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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. Chemistry on snow grains is simulated assuming a liquid-like layer (LLL), treated as an aqueous layer on the snow grain surface. 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 by approximately a factor of 2. We show for the first time, using an unconstrained 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. 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.

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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). While not directly observed, constrained chemical box model calculations 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). Observations of interstitial ozone show that mixing ratios decrease in the snowpack relative to

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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 H₂O₂ 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 because they result in additional HO_x (HO_x = OH + HO₂) formation upon photolysis. Indirect evidence for the impact of halogen chemistry on HO_x levels at Summit, Greenland was provided by unusually high OH:(HO₂ + RO₂) ratios that have been measured during summer (Sjostedt et al., 2007; Liao et al., 2011).

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°34' N, 38°29' W, altitude = 3.3 km), where HO_x and halogen cycling was studied in summer 2008. Ground based measurements, including hydroxyl and peroxy radicals (OH and HO₂ + RO₂), ozone (O₃), nitrogen oxide

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(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).



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



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In remote polar regions, OH is converted to both HO₂ and RO₂ 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 HO₂ because of conversion of the hydroperoxyl radical back to OH (Reaction R8).



Conversion of RO₂ to HO₂ can also occur. For example, NO reacts with the methyl peroxy radical and O₂ to form formaldehyde (HCHO) and HO₂ (Reaction R9).



These reactions compete with the self and cross reaction of HO₂ and RO₂ to form peroxides, for example Reactions (R10) and (R11).



20 The levels of NO_x are crucial in determining whether the OH/HO₂ cycle is propagated (Reaction R8) or terminated.

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Because the photolysis of NO₂, followed by the reaction of the oxygen atom with O₂, 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 NO₂ levels, is therefore important for determining both the oxidative capacity of the boundary layer as well as ozone concentrations.

10 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/HO₂ ratio:



15 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.

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).



20 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

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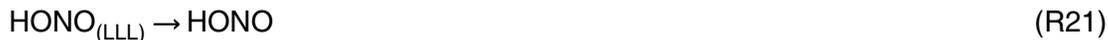


production, while bromine destroys ozone via a well known catalytic cycle. Both NO_x and bromine shift the $\text{OH}:\text{HO}_2$ ratio towards OH. HONO, H_2O_2 and HCHO emitted from the snowpack produce additional OH upon photolysis, therefore also increasing the amount of OH in the boundary layer. The connections between $\text{HO}_x + \text{RO}_2$ cycling and H_2O_2 , 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, the processes in the snowpack as well as their coupling to overlying atmosphere needs to be carefully considered. Many of these processes have already been described in Thomas et al. (2011) and will only be briefly reviewed here. Because of the need to differentiate between liquid-like and gas phase species in this section, we use the subscript (LLL) to refer to species in the liquid-like layer at the surface of snow grains.

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–R21).



The resulting NO_2 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

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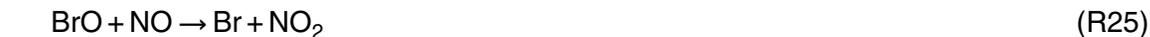
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(Thomas et al., 2011). Photochemical production of Br₂ in a LLL that covers snow grains results in halogen release from the snowpack (Reactions R22 and R23). BrO in both interstitial air and the atmosphere is formed from photolysis of Br₂ (Reaction R24) 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 R25 and R26).



In the condensed phase, bromine and nitrogen species also react (for example Reaction R27)



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.

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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, $\text{HO}_2 + \text{RO}_2$, and ozone (Sect. 4).

2 Description of the model and overview of runs

To model coupled snow-atmosphere chemistry and physics, we use the unconstrained 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 airmass 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 unknown partitioning of nitrate and bromide between the bulk snow and LLL were adjusted in the model. 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 (Rosenberg, 2005) in which chemistry occurs. 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, heterogenous reactions on aerosols are included in the atmosphere. A complete list of reactions, including both

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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 $\epsilon_\lambda = 10$ 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). 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). 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 $C_{LLL} = \phi \times C_{snow}$, where C_{snow} is the concentration in melted surface snow measured by liquid 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 $C_{LLL}(\text{NO}_3^-) = C_{LLL}(\text{H}^+)$. 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 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 of ±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

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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 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 airmass 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).

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BrO was measured by two different instruments. A longpath 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 times between 0.3–1 ppt with an accuracy of 4–7%. BrO was also measured at similar levels during these period 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 species 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 (R25), 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), 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(LLL)}⁻, which is an important intermediate species in Br_{2(LLL)} production, also reacts quickly with NO_{2(LLL)}⁻ producing NO_{2(LLL)} (Reaction R27). NO_{2(LLL)} is then transported to the gas phase (Reaction R19) where it undergoes photolysis to form NO. Reaction (R27) is in competition with the reaction of NO_{2(LLL)}⁻ with H⁺ forming HONO_(LLL) (Reaction R20), which can also escape into the gas phase and undergo photolysis forming NO. In the absence of bromide, the concentration of NO_{2(LLL)} is reduced because the reaction channel (R27) 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.

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indicates that snow-atmosphere exchange is described reasonably well in the model. The HONO photolysis rate calculated online by the model also 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 snowpack 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.

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 opposite influence of NO_x and bromine on ozone, we investigate their influences on ozone separately using sensitivity runs.

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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 air mass, 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 impact ozone formation directly via the destruction of ozone through Reaction (R16) and indirectly via lowering NO_x levels Reaction (R26). 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.

4.3 Formaldehyde and hydrogen peroxide snow and boundary layer chemistry

Formaldehyde (HCHO) is an important precursor of HO_2 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; Dominé 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. However, the general agreement suggests that this is less important than might be expected at Summit.

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

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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.

5 Snow sourced hydrogen peroxide, H₂O₂, can contribute to the OH budget and the boundary layer oxidizing capacity over snow upon photolysis. As no H₂O₂ measurements were made during GSHOX we also compare H₂O₂ modeled in the base case with prior measurements (Jacobi et al., 2004) at Summit, Greenland to determine if we correctly capture the mixing ratios, temporal behavior, and impact on atmospheric
10 oxidation (Fig. 9). H₂O₂ shows similar diurnal patterns as HCHO, with higher mixing ratios at noon. The modeled mixing ratios reproduce the observed H₂O₂ 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 H₂O₂ fluxes in June 1996 suggested a daytime H₂O₂ release from
15 the surface snow and redeposition at night (Jacobi et al., 2002, 2004). However, shading experiments did not impact H₂O₂ concentrations in the firn air, therefore the H₂O₂ is most likely not photochemically produced in the snowpack (Jacobi et al., 2004). In our model, most of the H₂O₂ results from the gas phase self reaction of HO₂ in the boundary layer, rather than release of peroxide from the surface snow. While the LLL
20 chemistry in our model may be oversimplified to correctly predict the flux of hydrogen peroxide out of the snowpack, we do show that gas phase chemistry in the boundary layer can largely explain measured H₂O₂.

4.4 HO_x chemistry of the boundary layer

The previous sections showed that snow photochemistry influences many species that
25 directly or indirectly impact OH, HO₂, and RO₂ radical concentrations. In this section we compare the modeled and measured OH and HO₂ + RO₂ in order to quantify the impact of snow chemistry on boundary layer oxidation capacity. Before analyzing the details of this chemistry we will first compare the model results with observations of

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OH and HO₂ + RO₂ 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).

5 We then calculate hourly averaged OH and HO₂ + RO₂ 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
10 11. As reported by Liao et al. (2011) the systematic uncertainties due to the calibration of the CIMS for OH is ~30 % and that for HO₂ + RO₂ is ~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 ~10 %, which is much less than the systematic uncertainty in the OH
20 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
25 the model.

The CIMS technique is sensitive to both the hydroperoxyl radical and organic peroxy radicals (HO₂ + RO₂) (Liao et al., 2011), we therefore sum HO₂ + RO₂ species in the model for comparison (Fig. 11). The base case model correctly predicts the total midday peroxy radical concentration of 5×10^8 molecules cm⁻³, and nighttime values of

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0.7×10^8 molecules cm^{-3} . The data and the model show a 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 $\text{HO}_2 + \text{RO}_2$ 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 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). 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

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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 HO₂. The second most important OH formation reaction is the one between HO₂ and ozone. In contrast to the other OH formation mechanisms this reaction continues to recycle HO₂ 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 NO + HO₂ reaction. Another chemical ozone loss shown in Fig. 12 is the O(¹D) + H₂O reaction (R2). The third, more indirect, ozone loss reaction is the photolysis of HOBr, which is formed through the reaction of HO₂ and BrO (Reaction R14). This constitutes ozone destruction because one 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 NO + HO₂ 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 HO₂ (Fig. 12b). Another OH loss reaction is OH + NO₂ 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 HO₂ in the model (Fig. 12c). As expected, OH + CH₄ is the main source of RO₂.

The main recycling pathways for HO_x, which we discussed as OH sources above, are also some of the most important HO₂ loss mechanisms (Fig. 12d). Formation of organic peroxides from reaction of HO₂ with RO₂, the reaction of HO₂ with OH, and HO₂ loss to aerosol are the most important terminal loss process for HO_x. Together with the OH + NO₂ reaction and reaction of HO₂ with NO₂ they balance the primary OH formation pathways. All the loss processes show the expected diurnal cycle, with

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photochemistry fastest at solar noon, that is also found in the HO₂ 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 NO + HO₂ 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 H₂O₂ released from surface snow increased the average boundary layer H₂O₂ concentrations (×7) and increased the boundary layer OH concentrations by 70 % and the HO₂ concentrations by 50 %. If the predicted H₂O₂ concentrations are correct, hydrogen peroxide contributed less significantly to OH production in the boundary layer during 2008. In addition, in the model H₂O₂ has a more important impact on OH through gas phase recycling of HO₂ to OH, rather than snowpack emissions of H₂O₂. HCHO photolysis to form HO₂ is a minor source of HO_x in the model (Fig. 12c). Together, in our model, snow emissions of HCHO and H₂O₂ 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.

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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. 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. 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 more than doubles the predicted mid-day OH concentration.

5 Summary and conclusions

We have presented results using an unconstrained 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 coupled air-snow system.

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 HO₂, and thus a shift in the OH:HO₂ ratio towards OH. Under the investigated conditions, bromine has a less important impact, increasing OH levels by 6–20 %, also shifting the OH:HO₂ 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 (BrNO₃) in the gas phase results in higher bromine concentrations without nitrate chemistry in the snowpack. Without bromine in the liquid layer, NO₂ 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.

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– 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 H₂O₂ are in agreement with prior measurements at Summit. 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 H₂O₂ in the boundary layer from the HO₂ self reaction sustains boundary layer H₂O₂ concentrations. The impact of H₂O₂ on boundary layer OH concentrations is primarily via recycling of HO₂ back to OH, with limited impact of snowpacks emissions. However, this model was not developed specifically to study H₂O₂ or HCHO, therefore the chemical scheme may be inadequate to correctly predict LLL concentrations. Model predicted H₂O₂ 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 the specific case of Summit, Greenland, the identified mechanisms will also be active at other snow covered locations. Our study thus shows that photochemical processing in snow is essential to accurately describe the boundary layer ozone chemistry and oxidation capacity, and should be considered when calculating lifetimes of CO and methane in the atmosphere over snow.

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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.

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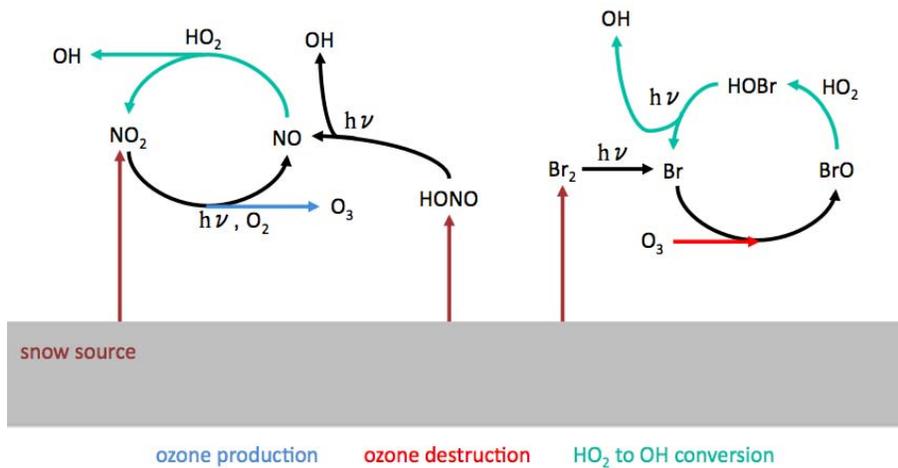


Fig. 1. Schematic of snow sourced NO_x , HONO, and bromine and their impact on ozone production and destruction. The figure also captures the impact of snow emissions on OH, both NO_x and bromine cycling shift the OH: HO_2 ratio towards OH. Snow sourced HONO is a direct source of OH.

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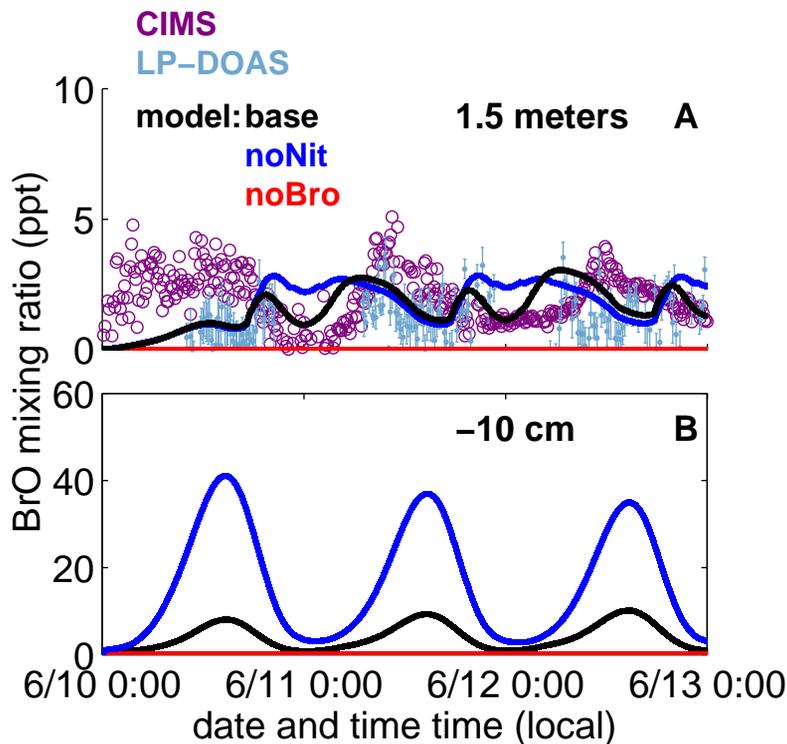


Fig. 2. Model predicted BrO for a three day model run for the base, noNit, and noBro cases compared to measurements of BrO using CIMS and LP-DOAS techniques during 10–13 June 2008. Without bromide in the liquid layer, no BrO is predicted showing that snow sourced bromine is the only source of reactive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

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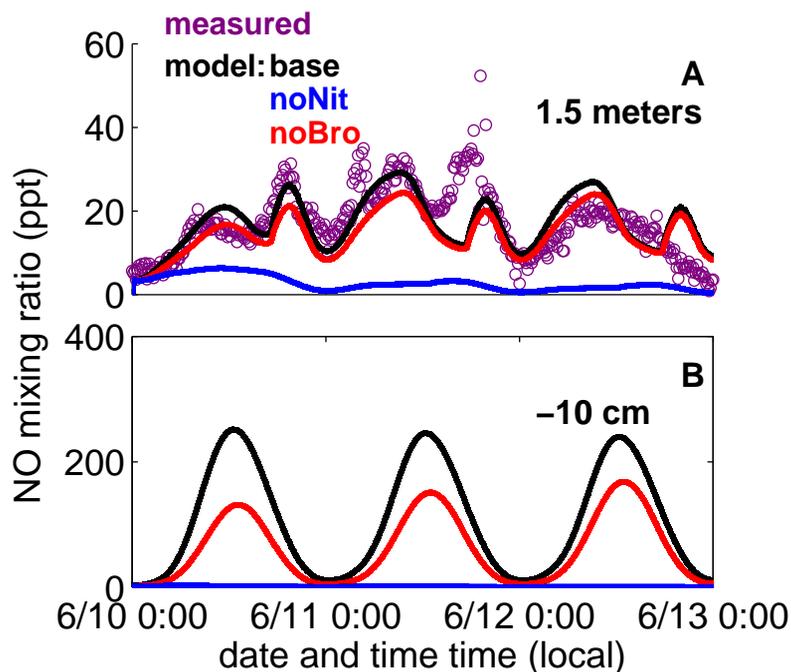


Fig. 3. Model predicted NO for a three day model run for the base, noNit, and noBro cases compared to measurements of NO taken on 10–13 June 2008. Without bromide in the liquid layer, the amount of NO predicted decreases. Without snow sourced NO_x enhanced NO is not predicted in the interstitial air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

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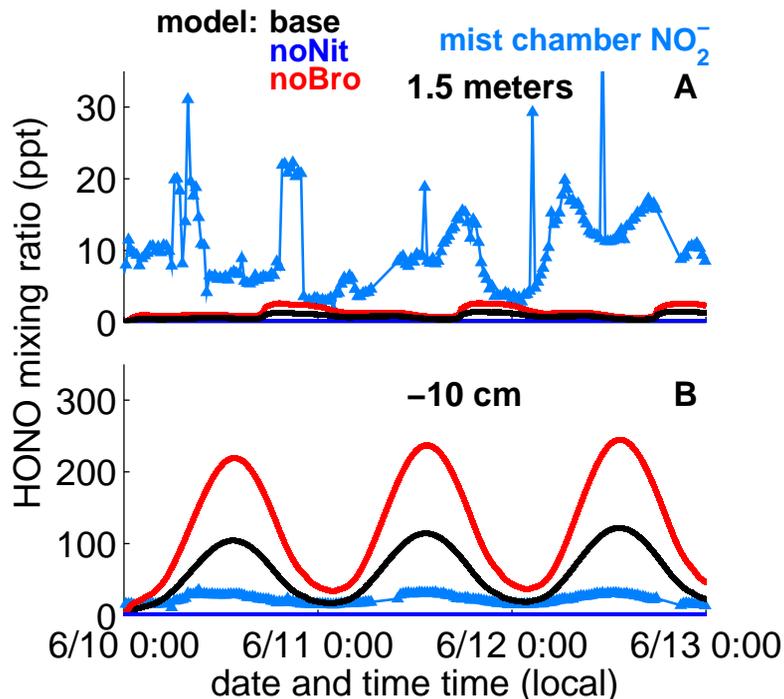


Fig. 4. Model predicted HONO for a three day model run (10–13 June 2008) for the base, noNit, and noBro cases compared to mistchamber measurements of soluble nitrite with one inlet 1.5 m above the snow surface and one inlet 10 cm below the snow surface, sampling interstitial air.

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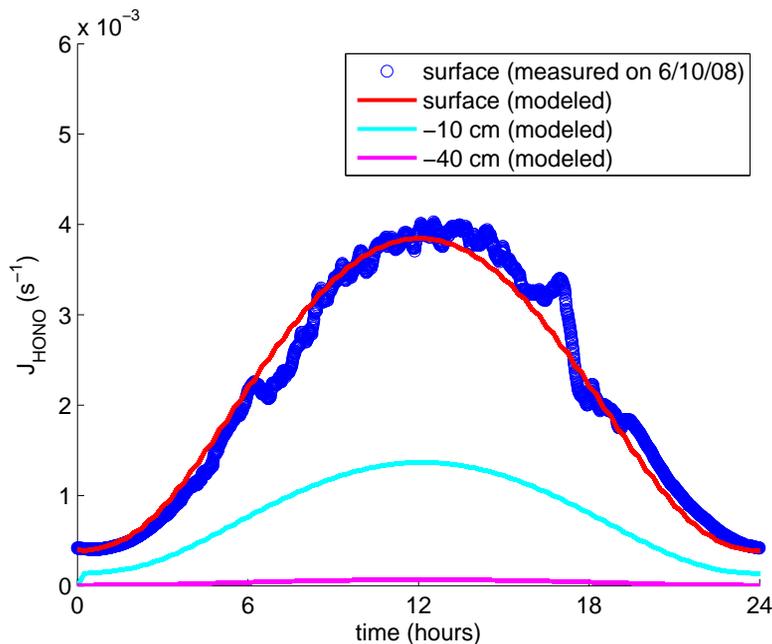


Fig. 5. Model predicted J_{HONO} on 10 June 2008 compared to the measured J_{HONO} . The excellent agreement between ambient and measured J_{HONO} indicates that the rate of HONO loss in the boundary layer due to photolysis is correctly represented in the model. At the surface at solar noon the HONO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

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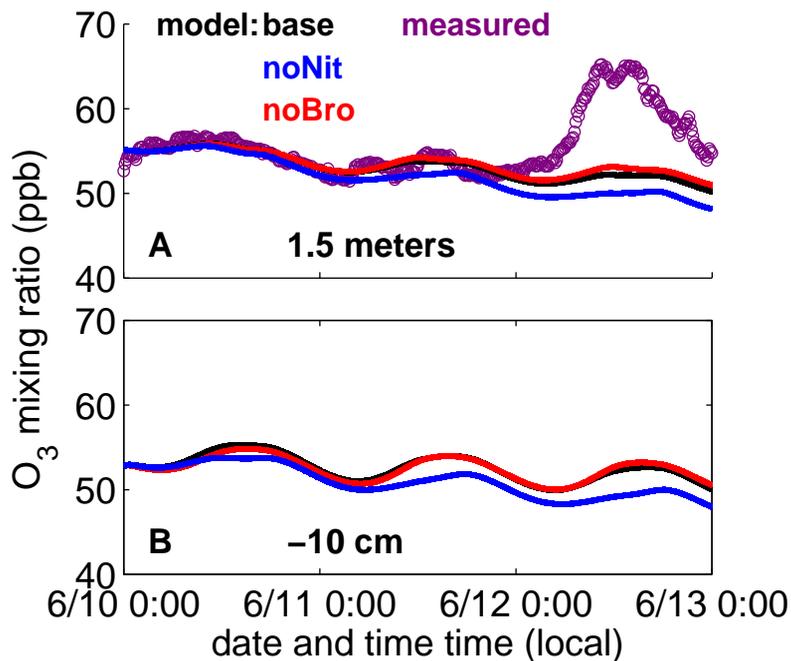


Fig. 6. Model predicted O₃ compared to measurements above the snow surface for a three day model run (10–13 June 2008) for the base, noNit, and noBro cases.

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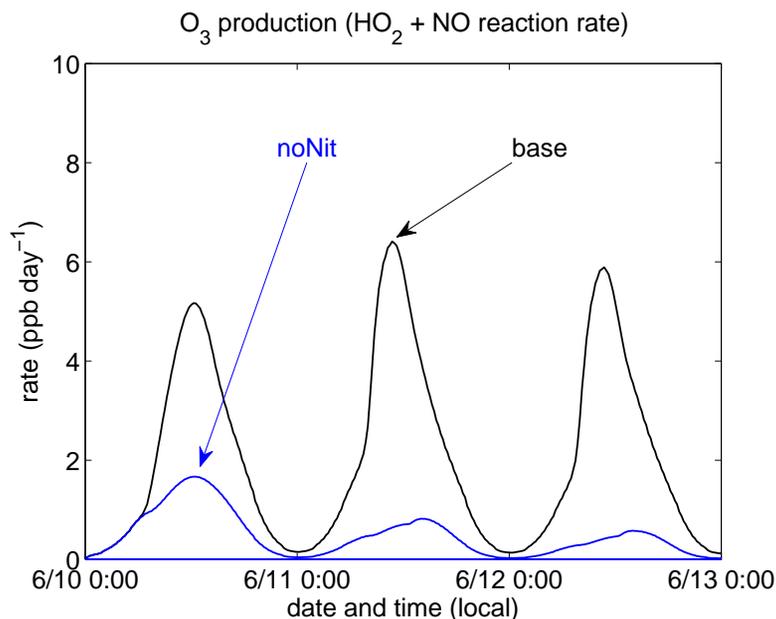


Fig. 7. Ozone production from NO to NO₂ conversion reaction (R8). The average ozone production rate from snow sourced NO_x results in an additional 2 ppb of O₃ in the boundary layer at Summit.

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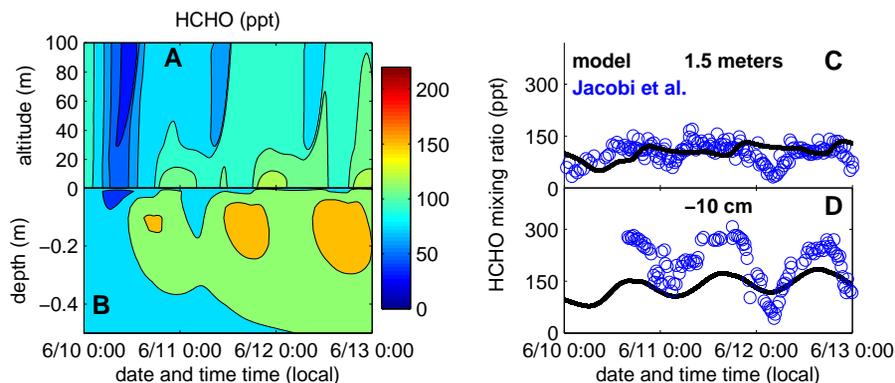


Fig. 8. Model predicted HCHO for the base case. Model results are compared with measurements taken in June 2000 originally published by Jacobi et al. (2004) (c and d). Measurements in the interstitial air during shading experiments have been removed from the comparison.

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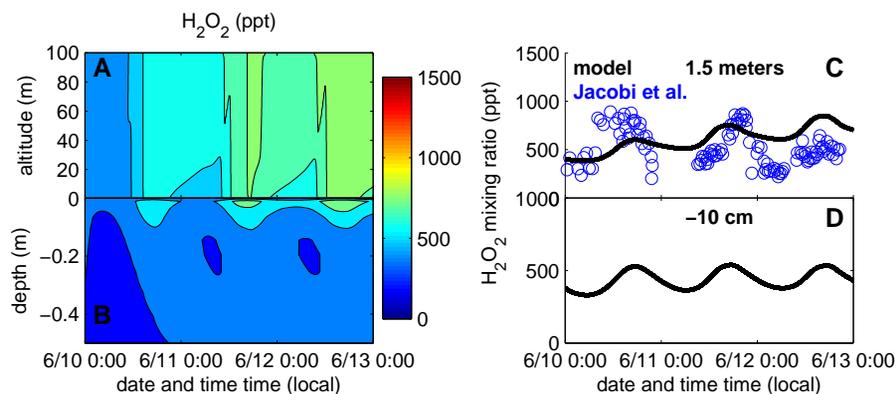


Fig. 9. Model predicted H₂O₂ for the base case. Model results are compared with measurements taken in June 2000 originally published by Jacobi et al. (2004) (panel c).

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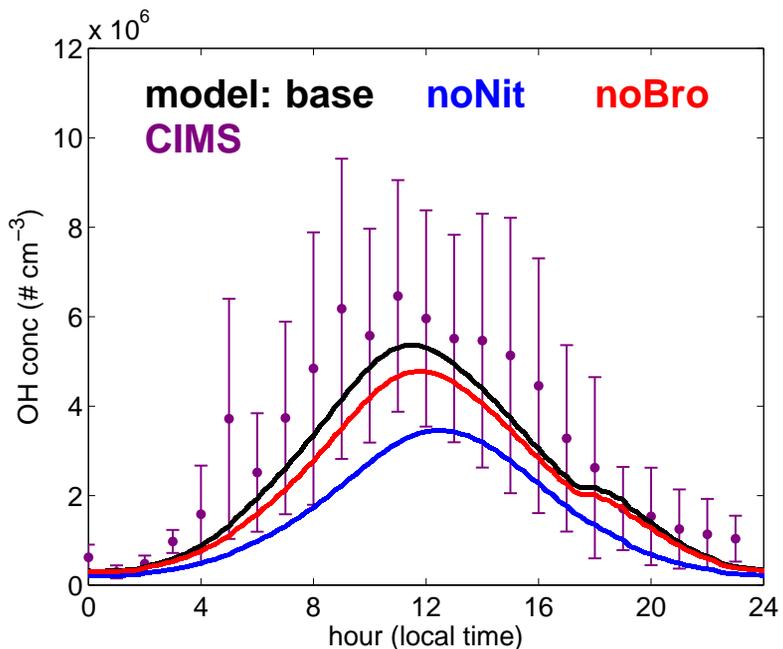


Fig. 10. Model predicted OH concentrations for the second day of the three day model run for the base, noNit, and noBro cases compared to hourly averaged OH concentrations for the time periods classified as influenced by local air. The error bars on the OH measurements indicate the standard deviation 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.

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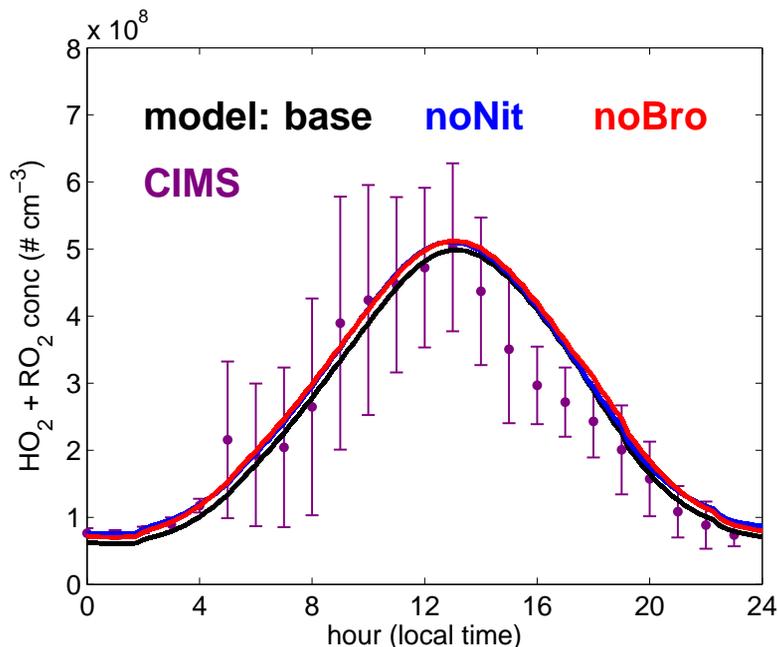


Fig. 11. Model predicted $\text{HO}_2 + \text{RO}_2$ (where RO_2 represents the sum of all organic peroxy radicals for both the measurement and the model) concentrations for the second day of a three day model run for the base, noNit, and noBro cases compared to hourly averaged $\text{HO}_2 + \text{RO}_2$ 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.

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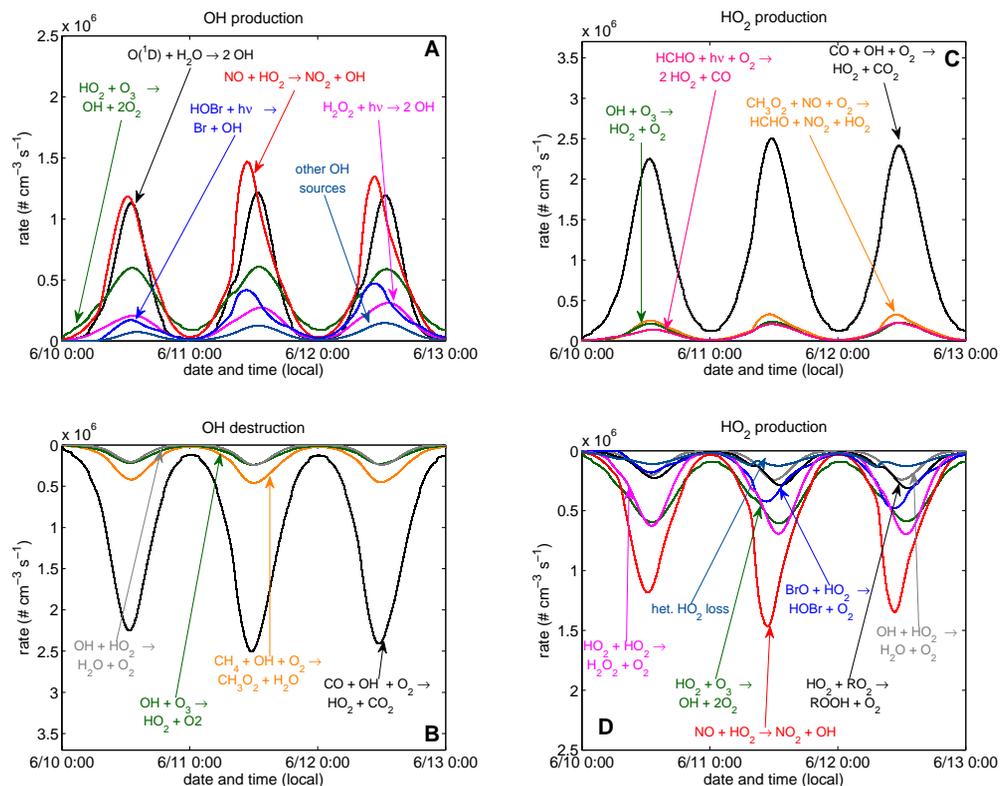


Fig. 12. OH and HO₂ production and destruction reaction rates in panels (a–d), including primary production, HO₂ to OH cycling reactions, and terminal loss processes.

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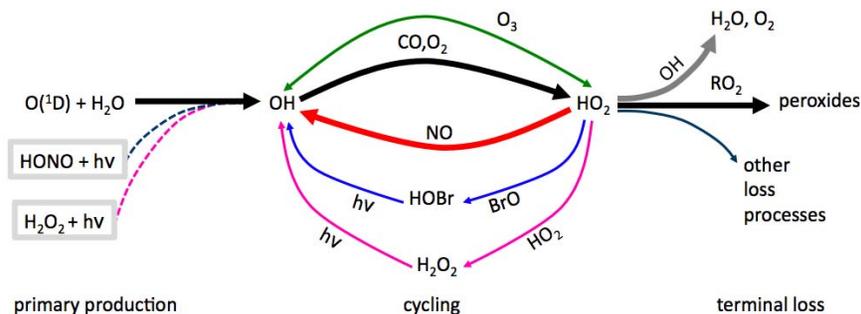


Fig. 13. Scheme of the major OH sources, HO_x interconversion reactions, and HO₂ loss processes shown in Fig. 12. The large arrows indicate the most important processes in the model at Summit during the focus period. The gray boxes indicate primary OH sources that may be due to snow emissions.

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**Modeling chemistry
in and above snow at
Summit, Greenland –
Part 2**

J. L. Thomas et al.

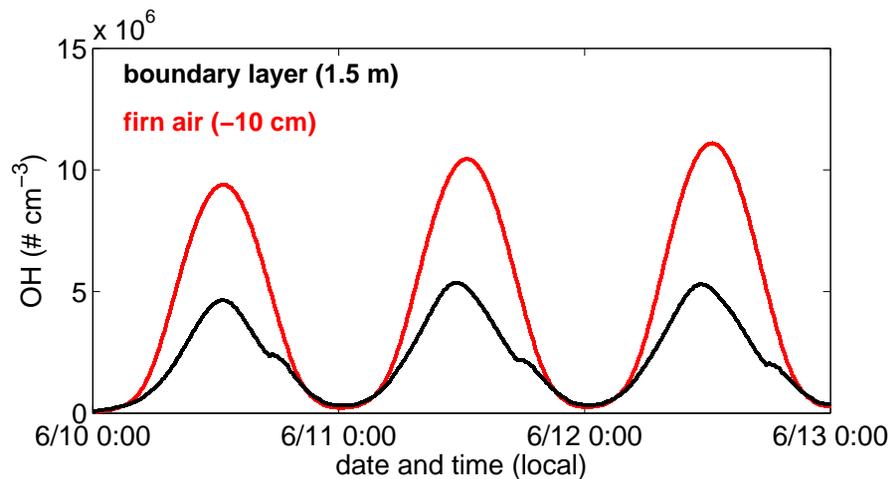


Fig. 14. OH concentrations predicted in the atmosphere and interstitial air for the base case. The model predicts a significantly enhanced oxidizing environment in the interstitial air.