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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.

K. M. Emmerson et al.

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We would like to thank both reviewers for thoughtful and constructive comments. We address the points below in turn. We present reviewer #1's comments followed by our response. We have indicated where changes will be made in the manuscript.

Reviewer 1

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).

We don't believe that such an action would improve clarity or significantly reduce the paper length and so would prefer to leave the figures as they are presented.

One thing I had hard time to understand is that the agreement in this study is very

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good, while in PUMA the model under-predicted OH and HO2 by a factor of approximately 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.

The TORCH campaign provided the UK atmospheric science community with the most comprehensive data-set downwind of an urban area to date. Undoubtedly, the quality of the measurement data was superior to that measured during PUMA (4 years previously), in terms of measurement quality, frequency and range. Indeed, many of the uncertainties from the PUMA campaign were used to drive the scientific objectives of the TORCH campaign (e.g. the need to measure the concentrations and quantify the impact of oxygenated species in the atmosphere) as we state on page 4 of the manuscript. The uncertainties in both model and measured output were higher for PUMA than for TORCH. For example, in PUMA, there were no HCHO measurements in winter, and many other parameters were not measured as well (or at all). There was only rudimentary aerosol information in PUMA (Fuchs surface area), and we have learnt from the SOAPEX and NAMBLEX campaigns (Sommariva et al., 2004, 2006; Haggerstone et al., 2005) that using the size distribution of aerosols and the diffusion/continuum model improves measured:modelled agreement dramatically. Having said that, the conditions during the TORCH and PUMA campaigns were quite different. PUMA took place on the edge of the city-centre of Birmingham, whilst TORCH was effectively a rural site, impacted by nearby urban conurbations (London was 25-miles downwind when the wind blew from the SW). As a result, average NOX concentrations during the PUMA summer campaign were 15.2 ppb compared to 10.8 ppb for TORCH.

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For instance, figure 8 shows that although the RO2+HO2 rates are similar for both campaigns, the RO2+NO rate is about 50% greater during PUMA. Radical termination through aerosol loss becomes more important at lower NOX (particularly so in the clean MBL). Heterogeneous loss would undoubtedly be less important for PUMA than TORCH given the NOX concentrations, although owing to the lack of relevant data, we can never say with any certainty, how much less. In order to address this point, we have added the following line to the conclusions:

"Indeed, this termination rate may have been underestimated during the PUMA campaign owing to a lack of relevant data, although the higher NOX concentrations experienced during the PUMA campaign mean that this loss route would likely be less important than for TORCH."

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.”

Changed as requested.

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.

Unfortunately, there were no detailed tests carried out on the TECO instrument during the campaign to quantify the impact of potential interference effects from PAN and HNO3. Therefore, it is only possible to speculate after the event, on what the possi-

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ble impacts might have been. Although there were two NO2 instruments during the campaign (there was also a TDLS instrument), the two instruments were located 50 m apart from each other and there are timing and averaging issues that arise when comparing the two instruments. However, a comparison for 10 days when both instruments were running produced a slope of 0.8 and an r2 of 0.3. By plotting the difference between the two instruments against PAN concentrations, we found no meaningful correlation. Note also that the model:measured comparison was not possible during the heat wave period owing to the absence of FAGE data and this period is when any PAN interference would have the greatest impact (as temperatures were highest). We believe, therefore, that interference by PAN was no greater than 20% in this instance. We have no information on measured HNO3 concentrations. Following through to the model calculations, if we have used too much NO2 in the model as a constraint (assuming some of the measured NO2 is really PAN and/or HNO3), the effect would be that the predicted OH concentrations would be lower than they should be (as more OH would be lost through OH+NO2 termination). In other words, the opposite effect to what is needed to explain the observed model over-prediction of OH. As we can't give a concrete uncertainty, and as such an uncertainty couldn't explain the model:measured results, we do not believe an addition to the text would be helpful in this context.

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

Corrected.

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.

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Sentence has been changed to:

"The concentrations are calculated using Facsimile for Windows software and averaged to 15 minutes to be consistent with the time interval of the input constraints, before being compared with the radical data."

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.

We agree that the absence of HONO measurements is regrettable and leads to a model uncertainty. However, we used the same technique to estimate concentrations during the PUMA campaign and the estimated concentrations were in reasonable agreement with the few concentrations available. In our further defence, the impact of HONO is likely to be greatest at dawn as shown through previous studies (Alicke et al., 2003) and the focus of the study here is on the hours around midday. In addition, our model tends to over-predict OH, the opposite to that expected if a significant amount of HONO were missing from our model. In conclusion, the omission of HONO is unlikely to be causing the over estimation of OH by the model. We have added the following to the conclusions:

"The absence of HONO measurements during the TORCH campaign was regrettable and leads to a model uncertainty. However, the same technique was used to estimate concentrations during the PUMA campaign, when estimated concentrations were in reasonable agreement with the few measured concentrations available (Emmerson et al., 2005a). In addition, the impact of HONO is likely to be greatest at dawn as shown through previous studies (Alicke et al., 2003) and the focus of the study here is on the

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hours around midday. Finally, the model tends to over-predict OH, the opposite to that expected if a significant amount of HONO were absent. In conclusion, the omission of HONO is unlikely to be causing the over estimation of OH by the model."

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

Information added as requested.

P.10536, L.24, change ";" to ":".

Changed as suggested.

P.10537, L.4, change "E is interesting:" to "E is interesting;".

Changed as suggested.

P.10539, L.22, I thought during PUMA HO2 was under-predicted as stated in Abstract of Emmerson et al. [2005a] that the modelled-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.

Our mistake - now corrected.

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 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.

Discussion now added - see above.

P.10542, L.3-4, a smaller peak in the observed [HO2+RO2] between 20:00 and 21:00

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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.

The feature shown in figure 7 appears on 9 out of 23 nights in the measured data, and is more pronounced on some nights than others (e.g. particularly pronounced on the 2nd of August). The feature is almost certainly produced through RO2 production from NO3 chemistry. The particular origins of the peak and the difference in the model RO2 predictions will be explored more thoroughly in a forthcoming nighttime paper.

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.

We have no explanation for this large difference and can only assume that the conditions during the TORCH campaign were unlike those observed elsewhere. The same ratio is not available during PUMA as peroxy radicals were not measured. The modelled ratio for PUMA campaign was 1.12, much closer to the BERLIOZ campaign. The experimental uncertainty for the FAGE OH and HO2 measurements, which is mainly controlled by the calibration accuracy, is given in the manuscript, and is 22% and 25% respectively (1 standard deviation) for OH and HO2. For [HO2+RO2] measured by PERCA the overall measurement uncertainty is 42% (see Fleming et al, 2006). We have added the following to the conclusions: Although the HO2 and RO2 concentrations are reproduced reasonably well by the model (the model in general overpredicts HO2 and underpredicts RO2), the high RO2:HO2 ratio of 6.8 is much higher than that predicted by the model (3.9). The reason for these high values compared with past campaigns (e.g. approx. 1 for BERLIOZ) and the difference between the modelled and

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measured ratios is currently unclear. It should be noted, however, that despite a significant difference between the modelled and measured ratio, both ratios during TORCH are considerably higher (e.g. factor of 4 for the model) than the ratios found during BERLIOZ.

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

The sentence is now 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.

Agreed and have now added the following to the end of the relevant paragraph: "However, meteorological conditions also have a large impact on ozone concentrations. The O3 production rate on the 9-10 August is lower than the 3-5 August, but the ambient ozone concentration is higher. These issues will be investigated further in future publications."

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.

See first response.

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 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 lower than this value.

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We agree which is why we emphasise the need for further relevant measurements in the future (end of paragraph 3).

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?).

Not sure why this happened but is now okay.

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