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

Reply to Anonymous Referee #1

We thank the reviewer for their careful reading of the manuscript, for their thoughtful questions, and their positive assessment of our work. In general we agree with their minor criticisms of our text and have made numerous small wording changes which we hope will assist the reader and will more clearly present and explain our results. Our detailed response to the reviewer's questions follows:

Reviewer's Summary:

This manuscript describes the application of a detailed (nearly explicit) photochemical box model to the simulation of Mexico City organic aerosol and investigates the simulated concentrations, elemental composition and relative contributions of precursors over Mexico City and downwind. The paper is quite clear and easy to follow, particularly in light of the complex model set-up and analysis. It also included a comprehensive discussion of the robust conclusions and uncertainties which was very balanced and thoughtful. I have some minor points below, mainly to add some clarifications. I recommend that this manuscript be published in ACP once these comments have been addressed.

Minor comments

1. Abstract, line 14 and page 17038, line 20: specify that the larger n-alkanes are estimated SVOC precursors

We agree and have added text to more clearly indicate the surrogate/estimated nature of our n-alkane emissions:

Abstract: "The majority (≥ 75%) of the model SOA stems from reaction products of the large n-alkanes, used here as surrogates for all estimated hydrocarbon emissions of similar volatility, with the remaining SOA originating mostly from the light aromatics. "

Page 17038: "In the model, the SOA is generated mainly from the estimated semi-volatile surrogate species (alkanes), and to a lesser extent from the lighter aromatics."

2. Page 17015, line 17: Technically, field observations do not measure SOA, the AMS analysis identifies OOA and HOA. Similarly, while SOA mass increases were postulated by de Gouw et al., this was not strictly measured. I suggest you re-phrase.

We have inserted new text and re-phrased to make clear the distinction between measured and theoretical classifications of OA:

"Instrumental techniques distinguish between two main types of organic aerosol; minimally oxygenated 'HOA' and highly oxygenated 'OOA', usually interpreted as analogues for POA and SOA, respectively. Field observations show that OOA mass generally outweighs HOA mass even in urban source regions (Zhang et al., 2007), and that OOA mass dominance increases downwind and regionally as OA ages and photochemistry progresses (e.g. de Gouw et al., 2008; Zhang et al., 2007). The implied dominance of SOA in the OA budget calls for a deeper understanding of the chemical and physical processes involved in its formation and evolution, as complex as they may be, to enable and improve prediction of OA and its many influences on the atmosphere."

3. Page 17016, lines 9-10: "improved agreement" is a little vague – could you specifically state that these treatments reduced the model bias?

We have clarified the direction of the model improvement:

"The VBS approach has been implemented for Mexico City in box models by Dzepina et al. (2009) and in three-dimensional chemistry-transport models (CTMs) by Tsimpidi et al. (2010), Hodzic et al. (2010a), and Li et al. (2011). These studies yielded aerosol mass concentrations that are larger and more consistent with observations than in previous parameterizations."

4. Section 1: The discussion of Section 4 answered many questions that came up as I read this manuscript. It would perhaps be worth noting explicitly at the end of Section 1 that you will discuss uncertainties and limitations in the model treatment in Section 4, so that the reader knows that they can expect this.

We are pleased that our discussion in Section 4 answered so many questions. We have re-worded the text at the end of Section 1, to assist the reader:
"We evaluate our model in Section 3 of this work by comparing with observations. In section 4 we place the results in context, discussing uncertainties and model limitations, and highlighting areas where further research is needed to improve our understanding of chemistry leading to SOA formation."

5. Page 17020, line 10: It would be nice to have the justification for neglect of dry deposition spelled out a bit. In particular, it seems that some gas phase organics would have significant dry deposition rates. Could you provide some values to compare to kent and kvent? It might be useful to indicate that this will be discussed further in Section 4.4 or move that discussion of dry dep to this section.

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. A back-of-the-envelope calculation suggests that dry deposition from a 3km bdy layer would be significantly slower than 1.3 day^{-1} (the rate for HNO_3), and in any case does not apply after our air parcel detaches from the surface in the Lagrangian simulation. 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."

6. Page 17021, line 4: why were the concentrations initialized with 24 hr concentrations rather than mean 0 LT concentrations?

The measurements were reported as daytime or as 24-hour averages. We judged the 24-hour average value to be more appropriate than the daytime value for night-time initialization of a box model representing the mean situation in the city because 24-hour means are less influenced by local emissions or by the specifics of the boundary layer depth. However, the specifics of the initialization are relatively unimportant because we ran the Eulerian simulation to a diurnally repeating state such that the results were no longer influenced by the initial conditions.

7. Page 17021, line 7: The assumption of zero background for some of the longer lived oVOCs is obviously incorrect. But perhaps it's irrelevant to the simulations here. If so, please state this explicitly. If not, perhaps aircraft observations from MILAGRO could constrain some of these values?

We do not expect background oVOCs to be major contributors to SOA mass, since, as we show, our modeled SOA is made up of molecules significantly larger than the most common oVOCs measured in background air (e.g. formaldehyde, acetaldehyde, methanol: Apel et al 2010). The other possible effect of background oVOC would be to modify the plume OH. Apel et al's aircraft measurements show that CO becomes progressively more important relative to OVOCs as the plume ages, and therefore CO is expected to dominate the OH reactivity in background air.

8. Page 17021, line 8: What does "based on the Mexico City emissions inventory" mean? The mean emissions for the region? A location in the center of Mexico City? At T0?

We mean the emissions in tons/yr for the entire city, as specified in Tie et al (2009). We have re-worded to clarify:
"Emissions of species listed in Table 2, and of CO and NO, were based on the emissions inventory and diurnal patterns for Mexico City used by Tie et al. (2009) in the WRF-Chem model,…"

9. Page 17022, top: Is there a diurnal profile on this background aerosol? Should there be? Particularly if it includes regional biogenic or fire influence? or is the temporal variability integrated over the regional background? Please detail and justify.

There should not be a diurnal profile on this prescribed regional background aerosol, because it is assumed to be both well aged and regionally well mixed, hence its concentration is the same inside and outside the city.

10. Page 17023, line 8: how is the 143 kg/km2/d value consistent with a 7.5 increase in 32 kg/km2/d given on the previous page (leading to 240 kg/km2/d)?

The POA flux value should have been 19 kg/km2/day. We thank the reviewer for pointing out our error and have corrected it. We also added the words "near the T0 site".

11. In the Figure 3 HO2 & HO2+RO2 panel: is the data for only HO2 or both? If the later, please comment on the large disagreement with the model.

The data is only for HO2. We have changed the y-axis label to reflect this.

12. Page 17024, line 18: note that for greater than C13 compounds the difference is over an order of magnitude.

The reviewer is correct. We have amended the text to reflect the larger difference.

13. Page 17025, lines 19-20: Why is afternoon SOA is so much higher than Hodzic et al?

We calculate vapor pressure for each aerosol constituent individually, while the parameterization of Robinson et al (2007) used by Hodzic et al applies a simple binned vapor pressure distribution. The Robinson parameterization has recently been suggested to be too evaporative (Dzepina et al, 2011). We have added additional explanation to our text:
"The difference is due to differences between the two modeled SOA vapor pressure distributions: the current model calculates vapor pressures for each individual aerosol constituent rather than parameterizing a bulk distribution across a discrete number of bins. Also, there is evidence (Dzepina et al, 2011) that the Robinson et al (2007) parameterization allows too much evaporation when the aerosol is warmed, as is the case in the afternoon."

14. Figure 7 caption (and perhaps in text): be clear that the C# refers to the C# of the precursor compound not final product.

Actually, Fig 7 shows the development of the aerosol composition in terms of C# of the individual aerosol constituents. We have added text to clarify this:
Pg 17025, line 25: Figure 7 illustrates the changing balance within the aerosol between POA (grey areas) and SOA (colored areas) in terms of carbon number of the aerosol constituent.

Fig 7 caption: Composition of simulated organic aerosol within Mexico City. SOA (colors) and POA (grey region) are sorted by carbon number of the individual aerosol constituents.

15. Discussion of Figure 7 and in Conclusions: It should be indicated that while no validation of C14+ alkanes is available for Mexico City, given that concentrations here exceed LA measurements by over an order of magnitude, the model may significantly overestimate the SOA from this source.

It is true that there is an order of magnitude difference between the LA n-alkanes and the values we use. However we are using the n-alkanes as surrogates for all NHMCs of similar volatility, as an exploration of one possible chemical distribution of the Hodzic et al / Robinson mass-and-volatility emissions distribution. In fact, the LA UCM contains more mass at higher carbon numbers than is included in our emissions, suggesting that our emissions may not after all be significantly overestimated. We have added the "Unidentified Complex Mixture" values from LA to Figure 5 to dispel confusion on this point, and edited our text accordingly:
End of Section 3.1: "Fraser et al. (1997) measured 16 $C_{\geq 11}$ n-alkanes totaling 3.1 μg m^{-3} (Fig. 5, and 13 specific branched and/or cyclic C_{18-28} 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 NOx-catalyzed oxidation of hydrocarbons can lead to SOA evolution."

16. Page 17026, line 11: The Lagrangian simulation results have not been presented yet. Section 3.4 should be moved prior to this.

We prefer to introduce the development of the aerosol chemical composition during the Lagrangian simulation as a logical follow-on from discussion of the composition of the Eulerian case aerosol. We have added a note at the end of Section 3.2 to remind the reader of the existence of the Lagrangian case, and to signal our intention to discuss in Section 3.4 the mass results from that run:
"OA mass development during our Lagrangian simulation, representing conditions in the outflow from the city, will be presented in Section 3.4."

17. Page 17028, line 16: to be specific "to -1 throughout the 6 days, and modeled SOA: : : "

We have re-worded this sentence:
"During the first 3 days, while modeled (SIGMA)OA composition is dominated by POA and SOA rather than by BGOA, its slope on the Van Krevelen diagram is close to -1. Modeled SOA…."
We have also replaced the word 'gradient' with 'slope' throughout this section, to be less confusing.

18. Section 4.4: can you explicitly discuss the contributions from the estimated SVOC/IVOC vs. other estimated precursors?

We already state (paragraph 3 of section 4.4) that C10-aromatics give rise to >30% of SOA. To help orient the reader, we have now slightly simplified the wording of paragraph 1 and added the following sentence:
"The estimated SVOC and IVOC precursors and their reaction products contribute about 70% of the resulting modeled SOA, with the remaining 30% originating mostly from single-ring aromatic precursors."

19. Page 17038, line 3: typo "agreement"

Corrected.

20. Page 17038, lines 3-5: Good agreement could also be obtained by a coincident underestimate of sources AND sinks.

This is a fair point. We have amended the text as follows:

“A good agreement despite ignoring several precursors and suspected or known SOA formation pathways suggests that either GECKO-A is too efficient at producing SOA, that the emissions of the unmeasured S/IVOCs were overestimated, or that both sources and sinks were underestimated.”