmelt, potentially affecting both aquatic and terrestrial environments. In order to investigate the behavior of organic contaminants in melting snow laboratory experiments were conducted using artificial snow spiked with the organic target substances naphthalene, phenanthrene, pyrene, benzo(ghi)perylene, lindane, and atrazine. The behavior of those substances during melting is dependent on their partitioning between the different phases present within the bulk snow. Very water soluble organic chemicals, such as atrazine, are preferentially released at an early stage of melting similar to inorganic ions. This first chemical flush becomes more pronounced when a deep, aged, and relatively homogeneous snow pack is exposed to intense melting. Hydrophobic substances attached to particles, such as high molecular weight polycyclic aromatic hydrocarbons, are often released at the very end of the melt period. Dirt cones at the surface of a deep snow pack amplify this late chemical enrichment. Whereas chemicals that are clearly hydrophilic or hydrophobic are likely to be released in pulse loads, the snowmelt behavior of chemicals with intermediate partitioning properties, such as lindane, is more dependent on the varying snow pack and melt characteristics. A notable fraction of volatile chemicals may transfer from the melting snow pack to the lower atmosphere due to evaporation. Shallow snow covers in temperate regions with depths below 10cm that are exposed to recurrent melt phases during the winter are less likely to lead to pulse releases. When the melt water runs off as overland flow over frozen ground, pollutants are directly transferred into catchment streams, and their water quality is affected most. Melt water flow along the soil subsurface dilutes and buffers organic contaminant loads. The findings of this laboratory study may assist in the development of contaminant fate models that includes snowmelt processes. The results may further help to explain observations of organic contaminants in natural snow environments.
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Chapter 1  Introduction and Thesis Structure

**Introduction.** Up to 50% of the landmass in the Northern hemisphere can be blanketed with snow covers. Those often contain thousands of square meters of internal surface area per square meter of ground referring to a large potential for sorption and storage of organic contaminants. Those substances are often released from melting snow in elevated concentrations. Pronounced concentration peaks of organic pollutants during the spring snowmelt period have been observed numerous times in lakes and catchment streams. Semi-volatile organic chemicals have also been measured in the air above snow covers. Acute high levels of organic pollutants may adversely affect the melt water receiving ecosystems. However, the snowmelt behavior of such substances is neither well understood nor has it been extensively investigated in the past. Laboratory experiments were implemented to study the snowmelt behavior of selected organic pollutants that cover a wide range of environmental partition properties. The development of realistic water quality and contaminant transport models requires an understanding of all the processes involved. An extended introduction to the topic is given in chapter one as part of a literature review (see Chapter 2).

The goal of this Ph.D. project was to implement controlled and laboratory based experiments in order to investigate the snowmelt behaviour of organic contaminants.

The following were the main goals of this Ph.D. project:

- To gain a mechanistic understanding of the processes that organic contaminants undergo during melting of a snow pack,

- To ascertain the timing and extent of the organic contaminant release in dependence on the chemical’s properties, the snow pack characteristics, and the melt conditions.

The findings of the project will contribute to the following long-term research objectives:

- Integration of snow in models of organic contaminant fate at catchment, regional and global scale,

- Assessment of the ecotoxicological effects of contaminant shock load releases to organisms in the melt water receiving ecosystems,
Assessment of the effect of climate change on organic contaminant fate in regions of high latitudes.

**Thesis Structure.** The Ph.D. thesis consists of seven chapters. The first chapter provides a short introduction into the theme and describes the structure of the thesis. In the last chapter, overall conclusions are drawn that comprise the findings of the Ph.D. project. Furthermore, an outlook on possible future research related to the topic is provided. Both chapters encompass four original papers and one book chapter, all of which are either published, accepted or in preparation for publication.

Chapter two consists of a critical review that provides an extended introduction and analyzes the past literature that is associated with the melt behavior of organic contaminants. The review is an original paper and published in the journal “Water Research”. Because of the scarcity of publications that are directly related to the topic of the thesis, the review includes findings about the melt behavior of inorganic ions and the hydrology of a melting snow pack. Emphasis was placed on the latter because the dynamics of the melt water determine the timing of the chemical’s release. The review surpasses a simple summarization of the published literature. It provides a method that enables the prediction of the elution pattern of an organic chemical based on its environmental partitioning properties and the snow pack characteristics. The review assisted in establishing hypotheses and in developing experimental scenarios that are tailored to the needs of this project.

Chapter three describes the entire experimental and analytical method. It consists of an original paper that is published in the journal “Environmental Science and Technology”. Several aspects of the method are novel such as the laboratory-based production of relatively large amounts of artificial snow that is spiked with organic target substances. The production of artificial snow that is reproducible in terms of physical and chemical properties was indispensable and provided the basis for the experiments. Also, relatively high contaminant concentrations within the melt water samples were necessary to generate elution sequences with sufficiently high resolution. The target substances that were injected into the snow comprise a wide variety of environmental partition coefficients. Accordingly, each substance represents a different chemical group. The complexity of a system that comprises organic substances in a melting snow pack requires permanent monitoring of the
physical properties of the bulk snow. Using Time Domain Reflectometry methods, the melt water content and the dry snow density could be measured online at different snow depths. The snow microstructure was traced using macro-photography. Accordingly, a permanent and comprehensive picture of the physical processes, that determine the melt behavior of organic chemicals, could be gained. An analytical method had to be developed enabling the separate extraction and analysis of both the dissolved and particulate melt water fractions. Both phases undergo a very different fate in a melting snow pack.

Chapter four and five represent the core of the thesis and provide the results of the laboratory experiments. Both are in preparation to be submitted to the journal “Environmental Science and Technology”. The presentation of the results was subdivided into two chapters because the melt behavior of organic pollutants is presented using two interdependent approaches. The chemical’s preferred partitioning between the bulk snow phases determines how easily it can become dissolved within the aqueous melt water phase and therefore can be released from the snow pack. Thus, chapter four describes the impact of the chemical’s partitioning properties on the melt behavior. The results that are presented in chapter five on the other hand, highlight the influence of the snow characteristics and the melt water content. The chemical enrichments during the snowmelt experiments were quantified for each scenario. This information will presumably be of most benefit for readers that are interested in a parameterization of such processes.

Chapter six is an invited book chapter and tentatively admitted for publication. This review is devoted to the exchange of organic chemicals between the snow pack and the lower atmosphere. Relatively volatile substances can be present within the interstitial gaseous phase to a large extent. The chemical properties, the snow pack characteristics, and the melt conditions decide how much of a substance will be released with the melt water and which fraction will leave the snow pack to the lower atmosphere due to evaporation. A decreasing internal surface area prior and during the melt period is associated with a declining storage capacity for organic chemicals. As a result, substantial amounts of volatile and semi-volatile organic chemicals can be released to the atmosphere. Wind pumping strongly enforces those processes (see Chapters 2, 6). An investigation of atmosphere-snow exchange processes on a laboratory basis was beyond the scope of this Ph.D. project. Chapter six is therefore an important supplement to the remaining part of the thesis.
Chapter 2: Organic Contaminant Amplification during Snowmelt

Torsten Meyer and Frank Wania

Contribution: Paper written under the supervision of F. Wania.

Abstract

The release of organic contaminants from melting snow poses risks to aquatic and terrestrial organisms and to humans that rely on drinking water and food production from regions that are seasonally snow-covered. Measured and model-predicted spring peak concentrations in waters receiving snowmelt motivate a thorough investigation of organic contaminant behaviour during melting. On the basis of the current understanding of snow metamorphosis, snowmelt hydrology and chemical partitioning in snow, this critical review aims to provide a qualitative picture of the processes involved in the release of organic contaminants from a melting snow pack. The elution sequence of organic substances during snowmelt is strongly dependent on their environmental partitioning properties and the physical properties of the snow pack. Water soluble organic contaminants can be discharged in greatly elevated concentrations at an early stage of melting, while the bulk of the hydrophobic chemicals attached to particles is often released at the end of the melt period. Melting of a highly metamorphosed and deep snow pack promotes such shock load releases, whereas a shallow snow cover over a relatively warm ground experiencing irregular melting over the winter season is unlikely to generate notable peak releases of organic substances. Melt water runoff over frozen ground directly transfers contaminant shock loads into receiving water bodies while permeable soils buffer and dilute the contaminants. A more quantitative understanding of the behaviour of organic contaminants in varying snowmelt scenarios will depend on controlled laboratory studies combined with field investigations. Reliable numerical process descriptions will need to be developed to integrate water quality and contaminant fate models.

2.1. Introduction

Falling snow efficiently scavenges contaminants from the atmosphere (Colbeck, 1981, Lei and Wania, 2004) and concentrates them in a snow cover that acts as a temporary storage medium. Snow covers up to 50% of the land mass in the Northern hemisphere (Robinson et al., 1993) where also the vast majority of anthropogenic contaminants are emitted. After deposition, snow metamorphosis and melt processes can further concentrate such contaminants which are eventually released during snowmelt. Reflecting ancient farmer’s knowledge, an early weather proverb describes snow as the "Poor Man's Fertilizer" referring to the concentrated release of
nutrients to cultivated soil prior to sowing. Organic contaminants may be similarly released from melting snow.

Pronounced spring concentration peaks of organic contaminants, coinciding with the snowmelt period, have been observed in a German Karst region (Simmleit et al., 1986), in the St. Lawrence River and four of its tributaries, Canada (Quémerais et al., 1994; Pham et al., 2000), at Bow Lake and its tributaries in the Canadian Rocky Mountains (Lafrenière et al., 2006), at Gorge Creek (Semkin et al., 1996) and in river catchments on Cornwallis Island, Arctic Canada (Loseto et al., 2004). Similarly, peaks in air concentrations of organic contaminants coinciding with the snowmelt period have been observed around the Laurentian Great Lakes (Hornbuckle et al., 1994; Gouin et al., 2002, 2005). The potential for snowmelt to cause temporary concentration maxima in water, air and soil has also been predicted by simulation models (Daly and Wania, 2004; Gouin et al., 2005; Hansen et al., 2006).

The timing of such pulse exposure relative to the seasonal cycle of ecosystems, populations and individual organisms is important. Snow and ice melt often coincide with time periods of intense biological activity. Specifically, the melting of the seasonal snow pack in temperate regions could result in a pulse exposure to contaminants in aquatic ecosystems during early spring, when many life forms are at a vulnerable stage of development (Hickie et al., 1995; Vieites et al., 2004). For example, amphibians that reproduce immediately after the melting of the ice cover in the spring may experience acute exposure to elevated levels of organic contaminants during arousal from hibernation, with potential effects on reproductive hormones and retinoid status (Leiva-Presa and Jenssen 2006). The endocrine system of developing organisms is very vulnerable and many organic contaminants are known or suspected to be endocrine disruptors (Clemons et al., 1998; Schultz and Sinks, 2002; Gross et al., 2003). Observations from a field study in the Canadian Arctic suggest that snowmelt processes also influence organic contaminant uptake in lichens, forming the basis of the caribou-wolf food chain (Kelly and Gobas, 2001). The mechanism and timing of organic contaminant delivery to various natural systems during snowmelt are thus of considerable interest.

Contaminant release from melting snow is expected to be mostly a concern if snowfall rates are high, such as occur at high altitudes or in snow-belt areas, or if contaminant loads in snow are high, such as in urban and roadside snow (Franz and Eisenreich, 2000; Boom and Marsalek, 2006).
The storage and disposal of the latter is a serious issue for many communities in regions of high latitudes, as both the storage on land as well as the dumping into rivers bears risks of contaminating valuable water resources below and above ground. The potential for organic contaminant amplification in melting snow is also relatively high in mountains (Blais et al. 1998; Daly and Wania, 2005). Large amounts of snow are deposited at high altitudes and especially semi-volatile organic substances appear to become preferentially trapped in cold regions (Wegmann et al., 2006). Millions of people rely on mountainous regions for their drinking water supply (Schindler, 1999) and lipophilic organic contaminants are known to accumulate in fat tissue of fish, including in lakes at high elevation (Blais et al., 2006).

Cryospheric regions will be impacted by global climate change sooner and more dramatically than other areas (IPCC, 2007). Precipitation patterns and snowmelt processes are very sensitive to temperature changes, evoking the question how global climate change may impact snow extent and coverage and ultimately the fate of organic contaminants in cold regions (Macdonald et al., 2003).

This review seeks to paint a comprehensive picture of what is currently known about organic contaminant fate during snowmelt. Starting with a review of the scant observational evidence on organic contaminant behaviour during snow melt (section 2.2.1), two primary types of contaminant enrichment are being identified (section 2.2.2). The two main sections of the review explore in detail the influence of chemical properties (section 2.3) and the characteristics of the melting snow pack (section 2.4) on these enrichment processes. Reference is made to physical snow processes, because contaminant behaviour in snow can only be understood in the context of snow metamorphism and melt water dynamics (Colbeck, 1981; Taillandier et al., 2006). Finally, we speculate on the extent to which different types of snow pack may be susceptible to organic contaminant enrichment processes (section 2.5).

2.2. Observational Evidence

2.2.1. Experimental Studies of the Release of Organic Contaminants from Melting Snow

Very few studies exist that have investigated the release of organic compounds from a melting snow pack. Nevertheless, those few studies provide an important starting point for any in-depth discussion of the processes controlling the fate of organic substances in melting snow. In a rare
laboratory-based study, Schöndorf and Herrmann (1987) investigated the fractionated release of five organic substances with widely variable partitioning properties (hexachlorocyclohexanes α-HCH and γ-HCH, and the polycyclic aromatic hydrocarbons, PAHs, fluoranthene Fla, benzo(a)pyrene BaP, and benzo(ghi)perylene BghiP) from cylindrical glass columns (inner diameter: 144 mm, height: 1 m) filled with aged, coarse snow. The first melt water fractions were highly enriched with the dissolved fractions of both HCH isomers (Fig. 2.1) along with a large fraction of the inorganic ions. Approximately 90% of the PAHs, which are more hydrophobic and therefore more likely to be attached to particles than the HCHs, were eluted with the last 20% of melt water (Fig. 2.1). A fraction of the HCHs, presumably also attached to particles, was enriched in the last sample. The very hydrophobic BghiP and BaP were more strongly enriched in the late melt water samples than the somewhat less hydrophobic Fla which was released more uniformly over the entire melt period. The concentration ratio between Fla and BghiP decreased after a short initial increase (Fig. 2.1). These findings were confirmed by preliminary results from a laboratory study (Meyer et al., 2006) which relied on a much larger, rectangular snow vessel (H 40-50 cm, W 100 cm, D 55 cm): Whereas particulate PAHs were released late, more water-soluble PAHs were eluted from the snow pack relatively uniformly. Approximately 85% of the very hydrophobic BghiP and benzo(k)fluoranthen (BkF) were released in the last third of the snowmelt. These two PAHs were completely sorbed onto particles while phenanthrene and pyrene occurred also within the dissolved phase.
Figure 2.1  Relative melt water concentrations of organic contaminants and concentration ratios during a laboratory experiment by Schöndorf & Herrmann (1987).

Simmleit et al. (1986) investigated the time-resolved release from melting snow in the field, relying on the same set of organic contaminants as Schöndorf and Herrmann (1987). Melt water was sampled from relatively shallow snow covers (height: 24 cm and 18 cm) over the course of two melt periods. The first period was characterised by very rapid melting lasting a few days while the second period lasted several weeks and was combined with large temperature fluctuations around the freezing point. During the first melt period, 65-80% of both HCH isomers were released with the first 40% of the melt water (Fig. 2.2), while during the second event 80% of the HCHs were released with the first 25% melt water. The ratio of more hydrophobic to more water-soluble chemicals increased during the snowmelt period, consistent with the laboratory study (Schöndorf and Herrmann, 1987). However, contrary to the lab-based findings, Simmleit et
al. (1986) observed the release of about 60-70% of the more hydrophobic contaminants (Fla, BaP, BghiP) in the first 40% melt water (Fig. 2.2). During the second melt event, 50% of those substances were found within the first 25% melt water. Irregular snowmelt events from very thin snow covers did not show any peak concentration of dissolved chemicals (Daub et al., 1994). Neither did melt water samples taken from a shallow snow pack (height = 10 cm) during a rain-induced melt event show any enrichment of organic contaminants (Simmleit et al., 1986).

Figure 2.2  Melt water concentrations of organic contaminants and H\(^+\) ions relative to the bulk snow concentrations at the onset of the melt event (Simmleit et al., 1986).

Although not analyzing melt water directly, several field studies reported increased stream water concentrations of organic contaminants coinciding with the spring melt period. Quémerais et al. (1994) found peak concentrations of PCBs in the dissolved aqueous phase of the St. Lawrence River and its tributaries during spring snowmelt but no additional peak related to particulate PCBs. Measured peak loads of DDT congeners in the St. Lawrence River (Pham et al., 2000) and of methylmercury in Lake Amituk on Cornwallis Island (Loseto et al., 2004) may be attributed to the mobilisation of particles. Semkin et al. (1996) observed high concentrations of the relatively water-soluble endosulfan, \(\alpha\)-HCH and \(\gamma\)-HCH in Gorge Creek on Cornwallis Island, Arctic Canada at the beginning of the snowmelt period followed by an exponential decrease. At the beginning of the melt, the ground was still frozen and the pulse load of water-soluble chemicals was transferred directly to the creek. Concentrations of more hydrophobic organic substances, such as PCBs and DDTs, were increasing over the course of the melt period. Lafrenière et al.
(2006) on the other hand, found enrichments of both water-soluble and hydrophobic organic contaminants within the first melt water fraction taken from an alpine snow field. Water-soluble substances were more enriched than the hydrophobic chemicals. A low content of particulate organic matter in the snowmelt water presumably kept even the more hydrophobic DDTs and PCBs dissolved within the water phase. Higher stream water concentrations were observed during a shorter melt period which was attributed to a lower potential for evaporative losses during the melt (Lafrenière et al., 2006). Relatively high organic chemical concentrations in glacial run-off were linked to very limited contact of the melt water with soil or vegetation while melt water from a non-glaciated catchment had partially run off as sub-surface flow (Lafrenière et al., 2006).

2.2.2. Patterns of Contaminant Enrichment of Organic Contaminants During Snowmelt

The observational evidence from both field and laboratory suggests that there are essentially two patterns of organic contaminant enrichment in snow melt water. One (Type 1) leads to preferential elution with the early melt water fractions and affects the more water soluble substances, and sometimes also particle-sorbed organic contaminants. The other pattern (Type 2) leads to enrichment of particle-sorbed substances in late melt water fractions. Both patterns can lead to temporarily increased contaminant exposure of aquatic organisms in water receiving snowmelt. The early studies by Hermann and co-workers also provided plausible mechanistic explanations for the observed melt behaviour, and in particular sought to explain the variable extent of observed enrichment and the reasons why particle-bound substances may be subject to either one of the two types of enrichment.

Type 1 enrichment, leading to a “first flush” of organic contaminants in early melt water fractions, mimicks the melt behaviour of inorganic ions, which is relatively well studied and understood (see section 2.3.4 below). This early release is attributed to a freezing-out of chemicals and small particles from the ice lattice during snow metamorphism occurring prior to snowmelt or during melt/freeze cycles. A downward percolating melt water front picks up the contaminants concentrated on the grain surface and thus becomes enriched. Differences in the extent of first flush behaviour may therefore be due to differences in either the extent of dry and wet snow metamorphism prior to melt (sections 2.3.4, 2.4.2) or the melt water hydraulics during the melt (sections 2.4.3 and 2.4.4). Alternatively, differential elution or organic compounds from a melting snow pack may be related to differences in the compounds’ distribution constants
between the ice grain surface and the melt water (section 2.3.4). Strong temperature fluctuations, causing intense melt/freeze cycles, were deemed responsible for the stronger first flush behaviour of the HCHs during the second melt event in the study by Simmleit et al. (1986). In the first melt event HCHs were washed out more uniformly, indicating that intense melting at the onset of melt may have led to strong preferential flow in confined flow fingers bypassing other areas of the bulk snow.

Type 2 enrichment, leading to the late elution of particle-bound substances, is generally attributed to the filtering of particles by the snow pack. For example, extended snow metamorphism prior to melting combined with particle coagulation efficiently prevented the particulate fraction from being washed out in the laboratory experiments until the last melt water sample was collected (Schöndorf and Herrmann, 1987, Meyer et al., 2006). Some particles were washed out at the very beginning of the snowmelt until increasing snow density and an improving snow filter capacity prevented further elution of particle-associated BghiP, while the somewhat more soluble Fla experienced a small but continuous discharge (Fig. 2.1). The two peak pattern of the HCHs (Fig. 2.1) may have been due to a separation of dissolved and particulate fractions during snow metamorphism, which were then washed out in separate shock loads at the beginning and end of the melt. The early elution of particle-bound substances in the field experiment by Simmleit et al. (1986) may be attributed to the shallowness of the sampled snow packs in which vertical flow channels at the onset of melting can easily break through to the ground creating shortcuts of melt water flow in which even larger particle coagulates washed out (Schöndorf and Herrmann, 1987). In the second melt event, enrichment of particulate substances was also observed in the last melt water sample (Simmleit et al., 1986). Presumably, melt/freeze cycles led to a denser snow pack with more efficient filtering of particles.

2.3. The Influence of Chemical Properties

2.3.1 Chemical phase partitioning in a dry snow pack

Chemical properties influence contaminant behaviour in snow primarily by determining how a contaminant is distributed between the various components of a snow pack. In dry snow organic chemicals can reside as gases in the pore space, attached to particles present in the snow, or adsorbed at the ice-air interface (Fig. 2.3). Incorporation within the ice lattice of the snow grains
is likely very minor for most organic chemicals, because it would cause large defects in the ice’s crystal structure (Workman, 1954; Kammerer and Lee, 1969; Davis, 1991).

**Figure 2.3** Major phases in dry and wet snow and the equilibrium phase partitioning coefficients $K$ that determine an organic chemical’s distribution between those phases.

The distribution in dry snow thus depends on the chemical’s relative affinity for the gas phase, the surface, and the particles contained in the snow. The surface of snow grains is commonly perceived to be a quasi-liquid layer (QLL), a gradual transition phase between ice and liquid water at sub-freezing temperatures. The nature of the QLL is disputed and especially its reported thickness varies widely among studies depending on the measurement technique (Toubin et al., 2001; Wei et al., 2001; Döppenschmidt and Butt, 2000; Dosch et al., 1996). However, it is generally agreed that its thickness increases with temperature and ionic solute concentration (Dominé and Shepson, 2002; Cho et al., 2002; Döppenschmidt and Butt, 2000). Whereas the partitioning of organic contaminants between the interstitial gas phase and the surface of the ice lattice within bulk snow has been estimated by extrapolating adsorption coefficients to the water surface beyond the freezing point (Hoff et al., 1995; see Wania et al., 1998), Dominé and Rauzy (2004) point to the dissimilarities of the properties of water and the QLL and consider adsorption on the solid ice surface the only process representing snow surface/air partitioning. Roth et al. (2004) have measured the sorption of numerous organic chemicals to snow and based on that empirical dataset derived an equation which allows estimation of an organic chemical’s snow surface/air sorption coefficient log ($K_{I/A}$/m).

If we assume that (a) the organic matter contributes most of the sorptive capacity of the particles in snow, and (b) humic acid is a good surrogate for organic matter, we may further express the affinity to the particles in snow with a humic acid/air partition coefficient log $K_{HA/A}$ (Niederer et
al., 2006) (Fig. 2.3). Specifically, we can plot the equilibrium phase distribution of organic chemicals within the dry snow pack in a two dimensional chemical partitioning space defined by $K_{IA}$ and $K_{HA/A}$ (Fig. 2.4). Within this space, regions of predominant sorption to the snow surface (blue), presence as gas in the snow pore space (red), and sorption to organic particles in the snow (brown) can be delineated. Because the phase distribution also depends on the snow pack properties, Fig. 2.4 describes two different types of snow pack. One represents recently fallen snow with a high specific snow surface area (SSA, 1000 cm²/g), a low density (0.05 g/cm³) and a moderate organic matter content (0.009 µg mL⁻¹ snow volume); the other refers to aged snow exhibiting a low SSA (125 cm²/g), a high density (0.40 g/cm³) and a larger organic matter concentration (0.18 µg mL⁻¹) due to snow compaction and dry deposition during ageing.

Figure 2.4 Chemical space plots of the phase distribution of different chemicals in two types of dry snow pack as a function of the snow surface/air sorption coefficient (log ($K_{IA}/m$) and the humic acid/air partition coefficient (log $K_{HA/A}$). $K_{IA}$ and $K_{HA/A}$ values were determined based on Roth et al. (2004) and Niederer et al. (2006).

The threshold $K$-values, at which a transition from one phase to another occurs, shift within an ageing snow pack as density, surface area and particle content change (Fig. 2.5). For example, during the rapid initial surface area loss the blue area in the upper right of Fig. 2.4 shrinks, and
more chemicals will be sorbing to particles or be present as vapours in the pore space. The latter may be partly offset by an increasing snow density, which reduces the pore volume and shifts the threshold to the left (Fig. 2.5). This compensation is the reason why the $K_{I/A}$ threshold for the transition from the air pore space to the ice interface is similar (0.0001 to 0.001 m) for both fresh and aged snow (Fig. 2.4). If the density of aged snow is very low, such as occurs in depth hoar, this transition occurs at larger $K_{I/A}$ values and more chemicals are present as gases in the pore space.

$K_{I/A}$ and $K_{HA/A}$ for selected organic contaminants as a function of temperature in the range of -20 to 0 °C were estimated using poly-parameter linear free energy relationships (Roth et al., 2004, Niederer et al., 2006). Details of these calculations are given in the supporting information. The contaminant groups, such as the PAHs, polychlorinated biphenyls (PCBs), HCHs, fluorotelomer alcohols (FTOHs) and chemicals from the BTEX group cover a wide range of partitioning properties. When the lines representing different chemicals are placed on the chemical space plots in Figure 2.4, we can infer their likely phase distribution within fresh and aged dry snow packs at different temperatures.

**Figure 2.5** Diagram illustrating how the various $K$-thresholds that indicate a transition from one snow-pack phase to another shift in response to various ageing processes in dry and wet snow.
2.3.2 Chemical phase partitioning in a wet snow pack

The phase distribution of an organic chemical in the melting snow pack is a crucial element in understanding the manner and timing of its release. To investigate the partitioning behaviour in a melting snow pack theoretically, a second set of chemical partitioning space maps similar to those in Fig. 2.4 was developed. A wet snow pack contains a liquid water phase in addition to all of the phases of the dry snow pack (Fig. 2.3). This necessitates the quantitative expression of additional phase equilibria between air and water and between water and organic matter. It also means that a single two-dimensional map is no longer sufficient. Figure 2.6 therefore displays plots defined by the air/water partition coefficient $\log K_{AW}$ and the organic matter/water partitioning expressed by the humic acid/water partition coefficient ($\log K_{HA/W}$) for four different $\log (K_{I/A}/m)$ values (-4, -2, 0, +2). Again, two types of snow packs are considered: one snow pack, referred to as urban snow, contains a large organic matter load per snow volume (9 µg mL$^{-1}$), the other, representing Arctic snow, contains very little organic matter (0.009 µg mL$^{-1}$). The water content was assumed to be 4% by volume which refers to intermediate melt intensity (Section 2.3.4). Density and SSA are the same as for the aged snow in Fig. 2.4. The plots delineate regions of predominant adsorption to the snow surface (light blue), presence as gas in the snow pore space (red), sorption to organic particles in the snow (brown), and dissolution in the aqueous melt water phase (dark blue). Selected organic chemicals are placed on the maps based on their estimated distribution properties at 0°C.

2.3.3 The behavior of volatile substances in snow

Not all of the organic chemicals deposited with and to snow will be released with the melt water. Relatively volatile substances, located in the upper left of the plots in Fig. 2.4, can evaporate before the onset of melting. E.g. ethylbenzene and p-xylene partition mostly into the air-filled pore space of a relatively warm snow pack. Such chemicals are likely to be released prior to the melt season due to evaporation and wind-induced ventilation within the bulk snow. Somewhat less volatile chemicals, such as naphthalene and shorter FTOHs, may also be released to the atmosphere especially in highly metamorphosed depth hoar exhibiting little surface area (Fig. 2.4). Even semi-volatile chemicals such as tri- and tetrachlorinated PCBs and three-ring PAHs, that are present in the gaseous pore space in very small fractions, can be susceptible to loss by evaporation if sufficient ventilation in snow provides rapid replacement of the air in the pore
space. The depleted quantity of gas phase chemical is then replenished by rapid desorption from the ice surface. For sufficiently volatile chemicals neither of the two types of contaminant enrichment described in section 2.2.2 would be expected to apply.

**Figure 2.6** Chemical partitioning space plots displaying the phase distribution of different chemicals in an urban and an Arctic snow pack as a function of the air/water partition coefficient (log $K_{AW}$) and the humic acid/water partition coefficient (log $K_{HA/W}$) for different log ($K_{UA/m}$) values. See supporting information for the derivation of partition coefficients for selected organic chemicals.

Indeed, decreasing contaminant concentrations in ageing dry snow have been observed (Gregor et al., 1995; Enge et al., 1998, Herbert et al., 2005, Burnistone et al., 2007) and attributed to evaporation driven by a loss of storage capacity of the snow (Herbert et al., 2005, Burnistone et al., 2007). The days immediately after snow deposition are characterized by an increase of snow density and a significant decrease of the internal snow surface area (Cabanes et al., 2002; Jellinek, 1967; Hanot and Dominé, 1999). Based on the decreased storage capacity for chemicals within the interstitial air and on the ice surface, it has been estimated that substantial amounts of
volatile and semi-volatile organic chemicals could evaporate to the atmosphere from ageing snow (Wania et al., 1998, Hansen et al., 2006, Taillandier et al., 2006). The interplay of wind turbulence and snow surface roughness is a major factor driving atmosphere-snow exchange processes and re-location within the bulk snow (Sturm and Johnson, 1991; Dominé et al., 2002; Albert, 2002). At the onset of the snowmelt period in the spring a substantial fraction of organic contaminants may have already left the snow cover (Halsall, 2004).

Snow intercepted by a boreal forest canopy is particularly susceptible to sublimation and evaporation processes. Sublimation of snow over the winter period substantially decreases the amount of melt water released during the melt period and typically accounts for 15 to 40% of the cumulative snowfall (see Marsh, 1999). Sublimation increases the concentration of non-volatile chemicals within the bulk snow. Interception and storage of snow within dense boreal forest canopies can amount up to 70% of cumulative winter snow fall (Pomeroy et al., 1997). The air-snow interface of intercepted snow greatly exceeds that of surface snow (Pomeroy and Schmidt, 1993) and wind ventilation velocities are an order of magnitude higher than in snow on the ground (Claasen and Downey, 1995). Hence, semi-volatile organic chemicals stored in canopy snow are likely to be much more effected by evaporation prior to melting than substances deposited in snow on the ground.

2.3.4 The behavior of water soluble substances in snow

Chemicals that partition appreciably into the liquid water phase of the wet snow pack (> 10%), i.e. are located toward the upper left of the diagrams in Fig. 2.6, can be expected to be subject to the first chemical enrichment mechanism identified in section 2.2.2 and therefore be flushed out of the snow pack with early melt water fractions. Such behaviour is predicted for the HCHs (Fig. 2.6C and G) and 4:2 FTOH (Fig. 2.6B and F) in both urban (Fig. 2.6B and C) and Arctic snow (Fig. 2.6F and G). In Arctic snow with little organic particles, also three ring PAHs and PCB-28 are predicted to partition appreciably into melt water (Fig. 2.6F), whereas in urban snow they are more likely to sorb to particles (Fig. 2.6B). BTEX substances and naphthalene also partition into melt water (Fig. 2.6A and E), but because of their preference for the gas phase in dry (Fig. 2.4) and wet snow (Fig. 2.6A and E) are more likely to be lost by evaporation than with melt water.

Figure 2.6 can only provide a snapshot of the phase distribution during snowmelt because the phase composition of the snow pack changes as snowmelt progresses (Fig. 2.5). As the melting
snow pack shrinks and becomes denser, the relative abundance of melt water and particles will increase at the expense of snow surface and pore space. This implies that the phase transition boundaries in Fig. 2.6 will in most cases shift to the upper right as melting proceeds (Fig. 2.5). This also implies that more and more chemicals that originally were sorbed to the snow surface will either start to dissolve in melt water or sorb to particles, depending on their location in the chemical partitioning space and the amount of particles in snow. In Arctic snow, even sparingly soluble substances, such as the PCBs and PAHs with more than three rings, may eventually become dissolved in melt water as the snow surface area vanishes (Fig. 2.6G and H). Indeed, even relatively hydrophobic organochlorine pesticides were found to be mainly present in the dissolved phase of glacial melt water streams characterized by low particle contents (Blais et al., 2001).

Already Schöndorf and Herrmann (1987) noted the similar elution behaviour of ions and dissolved organic chemicals, namely their enrichment in early melt water fractions (see section 2.2.2). The behaviour of the water soluble inorganic ions in melting snow has been the subject of frequent investigations both in the field and laboratory and may yield some insight into the behaviour of water soluble organic chemicals. Whereas all studies investigating the fate of inorganic solutes in melting snow observed preferential elution of ions, the order in which the different species are released varies from study to study (Johannessen and Henriksen, 1978; Marsh and Pomeroy, 1999; Stottlemyer, 2001; Suzuki, 2003; Ulén, 2003). While Na\(^+\) and Cl\(^-\) are frequently released at a later stage during snowmelt (Tsiouris et al., 1985; Tranter et al., 1992) the ions Mg\(^{2+}\), Ca\(^{2+}\), SO\(_4\)^{2-} are often discharged earlier (Eichler et al., 2001; Tsiouris et al., 1985; Tranter et al., 1992). The reason for preferential elution is disputed.

One school of thought maintains that the way in which a chemical is incorporated into the growing snowflake influences its eventual release from a melting snow cover. Particles that act as condensation nuclei by initiating freezing of super-cooled water droplets (Barrie, 1991) are incorporated into the bulk of the snow grain and chemicals associated with those particles may be released at a late stage during the snowmelt period (Cragin et al., 1996). On the other hand, fine rime structures on snow exhibiting large surface area efficiently sweep contaminants from the atmosphere (Barrie, 1991) resulting in their accumulation at the outside of the ice crystals (Davis, 1991) where they are available to be released from the snow pack with early melt water. Accordingly, the ions Na\(^+\) and Cl\(^-\), as major constituents of sea salt that acts as condensation
nuclei during snow formation, are released later in the snowmelt period, while atmospheric pollutants, such as \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \), are scavenged by snowflakes and located near the snow grain surfaces (Tsiouris et al., 1985, Tranter et al., 1986), and therefore are eluted earlier. Similar argument could be applied to organic chemicals which may be scavenged as vapours or while sorbed onto particles serving as condensation nuclei.

However, the distribution of a chemical between the surface and the interior of snow grains at the onset of melting is not only dependent on how it was incorporated into the snow in the first place, but also by redistribution processes occurring during snow ageing. For example, Johannessen and Henriksen (1978) attributed the accumulation of ions at the snow grain surface in a field study and laboratory measurements to melt/freeze cycles leading to intense wet snow metamorphism and the gradual purification of the snow grains. Redistribution of inorganic ions and organic chemicals can also occur during dry snow metamorphism, i.e. in the absence of thaw/freeze cycles. Dry snow metamorphosis, leading to snow grain growth and sintering, is most intense just after a snowfall and then abates exponentially (Colbeck, 1998). At sub-zero temperatures, macroscopic and microscopic temperature gradients, the latter caused by differences in snow grain curvature, are mainly responsible for water vapour flow and rearrangement of the snow grain structure. Large temperature gradients, in particular, can quickly change form and size of the snow grains (Dominé et al., 2003). Such dry snow metamorphism can lead to a gradual rejection of both chemicals and particles from the ice lattice of the snow grains and to their accumulation near the surface of the snow grains (Colbeck, 1981). Based on laboratory experiments, Cragin et al. (1996) concluded that the elution order of inorganic ions was indeed strongly influenced by ion exclusion and rearrangement during dry snow metamorphism, but not by chromatographic effects, i.e. the differential retention of different ions on the snow grain surface. If chemical redistribution in the ageing snow pack is important, then the extent of type 1 enrichment would depend on the extent of snow metamorphism occurring prior to melt (Taillandier et al., 2006).

No experiments exist that would allow a direct extension of these conclusions to organic substances. In particular, variations in exclusion and the extent of outfreezing may be less important for separating organics, because their inclusion into the ice lattice is likely to be minor in the first place, except for fairly small organic solutes. On the other hand, chromatographic effects may play a larger role in controlling the elution order for organic chemicals, because of
their wide variation in water/ice surface partitioning. The diagrams in Figure 2.6 can help to illustrate how the partitioning properties of organic chemicals may determine their elution order during early snowmelt. At the onset of melt, the liquid melt water content increases and snow surface area decreases, i.e. the dark blue area in the upper left increases at the expense of the light blue area in the upper right of the panels in Fig. 2.6. Depending on their location within the partitioning space, different organic chemicals will become dissolved in the melt water at different times during the melt process. For example, $\gamma$-HCH may be eluted somewhat earlier than $\alpha$-HCH, and FTOHs may become fractionated based on chain length (earlier elution of the shorter molecules). Using the same reasoning, Fig. 2.6 can also help to understand why the elution behaviour of certain chemicals (those with $K_{AW}$ values close to the vertical thresholds in Fig. 2.6, such as the HCHs) can differ depending on the snow pack properties and melt conditions. In a snow pack with a large SSA and low melt water content the log $K_{AW}$ threshold indicating the transition in distribution between liquid water and snow surface would be lower than in highly metamorphosed snow pack with low SSA and high liquid water content. In the former, a large fraction of $\gamma$-HCH would stay adsorbed on the ice surface during the melt process and the first melt water fraction would be expected to show only minor chemical enrichment. In the latter snow pack, on the other hand, we would expect the first melt water fractions to be highly enriched with $\gamma$-HCH.

2.3.5 The behaviour of chemicals sorbed to particles and to the ice interface in snow

Particles, and the chemicals associated with them, are present in snow, because they may act as condensation nuclei or because they are scavenged by falling snow flakes. Between snowfall events dry deposition of particles, consisting largely of mineral dust (Ginot et al., 2001), can add substantial amounts of contaminants to the snow pack (Golomb et al., 2001). They may remain between snow layers or may be transported deeper into the bulk snow by wind ventilation (Heintzenberg and Rummukainen, 1993). With decreasing temperature organic chemicals in dry snow tend to increasingly sorb to the ice surface (Fig. 2.4). The clustering of the contaminants along the diagonals in Figure 2.4 suggest that for most organic chemicals the distribution coefficient between the ice surface and organic matter $K_{I/HA}$ falls into a fairly small range of only 3 to 4 orders of magnitude. That range overlaps with the transition from predominant sorption to the ice interface (blue area) and predominant sorption to organic matter (brown area) (Fig. 2.4),
highlighting that it is the relative capacity of interface (SSA) and particles (organic matter content) that determines where most of the organic chemicals will be found. In clean, fresh snow the interface is favoured, whereas the distribution in aged, dirty snow will be shifted to the particles, i.e. snow ageing causes more chemicals to become associated with particles.

Melt/freeze cycles cause substantial coagulation of fine particles in snow (Nakamura and Okada, 1976a). During the freezing phase and with increasing dehydration groups of particles are pushed together and the resulting coagulates are held together by van der Waals forces (Nakamura and Okada, 1976b). Particles consisting of clay silicates tend to coagulate to a lesser extent, while small micro-soot particles always form aggregates (Drab et al., 2002), often with a density lower than water. During snowmelt such micro-soot coagulates, and any substances that sorb to them, may accumulate in the surface layer of the snow cover (Colbeck, 1981) or on top of surface dirt cones (Fig. 2.7). Due to the rapid snow densification occurring upon first wetting, large particle coagulates can clog the snow pore spaces and particle-bound contaminants are efficiently prevented from being washed out from the bulk snow until the end of the melt period (Schöndorf and Herrmann, 1987). Relatively small differences in the relative affinity of different chemicals for interface and organic matter could result in very different phase distribution in snow. For example, hydrophobic chemicals such as PCBs may become concentrated in large particle coagulates during dry snow metamorphosis that during melting clog the pore spaces and are accumulating at the snow pack’s surface. Chemicals such as HCHs and FTOHs may concentrate at the snow grain surface where they can be released from the snow pack with early melt water depending on their ice-water partitioning (Fig. 2.4).

In melting snow, sparingly soluble substances, such as the larger PCBs, PAHs, and FTOHs, are predicted to be associated with the snow surface or the particles (Fig. 2.6C,D,G and H). Similar to the situation in dry snow (Fig. 2.4), which of these phases dominates, depends strongly on the particle content of the snow. In urban snow, the particle phase is dominant (Fig. 2.6C and D) and we may infer that the fate of such organic chemicals is controlled by the fate of the particles during snowmelt. Field studies confirm that the extent of a chemical’s association with particles depends on its partitioning properties and the particle content in snow. The partitioning of different PCB congeners between the particulate and the aqueous phases in melt water was found to be clearly dependent on the chemicals hydrophobicity (Gustafsson et al., 2005). Daub et al.
(1994) observed a transfer of particulate phenanthrene and pyrene into the dissolved phase during snowmelt in correlation to the suspended solid concentration within the melt water.

Figure 2.7 Onset of melting in a homogeneous snow pack above warm and permeable grounds; runoff in saturated snow base layer and as sub-surface flow above impermeable soil layer.

2.3.6 The behaviour of degradable substances in snow

Heterogeneous chemical reactions within snow, initiated e.g. by nitrate photolysis, change the chemical snow composition (Honrath et al., 2000) and result in the formation of gas phase radicals such as ·OH (Tom-Sauntry and Barrie, 2002; Dominé and Shepson, 2002), which in turn may lead to the degradation of organic contaminants (Anastasio and Jordan, 2004; Atkinson, 1987; Pitts et al., 1978; Masclet et al., 2000, Klán and Holoubek, 2002). Such degradation is presumably most efficient within the upper snow layers because of the limited penetration depth of short-wave radiation (Atkinson, 1987). A 90% decrease of benzo(a)pyrene in snow from the Greenland ice cap over a 4 year period was attributed to degradation (Jaffrezo et al., 1994). Similarly, ratios of pp’-DDE/pp’-DDT and Endosulfan-II/I that increased during the ageing of a dry snow pack were interpreted as reflecting sun-light induced conversions (Burniston et al., 2007). Jones et al. (1991) proposed the possibility of biological degradation of organic contaminants. However, not much evidence has been presented yet. Degradation may often be incomplete and degradation products could be more toxic than the original molecule (Klán and
Holoubek, 2002). Neither of the two enrichment processes described in section 2.2.2 would apply to chemicals that are notably degraded in snow, but could of course apply to stable degradation products being formed in the snow.

2.4. The Influence of Snow Properties

2.4.1 Surface melting vs. bottom melting

A snow cover can melt at the surface due to irradiative forces or at the bottom if sufficient heat is transferred from the ground to the soil-snow interface (Fig. 2.7). The melt dynamics in the lower snow pack is determined by the temperature at the interface between soil and snow. In Arctic regions the ground heat contribution to snowmelt can usually be neglected (Koivusalo et al., 2001; Ling and Zhang, 2004). But even in temperate and sub-arctic regions the interfacial temperature is often close to the freezing point (French et al., 2002; Stottlemyer, 2001; Gustafsson et al., 2001) and its influence on the snowmelt is small or negligible (Sauer et al., 1998). However, when a thick snow cover has developed early in the fall (Schaetzl et al., 2005; Gustafsson et al., 2001; Zhang, 2005) higher soil surface temperatures can cause small but steady snowmelt over the entire winter season (Stottlemyer and Toczydlowski, 1999; Stottlemyer, 2001; Anderson, 1976; Marks and Winstral, 2001; Şensoy et al., 2006). A deep snow cover of low density efficiently insulates the upper soil layers against cooling and freezing (Groffman et al., 1999; Walker et al., 1999). A snow density increase caused by strong wind pressure can significantly diminish the contribution of the ground heat to snowmelt (Ling and Zhang, 2006).

The contribution of ground heat to snowmelt has important consequences for the release of chemicals. Melt water generated at the surface may percolate downwards due to gravity or capillary forces and may take up chemicals that are present at the snow grain edge. On the other hand, melt water generated at the snow base due to ground heat is generally not enriched with chemicals because melting is confined to the lowest part of the bulk snow. Thus, substantial melting at the snow base mitigates the effect of type 1 contaminant enrichment (Stottlemyer, 2001)

A warm upper soil layer is often permeable to water. The soil infiltration rate to a large extent determines whether the melt water flows laterally as overland flow, as sub-surface flow or percolates deeper into the soil (Marsh and Pomeroy, 1999) (Figs. 2.7,2.8). The overland flow
component of snowmelt runoff was observed to be as high as 100% (Dunne et al., 1976) and as low as 0% (Price et al., 1979). Soil freezing causes decreasing infiltration and increasing runoff within a saturated snow layer (Groffman et al., 1999). The extent of saturated lateral flow at the base of the snow pack can exceed the vertical flow under unsaturated conditions by six orders of magnitude (Colbeck, 1978). Thus, the vertical flow within the bulk snow controls the melt water flow at the catchment scale. The ion concentration in catchment streams depends on the extent to which the melt water enters the soil during run-off (Stottlemyer and Toczydlowski, 1999). Chemicals transported with overland flow stay more concentrated and are directly passed on to receiving rivers and lakes while a soil passage likely buffers and dilutes them (Figs. 2.7,2.8). The largest runoff component in both a pre-alpine and an alpine Swiss catchment was found to be the subsurface flow causing spring peak concentrations in melt water to be smoothed due to buffering and dilution in upper soil layers (Gurtz et al., 2003).

In water-permeable soils sufficiently hydrophilic organic chemicals can be expected to reach the groundwater while somewhat more hydrophobic substances should be efficiently retained by soils, which then act as long-term storage sites. Indeed, Simmleit et al (1986) found less than 3% of the total input of α-HCH, γ-HCH, Fla, BaP, and BghiP in a groundwater spring after the melt water had passed a Karst soil. Most of the rest was adsorbed within the top soil layer (Simmleit and Herrmann, 1987). Organic contaminants deposited to soil during snowmelt may be re-located during subsequent snowmelt events. Similarly, contaminants deposited to the ground prior to the snow season may be carried away by lateral melt water flow which could increase the contaminant load to the stream water (Colbeck, 1981).

2.4.2 Melt/freeze cycles prior to melt water discharge

Over the winter period the snow cover in temperate regions is often exposed to numerous melt/freeze cycles prior to the first melt water outflow due to large temperature fluctuations around the freezing point (Colbeck, 1981; Ho and Gough, 2006). Alternating partial thawing and freezing of the snow accelerates snow grain growth and the freezing out of chemicals and particles from the ice lattice (Colbeck, 1981). During a warm spring day, melt water may be generated and kept within the interstitial pores due to capillary forces or may percolate downwards while enriching itself with chemicals that are either in the dissolved phase or attached to small particles. Lower snow layers may then become enriched with contaminants that are ready
to be washed out from the snow pack with the first melt water (Colbeck, 1981; Akan, 1994; Lygren et al., 1984). During the following cold night, the water may re-freeze completely or only partially depending on the snow pack’s insulation capacity, the meteorological conditions, and the temperature of the soil-snow interface. Re-freezing, especially in snow above very cold ground, may lead to the generation of impermeable ice structures and can significantly delay the first melt water flush (Pfeffer et al., 1991; Marsh and Woo, 1984). This presumably smoothes contaminant peak releases.

2.4.3 Melt water hydraulics in homogeneous snow

Snow pack hydraulics determine the timing of the early melt water discharge that potentially contains high concentrations of dissolved organic substances. Melt water flow in aged and course-grained snow usually takes place within a relatively small range of water content (m$^3$ liquid water/m$^3$ bulk snow pack $\cdot$ 100 %) and is driven mainly by gravity (Colbeck, 1978). A melt water content of up to 3% is retained within such a snow pack by capillary forces and even during intense melting the water content generally does not exceed approximately 5% (see Colbeck, 1978). A snow pack that has undergone intense dry and wet snow metamorphism is also relatively homogeneous in terms of grain size distribution. The limited range of both melt water content and snow grain size facilitates the parameterization of the hydraulics in aged, melting snow (Colbeck, 1978). The melt water flow rate $F$ in homogeneous snow is very sensitive to changes of snow grain diameter $d$ and effective water saturation $S_e$, defined as the fraction of the pore volume occupied with mobile liquid water:

$$F \sim d^2 S_e^3,$$

and the percolation velocity $v$ is proportional to the flow rate to the two-thirds power: $v \sim F^{2/3}$ (Colbeck, 1978). The early melt water moving through relatively fine grained snow at the beginning of a melt period is often very slow and may take days to be discharged from a deep snow pack especially when substantial re-freezing occurs (Marsh and Woo, 1984). The presence of a stagnant water layer at the snow base due to capillary retention may further enhance this delay (Coléou et al., 1999). Snow density rapidly increases upon snow wetting and the snow grain diameter can grow very rapidly within a few days (Brun, 1988). Accordingly, in the course of a melt day a large and fast melt water flow may catch up and combine with a slower moving
first melt water front generated earlier in the morning, leading to a strong shock melt water front when released from the snow pack.

This initial melt water wave transports contaminants present at the snow grain surface (Colbeck, 1978) to receiving soils or water bodies. Accordingly, in temperate regions, a sequence of melt/freeze cycles (section 2.4.2) followed by slow melting enhances concentrations in the first melt water (Colbeck, 1981). The sequence of weather events leading to the first runoff determines the extent of contaminant enrichment in the first run-off fraction (Johannessen and Henriksen, 1978; Colbeck, 1981). Daily sub-peaks of contaminant load at the beginning of a melt period can occur due to nightly re-freezing after the release of a melt water fraction and renewed concentration of chemicals at the snow grain surfaces (Colbeck, 1981).

Figure 2.8  Melting in a layered snow pack along a hydraulic barrier and in a saturated snow base layer over frozen ground.

2.4.4. Inhomogeneity of Snow Covers

Even in the absence of distinct snow layers the melting of natural snow packs is often characterized by heterogeneous melt water flow (Glass et al., 1989). At the onset of melting the two-dimensional flow field in homogeneous snow quickly becomes unstable resulting in the generation of flow channels (Fig. 2.8). Marsh and Pomeroy (1999) suggested a two-component wetting pattern consisting of a background wetting front above which the snow is wet and isothermal at 0 °C and a finger wetting front covering approximately 20% of the horizontal area
that describes the deepest penetration of liquid water within the bulk snow (Marsh and Woo, 1985). Flow fingers may contain melt water stemming from whole snow grains of the snow pack surface layer, while the background wetting front only takes up the chemical present on snow grain surfaces. Thus, flow fingers contain lower solute concentrations than the background wetting front but accelerate the melt water arrival at the ground (Harrington et al., 1996). When the melting progresses the background wetting front soon comprises the entire snow pack (Marsh and Woo, 1984). Accordingly, the permeability to melt water increases and the water flow becomes more homogeneous and enriched with chemicals taken up from lower snow layers at the end of the elution sequence (Davis, 1991) (Fig. 2.8). The overall effect of inhomogeneous flow is to reduce type 1 enrichment.

A seasonal snow pack prior to melting usually consists of several snow layers (Dominé et al., 2002) reflecting the different snowfall events that occurred over a winter. Those layers differ in density and snow grain size and can constitute hydraulic boundaries to unsaturated flow. A typical hydraulic boundary is the fine-to-coarse transition of two snow layers where fresh and fine-grained snow is deposited on an aged snow layer made up of coarse grains. In cold snow water can flow laterally downslope over distances of tens of meters within a single stratigraphic horizon even without an impermeable layer (Pfeffer and Humphrey, 1996) (Fig. 2.8). Saturated melt water at a hydraulic barrier may also break-through or re-freeze thereby generating an impermeable ice layer that guides subsequent melt water in a lateral direction (Waldner, 2002; Pfeffer and Humphrey, 1996; Albert and Perron, Jr., 2000). Thus, snow layering in very cold regions may significantly delay the first melt water flush enriched with water soluble contaminants. In relatively warm snow of temperate and sub-arctic regions cohesive and prolonged impermeable layers are rarely present (Pfeffer and Humphrey, 1996).

Rain events can be regarded as a snowmelt phase because the effect of percolating rain water in snow and melt/freeze cycles is similar. Leachate of artificial rain passing a snow pack in the laboratory contained similar ion composition as snowmelt water (Tranter et al., 1992). The melt intensity is greatly accelerated during a rain event (Simmleit et al., 1986) and rain water may enlarge snow pores and flush fine particles from the surface through the bulk snow (Schöndorf and Herrmann, 1987). Accordingly, particle associated contaminants may not be retained until the end of the melt period and are released earlier depending on snow pack depth and rain intensity.
2.4.5. **Snow depth**

In mountainous regions the spatial pattern of snow accumulation mainly depends on wind, topography (Stottlemyer, 2001; Anderton et al., 2003), and vegetation (Green et al., 2002). Marsh and Pomeroy (1996) observed an accumulation of approximately one third of the total snow within deep snow drift areas covering only 8% of the catchment. The release of contaminants from melting snow within a catchment is thus often spatially and temporally heterogeneous, resulting in non-uniform soil contamination. Contaminants in deep snow drifts are released later than those that are stored in more sun-exposed and shallow snow packs, preventing strong concentration pulses in catchment streams during snowmelt (Marsh and Pomeroy, 1999; Boyer et al., 2000; Dunn et al., 2001). Marsh and Pomeroy (1999) observed a time delay of five days in the ion release from shallow snow packs and deeper drift areas near Trail Valley Creek, Arctic Canada. Deep drift snow is not only more protected from wind but also, because of its depth, exposed to smaller temperature gradients (Sturm et al., 1995), both of which should diminish the evaporation of organic chemicals prior to melting (Taillandier et al., 2006). A relatively short and intense snowmelt period reduces this time delay and provides a more synchronous melt water flow around the catchment (Marsh and Woo, 1985). The delivery of potential contaminant shock loads to aquatic and terrestrial ecosystems is then confined to a short time-frame.

2.5. **Organic Contaminant Enrichment in Different Types of Snow pack**

The timing of organic contaminant exposure of aquatic and terrestrial ecosystems during snowmelt not only depends on the physical snow processes on the micro- and meso-scale, but also on meteorological factors and terrain parameters. In an attempt to classify snow according to predominant climate variables, Sturm et al. (1995) distinguished six snow cover classes labelled tundra, taiga, alpine, maritime, prairie, and ephemeral (Table 2.1). Those classes are defined by physical characteristics of the snow pack and not necessarily by geography or vegetation. However, tundra snow can often be found in arctic regions while taiga snow is predominant in sub-arctic areas. It is illuminating to speculate which of these snow pack types may be more susceptible to generating contaminant shock loads upon melting (Table 2.1).
Table 2.1  Snow cover classes, snow metamorphism and likely contaminant release features.

<table>
<thead>
<tr>
<th>snow cover class</th>
<th>Temperature</th>
<th>typical snow characteristics in late winter</th>
<th>snow metamorphism</th>
<th>likely organic contaminant release behaviour during snowmelt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tundra</td>
<td>- thin (10-75 cm), cold, wind blown, isothermal - large density, large SSA - usually north of tree line - basal layer of depth hoar overlain by multiple wind slabs</td>
<td>- small temperature gradients - little dry snow metamorphism</td>
<td>- little release of semi-volatile chemicals to the atmosphere - minor peak concentrations due to a shallow snow cover and little metamorphism</td>
<td></td>
</tr>
<tr>
<td>Taiga</td>
<td>- thin to moderately deep (30-120 cm) and cold - large temperature gradients - low density, small SSA - cold forested regions with low wind impact - 50-80 % depth hoar covered with low-density new snow</td>
<td>- strong dry snow metamorphism</td>
<td>- strong release of semi-volatile chemicals to the atmosphere in spring prior to melting - heavy peak concentrations of both dissolved and particulate chemicals due to intense dry snow metamorphism especially if snow cover is deep</td>
<td></td>
</tr>
<tr>
<td>Alpine</td>
<td>- intermediate to cold and deep (75-250 cm) - small temperature gradients, large SSA - basal depth hoar and wind crusts common - occasional but insignificant melt features</td>
<td>- little dry snow metamorphism</td>
<td>- pronounced peak release if melt-freeze cycles imposed on a deep snow cover precede an intense melt period</td>
<td></td>
</tr>
<tr>
<td>Maritime</td>
<td>- warm and deep (75-500 cm) - small temperature gradients, large density and small SSA - coarse snow grains and melt features very common - basal melting common</td>
<td>- strong wet snow metamorphism</td>
<td>- heavy peak concentrations of both dissolved and particulate chemicals - a very warm ground smoothes peak releases</td>
<td></td>
</tr>
<tr>
<td>Ephemeral</td>
<td>- thin and extremely warm (0-50 cm) - basal melting and melt features common - consists of only 1-3 snow layers due to frequent melt periods over the winter</td>
<td>- strong dry and wet snow metamorphism</td>
<td>- negligible chemical concentration especially if the snow pack is very thin and exposed to strong basal melting</td>
<td></td>
</tr>
<tr>
<td>Prairie</td>
<td>- thin (0-50 cm) (except in drifts) and moderately cold snow cover; - often isothermal, large density - wind slabs and drifts common</td>
<td>- little dry snow metamorphism</td>
<td>- notable chemical peak release only if snow pack is relatively deep and imposed to melt/freeze cycles prior to the melt period</td>
<td></td>
</tr>
</tbody>
</table>
Tundra and taiga snow differ in terms of the storage capacity for organic trace compounds. Tundra snow is colder and compressed by wind force and thus maintains a relatively high SSA over a long time span. Sub-arctic regions tend to develop more permeable snow packs in form of depth hoar due to very large temperature gradients within the bulk snow (see Sturm and Benson, 1997; Taillandier et al., 2006). The effect of wind pumping in such snow is larger and more of the volatile and semi-volatile chemicals may be released prior to melting (section 2.3.3) which may diminish the exposure of aquatic and terrestrial environments to those chemicals (Taillandier et al., 2006). Furthermore, large temperature gradients in taiga snow drive intensive dry snow metamorphism (section 2.4.2) which could enhance the accumulation of chemicals at the snow grain edges. Presumably, water soluble and non-volatile organic chemicals will be enriched to a larger extent within the first fractions of melting taiga snow. The vertical melt water flow in coarse grained snow is relatively fast which may lead to a more synchronous release of melt water and contaminants in catchments. A brisk and uninterrupted melt period also promotes a more uniform runoff pattern. Such conditions can often be found in sub-arctic regions that are characterized by permafrost and a confined spring melt period but also in alpine regions if soils are water impermeable due to previously infiltrated and frozen melt water. Tundra snow and underlying soil are often extremely cold because of the long duration of subfreezing air temperatures and frequent blowing wind (Marsh and Woo, 1984). The soils are often permanently frozen and melt water flow mainly takes place as overland flow. Thus, contaminants released from taiga and tundra snow can be transported directly into catchment streams (Lafrenière et al., 2006).

Snow in mountain regions is very heterogeneous but may often be assigned to the maritime or alpine snow category whereby the former is warmer and exposed to stronger winds and higher precipitation rates compared to the latter (Sturm et al., 1995). Alpine snow covers are often exposed to only small temperature gradients due to their large depth (section 2.4.5). However, if the snow is relatively warm, wet snow metamorphism preceding the melt period may concentrate chemicals at snow grain surfaces and a subsequent melt phase may release both the dissolved and particulate contaminant fraction in two distinct flushes. In deeper snow packs particles are efficiently held back from being released early. Buffering by soils is often minor in temperate high altitude environments, as glacier melt water and associated contaminants have little contact to soils and sediment while the runoff occurs in channels on the glacier surface (Blais et al.,
A very common feature of the somewhat warmer, aged maritime snow are coarse snow grains likely within a narrow size range due to intense wet snow metamorphism. Such snow packs may be prone to generate highly concentrated contaminant releases. Maritime snow is warm enough to prevent notable re-freezing. The melt water flow is relatively homogeneous and may be led by a consistent shock water front enriched with chemicals.

Prairie snow covers are exposed to strong wind activity and considerable contaminant amplification during snowmelt may only occur if a relatively deep snow pack undergoes melt-freeze cycles prior to melting. Ephemeral snow covers, finally, are shallow and short lasting and can often be found in temperate regions with mean winter temperatures near or above freezing (Sturm et al., 1995) and notable contaminant enrichments can hardly be expected in such snow. Also, the infiltration rate of the soils in those regions is large and organic contaminants are efficiently buffered and diluted.

2.6. Conclusions

The presence of snow significantly influences the fate of organic contaminants in colder areas. Specifically, several amplification processes, operating on a microscopic, macroscopic and temporal scale, conspire to concentrate organic chemicals in snowmelt water (Wania, 1999, Macdonald et al., 2002).

- The scavenging of organic chemicals from the atmosphere by snow is a powerful solvent switching phenomenon (Macdonald et al., 2002), concentrating contaminants in a relatively thin snow cover. This process is driven by the high capacity of falling snow for organic chemicals, which in turn is due to its large surface area and low temperature (Lei and Wania, 2004).

- Upon deposition dry snow metamorphism and a rapidly decreasing surface area causes the snow to loose capacity for organic chemicals. This solvent depletion phenomenon (Wania, 1999, Macdonald et al., 2002) will drive up the chemical potential in the snow pack and lead to the loss of sufficiently volatile chemicals from the snow pack, whereas less volatile chemicals will be retained.

- The freezing-out of chemicals from the snow grain interior to the grain surface during dry and wet snow metamorphism may further concentrate the organic chemicals. The
- Months of contaminant accumulation over the winter is followed by a rapid release within a relatively short melt period, exemplifying the kinetic effect of contaminant amplification in time (Wania, 1999). The spatial concentration processes taking place during snow ageing can now manifest themselves in the release of two distinct peak loads containing the dissolved chemical fraction at the beginning of a melt period and the particulate phase at the very end.

The amplification processes will operate to a different extent in different snow packs. Contaminant shock releases are favoured by extensive dry and wet metamorphism of a warm, deep and relatively homogeneous snow pack followed by slow melting. Colder snow requires more intense melting to prevent notable re-freezing in order to release chemicals in peak concentrations. Heavy rain events can wash out substantial amounts of particulate chemicals at any time of a snow season depending on snow depth and rain intensity. Shallow snow covers in temperate regions exposed to recurrent melt phases during the winter that are often initiated by rain events are less likely to lead to pulse releases. The water quality of catchment streams is affected most when the melt water runs off as overland flow over frozen ground. Melt water flow along the soil subsurface dilutes and buffers organic contaminant loads. Wind packed snow exposed to relatively small vertical temperature gradients as typical for Arctic and to some extent also alpine regions has a higher storage capacity for semi-volatile organic chemicals and likely releases a relatively large fraction of them to aquatic and terrestrial ecosystems while in sub-arctic regions more of those substances are released to the atmosphere by wind ventilation prior to melting.

Considering the possibly severe impact of organic contaminant releases during snowmelt on water and soil quality, the scientific response to this challenge has clearly been insufficient. Whereas this review could provide a tentative picture, considerable knowledge gaps currently do not allow for a full mechanistic understanding, let alone a quantitative description, of the factors and processes that influence this release. Timing and extent of organic contaminant delivery to various ecosystems during snowmelt should be investigated through a combination of field work
and controlled laboratory studies. Reliable predictive models of organic contaminant fate need to be developed for melting scenarios of various types of snow packs and different environmental influences. The knowledge gained in the process would contribute to the integration of snow in models of organic contaminant fate in cold ecosystems, the assessment of the ecotoxicological effects of the pulse exposure of marine, freshwater, and terrestrial organisms to organic contaminants, and the assessment of the effect of climate change on organic contaminant fate in Northern ecosystems.

**Acknowledgements**

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**References**


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Supporting Information for:

**Organic Contaminant Amplification During Snowmelt**

Torsten Meyer, Frank Wania

**Calculation of the partition coefficients for Figures 1 and 4**

*Snow-air partition coefficient log \( (K_{IA}/m) \)*

The poly-parameter linear free energy relationship (pp-LFER) for the calculation of the snow-air partition coefficient was taken from Roth et al. (2004):

\[
\log K_{IA}(-6.8 \degree C) = 3.53 \sum \alpha^H_2 + 3.38 \sum \beta^H_2 + 0.639 \log L^{16} - 6.85,
\]

where \( \log L^{16} \) is the hexadecane/air partition coefficient at 25 \degree C, \( \sum \alpha^H_2 \) is the electron acceptor; and \( \sum \beta^H_2 \) is the electron donor of the particular substance. The solute descriptors are shown in Table 1. The \( \log K_{IA} \) values were temperature corrected using:

\[
\log K_{IA}(T) = \log K_{IA}(T_{ref}) + \frac{\Delta H_{IA}}{2.303 R} \left[ \frac{1}{T_{ref}} - \frac{1}{T} \right]
\]

where \( \Delta H_{IA} \) is the enthalpy of sorption (Table S1).

*Humic acid-air partition coefficient log \([K_{HA/A}/(L/kg)]\)*

The pp-LFER for the calculation of the humic acid – air partition coefficient at 15 \degree C was taken from Niederer et al. (2006a):

\[
\log [K_{HA/A}/(L/kg_{HA})] = lL - vV + bB + aA + sS - c.
\]

The temperature dependent sorbent descriptors were calculated from Table 1 in Niederer et al. (2006a). The solute descriptors are shown in Table S1.
Air-water partition coefficient \( \log K_{AW} \)

The \( \log K_{AW} \) values of the HCHs were calculated from FAVs by Xiao et al. (2004) and those of the PCBs were calculated from FAVs by Li et al. (2003).

The \( \log K_{AW} \) values of ethylbenzene, p-xylene, benzo(a)pyrene (BaP) and benzo(ghi)perylene (BghiP) were calculated from Henry’s law constant expressions in Mackay et al. (2006) (van’t Hoff eq. derived from literature data, Staudinger and Roberts, 2001).

The \( \log K_{AW} \) values of the PAHs except BaP and BghiP were calculated using the pp-LFER from Abraham and Al-Hussaini (2005):

\[
SP = c + eE + sS + aA + bB + vV,
\]

and the coefficients of the system “gas phase to water” from Table 2 in Abraham and Al-Hussaini (2005). The values were temperature corrected using expressions from deMaagd et al. (1998).

The \( \log K_{AW} \) values of the FTOHs at 0 °C were extrapolated using values of Table 3 in Goss et al. (2006).

Humic acid-water partition coefficient \( \log [K_{HA/W}/(L/kg)] \)

The humic acid-water partition coefficients of all substances except the FTOHs were estimated from the results of two calculations:

1. \( \log K_{HA/W} = \log K_{HA/A} + \log K_{AW} \)
2. using the pp-LFER from Niederer et al. (2006a): \( \log [K_{HA/W}/(L/kg_{HA})] = 0.29 \text{ L} + 2.50 \text{ V} - 3.29 \text{ B} - 0.21 \text{ A} - 0.79 \text{ S} + 0.01 \). The solute descriptors are shown in Table S1.

The \( \log K_{HA/W} \) values of the FTOHs at 0 °C were estimated from values of Table 3 in Goss et al. (2006).
Table S1  Solute descriptors and enthalpies used in the calculations.

<table>
<thead>
<tr>
<th>Substance</th>
<th>A (∑α²H)</th>
<th>B (∑β²H)</th>
<th>L (log L¹⁶)</th>
<th>V</th>
<th>S</th>
<th>E</th>
<th>ΔH₁₆ [kJ mol⁻¹]f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene</td>
<td>0.00</td>
<td>0.15</td>
<td>3.778</td>
<td>1.00</td>
<td>0.51</td>
<td>-46.1</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.00</td>
<td>0.16</td>
<td>3.839</td>
<td>1.00</td>
<td>0.52</td>
<td>-47.1</td>
<td></td>
</tr>
<tr>
<td>4-2 FTOH</td>
<td>0.55</td>
<td>0.25</td>
<td>2.52</td>
<td>1.35</td>
<td>0.20</td>
<td>-65.8</td>
<td></td>
</tr>
<tr>
<td>6-2 FTOH</td>
<td>0.55</td>
<td>0.25</td>
<td>2.96</td>
<td>1.78</td>
<td>0.20</td>
<td>-69.1</td>
<td></td>
</tr>
<tr>
<td>8-2 FTOH</td>
<td>0.55</td>
<td>0.25</td>
<td>3.47</td>
<td>2.22</td>
<td>0.20</td>
<td>-72.9</td>
<td></td>
</tr>
<tr>
<td>10-2 FTOH</td>
<td>0.55</td>
<td>0.25</td>
<td>3.9</td>
<td>2.65</td>
<td>0.20</td>
<td>-76.1</td>
<td></td>
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<tr>
<td>α-HCH</td>
<td>0.00</td>
<td>0.71</td>
<td>7.317</td>
<td>1.5798</td>
<td>0.73</td>
<td>-96.5</td>
<td></td>
</tr>
<tr>
<td>γ-HCH</td>
<td>0.00</td>
<td>0.68</td>
<td>7.467</td>
<td>1.5798</td>
<td>0.91</td>
<td>-95.9</td>
<td></td>
</tr>
<tr>
<td>PCB-28</td>
<td>0.00</td>
<td>0.15</td>
<td>7.904</td>
<td>1.6914</td>
<td>1.33</td>
<td>-79.9</td>
<td></td>
</tr>
<tr>
<td>PCB-52</td>
<td>0.00</td>
<td>0.15</td>
<td>8.144</td>
<td>1.8138</td>
<td>1.48</td>
<td>-86.0</td>
<td></td>
</tr>
<tr>
<td>PCB-101</td>
<td>0.00</td>
<td>0.13</td>
<td>8.868</td>
<td>1.9362</td>
<td>1.61</td>
<td>-89.3</td>
<td></td>
</tr>
<tr>
<td>PCB-105</td>
<td>0.00</td>
<td>0.11</td>
<td>9.594</td>
<td>1.9362</td>
<td>1.59</td>
<td>-90.3</td>
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<tr>
<td>PCB-138</td>
<td>0.00</td>
<td>0.11</td>
<td>9.772</td>
<td>2.0586</td>
<td>1.74</td>
<td>-93.1</td>
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</tr>
<tr>
<td>PCB-153</td>
<td>0.00</td>
<td>0.11</td>
<td>9.587</td>
<td>2.0586</td>
<td>1.74</td>
<td>-92.5</td>
<td></td>
</tr>
<tr>
<td>PCB-180</td>
<td>0.00</td>
<td>0.09</td>
<td>10.415</td>
<td>2.1810</td>
<td>1.87</td>
<td>-95.7</td>
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</tr>
<tr>
<td>Naphthalene</td>
<td>0.00</td>
<td>0.20</td>
<td>5.161</td>
<td>1.0854</td>
<td>0.92</td>
<td>1.340</td>
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</tr>
<tr>
<td>Anthracene</td>
<td>0.00</td>
<td>0.26</td>
<td>7.57</td>
<td>1.454</td>
<td>1.34</td>
<td>2.290</td>
<td>-81.9</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.00</td>
<td>0.20</td>
<td>6.922</td>
<td>1.3565</td>
<td>1.03</td>
<td>1.588</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.00</td>
<td>0.26</td>
<td>7.63</td>
<td>1.454</td>
<td>1.29</td>
<td>2.055</td>
<td>-81.9</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.00</td>
<td>0.29</td>
<td>8.83</td>
<td>1.585</td>
<td>1.71</td>
<td>2.808</td>
<td>-98.6</td>
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<tr>
<td>Benzo(a)pyrene</td>
<td>0.00</td>
<td>0.39</td>
<td>11.80</td>
<td>1.95</td>
<td>1.98</td>
<td>-119.9</td>
<td></td>
</tr>
</tbody>
</table>

a from Niederer et al. (2006a), Supplementary Data
b from Goss et al. (2006)
c from Abraham et al. (2002)
d from Abraham and Al-Hussaini (2005)
e from Goss (2005), Supplementary Data
References of the Supporting Information


Chapter 3: Measuring the Release of Organic Contaminants from Melting Snow under Controlled Conditions

Torsten Meyer, Ying Duan Lei, Frank Wania

Contribution: Method developed under the supervision of Y.D. Lei and paper written under the supervision of F. Wania.

Abstract
The release of organic contaminants from a melting snow pack may result in temporary concentration peaks in receiving water bodies and respective pulse exposure of aquatic organisms. It is thus of considerable interest to gain a mechanistic and quantitative understanding of the processes determining the dynamic behavior of organic chemicals during snow melt. Uniformly structured and contaminated snow was produced with the help of a newly designed snow gun and exposed to predetermined temperature conditions in a temperature controlled cold room. The dry density and liquid water content during four freeze-thaw cycles was recorded continuously at different layers within the snow pack using time domain reflectometry, providing information on melt water production and propagation as well as snow metamorphism. Fractionated melt water samples were filtered and the dissolved and particle phase analyzed for five polycyclic aromatic hydrocarbons (PAHs) using gas chromatography/ mass spectrometry. The distribution of the PAHs between the dissolved and particulate fractions of the melt water was strongly related to their hydrophobicity. Particle-bound PAHs were released late during the snowmelt, whereas PAHs in the dissolved phase were released uniformly during a two day melting period. Even though conductivity measurements indicated a preferential early elution of ions in the first melt water fractions, no such “first flush” behavior was observed for soluble PAH. The developed laboratory-based approach opens up for the first time the possibility of reproducible experiments on organic contaminant behavior in snow. Future experiments will explore in detail how the properties of organic chemicals, the physical and chemical properties of the snow pack, and the temperature variations before and during the time of melting interact to determine the timing of chemical release from a snow pack.

Brief
The time-resolved release of polycyclic aromatic hydrocarbons from a melting snow pack is studied in controlled cold room experiments.

3.1 Introduction
Snow and ice influence in a multitude of ways the fate of organic contaminants in the environment (1, 2). Snow melt, in particular, should strongly influence the extent and timing of the delivery of organic contaminants to aquatic and terrestrial ecosystems in high latitudes and altitudes. During snow melt, contaminants are released that have accumulated in the snow pack as a result of wet and dry atmospheric deposition processes during the winter, sometimes over time periods of many months. Pronounced spring concentration peaks of persistent organic contaminants, such as the
polychlorinated biphenyls and DDT, coinciding with the snow melting period, have been observed in the St. Lawrence River and four of its tributaries (3,4). Similarly, peaks in air concentrations of organic contaminants coinciding with the snow melt period have been observed around the Laurentian Great Lakes (5-7). The potential for snow melt to cause temporary concentration maxima in water, air and soil environments has also been confirmed by simulation models (7,8).

The potential for a period of elevated contaminant release during snowmelt has implications regarding increased exposure of aquatic and terrestrial organisms. Ecotoxicological effects are often different depending on whether the exposure occurs continuously and evenly or in short, but intense pulses (9). The timing of such pulse exposure relative to the seasonal life cycle of populations and individual organisms is also important. Snow and ice melt often coincide with time periods of intense biological activity. Specifically, the melting of the seasonal snow pack in temperate regions could result in a pulse exposure of contaminants in aquatic ecosystems during early spring, when many life forms are at a vulnerable stage of development (10). Observations from a field study in the Canadian Arctic suggest that snow melt processes influence organic contaminant uptake in lichens, forming the basis of the caribou-wolf food chain (11). The mechanism and timing of organic contaminant delivery to various natural systems during snow melt are thus of considerable interest.

Whereas investigations of the melting behavior of inorganic chemicals in snow and ice have been quite common in both the field and the laboratory (e.g. 12-18), the melting behavior of organic contaminants is less well studied. Field-based research on organic chemicals in snow is rarely aimed at providing a quantitative understanding of the processes that organic contaminants undergo during snow melt. In general, most studies are limited to reporting residue concentration in bulk snow, sea ice and melt water samples taken in urban, rural or remote areas (see refs. in 1). Unfortunately, the interpretation of these data is often compromised by a lack of understanding regarding the interaction between organic chemicals and melting snow.

In a rare process-oriented field study, Simmleit et al. (19) measured the concentrations of selected organic contaminants in two melting snow packs on a daily basis. They observed that less soluble chemicals became enriched in the remaining snow pack relative to the more water-soluble compounds. Other studies have indicated the importance of particles in transporting the less water-soluble organic compounds (20,21). In the Amituk Lake basin in the Canadian High Arctic, the concentrations of the most water-soluble organic contaminants in snow melt water were observed to be initially high, with levels decreasing as the melting period progressed, whereas concentrations of the sparsely soluble substances are more likely to increase during the melting period (22). This
preferential elution or ‘first flush’ melting behavior of relatively water soluble organic substances matches that of water soluble inorganic compounds (e.g. 12,13), indicating that similar mechanisms may be influencing their release from the melting snow pack.

A disadvantage of field studies is the difficulty encountered when trying to reproduce snow properties and melting conditions. This is further complicated by low levels of organic contaminants in natural snow, particularly in remote locations, and the high spatial variability that may exist. The only laboratory study on organic contaminants in melting snow (23) explained observations of a fractionated elution of organic contaminants from a snow-filled, double-walled glass column (height 104.5 cm, inner diameter 14.4 cm), which had been exposed to repeated freeze-thaw cycles, with the extent to which the chemicals were associated with particles: Water-soluble substances, such as the hexachlorocyclohexane isomers, eluted first, whereas less soluble substances were associated with the last melt water fractions, which also contained the particles. In this study a coolant was regulating the snow temperature and light bulbs were inducing the melt cycles. With a relatively large wall-to-volume ratio, column experiments may suffer from wall effects. The small scale of these experiments also limits the number of snow melt samples that can be taken and therefore the temporal resolution that can be achieved.

In this study, we build on the pioneering work of Schöndorf and Herrmann (23) by describing laboratory investigations into the behavior of organic chemicals during snow melt using a temperature controlled cold room. The objective of these controlled experiments, involving artificially produced snow, is to gain a mechanistic and quantitative understanding of the processes determining the release of organic chemicals from a melting snow pack. This contribution describes the experimental procedure in detail, including the making and spiking of artificial snow, the tracking of physical snow pack properties using time domain reflectometry (TDR), and the analysis of dissolved and particulate snowmelt samples for polycyclic aromatic hydrocarbons (PAHs).

3.2 Methods

Overall Experimental Design. A large rectangular stainless steel container (Fig. 3.1, 0.24 m³; height: 40-50 cm, width: 100 cm, depth: 55 cm) is filled with artificial snow, sealed with a Plexiglas lid, and exposed to predetermined temperature conditions in a cold room, which can be cooled to -30 °C. During the experiment the cold room is kept dark to prevent photo-degradation of organic contaminants. Changes in physical snow properties are recorded continuously as a function of snow depth using TDR. As the snow pack in the container gradually melts, the melt water fractions are collected in a drain at the bottom of the vessel and are sampled into 1 L amber glass bottles. The
water level within the bottles is marked for sample volume determination. The melt water samples are stored at a temperature of 1 °C until filtration and extraction.

![Figure 3.1](image)

**Figure 3.1** Schematic of the experimental setup used in the snow melt experiments, showing the placement of TDR-aluminum rods in the stainless steel vessel.

A refrigerated cooling liquid is circulated through the double-walled bottom of the vessel, which makes it possible to control the temperature at the bottom of the snow pack separately from the rest of the cold room. This allows for the simulation of realistic temperature gradients within the snow pack. The heat transfer between double bottom and overlaying snow is relatively high and to avoid accelerated freezing or melting of the bottom snow the temperature of the cooling liquid is kept at 0 °C. Fluctuating cold room temperatures are balanced with adjustments of the refrigerating bath that pumps the refrigerant through the double bottom.

In the experiment describe here, artificial snow containing both particles and a mixture of several PAHs comprising a wide range of partitioning properties was first exposed to four diurnal melt/freeze cycles without any melt water leaving the snow pack. Subsequently, the snow was completely melted within two melt cycles interrupted by a re-freezing phase. The samples were separately analyzed for the particulate and the dissolved PAH phase.

**Procedure for Making Artificial Contaminated Snow.** The necessity to have large amounts of snow with constant and comparable properties for the experiments led to the development of a method for producing artificial snow by means of a “snow gun” (see Fig. 3.S1 in the supporting information).
Air compressed at 340 kPa (Air compressor - Porter Cable CPL6025) and tap water exhibiting similar pressure are mixed and forced through a nozzle (size 2.4 mm) into the cold room. The nozzle was made by drilling a hole in a commercially available threaded plumbing cap whereby the size of the borehole was chosen to match the cold room size and the capacity of its cooling compressors. After leaving the snow gun the mixture consisting of tiny water droplets within a high pressure environment rapidly cools down due to expansion, convection, and evaporation and falls as pellet snow directly into the experimental vessel. To keep the wet bulb temperature sufficiently low, a temperature of -20 ºC is maintained within the experimental cold room. A system of water vapor traps prevents clogging of the cooling evaporator entry with snow. The produced snow exhibits properties similar to recently deposited natural snow with a density of around 0.16 g/cm³ (measured gravimetrically) and a snow grain size of approximately 0.1 mm. The formed ice pellets assemble within the vessel at random, leaving a relatively large air-filled pore space due to stickiness of the snow grains. Soon, dry snow sintering and melt/freeze cycles let the snow grains bond more strongly to one another rendering a relatively stable snow structure. The size of the snow grains was determined by means of snow macro-photography (Fig. 3.S2). A biological microscope (M Series) was attached on a digital camera (Canon D20) whereby the stage of the microscope was cooled with a refrigerated liquid flowing through a copper coil. The specific surface area (SSA) of the artificially produced snow was determined by applying a volumetric method and measuring the adsorption isotherm of krypton on the snow at 77.15 K (liquid N₂ temperature) (adapted from 24). After an initial density increase of approximately 15 percent the snow sample exhibited a SSA of 582 (± 45) cm²/g. The method allows the production of approximately 40L of spiked artificial snow per hour of snowmaking. The metamorphosis of natural snow and artificially produced snow during melt/freeze cycles is inherently similar except during the initial stage when the density of artificial snow increases relatively fast. Due to more consistent sterical assembly meltwater formation and flow is presumably more uniform in artificial than in natural snow.

Mixtures of solutions containing defined concentrations of PAHs either in the dissolved phase or attached onto fine particles are injected into the water stream leading to the snow gun by means of a pump. The injection flow rate is 6 mL/min while the flow rate before the snow gun is approximately 110 mL/min. After leaving the snow gun the water droplets freeze to ice within less than a second which is believed to lead to a uniform distribution of particles, ions and spiked chemicals within the snow grain and within the snow pack itself. Natural snow crystals grow slower and as a consequence chemical substances are partially concentrated at the edge of the ice lattice. For the experiment an
injection mixture consisting of 1 L ultra-pure water, PAH stock solution, and humic acid (Aldrich Corp., St. Louis, MO) was prepared. The stock solution contained PAHs in neat form dissolved in acetone and was stored at -10 °C. Accordingly, the water equivalent of the artificially produced snow contained ~10 μg/L humic acid, ~1200 ng/L of each individual PAH, and approximately 190 mg/L total solids present in the drinking water (25). Prior to use, the humic acid was filtered with an A/D glass filter (Pall Corp.) to exclude particles with a diameter larger than 3 μm. The most important fraction of airborne particles in snow for the purpose of this study is in the range of 0.1 to 2 μm in diameter (26). The PAH stock solution includes naphthalene, phenanthrene, pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene. These five compounds have octanol-water and air-water partition coefficients that range over three orders of magnitude (Tab. 1). Based on their water solubility, the higher and medium molecular PAHs with 4 to 6 fused rings in their molecular structure are expected to be primarily associated with particles, while the lower molecular PAHs are believed to stay within the dissolved phase of the melt water (27).

Table 3.1  Physical chemical properties of the polycyclic aromatic hydrocarbons used in the snow melt experiments at 0 °C.

<table>
<thead>
<tr>
<th></th>
<th>log K&lt;sub&gt;OW&lt;/sub&gt;</th>
<th>solubility in water (μg/L)</th>
<th>Henry’s constant (Pa m&lt;sup&gt;3&lt;/sup&gt;/mol)</th>
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<tr>
<td>Naphthalene</td>
<td>3.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13,700&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10.2&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.26&lt;sup&gt;a&lt;/sup&gt;</td>
<td>390&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.53&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4.87&lt;sup&gt;a&lt;/sup&gt;</td>
<td>49&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.28&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>5.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.426&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0092&lt;sup&gt;ce&lt;/sup&gt;</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>5.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.049&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.011&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
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</table>

<sup>a</sup>log K<sub>OW</sub> values (25°C) from ref. 47 except for pyrene (ref. 48); adjusted to 0 °C using Δ<sub>OW</sub>H values from ref. 49 (value of benzo[a]pyrene was applied to benzo[k]fluoranthene considering their similar molecule structure).

<sup>b</sup>measured values at 0°C from ref. 50.

<sup>c</sup>aqueous solubility values (25°C) from ref. 47; adjusted to 0 °C assuming Δ<sub>sol</sub>H = Δ<sub>OW</sub>H

<sup>d</sup>Henry’s constant’s (20°C) from ref. 47; adjusted to 0 °C using Δ<sub>WA</sub>H values from ref. 51.

<sup>e</sup>Henry’s constant’s (20°C) from ref. 47; adjusted to 0 °C using Δ<sub>WA</sub>H values from ref. 52.

**Time Domain Reflectrometry (TDR).** TDR measures the travel time of an electromagnetic pulse along a probe embedded in a medium of interest, which in the present case is snow. This travel time is dependent on both the probe characteristics and the permittivity of the medium around the probe. Snow mainly consists of ice and air, and during snowmelt periods liquid water presents a third component. These three phases differ in permittivity, which allows the water content of wet snow and the density of dry snow to be measured on-line using TDR (28,29). While the liquid water
content is measured during melting periods, the dry snow density can only be acquired in “night-

time” refrozen snow. Both parameters are calculated using approximations given in a review by

Frolov and Macheret (30). If the physical length of the probe is known, the apparent or measured
permittivity of the surrounding bulk snow can be determined using:

\[
\varepsilon_a = \varepsilon' \left(1 + \sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2}\right) / 2,
\]

(1)

where \(\varepsilon'\) is the real part and \(\varepsilon''\) is the imaginary part of the relative permittivity (29). The density of
dry snow is determined using:

\[
\varepsilon_d' = (1 + 0.845 \rho_s),
\]

(2)

where \(\varepsilon_d'\) is the real part of the dielectric permittivity of dry snow and \(\rho_s\) is the bulk snow density.
The apparent permittivity is assumed to correspond to the real part of the permittivity leaving its
imaginary part negligible (30-32). The volumetric water content then is:

\[
\varepsilon_s' = \varepsilon_d' + \Delta\varepsilon_s' = \varepsilon_d' + (16.7 W + 42.5 W^2)
\]

(3)

where \(\varepsilon_s'\) is the dielectric permittivity of the bulk wet snow, and \(\Delta\varepsilon_s'\) is the incremental dielectric
permittivity accounting for the water content \(W\) (30). The average bulk snow density is additionally
ascertained by measuring the level of the snow surface during the experiments. Sublimation and
evaporation of snow is assumed to be negligible because an air tight lid is covering the snow vessel
during the experiments.

Six handcrafted twin-rod TDR probes consisting of aluminum tubes (29), an epoxy resin probe head,
and coaxial cables are held in place in the snowmelt vessel using 0.1 mm nylon thread, prior to their
embedding in the bulk snow (Figs. 3.1 and 3.S3). Three TDR probes are stacked one upon each other
with a vertical distance of 5 cm. The temperature dependence of the electromagnetic pulse’s travel
time within the coaxial cable is neglected considering that only 1 m of it is exposed to temperature
variations (32). The probes are 90 cm long, exhibiting a rod spacing of 9 cm and a rod outer diameter
of 3.2 mm. A short rise-time cable tester (Textronik 1502B) sends electromagnetic pulses with a
frequency range of 10 MHz to 1 GHz along the probes, while a multiplexer (SDMX50, Campbell
Scientific Inc.) is alternately switching between them. The signals are sampled and evaluated using
the TDR software TACQ (33).

**Chemical Analysis.** All neat PAHs are from Aldrich Corporation (St. Louis, MO). The standards
containing naturally occurring PAHs, the surrogate standards and the internal standard are from
Cambridge Isotope Laboratories, Inc. (Andover, MA), all solvents from Caledon Laboratories Ltd.
(Georgetown, ON). All standards are stored at -10°C to ensure stability. Samples were extracted within three days of sampling. Separation of the particulate and dissolved phase of PAHs was achieved by suction filtration through 0.45μm nylon hydrophilic membrane filters (Pall Corporation, East Hills, NY, or Whatman, Brentford, UK). The bottle and filter funnel were rinsed with ice-cold water to prevent re-partitioning of the PAHs between dissolved and particulate phase. The PAHs in the dissolved phase were extracted by means of C$_{18}$ SPE cartridges (Supelco, Sigma-Aldrich, St. Louis, MO) with a flow rate of 5 mL/min and after conditioning with 5mL acetonitrile and 10mL tap water (34). The latter volume is very small compared to the sample volume rendering trace amounts of PAHs in the tap water negligible. At no time was the cartridge allowed to run dry. C$_{18}$SPE is commonly used to extract PAHs from aqueous solutions (35-39). The extract was eluted with 5 mL hexane (37) and the resulting aliquot was blown down to 0.5 mL using N$_2$. The filters containing the particulate fraction were placed in 8 mL amber vials and dried for 15 minutes using N$_2$. Extraction was achieved by adding acetone and subsequent ultra-sonification (VWR Aquasonic) for 30 min (40). After filtering through 0.45 μm nylon membrane syringe filters the solvent was exchanged with iso-octane and concentrated to 0.5mL using N$_2$. Both particulate and dissolved fractions were analyzed using gas chromatography/mass spectrometry with electron impact ionization (Agilent 6890 Series) and selected ion monitoring mode. Detail of the instrumental method is provided in the Supporting Information.

Quantification was achieved with six external calibration standards containing the applied natural PAHs. Quality control was provided with the internal standard mirex and recovery surrogate standards in deuterated form. Surrogate PAHs were added to every second sample directly after sampling. The recovery rates for the entire analytical method comprising both particulate and dissolved phase PAHs were 51 % for d$_8$-naphthalene (13.5 % RSD), 76 % for d$_{10}$-phenanthrene (9.2 % RSD), 93 % for d$_{10}$-pyrene (9.3 % RSD), 49 % for d$_{12}$-benzo(a)pyrene (10.8 % RSD), and 43 % for d$_{12}$-benzo(ghi)perylene (15.5 % RSD). The d$_{12}$-benzo(a)pyrene served as surrogate for benzo(k)fluoranthene. The average RSD was 11.6 %. The relatively low recovery rates for the 5-ring and 6-ring PAHs may have resulted from irreversible adsorption on glass (36,38,41). The samples could not be spiked with any organic solvent or surfactant and the bottles could only be rinsed with ice cold water to avoid re-partitioning. Because melt water concentrations are presented relative to each other and not in absolute terms, the recoveries are judged acceptable.

It is not possible to establish the overall mass balance of the PAHs injected into the water used for making the snow because an undetermined fraction of that snow does not fall into the experimental
vessel during the snowmaking process. Artefacts stemming from the vertical walls of the snowmelt vessel can be neglected since not only is the wall-to-volume ratio of the vessel relatively low but snow metamorphism also rapidly leads to compaction of the snow and hence to a gap between the bulk snow and the vessel wall. However, sorption of particle-associated PAHs to the sloped bottom of the vessel during the melting process may occur.

3.3 Results and Discussion

Snow Density and Liquid Water Content. During the experiment, TDR was used to measure the bulk snow permittivity, reflecting dry snow density (at temperatures below freezing) or wet snow water content (at temperature above freezing), at three different levels within the snow pack. The red, green and blue lines in Figure 3.2 refer to the measured dielectric permittivities of the three stacked TDR probes during the course of the experiment. Dry snow conditions correspond to the minima of these three wavelike lines. During those time periods the snow density can be measured directly because the bulk dielectric permittivity is influenced only by the two components air and ice. The three dashed lines interpolating these minima can thus be interpreted as the dry snow density of different layers within the snow pack. During the first four days of the experiment the temperature in the cold room fluctuated diurnally between -8 and +6 °C (yellow line in Fig. 3.2). During that time the density slowly increased from approximately 0.17 - 0.18 g/cm³ to values of approximately 0.19 - 0.22 g/cm³ (dashed red, green and blue lines). During the first day, a small gradient developed with lower snow layers (red) being slightly denser than the layers above them (green and blue) by an increment of approximately 0.01 g/cm³. The increasing snow density is presumably caused by compaction and snow metamorphism occurring as a result of the melt/freeze cycles.

The peaks of the wavelike graphs in Figure 3.2 correspond to permittivity increases resulting from the presence of liquid water within the bulk snow during a melt period. Thus, the water content can be calculated by interpolating the snow densities of the dry snow periods before and after a melting phase and interpreting the height of the superimposed permittivity peak in terms of liquid water. The blue peaks are much larger than the green peaks, which in turn are larger than the red peaks (Fig. 3.2). This implies that during melt cycles the upper probe experienced a higher liquid water content than the middle and lower probes suggesting that upper snow layers are most affected by such cycles. The liquid water peaks in the lower snow layers also occur slightly later than in the upper layers, indicative of the delayed penetration of heat from the surface of the snow pack.
During the first four days the temperature was kept low enough to prevent the creation of a downward propagating melt water front and hence, no melt water left the snowmelt vessel. Accordingly, relatively little melt water was produced; calculated liquid water contents for each of the three probes range between 0.1 and 1 % (Fig. 3.2). Assuming a specific surface area of 250 cm$^2$/g (42) of the snow around the upper probe at day 4, the water content of 1.0 % corresponds to an average thickness of approximately 2 μm of the water layer on the surface of the ice lattice. Such small amounts of water are held by surface forces and can not be transported downward by gravity (43). The lower dielectric permittivity of bound water near surfaces compared to free water has negligible influence on the calculated water content in this study considering an affected distance from the surface of only about 1 nm (44). The observations indicate a high insulation capacity of snow with a strong vertical gradient of melt water production within the snow pack. The time shift between temperature and responding water production within the snow pack presumably occurred because air movement around the snow vessel and above the snow surface was extremely limited. During days 5 and 6 the snow melted completely at temperatures of approximately +15 °C and the liquid water content in bulk snow peaked at approximately 6 % (data not shown).
**Specific Conductivity.** The specific conductivity of the melt water fractions, measured with a conductivity meter (VWR Scientific Model 2052), is a good indicator of the occurrence of ions in the dissolved aqueous phase. Melt-freeze cycles cause ions to freeze out of the snow grain lattice and accumulate in the quasi-liquid layer where they are available to enrich the downward percolating melt water. During recrystallization most of the ions can not easily be reintegrated into the ice crystal lattice causing their gradual segregation (13). During the melt phase on days 5 and 6 of the experiment, the specific conductivity of the melt water samples decreased rapidly from a maximum in the second sample, which was taken when the propagating melt water front reached the bottom of the vessel (Fig. 3.3). On both days, the decrease in conductivity was linear with respect to the sample order, but the rate of decrease was faster on the first melt day. Conductivities in the last two samples of the first melt day did not continue the decreasing trend. At this time the melt water was re-freezing again, causing the accumulation of ions in the remaining melt water. The relatively low conductivity in the melt water sampled at the beginning of the second melt day refers to the loss of ions on the previous day as a result of freezing-out from the snow grain and loss from the vessel with melt water. Previous studies using natural snow reported conductivity decreases with progressing sample order that are logarithmic or nearly linear (19,23). A comparison of the studies is complicated because of the different ionic composition of tap water and possibly also a different distribution of chemicals within the snow grain of artificial snow.

![Figure 3.3](image-url)  
*Figure 3.3*  Specific conductivity and melt water volumes vs. sample order.
**Snow Melt Behavior of the PAHs.** The distribution of the PAHs between the dissolved and particulate fractions of the melt water is strongly related to their hydrophobicity, as expressed by either the water solubility or octanol-water partition coefficient log $K_{OW}$ (Table 3.1). Naphthalene is the most water soluble of the PAHs and was only detected in the dissolved phase. Benzo(ghi)perylene and Benzo(k)fluoranthene are the least water soluble and were only present in the particulate fraction. Pyrene and phenanthrene with an intermediate hydrophobicity were present in both phases.

The relative concentration of five different PAHs in the dissolved and particulate phase of the snow melt water as a function of sample order is given in Figure 3.4. Particle-bound substances were released late during the snowmelt. Approximately 85% of the release of benzo(k)fluoranthene and benzo(ghi)perylene occurred during the last third of the snowmelt phase, when also the majority of particles was leaving the vessel (Fig. 3.4). Schöndorf and Herrmann (23) had observed a similar melt behavior of particle-bound PAHs in controlled laboratory experiments. A field study, however, reported peak concentrations of particle-bound PAHs at the beginning and at the end of a snow melt period (19). Snow metamorphosis and permeability are important factors determining the timing of particle release from the snow pack. The artificial snow used in this study has a relatively uniform structure due to the defined conditions during its production. It appears that metamorphosis and meltfreeze cycles rendered the artificial snow pack an effective filter for particles by clogging them within the interstitial snow volume.

The PAHs in the dissolved phase are released rather uniformly during the two day melting period. There is a slightly higher dissolved phase concentration of naphthalene in the middle and slightly lower concentrations toward the end of the snow melt period. However, no “first flush” behavior was observed for any of the PAHs. The reason could be that none of the PAHs is very water soluble, except naphthalene (Table 3.1). However, naphthalene has a relatively high Henry constant, causing it to volatilize easily into the interstitial air of the bulk snow or in the enclosed air space above it. This air space may have acted as a “buffer” that continuously supplied naphthalene to the melt water, leading to its rather uniform release from the snow pack. Experiments with substances of a similar aqueous solubility as naphthalene but substantially lower Henry constant could shed more light on this issue. The release of phenanthrene is more equally distributed during the melt phase in both the particulate and dissolved phase. Pyrene shows a elution behavior that lies between that of phenanthrene and benzo(k)fluoranthene.
Evaluation and Future Potential of the Method. The feasibility of highly controlled experiments on snow in a laboratory setting has been established. Not only is it possible to strictly control the melting conditions to which a snow pack is exposed, but by using artificially made and contaminated snow, it is further possible to assure uniformity of experimental snow packs in terms of snow structure and contaminant concentrations. The metamorphism of surface snow in a natural environment is not only dependent on a complex system of environmental conditions but also on the initial snow structure developed during growth within the atmosphere. The relatively uniform structure of the artificially produced snow in this method provides repeatable and comparable conditions that can hardly be achieved by using natural snow. Also, the ability to spike the artificial snow with selected contaminants and in sufficiently high concentrations facilitates the investigations. The trace analysis of organic substances in natural snow often requires time consuming extraction and clean up procedures (45). The use of a cold room and large dimensions of the snow container further minimise the possible artefact of wall effects, the importance of which should increase with
decreasing volume-to-surface ratio of the snow pack. This work therefore opens up for the first time the option of reproducible experiments on organic contaminant behavior in snow.

TDR is the ideal complement to such experiments, because it allows for the recording of physical snow properties in a spatially and temporally resolved fashion. By recording melt water content and dry snow density it provides valuable information regarding melt water production and propagation as well as snow metamorphism within the bulk snow. The fragile nature of snow usually does not allow the recording of such information without destruction of the snow structure. Not only does TDR lead to only minimal disturbance of the snow pack, but the recordings are made continuously with no need for interpolation. The hydraulic properties of bulk snow significantly change during snow metamorphism. Rapidly increasing snow grain size and an increasing density change flow characteristics and consequently the melt behavior of organic substances. Therefore, snow macro-photographs will be taken for different snow layers at different times in future experiments. Also, a temporary stagnant water layer at the bottom of the bulk snow will be observed by adjusting the lowest TDR probe accordingly.

Future experiments also will explore in detail how the properties of the organic chemical, the physical and chemical properties of the snow pack, and the temperature variations before and during the time of melting interact to determine the timing of chemical release from a snow pack with melt water. Accordingly, experiments will vary in terms of the type of snow and initial snow properties, and the ageing and melting conditions. A focus will be on understanding the differences in snowmelt behavior of organic contaminants in the dissolved and particle phase (19,23). Other possible applications of the presented approach include the investigation of the influence of the underlying surface on melting and melt water composition, the observation of flow fingers using dye tracers (46), the study of the influence of short-wave radiation on photo-degradation of organic contaminants in the upper snow layers, the headspace analysis of volatile and semi-volatile chemicals during the experiments, or the study of the impact of different snow layers on snowmelt behavior. Obviously, natural snow can also be allowed to accumulate in a snowmelt vessel and be exposed to controlled experimental conditions in a cold room.

Acknowledgements
We are grateful for funding from the Canadian Foundation for Climate and Atmospheric Sciences, and laboratory assistance by Ibrahim Muradi. Special thanks to Tian Jiang Ye for the specific surface area measurement.
Supporting Information Available
Description of the instrumental analysis; photograph and drawing of the “snow gun”; macro-photographs of artificial snow grains; photograph of the snowmelt vessel with TDR probes and multiplexer. This material is available free of charge via the Internet at http://pubs.acs.org.

3.4 References


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**Supporting Information for**
Torsten Meyer, Ying Duan Lei, Frank Wania

**Measuring the Release of Organic Contaminants from Melting Snow under Controlled Conditions**

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</table>
Description of the GC/MS method

The sample extracts were analyzed using an Agilent 6890 gas chromatograph with auto-sampler (Agilent 7683) and mass spectrometer (Agilent 5973 MSD). A volume of 1.0 μL was injected in pulsed spitless mode. Chromatographic separation was implemented using a DB-5MS column (J&W Scientific: 60m x 0.25mm i.d., 0.10μm film thickness) with helium carrier gas. The initial inlet temperature was 280 °C and the GC oven temperature was: 70 °C for 1 min, 10 °C/min to 90 °C for 1 min, 4 °C/min to 130 °C, 5 °C/min to 240 °C and 4 °C/min to 300 °C and held for 2 min. The interface between GC and MSD was set to 310 °C and the ion source and quadrupole temperatures were 230 °C and 150 °C, respectively. The five natural PAHs and five deuterated PAHs were detected and quantified using the following ions (target/qualifier): naphthalene (128/127), d₈-naphthalene (136/137), phenanthrene (178/179), d₁₀-phenanthrene (188/189), pyrene (202/200), d₁₀-pyrene (212/213), mirex (272/274), benzo[k]fluoranthene (252/253), d₁₂-benzo[a]pyrene (264/265), benzo[ghi]perylene (276/274), d₁₂-benzo[ghi]perylene (288/289).

Figure 3.S1  Photograph and drawing of the “snowgun”.

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Figure 3.S2  Macro-photographs of the artificial snow grains (a,b) just after snowmaking and (c) after three melt/freeze cycles.

Figure 3.S3  Photograph of the snowmelt vessel with TDR probes and multiplexer.
Chapter 4: Organic Contaminant Release from Melting Snow: I. Influence of Chemical Partitioning

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Contribution: Experiments implemented and paper written in consultation and under the supervision of F. Wania and Y.D. Lei. Sample extraction carried out by T. Meyer and I. Muradi.

In preparation for “Environmental Science and Technology”.
Abstract. A melting snow pack can deliver organic contaminants to terrestrial and aquatic ecosystems in the form of short and concentrated pulse loads. The mechanisms and dynamics of these processes need to be understood to successfully integrate them into contaminant and water quality models. Controlled laboratory-based snowmelt experiments using artificially produced snow enriched with organic target contaminants revealed how chemical behavior during melting is dependent on the partitioning between the different phases within the bulk snow. Behaving similar to inorganic ions, water soluble organic chemicals are preferentially released at an early stage of melting, because such chemicals, accumulated at the snow grain surface, dissolve in the downward percolating melt water front. Hydrophobic substances attached to particles are often released at the very end of the melt period, because particle coagulation and snow densification render the melting snow pack an efficient filter trapping the particles. A notable fraction of volatile chemicals may transfer from the melting snow pack to the lower atmosphere due to evaporation. Organic pollutants with intermediate partition properties can easily switch between the bulk snow phases and their elution behavior is therefore sensitive to varying snow and melt characteristics.

4.1 Introduction

Amplification processes occurring within the bulk snow prior and during melting can lead to the release of organic contaminants from melting snow in form of peak loads. Concentration peaks of organic contaminants during spring snowmelt have been measured several times in rivers and lakes. Similarly, elevated concentrations of the more volatile organic pollutants have been observed within the lower atmosphere during melting. Major melt events often occur at times of enhanced reproductive activity when organisms are at a very vulnerable stage of development. The endocrine disrupting effects of specific organic pollutants may interact with the hormonal development of developing organisms. Every winter highly polluted road-side snow is deposited at snow dump sites from where the melt water is often released untreated to adjacent ecosystems (see Meyer and Wania, 2008).

Arctic and subarctic regions are especially susceptible to global climate change processes. The balance between snow and rain as precipitation mode is controlled by
small temperature differences. Both snow and rain exhibit very different potential to scavenge contaminants from the atmosphere (Lei and Wania, 2004). It is therefore of interest in which way climate change will influence the snow related fate of organic contaminants in cold regions (see Meyer and Wania, 2008).

Whereas investigations of the melting behavior of inorganic chemicals in snow have been quite common in both the field and the laboratory, the fate of organic contaminants in melting snow is far less well studied. Most field based studies are limited to reporting residue concentration in bulk snow and melt water samples taken in urban, rural, or remote areas. Very few studies have been investigating the temporal elution sequences of organic chemicals during snowmelt (Simmleit et al., 1986; Schöndorf and Herrmann, 1987; Meyer et al., 2006). In their laboratory study, Schöndorf and Herrmann (1987) found concentration peaks of water soluble organic contaminants at the beginning of the melt period. The bulk of the more hydrophobic substances was released at the end of melting along with the particles. Schöndorf and Herrmann melted natural snow in a glass cylinder (length: 1m; inner diameter: 14cm) while monitoring physical and chemical snow properties. The enrichment of hydrophobic organic pollutants towards the end of melting has been confirmed by Meyer et al. (2006), who were using a large block-shaped snowmelt vessel (0.24 m$^3$) in their experiments. In the field study conducted by Simmleit et al. (1986) however, most of the particle associated organic compounds were released at the beginning of the melt period along with the dissolved fraction. The contaminant pulse load at the early stage of a snowmelt period is referred to as Type 1 enrichment and describes the uptake of chemicals from snow grain surfaces by the first downward moving melt water. Particles and associated chemicals are efficiently held back from being washed out early, due to filter-like processes as a result of particle coagulation and an increasing snow density during melting. The release of particle-bound organic pollutants at the end of melting is referred to as Type 2 chemical enrichment (Meyer et al., 2008).

In this study, we built on the pioneering work of Schöndorf and Herrmann (1987) by implementing laboratory investigations into the behavior of organic chemicals during snowmelt using a temperature controlled cold room. The objective of these controlled experiments, involving artificially produced snow, is to gain a mechanistic understanding
of the processes determining the release of organic chemicals from a melting snow pack. This paper focuses on the influence of a chemical’s partitioning properties between the different bulk snow phases. We provide a method to theoretically assess the probability of a chemical to reside in a particular bulk snow phase, on the basis of the substance’s partitioning coefficients and the snow properties. Results from the snowmelt experiments are presented and discussed in relation to chemical partitioning maps. Finally, results from this study are compared to the findings of the laboratory study conducted by Schöndorf and Herrmann (1987).

4.2 Materials and Methods
The experimental design, the methods used to produce artificial snow spiked with target substances and to monitor the physical snow properties on-line, as well as the chemical analytical method are described in detail elsewhere (Meyer et al., 2006). Only the main features of the methods and any changes from the previously published procedure are described herein. A rectangular stainless steel vessel (0.24 m$^3$; height: 40-50 cm, width: 100 cm, depth: 55 cm) with a conical shaped bottom disembooguing in a melt water outflow, was filled with artificial snow and exposed to different melt conditions in a walk-in cold chamber. Changes in physical snow properties were measured on-line by means of time domain reflectometry (TDR). In particular, the density of dry snow and the water content of the snow during melting were measured at various snow depths. The travel time of an electromagnetic pulse along TDR probes that are embedded in snow is proportional to the relative dielectric permittivity of the bulk snow. The latter is different for the individual bulk snow phases air pore space, ice interface, and melt water. Based on the permittivity variations and the length of the TDR probe, the density of dry snow can be calculated directly. By interpolating the density of melting snow from two subsequent dry snow periods, the water content during a melt phase can be calculated. The average density of the bulk snow was additionally recorded by measuring the snow volume and the remaining snow-water equivalent at different stages of melting.

To further study the physical snow properties the snow micro-structure was tracked at different melt stages by means of macro-photography. The approximate size and shape of the snow grains provide clues about the hydraulic properties and the storage capacity of
the snow. By combining the snow classification scheme by Colbeck et al. (1990) with the studies by Legagneux et al. (2002) and Dominé et al. (2007), relationships between snow density and the specific surface area (SSA) could be established. The SSA is a crucial parameter in estimating the sorptive capacity of the internal snow surface for organic chemicals.

A cooling liquid flowing through the double-walled bottom of the snowmelt vessel was ensuring natural temperature gradients within the bulk snow. By means of a “snow gun” artificial snow was produced exhibiting pellet-shaped snow grains with diameter of approximately 100 µm, a density of 0.16 (+0.01) g/cm³, and a specific surface area (SSA) of 580 (+50) cm²/g. Bulk snow densities were measured using gravimetric and volumetric methods and were compared to values obtained by TDR. The SSA was determined by applying a volumetric method and measuring the adsorption isotherm of krypton on the snow at 77.15 K (liquid N₂ temperature) (adapted from Legagneux et al., 2002). Mixtures of solutions containing six different organic target substances either in the dissolved phase or attached to particles were injected into the water stream leading to the snow gun. Thus, the target chemicals were incorporated into the snow grain structure. The spiked artificial snow contained average concentrations of 1500 ng/L snow-water equivalent (SWE) of four polycyclic aromatic hydrocarbons (PAHs) (naphthalene, phenanthrene, pyrene, benzo(ghi)perylene (BghiP), of atrazine, and of lindane (γ-HCH). The partition coefficients describing the equilibrium distribution between the internal snow surface, melt water, air pore space, and organic matter within snow range over several orders of magnitude for this group of six compounds. The water used for making the artificial snow was further spiked with 3.5 mg humic acid per Liter SWE.

Melting was enforced either by elevated cold room temperatures while keeping the snow bottom at 0 °C or by six 175 W infra-red lights whose heights above the snow surface was adjustable. The 2 ± 0.2 Liter melt water fractions were sampled at the bottom of the vessel, measured for their specific conductivity, filtered, extracted and eventually both the dissolved and particulate phase were analyzed separately for organic contaminants. At the end of melting a large fraction of the particles adhered to the bottom of the snow vessel. Deviating from the procedure described in Meyer et al. (2006), those particles were now rinsed with additional drinking water and wiped into the exit funnel using a
painter brush. The vessel bottom was subsequently rinsed with acetone and both rinses were extracted and analyzed. Separation between the dissolved and the particulate phases of each sample was achieved by suction filtration using 0.45 μm nylon hydrophilic membrane filters (Whatman, Brentford, UK).

All chemical standards come from Cambridge Isotope Laboratories, Inc. (Andover, MA), the solvents ethyl acetate (EA) and dichloromethane (DCM) are from Caledon Laboratories Ltd. (Georgetown, ON). The humic acid was purchased from Aldrich Corp. (St. Louis, MO). The contaminants in the dissolved phase were extracted by means of C_{18} SPE cartridges (Supelco, Sigma-Aldrich, St. Louis, MO). The extract was eluted with 5 mL each of EA, DCM:EA (1:1), and DCM (Usenko et al., 2005). The extraction of the particulate fraction was achieved by ultra-sonication (VWR Aquasonic) in acetone, filtering and solvent exchange to iso-octane. Both dissolved and particulate fractions were analyzed using gas chromatography-mass spectrometry with electron impact ionization and selected ion monitoring mode. Surrogate contaminants were added prior to analysis to obtain recovery rates and mass balances (Meyer et al., 2006).

The concentrations of particles within the melt water were measured by filtering 1 Liter of each sample through a GF/F glass fiber filter (Whatman, Brentford, UK) with an approximate cut-off size of 0.7 μm. The latter differs from the cut-off size used for the extraction of organic contaminants. The bulk of the air-borne particles have diameters in the range between 0.4 to 0.7 μm (Heintzenberg and Rummukainen, 1993). Although a notable fraction of the particles will form large coagulates that are retained on GF/F filters, the particle concentrations in the melt water samples can not quantitatively be associated with the concentrations of particle-bound organic substances. Most of the particles in the artificial snow originate from indoor air that is sucked into an air compressor which provides compressed air for the snow production. Those particles presumably exhibit similar organic carbon content as the surrounding outdoor air (Ho et al., 2004; Hoek et al., 2007). The particle concentration within the artificial snow amounted to approximately 30 mg/L SWE. Combined with the injected amount of humic acid, the organic matter content was roughly estimated to be 10 mg/L SWE (Andren and Strand, 1981; Davies et al., 1992).
The results presented in this first of two complementary articles refer to the moderate to fast melting of an aged snow pack (see Appendix, melt scenario B). The last particulate fraction in each of the elution sequences refers to chemicals that were adsorbed to the particles remaining at the vessel bottom.

A mass balance was calculated encompassing the chemical’s fate from the deposition of the snow into the vessel to the sampling of the melt water, whereby the average meltwater concentrations were compared to the concentrations in bulk snow samples collected just after snowmaking. The approximate percentage losses during the chemicals' presence within the melt vessel were: 8% atrazine, 17% lindane, 85% naphthalene, 35% phenanthrene, 26% pyrene, and 20% benzo(ghi)perylene. This implies that a notable fraction of naphthalene and, to a smaller extent, phenanthrene and pyrene evaporated during melting.

4.3 Results and Discussion

Phase Partitioning Maps. The fate of an organic chemical in melting snow is determined by its distribution between the individual components within the bulk snow. This distribution depends on the chemical’s relative affinity for each of the snow phases and can be expressed with partition coefficients. The latter are dependent on the chemical’s properties and are constant in an isothermal and melting snow pack. Chemicals can be present as gases in the pore space, attached to particles in the snow, adsorbed at the internal snow surface, or dissolved within the melt water (see Meyer et al., 2008). Incorporation within the ice lattice of the snow grains is presumably very minor for most organic chemicals, because it would cause large defects in the crystal structure (Kammerer and Lee, 1969; Davis, 1991). The equilibrium phase distribution of organic chemicals within the melting snow pack can be plotted in a two dimensional chemical partitioning space defined by the chemical’s air/water partition coefficient $K_{AW}$ and the humic acid/water partition coefficient $K_{HA/W}$ for a specific snow surface/air sorption coefficient $K_{IA/m}$ (Fig. 4.1) (see Chapter 2). Within this partitioning space, regions of predominant presence at the snow surface (bright-blue), within the interstitial pore space (red), sorption to organic matter in the snow (brown), or presence in the dissolved aqueous phase (dark-blue) can be delineated. The phase
distribution of an organic chemical also depends on the relative proportions of the bulk snow phases to each other.

Figure 4.1 illustrates the partitioning of the organic target substances, used in the experiments, at an early stage of melting of an aged snow pack that was previously exposed to several melt-freeze cycles. The artificial snow of the associated experiment exhibited a density of 0.26 g/cm³, a specific surface area of approximately 125 cm²/g (see Appendix – melt scenario B), and an estimated organic matter concentration of 2.6 µg/mL snow. Such organic matter contents may be found in snow of less polluted urban regions. The water content was assumed to be 6% by volume which refers to an intermediate to strong melt intensity (see Appendix). To accommodate the different ice-air partition properties of the chemicals, the maps were drawn for four log \( (K_{IA/m}) \) values (Table 4.1, Fig. 4.1). The target chemicals were placed on the partitioning maps based on their estimated distribution properties at 0 ºC.

### Table 4.1 Physical-chemical properties at 0 ºC of the organic contaminants used in this study.

<table>
<thead>
<tr>
<th></th>
<th>solubility in water (µg/L)</th>
<th>log ( (K_{IA/m}) )</th>
<th>log ( K_{HA/W} )</th>
<th>log ( K_{AW} )</th>
<th>log ( (K_{IW/m}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>15,000^b</td>
<td>1.2^c</td>
<td>2.2^d</td>
<td>-7.3^e</td>
<td>-6.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>13,700^b</td>
<td>-3.0^c</td>
<td>3.4^d</td>
<td>-2.6^g</td>
<td>-5.6</td>
</tr>
<tr>
<td>Lindane</td>
<td>2,500^b</td>
<td>-0.2^c</td>
<td>3.2^d</td>
<td>-4.8^f</td>
<td>-5.0</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>390^b</td>
<td>-1.4^c</td>
<td>4.5^d</td>
<td>-3.2^g</td>
<td>-4.6</td>
</tr>
<tr>
<td>Pyrene</td>
<td>49^b</td>
<td>-0.2^c</td>
<td>5.2^d</td>
<td>-3.8^g</td>
<td>-4.0</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.26^b</td>
<td>-0.7^c</td>
<td>5.2^d</td>
<td>-4.3^g</td>
<td>-5.0</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>0.049^b</td>
<td>1.7^c</td>
<td>6.2^d</td>
<td>-5.2^h</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

^a fluoranthene was used by Schöndorf and Herrmann, 1987
^b from Mackay et al. (2006).
^c calculated using pp-LFER from Roth et al. (2004).
^d calculated using pp-LFER from Niederer et al. (2006).
^e from Mackay et al. (2006).
^f calculated from FAVs by Xiao et al. (2004).
^g calculated using pp-LFERs from Abraham and Al-Hussaini (2005).
^h calculated from Henry’s law constant expressions in Mackay et al. (2006).
^i solute descriptors from Abraham et al. (2002) and Goss (2005); enthalpies calculated from eq. 8 in Lei and Wania (2004) based on the pp-LFER by Roth et al. (2002) and an empirical relationship by Goss and Schwarzenbach (1999).
^j calculated using log \( (K_{IW/m}) = \log (K_{IA/m}) + \log K_{AW} \).
The fate of those chemicals that are located in the transition regions between the bulk snow phases in Fig. 4.1 is very sensitive to the capacity of the internal surface area, the organic matter content, the melt water content, and the pore space. Chemicals that partition appreciably (> 50 %) into the liquid water phase of the wet snow pack, i.e. are located within the dark blue region toward the upper left of the diagrams in Fig. 4.1, are likely to be subject to the Type 1 chemical enrichment. When the melting becomes intense the dark blue areas in Fig. 4.1 will expand and more chemicals will dissolve into the downward moving melt water phase. In fresh, fine-grained and clean snow the interface is favored, whereas the chemical distribution in aged and dirty road-side snow will be shifted towards the particles. Semi-volatile chemicals may favor the gaseous interstitial space if the snow exhibits a very low density such as in fresh snow or in depth hoar.

The boundaries between the colored areas in Figure 4.1 constantly change during snowmelt because the phase composition of the snow pack also changes as snowmelt progresses. As the melting snow pack densifies and the snow grain size increases, the relative extent of melt water and particles will increase at the expense of snow surface and pore space. Accordingly, the phase transition boundaries in Figure 4.1 will in most cases shift to the upper right as melting proceeds. This also implies that more chemicals that originally were sorbed to the snow surface will either start to dissolve in melt water or sorb to particles, depending on their location in the chemical partitioning space and the amount of particles in snow.
Figure 4.1 Chemical space plots of the phase distribution of chemicals in a melting snow pack as a function of the snow surface/air sorption coefficient ($\log (K_{I/A}/m)$), the humic acid/water partition coefficient ($\log K_{HA/W}$), and the air/water partition coefficient ($\log K_{AW}$) (Table 4.1). $K_{I/A}$, $K_{HA/A}$ and $K_{AW}$ values were determined based on Roth et al. (2004) and Niederer et al. (2006).

The Release of Relatively Water Soluble Organic Contaminants. Chemicals like atrazine preferentially partition into the aqueous snow phase according to their chemical
properties (Fig. 4.1D). The elution pattern in Fig. 4.2A shows a pronounced Type 1 enrichment. The first quarter of the released melt water contained 74 % of the atrazine with an enrichment in the first sample of 5.0 compared to the average melt water concentration. This elution behavior is closely mimicking that of inorganic ions which is expressed by the relative specific conductivity (Fig. 4.2B). The melt behavior of ions has been extensively investigated in the past, enabled by the ease of measuring the conductivity in melt water. Such an ion flush along with the early melt water has been reported throughout most of the studies. However, peak releases of inorganic ions and those of water soluble organic substances are presumably caused by two fundamentally different processes. Ions accumulate at the snow grain surface mainly due to a gradual “out-freezing” during dry and wet snow metamorphism and then can be taken up by the first downward moving melt water. Organic substances, on the other hand are arranged around the snow grain surfaces because of their large molecule size. Differences of the snowmelt behavior of organic chemicals are likely due to chromatographic effects, i.e. a differential retention at the ice-water interface.

![Atrazine Conductivity](image)

**Figure 4.2** Relative elution sequence of atrazine and relative specific conductivity during snowmelt.

Lindane (γ-HCH) has a smaller tendency to dissolve in water than atrazine (Table 4.1) hence, it is placed in Figure 4.1 amid the transition region separating the chemical’s
preferential presence in the melt water phase and on the ice-air interface. Lindane partitions into both phases by 45% each, leaving its melt behavior very sensitive to the permanently changing snow properties. Small parts of lindane will also sorb to organic matter (Fig. 4.1) depending on the amount and composition of the particles in snow. Figure 4.3 shows the relative concentrations of both the dissolved and the particulate fractions of lindane during melting. Approximately 15% of the lindane was found within the particulate fraction of the sampled melt water (30%, if the last sample is included) compared to 10% as indicated in Fig. 4.1. This discrepancy may be caused by an incorrect estimation of organic matter in the artificial snow, by the aforementioned phase exchange after melting, and/or by an increasing relative proportion of particles during melting. The first quarter of the released melt water contained 49% of the lindane (excluding the last particulate sample). The amplification of lindane in the early melt water is notably smaller than that of atrazine. The tendency of lindane to adhere to the internal ice surface is simply larger, which is reflected by its higher log (K_{IW}/m) values (Table 4.1). A large part of the lindane was associated with the particles that remained at the vessel bottom after melting and is represented by the last brown bar in Fig. 4.3. This fraction made up 20% of all analyzed lindane. During melting lindane was segregated mainly into two fractions experiencing a very different fate, resulting in both Type 1 and Type 2 enrichment. Such segregation becomes stronger the higher the particle content in the snow and the higher the melt water content per volume (see Chapter 2).

The melt behavior of a substance like naphthalene is more difficult to predict because notable fractions of the chemical are present within all major phases of a melting snow pack (Fig. 4.1). The part of naphthalene that is dissolved in the aqueous melt water phase is released in elevated concentrations at an early stage of melting, similar to what is observed for atrazine and lindane (Fig. 4.4). The first quarter of the melt water contained 45% of the analyzed naphthalene. However, most of the chemical (between 75 and 95%) evaporated from the snow pack prior and during melting. According to Figure 4.1, naphthalene is the only compound that partitions appreciably into the snow pack air-filled pore space. Soon after the onset of melting the snow pack becomes denser and parts of naphthalene may become trapped in the interstitial pores. During melting the pore space
presumably acts as a reservoir which steadily supplies the melt water phase with naphthalene (Fig. 4.4).

**Figure 4.3** Relative elution sequence of lindane during snowmelt (blue columns: dissolved phase; brown columns: particulate fractions).

**Figure 4.4** Relative elution sequence of naphthalene during snowmelt (blue columns: dissolved phase; brown columns: particulate fractions).
The Melt Behavior of Hydrophobic Organic Contaminants. Melt/freeze cycles cause substantial coagulation of fine particles in snow (Nakamura and Okada, 1976a). During the freezing phase and with increasing dehydration groups of particles are pushed together and the resulting coagulates are held together by van der Waals forces (Nakamura and Okada, 1976b). During the melt period those coagulates clog the permanently decreasing pores and hydrophobic chemicals associated with the particles are efficiently held back from being eluted. When melting progresses and the snow surface subsides the particulate fraction of the chemicals are gradually accumulating in the upper snow pack until they are released at a late stage of melting. This peak release at the end of the melt period becomes more pronounced when the snow has undergone intense melt-freeze metamorphism and densification. Dirt cones on snow can concentrate particle-associated chemicals literally at the top of the snow surface leading to their retention until the very end of melting. The impact of dirt cones on the release of hydrophobic chemicals is described in Meyer et al. (2008b).

Benzo(ghi)perylene is exclusively attached to particles because of its high affinity to organic matter (Table 4.1). Thus, the bulk of this chemical was released within the very last sample together with most of the particles (Fig. 4.5). Pyrene and phenanthrene are somewhat less hydrophobic than BghiP and have a higher affinity towards the ice surface (Fig. 4.1, Table 4.1). The internal ice surface may act as a reservoir from which small fractions of pyrene and phenanthrene are constantly released to the melt water, whereby phenanthrene is more amenable to be become dissolved in the aqueous phase (Fig. 4.5). This behavior is consistent with the position of both chemicals on the chemical partitioning space in Fig. 4.1. However, most of both chemicals accumulates in the upper snow pack while being sorbed to particles.

The concentrations in the dissolved phases of phenanthrene and pyrene were expected to be higher than those in the particulate phases (except for the last sample). However, they were not. Parts of the chemicals presumably repartitioned in the meltwater after sampling (see Method section). Also, the recovery rate of the particulate fraction was higher than that of the dissolved fraction.
Figure 4.5  Relative elution sequences of phenanthrene, pyrene, and benzo(ghi)perylene during snowmelt (blue columns: dissolved phase; brown columns: particulate fractions).

Comparison of Two Studies. In the only other published laboratory study that investigated the fractionated release of organic contaminants in melting snow (Schöndorf and Herrmann, 1987), the chemicals’ elution patterns closely resemble those of this study (Fig. 4.6). The partition coefficients are similar for both pyrene and fluoranthene (Table 4.1) hence, their snowmelt behaviour should not differ very much. Schöndorf and Herrmann (1986) did not distinguish between dissolved and particulate phases. Nevertheless, we may infer that the two concentration peaks of lindane at the beginning and at the end of the melt period refer to the dissolved and the particulate fraction, respectively (Fig. 4.6). Their study shows a stronger amplification of lindane within the first melt water sample compared to this study. The snow column Schöndorf and Herrmann used in their experiments promotes such a first chemical flush. A snow pack with a depth of 100 cm contains a larger amount of lindane that is concentrated at the snow grain surfaces and that can be taken up by the first melt water. Furthermore, the small horizontal area of 154 cm$^2$ such as used in their study prevents the development of distinct flow fingers that could flatten this concentration peak.
Figure 4.6  Relative elution sequences of lindane, fluoranthene, pyrene and BghiP reported by Schöndorf and Herrmann (1987) (A) compared with those of this study (B). The horizontal line refers to an enrichment factor of 1. The particulate and dissolved fractions of this study were combined.
In both studies the bulk of the more hydrophobic substances fluoranthene, pyrene, and BghiP was retained in the snow pack until the very end of the melt period while attached to the particles. The concentration ratios of the three substances provide hints on how the partitioning properties affect the melt behavior (Fig. 4.6). Both ratios fluoranthene/lindane and pyrene/lindane increase in the second half of the melt period reflecting the higher water solubility of lindane. The latter was washed out in notable concentrations over the entire melt period. The release of fluoranthene and pyrene, on the other hand is characterized by a stronger Type 2 enrichment. The ratios of fluoranthene and pyrene, respectively, to BghiP are very similar in both studies. At the beginning of the melt period a slightly enhanced particle load is washed out until an increasing snow density and stronger particle coagulation hamper a further release of particles.

Both fluoranthene and pyrene are more water soluble than BghiP. Accordingly, their concentrations in relation to BghiP increase until a peak is reached. The subsequently decreasing ratios may be explained by decreasing amounts of fluoranthene and pyrene at the snow grain surfaces, that are available to become dissolved in the aqueous melt water phase. Furthermore, the transfer of fluoranthene or pyrene from the particulate into the dissolved phase decreases because parts of those substances are more strongly bound due to the formation of chemical bonds or by inclusion into coagulates (Schöndorf and Herrmann, 1986).

The fate of organic contaminants during snowmelt is clearly correlated to their partitioning between the phase contained within the melting snow pack. The dissolved and the particulate fractions of a chemical tend to move into opposite directions of the elution order. Sufficiently water soluble substances are released early during melting because a large fraction is taken up from the snow grain surfaces by early melt water. Organic contaminants adsorbed to particles tend to be released towards the end of a melt period. Melt-freeze cycles lead to particle coagulation and snow densification. As a consequence particle associated chemicals are efficiently retained within the snow pack until the end of melting. The more exclusively a chemical is either dissolved within the aqueous phase or sorbed to particles, the more pronounced is the associated peak release. Atrazine easily dissolves in melt water and most of the BghiP can be found in the particulate phase. Hence, those chemicals are exposed to the strongest amplification
during snowmelt. The prediction of the melt behavior of those substances is relatively simple because the physical snow properties are of less influence. On the other hand, the elution behavior of chemicals with intermediate partitioning properties such as lindane or naphthalene very much depends on the melt scenario, i.e. the melt water content, snow porosity, SSA, and organic matter content.

To aid in the assessment of whether a particular chemical is likely to show Type 1 or Type 2 chemical enrichment in a particular snow pack, we propose the calculation of an indicator value $R$, which quantifies the fraction of the chemical which is present in the liquid melt water phase of the snow pack. The $R$-value combines chemical properties and snow pack characteristics:

$$R = \frac{(K_{HA/W} \cdot V_{HA} + K_{IW} \cdot SSA + K_{AW} \cdot V_{Air})}{V_{W}},$$

where $K_{HA/W}$, $K_{IW}$ [m], and $K_{AW}$ are the equilibrium partition coefficients that describe the chemical’s distribution among the phases present in the melting snow pack, SSA [m$^2$/m$^3$] is the specific surface area, and $V_{HA}$ [m$^3$/m$^3$], $V_{Air}$ [m$^3$/m$^3$], and $V_{W}$ [m$^3$/m$^3$] are the volume fractions of humic acid, air pore space, and liquid water in the snow pack, respectively. Based on the results of the experiments in combination with the calculations of phase distribution we propose two threshold values for $R$. If a melt scenario is characterized by an $R$-value smaller than 0.1, i.e. if the chemical is predicted to be present within the melt water phase to $>90\%$, the release pattern of this chemical is likely to resemble that of the ions. In such situations the release profile of the organic contaminant from the melting snow pack can simply be approximated by the ion release, which is readily measured as electrical conductivity. With $R$-values larger than 9 the chemical is predicted to be present within the aqueous phase to $<10\%$. If the chemical at the same time exhibits relatively low volatility (log $K_{AW} < ~-3.5$), most of it is likely to accumulate with the particles at the snow pack surface to be released at the end of the melt period. We should note that since $V_{A}$ and $V_{W}$ tend to vary within a fairly limited range, it is the snow surface area and the organic matter content which will control melt behaviour in combination with the chemical properties.
4.4 Literature Cited


Chapter 5: Organic Contaminant Release from Melting Snow: II. Influence of Snow Pack and Melt Characteristics

Torsten Meyer, Ying Duan Lei, Frank Wania, Ibrahim Muradi

**Contribution:** Experiments implemented and paper written in consultation with and under the supervision of Y.D. Lei and F. Wania. Sample extraction was carried out by T. Meyer and I. Muradi.

In preparation for “Environmental Science and Technology”.
Abstract

Large reservoirs of organic contaminants in seasonal snow pack can be released in short pulses during spring snowmelt, potentially impacting the receiving ecosystems. In order to investigate the behavior of organic contaminants in melting snow laboratory experiments were implemented using artificial snow spiked with organic target substances. Whereas in a companion paper emphasis was placed on the influence of a chemical’s environmental partitioning properties on the elution behavior we highlight here the impact of snow properties and melt features. Water soluble organic substances are released in high concentrations at the beginning of a melt period when a deep and aged snow pack undergoes intense melting. Warm grounds can cause notable melting at the snow bottom leading to a delayed and dampened concentration peak. Hydraulic barriers in layered snow packs cause preferential melt water flow which also mitigates the early contaminant flush. Hydrophobic organic pollutants that are associated with particles accumulate near the snow surface and are released at the end of melting. Dirt cones at the surface of a dense snow pack enhance this enrichment. The findings of this laboratory study will help to describe the snowmelt behavior of organic pollutants in the more complex environment of natural snow covers.

Brief

Different processes control the early elution of water soluble organic chemicals and the late elution of particle-bound substances from artificially generated snow packs melting under controlled conditions.

5.1 Introduction

The bulk of organic contaminants in snow is often released during melt in short and concentrated pulse loads that may affect aquatic and terrestrial environments and the people that depend on them (see Meyer and Wania, 2008). The snowmelt behavior of such substances is neither well understood nor has it been extensively investigated in the past, yet the development of realistic water quality and contaminant transport models for cold regions requires a conceptual and quantitative understanding of the processes involved. Laboratory experiments aimed at studying the snowmelt behavior of organic
contaminants under controlled and reproducible conditions should be well suited to address these knowledge gaps and, in particular, to identify the key processes leading to contaminant enrichments in melt water. In a companion paper we have shown that the partitioning properties of an organic chemical between the individual bulk snow phases (ice surface, pore space, liquid melt water, organic particles) to a large extent determine its elution behavior during snowmelt (Meyer et al., 2008). Chemicals with a high propensity to dissolve in the aqueous phase are usually washed out early during the melt period, similar to inorganic ions. Substances that are preferentially sorbed to organic particulate matter are often released at the very end of melting. We refer to contaminant amplifications at the beginning and at the end of melting as Type 1 and Type 2 enrichment, respectively (Meyer and Wania, 2008).

Many organic contaminants of environmental concern can, however, not be assigned unequivocally to only one phase within the bulk snow. These chemicals can easily switch between the phases depending on varying snow properties and melt conditions. The proportions and the storage capacities of the different snow pack phases change constantly not only during the melt period but already in dry snow and during melt-freeze cycles. Accordingly, the characteristics of the snow pack, as well as those of the ageing and melting period should have a considerable impact on the fate of organic contaminants during melting. The factors whose impact was investigated and will be presented here in detail include the snow pack depth, the temperature at the interface between soil and snow, the melt water content and the extent of the internal ice surface, as well as snow layering and preferential flow. Finally, factors that influence the release of particle-bound chemicals will be explored.

5.2 Methods

The complete experimental and analytical method is described elsewhere (Meyer et al., 2006; Meyer et al., 2008). Briefly, artificial snow (density: 0.16 g/cm³, grain diameter 100 µm, specific surface area 580 cm²/g) produced by a “snow gun” using water spiked with organic target substances (naphthalene, phenanthrene, pyrene, benzo(ghi)perylene, atrazine, and lindane or γ-HCH) is melted under temperature controlled condition. Two liter melt water samples, taken from the conical shaped bottom of the stainless steel snow
melt vessel (0.24 m$^3$), are filtered and the target analytes are quantified in the extracts of both the dissolved and particulate phase using gas chromatography – mass spectrometry. Dry snow density and the water content of melting snow are measured continuously using time domain reflectometry (TDR) (see Chapter 3 and Appendix). Snow microstructure is recorded using macro-photography. A cooling liquid circulating through the double bottom of the vessel creates temperature gradients within the bulk snow. Whereas the temperature at the interface between snow and bottom is kept at 0 °C in most experiments, in some cases melting at the snow base due to a warm ground is simulated by increasing the temperature of the cooling liquid within the double bottom to +1 °C. Two thermometers, attached to the vessel floor and insulated against the snow, provide temperature recordings from the snow-bottom interface. Melting at the surface is induced by six 175 W infra-red lamps. The heat transfer is regulated by switching the lamps on and off and by adjusting their height above the snow surface. Photochemical degradation of the organic contaminants in the wave-length range of the lamps is very limited.

In order to investigate the influence of snow cover depth on chemical release behavior, a “shallow” and a “deep” snow pack of 16 and 29 cm thickness, respectively, were melted; those depths are average values with respect to the conical shape of the vessel bottom. Aged and coarse grained snow was produced by repeatedly raising the cold room temperature to generate a melt water content of approximately 1% per snow volume, followed by subsequent re-freezing. This water content provides fast snow grain growth while at the same time preventing downward percolation of melt water (Brun, 1988). Natural dry snow metamorphism, leading to the generation of faceted snow grains, was simulated by exposing the snow pack to large macroscopic temperature gradients (Dominé et al., 2007a). The snow filled vessel was kept in a storage cold chamber at a temperature of -30 °C and the cooling liquid at the vessel bottom was adjusted to 0 °C, leading to a temperature gradient of approximately 80 °C/m. As a result, low density snow consisting of faceted snow grains was generated. A hydraulic barrier at the interface between two snow layers was achieved by depositing fresh and fine grained snow above an aged and coarse grained snow layer whereby the interface was located at approximately two thirds of the overall snow pack height.
The elution sequences of the target chemicals are presented as relative melt water concentrations of a particular chemical within one experiment. After leaving the snowmelt vessel and during storage and filtering, the chemicals may have partially switched between the dissolved and the particulate phase. Therefore, the presented relative concentrations in both phases within one sample may not exactly mirror the partitioning at the time when released from the snow pack. The last particulate fraction refers to the particles that were left adhering to the vessel bottom after melting and needed to be rinsed in order to be sampled.

Reproducibility of the snowmelt method was tested by conducting two experiments with similar snow pack and melt conditions and comparing the enrichment of relatively water soluble chemicals within the first quarter of the melt period. The enrichment of atrazine, lindane, and conductivity differed by 4%, 2% and 3%, respectively.

5.3 Results and Discussion

The Influence of the Snow Depth. The thickness of natural snow covers varies widely in space and time, suggesting a need to understand its impact on the melt behavior of organic chemicals. Melt water generated at the snow pack surface percolates downwards while taking up organic contaminants from the snow grains. Because of their relatively large molecular size compared to ions, organic chemicals are likely sorbed to the snow grain surface. The progressing melt water front continuously takes up chemical, leading to Type 1 contaminant enrichment at an early stage of the melt period. To investigate how this first flush behavior depends on snow depth, the chemical release from two snow packs with different thicknesses was compared (melt scenarios A and B in Appendix).

Both snow packs were exposed to several melt-freeze cycles and subsequently melted within a relatively short time. Consistent with a percolating melt water front that collects chemicals from more snow grains during a longer passage, the deeper snow pack released the relatively water-soluble chemicals in more pronounced peak concentrations (Table 5.1, Fig. 5.1).
Table 5.1  The chemical fraction released within the first quarter of the melt water from two snow packs of different depth (the last particulate fraction of lindane was excluded from the calculations).

<table>
<thead>
<tr>
<th></th>
<th>conductivity (%)</th>
<th>atrazine (%)</th>
<th>lindane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>shallow snow pack (16 cm)</td>
<td>53</td>
<td>61</td>
<td>37</td>
</tr>
<tr>
<td>deep snow pack (29 cm)</td>
<td>64</td>
<td>74</td>
<td>49</td>
</tr>
</tbody>
</table>

Figure 5.1  Relative elution sequences of atrazine, lindane, and the relative specific conductivity from a shallow snow pack (melt scenario A) and a deep snow pack (melt scenario B) (blue columns: dissolved phase; brown columns: particulate fractions).
Natural snow packs often exhibit depths larger than those applied in this study. It is therefore of interest whether the above trend can be extrapolated to deeper snow packs. Although the deep snow pack had almost double the thickness of the shallow snow pack, the chemical amplification differed only by factors in the range between 1.2 and 1.4 (Table 5.1). The extent to which contaminants are taken up by the downward moving melt water should also depend on the chemical’s relative concentrations in the aqueous phase and on the ice interface. Within the upper snow pack more substance is expected to transfer into the melt water phase compared to lower layers. Upon establishment of equilibration of the chemical between both phases the net transfer from the ice surface to the melt water should cease. An increasing extent of preferential flow in confined flow fingers within deeper snow packs may also limit Type 1 enrichment. Flow fingers bypass large areas of the bulk snow where chemical uptake is delayed until the background wetting front arrives and generates a more homogeneous melt water flow (Marsh and Pomeroy, 1999).

Particles and associated chemicals are usually efficiently retained from being washed out early during melting due to filter-like processes and an increasing snow density during melting (Meyer and Wania, 2008). However, when the depth of the snow pack fell below about 10cm in the experiments, a strong melt event was able to wash out relatively large amounts of particles (results not shown). Then, the melt water breaks through the snow cover while dragging particle bound organic substances along.

**The Influence of the Temperature at the Snow Bottom.** A snow cover can melt at the surface due to irradiative forces or at the bottom if sufficient heat is transferred from deeper layers of the ground to the soil-snow interface. Melt water produced due to surface melt may become enriched with water soluble organic chemicals on its way to the snow base leading to Type 1 enrichment. On the other hand, melt water generated at the snow base at the beginning of melting is not enriched with chemicals. The insulating properties of snow initially confine melting to the lowest part of the snow pack. With progressing melt and increasing wetness in the lowest snow layer, the insulating capacity decreases rapidly. Thus, more heat can be transported upwards and more organic chemicals can be taken up from snow grain surfaces. Bottom melt can be substantial in temperate regions, especially when a thick snow cover develops early in the fall. Then,
small but steady snowmelt may occur over the entire winter season. Deep snow covers combined with low snow densities efficiently insulate the upper soil layers against cooling and freezing during the winter (see Meyer and Wania, 2008).

Figure 5.2 illustrates the melt behavior of atrazine, lindane, and inorganic ions in a snow pack that was melted at the surface, and additionally exposed to considerable melting at the bottom. The associated melt scenario C (see Appendix) is common in natural environments and comprises a melt period that lasted over several days, interrupted by nightly re-freezing. For the first three days the snow pack was exposed to relatively small melt intensity at the surface generating a melt water content within the upper snow pack of below 2%, whereby one sample per day was collected. A stronger melt event at day four coincides with the release of the melt water samples four to six. The latter displays the highest concentrations of all three analytes (Fig. 5.2). Sample five and six corresponded to the time when the downward moving melt water front reached the snow pack base (see Appendix), after scavenging notable amounts of organic chemicals on its way down to the bottom. The first four to five melt water samples were mainly generated due to bottom melt and therefore, were less enriched with chemicals. In the melt scenarios A and B (Fig. 5.1) melting was confined to the surface and the first sample corresponds to the arrival of the downward moving melt water front. Clearly, melting at the snow base delays and flattens the Type 1 peak contaminant release.

**Figure 5.2** Relative elution sequences of atrazine and lindane, and the relative specific conductivity from a snow pack influenced by melting at the bottom and the surface of the snow pack (blue columns: dissolved phase; brown columns: particulate fractions).
Melt Water Content And Internal Surface Area. A melting snow pack is usually isothermal. Therefore, the partitioning properties of chemicals are nearly constant during the melt. The snow and melt characteristics however, are permanently changing prior to and during melting. The size, form and chemical composition of the snow grains as well as the snow density vary during dry and wet snow metamorphism (Dominé et al., 2007a). Particularly, microscopic and macroscopic temperature gradients lead to constant snow grain growth which is accelerated in the presence of melt water. Fresh snow has a relatively large internal surface area which decreases considerably when the snow undergoes numerous melt-freeze cycles. At the same time the storage capacity of the snow grain surface decreases, causing the partial release of weakly sorbed chemicals to adjacent phases. A high melt water content in snow, brought about by intense melting, enhances the storage capacity of the aqueous phase. Chemicals with intermediate partitioning properties may then be taken up by the melt water and washed out from the snow pack. The theoretical phase distribution of a chemical in a snow pack, and its dependence on varying physical snow properties, can be assessed using chemical partitioning maps (Meyer et al., 2008b). Figure 5.3 compares the phase partitioning of lindane and pyrene in two very different snow packs: fresh and fine grained snow with a low melt water content (melt scenario E), and aged and coarse grained snow with higher water content (melt scenario D). In the snow with the relatively large surface area more than 50% of lindane is sorbed to the snow grain surface, while in the aged snow the same chemical is mostly dissolved within the melt water. The latter snow pack should therefore generate stronger chemical enrichments within the first melt water samples.

To study this behavior experimentally, one snow pack consisting of aged snow that had undergone extensive wet snow metamorphism was melted rapidly (melt scenario D). Another fresh and fine grained snow pack was melted slowly (melt scenario E). During the experiments TDR was used to measure the dielectric permittivity, reflecting the density in dry snow and the water content during melt periods (Meyer et al., 2006) (Fig. 5.4). During the early melt phase the strongly melting snow pack in melt scenario D contained between 6 to 10% melt water per snow volume compared to only 4 to 6% in the slowly melting fresh snow (melt scenario E). Natural snow is often melting even slower with melt water contents of 3 to 5%. Thus in reality, lindane and pyrene may be
present in melt water to an even smaller extent, compared to experimental scenario E. The sample flow rates during the early melt period were three to four times higher in scenario D compared to scenario E (see Appendix). Scenario D was further characterized by a snow density of 0.23 g/cm³ and an SSA in the range between 20 and 50 cm²/g (Dominé et al., 2007b). The snow in scenario E exhibited a density of 0.19 g/cm³, and the SSA was estimated to be between 450 and 500 cm²/g (Meyer et al., 2006).

![Chemical space plots of the phase distribution of lindane and pyrene in a melting snow pack as a function of the humic acid/water partition coefficient (log K_{HA/W}), and the air/water partition coefficient (log K_{AW}). Both chemicals exhibit a log (K_{I/A}/m) value of -0.2. K_{I/A}, K_{HA/A} and K_{AW} values were determined based on Roth et al. (2004) and Niederer et al. (2006). (melt scenario D): Aged and coarse grained snow pack with high water content; (melt scenario E): Fresh and fine grained snow pack with smaller water content.](image-url)
Figure 5.4  Change of snow density in dry snow and of snow melt water content during melt phases calculated from relative dielectric permittivity measurements using TDR methods. TDR probes 1-4 (from above to below) were stacked one upon each other with a vertical distance of 5cm (see Appendix).

As expected, Type 1 enrichment of lindane was stronger in scenario D (Fig. 5.5, Table 5.2), because the ratio of the storage capacities of melt water and internal surface area is larger than in scenario E. The enrichment of the very water soluble atrazine and the inorganic ions is nearly the same in both scenarios (Fig. 5.5, Table 5.2). Thus, Type 1
enrichment of very hydrophilic chemicals appears to be relatively independent of melt water content and internal surface area. The atrazine enrichment in melt scenario B (Table 5.1) is somewhat smaller than in the scenarios D and E, respectively. The snow-water equivalent within the snowmelt vessel was somewhat smaller in scenario B compared to the other two scenarios (see Appendix, Table A1).

![Figure 5.5](image)

**Figure 5.5** Relative elution sequences of atrazine and lindane, and the relative specific conductivity in a coarse grained snow pack with high melt water content (melt scenario D) and a fine grained snow pack with low melt water content (melt scenario E) (blue columns: dissolved phase; brown columns: particulate fractions).
Table 5.2 The fractions of the chemicals and of the specific conductivity that were released along with the first quarter of the melt water from two different snow packs (for lindane, the last particulate fraction was excluded).

<table>
<thead>
<tr>
<th>snow-melt feature</th>
<th>conductivity (%)</th>
<th>atrazine (%)</th>
<th>lindane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coarse grains – fast melt</td>
<td>70</td>
<td>82</td>
<td>55</td>
</tr>
<tr>
<td>fine grains – slow melt</td>
<td>70</td>
<td>80</td>
<td>39</td>
</tr>
</tbody>
</table>

Pyrene and phenanthrene can also be found within the transition regions of the partitioning maps (Fig. 5.3; map for phenanthrene not shown). Those chemicals are relatively hydrophobic and most of them are released at the very end of melting. Small amounts of both substances, however, are released over the entire melt period (Fig. 5.6).

Figure 5.6 Comparison of the elution sequences of phenanthrene and pyrene in rapidly melting aged snow (melt scenario D) vs. slowly melting fresh snow (melt scenario E) (blue columns: dissolved phase; brown columns: particulate fractions).
Those amounts are higher in scenario D where the snow contains more melt water and less internal surface area. In this case, the upper left region in Fig. 5.3 is expanded and more of both chemicals are dissolved into the melt water phase. Type 2 enrichment declines slightly in an intensely melting and aged snow pack, whereas Type 1 enrichment is stronger under the same conditions.

**Heterogeneous Snow Packs and the Role of Hydraulic Barriers.** Certain combinations of snow pack and melt characteristics can limit Type 1 enrichment considerably. For example, preferential flow in confined flow fingers or along the interface between two snow layers is very common in natural snow. An aged snow pack often consists of several snow layers that differ in terms of physical properties such as density, snow grain size and form. The melt water flow rate in such snow also varies because of its strong dependence on snow microstructure (Colbeck, 1978). When an aged and coarse grained layer is covered by fresh and low density snow consisting of fine snow grains, the interface between the two layers forms a hydraulic barrier. Downward moving melt water will be impounded, may flow laterally along the interface, or may break through and flow vertically within distinct flow fingers. Large parts of the snow pack are by-passed and temporarily exempted from chemical uptake until the more homogeneous background wetting front arrives. Re-freezing of melt water at the interface between two layers generates horizontal ice layers which also create preferential flow.

To generate a layered snow pack in the laboratory, one snow layer was exposed to numerous moderate melt-freeze cycles that generated coarse grained snow exhibiting relatively low density (see Method section). This pack was subsequently covered by a fresh and fine grained snow cover (Fig. 5.7, melt scenario F). Prior to melting, the lower layer exhibited a density of 0.23 g/cm³ and an estimated SSA laying in the range between 20 to 50 cm²/g (Dominé et al., 2007b), while the upper layer was characterized by a density of 0.17 g/cm³ and SSA of nearly 580 cm²/g (see Appendix). Figure 5.7 (melt scenario F) shows the elution pattern of atrazine, lindane, and inorganic ions from this snow pack. The early melt water is characterized by irregularly varying concentrations of water soluble organic substances because the melt water breaks through the hydraulic barrier unevenly. Accordingly, the amount of chemical that is transported to the snow pack base depends on the extent of the flow fingers that build up. Later during melting,
the snow pack becomes more homogeneous in terms of melt water flow, i.e. the background wetting front is now dominating the flow regime. From that point on the chemical release resembles more that from homogeneous snow and a relatively constant decline of concentrations can be observed. The chemical amplification at the early stage of melting is small compared to that in homogeneous snow (Table 5.1-5.3). Therefore, hydraulic barriers caused by fresh snow above aged snow or by horizontal ice layers can notably limit the extent of Type 1 enrichment. This effect is presumably enhanced in a deeper snow pack because flow fingers travel faster than the background wetting front and thus, the preferential flow regime is present for a longer time (Marsh and Woo, 1984). It should be possible to assess the extent of preferential flow by comparing the magnitude of enrichment of the most water soluble substances, i.e. atrazine and inorganic ions, in the different melt scenarios. As the chemical composition of the snow was similar in all experiments, a relatively small Type 1 enrichment of those substances indicates that melt water by-passes large areas of the snow pack. This assumption is further supported by the very similar ion enrichment in two snow packs that exhibited very different melt and snow pack characteristics, but were similar in terms of the absence of significant preferential flow (Table 5.2, Fig. 5.4, 5.5).

**Effect of Strong Melting on Snow of Low Permeability.** Another case where a combination of snow and melt characteristics leads to a lower Type 1 enrichment is related to a snow pack which is not very permeable to melt water while at the same time being exposed to intense melting at its surface (Fig. 5.7, melt scenario G, Table 5.3). The snow used for this experiment had previously undergone dry snow metamorphism (see Method section) resulting in low density snow that exhibited relatively small and facetted snow grains. The flow velocity in such snow is initially very low until the snow becomes denser and the snow grains grow and round. Intense melting at the snow pack surface generated a high water content in the upper snow layer because the melt water drainage was hampered. Under those conditions, little heat energy is diverted into the snow pack interior. As a consequence, the upper snow layer including the whole snow grains were melted. The downward moving melt water front became diluted, which led to a dampening of the observed contaminant enrichment (Fig. 5.7, Table 5.3) in the early melt water fractions.
Figure 5.7  Relative elution of atrazine, lindane, and the relative conductivity in (melt scenario F) layered snow and in (melt scenario G) low permeable snow that is exposed to strong melting (blue columns: dissolved phase; brown columns: particulate fractions).

Table 5.3  The fraction of specific conductivity and the chemical fractions that were released along with the first quarter of the melt water from two different snow packs (for lindane, the last particulate fraction was excluded).

<table>
<thead>
<tr>
<th>snow pack - melt feature</th>
<th>conductivity (%)</th>
<th>atrazine (%)</th>
<th>lindane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>layered snow</td>
<td>60</td>
<td>66</td>
<td>35</td>
</tr>
<tr>
<td>strong melting – low snow permeability</td>
<td>56</td>
<td>69</td>
<td>32</td>
</tr>
</tbody>
</table>
The Impact of Dirt Cones on the Release of Particulate Organic Chemicals. Dirt cones and ablation hollows are common features of snow pack surfaces. The detailed mechanism of dirt cone formation is disputed (Betterton, 2000; Rhodes et al., 1987), but their formation in natural snow packs is promoted by heat reflection and dissipation away from dirt particles down to ablation hollows. Lowering of the snow surface due to melt water ablation and filter-like effects cause particles to accumulate near the surface. When fine particles appear at a snow surface that features dirt cones, further melting is more likely to move them in a direction perpendicular to the sloped surface of a dirt cone than vertically towards the ground. For those particles adhesive forces are large compared to gravitational forces (Betterton, 2000). The transport away from ablation hollows towards the peaks of the dirt cones concentrates the particle associated chemicals at the highest elevations of the snow pack.

The near infrared light used in the experiments to induce melting, also generates dirt cones. Light in this wave length range is almost completely absorbed by the snow surface (Schöndorf and Herrmann, 1987). Particle layers on cone peaks insulate the underlying snow against irradiation while melting in the ablation hollows is enforced. In contrast to the hollows, the dirt cones maintain a low density and a high heat insulation capacity.

In the experiments particle accumulation on dirt cones caused most of the very hydrophobic BghiP to be released at the very end of the melt period (Fig. 5.8, melt scenario B). In scenario H the snow was melted by simply increasing the cold room temperature, a procedure that did not generate dirt cones. The particles coagulated to a lesser extent and were more evenly distributed than in scenario B involving the IR lamps. Thus, more of the BghiP was washed out during earlier stages of the melt period (Fig. 5.8, scenario H). While the last fraction in scenario B contained 96% of all released BghiP, only 70% was present in the last sample in scenario H.

The amount of particles that can be transported through a melting snow pack depends on the snow microstructure and the size of the moving particle. The snow in scenario H consisted of rounded grains and exhibited a low density combined with a very cohesive structure as a result of numerous moderate melt events. In this kind of snow pack,
particles can move more freely than e.g. in dense snow consisting of fine and facetted snow grains.

**Figure 5.8** Relative elution sequence of BghiP; melt scenario B – from a relatively high density snow pack covered by dirt cones and melt scenario H – from a lower density snow pack without dirt cones (see Appendix).

**Evaluation and Future Prospect.** Laboratory experiments have been implemented to study the snowmelt behavior of organic contaminants under different melt scenarios. Amplification processes prior and during melting often lead to the concentrated release of organic pollutants, whereby the contaminant load is split into two. Type 1 enrichment at an early stage of the melt period involves the more water soluble chemicals while the release of the particulate fraction at the end of the melt period represent Type 2 enrichment (Meyer and Wania, 2008). Those chemicals that are either very water soluble, such as atrazine, or very hydrophobic, as in the case of BghiP, are very likely to become enriched during melting. They are associated almost exclusively with only one phase in the snow pack. On the other side, the melt behavior of substances with intermediate partitioning properties is more dependent on snow pack composition, i.e. the relative proportions of the individual bulk snow phases. This implies that physical characteristics of snow cover and melt scenario determine to a large extent how those chemicals behave during snowmelt. Our experiments have shown that the early contaminant peak increases
with a greater snow pack depth and with a higher ratio of melt water content to internal ice surface. Thus, an aged and deep snow pack that has undergone extended melt-freeze cycles will suffer the strongest Type 1 enrichment. On the other hand, slow melting of a fresh and shallow snow pack has a mitigating effect. Hydraulic barriers due to snow layering can notably limit the enrichment of water soluble contaminants because preferential flow to the ground by-passes large snow pack areas. Intense melting at the surface of a sparsely permeable snow pack also dampens the early peak release. When the ground beneath the snow cover is relatively warm, as is often the case in temperate regions, melting at the bottom delays and flattens the Type 1 contaminant peak. Hydrophobic organic pollutants that are sorbed to organic particulate matter within snow are likely to be released at the end of the melt period. Dirt cones at the snow surface reinforce such behavior while accumulating particle-associated chemicals at the top of the snow cover. Rapid melting of a shallow snow pack can lead to melt water breakthrough with relatively large amounts of particle-bound substances being washed out.

It is hoped that the mechanistic knowledge gained in this study will be useful in investigation of the more complex fate of organic contaminants in natural snow environments. Large scale environmental influences such as topographic and terrestrial characteristics can only be considered in field investigations. Finally, reliable predictive models need to be developed to augment existing water quality and contaminant fate models.

5.4 References


Chapter 6: Chemical Exchange between Snow and the Atmosphere

Torsten Meyer, Frank Wania

**Contribution:** Paper written under the supervision of F. Wania.

6.1 Introduction

In cold regions at high altitudes and latitudes snow can play a significant role both in the environmental fate of contaminants (Wania et al. 1998, Halsall, 2004) and in the chemistry of the atmosphere (Dominé and Shepson, 2002). This motivates the desire for a mechanistic understanding and quantitative description of the transport processes of chemical species between a snow pack and the atmosphere. This chapter seeks to provide an overview of the key processes involved in gaseous atmosphere-snow exchange (Fig. 6.1) and of the parameterizations that have been used to describe such processes.

Figure 6.1 Chemical transport processes between a snow pack and the atmosphere.

Snow is an efficient scavenger of particles and gaseous contaminants from the lower atmosphere. Scavenging efficiencies of snow are often much larger than those of rain (Lei and Wania, 2004). The porous nature of a snow pack also facilitates the exchange of gases with the atmosphere. Snow metamorphism, in particular a decrease of the internal snow surface area, can lead to a substantial release of volatile and semi-volatile contaminants to the atmosphere. Peaks in air concentrations of organic contaminants coinciding with the snow melt period have been observed around the Laurentian Great Lakes (Hornbuckle et al., 1994; Gouin et al., 2002, 2005). The potential for snow ageing and melting to cause temporary concentration maxima in the atmospheric layer above
Snow has also been predicted by simulation models (Daly and Wania, 2004; Gouin et al., 2005; Hansen et al., 2006). Snow also greatly influences the oxidative capacity of the lower atmosphere in polar regions and may even affect global atmospheric chemistry (Dominé and Shepson, 2002). Arctic field studies indicate a strong relationship between snow pack chemistry and elevated atmospheric concentrations of hydroxyl radicals (Yang et al., 2002; Dominé and Shepson, 2002). A change of the total snow covered area due to climate warming may notably affect the oxidative potential in the higher latitude atmosphere (Dominé and Shepson, 2002) and the global distribution of persistent organic pollutants (Macdonald et al., 2003, Stocker et al., 2007).

Chemical exchange between snow and the overlying atmosphere may take place by gas exchange (absorption and volatilization), by rain or snow scavenging, dry particle deposition, snow blowing, and fog deposition. Because of its relative significance only the gaseous chemical exchange is discussed in this chapter. A mechanistic description and further references of wet deposition by falling snow can be found in Lei and Wania (2004). The principles of mass transfer with blowing snow and associated chemical concentration by sublimation are described in Pomeroy et al. (1991, 1997) and Woo and Marsh (2005).

Part two of this chapter presents a method for assessing the availability of chemicals for gaseous atmosphere-snow exchange. Part three provides a summary of mechanistic descriptions of air-snow gas exchange and part four is devoted to findings from field-based and laboratory measurements. Part five discusses key factors influencing air-snow exchange and part six provides a sample calculation of the chemical exchange with two different types of snow pack.

### 6.2 Chemical Phase Distribution in Snow and Availability for Atmosphere-Snow Exchange

The rate of trace gas exchange between snow and atmosphere is, in most cases, limited by the transport within the air-filled pore space of the snow pack. Thus, it is advisable to first investigate the extent of a chemical’s presence within the air-filled pore space of bulk snow.
6.2.1 Estimating Sorption to the Snow Surface

The availability of a chemical for gas exchange between snow pack and atmosphere depends on its phase distribution within the bulk snow. The chemical can reside as gas in the pore space, be embedded within the ice lattice of the snow grains, be attached to particles present in the snow, be sorbed to the snow surface, and - during melting – be dissolved within the liquid aqueous phase (Meyer and Wania, 2008). During snow ageing, chemicals accumulate near the surface of the snow grain while its interior becomes gradually purified (Colbeck, 1981).

The distribution of organic chemicals between the surface of the snow grains and the interstitial pore space can be expressed with a temperature dependent equilibrium snow surface/air sorption coefficient $K_{1A} = C_I / C_A$. If the concentrations on the surface $C_I$ and in the gas phase $C_A$ are in units of mol/m$^2$ and mol/m$^3$, respectively, $K_{1A}$ has units of length (m). Early, and only modestly successful, attempts at estimating $K_{1A}$ were based on assuming equivalence between sorption to the water and ice surface and on empirically regressing the sorption coefficient to the water surface with other commonly encountered physical chemical properties, such as the air-water partition coefficient, water solubility, vapor pressure or the octanol-water partition coefficient (see e.g. comparison in Wania et al., 1999). More recently, Roth et al. (2004) measured the propensity for sorption to a snow surface for a wide variety of organic vapours and developed a linear free energy relationship based on intermolecular interactions:

$$\log K_{1A} \left(-6.8 \, ^\circ C\right) = 3.53 \sum \alpha_2^H + 3.38 \sum \beta_2^H + 0.639 \log L^{16} - 6.85$$

where $\log L^{16}$ is the hexadecane/air partition coefficient at 25 °C, which expresses quantitatively the van der Waals interactions a chemical can undergo, and $\sum \alpha_2^H$ and $\sum \beta_2^H$ are measures of a compound’s ability to act as electron acceptor and donor, respectively. Equation (1) allows for the estimation of $K_{1A}$ for any organic non-electrolyte for which $\log L^{16}$, $\sum \alpha_2^H$ and $\sum \beta_2^H$ are known. It should, however, be applied cautiously to large and complex molecules, such as organochlorine pesticides (Goss, 2004; Schüürmann et al., 2006; Burniston et al., 2007). The log $K_{1A}$ value may be temperature corrected using:
\[
\log K_{IA} (T) = \log K_{IA} (T_{ref}) + \frac{\Delta_{ads} H_i}{2.303 R} \left[ \frac{1}{T_{ref}} - \frac{1}{T} \right],
\]

where \( R \) is the ideal gas constant and \( T_{ref} \) is the reference temperature (-6.8 °C = 266.3 K). Goss and Schwarzenbach (1999) provide relationships between enthalpies of adsorption on a water surface \( \Delta_{ads} H_i \) and corresponding adsorption constants.

### 6.2.2 Estimating the Presence of Organic Chemicals in the Pore Space of Bulk Snow

The availability of organic substances for atmosphere-snow exchange may be studied by displaying their equilibrium phase distribution in snow using a chemical space plot as a function of the snow surface/air sorption coefficient (log \( (K_{IA}/m) \)) and the organic matter/air distribution expressed by the humic acid/air partition coefficient (log \( K_{HA/A} \)) (Fig. 6.2, Meyer and Wania, 2008). The plot delineates regions of predominant sorption to the snow surface, presence as gas in the snow pore space, and sorption to organic particles in dry snow. Figure 6.2 represents recently fallen snow with an internal specific surface area (SSA) of 1000 cm\(^2\)/g, a density of 0.05 g/cm\(^3\) and an organic matter content of 9 ng·μL\(^{-1}\) snow volume. With snow metamorphism, the phase composition and thus also the chemical phase distribution in the snow pack will change. In particular, the \( K_{IA} \) threshold value indicating the transition from air pore space to ice surface would shift to the left with increasing snow density, and shift to the right with decreasing SSA (Meyer and Wania, 2008).

The initial days after snow deposition are characterized by an increase of the snow density and a significant decrease of the SSA (Cabanes et al., 2002; Jellinek, 1967; Hanot and Dominé, 1999). Measured SSA values range from 19 to 1558 cm\(^2\)/g (Dominé et al., 2007b). A rapid decrease in SSA due to snow compaction and metamorphism leads to the loss of a snow pack’s capacity to store chemicals within the interstitial air and on the ice surface. This can result in the release of substantial amounts of sorbed constituents from the snow pack (Wania et al., 1998, Hanot and Dominé, 1999, Herbert et al., 2005; Hansen et al., 2006, Taillandier et al., 2006; Burniston et al., 2007).
Selected organic contaminants covering a wide range of partitioning properties, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), fluorotelomer alcohols (FTOHs), chemicals from the BTEX group, light aldehydes (formaldehyde, acetaldehyde), and acetone are placed on the chemical space plots as a function of temperature in the range of -20 °C to 0 °C. With decreasing temperature the position of chemicals in the partitioning map shifts to the lower right, implying that those in the transition areas become increasingly sorbed to the snow surface. Volatile chemicals, such as the aldehydes, acetone, ethylbenzene and p-xylene, are predicted to partition predominantly into the air-filled pore space of the snow and should thus be highly susceptible to loss by evaporation, especially in depth hoar and at higher snow pack temperatures. Depth hoar is low density snow consisting of large
facetted crystals with sizes between 2 and 20 mm. Strong water vapor fluxes combined with rapid grain growth are the results of large temperature gradients (Dominé et al., 2007a). A notable fraction of somewhat less volatile substances, such as naphthalene and short FTOHs, is also predicted to be present as gases in snow (Figure 6.2) and should be available for gas exchange with the atmosphere. Even semi-volatile chemicals such as tri- and tetrachlorinated PCBs and three-ring PAHs can be susceptible to loss by evaporation if sufficient ventilation in snow provides rapid replacement of the air in the pore space. The depleted quantity of gas phase chemical is then replenished by rapid desorption from the ice surface. As a result, even small fractions in the gas phase may be important as illustrated in Fig. 6.2 by the lines delineating a presence of 1% and 0.1% of a chemical within the air pore space.

6.3 Theoretical Descriptions of Atmosphere-Snow Gas Exchange

6.3.1 The Two-Resistance Model of Snow Pack-Atmosphere Exchange

Mechanistic descriptions of atmosphere-snow exchange processes generally calculate a flux ($g \cdot m^{-2} \cdot h^{-1}$) as the product of the gradient between the gas phase concentrations in the lower atmosphere $C_A$ ($g \cdot m^{-3}$) and in the snow pore space $C_{AS}$ ($g \cdot m^{-3}$), and an overall mass transfer coefficient (MTC) $k_m$ ($m \cdot h^{-1}$) (Wania, 1997; Daly and Wania, 2004; Halsall, 2004; Hansen et al., 2006; Herbert et al., 2006):

$$F = k_m \left[ C_{AS} - C_A \right]$$  \hspace{1cm} (3)

By assuming equilibrium partitioning within the snow pack, the vapor concentration in the pore space $C_{AS}$ can be estimated from the bulk snow concentration $C_S$ (in $g \cdot m^{-3}$ melt water), which is accessible to measurements, and a dimensionless bulk snow/air partition coefficient $K_{SA}$.

$$C_{AS} = C_S / K_{SA}$$  \hspace{1cm} (4)

$K_{SA}$ can be estimated from the snow surface sorption coefficient $K_{IA}$ by multiplication with the specific snow surface area $SSA$ ($m^2 \cdot g^{-1}$) and the density $\rho$ of melt water ($g \cdot m^{-3}$)

$$K_{SA} = K_{IA} \times SSA \times \rho \times 100$$  \hspace{1cm} (5)
Equation (3) thus becomes:

\[ F = k_m \left[ \frac{C_S}{K_{th} \times SSA \times \rho} - C_A \right] \] (6)

The existing parameterizations of \( k_m \) treat the exchange across the atmosphere-snow pack interface on the basis of the Whitman two-film resistance model, which assumes that a chemical that moves from snow pack to atmosphere has to first transfer from the bulk of the snow pack to the snow pack’s surface, and then through the atmospheric boundary layer to the bulk atmosphere.

\[ \frac{1}{k_m} = \frac{1}{k_{bl}} + \frac{1}{k_s}, \] (7)

where \( k_{bl} \) is the snow-air boundary layer MTC and \( k_s \) is the bulk snow phase MTC. The limiting MTC determines the extent of the total mass transfer. The overall MTC \( k_m \) comprises most of the uncertainties associated with atmosphere-snow exchange. Accordingly, its parameterization varies between the studies.

6.3.2 Mass Transfer Coefficient \( k_{bl} \) for Transport through the Boundary Layer above Snow

Similar to the widely adopted model of air-water exchange (Schwarzenbach et al., 2003), the mass transfer from the snow pack-air interface to the bulk atmosphere is usually interpreted as occurring by molecular diffusion across a thin stagnant boundary layer film. Because the thickness of this boundary layer is unknown, some approaches (Wania, 1997; Daly and Wania, 2004) simply treat \( k_{bl} \) as a constant. In particular, it is assumed that \( k_{bl} \) adopts values similar to a typical MTC for the boundary layer above soil (e.g. 0.14 cm·s\(^{-1}\) or 5 m·h\(^{-1}\), Mackay and Stiver, 1991). In a more realistic approach, Hansen et al. (2006) allow for the influence of variable wind speed on \( k_{bl} \), which they expressed as:

\[ k_{bl} = k^2 U \frac{1}{\ln \left( \frac{z_w}{z_0} \right) \ln \left( \frac{z_{ref}}{z_0} \right)} \] (8)

where \( U \) is the wind speed, \( z_0 \) is the aerodynamic surface roughness length (a generic value of \( z_0=0.001 \text{ m} \) was applied), \( z_w \) is the wind height, \( z_{ref} \) is the reference wind height,
and $k = 0.4$ is the von Karman’s constant.

6.3.3 Mass Transfer Coefficient $k_s$ for Transport through Bulk Snow

Some models of atmosphere-snow exchange assume that transport within the snow pack occurs in parallel both in the air and water-filled interstitial snow pores (Hoff et al., 1995, Wania 1997, Daly and Wania, 2004, Stocker et al., 2007):

$$k_s = \frac{k_{sw}}{K_{AW}} + k_{sa}, \quad (9)$$

where $k_{sw}$ is the snow-water phase MTC, $k_{sa}$ is the snow-air phase MTC, and $K_{AW}$ is the air-water partition coefficient. However, the liquid water content in aged and coarse grained snow rarely exceeds 5% of the snow pack’s volume (Colbeck, 1978). Because of the relatively small pore volume filled by water and the slower diffusivity in water compared to air, $k_{sw}/K_{AW}$ is typically much smaller than $k_{sa}$, even for chemicals with a very low $K_{AW}$. Accordingly, some studies (Hansen et al., 2006) neglect chemical transport within the water-filled pore space and assume:

$$k_s = k_{sa} \quad (10)$$

Initially, most studies of air-snow exchange assumed that transport within the snow pack occurs by molecular diffusion through the pore space only. The parameter $k_{sa}$ is then calculated from the molecular diffusivity in air $D_A$, the diffusion path length $dpl$, and a factor $pt$ accounting for the porosity of the snow pack and the tortuosity of the diffusion pathway:

$$k_{sa} = D_A \cdot pt / dpl \quad (11)$$

The diffusion path length $dpl$ has variably been assumed to be equal to the snow pack depth $z$ (Herbert et al., 2006), $z$ divided by two (Hansen et al., 2006), or $\ln(2)$ or 0.69 times $z$ (Wania et al. 1997, Daly and Wania, 2004, Stocker et al., 2007). The porosity-tortuosity term $pt$ is typically expressed as a function of the volume fraction of air in bulk snow, or porosity, $v_{sa}$, which is equal to 1 minus the ratio of the bulk snow density $\rho_{snow}$ and the density of ice $\rho_{ice}$ (0.917 g/cm$^3$):

$$pt = v_{AS^n} = (1 - \rho_{snow} / \rho_{ice})^n \quad (12)$$
The exponent \( n \) in equation (12) has been assumed to be either 1.5 (Albert and Shultz, 2002, Hansen et al., 2006), or 4/3 (Wania et al. 1997, Daly and Wania, 2004, Stocker et al., 2007), or 2/3 (Herbert et al. 2005). Equivalent expressions are used if diffusion in the water-filled pore space is considered (Wania et al. 1997, Daly and Wania, 2004, Stocker et al., 2007).

### 6.3.4 The Role of Snow Ventilation or Wind Pumping

Equation (11) and (12) state that with increasing snow pack depth \( z \) and decreasing snow porosity \( v_s \), the resistance to molecular diffusive transport increases. Accordingly, a shallow snow pack exhibiting a low density has the highest predicted \( k_s \). However, because of the slow rate of molecular diffusion, this approach generally predicts negligible volatilization rates in all but extremely shallow snow packs. Such low volatilization rates are clearly not reconcilable with the observational evidence (e.g. Herbert et al., 2005 Burniston et al., 2007). In response, Daly and Wania (2004), citing studies on the importance of wind ventilation (Albert and Shultz, 2002), incorporated the process of wind pumping into their description of atmosphere-snow exchange. Modifying equation (10), the mass transfer in the bulk snow was described as:

\[
k_s = \text{wpf} \times k_{sa},
\]

where the wind pumping factor \( \text{wpf} \) varies with snow depth and was selected - somewhat arbitrarily - so that both resistances in the air-filled pores space and in the atmospheric boundary layer are of similar magnitude, i.e. \( \frac{\text{wpf}}{k_{bl}} \approx 1 \). This assumes moderate wind ventilation at all times, making the atmosphere-snow interface relatively permeable.

Hansen et al. (2006) developed an Arctic snow model, in which the bulk snow MTC was calculated using:

\[
k_s = k_{sa} \times K_{SA}
\]

Although the appearance of the snow-air partition coefficient \( K_{SA} \) in equation (14) is theoretically not correct (Halsall et al., 2008), \( K_{SA} \) effectively adopts a role similar to that of the wind pumping factor in eq. (13), greatly increasing \( k_s \) to the point that the resistance posed by transport within the snow pack \( 1/k_s \) is no longer much larger than that
posed by the boundary layer resistance $1/k_{BL}$. The rapid gas exchange predicted using eq. (14) is consistent with the windy conditions in polar regions (Hansen et al., 2006, Halsall et al., 2008) and the observation of volatilisation loss from aging snow packs (Herbert et al. 2005) and highlights further that it is often not appropriate to assume that chemical transport in the snow pack occurs by molecular diffusion only (Halsall et al., 2008).

Although the simple approaches described in this section provide an expedient way to describe air-snow gas exchange on the scale of several days or weeks, they provide only limited quantitative insight. They can, however, serve to identify the most important processes, and thus the key parameters that need to be further investigated. In particular, it is important to accurately define the impact of permeability, snow layering, and wind on snow ventilation (Daly and Wania, 2004).

### 6.4 Measurements of Atmosphere-Snow Exchange Transport Parameters

Several studies have investigated empirically the flux of chemicals within snow or between snow and the atmosphere (Guimbaud et al., 2002, Albert and Shultz, 2002, Herbert et al., 2006). In particular, measured concentration gradients within the atmospheric boundary layer or within the snow pack have been used to calculate a chemical’s flux into or out of the snow pack. This approach has resulted in miscellaneous parameterizations to calculate fluxes of e.g. carbonyl compounds and NO$_x$ species from the snow pack as a result of photochemical processes in snow (Dominé and Shepson, 2002; Hutterli et al., 1999; Guimbaud et al., 2002; Grannas et al., 2002). However, flux measurements can only be used to derive kinetic transport parameters, such as diffusivities and mass transport coefficients, if the chemicals involved are reasonably persistent and do not undergo rapid conversions within the snow pack. For example, measurements of the flux of carbonyl compounds out of snow are more likely to reflect the kinetics of formation in the snow pack than the kinetics of snow-air gas exchange. As a result, there is a very limited number of experimental studies that provide quantitative information on the rate of chemical transport in snow.

Albert and Shultz (2002) used the stable and inert trace gas sulphur hexafluoride (SF$_6$) to study both diffusive and advective transport in Arctic snow at Summit, Greenland.
Chemical diffusivity in windpacked surface snow was determined by measuring the rate of disappearance of SF$_6$ from the headspace of a steel cylinder inserted into the snow pack. Windpack is high density snow and consists of small solid rounded crystals, generated by strong and cold winds (Dominé et al., 2007a). The effective diffusivity $D_{eff}$ was 0.06 cm$^2$·s$^{-1}$. The reduction of the molecular diffusivity by the presence of the snow pack was well described by equation (12) and the empirically derived exponent $n$ was close to the theoretically expected value of 1.5.

Transport velocities in snow due to wind ventilation, $k_v$, as in equation (13), were determined by injecting SF$_6$ into a 15 cm deep hoar layer beneath a dense windpack in a snow pack with little surface roughness. The arrival of the SF$_6$ pulse 1 m upwind and 1 m downwind of the injection point was measured as a function of time (Albert and Shultz, 2002). At lower wind speeds ($U_{10} = 3$ m·s$^{-1}$) arrival at upwind and downwind locations occurred at the same time, indicating that there was no ventilation effect on the chemical’s transport, even though the measured transport velocities were faster than what would be expected based on molecular diffusion alone. Under higher wind speed conditions ($U_{10} = 9$ m·s$^{-1}$) the SF$_6$ arrived much quicker at the downwind location, indicative of strong wind ventilation. The transport velocity was 1.3 cm·s$^{-1}$ (46.8 m·h$^{-1}$). This study revealed that strong winds allow for substantial ventilation in deeper more permeable snow layers even in the absence of notable surface roughness and in the presence of a dense and poorly permeable surface layer (Albert and Shultz, 2002).

In a modification of the approach by Albert and Schultz (2002), Herbert et al. (2006) measured the diffusion of several semi-volatile organic chemicals ($\gamma$-HCH, $\alpha$-HCH, HCB) into fresh and aged snow by maintaining a constant air concentration for 24 hours in the head space of a cylinder inserted into the snow pack. Subsequently, the concentration gradient with depth was measured in the melted snow and used to derive an effective diffusivity. By dividing this measured diffusivity (m$^2$·h$^{-1}$) by the snow pack depth $z$ (0.4 m), they estimated MTCs $k_{sa}$ of $1.2 \cdot 10^{-3}$ cm·s$^{-1}$ (0.043 m·h$^{-1}$). Those empirically derived MTCs were of the same order of magnitude as those estimated theoretically using an equation of type (11).

In the only known laboratory study of atmosphere-snow gas exchange the volatilization
flux of PAHs covering a wide range of partitioning properties were determined by measuring the air concentrations in an air stream passing over an homogeneous snow pack of 35 cm depth which was artificially contaminated with those PAHs (Daly et al., 2007). The wind speed was negligible because the air velocity above the snow surface was kept at approximately 0.1 cm·s⁻¹. Mass transfer coefficients $k_m$ of the three relatively volatile PAHs naphthalene, acenaphthylene, and fluorene were found to be on the order of $6 \cdot 10^{-6}$ to $6 \cdot 10^{-5}$ cm·s⁻¹ ($2 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ m·h⁻¹). Those values are smaller than those estimated using an equation of type (11).

6.5 Factors Influencing the Rate of Atmosphere-Snow Gas Exchange

6.5.1 Influence of Surface Roughness on Boundary Layer Resistance

The resistance to the transport of chemicals through the boundary layer above snow ($1/k_{bl}$ in equation 7) may be neglected, when the flow within the atmospheric boundary layer is sufficiently rough to prevent the formation of a laminar sublayer where chemicals only move due to molecular diffusion. If this happens above snow, only the MTC $k_s$ becomes important. The aerodynamic roughness length $z_0$ in combination with the friction velocity $u^+$ and the kinematic viscosity $\nu$ are commonly used to describe whether the flow at the boundary layer between two media is rough or smooth (Seinfeld and Pandis, 1998). Specifically, the shear Reynolds number which is the product of the roughness length and friction velocity divided by the kinematic viscosity of air is used to distinguish rough vs. smooth flow. Empirically, it was found that $u^+ z_0 / \nu > 2.5$ means rough flow while $u^+ z_0 / \nu < 0.13$ refers to smooth flow.

The roughness length $z_0$ is defined as the height above the surface at which the downward extrapolated logarithmic wind profile assumes zero wind velocity (Brock et al., 2006), and must not be confused with the surface roughness amplitude $A_{sr}$ (Albert and Hawley, 2002). Empirical studies indicate the relationship (Seinfeld and Pandis, 1998):

$$z_0 \approx A_{sr}/30.$$  \hfill (15)

Typical values for friction velocities $u^+$ in the lower atmosphere fall in the range of 10-80
cm$\cdot$s$^{-1}$ (Weber, 1999) and the kinematic viscosity $\nu$ of air is approximately 0.1 cm$^2$·s$^{-1}$. With prevalent snow roughness lengths $z_0$ ranging between 0.01 cm and 0.50 cm (see Brock et al., 2006), the atmospheric boundary flow would be considered rough under most circumstances. However, roughness lengths can vary widely from as low as 0.0004 - 0.0150 cm for Antarctic plateau snow to 3 cm for tropical glacier snow penitentes (Brock et al., 2006).

6.5.2 Influence of Wind Speed and Surface Roughness on Snow Ventilation

As discussed in section 3.4 above, advective transport due to wind-induced air flow is generally much faster than diffusive transport through snow and can thus greatly enhance atmosphere-snow exchange and the snow depth involved in such processes (Albert and Shultz, 2002). Wind pumping can cause vapor movement in snow covers at depths of several meters and enhances the available internal snow surface area for uptake and release of chemical substances (Albert et al., 2002). Wind ventilation in snow is caused by “form drag” pressure variations across snow roughness features and by pressure variations due to wind turbulence (Albert and Hawley, 2002). The intensity of snow ventilation depends on the wind speed above the snow surface, the profile of the surface roughness features, and the snow permeability. A common roughness feature in Arctic and Antarctic regions are sharp and irregularly shaped sastrugi that can move in time and may seasonally vary in size (Albert and Hawley, 2002). Surface roughness amplitudes $A_{sr}$ for different kinds of snow packs may be estimated using equation (15) and surface roughness lengths $z_0$ listed in Brock et al. (2006).

Albert and Hawley (2002) modeled the wind induced airflow in snow at Summit using measured snow permeability profiles within the snow pack. The amplitude of the maximum pressure difference caused by a steady flow over a sinusoidal snow surface is accordingly:

$$p_0 = C \rho_{air} U_{10}^2 A_{sr}/\lambda,$$  \hspace{1cm} (16)

where $p_0$ is the amplitude of the pressure (Pa), $\rho_{air}$ is the density of air (kg·m$^{-3}$), $A_{sr}$ is the amplitude of the surface roughness (m), and $\lambda$ is the wavelength of the surface roughness (m). The proportionality constant $C$ was determined by Colbeck (1989) to be approximately 3. During the summer the surface roughness profiles were smoothly
curved and approximately 5 cm high, while in the winter those profiles increased to a height of roughly 20 cm which strongly impacts the wind ventilation in snow. Under winter surface roughness conditions the transport velocity within the dense and windpacked surface layer is three times that during the summer assuming similar strong wind conditions \( U_{10} = 12 \text{ m·s}^{-1} \). A relatively short surface roughness wave length \( \lambda \) of 5 m induces ventilation down to 2 m depth in the snow pack, while a longer wavelength causes ventilation even in 4 m snow depth (Albert and Hawley, 2002). An increasing distance between surface roughness features causes a deeper air flow penetration within the snow pack. However, the air flow velocity in the upper layers decreases.

A similar calculation using measurements of physical snow properties and interstitial ozone concentrations further confirmed the significance of surface roughness features for a chemical’s transport in snow (Albert et al., 2002). Beneath moderate winds \( U_{10} = 7-9 \text{ m/s} \), surface roughness amplitudes of ~10 cm and roughness wavelengths of ~10-20 m almost the entire approximately 40 cm deep snow pack was subject to ventilation.

### 6.5.3 Influence of Snow Permeability on Snow Ventilation

Snow permeability is crucial for the transport of chemicals by wind ventilation (Albert and Shultz, 2002) and is substantially influenced by snow layering and snow microstructure. Increasing snow grain size and homogeneity enhances the permeability (Albert and Perron Jr., 2000). The grain size increase is fast when exposed to large macroscopic temperature gradients. However, well rounded and uniform snow grains usually develop under isothermal conditions. Figure 6.3 depicts snow crystals in different stages of metamorphism in isothermal snow. As a result of the development of larger, rounded ice crystals, the permeability is considerably enhanced. Although commonly applied to describe permeability variations, the snow density is poorly correlated to snow permeability (Albert et al., 2000).

The snow permeability \( P \) \( (\text{m}^2) \) is defined as the proportionality factor between the pressure gradient and the flow velocity within the bulk snow, known as Darcy’s Law:

\[
k_{sa} = -\frac{P}{\mu} \frac{\partial p_0}{\partial x},
\]

where \( \partial p_0 / \partial x \) is the pressure drop \( (\text{Pa·m}^{-1}) \) and \( \mu \) \( (\text{Pa·s}) \) is the fluid viscosity.
Snow crystal sketches describing recently deposited dendritic snow with large surface area (left) and isothermal aged snow crystals with small surface area (right); both exhibit similar porosity. (Dendritic snow consists of six-branched crystals with a diameter of a few mm and a thickness of a few tens of μm (Dominé et al., 2007a)).

The permeability of seasonal snow varies within two orders of magnitude depending on grain size and shape, porosity, and the type of snow (Dominé et al., 2007a). Albert et al. (2000) measured variations by almost an order of magnitude in different snow layers within the top two meters of a snow pack at Siple Dome, Antarctica. A typical permeability of newly deposited seasonal snow is 30 to 70·10^{-10} m². After months of ageing and metamorphism, the permeability of that snow may have decreased to 8 to 50·10^{-10} m² (Jordan et al., 1999). Snow containing notable fractions of re-frozen melt water exhibited permeability of 1 to 19·10^{-10} m² (Albert et al., 2000; Albert and Perron Jr., 2000). While Arctic windpack typically features permeability of 5 to 30·10^{-10} m², that of depth hoar usually is very high, between 100 and 600·10^{-10} m² (Dominé et al., 2007a). The latter two types of snow packs characterize typical snow in the Arctic and in the Subarctic, respectively.

### 6.6 Case Study

The influence of the various environmental parameters on atmosphere-snow exchange of organic chemicals is illustrated by a conceptual case study using the semi-volatile...
pesticide PCB-28 as an example (Table 6.1). The mass transfer of PCB-28 between two different types of snow pack and the overlaying atmosphere is estimated for windstill and moderately windy conditions. Under windstill conditions, chemical transport is assumed to be controlled by molecular diffusion, while stronger winds cause chemical movement in snow to be controlled by advection. One snow pack, consisting mostly of depth hoar, is typical for Subarctic regions and the other, a high density windpack, can often be found in the Arctic. Snow packs in Subarctic and Arctic regions are the most extended snow covers on Earth in terms of area and duration. At the same time, they are relatively easily distinguishable from each other (Taillandier et al., 2006). The applied parameters and estimation results are shown in Table 6.1.

Surface roughness features are highly variable and it is difficult to assign typical values for the two types of snow covers. Therefore, roughness amplitude $A_{sr}$ and wavelength $\lambda$ were assumed to be the same for Subarctic and Arctic snow packs. With a $\lambda$ between 0.05 m and 10 m, the ratio $A_{sr}/\lambda$ is approximately 0.15 and 0.025 for smaller and larger surface roughness features, respectively (see Colbeck, 1989). Here, we assume a relatively high $A_{sr}$ (Albert et al., 2002). The calculation does not consider the influence of $\lambda$ on the depth of the snow pack that will be affected by ventilation.

The depth-averaged MTC $k_s$ was estimated using equations (16) and (17) whereby $\ln 2z$ is used for the mean diffusion path length.

$$k_{sa} = - \frac{P}{\mu} \frac{P_0}{\ln 2z}$$  \hspace{1cm} (18)

The dimensionless snow-pore space partition coefficient $K_{SA}$ is notably lower in the Subarctic snow pack largely because of the influence of temperature on $K_{IA}$ (see equation 2). The bulk of the snow pack in Subarctic regions consists of depth hoar that exhibits both low density and SSA, which further contributes to this discrepancy. The differences in partitioning of PCB-28 within the Subarctic and Arctic snow pack cause significantly different concentration gradients between snow cover and lower atmosphere and thus, different exchange behavior. While PCB-28 is released from the Subarctic snow pack, the comparably low pore space concentration in the Arctic snow leads to a net deposition of this chemical (Table 6.1).
<table>
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<th>Parameter</th>
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<th>Arctic Snow</th>
<th>Reference / Equation</th>
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<td>$C_{AS}$-$C_A$ [g·cm$^{-3}$]</td>
<td>$7.1\cdot10^{-17}$</td>
<td>$-3.0\cdot10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>Air density [kg·m$^{-3}$]</td>
<td>1.34</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>Wind speed $U_{10}$ [m·s$^{-1}$] (in the case of advection controlled chemical movement in snow)</td>
<td>7</td>
<td>10</td>
<td>Canadian Wind Energy Atlas (2003)</td>
</tr>
<tr>
<td>Surface roughness amplitude $A_{sr}$ [m]</td>
<td>0.1</td>
<td>0.1</td>
<td>Albert et al., 2002; Brock et al., 2006 ; Equation 15</td>
</tr>
<tr>
<td>Surface roughness wavelength $\lambda$ [m]</td>
<td>5</td>
<td>5</td>
<td>Albert et al., 2002</td>
</tr>
<tr>
<td>Pressure amplitude $p_0$ [Pa]</td>
<td>3.9</td>
<td>8.6</td>
<td>Equation 16</td>
</tr>
<tr>
<td>Snow permeability $P$ [m$^2$]</td>
<td>$2\cdot10^{-8}$</td>
<td>$2\cdot10^{-9}$</td>
<td>Albert and Shultz, 2002</td>
</tr>
<tr>
<td>Air viscosity $\mu$ [Pa·s]</td>
<td>$1.68\cdot10^{-5}$</td>
<td>$1.58\cdot10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Snow depth $z$ [m]</td>
<td>0.7</td>
<td>0.4</td>
<td>Sturm et al., 1995</td>
</tr>
<tr>
<td>Diffusion coefficient $D_{eff}$ [cm$^2$·s$^{-1}$] (molecular diffusion controlled)</td>
<td>0.06</td>
<td>0.04</td>
<td>Dominé et al., 2007a</td>
</tr>
<tr>
<td>MTC in snow $k_s$ [cm·s$^{-1}$]</td>
<td>0.97</td>
<td>0.39</td>
<td>Equation 18</td>
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<tr>
<td>advection controlled</td>
<td>0.0017</td>
<td>0.0020</td>
<td>$k_s = 2 \frac{D_{eff}}{z}$ (Hansen et al. 2006)</td>
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<tr>
<td>molecular diffusion controlled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flux from snow [ng·m$^{-2}$·day$^{-1}$]</td>
<td></td>
<td></td>
<td>Equation 3</td>
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<tr>
<td>advection controlled</td>
<td>59.0</td>
<td>-1.02</td>
<td></td>
</tr>
<tr>
<td>molecular diffusion controlled</td>
<td>0.105</td>
<td>-0.005</td>
<td></td>
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</table>
The Subarctic snow pack exhibits permeability that is approximately one order of magnitude larger than that in Arctic snow, which significantly increases the chemical exchange in the former. 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.

6.7 Conclusion

A variety of models of air-snow exchange have been developed in recent years that have been modified along with, and on the basis of, progressing field measurements. There is still need to perform field and laboratory measurements to explore the influence of physical snow properties, wind and a chemical’s partitioning properties on the exchange dynamics. The models differ most in terms of their description of chemical movement within the bulk snow, which is in most cases also the limiting factor of atmosphere-snow exchange. Whether snow ventilation due to wind pumping needs to be more mechanistically described depends on the particular model application. For some scenarios the application of a generic wind pumping factor may be sufficient, e.g. when long-term processes such as the release of chemicals from snow in the course of weeks or months are the scope of the investigation. When the atmospheric boundary conditions are extremely static, mere molecular diffusion may represent such processes well, and an effective molecular diffusion coefficient is sufficient. However, the description of diurnal exchange processes within the upper snow layers of substances, such as those generated by photolytic reactions, will requires a more specific parameterization of wind ventilation in snow.

6.8 References


Halsall, C.J., Hansen, K., Christensen, J. (2008): Correction to: ”A dynamic model to study the exchange of gas-phase persistent organic pollutants between the air and a seasonal snow pack”. *Environmental Science & Technology* **42** ASAP.


Chapter 7  Synthesis, Conclusions and Outlook

Synthesis. All chapters in this thesis are closely related to each other and each part builds upon the previous ones. The review in chapter two is providing an extended introduction into the topic of the Ph.D. project, is detailing the present knowledge and identifies the major knowledge gaps. Based on the latter an experimental setup was conceived which is suitable to address those gaps. Consequently, chapter three comprises the entire experimental and analytical method. The results of the experiments are presented in the chapters four and five where the melt behavior of organic pollutants is described using two interdependent approaches. In chapter four emphasis was placed on the impact of the chemical properties while the influence of the snow pack and melt characteristics is illustrated in chapter five. Since organic chemicals may also leave the snow pack by evaporation processes, the last chapter contains a critical review that addresses the fate of the more volatile chemicals in snow. The chapters two to six are preceded by a short introduction to the topic and followed by an overall conclusion, the latter including an outlook on possible future research.

Conclusions. The presence of snow significantly influences the fate of organic contaminants. Several amplification processes occurring prior to and during the melt period can lead to the release of organic chemicals in the form of short and concentrated pulses. The main conclusions from the experimental part of the Ph.D. project are:

1) Chemicals with a high propensity to dissolve in the aqueous phase of the melt water, i.e. those exhibiting log \( K_{1W/m} \) values of < -5 and log \( K_{HA/W} \) values of < 3.4, are usually washed out early during the melt period similar to inorganic ions. Organic substances are accumulated at the snow grain surfaces from where they can be taken up by the first downward moving melt water. Substances that are preferentially adsorbed to the organic matter of particles and exhibit log \( K_{HA/W} \) values of 4.5 and higher, are often released at the very end of melting. Particles and associated chemicals are efficiently retained from being released at an early stage of melting due to particle coagulation processes, filter-like effects and an increasing snow density during melting. Both contaminant amplifications at the beginning and
2) The melt behavior depends to a large extent on the chemical’s partitioning properties that describe the preferential presence within one of the main bulk snow phases (ice surface, pore space, liquid melt water, organic particles). The more exclusively a chemical is either dissolved within the aqueous phase or sorbed to particles, the more pronounced is the associated peak release. The prediction of the melt behavior of those substances is relatively simple because the physical snow properties are of less influence. On the other side, the elution behavior of chemicals with intermediate partitioning properties very much depends on physical properties such as the melt water content, internal surface area, and organic matter content.

3) Large parts of sufficiently volatile chemicals can leave the snow pack to the overlying air due to evaporation processes. Semi-volatile organic substances that are sorbed to the internal snow surface may transfer into the gaseous pore space when the surface area and the associated storage capacity decrease. Thus, snow grain growth due to melt-freeze cycles promotes the release of those substances from snow to the atmosphere.

4) Type 1 chemical enrichment becomes more distinct when the snow pack is deeper because the downward moving melt water front picks up more water soluble chemicals from the snow grain surfaces. Accordingly, the initially released melt water experiences a larger chemical enrichment. However, with an increasing concentration of the downward moving melt water front the chemical transfer into the aqueous phase slows down until equilibrium is reached.

5) Type 1 peak release of somewhat less water soluble chemicals becomes more pronounced when the ratio of the melt water content in snow to the internal ice surface is relatively high. Thus, strong melting of an aged snow pack that has undergone extended melt-freeze cycles prior to the melt period, is likely to cause strong Type 1 enrichment. On the other, hand slow melting of a fresh snow pack has a mitigating effect.
6) Hydraulic barriers formed at the interface between an aged and coarse-grained snow layer beneath a fresh layer consisting of fine snow grains, cause extended preferential flow within confined flow fingers. Large areas of the snow pack are bypassed by the first downward moving melt water front. As a consequence, Type 1 enrichment is diminished. Such conditions occur when a snow pack is exposed to melt-freeze cycles due to temperature fluctuations around the freezing point, followed by a fresh snowfall event.

7) As a result of intense melting at the surface of a sparsely permeable snow pack, the upper snow layer including whole snow grains is melted before notable amounts of melt water can percolate towards the ground. The first downward moving melt water is diluted and the Type 1 contaminant peak is flattened.

8) When the ground beneath the snow cover is relatively warm as often occurs in temperate regions, melting at the bottom delays and flattens the Type 1 peak. The melt water generated at the snow base at the onset of melting is not enriched with chemicals. The high insulating property of snow confines melting to the lowest part of the snow pack. A typical scenario is the deposition of a deep snow cover early in fall. If the snow maintains low density, the upper soil layers are efficiently insulated against cooling and freezing during the winter (Chapter two).

9) Type 2 chemical enrichment, involving the more hydrophobic organic pollutants, increases when the snow density is relatively high. The snow density increases during melt events and under the influence of strong wind pressure. Low density snow consisting of rounded snow grains allows more particles and associated chemicals to pass through the melting snow pack. The latter conditions can be the result of numerous moderate melt-freeze cycles that renders the snow pack very cohesive and less dense.

10) Parts of somewhat less hydrophobic chemicals can transfer into the aqueous melt water phase when a snow pack with small internal surface area is exposed to intense melting. Then, a small but steady release of such chemicals over the entire melt period slightly diminishes Type 2 enrichment. Type 1 enrichment however, increases under the same conditions (see point 5).
11) Dirt cones at the snow surface significantly increase Type 2 enrichment of particle associated organic contaminants. The particles accumulate at the highest elevations of the snow pack and will not be released until the snow pack is completely melted. Dirt cones can be formed when the irradiated energy is almost completely absorbed by the snow pack. Then, the dirt coating insulates the cone below while the snow in ablation hollows is melted.

12) Strong melting of a shallow snow pack can lead to melt water breakthrough and to the release of large amounts of particles along with hydrophobic substances. As a consequence, Type 2 contaminant enrichment is diminished.

Additional conclusions that have been derived from the literature reviews:

13) The water quality of catchment streams is affected most when the melt water runs off as overland flow over frozen ground. Melt water flow along the soil subsurface dilutes and buffers organic contaminant loads.

14) The release of contaminants from melting snow within a catchment is often spatially and temporally heterogeneous. Contaminants in deep snow drifts are released later than those in more sun-exposed and shallow snow packs. As a consequence, catchment streams are likely less affected by contaminant pulse loads than individual snow packs during snowmelt.

15) Wind packed snow exposed to relatively small vertical temperature gradients as typical for Arctic and to some extent also alpine regions has a higher storage capacity for semi-volatile organic chemicals. This kind of snow maintains a large internal surface area over the winter. Thus, a relatively large fraction of semi-volatile substances can be released to aquatic and terrestrial ecosystems with the melt, while in sub-arctic regions more of those substances are released to the atmosphere by wind ventilation prior to melting. Snow in sub-arctic regions often consists of coarse grained snow exhibiting low density.

16) Heavy rain events can wash out substantial amounts of particulate chemicals at any time during a snow season depending on snow depth and rain intensity. Rain events can be regarded as a snowmelt phases (see point 12) during which the melt intensity is greatly accelerated. Accordingly, Type 2 enrichment is smaller.
17) Shallow snow covers in temperate regions exposed to recurrent melt phases during the winter that are often initiated by rain events are less likely to lead to pulse releases.

18) The extent to which semi-volatile chemicals are released to the atmosphere prior to or during melting mainly depends on the snow microstructure, the snow temperature, the wind impact and the roughness of the snow surface. In relatively warm snow packs that exhibit low density and large permeability more semi-volatile organic substances partition into the gaseous pore space from where they can be released. Wind pumping substantially enhances the exchange of gases between snow and the atmosphere. Snow-atmosphere mass transfer coefficients are by two to three orders of magnitudes larger under the influence of moderately strong winds compared to wind still conditions.

The results of this study provide a mechanistic understanding of organic contaminant behavior in melting snow packs for a wide variety of chemical properties and snow pack characteristics. The insights gained can contribute to the development of reliable models that integrate snow in water quality, contaminant fate, and ecotoxicological models. Furthermore, the results can help to incorporate snow into predictive climate change models. The results from the experiments may directly be transferred to the catchment scale under certain topographic, terrestrial and meteorological conditions as discussed below. This may be of interest to governmental and consulting agencies that are concerned with the conservation and management of natural resources. Finally, the results will help to deepen the understanding of the hydraulics of a melting snow pack, which may concern people that are interested in water resources management, forestry, agriculture, and avalanche research.

**Outlook.** Investigations into the fate of organic contaminants in melting snow require different interacting approaches. Experimental studies, modeling studies, and field investigations complement one another and build upon each other. Insights gained from the experiments of this Ph.D. project may now be used to further develop simulation models and to undertake comprehensive field studies.

Those field studies should comprise different environments, varying in spatial and temporal scale. The experiments of this Ph.D. study were considering the fate of organic chemicals
during the period between snow deposition and the release of the melt water from the snow pack base. However, in natural snow environments the melt water and associated organic pollutants can be transported over longer distances depending on large scale influences such as topographic and terrestrial characteristics. Further amplification or dilution processes may take place. For example, substances that are released at the beginning of a melt period within the aqueous melt water phase can infiltrate porous soils and may travel further downward until reaching the aquifer. On the other hand, the melt water may flow laterally within the lower layer of the snow pack on top of frozen soils. In the latter flow mode the organic contaminants are transferred directly and undiluted into streams and rivers. Often, the melt water is diluted and buffered while flowing as sub-surface flow above a dense soil layer. Chemicals released in Type 2 enrichment mode can be retained within the upper soil layers or dragged along into catchment tributaries. In order to study the impact of contaminant peak loads on the environment, field studies should include measurements of concentrations in all media to which organic chemicals can be released during melting.

Based on the findings gained from the experimental studies and from field campaigns, the simulation of the snowmelt behavior of organic contaminants should be advanced. Models at the small-scale can help to enhance the quantitative understanding of the processes. They can identify those parameters that cause large sensitivity and uncertainty to the model output. The impact of those “uncertain” parameters could be investigated by implementing further experiments. Other models should simulate the melt behavior of organic chemicals at the regional scale and at the global scale. Relatively simple modules could be developed that would be included in already existing large scale contaminant fate and water quality models.

The knowledge gained in this study may assist in explaining and predicting concentration patterns of organic contaminants in tributary streams over the course of a melt period. In glacier environments and other catchments where the melt water is preferentially flowing above the surface the early melt period should coincide with higher concentrations of water soluble organic chemicals in stream tributaries. The melt water flow in aged and coarse grained snow as well as the saturated lateral flow at the base of the snow pack is usually very fast (see Chapter 2). Accordingly, strong melting of aged snow at the beginning of the
melt season may lead to a relatively simultaneous arrival of water soluble chemicals in receiving aquatic ecosystems. Such a melt scenario is described in Chapter 5 of this thesis and refers to a pronounced Type I chemical enrichment. Similarly, intense melting towards the end of the melt period is presumably dragging along a large fraction of particle associated organic chemicals into surface waters. Peak concentrations of water soluble organic pollutants in glacial stream water during the early stage of melting followed by an exponential decrease have previously been observed (see Chapter 2). The ratio of hydrophobic substances to hydrophilic chemicals was increasing over the course of the melt period, which leads to the assumption that Type I and Type II chemical enrichments in a melting snow pack may be extrapolated to stream water enrichments. Future investigations may also find correlations between organic pollutant enrichments in tributaries depending on the chemical’s partitioning properties in melting snow.

Simultaneous to this Ph.D. project a field study has been conducted that seeks to describe the snowmelt behavior of organic contaminants in an urban watershed, whereby the same chemicals are investigated that were used in the experiments. The subject of this ongoing study is the Highland Creek watershed in Scarborough, Toronto. This urban catchment is cut in half by the Highway 401, which is widely considered to be the “busiest” highway in North America. During snowmelt large loads of PAHs that are emitted from car exhausts may enter the river system via storm water outfalls. During the sampling campaign in the winter 2006/2007 samples were taken from different representative sites along the river system prior to the first snowfall and at several times during the melt season. During the winter 2007/2008 samples were taken only from the furthest downstream site (Fig. 7.1) but in a higher temporal resolution as in the previous year. Upon sampling the river water was analyzed for specific conductivity and particulate matter concentration. The samples from the winter 2006/2007 are partially extracted and stored at -18 ºC to prevent chemical degradation, but have not been analyzed yet.

First results from the field study provide a glimpse at the fate of pollutants in this watershed. The specific conductivity of the melt water is a good indicator of the occurrence of ionic pollution in the dissolved aqueous phase. At the same time, this is a quantity which is very conveniently measurable. In Figure 7.1 specific conductivities of Highland Creek water samples from five snowmelt events and one sample taken on a date prior to the snow
season are assigned to eight sampling sites. The melt water taken on the first melt day is characterized by a relatively high conductivity especially in the upper part of the Creek at the sites 3 and 5-8. This area receives large amounts of pollutants from main roads and the Highway 401 via storm water outfalls. The water sampled at sites 1, 2 and 4 is diluted by less polluted melt water from forested areas and from groundwater that is feeding the river subterraneously South of Ellesmere Rd (TRCA, 1999).

![Image of a map of the Highland Creek watershed with conductivity bars showing data points for different days of sampling during the snowmelt period.](https://example.com/map.png)

Figure 7.1  Specific conductivities of Highland Creek river water during a complete melt period. The y-axis quantifies the specific conductivity and the x-axis (from left to right) refers to the days of sampling during the snowmelt period March 02, 10, 12, 13, 14, 2007 (purple columns) and to a sampling day where the river water was unaffected by snow Nov 28, 2006 (blue column).

Dissolved organic pollutants are expected to be released early during the snowmelt period in a similar fashion as the inorganic ions while hydrophobic substances attached to particles may enter the river at a later stage (Chapter 2). Upon analysis of all samples an elaborate
evaluation of the results will include information from meteorological records provided by a nearby weather station, stream discharge records from the Toronto and Region Conservation Authority (TRCA, 1999) as well as information about storm water outfalls and groundwater inflow into the river system.

Investigations in the release of organic pollutants from melting snow can also adopt a semi-controlled approach where natural snowmelt conditions are monitored using laboratory devices. Along with the field study, an experiment on the roof of the Science wing at the University of Toronto Scarborough was implemented. A large snowmelt vessel (0.43 m$^3$) was placed near the campus owned weather station. This station provides hourly data of temperature, relative humidity, pressure, wind direction, wind speed, precipitation, and solar radiation. Thus, a unique opportunity was available to investigate the melt water behaviour and composition in dependence of the environmental conditions. During the winter 2006/2007, a complete melt period was covered by the experiment. During several snowfall events the snow was naturally deposited into the snowmelt vessel. However, additional snow from the roof was manually added which led to a completely snow filled vessel prior to the melt period. The snowmelt water was then taken at the bottom of the vessel and subsequently treated in the same way as the samples from the Highland Creek field study whereby the final extraction and analysis has yet to be done.

First results from the experiment show a rapid decrease of the specific conductivity within the melt water samples over the course of six melt days (Feb 28, Mar 02, and Mar 10-13) and the release of the majority of the particulate matter within the very last sample (Fig. 7.2). The conductivity and particle release sequences are very similar to those found in the experiments which lends support to the suggestion that the knowledge of the organic chemical behavior can be transferred to natural snowmelt conditions. Very water soluble organic contaminants were presumably released early during snowmelt in a similar way as the ions and the particulate contaminants presumably left the vessel at the very end of the melt period while attached to the bulk of the particles (Chapter five).
Finally, several proposals for future research on the fate of organic pollutants in melting snow are provided:

1) Influential and at the same time uncertain parameters could be more closely investigated by implementing further target-oriented experiments. For example, the extent of preferential flow depending on snow and melt characteristics and its impact on the chemical release remains relatively undefined. Those processes can be studied using dye and fluorescent tracers (Waldner et al., 2004) combined with Time Domain Reflectometry methods. Furthermore, the capacity of different types of soils to retain contaminants that originate from infiltrating melt water, could be investigated under laboratory conditions. Other experiments can include the study of the influence of short-wave radiation on the photo-degradation of organic contaminants in the upper snow layers, or the headspace analysis of volatile and semi-volatile chemicals during the experiments.

2) The release of semi-volatile organic chemicals from natural snow covers to the atmosphere can be studied by sampling and analyzing air from above the snow surface. Specifically, a number of air samplers could be placed around a river catchment and samples could be taken prior and during the melt period. One field
study could be implemented in a sub-arctic catchment that is characterized by mainly depth hoar that exhibits low density and coarse grained snow. A complementary study could investigate the contaminant release from an alpine catchment whose snow cover mainly consists of wind packed and fine grained snow. In the former catchment the release of semi-volatile chemicals to the lower atmosphere is expected to be higher (see Chapter 2). This would also confirm the measurements and calculations from Taillandier et al. (2006).

3) Halogenated acetic acids are known for their phyto-toxicity and suspected carcinogenicity. Those substances are widespread in various ecosystems (see Scott and Alaee, 1998) and have been found at notable concentrations in snow (Berg et al., 2000; Scott and Alaee, 1998). However, the knowledge of their environmental fate is scarce. During the melt period samples could be taken from melt water receiving streams and lakes. Halogenated acetic acids are relatively water soluble which may lead to their release at an early stage of the melt period (Chapter 2, 4, 5).

4) Every winter large amounts of snow are deposited at snow dump sites in Northern urban areas. The generated melt water is usually released untreated into aquatic and terrestrial ecosystems. This snow is for the most part collected from streets and highways of urban regions and expected to contain exceptionally high concentrations of organic contaminants. Snow constituents may include combustion residues from car exhausts such as polycyclic aromatic hydrocarbons (PAHs) or contaminants originating from industrial plants. During the soil passage of the melt water a large part of the PAHs are expected to become sorbed within upper soil layers. Rain events occurring after the melt season may cause re-mobilization of those chemicals and further transport into aquatic systems. A study involving snow dump sites should include the sampling of soil at different depths and after major rain events occurring during summer and fall.

5) Every year in spring, the soil of agricultural land receives the melt water originating from the overlying snow cover. This is usually the first water that supplies the growing plants with nutrients. Ancient farmer’s knowledge refer to snow as the "Poor Man's Fertilizer", referring to the concentrated release of nutrients to cultivated soil prior to sowing. Organic contaminants may be similarly released
from melting snow. It may be worthwhile to measure contaminant concentrations in cropland soil that is located in downwind from large emitters, such as industrial plants or highways.

References


Toronto and Region Conservation Authority (TRCA) State of the watershed report: Highland Creek watershed. Prepared by the City of Toronto and TRCA, 1999.

Appendix

Content of the Appendix

<table>
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<th>Material</th>
<th>Page</th>
</tr>
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<td>description of melt scenarios from chapters four and five</td>
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<td>sample flow rate vs. sample order in melt scenarios D and E</td>
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<td>dirt cones on top of the snow pack surface</td>
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</table>
Table A1  Physical snow pack properties at the onset of melting and the approximate melt water content per snow volume during sampling of the first quarter of the melt water. The water content in scenario C is related to the fourth day of melting. F1 refers to the upper snow layer and F2 describes the properties of the lower layer in melt scenario F. The specific surface area (SSA) values were estimated using snow density-SSA relationships from Dominé et al. (2007) and the measurement from Meyer et al. (2006).

<table>
<thead>
<tr>
<th>Melt Scenario</th>
<th>Density [g·cm$^{-3}$]</th>
<th>Estimated SSA [cm$^2$·g]</th>
<th>Average snow depth [cm]</th>
<th>Snow-water equiv. [L]</th>
<th>Average melt water content [%]</th>
</tr>
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<tbody>
<tr>
<td>A: shallow snow pack</td>
<td>0.25</td>
<td>100 - 200</td>
<td>16</td>
<td>19.7</td>
<td>approxim. 5</td>
</tr>
<tr>
<td>B: deep snow pack</td>
<td>0.26</td>
<td>100 - 200</td>
<td>29</td>
<td>38.5</td>
<td>5 - 7</td>
</tr>
<tr>
<td>C: bottom melt</td>
<td>0.22</td>
<td>20 - 50</td>
<td>22</td>
<td>30.4</td>
<td>5 - 7</td>
</tr>
<tr>
<td>D: high melt water to surface area ratio</td>
<td>0.23</td>
<td>20 - 50</td>
<td>36</td>
<td>43.5</td>
<td>6-10</td>
</tr>
<tr>
<td>E: low melt water to surface area ratio</td>
<td>0.19</td>
<td>450 - 500</td>
<td>43</td>
<td>43.0</td>
<td>4 - 6</td>
</tr>
<tr>
<td>F1: fine grained snow</td>
<td>0.17</td>
<td>500 - 580</td>
<td>37</td>
<td>41.5</td>
<td>3.5 – 6.5</td>
</tr>
<tr>
<td>F2: coarse grained snow</td>
<td>0.23</td>
<td>20 - 50</td>
<td>37</td>
<td>41.5</td>
<td>3.5 – 6.5</td>
</tr>
<tr>
<td>G: strong melting on low permeable snow</td>
<td>0.20</td>
<td>150 - 250</td>
<td>39</td>
<td>41.8</td>
<td>8 - 10</td>
</tr>
<tr>
<td>H: snow pack without dirt cones</td>
<td>0.20</td>
<td>100 - 200</td>
<td>39</td>
<td>42.0</td>
<td>5 - 7</td>
</tr>
</tbody>
</table>


The Figures S1 to S5 show the relative dielectric permittivities measured with TDR methods. The TDR probes were stacked one upon each other, whereas the colors in the line charts reflect the heights above the base of the vessel wall - blue: 20cm, green: 15cm, plum: 10cm, red: 5cm (the probes bend into the conical shaped lower part of the vessel during snow compaction). Early endings of the chart lines are either caused by malfunction or due to ablation and lowering of the snow surface and associated probe exposure.

**Figure A1**  Relative dielectric permittivity reflecting melt water content and dry snow density vs. time for different snow depths; describes the early melt phase in scenario A.
Figure A2  Relative dielectric permittivity reflecting melt water content and dry snow density vs. time for different snow depths; describes the early melt phase in scenario B.

Figure A3  Relative dielectric permittivity reflecting melt water content and dry snow density vs. time for different snow depths; describes the first four melt cycles in melt scenario C.
**Figure A4**  Relative dielectric permittivity reflecting melt water content and dry snow density vs. time for different snow depths; describes the first melt cycle in scenario F.

**Figure A5**  Relative dielectric permittivity reflecting melt water content and dry snow density vs. time for different snow depths; describes the early melt phase in scenario G.
Figure A6  Sample flow rate vs. sample order in melt scenarios D and E during the first melt day.
Figure A7 Macro-photographs of the snow grains (a) shortly after snowmaking, (b) after dry snow metamorphism, during which the snow pack was exposed to large macroscopic temperature gradients, and (c) after several melt-freeze cycles.

Figure A8 Dirt cones at the snow surface.

References