Key: Solid Blue = Responses, *Italicized blue = new text,* Quotation marks = new and existing text from the manuscript.

We would like to thank the reviewers for taking the time to review our paper and for their thoughtful comments. Their comments 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 new text added to the manuscript is given in blue Italics and the original text from the submitted manuscript remains un-italicized. We would also like to point out that the numbering of the figures from the revised manuscript is used here in the responses and that the figures only used for responses are noted with the prefix ''R''.

Referee 1 Comments

R1.1. This paper is interesting in that new constraints on S/IVOC emissions are used together with recent VBS yield suggestions, and the results compared to a wide range of measurements. The measurement data range from near-surface to aircraft data, all evaluated using the concept of photochemical age and with SOA/CO ratios. The use of OFR data is also beneficial I think, in helping to place limits on the SOA formation and ageing-process at long photochemical ages.

Although the paper does present some interesting analysis, I think that there are some significant problems, and I cannot recommend the paper for publication until these are addressed. One problem is that there have been so many papers by now in which somebody identifies a problem with model-measurement discrepancies in SOA, and by tweaking the VBS parameters in some way one can get better agreement. This paper falls into that pattern, and although the authors have good reasons for their particular choice of parameter-tweaking the fact remains that there are an infinite number of ways of improving SOA predictions. The authors need to demonstrate some advantage of their schemes over others, and this requires a reliable model study.

We address to this comment by kindly referring the reviewer to the following paragraph written in the submitted manuscript (p. 5, L152) and by adding some sentences (in *Italics*) for clarity:

"The goal of this study is to use several recently published results to better evaluate and constrain the box model introduced in our previous work, and thus facilitate the identification of parameterizations that can be eventually incorporated into 3-D air quality models to accurately predict SOA for the right reasons. *It is important to note that parameterizations used in the box model are based on several published measurements taken from laboratory experiments and field studies that provide more realistic constraints than in previous versions and that were not available to be implemented in Hayes et al. (2015).* In particular, our work here improves the box model by incorporating recently published measurements of P-IVOCs and P-SVOCs that allow better constraining of the concentration, reactivity, yields, and volatility of these precursors (Worton et al., 2014; Zhao et al., 2014). In addition, given that experiments in environmental chambers may underestimate SOA yields for the VOCs due to losses of semi-volatile gases to the chamber walls (Zhang et al., 2014), the SOA yields from VOCs have been re-estimated using a very recent

parameterization of these wall-losses (Krechmer et al., 2016). The wall-loss corrected yields obtained are then used in the model in a sensitivity study to evaluate the corresponding change in the modeled SOA concentrations. *The model is modified based on these literature constraints. No model tuning is performed with the goal of improving the agreement with the observations."*

We also want to clarify that, contrary to the statement from the reviewer, no model tuning is performed in our work at all. That is to say, we test SOA models and parameters based on the literature, and we do not derive new versions based on fitting the observations. The results are obtained by directly incorporating into the model the results mentioned above from each study (P-IVOC concentrations, volatility, etc.) with no *a priori* knowledge that those model cases would have better (or worse) model/measurement agreement. In other words, in the development of the model cases model/measurement agreement with respect to SOA concentration was not used to determine the model parameters and the parameters in each case are not "tuned".

Why a box-model?

R1.1.1 In order to demonstrate that the merits of the tweaks used here are real, I would have wanted to see a thorough demonstration of improved model-observation performance across a range of scales. The box model used here cannot in my opinion provide such a demonstration; this study should have been conducted with a well-evaluated 3-D chemical transport model. In fact, with only four mechanisms being evaluated, and over a short period, I cannot think of any reason not to use a CTM.

Although box models are often useful for examination of, for example detailed chemical processes, or basic principles, they are not well suited to studies where comparison with ambient measurements is in focus. This has been well established for years, and is a major reason why air pollution modelling moved from the earlier EKMA-type moving box models to 3-D models such as CAMx or CMAQ. The measurements used in this study also range from near-surface data to aircraft, which places additional constraints on the abilities of a box model. Although the authors (and those of the previous Hayes et al 2015 study which preceded this work) have put a lot of effort into the box model setup, I do not believe that any amount of effort can overcome the basic limitations of such models. Box models simply cannot account for the 3-D nature of atmospheric dispersion, and they cannot be expected to cope with pollutant situations where nonlinearity of photochemical/SOA production is expected.

We very strongly disagree with these statements about 3-D models always being superior to box models, and in fact think that the opposite is the case in some cases, as already documented by many prominent papers in the literature. We address to this comment by kindly referring the referee to the following paragraph written in the submitted manuscript (p. 4, L138) and by adding some sentences (in *Italic*) for clarity:

"**Recently, we evaluated three parameterizations for the formation of S-SOA and I-SOA using a constrained 0-D box model that represents the South Coast Air Basin during the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign (Hayes et al., 2015).** ***Box models are often used to compare with ambient measurements, and have been shown to be of similar usefulness or even superior to 3D models if the emissions and atmospheric transport affecting a given case study***

are well constrained, and if the use of ratios to tracers can be used to approximately account for dispersion (e.g. Volkamer et al., 2006; Dzepina et al., 2009; Yuan et al, 2015; Hayes et al., 2015). A box model allows the evaluation of multiple model parameterizations either previously proposed in the literature or developed from recent field and laboratory data sets, as well as the performance of sensitivity studies, all of which would be difficult to carry-out in more computationally demanding gridded 3D models. There are six model cases presented in this paper that are described in further detail below. Given the number of model cases (including three additional model cases from Hayes et al. 2015), it would be computationally expensive to use a 3-D model to evaluate all the cases.

Moreover, there are important limitations to traditional comparisons of 3-D models predicted concentrations against measurements, as for example discussed for the Pasadena ground site in Woody et al. (2016). In that study, the SOA predicted by the Community Multiscale Air Quality (CMAQ) model with a VBS treatment of OA is a factor of 5.4 lower than the measurements during the midday peak in SOA concentrations. This underestimation was attributed to several different factors. First, the model photochemical age for the site was too low by a factor of 1.5. In the box model presented in this current work, that problem is eliminated as the photochemical aging of the urban emissions in the model is instead determined from the measured ratio of 1,2,4-trimethylbenzene to benzene as described previously (Parrish et al., 2007; Hayes et al., 2013). Second, it is difficult to distinguish errors due to model dispersion from those due to emission inventories and photochemical age. Woody et al. (2016) conclude that excessive dispersion or low emissions account for an error of about a factor of 2. Those errors are also eliminated by the use of emission ratios in this work. After those errors are accounted for, by analyzing the 3D model output using similar techniques as in our box model, the real under-prediction of SOA formation efficiency by a factor of 1.8 emerged, compared to the initial value of 5.4 from the concentration comparisons. These errors (of approximately 300%) in the interpretation of 3D model comparisons, which are ignored in most 3D model studies, are far larger than the uncertainties due to emission ratios or dispersion in our box model (about 10 - 20%), as demonstrated in section 2.4.

In addition, there are uncertainties in the P-S/IVOC emissions inventories used in 3-D models and in the methods used to estimate P-S/IVOC emissions from the traditional POA inventories. In our box model, as described in further detail below, we incorporated recently published field measurements of P-S/IVOCs to better constrain the concentration of these species. Thus, while 3-D models are essential for simulating spatially and temporally complex environments under the influence of many sources, in cases where transport is relatively simple and there is a well-defined urban plume such in Pasadena during the CalNex campaign, the box model is a valuable complementary or even superior approach that is less susceptible to the convoluted uncertainties in 3-D models discussed above. Another reason to use a box model is that it allows a direct comparison against OFR measurements taken in the field (Ortega et al., 2016). The OFR provided (every 20 minutes at the Pasadena ground site) a measure of SOA formation potential for a photochemical age of up to two weeks. To the best of our knowledge, 3-D models have not yet been adapted for comparison against OFR data. Finally, box models are more widely usable by experimental groups (such as ours) due to reduced complexity, while 3-D models are almost exclusively used by modeling-

only groups, who tend to be more distant from the availability, use, and interpretation of experimental constraints. Thus the use of a range of models by a range of different groups is highly beneficial to scientific progress."

R1.1.2 The authors may argue that by scaling with CO that they remove dispersion errors but this is only partly true. This does not account for the fact that SVOC partitioning is dependent on absolute OA concentrations, and so requires simulation of e.g. urban plumes and vertical gradients.

This is a small effect, which we had already addressed previously with a sensitivity study in Dzepina et al. (2009). We address this comment by adding the following section in the text:

Section 2.4 Correction for changes in partitioning due to emissions into a shallower boundary layer upwind of Pasadena

''As described in Hayes et al. (2015), during the transport of the pollutants to Pasadena, the planetary boundary layer (PBL) heights increase during the day. Using CO as a conservative tracer of emissions does not account for how the shallow boundary layer over Los Angeles in the morning influences gas-particle partitioning due to lower vertical mixing and higher absolute POA and SOA concentrations at that time. Thus, as shown in the gas-particle partitioning equation above, there will be a higher partitioning of the species to the particle phase and less gas-phase oxidation of primary and secondary SVOCs. Later in the morning and into the afternoon the PBL height increases (Hayes et al. 2013) diluting the POA and urban SOA mass as photochemical ages increases. However this is a relatively small effect as the partitioning calculation in the SOA model is relatively insensitive to this effect and the absolute OA concentrations (Dzepina et al., 2009; Hayes et al., 2015). Our previous work (Hayes et al., 2015) found in a sensitivity study a +4/-12% variation in predicted urban SOA when various limiting cases were explored for simulation of the PBL (e.g. immediate dilution to the maximum PBL height measured in Pasadena versus a gradual increase during the morning).

To account for the effect of absolute OA mass on the partitioning calculation, the absolute partitioning mass is corrected using the following method. A PBL height of 345 m is used for a photochemical age of 0 h and it reaches a height 855 m at a photochemical age of 9.2 h, which is the maximum age for the ambient field data. Between the two points, the PBL is assumed to increase linearly. The boundary layer heights are determined using ceilometer measurements from Pasadena at 6:00 - 9:00 and 12:00 - 15:00 local time, respectively (Hayes et al. 2013). The second period is chosen because it corresponds to when the maximum photochemical age is observed at the site. The first period is chosen based on transport times calculated for the plume from downtown Los Angeles (Washenfelder et al. 2011) that arrives in Pasadena during the afternoon. There are certain limitations to this correction for the partitioning calculation. First, the correction is based on a conceptual framework in which a plume is emitted and then transported to Pasadena without further addition of POA or SOA precursors. A second limitation is that we do not account for further dilution that may occur as the plume is advected downwind of Pasadena. However, such dilution is not pertinent to the OFR measurements, and so for photochemical ages beyond ambient levels observed at Pasadena, we focus our analysis on the comparison with the OFR measurements.''

R1.1.3 More fundamentally, the assumption in this box-model work is that one can predict ΔVOC concentrations from ΔCO alone. There may be some merit in this for transport derived VOC (and the VOC profiles shown in Hayes et al 2015 show surprisingly good agreement for such VOC), but such a relationship cannot hold for VOC from solvents and various production processes. Thus, we have sources of VOC and hence SOA which are not constrained. I didn't find a discussion of this in the paper.

We address to this comment by adding the following paragraph in the experimental section.

''It should be noted that the use of VOC emission ratios to CO to estimate VOC emissions does not assume that VOCs are always co-emitted with CO. Rather, it assumes that VOC emission sources are individually small and finely dispersed in an urban area, so that they are spatially intermingled with the sources of CO. Moreover, previous studies have measured the emission ratios of anthropogenic VOCs with respect to CO and the results show that vehicle exhaust is a major source of VOC and CO (Borbon et al. 2013, Warneke et al. 2007). Furthermore, the ratios are consistent both temporally and spatially. Thus, when thinking of the entire urban area as a source, the use of emission ratios to CO is justified. As shown in Hayes et al. (2015) in the supporting information, the modeled VOC concentrations are consistent with the measurements indicating that major VOCs sources have not been omitted, and the smooth time variations of the VOC concentrations support the use of a "global urban source".''

R1.1.4 These problems are even more difficult to deal with when comparing SOA formation at longer photochemical ages, e.g. 3 days as is done here. I would expect problems with any pollutant when running a box model over such time-scales.

We address to this comment by adding the following paragraph in section 3.1 of the submitted manuscript:

''As displayed in the graphs for Fig. 3, it should be noted the measurements from the OFR (Ortega et al. 2016) and from the NOAA P3 research aircraft (Bahreini et al. 2012) give quite similar results for SOA/ΔCO. The OFR measurements are not affected by particle deposition that would occur in the atmosphere at long timescales or photochemical ages. Only a few percent of the particles are lost to the walls of the reactor, and this process has been corrected for already in the results of Ortega et al. The similarity in the two types of observations suggests that ambient particle deposition and plume dispersion do not significantly change the SOA/ΔCO ratio over the photochemical ages analyzed here.''

R1.1.5 The authors (also in Hayes et al. 2015) do not even demonstrate that the model is capable of reproducing pollutants such as CO or NO2 reliably, and without this it is impossible to explain model-measurement discrepancies in SOA in terms of VBS parameters alone.

It was disturbing that the text didn't acknowledge these limitations, but instead all model-measurement discrepancies are assigned to VBS/SOA formation parametrizations.

As the NO_X levels and CO are constraints already used in the model set-up, it would not be meaningful to perform the diagnostics described by the reviewer, although we certainly agree that those comparisons would be worthwhile for (unconstrained) 3-D models. The ability to constrain important parameters is one key advantage of constrained box models for this type of application. To better explain how the model set-up is evaluated we have added the following text in section 2.2 of the manuscript.

"It should be noted that the model uses CO and NO_x as inputs to constrain the model and the SOA yields for high-NO_X conditions are used, based on our previous work (Hayes et al. 2013; 2015). Therefore, to verify model performance both predictions of VOC and POA concentrations have been compared against field measurements and the model performance appears to be satisfactory (Hayes et al. 2015)."

We agree with the reviewer that it is useful if the conclusions drawn from this study more clearly acknowledge the model uncertainties, which appear to be confusing in the submitted version. Therefore, we have updated the text as described in our response to comment R1.5.12 below.

R1.1.6 Given that CTM models have already been set up and used for the CalNex campaign (Baker et al., 2015, Hayes et al., 2015, Woody et al., 2016), I would suggest that the authors re-do their work in collaboration with one of these teams.

Based on our points described above, especially R1.1.1, it seems reasonable to conclude that a box model provides important scientific value that complements 3-D models and is superior to those models for some scientific questions. Indeed, we have contributed to both box modeling as well as collaborated closely in several 3-D modeling studies for CalNex. From those experiences, we have concluded that the box model can be superior to a 3-D model for this application, as it eliminates or greatly reduces many potential errors in, e.g., the photochemical age, dispersion, and emissions, by the use of constraints. We are not saying that box models can always provide a comparable alternative to 3-D models to study chemical processes in all cases, but this is clearly the case when source regions and transport are simple and well-characterized as in this study.

2 Experiment design

R1.2.1 I found the approach confusing in several respects.

To start with, the paragraph at the end of P9 (start of 2.2.2) is worrying. The initial POA is calculated from ΔPOA/ΔCO emissions, which implies that POA is an inert pollutant. At the same time the authors use Robinson's volatility distribution to estimate all emitted P/S/IVOCs. How can this be reconciled?

This topic has been discussed extensively in previous work (e.g. Dzepina et al., 2009, 2011; Hayes et al., 2015). We address this comment by updating the text below in the submitted manuscript (p. 9, L324).

"The initial POA concentration is determined from the product of the background-subtracted CO concentration and the ΔPOA/ΔCO emission ratio (Hayes et al., 2015). ***While this ratio may change due to evaporation/condensation or photochemical oxidation of POA, our previous work (Hayes et al. 2013) has shown that ΔPOA/ΔCO does not change significantly at the Pasadena ground site with observed photochemical age indicating that the ratio is insensitive to the extent of photochemical oxidation. Furthermore, it was calculated that the ratio would increase by 28% for an increase of OA concentration from 5 to 15 μg m^{-3}, concentrations that are representative of this study. This possible source of error is substantially smaller than current errors suggested for P-S/IVOC emission inventories in 3-D models, where current schemes are based on scaling POA emission inventories with scaling factors that are not well constrained (Woody et al. 2016)."***

R1.2.2 At the end of 2.2.2 (P10) we read that the important ratios of IVOC or VOC to CO are derived from measurements made between 00:00 and 06:00 local time in Pasadena, 'when the amount of photochemical ageing was very low'. There are several problems here, associated with the reliability of such ratios for daytime modelling, and the assumption that other ageing processes are negligible. My guess would be that CO concentrations have a larger component of long-range transport than IVOC for example, and also that night-time chemistry would be more important than assumed here.

CO is well-known to have a background from long-range transport, which is estimated and always subtracted before taking ratios, as described in Hayes et al. (2013) and references therein. Thus ΔCO represents the urban contribution to CO and is the appropriate quantity to use here. For clarity, we update the sentence below in the submitted manuscript (p. 10, L345-346):

"During the regression analyses the x-intercept was fixed at 105 ppbv CO to account for the background concentration of CO determined in our previous work (Hayes et al., 2013). Thus, the slope of the resulting line corresponds to the estimated emission ratio (ΔIVOC/ΔCO)."

We further address the potential uncertainty in IVOCs suggested by this comment by running a sensitivity case in which the IVOC initial concentration is calculated using the observed photochemical age, the IVOC measurements at Pasadena, and the estimated IVOC oxidation rate constants following Zhao et al. (2014). This alternate approach does not rely on the nighttime ratios of IVOC to CO.

For comparison, we also include here the SOA formation results before running this sensitivity study that are in the manuscript.

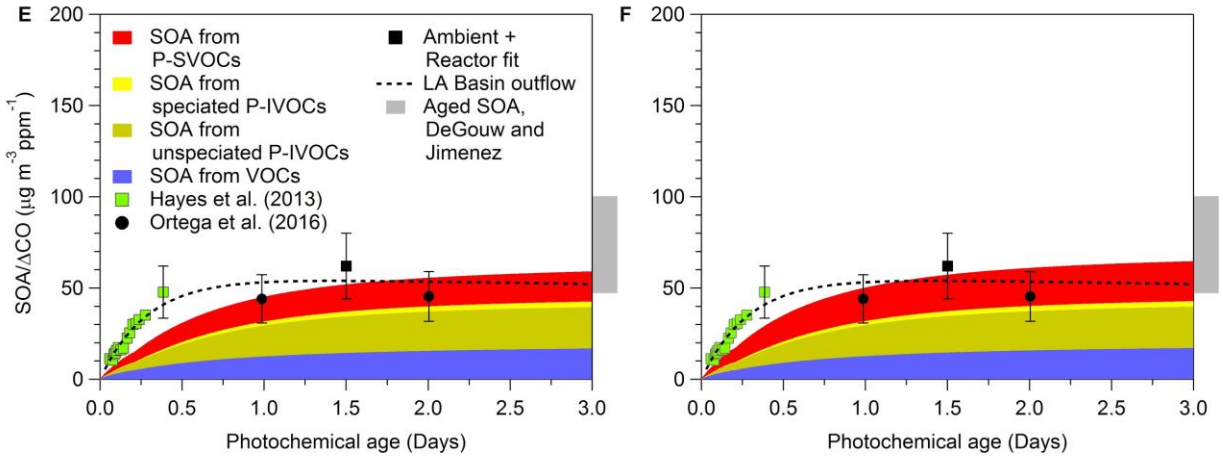


Figure 3. Predicted urban SOA mass for the E) ROB + ZHAO + MA and F) WOR + ZHAO + MA cases with the original model set-up for this work.

The figure below represents the SOA formation for the same two cases as above but for initial IVOC concentrations calculated without using the IVOC to CO ratios (as described above).

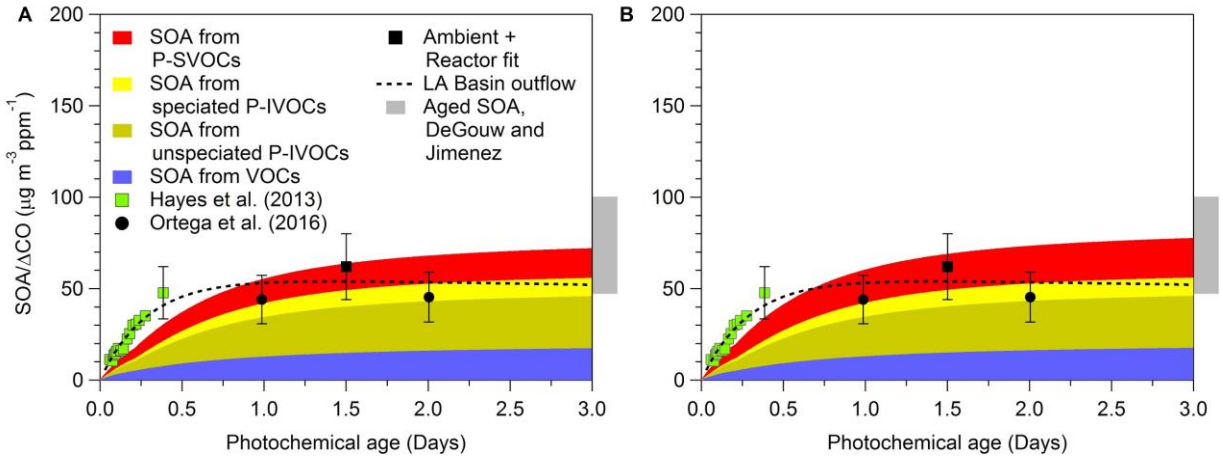


Figure S10. Predicted urban SOA mass for the A) ROB + ZHAO + MA and B) WOR + ZHAO + MA cases when using IVOC initial concentrations determined using photochemical age, the Pasadena IVOC concentrations, and the estimated IVOC oxidation rate constants.

To summarize these findings, we have added the paragraph below in the manuscript in section 3.3 and included Figure S10 in the supporting information.

''To further explore the impact of potential errors in the initial IVOC concentrations, a sensitivity study has been carried out using initial concentrations calculated based on the observed photochemical age and measured IVOC concentrations at Pasadena as well as the estimated IVOC oxidation rate constants (Zhao et al., 2014). This alternate approach is implemented for the ROB + ZHAO + MA and WOR + ZHAO + MA cases and does not use nighttime IVOC-to-CO ratios. The results when using this alternative approach are shown in the supporting information (Figure S10). When comparing Fig. S10 with Fig. 3, differences are minor. The model/measurement agreement improves slightly at shorter photochemical ages (less than 1 day). At the same time a slightly larger over-prediction is observed at longer photochemical ages. However, the formation of SOA modeled in this sensitivity test is similar to the original cases from Fig. 3 with an average difference of only 21 %, which represent a relatively small error compared to other uncertainties in SOA modeling. The IVOC initial concentrations used in this sensitivity test are slightly higher than those calculated using the IVOC-to-CO ratio, which explain the small increase of modeled SOA/ΔCO. Ultimately, the different approaches for determining the initial IVOC concentration in the model are reasonably consistent, and both approaches perform similarly given the model and measurement uncertainties.''

R1.2.3 Thirdly, it is usually a good idea to change one aspect at a time of model simulations, in order to investigate the effect of that one change. Here though the authors move from a set of 'Tsimpidi' cases to cases where wall-loss are accounted for. At the same time they switch off the ageing of secondary SVOCs. Thus, one cannot evaluate the importance of the ageing effect alone. This would have been a useful step between the TSI and the various wall-loss cases.

We address this comment by kindly referring the reviewer to the updated texts below, which are copied from the revised manuscript (page and line numbers written next to each section) where we discuss the inclusion of the ''aging'' mechanisms in the model.

From the Introduction (text added at p. 4, L125 in original manuscript):

''These "aging" mechanisms increase VOC yields to levels much higher than those observed in chamber studies since it was perceived that the yields may be too low in chambers compared to the real atmosphere. The "aging" mechanisms were added to chamber yields that were obtained without using aging as part of the fits of the chamber data. In some model applications they improve model agreement with field measurements (Ahmadov et al., 2012), while at long photochemical ages they lead to model SOA formation that is substantially larger than observed (e.g. Hayes et al., 2015; Dzepina et al., 2011).''

From section 2.2 (text added at p. 8, L289 in original manuscript):

''The three model cases accounting for wall losses of organic vapors are named ROB + MA, ROB + ZHAO + MA, and WOR + ZHAO + MA. For these cases, the aging of the secondary SVOCs formed from the oxidation of VOCs was not included, since multi-generation oxidation is not well-constrained

using data from chamber studies that are run over relatively short time-scales (i.e. hours). In addition, aging and correcting for wall-losses of organic vapors have been separately proposed to close the gap between observed and predicted SOA concentration from pre-2007 models*, and are thought to represent the same "missing SOA mass." Therefore, we run the model with one of these options at a time, as they are conceptually different representations of the same phenomenology.* The aging of secondary SVOCs formed from the oxidation of P-IVOCs (and P-SVOCs) has been kept for all of the MA cases, however. *To our knowledge, P-IVOC and P-SVOC mechanisms proposed in the literature have always included aging."*

As discussed in the submitted manuscript, the use of "aging" mechanisms were introduced to represent processes that increase SOA yields in the real world compared to chambers, and that are now known to be mostly due to vapor losses to chamber walls.

R1.2.4 Further, on p8-9, we read that ageing of secondary SVOC from 'VOC' is not included, partly because of poorly-constrained chamber data, but ageing of secondary SVOC from P-IVOCs and P-SVOCs is included for the MA cases. These choices feel rather random, and indeed seem like tweaks to give the model a decent chance of fitting the observations.

We address to this comment by clarifying that the choices are not random and we kindly refer the reviewer to our response in R1.2.3. As discussed in our previous response, the VOC aging is conceptually replaced by the correction for vapor wall losses on chamber walls. Therefore our choices are self-consistent, and they are the simplest choices that can be made based on the literature.

R1.2.5 Finally, the text on p9, L301-304 anyway seems to confirm that the refit was not able to reproduce the chamber data. Although non-equilibrium reasons are given for this, I am a little confused about the benefit of a refit that cannot reproduce the data.

To clarify, the refit *was able* to reproduce chamber data very well for the oxidation of VOCs. Therefore, it seems reasonable to conclude that refitting the data for the VOCs is beneficial, since wall-loses appear to be an important process that should be accounted for as best as possible. The refitting procedure was unsuccessful only in the case of the IVOCs. We have updated the text to more clearly explain these results.

"Indeed, when trying to refit the VOC and IVOC yield curves, the model assuming equilibrium partitioning between particles, the gas phase, and the walls was able to reproduce the yield curves for VOCs, but not for IVOCs. This difference in the results is consistent with equilibrium not having been reached during the chamber studies on the IVOCs, which produce a greater amount of lower volatility SVOCs when compared to VOCs during oxidation. These lower volatility SVOCs have relatively slow evaporation rates from the particles, which prevents the chamber system from reaching equilibrium (Ye et al. 2016)."

Yield data?

R1.3. Can the yields in Table S4 be correct? According to the manuscript (p8,L277-), this Table presents the upper limits of the SOA yields, but the numbers look rather odd compared to Table S1 which is supposed to be the lower limit. For isoprene the total yield is 0.039 in both Tables, and for other compounds the differences are sec are quite small (0.194 vs 0.200 for Ole1, 0.382 vs 0.392 for Ole2, 0.932 vs 0.939 for Aro2, 0.835 vs 0.855 for Terp). The main difference seems to be that Table S4 has mainly 0.0 for the 19 ug/m3 bin. A mistake maybe?

Firstly, we confirm that the SOA yields in Table S4 are indeed correct given our methodology.

Second, it is important to distinguish between total SOA yield , Y (particle-phase only), and the lumped SVOC yields, α_i (gas plus particle phases in a single volatility bin), which are related by the equation below (in the absence of wall-losses), and where C_{OA} is the particle concentration.

$$Y = \alpha_1 \left(1 + \frac{1}{C_{OA}}\right)^{-1} + \alpha_{10} \left(1 + \frac{10}{C_{OA}}\right)^{-1} + \alpha_{100} \left(1 + \frac{100}{C_{OA}}\right)^{-1} + \alpha_{1000} \left(1 + \frac{1000}{C_{OA}}\right)^{-1} \quad (1)$$

The equation above can be modified as discussed in our manuscript to include the partitioning of the organics to the wall where C_W is the effective wall mass concentration.

$$Y = \alpha_1 \left(1 + \frac{1}{C_{OA}} + \frac{C_{w,1}}{C_{OA}}\right)^{-1} + \alpha_{10} \left(1 + \frac{10}{C_{OA}} + \frac{C_{w,10}}{C_{OA}}\right)^{-1}$$

$$+ \alpha_{100} \left(1 + \frac{100}{C_{OA}} + \frac{C_{w,100}}{C_{OA}}\right)^{-1} + \alpha_{1000} \left(1 + \frac{1000}{C_{OA}} + \frac{C_{w,1000}}{C_{OA}}\right)^{-1} \quad (2)$$

According to equations 1 and 2, at low C_{OA} the observed Y will be lower than that observed in the absence of wall losses. On the other hand, when C_{OA} is much higher than C_W, the term $C_{W,i}/C_{OA}$ converges to 0 and equation 2 becomes identical to equation 1. Furthermore, at very high C_{OA}, Y is simply the sum of the α_i values. Therefore, Y at very high C_{OA} concentrations is the same with or without wall losses and thus the sum of α_i is also the same with or without wall loses. Therefore, the observation that the total SVOC yields are quite similar between Table S1 and S4 is not surprising, and actually expected. However, the difference in the volatility distribution of the yields, with a shift towards lower volatility when wall losses of organic vapors are accounted for, means that Y will be higher for low OA concentrations (typical of ambient conditions) and thus OA will have a tendency to form faster at low photochemical aging.

To clarify this point we have added the following text to the manuscript in section 2.2.

''Furthermore, as described in the supporting information, the updated SOA yields for VOC oxidation result in distribution of SVOC mass into lower volatility bins compared to the original parameterization, although the sum for the SVOC yields (α_i) remains similar. In the absence of aging, the SOA yields, Y, resulting from the wall-loss correction should be considered upper limits (MA parameterization), whereas the original yields serve as lower limits due to the considerations discussed above (TSI parameterization without aging). As shown in the supporting information (Figures S1 - S7) when aging (TSI parameterization with aging) is included the SOA yields increase beyond those observed when applying the wall loss correction for most of the VOC classes at longer photochemical ages. (It should be noted that SOA masses in Figues S1 – S7 were calculated using the same background as for the other model cases, 2.1 $\mu g\ m^{-3}$.) This feature of the aging parameterization is likely to blame for SOA over-predictions observed at long aging times when comparing with ambient data (e.g. Dzepina et al., 2011; Hayes et al., 2015).''

3-day simulations?

R1.4. As noted above, I have grave reservations about the use of a box model for this study, and the extension of the simulations to 3-days in Sect. 3.1. seems hard to defend. The authors suggest that they limited the runs to 3-days to minimize the importance of missing processes such as deposition, but a box model misses all processes of dispersion, transport and even chemistry in the correct photochemical regimes when run over such a long time. I simply do not believe that such long runs with such an artificial setup can be compared with measurements in other than a superficial way.

In any case, many SVOC species will show substantial deposition over 3-days (Karl et al, 2010, Hodzic et al, 2016), as indeed would ozone and various NOy species (e.g. N2O5).

We refer the reviewer to our response to comment R1.1.4. In addition, we have clarified the manuscript in order to focus on the comparison of our results with the OFR measurements, which are completely consistent with the model set-up, where deposition is also not important. We note that the box model is run for the conditions of the OFR itself, which is not problematic. The consistency of the OFR and aircraft results indicates that deposition does not have a major influence on the model results over short timescales.

Some other questions

R1.5.1 p3, L86 and generally. Actually VOCs are the only precursor of SOA (though of course other precursors such as NOx can be involved). VOC is a general term (defined here on L80-81) which includes SVOC and IVOC. If the authors want to use the term VOC for volatile organic compounds which are not S/IVOC then they need to refine and clarify their notation.

This is a semantic difference. In our work we use the term VOC as separate from S/IVOCs, while other authors (and reviewer 1) include S/IVOCs as part of the term VOCs. Different definitions are often used in the scientific literature for many terms, which is fine as long as each paper is clear on which definition is used. Thus, we address this comment by adding the following sentences in the introduction section.

''The notation used when discussing SOA precursors in this paper is similar to Hayes et al. (2015). We differentiate VOCs, IVOCs and SVOCs by their effective saturation concentration (c*). Therefore, SVOCs and IVOCs have volatilities ranging from c* = 10^{-2} to 10^{2} and 10^{3} to 10^{6} μg m^{-3} respectively, while VOCs are in the bins of c* ≥ 10^{7} μg m^{-3}.''

R1.5.2 p3, L99. I was surprised not to see some more recent references here, since much has been done in the last years. For example, Hodzic et al 2016 seem to cover some of the same themes (wall-loss corrected VBS) as this paper, with an evaluation at global scale. Another relevant work would be that of Dunmore et al 2015 and Ots et al. 2016, where IVOC emissions from diesel were suggested to be a major source of ambient SOA.

We add the references Dunmore et al. 2015 and Ots et al. 2016 in the introduction section when discussing P-S/IVOCs as important precursors to SOA.

We also added the following sentences in the experimental section (at p. 7, L237 in the original text) when describing the way which the IVOC parameters were estimated.

''In particular, the measured concentrations of speciated and unspeciated IVOCs and their estimated volatility are used to constrain the initial concentration of these species (as discussed in Section 2.2.2 below) as well as to estimate their yields (Zhao et al., 2014). ***Hodzic et al. (2016) have also estimated the IVOC yields while accounting for wall-losses using recent laboratory studies. However, the yields reported in that study are for a single lumped species, whereas in our work we estimate the yields using 40 IVOC categories, each representing a single compound or a group of compounds of similar structure and volatility. This method allows a more precise representation of IVOC yields and rate constants in the SOA model.''***

R1.5.3 p4, L105-107. If discussing VBS as a conceptual model, the 2-D version (Jimenez et al., 2009) deserves a mention. Actually, why was this version not used? Box/Lagrangian models have few restrictions on CPU usage, so would be a natural place to test 2-D VBS schemes.

We address this comment by adding the following paragraph at the end of section 2.2:

''Simulations of O:C have been previously evaluated in Hayes et al. (2015) using laboratory and field data from CalNex to constrain the predicted O:C. It was concluded in that work that it was not possible to identify one parameterization that performed better than the other parameterizations evaluated, because of the lack of constraints on the different parameters used (e.g. oxidation rate constant, oxygen mass in the initial generation of products and that added in later oxidation generations, SOA yields, and emissions). Therefore, incorporating O:C predictions into the current box model and using those results in the evaluation discussed here would not provide useful additional constraints.''

We also want to mention that such a discussion would add length to the manuscript, which might be undesirable as suggested by the reviewers. Not every available parameterization can be tested in each manuscript, and we have chosen to focus on the 1D VBS parameterizations that are most commonly used in regional and global models.

R1.5.4 p4, L118. loses should be losses. (There are other some small typos/English problems throughout, which should be checked.)

We correct ''loses'' to ''losses'' as suggested and have carefully proofread the revised manuscript.

R1.5.5 p6, L185-189. The text states that the potential source of error from omission if cold-starts does not apply to the total amount of vehicular POA emissions. This may be true if the absolute emission rates are not used, but surely the volatility distribution of cold-start VOC is different to that of warm-running engines?

We agree with the reviewer that the volatility distribution of POA emissions during cold-starts could be potentially different from that of warm-running engines, although no information on that comparison has been published to our knowledge. We have added the sentences below to the text in Section 2.2.2 to clarify this point.

''It should be noted that the tunnel measurements do not include emissions due to cold starts of vehicles. In the box model, only the relative volatility distribution of vehicular POA measured during the tunnel study is used, and thus this potential source of error does not apply to the total amount of vehicular POA emissions in the model. However, it is still possible that the volatility distribution of POA is different during cold-starts compared to that of POA emitted from warm-running engines. To our knowledge, measurements of the volatility distribution of POA during cold-starts are not available at this time. By comparing the SOA model results using two different POA volatility distributions (Robinson et al. 2007; Worton et al. 2014), we can evaluate to a certain extent the sensitivity of the simulated SOA concentration to the initial POA volatility distribution.''

R1.5.6 On the same paragraph though, presumably the Worton et al data could be used to produce a new estimate of total vehicle (S/I)VOC emissions. Why wasn't this done?

It is possible to calculate the P-S/IVOC emissions from the Worton et al. data in the following manner. The emission ratios (in g C L^{-1}) for both diesel and gasoline are multiplied by the volume of each fuel sold in Los Angeles county [Gentner et al. Proc. Natl. Acad. Sci. U.S.A. 109, 18318-18323, 2012] to obtain the total emission (in g C) for each of the fuel types. To then implement these total emissions into the box model framework, they are summed and divided by the total CO emissions [Gentner et al. Environ. Sci. Technol. 47, 11837-11848, 2013], which are calculated in a manner analogous to that used for the P-S/IVOCs. A POA/ΔCO ratio of 3 μg m^{-3} ppm^{-1} is obtained, which is lower than the ratio currently used in the box model, 6 μg m^{-3} ppm^{-1} . The difference could be due to a greater influence of diesel emissions at the Pasadena site than is indicated by the fuel sales data or cold starts. These possible sources of error are the reason that the observed POA/ΔCO ratio was chosen for constraining the P-S/IVOC emissions rather than the approach suggested in this comment.

R1.5.7 p8,L276-279, 281-288. Quantify these time-scales for the reader.

We have modified the text as follows in Section 2.2.

"Specifically, at lower volatilities (c* ≤ 1 μg m^{-3}), the partitioning kinetics of the organic mass from the particles to the chamber walls have an effective timescale of more than an hour, which is similar or longer than typical chamber experiments (Ye et al., 2016). The limiting step in the partitioning kinetics is evaporation of SVOCs from the particles to the gas phase, and therefore the exact rate of evaporation depends on the OA concentration in the chamber."

"According to Krechmer et al. (2016) and other chamber experiments (Matsunaga and Ziemann, 2010), the gas-wall equilibrium timescale doesn't vary strongly with the chamber size. ***The timescale for gas-wall equilibrium reported in these previous studies was 7 - 13 minutes."***

R1.5.8 P11, L370 and elsewhere. Define whether mass or volume fractions and stoichiometry are used. This can be an easy error, especially when the cited Donahue paper redefined Raoult's law in terms of mass rather than mole fractions.

We have updated the text as shown below.

"Where $x_{p,i}$ is the particle phase fraction of lumped species i (expressed as a mass fraction); C_i is the effective saturation concentration, and C_{OA} is the total mass of organic aerosol available for partitioning (μg m^{-3})."

R1.5.9 P11, L396. 'shorter' ... than what?

We now specify exactly the photochemical age in the text.

"The ambient urban SOA mass at the Pasadena ground site is generally measured under conditions corresponding to photochemical ages of 0.5 days or less (Hayes et al., 2013)."

R1.5.10 P15, L519-523. Too wordy and repetitive.

We address this comment by updating the text below in the submitted manuscript (at p. 15, L517 in the original text):

"To make this comparison, the simulated SOA is apportioned between fossil S-SOA, fossil I-SOA, fossil V-SOA, cooking S-SOA, and biogenic V-SOA. The last two apportionments correspond to non-fossil carbon. ***This evaluation is possible following an approach similar to Hayes et al. (2015) where the identity of the precursor is used to apportion SOA."***

R1.5.11 P15, L531. The work of Dunmore and Ots mentioned above would support this statement.

As suggested, we have added references to Dunmore et al. 2015 and Ots et al. 2016 in the line indicated by the reviewer.

R1.5.12 P15, L543 on. This paragraph is a good example where the authors attribute all problems to SOA mechanisms. It may well be that the box model setup is responsible for the problems.

We address this comment by updating the conclusions about our results. We kindly refer the reviewer to our updated texts below, which are copied from the updated manuscript.

From Section 3.1

"Finally, the ROB + ZHAO + MA and the WOR + ZHAO + MA cases both better represent SOA formation and exhibit better model/measurement agreement among the different cases used in this work. They are both consistent with the OFR reactor data at longer photochemical ages as shown in Figs. 3 and 4 compared with the other cases. At a qualitative level, the MA parameterization simulations are more consistent with the fit of the OFR measurements in which the SOA mass remains nearly constant at longer photochemical ages. In contrast, the cases with the TSI parameterization do not follow this trend as the SOA mass keeps increasing between 2 and 3 days age, which is not observed in the measurements. As already mentioned, the model used for this work does not include fragmentation reactions, and including these reactions, in particular branching between functionalization and fragmentation during gas-phase SVOC oxidation, may improve the cases using a potential update of the TSI parameterization as discussed below. **Fig. 4F indicates that including additional P-SVOC mass in the model and accounting for gas-phase wall losses in chamber studies improves SOA mass concentration simulations with respect to the measurements. However, in the WOR + ZHAO + MA case there is still a slight under-prediction of SOA formed at shorter photochemical ages (between 0.05 and 0.5 days), and this discrepancy is observed in all the other model cases.** ***Given the uncertainties in the model set-up discussed in the experimental section, it is not possible to conclude if one of the four cases (i.e. ROB + ZHAO + TSI, WOR + ZHAO + TSI, ROB + ZHAO + MA, WOR + ZHAO + MA) more accurately represents SOA formation in the atmosphere."***

We also want to mention that we explain the importance of fragmentation reactions as a response to comment R2.2.1.

From Conclusions:

"Therefore, the model cases with updated VOC yields that account for chamber wall-losses best reproduce the ambient and OFR data. However, while the WOR + ZHAO + MA case appears to represent a slight improvement over the ROB + ZHAO + MA case, as well as over the ROB + ZHAO + TSI and WOR + ZHAO + TSI cases, it is not possible to conclude that one set of parameters is better than the other since the difference in the predictions for these 4 cases (15 % on average) is likely smaller than the uncertainties due to the model setup as well as the lack of a gas-phase fragmentation pathway during aging."

R1.5.13 P17, Sect. 3.2. Given my reservations about the validity of the box-model, and its obvious lack of treatment of VOC degradation with transport time, I wasn't convinced that this section had a good basis. In addition, the manuscript is already quite long, and this section feels like a side-issue.

The model includes in fact a detailed treatment of VOC degradation in which the reduction in concentration with photochemical age is simulated. In fact, the treatment of VOC degradation in the box model is more rigorous than in 3-D gridded models in that there is no lumping of VOCs and the IVOCs are speciated, which allows the use of more precise oxidation rate constants. To respond to the concern regarding manuscript length, we have shortened this section to one paragraph.

Referee 2 Comments

General Comments:

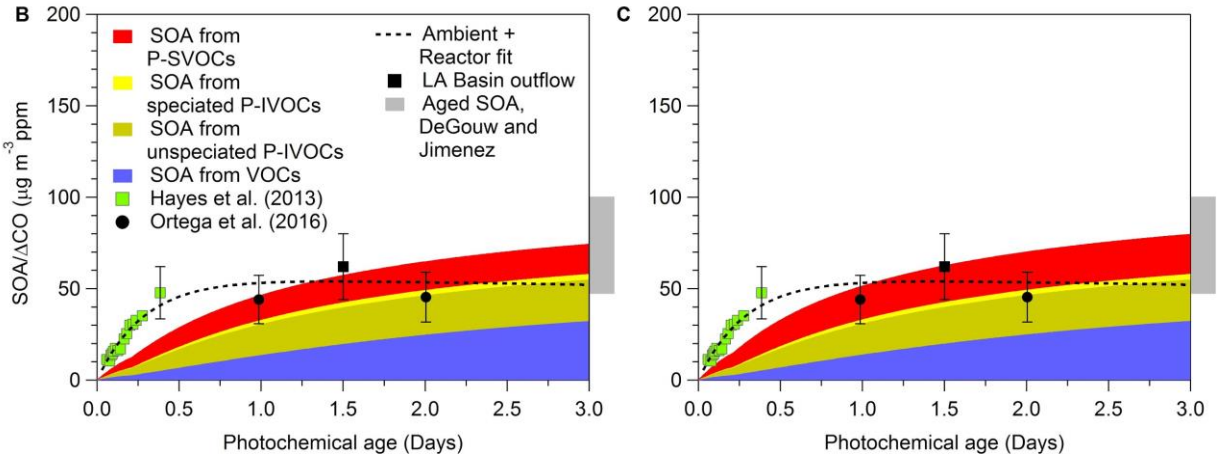
R2.1 Ma and coauthors present a follow-up to the work in Hayes et al. (2015), adding more recent parameterizations for I/S-VOC emissions and yields as well as very recent approaches to correcting chamber yields for wall losses. I am satisfied with the application of the box model to the Pasadena data given the lack of quantitative statistics presented. The important limitations of the aging mechanisms and over-exuberant IVOC formation pathways is demonstrated more qualitatively than quantitatively. Also, the authors are careful to avoid strong conclusions about the dominance of SOA from IVOCs over SVOCs or vice-versa. I do urge the authors to move toward a 3D-CTM analysis in the future, particularly since I'm pretty sure input datasets exist for all the major CTMs. Although the conclusions are not exactly novel (other studies have shown that the VBS functionalization mechanisms overpredict at long photochemical lifetimes), I appreciate the demonstration of the improved parameterizations, particularly the chamber wall-loss correction. I found some aspects of the experimental design to have unnecessary limitations. Moreover, I encourage the authors to consider improving several aspects of the presentation before I recommend publication of this manuscript.

We thank the reviewer for their thoughtful comments, and have provided point-by-point responses below. As discussed in response to, e.g., R1.1.1, we disagree with the notion that a 3D-CTM is superior in all cases. In some cases a box model can be complementary and even superior to a 3D-CTM for some applications.

Specific Comments:

R2.2.1 My primary question/criticism is why do the authors not investigate aging mechanisms with fragmentation given the emerging global/regional model implementations of these pathways and the low computational overhead of their own box model? This would seem like an ideal application given the experimental data available to them from CalNex. Why not use measured AMS elemental ratios to help constrain the configuration choices here? Potentially, that analysis could give complementary information to the analysis in Section 3.2 and Fig. 6.

We address to this comment by running two model cases and including a fragmentation process due to heterogeneous oxidation of the particles. The fragmentation is parameterized as an exponential decay of OA concentration with a lifetime of 50 days as reported in Ortega et al. 2016.



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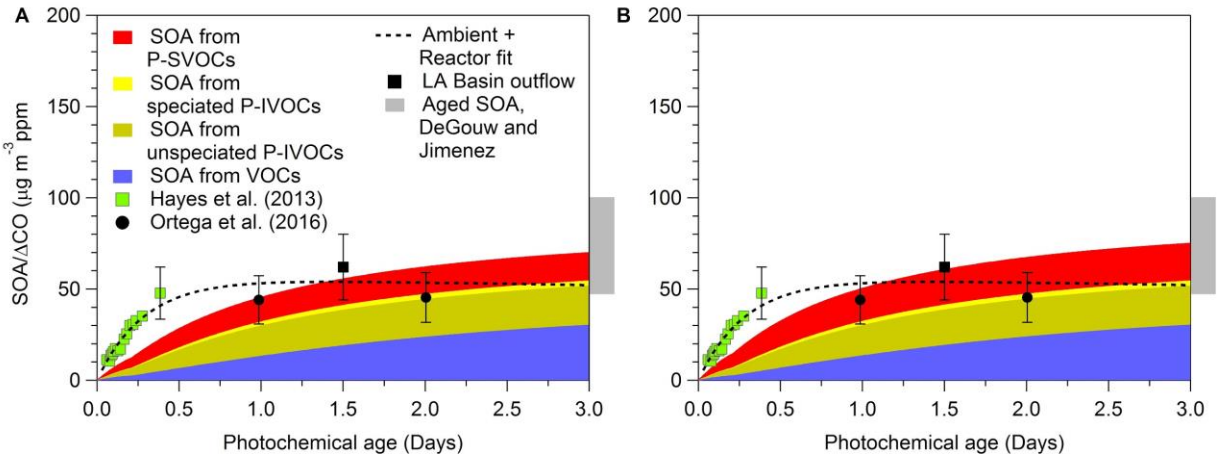
575 Figure 3. Predicted urban SOA mass for the B) ROB + ZHAO + TSI and C) WOR + ZHAO + TSI cases with
576 the original model set-up for this work.



577

578 Figure R1. Predicted urban SOA mass by the A) ROB + ZHAO + TSI and B) WOR + ZHAO + TSI cases when
579 including fragmentation.

580 To summarize these findings, we have updated the text in the manuscript and added a discussion of the
581 different fragmentation mechanisms. We only show results for two cases (those above), but all six
582 model cases give similar results when including fragmentation.

583 ***"According to the OFR data from Ortega et al. (2016), the mass of OA starts to decay due to***
584 ***fragmentation after heterogeneous oxidation at approximately 10 days of photochemical aging. The***
585 ***results are consistent with other OFR field measurements (George and Abbatt, 2010; Hu et al., 2016;***
586 ***Palm et al., 2016). In this work, the model is run only up to 3 days, which is much shorter than the age***
587 ***when heterogeneous oxidation appears to become important. In fact, when including a fragmentation***
588 ***pathway for each of the model cases, a reduction of OA of only 6 % is observed compared to the cases***
589 ***without fragmentation at 3 days of photochemical aging. In this sensitivity study, the fragmentation is***
590 ***parameterized as an exponential decrease in OA concentration that has a lifetime of 50 days following***

Ortega et al. (2016). Given the results, the inclusion of fragmentation due to heterogeneous oxidation in the model does not significantly change the model results or the conclusions made in this work.

More generally, there are at least three different fragmentation mechanisms that could be responsible for the decrease of SOA formation at very high photochemical ages. The first mechanism is the reaction of oxidants (e.g. OH) with the surface of an aerosol particle and decomposition to form products with higher volatility, i.e. due to the heterogeneous oxidation just described. The second type of fragmentation that may be important for very high photochemical ages in the OFR (Palm et al., 2016) is due to the high concentration of OH. Most of the molecules in the gas phase will react multiple times with the available oxidants before having a chance to condense, which will lead to the formation of smaller products too volatile to form SOA. However, this is only important at very high photochemical ages in the OFR, which are not used in this work. A third type of fragmentation can occur during the aging of gas-phase SVOCs (Shrivastava et al., 2013; 2015). The TSI parameterization used in the model from this work and from previous modeling works (Robinson et al., 2007; Hodzic et al., 2010; Shrivastava et al., 2011) only includes the functionalization of the SVOCs and neglects fragmentation reactions. More recently, Shrivastava et al. (2013) have modified the VBS approach in a box model by incorporating both pathways and performed several sensitivity studies. The results when including fragmentation generally exhibit better agreement with field observations, but as noted in that work the agreement may be fortuitous given that both the emissions as well as the parameters representing oxidation in the model are uncertain. This third type of fragmentation is not simulated in our sensitivity study using the approach above, and it remains poorly characterized due to the complexity of the chemical pathways and the number of compounds contributing to SOA formation as described in Shrivastava et al. (2013).''

R2.2.2 The authors discuss extensively the problems with aging VOC oxidation products and the tendency for mechanisms to accumulate mass at long photochemical lifetimes. It is important that they emphasize (stronger than they already do) that this aging approach is likely problematic precisely because it does not consider fragmentation. One of the main conclusions I read from the paper is that wall-loss corrected VOC yields should be used and aging mechanisms turned off. Conceivably, a future study will conclude that turning off aging is a bad idea because even though the OA mass is better predicted at long time, the O:C is underpredicted. The models of the future will hopefully have both more accurate yields and probably aging with both functionalization and fragmentation adequately described. To avoid confusion in the meantime, I recommend the authors refer everywhere to the TSI aging as "aging by functionalization only" or something similar, with an appropriate acronym for readability.

We have addressed this comment in our responses to comments R2.2.1 and R1.5.12. We have not changed the abbreviations in the text to "TSI with aging by functionalization only", since that would be very cumbersome terminology. Instead we very clearly address this important issue in the abstract and the conclusions as well as in new text quoted in our responses to R2.2.1 and R1.5.12.

R2.2.3 L390-394 and L480-483: The authors repeatedly refer to the OFR work of Ortega et al. (2016) to justify not including fragmentation in any model case. This argument relies on the assertion that fragmentation only played a dominant role when the OA mass began to decrease after it had plateaued for a couple of days in photochemical age space. But the OA concentrations started leveling off in that study at about 1 day. As with any competition, the manifestation of a plateau indicates to me that fragmentation is playing a role equal to that of functionalization. So sentences like L477-480 and L482-483 are pretty confusing, if not misleading.

We completely agree with the reviewer and have modified the text to clarify the manuscript.

At L390 - 394, the new text reads as follows:

"*Since fragmentation and dry deposition are not included in the model, it has only been run to 3 days in order to minimize the importance of these processes with respect to SOA concentrations (Ortega et al., 2016). *Nevertheless, it is very likely that gas-phase fragmentation of SVOCs (e.g. branching between functionalization and fragmentation) occurs during oxidative aging over these photochemical ages as is discussed in further detail below."

At L480 - 483, the text has been changed already in response to comment R1.5.12 and can be viewed in our response to that comment.

R2.2.4 The application of the wall-loss corrected chamber yields seems problematic to me. First of all, many of the studies used to inform the Tsimpidi et al. (2010) yield set included seed aerosol in their experiment. As the authors point out multiple times, the data they have included in Table S4 should be considered an upper bound. However, I fear that their demonstration of this approach will encourage others to blanket apply the parameters of Krechmer et al. (2016) to historical chamber yields without considering the details and possible interferences. I encourage the authors to describe in detail the problems with applying the narrowly defined Krechmer Cw's to existing data and repeat that paper's call for more detailed analysis of chamber data before the community gobbles this simple approach and then moves on to the next hot SOA formation topic.

We are aware of multiple groups that are working on further characterizing vapor wall losses and their impact on SOA formation experiments. In that context, it seems very unlikely that our simple approach would become "dominant" in the SOA modeling field. We still believe that it provides one useful sensitivity study about the impact of the vapor loss problem. We address this comment by adding the following sentence in the conclusion section of the manuscript.

''Moreover, uncertainties in the vapor wall-loss corrected yields remain, and the correction of the yields has been performed here using data from a limited number of laboratory studies. In particular, the effect of temperature and humidity on gas-wall partitioning needs to be characterized. The results obtained in our work motivate future studies by showing that SOA models using wall-loss corrected yields reproduce observations for a range of photochemical ages at a level of accuracy that it is as good as or better than parameterizations with the uncorrected yields.''

R2.2.5 Why is the SOA mass in Fig. 5 not also divided by CO concentrations to correct for dilution?

As suggested, we have included a right-side axis in the Fig. 5A bar graph representing the SOA mass to ΔCO concentration ratios.

R2.2.6 L257-258: Woody et al. (2016) proposed a meat cooking volatility distribution. Why not try this one in a sensitivity test?

We performed a sensitivity study running the model using the meat cooking volatility distribution proposed by Woody et al. (2016) as suggested by the reviewer. For ease of comparison, we include here the original results obtained before the sensitivity study and taken from the submitted manuscript.

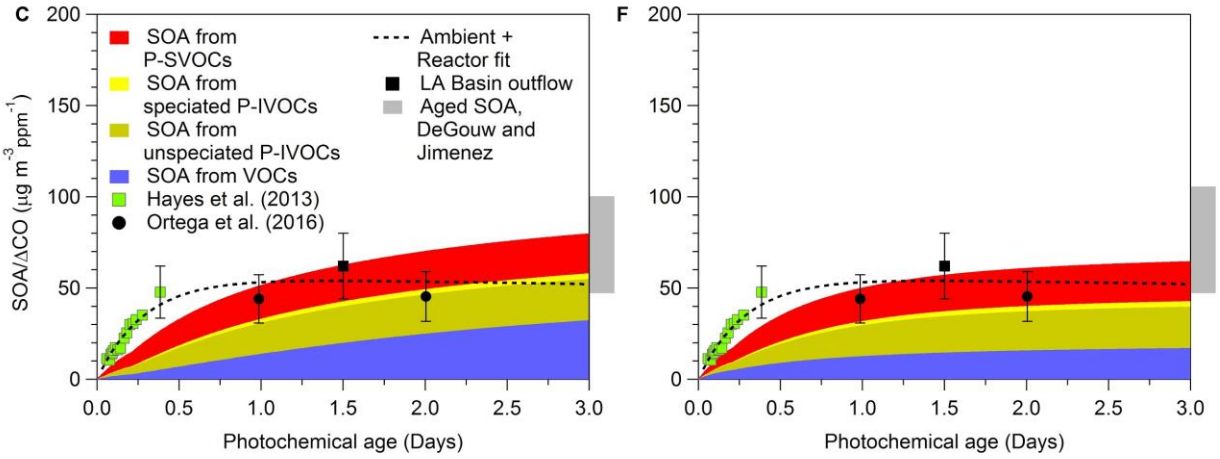


Figure 3. Predicted urban SOA mass for the C) WOR + ZHAO + TSI and F) WOR + ZHAO + MA cases with the original model set-up for this work.

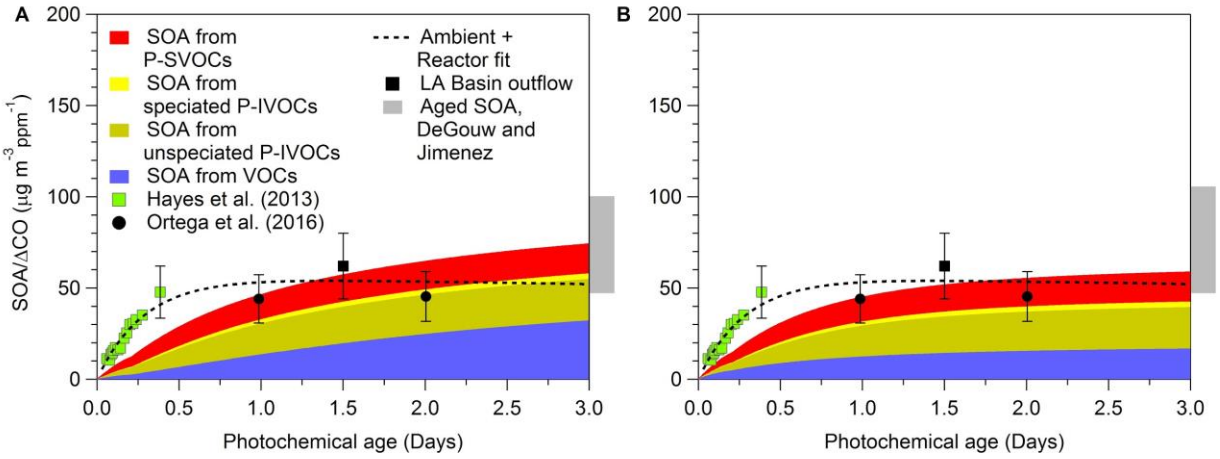


Figure S8. Predicted urban SOA mass for the A) WOR + ZHAO + TSI and B) WOR + ZHAO + MA cases when using the meat cooking volatility distribution reported in Woody et al. (2016).

We have added the figure above in the supporting information and the paragraph below in the manuscript to summarize the findings.

''Finally, Woody et al. (2016) recently proposed a meat cooking volatility distribution and therefore we perform a sensitivity study by using this distribution in our model for P-SVOCs coming from cooking sources. The results are displayed in the supporting information (Figure S8), where this alternate approach has been implemented for the WOR + ZHAO + TSI and WOR + ZHAO + MA cases. By comparing the results obtained from this sensitivity study with Fig. 3, the two cases in the sensitivity study display a slight decrease of SOA/ΔCO values over 3 days of photochemical aging with a difference of approximately 8% at 3 days. Thus, the model-measurement comparison does not change significantly relative to the base case. Given the similarities between the sensitivity study and Fig. 3, as well as the possibility of cooking SOA sources other than meat-cooking (i.e. heated cooking oils, Liu et al. (2017)), the remainder of our work uses the Robinson et al. volatility distribution for P-SVOCs from cooking sources.''

R2.2.7 Can the authors clarify more directly why the model with the Worton parameters for SVOCs gives more OA than that with the Robinson parameters? The volatility distribution and Fig. 2 show pretty clearly that the emissions are substantially higher in volatility. Is the difference really from the added 7.5% mass that comes with the 1-bin aging mechanism? If that's the case, please emphasize more clearly the uncertainty in this parameter/approach to put the differences in these two model runs into context.

We want to clarify that the difference between the results for the Worton and Robinson parameters is not due to the added 7.5% mass during aging but rather the ratio of SVOC/POA at the beginning of the SOA formation. We kindly refer the reviewer to the paragraph below from the submitted manuscript (p. 12, L439). For clarity, we have updated the text.

"The more rapid SOA formation is due to the updated SVOC volatility distribution in this model case compared to the cases that use the Robinson et al. (2007) distribution. ***Specifically, as shown in Fig. 2F, there is a higher relative concentration of gas phase SVOCs in the c* = 10^2 bin and thus a higher ratio of P-SVOC to POA. Given that in the box model (and in most air quality models) the P-SVOC emissions are determined by scaling the POA emissions according to their volatility distribution, a higher P-SVOC to POA ratio will then result in a higher initial P-SVOCs concentration. Furthermore, SOA formation from P-SVOCs is relatively fast. Together these changes lead to increases in SOA formation during the first hours of photochemical aging when using the Worton et al. volatility distribution.''***

R2.2.8 Section 3.2 and Fig. 6: This analysis is an interesting idea but I don't think the slight differences among the model cases warrant such a long-winded discussion and detailed figure. It would be enough to add a comment to section 3.1 that the WOR cases give more SOA from precursors with kOH in the range identified by Ortega et al. (2016). The abstract and conclusions would need to be correspondingly reduced.

We have shortened the discussion in Section 3.2 as suggested to one paragraph. We have also reduced the relevant paragraph in the conclusions.

R2.2.9 L716-718 and L796-797: Why do the authors not discuss the limitations of their aging mechanisms that only reduce volatility by one bin at a time? It is possible that a compound can shift more than one generation in volatility upon oxidation; the more recent 2D-VBS approaches and the SOM methods allow for multi-decadal shifts in volatility. Approaches like these might push the products below the "oxidation-partitioning barrier" manifested when compounds are protected from gas-phase oxidation.

We address this comment by kindly referring the reviewer to the paragraph below in the submitted manuscript (p. 20, L712). We have also updated this paragraph for clarity.

"With these considerations in mind, the volatility distribution of the SVOCs is somewhat different in the model compared to the measurements. Most notably, the model does not form a significant amount of lower volatility SOA in the 10^{-2} µg m^{-3} bin, whereas the measurements have a much higher concentrations in this bin. A factor that may explain this difference between the volatility distributions is the lack of particle phase reactions that continue to transform SOA into lower volatility products, a process which is not considered in the model. ***One example of a particle phase reaction is the formation of SOA within deliquesced particles, including the partitioning of glyoxal to the aqueous phase to produce oligomers as discussed in Ervens and Volkamer (2010), although that specific mechanism was of little significance during CalNex (Washenfelder et al., 2011; Knote et al., 2014). Alternatively, the use of an aging parameterization where the volatility may decrease by more than one order of magnitude per oxidation reaction would also distribute some SOA mass into lower c* bins. Hayes et al. (2015) previously evaluated different parameters for aging. However, the results from this previous study showed that substantial over-prediction of SOA was observed when using the Grieshop et al. (2009) parameterization in which each oxidation reaction reduced volatility by two orders of magnitude. New parameterizations may be necessary to produce the observed SOA volatility and concentration simultaneously (Cappa et al. 2012). However, we note that the additional low volatility organic mass will not significantly change SOA predictions in urban regions where OA concentrations are relatively high."***

R2.2.10 L760-762: How do these reaction rate constants compare to estimation methods developed for the 2D-VBS? If you used those approximations (based on C* and assumed O:C) would you do better?

We are not sure exactly what version of the 2-D VBS the reviewer is referring to, but 2-D VBS parameterizations have used a single rate constant of 4 x 10^{-11} cm^3 $molec^{-1}$ s^{-1} for oxidation and aging of IVOCs [Murphy et al. Atmos. Chem. Phys. 12, 10797-10816, 2012]. This rate constant is generally higher than that used in our own work for the initial oxidation reaction, and thus would be expected to improve the model/measurement agreement at short photochemical age. At the same time, such a result is not surprising given that the rate constant used in the 2-D VBS was tuned to best match laboratory and field observations. In contrast, the rate constants from our work are estimated based on the precursor structure as described in the manuscript as well as in Zhao et al. (2014), and thus they are better constrained. Furthermore, it should be noted that the aging rate constant used in the box model for subsequent oxidation reactions is the same as that used in the reference above (4 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}).

Furthermore, in the statistical oxidation mode (SOM) [Cappa et al. Atmos. Chem. Phys. 12, 9505-9528, 2012] the reaction rates constants are parameterized using both carbon and oxygen number. When comparing our rate constants in the supporting information against those summarized in Figure S1 of the supporting information of Cappa et al., the rate constants are very similar. This result is not surprising given that both are based on the same structure-activity relationship [Kwok and Atkinson *Atmos. Environ.* 29, 1685-1695, 1995].

Minor Changes/Typos:

R2.3.1 L48-50: This sentence should say something about how the two methods predict similar mass at short to moderate photochemical ages.

We address to this comment by updating the sentence below in the manuscript.

''The model predicts similar SOA mass at short to moderate photochemical ages when the "aging" mechanisms or the updated version of the yields for VOC oxidation are implemented."

R2.3.2 L82: Consider replacing "nucleate" with "form".

We replace ''nucleate'' by ''form'' in the text as suggested by the reviewer.

R2.3.3 L742-743: Make sure to also mention that Woody et al. (2016) cited excessive model dispersion as a potential complicating factor.

This is an excellent suggestion and we have updated the sentence below in the manuscript.

"As stated in Woody et al. (2016), the higher ratio may compensate for other missing (or underrepresented) formation pathways in SOA models or excessive dispersion of SOA in their model."

R2.3.4 I recommend adding figures with SOA mass curves (not just the yields) for each of the VOC product species to the supporting information, thereby visually demonstrating the effects of the upper- and lower-bound yield parameterizations. It would be a good idea to assume a background concentration equal to 2.1 ug m^{-3} (or greater if you just want to take an average of your total OA, model wide) like in the model so that you get relevant partitioning.

We address this comment by adding figures with SOA mass curves for each of the VOC classes in the supporting information as suggested. These figures are also displayed below.

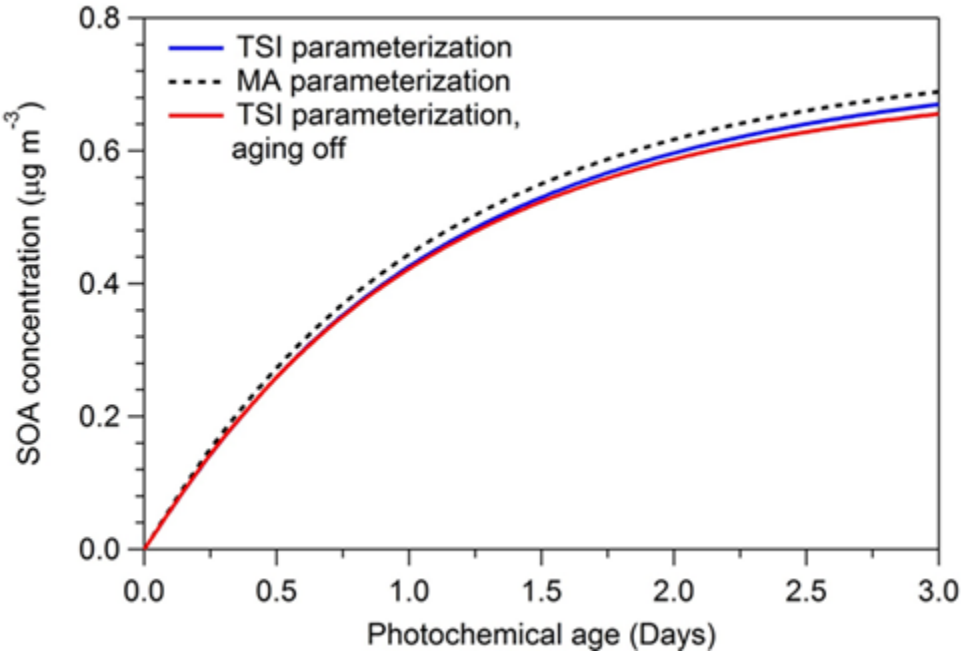


Figure S1. Predicted urban SOA mass from the alkane VOCs (Alk5) for different SOA formation parameterizations.

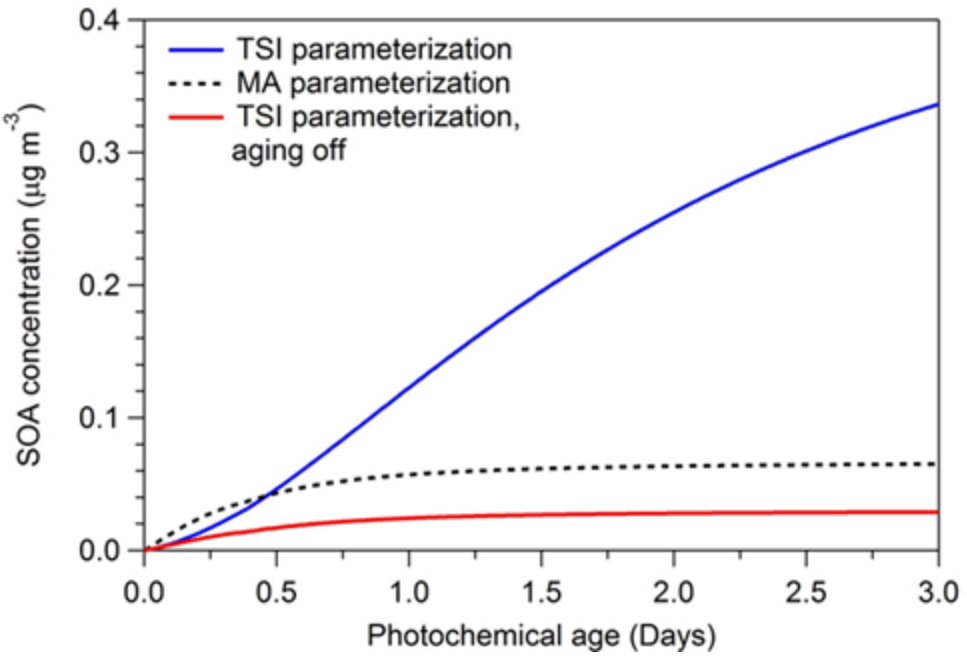


Figure S2. Predicted urban SOA mass from the olefin VOCs (Ole1) for different SOA formation parameterizations.

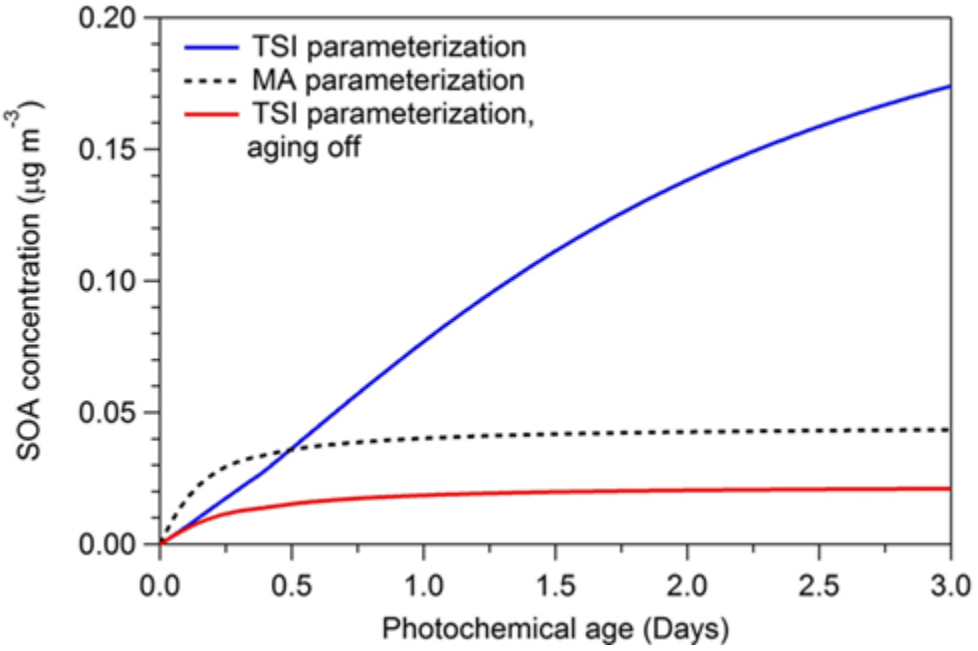
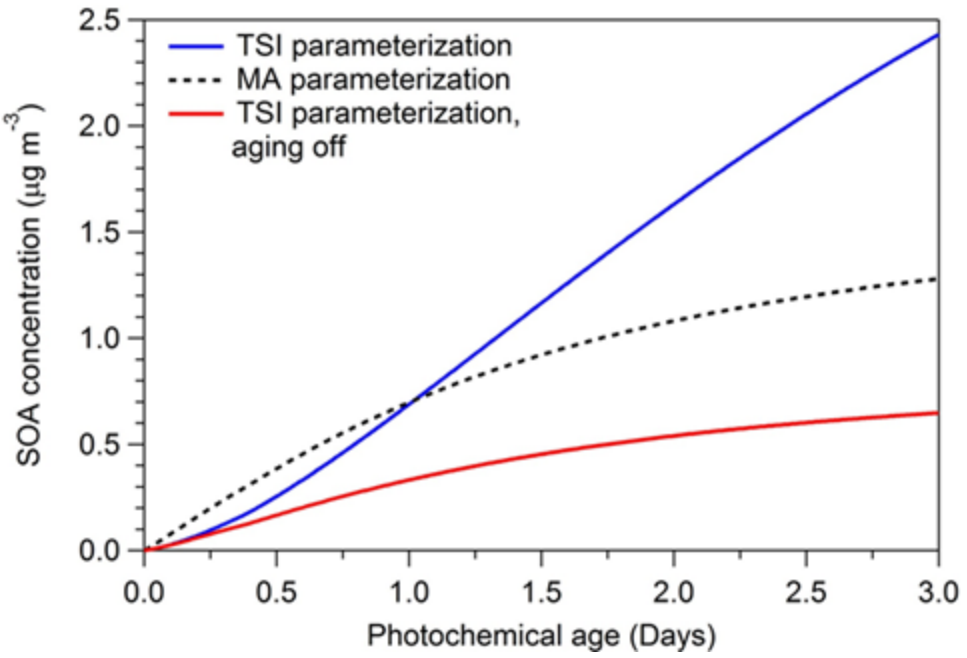
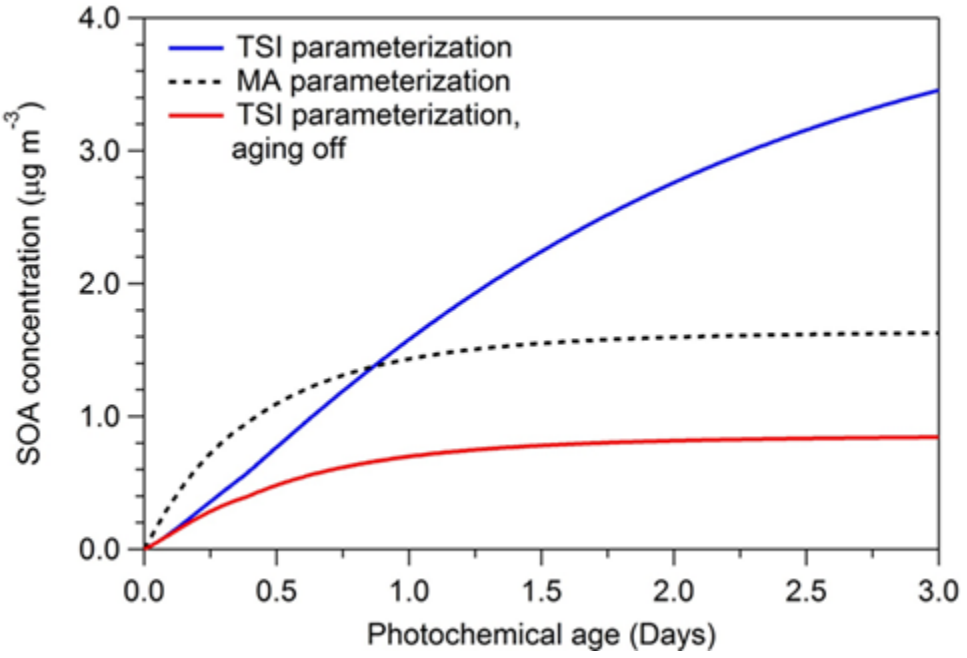


Figure S3. Predicted urban SOA mass from the olefin VOCs (Ole2) for different SOA formation parameterizations.



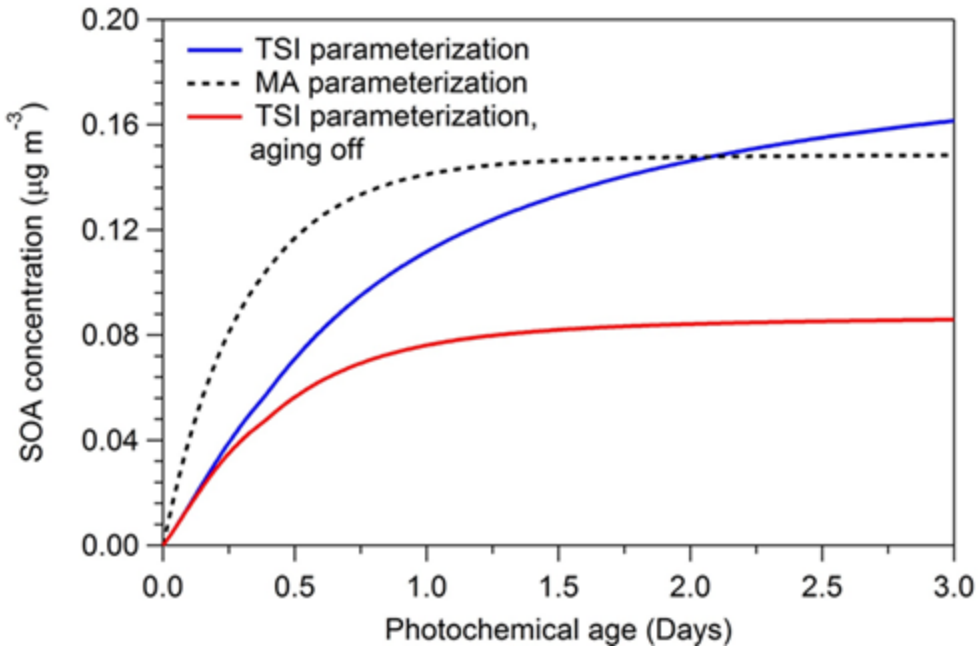
797

798 Figure S4. Predicted urban SOA mass from the aromatic VOCs (Aro1) for different SOA formation
799 parameterizations.



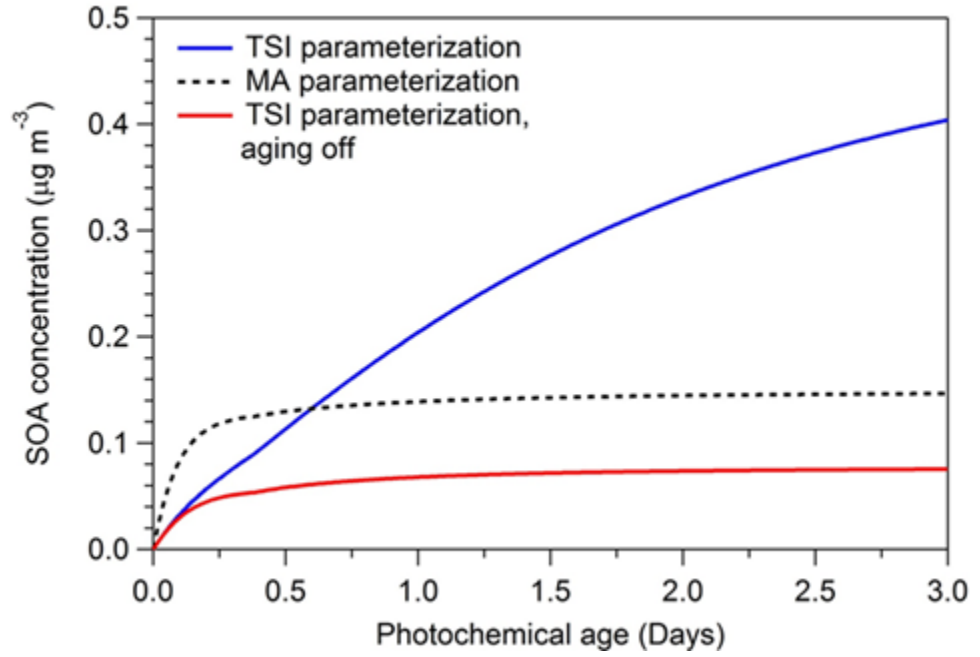
800

801 Figure S5. Predicted urban SOA mass from the aromatic VOCs (Aro2) for different SOA formation
802 parameterizations.



803

804 Figure S6. Predicted urban SOA mass from isoprene (Isop) for different SOA formation
805 parameterizations.



806

807 Figure S7. Predicted urban SOA mass from terpenes (Terp) for different SOA formation
808 parameterizations.

809

To summarize these findings, we have added the paragraph below in the manuscript in section 2.2 and include the Figures S1 to S7 in the supporting information.

''Furthermore, as described in the supporting information, the updated SOA yields for VOC oxidation result in distribution of SVOC mass into lower volatility bins compared to the original parameterization, although the sum for the SVOC yields (α_i) remains similar. In the absence of aging, the SOA yields, Y, resulting from the wall-loss correction should be considered upper limits (MA parameterization), whereas the original yields serve as lower limits due to the considerations discussed above (TSI parameterization without aging). As shown in the supporting information (Figures S1 - S7) when aging (TSI parameterization with aging) is included the SOA yields increase beyond those observed when applying the wall loss correction for most of the VOC classes at longer photochemical ages (it should be noted that SOA masses in Figures S1 - S7 were calculated using the same background as for the other model cases, 2.1 µg m^{-3}). This feature of the aging parameterization is likely to blame for SOA over-predictions observed at long aging times when comparing with ambient data (e.g. Dzepina et al., 2011; Hayes et al., 2015).''

R2.3.5 SI, L6-22: I found the derivation of the wall-loss correction confusing. First, the quantity in parentheses in equations 5 and 6 should be the reciprocal. I assume they used the correct form for the calculation because I calculated the adjusted ARO2 and it would have been way off using the equation as it is written. Also, [VOC] should be replaced with something more accurate like [ΔROG] or [ΔVOC]. It would be helpful to explain briefly why the mass of compounds on the walls, Cw, is a function of C* alone and not Ctot, Cg or Cp. This is essentially a consequence of the equilibrium assumption in the chamber analysis, as I understand it.

We have corrected equations 5 and 6. We also replace [VOC] by [ΔVOC] as suggested. We also address this comment by clarifying that c_w is the equivalent organic mass concentration of the walls. The notation c_w is used by Krechmer et al. (2016) and we have kept it for consistency. We add the text below in the supporting information for clarity.

''For clarity, c_w is the equivalent organic mass concentration of the walls, and it is an empirically determined value. Equations 2 and 3 are the partitioning equations that describe either the partitioning between the gas phase and walls or the gas phase and the particles, which both depend on the volatility of the organic vapors, c*. The significance of c_w can be understood by comparing equations 2 and 3. In equation 3, the partitioning is dependent on the total particle phase, c_{OA}. Similarly, the parameter c_w is the amount of mass in the chamber walls available for partitioning expressed as an effective mass concentration based on the work of Krechmer et al. (2016). However, the value of c_w is a function of c* as shown in equation 1.''

Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA

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ABSTRACT

Secondary Organic Aerosols (SOA) are important contributors to fine PM mass in polluted regions, and their modeling remains poorly constrained. A box model is developed that uses recently published literature parameterizations and data sets to better constrain and evaluate the formation pathways and precursors of urban SOA during the CalNex 2010 campaign in Los Angeles. When using the measurements of IVOCs reported in Zhao et al. (2014) and of SVOCs reported in Worton et al. (2014) the model is biased high at longer photochemical ages whereas at shorter photochemical ages it is biased low, if the yields for VOC oxidation are not updated. The parameterizations using an updated version of the yields, which takes into account the effect of gas phase wall-losses in environmental chambers, show model/measurement agreement at longer photochemical ages, even though some low bias at short photochemical ages still remains. Furthermore, the fossil/non-fossil carbon split of urban SOA simulated by the model is consistent with measurements at the Pasadena ground site.

Multi-generation oxidation mechanisms are often employed in SOA models to increase the SOA yields derived from environmental chamber experiments in order to obtain better model/measurement agreement. However, there are many uncertainties associated with these ‘‘aging’’ mechanisms. Thus, SOA formation in the model is compared against data from an oxidation flow reactor (OFR) in order to constrain SOA formation at longer photochemical ages than observed in urban air. The model predicts similar SOA mass at short to moderate photochemical ages when the ‘‘aging’’ mechanisms or the updated version of the yields for VOC oxidation are implemented. The latter case though has SOA formation rates that are more consistent with observations from the OFR. Aging mechanisms may still play an important role in SOA chemistry, but the additional mass formed by functionalization reactions during aging would need to be offset by gas-phase fragmentation of SVOCs.

All the model cases evaluated in this work have a large majority of the urban SOA (69 – 83 %) at Pasadena coming from the oxidation of P-SVOCs and P-IVOCs. The importance of these two types of precursors is further supported by analyzing the percentage of SOA formed at long photochemical ages (1.5 days) as a function of the precursor rate constant. The P-SVOCs and P-IVOCs have rate constants that are similar to highly reactive VOCs that have been previously found to strongly correlate with SOA formation potential measured by the OFR.

Finally, the volatility distribution of the total organic mass (gas and particle phase) in the model is compared against measurements. The total SVOC mass simulated is similar to the measurements, but there are important differences in the measured and modeled volatility distributions. A likely reason for the difference is the lack of particle-phase reactions in the model that can oligomerize and/or continue to oxidize organic compounds even after they partition to the particle phase.

1. INTRODUCTION

Atmospheric aerosols are important climate forcing agents (Christensen et al., 2013), negatively impact human health (Dockery and Pope, 1994) and reduce visibility by scattering and absorbing light (Watson, 2002). However, predicting quantitatively the composition and concentrations of aerosols is challenging, in part because of their complex composition and the variety of emission sources and chemical pathways that contribute to aerosol loadings in the atmosphere (Heald et al., 2011; Spracklen et al., 2011). Atmospheric aerosols are composed of black carbon, inorganic, and organic matter, and the latter is a mixture of hundreds to thousands of compounds (Gentner et al., 2012).

Due to this complexity, organic aerosol is often categorized into two groups. Primary organic aerosol (POA) is directly emitted into the atmosphere from sources such as motor vehicles, food cooking, and biomass burning (Hallquist et al., 2009). On the other hand, secondary organic aerosol (SOA) is the product of diverse chemical reactions occurring in the atmosphere that transform more-volatile precursors such as volatile organic compounds (VOCs) into lower volatility products that are either incorporated into existing particles or form new particles. Many previous studies have shown that SOA is an important fraction of OA globally often representing more than half the total OA concentration (Zhang et al., 2007; Jimenez et al., 2009).

In SOA parameterizations for use in regional and global models, a semi-empirical approach is used in which VOCs, often the only SOA precursors considered, react with OH radicals and other oxidants to form secondary products with lower volatility at a given mass yield. These secondary semi-volatile organic compounds (SVOCs) can partition to the particle phase to form SOA (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006). The parameters used in the models for the VOCs, such as the yields and product volatilities, are often determined from published chambers studies (e.g. Kroll et al., 2006; Chan et al., 2009; Hallquist et al., 2009; Presto et al., 2010). Over the past decade a number of studies have shown that traditional models that consider only the oxidation of VOCs alone predict SOA concentrations much lower than those observed in polluted urban regions (Volkamer et al., 2006; Dzepina et al., 2009; Hodzic and Jimenez, 2011; Hayes et al., 2015). As a result, several updates have been proposed in the literature to improve SOA models including new pathways for SOA formation, new SOA precursors, and increased yields for known precursors (e.g. Ng et al., 2007; Robinson et al., 2007; Ervens and Volkamer, 2010).

The volatility basis-set (VBS) approach (Donahue et al., 2006) has been used in most recent parameterizations of SOA yields. In this approach, the organic mass is distributed in logarithmically spaced volatility bins, and the SOA forming reactions then redistribute the mass from precursors such as anthropogenic and biogenic VOCs, into

bins with generally lower volatility (except for fragmentation reactions) leading to increased OA concentrations (Robinson et al., 2007; Tsimpidi et al., 2010). While the VBS provides a valuable conceptual framework for SOA modeling, substantial uncertainties remain in the correct parameters for different precursors and conditions.

In this paper we focus on investigating three interrelated questions that are responsible for important uncertainties in urban SOA modeling. The first is how to best incorporate SOA from primary semi- and intermediate volatility compounds (P-S/IVOCs), two recently-proposed types of SOA precursors. While there is now ample evidence that P-S/IVOCs are important contributors to SOA (Robinson et al., 2007; Zhao et al., 2014; Dunmore et al., 2015; Ots et al., 2016), the emissions of these precursors as well as the parameters that govern their oxidation and SOA formation are not well constrained. Also, it is well known that models of SOA that incorporate P-S/IVOCs often do not agree with measurements across a range of photochemical ages, although the modeled SOA mass varies substantially with the parameterization used (Dzepina et al., 2009; Hayes et al., 2015; Fountoukis et al., 2016; Woody et al., 2016). The second question is whether losses of semi-volatile gases to the walls of environmental chambers (Matsunaga and Ziemann, 2010; Krechmer et al., 2016) have resulted in low biases for the yields of some or all precursors, especially VOCs, as has been recently reported (Zhang et al., 2014). The third question is the appropriateness of including "aging" mechanisms in the VBS parameterization of SOA from VOCs, in which the initial oxidation reaction is followed by subsequent oxidation reactions of the first and later generation products, with each reaction resulting in a reduction of the organic volatility by, for example, an order of magnitude. These "aging" mechanisms increase VOC yields to levels much higher than those observed in chamber studies since it was perceived that the yields may be too low in chambers compared to the real atmosphere. The "aging" mechanisms were added to chamber yields that were obtained without using aging as part of the fits of the chamber data. In some model applications they improve model agreement with field measurements (Ahmadov et al., 2012), while at long photochemical ages they lead to model SOA formation that is substantially larger than observed (e.g. Dzepina et al., 2011; Hayes et al., 2015). While the inclusion of some of these new SOA precursors, updated yields, and aging can provide in some cases better agreement with measurements, the relative amount of SOA formed from VOCs (V-SOA), P-IVOCs (I-SOA), and P-SVOCs (S-SOA) is highly uncertain, and changes strongly depending on which of the above updates are implemented in a specific model. In addition, the fact that different subsets and variants of these updates can allow specific models to match SOA measurements raises important questions regarding whether or not the model mechanisms are representative of actual SOA forming processes in the atmosphere.

The notation used when discussing SOA precursors in this paper is similar to Hayes et al. (2015). We differentiate VOCs, IVOCs and SVOCs by their effective

saturation concentration (c*). Therefore, SVOCs and IVOCs have volatilities ranging from c* = 10^{-2} to 10^{2} and 10^{3} to 10^{6} μg m^{-3} respectively, while VOCs are in the bins of c* ≥ 10^{7} μg m^{-3}.

Recently, we evaluated three parameterizations for the formation of S-SOA and I-SOA using a constrained 0-D box model that represents the South Coast Air Basin during the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign (Hayes et al., 2015). Box models are often used to compare with ambient measurements, and have been shown to be of similar usefulness or even superior to 3-D models if the emissions and atmospheric transport affecting a given case study are well constrained, and if the use of ratios to tracers can be used to approximately account for dispersion (e.g. Volkamer et al., 2006; Dzepina et al., 2009; Hayes et al., 2015; Yuan et al., 2015). A box model allows the evaluation of multiple model parameterizations either previously proposed in the literature or developed from recent field and laboratory data sets, as well as the performance of sensitivity studies, all of which would be difficult to carry-out in more computationally demanding gridded 3-D models. There are six model cases presented in this paper that are described in further detail below. Given the number of model cases (including three additional model cases from Hayes et al. (2015)), it would be very computationally expensive to use a 3-D model to evaluate all the cases.

Moreover, there are important limitations to traditional comparisons of 3-D models' predicted concentrations against measurements, as for example discussed for the Pasadena ground site in Woody et al. (2016). In that study, the SOA predicted by the Community Multiscale Air Quality (CMAQ) model with a VBS treatment of OA is a factor of 5.4 lower than the measurements during the midday peak in SOA concentrations. This underestimation was attributed to several different factors. First, the model photochemical age for the site was too low by a factor of 1.5. In the box model presented in this current work, that problem is eliminated as the photochemical aging of the urban emissions in the model is instead determined from the measured ratio of 1,2,4-trimethylbenzene to benzene as described previously (Parrish et al., 2007; Hayes et al., 2013). Second, it is difficult to distinguish errors due to model dispersion from those due to emission inventories and photochemical age. Woody et al. (2016) conclude that excessive dispersion or low emissions account for an error of about a factor of 2. Those errors are also eliminated by the use of emission ratios in this work. After those errors are accounted for, by analyzing the 3-D model output using similar techniques as in our box model, the real under-prediction of SOA formation efficiency by a factor of 1.8 emerged, compared to the initial value of 5.4 from the concentration comparisons. These errors (of approximately 300%) in the interpretation of 3-D model comparisons, which are ignored in most 3-D model studies, are far larger than the uncertainties due to emission ratios or dispersion in our box model (about 10 - 20%), as demonstrated in section 2.4.

In addition, there are uncertainties in the P-S/IVOC emissions inventories used in 3-D models and in the methods used to estimate P-S/IVOC emissions from the traditional POA inventories. In our box model, as described in further detail below, we incorporated recently published field measurements of P-S/IVOCs to better constrain the concentration of these species. Thus, while 3-D models are essential for simulating spatially and temporally complex environments under the influence of many sources, in cases where transport is relatively simple and there is a well-defined urban plume such in Pasadena during the CalNex campaign, the box model is a valuable complementary or even superior approach that is less susceptible to the convoluted uncertainties in 3-D models discussed above. Another reason to use a box model is that it allows a direct comparison against OFR measurements taken in the field (Ortega et al., 2016). The OFR provided (every 20 minutes at the Pasadena ground site) a measure of SOA formation potential for a photochemical age of up to two weeks. To the best of our knowledge, 3-D models have not yet been adapted for comparison against OFR data. Finally, box models are more widely usable by experimental groups (such as ours) due to reduced complexity, while 3-D models are almost exclusively used by modeling-only groups, who tend to be more distant from the availability, use, and interpretation of experimental constraints. Thus the use of a range of models by a range of different groups is highly beneficial to scientific progress.

The results obtained in our previous work (Hayes et al., 2015) using a box model indicated that different combinations of parameterizations could reproduce the total SOA equally well even though the amounts of V-SOA, I-SOA, and S-SOA were very different. In addition, the model over-predicted SOA formed at longer photochemical ages (≈ 3 days) when compared to observations downwind of multiple urban sites. This discrepancy suggests that the ratio of P-S/IVOCs-to-POA may have been too high in the parameterizations evaluated. Also, as mentioned previously and discussed in Hayes et al. (2015), the implementation of aging for VOC products remains uncertain.

The goal of this study is to use several recently published results to better evaluate and constrain the box model introduced in our previous work, and thus facilitate the identification of parameterizations that can be eventually incorporated into 3-D air quality models to accurately predict SOA for the right reasons. It is important to note that parameterizations used in the box model are based on several published measurements taken from laboratory experiments and field studies that provide more realistic constraints than in previous versions and that were not available to be implemented in Hayes et al. (2015). In particular, our work here improves the box model by incorporating recently published measurements of P-IVOCs and P-SVOCs that allow better constraining of the concentration, reactivity, yields, and volatility of these precursors (Worton et al., 2014; Zhao et al., 2014). In addition, given that experiments in environmental chambers may underestimate SOA yields for the VOCs due to losses of

semi-volatile gases to the chamber walls (Zhang et al., 2014), the SOA yields from VOCs have been re-estimated using a very recent parameterization of these wall-losses (Krechmer et al., 2016). The wall-loss corrected yields obtained are then used in the model in a sensitivity study to evaluate the corresponding change in the modeled SOA concentrations. The model is modified based on these literature constraints. No model tuning is performed with the goal of improving the agreement with the observations. The results obtained from the new box model are compared against ambient ground site and airborne measurements, and also against recently-published oxidation flow reactor (OFR) measurements (Ortega et al., 2016). This combination of data sets allows the model to be evaluated for photochemical ages ranging up to 3 equivalent days (at 1.5×10^6 molec OH cm^{-3}) providing a means to evaluate the aging mechanisms of the VOCs in the VBS.

2. EXPERIMENTAL SECTION

2.1 Measurement and sampling site

The box model is constructed in order to represent the South Coast Air Basin during CalNex in spring/summer 2010. The measurements of aerosols used in this study were conducted in Pasadena, California (34.1406° N 118.1224° W), located to the northeast of downtown Los Angeles (Hayes et al., 2015). An overview of CalNex has been published previously (Ryerson et al., 2013). The location and the meteorology of the ground site at Pasadena are described in further detail in Hayes et al. (2013). Pasadena is a receptor site for pollution due to winds that transport emissions from the Ports of Los Angeles and Long Beach and downtown Los Angeles. Airborne measurements of aerosols were also carried out in the South Coast Air Basin as part of the CalNex project. A detailed description of the airborne measurements is given in Bahreini et al. (2012). Furthermore, measurements of POA composition and volatility taken at the Caldecott Tunnel in the San Francisco Bay Area reported in previous work (Worton et al., 2014) are also used to constrain the model as described below. The tunnel air samples were collected during July 2010.

Two additional datasets are used to evaluate the model. In addition to sampling ambient air, an aerosol mass spectrometer (AMS) sampled air that had been photochemically aged using an oxidation flow reactor (OFR) (Ortega et al., 2016). The OFR exposed ambient air to varying concentrations OH radicals in order to obtain photochemical ages much higher than the ambient levels observed at the Pasadena site, and the amount of SOA produced was quantified as a function of OH exposure. Moreover, radiocarbon (^{14}C) analysis has been performed on filter samples and results were combined with positive matrix factorization (PMF) data to determine fossil and non-fossil fractions of the SOA components as reported in Zotter et al. (2014). The ^{14}C

results are used for subsequent comparison against the box model from which fossil and non-fossil SOA mass can be estimated.

2.2 Model set-up

The SOA model is set-up to include 3 types of precursors: VOCs, P-IVOCs, and P-SVOCs. The parameters used in the box model to simulate the formation of SOA from these precursors are listed in Tables S1 to S3 of the supporting information. The box model dynamically calculates the evolution of organic species in an air parcel as it undergoes photochemical aging, hence producing SOA. The total SOA also includes background SOA (BG-SOA) at a constant concentration of 2.1 $\mu g\ m^{-3}$, as determined in our previous work (Hayes et al., 2015). The model accounts for P-SVOC emissions from vehicular exhaust and cooking and treats POA as semi-volatile (Robinson et al., 2007). It should be noted that the model uses CO and NO_x as inputs to constrain the model, and the SOA yields for high-NO_X conditions are used, based on our previous work (Hayes et al., 2013; 2015). Therefore, to verify model performance both predictions of VOC and POA concentrations have been compared against field measurements and the model performance appears to be satisfactory (Hayes et al., 2015).

A schematic of the model is shown in Figure 1. All the model cases are listed in Table 1, and all the parameterizations are shown schematically in Figure 2. The first model case (ROB + TSI) incorporates the Robinson et al. (2007) parameterization for SOA formation that models P-IVOCs and P-SVOCs (i.e. P-S/IVOCs) using a single volatility distribution and oxidation rate constant. The ROB + TSI case also uses the Tsimpidi et al. (2010) parameterization for SOA formation from VOCs. A detailed description of the parameters used in ROB + TSI can be found in Hayes et al. (2015), and the ROB + TSI model case used here is identical to the case of the same name used in that paper. Briefly, as displayed in Fig. 2A, the Tsimpidi et al. (2010) parameterization proposes that the VOCs undergo an initial oxidation step that will form four lumped products with different volatilities ($c^* = 1, 10^1, 10^2, 10^3\ \mu g\ m^{-3}$, where c^* is the effective saturation concentration). The first-generation oxidation products can be further oxidized, decreasing their volatility by one order of magnitude (i.e. aging). This "bin-hopping" mechanism repeats until the lowest volatility product is reached ($c^* = 10^{-1}\ \mu g\ m^{-3}$ in this study and $1\ \mu g\ m^{-3}$ in other studies such as Tsimpidi et al. (2010) and Hayes et al. (2015). The Robinson et al. (2007) parameterization proposes that the P-S/IVOCs are initially distributed in logarithmically spaced volatility bins ranging from $c^* = 10^{-2}$ to $10^6\ \mu g\ m^{-3}$. Thereafter, the oxidation of P-S/IVOCs decreases their volatility by one order of magnitude until the lowest volatility product is reached ($c^* = 10^{-2}\ \mu g\ m^{-3}$). The lowest volatility product possible is not the same for the oxidation of VOCs versus the oxidation of the P-S/IVOCs (10^{-1} vs. $10^{-2}\ \mu g\ m^{-3}$, respectively). However, whether the mass is

distributed into either bin has a negligible effect on the SOA mass simulated in the box model because of the relatively high SOA concentrations during the case study.

In this work, 5 model parameterizations are tested that incorporate new measurements of IVOCs and P-SVOC volatility as well as updated VOC yields that account for wall-losses of vapors (Zhang et al., 2014; Krechmer et al., 2016). For the first new case (ROB + ZHAO + TSI), we incorporate IVOC data measured in Pasadena during the CalNex campaign as reported from Zhao et al. (2014). In particular, the measured concentrations of speciated and unspeciated IVOCs and their estimated volatility are used to constrain the initial concentration of these species (as discussed in Section 2.2.2 below) as well as to estimate their yields (Zhao et al., 2014). Therefore, we replace the inferred concentrations of IVOCs that were used in our previous work and based on the volatility distribution of Robinson et al. (2007) with concentrations that are directly constrained by measurements. In the ROB + ZHAO + TSI case the SOA formation parameters used (e.g. yields, oxidation rate constants) are taken from Zhao et al. (2014) for the IVOCs and from Hayes et al. (2015) for the VOCs and SVOCs. Hodzic et al. (2016) have also estimated the IVOC yields while accounting for wall-losses using recent laboratory studies. However, the yields reported in that study are for a single lumped species, whereas in our work we estimate the yields using 40 IVOC categories, each representing a single compound or a group of compounds of similar structure and volatility. This method allows a more precise representation of IVOC yields and rate constants in the SOA model.

For the second new case (WOR + ZHAO + TSI), the volatility distribution of P-SVOCs is updated using measurements of POA performed at the Caldecott tunnel in the California Bay Area (Worton et al., 2014). In the previous two cases described above, the relative volatility distribution of P-SVOCs was taken from the work of Robinson et al. (2007). In this distribution, the relative concentration of SVOCs increases monotonically between the $c^* = 10^{-2}$ and 10^2 $\mu g\ m^{-3}$ bins. The P-SVOC volatility distribution in the WOR + ZHAO + TSI case increases monotonically as well, but the relative concentrations in each bin are different and notably there is a much higher relative concentration of SVOCs in the $c^* = 10^2$ $\mu g\ m^{-3}$ bin (see Fig. 2 and Table S3 in the supporting information). In this model case, the updated P-SVOC volatility distribution is only applied to vehicular P-S/IVOCs whereas the volatility distribution proposed by Robinson et al. (2007) is still used for cooking emissions.

Several recently published papers have found that chamber experiments may underestimate SOA yields due to the loss of semi-volatile vapors to chamber walls (Matsunaga and Ziemann, 2010; Zhang et al., 2014; Krechmer et al., 2016). A sensitivity study has been performed to explore this uncertainty by running the three model cases described above (ROB + TSI, ROB + ZHAO + TSI, and WOR + ZHAO + TSI) with a

revised version of the SOA yields for VOCs that accounts for these wall losses. A detailed description of how these updated yields were estimated is provided in the supporting information and the values can be found in Table S4. Briefly, equilibrium partitioning is assumed to hold for the organic mass found in the gas phase, particle phase, or chamber walls. The SOA yields are then obtained by refitting SOA chamber yield curves using a model that accounts for partitioning between the three compartments (particle, gas, and wall) and incorporates the equivalent wall mass concentrations published in Krechmer et al. (2016), which are volatility dependent. The SOA chamber yield curves that were refitted were first calculated using the parameters published in Tsimpidi et al. (2010). There are limits to the assumption that partitioning between the three phases occurs on short enough timescales for all four VOC product volatilities that equilibrium is reached during an SOA chamber study. Specifically, at lower volatilities ($c^* \leq 1$ μg m^{-3}), the partitioning kinetics of the organic mass from the particles to the chamber walls have an effective timescale of more than an hour, which is similar or longer than typical chamber experiments (Ye et al., 2016). The limiting step in the partitioning kinetics is evaporation of SVOCs from the particles to the gas phase, and therefore the exact rate of evaporation depends on the OA concentration in the chamber.

Furthermore, as described in the supporting information, the updated SOA yields for VOC oxidation result in distribution of SVOC mass into lower volatility bins compared to the original parameterization, although the sum for the SVOC yields (α_i) remains similar. In the absence of aging, the SOA yields, Y, resulting from the wall-loss correction should be considered upper limits (MA parameterization), whereas the original yields serve as lower limits due to the considerations discussed above (TSI parameterization without aging). As shown in the supporting information (Figures S1 - S7) when aging (TSI parameterization with aging) is included the SOA yields increase beyond those observed when applying the wall loss correction for most of the VOC classes at longer photochemical ages. (It should be noted that SOA masses in Figures S1 - S7 were calculated using the same background as for the other model cases, 2.1 μg m^{-3}.) This feature of the aging parameterization is likely to blame for SOA over-predictions observed at long aging times when comparing with ambient data (e.g. Dzepina et al., 2009; Hayes et al., 2015).

According to Krechmer et al. (2016) and other chamber experiments (Matsunaga and Ziemann, 2010), the gas-wall equilibrium timescale doesn't vary strongly with the chamber size. The timescale for gas-wall equilibrium reported in these previous studies was 7 - 13 minutes. Similar timescales have been calculated for a variety of environmental chambers, including chambers that were used to determine many of the yields used in this paper. In addition, Matsunaga and Ziemann found that partitioning was nearly independent of chamber treatment, reversible, and obeyed Henry's law. Thus, the

effective wall concentrations determined from the chamber experiments reported in Krechmer et al. (2016) are likely applicable to other chambers with different sizes.

The three model cases accounting for wall losses of organic vapors are named ROB + MA, ROB + ZHAO + MA, and WOR + ZHAO + MA. For these cases, the aging of the secondary SVOCs formed from the oxidation of VOCs was not included, since multi-generation oxidation is not well-constrained using data from chamber studies that are run over relatively short time-scales (i.e. hours). In addition, aging and correcting for wall-losses of organic vapors have been separately proposed to close the gap between observed and predicted SOA concentration from pre-2007 models, and are thought to represent the same "missing SOA mass." Therefore, we run the model with one of these options at a time, as they are conceptually different representations of the same phenomenology. The aging of secondary SVOCs formed from the oxidation of P-IVOCs (and P-SVOCs) has been kept for all of the MA cases, however. To our knowledge, P-IVOC and P-SVOC mechanisms proposed in the literature have always included aging. A similar approach for correcting the yields as described above cannot be applied to P-IVOCs because organics with low volatilities ($c^* < 10$ μg m^{-3}) will partition to chamber walls very slowly, and SVOCs from P-IVOC oxidation tend to have lower volatilities than the SVOCs formed from VOC oxidation (Tables S1 and S2). Indeed, when trying to refit the VOC and IVOC yield curves, the model assuming equilibrium partitioning between particles, the gas phase, and the walls was able to reproduce the yield curves for VOCs, but not for IVOCs. This difference in the results is consistent with equilibrium not having been reached during the chamber studies on the IVOCs, which produce a greater amount of lower volatility SVOCs when compared to VOCs during oxidation. These lower volatility SVOCs have relatively slow evaporation rates from the particles, which prevents the chamber system from reaching equilibrium (Ye et al., 2016).

Simulations of O:C have been previously evaluated in Hayes et al. (2015) using laboratory and field data from CalNex to constrain the predicted O:C. It was concluded in that work that it was not possible to identify one parameterization that performed better than the other parameterizations evaluated, because of the lack of constraints on the different parameters used (e.g. oxidation rate constant, oxygen mass in the initial generation of products and that added in later oxidation generations, SOA yields, and emissions). Therefore, incorporating O:C predictions into the current box model and using those results in the evaluation discussed here would not provide useful additional constraints.

2.2.1 IVOC oxidation parameterizations

An important difference between the ROB + TSI and ROB + MA cases and the other four cases that have been updated with the IVOC measurements of Zhao et al. (2014) is that in the ZHAO cases, the first generation of IVOC oxidation distributes part

of the product mass into four different volatility bins ($c^* = 10^{-1}$, 1, 10^1, 10^2 μg m^{-3}) as is displayed in Fig. 2E. This IVOC oxidation scheme is similar to that used for the first step of VOC oxidation (Tsimpidi et al., 2010) as displayed in Fig. 2A and D, and has been used to model chamber measurements of SOA from IVOCs (Presto et al., 2010). Contrastingly, in the ROB + TSI and ROB + MA cases, a "bin-hopping" approach is used for all P-S/IVOCs where oxidation lowers volatility by only one order of magnitude (see Fig. 2B and C). The Robinson et al. (2007) parameters are still used for the formation of SOA from P-SVOCs in the ROB + ZHAO + TSI and ROB + ZHAO + MA cases, but the parameters are only applied to primary emissions in c* bins between 10^{-2} and 10^2 μg m^{-3} inclusive (i.e. the volatilities corresponding to P-SVOCs).

2.2.2. Determination of initial precursor concentrations

In the ROB + TSI and ROB + MA cases, the initial concentration of P-S/IVOCs is estimated as follows. The volatility distribution determined by Robinson et al. (2007) is assumed to represent all P-S/IVOCs emitted (Dzepina et al., 2009). The total concentration of P-S/IVOCs is then set so that the amount of P-S/IVOCs in the particle phase is equal to the initial POA concentration. The initial POA concentration is determined from the product of the background-subtracted CO concentration and the ΔPOA/ΔCO emission ratio (Hayes et al., 2015). While this ratio may change due to evaporation/condensation or photochemical oxidation of POA, our previous work (Hayes et al., 2013) has shown that ΔPOA/ΔCO does not change significantly at the Pasadena ground site with observed photochemical age indicating that the ratio is insensitive to the extent of photochemical oxidation. Furthermore, it was calculated that the ratio would increase by 28% for an increase of OA concentration from 5 to 15 μg m^{-3}, concentrations that are representative of this study. This possible source of error is substantially smaller than current errors suggested for P-S/IVOC emission inventories in 3-D models, where current schemes are based on scaling POA emission inventories with scaling factors that are not well constrained (Woody et al., 2016). The same method is used for the other four model cases, but only the initial concentration of P-SVOCs is estimated by this method and the initial concentration of P-IVOCs is estimated separately as described in the next paragraph. In addition, in the WOR + ZHAO + TSI and WOR + ZHAO + MA cases the volatility distribution of vehicular P-SVOCs reported in Worton et al. (2014) is used for estimating the initial concentration of vehicular P-SVOCs whereas the volatility distribution of Robinson et al. (2007) is used for estimating the initial concentration of cooking P-SVOCs.

It should be noted that the tunnel measurements do not include emissions due to cold starts of vehicles. In the box model, only the relative volatility distribution of vehicular POA measured during the tunnel study is used, and thus this potential source of error does not apply to the total amount of vehicular POA emissions in the model.

However, it is still possible that the volatility distribution of POA is different during cold-starts compared to that of POA emitted from warm-running engines. To our knowledge, measurements of the volatility distribution of POA during cold-starts are not available at this time. By comparing the SOA model results using two different POA volatility distributions (Robinson et al., 2007; Worton et al., 2014), we can evaluate to a certain extent the sensitivity of the simulated SOA concentration to the initial POA volatility distribution.

The initial concentrations of VOCs and IVOCs are calculated by multiplying the background-subtracted CO concentrations measured at Pasadena by the emission ratios ΔVOC/ΔCO or ΔIVOC/ΔCO. In the ROB + TSI and ROB + MA cases this method is only applied to the VOCs. The initialization method for the concentrations of the VOCs is the same for all six cases in this paper. For the biogenic VOCs, we follow the same method as Hayes et al. (2015) to determine the initial concentrations since these compounds are not co-emitted with CO. The emission ratios are taken from the literature when available (Warneke et al., 2007; Borbon et al., 2013). For most of the IVOCs and some VOCs, emission ratios are not available in the literature. The ratios are instead determined by performing linear regression analyses on scatter plots of the IVOC or VOC and CO concentrations measured in Pasadena between 00:00-06:00 local time when the amount of photochemical aging was very low. During the regression analyses the x-intercept was fixed at 105 ppbv CO to account for the background concentration of CO determined in our previous work (Hayes et al., 2013). Thus, the slope of the resulting line corresponds to the estimated emission ratio (ΔIVOC/ΔCO).

It should be noted that the use of VOC emission ratios to CO to estimate VOC emissions does not assume that VOCs are always co-emitted with CO. Rather, it assumes that VOC emission sources are individually small and finely dispersed in an urban area, so that they are spatially intermingled with the sources of CO. Moreover, previous studies have measured the emission ratios of anthropogenic VOCs with respect to CO and the results show that vehicle exhaust is a major source of VOC and CO (Warneke et al., 2007; Borbon et al., 2013). Furthermore, the ratios are consistent both temporally and spatially. Thus, when thinking of the entire urban area as a source, the use of emission ratios to CO is justified. As shown in Hayes et al. (2015) in the supporting information, the modeled VOC concentrations are consistent with the measurements indicating that major VOCs sources have not been omitted, and the smooth time variations of the VOC concentrations support the use of a "global urban source".

2.3 SOA model

The VOC yields are taken from Tsimpidi et al. (2010) or determined in this work as described below. The estimation of the IVOC yields (based on values taken from Presto et al. (2010) and of the OH reaction rate constants for IVOCs follows the same

approach used by Zhao et al. (2014). However, instead of using the total SOA yield, *Y,* for a fixed OA concentration as reported in Zhao et al. (2014), we use the SVOC yield, α, of each c* bin. It is important to note here that the SOA yields taken from Tsimpidi et al. and Presto et al. use a four-product basis set with c* = 10^0, 10^1, 10^2, 10^3 µg m^{-3} and c* = 10^{-1}, 10^0, 10^1, 10^2 µg m^{-3} respectively. For this box model, it is more appropriate to have a uniform VBS in terms of the bin range utilised so a bin with a lower volatility (c* = 10^{-1} µg m^{-3}) has been added to the VBS distribution of Tsimpidi et al. (2010). The yield for bin c* = 10^{-1} µg m^{-3} is 0 for VOC oxidation, but when aging occurs mass can be transferred into this bin. However, the change in the total V-SOA mass is negligible because for both bin c* = 10^{-1} and 10^0 µg m^{-3} the secondary products almost completely partition to the particle phase.

The OH reaction rate constants are taken from the literature (Atkinson and Arey, 2003; Carter, 2010) as described previously in Hayes et al. (2015). During aging, the oxidation products undergo subsequent reactions with OH radicals with a reaction rate constant of 1 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} and 4 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} for the products of VOC oxidation and P-S/IVOC oxidation respectively (Hayes et al., 2015). For each oxidation step during aging, there is a mass increase of 7.5 % due to added oxygen.

The gas-particle partitioning is calculated in each bin by using the reformulation of Pankow theory by Donahue et al. (2006).

$$x_{p,i} = \left(1 + \frac{C_i}{C_{OA}}\right)^{-1}; C_{OA} = \sum_i [\mathrm{SVOC}]_i \, x_{p,i}$$

Where $\chi_{p,i}$ is the particle phase fraction of lumped species i (expressed as a mass fraction); C_i is the effective saturation concentration, and C_{OA} is the total mass of organic aerosol available for partitioning (in µg m^{-3}). Only species in the gas phase are allowed to react with OH radicals in the model, since aerosol species react at much lower rates (Donahue et al., 2013).

The simulated SOA mass from the model is compared against field measurements of aerosol composition including results from PMF analysis of aerosol mass spectrometry data (Hayes et al., 2013; 2015). Specifically, the model predictions of urban SOA (i.e. SOA formed within the South Coast Air Basin) are compared against the semi-volatile oxygenated organic aerosol (SV-OOA) concentration from the PMF analysis. The other OA component also attributed to SOA, low-volatility oxygenated organic aerosol (LV-OOA), is primarily from precursors emitted outside the South Coast Air Basin and is used to estimate the background secondary organic aerosol (BG-SOA) as discussed previously (Hayes et al., 2015).

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

As described in Hayes et al. (2015), during the transport of the pollutants to Pasadena, the planetary boundary layer (PBL) heights increase during the day. Using CO as a conservative tracer of emissions does not account for how the shallow boundary layer over Los Angeles in the morning influences gas-particle partitioning due to lower vertical mixing and higher absolute POA and SOA concentrations at that time. Thus, as shown in the gas-particle partitioning equation above, there will be a higher partitioning of the species to the particle phase and less gas-phase oxidation of primary and secondary SVOCs. Later in the morning and into the afternoon the PBL height increases (Hayes et al., 2013) diluting the POA and urban SOA mass as photochemical ages increases. However this is a relatively small effect as the partitioning calculation in the SOA model is relatively insensitive to this effect and the absolute OA concentrations (Dzepina et al., 2009; Hayes et al., 2015). Our previous work (Hayes et al., 2015) found in a sensitivity study a +4/-12% variation in predicted urban SOA when various limiting cases were explored for simulation of the PBL (e.g. immediate dilution to the maximum PBL height measured in Pasadena versus a gradual increase during the morning).

To account for the effect of absolute OA mass on the partitioning calculation, the absolute partitioning mass is corrected using the following method. A PBL height of 345 m is used for a photochemical age of 0 h and it reaches a height 855 m at a photochemical age of 9.2 h, which is the maximum age for the ambient field data. Between the two points, the PBL is assumed to increase linearly. The boundary layer heights are determined using ceilometer measurements from Pasadena at 6:00 - 9:00 and 12:00 - 15:00 local time, respectively (Hayes et al., 2013). The second period is chosen because it corresponds to when the maximum photochemical age is observed at the site. The first period is chosen based on transport times calculated for the plume from downtown Los Angeles (Washenfelder et al., 2011) that arrives in Pasadena during the afternoon. There are certain limitations to this correction for the partitioning calculation. First, the correction is based on a conceptual framework in which a plume is emitted and then transported to Pasadena without further addition of POA or SOA precursors. A second limitation is that we do not account for further dilution that may occur as the plume is advected downwind of Pasadena. However, such dilution is not pertinent to the OFR measurements, and so for photochemical ages beyond ambient levels observed at Pasadena, we focus our analysis on the comparison with the OFR measurements.

3. RESULTS AND DISCUSSION

3.1 Evolution of SOA concentration over 3 days

We follow an approach similar to Hayes et al. (2015) in order to analyse the model results. The model SOA concentration is normalized to the background subtracted CO concentration to account for dilution, and the ratio is then plotted against photochemical age rather than time to remove variations due to diurnal cycles of precursor and oxidant concentrations. The photochemical age is calculated at a reference OH radical concentration of 1.5×10^6 molec cm^{-3} (DeCarlo et al., 2010). Figure 3 shows this analysis for each model case for up to 3 days of photochemical aging. Since fragmentation and dry deposition are not included in the model, it has only been run to 3 days in order to minimize the importance of these processes with respect to SOA concentrations (Ortega et al., 2016). Nevertheless, it is very likely that gas-phase fragmentation of SVOCs (e.g. branching between functionalization and fragmentation) occurs during oxidative aging over these photochemical ages as is discussed in further detail below.

In each panel of Fig. 3, field measurements are included for comparison. The ambient urban SOA mass at the Pasadena ground site is generally measured under conditions corresponding to photochemical ages of 0.5 days or less (Hayes et al., 2013). The airborne observations of SOA in the Los Angeles basin outflow are also shown as the average of all data between 1 and 2 days of photochemical aging (Bahreini et al., 2012). The gray region on the right serves as an estimate for very aged urban SOA based on data reported by de Gouw and Jimenez (2009). The data from the OFR and a fit of the ambient and reactor data (dotted black line) are also displayed in Fig. 3 (Ortega et al., 2016). In addition, Figure 4 shows the ratio of modeled-to-measured SOA mass on a logarithmic axis to facilitate evaluation of model performance.

As displayed in the graphs for Fig. 3, it should be noted the measurements from the OFR (Ortega et al., 2016) and from the NOAA P3 research aircraft (Bahreini et al., 2012) give quite similar results for SOA/ΔCO. The OFR measurements are not affected by particle deposition that would occur in the atmosphere at long timescales or photochemical ages. Only a few percent of the particles are lost to the walls of the reactor, and this process has been corrected for already in the results of Ortega et al. The similarity in the two types of observations suggests that ambient particle deposition and plume dispersion do not significantly change the SOA/ΔCO ratio over the photochemical ages analyzed here.

In ROB + TSI, as described in previous work (Hayes et al., 2015), there is a large over-prediction of SOA mass at longer photochemical ages. As displayed in Fig. 3, the amount of SOA produced in the model is higher than all of the field measurements taken

at a photochemical age longer than 0.5 days. Moreover, the ratios of model to measurement are higher than the upper limit of the gray bar representing the ratios within the measurement uncertainties. There is an agreement with the measurements at moderate photochemical ages (between 0.25 and 0.50 days), but the SOA mass simulated by the model is slightly lower than the measurements at the shortest photochemical ages (less than 0.25 days) even when accounting for measurement uncertainties. In this parameterization, most of the SOA produced comes from the P-S/IVOCs, and uncertainties in the model with respect to these compounds likely explain the overestimation observed at longer photochemical ages. As discussed in the introduction, a major goal in this work is to better constrain the amount of SOA formed from the oxidation of P-S/IVOCs, and the following two model cases (ROB + ZHAO + TSI and WOR + ZHAO + TSI) seek to incorporate new measurements to better constrain the box model with respect to the P-S/IVOCs.

When the yield, rate constants, and initial concentrations of P-IVOCs are constrained using the field measurements reported in Zhao et al. (2014) (ROB + ZHAO + TSI), the SOA mass simulated by the model shows much better agreement with the measurements at longer photochemical ages (Fig. 3 and 4). There is a slight over-prediction at 2 days of photochemical aging, but the model is still within the range of measurements of very aged urban SOA reported by De Gouw and Jimenez (2009). The parameterization reported in Robinson et al. (2007) for P-S/IVOCs is based on one study of the photo-oxidation of diesel emissions from a generator (Robinson et al., 2007). The results obtained here for the better constrained ROB + ZHAO + TSI case indicate that the initial concentrations of P-IVOCs as well as the P-IVOC yields within ROB + TSI are too high which leads to over-prediction of SOA concentration at longer photochemical ages. On the other hand, the SOA mass simulated in ROB + ZHAO + TSI is biased low at shorter photochemical ages (less than 1 day). Similar to other recent studies (Gentner et al., 2012; Hayes et al., 2015; Ortega et al., 2016), there may be unexplained SOA precursors not included in the model which rapidly form SOA or yields for fast-reacting species including certain VOCs may be biased low. Both of these possibilities are explored in the other model cases discussed below.

The WOR + ZHAO + TSI case simulates higher SOA concentrations at shorter photochemical ages compared to the previous case (ROB + ZHAO + TSI), but it is still biased low at shorter photochemical ages. The more rapid SOA formation is due to the updated SVOC volatility distribution in this model case compared to the cases that use the Robinson et al. (2007) distribution. Specifically, as shown in Fig. 2F, there is a higher relative concentration of gas phase SVOCs in the $c^* = 10^2$ bin and thus a higher ratio of P-SVOC to POA. Given that in the box model (and in most air quality models) the P-SVOC emissions are determined by scaling the POA emissions according to their volatility distribution, a higher P-SVOC to POA ratio will then result in a higher initial P-

SVOCs concentration. Furthermore, SOA formation from P-SVOCs is relatively fast. Together these changes lead to increases in SOA formation during the first hours of photochemical aging when using the Worton et al. volatility distribution. This case suggests that P-SVOCs in their highest volatility bin ($c^* = 10^2$ μg m^{-3} bin) that are emitted by motor vehicles may be responsible for some of the observed rapid SOA formation within the South Coast Air Basin. When observing the SOA mass simulated at photochemical ages higher than 1 day, the simulation is similar to ROB + ZHAO + TSI. There is better model/measurement agreement than for the ROB + TSI case, but a small over-prediction is observed in the comparison to the reactor data at 2 days of photochemical aging.

Also shown in the right-hand panels of Fig. 3 and 4 are the results with the updated yields for the VOCs that account for gas phase chamber wall losses. For these last three cases (ROB + MA, ROB + ZHAO + MA, and WOR + ZHAO + MA), the rate of SOA formation at short photochemical ages is faster because the secondary SVOC mass from the oxidation of the VOC precursors is distributed into lower volatility bins compared to the Tsimpidi et al. (2010) parameterization. In the ROB + MA case (Fig. 3D and 4D), similar to ROB + TSI, an over-prediction is obtained at longer photochemical ages. There is an improvement in the model at the shortest photochemical ages, but the simulated mass is still lower than the measurements even when considering the measurement uncertainty. Both of these cases perform less well for SOA formation within the South Coast Air Basin, and therefore the remainder of this study is focused on the other four model cases. Overall, the model cases using the updated yields for V-SOA show improvement for the shorter photochemical ages, and the evolution of SOA concentration as a function of photochemical age better corresponds to the various measurements taken at Pasadena and from the OFR.

Specifically, the ROB + ZHAO + MA and the WOR + ZHAO + MA cases both better represent SOA formation and exhibit better model/measurement agreement among the different cases used in this work. They are both consistent with the OFR reactor data at longer photochemical ages as shown in Figs. 3 and 4 compared with the other cases. At a qualitative level, the MA parameterization simulations are more consistent with the fit of the OFR measurements in which the SOA mass remains nearly constant at longer photochemical ages. In contrast, the cases with the TSI parameterization do not follow this trend as the SOA mass keeps increasing between 2 and 3 days age, which is not observed in the measurements. As already mentioned, the model used for this work does not include fragmentation reactions, and including these reactions, in particular branching between functionalization and fragmentation during gas-phase SVOC oxidation, may improve the cases using a potential update of the TSI parameterization as discussed below. Fig. 4F indicates that including additional P-SVOC mass in the model and accounting for gas-phase wall losses in chamber studies improves SOA mass

concentration simulations with respect to the measurements. However, in the WOR + ZHAO + MA case there is still a slight under-prediction of SOA formed at shorter photochemical ages (between 0.05 and 0.5 days), and this discrepancy is observed in all the other model cases. Given the uncertainties in the model set-up discussed in the experimental section, it is not possible to conclude if one of the four cases (i.e. ROB + ZHAO + TSI, WOR + ZHAO + TSI, ROB + ZHAO + MA, WOR + ZHAO + MA) more accurately represents SOA formation in the atmosphere.

According to the OFR data from Ortega et al. (2016), the mass of OA starts to decay due to fragmentation after heterogeneous oxidation at approximately 10 days of photochemical aging. The results are consistent with other OFR field measurements (George and Abbatt, 2010; Hu et al., 2016; Palm et al., 2016). In this work, the model is run only up to 3 days, which is much shorter than the age when heterogeneous oxidation appears to become important. In fact, when including a fragmentation pathway for each of the model cases, a reduction of OA of only 6 % is observed compared to the cases without fragmentation at 3 days of photochemical aging. In this sensitivity study, the fragmentation is parameterized as an exponential decrease in OA concentration that has a lifetime of 50 days following Ortega et al. (2016). Given the results, the inclusion of fragmentation due to heterogeneous oxidation in the model does not significantly change the model results or the conclusions made in this work.

More generally, there are at least three different fragmentation mechanisms that could be responsible for the decrease of SOA formation at very high photochemical ages. The first mechanism is the reaction of oxidants (e.g. OH) with the surface of an aerosol particle and decomposition to form products with higher volatility, i.e. due to the heterogeneous oxidation just described. The second type of fragmentation that may be important for very high photochemical ages in the OFR is due to the high concentration of OH (Palm et al., 2016). Most of the molecules in the gas phase will react multiple times with the available oxidants before having a chance to condense, which will lead to the formation of smaller products too volatile to form SOA. However, this is only important at very high photochemical ages in the OFR, which are not used in this work. A third type of fragmentation can occur during the aging of gas-phase SVOCs (Shrivastava et al., 2013; 2015). The TSI parameterization used in the model from this work and from previous modeling works (Robinson et al., 2007; Hodzic et al., 2010; Shrivastava et al., 2011) only includes the functionalization of the SVOCs and neglects fragmentation reactions. More recently, Shrivastava et al. (2013) have modified the VBS approach in a box model by incorporating both pathways and performed several sensitivity studies. The results when including fragmentation generally exhibit better agreement with field observations, but as noted in that work the agreement may be fortuitous given that both the emissions as well as the parameters representing oxidation in the model are uncertain. This third type of fragmentation is not simulated in our

sensitivity study using the approach above, and it remains poorly characterized due to the complexity of the chemical pathways and the number of compounds contributing to SOA formation as described in Shrivastava et al. (2013).

Finally, Woody et al. (2016) recently proposed a meat cooking volatility distribution and therefore we perform a sensitivity study by using this distribution in our model for P-SVOCs coming from cooking sources. The results are displayed in the supporting information (Figure S8), where this alternate approach has been implemented for the WOR + ZHAO + TSI and WOR + ZHAO + MA cases. By comparing the results obtained from this sensitivity study with Fig. 3, the two cases in the sensitivity study display a slight decrease of SOA/ΔCO values over 3 days of photochemical aging with a difference of approximately 8% at 3 days. Thus, the model-measurement comparison does not change significantly relative to the base case. Given the similarities between the sensitivity study and Fig. 3, as well as the possibility of cooking SOA sources other than meat-cooking (i.e. heated cooking oils, Liu et al. (2017)), the remainder of our work uses the Robinson et al. volatility distribution for P-SVOCs from cooking sources.

3.1.1 SOA concentration estimated at Pasadena: fossil and non-fossil fractions

In the top panel of Figure 5, the box model is compared against the urban SOA determined by PMF analysis of the AMS measurements at Pasadena (Hayes et al., 2013). In the bottom panel of the same figure the model is compared against the fossil and non-fossil fraction of urban SOA as obtained from ^{14}C measurements reported in Zotter et al. (2014). Both panels show measurements and predictions corresponding to 12:00 – 15:00 local time, when SOA concentrations peaked due to longer photochemical ages (5 hours on average) as well as the arrival of emissions transported from source-rich western regions of the South Coast Air Basin.

Similar to the results in Fig. 3 and 4 for short photochemical ages, the SOA mass simulated by the ROB + ZHAO + TSI case is biased low in Fig. 5A. The ROB + ZHAO + MA, WOR + ZHAO + TSI, and WOR + ZHAO + MA cases show better model/measurement agreement as the simulated SOA mass is within the measurement uncertainty or essentially equal to the lower limit of the concentration that is defined by the measurement uncertainty. Fig. 5A also allows evaluation of the contribution of each precursor type to the SOA at Pasadena. For the four cases displayed, the P-SVOCs and P-IVOCs are responsible for 69 – 83 % of the urban SOA formation. Thus, more than half of the urban SOA is attributed to these precursors even in the MA parameterizations where the model is run with the updated yields, which doubles V-SOA compared to the cases using the yields reported from Tsimpidi et al. (2010). Furthermore, 8 – 29 % of the measured urban SOA is due to V-SOA where the range of values is due to the uncertainty

747 in the measurements as well as the difference in simulated V-SOA concentration for each
748 case.

749 According to the ^{14}C measurements, an average of 71 ± 3 % of urban SOA at
750 Pasadena is fossil carbon, which is thought to be due to the importance of vehicular
751 emissions, especially during the morning rush hour (Bahreini et al., 2012; Zotter et al.,
752 2014; Hayes et al., 2015). In general, the box model gives results consistent with the ^{14}C
753 measurements. To make this comparison, the simulated SOA is apportioned between
754 fossil S-SOA, fossil I-SOA, fossil V-SOA, cooking S-SOA, and biogenic V-SOA. The
755 last two apportionments correspond to non-fossil carbon. This evaluation is possible
756 following an approach similar to Hayes et al. (2015) where the identity of the precursor is
757 used to apportion SOA. Briefly, the fossil S-SOA is formed from P-SVOCs emitted with
758 hydrocarbon-like OA (HOA), which is a surrogate for vehicular POA. Second, cooking
759 S-SOA is formed from P-SVOCs emitted with cooking-influenced OA (CIOA). The
760 concentrations of HOA and CIOA were determined previously using PMF analysis.
761 Fossil V-SOA is formed from aromatics, alkanes, and olefins while isoprene and terpenes
762 are responsible for biogenic V-SOA. The treatment of IVOCs in the comparison with the
763 ^{14}C measurements has been updated from our 2015 study. Previously, it was assumed that
764 P-IVOCs were co-emitted with cooking-influenced OA, but the recent work of Zhao et
765 al. (2014) and others indicates that petroleum sources contribute substantially to IVOC
766 emissions (Dunmore et al., 2015; Ots et al., 2016). Therefore, the IVOCs are considered
767 entirely fossil carbon in order to obtain the results shown in Fig. 5B.

768 As seen in Fig. 5B, for all the model cases, cooking S-SOA dominates the non-
769 fossil fraction and biogenic VOCs have only a small contribution to non-fossil urban
770 SOA. This result is consistent with our previous work, and indicates agreement between
771 the model and ^{14}C measurements cannot be achieved without including an urban source
772 of non-fossil carbon such as P-SVOCs from cooking. With respect to fossil SOA, more
773 S-SOA is formed when using the volatility distribution of vehicular POA reported from
774 Worton et al. (2014) due to the greater proportion of gas-phase of P-SVOCs. When the
775 V-SOA yields are updated in the model (MA parameterizations), there is a corresponding
776 increase in both fossil and non-fossil V-SOA.

777 When comparing the fossil/non-fossil carbon split, all the cases are either in
778 agreement with the measurement within its uncertainty, or slightly lower. Starting with
779 the ROB + ZHAO + TSI case, the fossil fraction increases from 74 % to 79 % in each
780 case as VOCs or P-SVOCs from vehicle emissions have greater importance for SOA
781 formation. While the uncertainties reported in Zotter et al. (2014) were 71 ± 3 %, there
782 are likely additional errors due to different factors that may influence the model or
783 measurements. For example, a portion of the P-IVOCs may be from cooking sources
784 rather than entirely from fossil sources as is assumed above (Klein et al., 2016). Taking
785 the WOR + ZHAO + MA case as an example, since it is the best performing case in this

786 work according to Fig. 5A, model/measurement agreement is obtained within
787 measurement uncertainties if one assumes that 18 – 41 % of P-IVOCs come from
788 cooking emissions. Ultimately, the differences observed in the comparison with the ^{14}C
789 data are very likely smaller than these errors discussed here, and it is concluded that all
790 the model cases perform equally well with respect to the fossil/non-fossil carbon split.

791 As reported in Gentner et al. (2012), emissions from petroleum derived fuels such
792 as diesel and gasoline have an important contribution to the formation of SOA. However,
793 there have been conflicting results regarding the relative contributions of diesel versus
794 gasoline emissions (Bahreini et al., 2012; Gentner et al., 2012). In this work, the relative
795 contribution of different SOA sources is estimated following a procedure similar to that
796 previously published in Hayes et al. (2015), and the results are shown in Figure S9 of the
797 supporting information. Briefly, the source apportionment method follows four steps.
798 First, after classifying the SOA mass from isoprene and terpenes as biogenic V-SOA, the
799 remaining V-SOA is attributed to gasoline emissions since the diesel contribution to V-
800 SOA is small (~3 %) (Hayes et al., 2015). Second, for the diesel and gasoline
801 contribution to S-SOA, 70(±10) % of HOA is emitted from diesel vehicles with the
802 remainder from gasoline vehicles (Hayes et al., 2013), and thus it is assumed for the
803 source apportionment that 70% (30%) of vehicular P-SVOCs are from diesel (gasoline)
804 vehicles. Third, the S-SOA from cooking sources is calculated separately in the model,
805 where the initial concentration of cooking P-SVOCs is estimated using the measured
806 CIOA concentration and the method described in Section 2.2.2 above. Lastly, the
807 fractional contributions to I-SOA mass is difficult to determine since there are still
808 uncertainties about the sources of IVOCs. According to Zhao et al. (2014), petroleum
809 sources other than on-road vehicles likely contribute substantially to primary IVOCs, but
810 evidence exists that cooking may be a source of IVOCs as well (Klein et al., 2016). Thus,
811 while we attribute I-SOA to these two sources, we do not distinguish the sources. The
812 estimated source apportionment in Fig. S9 attributes urban SOA as follows: 4% to
813 biogenic V-SOA, 23% to gasoline V-SOA, 9% to gasoline S-SOA, 20 % to diesel S-
814 SOA, and 17 % to cooking S-SOA. The remaining 27 % is I-SOA that is either due to
815 cooking or off-road emissions of P-IVOCs.

816 It should be noted that according to McDonald et al. (2015), the emissions from
817 vehicles have decreased over time (i.e. between 1970 and 2010) due to regulations in
818 California. Warneke et al. (2012) have observed also that the emission ratios of some
819 SOA precursors (i.e. $\Delta VOC/\Delta CO$) have remained constant between 2002 and 2010,
820 while absolute concentrations have decreased. On the other hand, cooking and off-road
821 emissions are subject to different regulations in California, and the ratios of cooking or
822 off-road emissions to vehicular emissions have likely changed with time, which means
823 that the source apportionment results for urban SOA presented here will be specific to
824 2010.

3.2 SOA formation versus precursor oxidation rate constant

Recent results from Ortega et al. (2016) point to the importance of fast-reacting precursors for urban SOA during CalNex, and we can use their results to further evaluate our box model. The fraction of SOA formed from each precursor class as a function of the precursor rate constant is displayed in Figure 6. The right-axis of Fig. 6 shows the correlation (R^2) of different VOCs with the maximum concentration of SOA formed using the OFR as a function of their oxidation rate constants as reported in Ortega et al. (2016). This analysis of the OFR data allows us to constrain the rate constants of the most important SOA precursors. A detailed description of how the R^2 values were obtained can be found in Ortega et al. (2016). According to the R^2 data, the VOC compounds that correlate best with maximum SOA formation potential are those that have log k_{OH} rate constants ranging from -10.5 to -10.0. When comparing the percentage of SOA mass simulated by the model with the observed R^2 values, all of the four cases are not entirely consistent with the R^2 data. According to the model, more SOA mass is formed from precursors in the bin ranging from -11.0 to -10.5 (the majority of mass formed comes from P-IVOCs) rather than the bin ranging from -10.5 to -10.0. In contrast, the R^2 value is higher for the more reactive bin. If either fast-reacting precursors were missing in the model, or if the rate constants of the currently-implemented precursors were too small, then correcting either error would shift the relative distribution shown in Fig. 6 towards faster-reacting SOA precursors. In turn, the trend in the percentage of modeled SOA mass may more closely follow the trend in R^2 values.

3.3 Volatility distribution of OA

Based on the evaluations carried out up to this point on the six model cases, the WOR + ZHAO + MA case seems to most closely reproduce the observations. Thus, the entire volatility distribution of the OA, precursors, and secondary gas phase organics is analyzed for this model case. Figure 7 shows this distribution for three selected photochemical ages: 0, 5, and 36 h. The figure allows us to track the evolution of SOA and secondary gas phase organics from each precursor class in terms of their concentration and volatility and also to evaluate the reduction of precursor concentrations. For the model results, the volatility distribution of all organics resolved by precursor class, except for the VOCs and P-IVOCs, can be taken directly from the model. To determine the volatility distribution of the VOCs and P-IVOCs, the SIMPOL.1 method (Pankow and Asher, 2008) is used to estimate the effective saturation concentration of each compound or lumped species in the model. Also included in Fig. 7, in the bottom-right panel, is the observed volatility distribution for the Pasadena ground site, which is an average of measurements collected during 12:00 – 15:00 local time and corresponds to 5 h of photochemical aging. For the measurements, the volatility distribution of VOCs was determined using GC-MS data (Borbon et al., 2013) whereas

the IVOC distribution is taken from Zhao et al. (2014). The volatility distribution of SVOCs was determined using combined thermal denuder AMS measurements (see the supporting information for further details).

For the volatility distribution of the model at time 0, the concentrations of P-SVOCs and P-IVOCs monotonically increases with the value of c*. However, a discontinuity in the mass concentration exists between the c* = 10^2 and 10^3 μg m^{-3} bins. This discontinuity can be explained by several factors. First, the measured IVOCs mass concentration the c* = 10^3 μg m^{-3} bin is very low, and since the initial concentrations of IVOCs in the model are constrained by the field measurements, the model will also have very low concentrations. Zhao et al. (2014) have already noted that the concentration of P-IVOCs in this bin is relatively low when compared to the volatility distribution from Robinson et al. (2007). Another possible explanation is the presence of cooking sources, which in the model are responsible for substantial P-SVOC mass (~50%) but may have a smaller contribution to the P-IVOC mass.

During oxidation the volatility distribution evolves and the concentration of secondary organics increases in the bins between c* = 10^{-1} and 10^3 μg m^{-3} (inclusive), and the largest portion of SOA is found in the c* = 1 μg m^{-3} bin. This result is due to the partitioning of the organic mass to the particle phase and the lack of particle phase reactions in the model, which leads to very slow oxidation rates for species found in the lower volatility bins. After 36 h, a large portion of the precursors have been reacted, although some primary and secondary material remains in the gas phase giving rise to more gradual SOA formation.

In Fig. 7, it is possible to compare the measured volatility distribution with the model simulation at 5 h of photochemical aging. It should be noted that the relatively high concentrations of VOCs in the model compared to the measurements are due to the model containing VOCs for which measurements were not obtained in Pasadena. There are 47 VOCs used in the model and only 19 VOCs were measured. However, the remaining VOCs have been measured in other urban locations (Warneke et al., 2007; Borbon et al., 2013) and thus it is assumed they are also present in the South Coast Air Basin. For this work, we include these 28 remaining VOCs by assuming that they are also emitted in the South Coast Air Basin with identical emission ratios (ΔVOC/ΔCO). When comparing only VOCs measured and modeled (shown in hollow black bars), the results are consistent (3.1, 3.6 and 2.2 μg m^{-3} from c* = 10^7 to 10^9 μg m^{-3} bins versus 3.8, 3.7 and 2.2 μg m^{-3} for the measurements). On the other hand, the model appears to have a low bias for the concentrations of P-IVOCs (0.16, 0.63, 0.89 and 2.3 μg m^{-3} ^{3} from c* = 10^3 to 10^6 μg m^{-3} bins versus 0.21, 1.39, 2.65 and 3.82 μg m^{-3} for the measurements). This low bias is seen for each volatility bin and could possibly be explained by either oxidation rate constants that are too high or ΔIVOC/ΔCO ratios that are too low. The

latter explanation seems more likely given that the rate constants estimated using surrogate compounds and structure-activity relationships for the unspeciated P-IVOCs are generally lower limits (Zhao et al., 2014), which would result in a high bias rather than a low bias. The ΔIVOC/ΔCO ratios may be low because the photochemical age between 00:00 – 6:00 local time is not strictly zero, and some oxidation may have occurred during the period used to determine the ratio values. Emission ratios such as ΔIVOC/ΔCO facilitate incorporating P-IVOC emissions into 3-D models that already use CO emissions inventories, and the ΔIVOC/ΔCO ratios reported here could be used for this purpose. However, the resulting I-SOA concentrations should be considered lower limits given that the emission ratios, and also the rate constants, are likely themselves lower limits.

To further explore the impact of potential errors in the initial IVOC concentrations, a sensitivity study has been carried out using initial concentrations calculated based on the observed photochemical age and measured IVOC concentrations at Pasadena as well as the estimated IVOC oxidation rate constants (Zhao et al., 2014). This alternate approach is implemented for the ROB + ZHAO + MA and WOR + ZHAO + MA cases and does not use nighttime IVOC-to-CO ratios. The results when using this alternative approach are shown in the supporting information (Figure S10). When comparing Fig. S10 with Fig. 3, differences are minor. The model/measurement agreement improves slightly at shorter photochemical ages (less than 1 day). At the same time a slightly larger over-prediction is observed at longer photochemical ages. However, the formation of SOA modeled in this sensitivity test is similar to the original cases from Fig. 3 with an average difference of only 21 %, which represent a relatively small error compared to other uncertainties in SOA modeling. The IVOC initial concentrations used in this sensitivity test are slightly higher than those calculated using the IVOC-to-CO ratio, which explain the small increase of modeled SOA/ΔCO. Ultimately, the different approaches for determining the initial IVOC concentration in the model are reasonably consistent, and both approaches perform similarly given the model and measurement uncertainties.

For the measurements of SVOCs, all the mass in bins lower than 10^{-2} μg m^{-3} are lumped into this bin for Fig. 7 since the model does not contain lower volatility bins. In addition, the 10^{1} and 10^{2} μg m^{-3} bins are not well-resolved because the thermal denuder did not consistently reach temperatures low enough (less than 37°C) to resolve SVOCs in this range of volatilities. Thus, the 10^{1} μg m^{-3} bin may contain some higher volatility particulate mass although this contribution is expected to be small due to the low particle phase fraction of compounds in the 10^{2} μg m^{-3} bin. With these considerations in mind, the volatility distribution of the SVOCs is somewhat different in the model compared to the measurements. Most notably, the model does not form a significant amount of lower

volatility SOA in the 10^{-2} μg m^{-3} bin, whereas the measurements have a much higher concentrations in this bin. A factor that may explain this difference between the volatility distributions is the lack of particle phase reactions that continue to transform SOA into lower volatility products, a process which is not considered in the model. One example of a particle phase reaction is the formation of SOA within deliquesced particles, including the partitioning of glyoxal to the aqueous phase to produce oligomers as discussed in Ervens and Volkamer (2010), although that specific mechanism was of little significance during CalNex (Washenfelder et al., 2011; Knote et al., 2014). Alternatively, the use of an aging parameterization where the volatility may decrease by more than one order of magnitude per oxidation reaction would also distribute some SOA mass into lower c* bins. Hayes et al. (2015) previously evaluated different parameters for aging. However, the results from this previous study showed that substantial over-prediction of SOA was observed when using the Grieshop et al. (2009) parameterization in which each oxidation reaction reduced volatility by two orders of magnitude. New parameterizations may be necessary to produce the observed SOA volatility and concentration simultaneously (Cappa and Wilson, 2012). However, we note that the additional low volatility organic mass will not significantly change SOA predictions in urban regions where OA concentrations are relatively high. When comparing the total amount of particle phase SVOCs, it seems that the model reproduces reasonably well the measurements (6.6 versus 9.0 μg m^{-3}) as expected based on the comparisons of the total SOA concentration discussed above. In addition, the total amount of SVOCs (particle and gas phase) are similar (12.9 vs 11.8 μg m^{-3}), although it is difficult to determine from measurements the gas phase concentration of SVOCs in the 10^{2} μg m^{-3} bin due to the lack of particle mass in this bin under ambient concentrations as well as the limited temperature range of the thermal denuder system.

Recently, Woody et al. (2016) published a paper that modeled SOA over California using the Environmental Protection Agency's Community Multiscale Air Quality Model that had been updated to include a VBS treatment of SOA (CMAQ-VBS). As discussed in that paper, the modeled P-S/IVOC emission inventories remain an important source of uncertainty in 3-D grid-based models. In that previous study several different ratios of P-S/IVOCs-to-POA emissions were evaluated against measurements, and it was found that a ratio of 7.5 gave the best agreement between the CMAQ-VBS model and observations. From the results shown in Fig. 7 at a photochemical age of 0 h, a P-S/IVOC-to-POA ratio of 5.2 is calculated. This ratio is different from that determined by Woody et al. (2016), and may be biased low due to possibly low ΔIVOC/ΔCO emission ratios as discussed earlier in this section, but it serves as both a useful lower bound and has the advantage of being determined from empirical measurements of aerosols rather than by tuning a model to match measured SOA concentrations. As stated in Woody et al. (2016), the higher ratio may compensate for other missing (or

underrepresented) formation pathways in SOA models or excessive dispersion of SOA in their model.

4. CONCLUSION

We have used several data sets from recently published papers to better constrain and evaluate urban SOA formation pathways and precursors, especially P-SVOCs and P-IVOCs, within a custom-built box model. The use of the box model facilitates the incorporation of these new data sets as well as the evaluation of a number of model cases. All the model cases are able to correctly simulate the fossil/non-fossil carbon split at the Pasadena ground site providing support for the performance of the model. When measurements of IVOCs are used to constrain the concentrations of P-IVOCs, such as in the ROB + ZHAO + TSI and ROB + ZHAO + MA cases, a large improvement of the model at longer photochemical age is observed. However, these model cases are still biased low at shorter photochemical ages. By constraining the P-SVOCs additionally with measurements of those precursors, such as in the WOR + ZHAO + TSI case, better model/measurement agreement is obtained at shorter photochemical ages, yet the model is still biased low. Finally, the WOR + ZHAO + MA case, which incorporates state-of-the-art measurements of P-SVOCs and P-IVOCs and also accounts for the effect of chamber wall-losses on VOC yields, obtains model/measurement agreement within measurement uncertainties at long photochemical ages. Although, it displays also a low bias at short photochemical ages, which is similar to the ROB + ZHAO + MA case. This bias may be due to low ΔIVOC/ΔCO emissions ratios or IVOC oxidation rate constants for which the estimated values are too low. It is also possible that additional sources or SOA formation pathways are missing from the model. Moreover, a P-S/IVOC-to-POA ratio of 5.2 is determined, which can be combined with POA emission inventories to constrain the emissions of P-S/IVOCs in gridded chemical transport models.

In addition to evaluating the model performance with respect to SOA concentration, the rates of SOA formation are compared against measurements as well. This aspect of the study was enhanced by the use of OFR data to constrain SOA formation potential for up to 3 days of photochemical aging (at 1.5×10^6 molec OH cm^{-3}). The model cases that include multi-generation oxidative aging predict substantial SOA increases after 1.5 days of aging, which is not consistent with the OFR measurements. In contrast, model cases in which aging is omitted and instead SOA yields for VOCs are corrected for gas phase wall-losses in chamber experiments predict little change in the SOA concentration after 1.5 days. These results highlight the uncertainties associated with aging schemes for SOA from VOCs, which are often implemented in SOA models. Implementing instead corrected yields for VOCs results in similar amounts of SOA but formation rates versus time that are more consistent with observations.

Therefore, the model cases with updated VOC yields that account for chamber wall-losses best reproduce the ambient and OFR data. However, while the WOR + ZHAO + MA case appears to represent a slight improvement over the ROB + ZHAO + MA case, as well as over the ROB + ZHAO + TSI and WOR + ZHAO + TSI cases, it is not possible to conclude that one set of parameters is better than the other since the difference in the predictions for these 4 cases (15 % on average) is likely smaller than the uncertainties due to the model setup as well as the lack of a gas-phase fragmentation pathway during aging. Moreover, uncertainties in the vapor wall-loss corrected yields remain, and the correction of the yields has been performed here using data from a limited number of laboratory studies. In particular, the effect of temperature and humidity on gas-wall partitioning needs to be characterized. The results obtained in our work motivate future studies by showing that SOA models using wall-loss corrected yields reproduce observations for a range of photochemical ages at a level of accuracy that it is as good as or better than parameterizations with the uncorrected yields.

In all six of the model cases, a large majority of the urban SOA at Pasadena is the result of P-SVOC and P-IVOC oxidation. While this result alone cannot be taken as conclusive due to the uncertainties in the model parameters, further evidence for the importance of P-SVOCs and P-IVOCs is obtained by analyzing the percentage of SOA formed at long photochemical ages (~1.5 days) as a function of the precursor rate constant. The P-SVOCs and P-IVOCs have rate constants that are similar to highly reactive VOCs that have been previously found to strongly correlate with SOA formation potential measured by the OFR.

Lastly, the modeled volatility distribution of the total (gas and particle phase) organic mass between $c^* = 10^{-2}$ and 10^{10} ug m^{-3} is analyzed at three ages and compared against volatility-resolved measurements. While the total concentrations of gas and particle phase SVOCs are reasonably well simulated, at the same time there are important differences between the measured and modeled volatility distribution of SVOCs. These differences highlight the need for further studies of the chemical pathways that may give rise to SOA in low volatility bins at $c^* = 10^{-2}$ ug m^{-3} and lower.

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1345 **Table 1.** Summary of the model cases used in this paper.

Case	Notes	References
1) ROB + TSI	P-S/IVOCs: Robinson et al. parameterization, and all SOA treated within VBS framework VOCs: Tsimpidi et al. parameterization with aging	Hayes et al. (2015) Robinson et al. (2007) Tsimpidi et al. (2010)
2) ROB + ZHAO + TSI	P-SVOCs: Robinson et al. parameterization, and all SOA treated within VBS framework P-IVOCs: Zhao et al. parameterization with aging VOCs: Tsimpidi et al. parameterization with aging	Robinson et al. (2007) Zhao et al. (2014) Tsimpidi et al. (2010)
3) WOR + ZHAO + TSI	P-SVOCs: Worton et al. volatility distribution for vehicular P-SVOCs, Robinson et al. volatility distribution for cooking P-SVOCs P-IVOCs: Zhao et al. parameterization with aging VOCs: Tsimpidi et al. parameterization with aging	Robinson et al. (2007) Worton et al. (2014) Zhao et al. (2014) Tsimpidi et al. (2010)
4) ROB + MA	P-S/IVOCs: Robinson et al. parameterization, and all SOA treated within VBS framework VOCs: VOCs yields corrected for wall-losses, no aging of VOC oxidation products	Robinson et al. (2007) This work
5) ROB + ZHAO + MA	P-SVOCs: Robinson et al. parameterization, and all SOA treated within VBS framework P-IVOCs: Zhao et al. IVOC parameterization with aging VOCs: VOCs yields corrected for wall-losses, no aging of VOC oxidation products	Robinson et al. (2007) Zhao et al. (2014) This work
6) WOR + ZHAO + MA	P-SVOCs: Worton et al. volatility distribution for vehicular P-SVOCs, Robinson et al. volatility distribution for cooking P-SVOCs P-IVOCs: Zhao et al. IVOC parameterization with aging VOCs: VOCs yields corrected for wall-losses, no aging of VOC oxidation products	Robinson et al. (2007) Worton et al. (2014) Zhao et al. (2014) This work

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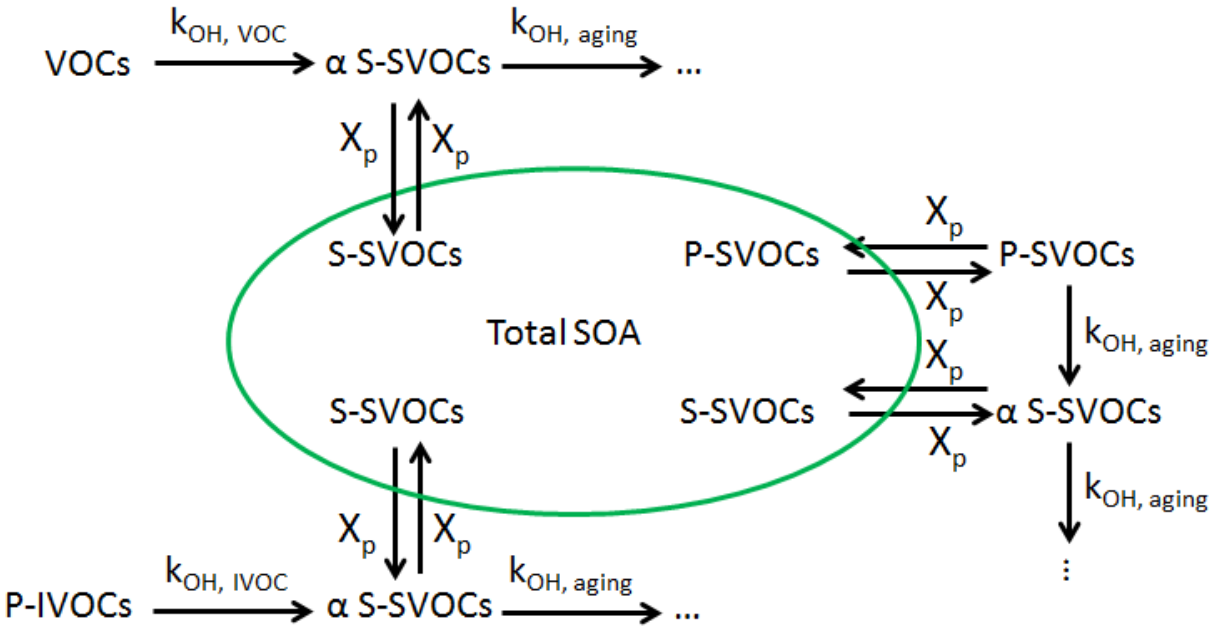

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1349 **Figure 1.** Schematic of the chemical pathways leading to the formation of SOA in the box model
1350 where α is the SOA yield, $k_{OH,VOC}$ and $k_{OH,IVOC}$ are the rate constants of a VOC or an IVOC
1351 species respectively for oxidation by OH radicals, and X_p is the particle-phase fraction of a
1352 species.

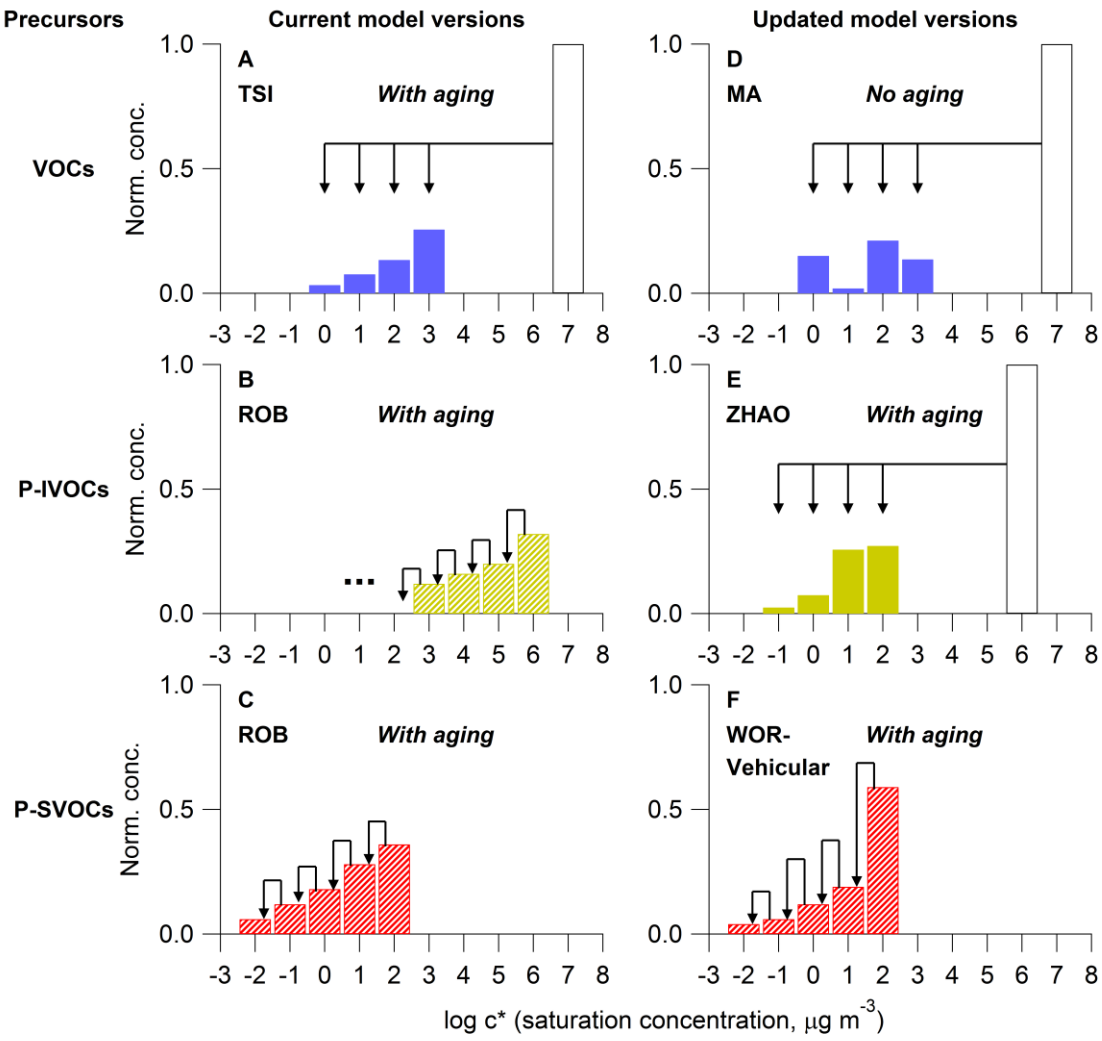


Figure 2. Schematic of the SOA formation parameterizations used in the model. The products formed are shown in different colors for each precursor. Note that the striped color bars indicate that the bins contain both primary and secondary organics. In panel **(A)** the parameterization of Tsimpidi et al. (2010) distributes the products of VOCs oxidation into four volatility bins. Panels **(B)** and **(C),** show the parameterization of Robinson et al. (2007) in which the volatility of the SOA precursors, specifically IVOCs and SVOCs, decrease by one order of magnitude per oxidation reaction. For P-IVOCs, aging continues to transfer mass to lower volatility bins (log c* < 2). Panel (**D**) shows the updated parameterization for VOC oxidation that accounts for gas phase wall losses, and Panel **(E)** shows the updated parameterization for P-IVOC oxidation that uses the speciated measurements of IVOCs from Zhao et al. (2014). In Panel **(F),** for the parameterization based on the measurements of Worton et al. (2014), the Robinson et al. (2007) volatility distribution is still used for the P-SVOCs emitted from cooking sources. Arrows representing the aging of SOA are omitted for clarity.

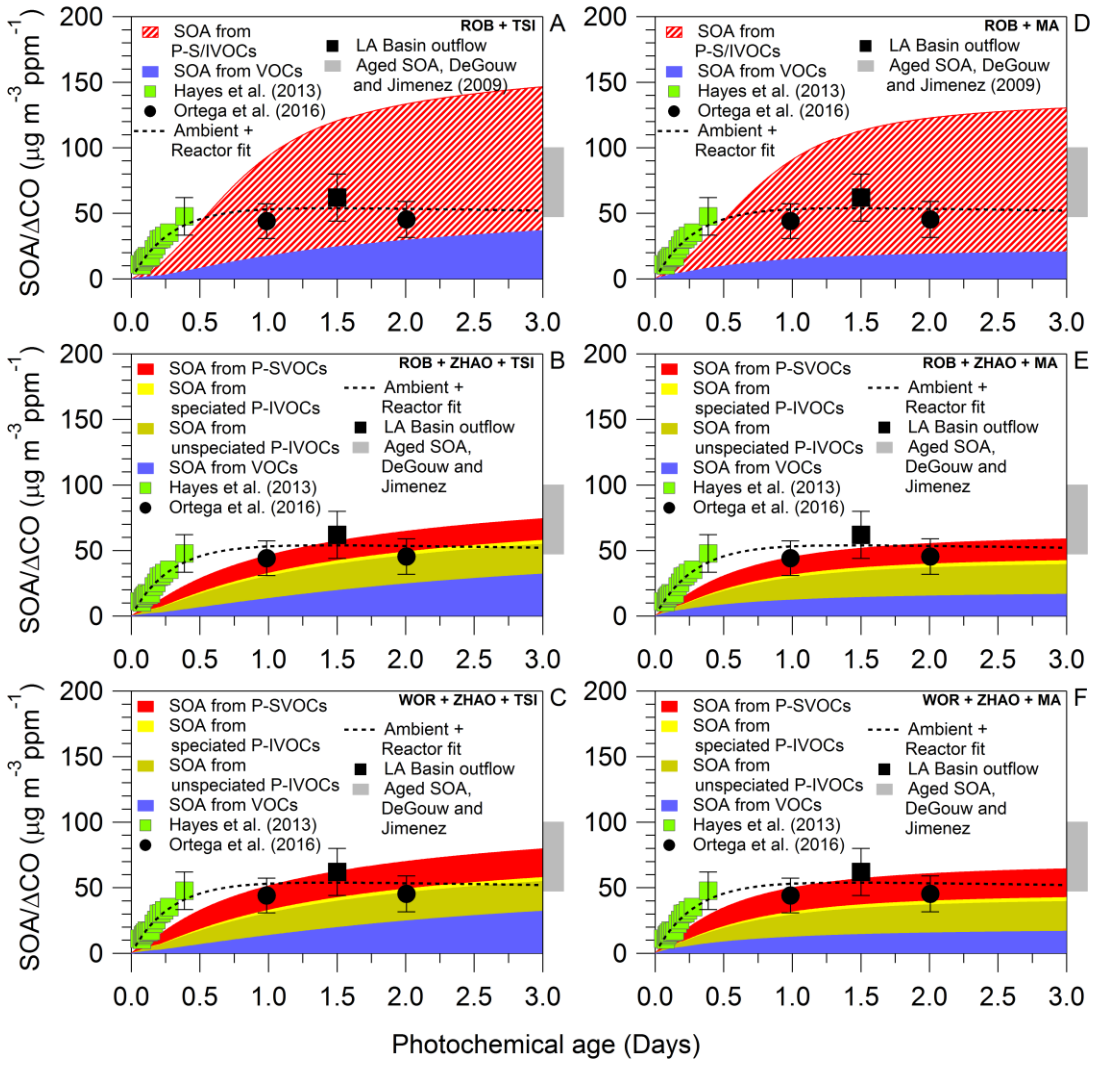


Figure 3. Predicted urban SOA mass by all six cases for up to 3 days of photochemical aging using a reference OH radical concentration of 1.5×10^6 molec cm^{-3}. Background SOA is not included in the figure. The SOA concentrations have been normalized to the background subtracted CO (ΔCO) concentration to account for changes in emission strengths and dilution. The SOA/ΔCO data determined from the ambient and OFR measurements at Pasadena as reported by Hayes et al. (2013) (green squares) and Ortega et al. (2016) (black circles) are shown. Also shown is SOA/ΔCO determined from measurements performed aboard the NOAA P3 research aircraft (black square) reported by Bahreini et al. (2012) and highly aged urban air masses (gray bar) reported by de Gouw and Jimenez (2009). The fit for ambient and reactor data reported by Ortega et al. (2016) is also shown (dotted black line).

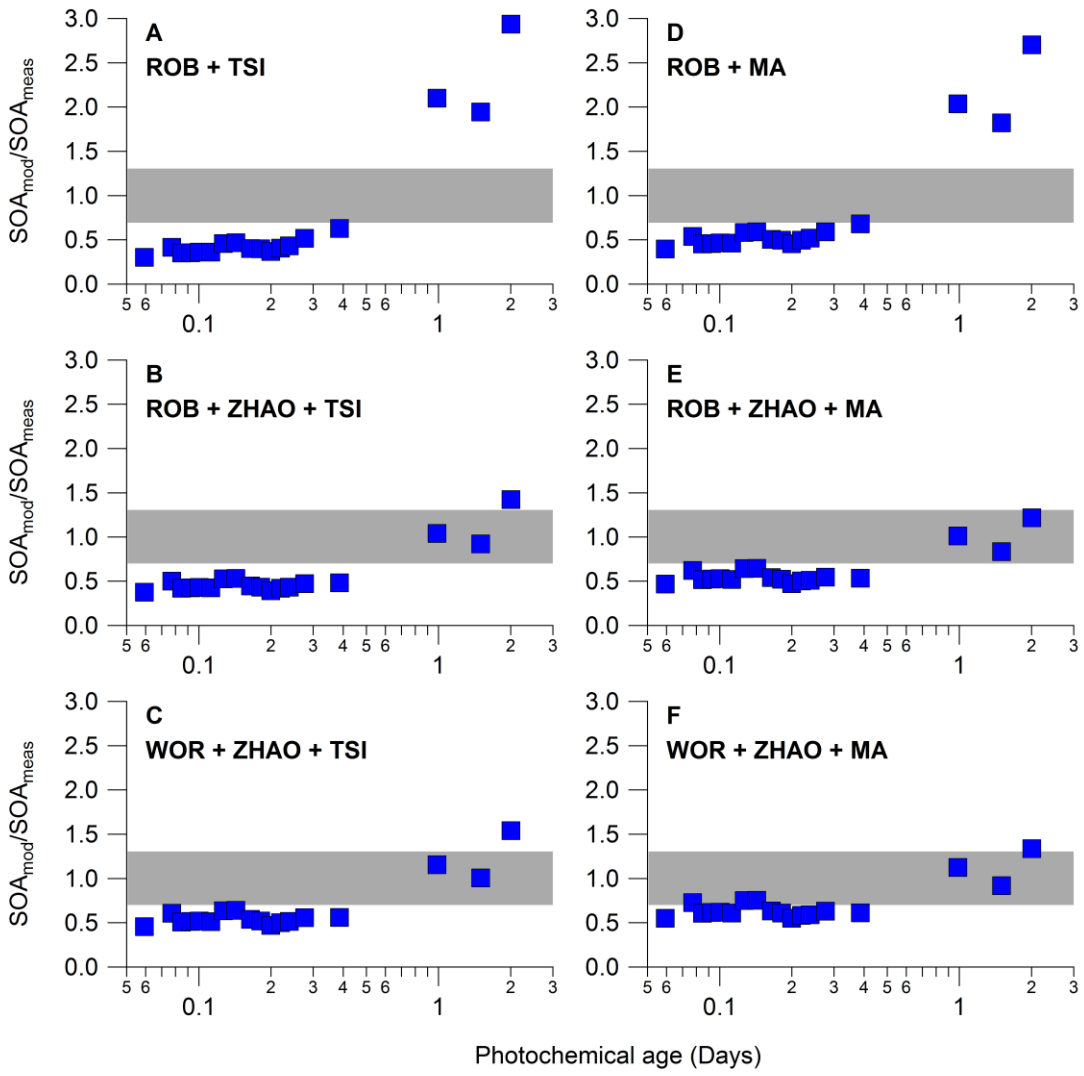
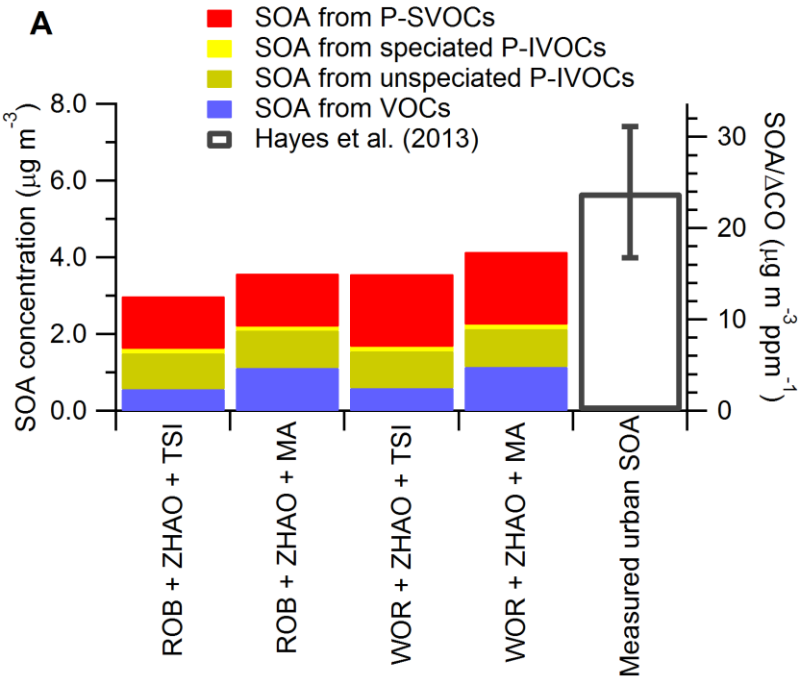


Figure 4. The ratio of the modeled-to-measured SOA concentrations (blue squares) for all model cases. The measurements are the same as used in Figure 3. The gray bar indicates ratios that would correspond to model results that are within the estimated ± 30 % uncertainty of the measurements.



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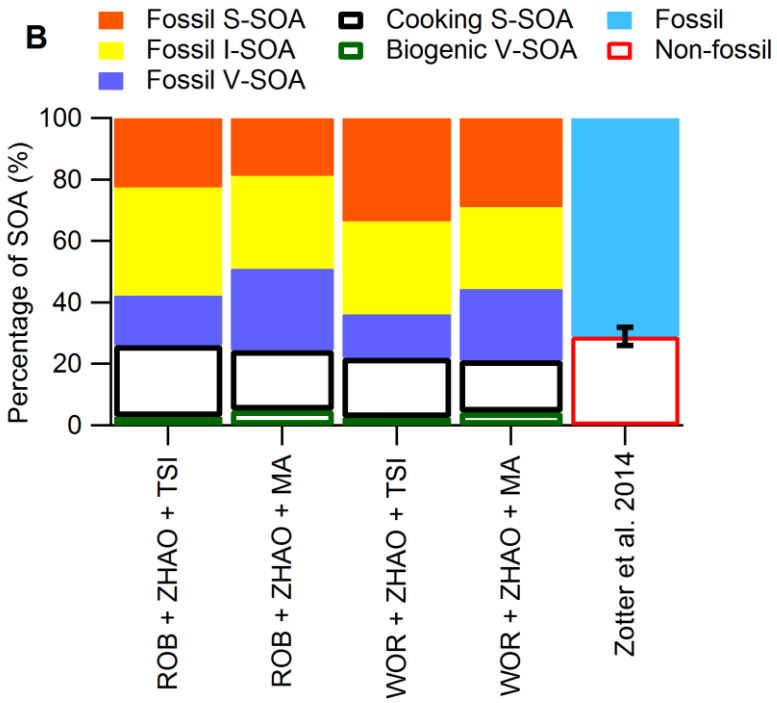

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1385 **Figure 5. (A)** Predicted and measured urban SOA mass for 12:00 – 15:00 local time at the
1386 Pasadena ground site. **(B)** The fractional mass of fossil S-SOA, fossil I-SOA, and fossil V-SOA,
1387 as well as cooking S-SOA and biogenic V-SOA for the same time and location. The percentage
1388 of urban SOA from fossil and non-fossil sources as reported in Zotter et al. (2014) is also
1389 displayed. The fossil sources are shown as solid bars and the non-fossil sources as hollow bars.

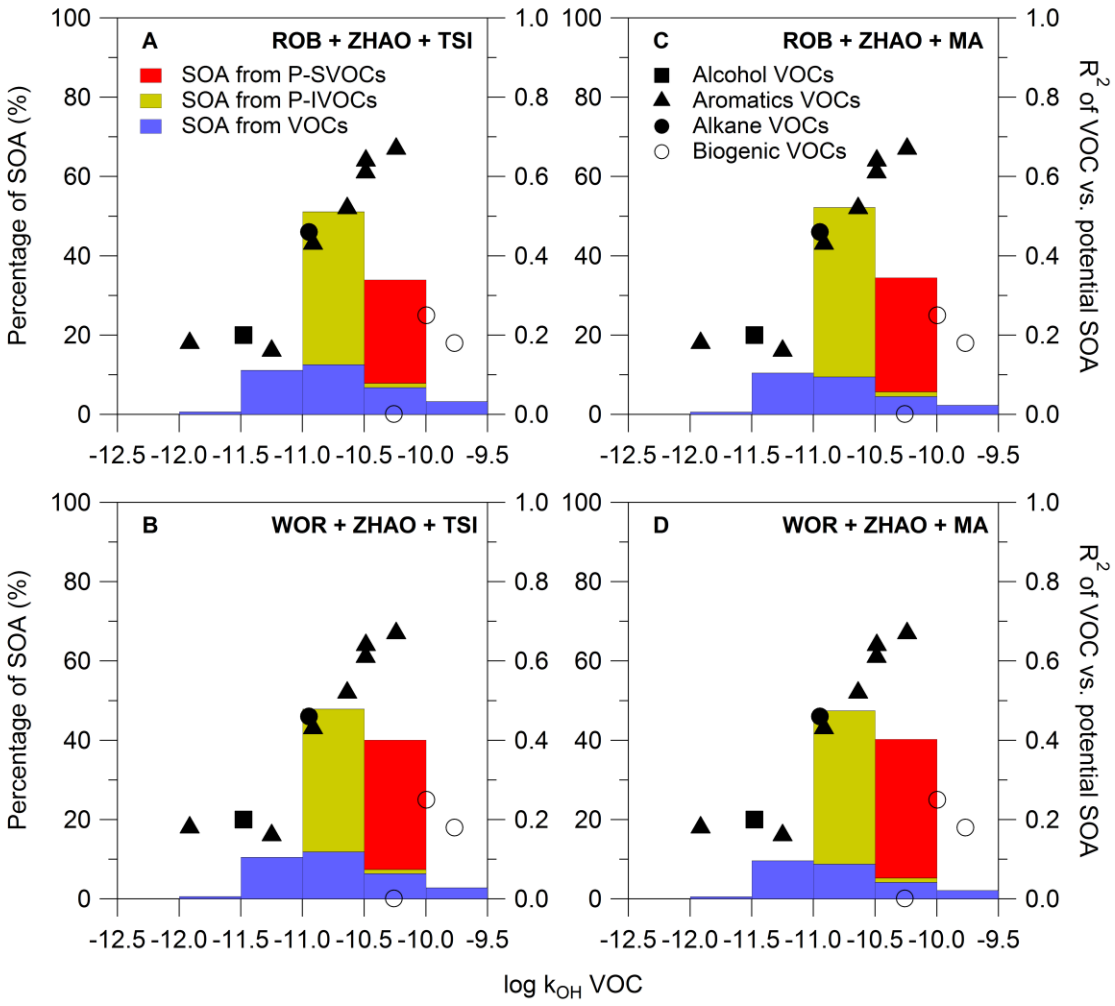

Figure 6. Percentage of SOA mass formed from different precursors at 1.5 days of photochemical aging (at 1.5×10^6 molec OH cm^{-3}) binned according to precursor rate constant. The correlations (R^2) between the concentrations of different VOCs and the maximum SOA concentration formed in the OFR as reported by Ortega et al. (2016) are represented by the markers. The shape of the marker indicates the chemical family to which each compound belongs. For the VOCs and the P-IVOCs the rate constant is the constant for the initial oxidation reaction. The measurements of IVOCs used here allow the rate constants of these precursors to be taken from published work or estimated using structure-activity relationships as described previously (Zhao et al., 2014). For S-SOA, the rate constant is the aging rate constant reported originally by Robinson et al. (2007).

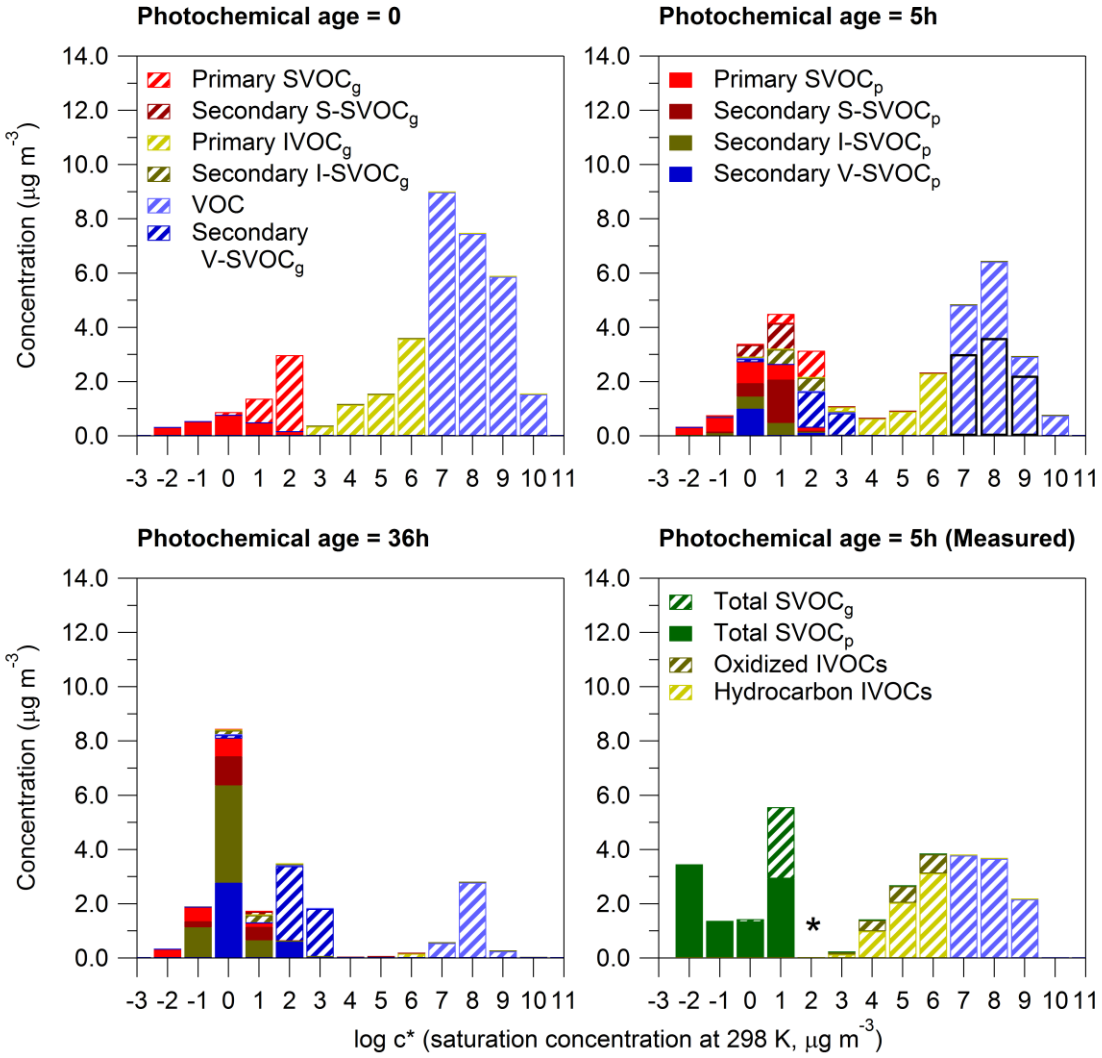

Figure 7. OA volatility distribution as simulated by the WOR + ZHAO + MA case displayed at different photochemical ages (0, 5, and 36 h). The partitioning of the species is indicated using patterned bars for gas phase and solid bars for particle phase mass. The bottom-right graph also shows the measured volatility distribution of OA. The SVOC volatility distribution is determined using a combined thermal denuder AMS system as described in the supporting information. The IVOC volatility distribution was previously published in Zhao et al. (2014), and the VOC distribution was determined from GC-MS measurements using the SIMPOL.1 model to estimate the volatility of each VOC. The asterisk in the bin log c* = 2 indicates that measurements are not available for this bin. It should be noted that not all the VOCs in the model were measured at Pasadena (see text for details). For direct visual comparison with the measurements, the simulated concentrations of only the VOCs measured at Pasadena are indicated by the black hollow bars in the bins log c* = 7, 8, and 9 μg m^{-3}.

Supporting Information for

Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA

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Estimation of SOA yields for the MA model cases by accounting for chamber vapor losses

The approach used here to estimate SOA yields for VOC oxidation that account for losses of gas phase organic compounds to the walls of Teflon environmental chambers uses a set of recently published parameters for modeling gas-wall partitioning in chamber experiments (Krechmer et al., 2016). This previous work found that the fraction of each compound that partitioned to the walls at equilibrium followed absorptive partitioning theory with an equivalent wall mass concentration that could be calculated from the following equation.

$$c_w = 16(c^*)^{0.6}\ \mu g\ m^{-3} \quad for\ c^* = 1, 10, 100, or\ 1000\ \mu g\ m^{-3} \qquad (1)$$

Our approach assumes equilibrium between the organic material found in the gas phase, particle phase, and the chamber walls. The limitations of this assumption and its potential impact on the model results are discussed below. The partitioning of the SVOCs between the particle and gas phases and the chamber walls can be calculated using the particle concentration, C_{OA} as well as the equivalent wall mass concentration calculated from Equation 1 above.

$$\frac{[SVOC]_w}{[SVOC]_g} = \frac{c_w}{c^*} \qquad (2)$$

$$\frac{[SVOC]_p}{[SVOC]_g} = \frac{c_{OA}}{c^*} \qquad (3)$$

Furthermore, the yield, α_i, is the total amount of SVOC at a given volatility, i, formed from a given VOC.

$$[SVOC]_{g,i} + [SVOC]_{p,i} + [SVOC]_{w,i} = \alpha_i\ [\Delta VOC] \qquad (4)$$

Combining Equations 2, 3, and 4, one can obtain the following equation.

$$[SVOC]_{p,i} = \alpha_i \left(1 + \frac{C_i^*}{C_{OA}} + \frac{C_{w,i}}{C_{OA}}\right)^{-1} [\Delta VOC] \qquad (5)$$

If a four bin basis set is used where i = 1, 10, 100, or 1000 μg m^{-3}, then the total SOA yield, Y, measured during an environmental chamber experiment can be fit with Equation 6, which is simply Equation 5 summed over the four volatilities and then rearranged.

$$Y = \alpha_1 \left(1 + \frac{1}{C_{OA}} + \frac{C_{w,1}}{C_{OA}}\right)^{-1} + \alpha_{10} \left(1 + \frac{10}{C_{OA}} + \frac{C_{w,10}}{C_{OA}}\right)^{-1} + \alpha_{100} \left(1 + \frac{100}{C_{OA}} + \frac{C_{w,100}}{C_{OA}}\right)^{-1} + \alpha_{1000} \left(1 + \frac{1000}{C_{OA}} + \frac{C_{w,100}}{C_{OA}}\right)^{-1} \quad (6)$$

The corrected yields in this work were determined by simulating yield curves using the parameters published in Tsimpidi et al. (2010) and then refitting the curves using Equation 6.

For clarity, c_w is the equivalent organic mass concentration of the walls, and it is an empirically determined value. Equations 2 and 3 are the partitioning equations that describe either the partitioning between the gas phase and walls or the gas phase and the particles, which both depend on the volatility of the organic vapors, c*. The significance of c_w can be understood by comparing equations 2 and 3. In equation 3, the partitioning is dependent on the total particle phase, c_{OA}. Similarly, the parameter c_w is the amount of mass in the chamber walls available for partitioning expressed as an effective mass concentration based on the work of Krechmer et al. (2016). However, the value of c_w is a function of c* as shown in equation 1.

As mentioned above, the approach described here assumes equilibrium between the particle and gas phases as well as the chamber walls. For higher volatility compounds (c* ≥ 10 μg m^{-3}), this assumption is reasonable given recently published results that show transfer of mass between particles and walls on the timescale of an hour (Ye et al., 2016). The same paper has shown however that for compounds with a volatility of c* = 1 μg m^{-3}, the organic material condensed on particles evaporates and partitions to the chamber walls on timescales that are longer than typical chamber experiments. The α value for the c* = 1 μg m^{-3} bin would then be biased high since the model described above would attribute mass to the chamber walls that is not actually present. Therefore, the amount of V-SOA in model cases that use the corrected yields determined here should be considered an upper limit. Furthermore, the original yields (without aging) should be considered lower limits.

Estimation of the SVOC volatility distribution at Pasadena from Thermonuder Aerosol Mass Spectrometry Measurements (TD-AMS)

The TD-AMS measurements at Pasadena were carried out using the system previously described by Huffman et al. (2008). Briefly, switching valves were used to sample both ambient air as well as ambient air passed through a thermodenuder (TD) that was scanned between 37 and 260°C. The mass fraction remaining (MFR) as a function of temperature, also known as a thermogram, is

then calculated from the ratio of the TD measurements and the linearly-interpolated ambient measurements. In order to compare against the model, the thermogram was only determined for the period between 12:00 – 15:00 local time, which corresponded to 5 h of photochemical aging at a reference OH concentration of 1.5×10^6 molec OH cm^{-3}. This thermogram is shown below in Figure S11. The thermogram is then converted to a volatility distribution using the method described by Faulhaber et al. (2009).

The lowest volatility bin modeled is c* = 0.01 μg m^{-3}, but similar to previous measurements (Dzepina et al., 2011), the TD volatility distribution extends to lower volatility bins. The mass in these lower bins is lumped into the c* = 0.01 bins to allow comparison with the model. In addition, since the background SOA is treated as non-volatile in the box model, we subtract the amount of background SOA from the lowest bin (c* = 0.01 μg m^{-3}) after lumping to determine the volatility distribution of urban OA at Pasadena. Both of these approximations will bias the measured urban OA towards higher volatilities. When subtracting the background SOA, this bias would be due to the possibility that some of the background SOA is found in c* bins greater than 0.01 μg m^{-3}. Thus, some of the mass subtracted from the c* = 0.01 μg m^{-3} bin should instead be subtracted from more volatile bins. Given the measured urban OA is already lower volatility than that predicted in the model, correcting these potential sources of error would not change the conclusion in the main text that the measured SOA is less volatile than the modeled SOA.

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Table S1. Parameters for VOC oxidation used in the model. The aging rate constant for the multi-generation oxidation of VOCs is 1×10^{-11} cm^3 $molec^{-1}$ s^{-1}.

Classification	Compounds	Molecular weight (g mol^{-1})	k_{OH} (cm^3 $molec^{-1}$ s^{-1})	ΔVOC/ΔCO (ppt ppb^{-1})	Stoichiometric SOA yield High-NOx, 298 K (μg m^{-3})				
					0.1	1	10	100	1000
Alk5	Methylcyclopentane	84.2	5.68×10^{-12}	0.566	0.000	0.150	0.000	0.000	0.000
	Cyclohexane		6.97×10^{-12}	0.285					
	Methylcyclohexane	98.2	9.64×10^{-12}	0.202					
	n-Heptane	100.2	6.76×10^{-12}	0.398					
	2-Methylhexane		6.89×10^{-12}	0.385					
	3-Methylhexane		7.17×10^{-12}	0.460					
	2,3-Dimethylpentane		7.15×10^{-12}	0.252					
	2,4-Dimethylpentane		4.77×10^{-12}	0.171					
	2,2,3-Trimethylbutane		3.81×10^{-12}	0.031					
	n-Octane	114.2	8.11×10^{-12}	0.197					
	3-Methylheptane		8.59×10^{-12}	0.131					
	2-Methylheptane		8.31×10^{-12}	0.171					
	2,2,4-Trimethylpentane		3.34×10^{-12}	0.476					
	2,3,4-Trimethylpentane		6.60×10^{-12}	0.171					
	2,3,3-Trimethylpentane		4.40×10^{-12}	0.194					
	n-Nonane	128.3	9.70×10^{-12}	0.220					
	n-Decane	142.3	1.10×10^{-11}	0.180					
	Undecane	156.3	1.23×10^{-11}	0.290					
Ole1	Propene	42.1	2.63×10^{-11}	3.740	0.000	0.001	0.005	0.038	0.150
	1-Butene	56.1	3.14×10^{-11}	0.340					
	1-Pentene	70.1	3.14×10^{-11}	0.112					
	2-Methyl-1-Butene		6.10×10^{-11}	0.250					
	3-Methyl-1-Butene		3.18×10^{-11}	0.058					
Ole2	1,3-butadiene	54.1	6.66×10^{-11}	0.350	0.000	0.003	0.026	0.083	0.270
	trans-2-pentene	70.1	6.70×10^{-11}	0.097					
	cis-2-pentene		6.50×10^{-11}	0.050					

Table S1 (continued).

Classification	Compounds	Molecular weight (g mol^{-1})	k_{OH} (cm^3 molec^{-1} s^{-1})	ΔVOC/ΔCO (ppt ppb^{-1})	Stoichiometric SOA yield High-NOx, 298 K (µg m^{-3})				
					0.1	1	10	100	1000
Ole2	Styrene	104.2	5.80×10^{-11}	0.220	0.000	0.003	0.026	0.083	0.270
Ald	Benzaldehyde	106.1	1.15×10^{-11}	1.15×10^{-9}	0.000	0.000	0.000	0.000	0.000
	o-Tolualdehyde	120.1							
	m-Tolualdehyde								
	p-Tolualdehyde								
	2,5-Dimethylbenzaldehyde	134.2							
Aro1	Toluene	92.1	5.63×10^{-12}	3.180	0.000	0.003	0.165	0.300	0.435
	Ethylbenzene	106.2	7.00×10^{-12}	0.570					
	i-Propylbenzene	120.2	6.30×10^{-12}	0.030					
	n-Propylbenzene		5.80×10^{-12}	0.110					
	Benzene	78.1	1.22×10^{-12}	1.300					
Aro2	*o*-Ethyltoluene	120.2	1.19×10^{-11}	0.120	0.000	0.002	0.195	0.300	0.435
	m/*p*-Ethyltoluene		1.52×10^{-11}	0.349					
	1,2,3-Trimethylbenzene		3.27×10^{-11}	0.240					
	1,2,4-Trimethylbenzene		3.25×10^{-11}	0.620					
	1,3,5-Trimethylbenzene		5.67×10^{-11}	0.310					
	m/*p*-Xylene	106.2	1.87×10^{-11}	1.790[a]					
	o-Xylene		1.36×10^{-11}	0.459[b]					
Isop	Anthropogenic isoprene	68.1	1.00×10^{-10}	0.300	0.000	0.001	0.023	0.015	0.000
	Biogenic isoprene			N/A					
Terp	α-pinene + β-pinene + limonene	136.2	9.82×10^{-11}	N/A	0.000	0.012	0.122	0.201	0.500

[a]Average of both emission ratios; [b]Zhao et al. 2014

Table S2. Parameters for P-IVOC oxidation used in the model. Measurements of the IVOCs were reported in Zhao et al. 2014. The aging rate constant for the multi-generation oxidation of P-IVOCs is 4×10^{-11} cm^3 $molec^{-1}$ s^{-1}.

Classification	Compounds	k_{OH} (cm^3 $molec^{-1}$ s^{-1})	ΔIVOC/ΔCO (ng m^{-3} ppb^{-1})	Stoichiometric SOA yield High-NOx, 298 K (μg m^{-3})				
				0.1	1	10	100	1000
Naph	Naphtalene	2.44×10^{-11}	0.341	0.000	0.165	0.005	0.516	0.881
	1-Methylnaphtalene	4.09×10^{-11}	0.058					
	2-Methylnaphtalene	4.86×10^{-11}	0.110					
	Phenanthrene	3.20×10^{-11}	0.187					
Alk10	B12 alkane	1.32×10^{-11}	1.718	0.000	0.150	0.000	0.000	0.000
Alk11	B13 alkane	1.51×10^{-11}	1.513					
Alk12	Dodecane	1.32×10^{-11}	0.446	0.000	0.014	0.110	0.160	0.000
	B14 alkane	1.68×10^{-11}	0.951					
	B12 cyclic	1.32×10^{-11}	8.950					
Alk13	Tridecane	1.51×10^{-11}	0.310	0.014	0.059	0.220	0.400	0.000
	Heptylcyclohexane	1.91×10^{-11}	0.049					
	B15 alkane	1.82×10^{-11}	0.574					
	B13 cyclic	1.51×10^{-11}	5.868					
Alk14	Tetradecane	1.68×10^{-11}	0.479	0.022	0.094	0.300	0.350	0.000
	Octylcyclohexane	2.05×10^{-11}	0.049					
	B16 alkane	1.96×10^{-11}	0.486					
	B14 cyclic	1.68×10^{-11}	5.009					
Alk15	Pentadecane	1.82×10^{-11}	0.277	0.044	0.071	0.410	0.300	0.000
	Nonylcyclehexane	2.19×10^{-11}	0.036					
	Pristane	2.44×10^{-11}	0.062					
	B17 alkane	2.10×10^{-11}	0.795					
	B15 cyclic	1.82×10^{-11}	2.758					
Alk16	Hexadecane	1.96×10^{-11}	0.204	0.053	0.083	0.460	0.250	0.000
	Decylcyclohexane	2.33×10^{-11}	0.029					
	Phytane	2.61×10^{-11}	0.031					
	B18 alkane	2.24×10^{-11}	0.278					

Table S2 (Continued).

Classification	Compounds	k_{OH} (cm^3 $molec^{-1}$ s^{-1})	ΔIVOC/ΔCO (ng m^{-3} ppb^{-1})	Stoichiometric SOA yield High-NOx, 298 K (μg m^{-3})				
				0.1	1	10	100	1000
Alk16	B16 cyclic	1.96×10^{-11}	1.855	0.053	0.083	0.460	0.250	0.000
Alk17	Heptadecane	2.10×10^{-11}	0.141	0.063	0.089	0.550	0.200	0.000
	Octadecane	2.24×10^{-11}	0.070					
	Nonadecane	2.38×10^{-11}	0.030					
	Eicosane	2.52×10^{-11}	0.015					
	Heneicosane	2.67×10^{-11}	0.010					
	B19 alkane	2.38×10^{-11}	0.123					
	B20 alkane	2.52×10^{-11}	0.072					
	B21 alkane	2.67×10^{-11}	0.028					
	B17 cyclic	2.10×10^{-11}	2.473					
	B18 cyclic	2.24×10^{-11}	0.939					
	B19 cyclic	2.38×10^{-11}	0.526					
	B20 cyclic	2.52×10^{-11}	0.311					
	B21 cyclic	2.67×10^{-11}	0.142					

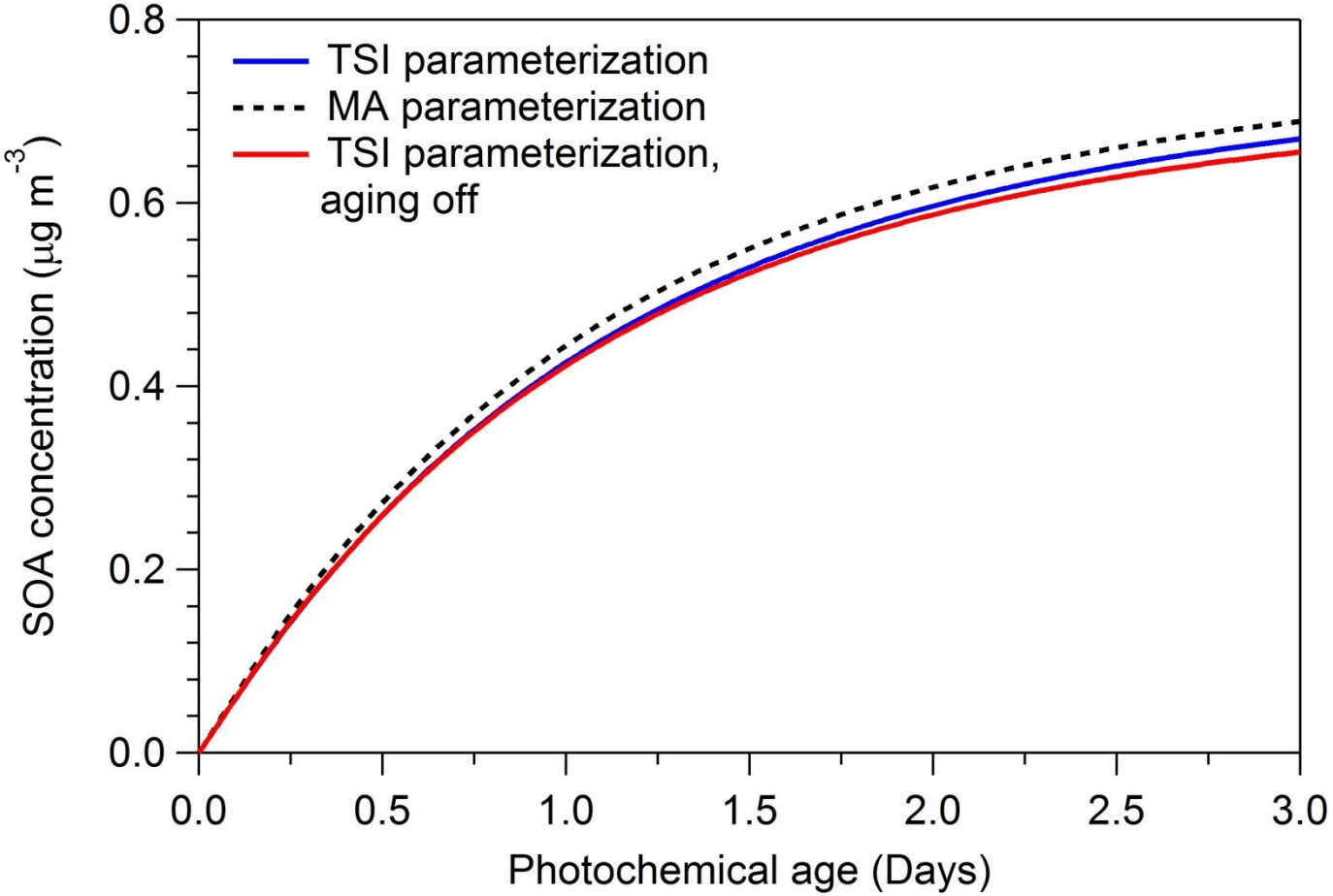
Table S3. Parameters for P-SVOC oxidation and the P-SVOC volatility distribution used in the model. The volatility distribution of P-SVOCs reported by Worton et al. (2014) is used for vehicular emissions whereas the volatility distribution of P-SVOCs reported by Robinson et al. (2007) is used for cooking emissions.

c* (μg m^{-3})	**ΔH_{vap} (kJ mol^{-1})**	**Molecular Weight (g mol^{-1})**	**Fraction of total P-SVOC (%)**	
ROB & WOR	ROB & WOR	ROB & WOR	ROB	WOR
10^{-2}	112	250	6	4
10^{-1}	106		12	6
10^{0}	100		18	12
10^{1}	94		28	19
10^{2}	88		36	59
K_{OH} (cm^3 $molec^{-1}$ s^{-1})	4×10^{-11}			
Oxygen mass gain per oxidation generation (%)	7.5			
Volatility decrease per oxidation generation	1 order of magnitude			

87 **Table S4.** Updated version of the SOA yields for VOCs accounting for losses of semi-volatile gases to chamber walls.

Classification	Stoichiometric SOA yield, High-NO_X, at 298 K (µg m^{-3})			
	1	**10**	**100**	**1000**
Alk5	0.157	0.000	0.000	0.000
Ole1	0.014	0.000	0.098	0.088
Ole2	0.052	0.000	0.183	0.157
Ald	0.000	0.000	0.000	0.000
Aro1	0.276	0.002	0.431	0.202
Aro2	0.310	0.000	0.420	0.209
Isop	0.034	0.000	0.005	0.000
Terp	0.210	0.000	0.348	0.297

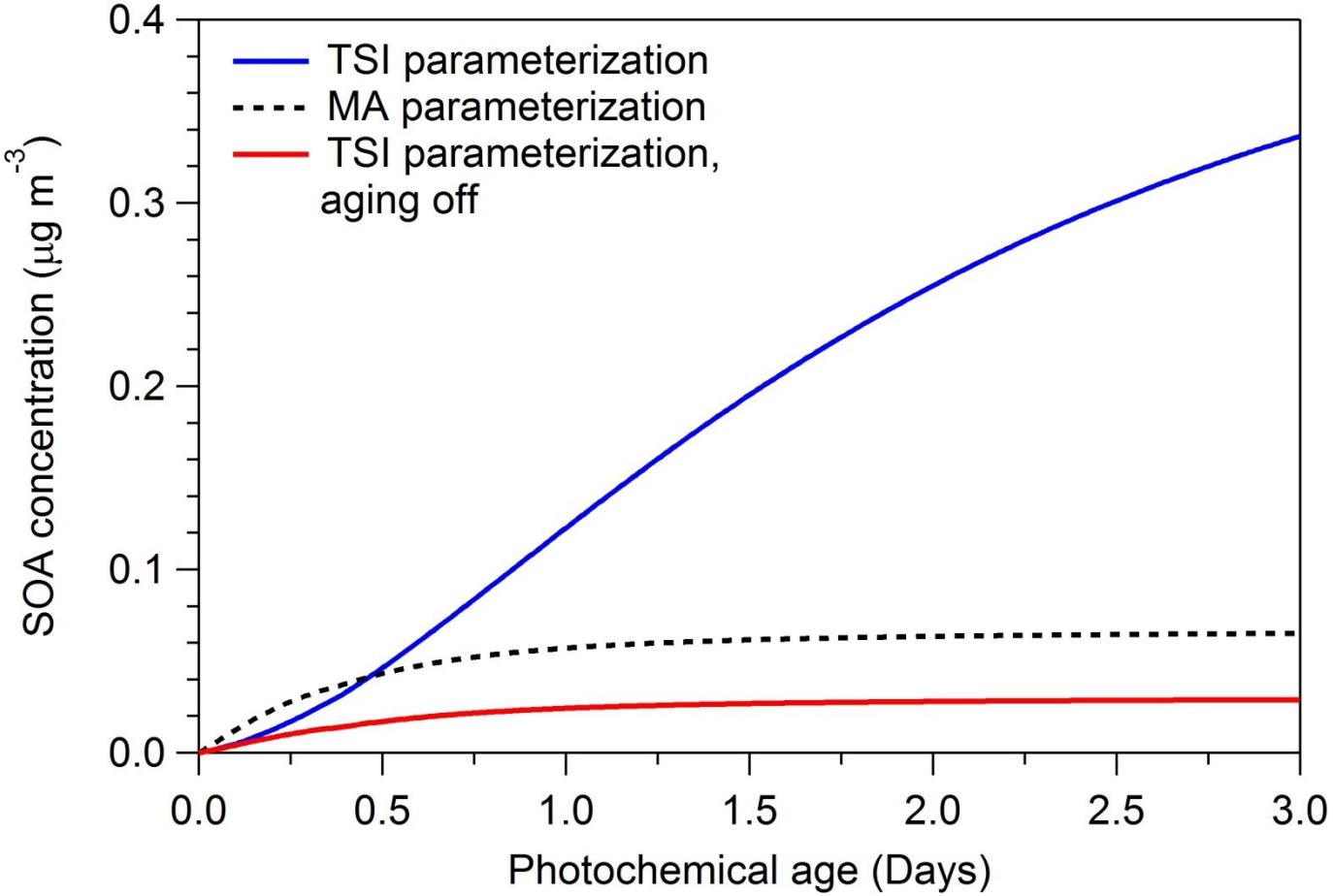
88



89

90 **Figure S1.** Predicted urban SOA mass from the alkane VOCs (Alk5) for different SOA formation parameterizations.

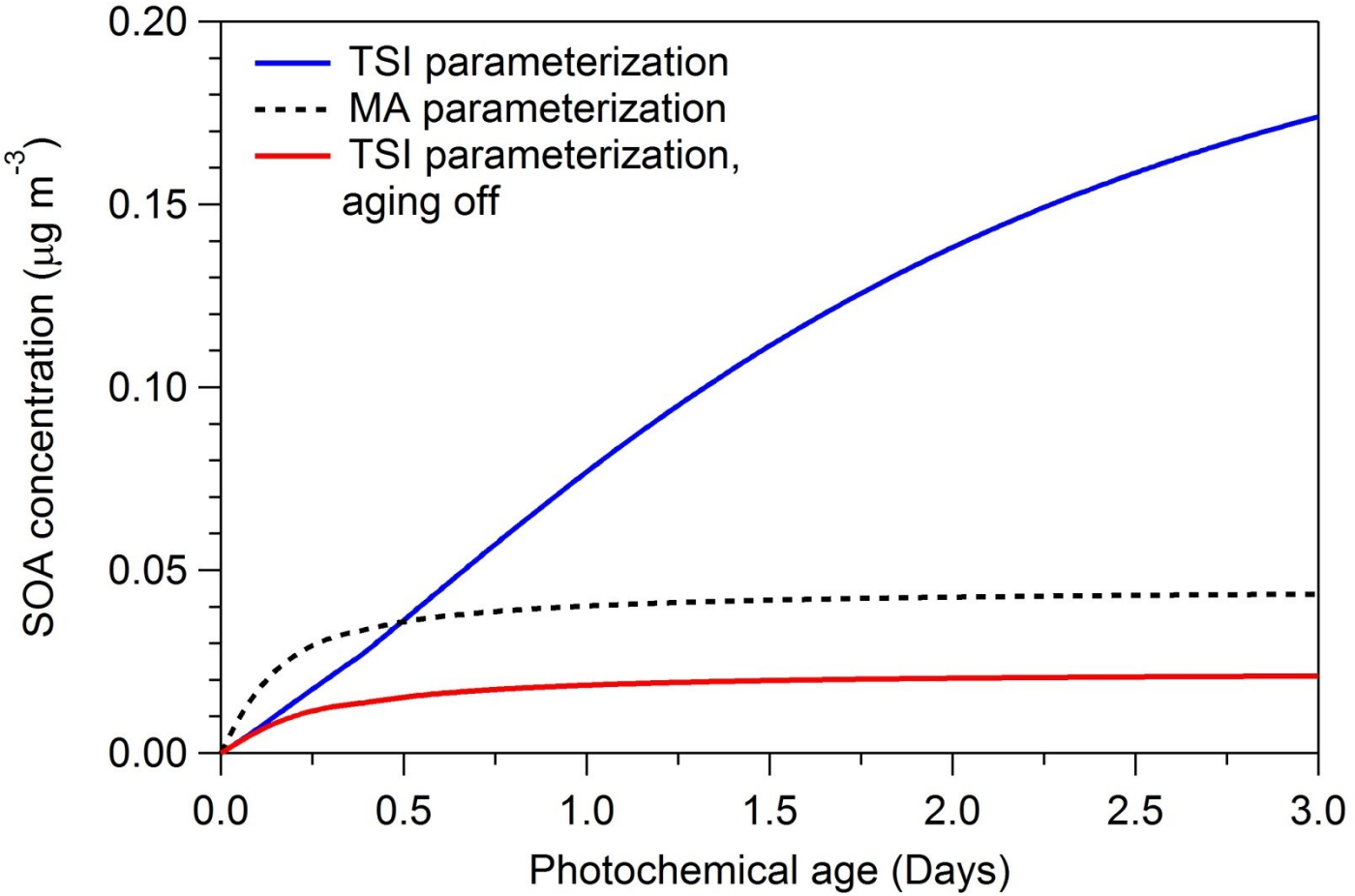
91



92

93 **Figure S2.** Predicted urban SOA mass from the olefin VOCs (Ole1) for different SOA formation parameterizations.

94



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96 **Figure S3** Predicted urban SOA mass from the olefin VOCs (Ole2) for different SOA formation parameterizations.

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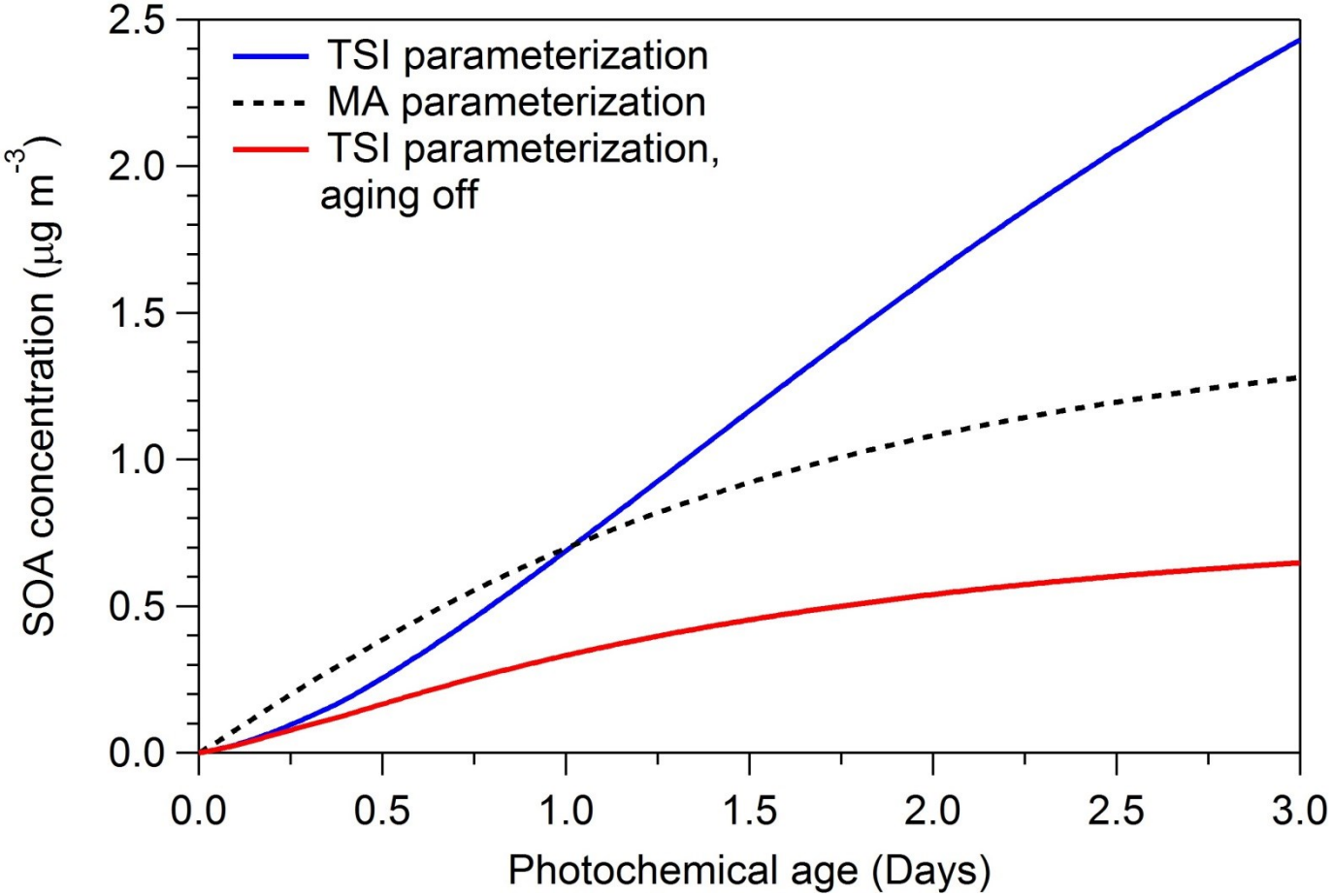
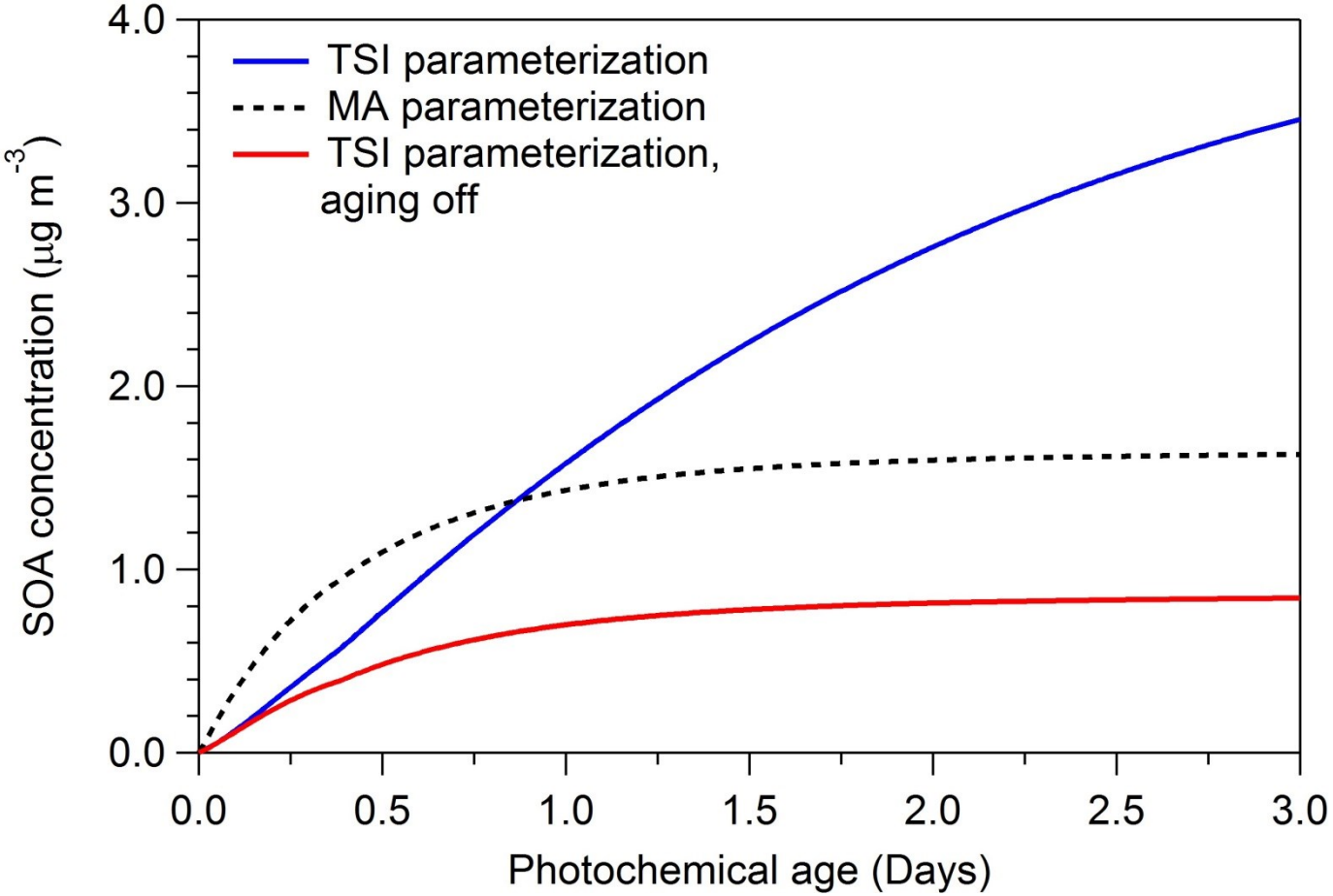


98

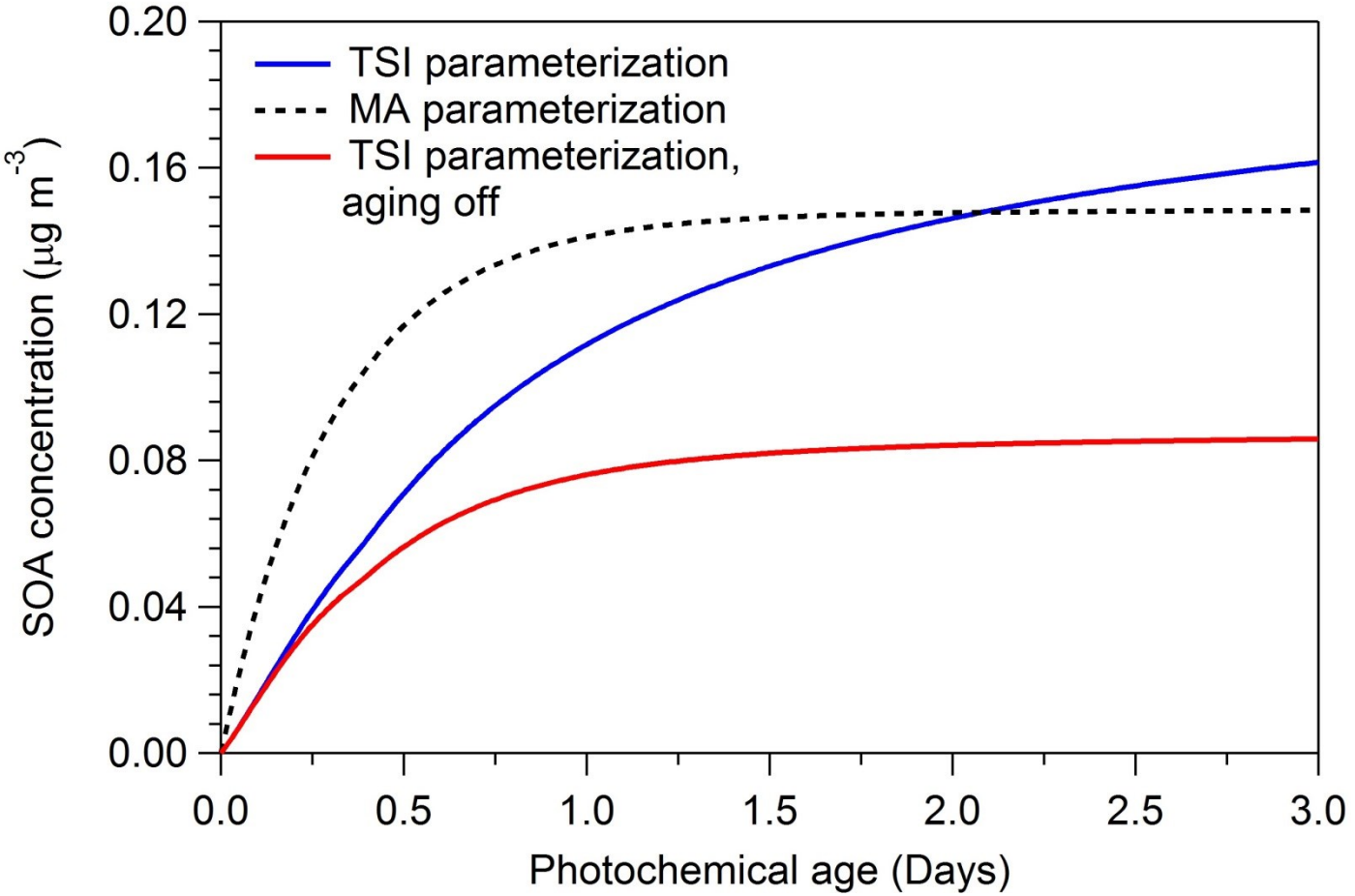
99 **Figure S4.** Predicted urban SOA mass from the aromatic VOCs (Aro1) for different SOA formation parameterizations.



100

101 **Figure S5.** Predicted urban SOA mass from the aromatic VOCs (Aro2) for different SOA formation parameterizations.

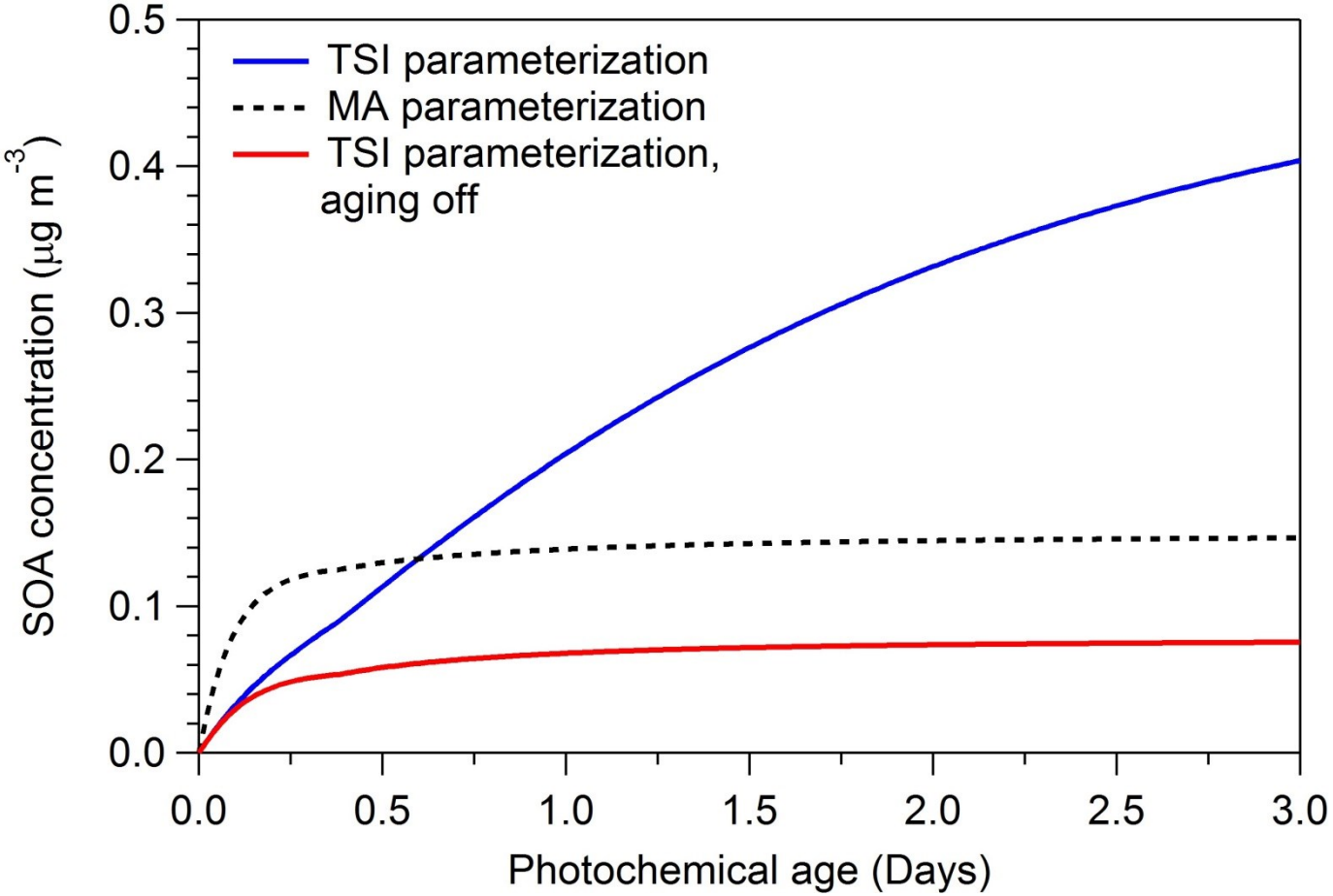
102



103

104 **Figure S6.** Predicted urban SOA mass from isoprene (Isop) for different SOA formation parameterizations.

105



106

107 **Figure S7.** Predicted urban SOA mass from terpenes (Terp) for different SOA formation parameterizations.

108

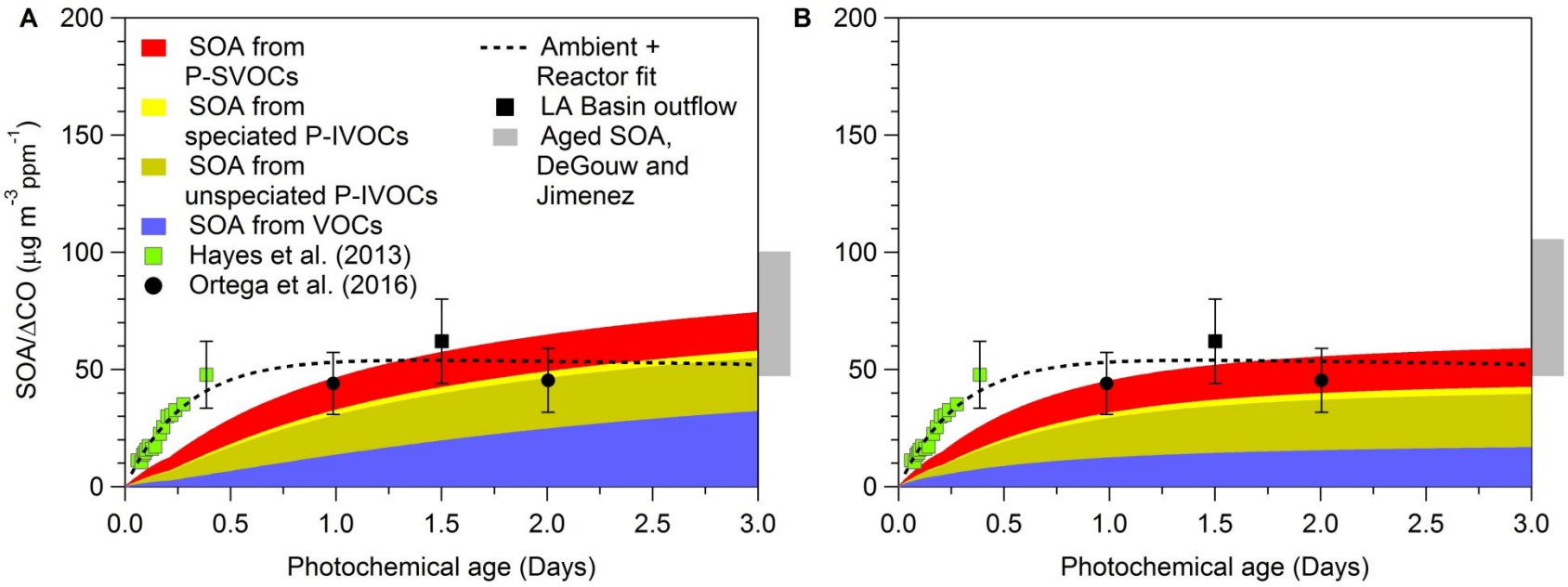
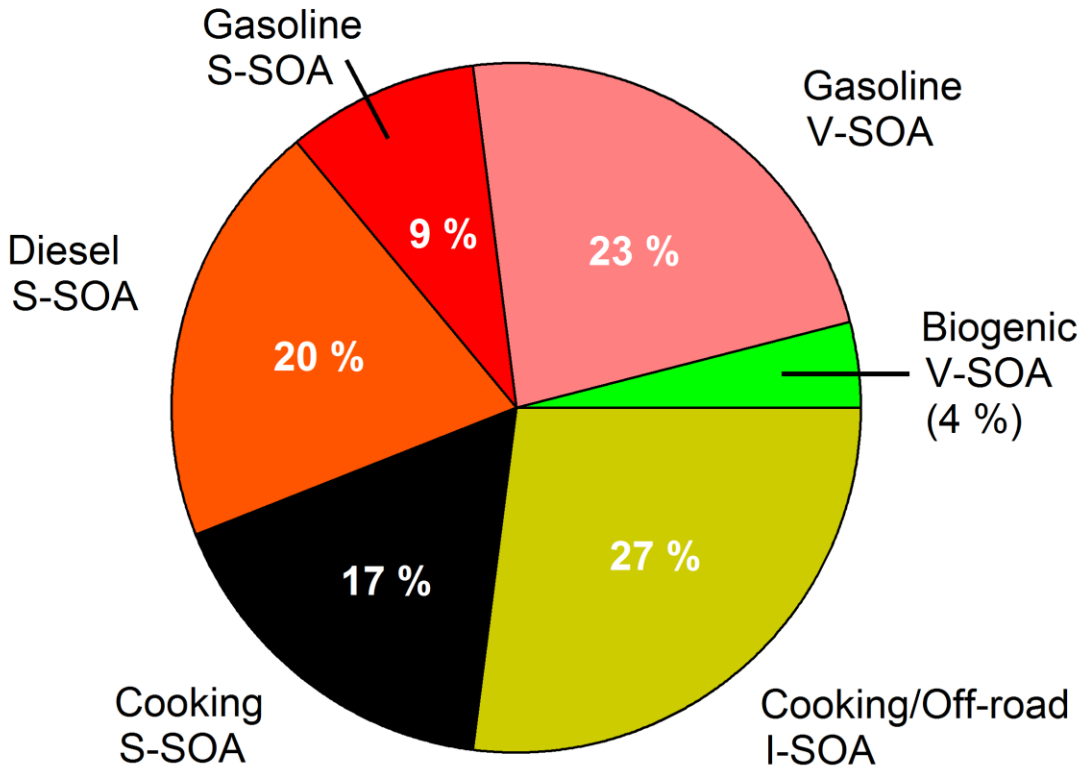


Figure S8. Predicted urban SOA mass by the A) WOR + ZHAO + TSI and B) WOR + ZHAO + MA cases when using the meat cooking volatility distribution reported by Woody et al. (2016).



113

114 **Figure S9.** Estimated fractional contributions to urban SOA mass concentration using the WOR + ZHAO + MA case.

115

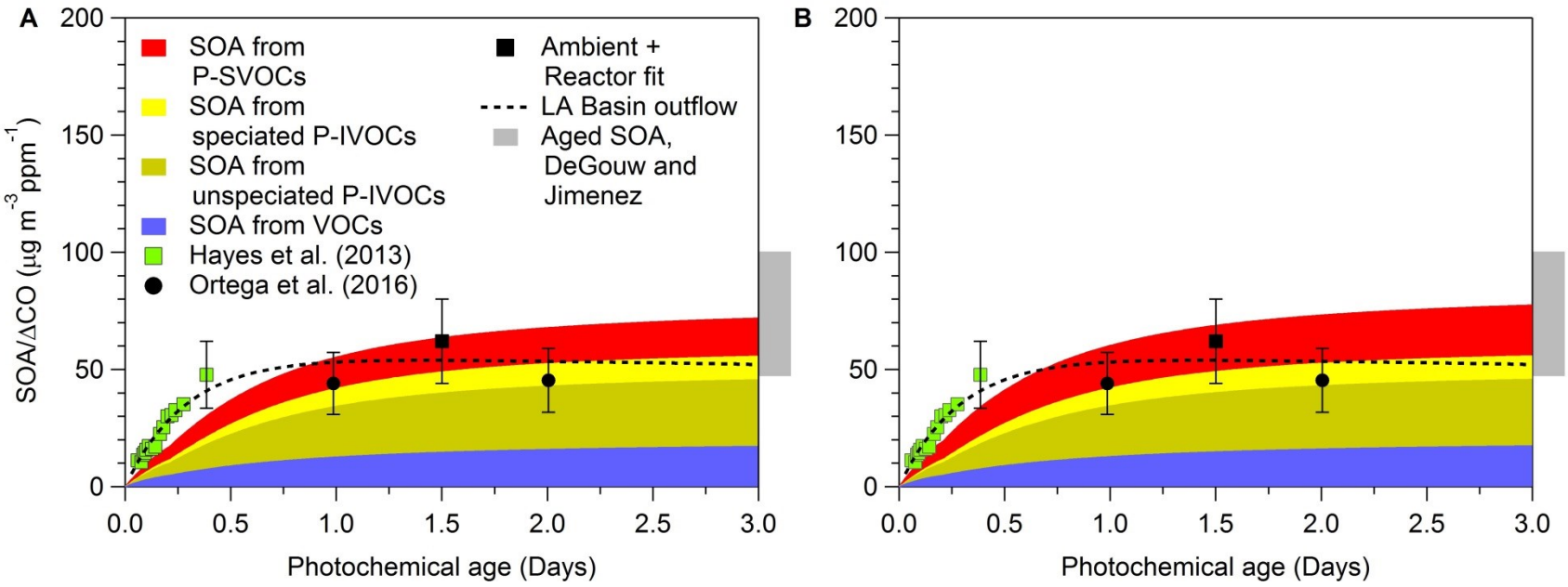


Figure S10. Predicted urban SOA mass for the A) ROB + ZHAO + MA and B) WOR + ZHAO + MA cases when using IVOC initial concentrations determined using photochemical age, the Pasadena IVOC concentrations and the estimated IVOC oxidation rate constants.

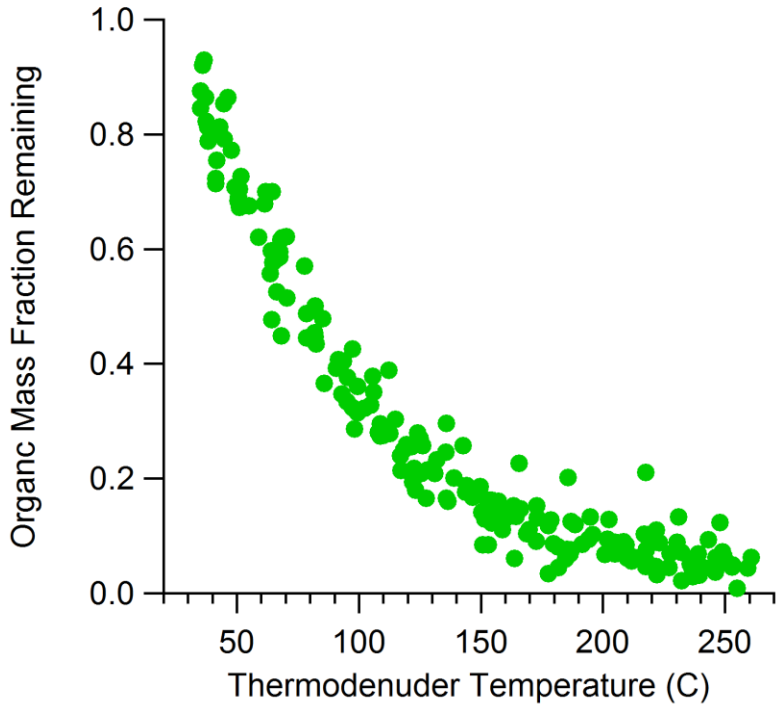


Figure S11. Organic mass fraction remaining as a function of temperature for Pasadena, California during CalNex 2010. Data correspond to 12:00 – 15:00 local time.