**Atmospheric
Chemistry
and Physics
Discussions**

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Comment

Interactive comment on "Systematic reduction of complex tropospheric chemical mechanisms using sensitivity and time-scale analyses" *by* L. E. Whitehouse et al.

Anonymous Referee #2

Received and published: 9 August 2004

General Comments:

In this paper, Whitehouse et al. discuss the use of established mathematical techniques for the reduction of a complex chemical reaction mechanism relevant to the polluted troposphere, namely the Master Chemical Mechanism v2.0. The motivation stems from the desire to use such a mechanism in 3-D Eulerian dispersion models, where the complete formulation of the mechanism is prohibitively expensive in terms of processor time. The authors present a lengthy dialogue concerning the application of different methods for removing redundant reactions based on rate and time-scale sensitivities. This results in a 5 stage reduction process. This paper is timely in that the area of regional air-quality modeling needs such mechanisms to be able to predict the

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local effects of anthropogenic emissions, such as the increase in tropospheric ozone.

Although the paper is relatively well written I feel that substantial improvements could be made regarding both the model description and visualization of the results. Therefore, I recommend that the paper should be published in ACP but only after the issues and queries raised below are adequately addressed.

Section 3: Simulation conditions for mechanism reduction :

The model description should be more compete. Below are some points which need clarity to provide the reader with a more robust overview :

Is the box model Eulerian (i.e.) fixed in space?? What is the air pressure used?? Why do the authors exclude deposition terms in their scenarios?? What are the consequences of continually increasing mass within the box on the chemical regimes prescribed in the model. Does the fate of OH change with respect to time over the simulation period due to the build-up of oxidation products (i.e.) the source and sink reactions at 36h and 60h?? Given that this simulation focuses on a polluted urban environment is it realistic to initialize most trace gas species at zero concentration?? (e.g) CO, CH4. One could initialise the [VOC] such that the initial ratio of [VOC]/NOX is essentially defined by the ratio applicable to a specific trajectory. Are the [VOC]/NOX ratios maintained throughout the simulation period or only obtained at the time of analysis??

What is the type of software used for these simulations and what is the integration time used?? The choice of the simulation period seems rather short. The authors make no mention of the 'spin-up' period in the model. If the simulation period is extended by another two days (to be compatible with the lagrangian simulations presented later on) then the reader could be assess whether the deviances noted at 90h and 120h are caused simply by the change in scenario.

The authors should comment on the dimensions of the box and state that all species are homogeneously mixed (i.e.) no profiles.

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Section 6: IDLM method:

The authors state that "very little will be gained by applying IDLM methods to a system with very few fast time-scales remaining". At Stage#5 most of these fast timescales have been removed by the application of the QSSA. Why not apply both the QSSA and IDLM reduction methods to Stage#4 of the mechanism and examine the resulting differences introduced into the final scheme. Currently, there is a full description of IDLM but no real application to MCM.

Section 7: Comparison between full and reduced schemes:

There should be more discussion related to some of the figures shown. Below I have highlighted some examples of plots on which further comment could be made:

Figure 4: Would tropospheric ozone ever reach 0ppbv in an urban setting ??

Figures 4 and 6: What causes the large differences between the diurnal behaviour of NO2 between these two trajectories.

Figure 7: The maximum [OH] reduces across the simulation period. I assume this is due to the increase in [VOC] (i.e) the sink reactions increase. If the simulation period was extended for another two days would all OH be scavenged instantaneously (i.e.) the resident [OH] would essentially drop to zero ??

Figures 4,6 and 8: the HCHO plot shows that the initial [HCHO] = 0ppbv but in Table 4 it states the initial [HCHO] = 41.3 ppbv. Can the authors comment on this inconsistency ??

There are no details regarding the initial conditions used for the lagrangian runs in the 1-D trajectory model therefore it is difficult for the reader to assess what over what type of scenario's the reduced mechanism has been tested. Deposition velocities should be altered in line with the emissions to account for the location of the air parcel.

Section 8: Discussion:

On P3756 the authors essentially summarise the results of the mechanism reduction in the first few paragraphs. This could be done much more succinctly by refering to table #8. Many of the details have been presented before (i.e. within Section 4.4). No real discussion is made regarding figures 4-9 and the reader is left to draw their own conclusions about the behaviour of key species.

Visualization:

Table#2: The text is too small making it difficult to read. Either the font should be increased or the table should be presented in a Landscape view.

Table#7: The units should be s-1.

Figures 4-9: All figures are too small and contain too many overlapping plots to be able to differentiate what the difference actually is (anything less than 2% is currently illegible). Why is stage #4 included when the difference between stage#3 and stage#4 is simply 8 reactions ? I recommend that only the full and stage#5 plots remain. An accompanying residual plot (stage#n/full) could be used in a limited number of cases where the authors consider that plotting two curves is too restrictive for certain species.

Typography

P.3725, line 11: Insert 'and' between the Roberts and Lightfoot references. P.3728, line 8: The word 'profile' should be replaced by 'scenarios'. Profiles implies height resolved concentrations of species but the emissions are homogeneously mixed in the box I assume. line 13: Table#3 is introduced before Table#2 in the text. Either the tables should be switched or the text should be re-written to introduce the tables in a sequential manner. P.3731, line1: The Turanyi references should be in chronological order. P.3732, line 5: Insert 'and' between vector and k. P.3735, line 4: should read 'within the scheme' P.3753, line 10: Table #5 should be Table#7. line 19: Table#6 should be Table #8. line 20: replace 'speed up' with 'increase' P3760, line 9: should read mechanism 'reduction'. P.3765, Table#1 : remove 'and' after 'concentrations' in

the table legend.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3721, 2004.

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