

Understanding the drivers for the 20th century change of hydrogen peroxide in Antarctic ice-cores

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[1] Observations and model simulations of an Antarctic ice-core record of hydrogen peroxide during the last ~150 years are analyzed. The observations indicate a relative increase in hydrogen peroxide by approximately 50% since 1900, with most of the change since the early 1970s. Using two model simulations spanning 1850 to present, we show that the modeled relative change in annual-mean surface hydrogen peroxide parallels the equivalent signal from the ice core record. In addition, we show that this relative change can be explained by the relative changes in tropospheric ozone concentration and mostly in ozone photolysis rates ($J(O^1D)$). The simulated signal is therefore intimately related to the changes in stratospheric ozone associated with increases in chlorofluorocarbons; this is further demonstrated using total ozone column observations and the associated observed change in ice-core hydrogen peroxide. **Citation:** Lamarque, J.-F., J. R. McConnell, D. T. Shindell, J. J. Orlando, and G. S. Tyndall (2011), Understanding the drivers for the 20th century change of hydrogen peroxide in Antarctic ice-cores, *Geophys. Res. Lett.*, 38, L04810, doi:10.1029/2010GL045992.

1. Introduction

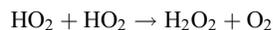
[2] The main production path for hydrogen peroxide (H_2O_2) in the remote atmosphere is the HO_2 self-reaction [Finlayson-Pitts and Pitts, 2000]. Once formed, hydrogen peroxide can be removed from the atmosphere by wet removal (uptake in cloud droplets), dry deposition, photolysis and reaction with OH [Sigg et al., 1992]. As a consequence, the lifetime of hydrogen peroxide ranges from a few hours to days in warm sunlit conditions [Jaegle et al., 2001] to several days during dark winter months [e.g., Snow et al., 2003]. Its presence in polar ice has been detected for over 25 years [Neftel et al., 1984].

[3] Hydrogen peroxide is reversibly deposited to snow, meaning that it continues to exchange between snow and air as environmental conditions change during the early stages of burial [Sigg et al., 1992; McConnell et al., 1998; Frey et al., 2006]. In general, high net snowfall rates and low air temperatures lead to higher preserved concentrations in

ice. In addition to atmospheric concentrations above the deposition site, hydrogen peroxide concentrations measured in ice cores, therefore, are affected by (1) changes in snow temperature because of temperature-dependent air-snow partitioning of hydrogen peroxide, (2) the seasonal timing of net snow accumulation at the site, and (3) the rate of burial (i.e., net annual snowfall), with the latter being the most important factor [McConnell et al., 1998]. More precisely, while photochemical reactions may modify the composition of snow and interstitial air near the surface, the post-depositional impacts on the snow concentrations are minimized at sites with annual accumulation rates higher than the e-folding depth of light penetration (~0.3 m); in that case, surface snow is quickly buried and so removed from solar radiation and chemical exchanges between the snow and overlying atmosphere are limited. Any temporal changes in post-depositional perturbations also are minimized in ice core records collected from sites with relatively constant accumulation rates [McConnell et al., 1998; Frey et al., 2006].

[4] It is also important to recognize that air-snow interactions driven by snowpack photochemistry can significantly perturb the air composition near the surface (<30 m) in the Polar regions, as comprehensively reviewed by Dominé and Shepson [2002] and Grannas et al. [2007]. However, Frey et al. [2006] indicate that H_2O_2 concentrations in fresh snow reflect ratios in clouds, indicating that the influence of boundary-layer chemistry is probably small.

[5] In the Antarctic troposphere, where NO and NO_2 concentrations are low (especially above the shallow boundary-layer but also more generally in the West Antarctic Ice Sheet [Frey et al., 2005], where the cores discussed here originate), the chemical reaction relevant to the production of hydrogen peroxide (H_2O_2) is [Finlayson-Pitts and Pitts, 2000]



indicating that hydrogen peroxide formation depends on the square of the HO_2 concentration. At steady-state, ignoring the contribution of RO_2 , which is significantly smaller than HO_2 in the Southern polar regions [Chen et al., 2001; Mauldin et al., 2004], the concentration of HO_2 can be expressed as [Finlayson-Pitts and Pitts, 2000]

$$[HO_2] \propto \sqrt{\{J(O^1D) \times [O_3]\}} \quad (1)$$

where $J(O^1D)$ is the rate at which ozone is photolyzed and forms an excited oxygen atom (O^1D). Note that, in particular, the potential role for CO in increasing the HO_2/OH ratio is explicitly used in the derivation of equation (1). Such square-root relationships between HO_2 and $J(O^1D)$ have also been

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observationally deduced [Bloss *et al.*, 2007]. Based on this analysis, we can therefore expect that, at steady-state,

$$[\text{H}_2\text{O}_2] \propto J(\text{O}^1\text{D}) \times [\text{O}_3] \quad (2)$$

indicating that hydrogen peroxide is mostly dependent on ozone, since $J(\text{O}^1\text{D})$ is approximately a simple function (power-law) of total ozone column [Madronich and Granier, 1992]. The overall sensitivity of tropospheric hydrogen peroxide to stratospheric ozone has been discussed in previous studies of global chemistry, such as Thompson [1991], Thompson *et al.* [1993] and Fuglested *et al.* [1994]; in addition, its role in the modulation of Arctic [e.g., Anklin and Bales, 1997] and Antarctic hydrogen peroxide has been postulated [e.g., Frey *et al.*, 2005]. Here we extend these analyses beyond the Antarctic ozone-hole period and compare the modeled change to ice-core observations.

[6] In this paper, we use continuous measurements in three recently collected, closely spaced ice cores from the West Antarctic Ice Sheet (WAIS) deep ice core site spanning several centuries to study the change in hydrogen peroxide, with a focus on the change since 1900. This is a relatively cold region (mean annual air temperature is -31°C) with high snowfall rates (>0.6 m of snow year^{-1}) where detailed chemical measurements in these ice cores show that no significant long term changes in snowfall have occurred during the past 200 years. In addition, we use results from simulations spanning 1850–2000 by two chemistry-climate models [Lamarque *et al.*, 2010] to identify the specific role of parameters driving the observed and simulated change in hydrogen peroxide. The paper is organized as follows: in section 2, we describe the ice-core data. Then, in section 3, the model and model simulations are described. The comparison with observations and analysis of the model simulations are done in section 4. Discussion and conclusions are in section 5.

2. Data Description

[7] We have constructed a composite record of annual hydrogen peroxide concentration (Figure 1) by combining measurements from three ice cores recently collected near the WAIS Divide ice core site in the dry snow zone of West Antarctica (79.5°S , 247.8°E). These include the ITASE00_1 core collected in late 1999 [Frey *et al.*, 2006] and the WDC05A and WDC05Q cores collected in 2005 [Banta *et al.*, 2008]. The WDC cores are located within 1 km of each other near the main deep borehole, while the ITASE00_1 core is located ~ 20 km to the northwest. Measurements from the selected ice-cores are very consistent with the high-accumulation sites of Frey *et al.* [2006]. Additional details can be found in the auxiliary material.¹

[8] Mean net snowfall rates from 1900 through 1999 C.E. were 200, 200, and 227 $\text{kg m}^{-2} \text{a}^{-1}$ for WDC05A, WDC06A, and ITASE00_1, respectively. In agreement with accumulation-rate-dependent post-depositional loss of hydrogen peroxide from the snow [McConnell *et al.*, 1998], concentrations at the higher snow accumulation ITASE00_1 site are consistently $\sim 10\%$ higher than in the lower accumulation WDC cores. Annual concentrations of hydrogen

peroxide also vary from core to core because of small differences in the amount and seasonal timing of net snow accumulation that primarily results from wind redistribution ($\sim 15\%$ of the annual average net snowfall at WAIS Divide [Banta *et al.*, 2008]). Despite these short-spatial-scale differences in snow accumulation, correlations between the individual annual hydrogen peroxide records reported here ranged between 0.324 and 0.466 for the 1900 through 1999 period common to all three cores, significant above the 99.9% confidence level [Banta *et al.*, 2008]. To reduce any impact of short-scale depositional differences, we combined the three individual records to obtain a composite, more regionally representative hydrogen peroxide record. Analysis of snowfall in these three ice core records indicates that there has been no significant long term change in snowfall during the past 100 years at WAIS Divide [Banta *et al.*, 2008] so the observed increase of both the individual and regional peroxide concentration profiles between the pre-1960s and the mid-1990s is likely not the result of changes in depositional processes.

3. Model Descriptions and Simulation Setup

[9] Model descriptions are limited to the specifics relevant to this study. In particular, the anthropogenic and biomass burning emissions are from Lamarque *et al.* [2010]. In addition, note that neither model has a representation of the specific polar boundary-layer chemistry related with air-snow exchanges (as discussed in the Introduction). The reader is referred to the auxiliary material for additional information.

3.1. CAM-chem

[10] We use the Community Atmosphere Model (CAM) version 3.5 [Gent *et al.*, 2009] modified to include interactive chemistry to calculate distributions of gases and aerosols. The model configuration used in this study includes a horizontal resolution of 1.9° (latitude) by 2.5° (longitude) and 26 hybrid levels, from the surface to ≈ 40 km with a timestep of 30 minutes; the transient simulation was performed continuously between 1850 and 2009. The chemical mechanism used in this study is formulated to provide an accurate representation of both tropospheric and stratospheric chemistry [Lamarque *et al.*, 2008; Lamarque and Solomon, 2010]. As the model top is ≈ 40 km, only wavelengths greater than 200 nm are considered in photolysis calculations. A flux lookup table (LUT) approach is used [Kinnison *et al.*, 2007], based on the 4-stream version of the Stratosphere, Troposphere, Ultraviolet (STUV) radiative transfer model (S. Madronich, personal communication, 2006). The transmission function is interpolated from the LUT as a function of altitude, overhead ozone column, surface albedo, and zenith angle. The temperature and pressure dependences of the molecular cross sections and quantum yields for each photolytic process are also represented by a LUT in this wavelength region. In all cases, the photolysis computation is performed every timestep (30 minutes) and takes into account the model distribution of ozone and clouds.

[11] In addition, the monthly-mean time-varying observed sea-surface temperatures (SSTs) and sea-ice distributions are taken from a 20th century CCSM-3 simulation [Meehl *et al.*, 2007]; as this simulation only extended from 1870 to present, the sea-surface temperature and ice extent between 1850 and 1870 are assumed to be the same as 1870.

¹Auxiliary materials are available in the HTML. doi:10.1029/2010GL045992.

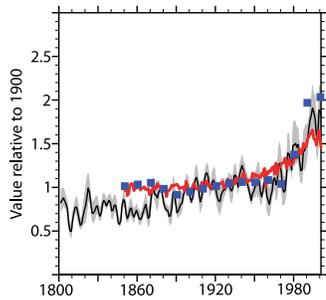


Figure 1. Time evolution of the relative change since 1900 in the observed annual mean H_2O_2 ice core concentration (black line, smoothed with a 3-year running average; grey shading indicates one standard deviation) and in the modeled annual mean H_2O_2 surface concentration (zonally-averaged over 80°S – 90°S) over Antarctica from CAM-chem (red line) and G-PUCCINI (blue squares).

3.2. G-PUCCINI

[12] Simulations were also performed with the Goddard Institute for Space Studies (GISS) model for Physical Understanding of Composition–Climate Interactions and Impacts (G-PUCCINI) [Shindell *et al.*, 2006]. The chemistry model is fully embedded in the GISS modelE climate model [Schmidt *et al.*, 2006]. The model was run at 2° latitude by 2.5° longitude Cartesian horizontal resolution. This configuration had 40 vertical hybrid sigma layers from the surface to 0.01 hPa (≈ 80 km). Time-slice simulations were performed every 20 years during the 1850–1930 period, and every 10 years from 1930–2000. Values during the 1850–1930 period were interpolated to give decadal means. Simulations were carried out for 8 years, with the average of the last 5 used for analysis. The GCM was driven by observed decadal mean sea-surface temperatures and sea-ice distribution [Rayner *et al.*, 2003]. Photolysis rates are calculated online every timestep (20 minutes) using the Fast-J2 scheme [Bian and Prather, 2002]; in particular, this scheme takes into account the model distribution of clouds, aerosols and ozone.

3.3. Surface Concentrations Over Antarctica

[13] As presented by Lamarque *et al.* [2010, see Figure 6], both models have a very realistic representation of surface ozone over the observational record (1970–2000); the only bias is for G-PUCCINI, with an underestimate of surface ozone (by about 4 ppbv) in the 2000 simulation. On the other hand CAM-chem seems to slightly overestimate ozone in the mid-1990s. In addition, analysis of the reconstructed CO change by Assonov *et al.* [2007] indicates an increase of approximately 40% between 1900 and 2000; this is quite well matched by the model results (Figure S2), especially for CAM-chem. Additional discussions on CO are given by Lamarque *et al.* [2010].

4. Analysis

[14] We discuss in this section results from the simulations described in section 3. Additional information on the simulations and associated results are given by Lamarque *et al.* [2010].

[15] As mentioned in section 2, hydrogen peroxide in the ice core is a record of its concentration when deposited at the surface through wet and dry deposition. We make here the assumption that the model representation of hydrogen peroxide in ice cores is proportional to its surface gas-phase concentration over Antarctica. Indeed, observations in the Northern Hemisphere high latitudes [Snow *et al.*, 2007] indicate a fairly small vertical gradient within the first 5–6 kilometers (also true in our model simulations, not shown). Modeled surface (i.e., lowest model layer) hydrogen peroxide is therefore a reasonable proxy for model tropospheric values at the level where its uptake by water (in any phase and subsequent snow/ice fall) or dry deposition occurs. Note that neither model has a representation of the snow and ice surface processes that can affect hydrogen peroxide concentrations [e.g., Hutterli *et al.*, 2001] in the deposited snow. As a consequence, it might be difficult to directly compare observed concentrations of hydrogen peroxide with modeled surface values. Instead, since hydrogen peroxide concentration over the Antarctic region is expected to be proportional to ozone (local and total column, equation (2)), we can expect observations and model simulations to exhibit similar relative changes.

[16] Therefore, we present in the subsequent analysis the various data (ice-core and modeled surface hydrogen peroxide) relative to their 1900–1909 values (Figure 1); note that the results shown in Figure 1 are from the full model simulations, not the application of equation (2). This period is chosen as no information on biomass burning emissions (the only emissions that are significantly changing in the Southern Hemisphere) before 1900 is available [Lamarque

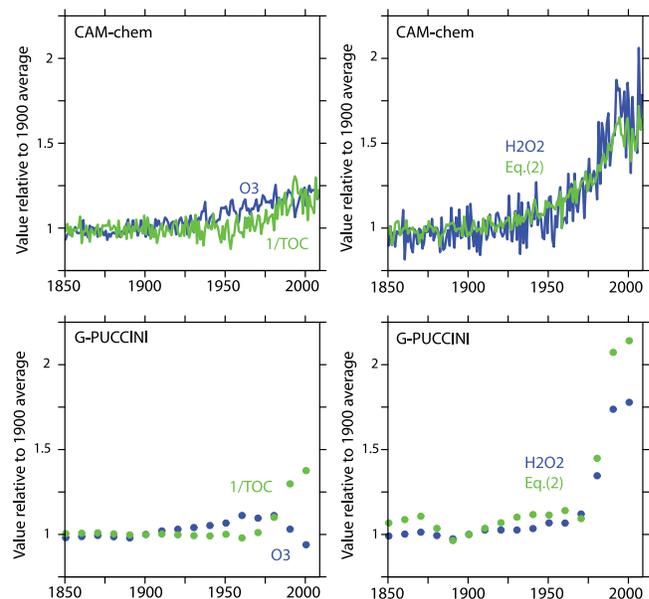


Figure 2. (top left) Time evolution of the relative change since 1900 in modeled annual mean surface O_3 (blue line) and the inverse of the total ozone column (1/TOC, green line) for the CAM-chem simulation. (top right) Time evolution of the relative change since 1900 in CAM-chem modeled annual mean H_2O_2 (blue line) and in the right-hand side of equation (2) (green line). (bottom) Same as Figure 2 (top) but for the G-PUCCINI simulation.

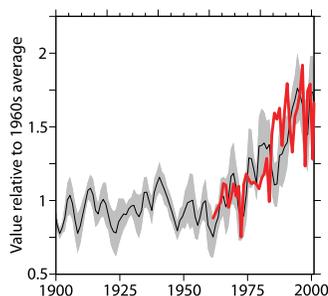


Figure 3. Time evolution of the relative change since the 1960s in the observed annual mean H_2O_2 ice core concentration (black line, smoothed with a 3-year running average; grey shading indicates one standard deviation); red line is the observed inverse of total ozone column squared. See text for details.

et al., 2010], meaning that the model simulations of H_2O_2 prior to 1900 could be affected by this simplification. Furthermore, this averaging period exhibits fairly constant values of ice-core hydrogen peroxide. Using this relative measure, we find that both model simulations (surface hydrogen peroxide concentration, annually-averaged over Antarctica to match the observational record) provide a reasonable representation of the long-term change in hydrogen peroxide (Figure 1) since 1900. In particular, we find that observations and simulations indicate a rapid rise starting in the 1970s.

[17] Following equation (2), we construct the timeseries of the relative change in surface ozone and in $J(\text{O}^1\text{D})$ from the simulations. As model results are not available for this latter quantity, we use instead total ozone column (TOC) inverse squared [Madronich and Granier, 1992]). The combination (as in equation (2)) of those relative changes for each model indicates a very good agreement with their respective change in simulated H_2O_2 (Figure 2); this comparison indicates therefore that equation (2) is a realistic representation of the H_2O_2 changes simulated by our full chemistry models. Note that the agreement of the G-PUCINI results is optimal with $\text{TOC}^{-2.5}$, still within the range of Madronich and Granier. It is not clear at this point why this exponent is different between models (a possible explanation is related to differences in the representation of photolysis rates, especially in low overhead ozone column), but this does not strongly affect our conclusion that the relative changes in hydrogen peroxide between 1900 and present are very closely following $[\text{O}_3] \cdot J(\text{O}^1\text{D})$, and are therefore mainly a function of ozone. More precisely, the relative change in surface ozone provides an explanation for the small relative change in hydrogen peroxide prior to the 1960s or 1970s. Over the most recent decades, it is however the decrease in total ozone column that provides the rapid increasing contribution to surface hydrogen peroxide in the model, as indicated in Figure 2 by the green lines in the left column. Indeed, the role of tropospheric ozone (a small steady increase over the 20th century but little change since 1980s in CAM-chem but a large decrease over that latter period in G-PUCINI, as mentioned in section 3) is then overwhelmed by the $J(\text{O}^1\text{D})$ signal. This analysis is therefore a complement to the results of Frey *et al.* [2006] where the variability in ice-core hydrogen peroxide in the pre-

1960 period was found to be related to internal modes such as the El Niño-Southern Oscillation.

[18] It is clear that other chemical compounds have significantly increased between 1900 and present. In particular, and of strong importance to the OH and HO_2 budget, is CO. However, while both models indicate a relative rise in CO of approximately 1.5 over that period (see discussion in section 3.3), its rate of increase (Figure S2) is much too rapid in the early part of the 20th century to be correlated with the H_2O_2 change and therefore cannot by itself explain this trend.

[19] To further analyze the role of long-term changes in total ozone column on hydrogen peroxide, we show (Figure 3; note that because of the limited ozone record, scaling is performed with respect to the decadal average 1960–1969 instead of 1900 as in Figures 1 and 2) the ice-core record of hydrogen peroxide (same as in Figure 1) in conjunction with the observed record of inverse total ozone column (using an average of all stations located poleward of 70°S) squared, as discussed above. Similar to the model results, we find that the long-term change of both signals over that period is quite similar in amplitude, as expected from equation (2) since surface ozone over South Pole has not changed much over that period [see Lamarque *et al.*, 2010, Figure 6; Helmig *et al.*, 2007, Figure 3]. It is, however, clear that the agreement between the two curves of Figure 3 is not perfect; this is possibly due to limitations in the data coverage (time and space) or modulation by missing mechanisms in our analysis; in particular, the proportionality factors implicit in equation (2) could exhibit variability and trends ignored in the present study.

5. Discussion and Conclusions

[20] We have shown that model simulations of the 20th century, driven by transient emissions and observed changes in long-lived gases, are able to reproduce the observed relative increase in hydrogen peroxide over Antarctica, as recorded in three closely spaced ice cores from West Antarctica. In particular, hydrogen peroxide in ice-cores has increased rapidly since the 1970s. Based on gas-phase chemistry of the remote atmosphere, we showed that, in our model simulations, this relative change is mostly driven by the combined changes in tropospheric and stratospheric ozone (through its influence on the ozone photolysis rates); however, over Antarctica, it is clear that most of the signal is associated with changes in stratospheric ozone, as was postulated by Frey *et al.* [2005]. This was further confirmed by the analysis of the change since the 1960s in ice-core hydrogen peroxide and in the observed total ozone column, as surface observations at the South Pole show little to no trends [Helmig *et al.*, 2007]. However, while the results of our study provide an explanation for long-term changes, the extent of the role of boundary-layer snow chemistry in inducing variability in ice-core hydrogen period remains to be quantified. It would therefore be interesting to include such chemistry in global models, and to improve the representation of depositional processes. Similarly, to further verify the validity of the correlations demonstrated here, frequent joint measurements of hydrogen peroxide, surface ozone column and total ozone column would be useful.

[21] This analysis highlights the potential for using ice-cores to understand long-term changes in ozone (tropospheric

and stratospheric) in the remote Southern Hemisphere, as ice core records extend beyond the period analyzed here. In particular, it might provide additional information on volcanic perturbations of stratospheric ozone since, in pre-CFC era, large volcanic eruptions likely led to an increase in stratospheric ozone [Tie and Brasseur, 1995], which could therefore be identified via the observation of a significant decrease in hydrogen peroxide and correlated with other volcanic signatures such as sulfur isotopes [Baroni et al., 2007].

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