Physically based inversion of surface snow concentrations of H$_2$O$_2$ to atmospheric concentrations at South Pole

Joseph R. McConnell, James R. Winterle, Roger C. Bales
Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona

Anne M. Thompson, Richard W. Stewart
NASA Goddard Space Flight Center, Laboratory for Atmospheres, Greenbelt, MD

Abstract. Inversion of chemical records archived in ice cores to atmospheric concentrations requires a detailed understanding of atmosphere-to-snow-to-ice transfer processes. A unique year-round series of surface snow samples, collected from November, 1994 through January, 1996 at South Pole and analyzed for H$_2$O$_2$, were used to test a physically based model for the atmosphere-to-snow component of the overall transfer function. A comparison of photochemical model estimates of atmospheric H$_2$O$_2$, which are in general agreement with the first measurements of atmospheric H$_2$O$_2$ at South Pole, with the inverted atmospheric record (1) demonstrate that the surface snow acts as an excellent archive of atmospheric H$_2$O$_2$ and (2) suggest that snow temperature is the dominant factor determining atmosphere-to-snow transfer at South Pole. The estimated annual cycle in atmospheric H$_2$O$_2$ concentration is approximately symmetric about the summer solstice, with a peak value of ~280 pptv and a minimum around the winter solstice of ~1 pptv, although some asymmetry results from the springtime stratospheric ozone hole over Antarctica.

Introduction

Ice cores provide a detailed record of past changes in atmospheric chemistry and meteorology. Chemical species are incorporated into snow and thence into the atmosphere through wet and dry deposition. Most aerosols are irreversibly deposited, meaning they are not emitted back to the atmosphere after deposition. More-volatile species such as hydrogen peroxide (H$_2$O$_2$), formaldehyde, and organic acids are reversibly incorporated in the snow. Some fraction of the deposited mass of these species returns to the atmosphere as precipitation ages and as surface and near-surface conditions change.

Quantitative interpretation of an ice core record requires detailed knowledge of the transfer processes that relate local atmospheric concentrations of chemical species to those found in snow, firm, and ice [Neffeltel, 1996]. This is particularly important for reversibly deposited species since post-deposition processes may play a more important role in determining the ice-core concentration than do depositional fluxes. H$_2$O$_2$, which shows strong post-deposition modification, is a good model for other reversibly deposited chemical species [Bales and Wolff, 1995]. A mathematical description of these transfer processes, referred to as the transport function, can be formulated in the forward sense that describes how H$_2$O$_2$ in air is incorporated into snow and firm. In an example of a forward model, McConnell et al. [1996b] developed an empirical, lumped-parameter model to simulate H$_2$O$_2$ concentrations in a snow pit given photochemical modeled estimates of the atmospheric concentration of H$_2$O$_2$ and a priori knowledge of the timing of snow accumulation from automatic depth gauges. Simulations were compared to observed profiles to define model parameters. The interpretation of the ice core record, however, requires inverse modeling, where ice core concentrations are inverted to an estimate of the atmospheric concentration. Non-linearities in the time-depth relationship and the convolution of those transfer processes active at the surface (e.g., partitioning between snow and air, post-depositional exchange with the atmosphere) with those active beneath the snow surface (e.g., diminished exchange during burial, redistribution of H$_2$O$_2$ by vapor phase diffusion in the snow pack) hamper inversion of ice core records.

In this study, we estimated year-round atmospheric concentrations of H$_2$O$_2$ at South Pole using a quantitative, physically based inversion of concentrations in snow samples. To test the inverse model, we used a unique, 14-month long series of surface snow samples, thereby avoiding both the non-linearities associated with the time-depth relationship in firm and the transfer processes active beneath the surface. We compared these inverted atmospheric concentrations with the first measurements of atmospheric H$_2$O$_2$ at South Pole and with steady-state photochemical model predictions.

Methods

Surface snow samples were collected by NOAA winter-overs staff in the Clean Air Sector at South Pole on approximately a weekly basis from November, 1994 through January, 1996. To mitigate spatial variability, each sample consisted of six surface snow scrapes with an average water-equivalent depth of 0.5 g cm$^{-2}$. The surface scrapes were aliquoted individually at South Pole and analyzed for H$_2$O$_2$ at our lab in Arizona. Continuous, short-term measurements of atmospheric H$_2$O$_2$ were made in November/December, 1994 and in Jan-
nary, 1996 at South Pole using a gas-phase detector [Bales et al., 1995a].

Model

The amount of H$_2$O$_2$ incorporated into precipitation is thought to be strongly temperature dependent and determined by co-deposition of water and H$_2$O$_2$ in proportion to their gas phase concentrations. Snow on the ground releases H$_2$O$_2$ since concentrations from co-deposition are supersaturated with respect to the solid phase [Bales et al., 1995]. The ice-air equilibrium relation, also a strong function of temperature (Figure 1), was confirmed by objective optimization of a lumped parameter model of the transfer function for H$_2$O$_2$ using snow-pit data in Greenland [McConnell et al., 1996b]. The time required to reach equilibrium in the solid phase is relatively long and surface conditions like temperature and atmospheric concentration of H$_2$O$_2$ change quickly, so the equilibrium concentration target is likely to be changing faster than the snow's ability to adapt. The result is a surface snow concentration that is essentially always out of equilibrium. This snow is eventually buried and cut off from contact with the atmosphere and so preserved in some state of disequilibrium, depending on how long it has remained at the surface after original precipitation, how quickly the snow can release or take up H$_2$O$_2$, how quickly surface conditions are changing, how quickly the snow is buried and the level of ventilation. Note that recent high-resolution snow pit data from South Pole [McConnell et al., 1996a] do not show any consistent loss of H$_2$O$_2$ after burial.

In laboratory experiments, the rate of H$_2$O$_2$ degassing from firn was found to be adequately described by a spherical diffusion model of individual snow grains within the firn:

\[
\frac{\partial C_r}{\partial t} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C_r}{\partial r} \right]
\]  

(1)

where $C_r$ is the local H$_2$O$_2$ concentration at any point in the ice sphere and $D_i$ is the diffusion coefficient in ice [Winter, 1996]. We use this spherical diffusion model with a strongly temperature-dependent $D_i$ (derived from independent laboratory experiments) to define a physically based snow response function to simulate how snow will uptake or release H$_2$O$_2$ as environmental conditions change.

The simulated response of snow to changes in temperature is given in Figure 2. For a temperature increase from -40 to -30 °C (Figure 2a), it takes nearly 15 weeks for the initial 20 µM snow concentration to approach the new 6 µM equilibrium. When the temperature is changed back to -40 °C, equilibrium at the original concentration is achieved after 20 weeks. In the second simulation (Figure 2b), the temperature is raised from -40 to -20 °C. The new equilibrium concentration of 2 µM is approached after only about 6 weeks because of the higher diffusion coefficient at this warmer temperature.

Year-around, monthly accumulation data from South Pole suggest that an individual surface snow sample is predominately "old" snow [McConnell et al., 1996a], meaning that snow found at the surface precipitated some months prior to sampling and has been in contact with the atmosphere for that time. The histogram of the gross monthly accumulation recorded at fifty accumulation stakes for the period September, 1988 through January, 1996 shows a distinct mode around zero (Figure 3).

From the cumulative distribution function, the relative probability that the surface elevation has changed by less than 2.5 cm in a month is about 50%. If the surface elevation has changed, it is likely that the added accumulation is "old" surface snow that has been redistributed by wind. We make the simplifying assumption that surface snow samples are composed of "old" snow. Hence, post-depositional processes at the surface dominate precipitation processes and H$_2$O$_2$ at South Pole is treated as a completely reversibly deposited chemical species.

We hypothesize that changes in surface snow concentrations are driven primarily by changes in surface temperature and atmospheric H$_2$O$_2$. Using the temperature-dependent spherical diffusion model and the computed skin temperature, the snow's response to changes in environmental conditions over the elapsed time between surface sampling is simulated to give $R_T$, the fraction of total equilibrium change in concentration.
achieved after some elapsed time. In Figure 2, $R_f$ starts at zero when the temperature is first changed from -40 °C to -30 °C, increases exponentially and approaches 1.0 after about 15 weeks. The equilibrium snow concentration is computed as:

$$S_{eq}(t) = \frac{S_{obs}(t-1) - S_{obs}(t)}{R_f}$$

(2)

where $S_{eq}$ is the equilibrium concentration (μM) of H$_2$O$_2$ and $S_{obs}$ is the observed concentration. With the temperature and the equilibrium snow concentration known, the atmospheric concentration is readily derived from the snow-atmosphere partitioning relationship ($K_D$) (Figure 1).

**Results**

Surface snow concentrations showed a pronounced, repeatable seasonal cycle with a maximum of (~22 μM) in early to mid-November, well before the summer solstice, and a broad minimum of (~2 μM) near the winter solstice (Figure 4). Spatial variability in surface concentration is generally far lower than temporal variability. Continuous atmospheric H$_2$O$_2$ measurements, presented as weekly averages (Figure 5), were 200-250 pptv in Nov/Dec, 1994 and 90-100 pptv in Jan, 1996. No diel cycle in atmospheric concentration was seen.

**Atmospheric Photochemical Model Estimates**

Steady-state photochemical model predictions at seven discrete times during the sunlit time of year were used to define a representative annual cycle in atmospheric H$_2$O$_2$ (Figure 5a). We used a photochemical box model that included a subset of the chemical reactions described in Stewart and Thompson [1996]. Annual cycles for air temperature, pressure, relative humidity, actinic flux, carbon monoxide (CO), and surface ozone (O$_3$) were taken from multi-year averages of measurements at South Pole. To our knowledge, no measurements of nitrogen oxide (NO) have been made so a concentration of 1 pptv was used throughout the year. In the model, O$_3$, CO, and NO were fixed and incident UV radiation computed using the latitude, time of year, and stratospheric ozone burden. Since H$_2$O$_2$ concentration is highly sensitive to actinic flux and water vapor, the error bars on Figure 5a represent the expected range due to short-term variations in the most sensitive input variables.

Because measured relative humidity was significantly higher around the 1995 summer solstice than around the 1994 solstice, the measured relative humidity without multi-year averaging was used to model atmospheric H$_2$O$_2$ for comparison to the snow inversion model results (Figure 5b).

**Inversion Model Results**

A parameter search was conducted to estimate the snow-atmosphere partitioning relationship ($K_D$). Using that reported by Conklin et al. [1993] resulted in atmospheric concentrations far higher than both observations and those predicted by the photochemical model. By comparing the estimate of the atmospheric concentration derived through surface snow inversion with that predicted by photochemical modeling, optimum parameters describing a quadratic shape of $K_D$ relationship with temperature were determined. Note that the entire 14 month surface snow record was used to define that 3 parameters in the $K_D$ relationship with temperature. The optimized annual atmospheric H$_2$O$_2$ cycle was inverted from the snow concentrations shown on Figure 4 using a $K_D$ double that given by Conklin et al. [1993] (Figure 1) and an effective snow grain radius of 70μm [Harder et al., 1996] (Figure 5b).

**Discussion**

The estimated annual atmospheric concentration cycle derived through inversion of the surface snow samples (Figure 5) is periodic and in good agreement with both photochemical model estimates and direct atmo-
spheric measurements made in late November and early December, 1994, although not with similar measurements made in January, 1996. During the latter period, there was significant local pollution from construction at the new Clean Air Facility at South Pole which may have reduced the measured levels of H$_2$O$_2$ somewhat. In addition, a constant NO concentration was used throughout the year in the photochemical modeling. Higher NO levels later in the summer would decrease the atmospheric H$_2$O$_2$ concentrations at that time, bringing the photochemical model and measurements into closer agreement. Atmospheric H$_2$O$_2$ levels are strongly sensitive to water vapor mixing ratio and actinic flux. Both are strongly seasonal at South Pole and the former is approximately symmetric about the summer solstice while the latter is, at present, asymmetric because of the springtime stratospheric ozone hole. The photochemical model and surface snow inversion estimates suggest that a sharp, approximately symmetric peak in the atmospheric H$_2$O$_2$ concentration (~280 pptv) occurs one to two weeks before the summer solstice while concentrations are very low (~1 pptv) throughout much of the winter.

The equilibrium snow-atmosphere partitioning relationship indicated in this study is greater than that previously reported from laboratory experiments. It should be noted, however, that only two individual laboratory experiments [Conklin et al., 1993] were made at the very cold temperatures generally found at South Pole, primarily because response of the snow is so slow as to require experiments of very long duration. Hence, the laboratory-based equilibrium partitioning relationship is essentially an extrapolation from much warmer temperatures (~30°C and ~8°C). In addition, reinterpration of the Conklin et al. [1993] data and incorporation of new laboratory data suggests that $K_D$ is probably higher than previously thought [Winterle, 1996].

While the surface-snow concentration cycle is clearly not symmetric about the solstice, the estimated atmospheric cycle is approximately so, demonstrating that the bulk of this asymmetry about the solstice is due to the very strong temperature dependence in the uptake capacity of H$_2$O$_2$ in snow. That is, the asymmetry in surface snow concentration is caused by the highly nonlinear, temperature dependent transfer function acting on a nearly symmetric atmospheric concentration, centered a few days to weeks before the solstice, and a symmetric surface temperature cycle that is centered about 10 days after the solstice.

Conclusions

By comparing direct short term measurements and photochemical model predictions with estimates of the annual atmospheric H$_2$O$_2$ concentration cycle that result from physically based inversion of surface snow sample concentrations, we conclude that surface snow acts as an excellent proxy for the annual atmospheric cycle. While this inversion of surface snow H$_2$O$_2$ concentrations to an estimate of atmospheric loading is an important step toward the objective of inverting snow-pit and ice-core records into a long-term, interannual evaluation of atmospheric H$_2$O$_2$ concentrations, it should be emphasized that transfer processes active beneath the surface have not been addressed here. To accomplish such an inversion will require a detailed understanding of the timing of accumulation at the core location and exchange between atmosphere and snow during burial. With no diel cycle, a long-duration, year-around instrumental record of atmospheric chemistry and meteorology, and year-round access by winter-over personnel, South Pole is an ideal location for the study of atmosphere-to-snow transfer processes.

Acknowledgments. This work was supported by a NASA Graduate Fellowship for Global Change and in part by National Science Foundation's Office of Polar Program. Atmospheric photochemical modeling at NASA was supported by the Goddard Director's Discretionary Fund. Field work at South Pole was conducted under a cooperative agreement with the NOAA Climate Monitoring and Diagnostics Laboratory. We very much appreciate the help of K. McNitt and R. Ramos of NOAA/CMDL for their help in collecting samples at South Pole throughout the year and S. Oltmans and P. Novell for access to the surface ozone and carbon monoxide data respectively.

References


J. R. McConnell, J. R. Winterle, and R. C. Bales, Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona, USA. (e-mail: jmc@hrw.arizona.edu; jimw@hrw.arizona.edu; roger@hrw.arizona.edu)

A. M. Thompson and R. W. Stewart, NASA Goddard Space Flight Center, Laboratory for Atmospheres, Greenbelt, MD, USA. (e-mail: thompson@gator1.gsfc.nasa.gov; stewart@oasis.gsfc.nasa.gov)

(Received October 22, 1996; revised January 13, 1997; accepted January 14, 1997.)