Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS

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Response to Reviewer #1

We appreciate the reviewer's thoughtful and insightful comments. In response to the reviewer's comments, we have made efforts to more clearly define our terminology, most notably POA, SOA, SVOCs, and IVOCs. We believe this clarification helps to address many of the comments provided by the reviewer. Below follows responses to specific comments, with the reviewer's original comment followed by our response in **bold**.

Specific Comments:

P26746, L12: What is meant here by "semi-explicit OA treatment" and "SOA lumped by parent hydrocarbon"? The products forming SOA in this model are semi-volatile, as they are in the VBS model, correct? And are not most species treated via a 2-product framework, with the exception of isoprene?

We have revised the abstract, clarifying our definitions of the CMAQ-AE6 OA treatment and the CMAQ-VBS OA treatment. Specifically for CMAQ-AE6, we have revised the text to read:

Traditionally, CMAQ treats primary organic aerosols (POA) as nonvolatile and uses a 2-product framework to represent secondary organic aerosol (SOA) formation.

P26748, L2: The authors seem to be implying that an O:C > 0.3 indicates a large contribution from SOA. If this is their intention, this thought should be made explicit.

We have clarified this statement, adding we believe O:C > 0.3 suggests significant contributions from SOA. The text now reads:

"Average OA O:C ratios exceed 0.3 in southern California (Craven et al., 2013) suggesting significant contributions from SOA,"

P26751, L4: I do not entirely follow the arguments resulting from the statement that fragmentation is more important for biogenic SOA than for POA. I would think the appropriate comparison is between biogenic SOA and anthropogenic SOA from aromatic compounds, which are the species to which ageing is applied by default. The comparison between biogenic SOA and POA does not seem relevant here.

We agree that that the comparison for fragmentation from biogenic SOA and POA lacks relevance in this context. Our intent was to highlight the importance of fragmentation for biogenic SOA which we have revised the text to indicate without the comparison to POA. The text now reads:

"In excluding aging of secondary biogenic SVOCs in all but our sensitivity simulation, we effectively assume that the net result of functionalization (aging) and fragmentation, an important process for accurate predictions of biogenic SOA (Donahue et al., 2012b), does not increase biogenic SOA concentrations (Fountoukis et al., 2011)."

P26751, L8: It would be could if the authors could clarify further what they mean when they say that "a portion...of the OA mass [is] shifted from the POA to the SOA set." It would seem more appropriate to me to have the "SOA" set include all vapors and the "POA" set to include only condensed-phase material.

We have clarified this in the text, indicating this is a modeling methodology to track O:C.

"a portion…of the OA mass shifted from the POA to the SOA set (Koo et al., 2014). The transfer of oxidized primary SVOCs (i.e. POA) to secondary SVOCs (i.e. SOA) is used as a modeling technique to maintain accurate O:C ratios, a feature of the 1.5-D VBS used in CMAQ (Koo et al., 2014), using existing POA and SOA basis sets and avoid additional computational burden of added model species (e.g. oxidized POA basis set)."

Also, in an effort to clarify what each of POA, SOA, SVOCs, and IVOCs refer to in our framework, we have made an effort to more clearly define each of these terms for our study.

"Traditional CMAQ-AE6 nonvolatile POA is replaced in CMAQ-VBS with semivolatile POA, referred to here as primary SVOCs, comprised of primary gas and particle phase organics located in the primary anthropogenic basis set. In this framework, CMAQ-VBS POA is therefore primary SVOCs located in the particle phase."

"CMAQ-VBS also includes a formation pathway of SOA from the oxidation of IVOC emissions, where IVOCs represent gas phase compounds with volatilities between SVOCs and VOCs (C* values ranging from 10^4 to 10^6 µg m^{-3}). Most of these compounds are generally considered to either be missing from emission inventories entirely or mischaracterized as non-SOA forming compounds. The inclusion of IVOCs represents an additional SOA precursor mass introduced into the model relative to CMAQ-AE6."

"CMAQ-VBS semivolatile SOA is represented using secondary SVOCs (gas and particle phase) located in the secondary anthropogenic and biogenic basis sets."

P26751, L10: It is not clear here what is meant by "oxidized POA". Does this refer to "POA" vapors that are oxidized? It would be useful if the authors were to clarify the distinction between gases and condensed-phase material more explicitly. I am finding the POA/SOA distinction here to be somewhat difficult to follow. Along these same lines, the terms SVOC and IVOC could be more explicitly defined for the reader (especially in the context of P26751, L6-14 and how this relates to the information on the previous page). I think that it could be helpful to move the paragraph starting on Line 15 on P26752 to earlier in this section, probably before discussion of the SOA treatment.

Please see the response to the previous comment, which clarifies our definitions of POA, SOA, SVOCs, and IVOCs. We have also moved the paragraph starting on Line 15 of P26752 to before the discussion of the SOA treatment as recommended.

P26753: The discussion of some of the caveats associated with estimating S/IVOC emissions, especially source-specific emissions, is very helpful, although it would be even better if the authors were to put this in the context of more recent measurements and constraints on S/IVOC emissions in addition to the relationship with other model treatments. Some of this is provided later in the manuscript (P26763), but it would seem appropriate to include some discussion here.

We have added the following text to the manuscript in an effort to provide better context to S/IVOC emission estimates across modeling studies:

“Therefore, modeled S/IVOC emissions can range from 2.5 to 7.5x existing POA inventories to match measurements (which makes direct comparisons to existing inventories difficult) and remains a source of uncertainty in conducting and comparing models that include S/IVOCs.”

Figure 1: It would be useful if the authors were to put a box around the LA area to guide the reader to that location.

We have added a box around Downtown LA and Pasadena to this figure and updated the figure caption to reflect the update.

Table 3: It would be useful if the authors were to provide the equations used to calculate the statistical metrics.

We have updated the table to include equations for the statistical metrics.

Regarding the supplemental figures, it would be useful if the authors were to (a) have the figures included in the main text in order and (b) to include mention of all supplemental figures in the main text. The reader should be made aware of the content of the supplemental within the main text.

We have referenced each of figures and tables located in the supplement in the main body of the manuscript.

P26755, L27: The authors note that larger model-measurement gaps were seen during photochemically active periods when OOA concentrations were higher. In looking at Fig. 2, this is not abundantly apparent to the reader. After estimating some numbers off of the figure, it seems to me that this is not universally true. For example, the observed/model ratio on 4-June (when OOA is higher) is only ~2.3 but is ~3.3 on 8-June when OOA is lower. It would be useful if the authors were to formalize this thought through an explicit demonstration, for example by plotting the observed/model ratio as a function of observed OOA concentrations.

We had intended the model to measurement gaps to refer to the difference in OA mass. However, as the reviewer points out, when one instead uses the ratio of observed to modeled concentrations, apparent occurrence of large "gaps" changes. In order to clarify, we have revised the text to read:

"with the largest differences in modeled to measured OA mass generally occurring during photochemically active periods (e.g. 4 to 7 June).

Fig. 4 vs. Fig. S8: To facilitate comparison, it would be useful if the Fig. S8 were modified to separate the CMAQ HOA and CIOA.

Fig. S8 does separate CMAQ-VBS HOA and CIOA. We believe the reviewer may instead be referring to Fig S9. That said, Fig. S8 was a combination of the data from Fig. 4 a and b (CMAQ-VBS vs. AMS data), with no new data being presented on Fig. S8. Therefore we have removed it from the supporting information. We have also moved the information on Fig. S9 (CMAQ-AE6 vs. AMS data) to Fig. 4 c and d to help facilitate comparisons. While ideally we would separate CMAQ-AE6 HOA and CIOA similar to CMAQ-VBS, CMAQ-AE6 does not track these separately and instead only reports POA.

P26756, L21: I find the meaning of this sentence to be somewhat unclear in terms of what is meant by "theoretical partitioning" in the context of "AMS measured OA". Do they mean that the larger CIOA concentrations lead to lower concentrations of semivolatile vapors due to enhanced partitioning? I think this is the case, but it could be stated more explicitly.

In an effort to clarify, we have revised the text to read:

"To determine if partitioning alone explained the underprediction in modeled midday CIOA concentrations, we considered two potential scenarios. In the first scenario, we removed model OA bias by replacing modeled OA with AMS measured OA and then calculated the theoretical partitioning of modeled semivolatile CIOA vapors. Using the higher AMS OA concentrations, more semivolatile CIOA vapors partitioned to the particle phase and increased modeled CIOA concentrations by approximately 10% in the afternoon. In the second scenario, we treated the modeled CIOA as nonvolatile…"

P26757, L3: The authors conclude that the underprediction of CIOA even using nonvolatile CIOA indicates that emissions were low. Couldn't an overestimate of the boundary layer height, especially at night, also be a contributing factor when considering absolute values? The authors might consider normalizing by background corrected CO, as they do with the SOA, to account for issues of dilution.

We agree that modeling bias in the boundary layer heights could have a role in model performance for CIOA. However, Kelly et al. (2014) found CMAQ model performance for the boundary layer was generally good with the exception of the evening transition. During these hours, CMAQ underpredicted mixing, which increased concentrations. In recognizing that low emissions may not be the only reason for the underprediction, we have also added underpredictions may also be attributable to too high of dispersion, similar to one of the factors we considered for SOA.

P26757, L18-21: The authors conclude based on the nighttime underprediction that low emissions are likely the reason for the underprediction during the daytime, rather than photochemistry. However, if the diurnal emissions profile is incorrect, it may be that the daytime underprediction is due to photochemistry (and low emissions) while the nighttime underprediction is due to low emissions alone. I suggest that the authors need to make a stronger argument as to how the nighttime underprediction truly constrains the reason for the underprediction during the daytime given an uncertain emissions timing. It is argued that the slower growth of the CIOA during the daytime compared to SV-OOA is suggestive of low emissions, as opposed to photochemical influence, but isn't it possible that the reaction rates are different, leading to differences in the timing when coupled with transport?

We agree that it is difficult to determine directly from the data if emissions or photochemistry are more likely the cause for the underprediction of CIOA. Therefore, we have revised the text to indicate both as plausible causes.

Figure S11: The meaning of "POA" in this figure is unclear. Is this CIOA + HOA (total POA) or just the HOA-type? In the main text, "POA" seems to be used to mean "non-CIOA POA" (Section 3.2.2). Similarly in Fig. S12 This should be clarified and terminologies used consistently throughout. Perhaps the authors could adopt the terminology “oPOA” to indicate “other POA” aka non-CIOA POA.

In an effort to clarify, we have defined non-CIOA POA as non-cooking POA (ncPOA) throughout. We chose not use “oPOA” since it is often used to mean oxidized POA.

P26759, L2: The “opposite” behavior of the modeled non-volatile oPOA compared to the observed HOA is similar to that of the semi-volatile oPOA, correct? As stated, this makes it seem that such “opposite” behavior is only for the non-volatile treatment, but Fig. 4 suggests that there is a similar “opposite” behavior for the semi-volatile case.

We agree that the semivolatile other POA diurnal pattern, albeit muted, is similar to the nonvolatile other POA diurnal pattern. We have therefore revised the text to read:

“The resulting diurnal pattern (Fig. S3) was higher in the morning and evening, with a minimum in the afternoon, similar to the more muted diurnal pattern of the semivolatile treatment (Fig. 4a) but opposite the AMS measurements (lower in the morning and evening, peaked in the afternoon).”

P26759, L17: Is this discussion associated with “ageing” in the context of POA indicating that including some SOA as POA would help? This is not entirely clear to me, I think in part due to my not entirely understanding the model definitions of POA and how/whether the “POA” category includes SOA (here, I think, referred to as oxidized POA). It would be useful if this could be clarified here and/or within the methods section.

We have attempted to clarify this both here and in the methodology section. In the methodology section, we have more clearly defined SVOCs, IVOCs, POA, and SOA and how oxidized POA is represented (66-90% POA depending on the level of oxidation). We have specifically revised the text here to read:

“Alternative aging schemes…generally produce more OA mass…and if applied to primary SVOCs could better represent the ncPOA midday peak (Hayes et al., 2015) since the majority of aged primary SVOCs (i.e. oxidized POA) remains as primary SVOCs/POA.”

P26759, L26: Regarding the conclusions associated with the NEI, again I think that it would be helpful if the authors were to more explicitly define their categorizations of what counts as POA. I find it somewhat difficult to understand how underestimates of SVOCs leads to underestimates of POA, unless oxidation of SVOCs produces POA. I think that it does in this model, but I am finding the terminology to be difficult to follow. I think that the authors could make this work more easily readable by adopting more precise language. For example, if their POA really equals POA + some fraction of oxidized SVOCs, then a better name would be POA+SVOCOA (or something like that, as I realize that is a cumbersome terminology). But even that might not be sufficient, because if I am understanding correctly some fraction of SVOCs contributes to a different SOA category. Ultimately, I strongly encourage the authors to rethink their overall terminology to make it more easily accessible to the reader.

We have made efforts to more clearly define our definitions of POA, SVOCs, SOA, etc in the methodology section which we believe will provide clarity here.

P26760, L9: It would be useful if the authors were to point the reader to a figure or table at this point. Perhaps Fig. 3 and Fig. 4. Along these same lines, it would be useful if the authors were to move some of the additional information (specifically the LV-OOA and SV-OOA diurnal profiles) in Fig. S8 to Fig. 4b.

We have added a reference to Fig. 4b here as well as added diurnal profiles of LV-OOA and SV-OOA from Fig. S8 to Fig. 4b.

P26760, L12-13: It would be useful if the authors were to note that the cited studies were not for LA but for other urban regions.

We have noted these studies were not specific for LA by revising the text as follows:

"This is consistent with many regional air quality studies (Volkamer et al., 2006; De Gouw et al., 2008), including CMAQ (Foley et al., 2010), which often underpredict urban SOA. Although those studies are not specific for LA, the similarity of tracer-normalized SOA concentrations across urban areas (e.g. De Gouw and Jimenez, 2009; DeCarlo et al.,2010; Hayes et al., 2015; Zhang et al.,2015) supports the occurrence of a general urban SOA under-prediction with models.

P26762, L2: The authors use –log(NOx/NOy) to estimate photochemical age and compare observed values at Pasadena to their modeled values. They conclude that the modeled photochemical age was too small by a factor of 1.5. However, doesn't this analysis also rely on the spatial distribution of NOx emissions being correct? NOx is converted to NOy over time, but if the NOx inputs are too low or too high along the transport pathway then the photochemical age will be incorrect. It could potentially be useful to also consider the NOx/CO ratio. Or, potentially, the toluene/benzene ratio (although the timescales may be too short for this to be a useful photochemical clock). Also, I find the second half of this sentence to be difficult to follow, in particular the section starting "...but not on SOA." I suggest the authors might be more explicit here.

We agree that NOx/NOy as a proxy for photochemical age has limitations. However, photochemical age estimated by measurements (Hayes et al., 2013) was similarly estimated using NOx/NOy. Therefore, it provided the best means to compare model and measurements. With regard to second half of the sentence, we have revised the text as follows:

"…which helps explain part of the underprediction in SOA concentrations (Figs. 3 and 4) but not underpredictions of SOA production efficiency (Fig. 5) (i.e. the efficiency per unit precursor at a given age)."

Fig. 5: What should the reader take away of the apparent intercept in Fig. 5a not being 0? If the fit were performed without constraining the fit to go through zero, a steeper slope would likely be obtained, correct? In Fig. 5b, is there a reason that the authors chose to not present the model results in the same manner as in Fig. 5a, i.e. using a Gaussian density kernel estimate to colorize the points? There seem to be a lot of points in the CMAQ-VBS simulations that fall along a line with much lower slope than the fit slope, which was forced through zero. The authors should also note in the main text (and/or the caption) that the fits were forced through zero.

Though the presentation of point density appears to suggest otherwise, we made no alterations to the slope or y-intercept (0.0002) of the best-fit line for CMAQ-VBS.

We chose not to include the Gaussian density kernel estimate of density on Fig. 5b since it includes points for both CMAQ-VBS and CMAQ-AE6 and adding another dimension (i.e. colors for density) would make the plot difficult to read and interpret.

P26763, L1-5: The authors concluded that the SOA production efficiency was underpredicted by a factor of 1.6-2. They note that Zhang et al. (2014) indicated a potential underestimate in SOA production by a factor of 2-4 from losses of SVOCs to chamber walls, but also that this was only for alkanes and toluene and was specific to the chamber used. They then conclude that SVOC wall loss does not likely account for the entire underestimate of SOA production efficiency. I do not entirely see how this conclusion is justified based on the statements given. As a hypothetical, what if the losses were greater in other chambers? Also, a factor of 2-4 is greater than a factor of 1.6-2. I suggest that the authors revisit the justification for this conclusion.

Our interpretation of the Zhang et al. (2014) results was that the 2-4 factor was an upper bound estimate based on other studies. However, we failed to reference these other studies in support of our conclusion. We have revised the text to include these references and provide further justification for our conclusion:

"However, the factor of 4 is for alkane systems (speciated long alkanes are not considered SOA precursors in CB05) and toluene and specific to the smog chamber used in Zhang et al. (2014). Other studies have generally reported lower values, ranging from 1.2 to 4.1 for low-NO_x conditions and 1.1

to 2.2 for high-NO_x conditions (Ng et al., 2007; Chan et al., 2009; Chhabra et al., 2011; Loza et al., 2012; Cappa et al., 2013). Therefore, the 2-4 factor likely represents an upper bound and SVOC wall loss does not likely account for the entire underestimate of SOA production efficiency."

P26763, L13: The authors note that the use of the results of Jathar et al. (2014) to update the IVOC emissions and parameterization in CMAQ-VBS could help to bridge the gap between model and measurements, and then go on to perform some sensitivity tests by scaling up the S/IVOC emissions. However, it would be useful if the authors were to more specifically make a connection with the Jathar et al. work. What does that work imply about what is correct? Are the test simulations consistent with those results?

Our hypothesis was that better constrained IVOC emissions from Jathar et al. (2014), who indicated SOA formed from IVOCs dominated total SOA formed from combustion emissions, and yields could account for some of the missing CMAQ-VBS SOA mass. Our goal was to test how much of the missing SOA mass S/IVOC emissions could account for using upper bound S/IVOC emissions. However, this connection was unclear. In an effort to clarify our intentions, we have revised the text to read:

"Current CMAQ-VBS IVOC emissions are scaled to primary SVOC emissions (1.5x) based on the results of a diesel generator (Robinson et al., 2007) and could potentially be updated to utilize more recent results, such as those reported by Jathar et al., 2014 who indicated unspeciated organics (S/IVOCs) dominated SOA mass formed from combustion emissions. Future work is needed to explore if better constraining IVOC emissions and yields in CMAQ would help improve model performance, but it would likely not account for the entire missing SOA mass based on sensitivity simulations using upper bound S/IVOC emissions. In these simulations, S/IVOC emissions were increased…"

P26764, L11: Are the measurements referred to here from Baker et al. (2015) or Zotter et al. (2014)? This should be clarified. Also, it would be useful if the authors could indicate (a) by how much >1 the non-fossil fractions were and (b) why contributions form a medical waste incinerator would lead to an estimated non-fossil fraction > 1.

The measurements were from Baker et al., (2015). To clarify, we have seperated the clauses referencing Baker et al. (2015) and Zotter et al. (2014). The text now reads:

"to compare CMAQ-VBS…against filter-based measurements collected at Pasadena (Fig. 6) (Baker et al., 2015). Those measurements indicated, on average, a near even split of non-fossil (48%) and fossil (52%) carbonaceous mass (Baker et al., 2015). The Baker et al. (2014) non-fossil measurements were also consistent with other collocated ^{14}C measurements collected during the same time period (51% non-fossil) (Zotter el al., 2014)."

The values for the non-fossil fractions > 1 ranged from 1.1 to 3.3. The fractions are based on an assumed non-fossil ^{14}C concentration of approximately 1.2 x 12^{-12} $^{14}C/C$ (Buchholz et al., 2013).

Medical incinerators emit ^{14}C tracers and can therefore produce ^{14}C concentrations > 1.2 x 12^{-12}, biasing the non-fossil fraction to values > 1. We have updated the text to reflect these clarifications as follows:

On 6 days the measured non-fossil fraction was >1 (values >1 ranged from 1.1 to 3.3)…The non-fossil fraction estimates assume a non-fossil ^{14}C concentration of 1.2 x 12^{-12} $^{14}C/C$ and emissions from medical incinerators, which contain ^{14}C, can bias the $^{14}C/C$ ratio (Buchholz et al., 2012).

Section 3.3: After reading through this section a few times, I suggest that addition of a summarizing table could be quite helpful that has entries for the different combinations of species considered (e.g. CMAQ-VBS fossil fraction with EC and without EC).

We have added a table summarizing the CMAQ-VBS and observed non-fossil C, fossil C with EC, and fossil C without EC.

Fig. 8: It would be very useful if the authors were able to split their “A_AGE” category into aged SOA originating from VOCs versus that from IVOCs. Also, I do not see the “B_IVOC” category in the figures, although one is indicated in the caption. To which species does this refer? Finally, it would be useful if the authors were to include the total AMS OOA on this figure, for comparison and reference to Fig. 4. Clearly, the predicted OOA is still greatly underpredicted even after addition of ageing of biogenic species.

We have split the “A_AGE” category into aged SOA originating from VOCs and IVOCs. The reference to “B_IVOC” was a typographical error and it has been removed from the figure caption.

We agree that including AMS OOA on the figure would help facilitate comparisons. However, given the large underprediction, including the measured OOA would alter the scale of the y-axis and compress the modeled contributions to the point they would be difficult to discern.

P26767, L21: While I agree that the ageing scheme represents a “technique to increase model SOA yields,” I find the words “similar to” in the context of the Zhang et al. (2014) findings to be a bit awkward as these refer to different physical processes. Additionally, Zhou et al. (2015, ES&T, 49, 2245−2254) demonstrate that the addition of ageing on top of existing parameterizations leads to an overprediction of SOA concentrations in chamber experiments, suggesting that such increases in SOA concentrations may result for the wrong reason. I suggest instead the authors state something to the effect of “The results indicate the majority of SOA was formed from aging, representing a technique to increase model SOA yields. Although via a different process, the resulting outcome is similar to that obtained if SOA yields are increased to account for SVOC losses to chamber walls, as proposed by Zhang et al. (2014) and used with CMAQ-AE6 in Baker et al. (2015). Also, although the inclusion of ageing reactions leads to an increase in SOA concentrations, this may be for the wrong reason as recent model-measurement comparisons with chamber experiments suggest that including ageing reactions on top of existing parameterizations can lead to overprediction of SOA concentrations (Zhou et al., 2015)." In other words, I think that a similar caveat as was included for the scaling up of S/IVOC concentrations is required.

We agree that the wording, particularly the use of "similar to", in the context of these two different physical processes could be improved. Based on the reviewer's recommendation, we have revised the text to read:

"Although via a different process, the resulting outcome is similar to that obtained if SOA yields are increased to account for SVOC losses to chamber walls, as proposed by Zhang et al. (2014) and used with CMAQ-AE6 in Baker et al. (2015). Also, although the inclusion of aging reactions leads to an increase in SOA concentrations, the model parameterization may overemphasize the contribution from aging as recent model to measurement comparisons with chamber experiments suggested the addition of aging reactions on top of existing parameterizations can lead to overpredictions of SOA concentrations (Zhou et al., 2015)."

P26767, L25: I suggest that this is reworded. The models do not, in my view, "utilize comparable SOA yields." The yields from the models are not constant values, but the result of specification of semi-volatile product yields that produce SOA. I suggest instead that they simply change "utilize" to "produce." Here, also, the Figure numbers should be given and the figures reordered.

We agree that "produce comparable SOA yields" is a more accurate statement and have revised the text to reflect this change. We have also provided the figure numbers for the yield curves in the supplement and reordered the figures.

SIMPLE model: I suggest that a line for the SOA/CO slope from the simple model be added to Fig. 5.

We have added the SIMPLE model slope to Fig. 5 as recommended.

General note on Figures: Many have relatively small axes labels. I encourage the authors to make sure that the labels are sufficiently large such that when formatted into a final article they remain easy to read.

We have increased the size of axes labels.

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Secondary Organic Aerosol with Smog-Chamber Experiments, Environ. Sci. Technol., 49, 2245–2254, 2015.

Response to Reviewer #2

We appreciate the reviewer's time and effort to provide thoughtful and thorough comments. We have incorporated the reviewer's comment into the manuscript in an effort to clarify the text.

Regarding the reviewer's comment of VBS SOA performance compared to other studies, the reasons for varying performance are numerous (e.g. differences in models, scales, VBS implementations, emission inputs, volatility split of emissions, chemical mechanisms, etc.). Specific to the studies that provide metrics for SOA performance (Hodzic et al., 2012; Shrivasta et al, 2011; and Fountoukis et al., 2015), two (Hodzic et al., 2012; Shrivasta et al, 2011) used considerably higher SVOC and IVOC emissions (7.5x POA inventory) to achieve good SOA performance compared to measurements.

Below are responses to the reviewer's specific comments, with the reviewer's original comment shown followed by our response in **bold**.

Abstract

1. Please explain briefly the general characteristics of CMAQ-VBS against the CMAQAE6 simulation runs so as the reader can understand why there is an underestimation. In line 9 and line 12 the authors report this in parenthesis but it is insufficient. Please delete the parenthesis and explain a little bit more in a separate sentence.

We provided a greater level of detail of how the OA treatment in CMAQ-AE6 differs from CMAQ-VBS. The text now reads:

"Traditionally, CMAQ treats primary organic aerosol (POA) as non-volatile and uses a 2-product approach to represent secondary organic aerosol (SOA) formation. CMAQ-VBS instead treats POA as semivolatile and lumps OA using volatility bins spaced an order of magnitude apart."

2. Line 10. Please replace NMdnB with NMB throughout the whole manuscript

NMdnB is commonly used to abbreviate normalized median bias to avoid potential confusion with normalized mean bias (NMB) (e.g. Appel et al., 2008; Foley et al., 2010; Bash et al., 2014). We have not made the reviewer's recommended change to also avoid confusion and to continue the precedence established by previous work.

3. Line 23. Please explain what the term "intrinsic SOA" means before starting using it.

The use of "intrinsic", or inherent, is used to describe the model's SOA formation efficiency ("intrinsic SOA formation efficiency"). We did not intend for it to be interpreted as a new term ("intrinsic SOA").

4. Line 20-24. This sentence is too big and too problematic. "based on species ratios", which species and what rations? "SOA parameterization from the observation", you mean SOA parameterization based on observations? In that case what kind of observations? The parenthesis used here are also confusing.

In an effort to provide clarification and answer questions raised by the reviewer, we have revised this sentence to read:

"We use two new methods, one based on species ratios (SOA/ΔCO and SOA/Ox) and another on a simplified SOA parameterization based on AMS observations, to apportion the SOA underprediction for CMAQ-VBS to too slow photochemical oxidation (estimated as 1.5×lower than observed at Pasadena using−log(NOx : NOy)), low intrinsic SOA formation efficiency (low by 1.6 to 2× for Pasadena), and too low emissions or excessive dispersion for the Pasadena site (estimated to be 1.6 to 2.3× too low/excessive)."

5. Line 27. "too low by about 7x". In comparison to what?

The 7x refers to comparisons against observations. We have revised the text to read:

"too low by about 7x compared to observations."

6. Page 26747, line 3-8. Too big sentence. Please make shorter. Replace "compared to " with "followed by"

We have broken the sentence into two to make it shorter as requested by the reviewer. However, we did not replace "compared to" with "followed by" since we are not intending to rank the sources (note: "other" sources, which comprise 13%, is listed last). The revised text now reads:

"From source-apportioned model results, we found most of the CMAQ-VBS modeled POA at the Pasadena CalNex site was attributable to meat cooking emissions (48%, and consistent with a substantial fraction of cooking OA in the observations). This is compared to 18% from gasoline vehicle emissions, 13% from biomass burning (in the form of residential wood combustion), and 8% from diesel vehicle emissions. All "other" inventoried emission sources (e.g. industrial/point sources) comprised the final 13%."

7. Page 26747. How you estimated the 1.7 factor? This is based on SVOCs measurements?

The 1.7 factor was estimated by comparing AMS measured to modeled POA concentrations. We have updated the text to include the factor was estimated using AMS measurements.

"Using AMS measurements, we estimated…"

Methodology

The structure of this section is inadequate. In several paragraphs the authors repeat same or similar information. The flow of the text would be greatly improved if the authors separate this section in subsections (i.e. 2.1 Model Description and Application, 2.2. Meteorology, 2.3 Emission Inventory, 2.4 Senstivity Simulations, 2.5 Measurements etc.). In addition this will help the reader to understand the main features of the model which unfortunately it is very difficult to be identified with the current format of this section.

As recommended, we have reorganized this section by adding the following subsections: Model Application; CMAQ-VBS OA Treatment; Emissions; Sensitivity Simulations; Meteorology, Boundary and Initial Conditions; and Measurements.

8. Page 26750, line 8. Please report the actual value of the C* for the non-volatility bin used in the model. If it is set to 0 then you can mention that under typical atmospheric conditions at Pasadena this bin can represent all the compounds with C*≤ 10-1 μg m-3.

For the nonvolatile bin, C* = 0. We have updated the text to include this and that this would represent compounds with a C*≤ 10^{-1} μg m^{-3} at typical ambient conditions in Pasadena.

9. Page 26750, line 10. Please rephrase. The sentence is too big and too confusing. From my understanding the authors assumed that IVOCs are represented as a naphthalene-like surrogate specie and therefore they used the aerosol yield of ARO2 (which includes naphthalene).

To clarify, we have rephrased this sentence to the following two sentences:
SOA yields from IVOC precursors are based on the Murphy and Pandis (2009) yields for the SAPRC ARO2 model species (Koo et al., 2014). ARO2 was used because it represents naphthalene (among other compounds), where naphthalene has previously been used as a surrogate to represent IVOCs (Pye and Seinfeld, 2010).

10. Page 26752, line 8. What is the 10% here? (a) The 10% of the oxidation product is allowed to move to SOA and the rest remains as POA? Or (b) all the oxidation product is moved to SOA which is calculated to be approximately 10% of the reacted POA? If the (a) is correct then explain more the rationale behind this assumption. If (b) is correct please report this in your results and not here.

The 10% is meant to represent (a). To clarify, we have revised the text as follows:
"…and a portion (~10%) of the OA mass shifted from the primary SVOC (POA) to the secondary SVOC (SOA) set (Koo et al., 2014). The transfer of oxidized primary SVOCs (i.e. POA) to secondary SVOCs (i.e. SOA) is used as a modeling technique to maintain accurate O:C ratios, a feature of the 1.5-D VBS used in CMAQ (Koo et al., 2014), using existing POA and SOA basis sets and avoid additional computational burden of added model species (e.g. oxidized POA basis set)."

11. Page 26752, line 12-14. So a compound after 4 oxidation steps is still considered as POA? This is not correct. It should be compared against OOA and not HOA.

We agree that oxidized POA should be compared against OOA rather than POA but the modeling framework does not allow such a comparison. We found that oxidized POA represented < 10% of OA mass and therefore has only a small impact on our results. We have also added the following text to acknowledge the added uncertainty in using this approach:

"With this treatment, the majority (~90%) of slightly aged POA (after a single aging reaction) resides as POA-like while very aged POA (after four aging reactions) would reside as two-thirds POA and one-third SOA. We acknowledge this approach, which prioritizes O:C ratios, adds uncertainty when model results are compared against AMS measurements and is an area where future research is needed to better understand that uncertainty. At Pasadena, our model predictions indicated~8% of modeled OA was comprised of oxidized POA and suggests this approach has only a small impact in this application."

12. Page 26752, line 11-14. How much of the total OA is coming from the boundaries in your domain? You have to make a simulation without emissions to verify the assumption that is reported here.

Based on a CMAQ-AE6 simulation, approximately 1% of total OA at Pasadena is attributable to boundary conditions. We have updated the text to the following:

"Neither larger scale simulation included CMAQ-VBS OA species, though the impact is likely small as a CMAQ-AE6 sensitivity simulation indicated most (99%) of the OA at Pasadena originates from local or regional sources located in our modeling domain."

13. Page 26752, the paragraph that begins in line 15. Here is an example of how confusing is this section. 4 paragraphs before this, the authors give some information of how SVOCs are treated in their model, then there is a paragraph with the model domain (which actually will fit better in the first paragraph of this section), then a paragraph with emissions used, then a paragraph with the meteorology, and then here they have an additional paragraph which again has information on emissions and how SVOCs are treated by their model. Please follow a more detailed structure and try not to repeat similar information.

As recommended, we have reorganized the entire methodology section.

14. Page 26752, line 26-28. Does the underlying chemical mechanism include species that are considered SVOCs or IVOCs ($C^* \leq 106$)? If yes please give a couple of examples. If it includes only VOCs then there is no double counting.

The technique to recycle OH in reactions with SOA precursors is commonly used in CMAQ (e.g. benzene and toluene) as these species are not explicitly represented in the gas-phase mechanism. Instead, generic model species (e.g. paraffins, olefins, nonreactive, etc.) are used to represent the gas-phase ozone chemistry and explicit species are used to represent the SOA chemistry. To clarify, we have revised the text as follows:

"OH is artificially recycled (i.e. not depleted) in oxidation reactions of IVOCs and SVOCs (primary and secondary) to prevent double counting and impacts to the gas-phase chemistry of the underlying chemical mechanism as these species are likely already represented in the model (e.g. paraffins, olefins, nonreactive, etc.). This technique is identical to that used by a number of existing CMAQ SOA precursors (e.g. benzene and sesquiterpene)."

Results and Discussion

15. Page 26755, line 2. Delete "modeled OA".

We have made the recommended deletion.

16. Page 26755, line 15. Replace "or improve" with "resulting in degraded"

We have made the recommended deletion.

17. Page 26756, line 6-8. If CMAQ-POA includes OA from biomass burning emissions you have to compare the CMAQ-POA against the sum of AMS HOA and BBOA. Furthermore, you have to add LOA in the comparison. Is there any indication (or interpretation) on what is LOA (oxidized or not)? If it is considered aged material it has to be added to the comparison against CMAQ-SOA while if it is considered fresh it has to be compared against POA. Overall, you cannot compare all CMAQ-OA components against part of the observed OA except if you assume that you are missing a specific OA source that is attributed to a specific AMS OA type.

The AMS measurements did not detect BBOA at Pasadena and therefore we chose to keep the CMAQ-VBS BBOA from residential wood combustion emissions separate from CMAQ-VBS POA. The AMS measured LOA was correlated with $PM_{1.15}$ Ti suggesting it may be related to paint or surface coatings (Hayes et al., 2013), a source which does not emit POA in CMAQ. Both types of OA do not contribute significantly to total OA (< 10%) and including/excluding them would have little to no impact on our results or conclusions.

18. Page 26755, line 9. The authors switch randomly from OA to OC concentration or SOA to SOC through the whole text which I found it rather confusing and hard to follow. I strongly suggest the use of "OA" instead of "OC" and "SOA" instead of "SOC" throughout the text. Either way, the authors should report the factor used to convert modeled OA to OC (or measured OC to OA).

Our use of OA vs. OC is defined by the measurement type. Comparisons with filter-based measurements (CSN, IMPROVE, and CalNex) use OC. Comparisons with AMS data use OA. In instances where both measurement types are used (e.g. Fig. 2a), OC is used. We have updated the text to indicate how CMAQ-VBS OA and AMS OA was converted to OC:

"When compared against the filter-based and routine monitoring network (CSN and IMPROVE) measurements of OC, CMAQ-VBS OA is converted to OC using OA/OC ratios reported in Koo et al. (2014)… When comparisons using both AMS and the filter-based OC measurements are made, AMS OA is converted to OC using OA/OC ratios reported in Hayes et al. (2013)."

19. Page 26756, line 24-27. Can you make a small comment on how this scenario affected CMAQ performance regarding SOA?

This estimate was made as a post-processing step outside of the model and therefore we unfortunately do not have corresponding SOA performance.

20. Page 26758, line 22-25. This sentence is confusing. Please rephrase.

We have rephrased the sentence to read:

“We calculated that when modeled OA concentrations were increased to match measured OA, partitioning of SVOCs increased POA-o concentrations by 20%. The 20% increase in modeled POA-o corresponded to a 2.3x underprediction of afternoon POA-o, with little change to morning and evening performance.”

21. Page 26758, line 26. Please delete the whole sentence in the parenthesis

We have made the recommended deletion.

22. Page 26759, line 26. Add “that” after “suggest”

We have made the recommended insertion.

23. Page 26759, line 27. Add “therefore” after “2x and”

We have made the recommended insertion.

24. Page 26760, line 2. Add “which” after parenthesis

We have made the recommended insertion.

25. Page 26760, line 3. Add “that” after “assume”

We have made the recommended insertion.

26. Page 26760, line 4. Add “the” before “missing”

We omitted using the article “the” prior to “missing emissions” to imply some ambiguity in the term and would therefore prefer to continue to omit the article.

27. Page 26760, line 4. Has less impact on what?

We have revised the text to indicate the impact is on POA predictions:

“However, we assume that this has less impact on POA predictions…”

28. Page 26760, line 5. Replace “or 25% excluding CIOA” with “(or 25% of POA excluding CIOA)”

We have made the recommended insertion.

29. Page 26761, line 16-19. Please rephrase. It is not clear how the numbers reported in this sentence suggest a factor of 2 error in the SOA precursor to CO emission ratio used by CMAQ

In an effort to clarify, we have added the following text”

“The relative good agreement of SOA precursor concentrations, along with the factor of two underprediction of CO, suggests the SOA precursor to CO emission ratio was incorrect by a factor of two.”

30. Page 26763, line 1. Add “that can” after “indicated”

We have made the recommended insertion.

31. Page 26763, line 13-20. Very confusing sentence. I can’t see any connection between the work of Jathar et al. (2014) and the sensitivities reported in this sentence. Therefore no conclusions can be made about the effect of Jathar et al. (2014) suggestions on CMAQ performance. Furthermore, the sensitivities reported here have not been presented earlier in the text. The authors should add a paragraph with all the sensitivities in the methodology section with their explanation and the rationale behind them. For instance, there is no point to use 7.5x POA emissions in this application. This has been chosen in Mexico City where the emissions where based on ambient measurements (which is not the case here).

We have included the SVOC sensitivity simulations performed in the methodology section and rational for each. For example, the 7.5x POA, which we note is based on Robinson et al. (2007) when a

POA emission inventory estimate is made before partitioning (and not specific to Mexico City), represents an upper bound of values used in the literature and simulations with it and a lower bound (1x POA emissions) provides constraints on CMAQ predicted SOA from IVOC emissions. We have also revised this paragraph to better connect the work by Jathar et al. (2014) with our sensitivity simulations. The revised text now reads:

"Current CMAQ-VBS IVOC emissions are scaled to primary SVOC emissions (1.5x) based on the results of a diesel generator (Robinson et al., 2007) and could potentially be updated to utilize more recent results, such as those reported by Jathar et al., 2014 who indicated unspeciated organics (S/IVOCs) dominated SOA mass formed from combustion emissions. Future work is needed to explore if better constraining IVOC emissions and yields in CMAQ would help improve model performance, but it would likely not account for the entire missing SOA mass based on sensitivity simulations using upper bound S/IVOC emissions. In these simulations, S/IVOC emissions were increased…"

32. Page 26766, line 7-8. Replace "the break down of POA was as follows:" with "POA comprised of"

We have made the recommended change.

33. Page 26766, line 24-25. Another example of bad writing. What kind of biogenics? More SOA at Pasadena than where? Or When? You can rewrite the sentence as: "The aging of biogenic SOA produced approximately 0.5 µg m-3 on average additional SOA at Pasadena throughout the day."

We have revised this sentence to read:

"In the simulation that aged secondary biogenic SVOCs, SOA concentrations were ~0.5 µg m^{-3} higher throughout the day at Pasadena compared to simulations that did not age secondary biogenic SVOCs…"

34. Page 26767, line 11-12. Again, what kind of biogenic? Replace the sentence with "On the other hand, biogenic VOCs emitted in the Central Valley and surrounding mountains are thought to be the major source of biogenic SOA observed in the LA basin"

We have made the recommended change.

35. Page 26767, line 13-14. "underprediction of monoterpenes": Do you mean under estimation of monoterpene emissions?

Yes, we were referring to monoterpene emissions and have added the word "emissions" for clarification. That portion of the sentence now reads:

"...if the underprediction of monoterpene emissions applies to other areas…"

36. Page 26767, line 17. Replace "contribution for" with "contribution of". Also, contribution to what? To predicted SOA concentrations?

We have made the recommended change and added "to predicted SOA concentrations" for clarification. The sentence now reads:

"Figure 8 also provides the contribution of the three standard SOA formation pathways in CMAQ-VBS (VOCs, IVOCs, and aging) to predicted SOA concentrations at Pasadena."

37. Page 26768, line 4-5. Delete "has been presented (Hodzic and Jimenez, 2011; Hayes et al., 2015) and" and "here"

We have made the recommended change.

38. Page 26768, line 11. Delete "when"

We have made the recommended change.

39. Page 26768, line 15. Delete "and"

We have made the recommended change.

40. Page 26768, line 16-18. Delete the whole sentence. Unnecessary information for the purpose of this study.

We have made the recommended change.

41. Page 26768, line 19-23. There is no need for this to be in a separate paragraph. Also, you can reverse the order of these two sentences as follows: “In our implementation in CMAQ-VBS we use an emission rate of 0.069 g VOC* g-1 CO and a KOH=1.25x 10-11 cm3 molec-1 cm-1. Hayes et al. (2015) found that using these optimal values, the SIMPLE parameterization...”

We have made the recommended change, combining paragraphs and changing the order of the sentences.

42. Page 26768, line 25. Replace “with the right diurnal cycle” with “following similar diurnal cycle” and place “(Fig. 9)” at the end of the sentence.

We have made the recommended change.

Conclusions

43. Page 26770, line 12. Add “from” after “50%” and “emissions” after “non-fossil”

We have made the recommended change.

44. Page 26770, line 15. Add “that” after “estimated” and add “the observed” after the “50% of”

We have made the recommended change.

45. Page 26770, line 16. Add “of SVOCs” after “66%”

We have made the recommended change.

46. Page 26770, line 20-27. I do not agree that is a matter of modelling needs and goals. During the last decade, the traditional treatment of OA has been proved to predict accurately the total OA in some cases (i.e., urban centers) but for the wrong reasons (overpredicts POA and underpredicts SOA). Therefore, the traditional treatment should not be considered appropriate anymore. The only advantage of the traditional approach was its computational efficiency compared to VBS but this doesn’t seem to be an issue anymore for VBS approach since during the last 5 years it has been applied even in global models with great success (Pye and Seinfeld, 2010; Farina et al., 2010; Jathar et al., 2011; Jo et al.,

2013; Tsimpidi et al., 2014). Please re-write the whole paragraph in order to highlight why the user has to switch to the CMAQ-VBS version by mentioning the great advantages of VBS (more accurate prediction of POA/SOA split without a significant computational cost).

We agree that the VBS approach in treating POA as semi-volatile is more appropriate than treating POA as non-volatile in the current AE6 formulation. However, the AE6 approach that explicitly relates parent VOC with SOA provides source specificity and chemical process information that is often useful for scientific and regulatory applications which is not available in the traditional VBS approach. Given that AE6 could be updated to treat POA and semi-volatile similarly to VBS and incorporate IVOC emissions for SOA formation the future may lead to a hybrid type of approach meaning an endorsement of the traditional VBS or AE6 would not be appropriate for this manuscript. Additionally, with respect to the VBS approach, there are number of uncertainties within VBS give us pause, including how best to apply existing POA emission inventories in a VBS framework or a number of empirical OA representations (aging only for anthropogenic SVOCs, lack of fragmentation, etc.). Given these uncertainties, it is reasonable to ask if VBS performs better for "the wrong reasons" by overemphasizing contributions from aging and/or IVOCS, excluding fragmentation, etc. The intent of this manuscript is to utilize routine and special study measurements to evaluate multiple approaches for estimating OA in a photochemical grid model and articulate the where improvements may be needed. We appreciate the reviewer's point of view here but we do not feel a technical manuscript is a venue for an endorsement of a particular approach. We have revised this paragraph to read:

"Regarding which OA treatment is more appropriate, CMAQ-VBS or CMAQ-AE6, depends on the user's modeling needs and goals. The traditional CMAQ-AE6 treatment, while it has known limitations (generally overpredicting POA and underpredicting SOA), more accurately predicts total OA measured at routine monitoring networks. Conversely, CMAQ-VBS treats primarily emitted OA as semivolatile and easily incorporates an estimate of IVOC emissions missing from the inventory to provide improved predictions on the total SOA mass and the POA/SOA split at Pasadena. The AE6 approach provides some utility in that parent VOCs and reaction processes are more clearly linked to SOA which is sometimes useful for scientific and regulatory model applications. Due to the difference in SOA/POA splits, the two CMAQ configurations may respond differently to VOC and/or NOx emission reductions, which should be examined in future work. Another area for future work is updating the POA emission inventory, originally developed for a non-volatile POA treatment, to account for semi-volatile POA and likely improving CMAQ-VBS total OA predictions."

Tables-Figures

47. Page 26781, line 10. Similar comment to the one above: the nonvolatile bin should represent all the compounds with C* ≤10-1 in Pasadena

Similar to the previous comment, we have indicated on the table that for the non-volatile bin C* = 0, which at typical ambient conditions at Pasadena represents compounds with C* ≤ 10^{-1}.

48. Page 26786, Figure 2a. Did you convert AMS-OA to AMS-OC? If yes, which factor did you use? Furthermore, why there is no data for AMS during the period of 18/5-30/5 in figure 2a? According to Figure 2b it seems that there is available AMS data during this period.

AMS-OA was converted to OC using AMS-measured OM to OC ratios (Hayes et al., 2013). Only days with at least 16 hours of AMS data are included in Figure 2a, as indicated in the caption. We have updated the caption to indicate how AMS-OA was converted to AMS-OC (and per an earlier comment included this in the text) and the days < 16 hours of AMS measurements were available (18/5, 20/5-26/5, 28/5, and 29/5).

"AMS measurements in (a) were converted to OC using OM to OC ratios reported in Hayes et al. (2013) and include only days with > 16 hourly measurements (i.e. 18/5, 20/5-26/5, 28/5, and 29/5 are excluded due to missing measurements).

References

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Bash, J. O., Carlton, A. G., Hutzell, W. T., & Bullock Jr, O. R. (2013). Regional Air Quality Model Application of the Aqueous-Phase Photo Reduction of Atmospheric Oxidized Mercury by Dicarboxylic Acids. Atmosphere, 5(1), 1-15.

Foley, K. M., Roselle, S. J., Appel, K. W., Bhave, P. V., Pleim, J. E., Otte, T. L., Mathur, R., Sarwar, G., Young, J. O., Gilliam, R. C., Nolte, C. G., Kelly, J. T., Gilliland, A. B., and Bash, J. O. (2010). Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. Geoscientific Model Development, 3(1), 205-226.

Response to Reviewer #3

We appreciate the reviewer's time and effort to provide thoughtful and thorough comments. Below are responses to the reviewer's specific comments, with the reviewer's original comment shown followed by our response in **bold**.

The abstract is generally a good representation of the paper, from the perspective of the presentation of a lot of results with limited synthesis and interpretation. The abstract is quite long, and it is suggested that some of the details be omitted. In addition, it is suggested that a synthesis of the results and their implications be included to highlight significance of the work.

As recommended by the reviewer, we have reduced the length of the abstract by omitting details. We have also attempted to synthesis the results and provide some implications by concluding the abstract with the following text:

"Overall, the CMAQ-VBS incorporates semivolatile treatment of POA and improves SOA model performance (though SOA formation efficiency is still 1.6-2× too low). However, continued efforts are needed to better understand assumptions in the parameterization (e.g. SOA aging) and provide additional certainty in how best to apply existing emission inventories in a framework that treats POA as semivolatile, which currently degrades existing model performance at routine monitoring networks. The VBS and other approaches (e.g.AE6) require additional work to appropriately incorporate intermediate volatility organic compounds (IVOCs) emissions and subsequent SOA formation."

p. 26749, line 17-18: The focus on the degree to which processes and/or sources characterized by CMAQ are at play in the ambient atmosphere is not particularly well connected to the focus on sources of OA as written.

In an effort to clarify, we have revised the text to read:

"Our analysis focuses on the degree to which processes and/or sources characterized in CMAQ v5.0.2 may be responsible for OA observed as part of CalNex."

The first three paragraphs of the introduction present many prior studies that are relevant to the research from the perspective of reporting previous OA measurement/modeling results in California, including during CalNEX. However, the information is poorly organized and it does little to build the motivation and need for the specific work presented. It is suggested that the authors consider reorganization of the introduction to better support their efforts in analyzing process/source contributions to measured and modeled OA.

We have reorganized the introduction as recommended to provide a clearer motivation for our work.

p. 26749, line 9: “indicates” should be “indicated” or “indicate”

We have made the suggested revision.

p. 26750, line 1-2: In the abstract and throughout the results, CMAQ-AE6 is differentiated from CMAQ-VBS; here however, they are described as the single approach to simulate aerosols (aerosols 6 module with the VBS approach). This needs to be reconciled.

We have clarified the aerosol treatments here by revising the text to read:

“Aerosols were simulated using the traditional aerosols 6 (AE6) module (CMAQ-AE6) and with an alternative version of AE6 which uses the volatility basis set (VBS) approach (Donahue et al., 2006) to model OA (CMAQ-VBS).”

It is suggested that the authors consider restructuring the methodology such that the paragraph starting on p. 26752, line 15, continues the discussion of SVOCs and POA from the paragraph starting on p. 26752, line 6; and then is followed by discussion of the emissions inventory and then modeling domain.

We have restructured the methodology section to better group related topics.

p. 26750, lines 10-20: The purpose of the additional references following Murphy and Pandis is unclear. In some cases, it seems as if the authors would like to reference the original data source, however, that is not made clear. What is the Koo et al. reference for? And Carlton et al. 2010? These are confusing given that the authors note that yields are based on Murphy and Pandis 2009.

Our intent was to reference the original data source but we have removed these references (with the exception of Hildebrandt et al., 2009) to avoid confusion since all relevant details are provided in Murphy and Pandis. The Koo et al. and Carlton et al. references were meant to point back to the CMAQ-VBS and CMAQ-AE6 descriptions of OA treatment. However, since these details are provided more clearly elsewhere, we have also removed these references here.

p26750-2751: The authors need to make it clearer that the order of magnitude reduction in volatility (e.g., line 25, p26750) occurs at each step.

We have clarified that each oxidation step for both POA and SOA reduces volatility by an order of magnitude.

"Primary SVOCs are aged/oxidized in the gas-phase by reactions with OH…with each oxidation step lowering volatility by an order of magnitude..."

"Anthropogenic SOA aging reactions form products with a vapor pressure reduced by one order of magnitude (10x) for each oxidation step.

p. 26755, line 25: It is suggested that the authors remove the imprecise language such as "were in reasonably good agreement", given that quantitative metrics follow.

We have made the recommended revision by removing imprecise language (e.g. "were in reasonably good agreement") when quantitative metrics are provided.

p. 26758, line 22: It is not clear whether "estimated" here means calculated or concluded based on simulations. Please clarify.

We have clarified by replacing "estimated" with "calculated".

p. 26763, line 6: Can the authors clarify what is meant by production efficiency? I was not expecting missing/mischaracterized IVOCs to be linked to production efficiency as is written.

SOA production efficiency is the efficiency per unit precursor at a given age. However, because of differences in how IVOC emissions are estimated, uncertainty in yields, and lack of SOA produced by IVOCs in CMAQ-AE6, we have categorized SOA formed from IVOCs as production efficiency.

p. 26763, line 25: Can the authors expand on what is meant by obtaining agreement for the wrong reasons? Can they give examples of what else would lead to the same conclusions?

We did not want the reader to interpret S/IVOC emissions accounted for all underpredictions in SOA production efficiency, though a factor of 7.5x would suggest that it does. Instead, other missing (or

underrepresented) pathways (e.g. low yields, missing precursors, oligomerization, etc.) could represent part of the underprediction in formation efficiency that increased S/IVOC emissions accounts for. Therefore, we have revised the text to read:

"However, the approximate agreement may be for the wrong reasons as increased S/IVOC emissions may account for SOA from other missing (or underrepresented) formation pathways and should not be over-interpreted as direct evidence of the presence of SOA formation efficiency of S/IVOCs.

p. 26767, line 11: Replace "biogenic" with "biogenics", or add "species"/"compounds"/etc.

We have revised the text to read: "…biogenic VOCs…"

p. 26768: It is not clear what is added by the application and discussion of the SIMPLE parameterization.

Our intent on the inclusion of SIMPLE was to answer the question as to how best can we improve CMAQ in the short term given many of the shortcomings highlighted in our work. We have clarified this by revising the text to read:

"Given the limitations in CMAQ-AE6 and CMAQ-VBS to accurately predict SOA at Pasadena and uncertainty in how best to improve predictions raises the question as to if other parameterizations can improve CMAQ performance in the near term. To this end, we have applied a simplified SOA parameterization…"

Largely absent from the results and conclusions is the role of oligomers (e.g., see review by Ziemann and Atkinson, 2012) and their lack of representation in models.

In recognizing the formation of SOA from oligomerization and the absence of a formation pathway in CMAQ-VBS, we have included the following paragraph in the SOA results section:

"Note that CMAQ-VBS does not include an oligomerization formation pathway in which heterogeneous/multiphase reactions form SOA (Ziemann and Atkinson, 2012). The lack of this pathway could account for underpredictions in production efficiency though it is plausible the SVOC aging parameterization already accounts for some of the mass formed through oligomerization. CMAQ-AE6, which does include an oligomerization formation pathway (Carlton et al., 2010), estimates approximately 20-25% of SOA at Pasadena is comprised of oligomers (Fig. S5), though because CMAQ-AE6 significantly underpredictions SOA, this equates to only a small amount of total mass (0.06 μg m^{-3} on average)."

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Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS

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Abstract

Community Multiscale Air Quality (CMAQ) model simulations utilizing the traditional organic aerosol (OA) treatment (CMAQ-AE6) and a volatility basis set (VBS) treatment for ~~organic aerosols~~ OA (CMAQ-VBS) were evaluated against measurements collected at routine monitoring networks (Chemical Speciation Network (CSN) and Interagency Monitoring of Protected Visual Environments (IMPROVE)) and those collected during the 2010 California at the Nexus of Air Quality and Climate Change (CalNex) field campaign to examine important sources of organic aerosol (OA) in southern California.

Traditionally, CMAQ treats primary organic aerosol (POA) as nonvolatile and uses a 2-product framework to represent secondary organic aerosol (SOA) formation. CMAQ-VBS ~~(OA lumped by volatility, semivolatile POA) underpredicted total~~ instead treats POA as semivolatile and lumps OA using volatility bins spaced an order of magnitude apart. The CMAQ-VBS approach underpredicted organic carbon (OC) at ~~CSN (−25.5 % Normalized Median Bias (NMdnB)) and IMPROVE (−63.9 % NMdnB) locations and total OC was underpredicted to a greater degree compared to the CMAQ-AE6 (9.9~~ IMPROVE and ~~−55.7 % NMdnB, respectively; semi-explicit OA treatment, SOA lumped by parent hydrocarbon, nonvolatile POA)~~CSN sites to a greater degree than CMAQ-AE6 due to the semivolatile POA treatment. However, comparisons to aerosol mass spectrometer (AMS) measurements collected at Pasadena, CA indicated that CMAQ-VBS better represented the diurnal profile and ~~the~~ primary/secondary split of OA. CMAQ-VBS ~~secondary organic aerosol (SOA)~~ SOA underpredicted the average measured AMS oxygenated organic aerosol (OOA, a surrogate ~~of~~ for SOA) concentration by a factor of 5.2~~(4.7 measured vs. 0.9 modeled),~~ , representing a considerable improvement to CMAQ-AE6 SOA predictions ~~, which were approximately~~ (factor of 24 ~~× lower than the average AMSOOA concentration.~~ lower than AMS).

We use two new methods, one based on species ratios ~~and~~ (SOA/ΔCO and SOA/O_x) and another on a simplified SOA parameterization~~from the observations~~, to apportion the SOA underprediction for CMAQ-VBS to ~~too~~ slow photochemical oxidation (estimated as 1.5×

lower than observed at Pasadena using $-\log(\mathrm{NO}_x : \mathrm{NO}_y)$), low intrinsic SOA formation efficiency (low by 1.6 to 2× for Pasadena), and ~~too~~ low emissions or ~~too high~~ excessive dispersion for the Pasadena site (estimated to be 1.6 to 2.3× too low/~~high~~excessive). The first and third factors ~~will be similar for~~ are common to CMAQ-AE6, while the intrinsic SOA formation efficiency for that model is estimated to be too low by about 7×. ~~For CMAQ-VBS, 90 % of the anthropogenic SOA mass formed was attributed to aged secondary semivolatile vapors (70 % originating from volatile organic compounds (VOCs) and 20 % from intermediate volatility compounds (IVOCs)).~~

From source-apportioned model results, we found most of the CMAQ-VBS modeled POA at the Pasadena CalNex site was attributable to meat cooking emissions (48 %, and consistent with a substantial fraction of cooking OA in the observations)~~,~~. This is compared to 18 % from gasoline vehicle emissions, 13 % from biomass burning (in the form of residential wood combustion), and 8 % from diesel vehicle emissions. All "other" inventoried emission sources (e.g. industrial~~/point~~, point, and area sources) comprised the final 13 %. The CMAQ-VBS semivolatile POA treatment underpredicted AMS hydrocarbon-like OA (HOA) + cooking-influenced OA (CIOA) at Pasadena by a factor of 1.8 ~~(1.16 modeled vs. 2.05 observed)~~ compared to a factor of 1.4 overprediction of POA in CMAQ-AE6, but did well to capture the AMS diurnal profile of HOA and CIOA, with the exception of the midday peak. ~~We estimated that using the National Emission Inventory (NEI)POA emissions without scaling to represent SVOCs underestimates SVOCs by ∼ 1.7 ×.~~

Overall, the CMAQ-VBS with its semivolatile treatment of POA, SOA from IVOCs, and aging of SOA improves SOA model performance (though SOA formation efficiency is still 1.6–2× too low). However, continued efforts are needed to better understand assumptions in the parameterization (e.g. SOA aging) and provide additional certainty in how best to apply existing emission inventories in a framework that treats POA as semivolatile, which currently degrades existing model performance at routine monitoring networks. The VBS and other approaches (e.g. AE6) require additional work to appropriately incorporate intermediate volatility organic compounds (IVOCs) emissions and subsequent SOA formation.

1 Introduction

Organic matter, comprised of primary organic aerosols (POA) and secondary organic aerosols (SOA), is a ubiquitous component of $PM_{2.5}$. ~~The~~ For example, the Los Angeles South Coast Air Basin and San Joaquin Valley are designated as $PM_{2.5}$ nonattainment areas (http://www.epa.gov/oaqps001/greenbk/ancl.html), and major ground sites for the California at the Nexus of Air Quality and Climate Change (CalNex) campaign (Ryerson et al., 2013) were located within these basins at Pasadena and Bakersfield, respectively. Forty-one percent of the submicron aerosol mass at Pasadena was organic during CalNex (Hayes et al., 2013), and several complementary measurements of the organics including radiocarbon, secondary organic aerosol (SOA) tracers, OC/EC, organic aerosol (OA) composition, and volatile organic compounds (VOCs) (Zotter et al., 2014; Baker et al., 2015; Hayes et al., 2013) were collected.

~~Even in urban areas,~~ Measurements have shown SOA is expected to be comparable to or dominate over ~~primary organic aerosol (POA)~~ POA, even in urban areas close to emission sources (Zhang et al., 2007). Average OA O : C ratios exceed 0.3 in southern California (Craven et al., 2013) suggesting significant contributions from SOA, and over 70 % of midday OA is estimated to be secondary in Riverside, CA (Docherty et al., 2008), Mexico City (Aiken et al., 2009), and Pasadena, CA (Hersey et al., 2011; Hayes et al., 2013). ~~Slightly more than half of the OC during CalNex was non-fossil in origin (Zotter et al., 2014; Baker et al., 2015). The dominant component of daytime SOA, semivolatile oxygenated organic aerosol (SV-OOA), at the Pasadena site was found to be highly correlated with measurements of fossil OC and markers of gasoline combustion indicating that fossil precursor gases are major contributors to its formation, consistent with an estimated 71 % fossil fraction (Zotter et al., 2014).~~

~~Several other studies have indicated that SOA from gasoline vehicles dominates over SOA from diesel vehicles as deduced from weekly cycles of non-fossil vs. fossil carbon and OA (Zotter et al., 2014; Bahreini et al., 2012; Hayes et al., 2013) as well as the higher potential for gasoline exhaust to form SOA in chamber oxidation~~

~~experiments (Jathar et al., 2014). Borbon et al. (2013) further show gasoline vehicle emissions dominate the hydrocarbon distribution in urban areas such as CalNex, though measurements were limited to VOCs and excluded SVOCs and IVOCs. However, an alternative analysis using a detailed characterization of organic emissions from diesel and gasoline vehicles and estimated SOA yields concluded that diesel is responsible for more than 65 % of vehicle-attributable SOA (Gentner et al., 2012). In contrast, Ensberg et al. (2014) conclude that either the SOA yields in the atmosphere are much larger than have been observed in chambers, or alternatively vehicles may not be the dominant source of anthropogenic fossil SOA in Los Angeles. Recent work also indicates that models underestimate~~ However, models tend to underestimate anthropogenic SOA from both known and unknown VOC precursors (Ensberg et al., 2014; Jathar et al., 2014; Zhang et al., 2014).

The Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006), which is used for research and regulatory purposes~~.~~, also tends to underpredict SOA in anthropogenically dominated locations (Foley et al., 2010; Baker et al., 2015). In CMAQ, POA is normally treated as nonvolatile (Simon and Bhave, 2012), and SOA forms mostly from gas-phase VOC oxidation to form lower-volatility products with contributions from cloud processing (Carlton et al., 2010). Simulations using this traditional OA treatment in CMAQ (CMAQ-AE6) during CalNex (Baker et al., 2015) indicate that predicted OA is dominated by POA with a small contribution of SOA from aromatic and biogenic VOC oxidation in contrast to the SOA dominated picture from observations. While anthropogenic parent VOCs are well represented in the model, secondary organic carbon (SOC) from aromatics is underestimated (Baker et al., 2015). The model is likely missing sources of fossil carbon and tracer-based apportionment methods for SOC are unable to capture the total OA concentration. Hayes et al. (2015) ~~indicates~~ indicated the SOA formed from the oxidation of VOCs alone is insufficient to explain observed SOA, and primary ~~semi- and intermediate volatility compounds (~~S/IVOCs ~~)~~ are likely needed to explain the observed mass.

In ~~this work, we examine the sources of OA in California with a focus on the 2010 CalNex-LA site in Pasadena, CA. In~~ recognizing the potential role for S/IVOC emissions to form SOA (Robinson et al., 2007; Dzepina et al., 2009; Ahmadov et al., 2012), we employ the publicly available version of the CMAQ-VBS model (Koo et al., 2014) and compare to the standard nonvolatile POA and SOA from VOCs in CMAQ v5.0.2, with a focus on the 2010 CalNex-LA site in Pasadena, CA. Our analysis focuses on the degree to which processes and/or sources characterized in CMAQ v5.0.2 may be responsible for OA observed as part of CalNex~~and the contribution of various sources to OA~~. We also identify whether underestimates in OA from CMAQ are due to emissions/dispersion, photochemical processing, or the OA treatment.

2 Methodology

2.1 Model Application

The CMAQ model version 5.0.2 was applied to estimate air quality in California from 4 May to 30 June 2010, which coincides with the CalNex campaign (May and July 2010). Gas phase chemistry was simulated with the Carbon Bond 2005 (CB05) chemical mechanism (Yarwood et al., 2005). Aerosols were simulated using the traditional aerosols 6 (AE6) module ~~with~~ (CMAQ-AE6) and an alternative version of AE6 which uses the volatility basis set (VBS) approach (Donahue et al., 2006) to model OA (CMAQ-VBS).

The model domain covered California and Nevada with a 4 km (317 × 236) grid resolution (Fig. 1). The vertical domain included 34 layers and extended to 50 mb. The first 11 days of the simulation were treated as a spin-up and results were excluded from the analysis to minimize the influence of initial conditions.

2.2 CMAQ-VBS OA Treatment

Details of the VBS treatment of organics in CMAQ are described in Koo et al. (2014) and comparisons of the POA and SOA treatments in the traditional CMAQ-AE6 and CMAQ-VBS and provided in the Supplement (Tables S1 and S2). Briefly, CMAQ-VBS includes four distinct basis sets/OA groups: primary anthropogenic (corresponding to hydrocarbon-like

OA (HOA) or POA), secondary anthropogenic (anthropogenic SOA), secondary biogenic (biogenic SOA), and primary biomass burning (biomass burning OA). Each of the ~~4~~ four basis sets is represented using ~~5 bins(4 bins~~ five bins. Four bins are used to represent C^* values ranging from 10^0 to 10^3 µg m^{-3} and ~~1 nonvolatile bin to represent~~ one bin (C^* ~~of~~ =0, which at typical ambient conditions at Pasadena would represent compounds with $C^* \leq$ 10~~$^{-2}$ and 10~~$^{-1}$ µg m^{-3}) represents nonvolatile particles.

Traditional CMAQ-AE6 nonvolatile POA is replaced in CMAQ-VBS with semivolatile POA, referred to here as primary SVOCs, comprised of primary gas and particle phase organics located in the primary anthropogenic basis set. In this framework, CMAQ-VBS POA is therefore primary SVOCs located in the particle phase. Primary SVOCs are aged/oxidized in the gas-phase by reactions with OH using a rate constant of 4×10^{-11} cm^3 molec.$^{-1}$ s^{-1} (Robinson et al., 2007), with each oxidation step lowering volatility by an order of magnitude and a portion (∼ 10 %) of the OA mass shifted from the primary SVOC (POA) to the secondary SVOC (SOA) set (Koo et al., 2014). The transfer of oxidized primary SVOCs (i.e. POA) to secondary SVOCs (i.e. SOA) is used as a modeling technique to maintain accurate O : C ratios. This feature of the 1.5-D VBS (Koo et al., 2014) uses existing POA and SOA basis sets to avoid additional computational burden of added model species (e.g. oxidized POA basis set). With this treatment, the majority (∼ 90 %) of slightly aged POA (after a single aging reaction) resides as POA-like while very aged POA (after four aging reactions) would reside as two-thirds POA and one-third SOA. We acknowledge this approach, which prioritizes O : C ratios, adds uncertainty when model results are compared against AMS measurements and is an area where future research is needed to better understand that uncertainty. At Pasadena, our model predictions indicated ∼ 8 % of modeled OA was comprised of oxidized POA and suggests this approach has only a small impact in this application.

CMAQ-VBS also includes a formation pathway of SOA from the oxidation of IVOC emissions, where IVOCs represent gas phase compounds with volatilities between SVOCs and VOCs (C^* values ranging from 10^4 to 10^6 µg m^{-3}). ~~Yields for semivolatile products of SOA~~ Most of these compounds are generally considered to either be missing from emission inventories entirely or mischaracterized as non-SOA forming compounds. The inclusion of IVOCs represents an additional SOA precursor mass introduced into the model relative to CMAQ-AE6. OH is artificially recycled (i.e. not depleted) in oxidation reactions of IVOCs and SVOCs (primary and secondary) to prevent double counting and impacts to the gas-phase chemistry of the underlying chemical mechanism as these species are likely already represented in the model (e.g. paraffins, olefins, nonreactive, etc.). This technique is identical to that used by a number of existing CMAQ SOA precursors (e.g. benzene and sesquiterpene) in CB05.

CMAQ-VBS semivolatile SOA is represented using secondary SVOCs (gas and particle phase) located in the secondary anthropogenic and biogenic basis sets. SOA yields from VOC precursors are the same as those used in Murphy and Pandis (2009) except for toluene (Hildebrandt et al., 2009). ~~Yields for semivolatile products of SOA~~ SOA yields from IVOC precursors are based on the ~~Murphy and Pandis (2009) reported~~ Murphy and Pandis (2009) yields for the SAPRC ARO2 model species~~, the model species that includes naphthalene (used in Pye and Seinfeld (2010)~~. ARO2 was used because it represents naphthalene (among other compounds), where naphthalene has previously been used as a surrogate to represent IVOCs ~~) (Koo et al., 2014)~~(Pye and Seinfeld, 2010). Photochemical reactions producing condensable vapors from aromatics (toluene, xylene, and benzene), isoprene, and monoterpenes utilize distinct high and low-NO_x yields (determined using $RO_2 + NO$ or $RO_2 + HO_2$~~; Chen and Griffin, 2005; Pfister et al., 2008; Carlton et al., 2010~~) while sesquiterpenes and IVOCs do not (IVOC NO_x-dependence excluded due to a lack of experimental data).

While experimental data suggests aging of both anthropogenic SOA (Hildebrandt et al., 2009) and biogenic SOA (Donahue et al., 2012) occurs, in CMAQ-VBS only anthropogenic SOA (formed from both VOCs and IVOCs) is aged via reactions of the gas-phase semivolatiles with OH using a rate constant of $2\times10^{-11}\ \mathrm{cm^3\ molec.^{-1}\ s^{-1}}$ (twice the rate previously assumed for anthropogenic SOA aging (Murphy and Pandis, 2009) and based on results from the 2-D VBS ~~; Donahue et al., 2013). Anthropogenic SOA~~ (Donahue et al., 2013).

Anthropogenic aging reactions form products with a vapor pressure reduced by one order of magnitude (10×) for each oxidation step. Biogenic aging is turned off in CMAQ-VBS by default as previous results, using a more conservative aging scheme than in CMAQ-VBS, indicated the VBS overpredicted OA in rural areas when biogenic SOA was aged (Lane et al., 2008; Murphy and Pandis, 2009; Fountoukis et al., 2011). In recognizing the aging of biogenic SOA does occur, we perform a sensitivity simulation with ~~biogenic~~ secondary biogenic SVOC aging on, the results of which are presented in Sect. 3.4.2. In excluding aging of ~~biogenic SOA~~ secondary biogenic SVOCs in all but our sensitivity simulation, we effectively assume that the net result of functionalization (aging) and fragmentation, ~~which is more important for biogenic SOA than POA~~ an important process for accurate predictions of biogenic SOA (Donahue et al., 2012), does not increase biogenic SOA concentrations (Fountoukis et al., 2011).

~~Primary SVOCs are aged in the gas-phase by reactions with OH using a rate constant of 4×10^{-11} (Robinson et al., 2007), lowering volatility by an order of magnitude and a portion ($\sim$ 10 %) of the OA mass shifted from the POA to the SOA set (Koo et al., 2014). This approach improves computational efficiency as it utilizes existing POA and SOA basis sets to represent oxidized POA and maintain the correct O : C ratios, avoiding the need for an additional oxidized POA basis set. With this treatment, the majority ($\sim$ 90 %) of slightly aged POA (after a single aging reaction) resides as POA-like while very aged POA (after four aging reactions) would reside as two-thirds POA and one-third SOA.~~

2.3 Emissions

~~The model domain covered California and Nevada with a 4 (317 × 236) grid resolution (Fig. 1). The vertical domain included 34 layers and extended to 50 . The first 11 days of the simulation were treated as a spin-up and results were excluded from the analysis to minimize the influence of initial conditions.~~

United States anthropogenic emissions were based on version 1 of the 2011 National Emissions Inventory (NEI) (US Environmental Protection Agency, 2014a). Stationary point sources reporting continuous emissions monitor (CEM) data were modeled with day and hour specific emissions matching the simulation period. Wildfire emissions were day specific although have little impact in Pasadena during this time period (Bahreini et al., 2012; Hayes et al., 2013). Biogenic emissions were day and hour specific using Weather Research Forecast (WRF) model temperature and solar radiation as input to the Biogenic Emission Inventory (BEIS) version 3.14 model (Carlton and Baker, 2011). Anthropogenic emissions from Mexico were projected to 2010 from 1999 (US Environmental Protection Agency, 2014b). All emissions were processed for input to CMAQ using the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system (Houyoux et al., 2000).

~~Gridded meteorological variables used for input to CMAQ and SMOKE were generated using version 3.1 of the WRF model, Advanced Research WRF core (Skamarock and Klemp, 2008). Details regarding the WRF configuration and application are provided elsewhere (Baker et al., 2013). In general, surface meteorology and daytime mixing layer heights were well represented for this period in California. A 36 CMAQ simulation covering the continental United States for the same time period was used to generate boundary conditions for this simulation. A global GEOS-CHEM (v8-03-02) (Bey et al., 2001) simulation provided boundary inflow for the 36 continental scale CMAQ simulation (Henderson et al., 2014). Neither larger scale simulation included~~ CMAQ-VBS ~~OA species, though the impact is likely small as we assume most of the OA at Pasadena originates from local or regional sources located in our modeling domain.~~

~~POA is treated as semivolatile (SVOCs) in CMAQ-VBS and allowed to partition between the gas and particle phase. CMAQ-VBS also includes a formation pathway of SOA from the oxidation of IVOC emissions, which represents additional SOA precursor mass introduced into the model relative to CMAQ-AE6. CMAQ-VBS~~ internally estimates SVOC and IVOC emissions at runtime based on traditional POA emission inventories. In the configuration used here, SVOC emissions are equivalent to the POA emissions input, i.e. no scaling of POA is applied to calculate SVOC emissions~~based~~. We base this on the assumption that ~~the POA emission inventory is reported before evaporation of semivolatile emissions (Robinson et al., 2007)~~NEI POA measurements are made at high concentrations and therefore all SVOCs are partitioned to the particle phase. Therefore, the total mass of

SVOC (gas and particle phase) emissions are equal to traditional POA emissions. IVOC emissions are estimated as 1.5 × SVOCs (Robinson et al., 2007), or 1.5× the traditional POA emission inventory. ~~OH is artificially recycled (i.e. not depleted) in oxidation reactions of IVOCs and SVOCs (primary and secondary) to prevent double counting and impacts to the gas-phase chemistry of the underlying chemical mechanism.~~ Although most modeling studies set IVOCs = 1.5 × SVOCs, the total amount of material introduced into the model varies depending on the study and leads to varying importance of SOA from S/IVOCs ~~and~~ vs. VOCS in different simulations. For example, in the box modeling studies of Dzepina et al. (2009) and Hayes et al. (2015) the POA was set equal to the measured HOA, then the SVOCs were calculated from equilibrium partitioning using the Robinson et al. (2007) volatility distribution, and then IVOC were set to 1.5 × SVOC. In grid-based model studies examining Mexico City OA (Hodzic et al., 2010; Tsimpidi et al., 2010; Shrivastava et al., 2011), the POA emission inventory was assumed to represent the fraction of aerosol remaining after evaporation of semivolatile emissions based on comparisons with observations and therefore SVOC emissions were set to 3 × traditional POA emissions and IVOC emissions were set to 1.5 × SVOC emissions leading to a total of S/IVOC = 7.5 traditional POA. Therefore, modeled S/IVOC emissions can range from 2.5 to 7.5× existing POA inventories to match measurements (which makes direct comparisons to existing inventories difficult) and remains a source of uncertainty in conducting and comparing models that include S/IVOCs.

The volatility split of SVOC emissions in CMAQ-VBS is provided in Table 1. By default, CMAQ-VBS assigns volatility distributions for POA emissions from gasoline vehicles (GV), diesel vehicles (DV), biomass burning (BB), nonvolatile sources (NV), and “other” sources (OP) (e.g. point~~/industrial~~, industrial, and area sources). In the absence of source specific POA emissions, the “other” profile is used. In our application, a significant portion of POA was associated with meat cooking activities (Table 2), which thermodenuder data suggests is of lower volatility compared to the other CMAQ-VBS source specific POA categories (Huffman et al., 2009). We ~~roughly~~ approximated a new volatility distribution for meat cooking SVOC emissions (Table 1) ~~by altering the CMAQ-VBS biomass burning SVOC volatility~~

~~distribution~~ based on comparisons of meat cooking and the MILAGRO average biomass burning thermodenuder measured volatility (Huffman et al., 2009). This is meant as a first approximation and represents an area where further research is needed. We note thermodenuder data provides some constraints on SVOCs but no constraints on IVOCs, therefore the IVOC emissions from meat cooking remained unchanged (1.5× of meat cooking POA emissions).

~~After~~

2.4 Sensitivity Simulations

In addition to evaluating the publicly available version of CMAQ-VBS, we performed a number of sensitivity simulations to examine the importance of OA sources in the model. For example, after input into CMAQ-VBS, anthropogenic POA emission source specificity is lost as anthropogenic POA is lumped into a single basis set. In order to leverage our source specific emission inputs, ~~in this study~~ basis sets for POA from gasoline vehicles, diesel vehicles, and meat cooking activities were added to provide anthropogenic POA source apportionment ~~.~~ (Sect. 3.4.1).

To evaluate how model predictions change with varying S/IVOC emissions, sensitivity simulations were conducted with primary SVOC emissions scaled by 1.5×, 2×, and 3× of NEI POA mass (Sect. 3.2.2 and 3.2.3). In each case, IVOC emissions were 1.5× of SVOC emissions, corresponding to factors of 2.25×, 3×, and 4.5× of NEI POA mass. The range of values are based on an assumption that the POA inventory is estimated before (3×) or after (1×) partitioning at ambient conditions (∼30 $\mu g\,m^{-3}$) and represent lower and upper bounds of scaling factors used in previous studies (e.g. Robinson et al., 2007; Dzepina et al., 2009).

Another set of sensitivity simulations quantified VBS SOA contributions from first-product oxidation of VOCs (i.e. no aging), anthropogenic and biogenic SVOC aging, and IVOCs (Sect. 3.4.2). In sensitivity simulations with aging of secondary biogenic SVOCs we also quantified in-basin vs. out of basin contributions at Pasadena from biogenic SOA precursor emissions by removing LA basin biogenic SOA precursors.

Lastly, given the tendency for regional air quality studies (Volkamer et al., 2006; De Gouw et al., 2008), including CMAQ (Foley et al., 2010; Baker et al., 2015), to underpredict anthropogenic SOA in urban areas, we evaluated a simplified SOA parameterization (SIMPLE) (Hodzic and Jimenez, 2011; Hayes et al., 2015). SIMPLE represents an alternative SOA modeling approach to the CMAQ-AE6 and CMAQ-VBS SOA treatments (Sect. 3.4.3) and has been shown to perform well for SOA predictions at Pasadena (Hayes et al., 2015) and for OA predictions in the Southeastern U.S. (Kim et al., 2015).

2.5 Meteorology, Boundary and Initial Conditions

Gridded meteorological variables used for input to CMAQ and SMOKE were generated using version 3.1 of the WRF model, Advanced Research WRF core (Skamarock and Klemp, 2008). Details regarding the WRF configuration and application are provided elsewhere (Baker et al., 2013). In general, surface meteorology and daytime mixing layer heights were well represented for this period in California. A 36 km CMAQ simulation covering the continental United States for the same time period was used to generate boundary conditions for this simulation. A global GEOS-CHEM (v8-03-02) (Bey et al., 2001) simulation provided boundary inflow for the 36 km continental scale CMAQ simulation (Henderson et al., 2014). Neither larger scale simulation included CMAQ-VBS OA species, though the impact is likely small as a CMAQ-AE6 sensitivity simulation indicated most (99%) of the OA at Pasadena originates from local or regional sources located in our modeling domain.

2.6 Measurements

Ground-based CalNex measurements were collected in Pasadena, CA from 15 May to 15 June 2010 (Ryerson et al., 2013). The Pasadena sampling site was located on the California Institute of Technology campus, northeast of the Los Angeles metropolitan area and south of the San Gabriel Mountains. Both filter-based carbon measurements and Aerosol

Mass Spectrometry (AMS) PM measurements were collected at this site. The filter-based measurements provide 23 h average concentrations of organic carbon, elemental carbon, and total carbon as well as the non-fossil vs. fossil carbon fraction. When compared against the filter-based and routine monitoring network (CSN and IMPROVE) measurements of OC, CMAQ-VBS OA is converted to OC using OA/OC ratios reported in Koo et al. (2014). Additional details of the filter-based measurements, including comparisons of those measurements against traditional CMAQ (CMAQ-AE6) results, can be found in Baker et al. (2015). The AMS data provide real time (sub-hourly) measurements of speciated sub-micron PM, including various organic components as determined using positive matrix factorization (PMF). The AMS organic components resolved at the site include two types of SOA (semivolatile oxygenated OA (SV-OOA) consistent with fresher SOA mostly from urban areas, and low-volatility oxygenated OA (LV-OOA) consistent with aged SOA); two types of POA (hydrocarbon-like OA (HOA) and cooking-influenced OA (CIOA)); and local OA (LOA). The source of LOA, which accounts for approximately 5 % of OA mass at Pasadena, is generally unknown, though large fluctuations in measured concentrations suggest a local source (Hayes et al., 2013). When comparisons using both AMS and the filter-based OC measurements are made, AMS OA is converted to OC using OA/OC ratios reported in Hayes et al. (2013). Additional details regarding the AMS measurements and PMF component analysis can be found in Hayes et al. (2013).

3 Results and discussion

3.1 Comparison against routine monitoring networks

Average OA concentrations predicted by CMAQ-VBS during 15 May to 30 June were highest in the Greater Los Angeles Area where the domain maximum concentration was 3.1 µg m^{-3} (Fig. 1). In this region, OA was approximately 30–50 % of total modeled PM$_{2.5}$ and ~~modeled OA~~ was generally evenly split between primary and secondary (i.e. SOA comprised 40–60 % of OA). In contrast, CMAQ-AE6 predicted the majority (80–90 %)

of OA was comprised of POA in LA. The shift from primary dominated to a more even primary/secondary split in CMAQ-VBS is due to both the semivolatile treatment of POA (lowering POA concentrations) and additional SOA formation pathways (SOA from IVOCs and SOA aging as discussed in Sect. 3.4.2).

Model performance comparisons at IMPROVE and CSN sites in California and Nevada indicated CMAQ-VBS ~~generally~~ underpredicted OC (Table 3). Model performance for OC was slightly degraded (i.e. greater underprediction) compared to CMAQ-AE6 predictions (~~see Table S3 and Fig. S9 of the Supplement for CMAQ-AE6 model performance~~Table 3). While CMAQ-VBS predicted higher concentrations of SOA due to additional SOA formation pathways (see Table S2 in the Supplement), including the introduction of IVOCs mass into the modeling system, the additional SOA production did not compensate enough for the evaporated POA ~~or improve~~ resulting in degraded performance relative to routine network measurements.

The degraded OC model performance (with the exception of slightly improved error) was more evident at CSN sites, which are often located closer to anthropogenic emission sources. At those sites, CMAQ-AE6 OC normalized median bias (NMdnB) and error (NMdnE) were 9.9 and 43.9 % compared to −25.5 and 36.5 % in CMAQ-VBS. At IMPROVE sites, CMAQ-AE6 NMdnB and NMdnE (−55.7 and 57.6 %) were comparable to CMAQ-VBS values (−63.9 and 64.6 %), with the negative bias indicating both consistently underpredicted OC.

CMAQ-VBS also underpredicted OC compared to filter-based and AMS measurements at the Pasadena CalNex site, ~~which were in reasonably good agreement with one another~~ (Fig. 2). CMAQ-VBS OC predictions were approximately 2 to 3× lower than measured OC, with the largest ~~gaps~~ differences in modeled to measured OA mass generally occurring during photochemically active periods (e.g. 4 to 7 June) when OOA concentrations were higher (Fig. 3), suggesting the model underpredicts SOA.

3.2 Comparison against CalNex measurements at Pasadena

Figures 3 and 4 compare CMAQ-VBS results against AMS measured submicron OA PMF components, where CMAQ-VBS POA from meat cooking sources was compared against AMS COA, CMAQ-VBS POA from all other sources including motor vehicles (referred to here as non-cooking POA or ncPOA) was compared against AMS HOA, and CMAQ-VBS SOA was compared against AMS SV-OOA + LV-OOA. Additional AMS measurements of LOA and CMAQ-VBS biomass burning OA (BBOA) from residential wood combustion are included in Fig. 4 but these measurements/model results do not have a direct corresponding AMS/model value.

3.2.1 Meat cooking OA

CMAQ-VBS COA concentrations averaged 0.65 $\mu g\,m^{-3}$ (28 % of modeled OA) at Pasadena during the modeling period with a diurnal profile that was generally flat throughout the day and peaked at night. This is compared to an average AMS COA concentration of 1.22 $\mu g\,m^{-3}$ (17 % of measured OA) and a diurnal profile that peaked in the afternoon and at night, ~~with peaks occurring~~ slightly later than typical mealtimes and likely due to transport time (Hayes et al., 2013). The AMS diurnal profile at Pasadena is consistent with AMS measurements from several major urban areas, including Barcelona, Beijing, London, Manchester, New York City, and Paris (Allan et al., 2010; Huang et al., 2010; Sun et al., 2011; Mohr et al., 2012; Freutel et al., 2013). CMAQ-VBS generally compared well to AMS measurements in the morning but underpredicted the afternoon peak by 3.8× and evening peak by 2.8×.

~~We examined the theoretical partitioning of modeled COA using AMS measured OA (in place of modeled OA) to~~ To determine if partitioning alone explained the ~~low bias~~ underprediction in modeled midday COA concentrations~~. This scenarioonly~~, we considered two potential scenarios. In the first scenario, we removed model OA bias by replacing modeled OA with AMS measured OA and then calculated the theoretical partitioning of modeled semivolatile COA vapors. Using the higher AMS OA concentrations, more semivolatile CIOA vapors partitioned to the particle phase and increased modeled CIOA concentrations by approximately 10 % in the afternoon. ~~If instead the modeled CIOA was treated~~ In the second scenario, we treated the modeled CIOA as nonvolatile (100 % of emissions ~~located~~ in the particle phase)~~, model~~ . Model concentrations increased by 30–40 % and generally improved model performance (−32 % normalized median bias compared to −51 % in the semivolatile treatment). However, the modeled CIOA ~~would still underpredict~~ still underpredicted the afternoon and evening peaks by 2.9× and 2×, respectively.

Even a nonvolatile treatment was unable to reproduce the measured peaks, suggesting the model CIOA emissions were low, particularly during afternoon and evening hours. This is expected since the 2011 emission inventory excludes residential meat cooking ~~due to uncertainty in emission fraction and activity data and~~ and the inclusion of these emissions would ameliorate some of the underprediction bias in evening hours and on weekends. To account for missing residential meat cooking emissions and potential underestimates in commercial meat cooking emissions, a doubling of CIOA emissions did well to reproduce the averaged measured value (1.28 µg m^{-3} modeled vs. 1.22 µg m^{-3} measured). However, the diurnal profile applied in SMOKE to the majority of CIOA emissions (profile 26) is a low arcing profile that peaks at 15:00 LST (see Fig. ~~S14~~ S1 in the Supplement). Additional mass of emissions applied to this profile helped to capture average CIOA and improved underpredictions of the evening peak (lowered from 2.8× to 1.3×) but overpredicted measurements in the morning and maintained the underprediction of afternoon AMS-measured CIOA (Fig. ~~S13~~S2), suggesting some morning emissions should be reallocated to occur in the afternoon. It is also possible that some of the measured CIOA peak was due to photochemistry, as the afternoon peak coincides with the peak in AMS SV-OOA. ~~Given the evening peak in measured CIOA occurs during a period of relatively low photochemistry (21:00 LST), it would seem emissions are a more plausible cause for the underprediction. Furthermore, trends in hourly data supports the theory that CIOA was more influenced by emissions than photochemistry, as CIOA concentrations do not increase as sharply as AMS SV-OOA during photochemically active periods (e.g. 4 to 7 June) (Fig. 3) and the~~

~~afternoon peak corresponds to the arrival of the morning emissions from downtown LA to the Pasadena site.~~

The highest observed ClOA value (8.9 µg m^{-3}) occurred on 30 May at 20:00 LST, which corresponds to the Saturday of the Memorial Day Holiday weekend. Results from Zotter et al. (2014), who reported a high non-fossil fraction of OA at the CalNex site on 30 May, corroborate the AMS data. SMOKE/CMAQ emission processing does not allocate more emissions to holidays like Memorial Day for meat cooking, when a larger number of people grill meat and emissions are likely to be higher than normal. Therefore, we would not expect CMAQ to reproduce such events. When the ClOA measurements during the Memorial Day weekend were excluded, the midday and evening AMS peaks were reduced by 0.2 µg m^{-3} and 0.5 µg m^{-3}, respectively, which corresponds to CMAQ-VBS underpredictions of 3.3× and 2.2× (or 2.5× and 1.6× for nonvolatile emissions and 1.4× and 1× for a doubling of ClOA emissions).

Given that the majority of both modeled and measured POA at Pasadena was attributable to cooking sources, further evaluation of the total ClOA emissions as well as the diurnal profile and volatility distribution applied to those emissions may help to improve POA model performance in urban areas.

3.2.2 ~~Other~~ Non-Cooking POA

Generally, CMAQ-VBS ~~POA results (excluding meat cooking)~~ non-cooking (ncPOA) results compared reasonably well against AMS HOA measurements (Fig. 4) in total magnitude, particularly during morning and evening hours. However, modeled ~~POA~~ ncPOA was biased low, more so in the afternoon. The modeled ~~POA~~ ncPOA underpredicted the AMS HOA peak (which occurred at 14:00 LST) by a factor of 3 compared to underpredictions of 7–55 % (average of 31 %) during morning (00:00–10:00 LST) and evening (19:00–23:00 LST) hours. The modeled ~~POA~~ ncPOA peak instead occurred at night (likely due to the collapse of the planetary boundary layer) which did correspond to a measured evening peak offset by ∼ 1 h.

We ~~estimated that when underpredictions in modeled total OA were accounted for, partitioning to the particle phase increased POA~~ calculated that when modeled OA concentrations were increased to match measured OA, partitioning of SVOCs increased ncPOA concentrations by 20 %~~and the afternoon underprediction of POA was reduced to~~. The 20 % increase in modeled ncPOA corresponded to a 2.3× ~~, though performance in the~~ underprediction of afternoon ncPOA, with little change to morning and evening ~~remained relatively unchanged. When POA~~ performance. When ncPOA was instead treated as non-volatile~~(CMAQ-AE6, where CMAQ-AE6 POA = CMAQ-VBS SVOC = NEI POA),~~ , the model overpredicted AMS measurements in the morning and evening (by 1.5 to 1.8×) and underpredicted measurements in the afternoon (by 1.5 to 1.6×). The resulting diurnal pattern (Fig. ~~S12,~~ S3) was higher in the morning and evening, with a minimum in the afternoon~~)~~ ~~was~~ , similar to the more muted diurnal pattern of the semivolatile treatment (Fig. 4a) but opposite the AMS measurements (lower in the morning and evening, peaked in the afternoon).

While neither ~~POA~~ ncPOA volatility treatment captured the afternoon peak in measured ~~POA~~ncPOA, the semivolatile treatment predictions during morning and evening hours suggest it to be the more appropriate model representation of the two. However, further considerations are needed to better account for the AMS measured midday peak in ~~POA~~ncPOA. The measured HOA peak followed a similar pattern to OOA both in the diurnal profile (Fig. 4) and on an hourly basis (Fig. 3), which may suggest that photochemistry served a role in the measured HOA peak as additional OA mass attributed to photochemistry could promote partitioning of semivolatile HOA to the particle phase. However, photochemical age and CO are correlated at this location due to the arrival of downtown LA plume in the early afternoon, so the observed correlation should not be over-interpreted. Alternative aging schemes to the Robinson et al. (2007) approach used in CMAQ-VBS, such as those proposed by Grieshop et al. (2009) and Pye and Seinfeld (2010) generally produce more OA mass than the Robinson et al. (2007) scheme and if applied to primary SVOCs could better represent the ~~POA~~ ncPOA midday peak (Hayes et al., 2015) ~~.~~ assuming the majority of aged primary SVOCs (i.e. oxidized POA) remains as primary SVOCs/POA. These alternative aging schemes may also degrade the morning and evening performance, though Hayes et al. (2015) found the Grieshop et al. (2009) scheme performed reasonably well throughout the day.

Average CMAQ-VBS ~~POA~~ ncPOA concentrations were approximately a factor of 1.6 lower than AMS measured HOA values at Pasadena (0.51 vs. 0.83 µg m^{-3}). Increasing the CMAQ-VBS ~~POA~~ ncPOA emissions by a factor of 1.5 produced average modeled ~~POA~~ ncPOA concentrations (0.78 µg m^{-3}) comparable to the AMS-measured HOA, though the model overpredicted HOA in the morning and evening and underpredicted HOA in the afternoon (Fig. ~~S15). These results suggest the~~ S4). The factor of 1.5–2 underprediction in ncPOA and CIOA, respectively, is similar to the 1.6–2.3 underprediction attributed to low emissions or excessive dispersion for SOA at the Pasadena site (Sect. 3.2.3). If the underprediction were entirely attributable to emissions, these results would suggest that the 2011 NEI underestimates non-cooking related SVOCs by $\sim 1.5\times$ and cooking related SVOCs by $\sim 2\times$ and therefore our SVOCs emissions are approximately 1.5 to $2\times$ lower than those estimated using measured HOA at Pasadena in Hayes et al. (2015). However, further work is needed to quatify the role of emissions vs. transport in CMAQ at the Pasadena site.

A source of uncertainty in the ~~POA~~ ncPOA results is the volatility distribution used for industrial~~/point~~, point, and area sources (i.e. "other" sources) which is based on measurements made from diesel generator exhaust (Robinson et al., 2007). However, we assume that this has less impact on ncPOA predictions than missing emissions since the nonvolatile ~~POA~~ ncPOA treatment underpredicted the measurements and ~~POA~~ ncPOA from these sources only comprises 13 % of total modeled POA ~~,~~ (or 25 % ~~excluding CIOA~~ of ncPOA (Sect. 3.4.1)).

3.2.3 SOA

Similar to the routine measurement comparisons of total OC, CMAQ-VBS underpredicted AMS OOA (SV-OOA + LV-OOA) ~~.~~ (Fig. 4b). This is consistent with many regional air quality ~~models~~studies (Volkamer et al., 2006; De Gouw et al., 2008), including CMAQ (Foley et al., 2010), which often underpredict urban SOA. Although those studies are not specific for LA, the similarity of tracer-normalized SOA concentrations across urban areas (e.g. De Gouw and Jimenez, 2009; DeCarlo et al., 2010; Hayes et al., 2015; Zhang et al., 2015) s the occurrence of a general urban SOA under-prediction with models. Other regional models that use high S/IVOC emissions to approximately match the observed POA do match or even exceed the urban observations (e.g. Hodzic et al., 2010; Shrivastava et al., 2011) though we found this not to be the case in CMAQ-VBS. The diurnal pattern of CMAQ-VBS SOA is generally more consistent with measurements of SV-OOA compared to LV-OOA (Fig. ~~S8~~4). The fact that LV-OOA is heavily oxidized and has relatively constant concentrations suggest it to be a background source, comprised of OA formed elsewhere and transported to Pasadena (Hayes et al., 2015). Note, the diurnal profile of CMAQ-AE6 SOA (Fig. ~~S9~~4) formed from particle oligomerization (a process not included in CMAQ-VBS) did follow a similar pattern to AMS LV-OOA (relatively flat throughout the day with a midday/afternoon bimodal peak) but model concentrations were significantly ($\sim 40\times$) lower (Fig. ~~S10~~S5).

CMAQ-VBS predicted considerably more SOA mass than CMAQ-AE6 ($\sim 0.9\,\mu\mathrm{g\,m^{-3}}$ at Pasadena in CMAQ-VBS compared to $\sim 0.2\,\mu\mathrm{g\,m^{-3}}$ for CMAQ-AE6). Overall, CMAQ-VBS SOA diurnal concentrations were approximately 4 to $5.4\times$ lower than the AMS OOA, with the largest underestimate corresponding to the peak AMS measurement (13:00 LST). The underprediction could be attributed to low emissions, low photochemical age, ~~too much~~ excessive dispersion or too little transport of emissions to the Pasadena site in the model, or low intrinsic SOA production efficiency.

Comparisons of modeled and measured CO normalized for background CO ($\triangle$CO, where $\triangle\mathrm{CO} = \mathrm{CO} - \mathrm{CO}_{\mathrm{background}}$ and modeled $\mathrm{CO}_{\mathrm{background}} = 75\,\mathrm{ppb}$, see Hayes et al. (2013) for CO background measurements) show 300 ppb measured $\triangle$CO vs. 150 ppb modeled $\triangle$CO. This observation suggests CMAQ anthropogenic CO emissions, which are often used as a proxy for anthropogenic emissions, may be a factor of two too low, or alternatively that ~~too high~~ excessive dispersion and/or too low transport of emissions to Pasadena in the model results in the lower modeled CO ~~.~~ (see Fig. S6 of the Supplement for CMAQ-VBS CO model performance). Baker et al. (2015), who also used the 2011 NEI, reported a similar model underprediction (approximately a factor of two) for total VOCs at Pasadena. However, Baker et al. (2015) reported the 2011 NEI based SOA precursor concentrations were in relatively good agreement with measured values, though xylene and toluene were generally overpredicted which could be attributed to underpredictions in photochemical age leading to insufficient xylene oxidation (e.g. at 0.1 day photochemical age, $\sim 75\,\%$ of emitted xylene would remain, but at actual ambient photochemical age a larger fraction would have reacted). CMAQ SOA precursor concentrations were a factor of 1.2 too low compared to 3 h measurements and a factor of 1.1 too high compared to 1 h measurements ~~, suggesting the~~ (Baker et al., 2015). The slight overprediction of SOA precursor concentrations, along with the factor of two underprediction of CO, suggests the SOA precursor to CO emission ratio was incorrect by a factor of ~~2.~~ two. Comparisons of the ratio of xylene and toluene emissions to CO emissions in LA and Orange Counties against observed xylene and toluene extrapolated to zero photochemical age (to account for photochemistry) to observed CO support this, as the emissions ratio (0.030) is approximately twice the observed ratio (0.014) and consistent with $\triangle$CO being low by a factor of two in the model.

The role of photochemical age in ~~SOA~~ underpredictions was explored at Pasadena by examining SOA formed (plotted as SOA/ΔCO to approximately correct for differences in emissions and dilution between times) in CMAQ-VBS vs. photochemical age (estimated using $-\log(\mathrm{NO}_x/\mathrm{NO}_y)$; Kleinman et al., 2008) (Fig. 5). The slope of the best fit line ($66\,\mu\mathrm{g\,m^{-3}\,ppm^{-1}}$) was low by $\sim 1.6\times$ compared to the measured value of $108\,\mu\mathrm{g\,m^{-3}\,ppm^{-1}}$ (Hayes et al., 2015). However, when the lower ΔCO in CMAQ is accounted for, the best estimate for the underprediction is $3.2\times$. Compared to the measured photochemical age (estimated by $-\log(\mathrm{NO}_x/\mathrm{NO}_y)$), the photochemical age component of CMAQ-VBS SOA was low by $\sim 1.5\times$, which helps explain part of the underprediction in SOA concentrations (Figs. 3 and 4) but not ~~on~~ underpredictions of SOA production efficiency (Fig. 5) ~~.~~ (i.e. the efficiency per unit precursor at a given age). For reference, Fig. 5 also includes the slope for CMAQ-AE6 predictions ($8\,\mu\mathrm{g\,m^{-3}\,ppm^{-1}}$), which was much lower than the slope for CMAQ-VBS and also much lower than observations for multiple urban areas (De Gouw and Jimenez, 2009).

Examining modeled SOA vs. odd oxygen ($O_x \equiv O_3 + NO_2$) (Herndon et al., 2008; Wood et al., 2010), which leverages high measured correlations of SOA and O_x with generally good model performance of O_x (true for Pasadena during CalNex; Kelly et al., 2014), the slope for CMAQ-VBS was 72 $\mu g\,m^{-3}\,ppb\,V^{-1}$ (Fig. 5). This is approximately a factor of 2 lower than observations at Pasadena (146 $\mu g\,m^{-3}\,ppb\,V^{-1}$) (Hayes et al., 2013), where measurements were comparable to other urban areas (Wood et al., 2010; Morino et al., 2014; Zhang et al., 2015). In comparison, CMAQ-AE6 (which has identical O_x concentrations to CMAQ-VBS) underpredicted the metric by a factor of 16, again suggesting that while CMAQ-VBS underpredicts SOA, it does considerably better than the traditional CMAQ-AE6 SOA treatment. Note, in CMAQ-VBS sensitivity simulations without aging reactions (Sect. 3.4.2) the slope of SOA vs. O_x (11 $\mu g\,m^{-3}\,ppb\,V^{-1}$) was nearly equivalent to the slope of CMAQ-AE6 (9 $\mu g\,m^{-3}\,ppb\,V^{-1}$). This indicates most of the CMAQ-VBS SOA mass was produced as a result of aging of SVOCs and is further discussed in Sect. 3.4.2.

Thus our analysis suggests that the SOA production efficiency in CMAQ-VBS is too low by 1.6 to 2×; photochemical age low by a factor of 1.5×, and the remaining underprediction (1.6 to 2.3×) attributed to other factors (emissions, transport, etc.). Combining both underestimates of the SOA/ΔCO (1.5× and 3.2×) implies that SOA concentrations should be too low by 4.8×, which agrees with the 5.2× underprediction of SOA compared to AMS OOA.

One possible reason for the underestimate of SOA production efficiency in CMAQ-VBS (and CMAQ-AE6) is that CMAQ SOA yields do not account for SVOC wall loss, which Zhang et al. (2014) indicated can reduce SOA production by 2 to 4× in chambers. However, the factor of 4 is for alkane systems (speciated long alkanes are not considered SOA precursors in CB05) and toluene and specific to the smog chamber used in Zhang et al. (2014). ~~Therefore,~~ Other studies have generally reported lower values, ranging from 1.2 to 4.1 for low-NO_x conditions and 1.1 to 2.2 for high-NO_x conditions (Ng et al., 2007; Chan et al., 2009; Chhabra et al., 2011; Loza et al., 2012; Cappa et al., 2013).

Therefore, the 2-4 factor likely represents an upper bound and SVOC wall loss does not likely account for the entire underestimate of SOA production efficiency.

Another possibility for the underprediction of SOA in CMAQ-VBS is SOA formed from missing or mischaracterized (as unspeciated VOCs) IVOC emissions. There is significant uncertainty currently associated with IVOC emissions and their SOA yields. Current CMAQ-VBS IVOC emissions are scaled to primary SVOC emissions (1.5×) based on the results of a diesel generator (Robinson et al., 2007) ~~. Jathar et al. (2014) recently published updated IVOC emission factors for unspeciated compounds and SOA yield parameterizations for diesel vehicles, gasoline vehicles, and biomass burning based on more recent source specific smog chamber results. Using the results of Jathar et al. (2014) to update the~~ and could potentially be updated to utilize more recent results, such as those reported by Jathar et al. (2014) who indicated unspeciated organics (S/IVOCs) dominated SOA mass formed from combustion emissions. Future work is needed to explore if better constraining IVOC emissions and ~~parameterization in CMAQ-VBS could help to bridge the gap between model and measurements, but likely would~~ yields in CMAQ would help improve model performance, but it would likely not account for the entire missing SOA mass ~~as CMAQ-VBS simulations where~~ based on sensitivity simulations using upper bound S/IVOC emissions. In these simulations, S/IVOC emissions were increased by 3.75 × (SVOC = 1.5 × POA to match HOA, IVOC = 1.5 × SVOC), 5 × (SVOC = 2 × POA to match CIOA, IVOC = 1.5 × SVOC) and 7.5 × (SVOC = 3 × POA, IVOC = 1.5 × SVOC) but CMAQ continued to underpredict both average (by factors of 4.4×, 3.7×, and 2.9×) and daily peak (by factors of 4.6×, 3,9×, and 2.8×) measured OOA. When the factor of 7.5× is used, the model is in approximate agreement with the observations once the lower model photochemical age and low emissions/~~high~~ excessive dispersion are taken into account, which is consistent with previous modeling efforts for CalNex and elsewhere (Dzepina et al., 2009; Hodzic and Jimenez, 2011; Hayes et al., 2015). However, the approximate ~~quantitative~~ agreement may be for the wrong reasons as increased S/IVOC emissions may account for SOA from other missing (or underrepresented) formation pathways and should not be over-interpreted as direct evidence of the presence ~~and~~ of SOA formation efficiency of S/IVOCs.

Note that CMAQ-VBS does not include an oligomerization formation pathway in which heterogeneous/multiphase reactions form SOA (Ziemann and Atkinson, 2012). The lack of this pathway could account for underpredictions in production efficiency though it is plausible the SVOC aging parameterization already accounts for some of the mass formed through oligomerization. CMAQ-AE6, which does include an oligomerization formation pathway (Carlton et al., 2010), estimates approximately 20-25% of SOA at Pasadena is comprised of oligomers (Fig. S5), though because CMAQ-AE6 significantly underpredictions SOA, this equates to only a small amount of total SOA mass (0.06 µg m^{-3} on average).

3.3 Non-fossil vs. fossil carbon

In addition to tracking POA from meat cooking activities separately in CMAQ-VBS, we also added the ability to track POA from gasoline vehicles, diesel vehicles, and "other" sources separately. Tracking POA from various sources provided the opportunity to compare CMAQ-VBS non-fossil vs. fossil carbon contributions against filter-based measurements collected at Pasadena (Fig. 6) (Baker et al., 2015). ~~Measurements~~ Those measurements indicated, on average, a near even split of non-fossil (48 %) and fossil (52 %) carbonaceous mass (Baker et al., 2015)~~, and the~~ . The Baker et al. (2015) non-fossil measurements were also consistent with other collocated ^{14}C measurements collected during the same time period (51 % non-fossil) (Zotter et al., 2014).

On 6 days the measured non-fossil fraction was > 1 (values > 1 ranged from 1.1 to 3.3) and therefore measurements on these days were excluded from our analysis as outliers. We believe these outliers were due to a plume from a nearby medical waste incinerator passing directly by the measurement site. The non-fossil fraction estimates assume a non-fossil ^{14}C concentration of 1.2×10^{-12} $^{14}\mathrm{C/C}$ and emissions from medical incinerators, which contain ^{14}C, can bias the $^{14}\mathrm{C/C}$ ratio (Buchholz et al., 2013). Other results were likely also influenced by the incinerator, though to a lesser extent, biasing the non-fossil carbon fraction high.

For the purposes of the comparison, we assumed non-fossil carbon was comprised of biogenic SOC, biomass burning POC, and all meat cooking POC (measurements suggest $\sim 75\,\%$ of meat cooking carbon is non-fossil but are likely biased due to imperfections of the PMF analysis; Hayes et al., 2013; Zotter et al., 2014). We assumed fossil carbon was comprised of EC, anthropogenic SOC, POC from gasoline and diesel vehicles, and all POC from "other" emission sources. Non-fossil carbon was always underpredicted in CMAQ-VBS (average predictions of $0.61\,\mu g\,C\,m^{-3}$ vs. average observation of $1.86\,\mu g\,C\,m^{-3}$) (Table 5) and the model predicted it to be dominated by meat cooking emissions. This suggests missing SOA formation pathways, low model SOA yields, or missing emission sources of non-fossil carbon at or upwind of Pasadena, including the substantial likely underestimate of cooking POA discussed above. Higher SOA formation from cooking emissions than parameterized here (Hayes et al., 2015) could account for some of the discrepancy, although this source is poorly characterized. In-basin biogenic SOA (e.g. formed from VOCs emitted within the LA basin) and advection of marine OA are estimated to be very small (Hayes et al., 2015), and are unlikely to account for the noted discrepancy. Not enough formation and/or advection of biogenic SOA from the North may account for some of the missing non-fossil SOA as well (Hayes et al., 2015).

Contrastingly, CMAQ-VBS did a reasonably good job of predicting fossil carbon at Pasadena (average predictions of $1.81\,\mu g\,C\,m^{-3}$ vs. average observation of $1.97\,\mu g\,C\,m^{-3}$) (Table 5), though the model tended to underpredict fossil carbon during days with higher measured OOA (e.g. 4 to 10 June, Fig. 3). Fossil carbon was generally dominated by EC and anthropogenic secondary organic carbon (ASOC). Comparisons of CMAQ-VBS EC (which has an identical treatment in CMAQ-AE6) concentrations (average of $1.01\,\mu g\,C\,m^{-3}$) against CalNex filter-based measurements at Pasadena ($0.51\,\mu g\,C\,m^{-3}$) suggest that CMAQ-VBS (and CMAQ-AE6) overpredicted EC and therefore over emphasizes its contribution to total carbon. Excluding EC, CMAQ-VBS predicted considerably less non-EC fossil carbon (average of $0.80\,\mu g\,C\,m^{-3}$) compared to observed ($1.46\,\mu g\,C\,m^{-3}$) (Table 5 and Fig. ~~S17~~S7). Additional details regarding the filter-based measurements and the EC / OC split in the NEI are reported in Baker et al. (2015).

Comparisons of the CMAQ-VBS diurnal profiles for non-fossil and fossil carbon at Pasadena against measurements made by Zotter et al. (2014) indicated the model did well to capture the overall pattern of the measurements (higher non-fossil carbon in the morning and evening with the minimum occurring in the afternoon) but was biased towards fossil carbon (see Fig. ~~S18~~ S8 of the Supplement). The fact that the model represented the measured diurnal pattern well but was biased suggests that it was missing both non-fossil (in the morning and evening) and fossil sources (in the afternoon). This is consistent with model underpredictions of meat cooking POA (non-fossil) in the morning/evening, minimal contributions from model SOA (non-fossil) throughout the day, and underpredictions of the afternoon peak in anthropogenic SOA (fossil).

3.4 CMAQ-VBS sensitivity analysis

3.4.1 POA source apportionment

Higher CMAQ-VBS predictions of POA from gasoline vehicles compared to diesel vehicles was true throughout southern California (Fig. 7). Most POA was comprised of meat cooking POA, followed by POA from gasoline vehicles, “other” sources, and finally diesel vehicles. Note that the diesel vehicle panel in Fig. 7 required a scale an order of magnitude lower than the other sources. At Pasadena, ~~the breakdown of POA was as follows~~POA was comprised of: 48 % meat cooking, 18 % gasoline vehicles, 13 % biomass burning (in the form of residential wood combustion), 13 % “other”, and 8 % diesel vehicles. This further emphasizes the relative importance of meat cooking activities relative to mobile sources as well as gasoline vehicle emissions compared to diesel vehicle emissions. We note that the predicted urban POA has larger non-fossil than fossil fraction.

Of note was the limited contributions of gasoline and diesel vehicle POC emissions to total carbon at Pasadena, where fossil OC was dominated by ASOC (Fig. 6). This result, coupled with the fact that the majority of ASOC precursor emissions originated from gasoline vehicles and point sources, suggest that gasoline vehicles dominated mobile source

OC contributions (Bahreini et al., 2012; Gentner et al., 2012; Ensberg et al., 2014; Hayes et al., 2015).

3.4.2 Contributions from CMAQ-VBS SOA formation pathways

As a sensitivity study, the aging of secondary biogenic SVOCs was turned on using the same oxidation pathways used for the aging of secondary anthropogenic SVOCs in CMAQ-VBS. That is, secondary biogenic SVOCs were aged by reactions with OH in the gas-phase using a rate constant of $2 \times 10^{-11}\,\mathrm{cm^3\,molec.^{-1}\,s^{-1}}$ and each aging step reduced the volatility by an order of magnitude. ~~The aging of biogenics produced more SOA at Pasadena (~~In the simulation with aging of secondary biogenic SVOCs, SOA concentrations were $\sim 0.5\,\mathrm{\mu g\,m^{-3}}$ higher throughout the day ~~)~~ at Pasadena compared to simulations that did not age secondary biogenic SVOCs (Fig. 8). The diurnal profile indicates aged biogenic SOA concentrations were essentially constant throughout the day, which is the same pattern as AMS LV-OOA. A scenario where LA basin biogenic SOA precursor emissions were zeroed out indicated almost all (95 %) of the predicted biogenic SOA originated from outside the basin, which is consistent with Hayes et al. (2015).

The additional non-fossil carbon mass from biogenic SOA would help to close the gap in the modeled vs. measured non-fossil carbon at Pasadena. Furthermore, the additional SOA mass improved overall OC model performance at routine monitoring network sites (Table 4) comparable to, if not better, than CMAQ-AE6 model performance. Monoterpene ~~emissions~~ concentrations were underestimated at Pasadena (Baker et al., 2015), although biogenic VOCs emitted in the LA basin make a very small contribution to SOA in Pasadena. Rather~~biogenic~~ , biogenic VOCs emitted in the Central Valley and surrounding mountains are thought to ~~contribute most of the~~ be the major source of biogenic SOA observed in the basin (Hayes et al., 2015). CMAQ-VBS could potentially overestimate biogenic SOA if the underprediction of ~~monoterpenes~~ monoterpene emissions applies to other areas of California. Further evaluation of the impacts of biogenic SOA aging are needed, particularly in areas dominated by biogenic SOA, such as in the southeastern US.

Figure 8 also provides the contribution ~~for~~ of the three standard SOA formation pathways in CMAQ-VBS (VOCs, IVOCs, and aging) to predicted SOA concentrations at Pasadena. These were estimated using sensitivity simulations without IVOCs, aging, or both and then taking the difference between results from the various scenarios. The results indicate the majority of SOA was formed from aging, representing a technique to increase model SOA yields~~similar to the 4×increase in SOA yields~~. Although via a different process, the resulting outcome is similar to that obtained if SOA yields are increased to account for SVOC losses to chamber walls, as proposed by Zhang et al. (2014) and used with CMAQ-AE6 in Baker et al. (2015). ~~Additionally,~~ Also, although the inclusion of aging reactions leads to an increase in SOA concentrations, the model parameterization may overemphasize the contribution from aging as recent model to measurement comparisons with chamber experiments suggested the addition of aging reactions on top of existing parameterizations can lead to overpredictions of SOA concentrations (Zhao et al., 2015). CMAQ-VBS predicted comparable SOA (considering first generation only) from VOCs to CMAQ-AE6, which one would expect given that they ~~utilize~~ produce comparable SOA yields (see Figs. S9-S15 of the Supplement for SOA yield curves). However, the inclusion of higher volatility semivolatile products (C^* of 100 and 1000) provides high yielding points along the yield curve missing in Odum 2-product framework of CMAQ-AE6. Thus, CMAQ-VBS transfers more mass from VOC precursor to semivolatile oxidation product but requires the aging process to lower the volatility of the semivolatile product to the point of condensing to form SOA.

3.4.3 Simplified SOA parameterization

~~A~~Given the limitations in CMAQ-AE6 and CMAQ-VBS to accurately predict SOA at Pasadena and uncertainty in how best to improve predictions raises the question as to if other parameterizations can improve CMAQ performance in the near term. To this end, we have applied a simplified SOA parameterization (SIMPLE) ~~has been presented (Hodzic and Jimenez, 2011; Hayes et al., 2015) and applied here~~ in CMAQ to provide an alternative SOA modeling budget for comparison with AE6 and VBS. SIMPLE was originally developed by Hodzic and Jimenez (2011) and recently shown to perform well in predicting anthropogenic SOA at Pasadena (Hayes et al., 2015). A key goal of the parameterization is to provide a quick way to estimate the amount of anthropogenic SOA formed from pollution sources, especially for studies in which mechanistic SOA formation description is not the goal, but ~~when~~ having the correct amount of aerosol present is important for the results of the simulation. It can also serve as a simple-to-implement benchmark to compare more complex parameterizations across different models~~, when many other parameters are also changing~~. The parameterization uses a single SOA precursor (VOC*) scaled to CO emissions ~~and~~ which reacts with OH. The oxidation product is treated as nonvolatile. ~~However, it will likely need to be re-fitted to ambient data in the future, when emission control strategies change the ratio of VOC precursors to CO, or their average SOA yield.~~

~~Hayes et al. (2015) found that the SIMPLE parameterization compared favorably to measurements and VBS box model results at Pasadena.~~ In our implementation in CMAQ-VBS, we use an emission rate of 0.069 g VOC* g^{-1} CO and a $k_{\mathrm{OH}} = 1.25 \times 10^{-11}\,\mathrm{cm}^3\,\mathrm{molec}^{-1}\,\mathrm{s}^{-1}$, based on the optimum values for Pasadena reported in Hayes et al. (2015). Hayes et al. (2015) found that the SIMPLE parameterization compared favorably to measurements and VBS box model results at Pasadena.

SIMPLE predicted more anthropogenic SOA mass than CMAQ-VBS (2.5× more at the afternoon peak) following a similar diurnal cycle (Fig. 9)~~with the right diurnal cycle~~. However, it still underpredicted the AMS measured SV-OOA by a factor of 2.3× at the afternoon peak. The slope of SOA/ΔCO vs. $-\log(\mathrm{NO}_x/\mathrm{NO}_y)$ for SIMPLE was 113 $\mu\mathrm{g\,m}^{-3}\,\mathrm{ppm}^{-1}$, which was slightly more than the measured 108 $\mu\mathrm{g\,m}^{-3}\,\mathrm{ppm}^{-1}$ and suggests that the SIMPLE parameterization is performing as expected and has an intrinsic SOA formation efficiency consistent with the observations. Underpredictions of photochemical age and low emissions/~~too high~~ excessive dispersion most likely explain the observed difference, as CO was underpredicted both in this study (see the Supplement) and in Baker et al. (2015). The factor of 2 difference in modeled vs. measured CO indicated in Sect. 3.2.3 are similar to the 2.3× underprediction in SIMPLE. This shows that the use of SIMPLE in a model can help diagnose model problems that are unrelated to the model intrinsic SOA formation efficiency.

CO inventories can also be estimated from ambient data (e.g. Brioude et al., 2013), providing an alternative ~~if the quality of official inventoriesdegrades in the future~~to bottom-up inventories.

4 Conclusions

The application of the CMAQ-VBS over California and Nevada in May and June 2010 was found to underpredict OC at routine monitoring networks, likely due to underpredictions of SOA (missing formation pathways, emissions, formation efficiency, etc.). The underprediction of CMAQ-VBS was more pronounced than CMAQ-AE6, particularly at CSN monitors (Table 3~~and Table S3~~) which are primarily located in urban areas and where modeled POA comprised a higher percentage of OC, and therefore likely attributed to the semivolatile treatment of POA in CMAQ-VBS. However, ~~the lower~~ CMAQ-VBS ~~POA appears to correct for a compensating bias of CMAQ-AE6 POA overpredictions as CMAQ-VBS~~ was able to better capture the POA/SOA split, total POA mass, and total SOA mass compared to AMS measurements at Pasadena. CMAQ-VBS predicted less POA (as a result of evaporation) and more SOA (90 % attributed to aging of anthropogenic SOA) compared to CMAQ-AE6.

CMAQ-VBS underpredicted the measured AMS OOA midday peak by 5.4×, albeit to a lesser extent than CMAQ-AE6 predictions (38×). Using two new methods, one based on species ratios and the other based on a simplified SOA parameterization from the observations, we apportioned the SOA underprediction from CMAQ-VBS to too slow photochemical oxidation based on $NO_x : NO_y$ (1.5× lower than observed at Pasadena), too low intrinsic SOA efficiency (1.6 to 2× too low for Pasadena), and too low emissions/~~high~~ excessive dispersion for the Pasadena site (1.6 to 2.3× too low/high). Individually, none of the recently proposed updates for SOA predictions (SVOC wall loss (Zhang et al., 2014), unspeciated IVOCs (Jathar et al., 2014), aging of biogenic SOA (Donahue et al., 2012), and aging of ~~SVOCs~~S/IVOCs) can resolve the model/measurement discrepancy, but a combination of the factors may.

POA at the Pasadena CalNex site was found to be mostly from meat cooking emissions (48 %) and to lesser extents from gasoline vehicle emissions (18 %), diesel vehicle emissions (8 %), biomass burning (13 %), and “other” emissions (13 %), and interestingly more than 50 % from non-fossil (cooking and biomass burning) emissions. Furthermore, the semivolatile treatment of POA better represented the measured AMS diurnal profile of HOA than nonvolatile POA, particularly during morning and evening hours. Using sensitivity simulations, we estimated that the NEI POA captures approximately 50 % of the observed meat cooking SVOCs and approximately 66 % of SVOCs from all other sources. However, CMAQ-VBS underpredictions of POA may also be attributed to the volatility distribution applied to emissions or missing/mischaracterized POA oxidation~~and~~. A sensitivity simulation suggested increasing CMAQ-VBS SVOC emissions by 1.5 to 2× would degrade POA model performance in the morning and evening.

Regarding which OA treatment is more appropriate, CMAQ-VBS or CMAQ-AE6, depends on the user’s modeling needs and goals. The traditional ~~treatment~~ CMAQ-AE6 treatment, while it has known limitations (generally overpredicting POA and underpredicting SOA), more accurately predicts total OA measured at routine monitoring networks~~(though due to possible compensating model biases, particularly at sites located in urban areas which are more influenced by POA)~~. Conversely, CMAQ-VBS ~~better represents the~~ treats primarily emitted OA as semivolatile and easily incorporates an estimate of IVOC emissions missing from the inventory to provide improved predictions on the total SOA mass and the POA/SOA split at Pasadena. The AE6 approach provides some utility in that parent VOCs and reaction processes are more clearly linked to SOA which is sometimes useful for scientific and regulatory model applications. Due to the difference in SOA/POA splits, the two CMAQ configurations may respond differently to VOC and/or NO_x emission reductions, which should be examined in future work. Another area for future work is updating the POA emission inventory, originally developed for a nonvolatile POA treatment, to account for semivolatile POA and likely improving CMAQ-VBS total OA predictions.

A future extension of this work includes enhancements to SOA from IVOCs in CMAQ. IVOC emissions are currently scaled to POA. Recent results published by Jathar et al.

(2014) provide new insights in how to better estimate IVOC emissions from gasoline and diesel vehicles and biomass burning. With updated IVOC emissions and parameterizations, coupled with comparisons of IVOC measurements made during CalNex (Zhao et al., 2014), ~~CMAQ-VBS~~ CMAQ predictions may be able to close the gap between measured and modeled SOA and provide additional certainty in both IVOCs and the SOA formed from IVOCs.

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Supplement. In addition to figures and tables already referenced in the text, the Supplement includes additional comparisons of CMAQ-AE6 and VBS (Fig. S16); comparisons of CMAQ-VBS inorganic aerosols against AMS measurements (Fig. S17); CMAQ-VBS non-fossil and fossil C at Bakersfield, CA (Fig. S18); CMAQ-VBS SOA contributions at Bakersfield, CA (Fig. S19); volatility distribution of CMAQ-VBS organic aerosols and vapors at Pasadena and Bakersfield (Fig. S20); and CMAQ-VBS modeled OH diurnal profile at Pasadena (Fig. S21).

Disclaimer. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official agency policy.

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Table 1. CMAQ-VBS volatility distribution of POA emissions from gasoline vehicles, diesel vehicles, biomass burning, nonvolatile (e.g. fugitive dust), meat cooking, and "other" sources.

Source	Non-Vol[a]	10^0	10^1	10^2	10^3
Gas Vehicles (GV)[b]	0.27	0.15	0.26	0.15	0.17
Diesel Vehicles (DV)[c]	0.03	0.25	0.37	0.24	0.11
Biomass Burning (BB)[d]	0.20	0.10	0.10	0.20	0.40
Nonvolatile (NV)	1.00	0.00	0.00	0.00	0.00
Meat Cooking (MC)[e]	0.35	0.35	0.10	0.10	0.10
Other (OP)[f]	0.09	0.09	0.14	0.18	0.50

[a] C^*=0 in the nonvolatile bin, which at typical ambient conditions at Pasadena would represent compounds with $C^* \leq 10^{-1}\,\mu\mathrm{g\,m^{-3}}$).

[b] May et al. (2013b).

[c] May et al. (2013c).

[d] May et al. (2013a).

[e] Estimated from Huffman et al. (2009).

[f] Robinson et al. (2007).

Table 2. Domain and modeling period (4 May to 30 June 2010) total 2011 NEI POA emissions (tons) for gasoline vehicles, diesel vehicles, biomass burning, nonvolatile (e.g. fugitive dust), meat cooking, and “other” sources.

Source	Emissions (t)
Gas Vehicles (GV)	1990
Diesel Vehicles (DV)	800
Biomass Burning (BB)	8550
Nonvolatile (NV)	540
Meat Cooking (MC)	1470
Other (OP)	2070

Table 3. CMAQ-VBS and CMAQ-AE6 organic carbon (OC) and elemental carbon (EC) model predictions evaluated against routine modeling network sites in the modeling domain (IMPROVE and CSN). Evaluation metrics include median bias (MdnB[a]), median error (MdnE[b]), normalized median bias (NMdnB[c]), and normalized median error (NMdnE[d]).

OA Treatment/ Species	Network	Mean Obs. (µg m^{-3})	Mean Model (µg m^{-3})	MdnB (µg m^{-3})	MdnE (µg m^{-3})	NMdnB (%)	NMdnE (%)
CMAQ-VBS	IMPROVE (247)	0.71	0.23	−0.38	0.38	−63.9	64.6
OC	CSN (159)	1.26	0.75	−0.31	0.44	−25.5	36.5
CMAQ-AE6	IMPROVE (247)	0.71	0.29	-0.33	0.34	-55.7	57.6
OC	CSN (159)	1.26	1.22	0.12	0.71	9.9	43.9
CMAQ-VBS	IMPROVE (249)	0.10	0.09	−0.02	0.03	−20.3	40.8
EC	CSN (159)	0.33	0.58	0.24	0.26	81.4	87.7
CMAQ-AE6	IMPROVE (249)	0.10	0.10	-0.01	0.03	-13.4	40.1
EC	CSN (159)	0.33	0.60	0.25	0.27	83.3	89.4

[a] $MdnB = median(model - obs)_N$

[b] $MdnE = median(|model - obs|)_N$

[c] $NMdnB = \frac{median(model-obs)_N}{median(obs)_N} \times 100\%$

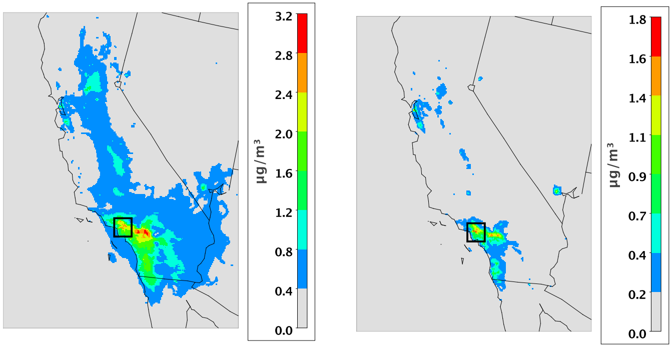
[d] $NMdnE = \frac{median(|model-obs|)_N}{median(obs)_N} \times 100\%$

Table 4. As in Table 3 but for CMAQ-VBS organic carbon (OC) model predictions in sensitivity simulations with aging of biogenic SOA.

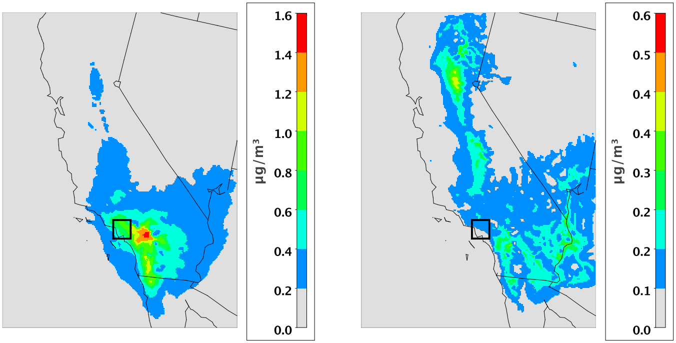
Species	Network	Mean Obs. (µg m^{-3})	Mean Model (µg m^{-3})	MdnB (µg m^{-3})	MdnE (µg m^{-3})	NMdnB (%)	NMdnE (%)
OC	IMPROVE (247)	0.71	0.42	−0.25	0.27	−41.8	45.0
	CSN (159)	1.26	1.00	−0.16	0.37	−13.4	30.6

Table 5. Comparisons of CMAQ-VBS non-fossil and fossil C against filter-based measurements (N=25).

	CMAQ-VBS (μg C m^{-3})	Obs. (μg C m^{-3})
Non-fossil C	0.61	1.86
Fossil C (with EC)	1.81	1.97
Fossil C (without EC)	0.8	1.46

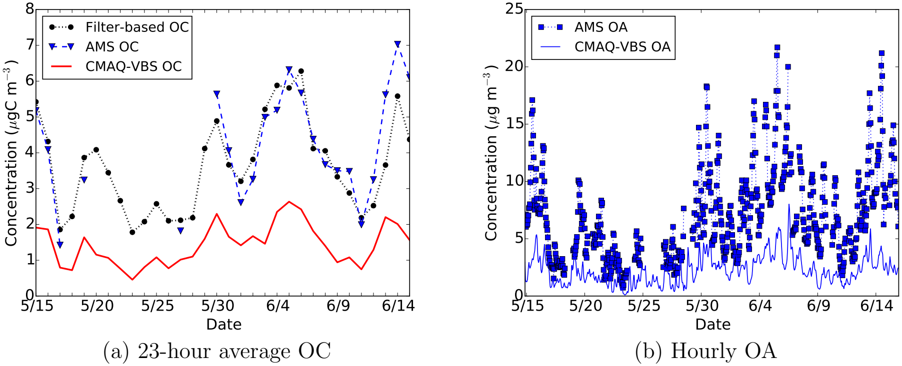


(a) Total OA (b) POA



(c) Anthropogenic SOA (d) Biogenic SOA

Figure 1. CMAQ-VBS modeling period average (15 May to 30 June 2010) concentrations of total OA **(a)**, primary organics **(b)**, anthropogenic SOA **(c)**, and biogenic SOA **(d)**. The black box indicates the approximate location of Downtown Los Angeles and Pasadena. Note each plot uses a unique scale.



(a) 23-hour average OC

(b) Hourly OA

Figure 2. **(a)** 23 h average modeled and measured (EPA filter-based and AMS) OC and **(b)** hourly modeled and AMS measured OA at Pasadena. AMS measurements in **(a)** were converted to OC using OM to OC ratios reported in Hayes et al. (2013) and include only days with $>$ 16 hourly measurements (i.e. 18/5, 20/5-26/5, 28/5, and 29/5 are excluded due to missing measurements).

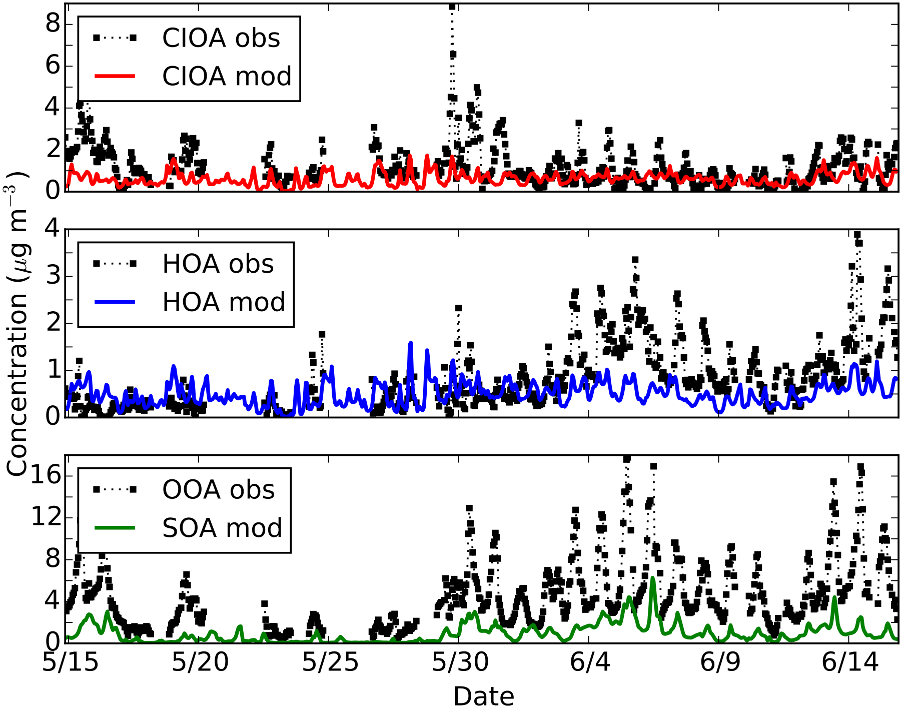
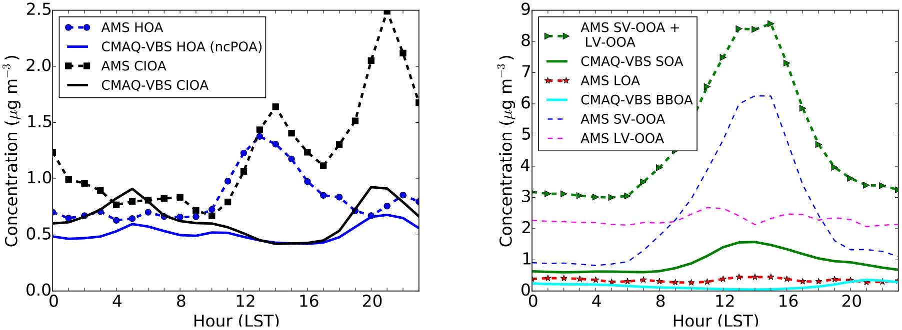
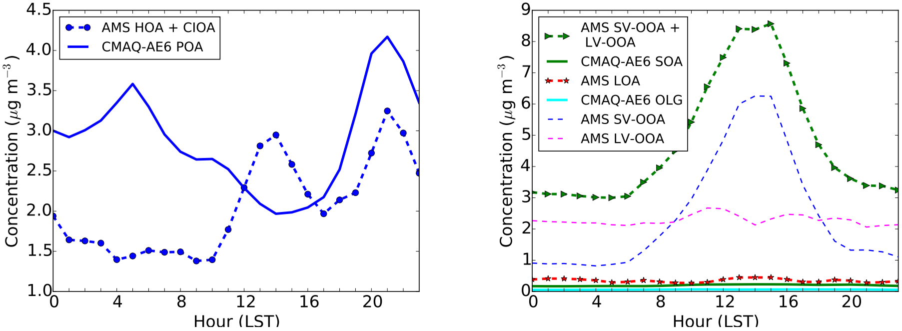


Figure 3. Hourly AMS measured (CIOA obs) and CMAQ-VBS predicted (CIOA mod) meat cooking POA (top), hydrocarbon-like OA (HOA) and ~~POA~~ ncPOA (middle), and OOA (SV-OOA + LV-OOA) and SOA (bottom) at Pasadena.



(a) CMAQ-VBS Primary-like (b) CMAQ-VBS Secondary/OOA-like



(c) CMAQ-AE6 Primary-like (d) CMAQ-AE6 Secondary/OOA-like

Figure 4. Diurnal profile of ~~CMAQ-VBS modeled and~~ AMS measured PMF OA components against CMAQ-VBS (a and b) and CMAQ-AE6 (c and d) predictions at Pasadena.

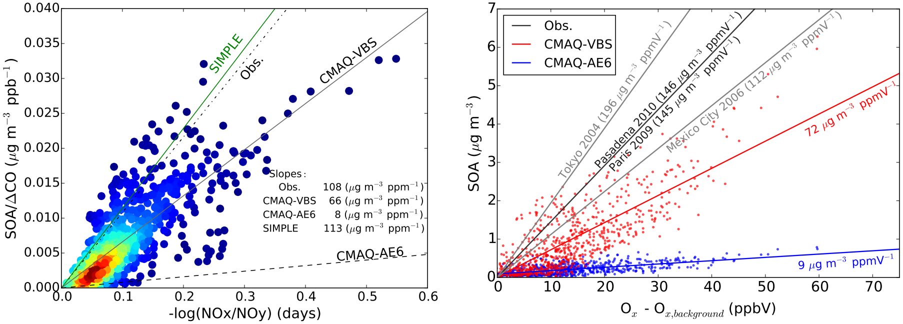
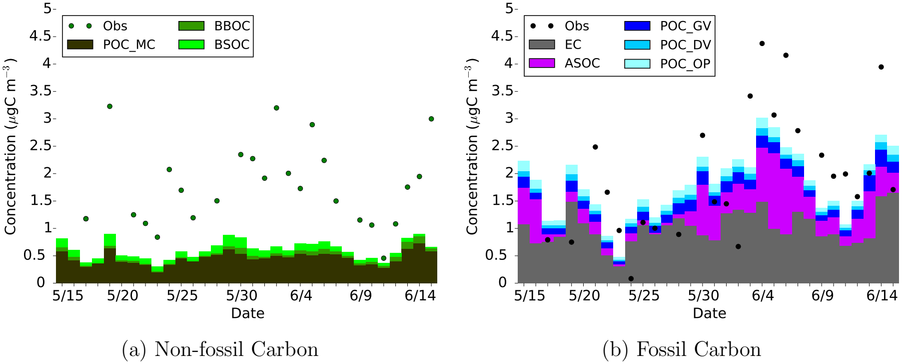
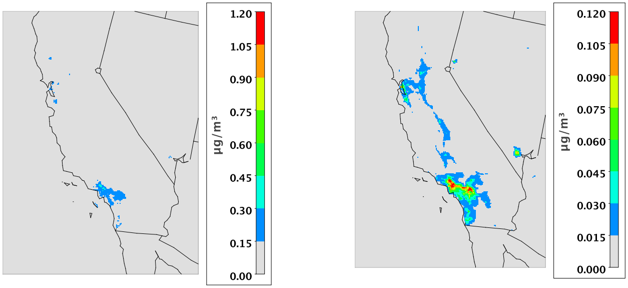


Figure 5. Left: CMAQ-VBS modeled SOA/△CO vs. photochemical age $[-\log(\mathrm{NO}_x/\mathrm{NO}_y)]$ at Pasadena. Colors indicate the relative density of points determined using the Gaussian density kernel estimate (red corresponds to high density and blue corresponds to low density). Also indicated are the slopes of the best fit lines for the same metric for observations (Hayes et al., 2015), CMAQ-VBS, ~~and~~ traditional CMAQ (CMAQ-AE6), and CMAQ with the SIMPLE SOA treatment (Sect. 3.4.3). Right: CMAQ-VBS and CMAQ-AE6 SOA vs. $\mathrm{O_x}$ ($\mathrm{O_3} + \mathrm{NO_2}$) minus $\mathrm{O_x}$ background at Pasadena. Also plotted are the slopes of the best fit line for the same metric for observations made from a number of urban areas, including Pasadena.

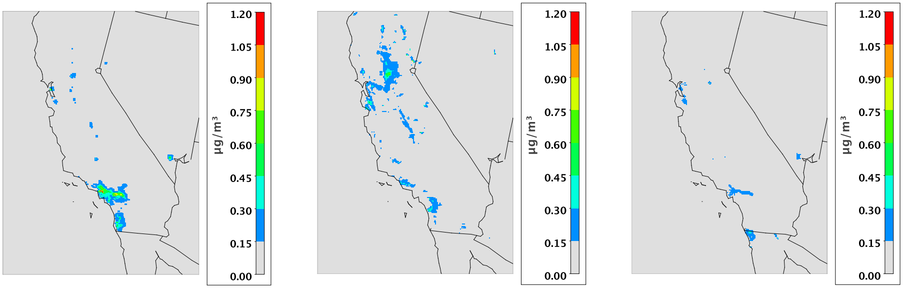


(a) Non-fossil Carbon (b) Fossil Carbon

Figure 6. Daily average CMAQ-VBS **(a)** non-fossil and **(b)** fossil carbon at Pasadena. Non-fossil carbon model species include primary organic carbon from meat cooking (POC_MC), biomass burning OC (BBOC), and biogenic secondary OC (BSOC) while fossil carbon model species include elemental carbon (EC), anthropogenic secondary OC (ASOC), and primary organic carbon from gasoline vehicles (POC_GV), diesel vehicles (POC_DV), and other sources (POC_OP).

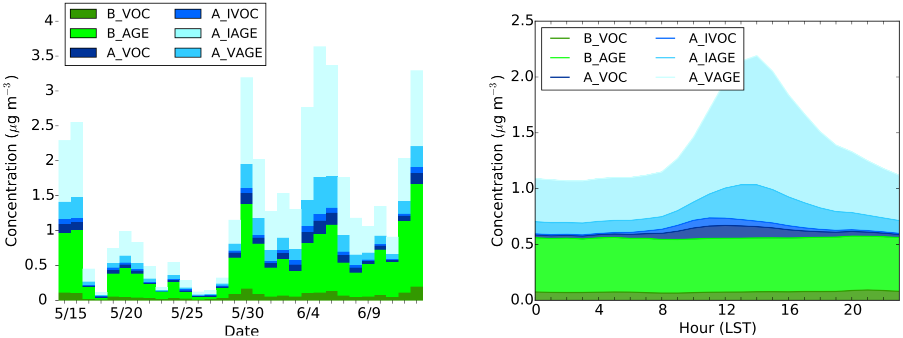


(a) Gas Vehicles (b) Diesel Vehicles



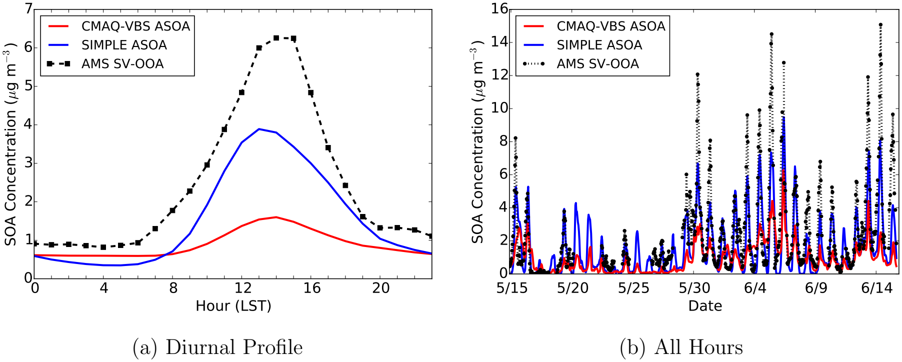
(c) Meat Cooking (d) Biomass Burning (e) Other

Figure 7. CMAQ-VBS modeled primary OA concentrations from gasoline vehicles **(a)**, diesel vehicles **(b)**, meat cooking **(c)**, biomass burning **(d)**, and "other" sources **(e).** Note the scale for diesel vehicles is an order of magnitude lower than for other sources.



(a) Daily Average (b) Diurnal Profile

Figure 8. Model contributions ~~of~~ to SOA at Pasadena from first-product anthropogenic and biogenic VOCs (A_VOC, B_VOC)~~,~~; first-product anthropogenic ~~and biogenic~~ IVOCs (A_IVOC, B_IVOC)~~,~~; and aging reactions of ~~anthropogenic and biogenic~~ secondary SVOCs originating from anthropogenic IVOCs (A_~~AGE~~IAGE), anthropogenic VOCs (A_VAGE), and biogenic VOCs (B_AGE)~~(originating from both VOCs and IVOCs) to SOA at Pasadena~~. Note, the aging of biogenic SVOCs was turned on only during sensitivity simulations.



(a) Diurnal Profile

(b) All Hours

Figure 9. Comparison of the SIMPLE SOA parameterization in CMAQ to CMAQ-VBS SOA and AMS OOA **(a)** diurnal cycle and **(b)** all hours at the Pasadena CalNex site.