

**Modeling chemistry
in and above snow at
Summit, Greenland –
Part 1**

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Abstract

Sun-lit snow is increasingly recognized as a *chemical reactor* that plays an active role in uptake, transformation, and release of atmospheric trace gases. Snow is known to influence boundary layer air on a local scale, and given the large global surface coverage of snow may also be significant on regional and global scales.

We present a new detailed one-dimensional snow chemistry module that has been coupled to the 1-D atmospheric boundary layer model MISTRA, we refer to the coupled model as MISTRA-SNOW. The new 1-D snow module, which is dynamically coupled to the overlaying atmospheric model, includes heat transport in the snowpack, molecular diffusion, and wind pumping of gases in the interstitial air. The model includes gas phase photochemistry and chemical reactions both in the interstitial air and the atmosphere. Heterogeneous and multiphase chemistry on atmospheric aerosol is considered explicitly. The chemical interaction of interstitial air with snow grains is simulated assuming chemistry in a liquid (aqueous) layer on the grain surface. The model was used to investigate snow as the source of nitrogen oxides (NO_x) and gas phase reactive bromine in the atmospheric boundary layer in the remote snow covered Arctic (over the Greenland ice sheet) as well as to investigate the link between halogen cycling and ozone depletion that has been observed in interstitial air. The model is validated using data taken 10 June–13 June, 2008 as part of the Greenland Summit Halogen- HO_x experiment (GSHOX). The model predicts that reactions involving bromide and nitrate impurities in the surface snow at Summit can sustain atmospheric NO and BrO mixing ratios measured at Summit during this period.

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1 Introduction

The significance of chemistry in surface snow and on ice was first discussed in the context of boundary layer ozone depletion events in the coastal Arctic during spring (Bottenheim et al., 1986; Oltmans and Komhyr, 1986; Hausmann and Platt, 1994; Barrie et al., 1988; Foster et al., 2001; Simpson et al., 2007). This ozone loss has been attributed to catalytic destruction of ozone by bromine released from frost flowers, open leads, first year sea ice, or recycling on aerosol (e.g. Kaleschke et al., 2004; Kalnajs and Avallone, 2006; Simpson et al., 2007; Piot and von Glasow, 2008; Zhao et al., 2008). At Summit (in the center of the Greenland ice sheet), where the total bromine loading is lower than in coastal regions, it has been hypothesized that active bromine chemistry may also occur and alter HO_x partitioning towards OH, increasing the oxidative capacity of the atmosphere (Sjostedt et al., 2007; Chen et al., 2007).

Snow-covered regions are also known to produce nitrogen oxides (NO_x=NO + NO₂) in the snowpack (e.g. Honrath et al., 1999, 2000, 2002; Jones et al., 2000; Davis et al., 2001; Dibb et al., 2002; Jacobi et al., 2004). Vertical gradients of NO_x and HNO₃ during summer 2000 (Honrath et al., 2002) as well as shading experiments and measurements of gases in interstitial air (Jacobi et al., 2004) suggest a photochemical NO_x source in the surface snow.

Model work on nitrate photolysis occurring in a liquid-like layer on snow grains has suggested NO₃⁻ in snow is the most likely source of NO_x in the atmosphere above remote, snow covered regions (Jacobi and Hilker, 2007; Boxe and Saiz-Lopez, 2008; Bock and Jacobi, 2010). HONO release from the remote snowpack has been measured in the Arctic (Zhou et al., 2001; Dibb et al., 2002; Honrath et al., 2002) and recent model work suggesting HONO is formed from NO₂⁻ on the surface of snow grains, followed by transfer to the interstitial air and mixing upwards via wind pumping was presented by Liao and Tan (2008).

Despite numerous observations demonstrating the importance of snow photochemistry, our quantitative understanding of the chemistry in the coupled snow, firn (snow

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that has been left over from past seasons), and atmosphere system is poor. Based on field and laboratory observations as well as modeling studies of snow physics and chemistry an initial picture of the mechanisms controlling this highly coupled system has emerged, shown in Fig. 1 (Domine and Shepson, 2002; Grannas et al., 2007; Domine et al., 2008). Well known tropospheric photochemistry of HO_x, NO_x, VOCs, and ozone occurs over snow covered surfaces. Reactive halogen chemistry also plays an important role in many environments and evidence for reactive halogen chemistry at Summit during 2007 and 2008 is presented by Stutz et al. (2010); Brooks et al. (2010); Liao et al. (2010b); Haman et al. (2010); and Dibb et al. (2010).

Vertical mixing and boundary layer evolution are important because they can modulate surface trace gas concentrations. Due to the particular properties of snow, i.e. low temperatures and high albedo, boundary layers can become very shallow during times of low and absent sun, i.e. during night or winter. A successful model description has to include the boundary layer evolution and related mixing processes in order to correctly model observed atmospheric mixing ratios. Observations of chemistry over snow and ice have resulted in increasing interest in the boundary layer processes that govern exchanges between the snow surface and the atmosphere, a recent review by Anderson and Neff (2008) provides an excellent overview of these processes in polar regions.

The strong influence of snow photochemistry on the overlying air is partly because snow is a highly porous medium. Interstitial air occupies approximately 70% of the snow volume and is efficiently exchanged with the overlying atmosphere through gas diffusion and wind pumping. Gases in the interstitial air undergo gas phase chemical reactions and because of the high ice surface to interstitial air volume ratio the air composition is highly dependent on heterogeneous/multiphase chemistry on ice surfaces. These processes are often driven by solar radiation making snow interstitial air a unique coupled physical-chemical system. Two recent papers Grannas et al. (2007); Domine et al. (2008) have reviewed these processes and have called for new photochemical models of snow that are based on a detailed description of snow chemistry and its coupling to the atmosphere.

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The development of the coupled model (MISTRA-SNOW) was motivated by the desire to explain previously observed elevated levels of NO_x at Summit, Greenland, as well as new measurements of NO and BrO during the 2007 and 2008 GSHOX experiments at Summit. In this study we provide a proof of principle that photochemistry in the snow is a source of gas phase nitrogen oxides and reactive bromine in the boundary layer at Summit and other snow covered areas. We investigate if local production of gas phase reactive nitrogen and bromine species in the surface snowpack can explain atmospheric measurements of BrO, NO, and O_3 made at Summit, Greenland during 3 days in June 2008. We focus on 2008 instead of 2007 because the boundary layer profiles of temperature and humidity were measured as part of the suite of measurements in 2008. The comparison also serves as a validation of the model framework. We also consider the current modeling results in the context of previous field experiments at Summit. In a companion paper, we will discuss the impact of halogen chemistry on HO_x and model sensitivity to a number of input parameters and environmental conditions including HONO, H_2O_2 and HO_x chemistry (Thomas et al., 2010).

2 Model description

In this section we present an overview of the new coupled atmosphere-snow model, MISTRA-SNOW, with a focus on the new snow module, and the initialization chosen for Summit, Greenland for June 2008. Figure 1 provides an overview of the physical and chemical processes included in the coupled model. The boundary layer model MISTRA was originally a microphysical model and was later expanded to include gas, aerosol, and cloud droplet chemistry (von Glasow et al., 2002a,b). MISTRA also includes a description of the dynamics and thermodynamics and treats feedbacks between radiation and particles, see von Glasow et al. (2002a,b) for a detailed description of MISTRA.

2.1 1-D vertical grid

The physical properties of the snowpack change rapidly with depth. The rate at which photochemical reactions proceed decreases rapidly with depth near the snow surface because the actinic flux decays exponentially with depth. To account for the fine spatial scale over which snowpack chemistry and physics changes, the snow/firn is represented as a one-dimensional vertical log scale grid to a depth of 3 m with a total of 20 grid cells. The atmosphere is represented by an evenly spaced grid with 1 m vertical grid spacing in the lowest 100 m and a logarithmically spaced grid from 100–2000 m. The fine grid spacing in the atmosphere is necessary to correctly simulate the shallow boundary layers that occur during evening hours over snow covered regions. The snowpack and atmosphere are coupled at the surface of the snowpack through gas flux that occurs by both diffusion and wind pumping (discussed below).

2.2 Physical properties of snow

The physical description of the snowpack in the model includes the liquid layer thickness, snow grain radius, density, liquid water content, and heat capacity. For calculation of mass transfer between the gas phase and the ice we assumed spherical snow grains. Snow grain radius (1 mm) and density ($\rho = 0.3 \text{ g cm}^{-3}$), respectively, were chosen based on typical conditions observed at Summit (Courville, personal communication, 2008). We treat the liquid layer as a 10 nm thick liquid layer on the surface of a spherical snow grain (Döppenschmidt and Butt, 2000; Rosenberg, 2005). Liquid water content was calculated based on density, snow grain radius, and liquid layer thickness.

2.2.1 Heat flux through the snowpack

The heat flux in the snowpack is explicitly calculated and the temperatures are used for snow chemistry and calculation of gas phase diffusion constants. The effective thermal conductivity of snow k_{eff} is the proportionality factor between the temperature gradient

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dT/dz and the heat flux q :

$$q = -k_{\text{eff}} \frac{dT}{dz} \quad (1)$$

k_{eff} has contributions from several physical processes including heat flux through the solid ice and interstitial air and has a wide range of measured values. For dry snow, values for k_{eff} range between $0.025\text{--}0.65 \text{ W m}^{-1} \text{ K}^{-1}$ and k_{eff} values of windpacked surface snow on polar ice sheets vary from $0.15\text{--}0.20 \text{ W m}^{-1} \text{ K}^{-1}$ for a density near 0.35 g cm^{-3} (Domine et al., 2008). Given these data, we used $k_{\text{eff}} = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ in the model run presented here. In order to calculate the temperature variation in the snowpack we use the time dependent equation:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\frac{k_{\text{eff}}}{\rho C_p} \frac{\partial T}{\partial z} \right) \quad (2)$$

where ρ is the density of the snowpack and C_p is the heat capacity.

To calculate the temperature of the surface and force a diurnal cycle in the atmospheric boundary layer, the upper boundary condition for integration of Eq. (2), is calculated according to:

$$T_{\text{surf}} = T_{\text{amp}} \left(1 + \sin \left[2\pi \left(\frac{t_h}{24} - \frac{t_{\text{min}} + 6}{24} \right) \right] \right) / 2 \quad (3)$$

where T_{surf} is the surface temperature, T_{amp} is the amplitude of the surface temperature oscillation, t_h is the hour in local time, and t_{min} is the hour when the surface temperature reaches a minimum. We use a diurnal variation in the snow surface temperature guided by snow surface temperature measurements (Seok and Helmig, personal communication, 2008) to drive the temperature variability in the snowpack. Similarly, we use this temperature as the lower boundary for the atmosphere ensuring consistency between the snow surface and the atmosphere. In future versions of the model we plan to solve for the surface energy budget in order to more completely treat snow-atmosphere heat flux.

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2.2.2 Gas transport in the firn

Gas transport in the snow and firn is treated as the sum of two process, wind pumping and molecular diffusion. The diffusion constant for gases, D_g , is approximated as $D_g = \lambda_{\text{air}} \bar{v} / 3$ (Gombosi, 1994) using the mean molecular speed ($\bar{v} = \sqrt{8RT / (M\pi)}$ where M is the molar mass) and the mean free path length (λ_{air}). The vertical wind pumping is calculated according to Cunningham and Waddington (1993):

$$u_{\text{firn}} = \frac{6k\rho_{\text{air}}}{\pi\mu\lambda_{\text{surf}}}\frac{h}{\lambda_{\text{surf}}}\frac{\sqrt{\alpha^2+1}}{\alpha}u_{10}^2\exp\left(-\frac{z}{\delta}\right) \quad (4)$$

using δ defined as

$$\delta = \frac{1}{2}\frac{\alpha}{\sqrt{\alpha^2+1}}\frac{\lambda_{\text{surf}}}{\pi} \quad (5)$$

where u_{firn} is the vertical wind pumping speed, k is the permeability, ρ_{air} is the density of air, μ is the dynamic viscosity of air, λ_{surf} is the relief wavelength, h is the relief amplitude, α is a horizontal aspect ratio of the relief relative to wind direction, z is the depth from the snow surface, and u_{10} is the horizontal wind speed 10 m above the snow surface. The parameters used for modeling wind pumping are summarized in Table 1. The horizontal and vertical relief size is chosen based on our visual observations in the field during the GSHOX campaign.

The total gas transport is the sum of both molecular diffusion and wind pumping. We calculate the effective diffusion constant κ (in m^2s^{-1}) as the sum of both contributing terms

$$\kappa = \tau D_g + U_{\text{firn}} \Delta z \quad (6)$$

where D_g is the gas phase diffusion constant, τ is the tortuosity, U_{firn} is the vertical wind pumping speed (both D_g and U_{firn} are a function of depth), and Δz is the grid spacing. Note that the second term of this equation represents an area-averaged effective vertical diffusivity arising from the wind pumping.

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2.3 Chemistry

The model treats gas and aqueous chemistry in the atmosphere and snowpack as well as transfer between the gas and aqueous phases, heterogeneous reactions on aerosols are included in the atmosphere. A complete list of reactions for the new model including both the gas and aqueous phases as well as the Henry's law constants and mass accommodation coefficients are included in the electronic supplement. The reaction set is based on von Glasow and Crutzen (2004) with updated rate constants according to Sander et al. (2006) and Atkinson et al. (2006). The aqueous reaction mechanism was originally developed for chemistry in aerosol particles and has been modified to be consistent with the mechanisms for NO_x release from snow grain recommended by Jacobi and Hilker (2007) as well as Boxe and Saiz-Lopez (2008). A reaction scheme including the most important chemical reactions discussed here is summarized in Fig. 2.

The prognostic equation for the concentration of a gas phase chemical species c_g (in mol/m³_{air}) including wind pumping, diffusion, chemical production and destruction, and exchange with the aqueous phases is given by

$$\frac{\partial c_g}{\partial t} = \frac{\partial}{\partial z} \left(\kappa \rho(z) \frac{\partial c_g / \rho(z)}{\partial z} \right) - D + P - k_t \left(w_l c_g - \frac{c_a}{k_H^{cc}} \right) \quad (7)$$

where κ denotes the sum of diffusion and wind pumping (described above). P and D are chemical production and loss terms, k_H^{cc} is the dimensionless Henry constant obtained by $k_H^{cc} = k_H RT$, where k_H is in mol/(m³Pa), w_l is the dimensionless liquid water content (m³_{aq}/m³_{air}) of the snow liquid layer. The last term in Eq. (7) describes the transport from the gas phase into the aqueous phase according to the formulation by Schwartz (1986) (see also Sander, 1999a). For a single snow grain, the mass transfer coefficient k_t is defined as

$$k_t = \left(\frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha} \right)^{-1} \quad (8)$$

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with the snow grain radius r , the mean molecular speed \bar{v} (defined above in Sect. 2.2.2), the accommodation coefficient α (see the electronic supplement), and the gas phase diffusion coefficient D_g (defined above).

2.3.1 Calculation of photolysis rates

5 Photolysis rates in the atmosphere are calculated online as a function of altitude using the method of Landgraf and Crutzen (1998) with a four stream radiation code. Photolysis rates in the snowpack are calculated according to:

$$E_\lambda(z) = E_\lambda(z=0)\exp(-\epsilon_\lambda^{-1}z) \quad (9)$$

10 where $E_\lambda(z)$ is the actinic flux at depth z , $E_\lambda(z=0)$ is the incident irradiance at the surface of the snowpack ($z=0$ at the surface of the snowpack), and ϵ_λ is defined as the e-folding depth (King and Simpson, 2001). We use an e-folding depth of $\epsilon_\lambda=10$ cm, measured for nitrate at Summit, Greenland (Galbavy et al., 2007) for all species that undergo photolysis. Surface and in snow photolysis rates for NO_2 are shown in Fig. 3. The modeled surface photolysis rates (J_{NO_2}) are in good agreement with measured rates on 10 June 2008. The measurements of J_{NO_2} show similar agreement with model results (not shown) for the remaining two days relevant for this model run.

2.4 Model initialization

20 The model is initialized with gas and aqueous phase concentrations, the initial surface gas phase and the liquid layer concentrations are summarized in Table 2. The initial gas phase mixing ratios in the interstitial air are vertically uniform for species with long atmospheric lifetimes (for example CO) and decay with snow depth for reactive species (for example O_3). Aqueous phase concentrations are initially equal to the Henry's law equilibrium concentration for volatile species. For non-volatile species (ions) the initial concentration is equal to:

$$25 C_{\text{liquid layer}} = \phi \times C_{\text{snow}} \quad (10)$$

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where C_{snow} is the concentration in melted surface snow measured by liquid chromatography at Summit during the days chosen from the GSHOX field campaign period for the model runs. Ion partitioning between the core and surface layer is represented by ϕ , an enhancement factor that accounts for the difference between the measured (bulk) concentration in melted snow and the concentration in the liquid layer. The fraction of the ions present in the liquid layer is given by ϕ/ϕ_{max} , where ϕ_{max} is determined by the properties of the snow grain and the liquid layer. The exact value of ϕ_{max} is determined by the ratio of liquid layer volume to the snow grain volume (for the parameters used to describe snow grains in our model $\phi_{\text{max}} = 3.3 \times 10^4$), while ϕ is determined by how ions segregate between the liquid layer and the ice-like core of the snow grain. Although ϕ is not well known, numerous studies have shown enhancement of ions on ice surfaces compared to the bulk ice composition (approximately equal to the composition of melted snow). Exclusion of non-volatile species from the ice matrix and formation of a surface brine during freezing is a well known phenomenon. Gas deposition followed by dissociation in the liquid layer (for example for HNO_3 deposition followed by dissociation to form H^+ and NO_3^-) will also increase surface ion concentrations compared to the bulk composition. The extent to which ions are mobile in the ice matrix, and how temperature cycling affects ion segregation at the surface of snow grains also affects ion partitioning.

Experiments suggest that chloride is concentrated at the surface of frozen sodium chloride solutions (Cho et al., 2002; Kahan et al., 2007). In addition, molecular dynamics simulations provide evidence that chloride is excluded from the ice matrix upon freezing (Vrbka and Jungwirth, 2005) and that chloride and bromide are more concentrated at the surface of liquid water solutions at ambient temperatures than nitrate (Jungwirth and Tobias, 2001, 2002; Mucha et al., 2005; Thomas et al., 2007). Based on these findings we chose $\phi_{\text{Cl,Br}}$ such that all bromide and chloride ions observed in melted surface snow are concentrated in the liquid layer. Much less information exists for nitrate partitioning between the ice and the liquid layer. We thus adjusted $\phi_{\text{NO}_3^-}$ such that 6% of the total available nitrate in melted snow is present in the liquid layer, so that

the modeled atmospheric NO mixing ratio matched the measured value. There is also evidence that the liquid layer thickness is a function of both the ion concentration and temperature (Cho et al., 2002), in the future the liquid layer thickness and composition will include an explicit description of the dynamic nature of the liquid layer to test model sensitivity to different representations of the liquid layer. The sensitivity of the model to the liquid layer composition will be discussed in an accompanying manuscript (Thomas et al., 2010).

Aqueous phase chemistry to oxidize bromide to bromine is known to be pH dependent, therefore particular care needs to be taken in initializing the pH in the liquid layer. Assuming that HNO_3 uptake is the major source of liquid layer acidity (noting that HCl makes a less significant contribution), we assume one NO_3^- ion has one corresponding H^+ ion. We therefore use the initial nitrate concentration in order to determine the initial H^+ concentration in the liquid layer.

The atmospheric aerosol number and size distribution was initialized by parameterizing aerosol size distribution measurements at Summit on 12 June 2008. The size distribution consists of fine aerosol particles primarily smaller than $0.1 \mu\text{m}$ with an average total aerosol number concentration of 168 \#/cm^3 . Particles are initialized with Cl^- , Br^- , NO_3^- , H^+ , and Na^+ based on collected filter samples during the same time period (Dibb et al., 2010), while also ensuring initial ion balance in the aerosol.

3 Results and discussion

We focused on three days of observations (10 June–13 June 2008) made during the GSHOX experiment at Summit, Greenland in order to test MISTRA-SNOW. This focus period was chosen due to consistent meteorological conditions during the three day focus period as well as simultaneous measurements of O_3 , NO , BrO , HO_x . In addition, FLEXPART emission sensitivity maps indicate that the air at Summit during this period had been cycling over the Greenland snowpack for at least three days prior to the focus period without influence of marine air (Stutz et al., 2010). Therefore, we anticipate that

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the composition of local air masses at Summit was strongly influenced by contact with the surface snowpack.

3.1 Boundary layer evolution and mixing

Atmospheric trace gas concentrations at Summit during this period, and above many other snow covered surfaces, are strongly modulated by diurnal boundary layer evolution. Radiative cooling at night causes the formation of shallow and stable temperature inversions, which often extend from the ground to 20–30 m in height. In the morning, solar surface heating leads to the breakup of this layer, forming a well mixed daytime boundary layer, typically 200–300 m high during the campaign. The three days chosen to test our model generally follow the described boundary layer behavior (Fig. 4). The evolution of temperature throughout the three day model run is shown in Fig. 4 panels a (atmosphere) and b (snow). Measured boundary profiles are shown in Fig. 4 panel c and modeled boundary layer profiles at the corresponding times are shown in panel d. Both the model and measurements show that a shallow inversion layer forms during the night time hours when the sun nears the horizon. At mid-day surface warming leads to rapid growth of the boundary layer. The comparison of measured and modeled temperature profiles at Summit during the 2008 campaign shows that the model accurately captures mixing between the boundary layer and the overlying air. The temperature evolution in the snowpack (Fig. 4 panel b) is also consistent with measured in snow temperature profiles at Summit during late June 2008 (Seok and Helmig, personal communication, 2008).

3.2 NO_x mixing ratios

A number of studies have reported high levels of atmospheric NO_x above the snow in Greenland as well as at South Pole Station in Antarctica and elsewhere (e.g. Honrath et al., 1999, 2000, 2002; Jones et al., 2000; Davis et al., 2001; Dibb et al., 2002). At Summit, the coupled MISTRA-SNOW model predicts NO and NO₂ mixing ratios in

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the atmosphere result from nitrate photochemistry occurring in the liquid layer (Figs. 5 and 6). In the model, nitrate in snow grains is photolyzed to form NO_2 (R1), which is subsequently transferred from the liquid layer to the gas phase (R2).



NO_2 in the interstitial air is in a pseudo steady state (PSS) with NO (R3 and R4).



The NO_x mixture produced in the snow is then mixed upwards and downwards via a combination of wind pumping and diffusion. As air is mixed downward, out of the region where photochemistry occurs, the PSS shifts to NO_2 due to the lower actinic fluxes deeper in the snow. As air is mixed upwards out of the snowpack and actinic flux increases the PSS shifts towards NO, until it reaches the atmospheric PSS at the surface. The surface NO_x mixing ratios are also modulated by boundary layer height (discussed below).

In order to model the absolute levels of NO in the atmosphere, the nitrate partitioning between ice and the liquid layer was adjusted so that 6% of the total nitrate in melted surface snow was present in the liquid layer. The initial nitrate concentration in the liquid layer is the only adjustable parameter used to model NO photochemistry. While there is no direct measurement that indicates how much nitrate should be in the liquid layer vs. the core of the snow grain, the derived value is reasonable and the resulting

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predicted NO mixing ratios are in excellent agreement with atmospheric measurements of NO during the selected 3 day period at Summit in 2008 (Fig. 5 panel c).

Plots of measured and modeled NO atmospheric mixing ratios (Fig. 5 panels a and c) clearly show the vertical distribution of NO is impacted by the boundary layer evolution.

Gas phase NO_x emissions from nitrate in the snow grains to the interstitial air peak with solar radiation, however the diurnal profile of atmospheric NO mixing ratios do not peak at solar noon. Fluxes out of the snowpack are modulated by the influence of mixing processes in the atmosphere. In the early morning NO is mixed upwards and confined to a shallow layer near the surface. The boundary layer breaks up later during the day and NO is rapidly mixed into a larger volume, then in the late afternoon NO is again confined to a shallow layer. The dip in mid-day NO mixing ratios is due to ventilation that occurs as the boundary layer grows, not due to a decrease in NO_x in the interstitial air.

A snow source of NO_x combined with atmospheric mixing explains the behavior of NO at 1.5 m altitude, resulting in NO peaks in the early morning and the later afternoon. It's important to note that NO does not disappear completely at night, as the NO₂ photolysis rate does not drop to zero during this time of the year at Summit. Agreement between model predicted NO mixing ratios and measurements provides strong evidence that the MISTRA-SNOW model contains a reasonable representation of snowpack NO_x chemistry and mixing processes. It should be noted here that the diurnal variation of NO mixing ratios are obtained without adjustment of the model parameters, while the absolute values were obtained by adjusting the nitrate partitioning between ice and the liquid layer.

Unlike NO, NO₂ was not measured during the GSHOX campaign. Therefore, there are no NO₂ measurements to directly compare to model calculations during this period. Figure 6 panels a and c show that the model predicts NO₂ peaks in the atmosphere during the night. The model predicts NO₂ mixing ratios up to a maximum of 60 ppt at night, which are confined to the lowest 20 m of the atmosphere. The majority of night time NO₂ in the atmosphere results from upward mixing of NO₂ in interstitial air,

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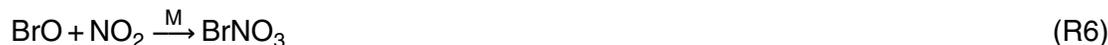
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where a large excess of NO_2 persists into the night. A small fraction of the night-time NO_2 is also produced from the conversion of NO to NO_2 . While this behavior does not reproduce the NO_x diurnal profiles measured at Summit in summer 1999, it is more consistent with measurements taken during summer of 2000 when the peak occurred later in the evening (Honrath et al., 2002). In order to definitively determine if the predicted NO_2 mixing ratios in both the atmosphere and interstitial air are reasonable direct comparison with simultaneous measurements of both NO and NO_2 would be required. However, the excellent agreement with measured NO mixing ratios suggests that the model contains a reasonable representation of NO_x chemistry.

Interstitial air NO and NO_2 mixing ratios have a clear diurnal profile modulated by available sunlight. NO mixing ratios have a maximum at 10 cm depth (230 ppt) as shown in Fig. 5 panels b and d. The loss by vertical mixing and transport is efficient near the surface, thus rapidly transporting NO to the atmosphere above from a depth of 10 cm. The shift in the NO_x PSS, on the other hand, leads to a decrease in NO with depth. Peak NO_2 mixing ratios of up to 700 ppt occur deeper in the snowpack (approx. 20 cm depth, Fig. 6 panels b and d) due to the longer lifetime of NO_2 as well as the shift in NO_x PSS towards NO_2 with depth.

There is some storage of reactive nitrogen as N_2O_5 (formed via R5) and BrNO_3 (formed via R6) in the snowpack during the evening hours. N_2O_5 mixing ratios increase with depth due to a decrease in actinic flux. Up to 40% gas phase nitrogen is present as N_2O_5 deep in the firn. BrNO_3 is only a small reservoir for gas phase nitrogen, but is significant as a reactive bromine reservoir (discussed below). A more detailed discussion of these species and model sensitivity to surface reactions involving BrNO_3 and N_2O_5 as well as their role in snowpack chemistry will be explored in a companion paper (Thomas et al., 2010).



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Cycling of reactive nitrogen species involves both emission of NO_x as well as deposition of reactive nitrogen back to the snowpack. In order to consider the current model results in context of prior field work at Summit, we have compared model results with vertical gradients of NO_x and HNO_3 measured in the lower 2 m above the snowpack at Summit, Greenland, during summer 2000 (Honrath et al., 2002). Honrath and co-workers measured the diurnal cycle of the difference between NO_x mixing ratios at 3.5 and 200 cm above the snow, resulting in a maximum difference during mid-day of approximately -25 ppt (representing a flux out of the snowpack), with larger errors during night-time hours. Because the first grid box in the model atmosphere is one meter in height, in order to compare with these vertical gradients, we calculated the gradient between the snow surface (top snow grid cell) and the concentration in the atmosphere at a height of 1.5 m. The model predicts a mid-day peak in the vertical gradient of -10 ppt, approximately a factor of 2 different than the vertical gradient values measured in 2000. Different conditions from year to year is one possible explanation for this difference. Strong gradients in near surface snow interstitial air mixing ratios are predicted by the model as a function of depth near the snow surface, as a result even a small increase in ventilation of the air at the top of the snowpack due to different meteorological conditions, different snow morphology, or perturbation of vertical NO_x gradients due to sampling near the snow surface could easily explain differences of a factor of 2 or more.

The diurnal cycle of HNO_3 mixing ratios at the same heights, 3.5 and 200 cm, were also measured by Honrath et al. (2002), with a maximum vertical gradient of 10 ppt at mid-day (representing a flux towards the snow surface). We have computed corresponding vertical gradients from the model results using the same method described above for NO_x . The model predicts a small flux of HNO_3 out of the snow during mid-day (max of ~ 1.5 ppt) and uptake of HNO_3 back to the snow at night, (max of ~ 0.25 ppt). Gas phase production of HNO_3 occurs in the interstitial air via the gas phase reaction of $\text{NO}_2 + \text{OH}$ (R7) during mid-day, due to elevated concentrations of both reactants in the interstitial air.



Disagreement between the predicted sign of the HNO_3 vertical gradient at mid-day between the model and could be due to difference in conditions between 2008 and 2000 (discussed above for NO_x) or an unknown input of atmospheric HNO_3 from an external source, for example atmospheric transport to Summit during measurements made during summer of 2000. The small values of the measured HNO_3 vertical gradient could also be subject to experimental error. Given this, further investigations of HNO_3 fluxes in the atmosphere and the model are warranted.

3.3 BrO mixing ratios

Contour plots of model predicted BrO mixing ratios in the atmosphere and interstitial air are shown in Fig. 7 a and b respectively. Atmospheric BrO shows a similar diurnal variation as NO (Fig. 5) with maxima of 2–3 ppt in the morning and late evening. Model BrO is compared with measurements of BrO by chemical ionization mass spectrometry (CIMS) and long-path differential optical absorption spectroscopy (LP-DOAS) in panel c and predicted interstitial air mixing ratios are shown in panels b and d. The model BrO generally agrees well with the observations within the uncertainty, although there are some differences during the first day of the model run, most likely due to a low initial gas phase reactive bromine mixing ratios in the model.

Atmospheric BrO mixing ratios in the model result from a small reactive halogen flux from bromine impurities in surface snow that undergo photochemistry and subsequent release from the snowpack (referred to as *local production*). Model predicted BrO in both interstitial air and the atmosphere is formed from photolysis of Br_2 (R8) followed by reaction with ozone (R9).



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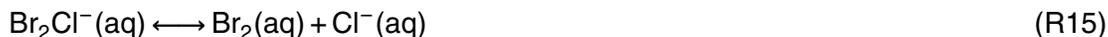
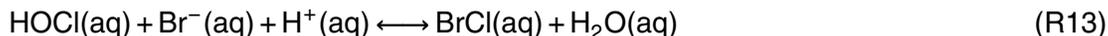
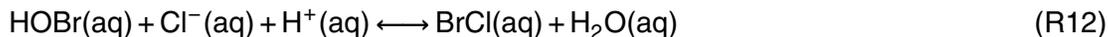
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Molecular bromine is formed via aqueous chemistry in the liquid layer by a series of reactions that begin with oxidation of the bromide ion (R10) and Br₂ formation includes many steps and reaction pathways including reactions involving Cl⁻, Br⁻, OH, HOBr, and H⁺ (see the electronic supplement for a complete list of reactions). OH is important as an oxidant in the liquid layer to initiate bromine production via reaction of OH with Br⁻ to form HOBr⁻.



Conversion of bromide to Br₂ is facilitated by the presence of Cl⁻ due to fast cycling between bromine and chlorine species in the liquid layer (for example R12 and R13). However, the model does not predict significant amounts of BrCl in the interstitial air because the Br:Cl ratio in the liquid layer is far in excess of that for sea water, therefore BrCl immediately reacts with bromine to form Br₂Cl⁻ (R14) followed by decomposition to Br₂ and Cl⁻ (R15). Molecular bromine formed in the liquid layer is transferred to the interstitial air (R11) where it can undergo gas phase photochemistry.



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In order to understand the mechanism for bromine release from the liquid layer, we have conducted three test runs (1) with no initial chloride in the liquid layer, (2) initially neutral pH in the liquid layer, and (3) with the $\text{Br}^- + \text{OH}$ reaction rate equal zero. Runs 1 and 2 (not shown) predict a negligible amount of bromine release from the liquid layer. Run 3 (also not shown) predicts initially a reduction in Br_2 by 50% with smaller reductions (both vary as function of depth) as the run progresses. The presence of bromide, chloride, acidity, as well as an initial oxidant are all important for bromine release from the liquid layer. A similar halogen activation mechanism was originally suggested by Vogt et al. (1996) and subsequent studies on halogen activation in aerosols have shown the importance of these processes in Br_2 and BrCl release from aerosols.

The bromide content of melted snow was measured as part of GSHOX at Summit (Dibb et al., 2010) and is known to be present in trace amounts in the remote snowpack. Bromide reacts with OH in the liquid layer formed from direct photolysis of H_2O_2 in the liquid layer (R16) and from photolysis of the nitrate ion (R1).



The relative contribution of liquid layer OH from H_2O_2 is between 60–90% of the total OH , with typical values of 85%. The remainder is primarily formed from nitrate photolysis, with the exact percent depending on the depth in the snowpack.

Release of liquid layer Br_2 also proceeds through the uptake of HOBr onto snow grains, which is formed in the gas phase via the reaction of BrO with the HO_2 radical (R17).



The gas phase Br_2 levels can also be impacted by the self reaction of BrO to form molecular bromine. However, as the role of the BrO self reaction depends on the square of the BrO concentration, it is less important for the relatively low BrO mixing ratios in our model run.

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In the interstitial air, where both elevated BrO and NO₂ mixing ratios are predicted, the gas phase reaction to form BrNO₃ proceeds rapidly (R6). A large portion of the total reactive gas phase bromine in the interstitial air is in the form of BrNO₃, near the surface between 15%–75% of the total bromine is present as BrNO₃ and deeper in the snowpack (where no photolysis occurs) close to 100% of the bromine is stored as BrNO₃. Br₂ recycling through the gas phase reaction of BrNO₃ with Br (R18) contributes between 40 and 50% of the total Br₂ formation in interstitial air.



Three processes contribute to loss of BrNO₃ in the interstitial air including conversion to Br₂ (R18), photolysis, and upward mixing. Gas phase reactions involving BrNO₃ are not a net source of bromine in interstitial air and only contribute to recycling of reactive bromine back to Br₂.

BrNO₃ plays an important role as a gas phase reservoir in the atmosphere as well. While during the day only a small fraction of the total bromine is stored as BrNO₃ in ambient air (average <10%) at night this fraction increases up to ~75% due to increased NO₂ mixing ratios (see discussion above). Bromine and NO_x chemistry are coupled through additional gas and aqueous reactions that will be discussed more in detail in a companion paper in this issue (Thomas et al., 2010). It is not clear if surface reactions involving gas phase BrNO₃ occur on the surface of ice, the importance of surface reactions involving BrNO₃ will be investigated in the context of a model sensitivity study in a corresponding paper (Thomas et al., 2010).

Transport of gas phase reactive bromine out of the snowpack occurs through upward mixing of a number of gas phase species including Br₂, BrNO₃, and BrO. The flux of bromine out of the snowpack peaks at solar noon, when photochemical production of Br₂ in the liquid layer is the most rapid. Molecular bromine is responsible for ~45% of the total bromine flux out of the snowpack at mid-day. BrNO₃ also plays an important role in transporting reactive bromine out of the snowpack into the atmosphere. During the day BrNO₃ transport contributes approximately 30% of the reactive

bromine transported to the atmosphere, with a larger percent at night when the total flux is at a minimum. Once BrNO_3 is in the atmosphere it is rapidly converted to Br_2 (R18), BrNO_3 does not form as rapidly in the atmosphere due to lower NO_2 mixing ratios than in the interstitial air.

5 Atmospheric aerosol also plays an important role in bromine recycling despite the low total aerosol number concentrations. It is known that aerosol particles are present at Summit can persist for some time above the snow surface at Summit (Ziemba et al., 2010). In order to investigate the role of aerosols in bromine cycling, a model run without atmospheric aerosol in the boundary layer resulted in 30% less BrO predicted
10 (compared to Fig. 7 c, not shown). Further investigation of the role of aerosol in bromine recycling at Summit is clearly warranted.

The diurnal profile of BrO, with peaks in the morning and early night, is similar to model predicted NO. As in the case of NO, lower BrO concentrations are observed as near surface air is actively mixed and diluted during mid-day. To investigate the influence of local snowpack emissions on the diurnal cycle of BrO we have compared model
15 predicted atmospheric mixing ratios to hourly averaged LP-DOAS measured BrO mixing ratios selected for times during the 2008 campaign when FLEXPART emission sensitivities indicate the source region for air sampled at Summit is primarily emissions from the surface of the Greenland ice sheet (Fig. 8). Agreement between modeled
20 and measured mixing ratios provides evidence that emissions from the surface of the Greenland ice sheet are the source of reactive gas phase halogens in the boundary layer, for a more detailed discussion see Stutz et al. (2010). Both the timing of the peaks as well as the absolute values of the mixing ratios are in good agreement, providing strong evidence that local air masses are influenced by snowpack emissions of
25 reactive bromine. Finally, it is important to note that the liquid layer in the snowpack is not significantly depleted in bromide during the three day model run, suggesting that bromine cycling resulting in at least 3 ppt of BrO can be sustained for longer time periods at Summit.

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3.4 O₃ mixing ratios

Predicted atmospheric and interstitial air ozone mixing ratios are shown in Fig. 9. The modeled and observed ozone mixing ratios show excellent agreement during the first 48 hours of the model run. On the final day of our focus period a rapid increase followed by a decrease in the measured ozone was observed, corresponding to a change in wind direction as noted by (Stutz et al., 2010). This most likely indicates an air mass change, however there is no corresponding change in the measured NO or BrO mixing ratios (see NO and BrO sections). FLEXPART emission sensitivity do not indicate a significant change in the source region for air sampled during the time when increased ozone was observed. Our model does not include the effect of an air mass change, but any change that occurred would only impact the final day of our model run.

The model run does not predict significant ozone loss in the snowpack, which was previously reported by Peterson and Honrath (2001). This can be explained by a combination of factors including only a moderate amount of BrO predicted in interstitial air (<15 ppt BrO), resulting in slower ozone destruction than occurs during typical ozone depletion events in the Arctic. Second, elevated hydroperoxyl radical concentrations in the interstitial air are predicted by the model (compared to ambient air). Consequently, there is some ozone production through NO conversion to NO₂ via the reaction with the hydroperoxyl radical. Third, fast downward mixing of ozone via mixing process from the overlying atmosphere results in replenishment of any ozone destroyed through gas phase bromine cycling in the firn air (in the current model run).

Although this model run does not predict depleted ozone mixing ratios in interstitial air, halogen chemistry is still a likely cause of reduced ozone mixing ratios that have been measured in interstitial air (see for example Peterson and Honrath, 2001). A delicate balance of many factors including interstitial air reactive bromine mixing ratios, bromide content in the snowpack, replenishment of ozone from the overlying atmosphere, NO_x mixing ratios, as well as the amount of HO_x present in the firn air all have a role in determining ozone concentrations. Rapid destruction of ozone by bromine

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in the interstitial air could potentially occur under different conditions than observed during the 2008 focus period.

4 Conclusions

A one dimensional air/snow multiphase chemical transport model (MISTRA-SNOW) was developed to simulate the vertical and temporal evolution of atmospheric chemistry at Summit, Greenland, and to test our understanding of sunlit snow as a chemical reactor. During periods when air masses were predominantly influenced by local chemistry, characterized by residence times on the Greenland ice sheet of at least 3 days, combined with stable diurnal meteorological conditions the model provides an excellent description of the observed NO and BrO mixing ratios and their diurnal profiles. The specific trends present in both the model and observations during the three day focus period are likely to be observed when there is a stable boundary layer at night, rapid venting during the day, and when an air mass has resided over the Greenland ice sheet for some time. A number of important mechanisms were identified to play a crucial role for the accurate description of boundary layer composition over sunlit snow:

- During the three day focus period in 2008 both the model and measurements show the atmospheric boundary layers exhibits a distinct diurnal behavior, with strong and shallow temperature inversions at night and in the early morning, and rapid mixing in the late morning to noon. The model, as well as field observations, clearly show that the boundary layer height is one of the main factors modulating surface trace gas mixing ratios over sunlit snow.
- Gas exchange processes including wind pumping and diffusion determine vertical redistribution of gases in the snowpack and impact the upward flux out of the snow. In our present model run, the effect of wind pumping dominates over gas diffusion at the surface of the snowpack, whereas gas diffusion dominates deeper

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in the snowpack. Considerable uncertainties in the representation of wind pump-
ing in the model remain and further studies are required to improve its description.

- Solar actinic flux is the main driver of nitrogen oxide and reactive bromine release from the liquid layer. The accurate description of this parameter requires detailed knowledge of the penetration of actinic flux into the snowpack.
- Aqueous photochemistry in a liquid layer on the snow grains yields a reasonable description of the release of nitrogen oxides and reactive bromine. Nitrate photolysis was the main driver of NO_x release, while a complicated reaction pathway leads to oxidation of bromide to Br_2 and results in release from the liquid layer. Br_2 release from the liquid layer depends on the concentration of liquid layer OH which, in our model, is formed through the photolysis of H_2O_2 and nitrate. A number of assumptions were made to describe the liquid layer including thickness (10 nm) and initial ion concentrations (6% of total nitrate and 100% of bromide and chloride measured in melted snow) in the liquid layer. We will investigate the sensitivity of the model results to these parameters in a companion paper (Thomas et al., 2010). Additional research on the physical and chemical properties of the liquid layer is imperative to further constrain these parameters.

Our results show that a model describing these mechanisms based on first principles can, despite the uncertainties in the physical and chemical processes, correctly describe coupled snow – atmosphere chemistry. Additional data, such as a new mechanism for nitrate photochemistry in snow developed by Bock and Jacobi (2010), will help to improve the existing model. New laboratory studies that study mechanisms for release of gas phase species from ice (for example Hellebust et al., 2010) and their influence on results will be evaluated in future work. The current model does not include chemistry on atmospheric ice particles during nocturnal fog events (observed during the focus period) and during blowing snow (not observed during the focus period), which can potentially influence atmospheric chemistry of NO_x and reactive bromine. Mercury chemistry and its link to reactive halogens are currently also missing in the

model. Further improvements in the model will address these and other issues to improve our knowledge of snow photochemistry. Direct comparison of the model results with measured interstitial air mixing ratios would also provide a needed constraint of snowpack chemistry, with the understanding that even small perturbations to vertical mixing at the snow surface could impact the ability to compare directly model results and measurements taken in this region. Continued efforts to characterize the chemical composition of interstitial air are essential. Sensitivity studies as well as a discussion of HONO, H₂O₂ and HO_x chemistry using the current model version will be presented in a companion paper in this issue (Thomas et al., 2010) to further the goal of understanding the significance of sunlit snow as a chemical reactor and its impact on atmospheric chemistry.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys-discuss.net/10/30927/2010/acpd-10-30927-2010-supplement.pdf>.

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Table 1. Parameters to calculate the vertical wind pumping speed and diffusion a Summit, Greenland. The horizontal wind speed was based on our observations in the field.

Parameter	Description	Value	Units	Reference
μ	dynamic viscosity of air	1.6×10^{-5}	Pa · s	List (1884)
λ_{surf}	relief wavelength	3.0×10^{-2}	m	see text
h	relief amplitude	1.5×10^{-2}	m	see text
α	horizontal aspect ratio of relief	1	unitless	Albert and Hawley (2002)
k	permeability	8.0×10^{-10}	m ²	Albert and Shultz (2002)
u_{10}	horizontal wind speed	3.0	m s ⁻¹	average of NOAA observations*
τ	tortuosity	0.5	unitless	Albert and Shultz (2002)

* Mefford (2010)

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Table 2. Initial gas and liquid layer concentrations for model runs conducted based measurements taken in June 2008 as well as previous measurements at Summit, Greenland.

Species unit	gas phase (surface) ppb	Reference	liquid layer M	ϕ	Reference
O ₃	55	measured	–	–	–
NO ₂	0.02	Jacobi et al. (2004) and Hutterli et al. (2001)	–	–	–
HNO ₃	0.01	Dibb et al. (2002)	–	–	–
HCHO	0.1	Jacobi et al. (2004)	2.0×10^{-5}	1	Henry's law based on Sander (1999b)
H ₂ O ₂	0.4	Jacobi et al. (2004) and Hutterli et al. (2001)	1.0×10^{-3}	1	Henry's law based on Sander (1999b)
CO ₂	388 (ppm)	NOAA (Flask) ¹	–	–	–
CO	130	measured	–	–	–
Br [–]	–	–	1.0×10^{-8}	3.3×10^4	Dibb et al. (2010)
Cl [–]	–	–	5.5×10^{-7}	3.3×10^4	Dibb et al. (2010)
NO ₃ [–]	–	–	3.5×10^{-6}	2.5×10^3	Dibb et al. (2010)
H ⁺	–	–	3.5×10^{-6}	2.5×10^3	equal to nitrate ²
Na ⁺	–	–	5.6×10^{-7}	3.3×10^4	counter ion ³

¹ Conway et al. (2009).

² assumed nitrate is primarily from from HNO₃ deposition (therefore $[H^+]_{t=0}$ is equal to $[NO_3^-]_{t=0}$).

³ counter ion for halides.

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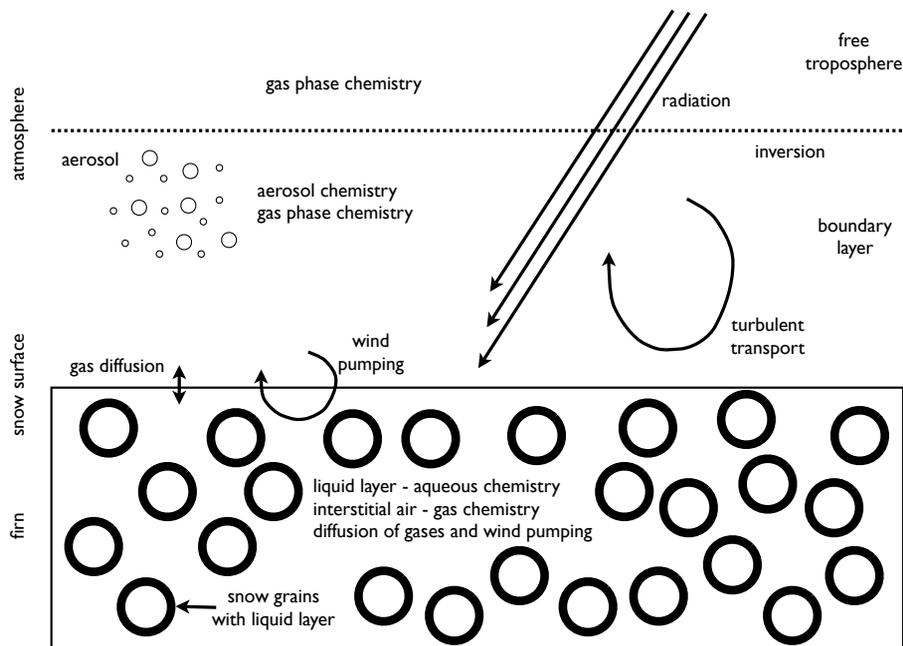


Fig. 1. Schematic depiction of the most important local processes controlling the atmospheric composition over sunlit snow. These processes are also included in the one-dimensional boundary layer model MISTRA-SNOW, where gas phase chemistry is calculated in all layers, aerosol chemistry is included in the boundary layer, and snow liquid layer chemistry is included below the snow surface.

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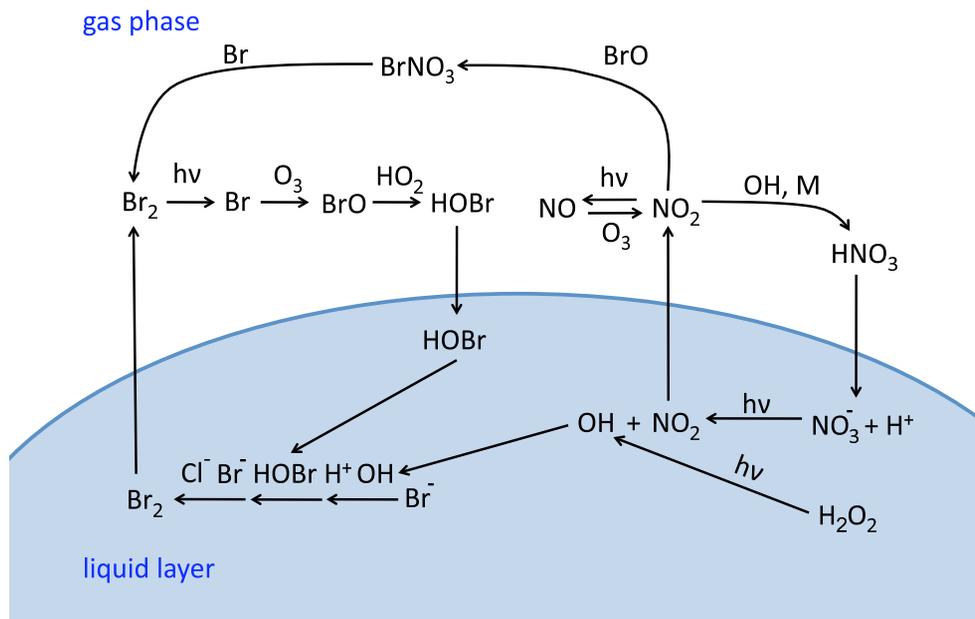


Fig. 2. Chemical pathways important for NO_x and reactive bromine cycling at Summit, Greenland.

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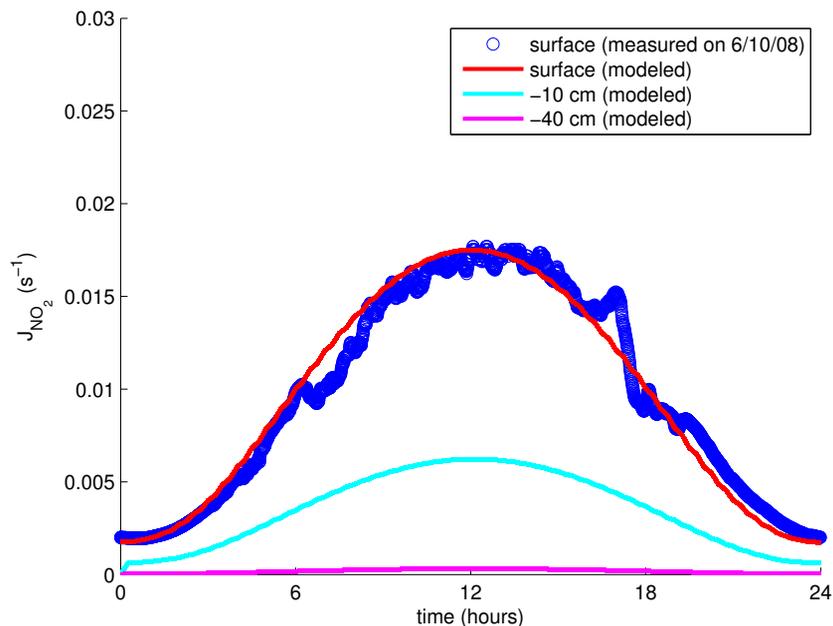


Fig. 3. J_{NO_2} measured on 10 June 2008 (in blue) compared with the modeled J_{NO_2} (in red) at the snow surface. Modeled J_{NO_2} data at depths of 10 cm and 40 cm are also shown.

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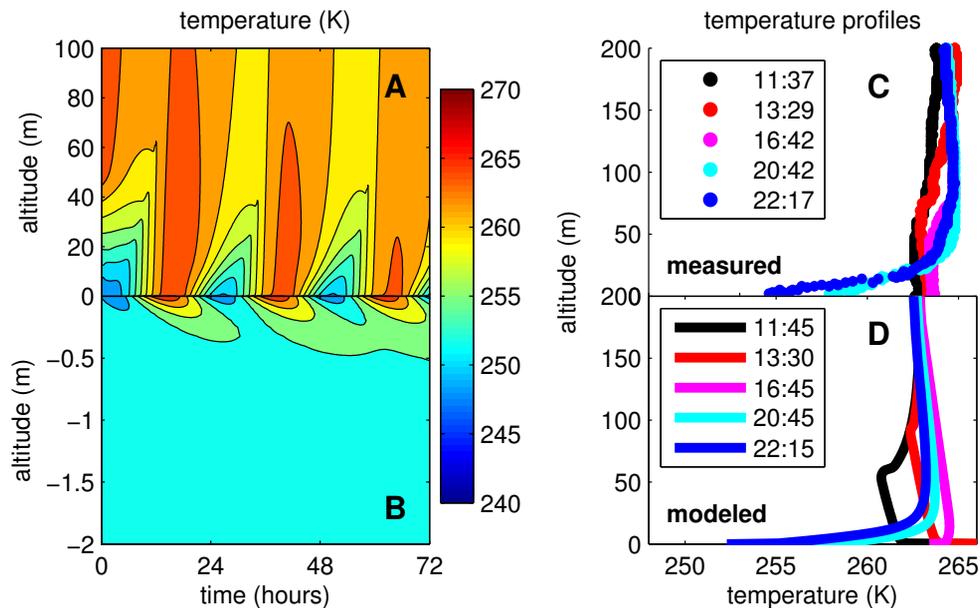


Fig. 4. Modeled temperature evolution of the atmosphere and firn in the upper panels (A) and (B). Tethersonde measurements (panel C) compared with modeled temperature profiles (panel D).

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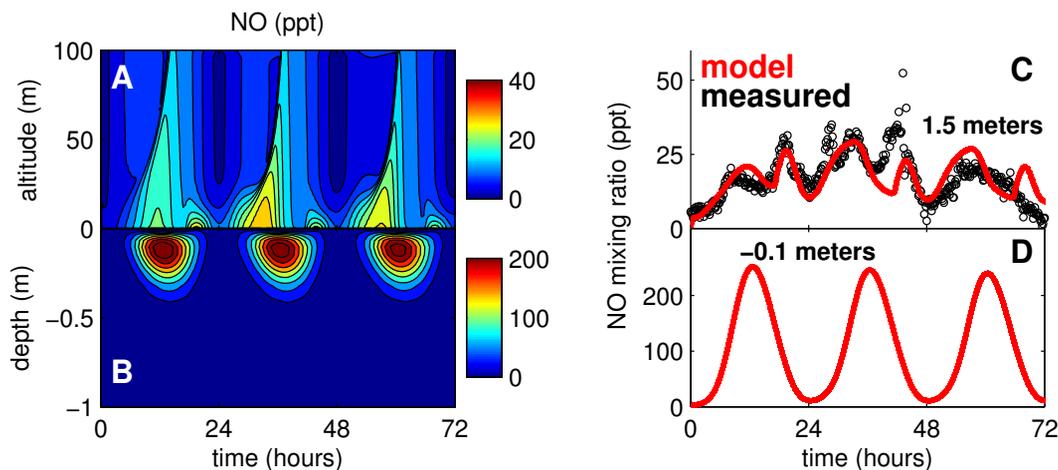


Fig. 5. Modeled NO mixing ratios in the atmosphere (**A**) and interstitial (**B**) air. Modeled mixing ratios in the atmosphere at an altitude of 1.5 m above the snowpack are compared with measurements in panel (**C**). Predicted interstitial air mixing ratios 10 cm below the snow surface are shown in panel (**D**).

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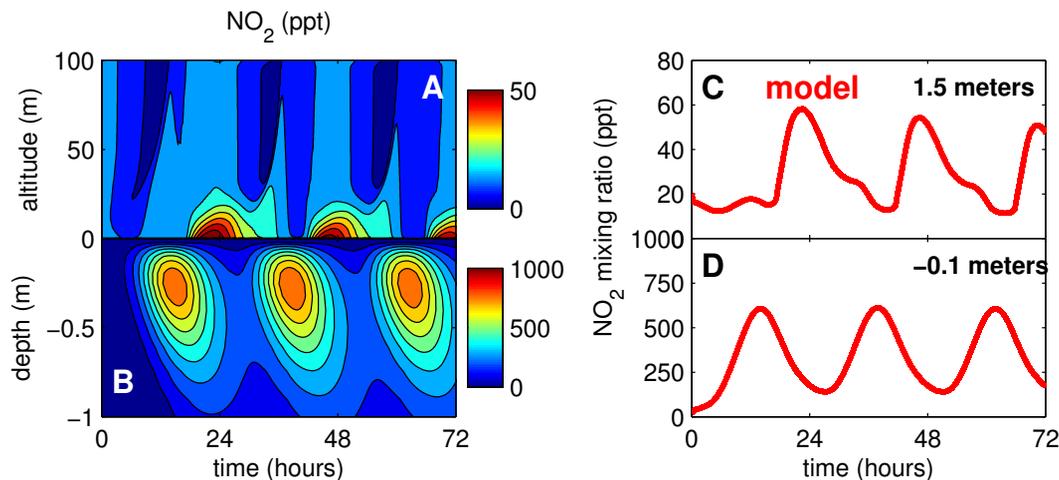


Fig. 6. Modeled NO₂ mixing ratios in the atmosphere (A) and interstitial (B) air. Modeled mixing ratios in the atmosphere at an altitude of 1.5 m above the snowpack are shown in panel (C), NO₂ was not measured during the field campaign. Predicted interstitial air mixing ratios 10 cm below the snow surface are shown in panel (D).

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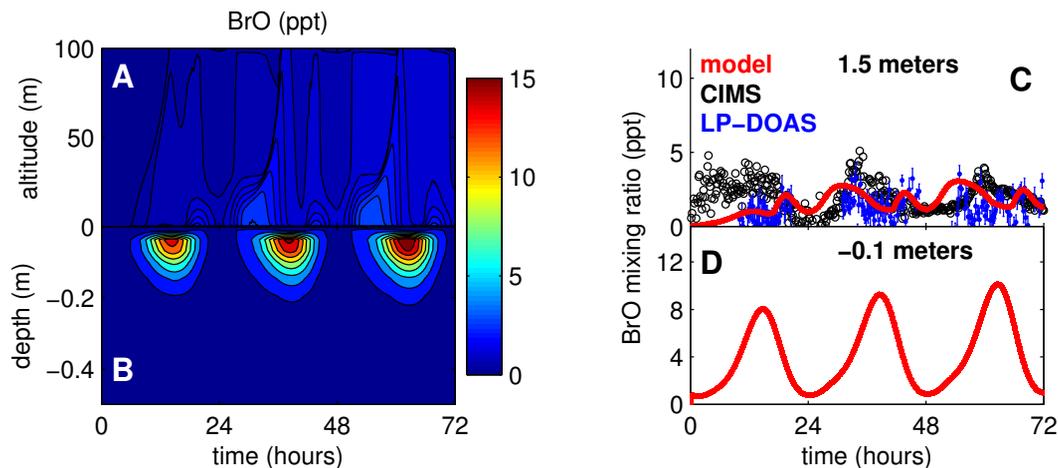


Fig. 7. Modeled BrO mixing ratios in the atmosphere (**A**) and interstitial (**B**) air. Modeled mixing ratios in the atmosphere at an altitude of 1.5 m above the snowpack are compared with both CIMS and LP-DOAS measurements in panel (**C**). Predicted interstitial air mixing ratios 10 cm below the snow surface are shown in panel (**D**).

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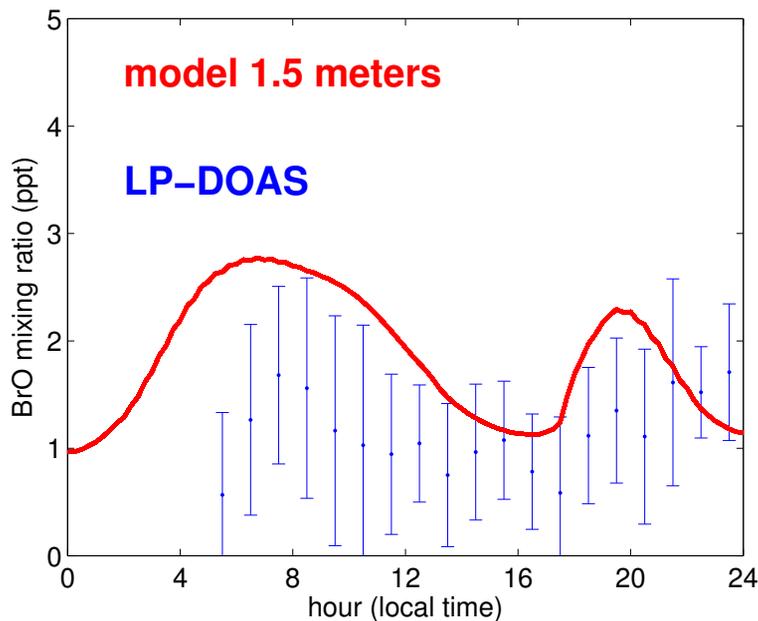


Fig. 8. Modeled BrO mixing ratios compared to the hourly averaged locally influenced BrO mixing ratios measured in air masses that have been over the ice sheet for at least 3 days before reaching Summit. Bars of the LP-DOAS data denote the variability of the data over the averaged days.

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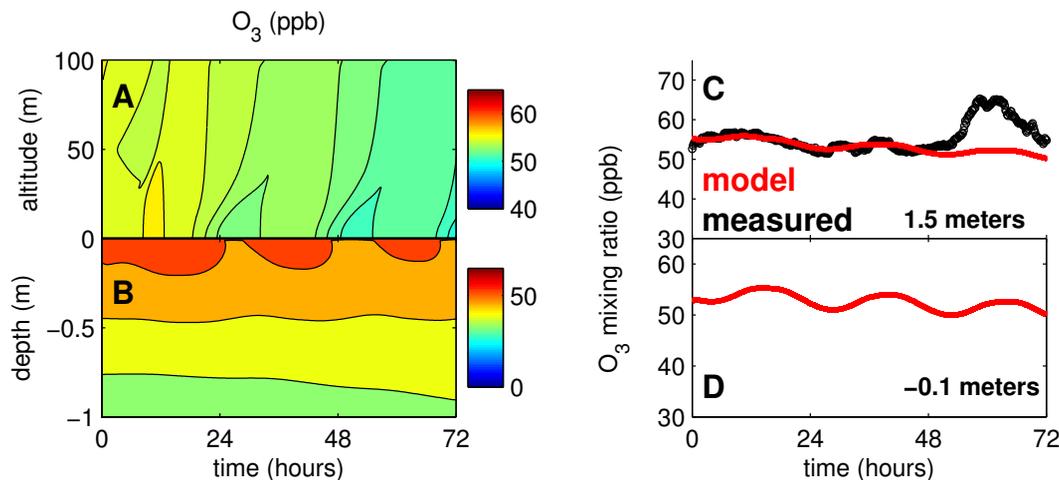


Fig. 9. Modeled O_3 mixing ratios in the atmosphere (A) and interstitial (B) air. Modeled mixing ratios in the atmosphere at an altitude of 1.5 m above the snowpack are compared with measurements in panel (C). Predicted interstitial air mixing ratios 10 cm below the snow surface are shown in panel (D).