Formaldehyde and Hydrogen Peroxide in Air, Snow and Interstitial Air at South Pole

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Abstract

Average H_2O_2 (HCHO) mixing ratios measured above the snowpack at South Pole were 278 pptv (103 pptv) in December 2000 and between 4 to 43 times (1.4 to 2.6) the expected value based on gas-phase photostationary state model calculations. The larger difference is realized if dry deposition of both species is included in the model. H_2O_2 and HCHO fluxes from the snowpack were independently determined from gradient measurements in the air above the snow surface, from firn air measurements and from the temporal concentration changes in near-surface snow. On average, the snowpack at South Pole was releasing on the order of 1 x 10^{13} and 2 x 10^{12} molecules m^{-2} s^{-1} of H_2O_2 and HCHO, respectively, in December 2000. This is consistent with the volumetric fluxes needed for the photostationary state model to reproduce the observed atmospheric mixing ratios of both H_2O_2 and HCHO. The highly elevated levels of both species found in firn air further support the above estimates. In the case of HCHO, it was also shown that there was good agreement between the measured flux and the physical air-snow exchange model as driven by changes in snow temperature from winter to summer. Shading experiments suggest that the net production of HCHO within the snow by heterogeneous photochemical processes most likely do not exceed photochemical destruction by more than 15% of the measured fluxes. The very rapid changes observed in atmospheric HCHO, which are also seen in NO and OH, can be understood in terms of dynamical processes that lead to rapid changes in the atmospheric mixing depth.

Keywords: interactions air/snow/ice, flux snow-atmosphere, snowpack chemistry, Antarctica, ISCAT 2000.

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1. Introduction

Formaldehyde (HCHO) and hydrogen peroxide (H_2O_2) are important constituents of atmospheric photochemistry and closely linked to the HO_x and NO_x cycles. Recent studies of the boundary layer photochemistry at South Pole (SP) showed unexpectedly high levels of NO (Davis et al., 2001) due to snowpack emissions of this species. Also observed were highly elevated levels of OH. The latter enhancement was shown to be a strong function of the NO level but also appeared to have some dependence on other snowpack emissions such as those involving HCHO and H_2O_2 (Chen et al., 2001). Both species have been shown to be released by Arctic snowpacks in spring and summer, implying significantly increased HO_x levels in the boundary layer (Hutterli et al., 1999; Hutterli et al., 2001; Jacobi et al., 2002; Sumner et al., 2002). Similar investigations have been missing in Antarctica.

Previous Antarctic atmospheric HCHO and H_2O_2 measurements have been reported from the coastal Neumayer Station (Riedel et al., 1999) and from the SP station (McConnell et al., 1997a; McConnell et al., 1997b; McConnell et al., 1998), respectively. In the first study HCHO was monitored year-round revealing elevated HCHO mixing ratios throughout much of the year with respect to photochemical model predictions. These results indicated that unaccounted local sources as well as long-range transport could be additional important processes. Observed diurnal atmospheric HCHO cycles intermittently present during the summer were attributed to temperature-driven cycling between the snow and the boundary layer. However, no actual HCHO flux measurements from the snow were reported. Recently, preservation of HCHO in snow and physical air-snow exchange was investigated at SP and other Antarctic sites based on snow pit data and numerical modeling (Hutterli et al., 2002a). The results predicted that temperature-driven release of HCHO from the snowpack could roughly triple the boundary layer HCHO mixing ratios in spring and summer at SP. Boundary-layer H_2O_2 mixing ratios were measured at SP during two summer seasons and related to surface snow concentrations in an investigation of the corresponding atmosphere-snow transfer (McConnell et al., 1997b).

The purpose of the present study was threefold: First, to determine the boundary layer HCHO and H_2O_2 mixing ratios at SP during the ISCAT 2000 project (see Chen et al., Davis et al., this issue). Second, to independently quantify HCHO and H_2O_2 fluxes across the snow-air interface with different methods and to compare the results with photochemical model predictions. And third, to investigate the origin of snowpack released HCHO and H_2O_2.

2. Methods

Gas-phase HCHO and H_2O_2 measurements were done from the Atmospheric Research Observatory building (ARO) at SP Station from December 5th-24th, 2000. HCHO was continuously scrubbed from the air (~0.55 L_{STP} min^{-1}) into a water stream (~0.16 mL min^{-1}) using a wet effluent diffusion denuder with a collection efficiency >96% as described by Hutterli et al., (1999). Similarly, H_2O_2 was quantitatively scrubbed from the air (~1.0 L_{STP} min^{-1}) into a water stream (~0.27 mL min^{-1}) using a glass coil. Subsequent continuous aqueous-phase HCHO and H_2O_2 analyses were done by fluorescence spectrometry using pentanedione and peroxidase-based reagents, respectively (Hutterli et al., 1999; Hutterli et al., 2001). Both instruments sampled air through the same ~15 m long heated and insulated 1/4" PFA intake line mounted to an automated 'mouse-elevator' situated on the snow ~5 m into the prevailing wind direction away from the ARO building. To determine gradients, the mouse elevator was programmed to change the height of the air intake intermittently between 0.05 m and 1.0 m above the snow surface. The protocol was to alternately sample 10 minutes each of HCHO and H_2O_2 free air (baseline), then atmospheric air from 0.05 m and from 1.0 m above the snow surface. HCHO and H_2O_2 free air was generated in excess by pumping outside air through a column filled with MnO_2-CuO catalyst (Carulite®) powder and was fed through a parallel tube to the tip of the sample line consisting of a Y-connector open to the atmosphere and connecting the two tubes. The intake line was checked for contamination and losses, but neither was detected. Airflow rates were continuously monitored with mass-flow meters. Liquid flow rates were measured several times a day by weighing the bottle containing the scrubbing water and corrected for evaporation in the coil and the denuder using the measured dew point of the ambient air and instrument temperature and assuming the air reaches saturation in the coil and denuder. Meteorological data used are available on the National Oceanic and Atmospheric Administration (NOAA) website www.cmdl.noaa.gov/info/ftpdata.html. Calibrations were done twice a day by running liquid standards through the denuder and glass coil while HCHO and H_2O_2 free air was sampled. The limit of detection defined as 3σ of the baseline noise based on the stored 15-second averages was generally below 40 pptv and 100 pptv for gas phase HCHO and H_2O_2 and below 15 pptv and 40 pptv respectively for 10-minute integrations. The accuracy of these observations is estimated to be better than 20% and 30% for HCHO and H_2O_2. However, this assumes that there are no interferences from other species. While there is no known interference in the HCHO method, the peroxidase-based reagent for H_2O_2 is also sensitive to organic peroxides. The highest sensitivity of the H_2O_2 instrument to organic peroxides is 0.3 for that of methylhydroperoxide (MHP) (personal communication M. Frey), which is also expected to show the highest mixing ratios (Riedel et al., 2000). Measurements in West

Antarctica revealed contributions of less than 20% of MHP to the total signal (personal communication M. Frey). However, average (maximum) modeled MHP mixing ratios at SP during ISCAT 2000 were 12 pptv (60 pptv) for the fully constrained simulation without deposition (see below), and would have contributed an equivalent of only 4 pptv (20 pptv) to the H_2O_2 signal.

Firn air (interstitial air) measurements were done by simply sticking the Teflon-coated tip of the intake into a ~5 cm diameter, 10 cm deep hole in the snow made with a clean Teflon tool. Depending on the experiment, the top of the hole was sealed with a cleaned 14 cm x 12.5 cm x 1 cm PTFE sheet or with surface snow. During one such experiment, an area of ~ 2 m x 2.5 m around the air intake was intermittently shaded with an aluminum coated nylon emergency blanket with most of the shaded area upwind of the air intake. The blanket was suspended at an angle of ~30° to the snow surface and ~0.5 m above the snow surface and several meters away from the intake line to minimize it's impact on the ventilation of the snowpack at the air intake. Snow samples were collected with stainless steel sampling tools and a HD-PE funnel and stored in airtight, clean glass bottles. All samples were analyzed no more than 2 days after collection and within 1 hour after melting using the same analytical method used for the water stream in the atmospheric measurements. The limit of detection defined as 3σ of the baseline was 0.19 ppbw and 1.1 ppbw for snow phase HCHO and H_2O_2, respectively, and accuracy was better than 10%.

The model used in this study is similar to that employed for the ISCAT 1998 analysis (Chen et al., 2001). It is a time dependent box model containing explicit HO_x-NO_x-CH_4 chemistry (71 reactions) and parameterized NMHC chemistry (184 reactions). The latter chemistry, however, has been further modified from the CAL scheme reported by Lurmann et al. [1986] (see e.g., Crawford et al., 1999). Typical model input consists of observational values for NO, CO, O_3, H_2O, ambient temperature, and pressure. In addition the model is capable of accommodating observational constraints based on measurements of OH, HO_2, HNO_3, HO_2NO_2, H_2O_2, HCHO, and HONO. The photolysis coefficients used are those derived from the in-situ actinic flux measurements (see Chen et al., this issue). Since no diurnal UV flux variations occur at SP during the Austral summer, photochemical steady state was assumed for all model-calculated species. The first order rates for heterogeneous removal of soluble species were adjusted to SP conditions. In this case, an average value of 9.3×10^{-5} sec^{-1} derived by Slusher et al. (2002) was used. For further detail concerning the model the reader is directed to Chen et al., (2001 and This Issue).

3. Results and Discussion

3.1. Atmospheric Measurements

H_2O_2 mixing ratios in the first meter above the snowpack varied from 23 pptv to 773 pptv with an average of 278 pptv (median 263 pptv) in December 2000 (Figure 1a). The mixing ratios were highest in the first part of December then gradually decreased to about half and remained low from December 13 to December 15 after which they rose to higher values again until December 23. These new measurements are of the same order as previous weekly averaged measurements at SP, which were between 180 pptv and 250 pptv during December, 1995, although they were substantially lower at 75 to 100 pptv in January, 1996 (McConnell et al., 1997b). The HCHO mixing ratios varied from 27 pptv to 184 pptv with an average of 103 pptv (median 108 pptv) over the whole period (Figure 1c). It will be noticed that there were several rather rapid decreases in the mixing ratios of HCHO followed by similarly fast increases with concentration changes of nearly 100 pptv.

The first of these HCHO shifts on 12 December (~12:00 GMT) was coincident with the formation of fog after a period with exceptionally large amounts of diamond dust in the air. At the same time the stratification of the planetary boundary layer changed from stable to unstable resulting in an increase in atmospheric mixing depth (Oncley et al., this issue). The fog cleared at around 7AM GMT on 13 December and was followed by a period of overcast weather until the last hours of 14 December, when HCHO mixing ratios quadrupled within a few hours. During the fog period, frost formed on suspended tubing and presumably on the snow surface. Previous results from Summit, Greenland have shown that fog deposition can effectively reduce boundary-layer mixing ratios especially of H_2O_2 (Bergin et al., 1996; Hutterli et al., 2001). Thus, the fact that the lowest H_2O_2 and HCHO mixing ratios were measured during this fog event can be at least partly attributed to scavenging processes operating within the boundary layer followed by deposition of frost, as indicated by the frost measurements discussed below.

3.2. Gradient Measurements

H_2O_2 gradients varied between –436 pptv m^{-1} to +210 pptv m^{-1} with 56% of the gradients being negative, indicating a flux from the snowpack to atmosphere (Figure 1b, 2a). The average of the 1280 independent gradient measurements was (–20±2) pptv m^{-1} (± standard deviation of the mean). For HCHO the gradients ranged from –48 pptv m^{-1} to +39 pptv m^{-1}. The average of the 827 values was (-4.9±0.4) pptv m^{-1} (± standard deviation of the mean) and 72% of the values were negative (Figure 1d, 2b), again indicating a flux out of the snowpack. Due to the 10-minute baseline intervals, gradient measurements were based on subsequent atmospheric mixing ratios that were separated either by less than 15 minutes or between 15 minutes and 30 minutes. As there was no significant difference between the distributions of both sets, all gradient measurements were used to calculate fluxes above the snowpack. While gradients indicate the general direction of the fluxes, the actual values of the latter depend strongly on the momentary values of the effective eddy diffusivity K_z. Fluxes based on the gradient measurements were calculated according to Monin-Obukhov Similarity theory using

$$F = -K_z \frac{\partial C}{\partial z} = -\frac{\kappa u_* z}{\phi(z/L)} \frac{\partial C}{\partial z} \tag{1}$$

where C is the atmospheric concentration, z is the height, F is the species flux, Kz is the effective turbulent diffusion coefficient between the two measurement heights, κ (set to 0.40) is the von Karman constant, u* is the friction velocity, and $\phi(z/L)$ is an empirically determined function defining the flux-profile relationship, which is assumed to depend only on the stability parameter z/L, with L the Monin-Obukhov length. The iterative method to obtain u* for different stability conditions is described in detail for similar studies on the Greenland ice sheet at Summit [e.g. (Hutterli et al., 2001; Jacobi et al., 2002)] and the same parameters and integrated ϕ functions were used here. The fluxes F were obtained for each gradient value using corresponding 10-minute averages of 0.5 m and 2.1 m air temperatures and wind speed at 3.1 m measured at the SP met tower (Oncley et al., this issue) and by integrating (1) from measurement heights z_1 to z_2 and inserting the observed atmospheric concentrations $C(z_1)$ and $C(z_2)$. Effective eddy diffusivities K_z closely followed wind speed and varied from 0.0006 $m^2\ s^{-1}$ to 0.04 $m^2\ s^{-1}$ with an average of 0.019 $m^2\ s^{-1}$ in the period from 4 to 25 December. The average H_2O_2 and HCHO fluxes out of the snow pack based on all individual 10-minute gradient measurements during which the necessary meteorological data were available were 9.5(±1.2)×10^{12} molecules $m^{-2}\ s^{-1}$ and 1.7(±0.1)×10^{12} molecules $m^{-2}\ s^{-1}$ (± standard deviation of the mean), with a total of 1119 and 778 10-minute values, respectively (Figure 2c, d).

Note that the standard deviations include the uncertainties due to the random errors and natural variability in both, the gradient and the turbulence measurements. We expect that the sequential 10-minute measurements of concentrations at the two levels contribute to the random error, but not to the systematic error. Significant systematic errors in the gradient measurements were avoided by using the identical setup including the intake line for both measurement heights. However, the single largest uncertainty in the average flux values stems from the fact that the gradient measurements had to be done close to the ARO building (~5m) and about 200 m away from where the micrometeorological data was acquired. The potential corresponding systematic error is expected to be less than a factor of 2.

The above-mentioned averages are representative for the actual time periods covered by the measurements (Figure 1), however, they could have been significantly different for different time periods covered. H_2O_2 fluxes e.g. were higher before 10 December 2.7(±0.3)×10^{13} molecules m^{-2} s^{-1} compared to 2.1(±0.9)×10^{12} molecules m^{-2} s^{-1} for the remainder of the season (± standard deviation of the mean, 331 and 788 values, respectively). During the latter, 6 out of 11 sequential 70-point flux averages were out of the snow above the 1-sigma confidence level (70 being the average number of H_2O_2 flux measurements per day). The remaining 5 were indistinguishable from zero at the 1-sigma level with 3 values into the snow. On 8 December, H_2O_2 fluxes were especially and consistently high, reaching values above 2×10^{14} molecules m^{-2} s^{-1}. HCHO fluxes out of the snowpack were relatively constant throughout the campaign. All 14 sequential 55-point flux averages (average number of HCHO flux measurements per day) were out of the snow at the 95% confidence level with values ranging from 0.9 x10^{12} to 2.9x10^{12} molecules m^{-2} s^{-1}.

The average measured H_2O_2 and HCHO fluxes at SP were both about 20% of those measured at Summit, Greenland in June 1996 (Hutterli et al., 1999; Hutterli et al., 2001). For a three-week period in June/July 2000 a net H_2O_2 deposition was reported for Summit, with the mean HCHO flux being about 50% of the SP value (Jacobi et al., 2002). The average measured HCHO flux falls within the range of values predicted for SP during the austral summer based on temperature-driven release from the snowpack (Hutterli et al., 2002a).

3.3. Photostationary State Calculations

A number of photostationary state (PSS) model calculations were performed in an effort to validate the measurements and to investigate the impact of the net snowpack fluxes on the composition of the Planetary Boundary Layer (PBL).

The calculated H_2O_2 level was no more than 2.3% of that measured when dry deposition was included and about 25% when dry deposition was excluced (Figure 3a, Table 1). This clearly suggests a missing source in the model consistent with the finding that the snowpack was releasing H_2O_2. The PSS model calculations also predicted lower atmospheric HCHO at no more than 39% and 74% of the measured values with and without dry deposition, respectively (Figure 3b, Table 1).

However, caution is warranted when directly comparing these PSS values with the observations. Due to the long photochemical lifetime of H_2O_2 and HCHO (median of 32 hours and 2.6 hours, respectively) compared to vertical mixing times from the snow surface to the measuring height (~ 1 minute), there is negligible effect of photochemistry on the flux-gradient relationship, and thus on the flux estimates in the region of measurement. This also implies, however, that the air close to the source cannot be assumed to be in PSS and could potentially have significantly elevated levels with respect to the average PBL value. Assuming no effect of photochemistry on the vertical profiles and K_z linearly increases with height ($u^* = 0.156$ m s^{-1}, and average PBL height 250 m Oncley et al, this issue), the estimated mean H_2O_2 and HCHO PBL mixing ratios are 47 pptv and 7 pptv lower than the corresponding measured 1-m averages.

When considering the entire PBL, the effect of photochemistry on the vertical profile is not negligible for HCHO. Using $u^* = 0.156$ m s^{-1} and a vertically averaged estimate of K_z obtained by Brost and Wyngaard (1978) for a neutral to slightly stable PBL, the characteristic height $h_\tau = (\tau \cdot K_z)^{1/2}$ (Lenschow, 1995) to which HCHO is mixed within one photochemical lifetime τ is about 150 m. Accounting for the photochemical loss with height results in an estimated average HCHO mixing ratio in this layer of ~93 pptv, i.e. 20 pptv above the PSS value.

The volumetric fluxes of H_2O_2 and HCHO necessary to reproduce observed mixing ratios can be calculated using the PSS model according to S = L – P with S defining the missing volumetric flux, P the total volumetric photochemical production rate and L the total loss rate of the species. For this case the model simulation was constrained by 215 pptv for H_2O_2 (estimated PBL mean) and 93 pptv for HCHO (estimated mean of the lower 150 m) (Table 1). The medians of the resulting volumetric fluxes were 2.4×10^4 molecules cm^{-3} s^{-1} and 1.1×10^4 molecules cm^{-3} s^{-1} for H_2O_2 and HCHO, respectively and about 250% and 6% of the corresponding photochemical production. Implicit in the model runs is the assumption that the layers investigated were on average in PSS and that the measured species used to constrain the model were representative for the whole layer. The first is not necessarily justified especially for H_2O_2, given that PBL heights sometimes changed by a factor of 5 within a period of a photochemical lifetime. To verify the second, vertical profile-measurements would be necessary.

Given the above constraints, the average volumetric fluxes of 3.8×10^4 molecules cm^{-3} s^{-1} and 1.2×10^4 molecules cm^{-3} s^{-1} obtained from the measured H_2O_2 and HCHO fluxes, and the average mixing heights of 250 m and 150 m are consistent with those determined from the PSS model runs. PSS estimates of the volumetric fluxes were 3.2×10^4 molecules cm^{-3} s^{-1} and 4.8×10^4 molecules cm^{-3} s^{-1} for H_2O_2 and HCHO using the measured mixing ratios to constrain the photochemical model, that is when simulating near-surface air rather than the average PBL composition. These values suggest that for the longer-lived H_2O_2 the snow source may dominate the H_2O_2 mixing ratios throughout the PBL and perhaps even affect the lower free troposphere; whereas, the impact of the surface flux from the shorter-lived HCHO would be limited mainly to the lower part of the PBL.

The PSS model results reproduce a strikingly similar pattern as that observed for atmospheric HCHO and OH (Figure 3c, 4b) throughout the campaign, indicating a close photochemical coupling of NO, OH and HCHO. The similar form of the measured and modeled results in Figure 4b suggests that near-surface HCHO is close to PSS, consistent with the above.

Note that while NO-driven photochemistry at SP explains the presence of both HCHO and H_2O_2, it cannot quantitatively explain the elevated levels of HCHO and H_2O_2 or the observed rapid concentration changes. As pointed out by Davis et al (2001, and This Issue) the rapid changes in boundary-layer NO mixing ratios are primarily driven by sudden changes in the mixing depth where the diluting air from the lower free troposphere has a much lower NO mixing ratio, being decoupled from any significant NO_x source. Similarly, HCHO mixing ratios should also decrease during these periods of major air mass exchange, which based on PSS model results should also contain lower OH, and hence, less HCHO. The near simultaneous variations in the levels of HCHO and NO mixing ratios thus support this hypothesis. However, these results do not imply that both species have the same snowpack source.

While all species are affected by changes in boundary layer mixing, they are likely to change by a different amount depending on their respective vertical profiles within the boundary layer and free troposphere as well as on the degree of photochemical processing. This apparently is the case for H_2O_2, which does not follow the same distinct pattern as HCHO and NO. While the H_2O_2 snowpack source tends to increase boundary-layer H_2O_2 during times of lower mixing heights (Hutterli et al., 2001), simultaneously increasing NO and OH levels tend to suppress photochemical production of H_2O_2 and increase its destruction rate, potentially dampening the expected increase.

3.4. Firn Air

Average H_2O_2 and HCHO mixing ratios in the firn air in the top centimeters of the snowpack were 884 pptv (range 375 pptv to 1515 pptv) and 747 pptv (range 425 pptv and 1238 pptv), respectively, and thus 5 to 10 times higher than those in the air above suggesting a net flux out (In all these experiments the sampling hole in the snow was sealed with the Teflon plate.). These observations were recorded on December 18, 19, 20 and 23 and covered a total of 23.5 hours. As expected, firn air values that were obtained by automatically moving the air intake into the uncovered hole in the snow resulted in much lower elevated values (H_2O_2: by ~10%, HCHO: by ~65%) due to the strong dilution of the sampled firn air with ambient air from above. In analogy to the calculations above, fluxes across the snow-air interface can be estimated based on the corresponding gradients between the firn air and the boundary layer. Vertical transport in the firn air in the top centimeters of snowpacks can be significantly increased at high wind speeds due to forced ventilation induced by pressure difference across sustrugis (Albert, 2002). Wind speeds during the firn air measurements were generally 4 m s^{-1} and always lower than 5 m s^{-1}. Reported velocity magnitudes of forced vertical air movement in the top centimeters of a snowpack at those wind speeds are of the order of 0.2 mm s^{-1} at SP (McConnell et al., 1998) and 1 mm s^{-1} at Siple Dome (Albert, 2002). This is less than 10% of the typical displacement of 10 mm s^{-1} for a HCHO or H_2O_2 molecule due to molecular diffusion in the porous firn (Hutterli et al., 2002b). Transport in the firn air during the firn air experiments is thus assumed to have been diffusion dominated. Using effective molecular diffusivities (1.9×10^{-5} m^2 s^{-1} at an atmospheric pressure of 690 mbar, -30°C, and a snow density of 350 kg m^{-3}) results in HCHO fluxes out of the snow between 7.5×10^{11} molecules m^{-2} s^{-1} and 3.0×10^{12} molecules m^{-2} s^{-1} with an average of $(1.5\pm0.7)\times10^{12}$ molecules m^{-2} s^{-1}. For H_2O_2 the corresponding fluxes are 3.6×10^{11} molecules m^{-2} s^{-1} and 4.3×10^{12} molecules m^{-2} s^{-1} with an average of $(1.4\pm1.0)\times10^{12}$ molecules m^{-2} s^{-1} (effective diffusivity of 1.7×10^{-5} m^2 s^{-1}). While only the firn-air measurements during which the hole was sealed were used, even in this case the sampled firn air is possibly diluted by atmospheric air that is drawn into the snowpack from above due to the porous nature of the firn. Thus these flux estimates should be considered as lower limits and true values could be several times higher. It is also important to note that the depth at which the firn air measurements were done (~10 cm) corresponded to snowlayers with relatively high HCHO but very low H_2O_2 content (Figures 5, 6). This most likely explains why the H_2O_2 flux is significantly underestimated, while the HCHO flux is similar to that determined with the gradient measurements.

Intermittent shading of the snow around the air intake for up to 90 minutes on three separate occasions on December 18 resulted in an ~15% drop in the HCHO firn air mixing ratio, whereas there was no consistent response detected in H_2O_2. The temperature of the shaded surface snow was consistently ~1˚C cooler than the nearby sunlit surface snow (in both cases the temperature probe was shaded to minimize measurement artifacts). Not only the snow surface, but also snowlayers in the top few tens of centimeters of the snowpack are expected to have cooled down during the shading (Colbeck, 1989) and at least part of the observed HCHO drop in the firn air might be attributed to less efficient thermal release. These results suggest that the net effect from photochemical formation (Sumner et al., 2002) and photochemical destruction of HCHO in the firn contributed less than 15% to the total flux observed at SP. Clearly, more elaborate and comprehensive measurements are needed to substantiate the latter. It is interesting to note that in order to maintain the measured H_2O_2 and HCHO fluxes out of the snowpack and assuming they originate in the top 20 cm of the snowpack, sources corresponding to a volumetric flux on the order of 1×10^7 molecules cm^{-3} s^{-1} are necessary. This is about 1000 times higher than the corresponding photochemical gas-phase production of H_2O_2 and more than 50 times higher than that for HCHO.

3.5. Snow

A few hours after the formation of the fog event on December 12 at ~8:30 P.M., H_2O_2 and HCHO concentrations in frost collected on clean Teflon tubing were 721 ppbw and 22.1 ppbw and about 2 and 20 times higher than surface snow concentrations, respectively. This supports previous results emphasizing the potential importance of fog deposition in replenishing surface snow and depleting the PBL (Bergin et al., 1994; Hutterli et al., 2001). About ten hours later, new frost samples contained 480 ppbw H_2O_2 and 12.2 ppbw HCHO, consistent with the lower atmospheric mixing ratios than earlier, however, they still contained much more than surface snow. H_2O_2 concentrations in the top meter of four snow pits sampled within 15 km of SP station all revealed seasonal cycles with maxima in summer and minima in winter layers (Figure 5) consistent with previous measurements (McConnell et al, 1998). However, the spatial variability as displayed by the differences among the various H_2O_2 profiles is much higher than the one seen in the HCHO profiles (Figure 5). The latter all show a distinct maximum in the last winter snow layers with constant values below, also confirming previous results (Hutterli et al., 2002a). While the H_2O_2 profile measured at the air intake adjacent to the ARO building was similar to the other profiles, the corresponding HCHO profile revealed concentrations in the deeper layers that were about double those in the other profiles. This is likely because of the disturbed snow accumulation patterns close to the ARO building. However, the top 50 cm of ARO pit profile was not significantly different from the other pit profiles suggesting that during the campaign the measured H_2O_2 and HCHO fluxes from the snowpack were representative for a large area around SP station.

HCHO concentrations in shallow pits of the top ~20 cm sampled within a meter of the air intake at three different times during the campaign decreased to about 40% within 16 days (Figure 6). The decrease from December 7th to 18th corresponds to a HCHO flux from the snow of 3.5×10^{12} molecules m^{-2} s^{-1} and the one from December 18th to 22nd to 4.0×10^{12} molecules m^{-2} s^{-1}. The temporal evolution of the HCHO air-snow exchange was simulated using the physically based air-snow transfer model described by (Hutterli et al., 2002a) using the measured air temperatures, measured atmospheric HCHO mixing ratios and the laboratory-determined air-ice equilibrium partitioning coefficient for HCHO (Burkhart et al., 2002). Starting with the measured HCHO snow concentrations from December 7 for the initial profile resulted in an average HCHO flux of 2.9×10^{12} molecules m^{-2} s^{-1} (range 1.3×10^{12} molecules m^{-2} s^{-1} to 4.3×10^{12} molecules m^{-2} s^{-1}) until December 23. The corresponding modeled average firn air mixing ratio at 10 cm depth was 741 pptv (range 503 pptv to 1036 pptv) in excellent agreement with the measurements.

H_2O_2 increased in the top 10 cm between December 7th and 18th. As there was no large fresh snow event during this period, the increase was most probably caused by accumulation of drifting snow on December 8 when wind speed exceeded 7 m s^{-1} and/or was due to inherent spatial variability. From December 18th to 22nd H_2O_2 concentrations in the top 20 cm decreased by 10%, corresponding to a H_2O_2 flux into the atmosphere of 7.6×10^{13} molecules m^{-2} s^{-1}. Because individual snow layers were not closely monitored related flux calculations are subject to considerable uncertainties. This is especially true for H_2O_2, where the spatial variability in the profiles can easily outweigh their temporal change over the time period investigated. However, within this limitation, these flux estimates are consistent with the other flux measurements. The air-snow exchange of H_2O_2 is most clearly visible in the unique time series of weekly surface snow samples collected at SP between November 1994 and December 2001 (Figure 7). The samples consist on average of only the top 0.055 g cm^{-2} water. Previous air-snow interaction modeling nicely reproduced the evolution of the H_2O_2 concentrations on a two-year subset of the data (see McConnell et al., 1998 also for experimental and modeling details). It implied that the distinct H_2O_2 increase in spring is due to efficient uptake by the cold snow of the H_2O_2 that starts to build up photochemically in the overlying boundary layer. The subsequent spring/summer H_2O_2 decrease and the associated release into the PBL, which is consistent with the flux measurements, is explained by increasing snow temperatures outplaying the simultaneously increasing PBL H_2O_2. Similarly the model also captured the smaller fall peak. The simulations assumed that the surface snow is entirely comprised of old snow and not affected by fresh snow or drifting snow events. The repeatability of the surface snow concentrations in the extended record as well as the lack of evidence of a sudden increase in fresh snow fall in October and November confirm the validity of those assumptions. The relatively low H_2O_2 content of the surface snow during the time of the field campaign suggest that the fluxes would be higher from mid November to early December.

4. Conclusions

The first HCHO gas-phase measurements at SP revealed elevated levels with respect to expected PSS calculations. This was to an even larger degree the case for atmospheric H_2O_2 mixing ratios. The measurements in all three compartments (air, firn air, and snow) confirmed that, like snowpacks in the Arctic, the snow at SP is also a strong source of H_2O_2 and HCHO in summer. The release of both species has a significant impact on the PBL photochemistry at SP. The agreement among the various independent flux estimates in the different compartments indicates that the net fluxes are dominated by physical, temperature-driven air-snow exchange.

For HCHO this is further supported by previous and new physically based air-snow transfer model results that reproduce average flux, firn air mixing ratios and snow profiles. While a proposed heterogeneous HCHO source cannot be excluded, the shading experiments suggest that the potential net contribution from photochemistry to the total flux was less than 15%.

The PSS calculations illustrate that the impact of the snowpack on the SP PBL photochemistry is smaller for HCHO than for H_2O_2 due its smaller flux and shorter photochemical lifetime. However, the available evidence also suggests that PBL photochemistry cannot be adequately described in many cases without invoking snowpack sources of HCHO and H_2O_2. The rapid concentration changes in HCHO and the close correlation with NO indicate that any understanding of the levels of this species at SP also requires a careful consideration of dynamical processes. Simultaneous measurements of vertical profiles of H_2O_2, HCHO and other key species extending into the free troposphere are needed to verify the estimated profiles and to quantify the interaction between the snowpack and the free troposphere, specifically for the longer-lived H_2O_2.

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Figure Captions

Figure 1. H_2O_2 and HCHO mixing ratios and gradients.

Figure 2. Distributions of H_2O_2 and HCHO gradients and corresponding calculated fluxes.

Figure 3. a,b) Measured and modeled H_2O_2 and HCHO mixing ratios. c) Measured NO mixing ratios and OH concentrations (Mauldin et al., Davis et al., this issue). In the unconstrained simulations, neither H_2O_2 nor HCHO were constrained by measurements, for the constrained H_2O_2 results, HCHO was constrained while H_2O_2 wasn't and for the constrained HCHO results vice versa. In all model simulations OH, NO, O_3, CO, H_2O, j-values, temperature, and pressure were constrained by measurements.

Figure 4. Comparison of measured versus modeled relationships between NO and H_2O_2 and HCHO, respectively.

Figure 5. H_2O_2 and HCHO concentrations in various snowpits at (ARO) or near South Pole. The pit names E30, B14 and B8 correspond to stake locations in the long-term accumulation array maintained by the Ohio State University (Mosley-Thompson et al., 1999) and the pits were located, 15km, 7km and 4km away from the station within or along the border of the clean air sector (for comparison: the sites correspond to the drilling locations of the shallow cores C, D and E, respectively, which were analyzed for H_2O_2 and HCHO the year before (Hutterli et al., 2002a)).

Figure 6. Temporal evolution of H_2O_2 and HCHO concentrations in near-surface snow at the air-sampling site.

Figure 7. Surface snow concentrations of H_2O_2 at SP from November 1994 to December 2001. Error bars show one standard deviation in replicate samples. Highlighted are the measurements from October to December 2000, the year and season corresponding to the field campaign. The multi-year average concentrations are also shown.

Tables

Table 1. Comparison of measurements with photostationary state modeling [a]

	H_2O_2			HCHO		
Case	pptv	%	%	pptv	%	%
Measured (1 m height)	262	100.0	121.9	110	100.0	118.5
Estimated PBL average [b]	215	82.1	100.0	93	84.5	100.0
Unconstrained with dry deposition [c]	4	1.5	1.9	38	34.5	41.0
Unconstrained without dry deposition [c]	55	21.0	25.5	73	66.4	78.1
Constrained with dry deposition [c]	6	2.3	2.6	43	39.1	45.9
Constrained without dry deposition [c]	66	25.2	30.7	81	73.6	87.6

[a]Averages of the 217 10-minute values for which OH, NO, HCHO, H_2O_2, CO, O_3 measurements were simultaneously available are reported. [b] HCHO: estimated mean of the lower 150 m, see text. [c] 'Unconstrained' and 'constrained' refers to whether H_2O_2 or HCHO measurements were used to constrain the model when calculating the PSS-values of other species. In all model simulations OH, NO, O_3, CO, H_2O, j-values, temperature, and pressure were constrained by measurements. Dry deposition was either turned on or off for both H_2O_2 and HCHO.

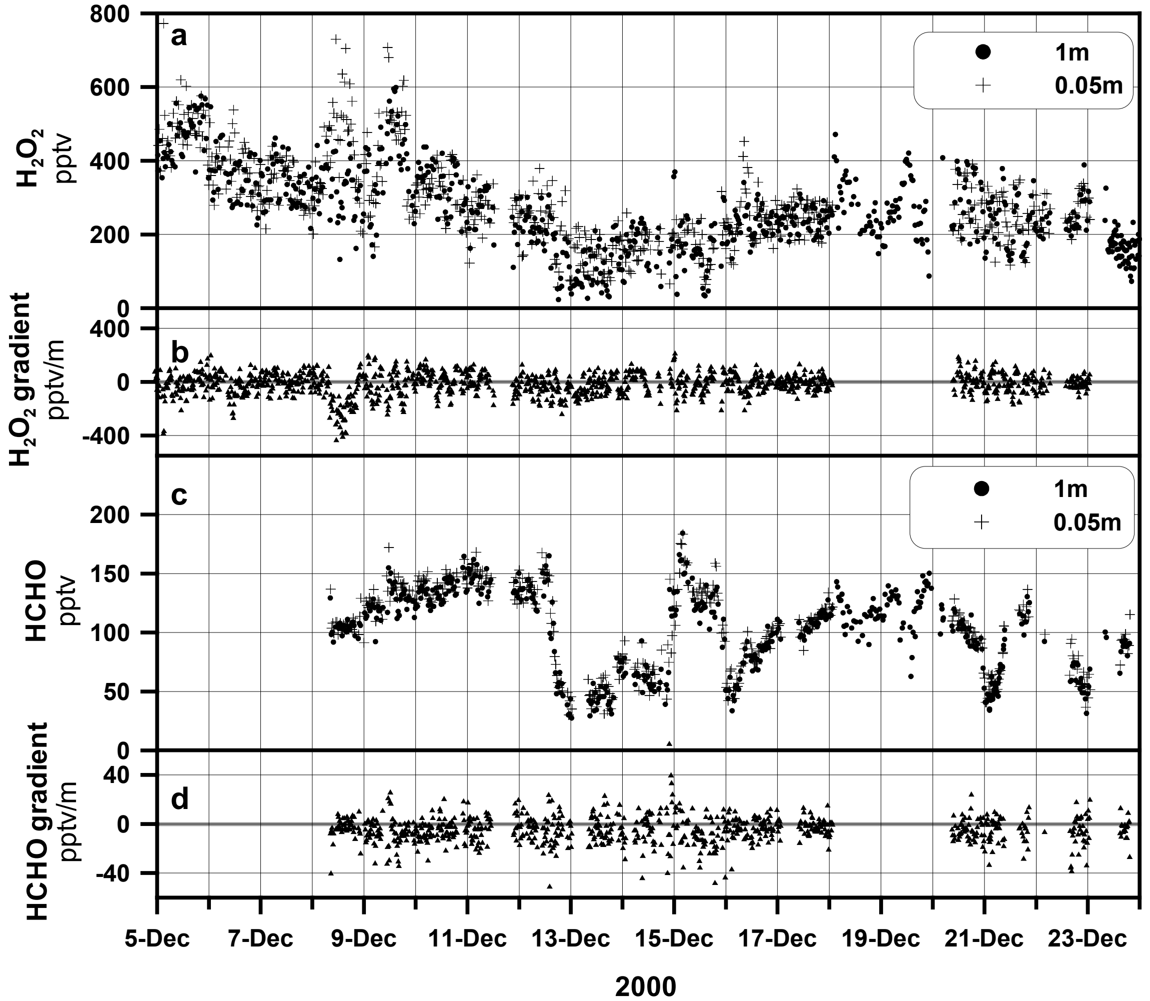


Figure 1.

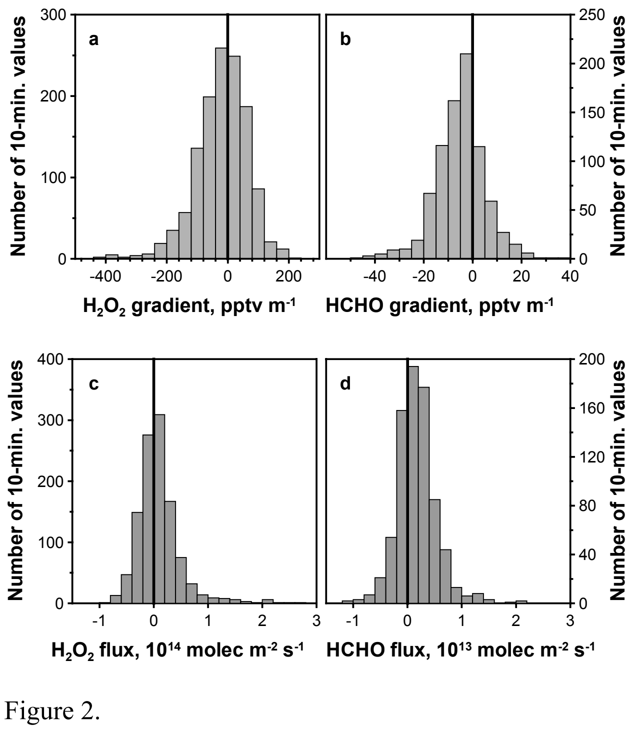


Figure 2.

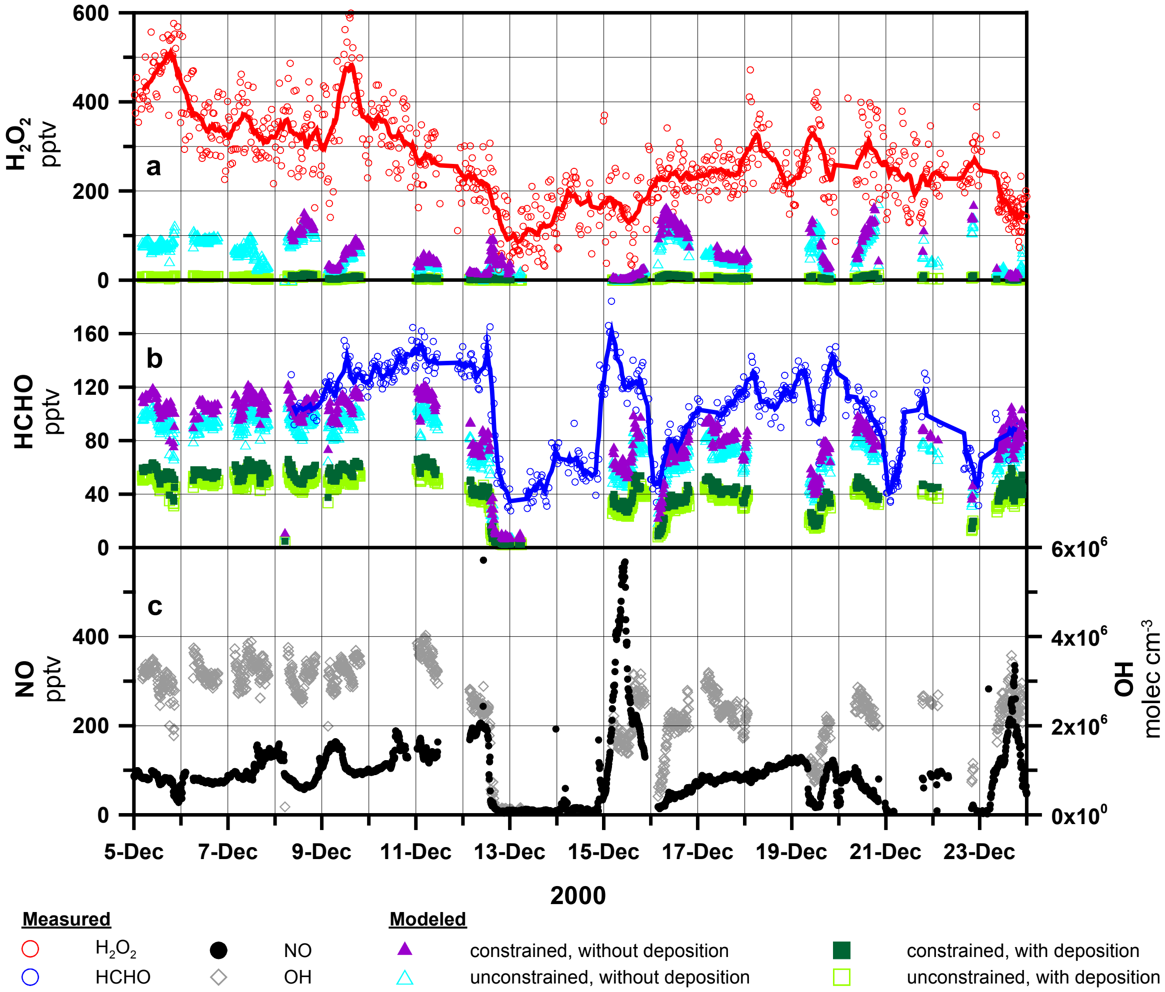
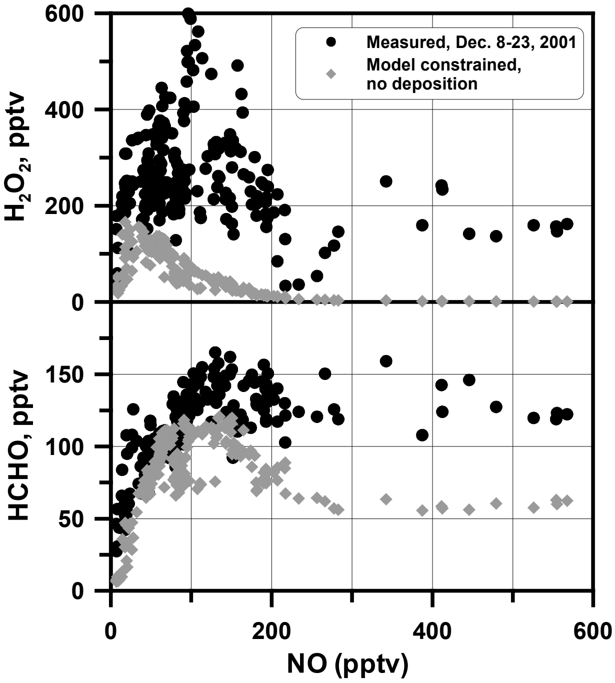


Figure 3.



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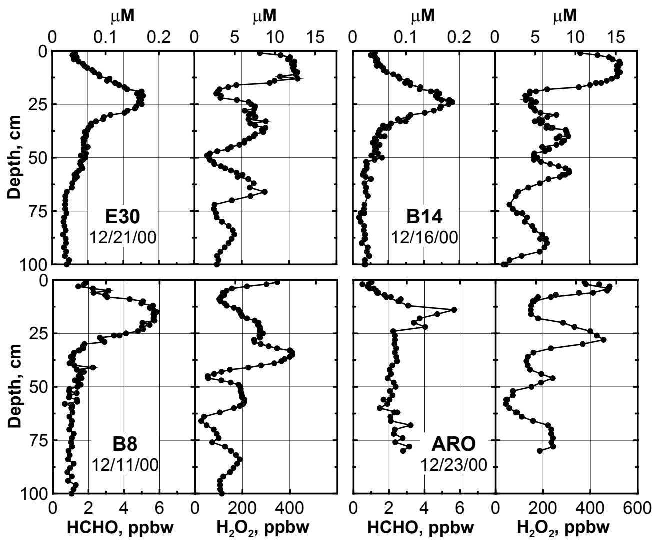

Figure 5.

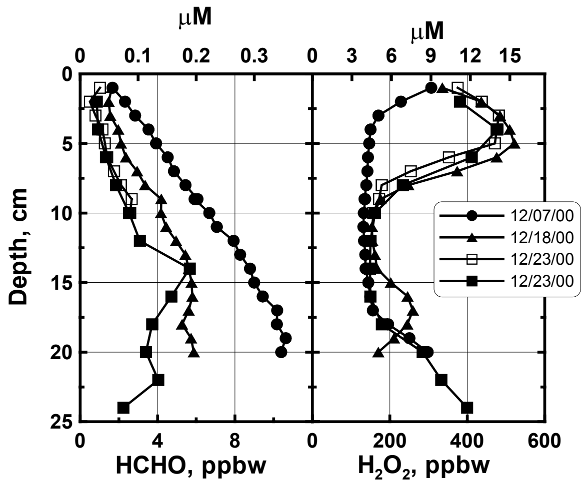

Figure 6.

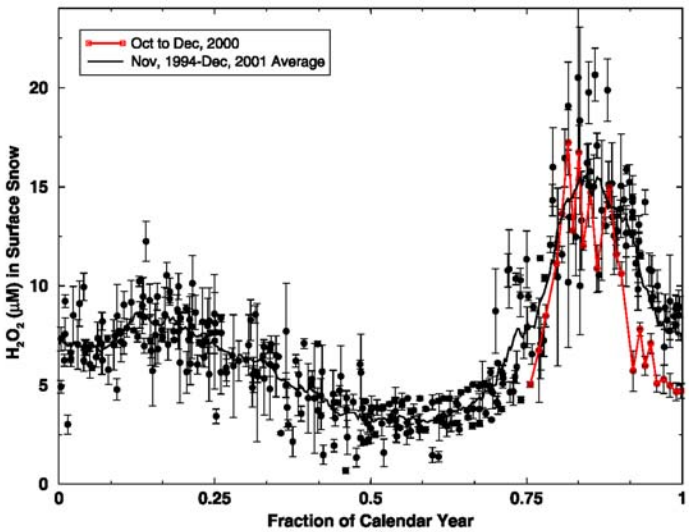

Figure 7.