We thank the reviewers for their thoughtful comments that have helped us clarify and improve the manuscript. We have reproduced the reviewer comments in black text. For ease of review, our responses are given in blue text, while the text added to the manuscript is given in *blue Italics.*

Referee 2 Comments

R2.1. Hayes et al. present results from box model simulations of in-basin SOA formation focusing on Pasadena, CA and measurements made during the CalNex 2010 study. Their box model is explicitly constrained by observations of ambient traditional VOC concentrations. They also include emissions of intermediate and semi-volatile organic compounds (I/SVOCs) that are not included in standard emissions inventories. They link their I/SVOC emissions to POA emissions and assume that all POA sources have identical volatility distributions. They also consider a first order estimate of the influence of chamber biases on SOA yields by multiplying their yields of semi-volatile VOC product species by 4. They have considered a number of different schemes for treating the oxidation of S/IVOCs and even of VOCs. They find that the various combinations all exhibit a diurnal profile shape consistent with the observations, but that certain model formulations perform better than others when the model results are compared with observations of the semi-volatile oxygenated organic aerosol (SV-OOA) factor determined from PMF analysis of the ambient organic aerosol time-series. They conclude that, overall, there is a need for some contribution of I/SVOCs to allow for simulation of SOA levels that are consistent with the average SV-OOA diurnal profile. They find that biogenics from within LA ("in-basin") contribute negligibly to the total in-basin SOA, although biogenic-SOA may contribute to the background OA burden. They find when they extrapolate their simulations based on these literature parameterizations to longer times that they overestimate the amount of SOA that should be formed.

Overall, the authors do a good job explaining what they have done, describing the results, and comparing between the different literature model formulations. I believe that this work should be publishable after they address the comments below.

We thank the referee for their thoughtful review and have provided point-by-point responses to their comments below.

R2.2. The authors apply a number of different model formulations, taken from the literature, for the simulation of SOA concentration diurnal profiles within a constrained box model. Each of these model formulations/parameterizations has particular limitations that ultimately lead to differences in the box model results. Some aspects of the model formulations are more constrained than others. For example, the VBS yields for the traditional VOCs are constrained from comparisons with chamber observations whereas the literature ageing scheme(s) applied have generally weak, or even no, constraints. The O/C parameterization for S/IVOCs are similarly underconstrained, while the O/C estimates for SOA from VOCs are guided by observations from laboratory studies. The S/IVOC emission scheme is linked to literature measurements of POA volatility, although connecting these observational constraints on the volatility distribution to actual emissions is challenged by a lack of knowledge regarding the conditions under which the emission inventory was determined. I therefore suggest that it would be useful if the authors were to note a bit more explicitly what aspects of the literature parameterizations are more/less constrained by previous observations. They already do a good job of describing the model formulations, but some minor addition regarding the nature of these formulations might facilitate greater understanding by the reader. I also suggest that, given the inherent uncertainties in the parameterizations, that the authors limit the scope of any conclusions regarding whether one particular parameterization is particularly better than another.

We generally agree with the descriptions of the reviewer in this comment. Some of the parameterizations are based on a larger amount of data than others, and some have only weak constraints. We have included all the constraints that we were aware of, but in some cases assumptions needed to be made due to the limitations of the available information. In all cases we have made what we thought was the most reasonable assumption, stated clearly what was done, and in multiple cases we have presented several model alternatives to illustrate the sensitivity of the results to different assumptions.

We have modified the abstract and the conclusions to better clarify these points. We have removed the sentence that stated that the GRI parameterization did better in reproducing the observations. In particular, the following text has been added to the abstract:

"The results from the 3 parameterizations show large differences (e.g. a factor of 3 in SOA mass) and are not well constrained, underscoring the current uncertainties in this area."

and

"The relative contribution of each source is uncertain by almost a factor of 2 depending on the parameterization used."

R2.3. Some additional clarification regarding the specification of the BVOC emissions would be useful.

We have added a paragraph to the manuscript to clarify the specification of the biogenic VOC emissions. As an example, we have also included in Figure SI-2 a comparison of the diurnal cycle predicted and measured for isoprene.

"The biogenic VOCs are not expected to be emitted proportionally with CO, and therefore the approach described in the previous paragraph cannot be used to specify the biogenic VOC emissions. Rather, the emissions of biogenic VOCs were adjusted empirically to match the observed concentrations of isoprene and terpenes, after accounting for anthropogenic isoprene using Δ(isoprene)/ΔCO (Borbon et al., 2013). Only ~4% of the daily average isoprene is from anthropogenic sources. In addition, the diurnal profile of emissions was assumed to be proportional to temperature.

The model consistency with the VOC measurements, including for biogenic VOCs, is evaluated by comparing the measured and modeled diurnal cycles. Some of the cycles compared are given in Figure SI-2 as an example. It is observed that the model is generally consistent with the biogenic VOC measurements."

R2.4. P32340: The authors should provide some brief discussion regarding their use of a constant [OH] in the simulations.

We have added substantially more discussion regarding the use of constant [OH] in the simulations. Please see the updated text below, which is from Section 2.3.

"The second consideration is that the purpose of using the ratio of VOC concentrations is to determine the ·OH exposure for the air mass at the Pasadena site. (·OH exposure is the concentration integrated over time for an air parcel.) While the ·OH exposure for the site is therefore well-constrained, the actual ·OH concentration in the modeled air parcel as a function of time is not as well-constrained. Thus, the photochemical ages used here (Figure 3) are calculated using an average ·OH concentration of 1.5×10^6 molec cm^{-3}, as described in our previous work (Hayes et al., 2013), and the model is run with the same concentration. Insofar as the model produces the same ·OH exposure as determined from measurements, which is always the case in this modeling study, the actual concentration of ·OH used in the model is not expected to substantially influence the results. In other words, while the concentration ·OH in the model is assumed to be 1.5×10^6 molec cm^{-3}, the integral of the ·OH concentration over time is constrained by the observed VOCs ratios. As expected, in the middle of the day the photochemical age will be longer than the transport age, and the opposite will be true during periods with low ambient ·OH."

R2.5. Section 2.6: Some clarification regarding the correction for "higher OA concentrations upwind of Pasadena" would be useful.

We have added a more in-depth introduction to this section in order to clarify this correction (see below). Perhaps, a useful way to understand this correction is the following: the initial concentration of precursors are calculated using the emission ratios to CO, which are multiplied by the measured excess CO (above the background level) to determine the initial precursor concentrations. Given that CO and precursors should undergo the same amount of vertical and horizontal dilution during transport, this approach implicitly dilutes the precursors by the appropriate factor <u>before oxidation occurs</u>. In reality, the species in the air parcel are oxidized

and diluted at the same time. This difference then means that the partitioning calculated in the model upwind of Pasadena will not be perfectly accurate. (However, the partitioning calculated at Pasadena is accurate.) We have applied a correction for this effect, although this correction is actually small due to the fact that the aerosol mass is distributed in volatility space over many orders of magnitude, whereas the OA concentration generally varies over a much smaller range (2 - 20 µg m^{-3} for Pasadena).

"2.6. Correction for changes in partitioning due to emissions into a shallower boundary layer upwind of Pasadena

To account for changes in partitioning due to lower planetary boundary layer (PBL) heights, and thus, increased OA concentrations upwind of Pasadena, the concentrations of POA, V-SOA, and SI-SOA are increased upwind of Pasadena beyond the amount already simulated in the model. This correction is necessary because using CO as a conservative tracer of emissions does not account for how the shallow boundary layer over Los Angeles in the morning influences partitioning between the gas and particle phases. Specifically, during the afternoon Pasadena is a receptor site for pollution from downtown Los Angeles that was generally emitted into a shallower boundary layer during the morning. The reduced vertical dilution will lead to higher concentrations of POA as well as any urban SOA formed, which in turn leads to higher partitioning to the particle phase and less gas phase oxidation of primary and secondary S/IVOCs."

R2.6. Questions and concerns regarding results and discussion:
I suggest that the introduction of the model variant that considers the influence of vapor wall losses be moved to methods.

In accordance with the reviewer's comment we have moved this subsection to the methods section.

R2.7. P32347/L10: The authors conclude here that their simulation results point to the "importance" of S/IVOCs. "Importance" is such a cagey word. I suggest that the authors be more

precise, stating that their results suggest that S/IVOCs contribute anywhere from X-Y% of the total SV-SOA.

We agree with the review that giving a percentage would be more precise, and so we have calculated the percentage of SOA formed from P-S/IVOCs in each model and added text describing the results to the manuscript (see quoted text below).

"Specifically, the contribution to total SOA from P-S/IVOCs in the box model is 65-75% (ROB+TSI), 80-87% (GRI+TSI), 80-92% (PYE+TSI), and 44-51% (ROB+4xV). The range indicates the variation in the contribution with the time-of-day. Thus, only in the ROB+4xV model variation is the estimated contribution to SOA from VOCs generally larger than or equal to that from the P-S/IVOCs. We note however these percentages include only the urban SOA and not the background OA, which is likely also SOA."

R2.8. Although the authors do clearly distinguish between SV-OOA and LV-OOA, in general, it could be useful if they take opportunities to remind readers more often that the SOA being investigated here excludes background OA, a fraction of which is likely SOA.

We have added several reminders of this point to the text. In particular, these reminders have been added to the 1st paragraph of Section 3.1.1., the first paragraph of Section 3.1.2., and the figure caption of Figure 6.

R2.9. Fossil vs. Modern: 1. The fossil/modern carbon analysis was determined for samples collected over only 7 days, a small subset of the overall campaign. The authors should note whether this week was generally representative of the overall campaign. 2. The authors might point out more strongly that the fossil/modern split determined here is linked to the assumptions regarding the assumed I/SVOC volatility distributions and emissions of these same compounds between sources.

In accordance with the reviewer's first comment we have added the following text to Section 2.4.

"In particular, the dates that the filters were collected were 30 May as well as 3, 4, 5, 6, 13, and 14 June 2010. Thus, these filters are more representative of the second half of the campaign that was more strongly influenced by pollution from the basin, compared to the first half of the campaign were regional advection played a more important role (Ryerson et al., 2013). Given the cost of the ^{14}C analyses, these days were chosen on the basis of the larger urban influence determined from the real-time measurements, and are therefore better suited to constrain urban sources (the subject of this paper) than if the analyses had been performed on filters from randomly-chosen days. However, it is noted that the relative concentrations of the different components of the OA were similar when averaging the second half of the campaign or the entire campaign: 14% vs. 12% for HOA, 5% vs. 5% for LOA, 12% vs. 17% for COA, 28% vs. 34% for LV-OOA, 40% vs. 34% for SV-OOA. Thus, it appears reasonable to assume that the relative results from the ^{14}C analysis are representative of the entire campaign. "

With respect to the second comment, we have added the following discussion to Section 3.1.2.

"It should be noted that the fossil/modern split from the box model that is described above depends on the initial P-S/IVOCs concentrations and volatility distribution assumed in the model. These parameters are not well constrained for cooking emissions, as discussed in further detail in Section 3.1.4 below. In addition, as discussed in the previous section (3.1.1) the concentration of primary IVOCs in the box model is higher than that measured. Thus, as an extreme sensitivity study, the model variations were also run under the assumption that cooking sources did not emit any P-S/IVOCs or, in the case of the PYE+TSI variation, any SVOCs (Figure SI-5). In this sensitivity study there is improved model/measurement agreement for primary IVOCs as shown in Table SI-3."

R2.10. SOA Apportionment: P32354/L14: I find the point associated with the mention of these PMF results from filters to be somewhat unclear. Are the authors simply saying that someone else said that diesel might contribute something?

Yes, that is correct. We have modified the text to make this point clearer (see quoted text below.)

"In addition, the existence of a diesel contribution in the model is consistent with PMF analysis of FTIR spectra of OA filter samples collected in Pasadena, in which, one SOA component exhibited relative peak intensities in the C-H stretching region that suggest some contribution from diesel emissions (Guzman-Morales et al., 2014), although the percentage of SOA from diesel could not be determined in this previous work."

R2.11. Evolution for 3 days: P32356/L12: I can see the concern raised regarding potential overestimates of OA downwind from urban regions in models. However, I think it is equally important to note that this is intimately tied to the model formulation that is used. Many models use very simple parameterizations that will not overpredict (necessarily), potentially even underpredicting (as shown with the WRF-CMAQ model). I think that the model dependency of this conclusion needs to be emphasized to a greater extent.

We have updated the text in this section (3.1.5) to more clearly state that this finding only applies to the parameterizations discussed in this section. The revised text reads:

"We also note that all of the parameterizations used in this section produce SOA/ΔCO ratios substantially larger (by factors of 2 or more) than those observed globally for aged air masses (i.e. photochemical ages greater than one day at an average OH concentration of 1.5×10^6 molec cm^{-3})."

R2.12. WRF-CMAQ box modeling: I think that the comparison here can go even further than what is already noted by the authors. The non-ageing VBS treatment of VOCs in the primary box model is essentially equivalent to the 2-product model in CMAQ. The only difference is really that there are four products instead of two. Yet in the primary box model if only the VOCs are considered the underprediction is not a factor of 25, as is seen when using CMAQ in box model form. It is more like a factor of 5 or 6. While still substantial, I think that this also indicates that there is a fundamental difference in the basic model parameters used in the CMAQ 2 product formulation vs. the VBS 4-product formulation. In other words, toluene in CMAQ does not equal toluene in VBS. The authors are encouraged to emphasize this upon revision. They may wish to

refer to (Barsanti et al., 2013) who discuss issues associated with refitting data to determine 2 product parameters.

The statement by the reviewer about the two parameterizations being "essentially equivalent" is incorrect. The two parameterizations of V-SOA are conceptually equivalent but produce substantially different results. As stated in P32357, L17-24, for this comparison we use the older V-SOA yields from Koo et al. (2003), which are significantly lower than those of the Tsimpidi et al. (2010) parameterization used in the rest of the paper. The latter parameterization was updated using more recent chamber results such as those of Ng et al. (2007). We use the Koo et al. (2003) parameterization when comparing the results of the box model to WRF-CMAQ because the parameterization in CMAQ is of the same vintage, and thus we can show that both models produce very similar results when using similar parameterizations. We have added the following text at the end of P32357 L24 to clarify this point:

"Note that the Koo et al. (2003) parameterization produces substantially lower V-SOA yields than the Tsimpidi et al. (2010) parameterization used in the rest of this work. The latter parameterization was updated using more recent chamber results (with higher yields) such as those of Ng et al. (2007). The use of the older Koo et al. (2003) parameterization for this specific comparison was motivated by the fact that the parameterization for urban SOA in the version of CMAQ used here is based on the same older data, and does not contain the higher updated yields in, for example, Tsimpidi et al. (2010)."

R2.13. Oxygen content comparison: The literature oxygenation (i.e. O/C) parameterizations used for S/IVOCs are particularly underconstrained. I suggest that the authors take care to note that, given these inherent uncertainties in the O/C model formulation, the results here should not necessarily be taken as an indication that one model performs better than another.

We certainly agree with the reviewer, and have added the following paragraph in Section 3.2 of the manuscript in order to highlight this important point.

"Lastly, we note that there are large uncertainties in the parameters used to predict O:C such as the distribution of O:C values as a function of volatility for V-SOA or the amount of oxygen mass added to the SI-SOA for each oxidation reaction. It is therefore not very meaningful to conclude from this study that one parameterization performs better than another. Rather, it is apparent that when using several different previously published SOA parameterizations (i.e. ROB+TSI, GRI+TSI, and TSI alone) it is possible to reproduce the observed O:C at the Pasadena ground site."

R2.14. The updated SOA budget: I suggest that the authors focus this discussion on the anthropogenic SOA budget, with less consideration given to the BVOC SOA budget, given that the (non-cooking related) urban SOA here is predominately anthropogenic in origin.

We agree with the reviewer that the BVOC SOA budget is highly uncertain and unrelated to the new constraints derived in this paper, and we have thus removed all references to this topic from the text.

R2.15. Conclusions: Given the differences between the different parameterizations regarding the relative contributions from S/IVOCs versus VOCs towards the urban SOA, I suggest that the authors further emphasize that the relative concentrations remain quite uncertain.

We agree with the reviewer and had already included a statement to this effect in the conclusions. However, we have added an additional sentence to the conclusions to emphasize the uncertainty in the relative contributions from each category of precursor. The updated text from the conclusions is quoted below.

"The relative importance of VOCs and P-S/IVOCs as contributors to urban SOA over different time and length scales remains unclear. Depending on the parameterization used in the box model, the amount of urban SOA from VOCs can range between 15 – 53% of the total predicted SOA for the Pasadena ground site. This range is 16 - 58% in a sensitivity study in which the IVOC emissions are reduced by one-half."

R2.16. Figures: Figure 1 is fantastic and is very helpful to the reader to understand how the model formulations work.

We are very happy to hear that the referee found Figure 1 to be helpful.

References.

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