

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 1 Comments**

**R1.1.** This paper describes modeling the secondary organic aerosol (SOA) formation in Los Angeles as measured during the CalNex study in May/June 2010. The paper evaluates a variety of different models/parameterizations – WRF-CHEM, WRF-CMAQ, and a box model with several different mechanisms. None of the models are novel, but applying them to CalNex is new (EPA has been doing some evaluation of the CMAQ model, e.g. a paper is up on ACPD right now <http://www.atmos-chem-physdiscuss.net/15/157/2015/acpd-15-157-2015.html>). Given the comprehensive nature of the CalNex dataset it is valuable to use it to evaluate SOA models. The analysis is similar to previous work the authors have published for Mexico City.

The conclusions from the work appear to be largely consistent with those of previous studies. The old, traditional SOA models that only consider a relatively small number of volatile organic compounds cannot explain the measured SOA, even if one makes extreme corrections to yields for potential vapor wall losses to chamber walls. The paper shows that mass closure on the SOA can be achieved if one includes semivolatile and intermediate volatility precursors in a model. The paper evaluates several different schemes for doing this. The paper evaluates models against SOA mass, degree of oxygenation, and fossil/modern split. The parameterization with IVOC/SVOC all appear to work reasonably well (but not perfectly), but are not well constrained with data. The simple IVOC/SVOC schemes the authors consider appear to overpredict the amount of SOA at longer time scales (~ 3 days), presumably (as mentioned by the authors) because they do not include any fragmentation. There is reasonable agreement between fossil/modern carbon data and their apportionment. Finally, the authors show that a simple parameterization they developed in Mexico City for SOA formation appears to work in LA as well. These are basically the same set of conclusions as the Mexico City work, with the addition of fossil/modern carbon.

This is a well written paper. It is long and very comprehensive, but I found it not difficult to read and follow. It makes a contribution. Its weakness is that it does not break much new ground. There is value to show that they largely reach the same conclusions as they did with Mexico City. I would recommend the paper for publication after the authors address the following comments.

We thank the reviewer for his/her good summary of the paper and comments.

We note that it is not obvious that the results from LA were going to be similar to those from Mexico City, and many scientists had expressed skepticism that this would be the case. For example a prominent EPA scientist stated in a public comment on a past ACPD paper that “I haven’t paid enough attention to Mexico City modeling studies in the past because [...] I did not expect the findings from intensive field campaigns in Mexico City to be generally transferable when modeling other less-polluted regions of the world.” [P. Bhave, Atmos. Chem. Phys. Discuss., 10, C878–C884, 2010].

**R1.2.** “The work presented here quantitatively demonstrates that PAHs are relatively unimportant compared to other precursors such as methylbenzenes” This statement is too strong. The model only included a few PAH (naphthalenes, methylnaphthalene). It seems clear that these PAHs do not appear to be major precursors, but large amounts of unspciated IVOCs include a fair number of more alkylated or funcationalized PAHs. The authors claim that unspciated IVOC are mainly alkanes, but that has not really been established. If a reasonable fraction (10s of %) were PAHs then PAHs could play an important role.

We have substantially modified the relevant discussion and, for reference, have pasted the new text below.

*“Figure 5B also shows a comparison for the naphthalenes. The tracer estimates are over an order-of-magnitude higher than the model predictions when using the SOA yields from the literature (which are ~20% for the conditions of our study) and the emission ratios determined from the regression analysis of nighttime measurements shown in Figure SI-3. The model is also*

run using the empirically adjusted emission ratios that better match the observed concentrations of the naphthalenes. The model for this variation is still much lower than the tracer estimate. As an additional sensitivity study, we also run the model with the adjusted emissions and a yield of 150% that places all the oxidized mass in the  $C^*=1 \mu\text{g m}^{-3}$  volatility bin. This last variation represents an upper limit estimate of SOA from naphthalenes, in which nearly all of the mass plus the added oxygen partitions to the particle phase, which is much higher than laboratory observations. The tracer estimate, however, is still about a factor of two higher than the model. It is known that the tracer estimate is an upper limit, because the tracer compound, phthalic acid, may not be a unique tracer, and it potentially could be emitted from primary sources (Kleindienst et al., 2012). However, there may be other alkylated or functionalized PAHs that are not explicitly accounted for in the box model, and some of them might produce the tracer.

The best estimate from the model with the adjusted emissions results in 0.7% of the predicted SOA being formed from the measured naphthalenes. Utilizing the upper limit of the model results for the PAHs, including that from the parameterization with a purposefully high yield, it is apparent that naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene account for less than 4% of the SOA mass. While previous work has suggested that PAHs are important precursors for SOA in the Los Angeles Basin (Hersey et al., 2011) these earlier findings were qualitative and based on the observation of phthalic acid in samples. The work presented here, both the modeling results as well as the tracer results, quantitatively demonstrates that SOA from identified PAHs is relatively small but not negligible when compared to the total SOA concentration. An upper limit for the contribution of this group of precursors is  $8(\pm 3)\%$  of the SOA. This percentage is calculated using the tracer method in which the SOA concentration from PAHs is higher than in the box model and a 30% uncertainty for the SV-OOA concentration. Lastly, we note that no suitable tracers for alkane oxidation have been identified yet, which prevents carrying out similar model/tracer comparisons with respect to the P-S/IVOCs, since these compounds are thought to be composed primarily, although not exclusively, of alkanes.”

**R1.3.** The authors should report the effective yields of the SI-SOA precursors. How do they compare of the recent work of Jathar (PNAS, 2014), which derived yields from chambers? How do they compare to the yields proposed by Zhao (EST, 2014) who performed this sort of model

with more extensive set IVOC data? How do they compare to smog chamber data for traditional precursors (alkanes, aromatics, etc.)?

The questions posed by the reviewer regarding the effective yields are very interesting. We have responded to them by adding the following paragraph to Section 3.1.1.

*“In addition, the effective SOA yields predicted in the box model for P-S/IVOCs can be compared against those determined in previous modeling and smog chamber studies. The effective yield is a function of photochemical aging, and thus for the purpose of this comparison we focus on the effective box model yields for 12:00 – 15:00 when there was a moderate amount of photochemical aging (5 h at an average OH concentration of  $1.5 \times 10^6$  molecules  $\text{cm}^{-3}$ ) comparable to the degree of aging typically achieved in chambers. During this period the effective yields for P-S/IVOCs were 12%, 27%, and 36% for ROB+TSI, GRI+TSI, and PYE+TSI, respectively. Zhao et al. (2014) recently carried out a modeling study of SOA formed in Pasadena that was constrained with an extensive set of IVOC data and found an overall SOA yield for IVOCs of 29%, which falls within the range of effective yields for P-S/IVOCs that are predicted by the box model for the three different parameterizations. Jathar et al. (2014) also recently estimated from chamber studies an effective SOA yield of 10 – 40% for unspciated organic emissions from combustion sources, which is also consistent with the P-S/IVOC yields from our box model. For reference, the effective yields for the aromatic VOCs m-xylene, toluene, and benzene under high- $\text{NO}_x$  conditions in chamber studies range from 4 – 28% depending on the precursor identity and chamber conditions (Ng et al., 2007). Similar chamber studies on 12-carbon alkanes determined effective yields ranging from 11% – 160%, where the highest yield corresponded to a cyclic alkane (Loza et al., 2014). In general, it appears that the effective yields resulting from the box model for the lower photochemical ages used here are similar to those determined from other chamber and modeling studies.”*

**R1.4.** The paper uses the results to apportion SOA to different sources. Since the SVOC and IVOC concentrations are scaled with primary organic aerosol; this apportionment is presumably the same as the primary organic aerosol. The authors should clarify this point in the manuscript. I

suspect it is highly uncertain. For example, gasoline vehicles emit relatively little POA but likely contribute significant SOA (Jathar et al. 2014).

The reviewer is correct that the initial SVOC and IVOC concentrations are scaled from primary organic aerosols. However, the apportionment of SOA from P-S/IVOCs is not the same as that for primary organic aerosol, because the amount of SOA from each source is also a function of the photochemical age. For example, there are substantial cooking emissions in the evening, but these produce little SOA over the urban scale considered here, due to the short ambient photochemical ages at that time. In addition, the SOA apportionment takes account of SOA from VOCs, which are largely emitted by gasoline vehicles, and which are not scaled to POA.

Still, the reviewer is correct that in scaling the P-S/IVOCs to POA we have assumed that the P-S/IVOCs to POA ratio as well as the volatility distribution of P-S/IVOCs is the same for the different sources, which may not be accurate. To explain this uncertainty we have added the following paragraph to Section 3.1.4.

*“The uncertainties in Figure 6 do not however account for certain assumptions that were made in order to perform the source apportionment. In particular, it was assumed that the P-S/IVOCs to POA ratio as well as the volatility distribution of P-S/IVOCs is the same for all sources, which is likely not the case. However, to our knowledge there is insufficient information in the literature to prescribe different volatility distributions for the different sources.”*

**R1.5.** Zhao (EST, 2014) recently reported measurements of more IVOCs, including an estimate of the unspiciated IVOC. It appears that the naphthalene data came from the same dataset? How do the author’s estimates of unspiciated IVOC inferred from primary organic aerosol compare to the measured data of Zhao et al.? How do the predictions of the authors compare to Zhao et al.?

In response to this comment we have added a table to the supporting information (Table SI-3) that compares the estimated IVOCs from the model versus the measured data of Zhao et al. (2014). The table is also included below for the reviewer’s convenience. We have also added a paragraph to Section 3.1.1 that discusses the comparison (see quoted text below).

In addition, we have performed a sensitivity study in which all the IVOC emissions from cooking as well as diesel/gasoline have been reduced by one-half. This sensitivity study is summarized in a new paragraph in Section 3.1.5 (text is also quoted below).

*“It is also possible to compare the predicted IVOC concentrations in the box model versus the concentrations measured by Zhao et al. (2014). The comparison is summarized in Table SI-3 of the supporting information. In total, the initial IVOC concentrations in the box model are two times higher compared to those determined from measurements ( $16 \mu\text{g m}^{-3}$  versus  $8(\pm 1) \mu\text{g m}^{-3}$ ). In addition, there is a larger difference for the  $C^* = 10^3$  bin ( $2.5 \mu\text{g m}^{-3}$  versus  $0.2(\pm 0.1) \mu\text{g m}^{-3}$ ). At the same time, the model used by Zhao et al. to predict urban SOA is lower than the measurements by 50% on the urban scale, whereas as the box model used here does not exhibit such a low bias. Given these differences we have run two sensitivity studies to explore how the model predictions depend on the IVOC emissions that are discussed in the following sections. The first sensitivity study reduces the emission of P-S/IVOCs from cooking emissions to zero (Section 3.1.2), and the second sensitivity study reduces all IVOC emissions by one-half (Section 3.1.5). Both of these variations greatly improve the agreement between the modeled and measured IVOC concentrations.”*

**“Table SI-3.** Initial concentrations of primary IVOCs predicted by the box model (ROB parameterization) in comparison with data from Zhao et al. (2014) as a function of the saturation concentration ( $C^*$ ) at 298 K. Note that the corresponding results for the GRI parameterization are very similar with the concentration being 8% higher due to differences in the  $\Delta H_{\text{vap}}$ .

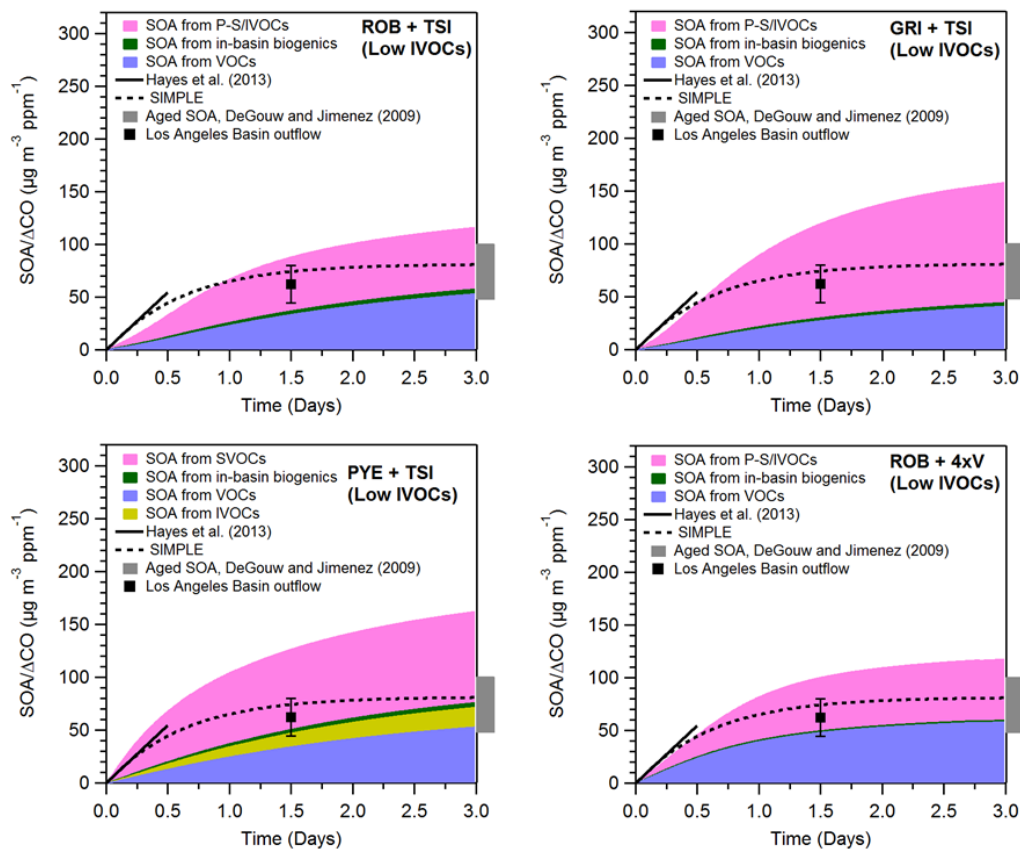
$C^*$ ( $\mu\text{g m}^{-3}$ )	Estimated Primary IVOCs ( $\mu\text{g m}^{-3}$ )	Estimated Primary IVOCs without cooking emissions ( $\mu\text{g m}^{-3}$ )	Measured Primary IVOCs ( $\mu\text{g m}^{-3}$ )
$10^3$	2.47	1.70	0.21 ( $\pm 0.07$ )
$10^4$	3.30	2.27	1.39 ( $\pm 0.29$ )
$10^5$	4.12	2.84	2.64 ( $\pm 0.64$ )
$10^6$	6.59	4.54	3.82 ( $\pm 0.99$ )

From Section 3.1.5:

*“A third explanation is the potential overestimation of IVOC emissions in the box model. As discussed in Section 3.1.1, the initial concentration of primary IVOCs in the model is a factor of 2 higher than the values determined from field measurements by Zhao et al (2014). To investigate this possibility, a sensitivity study was run in which the initial concentrations of primary IVOCs in the volatility bins  $C^*= 10^3, 10^4, 10^5, \text{ and } 10^6$  were decreased by one-half. The results of this sensitivity study are shown in Figure 8. In general, ROB+TSI, GRI+TSI, PYE+TSI, and ROB+4xV all show better agreement with measurements at long photochemical ages, although all four variants still overestimate the measurements. For shorter photochemical ages (in the urban scale) ROB+TSI under-predicts the SOA concentration, whereas GRI+TSI and ROB+4xV both predict SOA/ $\Delta\text{CO}$  ratios that are not significantly different from the measured values (Hayes et al., 2013), and lastly PYE+TSI overestimates the SOA concentration.*

Thus, IVOCs emissions that are too high in the box model may be responsible for some, but not all, of the overestimation of SOA concentrations at long photochemical ages.

For reference, we note that when the IVOC concentrations are halved the four variations all predict less SI-SOA for the Pasadena ground site (Figure SI-7), but the contribution of P-S/IVOCs to SOA formation remains important: 59 – 73% (ROB+TSI), 72 – 80% (GRI+TSI), 79 – 92% (PYE+TSI), 38 – 48% (ROB+4xV). Furthermore, all four variations still predict a fossil fraction of urban SOA consistent with the  $^{14}\text{C}$  measurements at the Pasadena site: 66( $\pm$ 9)%, 64( $\pm$ 10)%, 61( $\pm$ 12)%, 78( $\pm$ 6)%, respectively. Note that in calculating these fossil fractions the IVOCs emissions from cooking and gasoline/diesel were reduced by the same amount (i.e. one-half).”



“Figure 8: SOA concentration predicted by the ROB+TSI, GRI+TSI, PYE+TSI, and ROB+4xV parameterizations for up to 3 days of photochemical aging at a reference  $\cdot\text{OH}$  concentration of  $1.5 \times 10^6 \text{ molec cm}^{-3}$ . These predictions correspond to the sensitivity study in which the concentration of IVOCs in the volatility bins  $C^* = 10^3 - 10^6$  were reduced by one-half. Also



*shown in the three panels is the same result for the SIMPLE model using the optimized parameters (see Section 3.3 for further discussion). Note that the SOA concentrations have been normalized to the background subtracted CO concentration to account for changes in emission strengths, and the processed data are identified by the symbol SOA/ $\Delta$ CO. In addition, the SOA/ $\Delta$ CO data determined for the Pasadena site from the measurements of Hayes et al. (2013) are shown (black line) as well as similar airborne measurements downwind of Pasadena performed by Bahreini et al. (2012) aboard the NOAA P3 (black marker). The Bahreini et al. point corresponds to an average of all LA Basin outflow data between 1 – 2 days of photochemical aging. The OA/ $\Delta$ CO ratio reported by de Gouw and Jimenez (2009) is also indicated (gray box) to serve as an estimate of OOA/ $\Delta$ CO in highly aged air masses.”*

**R1.6.** “Indeed, decreases in SOA concentration at high photochemical ages have been observed in flow-tube studies, although typically at photochemical ages much longer than 3 days (George and Abbatt, 2010).” More recent flow tube studies (Lambe et al. EST 2013; Tkacik et al. EST 2014) suggest that the fall off may occur at shorter photochemical ages (between 2 and 3 days).

The shorter photochemical ages in the Tkacik et al. study are not a real difference, but rather the result of that study using a higher OH concentration for the calculation of the ages. The decrease in the Tkacik et al. data occurs at 5 days, when one uses the same OH =  $1.5 \times 10^6$  molec cm<sup>-3</sup> used in this paper. Lambe et al. (ES&T 2013) does not include any such data. The reviewer may have meant to cite Lambe et al. (ES&T 2012), for which the decreases are observed between 4-8 days of equivalent exposure at OH =  $1.5 \times 10^6$  molec cm<sup>-3</sup>.

In addition the apparent losses in recent flow tube studies where the SOA is formed in the reactor may be due to lack of SOA formation (e.g. due to oxidation of semivolatile species before they have time to condense, leading to fragmentation). The studies of George and Abbatt started with pre-existing OA and would not suffer from that potential problem, and thus we consider them more trustworthy for this point. Thus, we have not modified the text in response to this comment.

**R1.7.** SIMPLE parameterization is interesting. It is not clear how much fitting versus predicting is being done. This needs to be clarified in the manuscript. It appears that it has been retuned for

CalNex. If so then that is not as impressive – it is just a curve fit. If it is using previous parameters then that would be good. It would be interesting to better characterize the atmospheric conditions under which it may be applicable / influence SOA formation (VOC/NO<sub>x</sub>, etc.). Presumably LA and Mexico City are pretty consistent.

We have modified the text to clarify the discussion of the SIMPLE parameterization (see below). We agree with reviewer that it would be interesting to better characterize the performance of SIMPLE under various atmospheric conditions and have noted this now in the text. We also note that we are proposing this parameterization for urban SOA sources, and not for, e.g., biogenic SOA. It is difficult to carry out the characterization described by the reviewer for our case study, however, due to the limited set of atmospheric conditions explored. For example, in Los Angeles high-NO<sub>x</sub> conditions are generally observed. Thus, we recommend that future modeling studies also apply this parameterization to studies in other locations.

*“We replaced the SOA parameterizations discussed above with the SIMPLE parameterization just described, and ran the box model for a large number of possible parameter value combinations (i.e. emission ratio of VOC\*/CO and ·OH rate constant). Figure 11A shows the difference between model and measurements over that parameter space. The diurnal cycle predicted by the SIMPLE parameterization with the optimum parameters for Pasadena is shown in Figure 11B. The SIMPLE model with the optimized parameters performs comparably to the more complex parameterizations used in this work. At the same time, the SIMPLE parameterization is unable to capture perfectly the location of the peak in time because it depends solely on CO and photochemical age. The CO concentration at the site peaks at 12:00 and photochemical age peaks at 13:00 (Figure 3A) while the measured SOA has a broad peak between 14:00 – 16:00. The fact that SOA does not peak at the same time as CO and photochemical age indicates the assumption in SIMPLE that VOC\*/CO does not vary in time is probably not completely accurate. Still, the performance of the SIMPLE parameterization for urban SOA is sufficient for many applications and certainly far better than many models currently used.*

*Interestingly, the optimal model parameters for Mexico City and Pasadena are very similar. In other words, when tuning the model separately for each city, the parameters obtained*

*are identical within the estimated uncertainties. This result suggests SIMPLE, with the parameters reported for Mexico City or Pasadena, can be applied to other polluted urban regions as well. In addition, the optimal parameters for Pasadena (and Mexico City) are consistent with the OA/ $\Delta$ CO ratios observed for highly aged air masses by Bahreini et al. (2012) from the NOAA P3 aircraft in the LA basin outflow, as well as for other urban areas as summarized by de Gouw and Jimenez (2009) and shown in Figure 7. However, it should be noted that a range of SIMPLE parameter combinations still remains in which the different combinations perform similarly in the model/measurement comparison, and this range is indicated by the dashed box in Figure 11A. While the SIMPLE model is promising, additional work should be carried out to verify the optimal SIMPLE model parameters including analysis of data for a broad range of ages, e.g., by utilizing results from ambient air processed by oxidation flow reactors (Ortega et al., 2013). Also, the accuracy of the SIMPLE model for predicting urban SOA under a variety of atmospheric conditions should be explored (e.g. VOC/ $\text{NO}_x$  or relative amounts of gasoline versus diesel emissions.) Finally, we note that the SIMPLE model parameterizes urban SOA, and is not applicable to biogenic SOA.”*

**R1.8.** The importance cooking emissions to SOA formation is interesting. I am not aware of data to support this. I believe that the 1.5 factor of Robinson et al. (Science 2007) is based on data for combustion sources. Is there evidence from source test data that it might also apply to cooking? What evidence is there for SOA from cooking?

This is an excellent question. In essence, there is evidence for SOA from cooking, but the number of studies and thus constraints available for developing cooking SOA parameterizations is currently very limited. In particular the Prévôt group at PSI (coauthors in this paper) has a paper in preparation detailing results from one extensive study where significant SOA formation was clearly observed, and that has been presented at the AAAR Annual Meeting and other conferences.

We hope that our study will highlight the potential importance of cooking SOA and motivate further work on this topic. We have added the following paragraph to the end of Section 3.1.4 in

order to better explain the potential importance as well as the uncertainty regarding cooking SOA.

*“Lastly, the percentage of SOA attributed to cooking emission in this work also requires discussion. Compared to gasoline or diesel vehicles there is relatively little data on the SOA forming potential of cooking emissions, but nevertheless there is both direct and indirect data supporting the SOA forming potential of cooking emissions. First, it is clear from numerous source apportionment studies that cooking emissions are a source of organic matter in the atmosphere (e.g. Robinson et al., 2006; Mohr et al., 2011; Hayes et al., 2013). Second, molecular speciation of cooking emissions has demonstrated that cooking activities emit a variety of volatile and semi-volatile compounds that are known SOA precursors (Schauer et al., 1999, 2002). Third, chamber studies have demonstrated SOA formation from cooking emissions. The latter results have been presented at several major conferences, but not yet been published in the peer-reviewed literature (El Haddad et al., 2012). Thus, it is reasonable to conclude that SOA models should include the SOA resulting from chemical processing of cooking emissions, but there is a lack of chamber yields that could be used to develop specific SOA parameterizations. We have therefore assumed that SOA from cooking emission can be described using the same parameterizations as used for SOA from vehicular P-S/IVOCs. We also perform a sensitivity study where we assume that cooking emissions do not produce any SOA. Ultimately, the percentage of SOA from cooking emissions reported here should be considered a first-order estimate that should be updated when additional data regarding SOA from cooking emissions becomes available.”*

## **References.**

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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  $\Delta(\text{isoprene})/\Delta\text{CO}$  (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  $1.5 \times 10^6$  molec  $\text{cm}^{-3}$ , 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  $1.5 \times 10^6$  molec  $\text{cm}^{-3}$ , 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 before oxidation occurs. 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  $\mu\text{g m}^{-3}$  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 where regional advection played a more important role (Ryerson et al., 2013). Given the cost of the  $^{14}\text{C}$  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  $^{14}\text{C}$  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/ $\Delta$ CO 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  $1.5 \times 10^6$  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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