

Interactive comment on “Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere” by K. D. Lu et al.

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Response to Comments by Referee #2

We would like to thank the reviewers for their comments and questions which have helped to improve the manuscript. The reviewer comments are given below together with our responses and changes made to the manuscript.

General Comments

This paper described measurements, analysis and model simulations of HO_x radicals C14005

and related species performed in the Pearl river Delta region of China near Guangzhou. In particular, the paper follows up on a number of recent studies: Hofzumahaus et al. (Science, 2009) in which a significant model overestimate of the observed HO_x from PRIDE-PRD 2006 was first reported, the recently identified interference in LIF measurements of HO₂ from certain RO₂ radicals (Fuchs et al., AMT 2011) and a number of recent field observations and theoretical calculations relating to HO_x regeneration in the oxidation of isoprene (again, following observations of measurement/model exceedances under high BVOC, low NO_x conditions).

In the present work, the impact of the RO₂ interference in the measurement of HO₂ is evaluated by means of model simulations to calculate HO₂^{*}, the actual observed quantity, based upon the measured interference (where known) and modelled RO₂ (where speciated). The model-measurement HO_x discrepancy reported by Hofzumahaus et al. (2009) is found to persist, i.e. the qualitative conclusions of the Hofzumahaus study are found to hold even including this interference. The observed HO_x data is compared with that predicted under a range of model assumptions (i.e. differing HO_x recycling mechanisms), of which only the empirically tuned RO₂ / HO₂ + X method (with varying [X]) is found to successfully replicate the observed data, although the isoprene HO_x recycling mechanisms proposed by Lelieveld & co-workers and Peeters & co-workers go some way to resolving the discrepancy.

The paper addresses a critical area central to the remit of ACP. It is a well-written and comprehensive account of a key dataset likely to prove highly useful in disentangling the HO_x cycling issue in the future, with regard to which the level of detail included is appropriate. I recommend publication after consideration of the following (minor) points.

1 Comment

p.11323 were the O₃ interferences humidity dependent (due to O(1D) + H₂O - large range of H₂O over the absolute humidity range 2.5 - 4 %).

Response

Laboratory tests did not show a significant water vapor dependence of the ozone interference within the specified uncertainty of the correction ($\pm 30\%$). Therefore, the correction was applied as only ozone dependent. It should be noted that the resulting correction at PRD lies within the detection limit of OH and HO₂ and was not important for the daytime HOx concentrations. We will add a corresponding note in the revised paper.

2 Comment

p.11326 It would be useful to include a summary of the model sensitivity runs (in the Supplementary Info). Would the uncertainty obtained from this for HO₂* (40 %) include uncertainty arising from the lumping of the RO₂ species in the RACM mechanism, limiting scope to accurately calculate the retrieval of individual RO₂ as HO₂ (even if their individual interference factors were known, while in many cases they are not).

Response

In Section 2.4 (Model) of the revised paper, we have added a reference to a new section about 'model errors' which is now included in the supplement. In the revised supplement, we present a new table with a summary of the model sensitivity runs requested by the referee.

Fig. 12 can be used to estimate the uncertainty caused by a lumped model (RACM-MIM-GK, M0 scenario) versus a nearly explicit model (MCMv3.1, M7 scenario). Differences between RO₂(M0) and RO₂(M7) are small during daytime, introducing less than 10 % additional uncertainty in HO₂* compared to HO₂. This simple estimate does not consider the unknown uncertainty of the unmeasured $\alpha_{RO_2}^i$ values. Fig. 3 shows that the modelled (and measured) $\alpha_{RO_2}^i$ values for alkenes and aromatics have generally large values close to the upper limit of one. Thus, the calculated interference in HO₂* cannot become much larger, but rather must be considered an upper limit at a given

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amount of RO₂. The discussion of the model error of HO₂* is now also included in the supplement.

3 Comment

p. 11328 Is there information regarding the nighttime NO course in the CO data (which might be expected to reflect presence of "heavy duty" cars - a term which would do with refining - presumably you mean diesel (compression) engine light/heavy goods vehicles rather than passenger cars ? Or alternatively in any PM data which may be available ?

Response

We have replaced "heavy duty cars" by "diesel-powered trucks". The presence of strong nighttime emissions from diesel engines was identified by enhanced values of light-absorbing carbon (LAC) measured at the PRD site by Garland et al. (2008). They found that the ratio of LAC to CO was highly variable throughout the campaign indicating a complex mix of different combustion sources. We have included a corresponding remark with reference to Garland et al. in the revised paper (section 3.1).

4 Comment

p.11330 Clarify how VOC / NOx limitation is determined.

Response

Lines 22-23 (p. 11330) were meant to reemphasize our previous statement (lines 18-21) that the radical losses were controlled by reactions with NOx in the morning, while selfreactions of RO₂ dominated in the afternoon. The terms "VOC limited" and "NOx limited" are probably confusing at this point and not really needed here or elsewhere in the paper. We have therefore deleted the sentence in the revised paper.

5 Comment

p.11331 It would be interesting to calculate / plot the diurnal variation in the (OH) chain

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length, i.e. $p(\text{OH})/(\text{HO}_2 \rightarrow \text{OH})$, as a further metric for the diurnal variation in HOx behaviour - the denominator could be extended to include the $\text{RO}_2 \rightarrow \text{OH}$ contribution under the relevant extended model scenarios.

Response

The chain length is indeed a useful metric for radical cycling. We have prepared a new figure (Fig. S4) showing the mean diurnal variation of the chain length for the different model scenarios. The new figure is presented in the supplement of the revised paper. In section 4.3.1, we have added the following statement: "The effect of the additional recycling (M1, M2) on the OH chain length, defined as the ratio of the recycling rate ($\text{HO}_2 \rightarrow \text{OH}$, $\text{RO}_2 \rightarrow \text{OH}$) and $P(\text{OH})$, is to maintain the chain length at values around ten during daytime, whereas it drops from about ten in the morning to about 1–2 in the afternoon if no additional recycling is assumed (Fig. S4)."

6 Comment

p.11334 the independence of the observed OH to NO extracted from this simple empirical analysis, vs. the complex model behaviour, is a very interesting insight & should be flagged more prominently.

Response

We agree that the weak dependence of the observed OH to NO_x is very interesting. It stands in contrast to the theoretical expectation that OH first increases with NO_x due to increasing recycling by $\text{HO}_2 + \text{NO}$, but then decreases at even higher NO_x because of increasing OH loss by reaction with NO₂. This theoretical behaviour was confirmed for relatively clean rural air at POPCORN, where a nonlinear dependence with a maximum at 1 ppb NO₂ was found in good agreement for measured and modelled OH (Ehhalt, 1999). In the revised paper, we will highlight that the observed NO_x dependence is not only different from the POPCORN results, but disagrees in general with theoretical predictions made in various model studies (e.g., McKeen et al., 1997; Poppe et al.,

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1993; Weinstock et al., 1980). See also our response to referee #1 (comment 5).

7 Comment

p.11339 Can chamber data (e.g. with PERCA or MIESR) shed any light on observed vs modelled RO₂/HO₂ ratios, under high reactivity conditions similar to those encountered here ?

Response

Controlled chamber experiments with specific measurements of RO₂ and HO₂ by Matrix Isolation Electron Spin Resonance (MIESR; Mihelcic et al., 1990) would be very useful. However, chamber experiments with MIESR have so far not been performed at high reactivity conditions and MIESR is no more available at Juelich. PERCAs (peroxy radical chemical amplifiers; e.g. Kartal et al., 2010) can measure the sum of RO₂ and HO₂, but do not distinguish between RO₂ and HO₂. ROxLIF (ROx measurement by laser-induced fluorescence; Fuchs et al., 2008) can specifically measure RO₂ and HO₂, but needs NO for chemical conversion of the peroxy radicals. Thus, its ability to measure RO₂ to HO₂ ratios depends critically on the suppression of the interference by RO₂ in the HO₂ measurement mode (Fuchs et al., 2011). We are currently working on such technical improvement.

8 Comment

p.11343 In reality the aerosol uptake is likely to be in the transition regime where diffusion limitations can influence (reduce) the real HO₂ loss rate, so the 0.1 s⁻¹ is likely to be a further over-estimate beyond that from the gamma value alone.

Response

We agree that gas-phase diffusion will further reduce the HO₂ uptake, but the effect during the PRD campaign was small. The aerosol consisted mostly of submicron particles with an average particle-number size distribution peaking at a diameter of 100 nm (Yue et al., 2010). At such condition, the diffusive gas transport will reduce the uptake

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by roughly 10%, which has a much smaller effect than the uncertainty of the unknown γ value. We have added a comment on the influence of the gas transport in the text (section 4.3.4 in the original paper).

9 Comment

References -most seem to have spurious extra numbers after the end of the journal reference line ?

Response

The numbers are interactive links (included by the Journal) representing the page numbers where the reference has been cited in the paper. You may click back and forth between the citation in the text and reference list (does not work in the printer-friendly version).

10 Comment

Figure 11 / 12 - could consider shading the region corresponding to the systematic measurement uncertainty in OH and HO₂^{*}, to better indicate good / poor agreement with the simulations

Response

Besides systematic measurement uncertainties, also systematic modeling errors have to be taken into account to judge the model-measurement agreement/disagreement (as we have already done in the text). Shading the experimental and model curves would result in overloaded and unreadable figures. Therefore, we have made no changes to Figs. 11 and 12.

11 Comment

p.11317 line 1 "since many years" "is experiencing" please rephrase (ideally using precise dates)

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Response

Text changed to "In this subtropical region, air quality has been deteriorating over the past two decades owing to a fast growing economy and increasing urbanization"

12 Comment

p.11320 line 4 *the* asian monsoon

Response

Done.

13 Comment

p.11325 define GK part of the RACM-MIMN-GK model name

Response

A definition for GK has been included: "G = Geiger et al., 2003; K = Karl et al., 2006".

14 Comment

Fig 6 strictly L(ROx) and P(ROx) are equal in magnitude but not value (a trivial point).

Response

Done.

Additional References

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Garland et al., Aerosol optical properties in a rural environment near the mega-city Guangzhou, China: implications for regional air pollution, radiative forcing and remote sensing, Atmos. Chem. Phys. 8, 5161-5186, 2008.

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Kartal et al., Technical Note: Characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006, *Atmos. Chem. Phys.* 10, 3047-3062, 2010.

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