

## ***Interactive comment on “Free radical modelling studies during the UK TORCH Campaign in summer 2003” by K. M. Emmerson et al.***

**K. M. Emmerson et al.**

Received and published: 12 December 2006

We would like to thank both reviewers for thoughtful and constructive comments. We address the points below in turn. We present the comments of reviewer #2 followed by our response. We have indicated where a change in the manuscript will be made.

Reviewer 2

Specific comment: Impact of PANs on radicals.

Results from Figure 8 show that formation of PANs from RO<sub>2</sub> (via CH<sub>3</sub>CO<sub>3</sub>+NO<sub>2</sub>=>PAN and analogous reactions) is a major sink for radicals (OH+HO<sub>2</sub>+RO<sub>2</sub>). This represents 20-25% of the total radical sink and is comparable in magnitude to the other two large sinks (OH+NO<sub>2</sub>=>HNO<sub>3</sub> and HO<sub>2</sub>+aerosol). Presumably, this term represents net formation of PANs (i.e. the difference between

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production and PAN decomposition).

Yes.

In this type of calculation the net formation rate of PANs can be a model artifact, related to weaknesses in the 0-d calculation rather than to real net formation of PANs. The TORCH experiment coincided with very warm temperatures, and the resulting lifetime of PAN with respect to thermal decomposition is approximately 30 minutes (daytime). In this situation the PAN concentration should be close to its steady-state value with respect to  $\text{CH}_3\text{CO}_3$ . Several factors might cause PAN to deviate from its steady state value, resulting in net conversion from radicals to PAN or vice-versus. An increase in  $\text{O}_3$  with time would cause the steady-state PAN concentration to increase (due to the influence of the  $\text{NO}/\text{NO}_2$  ratio on the PAN steady state), resulting in net formation of PAN. A decrease in VOC precursor concentrations would cause PAN to decrease. Circulation within the convective mixed layer might lead to net thermal decomposition of PAN at the surface, because air at higher elevations within the mixed layer has lower temperatures and consequently higher steady-state PAN. The 0-d calculation used here does not include any of the above physical processes. Instead, net formation of PAN is based on calculated rates of formation from PAN precursors, which are derived or approximated from ambient measurements. (At least one major precursor, methyl glyoxal, is not measured directly.) Formation of PANs is complex and has many precursors, and any net imbalance between calculated sources and sinks is likely to represent imprecision in the calculation. The net imbalance between calculated PAN sources and sinks has the effect of introducing a source or sink for radicals. This net source or sink should be viewed as a possible model artifact. For this reason I believe it would be more accurate to set the PANs at steady state rather than to include net radical formation from PANs. Alternatively, net formation of PANs might be assumed to be proportional to the calculated increase in  $\text{O}_3$  (based on calculations showing that steady-state PAN increases in proportion to ambient  $\text{O}_3$ ).

I suggest the following changes in the manuscript: (i) Add some discussion of PANs

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as a source of radicals in the manuscript, and address the above issues. At present, PANs appear in Figure 8 as a radical source, but are not discussed. (ii) Consider showing results from an alternative calculation with PANs set at steady state. The current manuscript is worthy of publication without this addition, but it might be useful to show how results would change with this modification. (The same calculation would also illustrate the possible impact of the HO<sub>2</sub>-aerosol reaction, which is similar in magnitude to PAN as a source of radicals.)

One important point that tempers many of these concerns is that PAN is set to measured values in the model. Therefore, any changes in PAN concentration in the model are driven by observed changes and so the problems of ozone effects or convection are not of concern. The concentrations of the remaining PAN-type species in the model will depend partly on the NO<sub>2</sub> concentration (also fixed to observed concentrations) and those of the precursor hydrocarbons, which are mostly measured. PAN is the biggest component of the PAN-type species (40% on average). Therefore, we do not feel that an alternative calculation would reduce uncertainty given we use PAN measurements to constrain the model. We have, however, added a clarification to the end of the penultimate paragraph in section 4.4:

"Note that the point at which PAN species switch from being net radical sinks to sources is a complex function of NO<sub>x</sub>, O<sub>3</sub> and VOC concentrations as well as temperature."

Other specific comments. 1. Effect of additional VOC: Although not necessary, the authors might consider adding results that show how an increase in total VOC would affect OH, HO<sub>2</sub> and RO<sub>2</sub>. Total VOC represents a significant uncertainty in the 0-d calculation. If the input to the calculation relied solely on measured VOC, then it would be biased towards underrepresentation (since measured VOC is never 100% complete). This study avoids this bias by adjusting input VOC's based on a trajectory calculation with emissions. However, this also introduces uncertainty based on the accuracy of the emission inventory. This is important only because the model-measurement discrepancies for OH, HO<sub>2</sub> and RO<sub>2</sub> (underestimated RO<sub>2</sub>, overestimated OH, slightly

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overestimated HO<sub>2</sub>) suggest that the model underestimates total VOC, and that model-measurement agreement might be significantly improved if VOC were increased.

We agree with the referee that it is hard to be sure that all VOC are included. However, we believe our method of treating those VOC that were not measured during TORCH (see comment below) accounts for the missing carbon in a reproducible and relevant way for the UK, although we accept there are associated uncertainties. We have tried some tests where we introduced additional VOC (for instance, alpha-pinene). However, we couldn't get the agreement with OH to improve without worsening the agreement with either or both of the HO<sub>2</sub> and RO<sub>2</sub> predictions. Therefore, our feeling is that missing VOC are not the major problem.

2. The analysis of radical chemistry in the text is presented in terms of sources and sinks for summed radicals (OH, HO<sub>2</sub> and RO<sub>2</sub>), including sources, radical propagation and termination reactions. This is clear to readers familiar with OH photochemistry, but the writing is sometimes confusing. The text refers to "sources of OH" (e.g. p. 10525, line 21) and "OH initiation" (e.g. p. 10537, line 23, p. 10544, line 1, and in the conclusion). This is confusing because the term "sources of OH" usually refers to all direct sources of OH (including reactions viewed here as radical propagation). The term "OH initiation" is also ambiguous. The writing could be made clearer. The terms "initiation", "propagation" and "termination" are introduced on p. 10537 and are clearly defined, but I suggest using a term such as "radical initiation via OH" rather than "OH initiation". Also, the description in the introduction (beginning on p. 10525, line 20) is poor. The text begins with a discussion of "sources of OH" and a subsequent discussion of radical sources, propagation and termination. Only the subsequent discussion makes it apparent that "sources of OH" refers to radical sources through OH. Also, this discussion defines radicals as the sum OH+HO<sub>2</sub>, whereas the rest of the paper defines radicals as OH+HO<sub>2</sub>+RO<sub>2</sub>. Please clarify the introductory paragraphs on p. 10525-6 so that readers will understand that you are referring to the sources of all radicals (preferably, OH+HO<sub>2</sub>+RO<sub>2</sub>) rather than OH.

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Text clarified as requested.

3. The text refers to "PANs", but does not define them or say how they are determined in the 0-d model. The text notes that PAN is measured. How are the higher PANs set? Are they set based on the trajectory model? If so, are they set in proportion to PAN? Please clarify. 4. The text refers to a radical sink via OH through PANs. I am not familiar with this. There is a PAN+OH reaction, but its rate is normally very slow in the lower troposphere. It may be worth identifying these reactions in the text.

Some of the first question is dealt with above. The following sentence has been added where OH+PAN reactions are first discussed (p11) to clarify the other issues.

"There are 216 different PAN species in the model, which are formed when acetyl peroxy radicals (of general formula RCO<sub>3</sub>) react with NO<sub>2</sub>. They each react with OH to form carbonyl species, CO and NO<sub>2</sub>, albeit slowly, and the cumulative effect of these reactions can impact the resulting OH concentration under the right conditions."

5. With regard to HO<sub>2</sub>/OH: It may be worth discussing this in the context of results from Thornton et al., 2002 (JGR). Thornton et al argued for an OH source from isoprene (bypassing HO<sub>2</sub>) in order to explain their measured HO<sub>2</sub> at low NO<sub>x</sub>. The results here suggest that the model HO<sub>2</sub>/OH is overestimated versus measurements when NO is low (which may coincide with the conditions discussed by Thornton et al.) This appears to support the hypothesis of Thornton et al.

The impact of isoprene on OH, both through OH + isoprene and through O<sub>3</sub> + isoprene as a source, is fully accommodated through the isoprene measurements and through the MCM, which has the fractional production of OH as 0.27 (IUPAC 2006 has 0.25, 0.26 and 0.25). In addition, isoprene does not appear to effect the OH concentration during the modelled:measured comparison period of TORCH as pointed out in the manuscript (only 6% of the OH to RO<sub>2</sub> conversion): greatest concentrations were recorded when FAGE data were not available. The paper referred to by the referee by Thornton et al., [2002] proposes that the rate of reactions of the type HO<sub>2</sub>+RO<sub>2</sub>-

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ROOH+O<sub>2</sub> need to be reduced in order to explain modelled HO<sub>2</sub> at low NO<sub>x</sub>, especially for isoprene derivatives for which the kinetic data are poorly known. At a polluted site in Nashville it was estimated that isoprene-RO<sub>2</sub> intermediates may account for 40% of the total. These conditions are very different to TORCH. Therefore, whilst we agree that our data appear to support the hypothesis suggested by Thornton et al. [2002] that there may be an OH source from isoprene-RO<sub>2</sub> species that avoids HO<sub>2</sub>, we do not believe it is important in this instance.

6. Please clarify in the text: Is the trajectory calculation used only to add secondary VOC (which were not included in the measurements but which are produced from measured VOC), or is the calculation also used to add primary VOC (which were not included in the measurements but which were believed to be present based on emission inventories)? The text (p. 10532) refers to the addition of species in proportion to benzene, o-xylene and acetone. This may refer only to primary species. The 0-d model almost certainly included unmeasured secondary species such as methyl glyoxal. Were these included based on the ratio with primary species such as o-xylene in the trajectory calculation, or were they set to steady-state values in the 0-d calculation? (It might be more reasonable to set them in proportion to measured secondary species such as acetaldehyde, but this is minor in context.) Please clarify how these species were set.

The trajectory calculation was used to add primary VOCs which were not measured but believed to be present according to emission inventories. The secondary species were allowed to reach steady-state values by running the model for 4 days with the same input data as stated in the text. The text has been modified to make it clear that the relationships were used for primary emitted species only.

7. The text (p. 10532) includes the statement: “Consequently, there are model inputs for 84% of the primary emitted species in the model that are directly or indirectly based on measured values.” Please remove this sentence, which is probably a mistake. It raises a host of questions: Does this mean 84% of VOC based on the total number

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of species, or carbon content, or OH-reactivity? What are the other 16% of omitted species? (The text only described how unmeasured species were included indirectly and does not refer to species that were totally omitted.) Where does the 84% figure come from?

We meant that  $(74+39)=113/135$  or 84% of primary emitted species were initialized. However, given the context and the potential for misinterpretation, we have removed this sentence.

8. The introduction (p. 10526, line 13) states that the main sinks for HOx are the self and cross-reactions of HO<sub>2</sub> and RO<sub>2</sub> and formation of HNO<sub>3</sub>. This is the “classical” understanding. However, this study concludes that aerosol reactions are the dominant HOx sink. The introductory summary here should probably also mention the aerosol reaction.

Line added to intro in relevant place.

Additional references not in manuscript:

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Thornton, J.A., P. J. Wooldridge, R. C. Cohen, M. Martinez, H. Harder W. H. Brune, E. J. Williams, J. M. Roberts, F. C. Fehsenfeld, S. R. Hall, R. E. Shetter, B. P. Wert, and A. Fried, (2002). Ozone production rates as a function of NO<sub>x</sub> abundances and HO<sub>x</sub> production rates in the Nashville urban plume, *JOURNAL OF GEOPHYSICAL RESEARCH*, VOL. 107, NO. D12, 4146, 10.1029/2001JD000932.

Fleming, Z.L., P.S. Monks, A.R. Rickard, B.J. Bandy, N. Brough, T.J. Green, C.E. Reeves, and S.A. Penkett, Seasonal dependence of peroxy radical concentrations at a

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Northern hemisphere marine boundary layer site during summer and winter: Evidence for photochemical activity in winter, *Atmos.Chem.Phys.*, 6, 5415-5433, 2006.

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