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Atmospheric
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Discussions

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

Anonymous Referee #3

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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)?

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).

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?

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.

Typographical errors:

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

Page 17038, line 3: agreement.

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

References:

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F. and Wahner, A. Detection of HO2 by laser-induced fluorescence: calibration and interferences from RO2 radicals. Atmos. Meas. Tech., 4, 1209–1225, 2011.

Lim, Y. B. and Ziemann, P. J.: Kinetics of the heterogeneous conversion of 1,4-hydroxycarbonyls to cyclic hemiacetals and dihydrofurans on organic aerosol particles, Phys. Chem. Chem. Phys., 11, 8029–8039, 2009.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 17013, 2011.