Atmos. Chem. Phys. Discuss., 6, S4387–S4392, 2006
www.atmos-chem-phys-discuss.net/6/S4387/2006/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 4 November 2006

Review of Atmos. Chem. Phys. Manuscript (# acpd-2006-0260) "Free radical modelling studies during the UK TORCH campaign in summer 2003" by Emmerson et al.

1) Does the paper address relevant scientific questions within the scope of ACP? -Yes.

2) Does the paper present novel concepts, ideas, tools, or data? -Yes.

3) Are substantial conclusions reached? -Yes.

4) Are the scientific methods and assumptions valid and clearly outlined? -Yes, but see comments below.

5) Are the results sufficient to support the interpretations and conclusions? -Yes.

6) Is the description of experiments and calculations sufficiently complete and precise

to allow their reproduction by fellow scientists (traceability of results)? -Yes, but see the comments below.

7) Do the authors give proper credit to related work and clearly indicate their own new/original contribution? -Yes.

8) Does the title clearly reflect the contents of the paper? -Yes.

9) Does the abstract provide a concise and complete summary? -Yes.

10) Is the overall presentation well structured and clear? -Yes.

11) Is the language fluent and precise? -Yes.

12) Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? -Yes.

13) Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? - Figure 2, 4, 7 could be combined into one figure with subplots (a), (b), (c).

14) Are the number and quality of references appropriate? -Yes.

15) Is the amount and quality of supplementary material appropriate? -Not applicable.

General comments

This manuscript presents observations and model comparison during the TORCH study, conducted at a site influenced by London plumes. Field studies in polluted environments like this one are important to understand the atmospheric oxidation chemistry and exam fast photochemistry. This study provides a comprehensive measurement suite of important chemical species and physical parameter for model calculations to compare with the observations. Good agreement is achieved between observations and model calculations.

In the last few years, there are few similar studies on radical chemistry and atmospheric

ACPD

6, S4387–S4392, 2006

EGU

oxidation in urban environments. A closest study as this one is the PUMA summer campaign in which model-observation comparison was also made by the same group with the same mechanism, MCM. One thing I had hard time to understand is that the agreement in this study is very good, while in PUMA the model under-predicted OH and HO2 by a factor of ˜2. The authors mentioned that in this study, a different HO2 heterogeneous loss on aerosol surface was used and the termination of HO2 is a dominated by this heterogeneous loss, while in PUMA the HO2 loss is not important, at least not listed in Figure 4 of Emmerson et al., 2005b. Some discussion about the reasons for the difference in the agreement in the two studies is very necessary to see some consistence in this kind of comparison and to figure out why the model comparison results vary from time to time and from location to location. Could this be caused by problems in the measurements, or by problems in the model, or by the difference in physical and chemical conditions? This is my biggest concern.

In general the paper is well written, reports important results, and draws reasonable conclusions. I recommend it be published in ACP after revision, and ask the authors to consider the following comments in their revision.

Special Comments

P10524, L8-10, in Abstract, OH and HO2 were measured by LIF and HO2+RO2 was measured by CA. For clarification, change the statement to: “Between 25 July and 31 August, the concentrations of the hydroxyl radical and the hydroperoxy radical were measured using laser-induced fluorescence at low pressure and the sum of peroxy radicals was measured using the peroxy radical chemical amplifier technique.”

P10529, L25-27, it is known that a heated Molybdenum converter can partly convert some nitrogen species such as HNO3, PAN and cause interference in NO2 measurements. If this is the only NO2 measurement in this study and these NO2 measurements were constrained in the model, estimated uncertainties in the NO2 measurements and NO2 and thus in the model calculations should be mentioned.

ACPD
6, S4387–S4392, 2006

P10530, L25 and P10531 L2, I assume “Smith et al., 1995” should be “Smith et al., 2005”.

P10532, L14-16, here the authors state that the model was constrained with the observations in 15-min intervals. On the other hand, in P10533, L20-22, “The concentrations are calculated every minute using Facsimile for Windows software and averaged to 15 min to be consistent with the time interval of the input constraints, before being compared with the radical data.” If model inputs are in 15-min intervals, I assume the model outputs should be in 15-min intervals as well. Clarify this confusion.

It is a pity that there were no HONO measurements in this study because HONO photolysis is an important radical initiation process at least in the early morning. Between P10534 and P10535, HONO production rate is assumed based on the study by Kurtenbach et al. in a tunnel, which might be different from the situation in the open urban air. If this is true, then there would be some uncertainty in the model regarding the photolysis of HONO because contribution of HONO photolysis to radical production is comparable to that from O3 photolysis and O3+alkenes reactions.

P10536, L11, including the corresponding average time for the detection limit will be helpful. This is also true in P.10539, L.1.

P.10536, L.24, change “;” to “:”.

P.10537, L.4, change “Ĕ is interesting:” to “Ĕ is interesting;”.

P.10539, L.22, I thought during PUMA HO2 was under-predicted as stated in Abstract of Emmerson et al. [2005a]that the modeled-to-observed HO2 ratio is 0.56 for the summer campaign. So the reference Emmerson et al., 2005a should go to the under-predicted group, not the over-predicted group.

P.10540, in the 3rd paragraph, again back to my biggest concern about the consistency in the model-measurement comparison, HO2 heterogeneous loss on aerosol surface is so important in this study, but why in PUMA it is has little importance where HO2 was

ACPD

6, S4387–S4392, 2006

already under-predicted (if the HO2 heterogeneous loss in PUMA is as important as in this study, the model [HO2] would be even lower, resulting in even worse agreement in the PUMA study). Some discussion about this issue and the difference in the model comparison in the two studies is highly necessary.

P.10542, L.3-4, a smaller peak in the observed [HO2+RO2] between 20:00 and 21:00 is mentioned as show in figure 7. Some possible reasons for this peak and why the model couldn't capture this peak will be helpful.

P.10542, L.12-17, the observed RO2/HO2 ratio of 6.8 looks pretty high to me, which is also higher than both the model prediction and the value observed during BERLIOZ. Is there any possible explanation for this difference? Could this be caused by the measurement uncertainties because [HO2+RO2] and HO2 were measured by two different techniques? What about this ratio in a closer campaign like PUMA? It is also worthwhile to mention in either Abstract or Conclusions that the RO2/HO2 ratio can not be reproduced in the model, although the modeled and observed [HO2+RO2] and [HO2] are generally in good agreement.

P.10545, L.26, this sentence is not complete.

P.10546, L. 23-26, besides ozone production, the actual ambient ozone concentrations depend highly on meteorological conditions. For example, lower ozone production rates on 7 and 8 August than on 3-5 August actually result in higher ambient ozone concentrations. It is necessary to mention this point as well.

P. 10548, in the last paragraph of Conclusions, again it is also necessary to mention the reasons for the inconsistence in the model comparison such as TORCH v.s. PUMA and its implication for the future similar studies.

In Conclusions, the authors point out that "A major difference between this work and others such as PUMA is that termination of HO2 onto aerosol particles is a major pathway not previously considered in any detail, and could be important for all field

ACPD
6, S4387–S4392, 2006

EGU

campaigns with large sources and/or production rates of aerosol." In P.10534, an arbitrary accommodation coefficient of 0.5 was used for HO2 uptake to aerosol surface in the model. There is quite large uncertainty in this estimation and it may influence this conclusion if the actual accommodation coefficient is low than this value.

P.10554, in Table 1, the authors mentioned that "Heatwave period is highlighted in red" in the caption while this is not shown in the Table (4-10 August?).

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10523, 2006.