

“Explicit modeling of organic chemistry and secondary organic aerosol partitioning for Mexico City and its outflow plume” by J. Lee-Taylor et al.

Response to Anonymous Referee #3

We thank the Reviewer for their careful reading of our manuscript, and for their positive assessment of the value of our work. The reviewer raises some interesting questions, several of which we consider to be outside the scope of the current study, however we welcome the chance to discuss them below. For the other points, we have edited our text to clear up some apparent confusion regarding our prescribed emissions, and we have fixed the identified typos. Our specific responses follow:

Referee's Summary:

This paper presents the results of detailed, systematic and automated approach to simulating the chemical development of the Mexico City outflow plume, with a particular focus on the quantity and composition of SOA formed. The central component of the study is the detailed chemistry, which was developed using the previously documented GECKO-A generation methodology. This has allowed the degradation of a large number of emitted VOCs to be considered and represented at a very high level of detail, but with validated simplifications applied to reduce the mechanism to a manageable size. Given the inevitable uncertainties in many processes which need to be represented in the model, the results provide a remarkably good description of the observations. They also provide some fascinating insights into the chemical complexity of atmospheric chemistry, and an excellent illustration of the value of considering chemistry in detail to allow a reference benchmark against which to develop and/or evaluate reduced mechanisms which aim to retain those features of the chemistry which could not have been shown to be important without the initial detailed approach.

Importantly, the authors include a clear indication of those aspects of the results which are considered to be robust, and those which depend largely on model assumptions or for which more observational evaluation is required. Without this, it would be unclear to what extent the good results might have been artificially manufactured, or the extent to which compensating systematic errors might be contributing. The paper is generally clearly written and almost publishable in its submitted form. The authors may wish to consider the minor comments below when producing the revised manuscript.

Page 17022, final paragraph: the use of a given n-alkane as a surrogate for all S/IVOC alkanes of the same carbon number is described, with the explanation that branched alkanes of high carbon number retain linear character. This approach would seem to be essential, and the assumption is probably generally reasonable. However, the assumption will break down when the alkanes become sufficiently highly branched, and this will occur more readily for the more abundant IVOC at the small end of the range. Can the authors provide a judgement of the fractional contribution of such highly branched alkanes (as a further justification for the assumption)?

Unfortunately observational data are not available to support such an assessment. A systematic parameterization of the influence of branching would clearly be an interesting future study. We have re-worded our text, for clarity:

“In principle, branched alkanes may undergo more fragmentation than do n-alkanes, especially if the degree of branching is high enough to force fragmentation rather than radical isomerisation. However, since diesel fuel (which will be responsible for the majority of C12-C20 alkanes in Mexico City) is predominantly linear, we assume that the ratio of branching to chain length is sufficiently low that calculated SOA yields will not be significantly affected.”

Page 17024, first paragraph: a comparison of the simulations with observations of HOx radicals in Fig. 3 is given. Given the recent paper of Fuchs et al. (2011), the authors may wish to clarify whether the HO2 measurements might have a fractional contribution from some RO2 radical classes (specifically those from OH+alkenes and OH+aromatics).

Our model does indeed have detailed chemistry of OH with alkenes and aromatics in the ambient air, but does not consider how these reactions could interfere with the experimental detection of HO₂. The comparison in Fig. 3 is only intended as a semi-quantitative evaluation, as many other factors could affect HO₂ and its variability. It is true that RO₂ may interfere with detection of HO₂, however, critical discussion of measurement interferences is beyond the scope of our paper.

Page 17024, second paragraph: the measurements of the large alkanes are logically stated to be lower limits, owing to difficulties in measuring all contributors. Can the authors provide some further justification that a measured coverage of 20% (compared with the model) is a reasonable shortfall?

We are primarily using the Los Angeles results to compare the carbon-number distribution not the absolute concentrations, because our modeled n-alkanes are used as surrogates for all primary aliphatic compounds with similar vapor pressures. We have added to figure 5 the “Unidentified Complex Mixture” values from Los Angeles to dispel confusion on this point, and edited the text to clarify : “Fraser et al. (1997) measured 16 C_{≥11} n-alkanes totaling 3.1 μg m⁻³ (Fig. 5), and 13 specific branched and/or cyclic C₁₈₋₂₈ alkanes totaling 0.24 μg m⁻³. They also observed an unresolved complex mixture (UCM) of branched and cyclic alkanes, whose abundance outweighed that of the n-alkanes by over an order of magnitude. Figure 5 shows our simulated concentrations and distributions by carbon number of the larger n-alkanes in Mexico City to be comparable to those of the observed sum of n-alkanes and UCM in Los Angeles. Together, Figs. 3-5 confirm that our box model is a reasonable representation of the gas phase urban photochemical environment in which the NO_x-catalyzed oxidation of hydrocarbons can lead to SOA evolution.”

Page 17038 (and other points including Fig 9, abstract and conclusions): the authors comment that delta-hydroxy ketones are simulated to be important (and persistent) SOA contributors. A number of studies have demonstrated that these compounds isomerise to cyclic hemiacetals, with subsequent dehydration to produce highly reactive dihydrofurans. Given that a key paper reporting this process is already cited (Lim and Ziemann, 2009), it would seem that this specific relevant example of condensed phase chemistry should be mentioned. This would also seem important given that the authors highlight in the conclusions that further observational evaluation of their results is necessary “to identify the major chemical species contributing to the aerosol” – with specific mention of delta-hydroxy ketones. It would seem that they are unlikely to be observable.

The Lim & Ziemann (2009) result mainly applies under dry conditions. Under moderately humid conditions it is likely that, even if some conversion were to take place, a significant proportion of the delta-hydroxy ketones would persist. We agree that the reaction is worth mentioning in this section and have added the following text to page 17028:

“Lim and Ziemann (2009) observed di-substituted hydroxycarbonyls to undergo heterogeneous reactions, leading to products with greater volatility. However these reactions mainly occur under dry conditions and are not considered in our gas-phase model.”

Typographical errors:

Page 17024: A reference to Fig. 3 is required.

We have added a reference to Fig 3 to the discussion of OH and HO_x.

Page 17038, line 3: agreement.

Corrected.

Page 17030, line 30: doi appears to be incorrect for this paper.

The appropriate doi is: 10.1039/b904333k. We have made the correction and thank the reviewer for their attention to detail.