

## An assessment of the polar HO<sub>x</sub> photochemical budget based on 2003 Summit Greenland field observations

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### Abstract

An interpretative modeling analysis is conducted to simulate the diurnal variations in OH and HO<sub>2</sub> + RO<sub>2</sub> observed at Summit, Greenland in 2003. The main goal is to assess the HO<sub>x</sub> budget and to quantify the impact of snow emissions on ambient HO<sub>x</sub> as well as on CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. This analysis is based on composite diurnal profiles of HO<sub>x</sub> precursors recorded during a 3-day period (July 7–9), which were generally compatible with values reported in earlier studies. The model simulations can reproduce the observed diurnal variation in HO<sub>2</sub> + RO<sub>2</sub> when they are constrained by observations of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. By contrast, model predictions of OH were about factor of 2 higher than the observed values. Modeling analysis of H<sub>2</sub>O<sub>2</sub> suggests that its distinct diurnal variation is likely controlled by snow emissions and loss by deposition and/or scavenging. Similarly, deposition and/or scavenging sinks are needed to reproduce the observed diel profile in CH<sub>2</sub>O. This study suggests that for the Summit 2003 period snow emissions contribute ~25% of the total CH<sub>2</sub>O production, while photochemical oxidation of hydrocarbon appears to be the dominant source. A budget assessment of HO<sub>x</sub> radicals shows that primary production from O(<sup>1</sup>D) + H<sub>2</sub>O and photolysis of snow emitted precursors (i.e., H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O) are the largest primary HO<sub>x</sub> sources at Summit, contributing 41% and 40%, respectively. The snow contribution to the HO<sub>x</sub> budget is mostly in the form of emissions of H<sub>2</sub>O<sub>2</sub>. The dominant HO<sub>x</sub> sink involves the HO<sub>2</sub> + HO<sub>2</sub> reaction forming H<sub>2</sub>O<sub>2</sub>, followed by its deposition to snow. These results differ from those previously reported for the South Pole (SP), in that primary production of HO<sub>x</sub> was shown to be largely driven by both the photolysis of CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> emissions (46%) with smaller contributions coming from the oxidation of CH<sub>4</sub> and the O(<sup>1</sup>D) + H<sub>2</sub>O reaction (i.e., 27% each). In sharp contrast to the findings at Summit in 2003, due to the much higher levels of NO<sub>x</sub>, the SP HO<sub>x</sub> sinks are dominated by HO<sub>x</sub>–NO<sub>x</sub> reactions, leading to the formation and deposition of HNO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub>. Thus, a comparison between SP and Summit studies suggests that snow emissions appear to play a prominent role in controlling primary HO<sub>x</sub> production in both environments. However, as regards to maintaining highly elevated levels of OH, the two

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environments differ substantially. At Summit the elevated rate for primary production of HO<sub>x</sub> is most important; whereas, at SP it is the rapid recycling of the more prevalent HO<sub>2</sub> radical, through reaction with NO, back to OH that is primarily responsible.

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## 1. Introduction

Polar photochemistry has been the focus of several field studies during the past decade (Dominé and Shepson, 2002; Davis et al., 2001, 2004; Dibb et al., 2007). This was sparked by the observations of highly enhanced levels of chemically reactive species, e.g., NO, CH<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, and HONO, above the snowpack (e.g., Dibb et al., 2002; Honrath et al., 1999; Hutterli et al., 1999, 2001, 2003; Ridley et al., 2000; Davis et al., 2001). These species can dramatically increase the oxidative capacity directly above the snow surface (e.g., Chen et al., 2001, 2004; Hutterli et al., 2001; Yang et al., 2002). The observations of summertime OH in both Arctic and Antarctic showed similar or even higher levels than those seen in the tropical marine boundary layer (Mauldin et al., 2001, 2004; Sjostedt et al., 2007).

Along with field observations, diagnostic modeling studies have been carried out to assess the impact of snow emissions on HO<sub>x</sub> chemistry and to explore whether our understanding of that chemistry is complete. In an earlier Summit Study, Hutterli et al. (2001) estimated that the impact from the measured levels of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O, resulting from snow emissions, increased summertime OH and HO<sub>2</sub> concentrations by ~70% and 50%, respectively. In another Summit study, Yang et al. (2002) used a steady-state photochemical model to estimate OH and peroxy radical levels based on observations made during field campaigns in 1999 and 2000. Although these investigators had no direct OH or HO<sub>2</sub> observations to compare with, they did carry out a HO<sub>x</sub> budgetary analysis based on their modeling results which showed that gross HO<sub>x</sub> production from the photolysis of HONO, CH<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub> to be over a factor of 2–3 times larger than that resulting from the photolysis of ozone followed O(<sup>1</sup>D)+H<sub>2</sub>O reaction. It should be noted, however, that this analysis did not distinguish between snow emissions and photochemical sources of the above cited species. Based on modeled peroxy radical levels, Yang et al. (2002) also estimated the rate of net ozone

production to range from 2 to 3 ppbv/day. The first direct observations of OH and peroxy radicals (HO<sub>2</sub>+RO<sub>2</sub>) at Summit, Greenland were those reported in the summer of 2003 (Sjostedt et al., 2007). In addition, a more comprehensive set of precursor measurements were recorded which included O<sub>3</sub>, NO, CO, H<sub>2</sub>O, light non-methane hydrocarbons, H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, and HONO. Photolysis frequencies based on spectroradiometer observations were also available for this study. Collectively, these new observations permitted a more detailed photochemical modeling analysis to evaluate the impact of snow emissions on HO<sub>x</sub> as well as to test our understanding of polar photochemical processes. In this context, Sjostedt et al. (2007) have now reported a comparison of observed OH and observed total peroxy levels with steady-state model predictions as constrained by precursor observations. These authors found excellent agreement for HO<sub>2</sub>, but the model underestimated OH by nearly a factor of 2. Similar to the results from Yang et al. (2002), Sjostedt et al. (2007) also found that the combined photolysis of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O yielded nearly the same contribution to the primary production of HO<sub>x</sub> as did the O(<sup>1</sup>D)+H<sub>2</sub>O reaction channel.

Building upon these earlier Summit studies by Sjostedt et al. (2007) and Yang et al. (2002), the main goal of this work is to assess the HO<sub>x</sub> budget and to quantify the impact of snow emissions on HO<sub>x</sub> levels as well as those for CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. This study has used a time-dependent photochemical-box model having the same chemistry as Sjostedt et al. (2007). The resulting budget analysis from this study has been based on a series of simulations in which the model was constrained by the observed diurnal profiles for all critical HO<sub>x</sub> precursor species. The results have been contrasted to those from previous Summit studies as well as those at the South Pole (SP). Since the major two studies that will be compared are those by Yang et al. (2002) and Chen et al. (2004), we have labeled these as YJ02 and CG04. This study will be referred to as Summit 2003.

## 2. Observational data

A comprehensive suite of photochemical species and parameters was recorded at 2 m above snow surface during Summit 2003. The list includes O<sub>3</sub>, CO, NO, H<sub>2</sub>O, CH<sub>4</sub>, and light-weight non-methane hydrocarbon (NMHC) species, OH, HO<sub>2</sub>+RO<sub>2</sub> (total peroxy radicals), H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, HONO, and spectral actinic flux. Detailed descriptions of the instruments involved in these measurements have been provided by Sjostedt et al. (2007) and will not be repeated here except in table format (Table 1) which summarizes the techniques, uncertainties, and affiliated institutions. The ambient and snow surface temperature data used in this study were recorded at a site approximately 1 km away. The investigating team there was from the Institute for Atmospheric and Climate Science, Swiss Federal Institute of Technology ETH, Zurich, Switzerland. Wind speed and direction data were those reported by a University of Colorado Automatic Weather Station (AWS) located about 1.8 km from the Summit 2003 chemical measurement site.

During the 2003 summer field campaign, concurrent measurements of HO<sub>2</sub>+RO<sub>2</sub> and OH were carried out during the time period between June 26 and July 10. As described by Sjostedt et al. (2007), observed midday HO<sub>2</sub>+RO<sub>2</sub> values varied from 2.2 to 6.5 × 10<sup>8</sup> mol cm<sup>-3</sup>. A still larger variation was seen in midday OH, where values ranged from 0.3 to 2.3 × 10<sup>7</sup> mol cm<sup>-3</sup>. Some of the variations in HO<sub>x</sub> were linked to wind speed. For example, the highest OH was observed on a day having the highest wind speed of the 2003 field campaign, 10–14 m s<sup>-1</sup>, June

28th. Sjostedt et al. (2007) have suggested that a potential OH measurement bias might occur when wind speeds are above 6 m s<sup>-1</sup>. To minimize the possible impact from this bias, this analysis has focused only on three rather calm days having continuous concurrent OH and HO<sub>2</sub>+RO<sub>2</sub> measurements, i.e., July 7–9, 2003. Retroplume trajectory calculations (Stohl et al., 2003) using the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005) have shown that the air masses sampled during these days were close to the snow surface in the vicinity of Summit for three or more days during this period. In Fig. 1 the four panels shown represent the time series plots of several select species before, during, and after the selected analysis time period (shaded area). In particular, Fig. 1c reveals that the wind speed gradually weakened from July 6 to July 11, 2004; and it was under ~2 m s<sup>-1</sup> by the end of experiment, i.e., July 9th and 10th. There were, however, unexpected enhancements in NO (Fig. 1b) during these two days, reflecting the influence of nearby power generator emissions. The NO enhancement in the afternoon of July 9th exceeded the 97th percentile for the entire experiment period. We suspect that this NO enhancement was mostly influenced by factors other than snow emissions and opted to exclude these data from our analysis.

Fig. 1a shows that the diurnal trends for OH and HO<sub>2</sub>+RO<sub>2</sub> were quite consistent within the selected period. Furthermore, the HO<sub>2</sub>+RO<sub>2</sub> profile exhibits a high level of consistency with *j*(O<sup>1</sup>D), suggesting that the HO<sub>x</sub> diurnal variation was likely driven by photochemical processes. Finally, the

Table 1  
Summary of Summit, Greenland measurements

Species	Technique	Uncertainty	Institution
O <sub>3</sub>	UV absorption	<5%	Georgia Tech
NO	Chemiluminescence	10%	Georgia Tech
H <sub>2</sub> O	Cryo-hydrometer	10%	Georgia Tech
CO	GC/Canister	<5%	UCI
CH <sub>4</sub>	GC/Canister	<5%	UCI
NMHC	GC/Canister	<5%	UCI
H <sub>2</sub> O <sub>2</sub>	Scrubber/fluorescence spectrometry	15%	U. Arizona
CH <sub>2</sub> O	Scrubber/fluorescence spectrometry	20%	U. Arizona
HONO	Mist chamber	15%	UNH
OH	CIMS	25%	Georgia Tech
HO <sub>2</sub> +RO <sub>2</sub>	CIMS	32%	Georgia Tech
Actinic flux	SAFS	10%	NCAR/U. Houston
Temperature	Thermocouples	± 0.7 °C	IAC ETH Zurich
Wind speed	AWS	2% at 10 m s <sup>-1</sup>	UCO

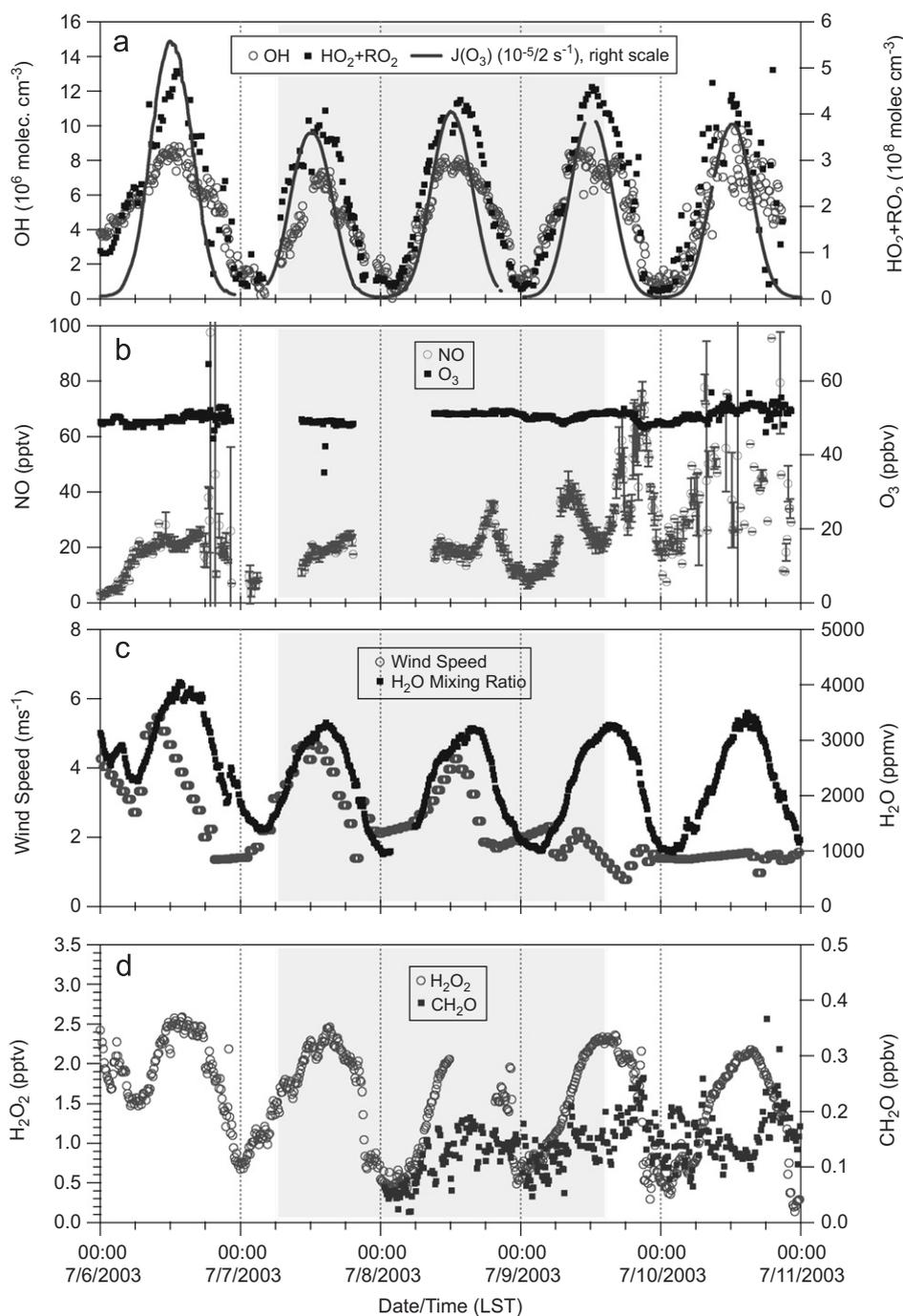


Fig. 1. Time series plot of: (a) OH, HO<sub>2</sub> + RO<sub>2</sub>, and  $j\text{O}(^1\text{D})$  (multiplied by 2), (b) NO and ozone, (c) wind speed and H<sub>2</sub>O mixing ratio, and (d) H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. The shaded area indicates the period of interest for this study.

smoothness in  $j$  value profile is indicative of clear sky conditions during the period of interest. This is a favorable condition for model simulations.

The observational data from the selected period, i.e., July 7–9, 2003, were averaged and used for

model simulation of OH and HO<sub>2</sub> + RO<sub>2</sub>. Hourly averages were calculated according to local sun time (LST). The diurnal profiles were constructed using the hourly averages of NO, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, H<sub>2</sub>O, temperature and photolysis coefficients.

This approach is one effective way to minimize the impact of data gaps shown in Fig. 1. For some other species, the observational data could not be used to represent diurnal variations due to either low sampling frequencies or large data gaps. In these cases, observational medians were used as the fixed values for these variables throughout the diurnal cycle. As one example, HONO was fixed at the median value of 10 pptv for the selected period. This choice was based on the fact that observed HONO had small daytime variations and that nighttime data was absent. Median values were also used for species measured from canister sampling, e.g., CO, CH<sub>4</sub>, and light-weight NMHC species. The NMHC mix consisted of ethane, propane, and butane with representative values for these species being 1.0, 0.07, and 0.04 ppbv, respectively. Other species, including more reactive NMHC's (e.g., ethene), were at levels near the limit of detection and not used in modeling runs. A more detailed discussion related to the Summit NMHC observations can be found in Swanson et al. (2002).

To put this study in perspective with other polar investigations, Table 2 provides a comparison between Summit 2003, CG04, and YJ02. The values for the Summit 2000 and Summit 1999 studies were taken from Table 2 of YJ02 and the entries for the

South Pole 2000 studies were those derived from the model input values used in CG04. It is noted here that the values given in Table 2 for this study are those derived from the selected period and they should not be considered as the typical values for the entire 2003 summer study which spanned from 10th June to 12th July. Table 2 shows that levels of NO, O<sub>3</sub>, and CO are quite consistent among all three Summit studies. For example, the variation in NO averages is <25%. Larger differences are seen in H<sub>2</sub>O, having a total range in levels of nearly a factor of 2. This difference is likely related to ambient temperature shifts at the times of the sampling. Of the species derived from snow emissions, the average HONO level for all three Summit studies is within a factor of 2 of the extremes. Summit 2003 H<sub>2</sub>O<sub>2</sub> levels are also generally consistent with those recorded in Summit 1999, Summit 1996 (Hutterli et al., 2001), and Summit 1990 (Sigg et al., 1992); but all of these values are significantly higher than those reported during the Summit 2000 study. The average Summit 2003 CH<sub>2</sub>O level is in agreement with the Summit 2000 and Summit 1996 investigations (Hutterli et al., 1999); but both are almost a factor of 7 lower than that reported for Summit 1999. Quite interestingly, the pattern of change between field studies is similar

Table 2  
Summary of model input parameters and comparison with previous polar HO<sub>x</sub> studies

Species/parameter	Summit 2003 (July 7–9)		Summit 2000 <sup>a</sup> (June–August)		Summit 1999 <sup>a</sup> (June–July)		South Pole 2000 <sup>b</sup> (November–December)	
	Average	Range	Average	Range	Average	Range	Average	Range
NO (pptv)	21	7–42	16	4–37	25	8–41	103	2–570
O <sub>3</sub> (ppbv)	50	35–52	52	40–63	41	28–49	32	17–51
CO (ppbv)	108	106–109	110		90		37	31–42
H <sub>2</sub> O <sub>2</sub> (ppbv)	1.45	0.43–2.46	0.72	0.22–1.52	1.78	0.85–2.77	0.26	0.03–0.56
CH <sub>2</sub> O (ppbv)	0.09	0.05–0.20	0.12	0.06–0.20	0.74	0.03–1.9	0.10	0.02–0.17
HONO (pptv)	11	5–22	7.2	1.1–19	13	3.1–27	26	12–33
CH <sub>4</sub> (ppmv)	1.82	1.81–1.82	1.82	1.79–1.84	1.80	1.80–1.82	1.71	1.70–1.73
H <sub>2</sub> O (% v/v)	0.22	0.09–0.33	0.29	0.13–0.50	0.40	0.17–0.60	0.067	0.003–0.1
<i>j</i> (O <sup>1</sup> D) (noon) <sup>c</sup> (10 <sup>-5</sup> s <sup>-1</sup> )	2.73	2.30–3.04	3.2	2.4–4.3	3.4	2.3–4.3		
<i>j</i> (NO <sub>2</sub> ) (noon) <sup>c</sup> (10 <sup>-2</sup> s <sup>-1</sup> )	1.42	1.35–1.48	1.5	1.6–2.1	2.0	1.6–2.3		
<i>j</i> (HONO) (noon) <sup>c</sup> (10 <sup>-3</sup> s <sup>-1</sup> )	3.19	3.02–3.33	4.4	3.6–5.0	4.2	3.4–4.7		
<i>j</i> (O <sup>1</sup> D) (avg.) <sup>d</sup> (10 <sup>-5</sup> s <sup>-1</sup> )	1.05		1.23		1.31		0.72	0.40–1.11
<i>j</i> (NO <sub>2</sub> ) (avg.) <sup>d</sup> (10 <sup>-2</sup> s <sup>-1</sup> )	0.84		0.88		1.18		0.99	0.60–1.25
<i>j</i> (HONO) (avg.) <sup>d</sup> (10 <sup>-3</sup> s <sup>-1</sup> )	1.84		2.53		2.42		2.14	1.32–2.66

<sup>a</sup>Data taken from Yang et al. (2002), Table 1.

<sup>b</sup>Data used in Chen et al. (2004).

<sup>c</sup>*j* values averaged between 10:00–14:00 LST to be consistent with the values reported by Yang et al. (2002).

<sup>d</sup>*j* values averaged over 24 h, Summit 2000 and 1999 data were scaled by a diurnal variation factor derived from this study.

for  $\text{H}_2\text{O}_2$  and HONO, but is radically different for  $\text{CH}_2\text{O}$ . The difference between  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  may be the result of shifts in time/season sampling, different meteorological conditions, different snow emissions or differences involving other factors not yet completely understood. For photolysis rate coefficients some differences are seen among the various Summit studies. This is partially due to the difference in the overhead ozone column density and solar zenith angle for the time period that each field campaign was carried out. In addition, the Summit 2000 and Summit 1999  $j$  values were calculated using a Phodis radiative transfer model Version 0.40 which was constrained by the measured  $j(\text{NO}_2)$  downwelling component, while  $j$  values for Summit 2003 were those computed from observations of a Scanning Actinic Flux Spectrometer (SAFS).

When comparing against the SP 2000 study, Table 2 shows that the observed levels of  $\text{O}_3$ , CO,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{O}$  at Summit were much higher than those of SP. The difference in CO is seen as nearly a factor of 3. Even larger differences can be seen in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  where the Summit values typically range from factors of 3 to more than 6 times higher than those at SP. In the case of NO, the average SP levels are about a factor of 5 higher and the SP variation in NO is also much larger. Of some significance here is the fact that the SP NO values recorded during the summer of 2000 were also well below the summertime levels observed during 1998, 2003 (Davis et al., 2001, 2004), and 2005 (L. G. Huey, private communication). The SP  $\text{CH}_2\text{O}$  values are seen as generally comparable to those from Summit 2003 and Summit 2000, while Summit 1999 yielded values that were over a factor of 7 higher than SP. Like Summit 2003, the SP  $j$  values were derived from SAFS measurements. Since the SP solar zenith angle does not undergo significant diurnal change, it is more meaningful to compare with Summit diurnal averages. In this case, the values for Summit 2000 and Summit 1999 were estimated using the noon time value and a diurnal variation factor derived from Summit 2003 observations. As shown in Table 2, the differences seen in the respective  $j$  values are generally modest. It is interesting to point out that the SP average  $j(\text{O}^1\text{D})$  values are lower than that at Summit by 46–82%. The other SP  $j$  values typically fall within the range of the Summit values. Interestingly, the average solar zenith angle is about the same for Summit 2003 and SP 2000.

### 3. Modeling approach and description

The key questions to be addressed in this study are: (1) what are the processes controlling the sources and sinks of  $\text{HO}_x$  and (2) of these, what is the role of snow emissions? Here, we opt to use an expanded definition of  $\text{HO}_x$  as the sum of OH and  $\text{HO}_2 + \text{RO}_2$ . As will be shown later,  $\text{HO}_2$  is the dominant component of  $\text{HO}_2 + \text{RO}_2$ .

From a budget analysis one can typically define the important sources and sinks of  $\text{HO}_x$ ; however, the second question is much more complicated. For example, it has been documented that snow emissions impact  $\text{HO}_x$  mainly through the release of  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and HONO; but just exactly how these three species impact the levels of  $\text{HO}_x$  still remains unclear at Summit (e.g., Hutterli et al., 2001, 2003, 2004; Yang et al., 2002). A simple illustration of the snow emission impact on  $\text{HO}_x$  can be obtained through a comparison of model runs that are constrained vs. not constrained by  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and HONO. However, because these species all have additional photochemical sources, a more quantitative way to assess the impact from snow emissions requires that one start with a good understanding of the relative importance of snow emissions vs. photochemistry as sources of these species. Here we have carried out in this study using a time-dependent model to simulate the observed diurnal profiles of these species, thus reflecting the net effect from their sources and sinks. Note, as discussed earlier, since the HONO observations were quite limited, no such analysis was done for this species.

The model used in this study is a modified version of that described in detail by Crawford et al. (1999, 2001) and Olson et al. (2006). Briefly, the model contains explicit  $\text{HO}_x$ – $\text{NO}_x$ – $\text{CH}_4$  chemistry and parameterized NMHC chemistry derived from Lurmann et al. (1986). The kinetic rate coefficients have been updated according to Sander et al. (2003) and Atkinson et al. (2003). Quantum yields and absorption cross-sections have also been updated according to recent publications (e.g., Blitz et al., 2004; Roehl et al., 2002). To better simulate the Summit OH and  $\text{HO}_2 + \text{RO}_2$  diel profile and take full advantage of the observations, the model was modified to allow constraint of observed diurnal profiles. Input diurnal profiles for selected species were constructed using the hourly averages as described in Section 2. The profiles are then incorporated into the time-dependent model calculation,

with a cubic spline interpolation used to determine the species concentrations for each 10 min model time step between the hourly averaged values. Observational profiles of  $O_3$ ,  $CO$ ,  $NO$ ,  $H_2O$ , temperature, pressure, and photolysis rate coefficients were provided to model as basic input for all simulations. For selected simulations, the observed diurnal profiles of  $H_2O_2$ ,  $CH_2O$ ,  $OH$ , and  $HO_2 + RO_2$  were also incorporated into the model, rather than allowing the model to predict them. In all cases the levels of  $CH_4$ ,  $HONO$ , and  $NMHC$  were held constant at their median observed values. Emission and deposition loss terms were introduced to the model to describe the snow emissions and the deposition losses of  $H_2O_2$  and  $CH_2O$ . The model uses a Gear solver and is initialized by steady-state solutions. For a typical run, a quasi-steady state is reached for longer lived species in  $<10$  days in that repetitive diurnal profiles are obtained.

#### 4. Results and discussion

Three model cases were designed to examine the impact of the constraint of  $CH_2O$ ,  $H_2O_2$ , and  $HONO$ . In Model 1, none of these species are constrained, so that their concentrations are determined solely by gas-phase photochemistry. Model 2 constrains  $CH_2O$  and  $H_2O_2$  to their observed profiles, and Model 3 constrains  $HONO$  as well as  $CH_2O$  and  $H_2O_2$ . The comparison of these model results with observations is discussed in Section 4.1. In addition, model exercises were carried out to evaluate the relative importance of snow emissions vs. photochemical processes in controlling the diel variations of  $H_2O_2$  and  $CH_2O$  (see Section 4.2). Finally, a budget assessment was performed to identify the key sources and sinks of  $HO_x$  and to quantitatively illustrate the effect of snow emissions on Summit photochemical processes over the snowpacks.

##### 4.1. Comparison of model simulated $HO_x$ with observations

Fig. 2 depicts  $OH$  and  $HO_2 + RO_2$  model predictions along with their observed diurnal profiles. The three model curves correspond to the three model cases discussed above in Section 4. The error bars on observational profiles are overall uncertainties including both instrumental uncertainties and ambient fluctuations. The model error bars (shown in Model 2 curves) are those propagated from model

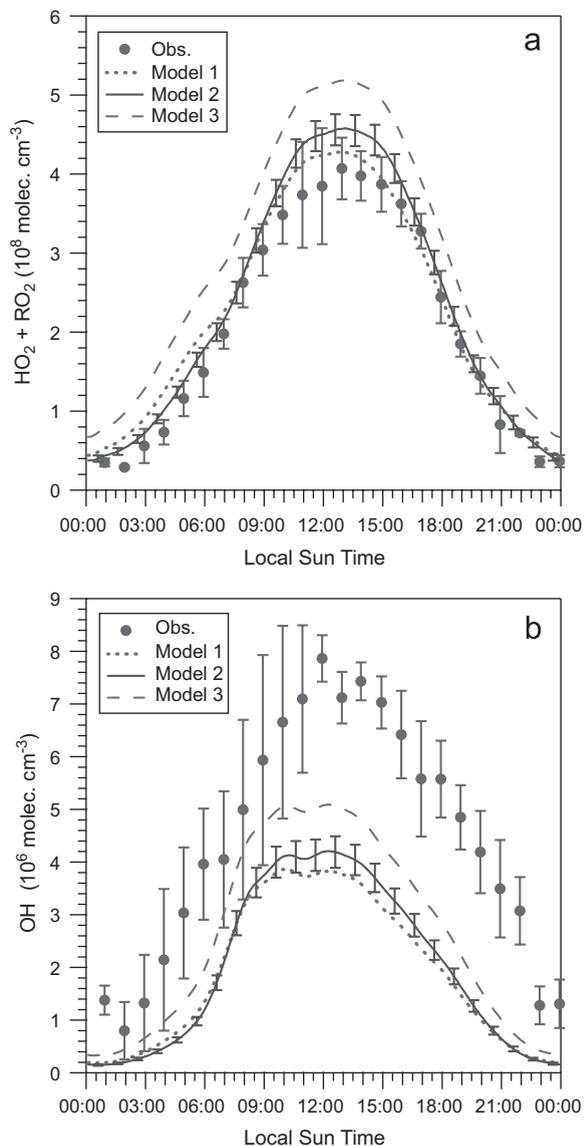


Fig. 2. Comparison of observations with model predictions for: (a)  $HO_2 + RO_2$  and (b)  $OH$ . Model 1: calculations without constraining snow influenced precursors; Model 2: calculations constrained by  $H_2O_2$  and  $CH_2O$ ; and Model 3: calculations constrained by  $H_2O_2$ ,  $CH_2O$ , and  $HONO$ .

input uncertainties as shown in Table 1. Monte Carlo calculations suggest that the potential systematic bias in the model due to  $HO_x$  uncertainties associated with kinetic rate coefficients (Sander et al., 2003; Atkinson et al., 2003) could be as much as  $\sim 20\%$  (at midday) to  $45\%$  (at midnight).

As discussed earlier, the effect of snow emissions is likely to be reflected in enhanced concentrations of  $CH_2O$ ,  $H_2O_2$ , and  $HONO$ . Therefore, the

differences between models 1, 2, and 3 provide an illustrative measure of the impact of snow emission on OH and HO<sub>2</sub> + RO<sub>2</sub>. Note that model-calculated HO<sub>2</sub> + RO<sub>2</sub> consists of HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, and RO<sub>2</sub> (C<sub>2</sub> and higher peroxy radicals), with estimated relative contributions of ~73%, 21%, and 6%, respectively. The model-estimated HO<sub>2</sub> to HO<sub>2</sub> + RO<sub>2</sub> ratio is generally consistent with the value assumed by YJ02.

For the HO<sub>2</sub> + RO<sub>2</sub> comparison shown in Fig. 2a, both Models 1 and 2 are generally consistent with the observations within the combined uncertainties. By contrast, Model 3 is about a factor of ~1.3 (midday) higher than the observations. This suggests that constraining HONO gives the largest increase in HO<sub>2</sub> + RO<sub>2</sub>, while constraining the model with profiles of CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> do not result in HO<sub>x</sub> values that exceed the uncertainties in the observations.

For the OH comparison, Fig. 2b shows that all model calculations significantly underestimate the observed levels, by about a factor of 1.5–3. A high degree of consistency, however, is revealed when both observed and modeled diurnal profiles are normalized by their maximum values. This suggests that the difference between model and observations as related to OH can be characterized as being systematic in nature, and thus, can be reconciled by a common factor. We note that these modeling results are consistent with those of Sjostedt et al. (2007). These authors have also suggested that presence of low levels of BrO and IO may significantly reduce the OH to HO<sub>2</sub> + RO<sub>2</sub> ratio difference between model and observations.

It is worth noting that based on 1999 field observations the YJ02 model predicted midday OH values close to those reported during Summit 2003. However, these 1999 calculations are based on conditions for which all variables related to HO<sub>x</sub> production (with the exception of ozone) were significantly enhanced relative to those reported here for the 2003 study (e.g., see Table 2). More importantly, the 1999 calculations result in HO<sub>2</sub> + RO<sub>2</sub> values more than a factor of 2 greater than 2003 observations, thus demonstrating the incompatibility between the relative levels of OH and HO<sub>2</sub> + RO<sub>2</sub> observed in 2003.

Model predictions from Model 3 show a modest model overestimation of HO<sub>2</sub> + RO<sub>2</sub> because of constraining HONO in addition to H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. However, constraining HONO does increase predicted OH, it does little to close the very large

difference between the model and observations. The estimated 24-h average HONO photolysis lifetime is < 10 min, ranging from 5 min at midday to 50 min at midnight while the NO<sub>x</sub> photochemical lifetime is about 12 h, due to net loss of NO<sub>2</sub> through formation of HNO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub>. Even so, the diurnal average NO<sub>x</sub> level is only about 5.5 times larger than that of HONO. This inconsistency between concentration ratio and lifetime ratio is quite similar to that encountered in the CG04 SP study. In the latter study, it was pointed out that one of the reasons for this discrepancy was that the HONO observations were based on the measurements of dissolved nitrite, instead of direct observations of HONO itself. In addition, one cannot rule out the possibility of significant HO<sub>x</sub> and NO<sub>x</sub> sinks still missing in all forms of the model now being used. It is speculated here that the resolution of the HONO discrepancy will require the development of a direct measurement technique with the capability of measuring very low levels (≤ 5 pptv). With the available evidence at this time, we believe that Model 2 represents the best model HO<sub>x</sub> simulation for Summit 2003 study among the three model simulations as this simulation was constrained by all observed precursors other than HONO.

#### 4.2. Simulation of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O diurnal variation

Observed diurnal variations of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O are shown in Fig. 1. These data clearly exhibit diurnal variations; but in the case of CH<sub>2</sub>O, they show a broad maximum that occurs somewhat later than for H<sub>2</sub>O<sub>2</sub>, and have a significantly reduced diurnal amplitude. It has been established that H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O in Polar regions are influenced by snow emissions and that both species can be important HO<sub>x</sub> precursors (e.g., Hutterli et al., 2001, 2002, 2004; Chen et al., 2001, 2004; Sumner et al., 2002; Yang et al., 2002). In their earlier work, however, Hutterli et al. (1999, 2001, 2002, 2003) have suggested that the air–snow exchange of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O are primarily dependent on snow temperature, and proposed a specific formulation for CH<sub>2</sub>O (1999). This formulation is based on an assumption that the bi-directional H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O fluxes between the snow and air (emission and dry deposition) are driven by temperature following an exponential law, which is at first order consistent with earlier studies (Burkhart et al., 2002; McConnell et al., 1997). As many of the parameters involved in the original formula were not available

in this study, a simplified approach (Eq. (1)) has been used here to examine the snow contribution to  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$ .

$$\frac{F_{\text{SNOW}}}{h} = A * \exp\left(\frac{B}{T_S}\right) - C[X]. \quad (1)$$

In this formulation, the term  $F_{\text{SNOW}}$  is the net result of the air–snow exchange, i.e., snow emission vs. deposition;  $h$  is boundary layer height;  $T_S$  is the effective snow temperature representing an average temperature of the snow layers dominating the air–snow exchange;  $[X]$  represents the ambient mixing ratio of either  $\text{H}_2\text{O}_2$  or  $\text{CH}_2\text{O}$ ; and  $A$ ,  $B$ , and  $C$ , are the adjustable constants.

It is assumed here that the air–snow exchange can be described as two competing processes: emission and deposition. The first term on the right-hand side describes the exponential temperature dependence of the emission from the snow; while the second term defines the magnitude of first-order physical loss, most likely associated with deposition processes. The current simplification assumes that deposition to the snow surface has a weak dependence on snow temperature and can be considered constant, as a first-order approximation for the temperature range observed during the 3-day period of this study. An implicit assumption adopted in this study is that the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$  in the snow did not significantly change over the 3-day period investigated. This assumption would appear to be in keeping with observations which showed no significant change in snow  $\text{H}_2\text{O}_2$  levels over this period while  $\text{CH}_2\text{O}$  increased by  $\sim 10\%$  in the top 20 cm of the snowpack (M. A. Hutterli private communication).

Calculations using Eq. (1) in the model were performed for  $\text{H}_2\text{O}_2$  and for  $\text{CH}_2\text{O}$  individually, with the parameters  $A$ ,  $B$ , and  $C$  adjusted to best fit the observational diurnal profiles by minimizing the chi-square value. Snow emission and deposition terms were then assessed and directly compared with photochemical production and loss terms. For this exercise, the concentrations of OH and  $\text{HO}_2$  were constrained to the model results labeled as “Model 2” in Fig. 2 since these values were determined to best represent ambient levels.

Fig. 3a displays the hourly averaged observations of  $\text{H}_2\text{O}_2$  from the selected time period shown in Fig. 1. Also plotted are two model profiles. One of these, Model A, shows the results without consideration of snow emissions or loss of  $\text{H}_2\text{O}_2$ , and is thus defined

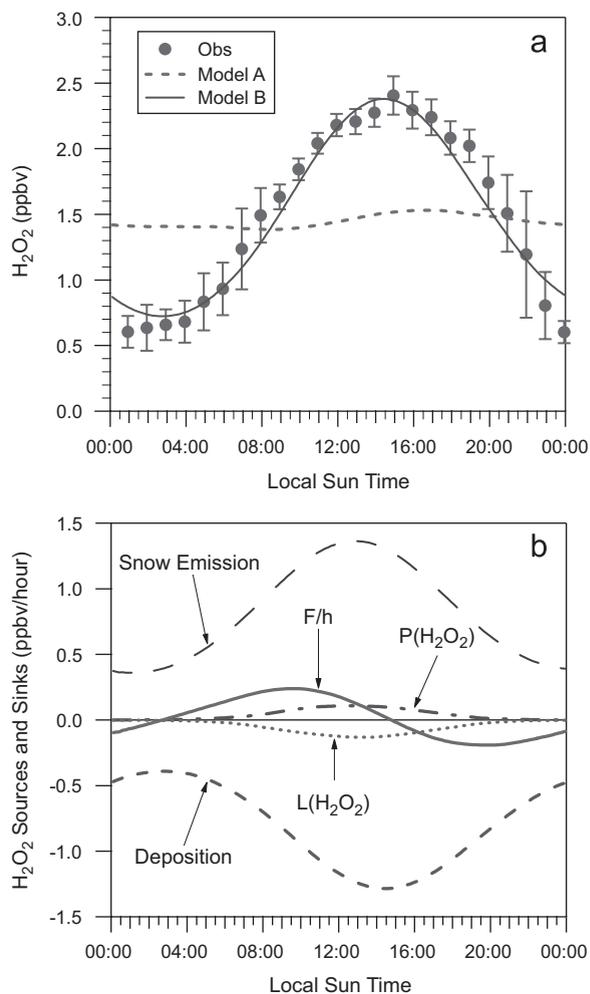


Fig. 3. Plots of: (a) comparison of observations with model predictions for  $\text{H}_2\text{O}_2$  and (b) diurnal variations of the sources and sinks of the Summit  $\text{H}_2\text{O}_2$  derived from Model B case. Model A: gas phase chemistry only and Model B: snow emission and deposition included in the model as described in Eq. (1).  $P(\text{H}_2\text{O}_2)$  and  $L(\text{H}_2\text{O}_2)$  are photochemical production and losses and  $F/h$  is the net snow contribution as defined in Eq. (1).

by photochemistry only. In this case, it can be seen that the model-predicted  $\text{H}_2\text{O}_2$  level is within a factor of 2 of the observations throughout the day, but the amplitude of the diurnal variation is significantly suppressed. By contrast, the second curve labeled as Model B, which utilize Eq. (1), matches the observations quite well. This suggests that, to a first approximation, observed  $\text{H}_2\text{O}_2$  at Summit can be reasonably reproduced by a temperature driven snow emission rate and a diurnally constant first-order loss reflecting dry deposition to the snow.

Additional modeling exercises suggest that the observed  $\text{H}_2\text{O}_2$  profile can also be simulated using a snow emission term that is driven by other diurnal varying variables other than snow temperature, e.g., photolytic processes. The temperature driven snow emission argument, however, is more convincing due to the strong correlation (i.e.,  $R^2 = 0.56$ ) found between observed  $\text{H}_2\text{O}_2$  and snow surface temperature for the entire Summit 2003 data set (see Fig. 4); while no other significant correlations were found between  $\text{H}_2\text{O}_2$  and other meteorological variables, i.e.,  $R^2$  values  $< 0.1$ .

Fig. 3b displays the diurnal variations of the terms representing photochemical  $\text{H}_2\text{O}_2$  production and loss, snow emission and snow deposition as well as  $F/h$  (the net snow effect) for the “Model B” exercise. It can be seen that snow emissions peak in the early afternoon when the snow surface temperature maximizes. It is also shown that the snow emission is the dominant source of  $\text{H}_2\text{O}_2$ , contributing about 95% of the total diurnal average source. This assessment suggests that the diurnal average impact of  $\text{H}_2\text{O}_2$  from snow on the  $\text{HO}_x$  budget would be 95% of the OH formation rate from  $\text{H}_2\text{O}_2$  photolysis. The dominant sink of  $\text{H}_2\text{O}_2$ , also shown in Fig. 3b, is deposition (94% of the diurnal average total), which corresponds to a lifetime of  $< 2$  h. The net snow contribution is about 25% of the gross photochemical production of  $\text{H}_2\text{O}_2$ . Thus, for this

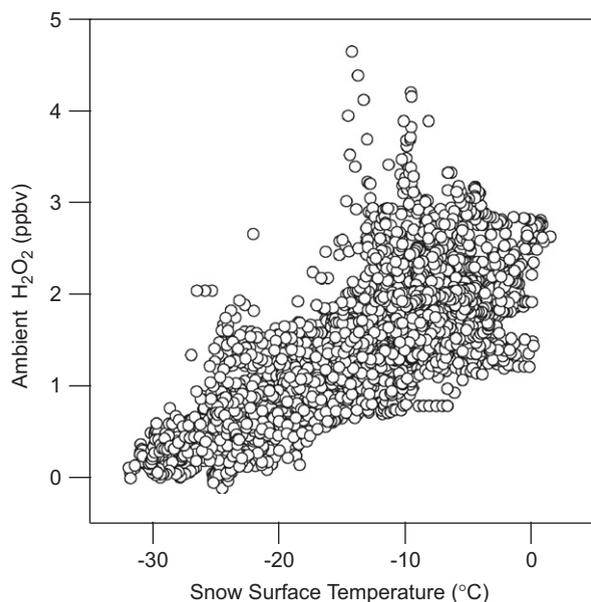


Fig. 4. Correlation plot of ambient  $\text{H}_2\text{O}_2$  and snow surface temperature. All data from Summit 2003 are used.

best fit exercise, the  $\text{H}_2\text{O}_2$  diurnal variation is heavily dictated by snow emission and deposition. This conclusion is supported by the finding that there is a significant lack of correlation between observed  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  ( $R^2 < 0.21$ ) for the entire Summit 2003 study period. Given the short lifetime of  $\text{H}_2\text{O}_2$ , one would expect a strong correlation between  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  if photochemistry were the dominating factor.

As shown in Fig. 5, when one shifts to a more detailed examination of  $\text{CH}_2\text{O}$ , the data reveals that the hourly averaged observations for this species are

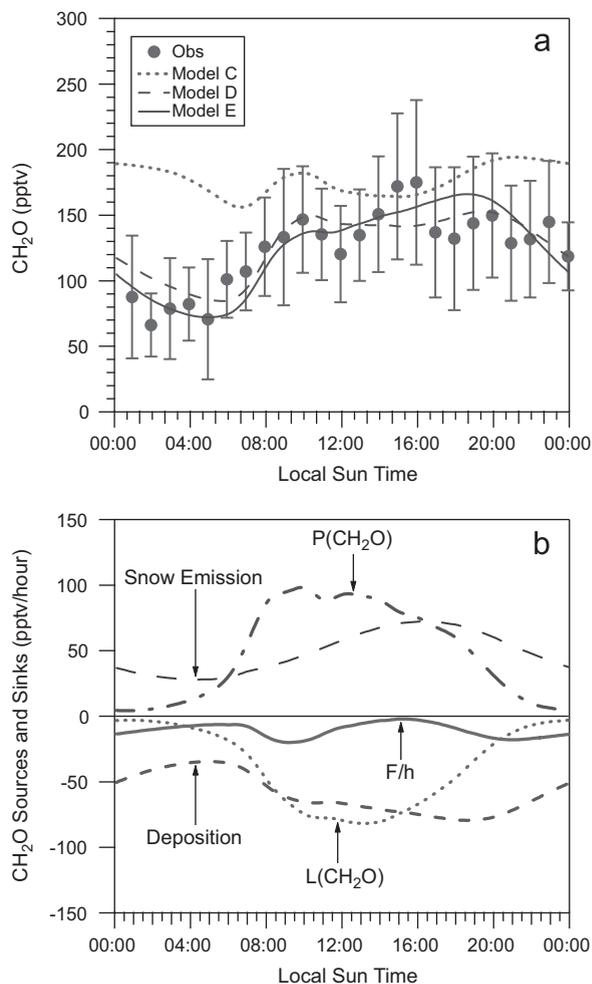


Fig. 5. Plots of: (a) comparison of observations with model predictions for  $\text{CH}_2\text{O}$  and (b) diurnal variations of the sources and sinks of the Summit  $\text{CH}_2\text{O}$  derived from Model E case. Model C: gas phase chemistry only; Model D: a constant physical loss term included; and Model E: snow emission and deposition included in the model as described in Eq. (1).  $P(\text{CH}_2\text{O})$  and  $L(\text{CH}_2\text{O})$  are photochemical production and losses and  $F/h$  is the net snow contribution as defined in Eq. (1).

associated with large uncertainties. For example, the  $1-\sigma$  standard deviation is nearly 35% of the average value. Such a large variation is a result of both the large ambient variability in this species over the averaging time period as well as poorer measurement precision at the low levels seen for  $\text{CH}_2\text{O}$ . Of the model profiles shown in Fig. 5, “Model C” gives a profile where neither snow emission nor deposition were included. In this case,  $\text{CH}_2\text{O}$  is controlled only by photochemistry, and one sees that in the results that the model persistently overestimates the observations by a significant factor, especially at pre-dawn times. The diurnal average photochemical lifetime estimated for this case is  $<3.4$  h. In Model D curve, a first-order loss term is included to represent additional physical losses (i.e., dry deposition), the equivalent lifetime of which is estimated at 12.1 h. This deposition loss thus becomes the dominant sink between 21:00 and 03:00 h while it contributes  $<15\%$  of the total at midday. In “Model E”, still additional terms were added to cover the possibilities of both depositional loss to the snow as well as emissions from the snow as described earlier in Eq. (1). For this parameterization, snow emissions were modulated using the observed snow temperature at 10 cm below the surface. This is in line with the studies by Hutterli et al. (2001, 2003) which have suggested that the top 20 cm of snow provide the major modulation of  $\text{CH}_2\text{O}$  in its diurnal cycle. The  $\text{CH}_2\text{O}$  diurnal trends for snow emission and deposition, along with photochemical production and loss, are those shown in Fig. 5b. In contrast to  $\text{H}_2\text{O}_2$  case, one sees the photochemical terms and snow terms are generally comparable. Even though, the snow emission and photochemical production peak at different times, each contributes about 50% of the diurnal averaged total. It is noteworthy that the diurnal variation resulting from photochemical production is mostly controlled by the levels of OH and NO, while the diurnal variation in snow emissions is solely determined by snow temperature. The deposition loss, corresponding to a lifetime of  $\sim 2.1$  h, is a strong sink for the most of day contributing  $\sim 46\%$  of the total. The net snow effect defines a net minor sink for  $\text{CH}_2\text{O}$  which is about 12% of the photochemical loss. This is inconsistent with previous studies (e.g., Hutterli et al., 1999, 2001, 2003) which have suggested snow to be a net source of ambient  $\text{CH}_2\text{O}$ . This may reflect the lower temperatures (i.e.,  $5^\circ$  lower than days before) encountered during the 3-day period of this study

which may also explain the unusually low  $\text{CH}_2\text{O}$  concentrations observed during this time period.

That “Models D” and “E” have provided similarly good fits to the observational  $\text{CH}_2\text{O}$  profile, suggests that the contribution from snow emissions most likely falls between the rather large range of 0–50%. A more precise assessment would require smaller uncertainties in the observational profile. Another potential complication factor would involve presence of bromine chemistry. A few pptv of BrO would be able to balance the  $\text{CH}_2\text{O}$  budget without invoking snow deposition; while significant higher levels, e.g.,  $>10$  pptv, would require a net snow  $\text{CH}_2\text{O}$  source. In this study, we have assumed the mid-point value of 25% to represent the relative contribution of snow emissions to atmospheric  $\text{CH}_2\text{O}$  for the temperature and light conditions of the study period. Thus, the reported results should not be extrapolated to periods when temperature and/or snow  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$  concentrations are significantly different from the studied period or and places with different  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  concentrations in the snow.

It is to be noted that visual observations of nighttime fog were reported at the site during the investigation period, which can lead to significant scavenging losses. The model simulations reported here cannot distinguish the difference between these two processes (i.e., deposition vs. scavenging) with currently available data. However, this is an important issue to understand in order to fully assess the snow impact on  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$ . Thus, direct flux measurements in future studies would be a better way to determine the nature of the physical loss.

#### 4.3. $\text{HO}_x$ budget assessment

Fig. 6 displays the significant summertime sources and sinks of Summit  $\text{HO}_x$ . This budget assessment is based on model calculations constrained by both  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  (the Model 2 curves in Fig. 2), with the snow surface emissions and losses apportioned as indicated by the simulations described in Section 4.2. As seen in the figure, the two dominant primary  $\text{HO}_x$  sources are the  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  reaction (41% of the gross source) and the photolysis of  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  from snow emissions (40% of the gross source).  $\text{H}_2\text{O}_2$  is the largest of the snow emission  $\text{HO}_x$  sources, contributing 37% to the gross source, compared to just 3% from  $\text{CH}_2\text{O}$ . Other  $\text{HO}_x$  sources include the photochemical oxidation of  $\text{CH}_4$

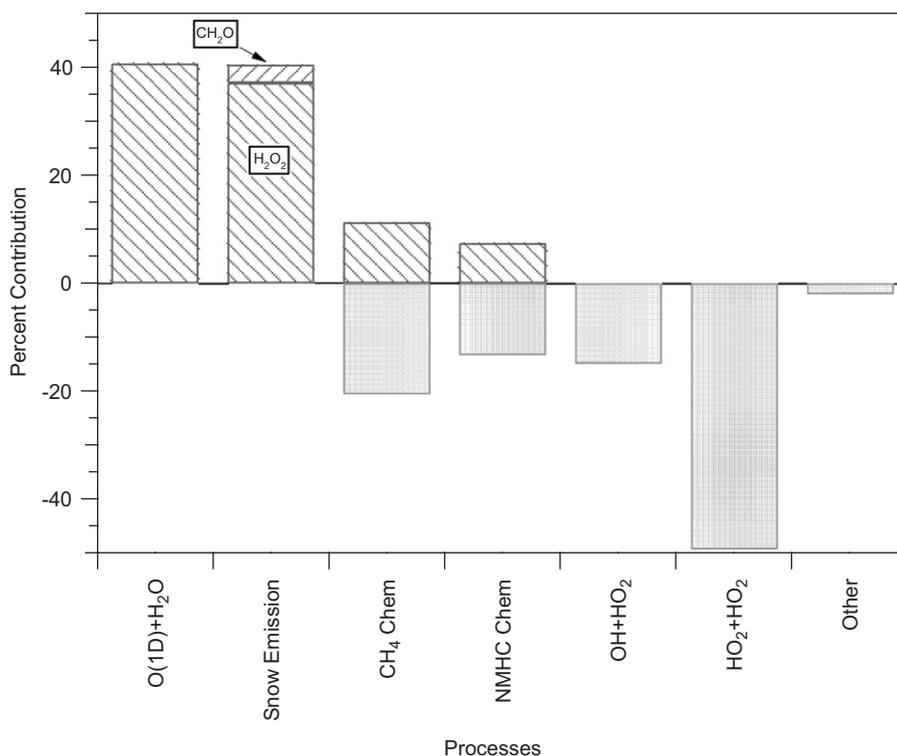


Fig. 6. Diurnal average photochemical HO<sub>x</sub> budget. Source terms are indicated by positive bars while negative bars denotes the sink terms.

and NMHCs. Although both are ultimately net sinks of HO<sub>x</sub>, their production terms contribute about 11% and 7% respectively, to the gross production. The HO<sub>x</sub> production from CH<sub>4</sub> and NMHC oxidation is primarily through formation and photolysis of CH<sub>2</sub>O and higher aldehydes, while the remainder is mostly from photolysis feedback of organic peroxides. It is noted here that constraining the model with observations of HONO would increase the gross production rate by about 40%. However, this source manifests itself in terms of predicted HO<sub>x</sub> levels as only a 15% increase (Models 2 vs. 3 in Fig. 2), suggesting that HONO, even at the Summit 2003 observed levels, is a significant, but not overwhelming perturbation to HO<sub>x</sub> source contributions.

The HO<sub>2</sub> + HO<sub>2</sub> reaction is identified as the single most important sink of Summit HO<sub>x</sub>, contributing nearly 50% of the total. This reflects the fact that the deposition term assumed for H<sub>2</sub>O<sub>2</sub> in Section 4.2 accounted for ~94% of the total H<sub>2</sub>O<sub>2</sub> loss. The consumption of OH and HO<sub>2</sub> via peroxy–peroxy reactions during the degradation processes of CH<sub>4</sub> and NMHC makes up 20% and 13% of total HO<sub>x</sub> losses, respectively. Another prominent HO<sub>x</sub> sink

involves the OH + HO<sub>2</sub> reaction, contributing ~15% to the total sink. Reactions involving the formation of HNO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub> (included under “Other” in Fig. 6) appear as only minor sinks for HO<sub>x</sub>, the total contribution being less than 2%.

The Summit HO<sub>x</sub> budget presented here is quite different from that at SP as reported in CG04. For example, the total Summit 2003 HO<sub>x</sub> burden is more than three times higher than that of SP, and the Summit HO<sub>x</sub> production rate is over a factor of 4 higher. The average HO<sub>2</sub> to OH ratio is 112 for Summit 2003 and 20 for SP. Interestingly, the HO<sub>x</sub> lifetime is also about 30% longer at Summit. The slower HO<sub>x</sub> production rate at the SP is a reflection of the much lower concentrations for H<sub>2</sub>O and O<sub>3</sub> (see Section 2), resulting in an OH formation rate from O(<sup>1</sup>D)+H<sub>2</sub>O that is over a factor of 7 times smaller than that at Summit. Similarly, the snow emission contribution to HO<sub>x</sub> at the SP is nearly a factor of 4 times lower than that found in the Summit study. The one notable contribution to HO<sub>x</sub> production from snow emissions at the SP was shown to be from CH<sub>2</sub>O, unlike that for Summit (e.g., H<sub>2</sub>O<sub>2</sub>). This suggests that the overall impact of snow chemistry at Summit may be quite different

than at SP. This can be seen in the median NO level used in CG04 for the SP which was 90 pptv, a level that greatly suppresses HO<sub>x</sub> radical–radical reactions and promotes the production of HO<sub>2</sub> from hydrocarbon oxidation. Thus, CH<sub>4</sub> chemistry becomes a net source of HO<sub>x</sub> under SP conditions, unlike the case for Summit. Additionally, the high levels of NO<sub>x</sub> and low temperature at the SP enable the formation of HO<sub>2</sub>NO<sub>2</sub> and HNO<sub>3</sub> followed by deposition to snow. The latter then dominate SP HO<sub>x</sub> losses (Slusher et al., 2001, 2002). In all, NO<sub>x</sub> related HO<sub>x</sub> sinks contributed nearly 70% to the total loss at the SP. By contrast, the low NO<sub>x</sub> levels at Summit greatly limits the significance of these reactions. In summary, the summertime SP HO<sub>x</sub> chemistry is considerably more complex because of its close interactions with NO<sub>x</sub> chemistry.

## 5. Summary and conclusions

Modeling analysis of the Summit 2003 field data were conducted so as to compare the results with those from previous field campaigns at this site and to also explore differences with the modeling results from SP. The comparison with previous Summit studies revealed that the levels of HO<sub>x</sub> precursors recorded during Summit 2003 are generally within the range of values reported by Yang et al. (2002). We found that the Summit 2003 HO<sub>x</sub> model simulations, when constrained by H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O, can well reproduce the observed diurnal variations of HO<sub>2</sub>+RO<sub>2</sub> while they systematically underestimate OH by about a factor of 2. However, the model tends to have a modest overestimation (i.e., 30% in midday) of HO<sub>x</sub> when further constrained by HONO. In the case of the H<sub>2</sub>O<sub>2</sub>, comparison between model and observations showed that the observed diurnal variation cannot be explained by photochemical sources and sinks alone. Temperature driven snow emissions and physical removal appear to have the dominant influences on H<sub>2</sub>O<sub>2</sub>. By contrast, model simulations of Summit 2003 CH<sub>2</sub>O suggest that photochemical production contributes 50% or more of the total; but additional physical removal of CH<sub>2</sub>O is needed to reproduce the observed diurnal profile. The assumed physical removal process is likely to be either dry deposition, scavenging by fog, or a combination of both.

A HO<sub>x</sub> budget analysis suggests that O(<sup>1</sup>D)+H<sub>2</sub>O and snow emissions are of equal importance as HO<sub>x</sub> sources during summertime at Summit, both

contributing roughly 40% of the total. Unlike conditions at SP, the impact of snow emissions is mainly linked to H<sub>2</sub>O<sub>2</sub> and, to a much lesser extent, CH<sub>2</sub>O. Oxidation of CH<sub>4</sub> is a net sink of Summit HO<sub>x</sub>, while providing a major HO<sub>x</sub> source at SP. At Summit, the effect of NMHC reactions is estimated to be a minor net sink. The major Summit HO<sub>x</sub> sink is found to be the HO<sub>2</sub>+HO<sub>2</sub> reaction followed by deposition of H<sub>2</sub>O<sub>2</sub> to the snow surface. The reaction of OH+HO<sub>2</sub> is also a significant sink, contributing ~15% of the total. This finding again differs from SP where the HO<sub>x</sub> sink is dominated by reactions involving formation of HO<sub>2</sub>NO<sub>2</sub> and HNO<sub>3</sub> and their deposition to the surface. Thus, the major differences between SP and Summit HO<sub>x</sub> are ultimately related to major differences in H<sub>2</sub>O (reflecting much lower temperatures) and NO levels. The high H<sub>2</sub>O level together with snow emissions result in Summit HO<sub>x</sub> levels being predominantly driven by primary production, i.e., O(<sup>1</sup>D)+H<sub>2</sub>O reaction, and photolysis of snow emitted H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. By contrast, SP HO<sub>x</sub> levels are controlled by snow emissions as well as secondary production through CH<sub>4</sub> chemistry at highly elevated NO levels. As for the atmospheric cleanser, OH, both Summit and SP have elevated values, but driven by quite different factors. At Summit it is mostly due to the primary production of HO<sub>x</sub>; while, at SP it is primarily due to partitioning of HO<sub>x</sub> driven by high levels of NO.

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