



Diffusion of VOC
through snow

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Diffusion of volatile organics through porous snow: impact of surface adsorption and grain boundaries

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Abstract

Release of trace gases from surface snow on Earth drives atmospheric chemistry, especially in the polar regions.

The gas-phase diffusion of methanol and of acetone through the interstitial air of snow was investigated in a well-controlled laboratory study in the temperature range of 223 to 263 K. The aim of this study was to evaluate how the structure of the snowpack, the interaction of the trace gases with the snow surface, and the grain boundaries influence the diffusion on timescales up to 1 h.

The diffusive loss of these two volatile organics into packed snow samples was measured using a chemical ionization mass spectrometer. The structure of the snow was analyzed by means of X-ray computed micro-tomography. The observed diffusion profiles could be well described based on gas-phase diffusion and the known structure of the snow sample at temperatures ≥ 253 K. At colder temperatures surface interactions start to dominate the diffusive transport. Parameterizing these interactions in terms of adsorption to the solid ice surface, i.e. using temperature dependent air–ice partitioning coefficients, better described the observed diffusion profiles than the use of air–liquid partitioning coefficients. No changes in the diffusive fluxes were observed by increasing the number of grain boundaries in the snow sample by a factor of 7, indicating that for these volatile organic trace gases, uptake into grain boundaries does not play a role on the timescale of diffusion through porous surface snow.

In conclusion, we have shown that the diffusivity can be predicted when the structure of the snowpack and the partitioning of the trace gas to solid ice is known.

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1 Introduction

1.1 Environmental relevance

Snow cover on the Earth's surface is of significant environmental importance (Bartels-Rausch et al., 2012a). For example, the Arctic surface snow can hold a high concentration of volatile organic molecules (Shepson and Sumner, 1999). Snow also covers large parts of the Northern Hemisphere in winter and high concentrations of volatile organics have been found in such surface snows (Kos and Ariya, 2010). Both in the Arctic, where volatile organics in snow are investigated as photochemical products, and in non-polar regions, where volatile organics mostly originate from biological soil emission (Swanson, 2005; Groffman et al., 2001) or from polluted air masses (Kos and Ariya, 2010), the fluxes between the snow and the air might impact air quality and climate change (Seok et al., 2009; Domine and Shepson, 2002; Grannas et al., 2007).

At low wind conditions, fluxes between the porous surface snow and the overlaying atmosphere are driven by diffusion through the interstitial air (Domine et al., 2008). Diffusion describes the transport of gases in a single-phase system driven by a concentration gradient and its rate is given by the diffusion coefficient or diffusivity. In porous materials, such as surface snow, diffusive transport through the open space (i.e. gas phase) is generally described by an effective diffusivity in the two-phase sample (Schwarzenbach et al., 2003). In Eq. (1), the effective diffusivity (D_{eff}) is described by the gas-phase diffusion coefficient (D_{air}), the free volume in the porous material (porosity, ρ), and the microscopic shape of the pores (tortuosity, τ). For trace gases that interact with the surface of the porous material by surface adsorption, the gas-solid partitioning coefficient (K_j), the ice- to air volume ratio (r_{sp}), and the specific surface area SSA are additionally included in the parameterization of D_{eff} (Herbert et al., 2006a; Schwarzenbach et al., 2003; Domine et al., 2008). The effective diffusivity of any gas can thus be calculated based on known gas-phase diffusivity, microstructure

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of the porous medium and sorption characteristics.

$$D_{\text{eff}} = D_{\text{air}} \times \frac{\phi}{\tau} \times \frac{1}{1 + r_{\text{sp}} \times K_i \times \text{SSA}} \quad (1)$$

In polar and subalpine snow or firn, the above correlation between the structure and the effective diffusivity has been empirically confirmed for non surface interacting gases such as CO₂, CH₄, O₂, and SF₆ (Fabre et al., 2000; Schwander et al., 1993; Seok et al., 2009). Going one step further, Pinzer et al. (2010) have recently carefully verified the structure–diffusivity relationship for NO by bringing together precise structural information gained from X-ray computed tomography with observed effective diffusivities in well-defined laboratory experiments.

1.2 Diffusion and surface interaction

Pinzer et al. (2010) have further confirmed that species that interact strongly with ice surfaces, such as HONO (Chu et al., 2000; Kerbrat et al., 2010; Bartels-Rausch et al., 2002), exhibit a much lower effective diffusivity. The effective diffusivity at temperatures of 250 to 270 K is 2–3 orders of magnitude smaller for HONO compared to non-interacting gases such as NO and NO₂. The authors found that the lower effective diffusivity could be directly linked to HONO's strong air–ice partitioning coefficient. This finding of slow gas transport of interacting gases in snow is in agreement with a number of earlier field observations on the diffusion of SO₂ (Choi et al., 2000), volatile- (Helmig et al., 2009), and semi-volatile organics (Herbert et al., 2006a,b). For example, Herbert et al. (2006a) found that the effective diffusion of semi-volatile organics scaled with their tendency to stick to snow surfaces. However, in these field studies temperatures approached (and even exceeded) the melting point of ice and consequently the snow held liquid water. Even the presence of a small fraction of liquid in wet snow can significantly modify the trace gas–snow interaction, as both adsorption to the solid ice surface and dissolution into the liquid fraction might occur simultaneously (Choi et al., 2000; Bartels-Rausch et al., 2012b). Consequently, it was found that using the air–ice

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partitioning coefficient to model transport of semi-volatile organics in snow largely underestimated the diffusivities, questioning the application of these gas–solid partitioning data to derive the effective diffusivity for such wet snows (Herbert et al., 2006a,b). The authors suggest that the air–water partitioning might dominate the interaction and that the gas–liquid partitioning coefficient (i.e. Henry’s law coefficients) might be better suited to describe diffusion in snow even at temperatures well below the melting point. However, no direct measurement of the effective diffusivity was made in these studies and so the validity of using Henry’s law coefficients has yet to be determined.

The suggestion that the air–liquid partitioning might be of importance for the interaction of trace gases with snow even in absence of liquid is often motivated by the increasing recognition that, at temperature approaching the melting point, the air–ice interface is disordered at a molecular level (Bartels-Rausch et al., 2012b). The surface disorder triggers two key-questions that are a topic of on-going controversy in atmospheric and cryospheric science (Knight, 1996b; Baker and Dash, 1996; Knight, 1996a; Bartels-Rausch et al., 2012b). Does the surface disorder change the interaction with trace gases compared to a more rigid surface at colder temperatures? And, does it interact with trace gases in a similar way than liquid water would? In their pioneering work, McNeill et al. (2006, 2007) addressed the first question and concluded that surface disorder on ice changes the uptake of trace gases, i.e. HCl, drastically: instead of a short-term and limited uptake as typically observed for surface adsorption of trace gases to ice, a long-lasting uptake regime was observed on ice samples that showed a pronounced surface disorder. These results imply that uptake in the presence of surface disorder is based on fundamentally different processes compared to adsorption to solid surfaces and thus calls for a specific parameterization. Even though the surface disorder is not a true liquid and has distinctly different structural properties from a liquid (Bartels-Rausch et al., 2012b), its existence is often used to justify the use of air–water partitioning coefficients to parameterize the interaction of trace gases with ice surfaces or with snow at temperatures well below the melting point (Thomas et al., 2011).

The first aim of this study was thus to determine the extent to which sorption processes impact the diffusion of volatile organics through a dry snowpack. By comparing observed diffusivities to simulations based on the air–liquid partitioning coefficients and on the air–solid partitioning the focus is placed on the question concerning which of the two parameterisations is superior to describe the interaction of trace gases with snow. A previously developed experimental set-up that allows the diffusion of trace gases into artificial snow samples to be quantified was used (Pinzer and Schneebeli, 2009; Pinzer et al., 2010). A key feature is that the structure of the snow is analysed in detail using X-ray computed tomography (Kerbrat et al., 2008).

1.3 Surface interaction and grain boundaries

Grain boundaries are defined as contact area between individual ice grains. Diffusion along grain boundaries is naturally faster than diffusion through ice crystals (Thibert and Domine, 1997; Huthwelker et al., 2006) and diffusion into the volume that they enclose might possibly be another explanation for the observed long-lasting uptake of trace gases to ice and snow (Huthwelker et al., 2006; Kerbrat et al., 2010; Bartels-Rausch et al., 2012b). Indeed, Kerbrat et al. (2010) observed a significant diffusive bulk uptake of HONO into polycrystalline ice that increased the overall uptake of HONO to snow at temperatures $\geq 240\text{K}$. In contrast, in experiments with natural snow samples – which tend to be composed of single crystal snow grains and thus have a low grain boundary density – no bulk uptake was detected (Pinzer et al., 2010). The authors argued that the difference in the grain boundary content might explain the different long-term fate of HONO for the two samples, but conclusive results could not be drawn as a detailed analysis of the grain boundaries was lacking. Additional uncertainty comes from the use of two different experimental techniques, a snow diffusion experiment – as used in this study – for the natural snow, and a packed bed flow tube study for the polycrystalline snow.

In this light, a second aim of this study was to explore whether or not the effective diffusivity of a trace gas is reduced in samples that have an artificial high amount of

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grain boundaries, but else similar geometric properties. To do this, we took advantage of recent, in-detail characterisations of grain boundaries in snow samples (Riche et al., 2012b,a).

1.4 Affinity of trace gases to snow

5 In this study, acetone and methanol were chosen to investigate the diffusivity in snow and the impact of grain boundaries. First, both are of environmental significance, because volatile organics are an important source of atmospheric HO_x radicals. Second, the surface adsorption has been studied for both compounds in great detail in laboratory experiments and molecular dynamics simulations (Starr et al., 2011; Hammer
10 et al., 2009; Abbatt et al., 2008; Hantal et al., 2008; Bartels-Rausch et al., 2005, 2004; Peybernès et al., 2004; Guimbaud et al., 2003; Hudson et al., 2002; Winkler et al., 2002; Marinelli and Allouche, 2001; Picaud and Hoang, 2000; Jedlovszky et al., 2006; Collignon and Picaud, 2004; Domine and Rey-Hannot, 2002; Behr et al., 2006). These studies give a sound basis for investigating the role of surface adsorption on diffusive
15 transport in snow. Third, molecular dynamics studies show that methanol is preferentially incorporated into the upper ice surface region at temperatures of 250 K, while at lower temperatures it exclusively stays on the surface (Collignon and Picaud, 2004). Molecular dynamic simulations at such high temperatures have not been done to study the acetone adsorption. Intuitively, one would expect that the larger acetone is less well
20 taken up into the ice compared to the smaller methanol. Taken together, these results indicate that methanol uptake might be more affected by bulk uptake than that of acetone. In these study, both trace gases were dosed simultaneously to the same snow sample to directly compare how the long-term interaction with ice impacts diffusion.

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2 Experimental method

The experimental set-up has been adapted from Pinzer et al. (2010) and is illustrated in Fig. 1. Central to the experimental procedure is that trace gases are passed over a snow sample and their slow diffusive loss into the porous snow sample is monitored using a chemical ionization mass spectrometer.

2.1 Sample preparation and characterisation

Two types of artificial snow were used in this work: one type, which we refer to as snow-maker snow, was prepared by exposing thin nylon wires to water vapour in a cold room at 248 K (Löwe et al., 2011). Sublimation of de-mineralized water kept at 303 K produced the required water fluxes. Its production thus mimics how snow flakes nucleate in the atmosphere. The produced snow was stored for 6 weeks at 268 K. The accelerated sintering and isothermal metamorphism during this storage resulted in small rounded grains. For the other snow type, hereafter shock-frozen snow, small ice spheres were rapidly frozen by spraying ultra pure water (MilliQ quality, 0.05 μ S) into liquid nitrogen. The initially amorphous samples were annealed at least for 10 days at 243 K, during that time their appearance changed from milky-white to shiny-clear indicating that crystallization had occurred. Samples were prepared from either snow type by sieving the snow to a fraction of 500–600 μ m in diameter, filling it into the sample holder – referred to as the snow diffusion chamber (Sect. 2.2), and purging over night with a stream of nitrogen in order to minimize contamination with volatile organics. This handling was done in a freezer at 243 K and the purge gas was humidified to the vapour pressure over the snowpack sample. Prior to use, the purge gas was disconnected and the gas inlet on the snow diffusion chamber was sealed.

The porosity and surface area of the snow in the snow diffusion chamber were extracted by image processing from X-ray computed micro-tomography reconstructions derived on a Scanco μ CT80 (Kerbrat et al., 2008; Pinzer and Schneebeli, 2009; Riche et al., 2012b,a). For this, the sample was sieved to a fraction of 500 to 600 μ m in

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diameter, stored in a closed glass vessel for 1 day, and filled into a cylindrical to-
mography sample holder (0.4 × 8 cm) to create the porous snow sample. Before the
X-ray computed micro-tomography, the snow-maker samples were stored at 243 K for
1 week, the shock-frozen samples at 254 K for 3 weeks. The tortuosity was calculated
5 based on this microstructure by a finite element simulation of the temperature field in
porous snow samples, as described by Kaempfer et al. (2005). The grain boundaries
of the shock-frozen samples were analysed using a stereological method (Riche et al.,
2012b). For these measurements the structure of the porous snow samples was fixed
with diethyl phthalate. Then, in a walk in cold room at 253 K, thin sections of 1 to 2 cm²
10 and 150 μm thickness were cut, and analysed under a polarized microscope.

2.2 Experimental set-up

Acetone and methanol concentrations of 1×10^{11} molecules cm⁻³ and $2 \times$
 10^{11} molecules cm⁻³ respectively were simultaneously dosed to the headspace
of the snow diffusion chamber by passing a carrier gas (N₂, Carbagas, 99.999 %) over
15 permeation tubes (VICI dynamical) inside a permeation oven (VICI dynacalibrator).
Flows of the carrier gas were controlled by mass flow controllers (Brooks 5850) or flow
regulators (Voegtlin red-y) with an accuracy of 1 % or better. Before entering the snow
diffusion chamber, the gas flow was cooled to the temperature of the snow sample
and humidified by passing it over an ice surface so that the dew point of water in the
20 gas flow matched the temperature of the snow sample. Additionally, traces of NO were
dosed to the carrier gas.

The loss of methanol and acetone from the carrier gas and the time profiles for
their recovery were the main observables of this study. Methanol and acetone were
detected using a chemical ionization mass spectrometer, previously described (Ulrich
25 et al., 2012; Bartels-Rausch et al., 2005). Water clusters from a Po-210 source or from
a corona discharge served as ionization reagents at 20 mbar pressure. Methanol and
acetone were detected as their positively charged water clusters. The NO concentration

profile was recorded simultaneously to the mass spectrometry data by means of a chemiluminescence analyser (eco physics).

The central part of the experiment was the snow diffusion chamber: a gas-tight, cylindrical sample holder that is made entirely of polytetrafluoroethylene (PTFE) teflon and consists of two parts. The upper part serves as empty headspace with the gas dosing and exit. It has a volume of 20 mL and the carrier gas passes through it at atmospheric pressure with a flow rate of 160 mL min^{-1} (given at standard temperature and pressure). Below that, the porous snow sample fills a total volume of 96 mL. This $\approx 10 \text{ cm}$ deep porous snow sample has contact to the gas in the headspace with an area of this interface of $\approx 10 \text{ cm}^2$. The entire snow diffusion chamber rests inside a temperature regulated thermo-jacket. Neither methanol, nor acetone showed any retention in the empty sample holder down to 223 K.

2.3 Diffusion profiles

The loss of either trace gas from the carrier gas and the time profile of recovery were the main observables of this study. To derive these recovery profiles, the signal intensity in the absence of methanol and acetone was recorded for 15 min (background), then the intensity in presence of both organics and with the sample holder and headspace by-passed for 30 min (full intensity), then the flow was passed via the sample holder for 60 min, followed by measurements of the full intensity and of the background. Any drifts in the background or in the full intensity signal were corrected by fitting the respective traces. The data shown in this work are averages of 2–3 individual experimental runs. NO does not interact with the ice surfaces and its diffusion behaviour has been well characterized (Pinzer et al., 2010). Its profiles were carefully examined to identify and discard experiments where systematic errors such as small leaks in the sample holder, or cracks in the snowpack sample occurred.

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2.4 Simulation

To derive the diffusive loss of volatile organics from the headspace into the snowpack sample, a numerical simulation was used. For non-interacting species, the term $1/(1 + r_{\text{sp}} \times K_i \times \text{SSA})$ in Eq. (1) is negligible and Pinzer et al. (2010) have developed an analytic solution to the one dimensional diffusion problem into a finite volume (Fick's second law)

$$\frac{\partial c}{\partial t} = D_{\text{eff}} \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where c is the concentration of trace gas in the interstitial air of the porous snow sample. The analytic solution was successfully used to describe the loss of NO and NO₂ from the headspace into the porous snow sample (Pinzer et al., 2010). However, it is only applicable if the flux into the snow is small, because a constant gas-phase concentration at the snow air interface at $c(x = 0)$ was employed as boundary condition.

For the general case of strong uptake to the ice, the gas-phase concentration in the headspace drops rapidly when the carrier gas is first routed through the snow diffusion chamber. This is due to fast adsorption to the top surface of the porous snow sample; eventually the gas-phase concentration in the headspace relaxes back to equilibrium. Thus, the approximation of a constant boundary condition cannot be applied. Instead, we treat the full flux balance in the headspace numerically. The flux balance is given by

$$c_0 \times F = c_{\text{out}} \times F + j_{\text{diff}} \times A. \quad (3)$$

Here, c_0 is the concentration of trace gas entering the headspace with the carrier gas, c_{out} is the concentration of trace gas in the carrier gas at the exit of the headspace, F is the gas flow through the headspace, A is the cross-section area of the snow cylinder, and j_{diff} is the diffusion flux into the porous sample. We assume ideal mixing in the headspace volume, so that the concentration right above the snow equals c_{out} . This assumption seems well justified, because the total flux of trace gases from the

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headspace to the snow sample rarely exceeds 20%. With the diffusion flux through a porous medium as given in Eq. (2) (Schwarzenbach et al., 2003), Eq. (3) can be rearranged to yield the boundary condition at the snow–air interface:

$$c_0 \times F = c(x = 0) \times F - A \times \phi \times D_{\text{air}} \frac{\partial^2 c(x = 0)}{\partial^2 x}. \quad (4)$$

Calculations and analysis were done with MATLAB.

3 Results

3.1 Diffusion profiles

We first studied the diffusive transport of the volatile organics acetone and methanol through a snow-maker snow sample, the freezing process of which mimics nucleation of ice crystals in the atmosphere. Figure 2 shows the primary observable of these experiments, the mean experimentally observed recovery profiles. The observed profiles of individual experimental runs at each temperature were almost identical: the standard deviation of the three individually measured recoveries at 10 min, 30 min, and 60 min were around 10% or better. The reproducibility of the experiments at 243 K was with $\approx 1\%$ significantly better and the scatter in the profiles much less pronounced, because different ionization conditions in the mass spectrometer were used that improved the signal to noise ratio.

The first observation is that the gas-phase concentrations in the headspace recover quickly indicating that the overall losses from the overlaying gas phase by gas-phase diffusion into the porous snowpack are small, and have a pronounced temperature dependence. At 263 K the observed profiles show, within the reproducibility of 10%, an immediate recovery to the initial gas-phase concentration of acetone and methanol and resemble thus the profiles of NO (Pinzer et al., 2010), a trace gas that does not interact with the ice surface at those temperatures (Bartels-Rausch et al., 2002). Similar

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fast recoveries have been observed at 253 K (data not shown). This indicates that under these warm conditions, diffusion through the dry snowpack is fast for both volatile organics. Given the small air volume of 55 cm³ in the porous snow sample, the concentration gradient is eliminated rapidly and diffusion from the carrier gas stops.

The effective diffusive loss into the snowpack is significantly enhanced at cold temperatures for both acetone and methanol and at the lowest temperature studied (223 K) neither volatile organic fully recovers during the course of this experiment. The observed slower diffusive transport is driven by air–ice interactions of either trace gas. First, recovery profiles of non interacting trace gases, such as NO, do not show such a strong temperature dependence (Pinzer et al., 2010). Second, methanol recovers slower than acetone, which is consistent with its stronger interaction with ice (Crowley et al., 2010).

3.2 Simulation – Langmuir vs. Henry

To extract more quantitative data from the experiments, the observed recovery profiles were compared to simulations based on the snow sample's porosity and tortuosity, as well as on the specific interactions of methanol and acetone with ice as given in Eq. (1). Table 1 lists calculated values of the effective diffusivity for acetone and methanol through the porous snow samples at 243 K. In this particular sample, the effective diffusivity is slower than the diffusivity in air by a factor of 50 or more. For this calculation, and the simulations shown in Fig. 2, the gas-phase diffusion constants were taken from Winkelmann (2007b,a) and extrapolated to the temperature of the experiment based on the reported temperature dependence of methanol gas-phase diffusion (Winkelmann, 2007a); K_{LinC} and their temperature dependence were taken from Crowley et al. (2010); r_{sp} was calculated based on the porosity and the snow density as measured in this study and given in Table 2. Also shown is the uncertainty in the simulation results (Fig. 2 and Table 1). The uncertainty was assessed by repeating the calculations taking the published error range of K_{LinC} (Crowley et al., 2010) as input and changing the other input parameters by 10 % each.

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The results show that acetone recoveries are very well captured and follow the simulations closely (Fig. 2). One exception is data at 223 K where the mean of the experimental runs lies on the lower edge of the simulation. Given the uncertainties of the experimental results and in the simulation, the agreement is good. Methanol shows a very good agreement except at 263 K, where the observed recovery is faster than the simulation and also compared to the recovery of NO. This is presumably an artifact by the ionization schemes in the mass spectrometer. Release of methanol from potentially contaminated samples was excluded as a reason for these high recoveries.

Two conclusions can be drawn. First, surface interactions have a strong impact on diffusive transport through the open pore space of dry snow and dominate the diffusivity at temperatures where adsorption equilibrium predicts a significant surface concentration. Second, the Langmuir coefficient, used to parameterize the reversible surface adsorption of trace gases to ice, describes the interaction of trace gases with the ice surface during diffusion well.

We also simulated the diffusive loss into the dry snowpack based on the reversible uptake to a liquid layer covering the surface of the individual ice spheres using Henry's law air–water partition coefficients. The results of these simulations are compared to the observed recovery profiles in Fig. 3. Such an approach is often used in current snow chemistry models to parameterise air–snow exchanges with dry snow (Thomas et al., 2011; Bartels-Rausch et al., 2012b). As shown in Fig. 3, the air–liquid partitioning is not suited to describe the observed recovery profiles at temperatures at and below 243 K. For these simulations, the distribution of the volatile organics between ice and air was parameterized as uptake into a 1–30 nm thick liquid covering the total specific surface area of the snow sample. Henry's law coefficients were taken from Snider and Dawson (1985) and extrapolated to the temperatures of the snow sample. The calculations reveal that at 263 K the results are invariant to the simulations based on the air–ice partitioning coefficient, as both results show a negligible influence of partitioning to the snow surface on the diffusive transport (Figs. 2 and 3). At colder temperatures the simulations based on Henry's law coefficients predict faster recoveries than observed

for acetone, but even more so for methanol (Fig. 3). At 223 K Henry's law coefficients still predict a negligible influence of partitioning to the snow surface for the diffusion of both methanol and acetone.

From this we conclude that the surface interaction with dry snow during the diffusive process can be better described as air–solid partitioning at temperatures up to 263 K. This conclusion is in-line with a number of earlier measurements that determined the reversible adsorption of volatile trace gases to ice and showed that the interaction of trace gases with ice is generally well described by a air–solid partitioning constant at temperature up to ≈ 240 K and for some species, such as HONO, even up to 260 K (Crowley et al., 2010). To describe interactions with ice surfaces based on properties of liquid water is very controversially discussed (Bartels-Rausch et al., 2012b). Our results show that parameterizing the ice surface with properties of a super-cooled solution is indeed an over-simplification. For dissolution into the disordered interface at the ice surface to be an important factor, the volume of this interface needs to be large enough to accommodate significant amounts of solutes and the solvation mechanism needs to be similar to that of liquid water. Current investigations of the thickness of this disordered interface give no conclusive picture, but most agree that it is a few tens of nm at most at temperatures below 263 K (Bartels-Rausch et al., 2012b). It has been argued that strong acids enhance the thickness of the disordered interface significantly and that this might provide a feedback that enhances the uptake (McNeill et al., 2006, 2007). Similar processes might also operate during the adsorption of volatile organics. However, recent direct surface sensitive observations of the structure of water molecules upon adsorption of volatile organics, such as acetone and acetic acid, clearly showed that at temperatures of 243 K the thickness of the disordered interface is not significantly increased, as those measurements give no indication that the thickness is larger than a few nm upon adsorption of these organic traces (Starr et al., 2011; Krepelova et al., 2013). These surface sensitive studies further clearly show that the adsorbed volatile organics remain on the surface of the ice and do not enter deep into the crystal structure. Based on depth profiles of carbon (from acetic acid) in the

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ice surface, Krepelova et al. (2013) showed that acetic acid does not reach depths deeper than 2 nm and concluded that reversible surface adsorption describes this situation well. Concluding, this study gives clear evidence that – at temperatures where the surface disorder is thin – air–liquid partitioning does not adequately describe the interaction with the ice surface. That the interaction of many volatile organics with ice is a purely surface process is supported by surface sensitive spectroscopy that give no indication for dissolution of acetic acid in the ice. An exception for this adsorption dominated interaction is formaldehyde. Barret et al. (2011b) have shown that this small organic trace gas forms solid solutions with ice and that this solution equilibrium with the ice crystal can explain observed formaldehyde exchanges between the air and the surface snow in the Arctic Barret et al. (2011a).

At temperatures approaching the melting point, but low enough to prevent (partial) melting, the surface interaction of these volatile organics is too small to significantly impact the diffusion in dry snow and this is reflected by both parameterisations.

3.3 Impact of grain boundaries

To study the effect of grain boundaries on the diffusion of trace gases through porous snow, experiments were performed with a second type of snow sample with a very high grain boundary content. Figure 4 shows the morphology of the shock-frozen snow as viewed under a polarization microscope. The contact area between individual ice spheres per volume of the snow sample, hereafter specific grain boundary area, adds to $2 \text{ mm}^2 \text{ mm}^{-3}$ (Riche et al., 2012a). Additionally, about 60–70 % of those spheres consist of several smaller ice crystals so that the total specific grain boundary area equals $10 \text{ mm}^2 \text{ mm}^{-3}$ (Riche et al., 2012a). In contrast, natural snow freezes by condensation of vapour in the gas phase and individual snow spheres are always single crystals (Riche et al., 2012b). The snow-maker snow used in this study was not analysed for its grain boundary content, but we argue that it is also composed of single crystals and the total grain boundary area is only given by the contact area between individual ice grains. Based on the measured contact area of ice spheres in the shock-frozen snow

and accounting for the lower density of snow-maker snow (Table 2), one can estimate a total specific grain boundary area of $1.5 \text{ mm}^2 \text{ mm}^{-3}$. Using this estimate, the specific grain boundary area in the two snow samples differs by a factor of 7.

The impact of this large difference in grain boundary content on the diffusion of methanol and acetone through dry snow is shown in Fig. 5. Here, the experimental recovery profiles are plotted as a ratio snow-maker/shock-frozen snow, for three temperatures. Figure 5 clearly shows that a larger grain boundary content does not enhance the interaction of methanol and acetone with the ice phase during diffusion through porous snow. The recovery profiles over packed shock-frozen, polycrystalline ice spheres agree within 10 % to the recovery profiles over snow-maker snow. That is, the plotted ratio in Fig. 5 lies within the 90–110 % interval. A better agreement of the observed profiles was not expected, as the samples differed slightly in surface area and microstructure (Table 2). This negligible impact of grain boundaries in dry snow holds for temperatures spanning 263 K to 223 K. In principle, grain boundaries have the potential to impact the uptake of trace gases in two ways. First, the microscopic surface structure differs at grain boundaries from the free surface and this may directly impact the adsorption equilibrium, i.e. by providing sites of energetically preferred adsorption (Donaldson et al., 2012). For example, McNeill et al. (2007) have observed two different adsorption modes for ice samples with varying grain size and have suggested that a particular reversible adsorption mode takes place at grain boundaries. Second, grain boundaries may also provide a channel through which adsorbates can diffuse rapidly away from the surface (Thibert and Domine, 1997) and which may serve as long-term reservoirs for adsorbates (Huthwelker et al., 2006).

Our results show that for acetone, the number of grain boundaries in the sample affects neither the short-term nor the long-lasting uptake. This finding is in agreement with results from earlier experiments of our group, where the adsorption of acetone to single crystalline ice and polycrystalline ice was investigated in a packed bed flow tube (Bartels-Rausch et al., 2005). This study verifies this conclusion and expands it to warmer temperatures and longer time scales, where diffusive processes become

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increasingly dominating (Kerbrat et al., 2010) and by using a well characterized snow sample. The earlier experiments were done in the temperature range of 198 K to 223 K, and lasted approximately 20 min. Further support for the irrelevance of grain boundaries for short-term adsorption comes from molecular dynamics calculations that have shown that interaction of acetone with the neat ice surface is energetically more favourable than the interaction with ice at grain boundaries (Hammer et al., 2009).

The interaction of methanol with different types of ice has not been investigated before. Results from a molecular dynamics study indicate that methanol adsorbs to ice by forming hydrogen bonds at the surface at 210 K and by dissolving into the upper water molecule layers of the ice crystal at 250 K. Given that a “dissolved” molecule may diffuse more easily into grain boundaries, one would have expected different recovery profiles of methanol on the two types of snow in our experiments. However, the results presented here show that even for this highly soluble molecule with its rather small size, surface adsorption dominates its interaction with polycrystalline ice on time scales of one hour. Concluding, solid-phase diffusion into grain boundaries does not impact the gas-phase transport of acetone and methanol and probably other volatile organics through a porous snow on timescales relevant for diffusive transport. This conclusion might not hold for those species that easily diffuse into the ice lattice and form solid solutions there. For those species, for example formaldehyde, air–snow exchanges can be dominated by diffusion and uptake into the bulk ice (Barret et al., 2011a,b). It would be interesting to study, if these molecules with their high affinity for solid-state diffusion dominates the interaction with snow on timescales relevant for diffusive transport.

4 Conclusions

In this study the diffusive transport of methanol and acetone into porous snow was investigated by monitoring the concentration of the two gases in the air above a dry snow sample.

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- At temperatures above 243 K diffusion of methanol and acetone into porous snow is fast and identical to that of NO, a gas that does not interact with ice surfaces. At lower temperatures (243 K and 223 K) diffusion of both organics is significantly slowed with methanol diffusing slower than acetone. This trend reflects the tendency to adsorb to ice surfaces.
- The effective diffusivities of both gases, as well as their temperature dependence, can be well described by taking into account the snow geometric properties and surface interactions. Results from our numerical simulations show that surface interactions can dominate diffusivity at low temperatures, and that the air–solid partitioning coefficient describes the reversible interaction with trace gases well.
- By comparing the diffusion profiles of acetone and methanol through porous snow samples which differed in their total grain boundary content, we found that grain boundaries neither enhance surface adsorption nor impede diffusion through the open pore space of snow on the time scales of 1 h.

5 Atmospheric implication

This study shows that the diffusion of acetone and methanol through surface snow under most temperatures typical for the Arctic and the non-polar cryosphere is fast. As a consequence, the release of acetone and methanol from the snowpack to the overlaying air is rapid, ensuring an almost instant exchange with the air masses, where acetone and methanol are important source of radicals (Heard et al., 2006). Further, the fast diffusion limits their residence time in the snowpack and thus the probability for chemistry there. Only under very cold conditions, that may prevail in Antarctica or rarely in the Arctic, will surface adsorption significantly slow the diffusive transport through snow.

More importantly, this study verifies the use of Eq. (1) to predict the diffusivity of these atmospheric trace gases through a snowpack and shows that surface adsorption

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is a key-factor controlling this transport. Knowing the snowpack geometric properties, gas-phase diffusion, and partitioning equilibrium is sufficient to predict the diffusivity.

The air–liquid partitioning does not adequately describe the interaction with dry snow. We propose that this might also be applied to other volatile and, more interesting, semi-volatile species, for which surface adsorption dominates the interaction with snow. It should also apply to surface snow of different microstructure – as long as the snow is dry and liquid water is not present. The interaction of trace gases with wet snow differs significantly from dry snow (Clapsaddle and Lamb, 1989; Herbert et al., 2006b; Bartels-Rausch et al., 2012b).

The (potential) flux of these organic compound into the grain boundaries is too small to impact their diffusive transport in the gas phase, and this will likely also hold for most, larger organic molecules. For other species, such as inorganic acids or formaldehyde, grain boundaries may still present a significant sink (Kerbrat et al., 2010; Huthwelker et al., 2001).

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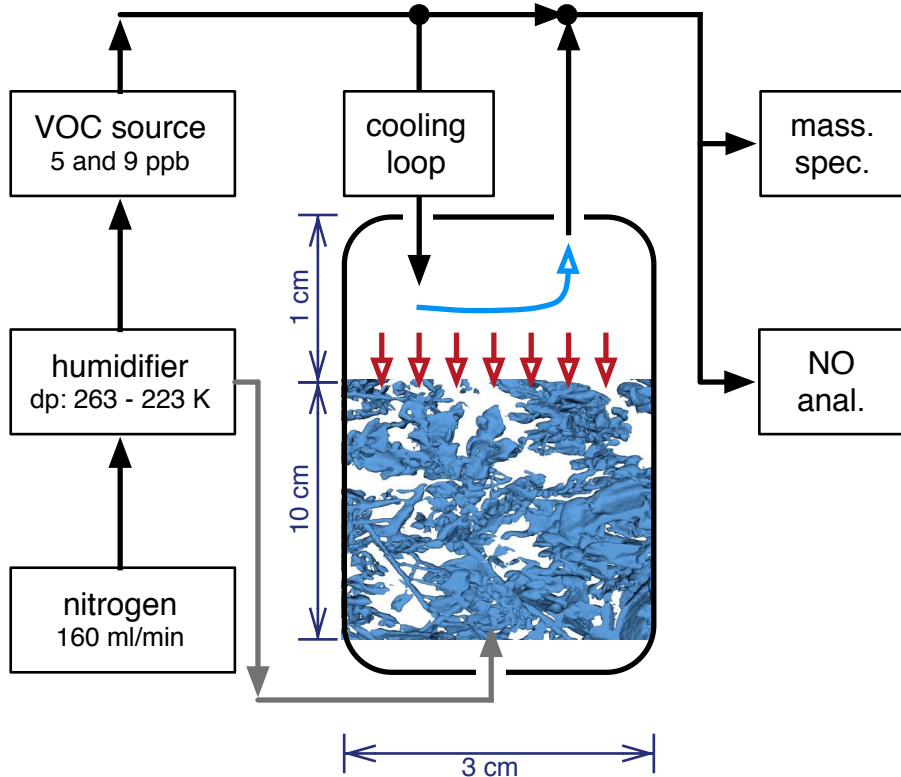


Fig. 1. Illustrative scheme of the experimental set-up showing the snow diffusion chamber. A N_2 flow containing traces of both acetone and methanol is passed over a snow sample (blue arrow). The trace gases diffuse into the porous snow sample from the headspace (red arrows). Before the experiments the sample can be purged to remove volatile impurities (grey arrow). Dew point is denoted as dp, filled circles represent three-way valves.

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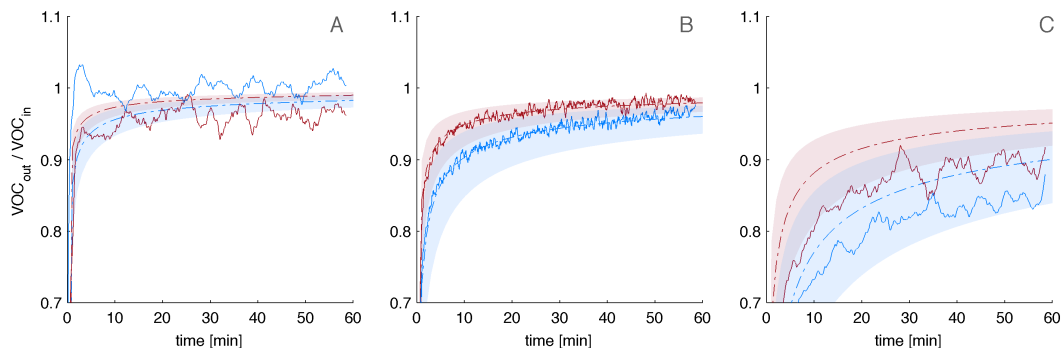


Fig. 2. Mean experimental recovery profiles (solid lines) of methanol (blue) and acetone (red) at different temperatures (**A** 263 K ($n = 3$), **B** 243 K ($n = 2$), **C** 223 K ($n = 3$)) in packed snow-maker snow. Also shown are results from numerical simulations of the recovery (dashed line) with uncertainties (shaded area), where the air–ice partitioning (Langmuir coefficient) was used to parameterize the effective diffusivity.

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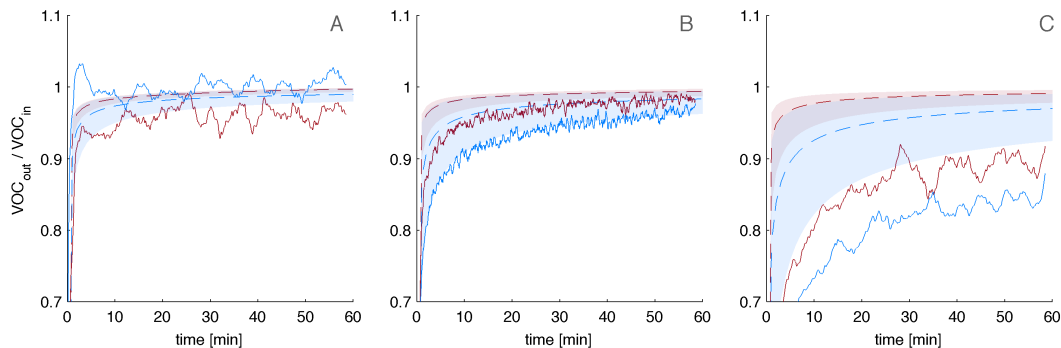


Fig. 3. Experimental recovery profiles (solid lines) of methanol (blue) and acetone (red) at different temperatures (**A** 263 K, **B** 243 K, **C** 223 K) in snow-maker snow. Also shown are results from numerical simulations of the recovery (dashed line) with uncertainties (shaded area), where the air–water partitioning (Henry’s law coefficient) was used to parameterize the effective diffusivity.

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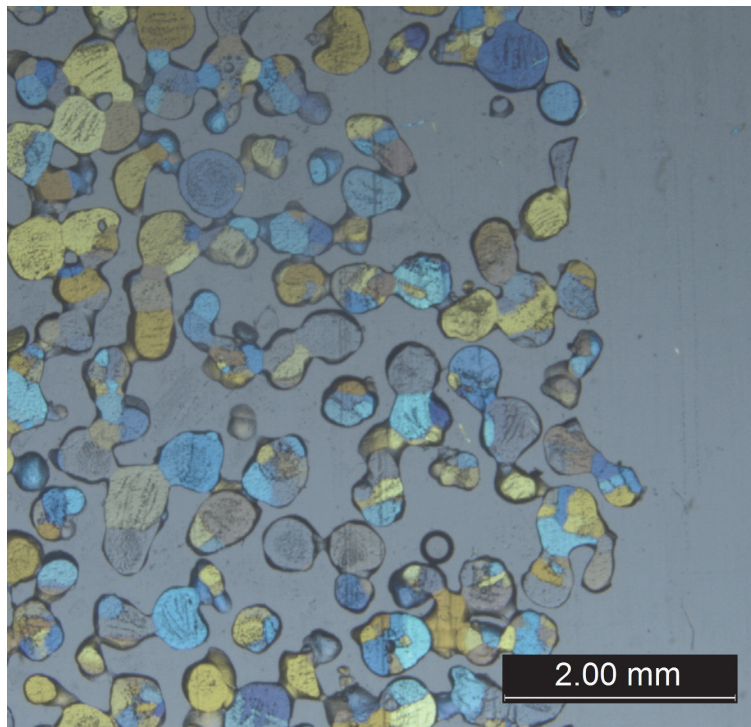


Fig. 4. Thin slice of a polycrystalline ice sample as seen under a polarisation microscope. Coloured areas visualize individual ice crystals. The slice also shows the porosity of the snow sample.

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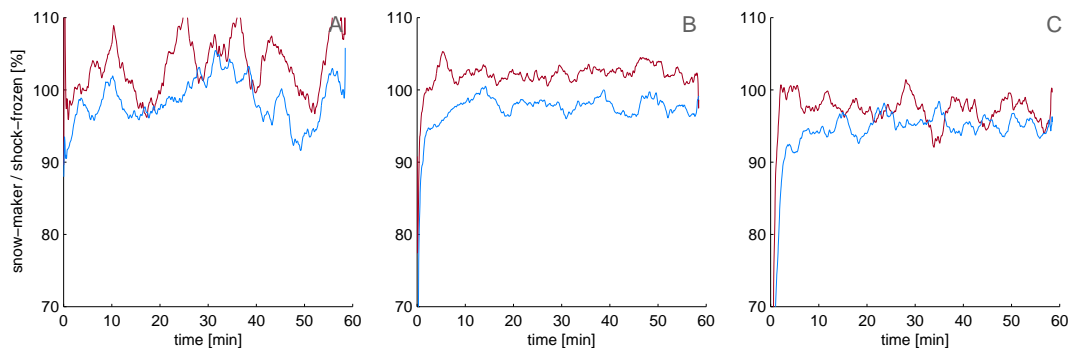


Fig. 5. Comparison of diffusivities in polycrystalline and single crystalline samples. Shown is the ratio of the observed recovery profiles of methanol (blue) and acetone (red) at different temperature (**A** 263 K, **B** 243 K, **C** 223 K) for a single crystalline to polycrystalline samples.

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