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Observations of hydroxyl and peroxy radicals and the impact of BrO at Summit, Greenland in 2007 and 2008

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Abstract. The Greenland Summit Halogen-HOx (GSHOX) Campaign was performed in spring 2007 and summer 2008 to investigate the impact of halogens on HOx (≡OH + HO2) cycling above the Greenland Ice Sheet. Chemical species including hydroxyl and peroxy radicals (OH and HO2 + RO2), ozone (O3), nitrogen oxide (NO), nitric acid (HNO3), nitrous acid (HONO), reactive gaseous mercury (RGM), and bromine oxide (BrO) were measured during the campaign. The median midday values of HO2 + RO2 and OH concentrations observed by chemical ionization mass spectrometry (CIMS) were 2.7 × 108 molec cm−3 and 3.0 × 106 molec cm−3 in spring 2007, and 4.2 × 108 molec cm−3 and 4.1 × 106 molec cm−3 in summer 2008. A basic photochemical 0-D box model highly constrained by observations of H2O2, O3, CO, CH4, NO, and J values predicted HO2 + RO2 (R = 0.90, slope = 0.87 in 2007; R = 0.79, slope = 0.96 in 2008) reasonably well and under predicted OH (R = 0.83, slope = 0.72 in 2007; R = 0.76, slope = 0.54 in 2008). Constraining the model to HONO observations did not significantly improve the ratio of OH to HO2 + RO2 and the correlation between predictions and observations. Including bromine chemistry in the model constrained by observations of BrO improved the correlation between observed and predicted HO2 + RO2 and OH, and brought the average hourly OH and HO2 + RO2 predictions closer to the observations. These model comparisons confirmed our understanding of the dominant HOx sources and sinks in this environment and indicated that BrO impacted the OH levels at Summit. Although, significant discrepancies between observed and predicted OH could not be explained by the measured BrO. Finally, observations of enhanced RGM were found to be coincident with under prediction of OH.

1 Introduction

Summit, Greenland (72°34′ N, 38°29′ W, alt = 3.3 km) is located in the middle of the Greenland Ice Sheet and has been the site of a series of scientific studies beginning with ice coring in the 1980s (e.g. Hammer et al., 1980; Mayewski and Bender, 1995). In more recent years, the interaction between photochemically active species in the snowpack and the overlying atmosphere has been studied in detail at Summit and other polar stations (e.g. Dibb and Jaffrezo, 1997; Grannas et al., 2007; Jones et al., 2008; Davis et al., 2001; Huey et al., 2004). Elevated levels of species emitted from surface snow such as nitric oxide (NO), formaldehyde (CH2O), and hydrogen peroxide (H2O2) have been observed over sunlit snow in a series of campaigns (Dibb et al., 2002, 2004; Honrath et al., 1999, 2002; Hutterli et al., 1999, 2001, 2004; Davis et al., 2001; Slusher et al., 2002; Helmig et al., 2008). Snowpack emissions of radical precursors (nitrous acid (HONO),
H$_2$O$_2$, and CH$_2$O) and NO$_x$ (NO + NO$_2$) have the potential to significantly enhance HO$_x$ (hydroxyl (OH) + hydroperoxyl (HO$_2$) radicals) photochemistry in these locations (e.g. Yang et al., 2002; Chen et al., 2001). The OH and peroxy radicals (HO$_2$ + RO$_2$) have been measured in a few polar locations and the concentrations vary based on the radical sources as well as environmental conditions. The daytime mean value of OH observed at Palmer station (64°46′S, 64°3.0′W) in Antarctica was $3 \times 10^5$ molec cm$^{-3}$ in austral summer (Jefferson et al., 1998). The low OH levels were found to be consistent with the high solar zenith angle, extensive cloud coverage, no snow coverage, and low NO$_x$ levels (typically near detection limits of 2–4 pptv) (Jefferson et al., 1998). OH concentrations observed at South Pole were unexpectedly high, with an average value of 2.0 ($\pm 0.9$) $\times 10^6$ molecule cm$^{-3}$ in November and December from three field campaigns ISCAT 98, ISCAT 00 and ANTCI 03 (Mauldin et al., 2001, 2004, 2010; Grannas et al., 2007). The high OH levels at South Pole were due to low boundary layer height and snowpack emissions that gave high levels of NO$_x$ and to a lesser extent formaldehyde (Davis et al., 2001; Hutterli et al., 2004). A photochemical model constrained to CH$_3$O and H$_2$O$_2$ measurements predicted OH levels with a median modeled to observed (M/O) ratio of 1.27 (Chen et al., 2001, 2004). The model over predicted OH significantly at low NO (NO < 50 pptv; M/O > 1.5) and high NO (NO > 150 pptv; M/O = 1.5) levels but agreed better at moderate levels of NO (Chen et al., 2004). Sjostedt et al. (2007) measured OH (mean 6.3 $\times 10^6$ molec cm$^{-3}$) and HO$_2$ + RO$_2$ (mean 2.8 $\times 10^6$ molec cm$^{-3}$) levels at Summit, Greenland during summer 2003. The observed HO$_2$ + RO$_2$ levels agreed well with the model predictions, although the measured OH levels were elevated compared to the predictions (Sjostedt et al., 2007; Chen et al., 2007). Sjostedt et al. (2007) suggested that halogen may be present at Summit, perturbing the HO$_x$ cycling and enhancing OH levels. In contrast, a later study at Halley Bay, Antarctica (75°35′S, 26°19′W) found average OH levels of 3.9 $\times 10^5$ molec cm$^{-3}$ in February with typical maximum (local noontime) levels of 7.9 $\times 10^5$ molec cm$^{-3}$ (Bloss et al., 2007, 2010). The OH levels at Halley Bay were slightly higher than measured at Palmer station in the same season of the year but significantly lower than observed at South Pole. The low levels of OH were surprising as mean diurnal NO levels of up to $\sim 14$ pptv and significant iodide oxide (IO) and bromide oxide (BrO) levels of up to $\sim 7$ pptv and $\sim 9$ pptv were observed. A photochemical box model including halogen reactions significantly over predicted observed levels of OH and HO$_2$, although the model well predicted the mean levels and diurnal patterns of NO$_x$ (NO and NO$_2$) (Bloss et al., 2007, 2010). The mean daily maximum M/O ratio of OH was 3.8 and of HO$_2$ was 2.8. The mean observed HO$_2$ to OH ratio of 46 was in good agreement with the mean predicted value of 44 from the model considering bromine and iodine chemistry, and no elevated OH was observed.

Prior to the GSHOX campaign, there was only indirect evidence that BrO may exist at Summit, Greenland. Although the overall reservoir of bromine at Summit is much less than in the coastal Arctic where ozone depletion events (ODEs) are typically observed, vertical profiles of ozone obtained from balloon borne sensors have demonstrated that ozone in the boundary layer is consistently depleted relative to the air above (Helming et al., 2002). However, the reaction of NO ($\sim 20$ pptv) and RO$_2$ ($\sim 10^6$ molec cm$^{-3}$) in the boundary layer at Summit should give a local ozone production of $\sim 2$ ppbv day$^{-1}$ (Sjostedt et al., 2007). This type of ozone production is evident in the NO$_x$ (NO + NO$_2$) rich South Pole boundary layer (Crawford et al., 2001) where boundary layer ozone is elevated relative to the air above (Helming et al., 2002). In addition, mercury oxidation in snow has been observed at Summit, Greenland (Fain et al., 2008, Brooks et al., 2011). As Br + H$_2$O (GEM) $\rightarrow$ Hg$^{2+}$ (RGM) is the only well established reaction that can initiate such rapid conversion of gaseous element mercury (GEM) to reactive gaseous mercury (RGM) (Ariya et al., 2002; Donohoue et al., 2006), depleted GEM and elevated RGM may be a signature of active bromine chemistry as RGM is a relatively short lived species (Steffen et al., 2008).

High levels (up to 30–40 pptv) of BrO are typically found in the polar marine boundary layer near large sources of halides during ODEs (Tuckermann et al., 1997; Hausmann and Platt, 1994; Saiz-lopez et al., 2007; Liao et al., 2011a). However, significant levels of BrO have been observed in a variety of other marine locations. For example, BrO was observed in the tropical marine boundary layer within the Cape Verde archipelago by Read et al. (2008) with an average daytime level of 2.5 pptv. Up to $\sim 7$ pptv of BrO was observed in the mid-latitude marine boundary at Roscoff, France (48.7°N, 4.0°W) (Mahajan et al., 2009) and at the Mace Head Atmospheric Research Station, Ireland (53.33°N, 9.90°W) (Saiz-lopez et al., 2006).

To investigate the hypothesis that BrO is present at Summit and that it impacts HO$_x$ photochemistry, a suite of instruments were used to measure OH, HO$_2$ + RO$_2$, BrO and other species at Summit, Greenland in spring 2007 and summer 2008. The observations of OH and HO$_2$ + RO$_2$, and their comparison to photochemical models are presented in this paper. The BrO observations and the associated snowpack chemistry are discussed by Stutz et al. (2011) and Thomas et al. (2011), respectively.

2 Methods

A comprehensive collection of instruments were used at Summit, Greenland during May–June 2007 and June–July 2008 to measure trace gases and radicals, aerosols, actinic fluxes, and meteorological parameters. Table 1 provides a
summary of the measurements during the campaign. The details of measurement techniques not specifically summarized are presented in the references in Table 1. Most of the measurements were located in a satellite camp ~1 km to the south of the main station. The layout of the experiment is shown in Fig. 1.

2.1 HO$_x$ measurement by CIMS

The chemical ionization mass spectrometry (CIMS) instrument to measure HO$_x$ (OH and sum of HO$_2$ + RO$_2$) is nearly identical to that used to measure HO$_2$ in 2003 (Sjostedt, 2006 and Sjostedt et al., 2007). The basic methods are based on the work of Tanner et al. (1997). The CIMS was calibrated for OH and HO$_2$. Because many of the simple RO$_2$ species (e.g. CH$_3$O$_2$) are efficiently converted to HO$_2$ by this method (Edwards et al., 2003), we assumed that the sensitivities for RO$_2$ were the same as for HO$_2$. The CIMS was located in the satellite camp (Fig. 1) and the inlet was about 1.5 m above the snow surface. The dominant uncertainty in the OH and HO$_2$ + RO$_2$ measurements is the accuracy of the calibration source (Sjostedt et al., 2007). The combined uncertainties are estimated to be ~30 % for OH measurements and ~35 % for HO$_2$ + RO$_2$ measurements. The calibration standards for both OH and HO$_2$ measurements are produced from the photolysis of ambient water vapor, consequently, the uncertainty in the ratio of observed OH to HO$_2$ + RO$_2$ is smaller than the absolute uncertainties.

2.2 BrO measurement by CIMS

The CIMS used to measure BrO levels at Summit is essentially identical to the low pressure CIMS systems used to measure halogens on the NASA DC-8 and NOAA P3 aircrafts during the ARCTAS and ARCPAC campaigns (Neuman et al., 2010), and at Barrow, Alaska during the OASIS 2009 campaign (Liao et al., 2011a). The details of the instrument and air sampling inlet are described in (Liao et al., 2011a) and only significant differences are described here.

SF$_6^-$ was used as a reagent ion to ionize BrO and other species such as SO$_2$.

\[
\text{SO}_2 + \text{SF}_6^- \rightarrow \text{F}_2\text{SO}_2 + \text{SF}_4 \quad \text{(R1)}
\]

\[
\text{BrO} + \text{SF}_6^- \rightarrow \text{BrO}^- + \text{SF}_6 \quad \text{(R2)}
\]

\[
\text{Br}_2 + \text{SF}_6^- \rightarrow \text{Br}_2^- + \text{SF}_6 \quad \text{(R3)}
\]

The charge transfer reaction of SF$_6^-$ with BrO (Reaction R2) was observed for the first time as part of this work. The rate constant for this reaction was determined relative to that of SF$_6^-$ with Br$_2$ (Reaction R3) (Streit, 1982). BrO was synthesized from the reaction of O$_3$(P) with Br$_2$ in excess ozone as described in Liao et al. (2011a). The ratio of the rate constant for Reaction (R3) to Reaction (R2) was determined to be 1.0 ± 0.25 % in the laboratory. The rate constant for Reaction (R2) derived from this work is $(5 \pm 2) \times 10^{-10}$ molec cm$^{-3}$ s$^{-1}$. 

SO₂ was used as our primary calibration gas for determining the sensitivity of the CIMS system in the field (Kim et al., 2007; Slusher et al., 2001) and as a proxy to track the sensitivity of BrO. The ratio of the sensitivity of BrO to that of SO₂ was determined in the laboratory after the campaign as a function of dew point (dewpt). The average sensitivity of SO₂ was ∼4 Hz pptv⁻¹ in 2007 and ∼60 Hz pptv⁻¹ in 2008 summit campaign. The sensitivity ratio of SO₂ to BrO was determined as Eq. (1)

\[
\frac{SO_2}{BrO} = \frac{0.76 - 0.096 \times \text{dewpt} - 0.00154 \times \text{dewpt} \ (\text{dewpt} > -35^\circ C)}{2.2} \ (\text{dewpt} < -35^\circ C). \tag{1}
\]

The background signal level of BrO during the 2007 Summit campaign was determined by periodically scrubbing the sampled air with an active carbon filter, similar to that used before for removal of SO₂, HO₂NO₂, and HNO₃. In 2008 the background was determined by using glass wool because it was found to effectively remove halogen species (Neuman et al., 2010).

The detection limits of BrO measurements are estimated to be ∼1.8 pptv in 2007 and ∼0.7 pptv in 2008. Considering the uncertainty in SO₂ standard concentration (∼10 %), the uncertainties in the sensitivity ratios between BrO and Br₂ (∼25 %) and between Br₂ and SO₂ (∼5 %), the total uncertainty in BrO measurements is estimated to be ∼36 %. The concentrations of BrO at Summit in spring 2007 and summer 2008 were often near the detection limits of both instruments (detection limit of LP DOAS = 0.5–2 pptv; detection limit of CIMS = ∼1–2 pptv). Moreover, the measurements of BrO at Summit were the earliest applications of CIMS to measure ambient BrO. SF₆ was used as the reagent ion to detect BrO at that time. After these campaigns the more selective reagent ion, I⁻, was found to sensitively detect BrO (Neuman et al., 2010). In addition, the capability of CIMS, using I⁻, to accurately and sensitively measure BrO was demonstrated in Liao et al. (2011a). Moving forward, CIMS observations of BrO with I⁻ are preferred to SF₆ as the latter ion is more prone to interferences as it is more reactive (Huey et al., 1995). Consequently, conclusions drawn from the CIMS BrO observations in this study must be considered in the context of potential interferences, although the specific candidates for the interference are not known at this time.

### 2.3 BrO measurement by DOAS

The primary BrO measurement during the Summit campaign was a long path differential absorption spectrometer (LP DOAS). The techniques of the LP DOAS instrument were based on the work of Stutz and Platt (1997). The LP DOAS measured BrO over a path of either 2 km or 5 km (2007)/4 km (2008). The optical paths were 1.5–3 m above the snow. The LP DOAS telescope was located at the edge of the clean air boundary in the south of the station and two reflectors were located 2 km and 5 km (2007)/4 km (2008) to the South of the light source (Fig. 1). The details of BrO measurement by LP DOAS are provided by Stutz et al. (2011).

### 2.4 Mercury measurement

Tekran models 2537a/1130/1135 (Brooks et al., 2008) were used to measure gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), also known as gaseous oxidized mercury (GOM), and fine particle mercury (FPM) via cold vapor atomic fluorescence. The details of the mercury measurements are described in the work of Brooks et al. (2011).

### 2.5 Actinic Fluxes measurement

Actinic Fluxes were measured by a Scanning Actinic Flux Spectrometer (SAFS) (Shetter and Muller, 1999) by University of Houston. The photolysis rate coefficients (J values) of atmospheric compounds were calculated based on the sum of downwelling and upwelling Actinic Fluxes.
2.6 Photochemical models

A 0-Dimensional steady-state HOx-NOx-CH4 model is used to evaluate the HOx chemistry at Summit. The model is identical to that described in Sjostedt et al. (2007) and is denoted as the base model (BM). The BM involves 46 chemical reactions which include 8 photolysis reactions and is constrained by the measurements of photolysis rate coefficients (J values) and the following gases: H2O, O3, CO, CH4, and NO. The model only considered CH4 chemistry because previous studies by Chen et al. (2007) and Sjostedt et al. (2007) found that including nonmethane hydrocarbons (NMHC) decreased OH number densities and increased HO2 + RO2 number densities less than 10% and that most of the RO2 is CH3O2 at Summit, Greenland. Typical levels of the dominant NMHC species ethane, propane, and butane are 1.0 ppbv, 0.07 ppbv, and 0.04 ppbv, respectively. The NMHC measured in 2007 and 2008 were generally consistent with the measurements in 2003. The average ethane, propane and butane levels were 1.1 ppbv, 0.14 ppbv, 0.03 ppbv, respectively in spring 2007 and 0.9 ppbv, 0.07 ppbv, 0.02 ppbv respectively in summer 2008. Because Summit Greenland is in the middle of Greenland Ice Sheet far away from biogenic and anthropogenic volatile organic carbons (VOCs) sources, we do not expect high levels of oxygenated VOCs reacting with OH at Summit, Greenland. Measurements of larger oxygenated VOCs at Summit, Greenland are needed to validate our assumption. The input data used to constrain the model were averaged to a 10 min basis. A spin-up time of 1000 s was used for model calculations of relatively long-lived species (e.g. H2O2 and HCHO). The model predictions are compared to OH and HO2 + RO2 measurements (assuming RO2 is primarily CH3O2). The rate constants are taken from the JPL compilation (Sander et al., 2006), and the J values are derived from the measured actinic fluxes (Shetter and Muller, 1999). Similar to the work of Sjostedt et al. (2007), the model can be run either constrained or unconstrained to HONO measurements. This allows evaluation of the impact of HONO on HOx levels and the radical budget. The model constrained to HONO observations is referred as BM-HONO.

To examine the impact of BrO on HOx levels, bromine reactions (see Table 2) were added to the BM. The model incorporating the bromine chemistry is referred as BM-BrO. Reaction (R6) in Table 2 acts as a source of HOx. HOBr serves as a temporary reservoir of HOx and heterogeneous loss of HOBr is effectively a loss of HOx. HOBr levels were assumed to be in steady-state and controlled by Reactions (R2), (R8) and (R9) in Table 2. This assumption was valid because the photolysis lifetime of HOBr is relatively short (∼5 min) at Summit Greenland in the daytime. The assumption was also found to reasonably predict the observed HOBr in Liao et al. (2011b). The box model is constrained by BrO measurements from CIMS and LP DOAS to illustrate the effect of two BrO datasets on HOx levels. The mass accommodation coefficient of HOBr is assumed to be 0.6 (Wachsmuth et al., 2002). This allowed predictions of OH and HO2 + RO2 when BrO measurements were available. The model did not include the heterogeneous sinks of BrONO2 because the model is constrained to BrO measurements and BrONO2 does not directly impact the budget of OH and HO2 + RO2. The impact of BrONO2 on daytime NO2 levels is also small due to the low BrO concentrations. Daytime NO2 levels increased ∼5% in 2007 and ∼2% in 2008 when the model considered bromine Reactions (R4) and (R5) in the Table 2. As the photochemical lifetime (∼2 min) of HO2 is much shorter than the lifetime due to heterogeneous loss (∼150 min) with a uptake coefficient of 0.1 (Mao et al., 2010), the model did not consider the heterogeneous loss of HO2.

One significant difference from the work of Sjostedt et al. (2007) is that observations of CH3O and H2O2 were not available. For this reason, the BM was used to predict CH3O and H2O2 levels. In order to test the ability of the model to calculate these species, predictions of CH3O and H2O2 using data from the 2004 Summit campaign were compared to observations. Both CH3O and H2O2 predictions are in reasonable agreement with the measurements (CH3O: Р = 0.68, mean M/O = 1.3; H2O2: Р = 0.72, mean M/O = 2.4), which suggests that the steady state model is viable for estimation of CH3O and H2O2 within about a factor of two. The impact of this relatively high uncertainty in mixing ratios of CH3O and H2O2 on predictions of HOx and its partitioning are discussed in Sect. 4.2.

3 Results

3.1 OH and (HO2 + RO2) observations

The time series of observations of OH, HO2 + RO2, J(O1D), BrO, NO, HNO3, HONO, O3, RGM, temperature, wind speeds and wind directions on a 10 min time base in spring 2007 and summer 2008 are shown in Fig. 2. The observations of OH and HO2 + RO2 were filtered to exclude the periods when NO > 50 pptv. High NO mixing ratios at Summit are almost always due to pollution plumes from the station power generator. High NO dramatically brought down the HO2 + RO2 concentrations and raised the OH concentrations (Fig. 3). Similar phenomena were observed by previous works as well (e.g. Sjostedt et al., 2007; Bloss et al., 2007). The HOx instrument was shut down to save reagent gases at night (22:00–06:00 Western Greenland Standard Time (WGST)) when the OH concentrations decreased to near detection limit (10^5 molec cm^{-3}). The gaps in the data other than night time and high NO periods are due to instrument maintenance or malfunction.

Diurnal profiles of OH and HO2 + RO2 largely followed the patterns of J(O1D) with a maximum at local noon, consistent with the behaviors of short-lived photochemically active species. Although 24 h of daylight are present in
summer time at Summit, $J(O^1D)$ decreased by approximately a factor of 100 from noon to midnight. The maxima mid-day levels of OH and HO$_2$ + RO$_2$ increased as temperature, $J(O^1D)$ and O$_3$ increased, which were consistent with the previous finding that O$_1D$ reacting with H$_2$O and snow emissions of H$_2$O$_2$ were the dominant HO$_x$ sources at Summit (Chen et al., 2007) (Mid-day is defined as 10:00–15:00 WGST). Overall, the maximum mid-day OH and HO$_2$ + RO$_2$ concentrations increased during the measurement period in spring 2007 as the summer solstice was approached. There was no significant trend in the maximum mid-day OH and HO$_2$ + RO$_2$ concentrations during summer 2008 (12 June 2008–8 July 2008) as the measurement period was centered about the solstice. The average mid-day OH and HO$_2$ + RO$_2$ concentrations were higher in summer 2008 than that in spring 2007, likely a result of the higher radiative fluxes ($JO_3$ 2007/JO$_3$ 2008 = 1:1.4) and dew points in summer time. The midday median ratio of HO$_2$ + RO$_2$ to OH was 107:1 in spring 2007 and 102:1 in summer 2008 and the midday mean ratio of HO$_2$ + RO$_2$ to OH was 109:1 with a standard deviation of 23 in spring 2007 and 108:1 with a standard deviation of 37 in summer 2008. The HO$_2$ + RO$_2$ to OH ratios are comparable to other measurements performed in the lower troposphere in mid latitudes (Ren et al., 2008). The mid-day median and mean values of OH and HO$_2$ + RO$_2$ observations, as well as $J(O^1D)$, $J(No_2)$, NO, HNO$_3$, HONO, O$_3$, BrO, RGM and temperature in spring 2007 and summer 2008 are summarized in Table 3.

3.2 NO, HNO$_3$ and HONO observations

Diurnal profiles of NO and HONO were also observed at Summit. The average mid-day concentrations of NO and HONO were $\sim$12 pptv and $\sim$6 pptv, respectively. HONO levels were obtained from measurements of soluble nitrite (NO$_2^-$) from the mist chamber (Dibb et al., 2002). However, it should be noted that the derived HONO levels must be considered an upper limit to gas phase HONO as other species might also produce nitrite in solution. Following the simple NO$_3$ and HONO lifetime arguments in Chen et al. (2004); NO levels of 12 ppt and HONO levels of 6 ppt would seem to indicate that the soluble nitrite measurement includes species other than HONO. Due to the increase of the boundary layer height through the day, the diurnal profiles of NO had a local minimum at noon (Thomas et al., 2011). Elevated HNO$_3$ was observed by mist chamber during the days when photochemically enhanced NO was observed. Higher NO, HNO$_3$ and HONO concentrations were observed in spring 2007 than in summer 2008.

3.3 RGM and GEM observations

Up to $\sim$250 pg m$^{-3}$ RGM were observed in the spring 2007 campaign. Clear diurnal profiles of RGM were observed when RGM was greater than 100 pg m$^{-3}$. Because bromine atoms are one of the few established species that efficiently converts GEM into RGM (Ariya et al., 2002; Donohoue et al., 2006), elevated RGM peaks indicated that significant levels of BrO may be present. Higher RGM levels were observed in spring 2007 than in summer 2008, which suggests that the concentrations of BrO at Summit might be higher in spring 2007 than in summer 2008. High RGM appeared to coincide with photochemically enhanced NO and HONO in most cases. This is consistent with snow photochemistry activating bromine chemistry as described in Thomas et al. (2011).

3.4 BrO observations

BrO mixing ratios detected by the LP DOAS ranged from below detection limit to 5.5 pptv with an average value of 1.6 pptv in 2007 at Summit. BrO was also measured by CIMS in the later period of the 2007 campaign with a mean value of 1.7 pptv, ranging from below detection limit to 6.4 pptv. Lower BrO mixing ratios were observed by both LP DOAS ($\langle BrO_{\text{mean}} \rangle = 0.9$ pptv for all data available) and CIMS ($\langle BrO_{\text{mean}} \rangle = 1.5$ pptv for all data available) in summer 2008. BrO mixing ratios in 2008 generally ranged from below detection limit to 4 pptv and 5 pptv detected by LP DOAS and CIMS respectively. To be noted, the BrO concentrations at Summit were often near detection limits of both instruments. Diurnal patterns of BrO were observed in spring 2007 and the early part (10 June to 13 June) of summer 2008 by the CIMS with maximum concentrations in the daytime, which is consistent with BrO as a photochemically active product. No significant diurnal patterns of BrO were observed by the CIMS in the later period of summer 2008 as the daytime BrO levels were near the detection limit.

4 Discussion

4.1 Model comparison

4.1.1 Base Model (BM)

The predicted OH and HO$_2$ + RO$_2$ from the BM are plotted against the observations in Fig. 4. Note that, the discrepancy between HO$_x$ observations and predictions increased at high wind speeds (WS $> 8$ m s$^{-1}$) and were excluded from the comparisons. On average 26 % of the HO$_x$ data were excluded and the correlation coefficients were improved ($R$ increase 0.03 on average for BM_model) when HO$_x$ data were filtered at high wind speed conditions. Higher wind speed conditions did not clearly correspond to low photolysis rate or lower NO$_x$ levels. The correlation coefficient ($R$) between photolysis rate and wind speeds were $< 0.1$ in 2007 and 2008. The correlation coefficient ($R$) between predicted NO$_2$ and wind speeds were $- 0.35$ in 2007 and $- 0.29$ in 2008. There is no clear systematic bias introduced when the HO$_x$ data were filtered at high wind speeds but this filter excluded the
Table 2. Bromine reactions included in the HO_x model.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reactions</th>
<th>Reaction rate coefficient ( k ) (cm³ molec⁻¹ s⁻¹ or s⁻¹)</th>
<th>( k(T = 250,\text{K}) ) (cm³ molec⁻¹ s⁻¹ or s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br + O_3 → BrO + O_2</td>
<td>( 1.7 \times 10^{-11} \exp(-800/T) )</td>
<td>( 6.9 \times 10^{-13} )</td>
</tr>
<tr>
<td>2</td>
<td>BrO + H_2O → HBrO + O_2</td>
<td>( 4.5 \times 10^{-12} \exp(460/T) )</td>
<td>( 2.8 \times 10^{-11} )</td>
</tr>
<tr>
<td>3a</td>
<td>BrO + BrO → 2Br + O_2</td>
<td>( 2.4 \times 10^{-12} \exp(40/T) )</td>
<td>( 2.8 \times 10^{-12} )</td>
</tr>
<tr>
<td>3b</td>
<td>→ Br_2 + O_2</td>
<td>( 2.8 \times 10^{-12} \exp(860/T) )</td>
<td>( 8.7 \times 10^{-13} )</td>
</tr>
<tr>
<td>4</td>
<td>BrO + NO → Br + NO_2</td>
<td>( 8.8 \times 10^{-12} \exp(260/T) )</td>
<td>( 2.5 \times 10^{-11} )</td>
</tr>
<tr>
<td>5</td>
<td>BrO + NO_2 + M → BrONO_2 + M</td>
<td>( k_0=5.2 \times 10^{-31} \exp(T/300)^{-3.2} )</td>
<td>( 5.3 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{\infty}=6.9 \times 10^{-12} \exp(T/300)^{-2.9} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Br + CH_2O → HBr + HCO</td>
<td>( 3 \times 10^{-3} ) − ( 4 \times 10^{-3} )(at noon)</td>
<td>( \sim 1 \times 10^{-4} )</td>
</tr>
<tr>
<td>7</td>
<td>BrO + hv → Br + O</td>
<td>0.06–0.08 (at noon)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>HOBr + hv → Br + OH</td>
<td>( 3 \times 10^{-3} ) − ( 4 \times 10^{-3} )(at noon)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Uptake of HOBr on heterogeneous surface</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Time series of measurements of HO_2 + RO_2, OH, J(O^1D), BrO, temperature, NO, HNO_3, HONO, O_3, RGM, wind speeds and directions on a 10 min time base in spring 2007 (top panel) and summer 2008 (bottom panel) Summit campaign.
Table 3. Photochemical species concentrations and parameters in the mid-day (10:00–15:00 WGST) at Summit, Greenland in 2007–2008. (Note: HOx predictions are from the base model.)

<table>
<thead>
<tr>
<th>Species</th>
<th>Year 2007 (13 May–13 June)</th>
<th>Year 2008 (10 June–8 July)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>Average</td>
</tr>
<tr>
<td>OH ($10^6$ molec cm$^{-3}$)</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>HO$_2$ + RO$_2$ ($10^8$ molec cm$^{-3}$)</td>
<td>2.7</td>
<td>3.3</td>
</tr>
<tr>
<td>OH pred ($10^6$ molec cm$^{-3}$)</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>HO$_2$ + RO$_2$ pred ($10^8$ molec cm$^{-3}$)</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>NO (pptv)</td>
<td>12.8</td>
<td>17.2</td>
</tr>
<tr>
<td>O$_3$ (ppbv)</td>
<td>54.6</td>
<td>55.3</td>
</tr>
<tr>
<td>BrO$_{LPDOAS}$ (pptv)</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>BrO$_{CIMS}$ (pptv)</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>RGM (pg m$^{-3}$)</td>
<td>41.8</td>
<td>64.8</td>
</tr>
<tr>
<td>HNO$_3$ (pptv)</td>
<td>12.9</td>
<td>15.9</td>
</tr>
<tr>
<td>HONO (pptv)</td>
<td>6.5</td>
<td>7.3</td>
</tr>
<tr>
<td>J(0$^1$D) ($10^{-5}$ s$^{-1}$)</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>JNO$_2$ (s$^{-1}$)</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td>Temperature ($^{\circ}$C)</td>
<td>−19.5</td>
<td>−18.2</td>
</tr>
</tbody>
</table>

Fig. 3. An example of elevated OH and depleted HO$_2$ + RO$_2$ at high NO conditions. The spikes in NO and the responses in OH and HO$_2$ + RO$_2$ are due to the measurement cite being impacted by the plume of the generator.

most scattered points. It is possible that the uncertainty in the CIMS calibration increases at high wind speeds (>8 m s$^{-1}$) due to turbulent flow in the inlet as suggested in Sjostedt et al. (2007). Overall, the observed and predicted OH and HO$_2$ + RO$_2$ from the BM were well correlated (HO$_2$ + RO$_2$: $R = 0.90$, OH: $R = 0.83$ in 2007; HO$_2$ + RO$_2$: $R = 0.79$, OH: $R = 0.76$ in 2008). The BM well predicted the magnitude of HO$_2$ + RO$_2$ and under predicted OH, especially in summer 2008 (HO$_2$ + RO$_2$: slope = 0.87, OH: slope = 0.72 in 2007; HO$_2$ + RO$_2$: slope = 0.96, OH: slope = 0.54 in 2008). The slopes were given by equally weighted bivariate regressions. The agreement between the predicted and observed HO$_2$ + RO$_2$ (which is dominated by HO$_2$) indicates that we have a good understanding of the major sources and sinks of HO$_2$ which dominates the HO$_x$ family. However, our understanding of the OH sources and sinks is clearly lacking especially during periods of elevated RGM (see Sect. 4.4). The model predicted an average midday HO$_2$ + RO$_2$ to OH ratio of 121:1 in 2007 and 125:1 in 2008, consistent with the values predicted by Chen et al. (2007) using input data from the summit 2003 campaign. The observed average midday HO$_2$ + RO$_2$ to OH ratios were 109:1 in 2007 and 108:1 in 2008. The predicted and observed HO$_2$ + RO$_2$ to OH ratios indicate that a mechanism rolling HO$_2$ back to OH may be missing, with halogen chemistry a likely prospect.

4.1.2 Base Model constrained to HONO measurements (BM_HONO)

The correlation coefficients and slopes between predictions from the BM_HONO and observations are shown in Fig. 5 (HO$_2$ + RO$_2$: $R = 0.84$, slope = 0.90 in 2007 and $R = 0.79$, slope = 1.09 in 2008; OH: $R = 0.78$, slope = 0.92 in 2007 and $R = 0.78$, slope = 0.72 in 2008). The slopes were given by equally weighted bivariate regressions. The correlation coefficient ($R$) between predicted and observed HO$_x$ did not improve when the model included HONO source. In 2007, the average modeled to observed (M/O) ratios of HO$_2$ + RO$_2$ and OH were 1.18 and 0.87 from the BM, and were 1.25 and 0.84 from the BM_HONO. In 2008, the average M/O ratios
of HO$_2$ + RO$_2$ and OH were 1.06 and 0.87 from the BM, and were 1.22 and 1.05 from the BM_HONO. The predictions of both OH and HO$_2$ + RO$_2$ from the BM_HONO were higher than that from the BM as this adds in a HO$_X$ source. However, the ratio of HO$_2$ + RO$_2$ to OH changed by less than 10% on average. As the HO$_X$ predictions from the BM had more data points, the correlation between predicted and observed HO$_X$ did not improve when HONO was included in the model, and the observed HONO is likely to have interferences (Stutz et al., 2010; Sjostedt et al., 2007), the BM is preferred for comparison to HO$_X$ observations in this work.

4.1.3 Model incorporating halogen chemistry (BM_BrO)

To investigate the impact of BrO on HO$_X$, predicted OH and HO$_2$ + RO$_2$ from the BM_BrO unconstrained by HONO measurements and constrained by BrO measurements from the CIMS (BM_BrOCIMS) and LP DOAS (BM_BrOLPDOAS) in 2007 and 2008 are also plotted against the observations (Fig. 6). Overall, the correlation coefficients between the observed and predicted OH and HO$_2$ + RO$_2$ were slightly improved (increased 0.03 except HO$_2$ + RO$_2$ in 2007) by incorporation of bromine chemistry with the BrO constrained to the CIMS observations. When the model included bromine chemistry and was constrained to CIMS BrO, the intercept increased from 1.12 × 10$^5$ molec cm$^{-3}$ to 1.65 × 10$^5$ molec cm$^{-3}$ and the slope increased from 0.72 to 0.78 in 2007 and the intercept increased from 8.64 × 10$^5$ molec cm$^{-3}$ to 9.23 × 10$^5$ molec cm$^{-3}$ and the slope increased from 0.54 to 0.56 in 2008 for OH. When the model included bromine chemistry and was constrained to LPDOAS BrO, the intercepts increased from 5.67 × 10$^7$ to 3.76 × 10$^5$ and the slope increased from 0.84 to 0.76 in 2007 and the intercept increased from 8.46 × 10$^5$ to 3.10 × 10$^7$ and the slope slightly decreased from 0.78 to 0.72 in 2008 for OH. To give a general idea of the difference between predicted OH and HO$_2$ + RO$_2$ from the BM and BM_BrO, the average ratios of OH and HO$_2$ + RO$_2$ from both models as well as the slopes and intercepts from linear equally weighted bivariate regression are also provided. Predicted OH increased 12 % ([OH]$_{\text{pred()}, \text{CIMS}/[\text{OH}]_{\text{pred(),avg}}}$ in 2007 and 10% in 2008, and predicted HO$_2$ + RO$_2$ decreased 10% in 2007 and 8% in 2008 on average when the BM_BrO was constrained to CIMS BrO. Predicted OH increased 10% in 2007 and 4% in 2008, and predicted HO$_2$ + RO$_2$ decreased 8% in 2007 and 3% in 2008 on average when the BM_BrO was constrained to LP DOAS BrO. These results indicate that BrO impacted the concentrations of OH and HO$_2$ + RO$_2$ at Summit, although all of the enhancement in observed OH relative to model predictions cannot be explained by the influence of BrO.

4.1.4 Impact of H$_2$O$_2$ and CH$_2$O

Because CH$_2$O and H$_2$O$_2$ were not observed, they had to be predicted with the photochemical model which may lead to under estimation of them as they are emitted to the atmosphere from the snowpack (Hutterli et al., 1999, 2001). Under estimation of CH$_2$O and H$_2$O$_2$ results in under prediction of OH and HO$_2$ + RO$_2$, but does not significantly impact the ratios of OH/ HO$_2$ + RO$_2$. For example, a 30% increase in
Fig. 6. HO$_2$ + RO$_2$ and OH predictions from the base model incorporating bromine chemistry constrained by BrO measurements by CIMS (BM, BrO$_{CIMS}$) and LPDOAS (BM, BrO$_{LPDOAS}$) plotted versus the observations in 2007 and 2008. The data are averaged on a 10 min time base. The correlation coefficient (R) and the slope and intercept from an equally weighted bivariate regression (red line) for each panel are also denoted in the figure. The units of slope and intercept from an equally weighted bivariate regression were added to the BM.

\[
\begin{align*}
\text{Intercept} & = 2.27 \times 10^6 \\
\text{Slope} & = 0.85 \\
\text{R} & = 0.89
\end{align*}
\]

\[
\begin{align*}
\text{Intercept} & = 3.20 \times 10^5 \\
\text{Slope} & = 0.78 \\
\text{R} & = 0.86
\end{align*}
\]

\[
\begin{align*}
\text{Intercept} & = 1.15 \times 10^6 \\
\text{Slope} & = 0.79 \\
\text{R} & = 0.79
\end{align*}
\]

\[
\begin{align*}
\text{Intercept} & = -2.34 \times 10^7 \\
\text{Slope} & = 0.76 \\
\text{R} & = 0.76
\end{align*}
\]

The model production rate of H$_2$O$_2$ or CH$_2$O would increase HO$_2$ levels by \sim 5\% and \sim 10\% but would impact the ratio of OH to RO by less than 2\%. According to the study of HO$_4$ at Summit in 2003 by Chen et al. (2007), H$_2$O$_2$ is the largest snow emitted HO$_4$ sources at Summit, contributing to 37\% of the net HO$_4$ sources compared to only 3\% from CH$_2$O. As snow emissions of H$_2$O$_2$ increase with temperature (Chen et al., 2007), the warmer temperature in summer 2008 may have contributed to the lower concentration between predicted and observed HO$_4$ in that year. For this reason, temperature dependent snow emissions of H$_2$O$_2$, based on net snow-air exchange rate shown as the following equation, were added to the BM.

\[
d[H_2O_2]/dt = A \times \exp(B/\text{Temperature}_{\text{snow}}) - C \times [H_2O_2] (\text{molec cm}^{-3} s^{-1} \text{ or ppbv hr}^{-1})
\]

\[
A, B \text{ and } C \text{ are adjustable constants. Temperature is assumed to be ambient temperature instead of snow temperature. [H$_2$O$_2]$ represents ambient H$_2$O$_2$ concentration (Chen et al., 2007). No significant improvement of the correlation was found between predicted and observed HO$_4$. However, as observations of H$_2$O$_2$ and CH$_2$O were not carried out in 2007 or 2008, enhanced snow photochemistry producing these and potentially other radical precursors in 2008 cannot be ruled out.}

4.2 Average comparison

Figure 7 shows the average diurnal profiles of hourly OH and HO$_2$ + RO$_2$ concentrations from observations and predictions from the BM and the BM, BrO constrained to CIMS measurements in 2007 and 2008. The error bars of the observations are the overall uncertainties including the measurement uncertainties and ambient fluctuations. The error bars of the predictions are the propagated uncertainties from the model inputs uncertainties and variations. The BM simulated the concentrations of OH and HO$_2$ + RO$_2$ within the combined uncertainties, except for the OH concentrations in the late afternoons in summer 2008. This confirms that the BM captures the dominant HO$_4$ sources and sinks. The BM also under predicts the OH concentrations in both 2007 and 2008. The midday median modeled to observed (M/O) ratio of OH was 0.88 and 0.87 in 2007 and 2008, and the midday median M/O ratio of HO$_2$ + RO$_2$ was 0.97 and 1.08 in 2007 and 2008. A low M/O ratio of OH was also reported in Sjostedt et al. (2007). The average hourly HO$_2$ + RO$_2$ and OH predictions from the BM, BrO constrained to CIMS BrO measurements in 2007 slightly over estimated their concentrations due to the absence of CIMS BrO measurements in the early period of the 2007 campaign and the increase in HO$_4$ levels in the late period of the 2007 campaign relative to the early period. The OH concentrations predicted from BM, BrO were higher compared to the results from the BM, and the average hourly predicted HO$_2$ + RO$_2$ concentrations slightly decreased when BM incorporated bromine chemistry in 2008. The model including bromine chemistry brought the predictions both of OH and HO$_2$ + RO$_2$ closer to the observations in 2008. The impact of bromine chemistry on HO$_2$ + RO$_2$ concentrations was smaller than on OH concentrations. The box model consistently under predicts the OH concentrations in the later afternoons, which indicates that box model underestimates the sources of OH as the radiation flux and boundary layer height decrease or there may be a change in the sinks or cycling. A similar behavior was observed by Sjostedt et al. (2007). Snow emitted compounds with higher concentrations or steeper vertical gradients in the later afternoon not included in the photochemical box model may contribute to the under predictions of OH and impact the photochemistry at Summit in the later afternoon.
4.3 Enhanced OH and RGM

Due to the limitations of BrO measurements discussed earlier, observations of RGM were also investigated as a proxy for bromine and potentially other chemistry. The correlations between the BM predictions and observations of HO$_x$ were examined for enhanced RGM levels (gray dots in Fig. 8) and low RGM levels (black dots in Fig. 8). RGM levels were considered to be enhanced when they were above average levels.
of RGM were present during the same period, with a maximum concentration of near 250 pg m\(^{-3}\). The RGM peaks indicate that certain levels of Br and BrO may be present during these periods. Small \(O_3\) concentration drops also occurred with the RGM peaks, possibly a result of bromine catalyzed \(O_3\) depletion. Up to 5 pptv of BrO were observed by LP DOAS and no CIMS BrO measurements were available during this time. OH predictions from BM\_BrO constrained by LP DOAS BrO measurements cannot account for the enhanced OH observed.

Figure 9b shows the early period of 2008 campaign including three days (12 June–14 June 2008) with obvious under prediction of OH. The RGM peaks during this period were the highest values in 2008 campaign with a maximum of \(\sim 80\) pg m\(^{-3}\). During this period, up to 4–5 pptv of BrO were observed by CIMS, and up to \(\sim 3\) pptv of BrO were observed by LP DOAS. The BrO levels were near the detection limits of the LP DOAS and CIMS instruments. The gaps of BrO and \(HO_3\) measurements during 12 June–14 June 2008 were due to the extremely high wind speeds (> 12 m s\(^{-1}\)). The OH predictions from BM\_BrO constrained by CIMS BrO measurements are also shown in Fig. 9b. These levels of BrO were not large enough to explain the under prediction of OH. The BrO concentrations during 12 June–14 June 2008 only contribute \(\sim 10\%\) to the OH production rate.

5 Conclusions

The median midday values of \(HO_3 + RO_2\) and OH concentrations observed by CIMS were \(2.7 \times 10^8\) molec cm\(^{-3}\) and \(3.0 \times 10^6\) molec cm\(^{-3}\) in spring 2007, and \(4.2 \times 10^8\) molec cm\(^{-3}\) and \(4.1 \times 10^6\) molec cm\(^{-3}\) in summer 2008 at Summit. The BM was reasonably accurate for \(HO_3 + RO_2\) \((R = 0.90, \text{ slope } = 0.87\) in 2007; \(R = 0.79, \text{ slope } = 0.96\) in 2008\) but under predicted OH \((R = 0.83, \text{ slope } = 0.72\) in 2007; \(R = 0.76, \text{ slope } = 0.54\) in 2008\). This confirmed our understanding of the dominant \(HO_3\) sources and sinks in this environment and that there may be mechanisms perturbing \(HO_3\) cycling and enhancing OH above the snowpack. Inclusion of HONO source in the model did not impact the correlation between predictions and observations of \(HO_3\) significantly and did not improve the ratio of OH to \(HO_3 + RO_2\). BrO levels detected by CIMS and LP DOAS generally ranged from below detection limits to \(\sim 6\) pptv and \(\sim 5\) pptv, respectively. The correlation between observed and predicted \(HO_3 + RO_2\) and OH from the BM\_BrO\_CIMS slightly improved relative to the BM. The model incorporating bromine chemistry brought the average hourly OH and \(HO_3 + RO_2\) predictions closer to the observations in 2008. This indicates that BrO at Summit impacted the \(HO_3\) levels, although most of the discrepancies between observations and models cannot be explained by the influence of detected BrO. High levels of RGM were found to be coincident with the significant under predictions of OH, and exclusion of high RGM periods significantly increased the agreement.
between predicted and observed OH. This is consistent with bromine chemistry and potentially other chemistry leading to elevated RGM and impacting the production OH from HO$_2$ and RO$_2$. Enhanced snow photochemistry producing H$_2$O$_2$, CH$_3$O and potentially other radical precursors at higher temperature may have contributed to the larger discrepancy between predicted and observed HO$_x$ in summer 2008.

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