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Atmospheric
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Discussions

Interactive comment on “The annual cycle of hydrogen peroxide: is it an indicator of chemical instability?” *by* R. W. Stewart

R. W. Stewart

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The following are responses to comments offered by anonymous referee #2. The points to which the following paragraphs respond will be numbered. Citations to published papers and references to figures are to those in the original manuscript with the exception of one new reference included at the end of this comment.

1. Relevance to atmospheric science.

The referee raises the question as to the degree to which this paper is relevant to atmospheric science. The principal concern in this regard is the lack of comparison of model results with existing observations. I agree that more discussion of observations is warranted and I will include such a discussion in this response and in a revised manuscript.

As noted in the introduction to the paper, there are two sets of H2O2 measurements that cover one or more annual cycles and are thus of particular interest to this model study. One of these is the Cape Grim, Tasmania measurements of Ayers, et al. (1996), the other the measurements of Sakugawa and Kaplan (1989) at Westwood, CA in the Los Angeles basin. These clearly represent different pollution backgrounds. The Cape Grim observations are characteristic of clean maritime air while those near Los Angeles are characteristic of more polluted air, having mean NOx over the measurement period of 36 ppb.

The Cape Grim measurements are presented as hourly average concentrations of total peroxide between early February 1991 and late March 1992. The monthly mean concentrations show a seasonal cycle with a range of values from ˜200 ppt in winter to 1.4 ppb in summer. The background atmosphere is low-NOx, ozone-destroying throughout the year as evidenced by the high winter and low summer ozone concentrations. These data are thus comparable to the low-NOx cycle shown in Figure 2. The summer maximum in Figure 2b is larger than that in the Cape Grim data, 2 ppb of H2O2 as compared to the monthly mean 1.4 ppb total peroxide. Maximum total peroxide concentrations during summer at Cape Grim did sometimes exceed 2 ppb. The NO concentrations during the measurement period are unknown, but a value of 3 ppt was assumed by Ayers et al. (1996) in modeling their data. If this is reasonably accurate then the range of 40 to 80 ppt in the model shown in Figure 2 would be expected to result in higher peroxide. The principal feature to note in both the model and data is the lack of a sharp winter/summer transition in H2O2 concentrations. The Cape Grim monthly mean peroxide values as well as the model calculations presented by the authors, both shown in their Figure 4, show a gradual rise from the July winter low to the December summer high concentrations. The change may be described as following a more or less sinusoidal curve.

The Sakugawa and Kaplan data cover the annual variation of H2O2 over three years from August 1985 through September 1988 at Westwood, CA. Two complete annual cycles for years 1986 and 1987 are shown as well as part of the 1985 and 1988 cycles.

The H_2O_2 concentrations are 4-hour averages (1200-1600 hr) taken on selected days (clear to partly cloudy skies) during each month. Mean, maximum and minimum values of NOx, NMHC and other pollutants over the entire observation period are reported. The mean NOx level of 36 ppb is within the range of values used in the model calculations shown in Figures 3 and 4. In contrast to the Cape Grim data and the low-NOx cycle shown in Figure 2, the Westwood cycles show rapid changes between winter and summer conditions, especially in the spring. For example, the 1986 [H_2O_2] values remain relatively low until June at which time a change to summer concentrations occurs. The temporal resolution of the data doesnŠt permit an evaluation of the time taken for this transition, but it is clearly completed in the month of June. The summer data for this particular year are sparse, but the return to winter concentrations is completed by the beginning of September. The overall appearance of this cycle is that of a ŚspikeŠ, sharper than the model profile in Figure 4b. There is no obvious difference in the rapidity of spring and fall transitions in the 1986 cycle, but there are fewer data points by which to judge than in the following year. The 1987 cycle also shows a rapid winter to summer transition beginning in April with some high H_2O_2 values extending into October. Here, there is a suggestion of a difference in rapidity with which the spring and fall transitions occur with high H_2O_2 values extending, with decreasing frequency, into October.

Some features of the Sakugawa and Kaplan time series differ from the more polluted profiles (Figures 3 and 4) in the present model. Foremost among these is the range of winter to summer values. Observed summer [H_2O_2] had a mean value ˜1.0 ppb while the model calculations reach or exceed 2 ppb in any model with a low-NOx summer. Observed winter [H_2O_2] had a mean value ˜0.2 ppb whereas it is essentially 0 in the model calculations with a high-NOx winter. Since the NMHC chemistry considered in the model is limited it is probable that winter production of H_2O_2 resulting from NMHC oxidation by O_3 and NO_3 is underestimated. In a model study based on Westwood conditions Sakugawa et al. (1990) calculated maximum H_2O_2 concentrations of ˜3.2 ppb in summer (July) and 0.05 ppb in winter (January).

The Westwood CA data do not contain enough information to calculate radical production and loss rates like those carried out by Kleinman (1991) thus confirming a high-NOx winter to low-NOx summer transition. Nonetheless, the morphological differences in the clean air Cape Grim observations and the more polluted Westwood observations and the similar changes in model profiles shown in this paper as NOx background increases (Figures 2b through 4b) suggest that such transitions occur.

The main features shown by the model calculations are the following: first, an increase in the sharpness of the winter high-NOx to summer low-NOx transition as NOx concentration increases; second, an asymmetry in both rapidity and time of the spring and fall transitions, the time of transition shifting towards the fall side of summer as NOx levels increase; and third, a correspondence between time-dependent high/low NOx transitions and instability in the underlying (steady-state) chemistry.

The data sets discussed above lend support to the first of these features. The change from winter low to summer high peroxide concentrations is much more gradual in the clean air observations of Ayers et al. (1996) than in the Sakugawa and Kaplan (1989) observations near Los Angeles. The 1987 annual cycle observed by Sakugawa and Kaplan (1989) are compatible with the second feature, but this is less clear in the 1986 cycle. Finally, the third feature would require additional observations sufficient to calculate radical production and loss rates. The correspondence cited in the third feature is not an observable, but is important in interpreting observations of change in peroxide concentrations as indicative of bistability in the chemical system.

2. Abstract and Introduction

The referee comments that the abstract and introduction gave the impression that the paper would be more related to observations. The above discussion will be included in the discussion and conclusion sections of a revised manuscript.

3. P. 1945, lines 6-7.

The statement cited by the referee as confusing will be replaced. A better statement is ŚThis implies that multiple concentration values can exist over a critical range of NOx emission ratesŠ. This is similar to the wording White and Dietz(1984) used in the introduction to their paper.

4. Level of detail included in section 2.1

Only the first two sentences in the first paragraph refer to ozone production in the stratosphere. Although these sentences concerning stratospheric ozone are statements of well known facts I thought them a useful introduction to the tropospheric description that follows. The mechanism described in this section captures the essential features of the full chemistry used in the model and is referred to throughout the discussion of the results presented in section 3.

5. Reaction R8

I believe the net stoichiometry presented in reaction R8 is a useful adjunct to the discussion that follows and the results presented in Figures 2 through 5, especially part (d) of these figures. Although the chemistry summarized in R8 is a simplification of that used in the calculations, the switching mechanisms diagramed in Figure 1 and the transition points calculated in Figures 2 Ű 5 may be interpreted as resulting from the mechanisms indicated by R8.

6. Physical Description of the Model

The model is a single-box model with physical sources and losses included for some species. These physical sources and loss coefficients are derived from prescribed fluxes and deposition velocities by dividing by the box height. It is assumed that the O3 flux is the same as the cross-tropopause flux from the stratosphere. Although the model does provide for exchange with a fixed ambient atmosphere this was not included in the calculations described in this paper. Some revision has been made to section 2.2.1 in an attempt to clarify the calculation of physical source strengths and

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loss coefficients in the model.

7. P. 1952, lines 16-22, Noon Concentrations.

A better description of the steady-state concentrations is that they are calculated on successive days of the year using noon photolysis rates multiplied by the daylight fraction. The manuscript will be revised accordingly.

8. Division of text in sections 3, 4 and 5

The comparison of model results with the Ayers et al.(1996) and Sakugawa and Kaplan (1989) observations is now included in the section 4 discussion. Section 4 will be titled ŚDiscussionŠ and section 5 ŚSummary and conclusionsŠ.

9. Sub-headings 2.1.1, 2.1.2, and 2.1.3.

These have been repositioned to encompass the introductory discussion as well as the reactions relating to the three phases of the chemical mechanism described in section 2.1

10. Labeling of reactions. The numbering of all reactions using R is necessary to comply with the Manuscript Preparation and Submission guidelines of ACP. It is true that the numbering in Table 2 doesnŠt correspond to that in section 2.1 of the paper, but both numbers are given in the first column of Table 2 for ease of reference. Since the ŚInitiationŠ reactions given in section 2.1 are consolidated into a single reaction in the model it wouldnŠt be possible to give a complete correspondence by renumbering the reactions.

Additional reference

Sakugawa, H, Wangteng, T., Kaplan, I. R., and Cohen, Y.: Factors controlling the photochemical generation of gaseous H2O2 in the Los Angeles Atmosphere, Geophys. Res. Lett., 17, 93-96, 1990.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1941, 2004.