

Interactive comment on “Comparison of tropospheric chemistry schemes for use within global models” by K. M. Emmerson and M. J. Evans

Anonymous Referee #1

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General comments:

This paper provides a comprehensive comparison of the reduced chemical schemes used in six different chemical transport models to the larger, more explicit Master Chemical Mechanism (MCM). The approach is to use a box model only (no transport, deposition, additional emissions, etc.) with different initializations of chemical composition, humidity and temperature, run for five days. The approach is useful in identifying differences in the various chemical schemes, particularly for species consumed or produced over shorter time scales, such as ozone and NO_x. Impacts on longer lived species such as methane are not directly apparent from the simulations,

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but can be inferred from the modeled OH concentrations. The limitations of the approach lie in the interpretation of differences due to chemical reactions in the absence of physical processes such as deposition or dilution, which can in turn feed back into the chemistry. However, the goal of the paper is to identify the differences that are due to chemistry alone, since one would expect different models to behave similarly in the most simplified case, which is examined here.

As the paper notes, the MCM is itself a model, and therefore its use as a "standard" does not identify which of the reduced schemes is likely to be more accurate. The paper is clear on this point in interpreting the differences between various model runs as areas of overall uncertainty common to all models rather than evaluations of the accuracy of any individual model.

In general, the paper is an informative comparison between different chemical schemes. It identifies four major areas of disagreement that require further treatment, including N₂O₅ hydrolysis, long range transport of NO_x in the form of PAN, representation of isoprene chemistry and nighttime chemistry of the NO₃ radical. I recommend publication, subject to consideration of the minor comments listed below.

Minor comments:

Page 19962: The statement that "we have switched off all heterogeneous chemistry" is justified in terms of providing a "consistent assessment." It is not clear why this makes the comparison more consistent. Is this just another simplification to ensure that the gas phase schemes themselves are correct? Further comment here would be helpful to the reader. It would also be useful to understand which heterogeneous reactions in particular are normally included in the different models that have not been considered here. The omission of heterogeneous reactions would seem to influence one of the most important conclusions of the paper regarding N₂O₅ hydrolysis. If the heterogeneous hydrolysis is not considered, but the gas phase reaction is, then the uncertainty in the latter may not be as important as suggested by the later results in

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the paper.

Page 19962: All model runs begin at midnight and run for five days. This choice highlights the importance of the nighttime chemistry identified later, but it should be explicitly noted at this point that an initialization at noon should reduce the differences due to nighttime chemistry seen in some simulations by consuming a larger fraction of the initial NO_x photochemically.

Page 19967: Comparison of models with gas phase N₂O₅ + H₂O included and removed. Based on prior comment, the removal of this reaction therefore results in no hydrolysis of any kind, homogeneous or heterogeneous? This should be stated explicitly, since the complete removal of any hydrolysis of this compound is likely not realistic and will result in a longer than expected NO_x lifetime and higher than expected NO₃ concentrations. This is apparent in Figure 1 and again in Figure 4a, which shows NO₃ in excess of 1 ppbv for relatively modest NO_x input (i.e., < 10 ppbv).

Page 19969: Differences in O₃ for the "full chemistry" / biogenic case are attributed mainly to the treatment of isoprene nitrates. The input to this scheme includes relatively little (120 pptv) NO_x. Does this suggest that in addition to the isoprene sensitivity study, an investigation of the NO_x dependence of this case would be useful? Previous model studies (e.g., von Kuhlmann, 2004), have suggested that a large fraction of isoprene nitrate production comes from reaction with NO₃ in addition to photochemical reaction of isoprene peroxy radicals with NO. Has this reaction been included in these simulations, and does it affect the outcome?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19957, 2008.

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