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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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This paper described measurements, analysis and model simulations of HOx radicals 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 HOx from PRIDE-PRD 2006 was first reported, the recently identified interference in LIF measurements of HO2 from certain RO2 radicals (Fuchs et al., AMTD 2011) and a number of recent field observations and theoretical calculations relating to HOx regeration in the oxidation of isoprene (again, following observations of measurement/model ex-

ceedances under hig BVOC, low NOx 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 HOx 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 HOx data is compared with that predicted under a range of model assumptions (i.e. differing HOx 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 HOx 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 HOx 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 :

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 %)

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).

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 ?

p.11330 Clarify how VOC / NOx limitation is determined

p.11331 It would be interesting to calculate / plot the diurnal variation in the (OH) chain length, i.e. p(OH)/(HO2 ïĆő OH), as a further metric for the diurnal variation in HOx behaviour – the denominator could be extended to include the RO2ïĆőOH contribution under the relevant extended model scenarios.

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.

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 ?

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

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

Minor points

p.11317 line 1“since many years” “is experiencing” please rephrase (ideally using precise dates) p.11320 line 4 *the* asian monsoon p.11325 define GK part of the RACM-MIN-GK model name Fig 6 strictly L(ROx) and P(ROx) are equal in magnitude but not value (a trivial point).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11311, 2011.