Chemical interactions with snow: Understanding the behavior and fate of semi-volatile organic compounds in snow

B.M.J. Herbert\textsuperscript{a,\*}, S. Villa\textsuperscript{b}, C.J. Halsall\textsuperscript{a}

\textsuperscript{a}Environmental Science Department, Lancaster University, Lancaster, LA1 4YQ, UK
\textsuperscript{b}Department of Environmental and Landscape Science, University of Milano Bicocca, Milan, Italy

Received 18 January 2005; received in revised form 14 May 2005; accepted 23 May 2005
Available online 20 July 2005

Abstract

Snow plays an important role in providing atmospherically derived semi-volatile organic compounds (SVOCs) to regions of high latitude and altitude. The accumulated winter snowpack serves as a reservoir for SVOCs, which may then be released to arctic/alpine catchments during seasonal snowmelt or entrained into deeper layers of snow and ice. This paper provides a review of the occurrence of SVOCs in snow, exploring sampling methodologies and field measurements. Furthermore, chemical fate following snowfall and the propensity of SVOCs to undergo revolatilization with snow metamorphosis are examined along with air–snow partitioning and the role of physical parameters such as snow density and snow surface area in controlling vapor-sorbed levels. Snowmelt and firnification processes are described, and the latter are related to SVOC measurements made in deeper snow layers and glacial ice cores. Evidence is provided that suggests that those SVOCs that possess relatively higher snow interfacial/air partitioning coefficients ($K_{ia\text{snow}}$) or lower Henry’s Law constants may be more efficiently retained in snow, with implications for the occurrence of currently used pesticides in the temperate mountain snowpack.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Arctic; Alpine; Polar; Persistent organic pollutants; Polychlorinated biphenyls

1. Introduction

The snowpack plays an important role in providing atmospherically derived pollutants to catchments in both polar and upland environments (Tranter et al., 1986; Gregor and Gummer, 1989; Gregor et al., 1995; Blais et al., 1998). Pollutants such as acidic ions and heavy metals have been observed to accumulate in the winter snowpack, being released during spring melt and affecting freshwater chemistry (Tranter et al., 1986) and aquatic biota, possibly at a sensitive stage of their life cycle with the onset of spring. A recent arctic study (Loseto et al., 2004) has shown that significant fractions of both methylmercury and total-mercury present in wetlands within the Canadian Arctic originate from snowmelt. Total-mercury concentrations in lakes and basin tributaries appear to show strong temporal trends that correspond to inputs during arctic snowmelt in late spring.

For polar, temperate, and upland environments, semi-volatile organic compounds (SVOCs) such as persistent organic pollutants (POPs) have also been reported in the seasonal snowpack (e.g., Kawamura and Kaplan, 1986; Gregor et al., 1995; Blais et al., 1998; Masclet et al., 2000; Carrera et al., 2001; Herbert et al., 2005). These chemicals have also been observed in older layers of firn and ice, providing accumulation time series (Peters et al., 1995; Donald et al., 1999; Villa et al., 2001; Maselet et al., 2000). Sea ice, for example, also provides a mechanism for the transpolar transport of POPs and other pollutants (Pfirman et al., 1995). The inclusion of organic contaminants such as pesticides into glacial ice (Donald et al., 1999; Villa et al., 2001) will ensure...
continued release into catchments during the future, which is likely to be exacerbated by the fast rates of loss of glacial ice in temperate mountain zones due to climate warming (Dyurgerov, 2003; Vincent et al., 2004). Spring snowmelt has now been shown to have a major impact on the loading of organochlorine (OC) pesticides to lakes in the Canadian Rockies, with the contribution from snow greatly exceeding the contribution from direct atmospheric deposition to lake surfaces (Blais et al., 2001a, b). The recent interest in mountain environments as possible repositories for atmospherically transported POPs is likely to prompt further interest in the mechanisms of snow contamination and subsequent accumulation of organic chemicals in the deeper snowpack and the role of snow in providing toxicologically relevant chemicals to sensitive habitats, such as mountain lakes (Carrera et al., 2001, 2002).

In the broader context, the area of the globe covered by snow and ice is vast, with seasonal snow occupying up to 33% of the Earth’s total land surface (www.nsidc.org). In the Arctic, the maximum extent of sea ice is \(14-16 \times 10^6 \, \text{km}^2\) (www.nsidc.org), while the terrestrial area (under Arctic Monitoring and Assessment Program (AMAP) boundaries) covers some \(13 \times 10^6 \, \text{km}^2\) (AMAP, 2004). The snow covering these areas can be considered to provide a porous homogenous surface (relative to snow-free surfaces), with a large internal surface area suitable for sorption of vapor-phase chemicals advected into the arctic atmosphere. The surface snowpack also plays an important role in the chemistry of reactive trace gases, providing a large surface area for sorption and/or heterogeneous chemical reactions (Sumner and Shepson, 1999; Houdier et al., 2002), and may play an important role in ozone and mercury depletion events observed during sunrise in the high Arctic (Boudries and Bottenheim, 2000).

The accumulation of SVOCs in the arctic snowpack may be driven by two related processes. First, the “cold condensation effect”, whereby lower temperatures will promote a shift of partitioning equilibria for chemicals in the vapor phase toward sorbed “condensed” phases, will serve to promote SVOC accumulation in cold environments (Wania et al., 1998; Lei and Wania, 2004). Secondly, precipitation in the form of falling snow and cold winter rain is highly efficient in removing SVOCs from the atmosphere (both vapor- and particulate-bound chemicals) (Franz and Eisenreich, 1998; Wania et al., 1999; Lei and Wania, 2004).

Cold temperatures coupled to the presence of snow are therefore likely to enhance air to surface transfer processes for SVOCs in polar and mountainous regions. To elucidate and predict chemical accumulation in snow, and quantify chemical transfer to meltwater and ice, post-depositional behavior needs to be examined and understood. There is growing evidence that a significant fraction of SVOCs deposited with fresh snow may volatilize from the snowpack with snow ageing, resulting in heavier, less volatile contaminants remaining in the snow until spring melt (Gregor and Gummer, 1989; Wania, 1997; Herbert et al., (unpublished); Villa et al., 2005). Importantly, those chemicals remaining in the snowpack may have the potential to undergo photochemical transformation, possibly to more persistent and/or toxic by-products (Klan et al., 2001; Klan and Holoubek, 2002). In this study we provide a review on the occurrence of SVOCs in snow and examine the relationship between snow properties and chemical behavior. We also explore factors that affect post-depositional behavior of SVOCs and their accumulation into deeper layers of firn and ice.

2. SVOC concentrations in snow

A number of studies over the past 15 years or so have identified organic chemical contaminants present in snow and measured their concentration and/or depositional flux to the snowpack (e.g., Gregor and Gummer, 1989; Donald et al., 1999; Herbert et al., (unpublished); Herbert et al., 2005). The chemicals usually measured include POPs such as polychlorinated biphenyls (PCBs) and OC pesticides. In addition, polycyclic aromatic hydrocarbons (PAHs), n-alkanes, and phthalates have been measured in arctic snow (e.g., Masclet et al., 2000; Garbarino et al., 2002). Table 1 provides a summary of snow contaminant concentrations from seven studies conducted in both alpine and arctic regions and, while not exhaustive, highlights the general paucity of POP concentrations in snow. These studies reveal a wide range in measured concentrations for the same chemical classes. This range in concentrations within data sets may, in part, be explained by temporal and spatial differences, reflecting changes in global emissions with time, and different regional usage patterns. For example, the highest snowpack concentrations of \(a\)-HCH (the major isomer comprising the pesticide technical-HCH) were from studies conducted during the 1980/1990s in the Arctic (e.g., Gregor and Gummer, 1989; Semkin, 1996) and were found to be an order of magnitude higher than concentrations reported in later snow studies in 2001 and 2003 (Herbert et al., (unpublished); Herbert et al., 2005). This may reflect the decline in technical-HCH usage following bans in North America during the 1970s and later by China and Russia in 1990 (Li, 1999). However, it is apparent that snowpack concentrations may vary by an order of magnitude within the same study. For example, Herbert et al. (unpublished) showed that surface snow layers in the Norwegian Arctic had polychlorinated biphenyl (\(\Sigma\)PCB) concentrations ranging from 160 to 2500 pg L\(^{-1}\) (snow-melt). This raises the question why such wide ranges in contaminant snow concentrations have been observed,
both between studies and within an individual study (Gregor et al., 1995; Herbert et al., unpublished; Herbert et al., 2005). There are possibly three factors that may account for this. First, different sampling and extraction methods may reduce the level of precision for measuring trace organics in snow. Second, fluctuating atmospheric concentrations may influence concentrations present in the snowpack. Third, varying snow physical properties may influence the capacity of snow to retain vapor-sorbed SVOCs. These three factors are discussed in more detail below. A further chemical loss process in surface snow and ice that should be taken into consideration and could account for variations in contaminant concentrations is chemical photodegradation by sunlight (photolysis). Photochemical reactions of contaminants at the snow surface may be initiated by direct solar irradiation or sensitization by other UV absorbers, resulting in either loss or transformation of the parent compound (Klan and Holoubek, 2002). In a study by Klan et al. (2001), it was shown that products of intermolecular photochemical reaction were often of greater toxicity and higher environmental risk than the parent compound (e.g., PCB formation). However, at present, data on the extent, rates, and products of photochemical reaction are scarce and therefore no quantitative estimates on the effects of photolysis in cold environments can be made.

3. Snow sampling methods

Currently, there is not an established protocol for the sampling and analysis of trace organics in snow. Sampling procedures usually involve taking large-volume grab samples, using equipment ranging from sealed-metal containers (Blais et al., 1998; Herbert et al., 2004) to polyethylene bags (Welch et al., 1991; Gröllert et al., 1997), followed by transport to laboratories for subsequent snow melt and extraction. In remote locations (such as the Arctic), melting and extraction may be conducted in situ (Masclet et al., 2000). For example, snow samples taken on the Agassiz ice cap (Ellesmere Island, Canada) were melted and extracted in a nearby ice camp (Peters et al., 1995). A summary of sample collection and extraction techniques is presented in Table 2. In most studies, due to logistical considerations and often inhospitable conditions, snow concentrations are derived from a relatively small number of snow samples \( n \leq 10 \), with few replicates (if any) being taken to assess sampling precision. The observed ranges in reported snowpack concentrations may therefore reflect the sampling/extraction technique or be indicative of the heterogeneous nature of snow, where concentration differences may be quite large over relatively small spatial scales (both horizontally and vertically through different snow layers). To assess
sampling equipment, the performance of a novel gas-tight, snow sampler (50L Snow Can) was conducted in the Italian Alps (Herbert et al., 2004). The study revealed a level of precision between replicate samples (relative standard deviation) taken from the same snow layer within an area of 4 m² of \( \frac{1}{24} \times 35\% \) PAHs, \( \frac{1}{24} \times 30\% \) PCBs, and \( \frac{1}{24} \times 25\% \) OC pesticides. This level of precision may be used as a benchmark to compare future field campaigns and highlights the suggestion that, for true environmental changes in snow concentrations to be observed, the concentration between samples would have to change by \( \frac{1}{24} \times 20–40\% \) depending on the contaminant in question.

### 4. Atmospheric concentrations

Chemical concentrations in the atmosphere will ultimately dictate the contaminant burden present in fresh snow (Lei and Wania, 2004). For example, snow samples taken in or near urban locations show markedly higher PAH concentrations than snow samples taken in rural areas (Schrimpff and Herrman, 1979; Sharma and McBean, 2001). Similarly, on a wider scale, regional differences in pesticide concentrations have been observed across Russia, reflecting the major areas of pesticide use (Poliakova et al., 2000). Therefore differences in spatial and temporal atmospheric concentrations will also be reflected in the snowpack.

There are now several long-term air monitoring programmes to measure POPs in Europe (Halsall et al., 1993), North America (Buehler et al., 2001; Buehler and Hites, 2002), and the Arctic (Halsall et al., 1997, 1998; Oehme et al., 1996). Air sampling across the Arctic, for example, has proven valuable in assessing temporal and spatial trends for a number of chemical groups including PCBs and OC pesticides (e.g., Oehme et al., 1996; Hung et al., 2001, 2002). These data reveal that contaminant levels across the Arctic generally exhibit a small range in concentrations over an annual time scale. For example, \( \Sigma PCB_{10} \) concentrations in the Canadian and the Siberian Arctic vary by a factor of <2, although differences between the Canadian and the Norwegian high Arctic are typically higher (AMAP, 2004).

Hung et al. (2001, 2002) used weekly air concentration data from a 5-year data set at Alert (Nunavut, Canadian high Arctic) to examine temporal trends in atmospheric

---

**Table 2**

Summary of snow collection and extraction protocols for SVOCs

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Sampling tool</th>
<th>Storage device</th>
<th>Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blais et al. (1998)</td>
<td>Canadian Rocky Mountains</td>
<td>Stainless steel chisel and</td>
<td>Sealed aluminum cans</td>
<td>Goulden extraction</td>
</tr>
<tr>
<td>Donald et al. (1999)</td>
<td>Canadian Rocky Mountains</td>
<td>Solvent-cleaned stainless</td>
<td>Snow/ice containers</td>
<td>Liquid/liquid (DCM)</td>
</tr>
<tr>
<td>Gregor et al. (1995)</td>
<td>Agassiz Ice Cap, Ellesmere</td>
<td>Aluminum snow cases</td>
<td></td>
<td>Liquid/liquid (DCM)</td>
</tr>
<tr>
<td>Haglund et al. (1987)</td>
<td>Stockholm, Sweden</td>
<td>Solvent-cleaned stainless</td>
<td>Gas-tight aluminum snow</td>
<td>Florosil (vapor phase), C(_{18})</td>
</tr>
<tr>
<td>Herbert et al. (2004a)</td>
<td>Punta Indren Ice Field,</td>
<td>Stainless steel shovel</td>
<td>can (50L)</td>
<td>trap (meltwater), GFF (particulate)</td>
</tr>
<tr>
<td>Melnikov et al. (2003)</td>
<td>Ob-Yenisey River</td>
<td>Scoop</td>
<td>Polyethylene containers</td>
<td>Liquid/liquid extraction</td>
</tr>
<tr>
<td>Carrera et al. (2001)</td>
<td>Alps (Europe)</td>
<td>Stainless steel corer</td>
<td>Stainless steel containers</td>
<td>Hexane</td>
</tr>
<tr>
<td>Herbert et al. (2004b)</td>
<td>Ny-Ålesund, Svalbard,</td>
<td>Solvent-cleaned stainless</td>
<td>Gas-tight aluminum snow</td>
<td>Florosil (vapor phase), C(_{18})</td>
</tr>
<tr>
<td>Gröllert et al. (1997)</td>
<td>Mt. Sonnblick, Austrian Alps</td>
<td>Polyethylene shovel</td>
<td>Polyethylene bags (6L)</td>
<td>empore disks (meltwater), GFF</td>
</tr>
<tr>
<td>Sonke et al.</td>
<td>Ekstroem Ice Shelf,</td>
<td>Metal shovel cleaned by</td>
<td>Stainless steel solvent</td>
<td>(particulate)</td>
</tr>
<tr>
<td>Welch et al. (1991)</td>
<td>Keewatin District, central</td>
<td>heating with gas burner</td>
<td>barrels (50L)</td>
<td>Liquid/liquid extraction</td>
</tr>
<tr>
<td>Peters et al. (1995)</td>
<td>Agassiz Ice Cap, Ellesmere</td>
<td>Clean steel shovel</td>
<td>Polyethylene bags</td>
<td>XAD-2 columns</td>
</tr>
<tr>
<td></td>
<td>Island, Canada</td>
<td>Solvent-cleaned stainless</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>steel shovel</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aluminum snow cases</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

B.M.J. Herbert et al. / Ecotoxicology and Environmental Safety 63 (2006) 3–16
levels of PCBs and OC pesticides. General declines in both ΣPCB (1993–1998) and OC pesticides (1993–1997) were observed over this period. While PCB and OC pesticide concentrations in the remote atmosphere appear to be decreasing, the rates of decline were relatively small, with chemical half-lives ranging between 3–20 years, and are unlikely to explain the wide variation in measured snow concentrations observed in studies conducted in the 1980s/1990s and in more recent snow measurements (e.g., Gregor et al., 1995; Herbert et al. (unpublished); Herbert et al., 2005). The influence of variable air concentrations is probably best examined through combined air and snow studies. Recently, Herbert et al., (2005) sampled air and snow every 24 h over an 11-day period in Tromsø in the Norwegian Arctic. Atmospheric ΣPCB and γ-HCH concentrations ranged from 7.9 to 76 pg m\(^{-3}\) and from 12.6 to 39.9 pg m\(^{-3}\), respectively. This variation can be explained in part by the influence of different air masses, with the lowest air concentrations occurring when the air originated from over the Arctic Ocean, as opposed to further south. Fig. 1 presents the mean air and snow concentrations for PCBs and a number of OC pesticides throughout the sampling period. PCB concentrations varied by ~16-fold in the snow compared to 8-fold in the air; similarly, γ-HCH varied by ~16-fold in the snow and by only ~4-fold in the air, illustrating the relatively small range in air concentrations compared to those in the snow.

5. Snowpack properties

Snow comprises a mixture of ice, air, water, and particles and can be viewed as a relatively homogenous porous surface compared to snow-free surfaces such as soil and vegetation (Bidleman and Leone, 2004; Meijer et al., 2003; Thomas et al., 1998; Smith et al., 2001). There are relatively few studies that have been undertaken to categorize and measure the properties of different snow types with respect to trace gas transfer between the snow surface and the atmosphere (e.g., Sumner and Shepson, 1999; Legagneux et al., 2002). Closer examination of the seasonal snowpack usually reveals a degree of stratification, with layers comprising different snow types, each of which is more or less homogenous within its own boundaries (Colbeck et al., 1990). Snowpack heterogeneity arises due to the accumulation of different snow layers, followed by snow metamorphosis brought about by changes in temperature, wind speed, relative humidity, and solar radiation both during and after snowfall (e.g., Colbeck, 1983). Different snow types are generally identified by visual observation of grain shape and size, designated “F” and “E,” respectively, both of which can usually be identified/classified in the field. For grain shape classification, there are nine basic grain types (1–9), which are then subclassified to further refine identification. The grain size of a homogenous snow layer is defined as the average size of its characteristic grains (Colbeck et al., 1990). The size of the grain is the measurement of the longest extension of the ice crystal (mm) and can then be used to deduce the corresponding grain size category (e.g., “very fine”<0.2 mm to “extreme”>5.0 mm). Both E and F are important parameters that will dictate the density (\(\rho\)) and specific surface area (SSA) of a snow layer (the latter usually expressed in units of cm\(^2\) g\(^{-1}\)) (Cabanes et al., 2003). Density is a measure of the mass of snow per unit volume (e.g., kg L\(^{-1}\)) and can be readily determined in the field by weighing snow of a known volume. SSA, however, is a difficult parameter to measure but a very useful property with respect to vapor sorption of trace gases and has been the focus of recent research in the sorptive capacity of different snow types (e.g., Hanot and Dominé, 1999; Legagneux et al., 2002). Measurement of SSA involves a technique based on CH\(_4\) adsorption, according to the Brunauer–Emmett–Teller (BET) isotherm. SSAs generally fall between 100 and 1500 cm\(^2\) g\(^{-1}\) depending on the age and “weathering” of the snow (Domine et al., 2002; Legagneux et al., 2002). Field observations of different snow types including measurements of E and F in addition to \(\rho\) and SSA have resulted in a number of empirical relationships that relate snow type and allow estimation of SSA (Legagneux et al., 2002). The total surface area (TSA) of the snowpack can then be calculated as a product of the SSA, \(\rho\), and snowpack depth.
Snow is a highly transient medium with physical properties open to rapid change, often over a period of hours following snowfall (Cabanes et al., 2002; Herbert et al., 2005). Fluctuating temperatures and wind speeds are processes that will change the physical structure of snow, affecting both \( \rho \) and SSA, which in turn affect the vapor-sorbed quantity of a chemical in the snow. Cabanes et al. (2002) examined the evolution of SSA and crystal morphology of fresh snow at Alert (Nunavut, Canada) and demonstrated that measured SSA values decreased with snow metamorphosis, with rates of decrease accelerated in periods of rising temperature and wind speed. The mechanisms involved in the reduction of SSA include the rounding of snow crystal edges, the sublimation of crystal microstructures, and the dilution of snow by surface hoar of a lower SSA (Cabanes et al., 2002).

6. Snow–chemical interaction

Fig. 2 illustrates the interaction of vapor- and particulate-bound SVOCs to a generic dendritic snow crystal. It is considered that penetration of the chemical (by diffusion) into the solid ice structure is negligible for the lifetime of the crystal and that chemical interaction is largely an ice surface phenomenon (Roth et al., 2004). Importantly, Fig. 2 highlights the influence of a quasi-liquid layer (QLL), which is believed to cover ice surfaces. The nature and extent of the QLL is open to some debate (Knight, 1996) but it could be essential in controlling vapor/ice partitioning. The interaction of low-polarity organic vapors with ice has been investigated in a number of laboratory studies (e.g., Orem and Adamson, 1969; Goss, 1993; Hoff et al., 1995). Several of these studies found that snow/ice–air partitioning was akin to that observed on water films (coated onto mineral surfaces) but at much higher temperatures. Hoff et al. (1995) examined the partitioning of a number of chlorinated volatile/semi-volatile chemicals directly to snow and concluded that partitioning at the ice–air interface (through derivation of experimental interfacial/air partitioning coefficients \( K_{ia} \)) was akin to that of water surfaces and can be estimated at temperatures near melting by extrapolating adsorption constants for the air–water interface. In this case, an interfacial/air partitioning coefficient for snow \( (K_{ia}^{\text{snow}}) \) can be calculated according to a chemical's aqueous solubility (subcooled) \( (C_w) \) and Henry’s Law constant \( (H) \) according to

\[
\log K_{ia} = -0.769 \times \log C_w - 5.97 + \log \frac{RT}{H}
\]  

(1)

where \( R \) is the universal gas constant, and \( T \) the temperature (293 K). Note that \( RT/H \) is the water–air
partition coefficient ($K_w$). $K_{ia,snow}$ values can be adjusted to subzero temperatures with knowledge of the heat of adsorption ($\Delta H_a$) for the chemical in question, assuming that the liquid water–ice interface is similar. At temperatures between −30 and 0 °C the ice surface is assumed to behave like a subcooled water surface with respect to sorption of volatile (often polar) organics (Sokolov and Abbatt, 2002).

The QLL is described as an interfacial region that can exist at temperatures below freezing, with liquid-like properties or disordered surface films present on the surfaces of ice crystals (Nenow, 1984). Knowledge of the QLL is of importance as it may control or influence chemical partitioning at the ice–air interface. Conklin and Bales (1993) estimated the thickness of the QLL by calculating the absorption of SO$_2$ to ice of an estimated surface area. Their study showed that the layer, assuming uniform thickness, ranged between 3–30 nm at −60 °C to 500–3000 nm at −1 °C. The depth of the QLL is influenced by both the salt content of the snow (important for the coastal or sea ice snowpack) and the ambient temperature. As the QLL is so thin it can be assumed that its volume will be proportional to the surface area of the ice crystal, although the existence and surface coverage of the QLL is open to some debate (Knight, 1996). Nevertheless, extrapolation of adsorption data from liquid water films to subzero temperatures (ice surfaces) has formed the basis of VOC/SVOC sorption to snow surfaces (Hoff et al., 1995).

At present the dominant sorptive process to the ice surface is still unknown. However, Roth et al. (2004) have measured $K_{ia,snow}$ for 57 organic compounds that covered a wide range of physical–chemical properties. $K_{ia,snow}$ was determined from compound retention volume using inverse gas chromatography for field snow cores at −6.8 °C. To test the Hoff et al. (1995) approach, Roth et al. (2004) compared the measured $K_{ia}$ sorption coefficients for the selected compounds of their study with water surface–air adsorption coefficients that had been extrapolated down to −6.8 °C. It was shown that sorption of both nonpolar and polar compounds to the snow surface was strongly underestimated by these extrapolated water values. This suggests that the sorptive process to snow is more complicated than simple adsorption to a subcooled water surface and that there is some uncertainty in extrapolating $K_{ia}$ values derived for water to those for ice surfaces at temperatures below freezing.

An approach adopted by Roth et al. (2004) to describe the sorption of organic vapors to snow uses polyparameter linear free energy relationships (pp-LFER). These use the molecular properties of the chemical including Van der Waals interactions and the electron donor/acceptor interactions to describe partitioning to environmental surfaces in general ($K_{surface/air}$) (Schwarzenbach et al., 2003) according to

$$\log K_{surface/air} = a \log K_{hexadecane/air} + b \Sigma \beta + c \Sigma \alpha + \text{constant}$$

(2)

where $\log K_{hexadecane/air}$ is the hexadecane/air partition coefficient at 25 °C (used to account for the Van der Waals forces alone), and $\Sigma \alpha$ and $\Sigma \beta$ are the sums of the electron acceptor and electron donor characteristics of the chemical, respectively. The regression coefficients $a$, $b$, and $c$ are related to the surface properties and the “constant” depends on the standard state of adsorption (Schwarzenbach et al., 2003). Roth et al. (2004), using the snow cores collected in the Alps, generated the “surface parameters” via multiple regression analysis of the experimental snow data and used the pp-LFER approach to derive an experimental fit to describe the sorption for their selected organic compounds ($n = 57$) to snow. $K_{ia,snow}$ is now given by

$$\log K_{ia,snow} = 0.639(\pm 0.037) \log K_{hexadecane/air} + 3.38(\pm 0.17) \Sigma \beta + 3.53(\pm 0.25) \Sigma \alpha - 6.85$$

(3)

Calculated $K_{ia,snow}$ using pp-LFER can then be extrapolated to relevant temperatures using the interface/air enthalpy of adsorption ($\Delta H_a$) for the chemical in question. However, $\Delta H_a$ values are available only for water films and again the assumption here is that the “interface” for liquid water is similar to that of ice. $K_{ia,snow}$ is given by

$$\log K_{ia,snow}(T_1) = \log K_{ia,snow}(-6.8^\circ C) + \Delta H_{ia}/2.303 R (1/T_1 - 1/T_{266.2})$$

(4)

where $T_1$ is the relevant snow temperature (K), $\Delta H_{ia}$ the interface/air enthalpy of sorption (kJ mol$^{-1}$), and $R$ the gas universal constant (0.008314 kJ mol$^{-1}$ K). While the pp-LFER approach does not identify the specific air–snow sorptive process, whether it is adsorption to the snow crystal surface, incorporation into the solid ice, or absorption into a QLL, it does appear to provide a useful tool to predict $K_{ia,snow}$ for a wide range of organic compounds.

Table 3

<table>
<thead>
<tr>
<th>$\gamma$-HCH (288 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ia,snow,Hoff}$ (m)</td>
</tr>
<tr>
<td>$k_{ia,Hoff}$</td>
</tr>
<tr>
<td>$C_{i,Hoff}$ (pg.m$^{-3}$)</td>
</tr>
<tr>
<td>$k_{ia,snow,LFER}$</td>
</tr>
<tr>
<td>$k_{ia,LFER}$</td>
</tr>
<tr>
<td>$C_{i,LFER}$ (pg.m$^{-3}$)</td>
</tr>
</tbody>
</table>
To illustrate the differences between $K_{ia\_snow}$ values calculated according to the Hoff et al. (1995) approach and those according to the Roth et al. (2004) pp-LFER approach, Table 3 predicts snow concentrations for the pesticide $\gamma$-HCH. This scenario assumes an air concentration ($C_a$) of 35 pg m$^{-3}$ (a typical value observed in the high Arctic; see Halsall et al. (1998)) and a “generic” snow with SSA of 55 m$^2$ kg$^{-1}$ and a density of 150 kg m$^{-3}$. A snow/air partitioning coefficient ($K_{ia}$) can be derived according to

$$K_{ia} = K_{ia\_snow} \times SSA \times \rho$$  \hspace{1cm} (5)

$C_s$ can be subsequently calculated by simply multiplying $K_{ia}$ (derived from Eq. (5)) with $C_a$. Comparison of the calculated $C_s$ values using the two different partitioning approaches reveals a notable difference. $C_s$ determined using the pp-LFER approach is 1.5 times greater than that using the Hoff et al. (1995) approach, indicating a higher degree of $\gamma$-HCH sorption to the snow. To examine the application of each approach, Fig. 3 compares the calculated $C_s$ values to observed snow concentrations (measured at similar environmental temperatures and snow conditions). Observed $C_s$ lies between the calculated values given by the two partitioning approaches. The Hoff et al. (1995) approach underestimates $\gamma$-HCH sorption to the snow by $\sim$30%, while the pp-LFER approach overestimates sorption by $\sim$20%. This scenario serves to highlight the importance of snow–air partitioning of vapor-phase SVOCs for controlling $C_s$. While uncertainty lies in both partitioning approaches, each predicts surface snow concentrations that are akin to measured values for this simple Arctic scenario.

7. Bulk chemical transfer between the atmosphere and the snowpack

The mechanisms that control the exchange of trace organic contaminants between the atmosphere and both falling snow and standing snowpack need to be resolved to incorporate winter snow cover into atmospheric and chemical fate models. The major processes, presented in Fig. 4, include vapor and particle scavenging by falling snow, vapor sorption/desorption to the snow surface, and diffusion of chemicals both into and out of the snowpack. These processes dictate the quantities of chemicals available to meltwater and for deeper burial in areas of permanent snow and ice.

Both vapor- and particle-phase SVOCs are subject to scavenging from the atmosphere via precipitation. A total scavenging ratio ($W_T$) (or washout ratio) can be calculated and represents a measure of the efficiency by which precipitation can remove SVOCs from the atmosphere (Ligocki et al., 1985). Values of $W_T$ have been reported from a number of empirical and theoretical studies for both winter rain and snowfall events (Franz and Eisenreich, 1998; Wania et al., 1999; Lei and Wania, 2004) and a summary of values are presented in Table 4.

Wania (1997) predicted that the scavenging of the vapor component of SVOCs ($W_v$) by falling snow was highly efficient, with $W_v$ strongly negatively correlated to a chemical’s vapor pressure (i.e., decreasing vapor pressure results in higher $W_v$). More recently Lei and Wania (2004) investigated whether rain or snow was more efficient at scavenging organic chemicals from the atmosphere. To compare the scavenging efficiency of snow and rain at different temperatures, total scavenging ratios $W_T$ (vapor- and particulate-bound) were calculated over a wide temperature range ($-25$ to $25^\circ C$) for a selection of chemicals. It was found that at 0°C rain was typically more effective in scavenging the vapors of “small” organic molecules than snow (i.e., phenolic compounds and lighter two-to-three-ringed PAHs) due to the larger sorptive capacity of the water droplets. In contrast, it was shown that snow with a large surface area ($>0.1$ m$^2$ g$^{-1}$, typical of fresh snow) is more efficient at scavenging vapors of larger nonpolar
organics, with lower solubilities (i.e., PCBs and heavy multiringed PAHs). For efficient snow scavenging, chemicals must have $K_{\text{ss}}$ values $>0.1$ m or particle–air coefficients ($K_{\text{pa}}$) $>10^{11}$ at temperatures $<0$ °C, properties typical of many environmental organic contaminants. In general $W_T$ increased as temperature decreased, due to the shift in partitioning from the vapor phase to liquid water droplets, atmospheric particles, and snow surfaces. Therefore Lei and Wania (2004) concluded that a reduced temperature effect was the main factor for snow scavenging ratios to be greater than those of rain and that snow scavenging increased significantly as temperature decreased to $<-10$ °C. In summary, precipitation in the form of snow plays an important role in the bulk transfer of airborne SVOCs to the standing snowpack, particularly at lower temperatures ($<-5$ °C). This appears to be confirmed by the higher values of $W_T$ measured in field observations (Franz and Eisenreich, 1998). $W_T$ values between snow events are large, making quantitative predictions of wet deposition fluxes difficult to obtain, and may explain the erratic and often large range in concentrations observed for fresh snow fall events (Franz and Eisenreich, 1998; Lei and Wania, 2004).

SSA has a controlling influence over the quantity of vapor sorbed chemicals in snow (Wania, 1997; Hanot and Domine, 1999). SSA is effectively the measure of the area available for gas exchange, providing the surface sorptive capacity for a given chemical (Wania et al., 1998). The importance of SSA for controlling the quantity of SVOCs present in different snowfalls was demonstrated by Herbert et al. (unpublished). They conducted a study in Ny-Ålesund in the Norwegian Arctic, whereby PCB and OC pesticide concentrations in fresh snow were measured and later related to the SSA of the separate snow types. For selected PCBs and OC pesticides a statistically significant relationship ($P<0.1$) between the measured sorbed snow concentration and the SSA of surface snow layers was apparent. For all measured contaminants the snow type that displayed the highest concentrations had the greatest SSA.

8. Diffusion processes

For VOC/SVOCs, diffusive vapor exchange will occur between the atmospheric boundary layer and the snow surface and will be dependent on a concentration gradient between the overlying atmosphere and the interstitial pore spaces in the surface snow. The Whitman two-film resistance model has been proposed to account for SVOC vapor fluxes between the snowpack and the atmosphere (Halsall, 2004; Hansen et al., unpublished), where the flux into surface snow can be represented by

\[
\text{Flux}(\text{pg m}^{-2} \text{ h}^{-1}) = k_s \left( \frac{C_s}{K_{\text{sa}}} - C_a \right),
\]

where $C_s$ and $C_a$ are the respective, snow and air concentrations, $K_{\text{sa}}$ is the snow/air partitioning coefficient (detailed earlier) and $k_s$ is the snow side mass transfer coefficient.

For the surface snowpack, diffusive vapor exchange will occur with the atmosphere; however, it is unlikely over the course of a winter season that equilibrium would be achieved for SVOCs, given the rapid metamorphosis experienced by fresh snow layers (i.e., surface area reduction) and the addition of fresh snow layers following repeated snowfall. Furthermore, deeper more dense snow and ice layers within the pack may greatly reduce air exchange with the overlying atmosphere. Nevertheless, sorption of vapor SVOCs to the standing snow may occur, particularly as wind serves to ventilate the seasonal snowpack (Albert and Shultz, 2002). Freshly fallen snow, having experienced a large volume of air during deposition and hence containing a significant contaminant burden, undergoes crystal size reduction (decrease in SSA) and subsequently releases SVOCs back to the atmosphere—an important process which is described further below.

Diffusion and ventilation are two important processes that affect the movement of a contaminant within a snowpack. Diffusion is a transport process driven by both concentration and temperature gradients (Albert and Shultz, 2002), whereas wind ventilation (or wind pumping) provides an advective transport process with interstitial pore space air movement within the snow-
pack. Experimental diffusivities and ventilation rates for a volatile tracer SF₆ (sulfur hexafluoride) have recently been determined in the snowpack at Summit, Greenland (Albert and Shultz, 2002). A diffusion coefficient for SF₆ of ~0.06 cm² s⁻¹ was calculated for the surface snowpack. Ventilation rates were determined at two windspeeds, “light” (~3 m s⁻¹) and “moderately strong” (~9 m s⁻¹). The study revealed that at the low wind speed the ventilation rate was ~0.2 cm s⁻¹, compared to ~1.3 cm s⁻¹ at the higher windspeed of 9 m s⁻¹. It was concluded that in the low-wind scenario the migration of SF₆ in the snowpack can be largely attributed to advective transport, while at high wind speeds the chemical migration is largely due to advective transport. It is estimated that the top 10–100 cm of snow are subject to wind ventilation. Scaling this up and using the earth’s area covered by snow, with a typical ventilation rate through snow of 0.5 cm³ s⁻¹, it is estimated that an air volume equivalent to the whole atmosphere passes through the snowpack within a period of ~3 months (Domine and Shepson, 2002). For SVOCs such as POPs, which possess high Kᵣ values, their effective diffusion rates are likely to be much lower than those for volatile chemicals such as SF₆. Nevertheless, the fraction of chemical released into snow pore spaces following changes in snow properties, such as SSA, will be subject to both advective and diffusive transport within the snowpack. These transport processes are likely to redistribute the chemical within the snowpack and/or alter the composition of the chemical mixtures (i.e., PCBs) over time.

9. Chemical fate following snow metamorphosis

Significant reductions in the burden of OC pesticides and other POPs in fresh snow have been observed with snow ageing (Gregor and Gummer, 1989; Hargrave et al., 1988; Herbert et al., 2005). For example, a study conducted in the Canadian high arctic (Hargrave et al., 1988) observed HCB in snow samples collected during May–June but not in snow collected in the same location in August–September. Similarly, in a study by Gregor and Gummer (1989) conducted on the Agassiz Ice Cap (Ellesmere Island, Nunavut), OC pesticide concentrations from the snow layer representing 1985/1986 were up to an order of magnitude higher than those measured in the subsequent year. Unfortunately, neither of the above studies provide detail on contaminant rates of loss or infer the physical processes that may have accounted for this loss.

Transformation of snow generally leads to a progressive decrease in SSA and snow porosity and to an increase in ρ. The metamorphosis of fresh snow to ice has been summarized in five key stages (Martini et al., 2001). In brief, fresh snow is typically characterized by ρ generally ranging between 0.01 and 0.1 kg L⁻¹ with a porosity of about 95%. Sublimation, wind action, and possible local melting are the dominant transformation processes reducing crystal size and increasing ρ. Furthermore, compaction from successive snowfalls results in the crushing of ice crystals, further accelerating snow metamorphosis. The product of the above transformation processes is then loosely termed “old snow”. Old snow contains rounded, closely packed ice crystals, with ρ ranging between 0.3 and 0.5 kg L⁻¹ with a porosity of ~50%. Snowpack density increases through further compaction and/or snow crystal sublimation, eventually resulting in firn. Firn comprises granular, rounded crystals ~1 mm in size, and ρ ~0.55 kg L⁻¹ and relatively low porosity compared to that of fresh snow. Firn transformation generally occurs due to the crushing, melting, and recrystallization of ice crystals, resulting in the production of intermediate firn–glacier ice. Further transformation of intermediate firn–glacier ice occurs through dynamic metamorphosis (i.e., by physical deformation caused by ice mass, temperature fluctuations, and other external forces), resulting in older glacier ice, with a density of about 0.9 kg L⁻¹ and is essentially impermeable.

In an attempt to quantify the rate of SVOC loss from a fresh snowpack (with snow ageing in mind), Herbert et al. 2005 took consecutive snow samples from a fresh snowfall layer over an 11-day period at Tromsø in the Norwegian Arctic. It was shown that the concentration of PCBs decreased significantly throughout the sampling period from an initial concentration of 2500 to 340 pg ΣPCB L⁻¹ (meltwater). The most rapid decrease was seen within the first 96 h, with ~75% of the total PCB burden being lost during this period (ΣPCB t₁/₂ = 65 h). Between 96 and 240 h the PCB concentration remained stable (~380 pg L⁻¹), with no significant change in concentrations between samples. Interestingly, PCB concentrations in this snow layer increased significantly from 300 to 5400 pg ΣPCB L⁻¹ after a fresh snowfall event (this fresh snow snow overlying the sample layer), indicating the propensity for contaminant exchange between snow layers and possible downward migration of chemicals into deeper snow layers.

Rates of loss in the snow (kₛ) were calculated for selected PCB and OC pesticides and were found to follow first-order kinetics. Values of kₛ were found to be similar for all PCB congeners, and for α- and, γ-HCH (kₛ = 0.01 h⁻¹). Surprisingly, a relationship between kₛ and physical/chemical properties, such as vapor pressure (Pᵥ) or H (r²<0.02), was not apparent, although the precision between samples may have blurred any relationship. The decrease in PCB and OC pesticide concentrations was mirrored by a steep increase in snow density of the sampled snow layer with a significant relationship (P<0.05) (fitted to all compounds studied) between the fraction of chemical remaining in freshly
fallen snow ($\phi_s$) and changes in snow density ($\Delta \rho$). This exponential relationship is given by

$$\phi_s = 0.6923e^{-6.2609\Delta \rho}$$

(7)

As an exponential decrease in $\phi_s$ was apparent, only a small increase in $\rho$ will result in a sizeable decrease in $\phi_s$. It must be noted, however, that this relationship may be applicable only for freshly fallen snow, since similar changes in $\rho$ for aged snow (months) are unlikely to result in an exponential decline in any remaining chemical residue. Importantly, the decrease in $\rho$ will result in a decrease in SSA and hence will reduce the capacity of the snow layer to retain the vapor-sorbed fraction. This will ultimately result in repartitioning of the chemicals from the ice crystal surface back into the interstitial pore spaces for subsequent migration within the snowpack or re-release to the overlying atmosphere. This process indicates that the loss of SVOCs from a fresh snowpack is rapid and that only a small fraction of vapor-sorbed chemical, initially deposited in fresh snow, remains within the snowpack after snow ageing. This finding supports previous studies that observed notable decreases in SVOC loading with time. A similar loss rate has been observed by Villa et al. (2005). In this study, a mixture of individual PCB congeners (Nos. 28, 52, 101, 138, 153, 180, and 209) and OC pesticides (z-HCH and p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT)) were spiked into surface snow and sub-samples were harvested daily over a 9-day period. A rapid loss of all the spiked contaminants was observed in surface snow, with half-lives ranging between 64 and 151 h, akin to the previous study by Herbert et al., 2005 (outlined earlier). However, unlike Herbert et al. a strong relationship was apparent between $k_s$ and both chemical vapor pressure ($P_o$) and $H$. In other words, rates of loss were reduced for those chemicals with lower vapor pressures and lower $H$ values ($P_o$ and $H$ were adjusted to the ambient air temperature). Distinguishing between either $P_o$ or $H$ as the controlling parameter was difficult, but a stronger relationship was observed for $H$ ($r^2=0.42$, $P < 0.05$). Similarly, comparison between contaminant concentrations in fresh and aged snow ($\sim 65$ days ageing) at the Lys glacier (Italian Alps) revealed losses of $> 90\%$, $80\%$, and $50\%$ for HCB, z-HCH, and $\gamma$-HCH, respectively, with the percentage loss again related to their respective $H$ values, whereby $H$ follows the order HCB > z-HCH > $\gamma$-HCH.

Current-use pesticides (CUPs), such as malathion and dacthal, generally have much lower $H$ values than OC pesticides and yet these chemicals have been observed in the snowpack and catchment waters at high-elevation sites in the national parks of the western United States (McConnell et al., 1997). Due to their semi-volatility, CUPs are likely to experience efficient removal from the atmosphere by snowfall and, importantly, are more likely to be retained within the aged snowpack due to their relatively lower $H$ values than those of POPs. The presence of CUPs in the Sierra Nevada mountains was primarily due to local/regional use of these chemicals in the Californian central valley. In this case, regional atmospheric transport provides the source of these chemicals to the high-altitude environment of the Sierra Nevada, where precipitation in the form of snow, coupled to the colder temperatures, is likely to result in pesticide accumulation in this environment.

Seasonal snowmelt may also result in re-emission of SVOCs from old snow back to the atmosphere but will importantly result in their release to meltwater and subsequently to catchment systems. During snowmelt, water is primarily lost from the snowpack by drainage and sublimation (Wania, 1997). At the start of snowmelt, liquid water released into the snowpack is generally retained in situ by capillary action and damming at the bottom of the snowpack (Wania, 1997). Once the snowpack water content increases to approximately $0.1 \text{ m}^3 \text{ m}^{-3}$ then substantial draining occurs (Bergstrom, 1975). During snowmelt the fate of organic contaminants present in the snow is largely dictated by the physical-chemical properties of the chemical; namely, solubility but also $K_{oa}$ and $K_{ow}$ may play roles in the repartitioning of SVOCs between meltwater/air spaces and particles originally present in the snow. Furthermore, a chemical with a relatively high $H$ such as HCB may also be lost via volatilization from the meltwater during the melting process. In contrast, for a chemical with a relatively high water solubility such as $\gamma$-HCH, a large fraction ($\sim 97.6\%$) is predicted to be released with the draining meltwater (Wania, 1997). There is large uncertainty with respect to the fate of SVOCs during snowmelt, but the limited observations in the field supported by modeling work suggest an elution order based on chemical solubility. The process of repartitioning to particulate matter and the fate of particle-bound chemicals are similarly unclear. Nevertheless, the findings from surface snowpack studies highlight that contaminant concentrations in fresh snow are not useful estimates of the quantities of chemicals likely to be released to either arctic or alpine catchments during spring melt.

10. Interpreting snow and ice records

Snow and ice cores have been used to evaluate SVOC accumulation in cold environments and have allowed the construction of accumulation time series. For example, Donald et al. (1999) examined the long-term depositional history of OC pesticides within a high-altitude Canadian glacier at Snow Dome Mountain in the Canadian Rocky Mountains. Snow and ice samples, taken within a crevasse, provided time series of every other year from 1959 to 1984 and annually from 1984 to
1995. The results indicated that, for many chemicals, namely ΣDDT, Echlordane, and ΣHCH, the peak deposition fluxes occurred in the 1980–1990s, some 10–20 years later than peak application rates for North America. Interestingly, between 1959 and 1975, the mean ratio of \( p,p' \)-DDT to \( p,p' \)-dichlorodiphenyldichloroethylene (\( p,p' \)-DDE) was 9.1 compared to a ratio of 2.1 during the 1990s. As \( p,p' \)-DDE is the metabolite of \( p,p' \)-DDT, the change in isomer ratios indicates a decline in DDT usage in the 1990s relative to previous decades (Donald et al., 1999). This study serves to illustrate the use of glaciers in providing a time series of depositional fluxes and indicating changes in chemical application rates over time. However, subsequent criticism of the work (Gregor and Peters, 2000) highlighted the points that significant chemical losses may have occurred prior to ice formation and that ice core time series really reflect “accumulation” rather than actual atmospheric deposition. Work detailed in earlier sections of this paper (e.g., Hargrave et al., 1988; Herbert et al., 2005) show that SVOC loss from snow is pronounced following snowfall. This would imply that the chemical composition of snow and/or lower \( K_{ia} \) snow or lower \( H \) values, and the effects of altitudinal fractionation on the chemical composition. Nevertheless, for those chemicals of sufficiently low volatility, ice and snow concentrations may give quantitative estimates of deposition fluxes. However, for chemicals of a higher volatility, measured concentrations in snow and ice may be largely underestimated and thus provide only qualitative indications of trends.

11. Future work

While progress in the measurement of SVOCs in both fresh and aged snow has been made there still remains uncertainty with regard to their snow–air partitioning, their fate following deposition, and the influence of snowmelt on both freshwater and marine systems. Both \( H \) and \( p,p' \)-LFERs have been demonstrated to give useful estimations of \( K_{ia} \) snow, but further refinement is required for their use in estimating \( K_{ia} \) snow values for SVOCs at subzero temperatures. This, coupled with a greater understanding of the dominant snow–air partitioning processes at relevant temperatures, will ultimately result in more accurate estimates of snowpack contaminant burden. This is of particular relevance for understanding chemical transfer and fate over large snow-covered areas such as the polar regions.

There is evidence to support rapid changes in snow contaminant concentrations with snow ageing, whereby SVOC concentrations decline over a relatively short time period (days). While such processes have been identified, further work is required to make a quantitative assessment of post-depositional behavior and relate this to particular physical–chemical properties such as \( K_{ia} \) snow or \( H \). Further knowledge in this area will allow quantitative assessments of chemical supply to the atmosphere, which may help to resolve issues such as the “spring-pulse” hypothesis, whereby elevated air concentrations have been observed following spring melt in temperate regions of Canada (Gouin et al., 2002). To date, modeling studies have provided the best insight into the release of SVOCs from a melting snowpack, with only limited observational data on chemical fate during snow/ice melt. Further work is required to help validate and improve current snowmelt models.

The atmosphere and long range atmospheric transport (LRAT) are viewed as the major sources of POPs to polar regions, but regional/local atmospheric transport may also provide significant quantities of CUPs to temperate mountain regions that are located close to agricultural and industrialized areas. The high-altitude snowpack is likely to provide a temporary sink for these
chemicals, and new field studies are required to assess the risk posed to upland catchments for both parent pesticide and potential degradates.

Acknowledgments

This work was supported by NERC Grant GR3/12930. BMJH is supported by NERC studentship NER/S/A/2001/06245.

References


Arctic Monitoring Assessment Program (AMAP), 2004. Assessment Report II, Oslo, Norway (chapter 2).


