"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 #2

We thank the reviewer for their positive assessment of our manuscript, and for their thoughtful comments and questions. We have made several minor edits to our text, to make our discussion clearer. Our specific responses follow:

Reviewer's Summary:

The manuscript describes the simulation of organic aerosol in Mexico City using a near- explicit photochemical chemical scheme in a 0-D model framework. It presents a fairly comprehensive discussion of the relative contributions of precursors to the magnitude and elemental compositions of modelled organic aerosol. The various sections of the manuscript are well laid out and easy to read and follow. In my view the material presented here gives additional useful insight in the modelling of organic aerosol and I recommend publication in ACP after the following clarifications and corrections are made.

General Comments

1. Page 17017, line 15 and discussed on page 17037 lines 23-27: The authors are using the vapour pressure equation of Myrdal and Yalkowsky with the Tb estimation method of Joback and Reid. This Tb estimation method has been repeatedly shown to give too high boiling points (for Tb values above about 550K) leading to a substantial underestimate in vapour pressure and consequently enhanced SOA mass. Why this choice when the authors know it overestimates SOA?

The MY + JR parameterization was used in the original formulation of the GECKO model (Camredon et al., 2007). We have been exploring alternative formulations, have begun some comparisons (see Valorso, 2011) and are currently evaluating which method is best for future simulations.

2. Page 17017 lines 15/16:- The Myrdal and Yalkowsky equation is not a group contribution method. Suggest this sentence is reworded to read ....using the method of Myrdal and yalkowsky (1997) with boiling points estimated using the group contribution method of Joback and Reid (1987) with the...

Thank you for the clarification. We have re-worded: "…using the method of Myrdal and Yalkowsky (1997) with boiling points estimated using the group contribution method of Joback and Reid (1987). The group contributions used for the …."

3. Page 17018, lines 18-20: why were nonadecane and eicosane reactions allowed to react to fifth generations (and 3rd generation for larger NMHCs). Is this for scientific or practical reasons?

This is for practical reasons, to mechanism size, but it also has a scientific basis. In addition to our sensitivity test (which we mention in the text) Fig 8 shows negligible abundance of products in the highest-allowed generation for each carbon number, justifying the approximation. We have added text to the discussion of Figure 8, referring back to the mechanism restriction:
"…(Presto et al, 2009). Incidentally, the lack of significant amounts of higher-generation products for the species with the longest carbon chains supports our computational strategy of limiting mechanism growth to 3 or 5 generations for these species. Smaller species show …"

4. Page 17020, line 7: "coeffiecients" should be "coefficients".

Corrected.

5. Page 17020, lines 8-9: The decision to neglect wet and dry deposition is odd. Were there any sensitivity studies that were done to validate this?

We agree that dry and wet deposition should be included in regional models, however we regard them as additional complications for our box model. We chose to represent non-rainy conditions (no wet deposition), to allow us to follow our simulated plume SOA for a number of days. For dry deposition, a back-of-the-envelope calculation suggests that, for HNO_3, with a deposition velocity of 3 cm s^{-1}, the lifetime would be on the order of 1 day. While this is not negligible in a regional model, in the present context it does not change our conclusions about the evolution of aerosol chemistry. In addition, the multi-day Lagrangian air parcel that we consider does not necessarily stay in contact with the surface, therefore we expect the surface deposition effect to be even smaller. We have amended our text as follows:

(Section 2.2) "Wet and dry deposition were neglected. The Mexico City region was generally dry for much of March 2006 (Fast et al., 2007), hence wet deposition may reasonably be omitted. Dry deposition may have some effect on our results, with removal rates of order of a day for the most labile compounds (e.g., HNO_3 with a deposition velocity of 3 cm s^{-1} in a 2 km BL) and could become important in multiday simulations if the air parcel remains in contact with the ground. In any case, parameters for dry deposition of SOA and its precursors are poorly known."

(Section 4.4) "Dry deposition can potentially reduce regional SOA loadings. We have performed a sensitivity calculation with a 3-D regional model (CHIMERE, as in Hodzic et al, 2010), which parameterized dry deposition at velocities similar to HNO_3 to get an upper estimate of its effect. The results (not presented in detail here) show maximum reductions in anthropogenic SOA within Mexico City on the order of 5 to 25% when compared to a non-deposition simulation. In the outflow simulation case, air parcel lofting further reduces the potential for dry deposition. Washout during rain events is, of course, a major sink for atmospheric aerosols but is not included in the dry-conditions simulation presented here."

6. Page 17021 line 7 and Table 2 on page 17056: Assuming zero background concentrations of VOCs such as ethane, propane etc does not seem right as it has the potential to perturb the simulated radical budget. Any justification for this and/or an explanation in your discussion how such an assumption would affect the conclusions.

We agree with the reviewer that background concentrations become progressively more important as the plume dilutes over the course of several days. However, Apel et al (2010) show that in the region sampled by the C130 aircraft, well outside the city, CO is the main contributor to OH reactivity and is far more important than other species such as ethane and propane. Thus the OH reactivity is dominated by plume hydrocarbons and CO plus background CO.

7. Page 17024 line 6: By how much is 2-pentene underrepresented in the emissions parameterisation and what is the impact in the simulated organic aerosol?

2-pentene is underrepresented by a factor of 4.4. This omission has no significant impact on the simulated aerosol because C5 species contribute only a miniscule proportion of condensed matter. It does reduce the calculated OH reactivity by ~5% (leading to a corresponding increase in OH concentrations), however the daytime net OH reactivity is only ~3% lower than that derived from the T0 observations, and the modeled OH compares well with measurements, so we see little cause for concern.

8. Page 17032, lines 13:16: Given the significant contribution of biogenic precursors to SOA, the omission of biogenic species is regrettable. Biogenics may be lower in concentrations that anthropogenics in Mexico City but they still have higher potential to impact SOA and thus, changing the magnitude and the elemental composition of simulated SOA. Perhaps the title could be changed to reflect that this is anthropogenic organic chemistry study?

We respectfully disagree. The work of Hodzic et al shows that biogenic precursors are too short-lived to be significant contributors to new aerosol in the city. Most biogenic aerosol in the city is highly aged (Hodzic 2010) & therefore does not participate in the chemistry of the new aerosol. Its mass contribution to the condensation equilibrium is important, and is represented by our chemically-inert BGOA.

9. Page 17038, line 3 should be "agreement"

Corrected.

10. Figure 1 caption is inadequate for this figure and needs to be improved with some explanation provided for all the lines.

We have amended the caption as follows:
“Figure 1. Meteorological parameters prescribed in the box model Eulerian simulations. Solid lines show boundary layer height (km, black, left axis) and temperature (K, red, right axis). Dotted lines show k_{ent}, the first-order rate of entrainment, i.e. vertical incorporation of free tropospheric air due to increasing boundary layer depth (expressed in units of day^{-1}, blue, left axis), and k_{vent}, the first-order rate of ventilation, i.e. lateral exchange with background air due to advection and mechanical mixing (in units of day^{-1},green, left axis).”