

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

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We thank reviewer #2 for their helpful comments and technical corrections. We address their comments in turn.

Comment 1.

The reviewer highlights an important point with our simulations. There are a large number of simulations that could have been run with varying degrees of complexity. We have generally adopted the least complex set of simulations we could that would provide useful information about the performance of models. We add the following text to the model to highlight the reviewer’s comments.

P 19971 L 3. We also show results including the constant NOX* boundary conditions (figure 5c). 'We note that these simulations probably underestimate the impact of the hydrocarbon chemistry on the reduced chemistry schemes. The short lived hydrocarbons are rapidly consumed by oxidants which means that the longer lived species remain and thus perturb the chemistry the most. This favours the skill of the reduced chemistry schemes.'

Comment 2 and 9.

We have used the version of CBM-IV described in Houweling et al. 1998 which includes extensions such as a methane oxidation and the OH+HO2 reaction described by the reviewer. We have updated the sentence and also include reference to the CBM-Z scheme mentioned by the reviewer

P 19962 L 4. Change text from

'The CBM-IV is used within the GISS model (Shindell et al., 2003) and Tracer Model 3 (Houweling et al., 1998) to study tropospheric chemical dynamics.'

to

'The CBM-IV has been extended for use in global models (inclusion of methane oxidation and some additional inorganic reaction) and is used within the GISS model (Shindell et al., 2003) and Tracer Model 3 (Houweling et al., 1998) to study tropospheric chemical dynamics. The scheme used in this comparison is that of Houweling et al. [1998]. It should be noted that other versions of the CBM-IV exist which may be more suitable for inclusion in a global model (e.g. Zaveri and Peters [1999]) however they are not used in global chemistry models and are thus not considered here.'

Comment 3.

The principal component analyses were designed to take into account the extreme regions of the troposphere. If the models are capable of simulating the extremes we have faith that they would be capable of reproducing the mean conditions. We have

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included this sentence in the text.

P 19964 L 19.

The two gridboxes which exhibit the most extreme behaviour (i.e. have the highest and lowest values of the component) from within each of these first three principal components are selected and their monthly mean concentrations used as the initial conditions for these model simulations. 'This will test the chemistry schemes under the extreme sets of conditions likely to be encountered. Success at these extremes is likely to (but given the non-linear nature of the chemistry not guaranteed to) mean success for all situations.'

Comment 4.

We agree with the reviewer that the speciation of VOCs from a mass to 'generic' VOC to a chemistry scheme specific VOC is complex and can be driven by a variety of factors. This is likely to be one of the leading sources of uncertainty in our analysis and for the sake of simplicity, robustness and consistency we have used the simplest formulation that we could i.e. to use the carbon number as the defining characteristic. Thus total carbon in the simulations is preserved. Other approaches to this mapping could have been adopted but they too would have suffered from other problems.

We have added the following to the text:

P 19965 L 14.

For all species which are not represented within a particular scheme, all alkanes are lumped into the highest alkane, all alkenes into the highest alkene, and all aromatics into the highest aromatic, maintaining the total mass of carbon. 'Other approaches could have been taken (mapping by functional group, OH reactivity etc) however all of these suffer from being one approximation or another. The approach taken here is clear and simple, however, the mapping of VOCs from a total emitted to chemistry scheme specific VOCs is non-trivial and plays an important role in determining the differences

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between models. A full investigation of its significance should be considered in the future.'

Comment 5.

The version of GEOS-CHEM used here is the updated scheme containing the updates mentioned, and not the original Bey et al. (2001) scheme. This is clarified in the text by replacing:

P 19961 L 10.

The GEOS-CHEM scheme (Bey et al., 2001; Evans and Jacob, 2005)

With

'The GEOS-CHEM scheme (Bey et al., 2001; Evans and Jacob, 2005) with subsequent amendments outlined on the Web (http://homepages.see.leeds.ac.uk/~lecmje/GEOS-CHEM/GEOS-CHEM_Chemistry.htm)'

Comment 6.

We agree that the differences between JPL and IUPAC reflects the uncertainties on the rate constants. We update the text from

P 19967 L 27.

Much of this disagreement lies within differences between the IUPAC and JPL kinetics. If at this basic level the schemes do not agree, then we suspect that inclusion of organic chemistry will make the calculated concentrations of OH, O₃ and NO_x diverge further. Future collaborative studies between the IUPAC and JPL kinetic data communities could yield a definitive set of rates for the inorganic chemistry.

To

Much of this disagreement lies within differences between the IUPAC and JPL kinetics and reflect the uncertainties on the rate constants from laboratory studies (Gao et

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al., 1996) rather than any significant difference in the inorganic chemistry scheme. Although these uncertainties cannot be removed, a consistent set of reaction rates from the IUPAC and JPL kinetic data communities would remove one source of difference between models.

Comment 7.

We include the following in the text:

P 19968 L 22.

therefore the different abilities of the chemical schemes to calculate PAN lead to concerns that the oxidizing capacities downwind of our box model will vary significantly. 'These differences reflect both differences in the mechanistic assumptions going into the different models (some models (MCM) include a PAN+OH sink and others do not (GEOS-CHEM)) and differences in the rate constants are assumed.'

Comment 8.

We thank the reviewer for pointing out this important omission. The error has arisen because the CBM-IV mechanism does not include a separate acetone species. We have included the initial concentrations of acetone in table 2, along with a footnote explaining that acetone has been incorporated into the CBM-IV scheme via the 'OLE' species. Table 2 is now complete.

The text has been changed to:

P 19968 L 15.

In figures 3b and 3d, the PAN concentration varies by up to a factor of 5 in the CBM-IV scheme. There is no separate acetone species in CBM-IV and the PAN precursor CH₃CO₃ is produced from CH₃CHO+NO₃, which is inefficient at low NO_x concentrations.

Comment 9.

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See above.

Comment 10.

We will include the Dentener et al (1993) along with the work of Evans and Jacob (2005) on the importance of N₂O₅ in global models.

We change: P 19960 L 4.

In this paper, six small and 'reduced' schemes currently employed in composition transport models are compared to a 'state of the science' explicit chemistry scheme.

To

In this paper, six small and 'reduced' gas-phase schemes currently employed in composition transport models are compared to a 'state of the science' explicit chemistry scheme. We do not consider heterogeneous reaction in our comparison. Heterogeneous chemistry is important for the composition of the atmosphere [Dentner et al., 1993; Evans and Jacob, 2005; etc] however considering uncertainties in its representation in models is beyond this scope of this exercise. It should be noted that the simulations performer here will be impacted by the lack of heterogeneous chemistry, This is especially the case for NO_x where the night-time lifetime is likely to be longer than in reality.

Comment 11.

We disagree with the reviewers comments about the NO + O₃ rate constant not impacting O₃. It does not do so directly but it does indirectly. For a given O₃ concentration the NO concentration is determined by the total NO_x concentrations, the photolysis of NO₂ and the rate of this reaction. Changes to the NO concentration will change the rate of production of O₃ through (NO+HO₂/RO₂) and thus change the O₃ concentration. Also changes in this rate impact the NO₂ concentration which impacts the rate of loss of NO_x which impacts O₃.

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Comment 12.

We have included more text here.

P 19970 L 11.

Some of these differences can be attributed to the different O₃ concentrations calculated (which compare the rate of NO₃ production through NO₂+O₃), however other significant differences exist in the treatment of NO₃+VOC and NO₃+RO₂ reactions. These are most significant for the biogenic cases. 'These differences include the lack of alkenes in some models which thus removes the NO₃+VOC sink in the model (TOM-CAT) or the lack of NO₃+RO₂ reaction in some models (GEOS-CHEM)'

Technical Corrections

We will make the technical corrections suggested by reviewer #2.

In particular, they comment on the confusion between NO_x and NO_x*. We use NO_x to mean NO+NO₂ and NO_x* to mean the sum of [NO]+[NO₂]+[NO₃]+2[N₂O₅]+[HONO]+[HO₂NO₂]. To avoid confusion we have changed all references to NO_x* to NO_xtot.

We have also removed references to 'constant boundary conditions' and 'constant NO_x boundary conditions' to avoid confusion. We have changed all incidences of these cases to the 'constant NO_xtot case'

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