



Formaldehyde in Arctic snow. Incorporation into ice particles and evolution in the snowpack

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Abstract

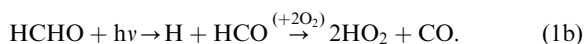
Formaldehyde was measured in the seasonal snowpack near Alert (Ellesmere Island 82.5°N, 62.3°W) during both winter and spring campaigns of ALERT2000. The time evolution of formaldehyde (HCHO) concentrations in fresh snow was monitored. Since snow metamorphism induces evaporation and condensation of both ice and its solutes, the evolution of snow microphysics was also studied. Simultaneous monitoring of the partial pressures of HCHO allowed the estimation of the partitioning of HCHO between the snowpack and the atmosphere. Assuming exchange layer thicknesses of 300 and 14 m during winter and spring, respectively, we calculated that over 80% of the total amount of HCHO in the (exchange layer + snow) system was in the snowpack. Snow is thus an important potential source of HCHO to the atmosphere. The mechanism of incorporation of HCHO in snow crystals must be known to understand its kinetics of exchange with the atmosphere. Tests were performed to determine whether HCHO was adsorbed on the ice surface, or dissolved in the ice crystalline lattice. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Increasing evidence indicates that reactive gases such as formaldehyde and NO_x are emitted from the snowpack to the atmosphere (e.g. Sumner and Shepson, 1999; Honrath et al., 1999; Jones et al., 2001). This partly explains why atmospheric chemistry over snow-covered surfaces cannot be simulated by models using gas-phase processes only (De Serves, 1994; Sander et al., 1997). The photolysis of formaldehyde (HCHO) produces 2 oxidizing radicals, (reaction (1b)) and the contribution of this process to the oxidizing capacity of the atmosphere can be important in polar regions,

where the usual source of OH, production from ozone photolysis, is reduced because of low solar flux and absolute humidity.



The emission of HCHO by snow will thus affect the atmospheric lifetime of numerous species, and determining the physical and chemical processes involved is necessary for an adequate representation of polar tropospheric chemistry. To contribute to this understanding, we have conducted simultaneous measurements of HCHO in the snow and in the atmosphere during the ALERT2000 campaign. Our snow studies focused on surface layers, whose microphysics were also

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studied to elucidate the interplay between physical processes and chemical evolution.

These studies were performed at Canadian Forces Station Alert, Nunavut, Canada (82.5°N, 62.3°W) during two intensive campaigns: the winter (dark) intensive from 31 January to 24 February 2000 and the spring (light) intensive from 8 April to 1 May 2000.

2. Experimental methods

2.1. Snow-phase HCHO analyses

All measurements were conducted from 8 to 20 February (winter campaign) and from 12 April to 1 May (spring campaign). Analyses were performed in the far transmitter building (FTX), located on a plateau approximately 180 m a.s.l. and 5.4 km SW of the Alert base. The main snow sampling site was located 300 m SE of the FTX and is hereafter identified as site A. Sampling was conducted at several spots having similar stratigraphies and within a few meters of each others. Some samples were collected 10 m South of the FTX (hereafter: FTX site).

The snow stratigraphies at site A during the winter and spring campaigns are detailed in Dominé et al. (this issue), and are briefly described here. The thickness, density and mean concentration of each snow layer is reported in Table 1. On 8 February, the layer nearest the ground (layer 1W) consisted of 5–15 cm of depth hoar, i.e. large faceted crystals, often cup-shaped. Above this layer was a hard to very hard (a pencil could not

penetrate it) wind-packed layer 10–25 cm thick (layer 2W). Two recently deposited fresh snow layers were present at the surface of the snowpack. The first one was discontinuous, and was deposited on 3 February (layer 3W) under moderate wind speeds, and formed accumulations in hollows and in the lee of Sastrugi. It was made up of submillimetric columns and bullet combinations, hereafter referred to as diamond dust. Another layer fell on 7 February under calm conditions and formed a continuous diamond dust layer (layer 4W), with most crystals being much smaller than those of the 3 February layer, as detailed in Cabanes et al. (this issue). Surface hoar grew continuously over this layer, until it was wind-blown on 22 February. Surface hoar and the 7 February diamond dust were sampled together, as separate sampling was not possible.

During the spring, the depth hoar (1S) and hard wind-packed (2S) layers observed in the winter (layers 1W and 2W) were still clearly visible, and no visible change in these layer had taken place over 2 months time. A soft discontinuous layer was present above the hard winter layer but was absent in about 20% of the sampling pits (layer 3S). Above this soft layer was a wind-packed layer (layer 4S), not quite as hard as the lower winter layer (a finger could penetrate it with difficulty). For this reason, it will be referred to as a semi-hard layer. Three thin layers were present near the surface. Crystal shapes of the lowest one (loose, layer 5S) suggested that this layer was deposited several days to 2 weeks before our arrival on 8 April (Dominé et al., 2002). The middle layer (layer 6S) was discontinuous and formed an easily breakable crust. These thin subsurface layers were covered by a

Table 1
Total HCHO in the winter snowpack, before 22 February and in the spring snowpack before 25 April, when layer 8S formed (see text)

Snowlayer	Layer number	Thickness (cm)	Density	[HCHO] _{snow} (ppbw)	HCHO snowpack loading (ng/cm ²)	Contribution (%)
<i>Winter Snowpack</i>						
7 February	4W	1	0.08	12.5	1	2.58
3 February	3W	1.5	0.15	8	1.8	4.64
Hard	2W	15	0.48	4.7	33.84	87.32
Depth hoar	1W	8	0.22	1.2	2.112	5.45
Total		25.5			38.8	100
<i>Spring snowpack</i>						
13–14 April	7S	0.3	0.16	6.5	0.31	0.52
Crusted snow	6S	1	0.16	7	1.12	1.86
Loose snow	5S	1.5	0.16	6.5	1.56	2.59
Semi-hard	4S	10	0.4	6.2	24.8	41.24
Soft	3S	5	0.3	6.2 ^a	9.3	15.47
Hard	2S	12	0.48	3.5	20.16	33.53
Depth hoar	1S	8	0.2	1.8	2.88	4.79
Total		37.8			60.1	100

^aNot measured: assumed to be the same as in the semi-hard layer.

thin diamond dust layer (layer 7S), that precipitated in 2 events on 13 and 14 April. This top layer grew in thickness with the progressive formation of surface hoar until it was wind-blown on 25 April. Again surface hoar and the underlying layer were sampled together. Rimed dendritic snow fell between 25 and 28 April (layer 8S), under strong northerly winds.

HCHO was measured every one or two days in surface layers (3W, 4W, 7S and 8S) as rapid exchange of gases can occur with the atmosphere (Hutterli et al., 1999). Measurements were less frequent for aged snow layers, whose concentrations were more stable. To evaluate possible snow heterogeneity, snow was sampled in triplicate. Values reported here are the mean, and error bars are the standard deviations. Snow was collected with a stainless-steel spatula and stored in 100 ml Duran glass bottles with polypropylene caps (Schott, Mainz, Germany), a few hours before being analyzed using DNSAOA derivation with fluorescence detection after HPLC separation of the different aldehyde adducts (Houdier et al., 2000). Formaldehyde concentrations in the snow ($[HCHO]_{\text{snow}}$) are reported in parts per billion by weight (ppbw). The detection limit is 0.3 ppbw or better, and the precision is estimated at 10%.

2.2. Other methods

Gas-phase HCHO measurements were conducted using a continuous flow injection analysis system (Fan and Dasgupta, 1994) as described by Sumner et al. (this issue). Data are reported in parts per trillion by mole (pptv) and are symbolized here as P_{HCHO} . We measured the specific surface area (SSA) of snow by CH_4 adsorption at liquid nitrogen temperature (77.15 K) using a volumetric method, as detailed in Hanot and

Dominé (1999) and Dominé et al. (2001, 2002). In practice, we measured the adsorption isotherm of CH_4 on the snow sample, to which a BET treatment is applied to extract the snow SSA (Dominé et al., 2001). To understand the evolution of the snow SSA, we also studied the changes in snow crystal morphology associated with snow metamorphism, using photomicrographs (Cabanes et al., 2002).

3. Results

3.1. Aged snow layers

Two aged snow layers were observed in February: depth hoar (1W) and hard wind-packed (2W). During spring, two other layers which deposited between winter and spring were classified as aged snow layers: soft (3S) and semi-hard layer (4S). Formaldehyde concentration was not measured in this soft layer.

The formaldehyde concentrations measured in aged layers are reported in Table 2. Concentrations measured in depth hoar (layers 1W and 1S) are spatially homogeneous as shown by the small standard deviations. Winter and spring concentrations are comparable and reinforce the theory that this layer is very homogeneous and stable in time. This is probably due to the depth hoar formation mechanism, in which strong water vapor fluxes (Marbouty, 1980) remobilize and homogenize volatile species. The hard wind-packed layer (2W and 2S) was formed by different precipitation and wind-blowing events (Dominé et al., 2002), which resulted in a high density and low permeability (Albert et al., 2002). This impeded exchanges within this layer and with the atmosphere, likely explains its heterogeneity after two or more months of aging. These

Table 2
HCHO concentrations in aged snow and surface hoar

Snow type	Layer number	Site	Sampling date	$[HCHO]_{\text{snow}}$ (ppbw)	S.D.
Hard	2W	A	9 February	4.7	0.8
Depth hoar	1W	A	10 February	1.2	0.1
Depth hoar	1W	A	13 February	1.4	0.2
Semi-hard	4S	A	13 April	5.9	0.22
Semi-hard	4S	A	13 April	6.2	0.14
Semi-hard	4S	A	20 April	7.5	2
Hard	2S	A	13 April	4.2	0.27
Hard	2S	A	13 April	2.7	0.12
Depth hoar	1S	A	20 April	1.8	0.06
Winter hoar frost	—	Guy wires of antennas	16 February	12.1	0.53
Winter hoar frost	—	Guy wires of antennas	19 February	9.5	0.24
Winter hoar frost	—	Guy wires of antennas	20 February	9.1	0.09
Spring surface hoar	—	Teflon sheet	24 April	6.9	0.44

suggestions are supported by measurements of ions and acetaldehyde (Dominé et al., 2002; Houdier et al., 2002), that are also heterogeneous. Semi-hard layer (4S) concentrations are in the range of 5.9–7.5 ppbw with a large standard deviation, which indicates a spatial heterogeneity caused by the same mode of formation as the hard wind-packed layer. $[\text{HCHO}]_{\text{snow}}$ in aged snow layers was similar in winter and spring, and exchanges of HCHO with the atmosphere between the 2 campaigns were probably limited.

3.2. Surface snow layers

The evolution of $[\text{HCHO}]_{\text{snow}}$ in surface layers is reported in Figs. 1–3. Interpretation of these data is facilitated by the use of P_{HCHO} and snow (SSA) values, that are also reported in the figures, whenever available.

$[\text{HCHO}]_{\text{snow}}$ in the 3 February layer (3W) (Fig. 1, top) decreased by more than a factor 2 between 9 and 12 February (from 13.3 to 5.5 ppbw). After this decrease, $[\text{HCHO}]_{\text{snow}}$ increased to about 8 ppbw and then showed only small variations around this value. The specific surface area of snow decreased by about a factor of 1.6 during this period.

$[\text{HCHO}]_{\text{snow}}$ in the 7 February layer (4W) (Fig. 1, bottom) displayed only small variations around a mean value of 13 ppbw, while snow SSA decreased by a factor of 2.5. While the gas-phase February HCHO data are somewhat sparse, they show a slow increase from about 150 to 200 pptv between 15 and 21 February, with

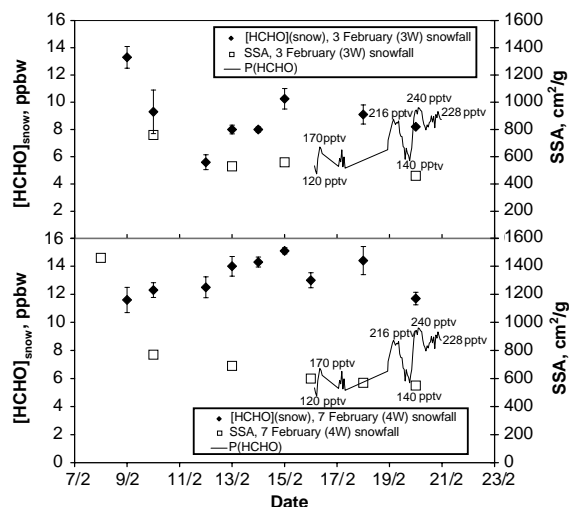


Fig. 1. $[\text{HCHO}]_{\text{snow}}$ (full symbols) and specific surface area (SSA, open symbols) for the 3 February snowfall (3W layer, top panel) and for the 7 February snowfall (4W, bottom panel). Samples were collected at site A. P_{HCHO} is represented by solid line.

variations up to 100 pptv. Surface hoar became visible on the snow on 16 February and represented about 50% of the mass of the 4W layer on 20 February. Since it was not possible to sample the surface hoar without the 7 February diamond dust, we measured the composition of the hoar frost that formed on guy wires near the site A. Hoar frost was growing faster than surface hoar and its composition could be different, but Table 2 shows that hoar frost concentrations are similar to those of the 7 February layer (4W).

In Fig. 2 top, we report the evolution of $[\text{HCHO}]_{\text{snow}}$ of the 13–14 April (7S) snowfall. We observe a decrease from 12.5 to 6.5 ppbw between 15 and 22 February, while snow SSA also decreased by a factor of 2. P_{HCHO} measurements do not show any trend, with variations around a mean value of 200 pptv. Surface hoar formed on this layer represents more than 80% of the layer mass on 19 April (Cabanès et al., this issue). To sample surface hoar separately, a Teflon sheet was placed down on the snowpack. On 24 April, $[\text{HCHO}]$ in surface hoar from the sheet was 6.9 ppbw (Table 2). To search for a possible diel cycle in $[\text{HCHO}]_{\text{snow}}$, intensive snow sampling was conducted at the FTX site starting on 18 April with 6 samples collected within 26 h. A decrease by a factor of 1.1 was observed during this period, while P_{HCHO} showed much larger variations indicative of a diel cycle (Grannas et al., 2002).

A decrease in $[\text{HCHO}]_{\text{snow}}$ was also observed for the 25–28 April snowfall (8W) from 6.5 to 4 ppbw within 2 days while SSA decreased to a third (Fig. 2, bottom). During this period, P_{HCHO} decreased from 250 pptv on April 26 to 50 pptv on April 28 with a sharp excursion to 380 pptv on April 27. This decrease was attributed to active halogen chemistry (Bottenheim et al., this issue; Sumner et al., this issue). P_{HCHO} recovered slowly to 150 pptv on 1 May.

HCHO concentrations in the crusted and loose surface snow layers (5S and 6S) were monitored from 12 to 22 April and are reported in Fig. 3. Contrary to the other surface layers analyzed during this period, both these layers were already several days to a few weeks old at the time of analysis. $[\text{HCHO}]_{\text{snow}}$ values were stable around a mean value of 7 ppbw for crusted snow and 6.5 ppbw for loose snow. SSA of the crusted snow (6S) decreased by a factor of 1.3 between 15 and 20 April. Only 2 values of SSA of the loose snow (5S) were measured, and they were very similar. As mentioned for layer 7S, P_{HCHO} values show no meaningful trend.

In summary, during spring, $[\text{HCHO}]_{\text{snow}}$ values decreased after deposition and reached a steady state. These steady-state concentrations were similar to those measured in the subsurface layers (5S and 6S, Fig. 3) which were deposited several days to weeks before the beginning of the spring campaign and had a stable $[\text{HCHO}]_{\text{snow}}$. During winter, the evolution is different:

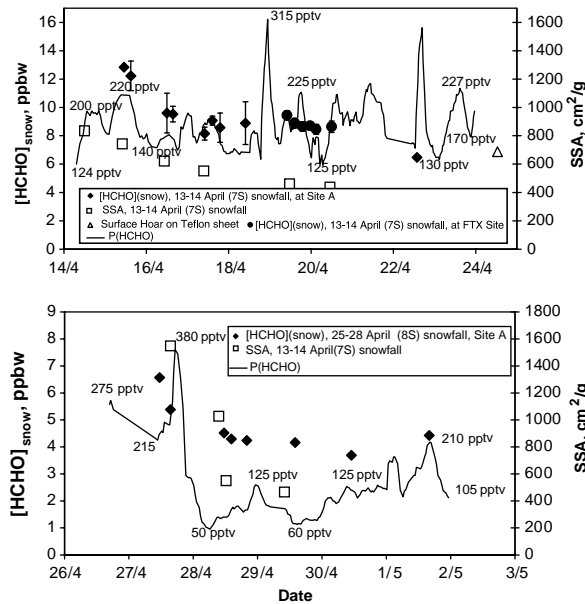


Fig. 2. $[HCHO]_{\text{snow}}$ (full symbols), and specific surface area (SSA, open symbols) for the 13–14 April snowfall (7S layer, top panel), and for the 25–28 April snowfall (8S layer, bottom panel). Samples were collected at site A. P_{HCHO} is represented by the solid line.

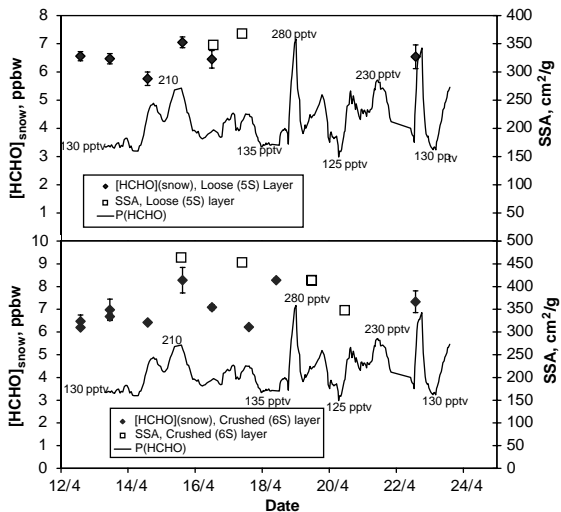


Fig. 3. $[HCHO]_{\text{snow}}$ (full symbols), specific surface area (SSA, open symbols) for the loose snow layer (5S layer, top panel) and for the crusted layer (6S layer, bottom panel). Samples were collected at site A. P_{HCHO} is represented by the solid line.

the very surface layer (4W) showed stable $[HCHO]_{\text{snow}}$ (Fig. 1, bottom), while the other surface layer (3W, Fig. 1, top) does show a decrease, but significant variations seem to precede a stabilization of $[HCHO]_{\text{snow}}$ to a lower value.

4. Discussion

4.1. Potential impact of the snowpack

Our data show that $[HCHO]_{\text{snow}}$ can evolve after deposition. The concentration decrease observed during spring is consistent with summer observations at Summit, Greenland of Hutterli et al. (1999), who attributed the decrease of HCHO to release to the atmosphere by physical processes: adsorption/desorption from the ice surface. In winter and spring, a similar trend was observed for acetaldehyde (Houdier et al., this issue).

If this is indeed the case, then snow does affect atmospheric composition. Release of HCHO from the snowpack will have a larger impact on P_{HCHO} in winter, as the HCHO lifetime is about 160 days (De Serves, 1994). The effect will be less visible in the spring, when the lifetime is ~ 6 h. (Grannas et al., 2002). Spring data suggest that release on a timescale of a few days is possible. However, the 7 February (4W) layer data show that release on short timescales is not always observed. Release on longer timescales appears possible, as deeper, warmer layers had much lower concentrations than fresh surface layers: a decrease by a factor of 10 decrease was observed between the very surface and the bottom of the snowpack, where temperature was about 10°C higher. To evaluate the impact of snow on atmospheric chemistry, we first quantify the partitioning of HCHO between the snow and the atmosphere and then evaluate

the kinetics of exchange with the atmosphere. This requires the knowledge of the incorporation mechanisms involved.

4.2. Formaldehyde snow/atmosphere partitioning

The mean formaldehyde mass per unit surface was calculated for each snow layer, using the density, thickness (Dominé et al., this issue) and mean $[\text{HCHO}]_{\text{snow}}$. The results are reported in Table 1. The total formaldehyde loading of the snowpack during winter and spring are 38.8 and 60.1 ng cm^{-2} , respectively.

The partitioning of formaldehyde between the snow and the exchange layer can be calculated. With a lifetime of 160 days in winter, HCHO can homogenize throughout the boundary layer. Guimbaud et al. (this issue) use a boundary layer height of 400 m in spring. We estimate that in winter, the greater atmospheric stability will reduce this height to 300 m. In spring, the lifetime of HCHO is only 6 h. With an eddy diffusivity coefficient of $K_z = 95 \text{ cm}^2 \text{ s}^{-1}$ (Guimbaud et al., this issue), emitted HCHO is destroyed at 14 m height. We then use an exchange layer height of 14 m. In the absence of vertical profiles, P_{HCHO} is assumed to be homogeneous in the mixing layer and we used 200 and 150 pptv as mean values for winter and spring, respectively. We calculated that 80.7% and 99.5% of the total formaldehyde were located in the snow during winter and spring, respectively. The snowpack does act as a HCHO reservoir, but only 7% and 5% of the total load of HCHO is located in the surface layers during winter and spring, respectively.

4.3. Possible incorporation mechanisms of HCHO in snow

HCHO in snow can be incorporated either by (i) adsorption onto the surface of snow crystals, (ii) dissolution into the ice volume, or (iii) a combination of both (Bales and Choi, 1996; Dominé et al., 1995; Dominé and Thibert, 1996; Thibert and Dominé, 1997, 1998).

4.3.1. Adsorption on the surface of ice crystal

If HCHO is adsorbed on the surface of snow crystals, then $[\text{HCHO}]_{\text{snow}}$ should be determined by temperature (T), P_{HCHO} , and the surface of snow accessible to gases i.e. snow SSA. Adsorption of molecules like aldehydes or ketones on ice are expected to occur via physisorption, and adsorption energies must be low or moderate (Schaff and Roberts, 1998; Picaud et al., 2000). Equilibration with the atmosphere should then occur on short timescales (less than a day). The HCHO mole fraction in snow (X_{HCHO}) should follow Eq. (1):

$$X_{\text{HCHO}} = A \times \text{SSA} \times (P_{\text{HCHO}})^{1/n} \exp\left(\frac{\Delta H_{\text{ads}}}{nRT}\right), \quad (1)$$

where A is a constant, n the number of entities created by the adsorption of a molecule of HCHO on the ice surface (Thibert and Dominé, 1997), and ΔH_{ads} the adsorption enthalpy of HCHO on ice.

4.3.2. Dissolution in the volume of ice crystals

Formaldehyde can dissolve in ice to form a solid solution, that can be in thermodynamic equilibrium with the atmosphere, or on the contrary, its concentration can be determined by kinetic processes (Dominé et al., 1995; Dominé and Thibert, 1996). If snow-phase HCHO is in equilibrium, then its mole fraction can be expressed as a function of P_{HCHO} and T as in Eq. (2) (Thibert and Dominé, 1997, 1998):

$$X_{\text{HCHO}} = A' \times (P_{\text{HCHO}})^{1/n'} \exp\left(\frac{\Delta H_{\text{sub}}}{n'RT}\right), \quad (2)$$

where A' is a constant and ΔH_{sub} is the partial molar enthalpy of sublimation of formaldehyde from ice and n' is the number of entities or defects created in the ice lattice. Changes in P_{HCHO} and temperature after formation of the crystals will result in a change in the equilibrium conditions, which will lead to exchanges with the atmosphere by solid-state diffusion.

If $[\text{HCHO}]_{\text{snow}}$ is governed by kinetic processes, then X_{HCHO} at the moment of incorporation will be determined by the relative number of HCHO and H_2O molecules that hit and stick to the ice surface (Dominé et al., 1995; Dominé and Thibert, 1996) given by Eq. (3):

$$X_{\text{HCHO}} = \frac{P_{\text{HCHO}}}{P_{\text{H}_2\text{O}}} \frac{\alpha_{\text{HCHO}}}{\alpha_{\text{H}_2\text{O}}} \sqrt{\frac{M_{\text{H}_2\text{O}}}{M_{\text{HCHO}}}}, \quad (3)$$

where α and M are the mass accommodation coefficients on ice and the molar masses. In both situations, equilibration with the atmosphere will proceed via solid-state diffusion. Note that sublimation/condensation cycles during metamorphism may also lead to exchanges with the atmosphere, as solute fluxes will accompany H_2O fluxes, but these exchanges will not necessarily drive $[\text{HCHO}]_{\text{snow}}$ towards equilibrium.

The timescale for metamorphism is on the order of several days to a few weeks (Cabanes et al., 2002). Evaluating the timescale for diffusion requires the knowledge of the diffusion coefficient of HCHO in ice, D , which has never been measured. Those of HCl and HNO_3 (Thibert and Dominé, 1997, 1998) and the self-diffusion of water in ice (Hobbs, 1974) have been measured and are in the range 10^{-12} – $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for the temperatures of interest here, and we assume that D falls within this range. The diameter of the columns and bullets of the snow falls of 3 and 7 February (3W and 4W), and of 13–14 April (7S), is $< 100 \mu\text{m}$, (Dominé et al., 2001; Cabanes et al., 2002) and they are hollow, so that the diffusion distance for equilibration, x , is about $30 \mu\text{m}$. The time constant for diffusion, given as $t = x^2/D$, is then 1–100 days, depending on the value

of D . Equilibration can therefore be expected to be much longer when volume processes are involved than if surface processes alone are involved.

4.4. Investigation of incorporation mechanisms of formaldehyde in snow

4.4.1. Adsorption

Since the correct value for n is not known, the values $n = 1$ and 2 were tested in Eq. (1). If formaldehyde is adsorbed on the snow surface, then assuming linear adsorption isotherms, $\ln[X_{\text{HCHO}}/(SSA \times P_{\text{HCHO}})]$ should depend linearly on $1/T$. Since exchanges with the atmosphere are expected to occur on short timescales, 24 h-averaged P_{HCHO} was used in the calculation when data were available. For early February, we used $P_{\text{HCHO}} = 150$ pptv. Since snow SSA was not measured as often as HCHO in snow, we interpolated the missing values from those measured by Cabanes et al. (2002). Temperatures were averaged over the hour preceding the snow sampling time.

Fig. 4, top shows that there is no correlation between $1/T$ and $\ln[X_{\text{HCHO}}/(SSA \times P_{\text{HCHO}})]$ for $n = 1$. The same null result was found for $n = 2$. Although we had to make several assumptions and approximations for this calculation, we then conclude that adsorption is not the dominant mechanism of incorporation of formaldehyde in ice crystals.

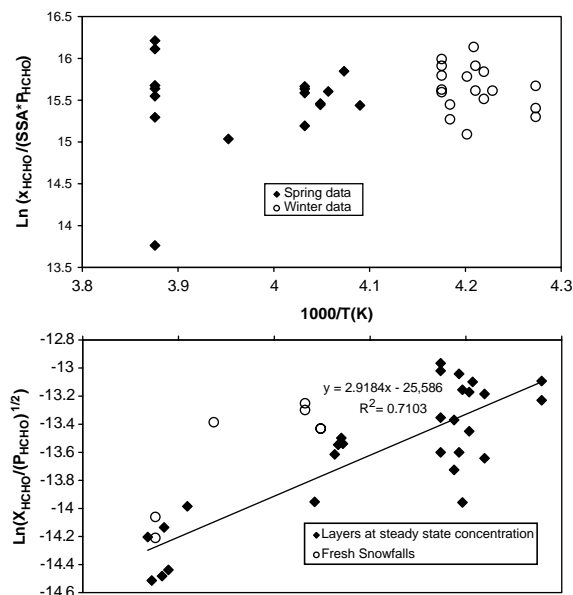


Fig. 4. Arrhenius-type plot to test the adsorption hypothesis. We used $n = 1$ in Eq. (1) (top panel) and Arrhenius-type plot to test the solid solution at thermodynamic equilibrium hypothesis. We used $n' = 2$ in Eq. (2) (bottom panel).

4.4.2. Solid solution at thermodynamic equilibrium (SSE)

This hypothesis was tested using Eq. (2) by plotting $\ln(X_{\text{HCHO}}/P_{\text{HCHO}})$ as a function of $1/T$ (Fig. 4, bottom). As in the case of adsorption, we used $n' = 1$ and 2 in the calculations. If formaldehyde is incorporated at thermodynamic equilibrium, the plot must be linear and the slope is $\Delta H_{\text{sub}}/R$ or $\Delta H_{\text{sub}}/(2R)$, respectively. Since solid-state diffusion, which is the equilibration process involved here, takes place on long timescales, we used only $[\text{HCHO}]_{\text{snow}}$ steady-state values (black diamonds). P_{HCHO} and T were 24 h-averaged and a value of 150 pptv was used for early February. For both values of n' , a trend was clearly visible: the correlation coefficients are 0.6 for $n' = 1$ ($\Delta H_{\text{sub}} = 24 \text{ kJ mol}^{-1}$) and 0.71 for $n' = 2$ ($\Delta H_{\text{sub}} = 48.5 \text{ kJ mol}^{-1}$). Thibert and Dominé (1997, 1998) observed that, for HCl and HNO_3 , partial molar enthalpies of evaporation from water, ΔH_{evap} , and partial molar enthalpies of sublimation from ice, ΔH_{sub} , were fairly similar in value. For instance, they measured $\Delta H_{\text{sub,HCl}} = 63.7 \text{ kJ mol}^{-1}$ (Thibert and Dominé, 1997), whereas $\Delta H_{\text{evap}}(\text{HCl})$ was about 74 kJ mol^{-1} (Fritz and Fuget, 1956). It is thus interesting that the value for $n' = 2$ of ΔH_{sub} is fairly similar to the partial molar enthalpy of evaporation of HCHO determined by Betterton and Hoffmann (1988): $\Delta H_{\text{evap}} = 59.8 \pm 1.8 \text{ kJ mol}^{-1}$. This suggests that the incorporation of HCHO in an SSE with $n' = 2$ is reasonable. It is implied that when $n' = 2$ formaldehyde forms 2 entities in ice. Dissociation of formaldehyde in the ice lattice appears unlikely and we therefore suggest that HCHO creates a defect in the ice lattice. HCHO is a larger molecule than H_2O , and a disruption of the crystalline lattice is indeed expected. However, n' need not be an integer, while other reasonable values could be tested.

In Fig. 4, bottom, the open circles are calculations for fresh snowfalls. Although only a few data points are available, they do not appear to fit the same curve and are all above the least-squares-fit line, which suggests supersaturation. For fresh snow layers, the hypothesis of a solid solution with concentrations governed by kinetic processes can therefore be tested.

4.4.3. Solid solution governed by kinetics processes

Eq. (3) was used to test whether $[\text{HCHO}]_{\text{snow}}$ in fresh snow was determined by condensation kinetics. Since α_{HCHO} is unknown, we calculated the ratio $\alpha_{\text{HCHO}}/\alpha_{\text{H}_2\text{O}}$ for different fresh snow layers, hoar frost and surface hoar. Assuming as a first approximation, that this ratio is independent of temperature in this range, it should not be dependent on snow layer. $P_{\text{H}_2\text{O}}$ values during the formation of the 7 February and 25–28 April snowfalls were determined using relative humidity and temperature-vertical profiles (Cabanes et al., 2002). $P_{\text{H}_2\text{O}}$ values for hoar formation were calculated using the ambient air

Table 3
Determination of $\alpha_{\text{HCHO}}/\alpha_{\text{H}_2\text{O}}$ to test the existence of a kinetic solid solution

Layer	7 February sampled on 9-02	Winter SH sampled on 16-02	Spring SH sampled on 23-04	Dendritic snowfall sampled on 27-04 at 11h30
$P_{\text{H}_2\text{O}}$ (Pa)	36.5	20	63	163
P_{HCHO} (Pa)	1.50×10^{-5}	1.50×10^{-5}	1.80×10^{-5}	2.40×10^{-5}
[HCHO] (ppbw)	11.8	12.1	6.9	6.6
X_{HCHO} (mol/mol)	7.08×10^{-9}	7.26×10^{-9}	4.14×10^{-9}	3.96×10^{-9}
$\alpha_{\text{HCHO}}/\alpha_{\text{H}_2\text{O}}$	2.22×10^{-2}	1.25×10^{-2}	1.87×10^{-2}	3.47×10^{-2}

temperature. Since HCHO vertical profiles were not available, P_{HCHO} was assumed to be the same at the ground and at the height of formation of the snow crystals. The calculated $\alpha_{\text{HCHO}}/\alpha_{\text{H}_2\text{O}}$ ratios, reported in Table 3, are all within a factor of 3 of each other. Considering the various experimental uncertainties, particularly on P_{HCHO} and X_{HCHO} just after deposition, and the probable dependence of this ratio on temperature, we conclude that these data are compatible with HCHO in fresh snow being incorporated in the ice volume and its concentration being governed by kinetic processes.

4.4.4. The particular case of rimed snow

The 25–28 April snowfall was composed of rimed dendritic crystals. Rimed ice crystals are formed in clouds that contain both ice crystals and supercooled water droplets that collide with and freeze on ice particles. The amount of riming was time-variable and was not easy to quantify. We estimate that rime made up 40 (± 20)% of the ice mass. Dendritic snow forms between -13°C and -17°C (Pruppacher and Klett, 1978) which corresponds, according to the temperature vertical profiles reported by Cabanes et al. (this issue), to an elevation between 500 and 1500 m. It fell under strong northerly winds that resulted in strong vertical mixing. P_{HCHO} can thus be assumed to be the same at the ground and at the height where snow formed. HCHO concentrations in these droplets can as a first approximation be predicted by Henry's law: $[\text{HCHO}]_{\text{aq}} = H_{\text{HCHO}} \times P_{\text{HCHO}}$. At -15°C , with $H_{\text{HCHO}} = 121 \times 10^3 \text{ mol atm}^{-1}$ (Betterton and Hoffmann, 1988) and $P_{\text{HCHO}} = 240 \times 10^{-12} \text{ atm}$, calculated $[\text{HCHO}]_{\text{aq}}$ is 870 ppbw, while measured $[\text{HCHO}]_{\text{snow}} = 6.5 \text{ ppbw}$. As any solute, HCHO is probably much less soluble in ice than in water and we deduce that only a small fraction of the HCHO is incorporated in the ice during riming, or that if it is incorporated, it is released very rapidly. The retention coefficient of HCHO during riming has never been measured, but Snider and Huang (1998) performed measurements in clouds and found that the retention coefficient for H_2O_2 was between 0.01 and 0.35. A value

closer to 0.01 for HCHO can be inferred from our measurements.

4.4.5. Interpretations

From our data, surface adsorption of formaldehyde can be rejected as the dominant incorporation mechanism. Incorporation of HCHO in the ice volume is the most likely mechanism. The concentrations measured in fresh snow and in surface hoar can be explained by incorporation being ruled by kinetic processes. When steady state is reached after a few days, snow-phase concentrations are stable and may be governed by thermodynamic equilibrium. The time constant observed to reach a steady state is between 1 and 3 days. With a diffusion distance of 30–50 μm and using $D = x^2/t$, a diffusion coefficient $D_{\text{HCHO}} = 3.5 \times 10^{-11} - 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for $t = 3$ days; $x = 30 \mu\text{m}$ and $t = 1$ day; $x = 50 \mu\text{m}$, can be, respectively, calculated. These values are close to those measured for HCl and HNO_3 (Thibert and Dominé, 1997, 1998) and H_2O (Hobbs, 1974). The $[\text{HCHO}]_{\text{snow}}$ evolution observed after deposition could then be explained by equilibration with the atmosphere via solid-state diffusion.

Another phenomenon which can contribute to the evolution of $[\text{HCHO}]_{\text{snow}}$ is metamorphism, but observations of photomicrographs showed that only a fraction of the ice is remobilized. This process cannot explain the whole evolution, but it can accelerate exchanges with the atmosphere.

We observed a difference in the steady-state concentrations between winter and spring that can be attributed to the temperature difference. As thermodynamics and Eq. (2) predict, solubility is positively correlated with $1/T$: the warmer the snow, the lower is the $[\text{HCHO}]_{\text{snow}}$. $[\text{HCHO}]$ in fresh spring snow layers decreased after deposition, as observed by Hutterli et al. (1999) in summer in Greenland. The 7 February layer (4W) may have been stable in $[\text{HCHO}]_{\text{snow}}$ if this snow was at equilibrium with the atmosphere when it was formed. This could be explained by 2 processes. The first is that most of this snow fall was formed at a temperature about 5°C warmer than the ground temperature. Thus, if it formed supersaturated in

HCHO, the colder temperature encountered on the surface may have brought it closer to equilibrium. The second one is that the crystals forming this snow were much smaller than those forming the other snowfalls studied here (Cabanes et al., 2002). Since this snow was sampled 2 days after its fall, it may already have had the time to reach equilibrium.

Regarding the 3 February layer (3W), we propose that the rapid and significant variations observed in this layer, formed by relatively large crystals, may be explained by its complex history of formation. Vertical temperature and relative humidity profiles show the snow formed at variable temperatures: warm at the beginning, and colder later so that snow may have been less concentrated at the beginning, and more later. Since the snow was wind-blown during deposition, it is possible that the snow sampled each day came from different periods of the precipitation and contained different HCHO concentrations.

Boudries et al. (2002), Grannas et al. (2002) and Guimbaud et al. (2002) found that HCHO, CH₃CHO, CH₃C(O)CH₃ had strong diel cycles in the snowpack air. Hutterli et al. (1999) found that snow was a source of HCHO to the atmosphere and proposed that this release of HCHO in snow was due to desorption from ice crystals when temperature increased. Such a mechanism should induce a diel cycle in the snowphase which was not observed during the frequent snow samplings of the surface layer during 18–19 April (Fig. 2, top). The suggestion made by Hutterli et al. is not compatible with our observations and we suggest instead that HCHO is incorporated in the ice volume. Sumner et al. (2002) proposed that it was possible to photochemically produce HCHO in the snowpack. This is compatible with our theory, if we assume that this production is from precursors located on the ice surface, followed by immediate release to the atmosphere. Such an immediate release is consistent with our observation that HCHO is not located on the ice surface and therefore has little affinity for it. Boudries et al. (2002) found that methanol was taken up by snow and this molecule could be a HCHO precursor. HCHO production in the ice volume appears unimportant, as this would have resulted in an increase in springtime HCHO, as observed for CH₃CHO (Houdier et al., 2002).

Finally, the snowpack may be a source of HCHO in winter, by out-diffusion of HCHO. We observed that HCHO decreased with depth in the snowpack. This is consistent with degassing of the snow that has been buried in deeper, warmer layers. The time scale for this process is long, (1–3 months), but still shorter than the HCHO lifetime in the Arctic winter. The impact of slow degassing can be evaluated with several assumptions. We assume that the time required for hard snow (2W) to reach equilibrium is one month. That is, at the time of snowfall, the HCHO concentration in this layer was

equivalent to that of the 7 February layer (4W, 12 ppbw) and the concentration decreased to 4.7 ppbw in one month. Examining a 1 cm² column, about 10 ng of HCHO degassed from the snowpack in one month. The degassing time is sufficiently shorter than the HCHO lifetime for degassing to be seen as a slow, cumulative addition of HCHO into the atmosphere, that increased P_{HCHO} by approximately 40%. This significant increase probably affects the whole arctic area, within which the residence time of air masses is about 20 days (Hopper and Hart, 1994), and may therefore have a significant impact on P_{HCHO} on a large scale. For air masses with a residence time shorter than the degassing time, the effect should be reduced in proportion. Slow release of HCHO by the winter Arctic snowpack may deserve consideration as an HCHO source in models.

5. Conclusions

Our measurements show that the snowpack contains most of the total (snow + mixing layer) HCHO: 80.7% and 99.5% during winter and spring, respectively. The snowpack therefore has the potential to impact atmospheric chemistry if the HCHO content is released to the atmosphere.

We propose that the most likely mechanism of incorporation of HCHO in snow is as follows:

1. Incorporation in the ice crystal volume, with the initial concentration possibly governed by kinetic processes.
2. Solid-state diffusion after deposition, leading to a steady-state concentration. The steady-state concentration is similar to the concentration of the solid solution in equilibrium with the atmosphere.

These results need, of course, to be confirmed by other field experiments and by laboratory measurements of the solubility and the diffusion coefficient of HCHO in ice.

If the snowpack is a spring-time photolytic source of HCHO, then we propose that HCHO thus formed is produced by photooxidation of organic species located on the ice surface. It is then rapidly released into the snow interstitial air and then on to the atmosphere. This implies that HCHO does not adsorb on ice surfaces, which needs confirmation by laboratory measurements of the adsorption isotherms of HCHO on ice.

Riming appears to have a minor impact on HCHO snow concentrations, which implies that the retention coefficient for HCHO could be as low as 0.01. This could be confirmed by freezing experiments of HCHO solutions.

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References

- Albert, M.R., Grannas, A.M., Bottenheim, J.W., Shepson, P.B., Perron Jr., F.E., 2002. Processes and properties of snow-air transfer in the high Arctic with application to interstitial ozone at Alert, Canada. *Atmospheric Environment Xref: 1352231002001188*.
- Bales, R.C., Choi, J., 1996. *Conceptual Framework for Interpretation of Exchange Processes in Chemical Exchange Between the Atmosphere and Polar Snow*, Vol. 43. NATO ASI, Springer, Berlin, pp. 319–338.
- Betterton, E.A., Hoffmann, M.R., 1988. Henry's law constants of some environmental important aldehydes. *Environmental Science and Technology* 22, 1415–1418.
- Bottenheim, J.W., Fuentes, J.D., Tarasick, D.W., Anlauf, K.G., 2002. Ozone in the Arctic lower troposphere during winter and spring 2000 (ALERT2000). *Atmospheric Environment Xref: S1352231002001218*.
- Boudries, H., Bottenheim, J.W., Guimbaud, C., Grannas, A.M., Shepson, P.B., Houdier, S., Perrier, S., Dominé, F., 2002. Distribution and trends of oxygenated hydrocarbons in the high Arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during ALERT2000 field campaign. *Atmospheric Environment Xref: S135223100200122X*.
- Cabanes, A., Legagneux, L., Dominé, F., 2002. Evolution of the specific surface area and of crystal morphology of fresh snow near Alert during ALERT2000. *Atmospheric Environment Xref: S1352231002001115*.
- De Serves, C., 1994. Gas phase formaldehyde and peroxide measurements in the arctic atmosphere. *Journal of Geophysical Research* 99 (D12), 25391–25398.
- Dominé, F., Thibert, E., 1996. Mechanism of incorporation of trace gases in ice grown from the gas phase. *Geophysical Research Letters* 23 (24), 3627–3630.
- Dominé, F., Thibert, E., Silvente, E., Legrand, M., Jaffrezo, J.-L., 1995. Determining past atmospheric HCl mixing ratios from ice core analyses. *Journal of Atmospheric Chemistry* 21, 165–186.
- Dominé, F., Cabanes, A., Taillandier, A.-S., Legagneux, L., 2001. Specific surface area of snow samples determined by CH₄ adsorption at 77 K, and estimated by optical microscopy and scanning electron microscopy. *Environmental Science and Technology* 35, 771–780.
- Dominé, F., Cabanes, A., Legagneux, L., this issue. Structure, microphysics, and surface area of the Arctic snowpack near Alert during the ALERT2000 campaign. *Atmospheric Environment*.
- Fan, Q., Dasgupta, P.K., 1994. Continuous automated determination of atmospheric formaldehyde at the part per trillion level. *Analytical Chemistry* 66, 551–556.
- Fritz, J.J., Fuget, C.R., 1956. Vapor pressure of aqueous hydrogen chloride solutions, 0° to 50°C. *Industrial and Engineering Chemistry* 1, 10–12.
- Grannas, A.M., Shepson, P.B., Guimbaud, C., Sumner, A.L., Albert, M., Simpson, W., Dominé, F., Boudries, H., Bottenheim, J.W., Beine, H.J., Honrath, R., Zhou, X., 2002. A study of photochemical and physical processes affecting carbonyl compounds in the Arctic atmospheric boundary layer. *Atmospheric Environment Xref: S1352231002001346*.
- Guimbaud, C., Grannas, A.M., Shepson, P.B., Boudries, H., Bottenheim, J.W., Fuentes, J.D., Dominé, F., Houdier, S., Perrier, S., Biesenthal, T.B., Splawn, B.G., 2002. Snowpack processing of acetaldehyde and acetone in the arctic atmospheric boundary layer. *Atmospheric Environment Xref: S1352231002001073*.
- Hanot, L., Dominé, F., 1999. Evolution of the surface area of a snow layer. *Environmental Science and Technology* 33, 4250–4255.
- Hobbs, P.V., 1974. *Ice Physics*. Clarendon Press, Oxford.
- Honrath, R.E., Peterson, M.C., Guo, S., Dibb, J.E., Shepson, P.B., Campbell, B., 1999. Evidence of NO_x production within or upon ice particles in the Greenland snowpack. *Geophysical Research Letters* 26, 695–698.
- Hopper, J.F., Hart, W., 1994. Meteorological aspects of the 1992 Polar Sunrise Experiment. *Journal of Geophysical Research* 99, 25315–25328.
- Houdier, S., Perrier, S., Defrancq, E., Legrand, M., 2000. A new fluorescent probe for sensitive detection of carbonyl compounds: sensitivity improvement and application to environmental water samples. *Analytica Chimica Acta* 412, 221–233.
- Houdier, S., Perrier, S., Dominé, F., Grannas, A.M., Guimbaud, C., Shepson, P.B., Boudries, H., Bottenheim, J.W., 2002. Acetaldehyde and acetone in the Arctic snowpack during the ALERT2000 field campaign. Snowpack composition, incorporation processes and atmospheric impact. *Atmospheric Environment Xref: S1352231002001097*.
- Hutterli, M.A., Rothlisberger, R., Bales, R.C., 1999. Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland. *Geophysical Research Letters* 26, 1691–1694.
- Jones, A.E., Weller, R., Anderson, P.S., Jacobi, H.-W., Wolff, E.W., Schrems, O., Miller, H., 2001. Measurements of NO_x emissions from the Antarctic snowpack. *Geophysical Research Letter* 28, 1499–1502.
- Marbouty, D., 1980. An experimental study of temperature gradient metamorphism. *Journal of Glaciology* 26, 303–312.
- Picaud, S., Toubin, C., Girardet, C., 2000. Monolayers of acetone and methanol molecules on ice. *Surface Science* 454–456, 178–182.
- Pruppacher, H.R., Klett, J.D., 1978. *Microphysics of clouds and precipitation*. Reidel, Dordrecht.
- Sander, R., Vogt, R., Harris, G.W., Crutzen, P.J., 1997. Modeling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring. *Tellus* 49B, 522–532.

- Schaff, J.E., Roberts, J.T., 1998. The adsorption of acetone on thin films of amorphous and crystalline ice. *Langmuir* 14, 1478–1486.
- Snider, J.R., Huang, J., 1998. Factors influencing the retention of hydrogen peroxide and molecular oxygen in rime ice. *Journal of Geophysical Research* 103, 1405–1415.
- Sumner, A.L., Shepson, P.B., 1999. Snowpack production of formaldehyde and its effect on the Arctic troposphere. *Nature* 398, 230–233.
- Sumner, A.L., Shepson, P.B., Grannas, A.M., Bottenheim, J.W., Anlauf, K.G., Worthy, D., Schreder, W.H., Dominé, F., Houdier, S., Perrier, S., 2002. Atmospheric chemistry of formaldehyde in the arctic troposphere at polar sunrise, and influence of the snowpack. *Atmospheric Environment Xref*: S135223100200105X.
- Thibert, E., Dominé, F., 1997. Thermodynamics and kinetics of the solid solution of HCl in ice. *Journal of Physical Chemistry B* 101 (18), 3554–3565.
- Thibert, E., Dominé, F., 1998. Thermodynamics and kinetics of the solid solution of HNO₃ in ice. *Journal of Physical Chemistry B* 102, 4432–4439.