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/Jun 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 (napthalenes, methylnaphthalene). It seems clear that these PAHs do not appear to be major precursors, but large amounts of unspeciated IVOCs include a fair number of more alkylated or funcationalized PAHs. The authors claim that unspeciated 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 μg* 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 napthalenes. 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(±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 x 10^6 *molecules* 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 unspeciated 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-*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 a 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 unspeciated IVOC. It appears that the naphthalene data came from the same dataset? How do the author's estimates of unspeciated 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 $\mu g\ m^{-3}$ *versus 8(±1)* $\mu g\ m^{-3}$*). In addition, there is a larger difference for the* $C^* = 10^3$ *bin (2.5* $\mu g\ m^{-3}$ *versus 0.2(±0.1)* $\mu g\ m^{-3}$*).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* ΔH_{vap}.

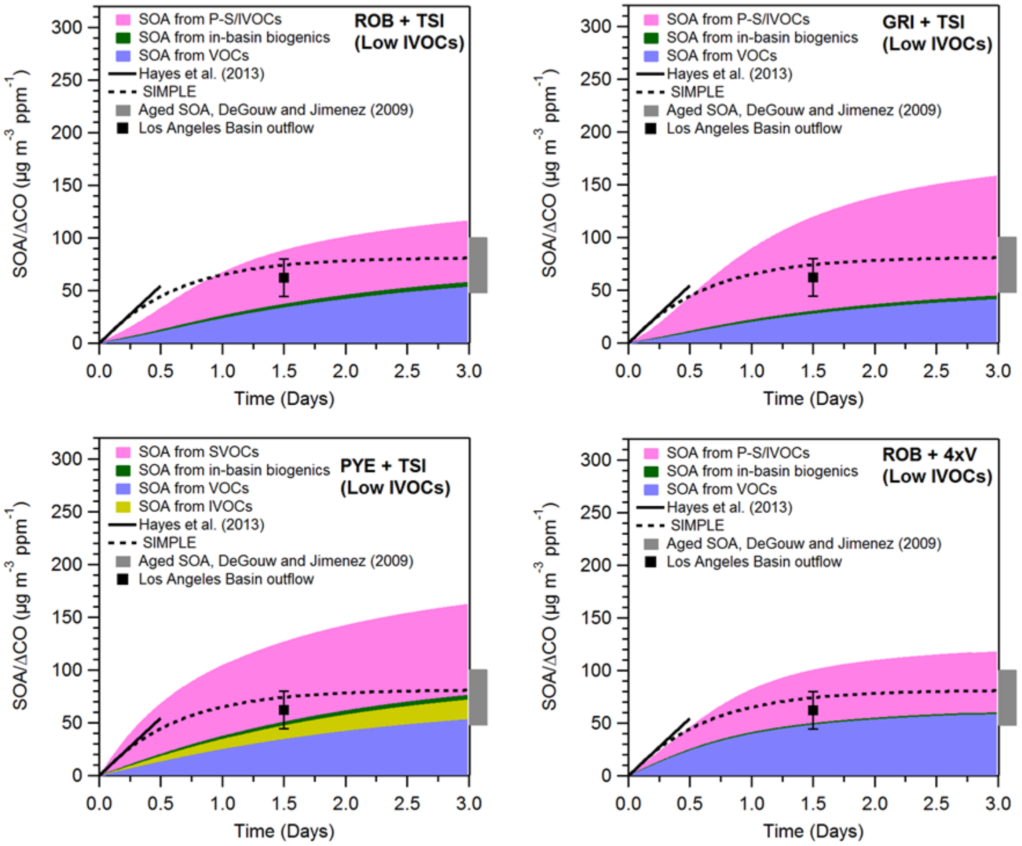
C* (µg m^{-3})	**Estimated Primary IVOCs (µg m^{-3})**	**Estimated Primary IVOCs without cooking emissions (µg m^{-3})**	**Measured Primary IVOCs (µg m^{-3})**
10^3	2.47	1.70	0.21 (± 0.07)
10^4	3.30	2.27	1.39 (± 0.29)
10^5	4.12	2.84	2.64 (± 0.64)
10^6	6.59	4.54	3.82 (± 0.99)

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, *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/ΔCO 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}C measurements at the Pasadena site: 66(±9)%, 64(±10)%, 61(±12)%, 78(±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 ·OH concentration of 1.5×10^{6} 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/ΔCO. In addition, the SOA/ΔCO 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/ΔCO ratio reported by de Gouw and Jimenez (2009) is also indicated (gray box) to serve as an estimate of OOA/ΔCO 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 x 10^6 molec cm^{-3} 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 x 10^6 molec cm^{-3}.

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/NOx, 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_X 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/ΔCO 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/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."

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