

Reactive trace gases measured in the interstitial air of surface snow at Summit, Greenland

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Abstract

Concentration measurements of nitric oxide (NO), nitrogen dioxide (NO₂), nitrous acid (HONO), nitric acid (HNO₃), formaldehyde (HCHO), hydrogen peroxide (H₂O₂), formic acid (HCOOH) and acetic acid (CH₃COOH) were performed in air filtered through the pore spaces of the surface snowpack (firn air) at Summit, Greenland, in summer 2000. In general, firn air concentrations of NO, NO₂, HONO, HCHO, HCOOH, and CH₃COOH were enhanced compared to concentrations in the atmospheric boundary layer above the snow. Only HNO₃ and H₂O₂ normally exhibited lower concentrations in the firn air. In most cases differences were highest during the day and lowest during nighttime hours. Shading experiments showed a good agreement with a photochemical NO_x source in the surface snow. Patterns of H₂O₂, CH₃COOH, and HNO₃ observed within the surface snow-firn air system imply that the number of molecules in the snow greatly exceeded that in the firn air. Deduced partitioning indicates that the largest fractions of the acids were present at the ice grain–air interface. In all cases, the number of molecules located at the interface was significantly higher than the amount in the firn air. Therefore, snow surface area and surface coverage are important parameters, which must be considered for the interpretation of firn air concentrations.

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1. Introduction

Recent experiments have demonstrated that surface snow in polar regions can act as a photochemical reactor influencing concentrations of a wide variety of important tropospheric trace gases like ozone and nitrogen containing compounds in the atmospheric boundary layer (ABL) over snow-covered regions (e.g. Honrath et al., 2000a, 2002; Jones et al., 2000, 2001; Peterson and Honrath, 2001). Moreover, the exchange of trace gases present in the snow (e.g. H₂O₂) with the ABL is of great

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importance for the interpretation of firn and ice core profiles of these gases (McConnell et al., 1997; Hutterli et al., 1999, 2001). Since firn air constitutes the link between the ABL and the snow, gases exchanging between the snow and the atmosphere pass through the firn air. Firn air comprises only a small portion of the ABL-snow system, making it sensitive to even small changes in temperature (through firn-air partitioning) or atmospheric concentrations.

In order to gain further insight into the role of the firn air, simultaneous measurements of key species in the firn air were performed during the summer 2000 on the Greenland ice sheet. In this paper, we report the first simultaneous observations of nitric oxide (NO), nitrogendioxide (NO₂), nitrous acid (HONO), nitric acid (HNO₃), formaldehyde (HCHO), hydrogen peroxide (H₂O₂), formic acid (HCOOH), and acetic acid (CH₃COOH) in the firn air at multiple depths with varying temperatures and radiation levels and investigate the extent to which concentrations are controlled by the partitioning between surface snow and firn air.

2. Experimental

Firn air was intensively sampled from 19 to 23 June, 2000 at the Summit Environmental Observatory on top of the Greenland ice sheet (72.6° N, 38.5° W, 3200 m elevation) using three different inlet lines. For the NO and NO₂ measurements a PFA-Teflon tube terminated with a PFA-Teflon filter pack was positioned at the bottom of a narrow hole, which was refilled with excavated snow. Firn air samples for the measurements of H₂O₂ and HCHO were drawn through a heated and insulated inlet line (0.635 cm ID PFA tubes) mounted in a PVC tube (6.03 cm OD, 5.08 cm ID) with a length of 43 cm. Another piece of the same PVC tube was used to drill holes into the surface snow. After placing the PVC tube with the inlet line into the hole, it was carefully sealed with surface snow (Fig. 1). A similar set-up with a 2-m length of heated 0.95 cm OD PFA tubing with a Teflon pre-filter was used for firn air sampling of HONO, HNO₃, HCOOH, and CH₃COOH (Dibb and Arsenaault, 2002). The distance between the inlets was <2 m. Applied flow rates were on the order of 20 l min⁻¹ for the acids and <2 l min⁻¹ for the other compounds. Measurements were made at depths of 10 and 30 cm below the snow surface. In each case, a second similar inlet line was used to sample either ambient air or, in the case of NO_x for certain periods, firn air at a different depth. Measurements were made with instruments described in detail previously, using a chemiluminescence technique for NO and NO₂ (Honrath et al., 2002), fluorometric detection for HCHO and H₂O₂ (Jacobi et al., 2002), and mist chamber sampling followed by ion chromatographic detection for HONO, HNO₃,

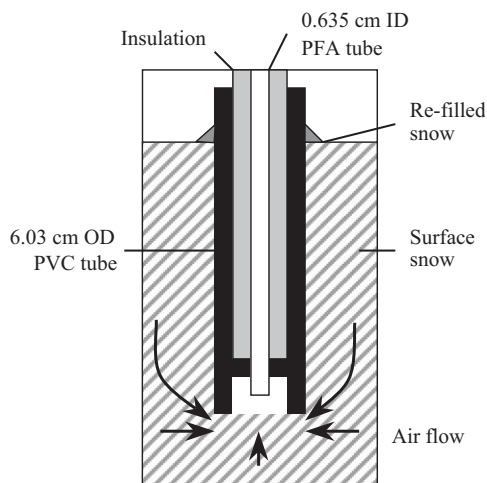


Fig. 1. Schematic drawing of the inlet line used for sampling H₂O₂ and HCHO in the firn air.

HCOOH, and CH₃COOH (Dibb and Arsenaault, 2002; Dibb et al., 2002). NO₂ photodissociation rate constants were determined with a 2- π Metcon filterradiometer (Yang et al., 2002).

Even with a perfect seal at the sampler-snow interface, significant amounts of atmospheric air is drawn down through the surface snow into the sample inlets (Albert et al., 2002). Air reaching the inlets has been filtered through firn at a range of depths and layers, and does not represent simply air that has been in contact with distinct snow layers (Bales et al., 1995a). In addition, the sampler-induced flow rates are at least an order of magnitude larger than flows induced by natural ventilation, and are many orders of magnitude higher than movement from diffusion (Albert et al., 2002); thus we cannot use models based on diffusion for quantitative interpretation of these data. Moreover, the inlets for different samplers have vastly different flow rates and were at different locations in the snow, inducing three-dimensional interstitial flow patterns that further complicate interpretation. In spite of these complications, the data are the first of their kind and do help to give insight into physical and photochemical interactions in the near-surface snow.

To investigate the influence of photochemical processes, the sampling area was shaded for periods of 30 min–2 h using pieces (~4 m²) of aluminum-covered insulation boards (20 June, 10:56–13:02 and 15:15–17:35; 22 June, 10:11–11:11, 12:22–13:25, 14:42–15:39 and 16:54–17:52), plexiglass (21 June, 8:59–11:04), or polyethylene (PE) film (22 June, 19:06–20:10) mounted ~15 cm above the snow surface. After finishing the firn air measurements, a snow pit was dug within the sampling area on 24 June. Snow samples of this pit were analyzed for concentrations of H₂O₂ and NO₃⁻,

density, and surface area. The surface area was determined from quantitative microscopy on two-dimensional thick sections of snow (Albert and Shultz, 2002). While the grain sizes determined by this method agree with visual observations, the surface area is sometimes affected by three-dimensional effects. Preliminary comparison of the side-by-side determination of the surface area of windpack and hoar in a thin snowpack at Alert, Canada by gas adsorption techniques (Dominé et al., 2002) and by imaging show differences as large as 25% (M. Albert, unpublished data).

3. Results

The firn air sampling was done near a tower that had been in place for many years, and the physical characteristics of the snow at the site had different characteristics than snow in undisturbed areas (Albert and Shultz, 2002), primarily due to foot traffic from previous years and drift patterns near the tower. Fig. 2 shows the stratigraphy and permeability profile of the snow at the sampling site. The snow was primarily fine-grained wind packed snow interspersed with layers of hoar. No dendritic forms were observed. The packed, low permeability snow below depths of 40 cm was trafficked snow that was deposited in the previous year, and the undisturbed snow from the current year lay above that. The specific surface area steadily decreased from $210 \text{ cm}^2 \text{ g}^{-1}$ near -13 cm depth to $130 \text{ cm}^2 \text{ g}^{-1}$ near -28 cm depth. The densities in the subsamples used for surface area determinations were essentially constant in the range $0.22\text{--}0.23 \text{ g cm}^{-3}$. Although these densities were lower than those shown in Fig. 2, we used the surface area ($210 \text{ cm}^2 \text{ g}^{-1}$) and density (0.22 g cm^{-3}) measured on the same sample from -13 cm depth in further analysis of the firn air measurements at -10 cm depth. H_2O_2 concentrations in the same snow pit decreased from $17.0 \text{ }\mu\text{M}$ at the surface (0 to -3 cm depth) to $4.9 \text{ }\mu\text{M}$ in the depth range of -24 to -28 cm . Between -7 and

-13 cm depth, the concentration was $11.5 \text{ }\mu\text{M}$. Similarly, NO_3^- decreased from $5.0 \text{ }\mu\text{M}$ at the surface to $0.6 \text{ }\mu\text{M}$ in the depth range of -24 to -27 cm . Between -9 and -12 cm depth, a NO_3^- concentration of $2.3 \text{ }\mu\text{M}$ was found.

Figs. 3–6 show time series of concentration measurements above and below the snow surface for the period 19–22 June. This period includes six shading experiments with the aluminum-covered insulation boards and single shading experiments using either plexiglass or PE film. The last shading experiment with the PE film, which is partly transparent to UV and visible radiation (the transmission increases from 30% at 350 nm to 50% at 600 nm), was conducted to investigate whether the shading would cause an effect due to a change in the ventilation between firn air and ABL. Since changes in firn air concentrations were not observed during this experiment, changes in air flow patterns due to the shading of the sampling area was neglected.

The most pronounced diel cycles in the firn air were observed for NO and NO_2 . NO concentrations in the firn air at -10 and -30 cm were similar, and were much higher than ambient concentrations during daytime (Fig. 3a). There were immediate, strong drops in NO at both levels during each shading period. During the longer shading experiments on June 20, the firn air concentrations dropped to ambient levels. NO levels immediately increased upon removing the shading, increasing to levels observed before the shading. NO_2 at -10 cm slowly decreased during the shading experiment whereas NO_2 at -30 cm first jumped to higher values followed by a steady decrease (Fig. 3b). Again, the opposite behavior was found after unshading. Even at night firn air NO_2 was elevated compared to ambient levels.

The diel cycle in the H_2O_2 concentration that was observed in the ABL was attenuated in the firn air at -10 cm (Fig. 4a). Ambient and firn air concentrations were comparable late at night. However, after sunrise ambient concentrations increased more than did those in the firn air, while firn air concentrations at -10 and -30 cm were comparable. Shading experiments did not affect H_2O_2 concentrations in the firn air.

Firn air concentrations of HCHO also exhibited a diel cycle at a depth of -10 cm (Fig. 4b). Late at night firn air and ambient concentrations were comparable. However, after sunrise firn air concentrations increased more than ambient concentrations and peaked around 19:00. At this time ambient and firn air concentrations at -10 cm differed by about 150 pptv. Although firn air concentrations at -30 cm on 22 June were further enhanced compared to firn air concentrations at -10 cm on the previous days, a diel cycle was less obvious. Firn air concentrations at -10 cm dropped by 50 to 60 pptv during the two shading periods on 20 June, while the experiments produced negligible effects on HCHO concentrations at -30 cm on 22 June.

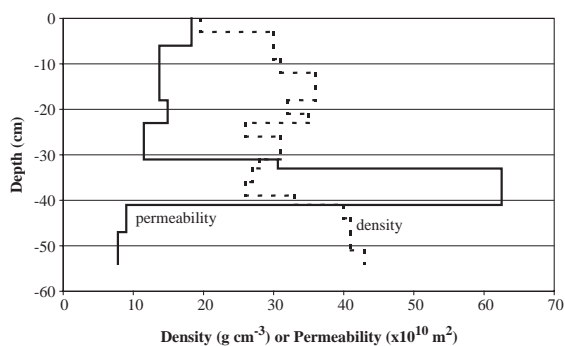


Fig. 2. Density and permeability measured in a snow pit within the firn air sampling area.

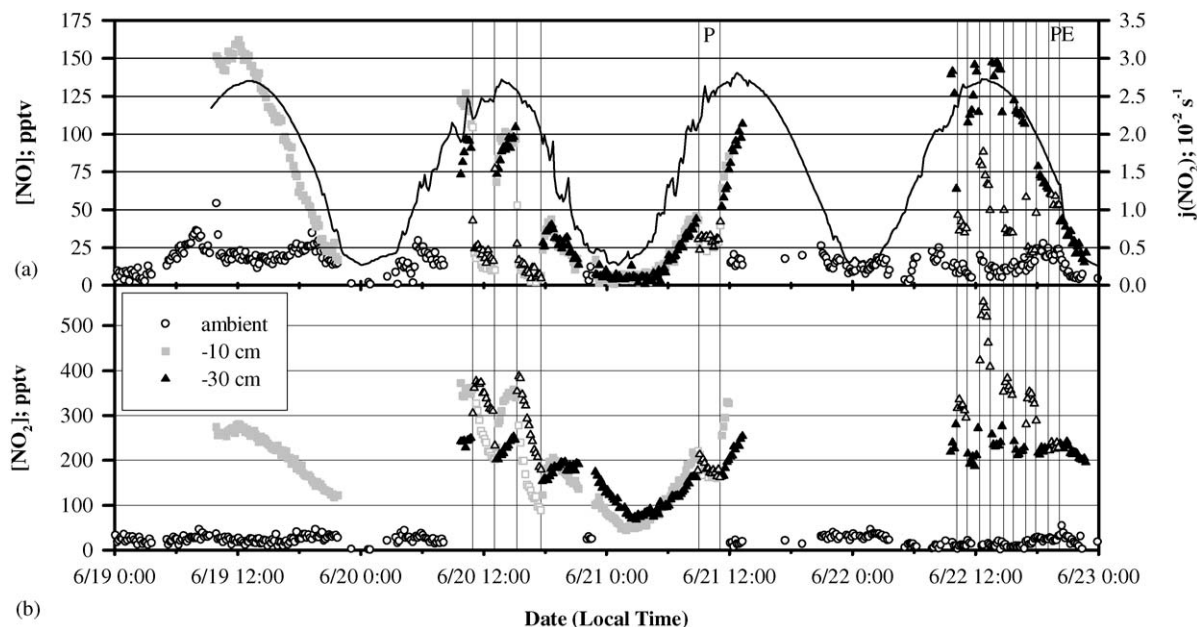


Fig. 3. Time series of 10-min averages of (a) NO and (b) NO₂ concentrations above and below the snow surface measured from 19 to 22 June. Also shown is the photolysis rate of NO₂ $j(\text{NO}_2)$ above the snow surface (a). Firn air concentrations during shading experiments are marked by open symbols with beginning and end of each experiment indicated by vertical lines (P: plexiglass, PE: PE film, others: aluminum; see text).

Quite high interstitial air concentrations were found for HCOOH and CH₃COOH (Dibb and Arsenaault, 2002). In contrast to ambient concentrations, which exhibited slightly higher concentrations during the day than at night, firn air concentrations were always in the range of 1500–4600 pptv for HCOOH and 2500–5500 pptv for CH₃COOH with no distinct diel cycle (Fig. 5). Also, concentrations were not affected during the shading experiments. HONO showed a behavior comparable to the organic acids; however, concentrations were much smaller (Fig. 6a). Shading experiments produced ambiguous results with the first shading experiment on 20 June resulting in a slight increase in HONO at –10 cm and with a strong decrease during the second shading experiment. HNO₃ exhibited the lowest firn air concentrations of all measured compounds (Fig. 6b). At –10 and –30 cm concentrations were comparable and remained below 20 pptv. The largest differences between firn air and ambient concentrations occurred at daytime, owing to the diel cycle of HNO₃ in the ABL.

4. Discussion

4.1. Relationship to fluxes measured above the snow surface

Firn air is connected both to the surface snow and the ABL above the snow. Therefore, we can expect that the

exchange measured above the snow surface correlates to the gradient between ambient and firn air concentrations. During the summer 2000 field season fluxes above the snow surface of NO_x, HONO, HNO₃, H₂O₂ and HCHO were measured (Honrath et al., 2002; Jacobi et al., 2002). Honrath et al. (2002) reported upward fluxes of NO_x and HONO and downward fluxes of HNO₃. The average diel cycle of each compound shows its maximum flux around noon, with negligible exchange during the night. These cycles agree well with the observed elevated firn air concentrations of NO_x and HONO and the reduced firn air concentrations of HNO₃. NO₂ and HONO firn air concentrations also remained higher than ambient levels at night and, thus, could cause emissions all day. However, at night very stable conditions normally develop in the ABL at Summit (Cullen and Steffen, 2001) limiting the turbulence to very low values. Therefore, even in the presence of large concentration gradients the exchange can remain negligible, in agreement with the measured fluxes.

The diel cycles of the exchange of H₂O₂ and HCHO followed similar patterns: emissions of both compounds during the day and a slight uptake at night (Jacobi et al., 2002). Daytime gradients of HCHO and nighttime gradients of H₂O₂ matched the previously reported direction of the fluxes above the snow surface, whereas those at other times did not. The reason for this disagreement could be that the fluxes of H₂O₂ and

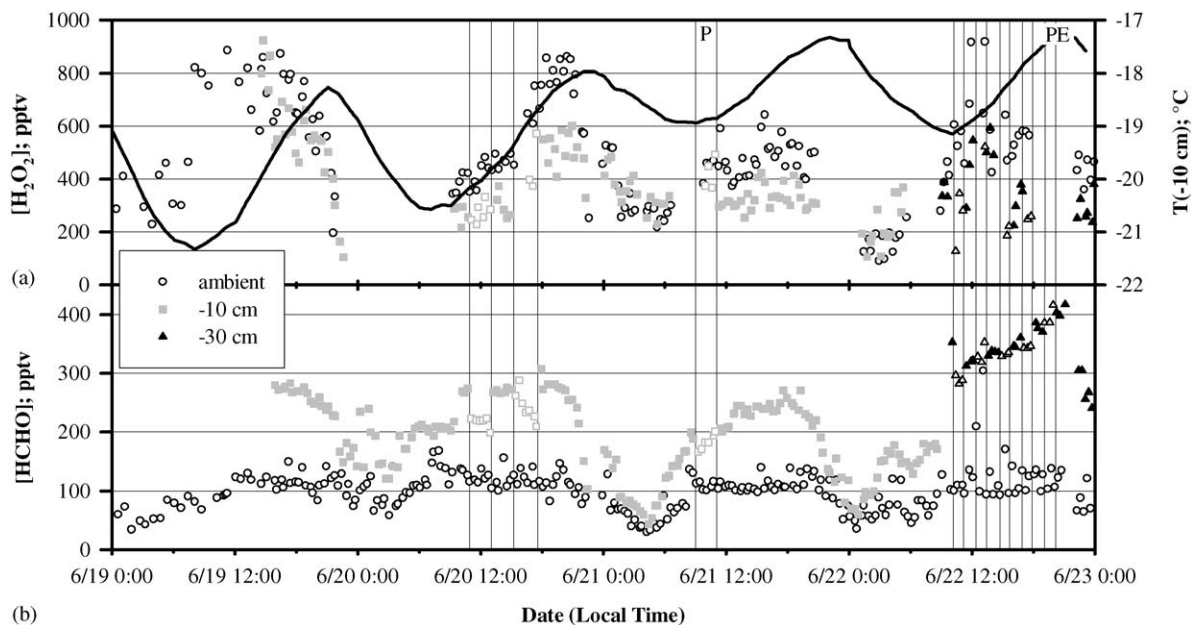


Fig. 4. Time series of 10-min averages of (a) H_2O_2 and (b) HCHO concentrations above and below the snow surface measured from 19 to 22 June. Also shown is the firn air temperature T at -10 cm (a). Firn air concentrations during shading experiments are marked by open symbols with beginning and end of each experiment indicated by vertical lines (P: Plexiglass, PE: PE film, others: aluminum; see text).

HCHO are dominated by the exchange with only the top few centimeters or millimeters of the snow surface (Hutterli et al., 2001). The amounts of H_2O_2 and HCHO stored in the top layer of the snow are sufficient to sustain the measured fluxes to the ABL as well as to deeper layers of the snow (Jacobi et al., 2002). However, differences between firn air and ambient concentrations may also be an artifact of the flow rates and patterns as described above, and points to the need for firn air sampling using much lower flow rates.

Thus, although gradients between ambient and firn air at -10 cm are considerably easier to quantify than gradients in the ABL, due to the much higher concentration differences, these gradients appear to be good indicators of fluxes between the surface snow and the ABL only for NO_x , HONO , and HNO_3 .

4.2. Photochemistry in the firn air

It has been demonstrated that the transfer of different trace gases between snow and air depends on temperature dependent physical and/or photochemical processes (Bales et al., 1995b; Sumner and Shepson, 1999; Hutterli et al., 1999, 2001; Couch et al., 2000; Honrath et al., 2000a; Jones et al., 2000). We can expect that the same processes also influence firn air concentrations. To investigate the effects of the physical and photochemical processes, we made a quantitative comparison using

maxima of the firn air concentrations and maxima of temperature and radiation in the surface snow. Radiation levels peak between 12:00 and 13:00. In contrast, snow temperatures peaked between 19:00 and 21:00 at -10 cm and between 21:00 and 23:00 at -30 cm. Thus, photochemically produced species should exhibit highest firn air concentrations at noon while maxima of species dominated by ice-air partitioning should occur concomitant with the temperature maxima at night. However, since the sampled firn air is not restricted to a distinct layer, the correlation with the temperature is probably rather weak. In contrast, the agreement with the radiation intensity should be much better because the maximum of the photochemical production occurs in all layers at the same time.

Accordingly, an unambiguous classification is only possible in the cases of NO and NO_2 . Highest firn air concentrations of NO and NO_2 normally occurred around noon (Fig. 3) indicating the photochemical production of NO_x ($=\text{NO}+\text{NO}_2$) in the surface snowpack (Honrath et al., 2000a; Jones et al., 2000, 2001), which has been attributed to the photolysis of the NO_3^- dissolved in the snow (Honrath et al., 2000b). Linear regressions of $[\text{NO}]$, $[\text{NO}_2]$, and $[\text{NO}_x]$ with the photolysis rate $j(\text{NO}_2)$ measured at -10 cm on 19 June gave correlation coefficients (R^2) of 0.89, 0.91, and 0.90, respectively. A similar simple interpretation of the results of the shading experiments is hampered by the

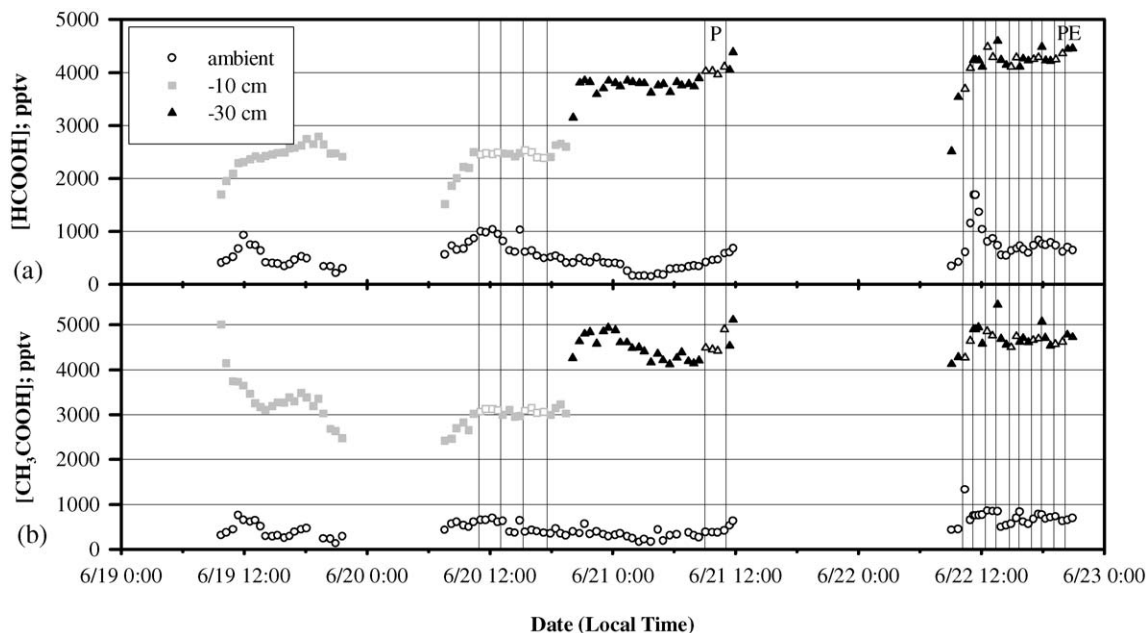


Fig. 5. Time series of (a) HCOOH and (b) CH₃COOH concentrations above and below the snow surface measured from 19 to 22 June. Sampling periods lasted between 19 and 38 min. Firn air concentrations during shading experiments are marked by open symbols with beginning and end of each experiment indicated by vertical lines (P: Plexiglass, PE: PE film, others: aluminum; see text).

fact that NO and NO₂ are connected by a very fast photochemical cycle involving the reactions of NO with O₃ and HO₂ and the photolysis of NO₂. However, the NO–NO₂ cycling has no effect on NO_x, which can be analyzed regarding the effect of the shading experiments. NO_x in the firn air decreased during all shading experiments and increased after unshading except after experiments late in the afternoon. These effects were more pronounced at –10 compared to –30 cm and are also in good agreement with a photochemical NO_x source in the snowpack. The shading immediately stops photochemical reactions in the snowpack as well as the photolysis of NO₂, while the reaction of NO with O₃ is much less affected due to the more steady O₃ concentrations. Therefore, the quick drop in firn air NO and the constant or increasing NO₂ concentrations immediately after shading may be attributed to the shift in the photochemical NO_x–O₃–cycle and the continuing steady decrease of both compounds due to the missing photochemical production in the snowpack.

H₂O₂ and HCHO also exhibited lower firn air concentrations at night versus daytime, indicating a possible photochemical contribution to elevated firn air values. However, maximum concentrations during the afternoon occurred later than the radiation maxima, but prior to temperature maxima. A better correlation might be obscured by the firn air sampling technique, which samples a mixture of ambient air and firn air from shallower depths, where the temperature maxima occur

earlier than at –10 and –30 cm. We assume that a combination of chemical and physical processes determined measured HCHO firn air concentrations. Since H₂O₂ concentrations in the firn air were lower than ambient values, a significant direct photochemical H₂O₂ source seems unlikely.

For HCOOH, CH₃COOH, HONO, and HNO₃ the results are more ambiguous because no full diel cycles were measured. The available data show rather constant concentrations for all compounds at –10 and –30 cm. This result is surprising in the case of HONO, which can also be a product of the NO₃[–] photolysis similar to NO_x (Mack and Bolton, 1999) and which normally exhibits higher firn air concentrations with increased radiation levels (Dibb et al., 2002; Zhou et al., 2001). Several effects can cause the differences in the behavior of HONO and NO_x. First, the very high flow rates for the sampling of the acidic compounds might have obscured any photochemical effect by diluting the firn air with a much larger volume of air mostly including ambient air. Second, even if HONO and NO_x are produced by the same photochemical mechanism in the snow, the release of HONO into the firn air could be affected by its properties in the surface region of the ice crystals, which is commonly called quasi-liquid layer (QLL) because it is less ordered and exhibits different properties than the solid ice. Such a QLL could act as a reservoir for HONO, but not for NO and NO₂. Thus, the HONO release could be dominated by

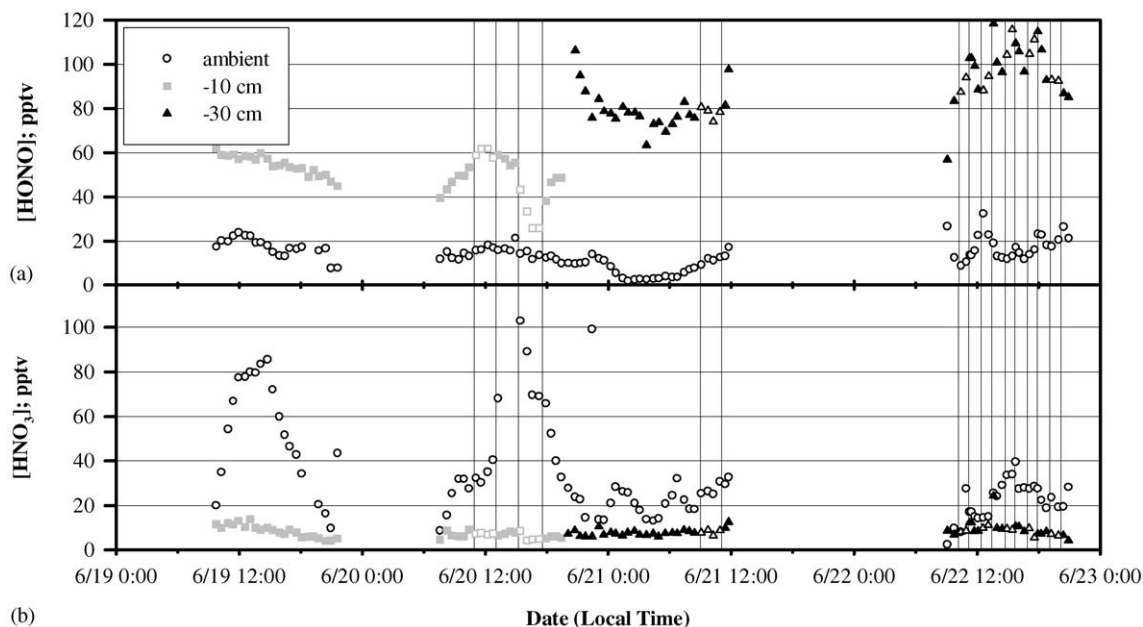


Fig. 6. Time series of (a) HONO and (b) HNO₃ concentrations above and below the snow surface measured from 19 to 22 June. Sampling periods lasted between 19 and 38 min. Firn air concentrations during shading experiments are marked by open symbols with beginning and end of each experiment indicated by vertical lines (P: Plexiglass, PE: PE film, others: aluminum; see text).

physical equilibria, which follow diel cycles different to the radiation cycles. Third, constant HONO concentrations could result if the most dominant sources and sinks follow similar diel cycles. For example, if the NO₃⁻ photolysis is the most important production process and the HONO photolysis the most important sink, both reactions would exhibit similar diel cycles that vary according to the radiation intensity. Nevertheless, the measurable nighttime HONO concentrations may also indicate a heterogeneous HONO production from NO₂ in the surface snow like observed in previous laboratory experiments (e.g. Finlayson-Pitts et al., 2003).

4.3. Air–snow partitioning

In order to further examine the influence of the temperature-dependent equilibrium between snow and firn air, we analyzed the air–snow partitioning considering the bulk ice, the ice grain–air interface, and the adjacent firn air. We assume that the equilibrium between the firn air and the interface is quickly established. Therefore, we used measured firn air concentrations to calculate surface coverages for the compounds, which have been measured directly in laboratory experiments or can be deduced from partitioning data. With the specific surface areas, the amounts located at the interface are calculated and subtracted from the amounts measured in the snow samples if necessary.

The distribution in Table 1 presents the results for H₂O₂, CH₃COOH, and HNO₃ following this procedure. The numbers reveal some important features for the air–snow partitioning of reactive trace gases. For example, the largest fractions are restricted to the condensed phase, with less than 0.1% present in the firn air in all three cases. The snow–air equilibrium constants are in the range of 2.9×10^4 , 230, and 4.6×10^5 M atm⁻¹ for H₂O₂, CH₃COOH, and HNO₃. The constant for H₂O₂ falls well in the range estimated from previous field studies (e.g. McConnell et al., 1997). Practically, all the H₂O₂ and HNO₃ are located in the bulk ice, while a significant fraction of CH₃COOH is present at the interface.

The different distribution of H₂O₂ and CH₃COOH in the condensed phase is somewhat surprising. However, it agrees well with several results of previous studies. First, bulk acetate concentrations in polar snow are very low compared to concentrations in rain in remote regions (Chebbi and Carlier, 1996) possibly due to low concentrations in the bulk ice (Table 1). On the other hand, the H₂O₂ uptake during the formation of fresh snow seems to be dominated by co-condensation leading to uniformly distributed H₂O₂ concentrations in the bulk ice of fresh snow (Sigg et al., 1992). Second, since large amounts of CH₃COOH are available at the interface, its degassing from aging snow can be expected to occur much faster than the degassing of H₂O₂, which is to a large extent limited by the slow diffusion within

Table 1
Properties of the ice-firn air system and partitioning of H₂O₂, CH₃COOH, and HNO₃ at a depth of –10 cm^a

		Bulk ice	Interface	Firn air
	Volume or surface area per volume unit	0.24 cm ³ cm ^{-3b}	46 cm ² cm ^{-3c}	0.76 cm ⁻³ cm ^{-3d}
H ₂ O ₂	Concentration or surface coverage	11.5 μM ^e	~ 10 ¹⁰ cm ^{-2f}	560 pptv ^g
	Number of molecules per volume unit	1.7 × 10 ¹⁵ cm ⁻³	4.6 × 10 ¹¹ cm ⁻³	8.2 × 10 ⁹ cm ⁻³
	Fraction	1	3 × 10 ⁻⁴	5 × 10 ⁻⁶
CH ₃ COOH	Concentration or surface coverage	0.38 μM ^h	3.8 × 10 ¹¹ cm ⁻²ⁱ	3000 pptv ^j
	Number of molecules per volume unit	5.5 × 10 ¹³ cm ⁻³	1.7 × 10 ¹³ cm ⁻³	4.4 × 10 ¹⁰ cm ⁻³
	Fraction	0.76	0.24	6 × 10 ⁻⁴
HNO ₃	Concentration or surface coverage	2.3 μM ^e		7 pptv ^k
	Number of molecules per volume unit	3.3 × 10 ¹⁴ cm ⁻³	2.5 × 10 ⁹ cm ^{-3l}	1.0 × 10 ⁸ cm ⁻³
	Fraction	1	8 × 10 ⁻⁶	3 × 10 ⁻⁷

^a Calculations for June 19, 15:00–22:00 ($T = -19^\circ\text{C}$; $\rho_{\text{air}} = 1.93 \times 10^{19} \text{ cm}^{-3}$).

^b Calculated with the measured snow density of 0.22 g cm⁻³ and the ice density of 0.92 g cm⁻³ at $T = -19^\circ\text{C}$.

^c Product of surface area (210 cm² g⁻¹) and volume density (0.22 g cm⁻³).

^d (1–0.24) cm³ cm⁻³.

^e Measured bulk snow concentration.

^f Clegg and Abbatt (2001).

^g see Fig. 4a.

^h Calculated with an average CH₃COOH bulk snow concentration of 0.5 μM (Dibb et al., 1994; De Angelis and Legrand, 1995; Legrand and Mayewski, 1997) taking into account the amount located at the interface.

ⁱ Sokolov and Abbatt (2002).

^j see Fig. 5b.

^k see Fig. 6b.

^l Calculated with a partitioning coefficient of $n_{\text{interface}}/n_{\text{firn air}} = 25$ obtained from the adsorption enthalpy and entropy of HNO₃ (Bartels-Rausch et al., 2002).

the ice matrix. Accordingly, field studies have shown that the loss of H₂O₂ from surface snow occurs over weeks to months (e.g. Bales et al., 1995b), while CH₃COOH in surface snow can significantly decrease within hours to days (Dibb et al., 1994; De Angelis and Legrand, 1995).

Molecular dynamics simulations demonstrate that HCOOH and CH₃COOH are trapped at the ice surface (Compoint et al., 2002). These calculations show that the incorporation of HCOOH in the bulk is more likely compared to CH₃COOH. Nevertheless, we assume that a somewhat lower, however still significant fraction of HCOOH is located at the interface of the crystals, since HCOOH concentrations in the firn and firn air behave similar to CH₃COOH.

To further investigate photochemical reactions occurring in the snow, it would be important to know if the reactive compounds are in the solid ice, dissolved in the QLL, or adsorbed on the ice crystal-air interface. For example, Honrath et al. (2000b) discussed that the photochemistry of NO₃⁻ is different in all three environments. Unfortunately, the laboratory studies of Clegg and Abbatt (2001) and Sokolov and Abbatt (2002) regarding the surface coverages of H₂O₂ and

CH₃COOH were performed at lower temperatures below 245 K and possibly without the presence of a QLL. Thus, these experimental results do not allow distinguishing between adsorbed amounts and amounts present in the QLL. In addition, Bartels-Rausch et al. (2002) stressed that their results are only valid for the amount of undissociated HNO₃ adsorbed at the surface of the ice crystal. Thus, the “bulk ice” quantity shown for NO₃⁻ in Table 1 includes NO₃⁻ in the QLL as well as in the bulk ice (but does not include adsorbed NO₃⁻ at the ice grain-air interface). Distribution coefficients for the partitioning of HNO₃ between ice and liquid water indicate that most of this NO₃⁻ is likely to be in the QLL. Gross (2003) obtained an average distribution coefficient (ice/liquid water) for NO₃⁻ of 2.3 × 10⁻⁴, in a series of experiments using NaNO₃ and KNO₃, while Thibert and Dominé (1998) reported a much smaller distribution coefficient for HNO₃ (5 × 10⁻⁶ at –19°C). Even if the QLL volume were only ~ 10⁻⁴ of the total (equivalent to a layer on the ice surface with a thickness of 2.5 × 10⁻⁶ cm), these distribution coefficients imply that 80–100% of the NO₃⁻ is present in the QLL.

Although HNO₃ is almost exclusively present in the condensed phase within the firn–firn air system, the

calculations suggest that by far the largest fraction is present in the QLL and, thus, available for release to the atmosphere. Indeed, substantial postdepositional losses from surface snow have been reported (e.g. Fischer et al., 1998; Wagnon et al., 1999). Moreover, the main source of the NO_x produced by irradiated surface snow is most probably the photolysis of nitrate present in the QLL rather than the photolysis of nitrate in the bulk ice.

Since considerably higher amounts of the trace gases are located at the interface compared to amounts in the firn air, firn air concentrations are expected to be very sensitive to physical parameters like temperature or surface area. For example, a simultaneous decrease of H_2O_2 and temperature at -10°C during the night from 20 to 21 June was observed (Fig. 4a). Between 22:00 and 7:00, the snow temperature dropped from about -18°C to -19°C , while H_2O_2 declined from around 500–300 pptv. Laboratory studies gave an enthalpy of $\Delta H^\circ = -55 \text{ kJ mol}^{-1}$ for the temperature dependence of the ice-atmosphere equilibrium of H_2O_2 below -11°C (Conklin et al., 1993). Therefore, the temperature drop would lead to a concentration decrease of $<10\%$ as long as all other parameters remain constant. This is much less than the observed decline of 40%, which would require a temperature drop of 5 K. Measurements of the H_2O_2 uptake on ice resulted in a more or less constant surface coverage in the temperature range between 218 and 238 K (Clegg and Abbatt, 2001). Nevertheless, a slight temperature dependence of the surface coverage well below the uncertainty of the laboratory experiments (Clegg and Abbatt, 2001) could explain a decrease of H_2O_2 in the firn air on the order of 200 pptv due to the exceeding amounts present at the surface compared to the firn air. In addition, Dibb and Arseneault (2002) noted that firn air profiles of CH_3COOH at Summit exhibited large fluctuations of 800–2200 pptv between profiles measured with time lags of 4–5 h. With the surface coverage given in Table 1, a change in the surface area of only 0.2% could explain fluctuations in firn air concentrations on the order of 2200 pptv.

Cabanes et al. (2002) studied trends of surface areas of Arctic snow. They found that the surface area of fresh snow decreased significantly with rates between 19 and $730 \text{ cm}^2 \text{ g}^{-1} \text{ day}^{-1}$. However, the surface area of older underlying snow remained rather stable (Dominé et al., 2002). The temperature gradients during this study were too low to induce metamorphism leading to an increase in the surface area. Therefore, decreasing surface areas can explain observed increases, but not the also observed quick drops in firn air concentrations of CH_3COOH . More likely are differences in firn air concentrations that may be related to snow characteristics and/or spatial variability at the sampling site.

Nevertheless, surface area and surface coverage are possibly as important as the temperature in determining equilibria between snow and firn air and thus firn air

concentrations. Cabanes et al. (2002) calculated that the surface area and the temperature-dependent adsorption could affect HNO_3 concentrations not only in the firn air, but even in the boundary layer. As discussed above, complications due to the varying flow rates and flow patterns make detailed model interpretation of the data untenable for the current study. However, small changes in the physical characteristics of snow, especially the surface area, may yield significant differences in firn air concentrations.

Exchange with the ABL also affects firn air concentrations. For example, the average H_2O_2 flux measured above the snow surface (Jacobi et al., 2002) during 20 June, 22:00–21 June, 7:00 resulted in a slight emission, on the order of $1.5 \times 10^8 \text{ molecules m}^{-2} \text{ s}^{-1}$, contributing to the drop in the measured firn air concentration at -10 cm . This small flux could remove the entire H_2O_2 amount in the firn air of the top 30 cm of the snow within $<1 \text{ h}$, were it not replenished from the condensed phase.

5. Conclusions

The comparison of trace gas concentration profiles above and below the snow surface during day and night and during shading experiments revealed that firn air concentrations are determined by photochemical reactions, temperature-dependent equilibria between the surface snow and adjacent firn air, and the exchange between the firn air and the air above the snow. Removal of NO_x during shading experiments confirms previous results demonstrating that considerable amounts are produced in the surface snow and released to the firn air due to photochemical processes. However, during the shading experiments two different regimes were identified indicating that the release from the snowpack is considerably slower than the rates in the photochemical NO_x - O_3 cycle. Nevertheless, features like elevated NO_2 firn air concentrations at night remain unexplained warranting a more detailed study of the mechanism of NO_x production in surface snow and the photochemical NO_x reactions in the firn air. Mixing ratios of H_2O_2 , CH_3COOH , and HNO_3 in the firn air mainly depend on gas and snow phase equilibria. The analysis of the firn air data indicate that a large fraction of CH_3COOH is present at the ice grain–air interface making adsorption to the snow and the surface area of the snow very important parameters for firn air concentrations. Despite the lack of laboratory data for HCOOH , we conclude that it is also mainly located in the QLL or at the grain–air interface based on the similarities in the behavior of HCOOH and CH_3COOH in the firn and firn air.

However, further laboratory studies of the ice-gas phase equilibria and surface coverage of ice at

temperatures close to the freezing point are needed. For example, the results could be used to analyze whether observed diel cycles of alkyl nitrates in the firn air (Swanson et al., 2002) are caused by phase partitioning or photochemical production. Since most of the NO_3^- is probably located in the QLL, it seems likely that the NO_x production is also governed by reactions in this layer. Therefore, laboratory experiments in a broad range of temperatures could demonstrate the importance of the QLL for the NO_3^- photolysis in ice and snow. For the correct description of the conditions within the firn and the firn air, further information about the nature and properties of the QLL of the snow grains is needed. For example, Dubowski et al. (2002) conclude that some properties of the QLL differ from those of supercooled water. The results underline the obvious need to characterize the amount and properties of this layer using for example NMR techniques (Cho et al., 2002) and to include this knowledge in models describing the transfer of trace gases between firn and firn air.

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