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Modeling chemistry in and above snow at Summit, Greenland – Part 2: Impact of snowpack chemistry on the oxidation capacity of the boundary layer

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Abstract. The chemical composition of the boundary layer in snow covered regions is impacted by chemistry in the snowpack via uptake, processing, and emission of atmospheric trace gases. We use the coupled one-dimensional (1-D) snow chemistry and atmospheric boundary layer model MISTRA-SNOW to study the impact of snowpack chemistry on the oxidation capacity of the boundary layer. The model includes gas phase photochemistry and chemical reactions both in the interstitial air and the atmosphere. While it is acknowledged that the chemistry occurring at ice surfaces may consist of a true quasi-liquid layer and/or a concentrated brine layer, lack of additional knowledge requires that this chemistry be modeled as primarily aqueous chemistry occurring in a liquid-like layer (LLL) on snow grains. The model has been recently compared with BrO and NO data taken on 10 June–13 June 2008 as part of the Greenland Summit Halogen-HO_x experiment (GSHOX). In the present study, we use the same focus period to investigate the influence of snowpack derived chemistry on OH and HO_x + RO₂ in the boundary layer. We compare model results with chemical ionization mass spectrometry (CIMS) measurements of the hydroxyl radical (OH) and of the hydroperoxyl radical (HO₂) plus the sum of all organic peroxy radicals (RO₂) taken at Summit during summer 2008. Using sensitivity runs we show that snowpack influenced nitrogen cycling and bromine chemistry both increase the oxidation capacity of

the boundary layer and that together they increase the mid-day OH concentrations. Bromine chemistry increases the OH concentration by 10–18 % (10 % at noon LT), while snow sourced NO_x increases OH concentrations by 20–50 % (27 % at noon LT). We show for the first time, using a coupled one-dimensional snowpack-boundary layer model, that air-snow interactions impact the oxidation capacity of the boundary layer and that it is not possible to match measured OH levels without snowpack NO_x and halogen emissions. Model predicted HONO compared with mistchamber measurements suggests there may be an unknown HONO source at Summit. Other model predicted HO_x precursors, H₂O₂ and HCHO, compare well with measurements taken in summer 2000, which had lower levels than other years. Over 3 days, snow sourced NO_x contributes an additional 2 ppb to boundary layer ozone production, while snow sourced bromine has the opposite effect and contributes 1 ppb to boundary layer ozone loss.

1 Introduction

Air-snow interactions are known to impact the composition of the polar boundary layer via deposition, chemical processing, and emission of chemical species (e.g. Dominé and Shepson, 2002; Grannas et al., 2007). Photochemistry on

snow grains and in interstitial air (air between snow grains in the snowpack) lead, for example, to the formation of nitrogen oxides (NO_x), formaldehyde (HCHO), hydrogen peroxide (H_2O_2), HONO, and reactive halogen species, which can then be released into the boundary layer above the snowpack. This release has been observed at Summit station (e.g. Hutterli et al., 1999, 2001; Honrath et al., 1999, 2002; Dibb et al., 2002, 2010; Jacobi et al., 2004; Sjostedt et al., 2007; Liao et al., 2011; Stutz et al., 2011) in the center of the Greenland ice sheet and in Antarctica (e.g. Davis et al., 2001; Jones et al., 2001), where concentrations of NO_x and other species far exceed those expected from gas phase and aerosol chemistry alone.

Fluxes of NO_x from surface snow into a shallow boundary layer have been shown to cause photochemical ozone production in Antarctica (e.g. Crawford et al., 2001; Helmig et al., 2008). In the center of the Greenland ice sheet, where NO_x fluxes have also been observed, large increases in boundary layer ozone similar to those observed at South Pole have not been directly measured (Dibb et al., 2002; Honrath et al., 1999, 2000, 2002). Constrained chemical box model calculations have shown that the reaction of NO and RO_2 in the boundary layer at Summit should result in ozone production (Sjostedt et al., 2007).

Rather than ozone production, it has been shown at Summit that ozone depletion occurs via either chemical or physical processes in the snowpack (Peterson and Honrath, 2001). The presence of reactive bromine at Summit has recently been confirmed (Dibb et al., 2010; Stutz et al., 2011; Liao et al., 2011) and most likely contributes to ozone destruction. Although, bromine is present at Summit in much lower concentrations than typically found in the coastal Arctic (summarized in Simpson et al., 2007 and Abbatt et al., 2012). Observations of interstitial ozone show that mixing ratios decrease in the snowpack relative to boundary layer (Peterson and Honrath, 2001), suggesting that ozone is predominantly deposited or chemically destroyed in snow (e.g. Helmig et al., 2007). Ozone depletion in the interstitial air suggests that bromine chemistry is more active in the snowpack (Peterson and Honrath, 2001; Helmig et al., 2002), implying a snow source of reactive bromine at Summit.

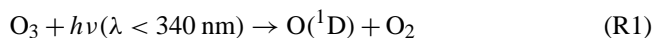
Snow sourced species may also produce additional HO_x radicals and perturb the OH: HO_x ratio via faster/additional HO_x interconversion reactions (e.g. Yang et al., 2002; Chen et al., 2007; Liao et al., 2011). Measurements have suggested that HONO, an important OH precursor, is released from the remote snowpack (Zhou et al., 2001; Dibb et al., 2002; Honrath et al., 2002; Bartels-Rausch and Donaldson, 2006) and from frozen nitrate in ice upon irradiation (Anastasio and Chu, 2009). Snowpack emissions of HCHO and H_2O_2 have also been measured (Hutterli et al., 1999; Jacobi et al., 2004; Hutterli et al., 2001; Sumner et al., 2002; Barret et al., 2011) and largely attributed to temperature induced cycling caused by radiative heating and cooling of the snow surface (Hutterli et al., 2001). These species may also be important be-

cause they result in additional HO_x ($\text{HO}_x = \text{OH} + \text{HO}_2$) formation upon photolysis. Indirect evidence for the impact of halogen chemistry on HO_x levels at Summit, Greenland was provided by unusually high OH:($\text{HO}_2 + \text{RO}_2$) ratios that have been measured during summer (Sjostedt et al., 2007; Liao et al., 2011). Prior modeling work using a constrained box model showed the importance of these species for OH budget at Summit (Chen et al., 2007).

While it has been clearly demonstrated that snow photochemistry influences the lower atmosphere, few attempts have been made to provide a quantitative physical and chemical description of the air-snow system. In particular, there is a need for studies that show how in-snow photochemistry and transport impact boundary layer radical and ozone chemistry. In this study, we will address this using a detailed 1-D snow-atmosphere chemistry and transport model (Thomas et al., 2011). The model will be applied to the conditions during the Greenland Summit Halogen- HO_x (GSHOX) Campaign at Summit, Greenland ($72^\circ 34' \text{ N}$, $38^\circ 29' \text{ W}$, altitude = 3.2 km), where HO_x and halogen cycling was studied in summer 2008. Ground based measurements, including hydroxyl and peroxy radicals (OH and $\text{HO}_2 + \text{RO}_2$), ozone (O_3), nitrogen oxide (NO), mistchamber nitrite (soluble NO_2^-), and bromine oxide (BrO), will be compared to model results. The model output for a base case and for several sensitivity runs is used to quantify how in-snow photochemistry of NO_x , HONO, and bromine impact the oxidation capacity of the boundary layer. We will also investigate how this chemistry impacts ozone formation over snow.

1.1 Atmospheric radical and ozone chemistry

It is instructive to begin a study of this system with a short review on how snow photochemistry can change boundary layer gas phase HO_x and ozone chemistry. The Arctic is a unique region where photolysis rates are enhanced by the high surface albedo over snow. Therefore, photolysis rates in the snow covered Arctic can be comparable to those at lower latitudes, despite the higher solar zenith angles encountered in polar regions (which would normally result in lower photolysis rates without snow cover). The primary OH source in the atmosphere is reaction of $\text{O}(^1\text{D})$, which results from ozone photolysis (Reaction R1), with gas phase water (Reaction R2).



HONO and H_2O_2 , both of which are known to be released from the snowpack, can also be significant sources of OH (Reactions R3 and R4).



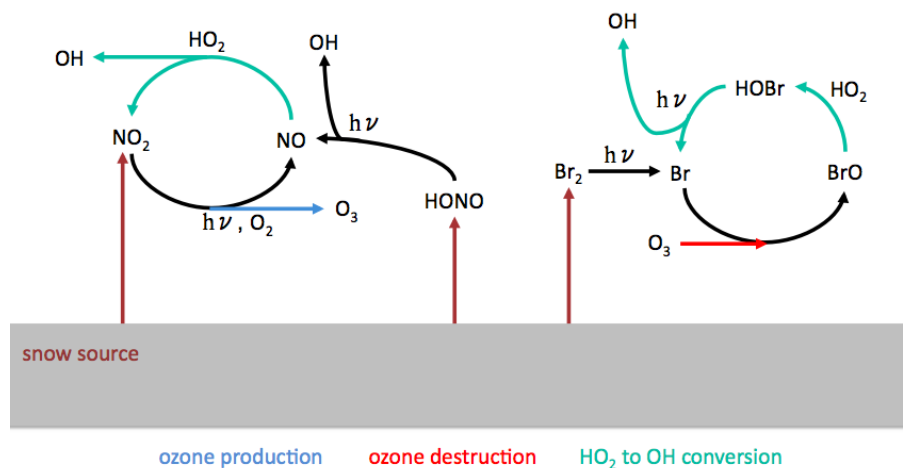
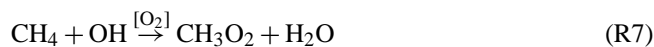


Fig. 1. Schematic of snow sourced NO_x , HONO, and bromine and their impact on ozone production and destruction. The figure also captures the impact of snow emissions on OH. Both NO_x and bromine cycling shift the OH: HO_2 ratio towards OH. Snow sourced HONO is a direct source of OH.

The photolysis of HCHO released from the snow forms HO_2 radicals, which can increase HO_x levels.



In remote polar regions, OH is converted to both HO_2 and RO_2 predominantly via reactions with CO, methane, and, to a minor extent, other organics. The most important OH loss reactions are with CO and methane (Reactions R6 and R7).



Methane and CO are not known to be influenced directly by the snow and their main sources are long-range transport to the remote Arctic or Antarctica. NO_x is also important for HO_x cycling, but is subject to loss during long-range transport to the remote Arctic, making even small local NO_x sources important. At levels above 10–20 ppt NO_x plays a key role in determining the ratio of OH to HO_2 because of conversion of the hydroperoxyl radical back to OH (Reaction R8).



Conversion of RO_2 to HO_2 can also occur. For example, NO reacts with the methyl peroxy radical and O_2 to form formaldehyde (HCHO) and HO_2 (Reaction R9).

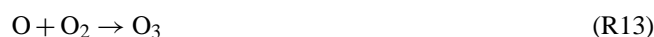


These reactions compete with the self and cross reaction of HO_2 and RO_2 to form peroxides, for example Reactions (R10) and (R11).



The levels of NO_x are crucial in determining whether the OH/ HO_2 cycle is propagated (Reaction R8) or terminated.

Because the photolysis of NO_2 , followed by the reaction of the oxygen atom with O_2 , is the only chemical source of ozone in the troposphere the levels of NO_x determine the ozone formation rate in the troposphere.



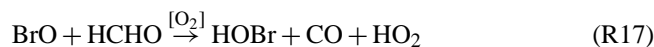
The formation and release of NO_x from the snowpack, which substantially increases surface NO and NO_2 levels, is therefore important for determining both the oxidative capacity of the boundary layer as well as ozone concentrations.

In the presence of reactive bromine, which can also be released from the snow, additional reactions can impact the cycling of HO_x and the OH/ HO_2 ratio:



The reaction cycle (R14)–(R16) is also known to destroy ozone, and is the dominant bromine catalyzed ozone destruction mechanism at BrO levels below 5 ppt. The Reactions (R14) and (R15) together convert HO_2 to OH.

It is also known that HCHO can play a role in halogen recycling, via reaction of BrO with HCHO to form HOBr (Reaction R17) as pointed out by Michalowski et al. (2000).



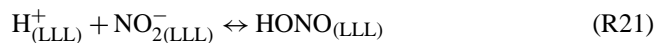
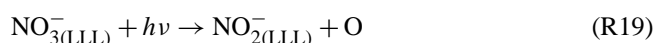
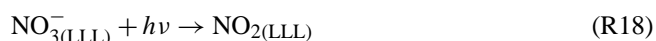
HOBr formed by either Reaction (R14) or (R17) can be taken up on aerosol particles or snow grains and contributes to Br₂ recycling.

This brief review shows how both nitrogen and halogen chemistry modify the fundamental radical cycles that determine ozone and OH concentrations in the troposphere. Figure 1 shows the main pathways by which emissions of reactive bromine and nitrogen oxides from snow impact ozone and OH. Snow sourced NO_x contributes to ozone production, while bromine destroys ozone via a well known catalytic cycle. Both NO_x and bromine shift the OH:HO₂ ratio towards OH. HONO, H₂O₂, and HCHO emitted from the snowpack produce additional OH upon photolysis, therefore also increasing the amount of OH in the boundary layer. The connections between HO_x + RO₂ cycling and H₂O₂, HCHO, halogens, HONO, and NO_x show that these processes cannot be considered separately, therefore we discuss the predicted concentrations of these species in the context of current and past measurements at Summit.

1.2 Snow chemistry and physics

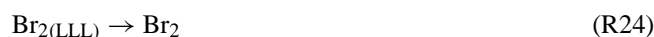
To fully describe the coupled snow-air system, chemistry occurring in snowpack needs to be treated explicitly. We use a simplified representation of the liquid-like layer (LLL) and its chemistry to represent the complex, but poorly understood, processes occurring in the snowpack. The modeled LLL is a disordered liquid-like interfacial layer on ice, which is a combination of the quasi-liquid layer (QLL) and brine layers (BL), which form for fundamentally different reasons (e.g. Kuo et al., 2011). The QLL is a disordered layer of waters at the surface of ice that forms even at very low or no impurity concentrations. On the other hand, brine pockets (BL) with high impurity concentrations form in ice with higher solute content. Both the QLL and BL should in principal grow with increased impurities and temperature. Given that there is a great deal of uncertainty that surrounds how to correctly represent the LLL in models, we represent the LLL and its chemistry in a simplified way. Our representation of snow chemistry will require improvements in the future as our understanding of both LLL physics and chemistry develops. In this section we differentiate between liquid-like and gas phase species by using the subscript (LLL) to refer to species in the liquid-like layer at the surface of snow grains. A description of the model has already been presented in Thomas et al. (2011), therefore the chemistry and physics will only be briefly reviewed here.

The source of NO_x and HONO in the snowpack is the photolysis of nitrate and reactions involving nitrite in a LLL on the snow grain surface (Reactions R18–R22).



The resulting NO₂ and HONO in the firm air undergo gas phase photochemical reactions as they are transported to the boundary layer by both diffusion and wind pumping, as discussed in Liao and Tan (2008) for HONO.

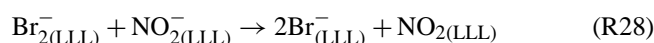
Model results have shown that BrO measured in the boundary layer at Summit during summer 2008 can result from photochemical release of bromide impurities in snow (Thomas et al., 2011). Photochemical production of Br₂ in a LLL that covers snow grains results in halogen release from the snowpack (Reactions R23 and R24). BrO in both interstitial air and the atmosphere is formed from photolysis of Br₂ (Reaction R25) followed by reaction with ozone (R16).



The chemical cycling of bromine and nitrogen species is directly connected via a number of chemical reactions. For example, in the gas phase BrO reacts with both NO and NO₂ (Reactions R26 and R27).



In the condensed phase, bromine and nitrogen species also react (for example Reaction R28)



Hydrogen peroxide (H₂O₂) and formaldehyde (HCHO) experience strong summertime cycling over the snowpack driven by temperature-induced uptake and release, which likely involves diffusion between the gas phase and solid ice matrix within snow grains (Barret et al., 2011; Hutterli et al., 1999, 2001). In the present study, we do not treat the solid diffusion process. Therefore, it is likely that we only capture a portion of this temperature driven cycling. These species are also photochemically produced and destroyed, which we model explicitly in the LLL and interstitial air using a simple chemical mechanism.

Another crucial process in understanding the impact of snow chemistry on the atmosphere is how efficiently ambient and interstitial air are exchanged. This process is still poorly constrained, as discussed in our previous study (Thomas et al., 2011). We use a parameterization including both gas phase diffusion and wind pumping (Cunningham and Waddington, 1993), combined with horizontal and vertical relief structure and a constant wind speed of 3 m s⁻¹, which led to an accurate description of surface trace gas mixing ratios in Thomas et al. (2011). We use the same parameters in

this study, however it should be noted that wind pumping has a large influence on surface layer trace gas mixing ratios and needs further study.

It is also essential to capture the effect of boundary layer vertical mixing processes as the boundary layer height determines concentrations of gases released from the snow (Anderson and Neff, 2008). Correctly modeling boundary layer mixing processes requires considering the high albedo and radiative heating that rapidly warms the boundary layer at solar noon in snow covered regions, which we model by constraining the snow surface temperature to measurements. The impact of boundary layer mixing at Summit was recently discussed in the context of BrO and NO measurements in Part 1 of this work (Thomas et al., 2011).

The correct description of the gas phase and surface/aerosol chemistry in the atmosphere and the snowpack, as well as the accurate quantification of the vertical transport processes in and above the snow are crucial for a correct description of the snow-air system in remote polar regions. The approach we employ is based on describing the coupled system using first principles by employing a 1-D chemistry and transport snow-atmosphere model (Sect. 2) that is compared with surface observations (Sect. 3). Through sensitivity runs and an analysis of the various chemical pathways, we will then investigate the budget of OH, HO₂ + RO₂, and ozone (Sect. 4).

2 Description of the model and overview of runs

To model coupled snow-atmosphere chemistry and physics, we use the model MISTRA-SNOW with an initialization chosen for Summit, Greenland for comparison with measurements taken in June 2008. For a detailed description of the model, methodology, and initialization we refer the reader to the companion paper (Thomas et al., 2011). The model includes a 1-D vertical grid in the snowpack and the atmosphere. 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.

Observations from the local air mass period during GSHOX 2008 and well known background concentrations were used to initialize the model run. The vertical mixing in the atmosphere and the extent of the boundary layer was simulated solely by constraining the surface temperature. The simulated temperature profiles showed excellent agreement with the observations (Thomas et al., 2011). Besides surface temperature, only the partitioning of nitrate and bromide between the bulk snow and LLL were adjusted in the model, which are not well characterized. The adjustment was performed such that the modeled surface levels of NO and BrO agreed with the observations. The best agreement was found for LLL nitrate being 6 % of total nitrate measured in melted

snow. In the case of bromide (and chloride) 100 % of the bulk snow ions were initialized in the LLL.

We represent the snowpack using spherical snow grains covered by a uniform 10 nm thick liquid layer (summarized in Rosenberg, 2005) in which chemistry occurs. We have chosen a liquid layer thickness in the mid-range of QLL measurements for pure ice in the temperature range of the model. Exactly how to represent the QLL and BL in models of snow chemistry is still under discussion, despite recent progress (Kuo et al., 2011). For the low ion concentrations at Summit, it's not clear if a true BL forms. According to Kuo et al. (2011) for a known melt concentration, very little or no brine formation is predicted for the solute concentrations measured in surface snow at Summit, which is consistent with the model initialization. We initialize the model using a snow grain radius (1 mm) and density ($\rho = 0.3 \text{ g cm}^{-3}$). Liquid water content was calculated based on density, snow grain radius, and liquid layer thickness.

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 boundary layer. A complete list of reactions, 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 of Thomas et al. (2011). Photolysis rates in the snowpack decrease exponentially with depth due to decreasing light penetration with depth in the snowpack. We use an e -folding depth of $\epsilon_\lambda = 10 \text{ cm}$, measured for nitrate at Summit, Greenland (Galbavy et al., 2007) for all species that undergo photolysis to describe how photolysis rates decay with depth in the snowpack.

The base case model run is initialized with gas and aqueous phase concentrations as described in Thomas et al. (2011), Table 2. Briefly, 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 O₃, H₂O₂, and HCHO). 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 $C_{\text{LLL}} = \phi \times C_{\text{snow}}$, where C_{snow} is the concentration in melted surface snow measured by liquid ion chromatography at Summit during the days chosen for the model runs and ϕ is a factor that relates this measured concentration to the LLL concentration in the model.

We assume HNO₃ uptake to be the major source of liquid layer acidity, therefore we use the initial nitrate concentration in the LLL (C_{LLL}) to determine the initial H⁺ concentration such that $C_{\text{LLL}}(\text{NO}_3^-) = C_{\text{LLL}}(\text{H}^+)$. The atmospheric aerosol number and size distribution was initialized by parameterizing aerosol size distribution measurements at Summit on 12 June 2008.

The focus of this paper is to investigate the impact of snow sourced trace gases on the oxidation capacity of the boundary

Table 1. Liquid layer concentrations for the base case and sensitivity model runs conducted based on measurements taken in June 2008 as well as previous measurements at Summit, Greenland.

Species	LLL concentration (M)			Reference
	base case ^a	no bromide (noBro)	no nitrate (noNit)	
Br ⁻	3.3×10^{-4}	0	base case conc.	Dibb et al. (2010)
Cl ⁻	1.8×10^{-2}	base case conc.	base case conc.	Dibb et al. (2010)
NO ₃ ⁻	8.8×10^{-3}	base case conc.	0	Dibb et al. (2010)
H ⁺	8.8×10^{-3}	base case conc.	base case conc.	equal to nitrate ^b
Na ⁺	1.9×10^{-2}	base case conc.	base case conc.	counter ion ^c
HCHO	2.0×10^{-5}	base case conc.	base case conc.	Henry's law based on Chameides (1984)
H ₂ O ₂	1.0×10^{-3}	base case conc.	base case conc.	Henry's law based on Lind and Kok (1994)

^a Additional details regarding the base case initialization can be found in Thomas et al. (2011). ^b Assumed nitrate is primarily from HNO₃ deposition (therefore $[H^+]_{t=0}$ is equal to $[NO_3^-]_{t=0}$). ^c Counter ion for halides.

layer using a set of sensitivity runs. We have completed runs with the initial bromide in the liquid layer set to zero (referred to as noBro) and with the initial nitrate in the liquid layer set to zero (referred to as noNit). The liquid layer initialization for the base case and the two sensitivity runs is summarized in Table 1.

3 Summary of measurements

To further interpret and evaluate our model results we will compare them to a number of observations during the GSHOX experiment. Most of these measurements have already been published and we will only give a brief overview here. We will focus here on the periods when FLEXPART (Stohl et al., 2005) emission sensitivities showed that the observed air mass resided over the Greenland Ice Sheet at least 3 days prior to the observations at Summit (Stutz et al., 2011). The restriction to these local air masses reduces the effect of advection and also removes meteorological biases.

Observation of OH and HO₂ + RO₂ radicals were performed by Chemical Ionization Mass Spectrometry (CIMS) 1.5 m above the snow surface as described by Liao et al. (2011). OH values showed the typical diurnal variation with mid-day median OH values of 6×10^6 molecules cm⁻³ (detection limit of 1×10^5 molecules cm⁻³) and concentration close to zero at night, with variations of around 30%. HO₂ + RO₂ values were 5×10^8 molecules cm⁻³ (detection limit of 1×10^7 molecules cm⁻³) and followed the diurnal behavior seen for OH. Liao et al. (2011) report the combined uncertainties of the CIMS as ~30% for OH measurements and ~35% for HO₂ + RO₂ measurements, predominantly due to the uncertainty in the instrument calibration.

NO was measured using a standard chemiluminescence technique with an accuracy of ±10% and a detection limit

of <3 ppt (Liao et al., 2011). The NO inlet was placed close to the other in-situ measurements during GSHOX at around 1.5 m height above the snow. It should be noted that the NO data, as well as other datasets used here were filtered for the influence of the emissions from Summit station, which typically increase NO levels during northerly winds. Ozone was measured by UV-absorption with an accuracy of better than ±5% (detection limit <1 ppb) close to the other in-situ inlets (Liao et al., 2011).

Actinic fluxes above the snow were measured by a 2π Scanning Actinic Flux Spectrometer (SAFS) (Shetter and Müller, 1999) operated by the University of Houston near the sampling location. The impact of the snow albedo was determined by intermittently turning the SAFS downward. The photolysis rates of various atmospheric compounds were then calculated based on downwelling flux and a correction factor that considered the reflection from the snow surface. The accuracy of the actinic flux measurements are on the order of 6% in the UV-B and 5% in the UV-A and precision of the measurements was 3% for the UV-B and 2% for the UV-A wavelength regions. The majority of the uncertainty in the photolysis frequencies calculated using the actinic flux measurements comes from the uncertainty in either the molecular absorption cross-section or the photolysis quantum yield, consequently the overall uncertainty for the individual *J*-values is typically 12–18%. Due to the high snow albedo and high elevation at Summit the photolysis rates were comparable to those typically found at lower latitudes. In addition, it should be noted that due to the northern latitude of Summit the sun did not set at night and thus photolysis continued, albeit at low rates, at night. The measured photolysis rates were predominantly used to evaluate the model representation of HONO photolysis.

Water soluble gas phase species were measured by mistchamber samplers and near-real-time by ion

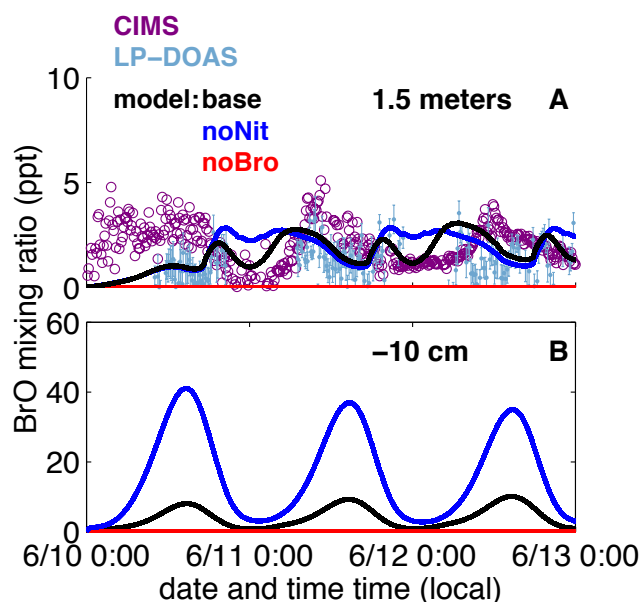


Fig. 2. Model predicted BrO for a three day model run for the base, noNit, and noBro cases compared to measurements of BrO using CIMS and LP-DOAS techniques during 10–13 June 2008. Without bromide in the liquid layer, no BrO is predicted showing that snow sourced bromine is the only source of reactive halogens in the model. Without snow sourced NO_x the amount of BrO predicted increases due to bromine loss processes that involve NO_x in the gas phase.

chromatography (MC/IC) during the campaign as described by Dibb et al. (2010). Here we focus mostly on the soluble nitrite observations in and above snow. During the local air-mass periods ambient soluble nitrite mixing ratios typically reached maxima of ~ 7 ppt around noon after increasing from typical nighttime levels of ~ 2 ppt. For the 27.5 min sample integration interval used at Summit the detection limits for the MC/IC system were 0.3 ppt. Uncertainty based on measured air and water volumes and precision of the concentrations determined by IC in sample solutions was $\pm(10\% + 0.1 \text{ ppt})$ for both nitric acid and soluble nitrite. The MC/IC system was also used to sample interstitial air during some periods of the campaign and the inlet was placed ~ 10 cm below the snow surface. The ion chromatograph was also used to determine the ionic composition of the surface snow as well as snow profiles at Summit during GSHOX 2008. Low levels of bromide and nitrate were found as described in detail by Dibb et al. (2010).

BrO was measured by two different instruments. A long-path Differential Optical Absorption Spectrometry system measured the BrO absorptions along two 2 or 4 km long open air absorption paths (Stutz et al., 2011). During the local air episodes in 2008 hourly averaged BrO mixing ratios were strongly modulated by solar radiation and boundary layer height, showing maxima of ~ 1.5 ppt in the morning and the evening with the LP-DOAS BrO detection limit during these

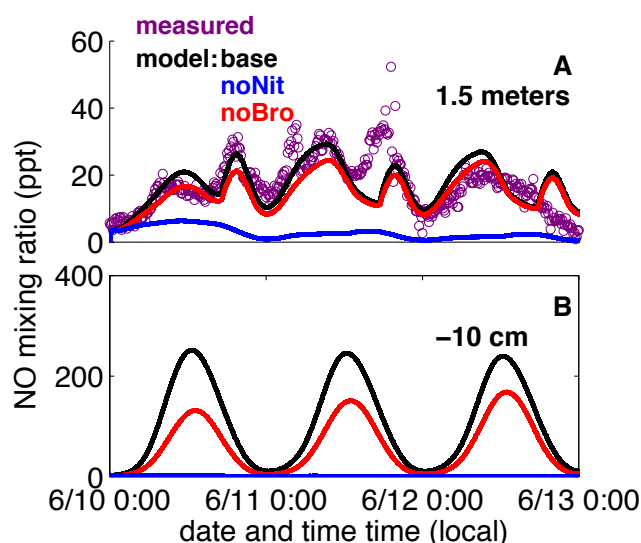


Fig. 3. Model predicted NO for a three day model run for the base, noNit, and noBro cases compared to measurements of NO taken on 10–13 June 2008. Without bromide in the liquid layer, the amount of NO predicted decreases. Without snow sourced NO_x enhanced NO is not predicted in the interstitial air and ambient NO is predicted to be well below measured values.

times between 0.3–1 ppt with an accuracy of 4–7%. BrO was also measured at similar levels during these periods by CIMS which sampled close to the OH/HO₂ CIMS instrument (Liao et al., 2011). The accuracy of the CIMS BrO measurements is $\pm 30\%$ – 36% with an estimated detection limit of 1–2 ppt.

4 Results and discussion

We begin our investigation of boundary chemistry by further analyzing the results of the model run already discussed in Thomas et al. (2011), referred to as the base run in the present study. To gain additional insight we expand our analysis of the snow-atmosphere chemical system by comparing a sensitivity run without snow bromide (noBro) and a separate run without snow nitrate (noNit) to the base case. These runs will also be used to investigate the impact of snow nitrate and bromide on surface ozone. We also compare model predicted mixing ratios for other radical sources with current and prior measurements at Summit. The last part of this section is dedicated to a detailed analysis of OH, HO₂, and RO₂ chemistry over snow.

4.1 Bromine, NO_x , and HONO in the boundary layer

Bromine and nitrogen chemistry are closely linked via chemistry in the gas and condensed phases. Using the sensitivity runs (noBro and noNit) we investigate the links between snowpack chemistry and predicted reactive bromine (BrO) and nitrogen (NO) in the boundary layer. As expected, without snowpack bromide, no bromine is predicted in the

boundary layer (Fig. 2). Similarly, without snowpack nitrate, little NO is predicted to remain in the boundary layer (Fig. 3).

The relationship between bromine and nitrogen chemistry is shown because without nitrate in the liquid layer the model predicts more BrO in both the ambient and interstitial air (Fig. 2a and b). Efficient formation of BrNO₃ through the BrO + NO₂ reaction (R26), results in an additional loss pathway for bromine with snow sourced NO_x. Without snow sourced NO_x, the partitioning of reactive gas phase bromine shifts from BrNO₃ to BrO and additional reactive halogens are predicted.

In the interstitial air, where there is higher NO_x than in the atmosphere, this effect is further amplified and there is significantly more BrO without NO_x production in the snowpack (Fig. 2b). The reactions between bromine and nitrogen species in the gas phase are also important because BrNO₃ has been shown to be a dominant source of nitrate deposited to surface snow in the coastal Arctic boundary layer (Morin et al., 2007, 2008), pointing to the importance of accurately understanding the connections between halogen and nitrogen cycling. Given this, one would expect that snow nitrate would strongly modulate BrO in the atmosphere and interstitial air and that lower BrO levels are expected in areas of high snow nitrate content.

The dependence of NO_x chemistry on bromide in the liquid layer is more complicated because bromine and nitrate species also react in the LLL. Br_{2(LL)}⁻, which is an important intermediate species in Br_{2(LL)} production, also reacts quickly with NO_{2(LL)}⁻ producing NO_{2(LL)} (R28). NO_{2(LL)} is then transported to the gas phase (Reaction R20) where it undergoes photolysis to form NO. Reaction (R28) is in competition with the reaction of NO_{2(LL)}⁻ with H⁺ forming HONO_(LLL) (Reaction R21), which can also escape into the gas phase and undergo photolysis forming NO. In the absence of bromide, the concentration of NO_{2(LL)} is reduced because the reaction channel (Reaction R28) is turned off, thus resulting in a lower NO₂ flux to the gas phase. This leads then to lower NO as reflected in (Fig. 3a and b). In the interstitial air NO mixing ratios halve in the absence of bromide during the first day.

The presence of bromide also influence the levels of HONO in the gas phase. Because HONO can be an important OH radical precursor, we also analyzed the model results for this species (Fig. 4). As expected from the competition between Reactions (R21) and (R28), HONO mixing ratios in the interstitial air double in the absence of snow bromide. Hence, the presence of bromine photochemistry in the condensed phase suppresses HONO formation by lowering the nitrite concentration (Reaction R28), which then changes HONO_(aq) formation rate (Reaction R21). A corresponding increase in boundary layer HONO is predicted for the noBro case (Fig. 4a).

The predicted HONO mixing ratios in all cases are significantly lower than the levels suggested by prior measurements at Summit (Honrath et al., 2002). Mistchamber measure-

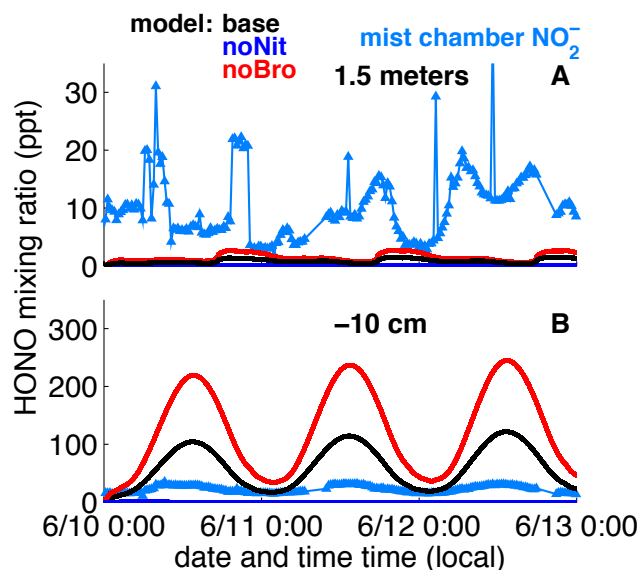


Fig. 4. Model predicted HONO for a three day model run (10–13 June 2008) for the base, noNit, and noBro cases compared to mistchamber measurements of soluble nitrite with one inlet 1.5 m above the snow surface and one inlet 10 cm below the snow surface, sampling interstitial air.

ments above the snowpack averaged ~ 10 ppt of HONO during the GSHOX focus period, while the base case model run only predicts a maximum of between 1 and 2 ppt of HONO. The model predicts a large HONO source from snow photochemistry (Fig. 4), however HONO photolysis is faster than HONO can be replenished via transport upward from the snowpack. Consequently, the majority of HONO formed in the snowpack is photolyzed just below the snow surface and only small concentrations are predicted in the atmosphere.

We also compare the model predicted interstitial air HONO at a depth of 10 cm with mistchamber measurements taken with one inlet placed below the snow surface (Fig. 4b). While the measurements do predict enhanced nitrite below the surface, they do not approach the large values (100 ppt) predicted by the base case model run. A complicating factor in this comparison is that the mistchamber likely sampled a mix of interstitial and ambient air due to the large flow rate required for sampling.

To further investigate if the model predicted atmospheric HONO is reasonable, we analyzed the major source and loss terms for boundary layer HONO, which are transport from the snowpack and photolysis. The excellent agreement of observed and modeled boundary layer NO and BrO strongly support that the transport rate of species out of the snowpack is reasonable in the model. In addition, current work measuring NO in the interstitial air at Summit as discussed in Thomas et al. (2011), also indicates that snow-atmosphere exchange is described reasonably well in the model. The HONO photolysis rate calculated online by the model also

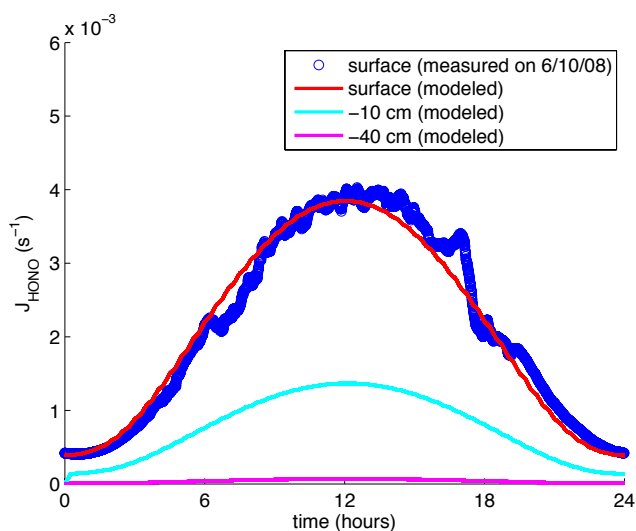


Fig. 5. Model predicted J_{HONO} on 10 June 2008 compared to the measured J_{HONO} . The excellent agreement between ambient and measured J_{HONO} indicates that the rate of HONO loss in the boundary layer due to photolysis is correctly represented in the model. At the surface at solar noon the HONO lifetime is 4.4 min, resulting in rapid photolysis to form NO and OH.

shows excellent agreement with measurements at Summit from 10 June 2008 (Fig. 5). It is also feasible that the mist-chamber technique samples another gas phase species as soluble nitrite (NO_2^-), which could explain the discrepancies between the model and measurements. However, HONO has also been observed at high levels in polar regions using a LOPAP instrument (LONG Path Absorption Photometer), which provides a specific measurement of HONO (Villena et al., 2011) and we have no clear evidence for such interfering species. We therefore, conclude that the most likely explanation for the observed elevated boundary layer HONO is a large missing HONO source. Any HONO source that is consistent with this study, would have to involve chemistry on atmospheric particles, in the gas phase, or chemistry occurring at the top of the snow-pack resulting in immediate release into the boundary layer. One example of a potential HONO source is photo-enhanced conversion of NO_2 in the LLL involving HULIS (humic-like substances) present in the surface snow (Beine et al., 2008), which is not modeled here.

In summary, bromine and nitrogen chemistry are connected via chemical reactions in both the aqueous and gas phase. We have noted that bromine chemistry in the snow-pack alters the ratio of HONO: NO_2 predicted by the model due to reactions between $\text{NO}_2^-(\text{LLL})$ and $\text{Br}_2^-(\text{LLL})$. Bromine chemistry is primarily impacted via gas phase loss processes, which are faster when additional NO_x is present.

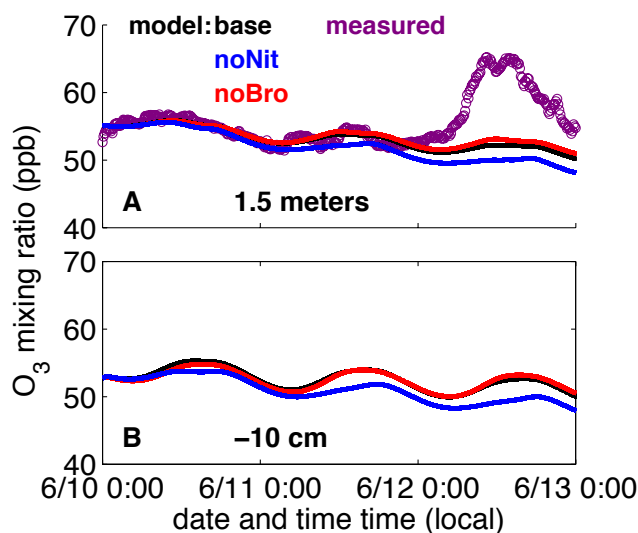


Fig. 6. Model predicted O_3 compared to measurements above the snow surface for a three day model run (10–13 June 2008) for the base, noNit, and noBro cases.

4.2 Influence of snow chemistry on ozone

Ozone in the boundary layer is also impacted by snow photochemistry. In the coastal Arctic reactive bromine is known to cause large ozone depletion events, while on the Antarctic plateau, NO_x emissions from snow cause large increases in ozone. At Summit, with lower levels of both bromine and NO_x , neither of these effects have been clearly observed. Given the opposing influence of NO_x and bromine on ozone, we investigate their influences on ozone separately using sensitivity runs.

In the base case model run, with active halogen and NO_x chemistry in the snowpack, measured ozone is reproduced well during the first two days (Fig. 6) as discussed in Thomas et al. (2011). The increase in observed ozone on the third day is caused by a change in airmass, which cannot be reproduced by our 1-D model. The influence of snow sourced NO_x and bromine on ozone is shown in Fig. 6. In all three cases a decrease in ozone mixing ratios is predicted, both in ambient and interstitial air. The comparison of the base and the noNit case shows that nitrate snow chemistry leads to the formation of an additional 2–3 ppb in the boundary layer. A comparison of ozone formation, given by the rate of the $\text{HO}_2 + \text{NO}$ reaction (R8) is shown in Fig. 7. Nitrate snow chemistry increases ozone formation rates at Summit approximately by a factor of four around noon. The result is an additional 2–3 ppb of O_3 in the boundary layer due to snow sourced NO_x (difference between the base and noNit cases) during the three day model run.

The noBro case shows a smaller difference to the base case. Over the three day model run bromine contributes 1 ppb of boundary layer ozone loss. This small effect can be explained by the very low BrO mixing ratios at Summit that

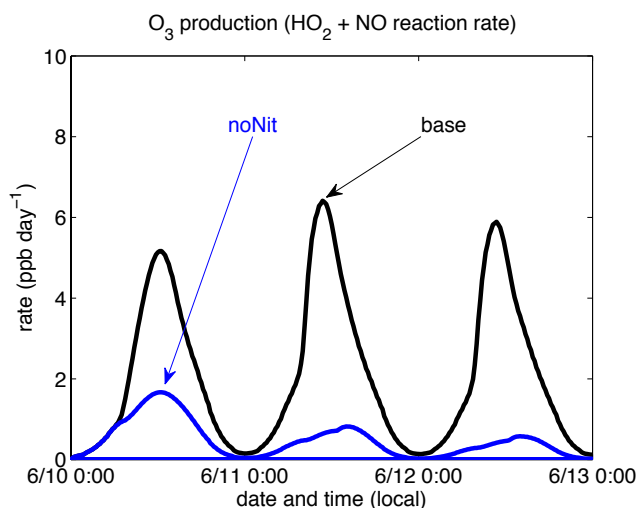


Fig. 7. Ozone production from NO to NO₂ conversion reaction (R8). The average ozone production rate from snow sourced NO_x results in an additional 2 ppb of O₃ in the boundary layer at Summit.

impact ozone formation directly via the destruction of ozone through Reaction (R16) and indirectly via lowering NO_x levels Reaction (R27). The comparison of the base case with the sensitivity cases shows that snow chemistry has a considerable impact on ozone levels on the Greenland ice sheet, where ozone lifetimes are quite long. Other processes, not involving halogen and nitrogen cycling, clearly also influence ozone levels at Summit.

The model does not predict strong ozone depletion in the snowpack, which has been observed at Summit (Peterson and Honrath, 2001). This is because of the relatively small halogen concentrations in interstitial and because ozone production from NO_x in the interstitial air offsets most ozone destruction that does occur. Alternatively, the model could under-predict halogen concentrations in interstitial air and the corresponding ozone destruction. It is also possible there is another (currently unknown) mechanism causing ozone destruction in interstitial air. Measurements of halogens and NO_x in the interstitial air are needed to compare with the model. However, measurements of undisturbed interstitial chemical concentrations are difficult and will likely require developments in measurement techniques.

4.3 Formaldehyde and hydrogen peroxide snow and boundary layer chemistry

Formaldehyde (HCHO) is an important precursor of HO₂ and a marker for VOC chemistry. It is also known to be released from snow to the atmospheric boundary layer (Hutterli et al., 1999, 2003; Sumner and Shepson, 1999; Domínguez and Shepson, 2002; Jacobi et al., 2004; Barret et al., 2011). As there were no HCHO measurements during GSHOX, we compare modeled HCHO mixing ratios with prior measurements at Summit, Greenland (Jacobi et al., 2004). It should

be noted, however, that due to differences in environmental conditions, such as snowpack temperature, the comparison should only be considered semi-quantitative. Despite the shortcomings of this comparison the model accurately reflects the HCHO mixing ratios one would expect in the boundary layer at Summit (Fig. 8). The modeled interstitial air HCHO mixing ratios are about 50–70 % of the noontime values observed by Jacobi et al. (2004), while the nocturnal values again show good agreement.

In the model HCHO is formed through the gas phase Reaction (R9) of NO with CH₃O₂, which results from the oxidation of methane. This reaction occurs in the atmosphere and in the top few centimeters of the snow, where photochemistry is still fast. Organics present in surface snow layers have been proposed to play an important role in HCHO production (Grannas et al., 2004). However, as these processes are largely unknown, our model does not include a sophisticated organic chemistry scheme in the LLL, and relies on a basic HCHO reaction scheme. It is possible that the discrepancy between the model and observations in the interstitial air at noon can be explained by organic chemistry in the snowpack. In addition, the measurements are likely a lower limit of interstitial air concentrations due to dilution while sampling. In the future, model improvements will be needed to fully represent this chemistry.

For the reactions included in the model (LLL and gas phase photochemistry of HCHO) neither chemical production or destruction of HCHO is as fast as mass transfer processes driven by temperature changes in the snowpack. Increases in HCHO mixing ratios (Fig. 8) correspond to changes in predicted snowpack temperature published in Thomas et al. (2011). This has been confirmed by recent work focused on physical processes involved in the HCHO air-snow exchanges during OASIS 2009 field campaign at Barrow, Alaska (Barret et al., 2011). In this study, HCHO concentrations in the solid phase were quantitatively explained by solid-state diffusion of HCHO within snow crystals, without considering the quasi-liquid layer present at the surface of ice crystals, showing that physical processing is essential for predicting HCHO concentrations.

Michalowski et al. (2000) showed the central role of HCHO in HOBr formation during halogen induced ozone depletion events in the coastal Arctic. At Summit where the halogen concentrations are lower, HOBr formation in the boundary layer is dominated by reaction of BrO with HO₂ (Reaction R14). In the surface snow interstitial air, where BrO peak concentrations are predicted, at most 3 % of HOBr formation occurs via reaction with HCHO (Reaction R17). Unlike the coastal Arctic, the influence of formaldehyde chemistry on bromine activation is much less important at Summit.

Snow sourced hydrogen peroxide, H₂O₂, can contribute to the OH budget and the boundary layer oxidizing capacity over snow upon photolysis. Multiple years of measurements of hydrogen peroxide have been made at Summit, Greenland

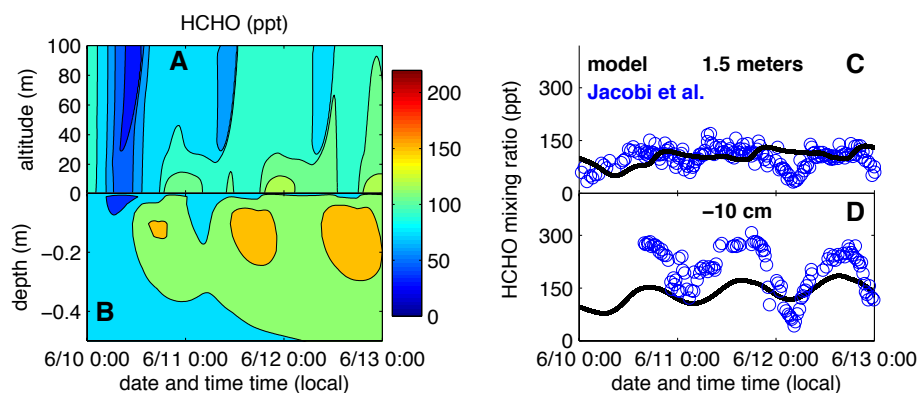


Fig. 8. Model predicted HCHO for the base case. Model results are compared with measurements taken in June 2000 originally published by Jacobi et al. (2004) (c and d). Measurements in the interstitial air during shading experiments have been removed from the comparison.

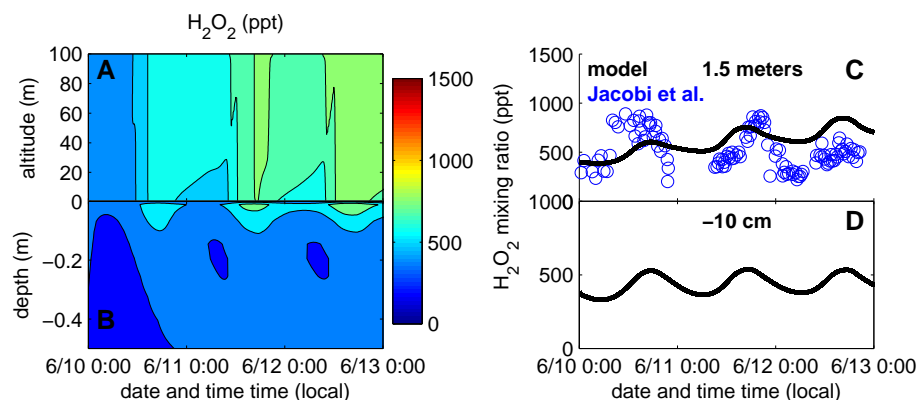


Fig. 9. Model predicted H_2O_2 for the base case. Model results are compared with measurements taken in June 2000 originally published by Jacobi et al. (2004) (panel c).

(e.g. Hutterli et al., 2001). As no H_2O_2 measurements were made during GSHOX we also compare H_2O_2 modeled in the base case with prior measurements during summer 2000 (Jacobi et al., 2004) (Fig. 9). H_2O_2 shows similar diurnal patterns as HCHO, with higher mixing ratios at noon. The modeled mixing ratios reproduce the observed H_2O_2 within a factor of two, but the model does not correctly capture the amplitude of the diurnal variation. However, this comparison is subject to the same shortcomings as discussed above for HCHO. Measured H_2O_2 fluxes in June 1996 suggested a daytime H_2O_2 release from the surface snow and redeposition at night (Hutterli et al., 2001). However, shading experiments did not impact H_2O_2 concentrations in the firn air, therefore the H_2O_2 is most likely not photochemically produced in the snowpack (Jacobi et al., 2004).

During other years, higher H_2O_2 and HCHO levels have been measured at Summit. Frey et al. (2009) presented H_2O_2 measurements at Summit from 2003 and 2004 which ranged from 1.4 ppbv in June/July to 100–300 pptv in March–early May. Summer 2000 H_2O_2 levels were lower, as shown by Jacobi et al. (2004), suggesting both seasonal and inter-annual

variability in radical sources may be important. But, given that H_2O_2 and HCHO were not measured during GSHOX the comparison with prior years can only be considered qualitative. To investigate the impact of higher primary OH sources on OH levels, we have completed a model sensitivity run with additional peroxide and formaldehyde (1.4 ppbv and 230 pptv respectively). These model results have been compiled and presented in the Supplement. This sensitivity study shows that a significant increase in these radical precursors only has a small impact on mid-day OH concentrations during the first day of the model run (a 3% increase). The lack of sensitivity of OH levels to additional hydrogen peroxide is not surprising, given that OH concentrations are well buffered and largely determined by recycling reactions, for example Reaction (R8).

In the base case, most of the H_2O_2 results from the gas phase self reaction of HO_2 in the boundary layer, rather than release of peroxide from the surface snow. While the LLL chemistry in our model may be oversimplified to correctly predict the flux of hydrogen peroxide out of the snowpack,

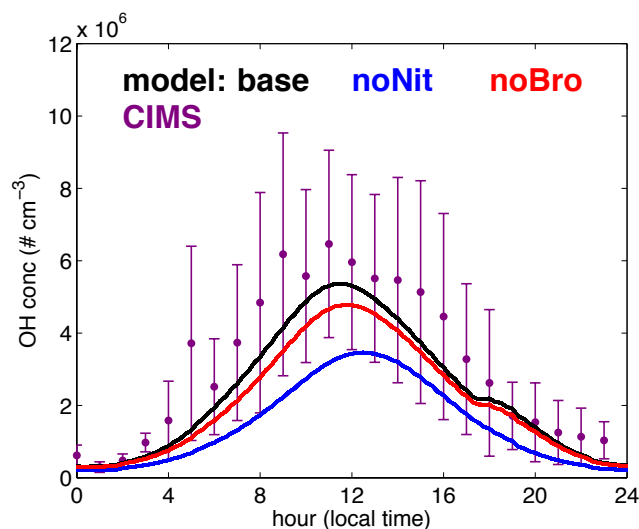


Fig. 10. Model predicted OH concentrations for the second day of the three day model run for the base, noNit, and noBro cases compared to hourly averaged OH concentrations for the time periods classified as influenced by local air. The error bars on the OH measurements indicate the standard deviation upon hourly averaging. The base case model predicted OH is below mean values of the measurements, but well within the error bars. Without bromine chemistry, OH is predicted to be lower than the base case. Without snow sourced NO_x chemistry, the OH concentrations are predicted to be much lower than the measured values.

gas phase chemistry in the boundary layer can largely explain the H_2O_2 levels measured during summer 2000.

4.4 HO_x chemistry of the boundary layer

The previous sections showed that snow photochemistry influences many species that directly or indirectly impact OH, HO_2 , and RO_2 radical concentrations. In this section we compare the modeled and measured OH and $\text{HO}_2 + \text{RO}_2$ in order to quantify the impact of snow chemistry on boundary layer oxidation capacity, which for the purposes of this study we define as the sum of OH, HO_2 , and RO_2 . Before analyzing the details of this chemistry we will first compare the model results with observations of OH and $\text{HO}_2 + \text{RO}_2$ during GSHOX to ensure that the model accurately describes this chemistry. As in the case of NO and BrO we will solely concentrate on time periods during which FLEXPART predicts air measured at Summit is influenced by snowpack emissions for at least 3 days (see details of these local air events in Stutz et al., 2011). We then calculate hourly averaged OH and $\text{HO}_2 + \text{RO}_2$ mixing ratios using the local air periods between 9–14 June 2008 and 23–26 June 2008 for the purpose of comparison with model results. Hourly averaging reduces the statistical error of the measurements and also removes day-to-day variability in the data. The averaged data together with the standard deviation from the hourly averaging (error bars) are shown in Figs. 10 and 11. As reported by

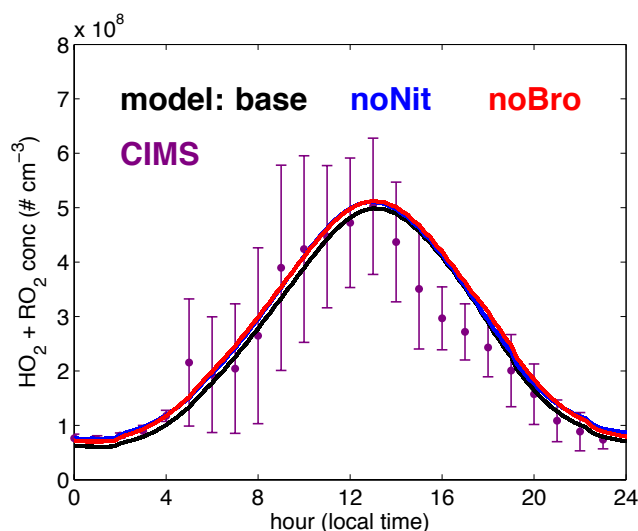


Fig. 11. Model predicted $\text{HO}_2 + \text{RO}_2$ (where RO_2 represents the sum of all organic peroxy radicals for both the measurement and the model) concentrations for the second day of a three day model run for the base, noNit, and noBro cases compared to hourly averaged $\text{HO}_2 + \text{RO}_2$ concentrations for the time periods classified as influenced by local air. The error bars on the $\text{HO}_2 + \text{RO}_2$ measurements indicates the standard deviation upon hourly averaging.

Liao et al. (2011) the systematic uncertainties due to the calibration of the CIMS for OH is $\sim 30\%$ and that for $\text{HO}_2 + \text{RO}_2$ is $\sim 35\%$. We can thus consider the error bars as a good measure of the observational uncertainty.

We compare model results at a height of 1.5 m with surface measurements made at a similar height above the snow surface. The observations show a diurnal profile with a clear maximum of 6×10^6 molecules cm^{-3} around noon and values of $0.5\text{--}1 \times 10^6$ molecules cm^{-3} at night. The base case model run including both nitrogen and bromine snow chemistry shows excellent agreement with the observations within the uncertainties. The model seems to under predict the average peak OH concentrations by $\sim 10\%$, which is much less than the systematic uncertainty in the OH measurement. The model OH follows the observed diurnal behavior well. It also shows a secondary peak around 18:00 LT that forms due to the onset of a stable inversion that traps NO_x and reactive bromine emissions in a shallow layer near the surface. It is difficult to clearly distinguish this effect in the measurements, but the observed OH in the hours before midnight is higher than in the early hours of the morning, as predicted by the model.

The CIMS technique is sensitive to both the hydroperoxy radical and organic peroxy radicals ($\text{HO}_2 + \text{RO}_2$) (Liao et al., 2011), we therefore sum $\text{HO}_2 + \text{RO}_2$ species in the model for comparison (Fig. 11). The base case model correctly predicts the total mid-day peroxy radical concentration of 5×10^8 molecules cm^{-3} , and nighttime values of 0.7×10^8 molecules cm^{-3} . The data and the model show a

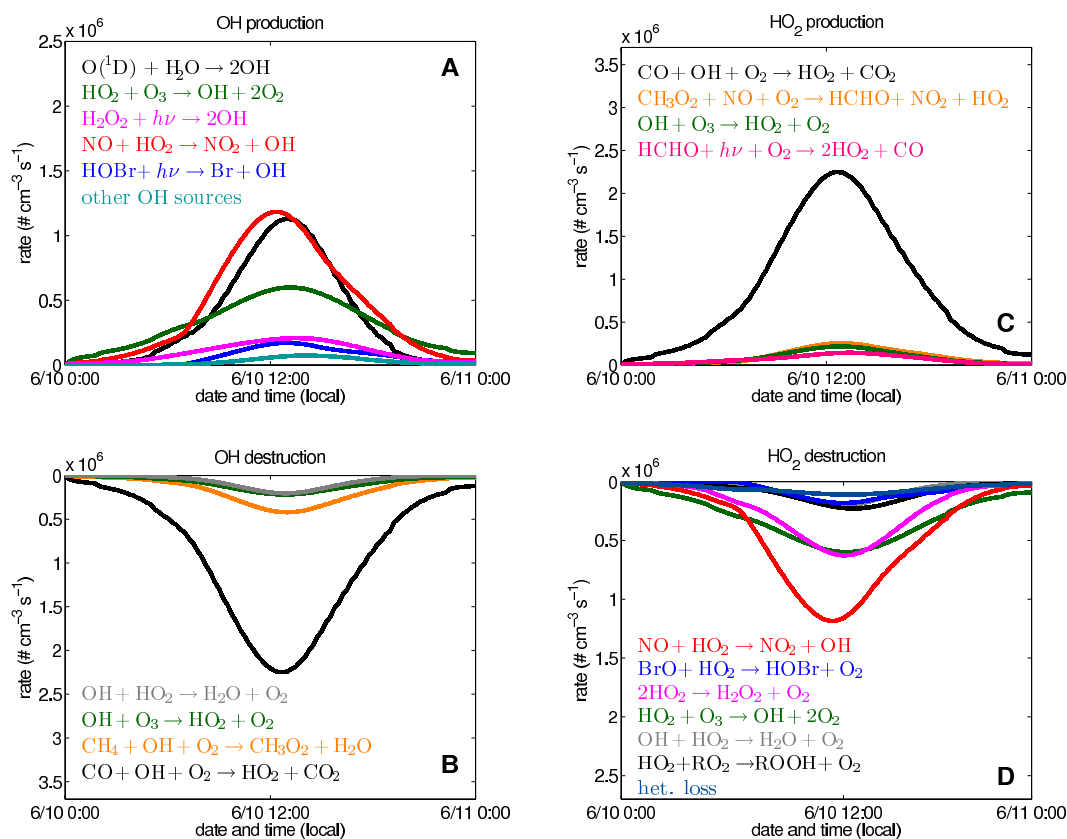


Fig. 12. OH and HO₂ production and destruction reaction rates in panels (a–d), including primary production, HO₂ to OH cycling reactions, and terminal loss processes on June 10, 2008.

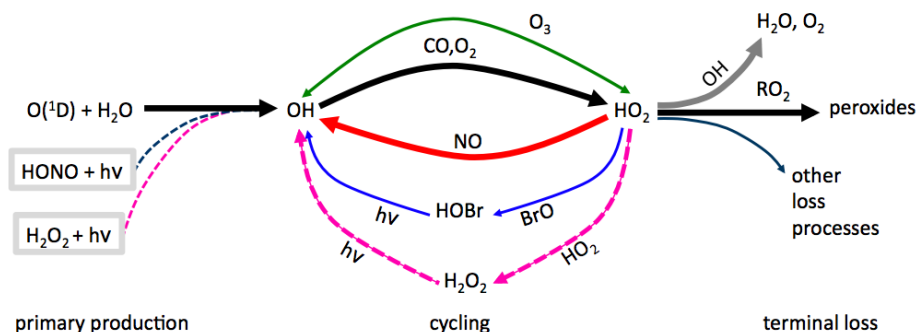


Fig. 13. Scheme of the major OH sources, HO_x interconversion reactions, and HO₂ loss processes shown in Fig. 12. The large arrows indicate the most important processes in the model at Summit during the focus period. The gray boxes indicate primary OH sources that may be due to snow emissions. H₂O₂ may contribute more to OH levels, as indicated by the dashed magenta line.

similar nocturnal asymmetry as OH, caused by the onset of the nocturnal inversion.

The successful comparison of the field observations with the model results for OH and HO₂ + RO₂ gives confidence that the model correctly describes the atmospheric radical chemistry over snow at Summit. We note that this is the first unconstrained model calculation (only the surface temperatures were constrained and the LLL partitioning of non-volatile species was adjusted at the beginning of the run) that

correctly represents HO_x chemistry and the oxidation capacity of the boundary layer over snow.

To demonstrate the effect of bromine and nitrogen chemistry on HO_x levels and the oxidation capacity of the boundary layer we compare the predicted OH concentrations for two sensitivity runs (noBro and noNit) to the base case model run in Fig. 10. There is almost a factor of 2 more OH due to emissions of NO_x to the boundary layer, depending on time of day. Similarly, gas phase bromine impacts boundary layer

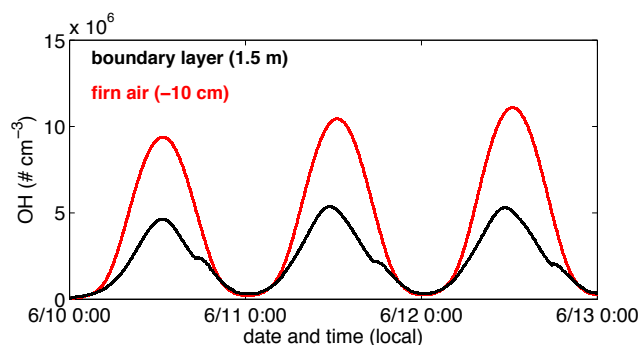


Fig. 14. OH concentrations predicted in the atmosphere and interstitial air for the base case. The model predicts a significantly enhanced oxidizing environment in the interstitial air.

OH concentrations, but less so than snow sourced NO_x . The sensitivity run shows there is between 6–20 % increase in OH upon including snow bromine chemistry, which is similar to the numbers predicted by Stutz et al. (2011). On the other hand snow sourced NO_x and halogens do not significantly impact the total peroxy radical concentration, shown by the sensitivity runs in Fig. 11.

In order to understand these results and HO_x cycling over snow in general, the OH production and HO_2 loss reactions were extracted from the model (Fig. 12). The most important primary OH source is $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ (Reaction R2) (Fig. 12a). Hydrogen peroxide photolysis (Reaction R4) also contributes to OH, only a small portion of this is a primary OH source (from snow emissions of H_2O_2). However, the sensitivity run presented in the Supplement shows that for a case with higher hydrogen peroxide concentrations the contribution of H_2O_2 to primary OH is consistent with the study of Chen et al. (2007). These higher concentrations likely result from snow-pack emissions of hydrogen peroxide. In the model the majority of H_2O_2 is formed in the gas phase via the HO_2 self reaction, and therefore constitutes HO_2 recycling back to OH. HONO is a minor source of OH in the boundary layer (included in other OH sources) because it rapidly photolyzes in snow (see Sect. 4.1) before reaching the boundary layer. Of the HO_x recycling reactions that convert HO_2 back to OH, the reaction of NO with HO_2 (Reaction R8) dominates. It should be noted that the rate of this reaction determines the chemical ozone formation rate at Summit, as discussed in Sect. 4.2. Bromine chemistry constitutes a small contribution to the OH in the boundary layer at Summit (via HOBr photolysis, Reaction R15), compared to recycling via the reaction of NO with HO_2 . The second most important OH formation reaction is the one between HO_2 and ozone. In contrast to the other OH formation mechanisms this reaction continues to recycle HO_2 back to OH at night, and is responsible for much of the nocturnal OH found at Summit. The reaction also constitutes an important chemical ozone loss mechanism in the model. In addition, it balances a portion

of the ozone formation that follows from the $\text{NO} + \text{HO}_2$ reaction. Another chemical ozone loss shown in Fig. 12 is the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction (R2). The third, more indirect, ozone loss reaction is the photolysis of HOBr, which is formed through the reaction of HO_2 and BrO (Reaction R14). This constitutes ozone destruction because one of the photolysis products for HOBr is the bromine radical, Br, which acts to destroy ozone (Reaction R16). The bromine reaction cycle through HOBr is somewhat less efficient in destroying ozone than the other two pathways, but nevertheless adds considerably to the ozone loss at Summit. Together the three reaction pathways destroy ozone at a higher rate than it is produced through the $\text{NO} + \text{HO}_2$ reaction (Reaction R8), explaining, together with the surface deposition of ozone, the slow ozone decrease in Fig. 6.

OH loss processes at Summit include reactions with CO (most important), methane, ozone, and HO_2 (Fig. 12b). Another OH loss reaction is $\text{OH} + \text{NO}_2$ to form nitric acid, however the channel is a minor OH loss process (not shown in the figure). The reaction of OH with CO (Reaction R6) is also the main sources of HO_2 in the model (Fig. 12c). As expected, $\text{OH} + \text{CH}_4$ is the main source of RO_2 .

The main recycling pathways for HO_x , which we discussed as OH sources above, are also some of the most important HO_2 loss mechanisms (Fig. 12d). Formation of organic peroxides from reaction of HO_2 with RO_2 , the reaction of HO_2 with OH, and HO_2 loss to aerosol are the most important terminal loss process for HO_x . Together with the $\text{OH} + \text{NO}_2$ reaction and reaction of HO_2 with NO_2 they balance the primary OH formation pathways. All the loss processes show the expected diurnal cycle, with photochemistry fastest at solar noon, that is also found in the HO_2 sources. The most important production, cycling, and loss processes for HO are summarized in Fig. 13.

Using this analysis and the results from our sensitivity study one can now understand how snow photochemistry influences OH levels and the atmospheric oxidation chemistry. As illustrated in Figs. 12 and 13 the emission of NO_x and bromine impact OH recycling reactions. In the absence of snow sourced NO_x the levels of NO would be significantly reduced (Fig. 3) and the cycling of HO_x through the $\text{NO} + \text{HO}_2$ channel have a corresponding reduction, with the net effect leading to 50 % lower OH concentrations as shown in Fig. 10. At the same time, reduced NO_x also slows the rate of ozone formation. It is clear from Fig. 10 that the OH budget at Summit cannot be closed without including snow photochemistry.

Similarly the absence of snow bromine chemistry decreases OH because the formation channel through HOBr photolysis is missing. However, the effect on ozone is negative as the HOBr cycle leads at the same time to ozone destruction. The absence of snow sourced bromine has a less important contribution to improving the comparison for OH between model and observations (Fig. 10).

Hutterli et al. (2001) suggested that H_2O_2 released from surface snow increased the average boundary layer H_2O_2 concentrations ($\times 7$) and increased the boundary layer OH concentrations by 70 % and the HO_2 concentrations by 50 %. If the predicted H_2O_2 concentrations are correct, hydrogen peroxide contributed less significantly to OH production in the boundary layer during 2008. In addition, in the model H_2O_2 has a more important impact on OH through gas phase recycling of HO_2 to OH, rather than snowpack emissions of H_2O_2 . HCHO photolysis to form HO_2 is a minor source of HO_x in the model (Fig. 12c). Together, in our model, snow emissions of HCHO and H_2O_2 have a minor impact on HO_x cycling in the boundary layer. There are shortcomings in our model representation of their chemistry, but the model predicted levels of these species is in line with prior measurements.

While the total air volume in the snow is much smaller than that of the overlying boundary layer, gas phase chemical processing of atmospheric species in the snow can impact atmospheric composition through the air exchanged between the boundary layer and snow. Little is known about the radical chemistry in interstitial air due to the inherent difficulty to sample interstitial air without at the same time sampling atmospheric air, and the necessity to use in-snow inlets and sampling lines. In an initial study, Beyersdorf et al. (2007) showed using hydrocarbon gas ratios in a transparent snow chamber with undisturbed surface snow that the lower limit to peak OH radical concentration on 10–12 July 2003 was $3.0 \times 10^6 \text{ cm}^{-3}$. It is useful to employ a coupled snow-atmosphere model to study the oxidizing environment of the interstitial air, which has implications for chemistry occurring in the snowpack (e.g. processing of mercury and persistent organic pollutants transported to the Arctic). We show in Fig. 14 that the environment of the interstitial air (10 cm depth) is predicted to be significantly more oxidizing than the boundary layer, with mid-day OH concentrations in the firn air approximately 2 times greater than in the boundary layer. There are several potential explanations for the discrepancy between Beyersdorf et al. (2007) and the present study. It's possible that the model over predicts NO_x concentrations present in interstitial air, therefore over predicting OH. In addition, it's possible that during sampling Beyersdorf et al. (2007) measured hydrocarbons from deeper in firn air, which would contain lower OH concentrations. Clearly, further investigation of the oxidizing environment in the interstitial air within the surface snowpack is needed.

We have shown that snow chemistry increases the amount of OH in the boundary layer, while leaving $\text{HO}_2 + \text{RO}_2$ unchanged. Faster recycling of HO_2 back to OH increases the steady state OH concentration compared to the halogen free atmosphere. Similarly, increased NO_x also contributes to faster recycling of HO_2 to OH. Together, snow sourced halogen and nitrogen chemistry in the boundary layer doubles the predicted mid-day OH concentration.

5 Summary and conclusions

We have presented results using a coupled air-snow chemistry model of radical chemistry over snow in the remote high Arctic. The modeled boundary layer concentrations of OH and $\text{HO}_2 + \text{RO}_2$ show excellent agreement with measurements performed during periods influenced by local air during the 2008 GSHOX experiment. Together with the previously reported agreement of the modeled NO and BrO mixing ratios with observations during these periods (Thomas et al., 2011), we conclude that the model represents accurately the influence of the snowpack on boundary layer chemistry during GSHOX. It should also be noted that the model correctly reproduces measurements, despite the assumptions made in representation of the LLL thickness, ion content, and chemistry. The current version of the model also contains a simplified representation of snowpack physics, which is a complex process that depends on temperature (e.g. Dominé et al., 2008). In the future, work towards a more complete description of snowpack physics and chemistry in one model is needed to create a model that accurately predicts the coupling between snow chemistry and physics with the overlying atmosphere.

We used the model to investigate how chemistry in the snow-pack influences the oxidation capacity and ozone levels in boundary layer air, using sensitivity runs and a detailed analysis of the HO_x reaction rates. The following general conclusions can be derived from our study:

- The major impact of snow chemistry on OH is due to the chemical formation of NO_x through the photolysis of nitrate, followed by the transfer of NO_x from the snowpack into the atmosphere. The snow NO_x sources leads to a near doubling of the predicted OH via reaction of NO with HO_2 , and thus a shift in the OH: HO_2 ratio towards OH. Under the investigated conditions, bromine has a less important impact, increasing OH levels by 6–20 %, also shifting the OH: HO_2 ratio towards OH. Together, snow emissions of NO_x and bromine double model predicted OH, increasing boundary layer oxidation capacity.
- Boundary layer ozone is impacted by both halogen and NO_x emissions from the surface snow. Nitrogen cycling contributes an additional 2 ppb of ozone in the boundary layer over the three day model run. Bromine emissions from the surface snow destroy 1 ppb of ozone over three days. In effect, the snowpack emissions offset would result in net ozone production, but other processes contribute and result in a slight ozone decrease (measured and modeled) during the focus period.
- Halogen and nitrogen cycling are connected via LLL reactions as well as gas phase reactions, therefore the ratio of bromide to nitrate in surface snow impacts the amount of reactive species released from the

snowpack, and thus indirectly the OH levels and the atmospheric oxidation capacity. Formation of bromine nitrate (BrNO_3) in the gas phase results in higher bromine concentrations without nitrate chemistry in the snowpack. Without bromine in the liquid layer, NO_2 formation in the LLL is reduced and results in lower predicted NO_x fluxes. However, increased nitrite concentrations in the liquid layer without bromide resulted in increased HONO release from the snowpack.

- A comparison of predicted and measured HONO (mistchamber soluble nitrite) shows that the model over predicts interstitial air HONO, but under predicts boundary layer HONO. Under no conditions are we able to predict 10 ppt of boundary layer HONO due to its rapid photolysis at the surface, which is in good agreement with measured photolysis rates at Summit. There is evidence for a large missing boundary layer HONO or soluble nitrite source that is yet to be identified. Given the agreement between the model and measurements for both OH and NO, any additional HONO source would have to be identified along with sinks for the additional OH and NO resulting from HONO photolysis. It is also possible there is another source of soluble nitrite in addition to HONO.
- Model predicted HCHO and H_2O_2 are in agreement with prior measurements taken in summer 2000 at Summit. However, measurements in summer 2000 were lower than other campaign periods (Hutterli et al., 2001; Frey et al., 2009). Temperature cycling dominates predicted HCHO in the model. HCHO plays a less important role in bromine recycling at Summit than in the coastal Arctic. Gas phase formation of H_2O_2 in the boundary layer from the HO_2 self reaction sustains boundary layer H_2O_2 concentrations. The impact of H_2O_2 on boundary layer OH concentrations is primarily via recycling of HO_2 back to OH, with limited impact of snowpacks emissions. However, this model was not developed specifically to study H_2O_2 or HCHO, therefore the chemical scheme may be inadequate to correctly predict LLL concentrations. Model predicted H_2O_2 and HCHO mixing ratios are adequate for the purposes of capturing their influence on oxidation capacity, but their LLL chemistry and cycling (including solid diffusion) will need to be investigated further in the future.

While these conclusions were derived for a specific case of Summit, Greenland, the identified mechanisms may also be active at other snow covered locations. Additional modeling studies, backed up by field observations as well as new laboratory studies, are needed to confirm that our results are representative for other snow covered locations. This in-depth research is needed to provide complete understanding, which can be used to develop predictive modeling capabilities and parameterizations of these processes for inclusion in regional

and global atmospheric chemistry models. Despite the simplified parameterization of processes, such as LLL physics and chemistry, air transport in and out of snow, etc., our study shows that photochemical processing in snow is essential to accurately describe the mechanisms controlling boundary layer ozone chemistry and oxidation capacity.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/12/6537/2012/acp-12-6537-2012-supplement.pdf>.

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