**Atmospheric
Chemistry
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Contrasting atmospheric boundary layer chemistry of methylhydroperoxide (CH$_3$OOH) and hydrogen peroxide (H$_2$O$_2$) above polar snow

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Abstract. Atmospheric hydroperoxides (ROOH) were measured at Summit, Greenland (72.97° N, 38.77° W) in summer 2003 (SUM03) and spring 2004 (SUM04) and South Pole in December 2003 (SP03). The two dominant hydroperoxides were H$_2$O$_2$ and CH$_3$OOH (from here on MHP) with average ($\pm 1\sigma$) mixing ratios of 1448 (± 688) pptv, 204 (± 162) and 278 (± 67) for H$_2$O$_2$ and 578 (± 377) pptv, 139 (± 101) pptv and 138 (± 89) pptv for MHP, respectively. In early spring, MHP dominated the ROOH budget and showed night time maxima and daytime minima, out of phase with the diurnal cycle of H$_2$O$_2$, suggesting that the organic peroxide is controlled by photochemistry, while H$_2$O$_2$ is largely influenced by temperature driven exchange between the atmosphere and snow. Highly constrained photochemical box model runs yielded median ratios between modeled and observed MHP of 52%, 148% and 3% for SUM03, SUM04 and SP03, respectively. At Summit firn air measurements and model calculations suggest a daytime sink of MHP in the upper snow pack, which decreases in strength through the spring season into the summer. Up to 50% of the estimated sink rates of 1–5×10^{11} molecules m^{-3} s^{-1} equivalent to 24–96 pptv h^{-1} can be explained by photolysis and reaction with the OH radical in firn air and in the quasi-liquid layer on snow grains. Rapid processing of MHP in surface snow is expected to contribute significantly to a photochemical snow pack source of formaldehyde (CH$_2$O). Conversely, summer levels of MHP at South Pole are inconsistent with the prevailing high NO concentrations, and cannot be explained currently by known photochemical precursors or transport, thus suggesting a missing source. Simultaneous measurements of H$_2$O$_2$, MHP and CH$_2$O allow to constrain the NO background today and potentially also in the past using ice cores, although it seems less likely that MHP is preserved in firn and ice.

1 Introduction

Atmospheric hydroperoxides (ROOH) contribute significantly to the tropospheric oxidizing capacity either directly as hydrogen peroxide (H$_2$O$_2$) or indirectly as HO$_x$ radical and ozone precursors in the remote and upper troposphere (Barth et al., 2007; Grannas et al., 2007, and references therein). Atmospheric oxidants play a key role for atmospheric composition and the so-called chemical climate feedback since they determine the lifetime of many natural and anthropogenic trace chemical species including pollutants (carbon monoxide, CO; nitrogen oxides, NO$_x$; non-methane hydrocarbons, NMHCs; sulfur dioxide, SO$_2$) and greenhouse gases (methane, CH$_4$; HFCs). However, the spatial and temporal variability of atmospheric oxidants including ROOH and specifically the role of heterogeneous chemistry are still poorly constrained (e.g. Thompson, 1992; Lawrence et al., 2001). For instance, only recently it has been recognized that the air above and within the snow pack of the high and mid latitudes is photochemically highly reactive driving chemical
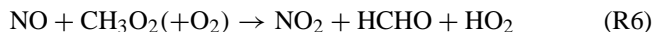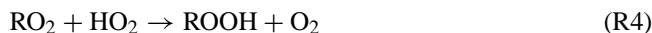
fluxes across the snow-air interface with important implications for atmospheric oxidant concentrations at regional and possibly also global scales (Dominé and Shepson, 2002; Grannas et al., 2007).

In the case of ROOH, the temperature driven release and uptake of H_2O_2 by the upper snow pack was found to have significant impact on H_2O_2 boundary layer (BL) concentrations above Greenland (Hutterli et al., 2001) and Antarctica (Hutterli et al., 2004; Frey et al., 2005). Subsequent HO_x radical budget assessments have then demonstrated that the H_2O_2 emitted from the snow is an important radical source above the polar ice sheets. At South Pole model results from a study in summer 2001 showed that snow emissions of H_2O_2 (14%) and HCHO (32%) contributed together almost twice as much to the HO_x budget than CH_4 oxidation and the ozonolysis reaction $O(^1D)+H_2O$ (both 27%) (Chen et al., 2004). Similarly at Summit, Greenland, it was found that the two most important primary sources of HO_x were production from ozonolysis (41%) and photolysis of snow emitted H_2O_2 (37%), followed by CH_4 (11%) and NMHC oxidation (7%) (Chen et al., 2007). In addition, due to its relatively high water solubility H_2O_2 is deposited in snow to the large ice sheets of Greenland and Antarctica and preserved for centuries (Sigg and Neftel, 1991; Anklin and Bales, 1997; Frey et al., 2006) and even millennia (Neftel et al., 1984). Significant post-depositional change complicates the quantitative reconstruction of past atmospheric H_2O_2 concentrations from ice cores, however recent progress in model, atmospheric and ice core studies demonstrate the potential to use H_2O_2 as a quantitative proxy of past oxidant levels (Hutterli et al., 2003; Frey et al., 2006, and references therein). In summary, a thorough understanding of speciation, sinks and sources and atmosphere-snow exchange of atmospheric ROOH above the polar ice sheets is paramount to evaluation of ROOH as a quantitative constraint on the atmospheric oxidant budget, to assessing the role of the snow pack on BL chemistry and finally to quantitative interpretation of ice core records.
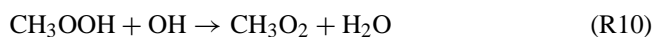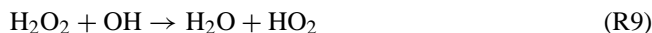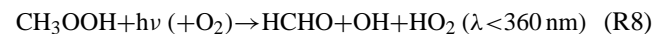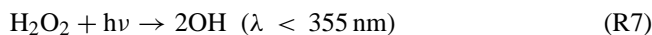
The known ROOH gas phase chemistry can be summarized as follows: in the presence of sunlight, water vapor and ozone (O_3), the short-lived OH radicals are produced and then converted in the oxidation reaction with carbon monoxide (CO), methane (CH_4) and other non-methane hydrocarbons to peroxyradicals (RO_2) (R1–R2).

$$CO + OH + O_2 \rightarrow CO_2 + HO_2 \qquad (R1)$$

$$CH_4 + OH + O_2 \rightarrow H_2O + CH_3O_2 \qquad (R2)$$

Under low NO_x conditions self and cross reactions of RO_2 produce H_2O_2 and alkylperoxides (ROOH) (R3–R4), while under high NO_x conditions, ROOH formation is suppressed and production of HCHO and NO_2 occurs instead (R5–R6) (Lee et al., 2000; Frey et al., 2005).

$$HO_2 + HO_2 \rightarrow H_2O_2 \qquad (R3)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (R4)$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (R5)$$

$$NO + CH_3O_2(+O_2) \rightarrow NO_2 + HCHO + HO_2 \qquad (R6)$$

A physical snow pack source has been recognized to be important for summer BL concentrations of H_2O_2 at Summit, Greenland (Hutterli et al., 2001), the South Pole (Hutterli et al., 2004) and above the West Antarctic Ice Sheet (WAIS) between 76 and 90° S (Frey et al., 2005). Sinks of ROOH include photolysis (R7-R8), attack by the OH radical (R9-R10), and wet and dry deposition.

$$H_2O_2 + h\nu \rightarrow 2OH \ (\lambda \ < \ 355\,nm) \qquad (R7)$$

$$CH_3OOH + h\nu \, (+O_2) \rightarrow HCHO + OH + HO_2 \ (\lambda < 360\,nm) \qquad (R8)$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \qquad (R9)$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \qquad (R10)$$

Recent observations in Antarctica have shown that MHP is the only higher important peroxide next to H_2O_2 occurring in the summer BL on the Antarctic Coast (Riedel et al., 2000), above the West Antarctic Ice Sheet (WAIS) (Frey et al., 2005) and the South Pole (Frey et al., 2005), while no direct measurements exist to date from Greenland. Photochemical box model calculations suggested that both chemical species are tightly linked to the tropospheric NO_x-HO_x budget and thus have the potential to provide a quantitative tool to constrain the current and, using ice cores, past oxidation capacity of the remote atmosphere (Frey et al., 2005). However, concurrent measurements of ROOH and NO_x-HO_x species have been lacking so far to test the model.

In this study we focus on the much less studied organic peroxides and compare speciation, levels and temporal variability of atmospheric ROOH in the BL above Greenland and Antarctica. We compare observations with photochemical box model calculations and investigate the role of the snow pack for the BL budget of organic peroxides. Finally, we discuss the potential use of ROOH for constraining the nitric oxide (NO) background and thus atmospheric oxidation capacity.

2 Methods

Atmospheric hydroperoxide measurements were carried out at the Amundsen-Scott South Pole station during the Antarctic Tropospheric Chemistry Investigation (Eisele et al., 2008) in December 2003 (from here on SP03) and at Summit, Greenland (72.97° N, 38.77° W) during the Greenland Snow Photochemistry Experiment in summer 2003 and spring 2004 (Dibb et al., 2007) (from here on SUM03 and SUM04). The remote location of South Pole and Summit allows investigation of the background chemistry of the atmospheric

BL above ice sheets in both hemispheres at an elevation of 2810 and 3200 m a.m.s.l. with annual mean temperatures of -49.3 and $-27.2°C$, respectively. At South Pole ROOH data were collected from the second floor of the NOAA operated Atmospheric Research Facility (ARO) in the clean air sector with sampling heights of 8 and 1 m above the snow surface between 8 and 28 December 2003. At Summit, Greenland measurements were carried out in the clean air sector 1 km from camp at 1 and 0.1 m above the snow from 8 June until 12 July 2003 and between 22 March and 2 May 2004. During spring 2004 firn air from the upper snowpack was sampled as well.

Atmospheric ROOH were measured with a 2-channel detector deployed previously on the US. International Trans-Antarctic Scientific Expedition (Frey et al., 2005). In brief, ambient air was pumped at 1.5 STP-L min^{-1} through intake lines, which were heated above ambient air temperature to prevent condensation losses. Hydroperoxides were scrubbed from the sample air stream into aqueous solution and analyzed using a fluorescence detection method (Jacobi et al., 2002; Frey et al., 2005). While in channel 1 the signal of total hydroperoxides was continuously measured, in channel 2 hydroperoxides were first separated on a INERTSIL ODS-2 HPLC column (metal free PEEK lining, Alltech Associates, Inc.) with EDTA containing 10^{-3} m H_2SO_4 solution as the mobile phase (Kok et al., 1995; Lee et al., 1995). Discrete 456 μl samples were injected automatically every 10 min into the HPLC channel with a 6-port HPLC injection valve (model C2 with PAEK body, Valco Instruments Co. Inc.) using a 2-position standard electric actuator (Valco Instruments Co. Inc.). Instrument response was calibrated 1–2 times per day with liquid H_2O_2 and MHP standards. MHP was synthesized in our lab after Rieche and Hitz (1929) from the reaction between dimethyl sulfate and H_2O_2 under strongly alkaline conditions. 38 ml of 40% KOH were added slowly over 40 min to a mixture of 45 ml of 30% hydrogen peroxide, 75 ml H_2O and 30 g dimethyl sulfate. Since the reaction takes place under release of heat, the mixture was stirred and cooled constantly in order to prevent disintegration of the reaction product. The liquid was acidified and about half of it distilled at 98°C yielding 0.9–1.5 m (4–7%) solutions of MHP. Permanganate titration to check for the presence of H_2O_2 was negative suggesting that H_2O_2 contamination of the synthesis product was less than 10^{-4} m. MHP standards were diluted to 10^{-1} m, filled into brown glass bottles with EDTA added and stored at 5°C. Pre and post field season calibration of H_2O_2 and MHP standard stock solutions using permanganate and iodometric titration with FeCl$_3$ as a catalyst, respectively, showed no significant concentration change. The decrease in MHP concentration of the stock solution after >1 yr of storage was less than 4%.

After linear baseline correction, signals were converted into liquid concentration based on the standard response. Chromatogram peaks were evaluated using height as the parameter related to concentration. Mixing ratios were derived with coil scrubber collection efficiencies (CE) calculated according to Henrys Law using monitored coil temperature and pressure and gas and liquid flow rates as described previously (Frey et al., 2005). The HPLC signals from sample and liquid standards were corrected based on regular blank runs. Injection of liquid standards after the glass coils required also a correction of the liquid flow rates to account for evaporation in the coil amounting to up to 10% of the final mixing ratio. To account for the interference of the fluorescence detection method to all hydroperoxides, a correction term in pptv H_2O_2-equivalent was calculated based on a 24-point running mean of the difference between HPLC derived signals of total observed peroxides (H_2O_2+MHP) and H_2O_2 and then subtracted from the continuous measurements in channel 1. H_2O_2 mixing ratios from both channels showed good agreement after correction with r^2 values calculated from concurrent data points of 0.66, 0.81 and 0.77 for SP03, SUM03 and SUM04, respectively. Deviations of r^2 from unity reflect in part the higher background noise in the HPLC data set.

Gas phase mixing ratios and calculated gradients and fluxes reported in this study are based on the HPLC method except ambient levels of H_2O_2 which are based on the continuous method (Table 1). The limit of detection (LOD), here defined as 3σ of the baseline of the continuous H_2O_2 measurements averaged over 1 min, was 10 pptv and the accuracy better than 15%. LOD and accuracy of the MHP measurements were 20 pptv and <20%, respectively.

Firn interstitial air was sampled during SUM04 by switching the instrument for 10 min each hour to a second intake line attached to a firn air probe used by all investigators participating in the Greenland Photochemistry Experiment (Dibb et al., 2007). Firn air experiments included depth profiles as well as shading experiments. All tubing connected to the PTFE firn air probe head was made of PFA. For protection the probe was placed into another tube made of plexiglass down to 0.5 m depth and of aluminium below. The heated inlets and the firn probe were tested regularly for systematic bias. ROOH ambient mixing ratios at 1 m above the snow surface were measured in parallel through both heated inlets for up to 12 h at a time. The comparison of 29 subsequent 10-min intervals from 5 April, 14 April and 2 May using parametric (two-sample t-test) and nonparametric (Wilcoxon signed rank test) statistics showed no significant difference between the two inlets at a 95% confidence level. However, the 1–2 times daily comparison of ambient ROOH levels sampled through the inlet, with and then without the firn air probe attached, revealed systematic losses of H_2O_2 but not for MHP. If condensation (deposition) of water vapor had taken place in the unheated firn air probe head, one might expect removal of H_2O_2 followed by release later on from evaporation (sublimation) of potential water droplets (ice crystals). However, losses did not show any temporal trend, were independent of ambient mixing ratios and no icing up of the probe was observed. In conclusion, the nature of the loss process remains uncertain. All H_2O_2

Table 1. Summary of ROOH observations in ambient air in Greenland and Antarctica.[a]

Site	Period	H_2O_2, pptv[b]	MHP, pptv[c]	Ratio[d]
SUM03	8 Juni–12 July	1448±688 (10–4642)	–	–
	27 Juni–12 July	1425±602 (23–3201)	578±377 (30–3202)	0.31±0.14 (0.11–0.83)
SUM04	22 March–2 May	204±162 (10–1259)	–	–
	27 March–2 May	207±167 (10–1259)	139±101 (30–562)	0.37±0.20 (0.01–0.94)
	27 March–7 April	107±79 (21–425)	144±139 (30–562)	0.45±0.29 (0.04–0.94)
	8–17 April	187±88 (48–477)	108±59 (30–303)	0.34±0.13 (0.12–0.78)
	18 April–2 May	302±208 (8–1259)	162±89 (30–410)	0.35±0.17 (0.01–0.69)
SP03	8–28 December	278±67 (89–459)	–	–
	19–26 December	236±60 (164–415)	138±89 (30–654)	0.35±0.07 (0.18-0.57)

[a] Mean ±1σ (range). [b] Based on 10 min averages of the continuous channel measured at 1 m above the snow pack, except for SUM03, when continuous measurements at 1 m and 0.1 m were combined with 1 m HPLC data. [c] Based on individual chromatograms of the HPLC channel measured at 1 m above the snow pack, except for South Pole 2003, when measurements at 1 m and 8 m were combined. [d] Based on 4 h averages of the ratio MHP/(MHP+H_2O_2).

firn air data were therefore corrected using a single factor of 2.91 estimated from a linear regression between mixing ratios measured with and without the probe.

The photochemical model used to compare with our measurements during SUM03 and SP03 is a time-dependent box model containing explicit HO_x-NO_x-CH_4 chemistry (71 reactions) and parameterized NMHC chemistry (184 reactions). Typical model inputs include NO, CO, O_3, H_2O, ambient temperature and pressure. In addition, the model can be constrained by observations of OH, HO_2, H_2O_2, HCHO, HNO_3, HO_2NO_2, HONO and photolysis rates derived from in situ actinic flux measurements. Further details on the model are described elsewhere (Chen et al., 2004, 2007). For SUM04 a steady state box model was used also containing explicit HO_x-NO_x-CH_4 chemistry with a reaction scheme similar to the mechanism described in Chen et al. (2004) and Sjostedt et al. (2007).

3 Results

3.1 Ambient air

Averages, standard deviations and ranges for ambient H_2O_2 were 1448±688 (<10–4642) pptv, 204±162 (<10–1259) pptv and 278±67 (<89–459) pptv during SUM03, SUM04 and SP03, respectively (Table 1, Fig. 1). At both sites, MHP was the only higher organic hydroperoxide detected with the HPLC method described and MHP mixing ratios in ambient air during the same seasons were 578±377 (<30–3202) pptv, 139±101 (<30–562) pptv and 138±89 (<30–654) pptv (Table 1, Fig. 1).

Averaging 2-h binned data of the 1-m gas phase concentrations over the entire field seasons confirmed the presence of a diurnal cycle of H_2O_2 at Summit, Greenland (Bales et al.,

1995) during summer 2003 and also during the spring season 2004 with maxima (minima) occurring between 13:00 and 17:00 (01:00 and 03:00) solar time and amplitudes of 760 and 137 pptv, respectively. At South Pole in summer, H_2O_2 does not show any significant diurnal variability, as expected from a nearly constant solar elevation angle (SEA). In the case of MHP a distinct diurnal cycle was only observed at Summit, Greenland during spring 2004 with a mean amplitude of 57 pptv.

Dividing the spring 2004 season into three subsequent 10-day periods revealed that during the spring transition from dark to 24-h sunlit conditions the diurnal cycles of H_2O_2 and MHP evolved in very different ways (Table 1, Fig. 2). H_2O_2 amplitudes almost triple from approximately 113 pptv during the first two time periods to 333 pptv from 18 April to 2 May (Fig. 2d–f). Early in the season between 27 March and 7 April MHP dominates the atmospheric hydroperoxide budget as reflected by the highest mean and maximum values of the MHP/(MHP+H_2O_2) ratio of 0.45 and 0.94, respectively (Table 1). At the same time the MHP diurnal cycle is out of phase with H_2O_2 and air temperature, with a night time maximum of 269 pptv (01:00–03:00 solar time) and an early afternoon minimum of 30 pptv (13:00–15:00 solar time) (Fig. 2a,d). The 8–17 April period shows then a decrease in the amplitude of MHP from 238 pptv to 48 pptv (Fig. 2e). Eventually, the diurnal pattern shifts by 180° with a nighttime minimum (01:00–03:00 solar time) during the 18 April to 2 May period of 109 pptv and a late afternoon maximum of 216 pptv (15:00–17:00 solar time) (Fig. 2f).

3.2 Firn air

Mean firn air concentrations of H_2O_2 and MHP at Summit, Greenland in spring 2004 were 250±230 and 95±71 pptv, respectively (Table 2).
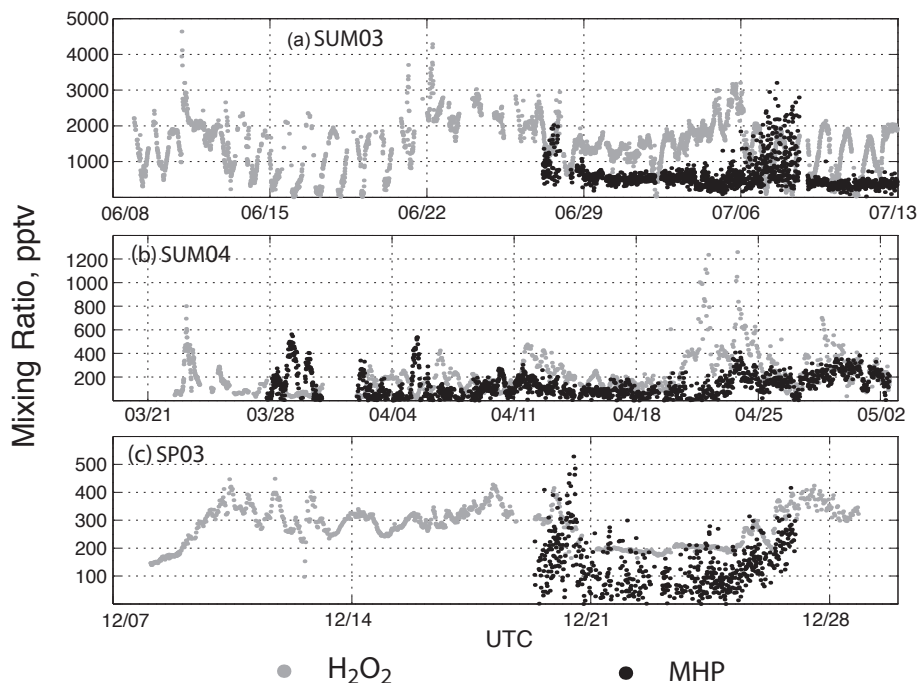
Fig. 1. Observations of atmospheric ROOH during **(a)** the Greenland Snow Photochemistry Experiment at Summit, Greenland in summer 2003 (SUM03) and **(b)** spring 2004 (SUM04), and during **(c)** the Antarctic Tropospheric Chemistry Investigation (ANTCI) at South Pole in December 2003 (SP03). Grey symbols represent 10 min averages of H_2O_2 measured with the continuous method at 1 m above the snow surface, except for SUM03 when 0.1 and 1 m measurements were combined with 1 m HPLC data. Black symbols show MHP levels derived from individual chromatograms and measured at 1 m above the snow pack, except at South Pole, where 1 m and 8 m measurements were combined.
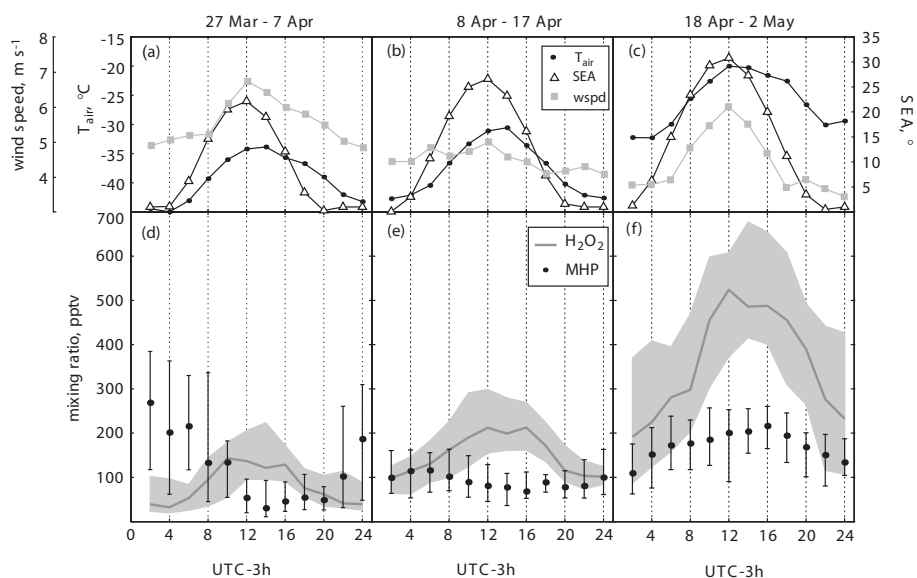

Fig. 2. Diurnal cycles of H_2O_2, MHP **(d–f)**, air temperature, solar elevation angle (SEA) and wind speed **(a–c)** are compared at Summit, Greenland over three 10-day periods in spring 2004. Median values of 2-h bins are shown, as well as the 0.25 and 0.75 quartiles of 2-h bins for atmospheric concentrations of H_2O_2 (grey line and shaded area) and MHP (black symbols and error bars).

Table 2. Results from ROOH firn air measurements at Summit, Greenland in spring 2004.[a]

Parameter	H_2O_2	MHP
Firn Air, pptv[b]	250 ± 230 (<10 to 1151)	95 ± 71 (<30 to 309)
1.0–0.1 m, pptv m^{-1}[c]	-42 ± 111, (-708 to 97)	3 ± 66 (-163 to 238)
0.1 m-firn, pptv m^{-1}[d]	232 ± 2034, (-4566 to 8913)	425 ± 584 (-1253 to 1689)
0.1 m-firn flux, molecules m^{-2} s^{-1}[e]	$3.5\times10^{10}\pm5.1\times10^{11}$ (-1.2 to 2.3×10^{12})	$9.0\times10^{10}\pm1.3\times10^{11}$ (-2.9 to 3.9×10^{11})

[a] Mean$\pm1\sigma$ (range) based on HPLC data between 12 April and 2 May, except firn air between 27 March and 2 May. [b] Including all measurements made between -5 and -25 cm below the snow surface. [c] Gradient calculated as $(c_{1.0\,m}-c_{0.1\,m})/0.9$ m. [d] Calculated as $(c_{0.1\,m}-c_{firn})/0.15$ m. [e] Diffusive flux estimate across the air-snow interface according to Fick's Law (see text); note that negative flux is equivalent to emission.

The frequency distributions of ROOH gas phase gradients between 0.1 m and firn air show that most of the time ambient levels of MHP exceeded those in firn air leading to predominantly positive gradients (Fig. 3d), while in the case of H_2O_2 the opposite was observed (Fig. 3c). No significant trend was found for MHP gradients between 1 m and 0.1 m above the snow (Fig. 3a), while H_2O_2 gradients were mostly negative (Fig. 3b). By convention negative (positive) gradients point upwards (downwards) driving the respective emission (deposition) flux.

Vertical profiles of ROOH in firn air were measured on 15 April and 26–27 April and compared to average ambient air levels during the 12 and 32 h long experiments (Fig. 4). During the first experiment MHP firn air levels dropped off from close to ambient air concentrations at 5 cm depth to levels at or below the LOD at 50 cm depth (Fig. 4a). During the second experiment MHP in firn air between 0 and 40 cm depth remained mostly in the $\pm1\sigma$ range of mean ambient air mixing ratios (Fig. 4b). In the deeper snow pack MHP declined rapidly to levels below the LOD (except at 60 cm and 130 cm depth) (Fig. 4b). Note that snow concentrations of MHP at Summit were below the detection limit as found also in Antarctica (Frey et al., 2005).

In the case of H_2O_2 mixing ratios in firn air showed large fluctuations across the top 1.5 m with maxima and minima mostly in phase with the seasonal extrema of H_2O_2 concentrations in snow, a pattern expected from physical uptake and release (Fig. 4c, d).

3.3 Model results

All model runs to calculate MHP were constrained by diurnal profiles of observed O_3, CO, NO, H_2O, air temperature, pressure, photolysis rate coefficients, H_2O_2 and HCHO, while CH_4 and NMHCs were held constant at their median observed level. HONO was calculated since predictions of HO_x radicals matched observations less well when it was constrained (Chen et al., 2007; Sjostedt et al., 2007). Unless otherwise noted deposition rates for MHP and other organic

peroxides were set to zero. During SUM03 model output was averaged for the 7–9 July period, when winds were low and conditions representative for the whole season, and then compared to observations from 9 July only (Fig. 5a). Data from 6–8 July were not included since MHP showed untypically high levels and variability, which we cannot explain by contamination, instrumental issues or any observed environmental parameter (Fig. 1a). Median ratios between modeled and observed concentrations of atmospheric MHP were 52%, 148% and 3% for SUM03, SUM04 and SP03, respectively (Fig. 5) and correlations between model and measurements were only significant during SP03 ($r^2=0.85$ at 95% confidence). Model output for SUM04 was only available for a few hours around solar noon each day and tracks the observed weekly trend of MHP quite well, however overpredicts at times the daily maxima (Fig. 5b).

4 Discussion

4.1 Speciation, levels and variability of ROOH

Our first time HPLC measurements of atmospheric hydroperoxides above the Greenland ice sheet show that MHP is the only significant organic peroxide occurring in the BL at Summit in summer and spring (Fig. 1a, b and Table 1). Likewise at South Pole, our results from December 2003 confirm a previous study during January 2003 that H_2O_2 and MHP are the two dominant atmospheric hydroperoxides, with the latter occurring at about 1.3 times the level reported previously (Frey et al., 2005) (Fig. 1c and Table 1). The summertime mean and maximum MHP concentrations at Summit of 578 (range 30–3202) pptv were among the highest measured so far in the polar regions, exceeding those in coastal Antarctica during the entire sunlit period of 190 (range 50–890) pptv (Riedel et al., 2000) and above the Antarctic Ice Sheet between 77 and 90° S of 310 (range 30–1100) pptv (Frey et al., 2005). Springtime MHP mixing ratios at Summit of 139 (range 30–562) pptv were similar to those observed at South Pole (Table 1) and previously above the East Antarctic
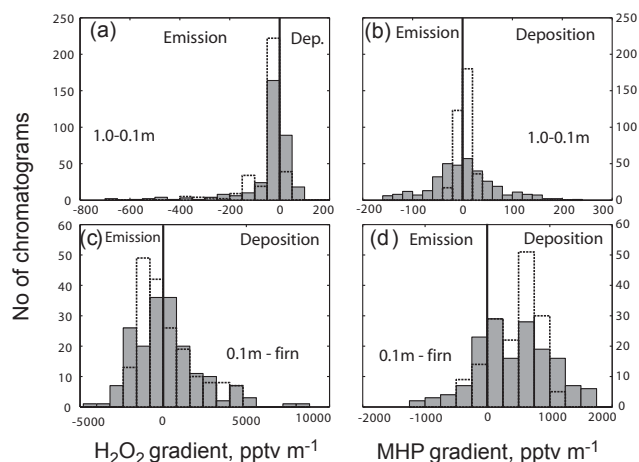
Fig. 3. Distributions of the 1.0–0.1 m and 0.1 m-firn gradients of H_2O_2 **(a, c)** and MHP **(b, d)** at Summit in spring 2004. Shown are results from single (grey) and smoothed (dotted line) HPLC measurements using a 12-point 2nd order filter.

Plateau in summer (Frey et al., 2005) but lower than the only other available Arctic measurements during this time of year, reported for Alert, Canada (82.5° N, 62.3° W) during the Polar Sunrise Experiment 1992 (de Serves, 1994). There the organic peroxide signal expressed as H_2O_2 was ~150 pptv in early April, which is equivalent to about 200 pptv MHP if a reduced coil scrubber uptake efficiency of 75% and the presence of MHP and H_2O_2 only are assumed (de Serves, 1994).

Below we compare the spatial and temporal variability of both hydroperoxides (Fig. 1) in order to demonstrate that photochemical and physical sinks and sources differ significantly between H_2O_2 and MHP.

At Summit, MHP mixing ratios exceed those of H_2O_2 frequently in early spring, while in summer H_2O_2 is higher (Fig. 1b), suggesting a transition from an organic peroxide dominated regime in winter/early spring to a H_2O_2 dominated regime in summer to take place in early April. The transition timing coincides with previous measurements in the Arctic (de Serves, 1994; Snow et al., 2003). Average MHP fractions of total peroxide were highest during SUM04 with 0.37±0.21 followed by SP03 and SUM03 with 0.35±0.07 and 0.31±0.14, respectively (Table 1), but lower than previously published values determined in the summer BL above the West Antarctic Ice Sheet of 0.39±0.15 (Frey et al., 2005) and coastal Antarctica of 0.57±0.26 (Riedel et al., 2000).

Simply assigning the total peroxide signal determined with the continuous method in channel 1 to H_2O_2 carries the risk of overestimating true concentrations as pointed out by Sigg et al. (1992). Therefore, the average MHP contribution to the total peroxide signal measured with the continuous method in channel 1 was calculated as H_2O_2-equivalent
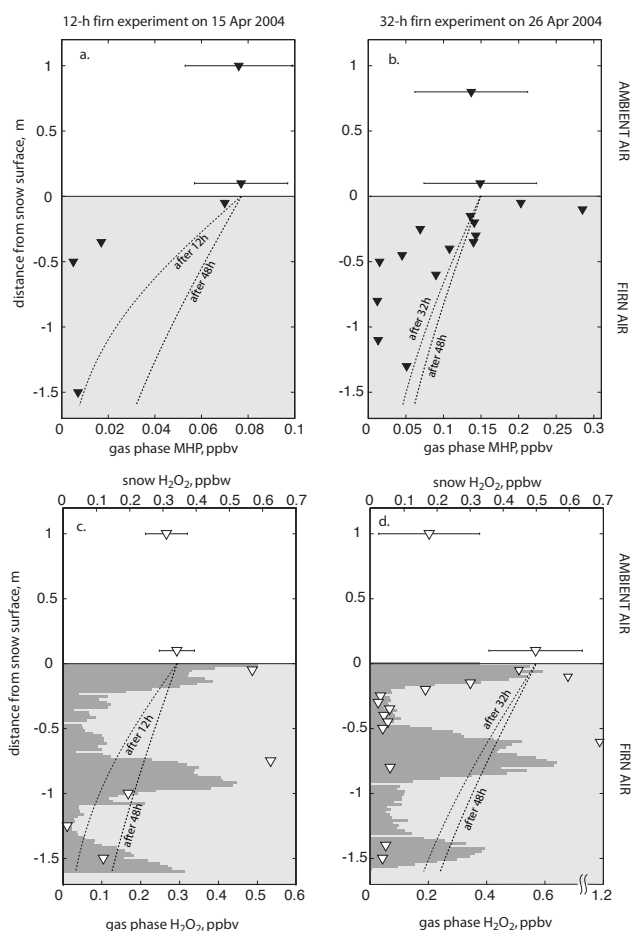

Fig. 4. Vertical profiles of H_2O_2 and MHP mixing ratios in firn and ambient air (triangles) at Summit, Greenland on 15 **(a, c)** and 26–27 April 2004 **(b, d)**. Firn air data are 1-h averages, while ambient air levels refer to mean±1σ for the entire duration of the experiment. Profiles of H_2O_2 concentration in snow are shown for comparison (horizontal bars in **c, d**). Dashed lines represent calculated firn air profiles based on molecular diffusion only and assuming constant ambient air levels (see text).

in pptv (fraction of the season mean of total peroxide in percent) using the HPLC data. The contribution of MHP to the total signal corresponded to 159 pptv (10%), 28 pptv (15%) and 19 pptv (6%) H_2O_2 during SUM03, SUM04 and SP03, respectively. Thus, in the polar BL the contribution of organic hydroperoxides to the total hydroperoxide budget can be significant and if not corrected for in the continuous peroxidase method can lead to an overestimate of H_2O_2 that is of the same order of magnitude as the accuracy of the method.

4.1.1 Inter-site differences

An inter-site comparison shows that summer concentrations of MHP at Summit were 4 times those observed at South Pole, while they were similar in spring (Table 1). H_2O_2 levels
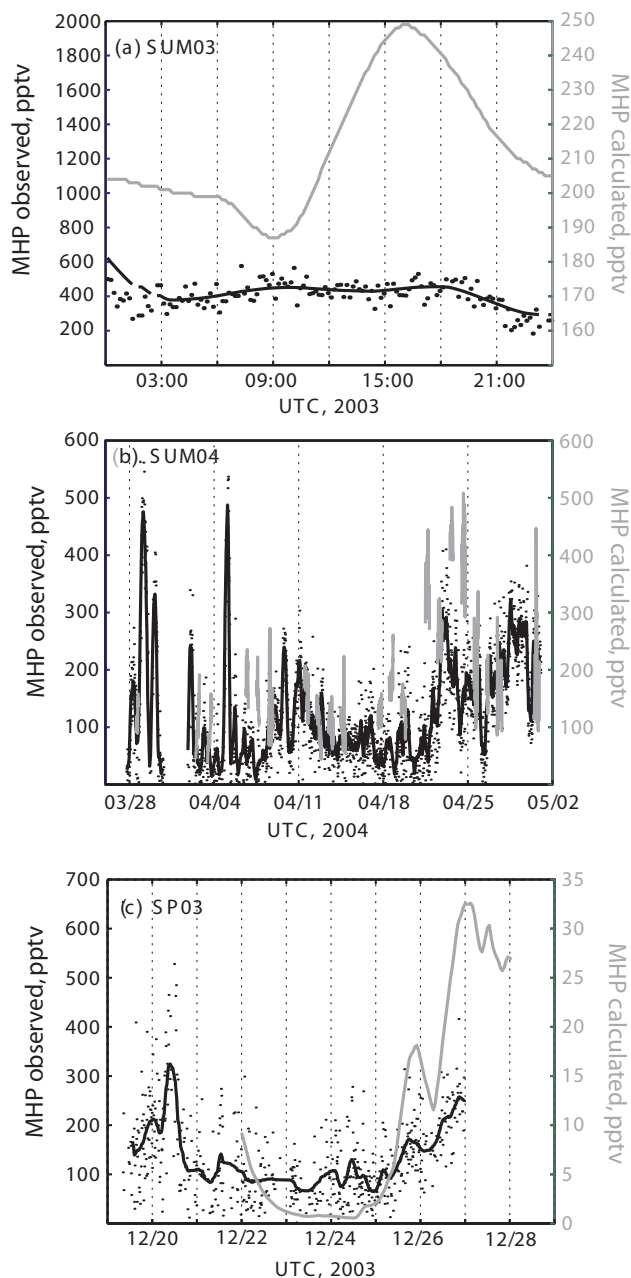
Fig. 5. Atmospheric MHP concentrations (black symbols and line) at Summit, Greenland **(a, b)** and the South Pole **(c)** are compared to highly constrained photochemical model runs (grey line). Note that the ordinate scale for the observations during SUM03 and SP03 is 20 times that of the model output.

showed an increase from 0.5 to 1.7 times the South Pole levels during spring 2004 reaching summer time mixing ratios as high as 5 times South Pole observations (Table 1). In the case of H_2O_2 one of the underlying causes is that concentrations of its main photochemical precursor CO at Summit were 160 ppbv and thus about 3 times the levels observed at South Pole (Table 3). This is due to the proximity of anthropogenic pollution sources in North America and Eurasia.

In addition, ambient summer temperatures are considerably higher at Summit than at South Pole, which has a twofold effect: first, higher temperatures lead to an elevated atmospheric moisture content and increased formation of HO_x radicals, which then readily recombine to form H_2O_2. This is consistent with the strong correlations between H_2O_2 and specific humidity at both sites (r^2 range 0.62–0.72, $p<0.05$). Contrary to South Pole, NO background levels were low at Summit (Table 3) and competing reactions with NO are not expected to inhibit H_2O_2 formation. Second, high ambient temperatures lead generally to an increase in the strength of a physical snowpack source of H_2O_2. Indeed, temperature-driven summer H_2O_2 fluxes at Summit, Greenland have been observed to be 5 times those measured at South Pole due to higher temperatures (Hutterli et al., 2001, 2004).

In the case of MHP a snow pack reservoir is not considered to be important as a physical source because the solubility of MHP is 3 orders of magnitude lower than that of H_2O_2 (Lind and Kok, 1994) and most likely even lower in snow and ice, since none has been detected so far in polar snow above the current LOD (Frey et al., 2005). Inter-site differences in MHP mixing ratios can be related to photochemical precursors such as CH_4, NMHCs and water vapor, which form peroxyradicals (HO_2 and CH_3O_2). CH_4 mixing ratios were similar at Summit and South Pole (Table 3). But evidence of the presence of a series of C2–C4 non-methane hydrocarbons in the Summit BL originating from the lower latitudes has been reported previously with a seasonal maximum in February and a minimum in the summer months due to photochemical removal (Swanson et al., 2003). High levels of water vapor (Table 3) in combination with enhanced MHP production inferred from the large NMHC removal rates explain higher MHP concentrations in summer compared to South Pole. In spring, precursor levels are higher since reaction rates are smaller. For example, atmospheric concentrations of ethene (C_2H_4), a CH_3O_2 precursor and potential MHP source (Horie et al., 1994), during SUM04 were twice those during SUM03 and SP03 (Table 3) and the highest levels during early spring before 4 April (30–60 pptv) coincide with elevated MHP (Fig. 1) suggesting a contribution to the ROOH budget. Summit is a site which is influenced by rapid transport of air masses from the lower latitudes (e.g. Swanson et al., 2003) therefore advection of non-locally produced MHP can be an additional source to the local ROOH budget especially in spring, when the atmospheric lifetime of MHP is on the order of days as discussed below. However, we did not find any significant correlation between mixing ratios and wind speed or direction to support this and therefore conclude that in spring most of the MHP is produced locally.

4.1.2 Temporal variability

The diurnal cycle of H_2O_2 present at Summit in summer and now observed also during spring has been shown to be largely determined by a temperature-driven cycle between

atmosphere and the upper snow pack with daytime emission and nighttime deposition (Bales et al., 1995; Hutterli et al., 2001). The importance of a physical snowpack source over photochemical formation is illustrated by significant correlations at both sites between H_2O_2 mixing ratios and air temperature, a good proxy of the temperature of the snow surface (r^2 range 0.60–0.70, $p<0.05$), while they are weak between H_2O_2 and solar elevation angle, a radiation proxy ($r^2<0.1$, $p<0.05$). On a seasonal time scale H_2O_2 concentrations at Summit increase throughout spring and peak in summer as expected from photochemical theory and observed previously in coastal Antarctica (Riedel et al., 2000).

In contrast, MHP did not correlate significantly with either temperature or SEA and its diurnal cycle at Summit in early spring (before 17 April) was out of phase with H_2O_2, suggesting build up of MHP when the sun was low or below the horizon and then a decline as the solar elevation angle increased reaching a minimum slightly after the SEA maximum (Fig. 2a, d).

Horizontal wind speed and thus turbulent vertical mixing exhibit also a diurnal variability correlated with SEA (Fig. 2a–c). This could lead to daytime minima through dilution with air from aloft, since upper tropospheric MHP levels in the high latitudes have been found to be lower than those in the BL (Snow et al., 2003). Since a daytime maximum of MHP is still observed during the 18 April to 2 May period when wind speed amplitudes were largest (Fig. 2c, f), we argue that dilution effects are small and the observed diurnal variability is due to changes in photochemical sink and source terms.

Comparison of atmospheric sinks shows that MHP is about 3 times more susceptible to attack by the OH radical, but photolyzes less readily than H_2O_2 (Atkinson et al., 1997). Significant differences in the atmospheric life time of these two hydroperoxides will mostly arise from differences in removal via dry and wet deposition. The dry deposition velocity of MHP is reported to be 30 times smaller than that of H_2O_2 (Hauglustaine et al., 1994) and wet deposition does not represent an important removal process for MHP due its lower solubility compared to H_2O_2 (Lind and Kok, 1994).

To quantify this further we calculated the atmospheric lifetime of MHP at both sites with respect to photolysis, reaction with OH, using measured photolysis rates and OH concentrations, and a dry deposition rate of $4.0\times10^{-7}\,\mathrm{s}^{-1}$ based on suggested deposition velocities (Hauglustaine et al., 1994) and assuming a BL depth of 250 m. Since the dry deposition velocity is small, results are not very sensitive to uncertainties in BL depth. Atmospheric lifetimes at solar noon (midnight) during SUM04 decreased from 96 (155) to 38 (142) h, while they were 7 (15) h during SUM03 and 22 (22) h during SP03. For comparison, H_2O_2 lifetimes with respect to photochemical sinks and dry deposition were only 11–17% of those for MHP for most of SUM04, 120% during SUM03 and 60% at South Pole. The atmospheric lifetime of MHP at Summit in early spring is not consistent

with the observed diurnal cycle suggesting the existence of an additional daytime sink.

On a seasonal scale MHP shows a similar trend as H_2O_2 with the highest values in the summer, in line with previous observations of MHP in coastal Antarctica (Riedel et al., 2000) reflecting a more active hydroxyl radical chemistry during the sun lit season. Contrary to H_2O_2, the individual MHP measurements did not correlate significantly with any of the observed environmental parameters, in part due to larger scattering.

4.2 Model comparison

Median ratios between modeled and observed concentrations of atmospheric MHP were 52%, 148% and 3% for SUM03, SUM04 and SP03, respectively, and suggest a missing source in summer and a missing sink in spring (Fig. 5).

Discrepancies between model and observations can be in part reconciled by changing the rate constant of the $CH_3O_2+HO_2$ reaction within the stated uncertainties, as a recent study using the NASA-GFSC point photochemical model has pointed out (Frey et al., 2005). However, at South Pole the model underestimate is particularly large, indicating that photochemical ROOH sources other than methane oxidation and not included in the calculations might be important. There are two likely possibilities. One is the ozonolysis of ethene (C_2H_4), which produces MHP under dry and wet conditions (Horie et al., 1994). However, model sensitivities suggest that increases in C_2H_4 (6–26 pptv, Table 3) have only a small effect on MHP at South Pole and quickly lead to unrealistic levels of calculated peroxyacetyl nitrate (PAN). The second is photo-oxidation of acetone ($CH_3(CO)CH_3$) (Finlayson-Pitts and Pitts, 1998), which is also found to be only a minor source of MHP, since increasing assumed acetone levels from the nominal value for the remote Northern Hemisphere of 300 pptv by one order of magnitude (based on few canister measurements available from South Pole) resulted only in a 10% increase in calculated MHP. And finally, the South Pole box model states that more than 75% of the CH_3OO radicals are formed from CH_4 oxidation, thus indicating that the radical source is off by at most a factor 2. In summary, at South Pole a significant part of observed MHP is unaccounted for by known gas phase photochemistry and contributions from transport are likely to be minor given atmospheric lifetimes of less than one day.

Conversely in spring model overestimates of noon time MHP levels suggest a missing sink. This holds true even though dry deposition was not included in the model runs as the following example shows. On 23 April modeled day time values MHP were 450 pptv or 1.5 times the observed levels. At a dry deposition velocity of 0.01 cm^{-1} (Hauglustaine et al., 1994) it would take about 20 (4) days to remove the excess MHP in a BL of 250 (50) m vertical extension.

Table 3. Overview of observed key parameters at Summit, Greenland and South Pole.[a]

Parameter	SUM03[b]	SUM04[c]	SP03[d]
O_3, ppbv	49 ± 4 (10–65)	55 ± 7 (32–81)	41 ± 9 (18–47)
NO, pptv	15 ± 23 (1–465)	11 ± 14 (0–100)	226 ± 173 (15–830)
CH_4, ppmv	1.81 ± 0.01 (1.81–1.83)	1.84 ± 0.01 (1.82–1.86)	1.70 ± 0.01 (1.68–1.71)
CO, ppbv	126 ± 6 (113–139)	162 ± 11 (132–187)	47 ± 4 (41–58)
C_2H_4, pptv	9 ± 22 (3–243)	22 ± 12 (11–66)	10 ± 8 (6–26)
T_{air}, °C	-13.4 ± 5.0 (−29.2–6.5)	-34.8 ± 8.7 (−56.8–13.8)	-25.0 ± 1.5 (−27.0–20.6)
OH, molec. cm^{-3}	6.4×10^6	2.5×10^5 (before 11 April)	1.7×10^6
		8.9×10^5 (after 11 April)	
(HO_2+RO_2),	2.2×10^8	2.2×10^7 (before 11 April)	7.1×10^{7e}
molec. cm^{-3}		9.5×10^7 (after 11 April)	
H_2O, g kg^{-1}	1.6 ± 0.6 (0.5–3.4)	0.4 ± 0.4 (0.1–1.9)	0.6 ± 0.1 (0.5–0.9)
SEA, °	22 ± 12 (5–41)	17 ± 9 (0–33)	23 ± 0 (23.3–23.5)
j-O_3, s^{-1}	$8.4\times10^{-6}\pm7.4\times10^{-6}$	$1.9\times10^{-6}\pm3.4\times10^{-6}$	$1.3\times10^{-5}\pm8.7\times10^{-7}$
	$(1.8\times10^{-7}-2.8\times10^{-5})$	$(2.4\times10^{-11}-1.5\times10^{-5})$	$(9.9\times10^{-6}-1.4\times10^{-5})$

[a] Median $\pm1\sigma$ (range). [b] Ref. period 10 Juni–12 July 2003; HO$_x$ data from Sjostedt et al. (2007). [c] Ref. period 22 March–2 May 2004; HO$_x$ data S. Sjostedt, personal communication, 2006. [d] Ref. period 20–27 December 2003. [e] Model estimate.

Table 4. Comparison of sink rates (S_{MHP}) and atmospheric life time (τ_{MHP}) of MHP at Summit.

	OH[a] molec. cm^{-3}	S_{MHP}^{b} molec. m^{-3} s^{-1}	S_{MHP} pptv h^{-1}	τ_{MHP}^{c} h
Firn profiles				
15 April 2004		5.3×10^{11}	96	0.8
26–27 April 2004		1.3×10^{11}	24	6
Ambient air				
15 April 2004	5.4×10^5	3.5×10^9	1	101
26–27 April 2004	2.6×10^6	4.9×10^{10}	9	24
10–12 July 2003	9.8×10^6	3.0×10^{11}	57	6
Firn air				
15 April 2004	1.1×10^6	6.0×10^9	1	59
26–27 April 2004	1.5×10^6	2.7×10^{10}	5	43
10–12 July 2003	3.2×10^6	1.2×10^{11}	24	15
Quasi-liquid layer				
15 April 2004		3.6×10^{10}	7	10
26–27 April 2004		3.6×10^{10}	7	33
10–12 July 2003		4.3×10^{11}	82	4

[a] Observed in ambient (Sjostedt et al., 2007; Dibb et al., 2007) and firn air (Beyersdorf et al., 2007).
[b] Sink rate estimates from firn air profiles are compared to calculated removal rates in ambient and firn air including photolysis, reaction with OH radicals and dry deposition (ambient air only) and to removal in the quasi-liquid layer on snow grains (see text).
[c] From dividing S_{MHP} by maximum ambient air MHP concentrations of 65, 218 and 358 pptv for 15 and 26–27 April 2004 and 10–12 July 2003, respectively.

4.3 The role of the snow pack on atmospheric ROOH

The firn air measurements made at Summit in spring 2004 allow to investigate further the role of the snow pack for BL concentrations of ROOH and highlight fundamental dif-

ferences between H_2O_2 and MHP. In order to estimate atmosphere-snow fluxes we applied Fick's 1st Law using measured concentration gradients and effective molecular diffusion coefficients (D_{eff}) in the open firn pore space

(Table 2). D_{eff} values include a downward correction to take into account tortuosity effects of the upper snow pack (after Schwander et al., 1989), typically on the order of 10% of the free air molecular diffusivities for Summit conditions (e.g. $D_{eff, MHP}$ 1.1×10^{-5} m^2 s^{-1}). It should be noted that our approach assumes a constant diffusivity coefficient and thus a linear concentration profile between the two measurement levels of 0.1 and -0.05 m and thus yields a lower limit of the true flux. However, if the turbulent exchange coefficient (K_{zz}) in the air above the snow was much larger than D_{eff}, vertical mixing of molecules in ambient air would be rapid and the main concentration gradient would occur only across the diffusion distance in snow leading to a flux three times our calculated values. In addition, forced ventilation from wind pumping is quite likely to occur at 0.05 m depth and will lead to larger D_{eff} and thus an underestimate of true fluxes. It should also be noted that pumping firn air at rates of several L min^{-1} will advect air from above (or below) to the firn air probe inserted into the snow, as discussed by Albert et al. (2002). This effect was reduced by using a circular transparent disk covering snow surface adjacent to the firn air probe. Any remaining mixing between air at the depth of the firn air probe head and air from a different depth will result in a bias in measured concentrations and calculated fluxes. This bias related to the sampling method is considered to be small in comparison to the uncertainties in D_{eff} and it is therefore safe to assume that our flux calculations yield lower limits of the true values.

H_2O_2 flux time series showed emission alternating with deposition with no significant trend (Fig. 6a). However, both gradient distributions suggest that emission dominated over deposition (Fig. 3a, c). Between 19 and 25 April H_2O_2 mixing ratios showed a sharp increase from 200 pptv to >1000 ppt (Fig. 1b). The concurrent increase in air temperature supports the conclusion that the warming snow pack released additional H_2O_2. However, firn air levels remained constant leading to gradients pointing into the snow and causing large deposition fluxes (Fig. 6a). Thus, H_2O_2 was likely formed in situ above the snow or regionally in a newly arriving air mass. Advective transport is supported by concurrent increases of specific humidity, O_3 and CO (data not shown). On the other hand, the radionuclide ^{210}Pb, the daughter product of the continental tracer ^{222}Rn did not show any unusual excursions during the same time period (Dibb , 2007).

The distribution of 0.1 m-firn air gradients and time series of MHP fluxes show predominantly deposition throughout the spring season suggesting that most of the time the snow pack acts as a net sink (Fig. 3d, 6b). However, on a daily time scale fluxes did not mirror the observed diurnal cycle of atmospheric mixing ratios and fluctuations had no obvious correlation to any other observed variable (Fig. 6b).

In order to assess further the nature of the snow pack sink we compare firn air observations with the theoretical profile of a conservative tracer which is subject to molecular diffusion only. To do this we apply the solution of the one-dimensional diffusion Eq. (1), assuming constant ambient mixing ratios, c_0, across the upper boundary as well as no change in the molecule-specific D_{eff} with depth z, and calculate the respective firn air mixing ratios c_g after time t (Crank, 1975):

$$c_g = c_0 \operatorname{erfc}\left(\frac{z}{2\sqrt{D_{eff}t}}\right) \qquad (1)$$

Ambient air levels and variability of both hydroperoxides during each experiment were similar to those up to 48 h before. Thus, if no other physical or chemical processes occured molecular diffusion would fill quickly the firn air column leading to vertical profiles of H_2O_2 and MHP as calculated for 12–48 h of downward diffusion (Fig. 4). However, firn air profiles of both hydroperoxides disagree with this simple diffusion model (Fig. 4).

The strong correlation between gas and snow phase concentrations of H_2O_2 indicates supersaturation (undersaturation) leading to release (uptake) in snow layers containing the summer maximum (winter minimum) of H_2O_2 (Fig. 4c, d) and confirms previous work that physical atmosphere-snow exchange needs to be included in such a H_2O_2 firn model (McConnell et al., 1998). In contrast to H_2O_2, MHP firn air concentrations show in general a decline with depth, starting right at the surface on 15 April or at 0.4 m depth as during the second experiment (Fig. 4a, b). The observed firn air profile slopes are steeper than those calculated for 12–48 h of diffusion, suggesting MHP is efficiently removed by a snow pack process at a higher rate than it can be supplied via downward diffusion or wind pumping (Fig. 4a, b). Snow phase levels of MHP below the detection limit indicate also that exchange with a snow reservoir is less likely important.

Mathematical relationships between mixing ratio and depth are obtained by fitting an exponential function to MHP firn air profiles. Multiplying the first and second derivative of those with the average D_{eff} of 1.1×10^{-5} m^2 s^{-1} yields flux as a function of depth and concentration as a function of time, corresponding to Fick's 1st and 2nd Law. MHP depositional fluxes right below the snow surface were 7 and 9×10^{10} molecules m^{-2} s^{-1} close to the seasonal mean flux based on the ambient-firn air gradient (Table 2), while concentration changes with time or volumetric fluxes were 1 and 5×10^{11} molecules m^{-3} s^{-1}, equivalent to 24 and 96 pptv h^{-1} during the first and second firn air experiment, respectively (Table 4). The large removal rates found lead to MHP lifetimes of only 0.8–6 h and would explain the observed diurnal variability in early spring (Table 4).

A likely candidate for MHP removal in snow is the reaction with OH radicals (R10) (a) in the open pore space and (b) in the quasi-liquid layer (QLL) on snow grains, where OH radicals are produced from H_2O_2 photolysis as suggested previously(Anastasio et al., 2007). Regarding (a), OH levels observed in firn air (Beyersdorf et al., 2007) exceeded ambient air concentrations on 15 April and removal rates were therefore higher in the snow pack than above, but still only
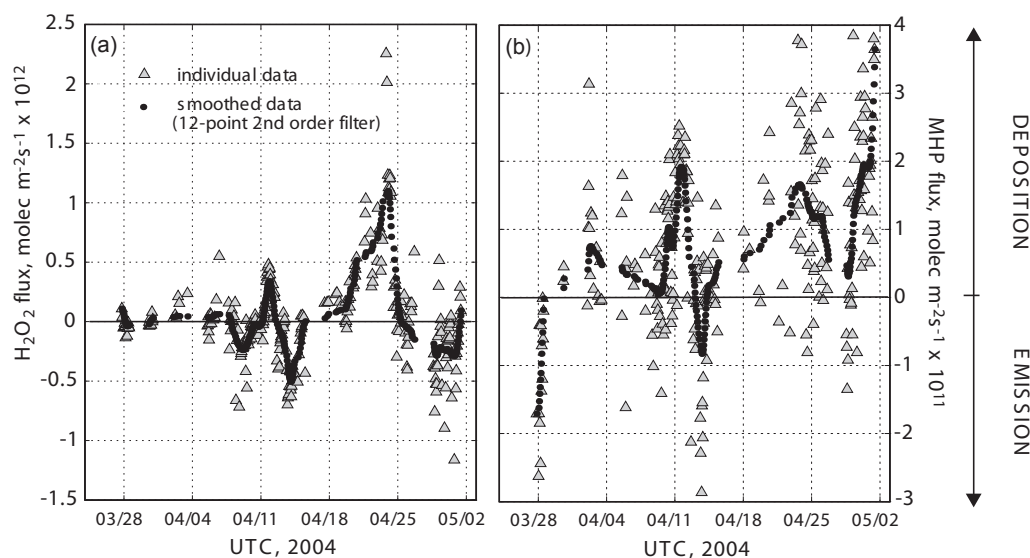
Fig. 6. Atmosphere-snow fluxes of H_2O_2 **(a)** and MHP **(b)** at Summit, Greenland during spring 2004 based on the 0.1 m-firn air gradient of gas phase concentrations (except before 12 April when only 1.0 m measurements were available).

1% of those derived from the firn profile (Table 4). With respect to (b), measured midday rates of OH radical production at Summit expressed with respect to the snow water equivalent of snow were 0.025 and 0.3 μm h^{-1} in spring 2004 and summer 2003, respectively (Anastasio et al., 2007). We assume that as an upper limit MHP destruction equals OH production, that MHP removal takes place predominantly in the water volume of the QLL and that its transport from the open pore space into the QLL is not rate limiting. The measured rates need then to be expressed as molecules of MHP lost per second and volume of air contained in the upper snow pack in order to allow to compare them with other MHP gas phase sinks. To do this we calculate the fraction of liquid water with respect to the volume of open pore space in snow, $w_{aq, open}$. Boxe and Saiz-Lopez (2008) estimated the liquid water fraction of a snow grain due to the existence of a QLL in the 250–265 K range to be 2.78×10^{-5}. Multiplying it with the ratio between measured snow density of 0.24 cm$^3_{aq}$ cm$^{-3}_{snow}$ and estimated open porosity of 0.74 cm$^3_{air}$ cm$^{-3}_{snow}$ (after Schwander et al., 1989) yields a $w_{aq, open}$ of 8.6×10^{-6}. Thus, by multiplying $w_{aq, open}$ with the OH production rates we obtain MHP removal rates of 3.6×10^{10} and 4.3×10^{11} molecules m^{-3} s^{-1} (Table 4). Assuming a Henry equilibrium between the QLL and the open pore space one can calculate upper limits of the MHP mass fraction X_{aq} residing in the QLL using $w_{aq, open}$, Henry's Law constant K_H (Lind and Kok, 1994), the ideal gas constant R and temperature T (2) (after Seinfeld and Pandis, 1998):

$$X_{aq} = w_{aq, open} \frac{K_H RT}{1 + w_{aq, open} K_H RT} \qquad (2)$$

The mass fraction X_{aq} is 75% in spring, decreasing to 40% in summer and suggests that a significant fraction of the total MHP present in the upper snow pack could be exposed to OH in the QLL. However, these values have to be considered as upper limits, since true solubilities of MHP in the QLL are possibly lower. In summary a combination of OH reactions in firn interstitial air and the QLL can explain up to 50% of the MHP sink rate based on the firn profiles in spring (Table 4).

As photochemistry intensifies in late spring and summer the snow pack sink should increase in strength, as for example MHP removal rates in the QLL suggest (Table 4). However, S_{MHP} derived from the firn profiles indicate rather a decrease with time, diurnal cycles show an afternoon maximum (Fig. 2c) and model calculations underpredict observations in summer. A possible explanation is the observed decrease of OH ratios between firn and ambient air from 1.7 in spring to 0.3 in summer (Table 4), thereby indicating that photochemical sinks and sources of MHP above the snow have become more important in comparison with the snow pack sink and control its budget.

4.4 Link to NO and atmospheric oxidative capacity

Nitrogen oxides (NO$_x$) are closely linked to the HO$_x$ radical budget and O$_3$ production and thus control the oxidizing capacity of the atmosphere. A previous model study using measurements from Antarctica showed that H_2O_2, MHP and CH$_2$O levels are very sensitive to the NO background in the remote atmosphere, since reaction of RO$_2$ radicals with NO competes directly with ROOH production via self and cross combination of RO$_2$ (Frey et al., 2005). Since RO$_2$+NO leads

to CH_2O formation, NO increases should concur with increases in CH_2O at the expense of H_2O_2 and MHP. It was hypothesized that combined measurements of ROOH and CH_2O have the potential to constrain the NO background and thus atmospheric oxidative capacity now and in the past, using ice cores (Frey et al., 2005). First time simultaneous measurements of all chemical species involved allow to test this hypothesis. Correlation plots of both hydroperoxides and CH_2O versus observed NO confirm model predictions, showing well defined relationships at South Pole and to a lesser extent at Summit in 2003 and 2004 (Fig. 7). The inter-site difference is mainly due to the absence of a diurnal cycle, which reduces scatter, and the large range of NO concentrations at South Pole. Modeled MHP mixing ratios from this study were included and despite the disagreement in the absolute values match the observed trends (Fig. 7a, c).

As expected, the highest levels of MHP are found at both sites in low-NO regimes of less than 25 pptv (Fig. 7b, c). The steep decline in MHP and H_2O_2 and the increase in CH_2O at higher NO then illustrate that suppression of ROOH formation concurs with enhanced CH_2O production (Fig. 7b, c, e, f, h, and i). Closer examination of H_2O_2 at South Pole reveales first an increase and a maximum at 30–50 pptv NO before the decrease, in agreement with previously reported measurements (Hutterli et al., 2004).

The observed differences in the response of H_2O_2 and MHP to rising NO are consistent with known photochemistry and have been discussed previously (Frey et al., 2005). ROOH and CH_2O are most sensitive to NO changes and thus useful as a NO constraint before they reach their plateau concentration, that is within the 0–25 pptv and 0–100 pptv range of NO at Summit and South Pole, respectively (Fig. 7). Combining the correlations from all three trace gas species allows also to determine if NO has exceeded that range (Fig. 7).

5 Conclusions

Atmospheric H_2O_2 and MHP were shown to be the two most important hydroperoxides ocurring in the BL above Antarctica and central Greenland. Sinks and sources of both chemical species differ significantly as reflected by the observed magnitude and variability of their mixing ratios (Figs. 1 and 2). While physical exchange between atmosphere and snow controls H_2O_2, photochemical processes dominate the MHP budget. To overcome the general lack of organic peroxide measurements in the polar atmosphere it has been common use in past modeling exercises to estimate MHP levels by simply setting them equal to H_2O_2 concentrations (e.g. Yang et al., 2002). However, our findings do not warrant this simplification. It was found that relative MHP contributions to atmospheric ROOH in the polar BL are larger at cold sites or during the early part of the sunlit season, when temperatures are low and the physical snow pack source strength of H_2O_2 is small. Under these conditions MHP is expected to

be an important atmospheric radical source, similar to other cold and water vapor limited regions such as the upper troposphere.

Spring time measurements of MHP in ambient and firn air at Summit suggest a daytime sink in the upper snow pack. This is supported by (a) the inconsistency of calculated lifetimes based on known atmospheric sinks with the observed diurnal cycle in early spring, (b) model overprediction, (c) predominantly deposition (Figs. 3 and 6), and (d) the discrepancy between the observed firn air profile and a simple diffusion model (Fig. 4). Up to 50% of the snow pack sink can be explained by photolysis and the reaction with the OH radical in firn air and the QLL on snow grains, but appears to be only important in spring, when firn air levels of OH radicals exceed those in ambient air.

One implication is the impact on formaldehyde (CH_2O) formation from MHP photolysis (R8) and reaction with OH (R10) followed by reaction with NO (R6). Using SUM04 seasonal averages of observed j-CH_3OOH, NO and CH_3OOH levels and a model estimate for CH_3OO of 1.16×10^7 molecules cm^{-3} we calculated a CH_2O production rate of 6 pptv h^{-1} at ambient and 37 pptv h^{-1} at firn air NO levels. MHP removal rates in firn air suggest that CH_2O could be formed at rates of up to 96 pptv h^{-1} (Table 4), much higher than ambient production rates and thus likely contributing to a photochemical source of CH_2O in the snow observed previously at South Pole (Hutterli et al., 2004). Assuming that a maximum CH_2O source strength of 5.3×10^{11} molecules m^{-3} s^{-1} (Tab.4) is constant across the top 0.05 m of snow translates into an areal flux of 2.7×10^{10} molecules m^{-2} s^{-1}. This is about 1% of CH_2O emission fluxes measured previously at Summit in summer, ranging between 1 and 9×10^{12} molecules m^{-2} s^{-1} (Grannas et al., 2007, and references therein). In spring however, when temperature driven emissions are reduced due to lower temperatures, it is expected that the MHP removal contributes a larger fraction to the total CH_2O emissions. More detailed work on CH_2O firn air photochemistry will be reported elsewhere (Hutterli et al., 2004).

In summer, model predictions of MHP at Summit and South Pole rather suggest a missing source. While contributions from other possible photochemical precursors of MHP are a plausible explanation at Summit, they are not at South Pole, where high NO levels suppress MHP production. Advection of non-locally produced MHP is also minor, thus known processes cannot currently account for the missing MHP source at South Pole. Flux studies combined with firn air profiles under well controlled conditions are still scarce, but are considered essential as this study has shown for quantifying the impact of snow covered areas in general on the composition of the local BL. The observed local relationships between ROOH, CH_2O and NO are useful in that they can help constrain the range of the current NO background. Developing atmospheric histories for these chemical gases from ice cores can potentially
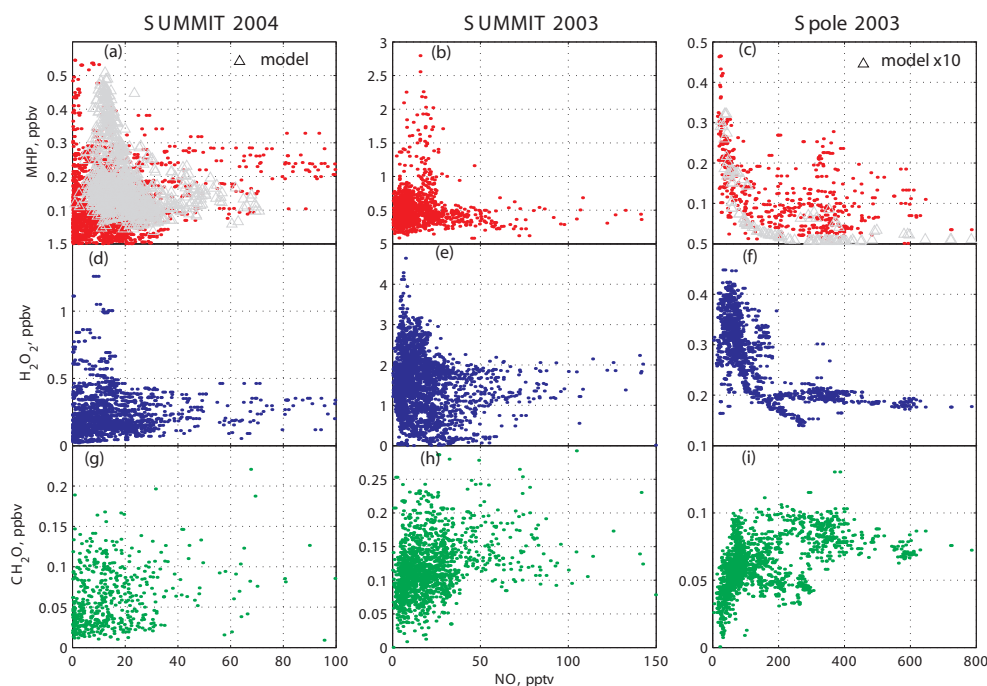
Fig. 7. Observed relationship between MHP (**a–c**), H_2O_2 (**d–f**) and HCHO (**g–i**) and NO at Summit and South Pole. Modeled MHP is shown for comparison (grey symbols in **a, c**).

extend these constraints into the past. However, our results do not raise much hope in finding a well preserved MHP record in firn and ice.

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