



Processes and properties of snow–air transfer in the high Arctic with application to interstitial ozone at Alert, Canada

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Abstract

Recent measurements of reactive chemical species in snow and firn at polar sites have served to underscore the importance of air–snow transfer processes in understanding changes in atmospheric chemistry. In this paper we present the first quantitative assessment of the impact of physical processes in the snow on air–snow chemical exchange of ozone. Measurements of snow properties, interstitial ozone concentrations, and an ozone kinetic depletion experiment results are presented along with two-dimensional model results of the diffusion and ventilation processes affecting gas exchange at Alert, Nunavut, Canada. The Arctic snowpack at Alert will allow rapid exchange of gases with the atmosphere. Even under natural ventilation conditions with moderate winds, the entire pack is exposed to air movement and therefore available for chemical exchange processes. Both measurements and model results indicate that ozone undergoes rapid depletion in the top centimeters of the snow—approximately within the top 5 cm under diffusion alone, and in the top 10 cm or less during ventilation. Due to the higher permeability of the snowpack on the sea ice site as compared to the terrestrial site, it is possible that chemical exchange processes could be even more rapid over the sea ice in the greater Arctic than at the terrestrial site. A quantitative discussion of complications that arise from current firn air sampling techniques is presented and possible improvements for future measurements are suggested. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A surge of atmospheric chemistry studies in recent years has indicated that it seems likely that photochemical and physicochemical processing in the snowpack strongly perturb the overall composition, oxidative state, and radical budget of the Arctic boundary layer. The glaciological community has long recognized that processes of air–snow transfer can alter chemical concentrations in the snow after deposition; these post-

depositional changes are of interest to the ice coring community for purposes of ice core interpretation. Only recently has it been fully realized that the processes of air–snow exchange may also have a large impact on the chemistry of the atmosphere. Field measurements of various species in the snow and in the atmosphere have been made at Alert, Canada (e.g., Sumner and Shepson, 1999; Zhou et al., 2002; Houdier et al., 2002), Greenland (e.g., Honrath et al., 1999; Peterson and Honrath, 2000), and Antarctica (Jones et al., 2000; Davis et al., 2001). Ozone is completely absent from the boundary layer at Alert during sunlit periods in the spring when the area is influenced by stable Arctic Ocean air masses. During the recent Polar Sunrise campaign, gradient measurements

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implicated a strong surface sink for O_3 , which was attributed to photochemical destruction within or upon the snowpack (Arnold et al., 2000). This paper discusses advective–diffusive air–snow transport processes, measurements of the properties that control those processes at Alert, measurements of interstitial ozone and ozone depletion rates in the snow, and model simulations of ozone transport and destruction within the snowpack.

2. Air–snow transfer processes

Chemical processes that occur in snow are dependent upon the physical properties of the snow and also upon the processes that occur in the interstitial space and within the snow crystals themselves. In dry snow, mass and chemical species transport can occur by diffusion and by advection because of airflow (ventilation) through the snowpack. Both diffusion and ventilation affect heat and chemical species transport in the snowpack (e.g., Cunningham and Waddington, 1993; Albert, 1993; McConnell et al., 1998). Diffusion is the relatively slow transport process that is driven by gradients in concentration or temperature. Ventilation is interstitial air movement within the snowpack caused by “form drag” pressure variations from wind blowing over surface roughness or by pressure variations due to wind turbulence. Because advective processes such as ventilation greatly increase both the rate and physical extent to which the air carrying the chemical constituents contacts the snow grains, ventilation can effectively increase the available surface area of snow grains for chemical interaction.

Our mathematical modeling builds upon an existing two-dimensional advection–dispersion transport model developed at CRREL for investigating transport within snow and firn (Albert, 1996). The model solves the system of coupled partial differential equations that describe conservation of mass, momentum, energy, water vapor, and chemical transport in the snow. Space considerations do not permit a listing of the governing differential equations here; they appear in Albert (1996). For the current calculations we neglect water vapor transport within the snow, and the chemical transport equation has been updated to include reaction. Because we have measured the rate of ozone destruction in the snow but the mechanism is unknown, we assume a first-order process and employ our experimentally determined rate coefficient, described in more detail below. Future modeling efforts will include photochemical and radical chemistry in the atmosphere, pore air, and within the snow grains for a variety of chemical species.

The finite element numerical technique is used to solve the two-dimensional coupled partial differential equations that describe the flow and transport. Finite elements are used so that the geometry of the modeled

physical space can be arbitrary, allowing for simulations of irregular surface and interior features.

3. Measurements of ozone in the firn–air

3.1. Method

Ozone was measured during the ALERT 2000 field campaign using a UV absorbance instrument (TECO Model 49) with a $2\text{-}\sigma$ precision of 1 ppbv. Measurements in the snowpack interstitial air were obtained by boring a hole to the desired depth in the snowpack using an open stainless steel tube (2.5-cm ID) and removing the snow. A filtered-inlet all-Teflon snow probe (2.5-cm OD) was then inserted to the base of the hole. A Teflon filter was slightly recessed from the end of the probe. Sample air from the probe tip was pumped through a 30 m heated $\frac{1}{4}$ -in PFA line at 2 lpm to the instrument housed inside the laboratory. Tests conducted during the field study indicate that line losses and pressure fluctuations (caused by attaching the instrument to a 30-m filtered inlet line) caused negligible changes in the measured ozone concentration.

3.2. Measurement results

Ozone measurements conducted for various depths within the snowpack are shown in Fig. 1. Three average depth profiles are shown. Data obtained during the dark (before the 28 February sunrise), twilight (between the 28 February sunrise and 9 March), and light (after the beginning of 24-h daylight) periods were averaged according to the depth of the measurement and radiation conditions. At each depth, the measured

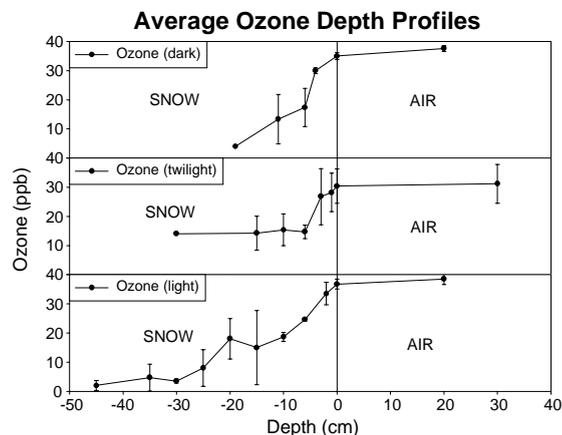


Fig. 1. Average ozone depth profiles obtained during dark (10–28 February), twilight (29 February–9 March), and light (15–30 March) conditions at Alert, Nunavut, Canada.

ozone concentration quickly achieved equilibrium, and varied by not more than ± 2 ppb. We found that artificial irradiation (using a Pyrex glass filtered 150 W Xe arc lamp) of the snow around the probe had no measurable effect on the measured ozone at any depth. It can be seen that during all radiation regimes, ozone is significantly depleted within the snowpack. This is clearly true, even though the sampled air is diluted with air from above the snowpack surface. Given that there is significant depletion of ozone within the Alert snowpack during the dark period, it is clear that this is not strictly a photochemical process. Photochemistry may play a role in ozone destruction within the snowpack after sunrise, but a dark destruction mechanism must also exist to explain the data obtained during the dark period of the ALERT 2000 field campaign.

Fig. 2 shows the diurnal variability of ambient and snowpack interstitial air ozone concentrations measured at three depths. In each case, the snowpack ozone concentration tracks the ambient ozone concentrations changes, indicating the importance of snowpack ventilation processes, some of which are caused by the

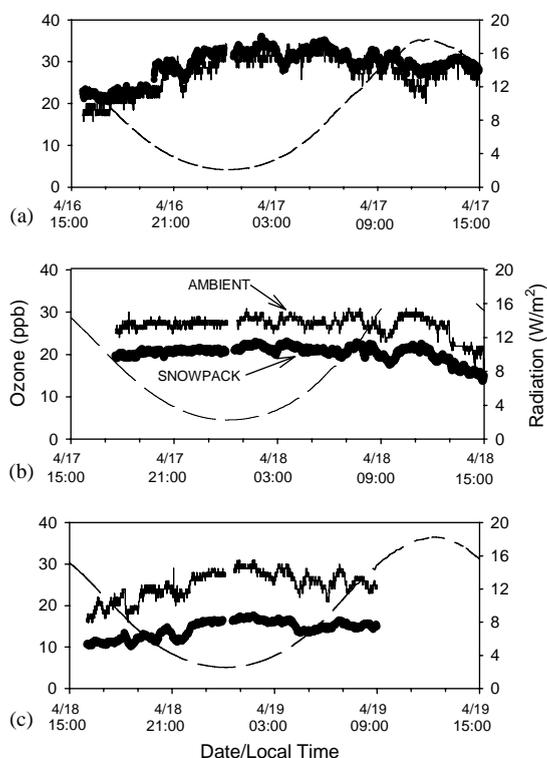


Fig. 2. Ambient (—) and snowpack interstitial air (---) ozone concentrations with radiation (· · ·) for 16–19 April 2000, at the Far Transmitter Building, Alert, Nunavut, Canada. Snowpack interstitial air measurements are obtained at (a) 2 cm below snowpack surface, (b) 5 cm below snowpack surface and (c) 10 cm below snowpack surface.

sampling itself, as discussed below. While ambient ozone concentrations ranged from about 20–30 ppb, the snowpack interstitial air ozone concentration was about 5–10 ppb lower than the ambient levels for depths below 2 cm. Because of the sampling flow rate of 2.0 lpm, significant forced ventilation occurs during sampling of the snowpack interstitial air. Consequently, the concentration of ozone measured within the snowpack interstitial air is partly determined by the mixing of depleted air within the snowpack with ozone-rich ambient air that is sampled nearly vertically through the snowpack. This implies that the concentration of ozone within the snowpack interstitial air is actually lower than that measured. It is also interesting to note that there is no apparent anti-correlation between the snowpack air ozone and radiation, as would be expected if the ozone loss were photochemical, as was observed in Summit, Greenland, by Peterson and Honrath (2000). They hypothesize that halogen chemistry occurring within the snowpack can lead to the catalytic destruction of O_3 , as shown in reactions (I) and (II). The source(s) of Br atoms



would be the photolysis of Br atom precursors, thus leading to a correlation between radiation and ozone loss. Such a radiation dependence is not observed in the Alert snowpack ozone concentration, which is interesting, as the snow at Alert is more halogen rich than at Summit. This may imply that the observed Summit ozone destruction in the snowpack is not mediated by halogen chemistry.

4. Kinetics of ozone destruction in snow

To investigate the efficiency of O_3 destruction in the snow at Alert, a chemical kinetic experiment was performed using a quartz cylindrical snow chamber (Beine et al., 2002). For this experiment the chamber was completely filled with snow from the loose surface layer (Domine et al., 2002), carefully collected near the Special Studies Trailer. The total volume of snow contained in the chamber was $\sim 23.5 \text{ dm}^3$ of snow. Ambient air was pumped through this chamber at a rate of 2 lpm, and the O_3 mole fraction was determined at the exit of the chamber with a TECO model 49 O_3 monitor. Ambient O_3 mole fractions were determined between the experiments by disconnecting the sample line from the chamber exit port. Before the start of these experiments no ambient air had been sampled from the chamber for at least 12 h, and at the beginning of the experiments, no O_3 signal was observed for a period of ~ 8 min. Assuming that all O_3 in the air before the start of the

experiment had been destroyed by chemical reactions, this would imply that the volume of air in the chamber was ~ 161 or 70% of the volume of snow, in excellent agreement with the estimate of Beine et al. (2002). We therefore assume that the flow through the snow-filled chamber was close to a plug-flow and channeling was unimportant. No cracks or gaps in the snow-filled space were observed.

The experimental procedure was as follows: ambient air was pumped through the chamber until a steady signal was obtained with the O_3 monitor connected to the exit of the chamber. The sample line was then disconnected from the chamber for variable lengths of time to allow the ozone in the chamber to react with the snow, and upon reconnecting the sample line the initial decrease in the O_3 mole fraction was determined. The experiments were performed both in the dark with the chamber covered by aluminum foil and snow, and under full natural sunlight irradiation. The latter experiments took place close to solar noon, implying a zenith angle of $\sim 71.1^\circ$ (21 April, latitude $82^\circ N$). The air temperature at the time of the testing was $\sim -20^\circ C$ during both of the tests.

Assuming the rate of O_3 reaction in the chamber to be a first-order loss process, the mole fraction after an exposure time t minutes to the snow can be expressed as

$$[O_3(t)] = [O_3(0)]\exp(-t/\tau), \quad (1)$$

where $[O_3(0)]$ is the ambient O_3 mole fraction, $[O_3(t)]$ is the O_3 mole fraction after exposure time t minutes (which is the sum of the time it takes to pump air through the chamber, i.e., 8 min, and the time the air was not pumped), and τ is the apparent lifetime of O_3 in the snow (i.e., $1/\mu_c$). The results of the experiments are

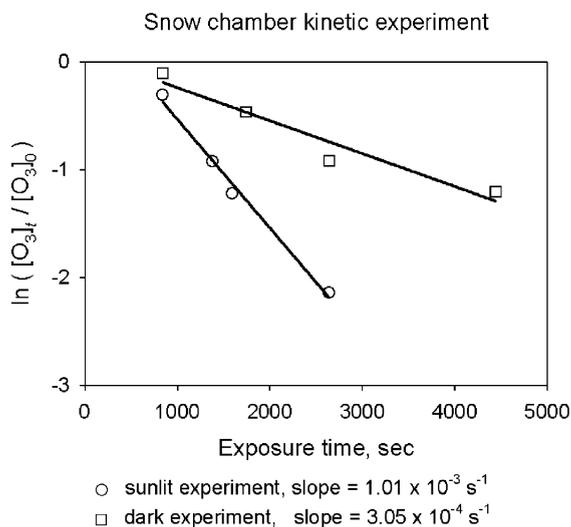


Fig. 3. Measurements of the experimental decay of ozone in a snow chamber.

presented in Fig. 3. As can be seen, surprisingly short O_3 lifetimes of 18 and 55 min were obtained for irradiated and dark conditions, respectively.

5. Snowpack properties affecting transport and exchange at Alert

Exchange processes between snow and the atmosphere are dependent upon atmospheric concentrations, meteorological conditions, and also upon the properties of the snowpack. The snow cover at Alert is seasonal (disappearing completely every summer) and is relatively thin, with a snowpack depth at peak accumulation of ~ 50 cm. The snowpack is highly layered and is generally characterized by pronounced layers of large-grained faceted crystals alternating with layers of finer-grained small windpacked crystals that are sometimes also faceted. A layer of very large-grained columns of depth hoar lies at the bottom of the snowpack. There was no evidence of melt since deposition for any of the layers, and no melt occurred in the course of the ALERT 2000 experiments.

A pit dug in a representative undisturbed area of the snowpack was examined for snow stratigraphy, density, permeability, and thick-section microscopy profiles near the transmitter site, where most of the firm air experiments were conducted, and also on the sea ice for comparison. In addition, several 100-m transects of snow-depth measurements, with depth measurements at 1-m intervals and stratigraphy examinations every 10 m, were made for estimates of spatial variability.

In the snow pit measurements, snow permeability was measured as a function of layer type. The permeability was measured using a custom air permeameter (Albert et al., 2000). Snow microstructure was examined through quantitative microscopy on thick sections made from preserved snow samples taken to profile the pit. The microscopy involved cutting an undisturbed section of snow into a sample container, pouring chilled pore filler (dimethyl phthalate) in the air space along the edges of the sample, allowing it to wick into the pore space of the sample, then freezing the sample for microtoming and imaging as in Perla (1982). Fig. 4a depicts the stratigraphy, density, and permeability plotted with samples of the thick section images of the snow microstructure for each layer at the transmitter (terrestrial) site. The permeability varies according to layer type and depth, and ranged from $1.5 \times 10^{-10} \text{ m}^2$ in the surface windpack, to $6.7 \times 10^{-10} \text{ m}^2$ in the underlying faceted layer, to $200 \times 10^{-10} \text{ m}^2$ and greater in the basal depth hoar layer.

At the terrestrial site, the snow depth ranged from 30 to 60 cm, with an average depth of 40 cm. The pack, which had a layer of very large-grained depth hoar at the bottom, had alternating layers of coarse-grained faceted

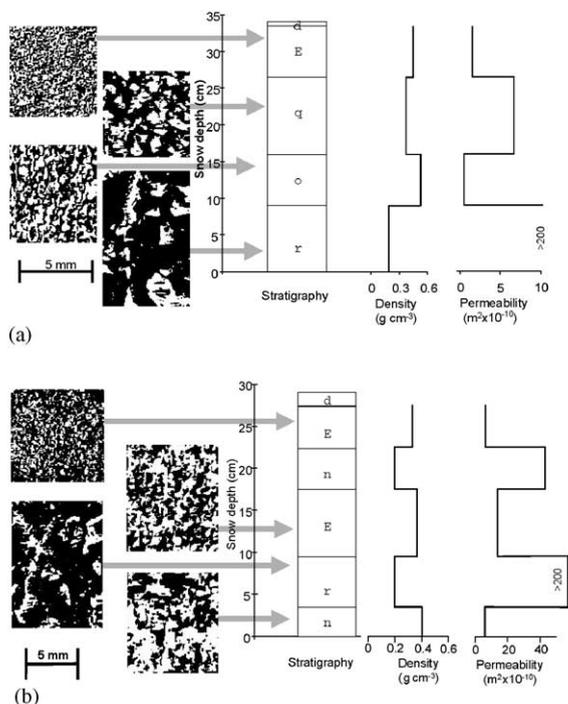


Fig. 4. Snowpack stratigraphy, density, permeability, and samples of thick-section microstructure images from Alert: (a) At the terrestrial measurement site at Alert and (b) At the sea ice site near Alert. Snow type symbols follow ICSI standards: (●) windpack, (▲) cups, (λ) columns of depth hoar, (□) faceted, (⊠) small faceted, (*) stellar dendrite.

crystals and aged windpack. At the sea ice site, the snow depth was much more variable due to uneven drifting and a small pressure ridge; snow depths ranged from 2 to 40 cm deep, with an average depth of ~ 25 cm. The snow characteristics at a representative site along the sea ice transect are plotted in Fig. 4b. With the exception of the layer of frozen brine pathways at the bottom of the sea ice snowpack, it is evident that the dominant layers in both the sea ice and the terrestrial pits are similar, indicating that both sites were formed from the same snow deposition events and subject to similar meteorology. However, the snow at the sea ice site has a greater overall permeability, with each layer having an almost fivefold increase in permeability over the corresponding layer at the terrestrial site. Because of this higher permeability, for equal wind conditions, the snow over the sea ice would be expected to have greater interstitial transport rates and therefore possibly greater air–snow exchange than the snow at the Alert terrestrial site. This is important in part because the halogen ion concentration is significantly greater in the snowpack over the frozen Arctic Ocean surface. In addition, the sea ice site has evidence of frozen brine pathways at the bottom of the pack that are not present at the terrestrial site; the

presence of this layer may affect some chemical reactions.

6. Discussion

These observations imply a heterogeneous destruction of ozone on snowpack surfaces. Oum et al. (1998) report the formation of gaseous Br_2 from the reaction of seawater ice with O_3 in dark conditions. The reaction of O_3 with sea salts is one possible dark mechanism for O_3 destruction within the snowpack, as well as a source of molecular halogens. As reported by Foster et al. (2002), significant concentrations of Br_2 and BrCl were observed at Alert in dark and twilight conditions, with elevated concentrations of Br_2 present in the snowpack (as compared to ambient air). These observations could imply that this mechanism is at least partly responsible for snowpack O_3 depletion in the Arctic.

There are a variety of other possible ozone destruction mechanisms. Several studies have discussed that activated carbon and black carbon surfaces can catalyze transformation of ozone into OH radicals (Jans and Hoigne, 1998, 2000; Stephens et al., 1986). Because of the shallow depth of snow at Alert (about 50 cm during ALERT 2000), crustal materials can easily be blown around and deposited onto the snow surface during windy conditions. Long-range transport would serve as a significant source of black carbon from anthropogenic combustion sources (Worthy et al., 1994). There is also some input from activities at the CFS Alert base. Consequently, one might expect the snow to have some carbon and crustal material content.

The ozone destruction potential of these reactions will be dictated by the amount of active surface area present in the Alert snowpack. Hopper et al. (1994) report a black carbon content of aerosols at Alert of ~ 300 ng/ m^3 . Assuming a dry deposition velocity of 0.05 cm/s, a particle radius of 1×10^{-5} cm and a particle density of 2.0 g/ cm^3 , we calculate a surface area concentration of carbon in snow of $\sim 4 \times 10^{-4}$ cm^2 (carbon)/ cm^3 (snow) assuming a constant deposition over a 120-day accumulation of the 54 cm snowpack depth. Given that these particles will be occluded in the snow crystal, we approximate that only 10% of the actual carbonaceous surface will be exposed to the ambient air, leading to an overall black carbon surface area concentration of 4×10^{-5} cm^2 (carbon)/ cm^3 (snow). We estimate snow surface area concentration, using the data of Domine et al. (2002) to be 150 cm^2 (snow)/ cm^3 (snow). Therefore, $\sim 2.6 \times 10^{-7}$ of the snow surface area could be black carbon.

Fendel et al. (1995) determined uptake coefficients (γ) for O_3 on small C(s) particles (10–100 nm), and obtained a γ of 3.3×10^{-3} at room temperature (300 K). Rogaski et al. (1997) determined uptake coefficients of

$1(\pm 0.5) \times 10^{-3}$ for amorphous carbon at 300 K. Smith et al. (1988) report that ozone/soot reactions are first order in ozone with CO, CO₂, and H₂O the only stable gaseous products formed. Stephens et al. (1986) measured CO, CO₂, and O₂ as products with one O₂ produced for every ozone reacted. Their measured uptake coefficients varied from 10^{-3} to 10^{-5} , depending on the type of carbon sample exposed and the amount of ozone exposure. Consequently, the ozone/carbon reaction probability is clearly dependent on the C(s) surface history. However, these measurements allow us to calculate a potential limit for the efficiency of ozone destruction via reaction with black carbon, as one of many possibilities that could explain the observed ozone loss. Given an assumed uptake coefficient of 0.0033, the first-order heterogeneous loss rate of ozone within the snowpack due to reaction with black carbon is calculated to be 3.8×10^{-4} /s, corresponding to an ozone lifetime in the snowpack of 44 min. Via this loss mechanism, the lifetime of gas phase ozone in a 400 m boundary layer height would be 22 days (assuming no entrainment from the free troposphere). We do not intend to imply that this is the operative mechanism, rather only that this is a possibility that could explain the quartz tube experimental data.

As an alternative possibility, Nawrocki and Kalkowska (1999) report ozone reaction with humic and fulvic acids in water samples. Because of local vegetation, algae, and soils, Alert snow could be expected to have a significant humic and fulvic acid content, although measurements of these have not been made for Alert snow. Interestingly, this destruction of ozone has been found to lead to the formation of aldehydes such as formaldehyde, acetaldehyde, and propanal (Nawrocki and Kalkowska, 1999; Gracia et al., 1996; Hureiki et al., 1998). In light of Boudries et al. (2002) Guimbaud et al. (2002), Sumner et al. (2002) and Grannas et al. (2002), ozonolysis of humic and fulvic substances in snow may also serve as a source of aldehydes in the snowpack.

7. Model simulations of advective–diffusive interstitial ozone transport

7.1. Natural ventilation driven by the wind

Natural ventilation is the interstitial airflow in snow due to varying surface pressures imposed by the wind on surface features across the top of the snowpack. At Alert the small surface sastrugi had irregular geometries, but from surveys of roughness heights and separation, we judged that characteristic roughness features had amplitudes of ~ 10 cm and wavelengths of ~ 10 – 20 m. In previous studies, we had measured surface pressures over snow roughness under a variety of wind speeds. For

the calculations presented herein we use the geometrical information measured at the site along with a range of surface pressures encountered in the previous studies, and we use the measured permeability profile depicted in Fig. 4a.

Fig. 5a shows the airflow velocity vectors for the calculated airflow pattern that would be expected from natural ventilation at the Alert transmitter (terrestrial) site. Because the wavelength of the pressure forcing is long relative to the depth of the snowpack, it is evident that essentially the entire snowpack is subject to interstitial airflow during wind events. Under light wind conditions (2–4 m/s) the calculated interstitial airflow is ~ 0.08 cm²/s near the surface, decreasing to 0.02 cm²/s near the ground. For moderate (7–9 m/s) winds, the snowpack ventilation in the top centimeters of snow is ~ 0.3 cm²/s, more than an order of magnitude larger

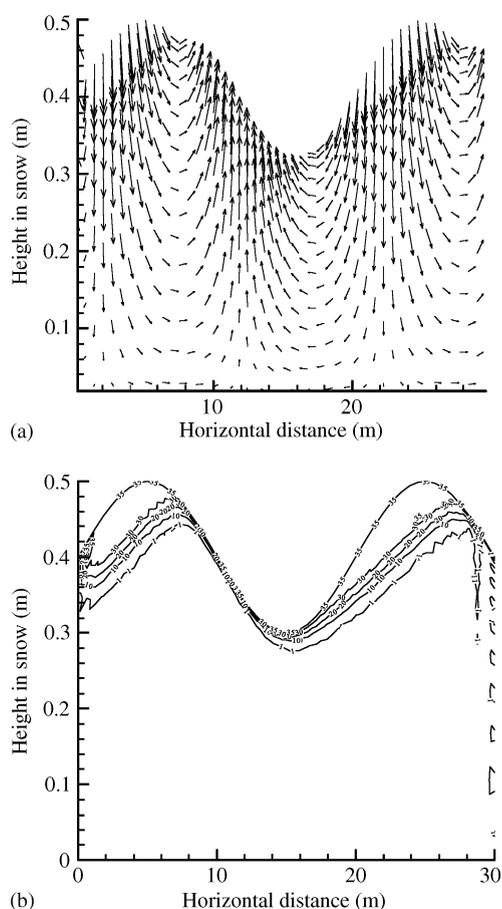


Fig. 5. Calculations of wind-driven ventilation of the snow at Alert: (a) Interstitial airflow velocity vectors for the terrestrial site; the surface velocity is ~ 0.3 cm/s for moderate winds and (b) Calculated ozone concentration in the snow under natural ventilation conditions; concentrations equal to atmospheric at the surface decrease by two orders of magnitude in the top 8 cm of snow.

than molecular diffusion rates in snow. Interstitial airflow under moderate winds follows the same flow paths shown in Fig. 5a except that the rate near the ground is near $0.05 \text{ cm}^2/\text{s}$. Higher winds produce larger surface pressure differences, which create higher interstitial airflow rates. The long wavelength of the surface roughness relative to the depth of the snow causes almost the entire pack to be subjected to ventilation, especially under moderate to high winds.

The ozone ventilation calculations assume that the interstitial air at the top of the snowpack is at the ambient ozone concentration, and that the ozone concentration at the bottom of the pack is zero. Fig. 5b depicts the calculated ozone concentration contours for moderate wind conditions. It is evident that the rapid rate of decay causes very little ozone to be present below about 8 cm in the snowpack. Also, the ventilation pattern induces some spatial variability in concentration of ozone with depth, depending on the location along the surface roughness. The calculated ozone profiles due to natural ventilation shown in Fig. 5b show a faster depletion of ozone with depth than the measured interstitial ozone profiles in Fig. 1. However, as stated earlier this is to be expected because the measurements involve additional induced ventilation of ambient ozone into the pack. Both the measurements and the calculations indicate that there is almost total depletion of ozone below approximately the top decimeter of the pack.

7.2. Simulation of the firn air sampling

The firn air chemistry measurements conducted for ALERT 2000, as well as those conducted in the past by this set of investigators and also by others reported in the literature, involve pumping of interstitial air from the snowpack. Because the chemical analysis detection limits often require flow rates on the order of liters per minute, the sampler withdraws air from locations in the snowpack that are not immediately adjacent to the intake. It is of interest to determine the nature of the flow and the resulting concentrations that arise from this advection-dominated situation.

For these calculations, the intake is simulated as a mass sink in the computational domain; the pressure at the sink is lowered until the simulated airflow rates into the sink match those at the actual intake. We assume that there are no ambient winds during the interstitial ozone tests, so that there is no pressure gradient along the top of the snowpack nor along the snow/ground interface. The firn-air ozone experiments were done at a location where most of the snowpack was composed of windpack, so for these simulations the permeability is assigned to that measured in the windpack at the Alert transmitter site. We also assume for these calculations that the intake port is in perfect contact with the surrounding snow for the entire length of the sampler

into the snow; these calculations do not therefore include possible fast-flow effects that may be possible should a gap exist between the sampler and the surrounding snow. Boundary conditions on the ozone are the same as for the natural ventilation calculations: zero concentration at the snow/ground interface, and ambient air ozone concentration in the top millimeter of firn air. The decay rate for ozone is again taken from the ozone kinetic chamber experiment.

Fig. 6a shows the airflow pattern in the snow for the intake at 10 cm deep in the snow. The airflow velocity for vectors in the snow shown near the intake is $\sim 7 \text{ cm/s}$, while those at 0.4 m away from the intake are $\sim 0.1 \text{ cm/s}$; the velocities approach zero farther away from the intake. Note that for clarity in Fig. 6a, the flow field is only shown out to a lateral extent of 0.4 m from the intake, but the entire calculation domain extends out to 3 m. At flow rates of 2 lpm in this shallow snowpack, most of the air is drawn down from the surface of the pack into the sampler, allowing little residence time in the snow. The resulting calculated contours of ozone

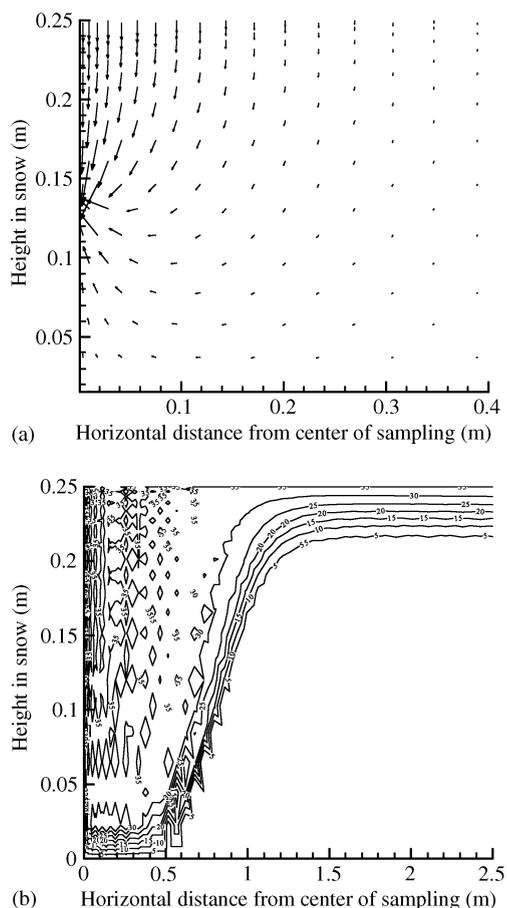


Fig. 6. Calculated airflow and ozone concentrations for firn probe sampling: (a) airflow velocity vectors and (b) ozone concentration.

concentration are shown in Fig. 6b; these contours are not significantly changed if the dark destruction rate coefficient is used in place of the light coefficient. It is evident that the concentration at the intake includes ambient air drawn at high speed through the pack; the concentration at that depth in the absence of the firn air sampler would probably be lower, as evidenced by the natural ventilation and diffusion simulations shown above. The ozone concentrations several meters away from the sampling intake in Fig. 6b represent the concentration dominated by molecular diffusion since the airflow velocity there is very small. Several meters away from the intake these calculations essentially indicate that, in the absence of interstitial airflow, the ozone depletion in the snow occurs within the top 5 cm of the pack. Thus the numerical calculations taken together indicate that in windless conditions, transport through the pack is by diffusion and ozone is depleted in the top ~5 cm; under natural wind-driven ventilation more ozone is transported into the pack by the wind so that the ozone is depleted in the top ~8 cm of the pack. Under high-speed ventilation induced by firn air sampling, the resultant ozone profile shows depletion in the top ~30 cm, but this concentration includes a contribution from ambient ozone from the air above the pack that was drawn at high speeds through the snow and into the sampler. All of the data and calculations show that ambient ozone becomes rapidly depleted within the snowpack.

Improved measurements of chemical concentrations in the snowpack interstitial air are needed for accurate sampling of trace species in firn air. Ideally, sampling instruments should measure chemical concentrations of distinct, small (e.g., 10–30 cm³) quantities of air extracted from the snowpack, rather than requiring continuous flow withdrawal. Unfortunately, for ozone and most other trace species of interest in firn air, the sampling devices require continuous flow on the order of liters per minute, which will necessarily result in advection-dominated flow and mixing of concentrations of various depths, as shown above. Alternatively, if continuous flow is required by the sampling instrument, the sampling technique should be modified so that the sampled flow would aggregate the flow from many low-flow sampling ports that are distributed horizontally but lie at the same depth and layer within the snow. In the field we have noticed that the concentrations vary much more with depth than with lateral (horizontal) location. The low flow at each low-flow port would help to improve the ratio of air from the desired depth to air withdrawn from other depths. In current research at Summit, Greenland, we are developing a new sampling apparatus following this idea, and also conducting inert tracer gas (SF₆) experiments for model validation of the flow regimes and for comparison to measured reactive species concentrations.

8. Conclusions

The Arctic snowpack at Alert will allow rapid exchange of gases with the atmosphere. Even under natural ventilation conditions with moderate winds, the entire pack is exposed to air movement and therefore available for chemical exchange processes. Measurements of interstitial ozone concentrations in the snow indicate rapid depletion of ozone as a function of depth in the snow, indicating that the snowpack plays a key role in depletion of ozone in the atmospheric boundary layer. A kinetic snow chamber experiment has allowed a first-order modeling of the exchange processes. In the case of ozone, rapid destruction rates of ozone cause most of the ozone destruction to occur within approximately the top 10 cm of the snowpack under natural ventilation conditions, and would likely be limited to the top 5 cm if the same destruction rates are valid with diffusion alone. Because of the higher permeability of the snowpack on the sea ice site, compared to the terrestrial site where the measurements were made, it is possible that chemical exchange processes could be even more rapid over the sea ice in the greater Arctic.

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