

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

Anonymous Referee #2

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General Comments

Although this paper was interesting, overall it did not leave me with an understanding of the relevance of its findings to atmospheric science. Using a steady-state and time-dependent model the annual cycle of hydrogen peroxide is calculated for different concentrations of NOx. For a range of NOx concentrations the steady-state model has two stable solutions for a period in spring and fall. This is qualitatively matched by a rapid change from low to high (spring) or high to low (fall) concentrations in the time-dependent model, which is thought to be a transition between two stable regimes. However, very few observations of peroxide were presented to validate these model results and in fact the author points out the difficulty of actually obtaining observations which would provide evidence of this chemical instability due to factors such as transport and heterogenous chemistry. The author points out that chemical instability is a

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mathematical characteristic and that the atmospheric consequences should be pursued. Therefore I struggle to understand the relevance of this work for atmospheric science.

In the Abstract (p. 1942, l. 3) and Conclusions (p. 1960, l. 11) the author states that the objective has been to see whether the observed changes in H₂O₂ concentrations from summer to winter may, under some circumstances, be interpreted as a manifestation of chemical instability. This paper has shown that in theory this may be so, but it has not attempted to see whether 'observed' changes in H₂O₂ concentrations can be used for this purpose. I therefore question whether the objective of this paper as set by the author has been met ?

Specific Comments

The Abstract gave me the impression that the paper would be more related to observations than it was.

Introduction: (p. 1942, l. 24) Again it states that the paper addresses the question of observable consequences.

There is only a very brief description of available observations in section 1.1 The observed annual cycle of H₂O₂. The observed annual cycle is only presented for Cape Grim, a clean maritime site, and no attempt is made to examine the seasonal cycle in more polluted conditions.

P. 1945, l. 6-7. This sentence is difficult to understand as it refers to both NO_x source value and NO_x emission rate, when it is not clear what these two things mean. Are they the same thing ? How do they differ ?

Although section 2.1 Tropospheric chemical regimes provides some very useful background I thought that some of it was a bit unnecessary, in particular the first bit comparing O₃ production in the stratosphere with that in the troposphere. Since the important ideas of tropospheric chemistry are elaborated in this section, much of the first para-

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graph could perhaps be removed.

I am not sure that all the detail relating to R8 is required in section 2.1.4 Net. It is important to describe the transition, but R8 is based on a simplification of the reaction scheme with only R1-R7 considered. Since the transition from ozone destruction to production is simplified to being approximately when $k4b[O_3]=k4a[NO]$, I am not sure that R8 adds anything. Further the presentation of the results and discussion refer more to switching between stable chemical regimes, whilst O₃ production and loss appears to be secondary.

It would help to have a little more detail about the physical description of the model, in terms of how the fluxes in and out of the boundary layer are dealt with. Is it a single box extending to the top of the boundary layer (BL) (1 km in height) ? Is it assumed that the flux of O₃ from the free troposphere (FT) in to the BL is the same as the flux from the stratosphere into the FT ? Are there any fluxes of species, particularly those emitted, from the BL to the FT ?

P. 1952, l. 16-22. Is it strictly correct to say that concentrations of species were calculated for noon when the photolysis rates were multiplied by a daylight fraction ?

It seemed to me that the division of text between the sections 3 Results, 4 Discussion and Summary and 5 Conclusions was not quite right. There was very little discussion in section 4, much of it was repeating or summarising the results. Some discussion appears in Results (e.g. paragraph beginning p. 1956, l. 25). New ideas and discussion are introduced for the first time in the penultimate paragraph of the Conclusions.

Technical Corrections

I felt that the sub-headings 2.1.1, 2.1.2 and 2.1.3 were in the wrong place since they came after the sentences each describing the initiation, chain propagation and termination.

The reactions referred to in the text and those in Table 2 are all called R although they

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refer to different reactions, as illustrated in Table 2. For ease of reference I think it would be easier if they were given different names.

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