

Diel variations of H₂O₂ in Greenland: A discussion of the cause and effect relationship

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Abstract. Atmospheric hydrogen peroxide (H₂O₂) measurements at Summit, Greenland, in May–June, 1993 exhibited a diel variation, with afternoon highs typically 1–2 parts per billion by volume (ppbv) and nighttime lows about 0.5 ppbv lower. This variation closely followed that for temperature; specific humidity exhibited the same general trend. During a 17-day snowfall-free period, surface snow was accumulating H₂O₂, apparently from nighttime cocondensation of H₂O and H₂O₂. Previous photochemical modeling (Neftel et al., 1995) suggests that daytime H₂O₂ should be about 1 ppbv, significantly lower than our measured values. Previous equilibrium partitioning measurements between ice and gas phase (Conklin et al., 1993) suggest that air in equilibrium with H₂O₂ concentrations measured in surface snow (15–18 μM) should have an H₂O₂ concentration 2–3 times what we measured 0.2–3.5 m above the snow surface. A simple eddy diffusion model, with vertical eddy diffusion coefficients calculated from balloon soundings, suggested that atmospheric H₂O₂ concentrations should be affected by any H₂O₂ degassed from surface snow. However, field measurements showed the absence of either high concentrations of H₂O₂ or a measurable concentration gradient between inlets 0.2 and 3 m above the snow. A surface resistance to degassing, that is, slow release of H₂O₂ from the ice matrix, is a plausible explanation for the differences between observations and modeled atmospheric profiles. Degassing of H₂O₂ at a rate below our detection limit would still influence measured atmospheric concentrations and help explain the difference between measurements and photochemical modeling. The cumulative evidence suggests that surface snow adjusts slowly to drops in atmospheric H₂O₂ concentration, over timescales of at least weeks. The H₂O₂ losses previously observed in pits sampled over more than 1 year are thought to have occurred later in the summer or fall, after the May–July field season.

Introduction

Hydrogen peroxide (H₂O₂) archived in polar ice cores offers the potential to help constrain model estimates of atmospheric hydroxyl radical (OH) concentrations in the past. Recent attempts to use the H₂O₂ records in

ice cores have assumed that concentrations found in the ice are related to those in the atmosphere at the time of deposition [Sigg and Neftel, 1991; Thompson et al., 1993] by a linear function that is constant over time. However, the atmosphere snow “transfer function” is neither constant over time nor linear; it depends on processes controlling H₂O₂ deposition, on postdepositional air–snow exchange, and possibly on chemical reactions in buried snow/firn/ice [Neftel et al., 1995].

The first continuous H₂O₂ gas phase observations at Summit, Greenland, were made by Sigg et al. [1992] in summer, 1990. They showed surprisingly high gas phase concentrations during midday, which were more than double the concentrations predicted from photochemical model calculations [Neftel et al., 1995]. In addition, a strong diel variation was apparent, with the lowest values from midnight to early morning. Sigg et al. [1992] suggested that the polar snow surface acts as a temporary storage for H₂O₂ at night. Neftel et al. [1995] also suggested that degassing of H₂O₂ from the snowpack could explain the discrepancy between the measured and predicted gas phase concentrations.

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The purpose of the work reported here was to test the hypothesis that on a daily basis, the surface snow is a temporary storage reservoir for H₂O₂, and that surface snow readily exchanges H₂O₂ with the atmosphere. We report experimental and monitoring results from field work at Summit, Greenland, during summer, 1993.

Methods

These studies were carried out at the Greenland Ice Sheet Project 2 (GISP2) camp at Summit, Greenland (72° 58' N, 38° 46' W), in May through July of 1993. (Note that at the summer solstice, solar zenith angles range from 50° at noon to 83° at midnight.) We measured H₂O₂ in the air at 0.2, 3, and 3.5 m above the snow and in surface snow. Because of logistical constraints, experimental investigations of the transfer function at most polar sites are currently possible only during summer months. Therefore responses of the snowpack to atmospheric concentrations could be observed over only a very limited range of atmospheric concentrations and for short times.

The atmospheric H₂O₂ detector involved drawing sample air and pumping H₂O₂-free water into a coil scrubber, where all of the H₂O₂ was transferred from the air to the water; the H₂O₂ content of the water was then analyzed using a peroxidase method [Sigg *et al.*, 1992]. Tubing and parts in contact with H₂O₂ containing fluids were perfluoroalkoxy (PFA) teflon or glass, plus a short length of peristaltic pump tubing that was tygon. Inlet lines were 8-mm ID PFA teflon. The detector automatically switched between H₂O₂-free air and sample air on a cycle of 6 to 20 min.

During most of the sampling period, one atmospheric detector system was located in a heated canvas laboratory building, with the sampling line extending outside to a height of 1 m above the building (3.5 m above snow surface). Line losses in this system (~3.5 m length) were estimated to be insignificant, based on a one-time measurement of a gas calibration source near the end of the sampling period. We also checked for line losses earlier by comparing measurements with and without the sampling tube; differences were insignificant. On a few of the days we moved the system outside to make side-by-side comparisons with a second system that was in a heated box located 100 m from the laboratory. The second system drew air through inlet tubes at 0.2 and 3 m sequentially during each cycle. Line losses in the second system were estimated to be 20–30%, based on three calibration measurements.

Micrometeorological data were taken from an automatic weather station [Stearns *et al.*, 1993], located approximately 500 m from the building and H₂O₂ sampling site (GISP2 AWS). Air temperature was measured at 0.2 and 1.8 m above the snow, and relative humidity, air pressure, wind direction, and wind speed were measured at 2 m above the snow surface. Because of instrument problems, relative humidity data were taken from a second micrometeorological station, which was located at the atmospheric sampling camp

30 km south of the GISP2 camp (Kenton AWS). Other measurements taken at both stations matched well.

Daily surface snow samples were collected at the atmospheric sampling camp; collection time depended on the availability of personnel. Five replicates were taken from the entire surface snow layer, defined by visual observation of grains and layering. The still-frozen samples were brought to the GISP2 camp, melted, and analyzed as soon as possible after melting; usually within 1 hour. Analyses were done on an instrument with the same design as used for the atmospheric measurements; the air pump was shut off and liquid samples were injected directly at the outlet of the coil (beginning of the liquid sampling loop). Aliquots were refrozen and analyzed in our laboratory in Tucson 3 months later, with comparable results. This lack of H₂O₂ loss is in contrast to sample handling methods used on other studies, where losses during transport were observed (unpublished data).

We collected depth samples of the top surface of the snow near the GISP2 camp by sequentially scraping a few tenths of a millimeter of water equivalent (few millimeters of snow) from a 10 × 10 cm area of the snow surface into a sampling container. Depths sampled were estimated from sample weights. Samples were generally melted and analyzed within 1 to 3 hours after collection. These are referred to as micropits.

Fog and fresh snow samples were collected on polyethylene trays set on poles 1 m above the snow. Trays were about 150 m upwind from the GISP2 drilling dome. Fog or snow was allowed to accumulate overnight and scraped into bottles at about 0630–0700 UT. Sample handling and analysis were as for the surface snow samples.

A balloon was used to make soundings of atmospheric pressure, wind speed and temperature at least twice daily, up to a height of 700–800 m.

Results

To evaluate H₂O₂ exchange between surface snow and the atmosphere, we focus on the first 17 days, when there were no major storms. Regular balloon soundings were made during these days as well. Hourly means of H₂O₂ measured in the atmosphere during summer 1993 are displayed in Figure 1a. They show a similar pattern as that reported by Sigg *et al.* [1992], with daytime highs generally between 1.0 and 2.0 parts per billion by volume (ppbv) and nighttime minima about 0.5 ppbv lower. H₂O₂ in surface snow showed a small but statistically significant increase over this 17-day period, from 15 to 18 μM (Figure 1b). The average daily increase and standard error were 0.18 ± 0.05 μM.

The diel variation in H₂O₂ was found to closely follow that for temperature (c.f. Figure 1a versus 1c). Relative humidity reflected a daytime low of 10–20%, and a nighttime high of 60–80% (data not shown). Diel changes in specific humidity were also apparent, and followed a diel cycle (Figure 1d). Values reached a maximum late in the evening and a minimum during the late morning hours.

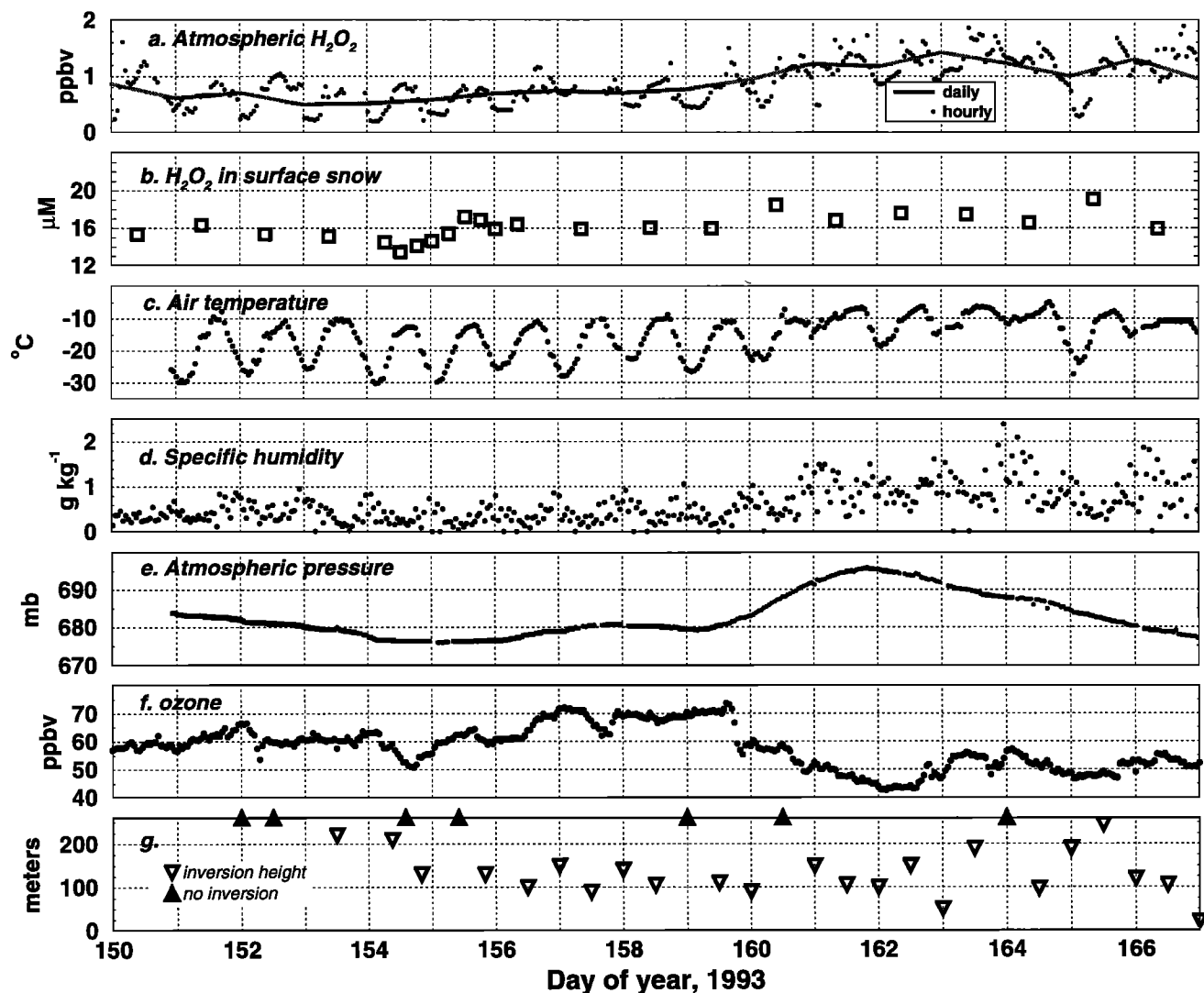


Figure 1. Hourly atmospheric and surface snow data. (a) H₂O₂ in the atmosphere at GISP2 camp. Points are hourly averages of two detectors for days 154–167, and a single detector for days 150–154. (b) H₂O₂ in the surface snow layer, from samples collected at the atmospheric sampling camp. (c) Air temperature measured at GISP2 automatic weather station (AWS). (d) Specific humidity, based on temperature and pressure from the GISP2 AWS, and relative humidity from the atmospheric camp (Kenton AWS). (e) Air pressure from GISP2 AWS. (f) Hourly ozone concentrations. (g) Inversion height from balloon soundings at GISP2. Day of year 150 was May 30.

A linear regression of H₂O₂ concentration as a function of temperature for the 17-day period shown on Figure 1 gave a standard error of 0.203; the standard error was 10% lower (0.183) with atmospheric pressure and specific humidity as additional dependent variables (Figure 2). Average H₂O₂ concentration for the period was 1.0 ± 0.4 ppbv, average temperature was -16°C , and average specific humidity was 0.6 ± 0.4 g kg⁻¹ (\pm standard deviation). For the period after day 167, the correlations were not as good, probably due to the highly variable weather and frequent snowfall (R. Bales, unpublished data, 1994). However, the daily trend in atmospheric H₂O₂, both for the period shown and later days, did closely follow changes in air pressure (Figure 1e), suggesting that shifts in sources of air masses were

important. Winds were out of the south (southeast to southwest) for the entire period (data not shown). Applying the same regression to the only previous continuous H₂O₂ data for Summit, the 1990 data of Sigg *et al.* [1992] and the Kenton AWS data, gave similar results (Figure 3). That is, atmospheric H₂O₂ variations closely followed changes in air temperature, specific humidity, and pressure.

During the 17-day period in 1993, the inversion height varied from 20 to 240 m, with an average of 150 m (excluding seven soundings with no inversion) (Figure 1g). The atmosphere below the inversion height on average contained about $4.2 \mu\text{mol m}^{-2}$ of H₂O₂ (at 1.0 ppbv). The average surface snow H₂O₂ concentration for the same period was $16.3 \mu\text{M}$, or $16.3 \mu\text{mol m}^{-2} \text{mm}^{-1}$.

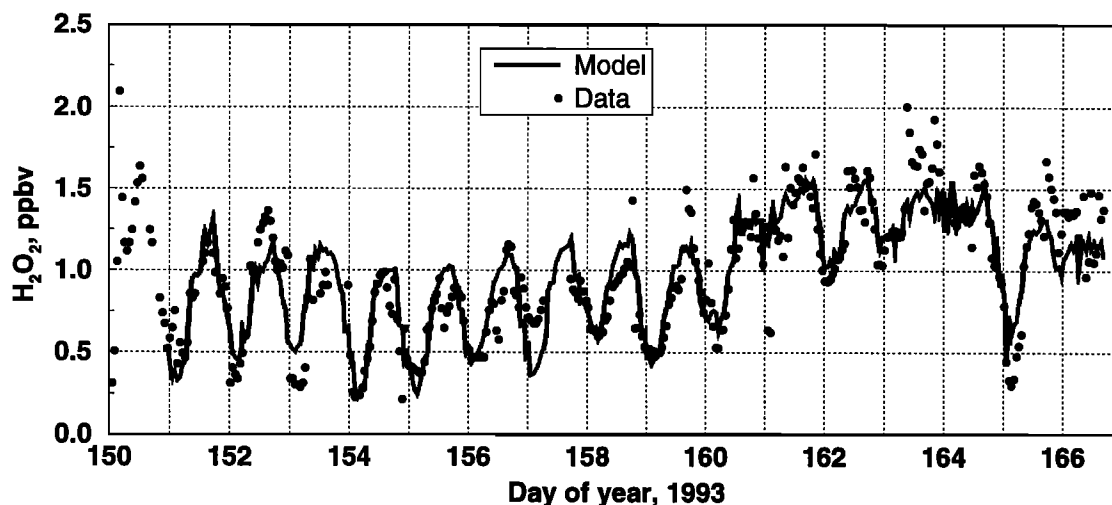


Figure 2. Correlation of H₂O₂ in the atmosphere with micrometeorological data for 17-day period shown on Figure 1.

Thus the top 0.26 mm of water equivalence (~ 2.6 mm snow) contained as much H₂O₂ as the entire atmosphere below the average inversion height.

The average amount of water contained in the atmosphere below the inversion height was 82 g m^{-2} for the period, or 0.082 mm. Thus a day-to-night change in specific humidity of only 50%, typical for the period, represents the top 0.04 mm of water (~ 0.4 mm snow). From visual observations of the surface snow each morning, it was apparent that there was hoar and/or rime deposition nearly every night. Further, there was fog

deposition in the night and early morning of days 154 and 160 (equivalent to 0.097- and 0.194-mm water, respectively).

Micropits showed that maximum H₂O₂ concentrations were at the top with lower concentrations below the surface snow. That is, the gradient of H₂O₂ was into, rather than out of the snow (Figure 4). There was a remarkable consistency among surface samples taken at different times with little temporal variation. We attribute differences between sample collections at different times to spatial variability rather than to changes

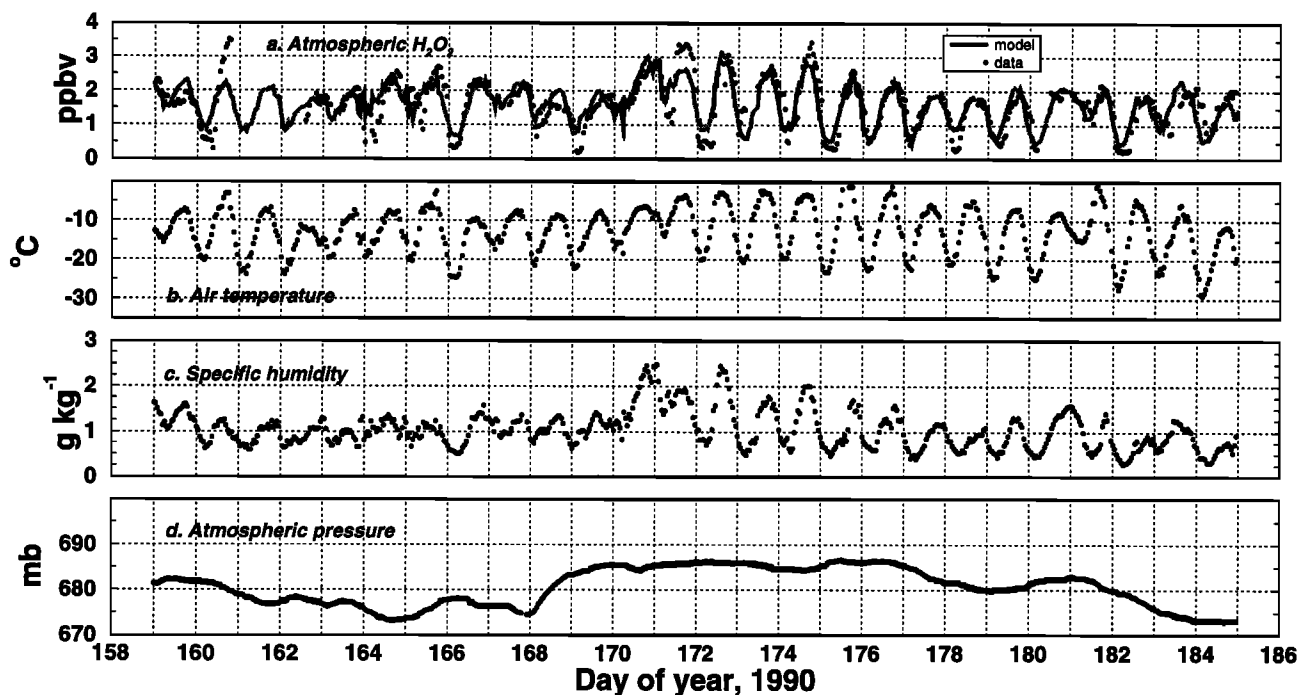


Figure 3. Hourly atmospheric data for 1990. (a) Hourly averages of H₂O₂ data from Sigg *et al.* [1992] as well as regression of H₂O₂ concentration with micrometeorological data. (b) Air temperature measured at Kenton AWS. (c) Specific humidity, based on temperature, pressure, and relative humidity at Kenton. (d) Air pressure from Kenton.

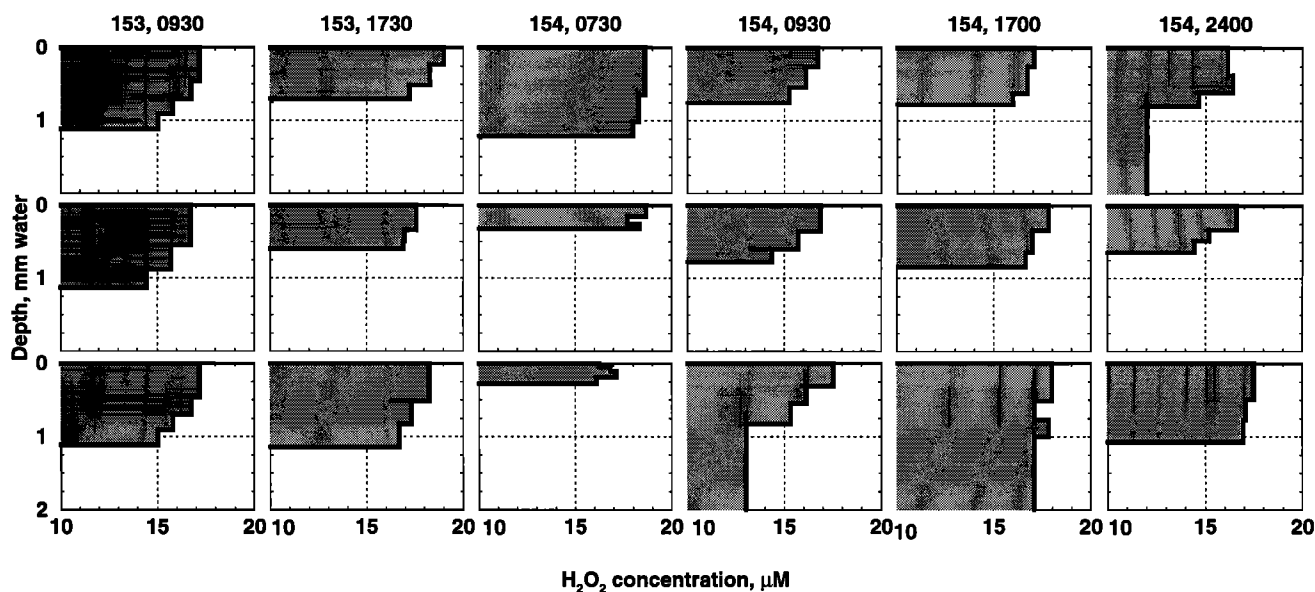


Figure 4. H₂O₂ in a series of replicate micropits during a period without snowfall or significant wind redistribution of surface snow. Day and time sampled are indicated.

in the surface snow. Micropit H₂O₂ concentrations were within a few percent of surface layer H₂O₂ concentrations shown on Figure 1b.

Wind data from 0.25- and 3.0-m heights at Summit were used to infer the aerodynamic roughness length z_0 and friction velocity u_* . The wind data consisted of scalar-averaged measurements of wind velocity over 15-min time intervals. The roughness length was computed from:

$$\ln(z_0) = \frac{u_2 \ln(z_1) - u_1 \ln(z_2)}{u_2 - u_1} \quad (1)$$

where z_1 and z_2 are the measurement heights of 0.25 and 3.0 m, and u_1 and u_2 are the respective wind measurements. This definition follows from the well-known logarithmic wind profile equation

$$u_i = u_* \kappa^{-1} \ln \frac{z_i}{z_0} \quad (2)$$

where κ is the von Karman constant, taken to be 0.4. The logarithmically averaged estimate of the roughness length for the 17-day period was 2×10^{-3} m, which compares favorably with the published values of z_0 for fresh snow of $\leq 10^{-3}$ m [Lettau, 1969; McRae et al., 1982]. The arithmetic mean was 10^{-2} m, with a variance of 6×10^{-4} m². Our data were insufficient to estimate a displacement height, inclusion of which should give a lower z_0 estimate.

Using the individual roughness length estimates for each 15-min interval (recognizing that surface snow conditions at Summit can change significantly from day-to-day), the friction velocity for each interval was computed. The average friction velocity estimate for the 20-day period was 0.35 m sec^{-1} and the variance $0.011 \text{ m}^2 \text{ s}^{-2}$.

In rough flow regimes, the laminar sublayer is nonexistent or negligible, while in smooth flow regimes the laminar sublayer is proportional to $\frac{\nu}{u_*}$, where ν is the kinematic viscosity and is equal to $0.14 \text{ cm}^2 \text{ sec}^{-1}$. The conditions for rough and smooth flow regimes have been experimentally determined to be [Seinfeld, 1986]:

$$\begin{array}{ll} \text{smooth flow regime} & \frac{u_* z_0}{\nu} < 0.13 \\ \text{rough flow regime} & \frac{u_* z_0}{\nu} > 2.5 \end{array} \quad (3)$$

Using these criteria, the 15-min data were classified into smooth and rough flow regimes. Ninety-seven percent of the samples were classified as rough, while less than 1% were classified as smooth. While our data were insufficient to estimate effects of atmospheric stability, we did the same classification assuming z_0 is 10% of those estimated from (1). In that case, 58% were classified as rough, with less than 1% classified as smooth. This analysis suggests that for most of the 17-day interval, there was little or no laminar sublayer present at Summit.

From an analysis of the vertical soundings we also calculated turbulent exchange coefficients for the atmosphere (K_{zz}) and used them to calculate concentration profiles in the atmosphere:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial C}{\partial z} \right) \quad (4)$$

Values ranged from less than 10^{-2} to $1.0 \text{ m}^2 \text{ s}^{-1}$ a few meters above the snow and generally increased with height (Figure 5). We calculated vertical profiles of H₂O₂ for the range of K_{zz} and inversion heights en-

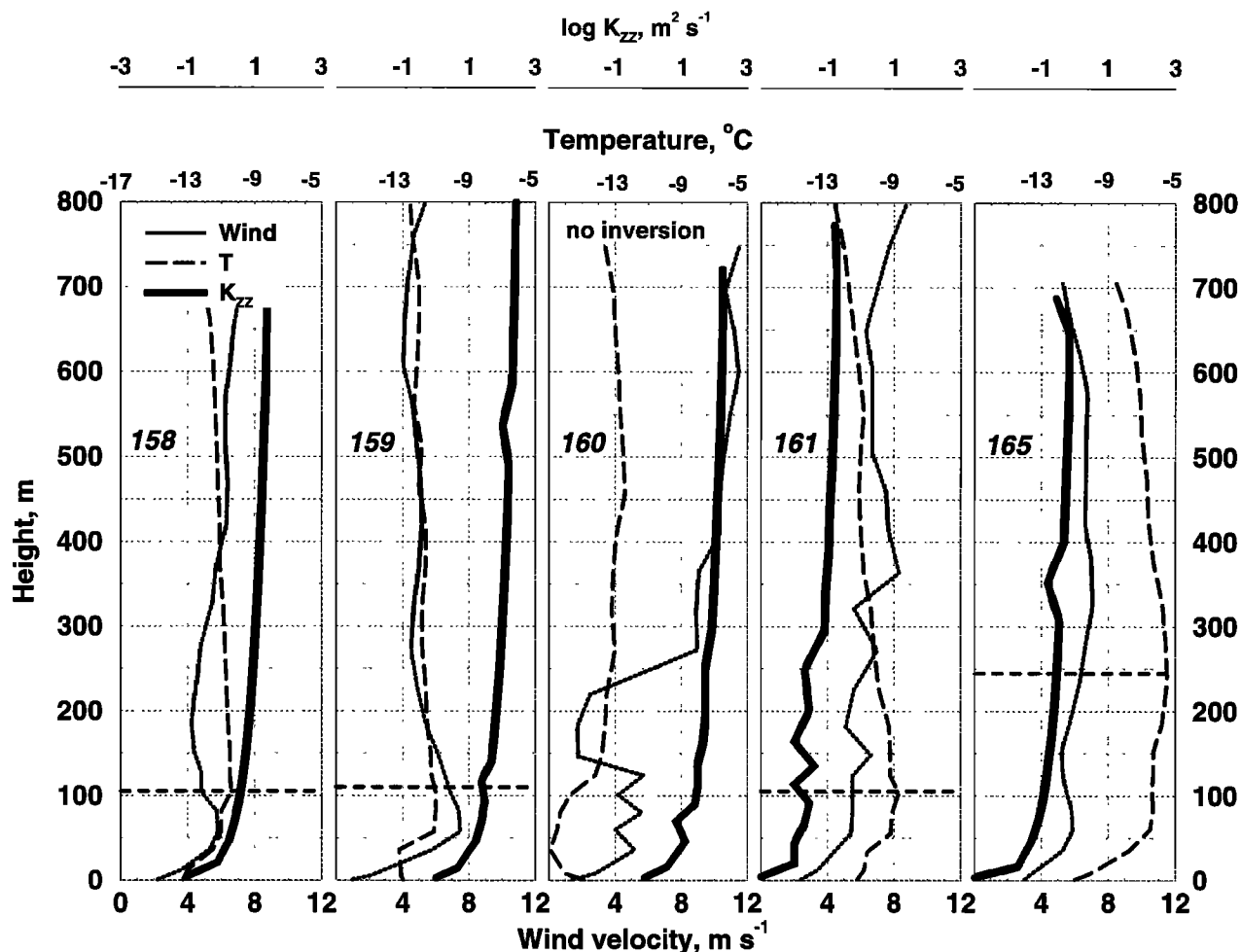


Figure 5. Temperature, inversion height (horizontal dashed line), wind velocity and K_{zz} from five typical balloon soundings at 1100 UT on the day of year indicated.

countered using (4). For this analysis we assumed an H₂O₂ concentration of 1 ppbv from homogeneous photochemical sources [Neftel *et al.*, 1995], and a boundary condition of 3.6 ppbv at the top of the snowpack. This is an assumed boundary condition, based on the gas phase H₂O₂ concentration in equilibrium with the surface snow [Conklin *et al.*, 1993]. In three of the profiles, days 158, 159, and 160, H₂O₂ rapidly mixed throughout the atmosphere below the inversion. K_{zz} values on these days were 0.1–1 m² s⁻¹ at a height of 4 m, up to 5–30 m² s⁻¹ at a height of 110 m. Two of these 3 days had medium inversion heights, while there was no inversion on day 160. On days 161 and 165, inversion heights were medium and high, respectively, but K_{zz} values were less than 0.3 m² s⁻¹ throughout the height below the inversion. On these days, the modeled H₂O₂ atmospheric profiles failed to reach steady state after 12 hours of degassing, and the H₂O₂ concentrations in the atmosphere were calculated to be well below those at the boundary (Figure 6). A second set of profiles was calculated using 2.0 ppbv as the boundary condition, which gave atmospheric values nearer those reported on Figure 1a, and gradients on the order of 0.1 μg m⁻⁴.

Discussion

The nighttime decrease in atmospheric H₂O₂, which followed temperature and humidity (Figures 1 and 3), can be explained by cocondensation of water molecules and H₂O₂ on the surface snow. Water was being deposited at night, and cocondensation of H₂O and H₂O₂ occurs. Even if cocondensation was not stoichiometric, H₂O₂ would still be removed by codeposition of H₂O₂ and H₂O molecules. Release of H₂O₂ did not necessarily follow coevaporation. On some days the morning increase in atmospheric H₂O₂ followed temperature more than specific humidity, suggesting that adsorption rather than absorption controlled short-term retention of H₂O₂ in the snow. But on other days, especially in the 1990 record, it closely follows specific humidity. Adsorbed H₂O₂ should desorb in response to a temperature increase, whereas absorbed H₂O₂ should be released with sublimation of water. It thus appears that both processes were important.

The H₂O₂ concentration in surface snow increased during the period shown on Figure 1, however. This suggests that net uptake was not restricted to a pure ad-

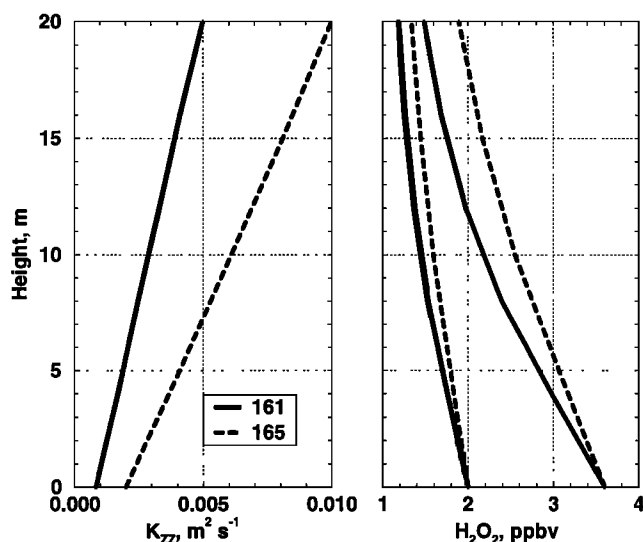


Figure 6. Calculated K_{zz} and H_2O_2 profiles for the lower 10 m of the atmosphere, for the conditions shown on Figure 5.

sorption/desorption at the surface, but that uptake/release of the bulk phase was involved. This was apparently the case for laboratory experiments reported previously [Conklin *et al.*, 1993]. Alternatively, the deposition could reflect deposition of diamond dust (clear sky precipitation) or light fog. The micropit profiles support this second explanation.

Whether or not the discrepancy between gas phase concentrations predicted from photochemical modeling [Nefstel *et al.*, 1995] and measured values can be explained by a degassing of H_2O_2 from the surface snow depends on the resistance to transport away from the surface of the snow. Only a small exhalation, of the order of 2 to 20 $ng\ m^{-2}\ s^{-1}$, is needed to approximately double the amount of H_2O_2 in the air below the inversion. Expected H_2O_2 gradients near the surface are of the order of 0.1 $\mu g\ m^{-4}$ (Figure 6). The atmospheric measurement system that we were using in 1993 was sufficiently sensitive to detect a difference of 0.15 ppbv ($\sim 0.15\ \mu g\ m^{-4}$). So over the 2.8-m distance we could have detected a gradient of this magnitude if it were present ($\sim 0.3\ \mu g\ m^{-4}$). Failure to detect an H_2O_2 concentration gradient above the snow is not necessarily in contradiction with this simple model, which assumed unchanging atmosphere and snow conditions over the day. Slow degassing of H_2O_2 from snow, kinetically controlled by release of H_2O_2 from the snow grains, could also be important.

H_2O_2 concentrations measured on all days were also below that predicted from equilibrium partitioning [Conklin *et al.*, 1993]. From this observation it can be inferred that either degassing in the field was kinetically limited, the equilibrium concentration was below that found in laboratory studies, or both. The fact that the concentration in the surface snow increased roughly in parallel with the atmospheric concentration argues against significant degassing. However, additions to the snow at night could well exceed degassing during

the day, because of codeposition at night. Because the H_2O_2 mass in surface snow is so much larger than that in the atmosphere below the inversion layer, degassing could cause a large increase in the atmospheric concentration but no detectable change in surface snow.

It could be speculated that the additional H_2O_2 originated from snow layers beneath the surface. This seems unlikely in view of the decreasing temperature with increasing depth in the summer snow, and the concentration gradients shown on Figure 4. Laboratory studies have shown that below about $-10^\circ C$, the partitioning of H_2O_2 from air to snow surfaces increases drastically as temperature decreases [Conklin *et al.*, 1993]. High frequency pressure pumping, known to disrupt the thermal regime in snowpacks [Albert and McGilvary, 1992], enhances ventilation of subsurface snow and could contribute to degassing of H_2O_2 . Pressure pumping was shown to enhance the flux of CO_2 from soil, through a seasonal snowpack, to the atmosphere by 18–34% [Massman *et al.*, 1995]; however, our H_2O_2 fluxes and gradients in snow/firn [Bales *et al.*, 1995] are much lower than CO_2 fluxes and gradients in seasonal snowpacks [Sommerfeld *et al.*, 1993].

The variations in daytime H_2O_2 concentration highs were most likely related to changing air mass origin and the passage of frontal systems. Note that the daily average H_2O_2 on Figure 1a generally follows that for atmospheric pressure (Figure 1e). Over the entire 40-day sampling period a linear regression of H_2O_2 concentration versus pressure gave a relatively good fit; the standard error was 0.3965. Ozone concentration, measured with a detector (Dashibi) located in the same canvas laboratory building as the first H_2O_2 detector, showed a drop from 65 ppbv on days 158–159, to 40 ppbv on days 161–162, and then a small rise in concentration (Figure 1f).

Conclusions

Our measurements showed that degassing of H_2O_2 from the snow surface was slow, and thus may not be a plausible explanation for the measured atmospheric values exceeding those estimated from model calculations. Lower measured versus predicted equilibrium H_2O_2 concentration just above the snow surface, and low H_2O_2 in firn gas [Bales *et al.*, 1995] both indicate that H_2O_2 is released slowly from the snow, if at all. Because surface snow contains so much more H_2O_2 than the atmosphere below the atmospheric inversion height, however, even a slow degassing would increase atmospheric concentrations. During the period analyzed, surface snow was accumulating H_2O_2 , even in the absence of snowfall, apparently from cocondensation of H_2O and H_2O_2 . Previous studies have reported H_2O_2 losses in pits sampled over more than 1 year. Our current work suggests that these losses must have occurred later in the summer or fall, after the May–July field season. The cumulative evidence suggests that surface snow adjusts slowly to drops in atmospheric H_2O_2 concentration, over time scales of at least weeks.

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