

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

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We thank the referee for his/her comments and respond to each in turn below.

> 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??

The model under which the reduction has taken place is a fixed, well mixed, box model and all trajectories have been performed at atmospheric pressure. The final comparisons between full and reduced schemes were performed for both the fixed box model trajectories over which the reduction was achieved, as well as the moving box Lagrangian trajectory. Due to the large number of variables in many comprehensive mechanisms it is not usually possible to apply reduction strategies within a full three dimensional Eulerian framework since the computational expense of the using the full

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model would be too large. A common strategy is therefore to devise a zero dimensional, well mixed, fixed box model which attempts to cover the main concentration regimes that would be encountered within a full reactive transport code by calculating a broad range of emissions or initial conditions. In this work we have devised such a model with the intention of achieving the range of concentrations of major species that are encountered in polluted tropospheric UK conditions. The concentration ranges of major species from all trajectories used in the reduction procedure have been compared with measured concentrations from UK urban monitoring sites to ensure that they are representative. Since the reduction analysis used is entirely local, it is in fact only the local concentrations of all species that are important and not the model from which they are generated. The intention was therefore to keep the box model as simple as possible and to aim to generate the range of concentrations found within UK urban environments and so deposition was not included. Deposition was however included in the Lagrangian test model as discussed below.

>What are the consequences of continually increasing mass within the box on the chemical regimes prescribed in the model?

The scenarios become progressively more polluted with regards to primary emissions over time. Simulations were terminated where concentrations were outside of the range desired for the reduction. Again, it is only the local concentrations that determine the suitability of a set of concentrations for use within the reduction procedure.

>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??

The daily maximum concentration of OH changes with each scenario used for the reduction. In general there is a slight decrease in the maximum concentration of OH on day 3 of the scenario reflecting increased scavenging of OH by VOCs as their concentrations build. Rate of production analysis (ROPA) for OH demonstrates that the rates of the reaction of OH with oxogenates increase over the 3 days of the simulation, leading

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to the decrease in concentration of OH later in the scenario.

> 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.

Within the urban environment CO and CH₄ can be considered to be of much lower importance than non methane VOCs. Their concentrations were not however zero for the reduction conditions chosen since their concentrations build up through the simulation. Because the concentrations of non methane VOCs dominate however, the reaction methane+OH was not found to be important under the box model scenarios although CO+OH was retained. In the test scenario which uses a Lagrangian trajectory starting from remote conditions, only the reaction CH₄+OH had to be replaced in order to achieve good accuracy at the start of the trajectory. We do not believe therefore that using scenarios with initial trace concentrations of CO and CH₄ would change the results since they would not compete with other VOCs in terms of being the most important pathways for say OH removal.

> One could initialise the [VOC] such that the initial ratio of [VOC]/NO_x is essentially defined by the ratio applicable to a specific trajectory. Are the [VOC]/NO_x ratios maintained throughout the simulation period or only obtained at the time of analysis??

The VOC/NO_x ratios quoted in the table are those obtained under maximum NO_x conditions for each trajectory. They are not necessarily maintained throughout the scenario. We will make this clearer in the final version of the paper. The emissions rates chosen were designed to achieve these ratios and are maintained throughout the simulation.

> What is the type of software used for these simulations and what is the integration time used??

The integration method used was the variable theta method that forms part of the Sprint package (Berzins and Furzeland, 1985). The integration time is determined through the

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control of numerical error and therefore depends on the local solution gradient. The periods of sunrise and sunset therefore tend to lead to much smaller time-steps. The Sprint package was chosen due to its high reported accuracy for the solution of large systems of stiff ordinary differential equations and its ability to solve coupled algebraic, differential equations required to test the QSSA method. A description of the method and reference will be given in the revised version of the paper.

Berzins M. and Furzeland R.M. A User's Manual for SPRINT - A Versatile Software Package for Solving Systems of Algebraic Ordinary and Partial Differential Equations: Part 1 - Algebraic and Ordinary Differential Equations. Report TNER.85.058, Shell Research Ltd, Thornton Research Centre, Chester (1985).

>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 box model runs were designed to cover concentration conditions found within re-active transport models using an Eulerian or Lagrangian framework. Such models may also include the use of the chosen chemical mechanism within the spin-up period and so it is realistic to test our reduced mechanism from zero initial concentrations of trace species through to conditions where significant concentrations of intermediates have built up. The scenarios were designed therefore to cover both these sets of conditions. At the suggestion of the referee we have performed 5 day simulations for the full and final reduced schemes for the selected trajectories used in the paper. The results do not differ qualitatively from the 3 day trajectories shown in the paper, in that those species which show a small deviation between the full and reduced scheme in the 3rd day of simulation show a slightly increased deviation on the 5th day. Those species that show very little deviation on the third day show a similarly small error on the 5th day.

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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.

The application of the ILDM methodology involves several stages. The first is to identify the number of variables necessary to describe the ILDM. The second requires the mapping of the ILDM in phase space and the third the selection of a method by which the time dependant behaviour of the model can be described on the ILDM. The latter has been achieved in previous applications for example via the use of look-up tables or fitted polynomial difference equations. In previous applications the methodology has been applied to systems with only low dimensional ILDMs. This means that the manifold has been mapped out in, for example, 3 or 4 dimensions and the use of a look-up table has been achievable. Lowe and Tomlin (2000) applied a polynomial repro-model methodology to a 9 dimensional slow manifold for a lumped atmospheric model. In the case of the MCM without any species lumping, the intrinsic dimensional of the manifold is far too high to be able to map out the ILDM or to apply the use of look-up tables. For this reason the relatively simple QSSA method has been used in this case in order to reduce the number of fast variables. The first stage of the ILDM methodology was described and applied here in order to highlight the high intrinsic dimensionality of the system and the differences between complex explicit mechanisms like the MCM compared to other types of chemical mechanism such as those used combustion applications (Maas and Pope) or lumped atmospheric schemes (Lowe and Tomlin, 2000). It would not be possible for us to compare the QSSA with the ILDM for the above reasons and we will try to make this point clearer in the manuscript. The purpose of this part of the study was to show that a much simpler methodology like the QSSA was extremely successful in reducing a complex mechanism such as the MCM and that the intrinsic time-scale structure of the MCM is different to many mechanisms

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where previous reduction studies have been applied.

>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??

0ppbv ozone concentrations would correspond to ozone being completely titrated by NO. Whilst this would not be expected to occur at an urban background location, it is conceivable that such conditions might arise close to traffic emissions sources where NO_x is dominated by NO. Large eddy simulations of urban streets for example, show pockets of extremely low ozone concentrations close to regions where NO emissions are high. It seems therefore to be realistic to include low ozone concentrations in the reduction scenarios since such conditions would be relevant to small scale urban studies.

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

The differences between the diurnal profiles of NO₂ for scenarios 7 and 25 reflect the large differences in emission rates for the two scenarios. Scenario 25 represents much lower VOC and NO_x emissions than scenario 7. In scenario 25 the NO₂ concentration is therefore always low (0-8 ppb) and shows a minimum in the late afternoon reflecting the maximum removal rate by photolysis and by nitrate formation. The maximum concentrations occur in the early morning reflecting reduced photochemical activity. The maximum NO₂ concentrations are much higher for the high VOC emission scenario shown in Figure 4 and these considerations result in only small variations in the overall rate of increase of the NO₂ concentration.

>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.)

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the resident [OH] would essentially drop to zero ??

Although the [OH] decreases slightly, OH is not completely scavenged on the 5th simulation day for this scenario. Furthermore, the reduced model gives a good representation of the [OH] concentration peak on the 5th day.

> 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 ??

The initial [HCHO] concentration in Table 4 should be 4.13ppbv and will be corrected in the revised document.

>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.

Initial conditions for the Lagrangian trajectory and further discussion of the figures will be added in the revised document.

>Deposition velocities should be altered in line with the emissions to account for the location of the air parcel.

The deposition velocities used in the Lagrangian trajectory model are a function of the species concentration, and the time dependant boundary layer depth as described in Derwent et al. 1996 (see paper for full reference). The deposition is therefore a function of the local species concentration depending on the position of the air parcel. We will amend the paper to clarify this point.

>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 referring 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.

The discussion will be amended in the revised document according to these comments.

>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.

Could the editors comment on whether it would be feasible to include Table 2 in Landscape in the final document?

>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.

We would like to maintain the presentation of the trajectories for the intermediate reduction stages in order to show the differences caused by each of the methods used. In particular it is interesting to note that the largest step deviation was caused by a reduction in the number of selected important species at the start of the procedure and extremely small errors are caused by the application of the QSSA. These points are discussed in the text and we believe it useful to give a visual demonstration. Residual plots could be considered as an alternative, although it would then be necessary to present a trajectory plot and a residual plot for each species and trajectory. This would lead to significantly more figures in the paper. Editorial guidance would be appreciated.

>Typography We thank the referee for the comments on typography. Each will be dealt with in the revised document.

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

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