

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

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26

27 **ABSTRACT**

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

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

51 All the model cases evaluated in this work have a large majority of the urban SOA (70 –
52 83 %) at Pasadena coming from the oxidation of P-SVOCs and P-IVOCs. The importance of
53 these two types of precursors is further supported by analyzing the percentage of SOA formed at
54 long photochemical ages (1.5 days) as a function of the precursor rate constant. The P-SVOCs
55 and P-IVOCs have rate constants that are similar to highly reactive VOCs that have been
56 previously found to strongly correlate with SOA formation potential measured by the OFR.

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

63

64 1. INTRODUCTION

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

73 Due to this complexity, organic aerosol is often categorized into two groups. Primary
74 organic aerosol (POA) is directly emitted into the atmosphere from sources such as motor
75 vehicles, food cooking, and biomass burning (Hallquist et al., 2009). On the other hand,
76 secondary organic aerosol (SOA) is the product of diverse chemical reactions occurring in the
77 atmosphere that transform more-volatile precursors such as volatile organic compounds (VOCs)
78 into lower volatility products that are either incorporated into existing particles or form new
79 particles. Many previous studies have shown that SOA is an important fraction of OA globally
80 often representing more than half the total OA concentration (Zhang et al., 2007; Jimenez et al.,
81 2009).

82 In SOA parameterizations for use in regional and global models, a semi-empirical
83 approach is used in which VOCs, often the only SOA precursors considered, react with OH
84 radicals and other oxidants to form secondary products with lower volatility at a given mass
85 yield. These secondary semi-volatile organic compounds (SVOCs) can partition to the particle
86 phase to form SOA (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006). The parameters
87 used in the models for the VOCs, such as the yields and product volatilities, are often determined
88 from published chambers studies (e.g. Kroll et al., 2006; Chan et al., 2009; Hallquist et al., 2009;
89 Presto et al., 2010). Over the past decade a number of studies have shown that traditional models
90 that consider only the oxidation of VOCs alone predict SOA concentrations much lower than
91 those observed in polluted urban regions (Volkamer et al., 2006; Dzepina et al., 2009; Hodzic
92 and Jimenez, 2011; Hayes et al., 2015). As a result, several updates have been proposed in the
93 literature to improve SOA models including new pathways for SOA formation, new SOA
94 precursors, and increased yields for known precursors (e.g. Ng et al., 2007; Robinson et al.,
95 2007; Ervens and Volkamer, 2010).

96 The volatility basis-set (VBS) approach (Donahue et al., 2006) has been used in most
97 recent parameterizations of SOA yields. In this approach, the organic mass is distributed in
98 logarithmically spaced volatility bins, and the SOA forming reactions then redistribute the mass
99 from precursors such as anthropogenic and biogenic VOCs, into bins with generally lower
100 volatility (except for fragmentation reactions) leading to increased OA concentrations (Robinson
101 et al., 2007; Tsimpidi et al., 2010). While the VBS provides a valuable conceptual framework for

102 SOA modeling, substantial uncertainties remain in the correct parameters for different precursors
103 and conditions.

104 In this paper we focus on investigating three interrelated questions that are responsible for
105 important uncertainties in urban SOA modeling. The first is how to best incorporate SOA from
106 primary semi- and intermediate volatility compounds (P-S/IVOCs), two recently-proposed types
107 of SOA precursors. While there is now ample evidence that P-S/IVOCs are important
108 contributors to SOA (Robinson et al., 2007; Zhao et al., 2014; Dunmore et al., 2015; Ots et al.,
109 2016), the emissions of these precursors as well as the parameters that govern their oxidation and
110 SOA formation are not well constrained. Also, it is well known that models of SOA that
111 incorporate P-S/IVOCs often do not agree with measurements across a range of photochemical
112 ages, although the modeled SOA mass varies substantially with the parameterization used
113 (Dzepina et al., 2009; Hayes et al., 2015; Fountoukis et al., 2016; Woody et al., 2016). The
114 second question is whether losses of semi-volatile gases to the walls of environmental chambers
115 (Matsunaga and Ziemann, 2010; Krechmer et al., 2016) have resulted in low biases for the yields
116 of some or all precursors, especially VOCs, as has been recently reported (Zhang et al., 2014).
117 The third question is the appropriateness of including “aging” mechanisms in the VBS
118 parameterization of SOA from VOCs, in which the initial oxidation reaction is followed by
119 subsequent oxidation reactions of the first and later generation products, with each reaction
120 resulting in a reduction of the organic volatility by, for example, an order of magnitude. These
121 “aging” mechanisms increase VOC yields to levels much higher than those observed in chamber
122 studies since it was perceived that the yields may be too low in chambers compared to the real
123 atmosphere. The “aging” mechanisms were added to chamber yields that were obtained without
124 using aging as part of the fits of the chamber data. In some model applications they improve
125 model agreement with field measurements (Ahmadov et al., 2012), while at long photochemical
126 ages they lead to model SOA formation that is substantially larger than observed (e.g. Dzepina et
127 al., 2011; Hayes et al., 2015). While the inclusion of some of these new SOA precursors, updated
128 yields, and aging can provide in some cases better agreement with measurements, the relative
129 amount of SOA formed from VOCs (V-SOA), P-IVOCs (I-SOA), and P-SVOCs (S-SOA) is
130 highly uncertain, and changes strongly depending on which of the above updates are
131 implemented in a specific model. In addition, the fact that different subsets and variants of these
132 updates can allow specific models to match SOA measurements raises important questions
133 regarding whether or not the model mechanisms are representative of actual SOA forming
134 processes in the atmosphere.

135

136 The notation used when discussing SOA precursors in this paper is similar to Hayes et al.
137 (2015). We differentiate VOCs, IVOCs and SVOCs by their effective saturation concentration
138 (c^*). Therefore, SVOCs and IVOCs have volatilities ranging from $c^* = 10^{-2}$ to 10^2 and 10^3 to 10^6
139 $\mu\text{g m}^{-3}$ respectively, while VOCs are in the bins of $c^* \geq 10^7 \mu\text{g m}^{-3}$.

140 Recently, we evaluated three parameterizations for the formation of S-SOA and I-SOA
141 using a constrained 0-D box model that represents the South Coast Air Basin during the
142 California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign (Hayes
143 et al., 2015). Box models are often used to compare with ambient measurements, and have been
144 shown to be of similar usefulness or even superior to 3-D models if the emissions and
145 atmospheric transport affecting a given case study are well constrained, and if the use of ratios to
146 tracers can be used to approximately account for dispersion (e.g. Volkamer et al., 2006; Dzepina
147 et al., 2009; Hayes et al., 2015; Yuan et al., 2015). A box model allows the evaluation of
148 multiple model parameterizations either previously proposed in the literature or developed from
149 recent field and laboratory data sets, as well as the performance of sensitivity studies, all of
150 which would be difficult to carry-out in more computationally demanding gridded 3-D models.
151 There are six model cases presented in this paper that are described in further detail below.
152 Given the number of model cases (including three additional model cases from Hayes et al.
153 (2015)), it would be very computationally expensive to use a 3-D model to evaluate all the cases.

154 Moreover, there are important limitations to traditional comparisons of 3-D models'
155 predicted concentrations against measurements, as for example discussed for the Pasadena
156 ground site in Woody et al. (2016). In that study, the SOA predicted by the Community
157 Multiscale Air Quality (CMAQ) model with a VBS treatment of OA is a factor of 5.4 lower than
158 the measurements during the midday peak in SOA concentrations. This underestimation was
159 attributed to several different factors. First, the model photochemical age for the site was too low
160 by a factor of 1.5. In the box model presented in this current work, that problem is eliminated as
161 the photochemical aging of the urban emissions in the model is instead determined from the
162 measured ratio of 1,2,4-trimethylbenzene to benzene as described previously (Parrish et al.,
163 2007; Hayes et al., 2013). Second, it is difficult to distinguish errors due to model dispersion
164 from those due to emission inventories and photochemical age. Woody et al. (2016) conclude
165 that excessive dispersion or low emissions account for an error of about a factor of 2. Those
166 errors are also eliminated by the use of emission ratios in this work. After those errors are
167 accounted for, by analyzing the 3-D model output using similar techniques as in our box model,
168 the real under-prediction of SOA formation efficiency by a factor of 1.8 emerged, compared to
169 the initial value of 5.4 from the concentration comparisons. These errors (of approximately
170 300%) in the interpretation of 3-D model comparisons, which are ignored in most 3-D model
171 studies, are far larger than the uncertainties due to emission ratios or dispersion in our box model
172 (about 10 - 20%), as demonstrated in section 2.4.

173 In addition, there are uncertainties in the P-S/IVOC emissions inventories used in 3-D
174 models and in the methods used to estimate P-S/IVOC emissions from the traditional POA

175 inventories. In our box model, as described in further detail below, we incorporated recently
176 published field measurements of P-S/IVOCs to better constrain the concentration of these
177 species. Thus, while 3-D models are essential for simulating spatially and temporally complex
178 environments under the influence of many sources, in cases where transport is relatively simple
179 and there is a well-defined urban plume such in Pasadena during the CalNex campaign, the box
180 model is a valuable complementary or even superior approach that is less susceptible to the
181 convoluted uncertainties in 3-D models discussed above. Another reason to use a box model is
182 that it allows a direct comparison against OFR measurements taken in the field (Ortega et al.,
183 2016). The OFR provided (every 20 minutes at the Pasadena ground site) a measure of SOA
184 formation potential for a photochemical age of up to two weeks. To the best of our knowledge,
185 3-D models have not yet been adapted for comparison against OFR data. Finally, box models are
186 more widely usable by experimental groups (such as ours) due to reduced complexity, while 3-D
187 models are almost exclusively used by modeling-only groups, who tend to be more distant from
188 the availability, use, and interpretation of experimental constraints. Thus the use of a range of
189 models by a range of different groups is highly beneficial to scientific progress.

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

198 The goal of this study is to use several recently published results to better evaluate and
199 constrain the box model introduced in our previous work, and thus facilitate the identification of
200 parameterizations that can be eventually incorporated into 3-D air quality models to accurately
201 predict SOA for the right reasons. It is important to note that parameterizations used in the box
202 model are based on several published measurements taken from laboratory experiments and field
203 studies that provide more realistic constraints than in previous versions and that were not
204 available to be implemented in Hayes et al. (2015). In particular, our work here improves the box
205 model by incorporating recently published measurements of P-IVOCs and P-SVOCs that allow
206 better constraining of the concentration, reactivity, yields, and volatility of these precursors
207 (Worton et al., 2014; Zhao et al., 2014). In addition, given that experiments in environmental
208 chambers may underestimate SOA yields for the VOCs due to losses of semi-volatile gases to
209 the chamber walls (Zhang et al., 2014), the SOA yields from VOCs have been re-estimated using
210 a very recent parameterization of these wall-losses (Krechmer et al., 2016). The wall-loss
211 corrected yields obtained are then used in the model in a sensitivity study to evaluate the
212 corresponding change in the modeled SOA concentrations. The model is modified based on these
213 literature constraints. No model tuning is performed with the goal of improving the agreement

214 with the observations. The results obtained from the new box model are compared against
215 ambient ground site and airborne measurements, and also against recently-published oxidation
216 flow reactor (OFR) measurements (Ortega et al., 2016). This combination of data sets allows the
217 model to be evaluated for photochemical ages ranging up to 3 equivalent days (at 1.5×10^6
218 molec OH cm⁻³) providing a means to evaluate the aging mechanisms of the VOCs in the VBS.

219 **2. EXPERIMENTAL SECTION**

220 **2.1 Measurement and sampling site**

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

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

244 **2.2 Model set-up**

245 The SOA model is set-up to include 3 types of precursors: VOCs, P-IVOCs, and P-
246 SVOCs. The parameters used in the box model to simulate the formation of SOA from these
247 precursors are listed in Tables S1 to S3 of the supporting information. The box model
248 dynamically calculates the evolution of organic species in an air parcel as it undergoes
249 photochemical aging, hence producing SOA. The total SOA also includes background SOA

250 (BG-SOA) at a constant concentration of $2.1 \mu\text{g m}^{-3}$, as determined in our previous work (Hayes
251 et al., 2015). The model accounts for P-SVOC emissions from vehicular exhaust and cooking
252 and treats POA as semi-volatile (Robinson et al., 2007). It should be noted that the model uses
253 CO and NO_x as inputs to constrain the model, and the SOA yields for high- NO_x conditions are
254 used, based on our previous work (Hayes et al., 2013; 2015). Therefore, to verify model
255 performance both predictions of VOC and POA concentrations have been compared against field
256 measurements and the model performance appears to be satisfactory (Hayes et al., 2015).

257 A schematic of the model is shown in Figure 1. All the model cases are listed in Table 1,
258 and all the parameterizations are shown schematically in Figure 2. The first model case (ROB +
259 TSI) incorporates the Robinson et al. (2007) parameterization for SOA formation that models P-
260 IVOCs and P-SVOCs (i.e. P-S/IVOCs) using a single volatility distribution and oxidation rate
261 constant. The ROB + TSI case also uses the Tsimpidi et al. (2010) parameterization for SOA
262 formation from VOCs. A detailed description of the parameters used in ROB + TSI can be found
263 in Hayes et al. (2015), and the ROB + TSI model case used here is identical to the case of the
264 same name used in that paper. Briefly, as displayed in Fig. 2A, the Tsimpidi et al. (2010)
265 parameterization proposes that the VOCs undergo an initial oxidation step that will form four
266 lumped products with different volatilities ($c^* = 1, 10^1, 10^2, 10^3 \mu\text{g m}^{-3}$, where c^* is the effective
267 saturation concentration). The first-generation oxidation products can be further oxidized,
268 decreasing their volatility by one order of magnitude (i.e. aging). This “bin-hopping” mechanism
269 repeats until the lowest volatility product is reached ($c^* = 10^{-1} \mu\text{g m}^{-3}$ in this study and $1 \mu\text{g m}^{-3}$
270 in other studies such as Tsimpidi et al. (2010) and Hayes et al. (2015). The Robinson et al.
271 (2007) parameterization proposes that the P-S/IVOCs are initially distributed in logarithmically
272 spaced volatility bins ranging from $c^* = 10^{-2}$ to $10^6 \mu\text{g m}^{-3}$. Thereafter, the oxidation of P-
273 S/IVOCs decreases their volatility by one order of magnitude until the lowest volatility product
274 is reached ($c^* = 10^{-2} \mu\text{g m}^{-3}$). The lowest volatility product possible is not the same for the
275 oxidation of VOCs versus the oxidation of the P-S/IVOCs (10^{-1} vs. $10^{-2} \mu\text{g m}^{-3}$, respectively).
276 However, whether the mass is distributed into either bin has a negligible effect on the SOA mass
277 simulated in the box model because of the relatively high SOA concentrations during the case
278 study.

279 In this work, 5 model parameterizations are tested that incorporate new measurements of
280 IVOCs and P-SVOC volatility as well as updated VOC yields that account for wall-losses of
281 vapors (Zhang et al., 2014; Krechmer et al., 2016). For the first new case (ROB + ZHAO + TSI),
282 we incorporate IVOC data measured in Pasadena during the CalNex campaign as reported from
283 Zhao et al. (2014). In particular, the measured concentrations of speciated and unspciated
284 IVOCs and their estimated volatility are used to constrain the initial concentration of these
285 species (as discussed in Section 2.2.2 below) as well as to estimate their yields (Zhao et al.,
286 2014). Therefore, we replace the inferred concentrations of IVOCs that were used in our
287 previous work and based on the volatility distribution of Robinson et al. (2007) with
288 concentrations that are directly constrained by measurements. In the ROB + ZHAO + TSI case

289 the SOA formation parameters used (e.g. yields, oxidation rate constants) are taken from Zhao et
290 al. (2014) for the IVOCs and from Hayes et al. (2015) for the VOCs and SVOCs. Hodzic et al.
291 (2016) have also estimated the IVOC yields while accounting for wall-losses using recent
292 laboratory studies. However, the yields reported in that study are for a single lumped species,
293 whereas in our work we estimate the yields using 40 IVOC categories, each representing a single
294 compound or a group of compounds of similar structure and volatility. This method allows a
295 more precise representation of IVOC yields and rate constants in the SOA model.

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

307 Several recently published papers have found that chamber experiments may
308 underestimate SOA yields due to the loss of semi-volatile vapors to chamber walls (Matsunaga
309 and Ziemann, 2010; Zhang et al., 2014; Krechmer et al., 2016). A sensitivity study has been
310 performed to explore this uncertainty by running the three model cases described above (ROB +
311 TSI, ROB + ZHAO + TSI, and WOR + ZHAO + TSI) with a revised version of the SOA yields
312 for VOCs that accounts for these wall losses. A detailed description of how these updated yields
313 were estimated is provided in the supporting information and the values can be found in Table
314 S4. Briefly, equilibrium partitioning is assumed to hold for the organic mass found in the gas
315 phase, particle phase, or chamber walls. The SOA yields are then obtained by refitting SOA
316 chamber yield curves using a model that accounts for partitioning between the three
317 compartments (particle, gas, and wall) and incorporates the equivalent wall mass concentrations
318 published in Krechmer et al. (2016), which are volatility dependent. The SOA chamber yield
319 curves that were refitted were first calculated using the parameters published in Tsimpidi et al.
320 (2010). There are limits to the assumption that partitioning between the three phases occurs on
321 short enough timescales for all four VOC product volatilities that equilibrium is reached during
322 an SOA chamber study. Specifically, at lower volatilities ($c^* \leq 1 \mu\text{g} \text{m}^{-3}$), the partitioning
323 kinetics of the organic mass from the particles to the chamber walls have an effective timescale
324 of more than an hour, which is similar or longer than typical chamber experiments (Ye et al.,
325 2016). The limiting step in the partitioning kinetics is evaporation of SVOCs from the particles
326 to the gas phase, and therefore the exact rate of evaporation depends on the OA concentration in
327 the chamber.

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

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

350 The three model cases accounting for wall losses of organic vapors are named ROB +
351 MA, ROB + ZHAO + MA, and WOR + ZHAO + MA. For these cases, the aging of the
352 secondary SVOCs formed from the oxidation of VOCs was not included, since multi-generation
353 oxidation is not well-constrained using data from chamber studies that are run over relatively
354 short time-scales (i.e. hours). In addition, aging and correcting for wall-losses of organic vapors
355 have been separately proposed to close the gap between observed and predicted SOA
356 concentration from pre-2007 models, and are thought to represent the same "missing SOA
357 mass." Therefore, we run the model with one of these options at a time, as they are conceptually
358 different representations of the same phenomenology. The aging of secondary SVOCs formed
359 from the oxidation of P-IVOCs (and P-SVOCs) has been kept for all of the MA cases, however.
360 To our knowledge, P-IVOC and P-SVOC mechanisms proposed in the literature have always
361 included aging. A similar approach for correcting the yields as described above cannot be applied
362 to P-IVOCs because organics with low volatilities ($c^* < 10 \mu\text{g m}^{-3}$) will partition to chamber
363 walls very slowly, and SVOCs from P-IVOC oxidation tend to have lower volatilities than the
364 SVOCs formed from VOC oxidation (Tables S1 and S2). Indeed, when trying to refit the VOC
365 and IVOC yield curves, the model assuming equilibrium partitioning between particles, the gas
366 phase, and the walls was able to reproduce the yield curves for VOCs, but not for IVOCs. This

367 difference in the results is consistent with equilibrium not having been reached during the
368 chamber studies on the IVOCs, which produce a greater amount of lower volatility SVOCs when
369 compared to VOCs during oxidation. These lower volatility SVOCs have relatively slow
370 evaporation rates from the particles, which prevents the chamber system from reaching
371 equilibrium (Ye et al., 2016).

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

380 **2.2.1 IVOC oxidation parameterizations**

381 An important difference between the ROB + TSI and ROB + MA cases and the other four
382 cases that have been updated with the IVOC measurements of Zhao et al. (2014) is that in the
383 ZHAO cases, the first generation of IVOC oxidation distributes part of the product mass into
384 four different volatility bins ($c^* = 10^{-1}, 1, 10^1, 10^2 \mu\text{g m}^{-3}$) as is displayed in Fig. 2E. This IVOC
385 oxidation scheme is similar to that used for the first step of VOC oxidation (Tsimpidi et al.,
386 2010) as displayed in Fig. 2A and D, and has been used to model chamber measurements of
387 SOA from IVOCs (Presto et al., 2010). Contrastingly, in the ROB + TSI and ROB + MA cases, a
388 “bin-hopping” approach is used for all P-S/IVOCs where oxidation lowers volatility by only one
389 order of magnitude (see Fig. 2B and C). The Robinson et al. (2007) parameters are still used for
390 the formation of SOA from P-SVOCs in the ROB + ZHAO + TSI and ROB + ZHAO + MA
391 cases, but the parameters are only applied to primary emissions in c^* bins between 10^{-2} and 10^2
392 $\mu\text{g m}^{-3}$ inclusive (i.e. the volatilities corresponding to P-SVOCs).

393 **2.2.2. Determination of initial precursor concentrations**

394 In the ROB + TSI and ROB + MA cases, the initial concentration of P-S/IVOCs is
395 estimated as follows. The volatility distribution determined by Robinson et al. (2007) is assumed
396 to represent all P-S/IVOCs emitted (Dzepina et al., 2009). The total concentration of P-S/IVOCs
397 is then set so that the amount of P-S/IVOCs in the particle phase is equal to the initial POA
398 concentration. The initial POA concentration is determined from the product of the background-
399 subtracted CO concentration and the $\Delta\text{POA}/\Delta\text{CO}$ emission ratio (Hayes et al., 2015). While this
400 ratio may change due to evaporation/condensation or photochemical oxidation of POA, our
401 previous work (Hayes et al., 2013) has shown that $\Delta\text{POA}/\Delta\text{CO}$ does not change significantly at
402 the Pasadena ground site with observed photochemical age indicating that the ratio is insensitive
403 to the extent of photochemical oxidation. Furthermore, it was calculated that the ratio would

404 increase by 28% for an increase of OA concentration from 5 to 15 $\mu\text{g m}^{-3}$, concentrations that are
405 representative of this study. This possible source of error is substantially smaller than current
406 errors suggested for P-S/IVOC emission inventories in 3-D models, where current schemes are
407 based on scaling POA emission inventories with scaling factors that are not well constrained
408 (Woody et al., 2016). The same method is used for the other four model cases, but only the initial
409 concentration of P-SVOCs is estimated by this method and the initial concentration of P-IVOCs
410 is estimated separately as described in the next paragraph. In addition, in the WOR + ZHAO +
411 TSI and WOR + ZHAO + MA cases the volatility distribution of vehicular P-SVOCs reported in
412 Worton et al. (2014) is used for estimating the initial concentration of vehicular P-SVOCs
413 whereas the volatility distribution of Robinson et al. (2007) is used for estimating the initial
414 concentration of cooking P-SVOCs.

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

425 The initial concentrations of VOCs and IVOCs are calculated by multiplying the
426 background-subtracted CO concentrations measured at Pasadena by the emission ratios
427 $\Delta\text{VOC}/\Delta\text{CO}$ or $\Delta\text{IVOC}/\Delta\text{CO}$. In the ROB + TSI and ROB + MA cases this method is only
428 applied to the VOCs. The initialization method for the concentrations of the VOCs is the same
429 for all six cases in this paper. For the biogenic VOCs, we follow the same method as Hayes et al.
430 (2015) to determine the initial concentrations since these compounds are not co-emitted with CO.
431 The emission ratios are taken from the literature when available (Warneke et al., 2007; Borbon et
432 al., 2013). For most of the IVOCs and some VOCs, emission ratios are not available in the
433 literature. The ratios are instead determined by performing linear regression analyses on scatter
434 plots of the IVOC or VOC and CO concentrations measured in Pasadena between 00:00-06:00
435 local time when the amount of photochemical aging was very low. During the regression
436 analyses the x-intercept was fixed at 105 ppbv CO to account for the background concentration
437 of CO determined in our previous work (Hayes et al., 2013). Thus, the slope of the resulting line
438 corresponds to the estimated emission ratio ($\Delta\text{IVOC}/\Delta\text{CO}$).

439 It should be noted that the use of VOC emission ratios to CO to estimate VOC emissions
440 does not assume that VOCs are always co-emitted with CO. Rather, it assumes that VOC
441 emission sources are individually small and finely dispersed in an urban area, so that they are
442 spatially intermingled with the sources of CO. Moreover, previous studies have measured the

443 emission ratios of anthropogenic VOCs with respect to CO and the results show that vehicle
 444 exhaust is a major source of VOC and CO (Warneke et al., 2007; Borbon et al., 2013).
 445 Furthermore, the ratios are consistent both temporally and spatially. Thus, when thinking of the
 446 entire urban area as a source, the use of emission ratios to CO is justified. As shown in Hayes et
 447 al. (2015) in the supporting information, the modeled VOC concentrations are consistent with the
 448 measurements indicating that major VOCs sources have not been omitted, and the smooth time
 449 variations of the VOC concentrations support the use of a “global urban source”.

450 **2.3 SOA model**

451 The VOC yields are taken from Tsimpidi et al. (2010) or determined in this work as
 452 described below. The estimation of the IVOC yields (based on values taken from Presto et al.
 453 (2010) and of the OH reaction rate constants for IVOCs follows the same approach used by Zhao
 454 et al. (2014). However, instead of using the total SOA yield, Y , for a fixed OA concentration as
 455 reported in Zhao et al. (2014), we use the SVOC yield, α , of each c^* bin. It is important to note
 456 here that the SOA yields taken from Tsimpidi et al. and Presto et al. use a four-product basis set
 457 with $c^* = 10^0, 10^1, 10^2, 10^3 \mu\text{g m}^{-3}$ and $c^* = 10^{-1}, 10^0, 10^1, 10^2 \mu\text{g m}^{-3}$ respectively. For this box
 458 model, it is more appropriate to have a uniform VBS in terms of the bin range utilised so a bin
 459 with a lower volatility ($c^* = 10^{-1} \mu\text{g m}^{-3}$) has been added to the VBS distribution of Tsimpidi et
 460 al. (2010). The yield for bin $c^* = 10^{-1} \mu\text{g m}^{-3}$ is 0 for VOC oxidation, but when aging occurs
 461 mass can be transferred into this bin. However, the change in the total V-SOA mass is negligible
 462 because for both bin $c^* = 10^{-1}$ and $10^0 \mu\text{g m}^{-3}$ the secondary products almost completely partition
 463 to the particle phase.

464 The OH reaction rate constants are taken from the literature (Atkinson and Arey, 2003;
 465 Carter, 2010) as described previously in Hayes et al. (2015). During aging, the oxidation
 466 products undergo subsequent reactions with OH radicals with a reaction rate constant of 1×10^{-11}
 467 $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ and $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ for the products of VOC oxidation and P-S/IVOC
 468 oxidation respectively (Hayes et al., 2015). For each oxidation step during aging, there is a mass
 469 increase of 7.5 % due to added oxygen.

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

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

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

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

484 **2.4 Correction for changes in partitioning due to emissions into a shallower** 485 **boundary layer upwind of Pasadena**

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

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

514 so for photochemical ages beyond ambient levels observed at Pasadena, we focus our analysis on
515 the comparison with the OFR measurements.

516 **3. RESULTS AND DISCUSSION**

517 **3.1 Evolution of SOA concentration over 3 days**

518 We follow an approach similar to Hayes et al. (2015) in order to analyse the model
519 results. The model SOA concentration is normalized to the background subtracted CO
520 concentration to account for dilution, and the ratio is then plotted against photochemical age
521 rather than time to remove variations due to diurnal cycles of precursor and oxidant
522 concentrations. The photochemical age is calculated at a reference OH radical concentration of
523 1.5×10^6 molec cm⁻³ (DeCarlo et al., 2010). Figure 3 shows this analysis for each model case for
524 up to 3 days of photochemical aging. Since fragmentation and dry deposition are not included in
525 the model, it has only been run to 3 days in order to minimize the importance of these processes
526 with respect to SOA concentrations (Ortega et al., 2016). Nevertheless, it is very likely that gas-
527 phase fragmentation of SVOCs (e.g. branching between functionalization and fragmentation)
528 occurs during oxidative aging over these photochemical ages as is discussed in further detail
529 below.

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

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

548 In ROB + TSI, as described in previous work (Hayes et al., 2015), there is a large over-
549 prediction of SOA mass at longer photochemical ages. As displayed in Fig. 3, the amount of

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

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

578 The WOR + ZHAO + TSI case simulates higher SOA concentrations at shorter
579 photochemical ages compared to the previous case (ROB + ZHAO + TSI), but it is still biased
580 low at shorter photochemical ages. The more rapid SOA formation is due to the updated SVOC
581 volatility distribution in this model case compared to the cases that use the Robinson et al. (2007)
582 distribution. Specifically, as shown in Fig. 2F, there is a higher relative concentration of gas
583 phase SVOCs in the $c^* = 10^2$ bin and thus a higher ratio of P-SVOC to POA. Given that in the
584 box model (and in most air quality models) the P-SVOC emissions are determined by scaling the
585 POA emissions according to their volatility distribution, a higher P-SVOC to POA ratio will then
586 result in a higher initial P-SVOCs concentration. Furthermore, SOA formation from P-SVOCs is
587 relatively fast. Together these changes lead to increases in SOA formation during the first hours
588 of photochemical aging when using the Worton et al. volatility distribution. This case suggests

589 that P-SVOCs in their highest volatility bin ($c^* = 10^2 \mu\text{g m}^{-3}$ bin) that are emitted by motor
590 vehicles may be responsible for some of the observed rapid SOA formation within the South
591 Coast Air Basin. When observing the SOA mass simulated at photochemical ages higher than 1
592 day, the simulation is similar to ROB + ZHAO + TSI. There is better model/measurement
593 agreement than for the ROB + TSI case, but a small over-prediction is observed in the
594 comparison to the reactor data at 2 days of photochemical aging.

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

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

627 ZHAO + MA, WOR + ZHAO + MA) more accurately represents SOA formation in the
628 atmosphere.

629 According to the OFR data from Ortega et al. (2016), the mass of OA starts to decay due
630 to fragmentation after heterogeneous oxidation at approximately 10 days of photochemical
631 aging. The results are consistent with other OFR field measurements (George and Abbatt, 2010;
632 Hu et al., 2016; Palm et al., 2016). In this work, the model is run only up to 3 days, which is
633 much shorter than the age when heterogeneous oxidation appears to become important. In fact,
634 when including a fragmentation pathway for each of the model cases, a reduction of OA of only
635 6 % is observed compared to the cases without fragmentation at 3 days of photochemical aging.
636 In this sensitivity study, the fragmentation is parameterized as an exponential decrease in OA
637 concentration that has a lifetime of 50 days following Ortega et al. (2016). Given the results, the
638 inclusion of fragmentation due to heterogeneous oxidation in the model does not significantly
639 change the model results or the conclusions made in this work.

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

661 Despite having higher SOA yields initially, over regional scales (i.e. photochemical ages
662 at and above approximately 2 days) the parameterizations with updated V-SOA yields and
663 without aging produce less SOA, because the organic mass in higher volatility bins ($c^* = 100$
664 and $1000 \mu\text{g m}^{-3}$) is not further oxidized by aging reactions to produce organics with sufficiently
665 low volatilities to form SOA (Fig. S1 – S7). Furthermore, large SOA overpredictions have been

666 shown to occur in gridded 3-D models when using parameterizations with aging that do not
667 include fragmentation reactions (Shrivastava et al., 2015). Fragmentation with aging reactions
668 may still play a role in determining SOA concentrations on such regional scales. However for the
669 photochemical ages studied here, our results as well as the recent findings regarding gas-phase
670 wall losses in chamber studies, suggest the inclusion of updated V-SOA yields as well as
671 accurate parameterizations for I-SOA and S-SOA and for the emissions of precursors is more
672 important for accurately predicting urban SOA concentrations.

673 Finally, Woody et al. (2016) recently proposed a meat cooking volatility distribution and
674 therefore we perform a sensitivity study by using this distribution in our model for P-SVOCs
675 coming from cooking sources. The results are displayed in the supporting information (Figure
676 S8), where this alternate approach has been implemented for the WOR + ZHAO + TSI and WOR
677 + ZHAO + MA cases. By comparing the results obtained from this sensitivity study with Fig. 3,
678 the two cases in the sensitivity study display a slight decrease of SOA/ Δ CO values over 3 days of
679 photochemical aging with a difference of approximately 9 % at 3 days. Thus, the model-
680 measurement comparison does not change significantly relative to the base case. Given the
681 similarities between the sensitivity study and Fig. 3, as well as the possibility of cooking SOA
682 sources other than meat-cooking (i.e. heated cooking oils, Liu et al. (2017)), the remainder of our
683 work uses the Robinson et al. volatility distribution for P-SVOCs from cooking sources.

684 **3.1.1 SOA concentration estimated at Pasadena: fossil and non-fossil fractions**

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

692 Similar to the results in Fig. 3 and 4 for short photochemical ages, the SOA mass
693 simulated by the ROB + ZHAO + TSI case is biased low in Fig. 5A. The ROB + ZHAO + MA,
694 WOR + ZHAO + TSI, and WOR + ZHAO + MA cases show better model/measurement
695 agreement as the simulated SOA mass is within the measurement uncertainty or essentially equal
696 to the lower limit of the concentration that is defined by the measurement uncertainty. Fig. 5A
697 also allows evaluation of the contribution of each precursor type to the SOA at Pasadena. For the
698 four cases displayed, the P-SVOCs and P-IVOCs are responsible for 70 – 83 % of the urban
699 SOA formation. Thus, more than half of the urban SOA is attributed to these precursors even in
700 the MA parameterizations where the model is run with the updated yields, which doubles V-
701 SOA compared to the cases using the yields reported from Tsimpidi et al. (2010). Furthermore, 8
702 – 27 % of the measured urban SOA is due to V-SOA where the range of values is due to the

703 uncertainty in the measurements as well as the difference in simulated V-SOA concentration for
704 each case.

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

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

731 When comparing the fossil/non-fossil carbon split, all the cases are either in agreement
732 with the measurement within its uncertainty, or slightly lower. Starting with the ROB + ZHAO +
733 TSI case, the fossil fraction increases from 75 % to 79 % in each case as VOCs or P-SVOCs
734 from vehicle emissions have greater importance for SOA formation. While the uncertainties
735 reported in Zotter et al. (2014) were 71 ± 3 %, there are likely additional errors due to different
736 factors that may influence the model or measurements. For example, a portion of the P-IVOCs
737 may be from cooking sources rather than entirely from fossil sources as is assumed above (Klein
738 et al., 2016). Taking the WOR + ZHAO + MA case as an example, since it is the best performing
739 case in this work according to Fig. 5A, model/measurement agreement is obtained within
740 measurement uncertainties if one assumes that 19 – 39 % of P-IVOCs come from cooking
741 emissions. Ultimately, the differences observed in the comparison with the ^{14}C data are very

742 likely smaller than these errors discussed here, and it is concluded that all the model cases
743 perform equally well with respect to the fossil/non-fossil carbon split.

744 As reported in Gentner et al. (2012), emissions from petroleum derived fuels such as
745 diesel and gasoline have an important contribution to the formation of SOA. However, there
746 have been conflicting results regarding the relative contributions of diesel versus gasoline
747 emissions (Bahreini et al., 2012; Gentner et al., 2012). In this work, the relative contribution of
748 different SOA sources is estimated following a procedure similar to that previously published in
749 Hayes et al. (2015), and the results are shown in Figure S9 of the supporting information.
750 Briefly, the source apportionment method follows four steps. First, after classifying the SOA
751 mass from isoprene and terpenes as biogenic V-SOA, the remaining V-SOA is attributed to
752 gasoline emissions since the diesel contribution to V-SOA is small ($\sim 3\%$) (Hayes et al., 2015).
753 Second, for the diesel and gasoline contribution to S-SOA, $70(\pm 10)\%$ of HOA is emitted from
754 diesel vehicles with the remainder from gasoline vehicles (Hayes et al., 2013), and thus it is
755 assumed for the source apportionment that 70% (30%) of vehicular P-SVOCs are from diesel
756 (gasoline) vehicles. Third, the S-SOA from cooking sources is calculated separately in the
757 model, where the initial concentration of cooking P-SVOCs is estimated using the measured
758 CIOA concentration and the method described in Section 2.2.2 above. Lastly, the fractional
759 contributions to I-SOA mass is difficult to determine since there are still uncertainties about the
760 sources of IVOCs. According to Zhao et al. (2014), petroleum sources other than on-road
761 vehicles likely contribute substantially to primary IVOCs, but evidence exists that cooking may
762 be a source of IVOCs as well (Klein et al., 2016). Thus, while we attribute I-SOA to these two
763 sources, we do not distinguish the sources. The estimated source apportionment in Fig. S9
764 attributes urban SOA as follows: 4% to biogenic V-SOA, 22% to gasoline V-SOA, 9% to
765 gasoline S-SOA, 20 % to diesel S-SOA, and 16 % to cooking S-SOA. The remaining 29 % is I-
766 SOA that is either due to cooking or off-road emissions of P-IVOCs.

767 It should be noted that according to McDonald et al. (2015), the emissions from vehicles
768 have decreased over time (i.e. between 1970 and 2010) due to regulations in California. Warneke
769 et al. (2012) have observed also that the emission ratios of some SOA precursors (i.e.
770 $\Delta\text{VOC}/\Delta\text{CO}$) have remained constant between 2002 and 2010, while absolute concentrations
771 have decreased. On the other hand, cooking and off-road emissions are subject to different
772 regulations in California, and the ratios of cooking or off-road emissions to vehicular emissions
773 have likely changed with time, which means that the source apportionment results for urban
774 SOA presented here will be specific to 2010.

775 **3.2 SOA formation versus precursor oxidation rate constant**

776 Recent results from Ortega et al. (2016) point to the importance of fast-reacting
777 precursors for urban SOA during CalNex, and we can use their results to further evaluate our box
778 model. The fraction of SOA formed from each precursor class as a function of the precursor rate
779 constant is displayed in Figure 6. The right-axis of Fig. 6 shows the correlation (R^2) of different

780 VOCs with the maximum concentration of SOA formed using the OFR as a function of their
781 oxidation rate constants as reported in Ortega et al. (2016). This analysis of the OFR data allows
782 us to constrain the rate constants of the most important SOA precursors. A detailed description of
783 how the R^2 values were obtained can be found in Ortega et al. (2016). According to the R^2 data,
784 the VOC compounds that correlate best with maximum SOA formation potential are those that
785 have $\log k_{OH}$ rate constants ranging from -10.5 to -10.0. When comparing the percentage of SOA
786 mass simulated by the model with the observed R^2 values, all of the four cases are not entirely
787 consistent with the R^2 data. According to the model, more SOA mass is formed from precursors
788 in the bin ranging from -11.0 to -10.5 (the majority of mass formed comes from P-IVOCs) rather
789 than the bin ranging from -10.5 to -10.0. In contrast, the R^2 value is higher for the more reactive
790 bin. If either fast-reacting precursors were missing in the model, or if the rate constants of the
791 currently-implemented precursors were too small, then correcting either error would shift the
792 relative distribution shown in Fig. 6 towards faster-reacting SOA precursors. In turn, the trend in
793 the percentage of modeled SOA mass may more closely follow the trend in R^2 values.

794 **3.3 Volatility distribution of OA**

795 Based on the evaluations carried out up to this point on the six model cases, the WOR +
796 ZHAO + MA case seems to most closely reproduce the observations. Thus, the entire volatility
797 distribution of the OA, precursors, and secondary gas phase organics is analyzed for this model
798 case. Figure 7 shows this distribution for three selected photochemical ages: 0, 5, and 36 h. The
799 figure allows us to track the evolution of SOA and secondary gas phase organics from each
800 precursor class in terms of their concentration and volatility and also to evaluate the reduction of
801 precursor concentrations. For the model results, the volatility distribution of all organics resolved
802 by precursor class, except for the VOCs and P-IVOCs, can be taken directly from the model. To
803 determine the volatility distribution of the VOCs and P-IVOCs, the SIMPOL.1 method (Pankow
804 and Asher, 2008) is used to estimate the effective saturation concentration of each compound or
805 lumped species in the model. Also included in Fig. 7, in the bottom-right panel, is the observed
806 volatility distribution for the Pasadena ground site, which is an average of measurements
807 collected during 12:00 – 15:00 local time and corresponds to 5 h of photochemical aging. For the
808 measurements, the volatility distribution of VOCs was determined using GC-MS data (Borbon et
809 al., 2013) whereas the IVOC distribution is taken from Zhao et al. (2014). The volatility
810 distribution of SVOCs was determined using combined thermal denuder AMS measurements
811 (see the supporting information for further details).

812 For the volatility distribution of the model at time 0, the concentrations of P-SVOCs and
813 P-IVOCs monotonically increases with the value of c^* . However, a discontinuity in the mass
814 concentration exists between the $c^* = 10^2$ and $10^3 \mu\text{g m}^{-3}$ bins. This discontinuity can be
815 explained by several factors. First, the measured IVOCs mass concentration the $c^* = 10^3 \mu\text{g m}^{-3}$
816 bin is very low, and since the initial concentrations of IVOCs in the model are constrained by the
817 field measurements, the model will also have very low concentrations. Zhao et al. (2014) have

818 already noted that the concentration of P-IVOCs in this bin is relatively low when compared to
819 the volatility distribution from Robinson et al. (2007). Another possible explanation is the
820 presence of cooking sources, which in the model are responsible for substantial P-SVOC mass
821 (~50%) but may have a smaller contribution to the P-IVOC mass.

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

829 In Fig. 7, it is possible to compare the measured volatility distribution with the model
830 simulation at 5 h of photochemical aging. It should be noted that the relatively high
831 concentrations of VOCs in the model compared to the measurements are due to the model
832 containing VOCs for which measurements were not obtained in Pasadena. There are 47 VOCs
833 used in the model and only 19 VOCs were measured. However, the remaining VOCs have been
834 measured in other urban locations (Warneke et al., 2007; Borbon et al., 2013) and thus it is
835 assumed they are also present in the South Coast Air Basin. For this work, we include these 28
836 remaining VOCs by assuming that they are also emitted in the South Coast Air Basin with
837 identical emission ratios ($\Delta\text{IVOC}/\Delta\text{CO}$). When comparing only VOCs measured and modeled
838 (shown in hollow black bars), the results are consistent ($3.1, 3.6$ and $2.2 \mu\text{g m}^{-3}$ from $c^* = 10^7$ to
839 $10^9 \mu\text{g m}^{-3}$ bins versus $3.8, 3.7$ and $2.2 \mu\text{g m}^{-3}$ for the measurements). On the other hand, the
840 model appears to have a low bias for the concentrations of P-IVOCs ($0.16, 0.63, 0.89$ and $2.3 \mu\text{g}$
841 m^{-3} from $c^* = 10^3$ to $10^6 \mu\text{g m}^{-3}$ bins versus $0.21, 1.39, 2.65$ and $3.82 \mu\text{g m}^{-3}$ for the
842 measurements). This low bias is seen for each volatility bin and could possibly be explained by
843 either oxidation rate constants that are too high or $\Delta\text{IVOC}/\Delta\text{CO}$ ratios that are too low. The latter
844 explanation seems more likely given that the rate constants estimated using surrogate compounds
845 and structure-activity relationships for the unspiciated P-IVOCs are generally lower limits (Zhao
846 et al., 2014), which would result in a high bias rather than a low bias. The $\Delta\text{IVOC}/\Delta\text{CO}$ ratios
847 may be low because the photochemical age between 00:00 – 6:00 local time is not strictly zero,
848 and some oxidation may have occurred during the period used to determine the ratio values.
849 Emission ratios such as $\Delta\text{IVOC}/\Delta\text{CO}$ facilitate incorporating P-IVOC emissions into 3-D models
850 that already use CO emissions inventories, and the $\Delta\text{IVOC}/\Delta\text{CO}$ ratios reported here could be
851 used for this purpose. However, the resulting I-SOA concentrations should be considered lower
852 limits given that the emission ratios, and also the rate constants, are likely themselves lower
853 limits.

854 To further explore the impact of potential errors in the initial IVOC concentrations, a
855 sensitivity study has been carried out using initial concentrations calculated based on the

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

871 For the measurements of SVOCs, all the mass in bins lower than $10^{-2} \mu\text{g m}^{-3}$ are lumped
872 into this bin for Fig. 7 since the model does not contain lower volatility bins. In addition, the 10^1
873 and $10^2 \mu\text{g m}^{-3}$ bins are not well-resolved because the thermal denuder did not consistently reach
874 temperatures low enough (less than 37°C) to resolve SVOCs in this range of volatilities. Thus,
875 the $10^1 \mu\text{g m}^{-3}$ bin may contain some higher volatility particulate mass although this contribution
876 is expected to be small due to the low particle phase fraction of compounds in the $10^2 \mu\text{g m}^{-3}$ bin.
877 With these considerations in mind, the volatility distribution of the SVOCs is somewhat different
878 in the model compared to the measurements. Most notably, the model does not form a significant
879 amount of lower volatility SOA in the $10^{-2} \mu\text{g m}^{-3}$ bin, whereas the measurements have a much
880 higher concentrations in this bin. A factor that may explain this difference between the volatility
881 distributions is the lack of particle phase reactions that continue to transform SOA into lower
882 volatility products, a process which is not considered in the model. One example of a particle
883 phase reaction is the formation of SOA within deliquesced particles, including the partitioning of
884 glyoxal to the aqueous phase to produce oligomers as discussed in Ervens and Volkamer (2010),
885 although that specific mechanism was of little significance during CalNex (Washenfelder et al.,
886 2011; Knote et al., 2014). Alternatively, the use of an aging parameterization where the volatility
887 may decrease by more than one order of magnitude per oxidation reaction would also distribute
888 some SOA mass into lower c^* bins. Hayes et al. (2015) previously evaluated different
889 parameters for aging. However, the results from this previous study showed that substantial over-
890 prediction of SOA was observed when using the Grieshop et al. (2009) parameterization in
891 which each oxidation reaction reduced volatility by two orders of magnitude. New
892 parameterizations may be necessary to produce the observed SOA volatility and concentration
893 simultaneously (Cappa and Wilson, 2012). However, we note that the additional low volatility
894 organic mass will not significantly change SOA predictions in urban regions where OA

895 concentrations are relatively high. When comparing the total amount of particle phase SVOCs, it
896 seems that the model reproduces reasonably well the measurements (6.2 versus $9.0 \mu\text{g m}^{-3}$) as
897 expected based on the comparisons of the total SOA concentration discussed above. In addition,
898 the total amount of SVOCs (particle and gas phase) are similar (11.2 vs $11.8 \mu\text{g m}^{-3}$), although it
899 is difficult to determine from measurements the gas phase concentration of SVOCs in the $10^2 \mu\text{g}$
900 m^{-3} bin due to the lack of particle mass in this bin under ambient concentrations as well as the
901 limited temperature range of the thermal denuder system.

902 Recently, Woody et al. (2016) published a paper that modeled SOA over California using
903 the Environmental Protection Agency's Community Multiscale Air Quality Model that had been
904 updated to include a VBS treatment of SOA (CMAQ-VBS). As discussed in that paper, the
905 modeled P-S/IVOC emission inventories remain an important source of uncertainty in 3-D grid-
906 based models. In that previous study several different ratios of P-S/IVOCs-to-POA emissions
907 were evaluated against measurements, and it was found that a ratio of 7.5 gave the best
908 agreement between the CMAQ-VBS model and observations. From the results shown in Fig. 7 at
909 a photochemical age of 0 h, a P-S/IVOC-to-POA ratio of 5.2 is calculated. This ratio is different
910 from that determined by Woody et al. (2016), and may be biased low due to possibly low
911 $\Delta\text{IVOC}/\Delta\text{CO}$ emission ratios as discussed earlier in this section, but it serves as both a useful
912 lower bound and has the advantage of being determined from empirical measurements of
913 aerosols rather than by tuning a model to match measured SOA concentrations. As stated in
914 Woody et al. (2016), the higher ratio may compensate for other missing (or underrepresented)
915 formation pathways in SOA models or excessive dispersion of SOA in their model.

916 **4. CONCLUSION**

917 We have used several data sets from recently published papers to better constrain and
918 evaluate urban SOA formation pathways and precursors, especially P-SVOCs and P-IVOCs,
919 within a custom-built box model. The use of the box model facilitates the incorporation of these
920 new data sets as well as the evaluation of a number of model cases. All the model cases are able
921 to correctly simulate the fossil/non-fossil carbon split at the Pasadena ground site providing
922 support for the performance of the model. When measurements of IVOCs are used to constrain
923 the concentrations of P-IVOCs, such as in the ROB + ZHAO + TSI and ROB + ZHAO + MA
924 cases, a large improvement of the model at longer photochemical age is observed. However,
925 these model cases are still biased low at shorter photochemical ages. By constraining the P-
926 SVOCs additionally with measurements of those precursors, such as in the WOR + ZHAO + TSI
927 case, better model/measurement agreement is obtained at shorter photochemical ages, yet the
928 model is still biased low. Finally, the WOR + ZHAO + MA case, which incorporates state-of-
929 the-art measurements of P-SVOCs and P-IVOCs and also accounts for the effect of chamber
930 wall-losses on VOC yields, obtains model/measurement agreement within measurement
931 uncertainties at long photochemical ages. Although, it displays also a low bias at short
932 photochemical ages, which is similar to the ROB + ZHAO + MA case. This bias may be due to

933 low $\Delta\text{IVOC}/\Delta\text{CO}$ emissions ratios or IVOC oxidation rate constants for which the estimated
934 values are too low. It is also possible that additional sources or SOA formation pathways are
935 missing from the model. Moreover, a P-S/IVOC-to-POA ratio of 5.2 is determined, which can be
936 combined with POA emission inventories to constrain the emissions of P-S/IVOCs in gridded
937 chemical transport models.

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

949 Therefore, the model cases with updated VOC yields that account for chamber wall-
950 losses best reproduce the ambient and OFR data. However, while the WOR + ZHAO + MA case
951 appears to represent a slight improvement over the ROB + ZHAO + MA case, as well as over the
952 ROB + ZHAO + TSI and WOR + ZHAO + TSI cases, it is not possible to conclude that one set
953 of parameters is better than the other since the difference in the predictions for these 4 cases (15
954 % on average) is likely smaller than the uncertainties due to the model setup as well as the lack
955 of a gas-phase fragmentation pathway during aging. Moreover, uncertainties in the vapor wall-
956 loss corrected yields remain, and the correction of the yields has been performed here using data
957 from a limited number of laboratory studies. In particular, the effect of temperature and humidity
958 on gas-wall partitioning needs to be characterized. The results obtained in our work motivate
959 future studies by showing that SOA models using wall-loss corrected yields reproduce
960 observations for a range of photochemical ages at a level of accuracy that it is as good as or
961 better than parameterizations with the uncorrected yields.

962 In all six of the model cases, a large majority of the urban SOA at Pasadena is the result
963 of P-SVOC and P-IVOC oxidation. While this result alone cannot be taken as conclusive due to
964 the uncertainties in the model parameters, further evidence for the importance of P-SVOCs and
965 P-IVOCs is obtained by analyzing the percentage of SOA formed at long photochemical ages
966 (~1.5 days) as a function of the precursor rate constant. The P-SVOCs and P-IVOCs have rate
967 constants that are similar to highly reactive VOCs that have been previously found to strongly
968 correlate with SOA formation potential measured by the OFR.

969 Lastly, the modeled volatility distribution of the total (gas and particle phase) organic
970 mass between $c^* = 10^{-2}$ and 10^{10} ug m⁻³ is analyzed at three ages and compared against volatility-

971 resolved measurements. While the total concentrations of gas and particle phase SVOCs are
972 reasonably well simulated, at the same time there are important differences between the
973 measured and modeled volatility distribution of SVOCs. These differences highlight the need for
974 further studies of the chemical pathways that may give rise to SOA in low volatility bins at $c^* =$
975 $10^{-2} \text{ ug m}^{-3}$ and lower.

976

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984

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1254 **Table 1.** Summary of the model cases used in this paper.

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