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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 #4

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This paper is a more detailed follow up from the Hofzumahaus et al paper published in Science in 2009. It is very much in scope for ACP and demonstrates clearly that under low NO_x conditions in this environment, our current understanding of sources of the OH radical are lacking. Since the 2009 paper, the Julich group has discovered an interference in HO₂ measurements, which comes from the decomposition of RO₂ radicals derived from certain VOCs, in particular alkene and aromatic species. The effect of this is that the true HO₂ concentration is lower than that measured, and the authors have attempted to allow for this by combining fractional sensitivities towards

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Discussion Paper

certain RO₂ species producing a HO₂ signal measured in the laboratory with a box model which calculates the distribution of RO₂ species. There are two main impacts of this. The first is that it is not necessary now to invoke both a RO₂+X = HO₂ and HO₂+X = OH step to bring the field measurements of OH and HO₂ into line with experiments (although this could still be an explanation), rather a single step HO₂+Y = OH could bring into agreement field measurements and model calculations within the combined uncertainties of model and measurements. Secondly, as the true HO₂ is lower, the HO₂+NO source of OH is lower than before, and the missing sink of OH becomes a larger fraction of the total production rate of OH, which is measured via $k'(\text{OH}) \times [\text{OH}]$, determined using the LIF OH instrument and the OH reactivity instrument.

The authors have also shown using a variety of models, with different mechanisms, the impact of including new chemistry that has been suggested over the last couple of years, for example the Peeters mechanism for decomposition of isoprene related RO₂ radicals into HO₂ and also products which generate further HO_x radicals (e.g. multifunctional carbonyls), the Paulot mechanism for reaction of isoprene related epoxide species generating HO_x, and also reactions of RO₂ with HO₂ which can regenerate HO_x radicals rather than acting as a termination step. It is shown that although some of these have a significant impact (e.g. Peeters), others do not, but that there is still an unknown source of OH from HO₂+Y (or RO₂+X = HO₂ and HO₂+X = OH). There are however, large uncertainties still in these mechanisms, with many rate parameters and yields unmeasured and an important conclusion is that further laboratory work is needed urgently to confirm. The absence of OVOC measurements in this study is a gap that needs filling for future campaigns in this type of environment, and these species represent large sinks for OH and candidate sources for some of the unexplained chemistry. It might have been nice to have had some discussion on exactly what X or Y are, but it would be speculative at this point, but maybe some candidates could be ruled out?

The paper also contains a nice synthesis of work done in similar environments, either

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Interactive
Comment

in urban centres or in regions impacted by high isoprene concentrations at low NO_x. It seems that although the mechanisms to explain the behaviour are unknown, there is at least consistent behaviour now observed between several groups. This is important as the OH and HO₂ measurements are very difficult. The authors have collected together a significant body of previous work for comparison. It seems that the unexplained behaviour in tropical forests, north American forests and this urbanised region in southern China may all have the same origins, although the NO concentration here, even at its lowest, is still significantly higher than in Amazonia or SE Asia tropical forests, and so the importance of RO₂+HO₂ reactions compared with RO₂ or HO₂ with NO is diminished.

In a later update posted by the authors, the MCM v3.2 is used rather than MCM v3.1 to compare the relative sensitivities for specific RO₂ compared with HO₂ – and there is better agreement. This provides a good validation of certain aspects of the update of the MCM. Also, the authors show that using RACM-MIM-GK, which has a lumped scheme for much of the chemistry, gave similar results to the MCMc3.1, and so any discrepancies with the field measurements is probably not due to lumping aspects of the RO₂ chemistry.

Another interesting result is that the OH concentration normalised for J(O₁D) does not show a strong dependence on NO, in contrast to previous studies, and in contrast to the model predictions.

I recommend publication in ACP. The paper is very well presented with very few technical errors, and the results are highly significant. There are a few further specific points below.

The night-time measurements are potentially very interesting given the significant OH and HO₂ that has been observed. Although a future paper is planned on the origins of the nighttime HO_x, given that the data are displayed in this paper, some discussion, albeit brief, of the major conclusions at night would round the paper off.

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Interactive
Comment

What is a heavy-duty car? Does this mean lorries? The NO profile is unusual, being pretty high in the mornings (many ppbs) yet going down to ~ 0.2 ppb in the afternoons. This ban in the afternoon certain types of traffic could be a unique feature which has allowed the conclusions from this study to be drawn.

Page 11341. Line 20, M5 is the Peeters mechanism, M4 is the Paulot mechanism and so do not concern peroxy-peroxy reactions? , or did (M3-M6) refer to the radical sink reactions? Perhaps some rewording to make this sentence clearer.

Page 11344, line 27, “ratio” not “ration”

Figure 13. Although the NO₂ concentration is quite high (up to 40 ppb fig 5, which presumably corresponds to the right hand pie-chart in fig 13), the loss of OH by reaction with NO₂ (which is in the “other” slice of the pie-charts) seems quite small?

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

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