Response to Anonymous Referee #4

We thank the Reviewer for their thoughtful and thorough reading of our manuscript, and for their helpful comments. We agree with all the points raised, and have implemented the suggested changes. In particular we have added several references to early literature, so that appropriate credit is given to pioneering researchers in the field. Our specific responses follow:

Referee’s Summary:

The subject manuscript by Lee-Taylor et al. reports on a chemical box model application of GECKO-A, a nearly explicit gas-phase chemical mechanism model with gas-particle partitioning. As presented in the subject manuscript, as well as in future applications, this model truly will advance the field, as the model provides insights into the gas-phase oxidation chemistry that forms condensable products in the atmosphere that can not be explored with the highly parameterized models typically used to represent ambient SOA formation. There are few, if any, other models that use this model approach, and thus it is a highly unique and valuable tool. The model approach and assumptions are clear and generally well-supported. The assessment of model performance (robust results) and sensitivity to initialization are very well described. After addressing the minor comments below, it is suggested that the manuscript be published in ACP.

Comments:

It isn’t always clear, both in body and figures, whether the results/discussion refer to the Eulerian scenario, Lagrangian scenario, or both. For example, on p. 17025, line 23 starts with Figure 7 and goes into the results without specifying which results are illustrated in Fig. 7; in Figure 10, the scenario is not specified. It is suggested that the authors revise the results, discussions, and figure captions as necessary to make the scenario distinction clearer (relabeling section headers, e.g., 3.2 and 3.3, would likely help).

We appreciate this suggestion, and have inserted numerous references throughout Section 3 (and subsections) to clarify which scenario is being discussed.

p. 17015, starting line 15: The cited references for formation of anthropogenic and biogenic SOA are inappropriate. Each of the cited papers has made a notable contribution to the field, but the formation of SOA from anthropogenic and biogenic precursors was pursued in much earlier work (early 90’s).

We have added the following early references (and references therein):


This was an oversight on our part. We have added the reference, and thank the reviewer for the opportunity to give appropriate credit to earlier researchers.

p. 17023, line18: Does the overestimation of ozone tell you anything about your assumed emissions?

A lower ozone could be achieved in the model by decreasing the VOC/NOx ratio because the city is in the NOx-inhibited, VOC-sensitive regime (Stephens et al., 2008; Tie et al., 2009; Li et al., 2011). But realistically, for a box model, this is pretty good agreement. We are comparing to city-wide monthly average ozone where the day-to-day variability of the individual data points is comparable to the model/measurement discrepancy, so we don’t think it’s a problem.


p. 17025, line 19: It is recommended that some suggestion(s) be made as to the general reasons for the discrepancies between the current model and the parameterized model of Hodzic et al. (2010a), given the similar treatment of emissions.

This is an interesting point. 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.”

p. 17034, line 12: Are the n-alkanes used as surrogates for "all" precursors of similar volatility? Or just the unmeasured NMHCs? It seems the latter is the case. If so, suggest specifying/clarifying here.

We have slightly re-worded: "... using n-alkanes as surrogates for all emitted organic precursor molecules of similar volatility...."

p. 17036, starting line 24: There are also earlier more appropriate references for aqueous phase chemistry.
We have added the following references:


p. 17037, line 24: The statement about the importance of C>11 n-alkanes in Mexico City seems unnecessary and largely unsupported, given the uncertainty in the emissions. It seems rather that (at least without some verification of the emissions) they represent a range of species with similar volatility/reactivity, as intended.

The statement referred to (on p 17038) is about alkanes in general (not n-alkanes) and is based on H/C & O/C ratios. We agree that it was somewhat speculative and have removed this sentence to avoid confusion.

p. 17039, starting line 10: While the discussion of aerosol formation in the Lagrangian scenario (3.4) was interesting and likely quite important, the related conclusions do not make much sense. The authors comment that partitioning theory predicts that particles evaporate as plumes are diluted, in the absence of chemical processing, and that “quite contrarily” their model predicts continuing growth. One, the partitioning portion of the GECKO-A model employs classic partitioning theory and so partitioning theory and the GECKO-A model (at least in terms of gas-particle partitioning) are the same. Two, it is not clear what is meant by chemical processing: : : if that means gas-phase oxidation chemistry, then the statement supports the model results, as it is the continued oxidation and subsequent partitioning that produces SOA in the diluted plume. Evaporation of SOA in dilute conditions assumes that there is no gas-phase source of condensable products. In the event that there is a gas-phase source of condensable products, as in the Lagrangian application of GECKO-A, then gas-particle partitioning would predict the formation of additional SOA (as in the Lagrangian application of GECKO-A). It is suggested that this part of the conclusions be rewritten to better capture the importance of the results as presented in 3.4.

The Reviewer is correct on both points, and as a result we modified slightly the wording. On point one: Indeed we also use partitioning theory, and we should have said more specifically that partitioning alone, i.e. condensation and evaporation in the absence of any further gas or particle chemistry, would predict a decrease in total aerosol mass (or, at most, a constant particle mass if vapor pressures approach zero). This also addresses the Reviewer’s second point, which emphasizes the importance of chemistry to the continuing growth of particles. We now state this issue this more clearly:

“In the absence of chemical processing, dilution of the urban plume by cleaner background air would lead to evaporation of the particles (or at most to constant particle mass if vapor pressures approach zero), because particle/gas partitioning is proportional to the mass concentration of particles (Pankow, 1994b; Odum et al., 1996). Quite contrarily, our model predicts continuing particle growth even after dilution (Fig. 11). The growth occurs because of continuing gas phase reactions of the hydrocarbon precursors and their partly oxidized intermediates, yielding molecules of progressively lower vapor pressures”

**Fig. 1:** Terms should be described either in a figure legend or in the caption.

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 $k_{\text{ent}}$, 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 $k_{\text{vent}}$, 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).”

Fig. 10: Suggest including the dotted red and blue lines in the legend for panel a.

We have done this. Thanks for the suggestion.