REVIEWER 1

Interactive comment on "Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield" by K. R. Baker et al.

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The authors present a detailed diagnostic evaluation of CMAQ model predictions for organic carbon during the CalNex study in California. Even after two decades of regional air quality model development, there still remains wide gaps between measurements and model predictions for gas and particle phase organic carbon. The manuscript nicely introduces the field of research and explains well the complexity of modeling organic aerosol. The manuscript is well written and figures and tables are nicely presented. The manuscript also places this work in the context of the state of science very well.

Overall, I wonder what is causing the day-to-day wide variations in carbon isotope at Pasadena. The model is not capturing this variation at all. Is this related to small-scale meteorological features, localized emission sources, grid spacing limitations? Clearly, more work is needed in the laboratory to parameterize SOA yields as a function of a wide range of precursors and aerosol compositions. The manuscript concludes that additional work is needed to characterize the volatility for ambient POA sources upon dilution and parameterize the unaccounted for IVOC (intermediate volatile) emissions. I would recommend the manuscript for publication with only minor comments, as listed below.

The reviewer is correct to point out some features of CMAQ model performance (e.g. day to day variation in modern carbon fraction of OA) are not fully explained and could be explored further with additional projects. We appreciate the positive comments and want to note that we are working on follow-up projects that include manuscripts showing POA/SOA CMAQ performance when using the volatility basis set approach for the same CALNEX period and modeling platform presented here and also a project examining the impacts of IVOC emissions on CMAQ estimated OA. These projects should provide more information about what is influencing the model's lack of skill in capturing the day to day variability in POA/SOA and contemporary-modern carbon fraction.

Introduction
Pg 4. Line 15. "Given the direct relationship between precursor VOC and OH radical abundance and SOA formation,...." Can you rephase this statement as it is not clear which species directly relate to which species? SOA formation also depends on other oxidants, particle phase concentration and components, and other met variables such as temperature, relative humidity.

Text has been changed to be clearer that we are not trying to compile a complete list of chemical species and physical processes that influence SOA formation, but note there is a relationship between VOC precursors, OH radicals, and OA. One of the primary objectives of this manuscript is to evaluate all 3 of these simultaneously to focus future work on OA model representation. The revised text follows.

> Given the relationships between precursor VOC, OH radical abundance and SOA formation, it is important to simultaneously evaluate the model representation of all three within the context of how organic species evolve in the atmosphere to diagnose persistent SOA model bias.

Methods

Pg 6. Line 15. Can the authors give more details on the nesting options used. For CMAQ, are the initial chemistry variables recycled from end of the last run or are they interpolated from the lower resolution parent model? For the high resolution WRF runs, do the initial conditions at each hour recycle from the last run (aerosol and cloud variables) or do they come from the regional WRF parent model and met analysis. Do the CMAQ met boundary conditions for the high resolution run come from the regional WRF model or from the high resolution WRF model. Is a spin-up time used to develop the clouds for the high resolution runs.

The CMAQ initial chemistry conditions are based on output from a coarser continental scale CMAQ simulation for the entire year of 2010. The coarse continental scale CMAQ simulation was run continuously from December 2009 and the first week of the 4 km fine scale CMAQ simulation is not used to minimize initial condition influence. The WRF model was run for the 4 km simulation and initialized from a 12 km (12NAM) meteorological analysis dataset that combines hemispheric scale prognostic meteorological model output with surface and upper air observation data. The WRF model was run in 5.5 day blocks and the first half day was not used to minimize initialization influence. Additionally, WRF was nudged to the underlying analysis field above the boundary layer to improve representation of mesoscale features. Weather during this time period and area was generally clear skies, meaning any discontinuities that may come about for clouds between 5 day blocks of WRF simulations should minimally impact the CMAQ model estimates. New manuscript text providing additional information about how initial conditions were treated follows.

> The coarser continental U.S. CMAQ simulation was run continuously from December 2009 through this study period and the first week of the finer 4 km CMAQ simulation was not used to minimize the influence of initial chemical conditions.

Pg 7. Line1. Change "was" to "were".

The reviewer is correct and this has been changed in the manuscript.

Pg 7. Line 9. Mobile emissions were generated from CARB. Can the authors expand a couple more lines and a reference as to how the mobile emissions were calculated, e.g. MOBILE, MOVES, traffic flow models?

Based on the reviewers comment, additional text has been added regarding the mobile emissions used for these applications. We used the SMOKE-MOVES tool that integrates the MOVES mobile model with SMOKE to generate mobile emissions estimates. An additional step was taken to adjust these emissions to match mobile emissions data reported by the California Air Resources Board (CARB). Revised text follows.

> Mobile source emissions were generated using the SMOKE-MOVES integration approach (United States Environmental Protection Agency, 2014) and then interpolated between totals provided by the California Air Resources Board for 2007 and 2011.

Pg 8. Line 11. What version of SAPRC07 was used...detailed, toxics, condensed?

The SAPRC07TB condensed mechanism was applied for these simulations. Text in the methods section has been updated to add this specificity about the version of the SAPRC mechanism used in CMAQ. Revised text follows.

> Gas-phase chemistry is simulated with the SAPRC07TB condensed mechanism (Hutzell et al., 2012) and aqueous-phase chemistry that oxidizes sulfur, methylglyoxal, and glyoxal (Carlton et al., 2008;Sarwar et al., 2013).

Pg 9, Line 2. I think fragmentation reactions should also be included as they produce the small carboxylic acids.

Based on this comment, text in the manuscript has been revised to indicate there are multiple processes being represented in CMAQ's aqueous-phase SOA representation. Here, we just name two of the various processes, one of which could potentially be fragmentation as noted by the reviewer. Revised text follows.

> Aqueous-phase organic chemistry represents multiple processes, including functionalization and oligomerization, because some photooxidation products are small carboxylic acids and others are high molecular weight species (Tan et al., 2010;Carlton et al., 2007).

Pg 18. Line 4. Are there any ship or aircraft-based CO measurements to help validate upwind boundary conditions?

We have reviewed the ship and aircraft measurements and were not able to clearly differentiate CO originating from the lateral boundary and that from local or regional sources such as shipping or other anthropogenic/biogenic sources. Modeled CO source contribution could be estimated using CMAQ source apportionment (Kwok et al., 2015). We agree that would be an interesting question to pursue but it would be outside the scope of this work given that CO is not a critical evaluation element. We plan to keep this in mind for future projects that have more emphasis on CO performance.

Results and Discussion

Pg 18, Line 5. Are there any results for total VOC reactivity? Stroud et al (2008) performed a comparison of total modeled and measured VOC OH reactivity to assess predictions of peroxy radical production rates.

This type of evaluation would be an interesting extension of the work done here to provide more information about how well this modeling system is predicting peroxy radicals. Here, we chose to focus on OH and HO2 directly as opposed to less direct methods to assess performance. This suggestion certainly has merit and will be kept in mind for future assessments.

Pg 20. Line 20. Should "exists" be changed to "does not exist" as the sentence states there is vegetation in the San Joaquin Valley.

Here, we are stating that the sesquiterpene SOC tracer methodology is clearly uncertain since we know sesquiterpene emitting vegetation exists in the area but none was measured, however this could also be due to the sesquiterpenes being oxidized before reaching the VOC measurement location.

Pg 21. Line 12. At Pasadena, I would think that SOA formation would be in the high NOx limit, so the SOA formation would be less dependent on HO2 than NOx.

We expect SOA to be formed through both high and low pathways and the CMAQ model does predict SOA from both pathways at Pasadena. SOA formation pathways are more dependent on the ratio of these species rather than mixing ratios or concentration, and since the low NO_X pathway has higher SOA yields it is difficult to determine which is more important even in an urban area that has an abundance of NO_X emissions. In general we agree with the reviewer that SOA at Pasadena during this time of year would be less dependent on HO2. Text in the manuscript presents a similar argument that SOA is largely formed from the high-NO pathway.

> Of these channels the IEPOX channel is thought to have the largest SOA production potential, but the chemistry in the LA basin is dominated by the high-NO channel (Hayes et al., 2014) and thus IEPOX is not formed from isoprene emitted within the LA basin. Consistent with that observation, the AMS tracer of IEPOX SOA is only detected at background level in the LA basin.

Pg 22. Line 18. The recent study by Stroud et al (2014) also required an increase in unaccounted for SOA precursor emissions (IVOCs and SVOC) to compare to rapid SOA formation observed downwind of a major highway. Their simulations of POA also improved by considering POA evaporation to form reactive SVOC species.

We appreciate the reviewer providing this relevant reference for this manuscript and we agree it broadly supports the need to follow up on treating POA as semi-volatile and better accounting for SOA from IVOC emissions. This paper is now referenced in this manuscript. In addition, we have been working on separate follow up projects that extend the work shown here to include CMAQ simulations using the volatility basis set to treat POA as semi-volatile and also a project looking at the impacts of better characterizing IVOC impacts on SOA for this CALNEX period.

Pg 23, Line 16. Water soluble organic aerosol can be useful to constrain sources.

This is an interesting suggestion and warrants further investigation as part of follow-up research in this area. It would be possible to compare water soluble organic aerosol with the other OA measurement methods made at Pasadena and look for relationships where measurements agree or disagree and postulate about sources or processes that could be contributing to differences. CMAQ does not currently differentiate water soluble OA. All PM2.5 are treated as an internally mixed particle so it would not be possible given CMAQ's current OA formulation to directly compare a measurement of water soluble OA with CMAQ. The observation based comparison is complex enough that it would warrant a follow-up project or be included as part of a follow-up project.

Figure 1. What are the blue colored species above MGLY and GLY that have the same names? Can you put an explanation in caption?

Hydrated glyoxal and hydrated methylglyoxal have higher molecular weights in CMAQ and different saturation vapor pressures (Table S3). The color scheme for Figure 1 has been changed based on this comment to clearly differentiate the hydrated forms of these species in CMAQ.

Table S1a. Is residential food cooking included in commercial food cooking? I would think they might be of similar magnitude.

Residential food cooking is not included in the 2011 NEI, only commercial food cooking. The reviewer raises a good point in that there is some amount of meat cooking emissions not being accounted for in this modeling study (and any modeling study based on the NEI). The relative amount of residential meat cooking compared to commercial cooking is difficult to approximate given the lack of reliable inventory data. However, it seems reasonable to expect residential meat cooking would be smaller than commercial meat cooking since commercial restaurants operate and cook throughout the daytime and evening hours and each day of the week where residential cooking would be most often over a few hours in the early evening and spread out on weekends. We are currently working on a follow up project where CMAQ is applied with VBS and we include a volatility set for meat cooking. Model estimates are generally comparable in magnitude to the meat cooking estimated using PMF/AMS observation data taken at the Pasadena site. However, it is notable that CMAQ's meat cooking estimates are slightly lower than the AMS estimates for that source and that seems reasonable considering residential meat cooking is not included in the inventory.

Figure S2. NO3-initiated isoprene oxidation could be a large source of semi-volatile production at night in an urban environment. Can any simple calculations be done based on predicted NO3 and SOA yields?

The reviewer raises a good point that the NO3 isoprene oxidation pathway is not included in this version of CMAQ and would contribute some amount of SOA. Given the low concentrations of isoprene at night in these areas it is expected that this would be a minor production pathway. This pathway is included in the next release of CMAQ (version 5.1) and new SOA estimates could be directly estimated and compared to OA estimated here with the current version 5.0.2 to determine the importance of that pathway. Unfortunately, that version of the model is not available at this time. This is a good idea and one that will be explored later in 2015 when the newer version of CMAQ is released.

REVIEWER 2

Interactive comment on "Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield" by K. R. Baker et al.

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Review of Baker et al, "Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield", submitted to ACP, 2015.

Overall I think this was a reasonable comparison of the CMAQ model to observations. I have some specific issues with regards to the methodology used – these require some clarifications in the text. A greater concern is that the authors are apparently unaware of previous and parallel work going on, some of which is in the same region, which suggests that much of the missing/unattributed SOC mass may be associated with the emission of intermediate volatility compounds, co-emitted from sources such as the mobile sector along with the precursor compounds resolved in the CMAQ dataset. This work needs to be referenced and discussed in the text – ideally, if emissions estimates of these compounds are readily attainable from the literature, an additional model run could be carried out to determine their impact on the results. However, the effort required for this additional run may be sufficiently large to be a subject of the next phase of this research.

The commenter is correct that additional work needs to be done using this model platform treating POA as semi-volatile and also accounting for IVOC emissions. We are currently close to submitting a second manuscript to ACP where CMAQ is applied for this case study using a volatility basis set approach. A third project is underway where we use available information in literature to better estimate IVOC emissions in the emission inventory to determine whether that improvement would improve model estimates of total PM2.5 organic carbon mass and the POA/SOA split. These are both substantial projects and build upon the work presented here.

Larger issues:

(1) Intermediate Volatility Compounds: Introduction, pages 160 to 162, and at various places throughout the text (see Minor Comments section following). The authors have not mentioned (and may be unaware of) the recent Intermediate Volatility compound research (c.f. Zhao et al, "Intermediate-volatility organic compounds: a large source of secondary organic aerosol, Env. Sci. & Tech., 48(23), 13743-13750, 2014, also studied during CalNex. The latter paper suggests that most of the southern California SOA mass originates in these compounds rather than oxidation of VOCs such as the aromatics and monoterpenes and the mechanism for SOC formation included within this version of CMAQ. There are other papers suggesting their importance (Tkacik et al, ES&T 46(16), 8773-8781, 2012; Presto et al., ES&T 43(13), 4744-4749, 2009; Helal et al, Atmos. Chem. Phys., 14, 10439-10464, 2014. This work suggests that a substantial proportion of what has up to this point classified as "secondary" organic aerosol, may originate in the high temperature emission of oxygenated species which condense once reaching ambient temperatures. This mechanism has been proposed as an alternative to the assumption of increasing the yield of SOA from oxidation of VOCs beyond that which is measured in the laboratory, as has been done

in the authors' paper. The above literature should be referenced and discussed in the Introduction, and the potential impact on the authors' results should be discussed as a caveat on their conclusions.

We agree this is an important aspect of OA formation in southern California that needs for exploration. As noted above, we are currently working with the PI that made IVOC measurements during the CALNEX field campaign on a new manuscript that illustrates the impact of IVOC emissions on this particular modeling platform and area. Additional references noted by this reviewer (Zhao et al., 2014) and the 1st reviewer (Stroud et al., 2014) should help emphasize the importance of better understanding IVOC contribution to OA in this manuscript as we did not intend to imply otherwise. Additional text has been added to the introduction section outlining the major findings of (Zhao et al., 2014).

> Lower volatility VOC measurements made at Pasadena have been estimated to produce approximately 30% of fresh SOA in the afternoon with a large contribution to these low volatility VOC from petroleum sources other than on-road vehicles (Zhao et al., 2014).

(2) Description of the air-quality model's SOC formation processes, e.g. page 163/line 26-164/5: This is a very brief and incomplete description of the air-quality model. Specifically, given that the issue at hand is the model's ability to simulate secondary organic aerosol, there needs to be a few pages describing how this specific version of the model creates SOA in its base case, here, not in the supplemental material (it is the key issue studied in this paper, hence should be described in some detail in the manuscript itself). Figure 1 shows the log10(C*) of the different species – how were these values determined? Laboratory measurements / structural relationships, etc? Each process by which organic aerosol formation takes place needs to be described in more detail, along with the sources of reaction rates used in the model parameterizations for these processes.

Additional information about CMAQ's SOA approach and underlying data are available in the Supporting Information for this manuscript. Details of the CMAQ treatment for SOA including reaction rates and the source of data for saturation vapor pressures are provided in great detail in (Carlton et al., 2010). The reaction rates, yields, and saturation vapor pressures have not changed in CMAQ since the publication of that manuscript so that information is up to date. We certainly appreciate the reviewer's sentiment to fully include all pertinent details into each manuscript but we feel that given word limit constraints and overall readability this information is best in the (Carlton et al., 2010) manuscript where a complete description is available.

(3) 164/27-165/8, and Table 2, page 167 lines 15-22, Page 165, lines 16-20, and section 3.5: Given that the methodology in linking observed tracers to SOC totals is crucial for evaluating the model's performance for same, some description of that methodology, and its likely error range, is needed within the text. What is the likely precision of the linkage between tracers and SOC mass in the methodology referenced in this section? There needs to be a discussion on the methodology used to create the "observed" SOC from the tracers, given that they are later used as a means to estimate model accuracy (e.g. in Figures 5 and 6). One question/concern I have here is that if some methodologies would provide an estimate of the SOC "associated with" aromatic compounds, for example, as opposed to an estimate of the SOC "created by oxidation of aromatic compounds". The former would allow for the co-emission of other condensable species in addition to the precursor aromatics being counted as "aromatic SOC" in the subsequent measurement analysis, and hence the authors inference through their sensitivity study that the aromatic oxidation yields of SOC may be too low. Can they eliminate the potential for co-emission of

IVOCs with aromatics and other VOC precursors of SOC as another, unaccounted for, source of SOC, in the use of tracers to estimate observed SOC sources?

Based on this comment we noticed that we failed to note in the manuscript that additional details regarding the observation based SOA tracer methodology are in the Supporting Information. We reviewed the material presented in the manuscript text and feel it provides an appropriate scope of information since this manuscript is not intended to present a detailed description of this approach which has been described elsewhere and in great detail in the Supporting Information. Since these tracers are specific compounds they would not include a contribution from IVOC. The relevant text for this approach in the manuscript is below with new text at the end pointing readers to the Supporting Information for more details on the methodology.

> An ambient-based approach is used here to estimate secondary OC from individual or groups of similar hydrocarbons (Kleindienst et al., 2010). Concentrations of specific compounds, tracers, are determined and used to estimate SOC contributions from the particular source groups based on measured laboratory tracer-to-SOC mass fractions (Kleindienst et al., 2007). Filter-based particulate matter sampling conducted at each site for 23-h periods starting at midnight (PDT) of the designated sampling day was used for tracer-based organic aerosol characterization. In total, there were 32 filter samples from Pasadena and 36 from the Bakersfield site (Lewandowski et al., 2013). The filter sampling protocols have been described in detail elsewhere (Kleindienst et al., 2010). For the analysis of the SOC tracer compounds, filters and field blanks were treated using the derivatization method described by Kleindienst et al. (Kleindienst et al., 2007). The mass spectral analysis for the organic compounds used as secondary molecular tracers has been described (Edney et al., 2003). The method detection limit (MDL) for the SOC tracer species is 0.1 ng m-3. Additional details of this methodology are provided in the Supporting Information.

Minor comments by page/line number:

159/27: “still too primary” might be better worded as “still contains a higher primary fraction than was observed”.

The text has been changed to reflect the reviewer’s suggestion.

> Modeled percent secondary contribution (22% at Pasadena) becomes closer to ambient based estimates but still contains a higher primary fraction than observed.

162/17: Did CMAQ and GEOS-CHEM use the same chemical speciation for gases and aerosols? If not, discuss the methodology used to match these between the models.

The reference (Henderson et al., 2014) noted in the methods section provides detailed gas phase mapping between the GEOS-CHEM mechanism and SAPRC07. CMAQ does not employ the exact same aerosol species and uses a different gas phase chemical mechanism. However, it is worth noting that observation based techniques and current conceptual models of OA formation in central and southern California suggest it is largely local in origin and not from other continents or other States meaning the VOC and PM2.5 boundary inflow into the continental US CMAQ simulation used to supply boundary conditions to this smaller domain would be minimally important for this particular area and time.

163/17: The text mentions green shading in Table 1. This is not in the table included with the paper. Some journals do not allow shaded backgrounds, but will allow a change in font – please consult with the journal and correct this.

The reviewer is correct, shaded backgrounds are not an option for these Tables and were not noticed and corrected during the proof review process. The Table 1 caption has been changed to reflect this information without color background shading. The new text follows.

> Table 1. Episode total anthropogenic emissions of primarily emitted PM2.5 organic carbon and the sum of benzene, toluene, and xylenes by emissions sector group. The Los Angeles (LA) total includes Los Angeles and Orange counties. The southern San Joaquin Valley (SSJV) total includes Kern, Fresno, Kings, and Tulare counties. Residential wood combustion, fugitives, and non-point area PM2.5 emissions are largely contemporary in origin.

168/11-12: Does this not also imply that the source apportionment (?) used to separate out the SOA mass is not including all of the species – that is, it's not the samples that are erroneous, but the methodology used to determine the amount of carbon mass that is in error?

The radiocarbon measurements are the contemporary fraction of the provided carbon aerosol mass. Measurement biases in this approach would not impact mass based measurements. Also, multiple measurements approaches for OA were undertaken at Pasadena and agreed well in terms of OA mass making it more likely the radiocarbon estimates are occasionally problematic.

168/26-169/6: Should also include some stats for the model performance here. What was the correlation between model and obs for SOA, for example?

Based on the reviewer's suggestion to include correlations we have added the estimated correlation coefficient for all modeled and observed species presented in Table 2. Additional correlation coefficient information is now provided for EC, OC, 4 different SOC tracers, 6 different 3-hourly VOCs, and 4 different hourly VOC species. See the revised Table 2 for this additional information.

170/19: Some discussion of IVOCs should appear here, see references in the Larger Issues section. The timing of events on Figure 4 looks relatively good, which implies the correlation coefficient may not be that bad – is the problem just a matter of offset in the bias or is the timing of events "off" as well? Correlation coefficients would help in addressing this question.

Missing or poorly characterized IVOC emissions have been included in the acknowledged list of known possible explanations for the difference in model estimates and observations. The model estimated primary component of OA at Pasadena is very consistent from day to day unlike the observations as shown in Figure S6. The updated manuscript text follows.

> The underestimation of SOC may result from underestimated precursor VOC, poorly characterized oxidants, underestimated semi-volatile yields, missing intermediate volatility VOC emissions (Stroud et al., 2014;Zhao et al., 2014), other issues, or some combination of each.

171/5: If the meteorology is poorly characterized, would this not also affect the aromatic compound transport?

The commenter makes a good point that meteorological characterization of micro scale flow features would similarly impact all precursors and formation processes. However, since biogenic precursors are largely located in nearby complex terrain features and aromatics are available in abundance in immediate proximity to these monitors (and not complex terrain) it is possible micro scale meteorology could impact biogenic precursors more than aromatics for this particular area differently than other locations.

171/16: CO underpredictions due to boundary conditions: the difference between maximum diurnal and minimum diurnal CO could be used to see if the model is resolving the local sources. Also, CO should be a tracer of mobile emissions – presumably the BTEX and CO should correlate well in time – another check on whether the local contribution has been adequately resolved.

This is an interesting suggestion to better differentiate the sources of CO in the model. The idea certainly has merit but may not be definitive. An alternative approach for an additional research project would be to track CO from specific sources using CMAQ source apportionment. CMAQ has recently been enhanced with CO source apportionment (Kwok et al., 2015) and that may be a better approach to take to differentiate CO origin between anthropogenic, biogenic, and boundary inflow. This would be an interesting endeavor and one we will consider for upcoming projects.

171/20-28: Labelling the model primary emitted "unexplained" here doesn't make sense – it is the amount the model generates for primary PM2.5, and the amount that the inventory has as primary PM2.5. They shouldn't be colored the same as the observations in Figure 4 either – they are not known to be the same.

The commenter is correct. Manuscript text and Figure 4 caption text has been modified to be clear that different information is being provided for the observations and model estimates. The Figure 4 legend provides a clear differentiation as suggested by the commenter and that should have also been made in the text and Figure caption. Both are now updated to be consistent with the Figure 4 legend and with the reviewer's comment. Revised text in the manuscript follows.

> Figure 4 shows modeled and measured total PM2.5 OC mass. Measured mass explained by fossil and contemporary SOC tracers are shown in the top row. The unexplained observed fraction is a mixture of primary, secondary, fossil and contemporary origin. Modeled mass is colored to differentiate primarily emitted OC and SOC.
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> Figure 4. Observed (top row) and modeled (middle and bottom rows) PM2.5 organic carbon at Pasadena and Bakersfield. Mass explained by SOA tracers shown in green (contemporary origin tracers) and brown (fossil origin tracers). Top row gray shading indicates mass not explained by known observed SOC tracers. Middle and bottom row gray shading shows modeled primarily emitted PM2.5 that is both contemporary and fossil in origin. Middle row shows baseline model estimates and bottom row model sensitivity results with increased SOA yields.

172/12: Again, what about IVOC, here? Did Hayes et al 2013 consider this possibility, or have the methodology to distinguish IVOC from SOC?

The commenter is correct that OA from IVOC could contribute to the observation based tracer mass being lower than measured OA at these locations. We consider that to be included in the statement "unidentified

SOC pathways" since SOC tracers from specific IVOC precursors have not been identified. We agree that IVOCs are important and have an ongoing project with the PI for the IVOC measurements at Pasadena and will have a manuscript looking specifically at the influence of IVOCs in CMAQ in the near future. This is a complex issue and one that deserves its own publication(s).

172/24-27: Presumably if the isoprene SOC was being formed elsewhere, so that the local isoprene concentrations are decoupled from the isoprene SOC, the model would show this – does it? Lines 27-3(next page): is there sufficient low-level cloud in the domain to allow for significant aqueous phase production? It looks like this possibility was investigated and rejected later (section 3.6) – should mention this here.

Unfortunately the model does not have the capability to differentiate isoprene SOC by geographic origin so we can not clearly differentiate whether the modeled isoprene SOC came from isoprene emissions near the monitor location or from somewhere else in the model domain. CMAQ Source apportionment exists for isoprene (Kwok et al., 2015) and thus be tracked back to specific regions but not SOC (Kwok et al., 2013). There were very few clouds during the CALNEX field campaign and cloud processes are not expected to provide notable SOA contributions at these monitors during this time period (Washenfelder et al., 2011) as the reviewer notes.

173/20: Mention the difference in SOA yields between the modelled (alpha pinene) and observed monoterpenes (limonene, myrcene, para-cymene).

This is a good suggestion and text has been added to this section noting the large differences in SOA yields estimates for different monoterpene compounds. The added text follows.

> This is important because yields vary among from different monoterpenes and limonene has a much larger SOA yield than pinenes (Carlton et al., 2010).

174/1-11: This argument needs clarification. It's not clear how overestimated hydroxyl radical could influence the low SOC levels in the manner described. Note also that both Figures 5 and 6 show an underprediction in the estimated SOC, though in Figure 5 the xylene+toluene is overestimated, and in figure 6 the xylene+toluene is underestimated. Wouldn't having OH too high in the model result in greater SOC formation from the precursors than would otherwise take place? If anything, I would expect that high OH concentrations are indicating that the model is creating even more SOC than it would if the predicted OH concentrations were slower. i.e. other factors must be responsible for the SOC formation than the mechanisms considered thus far.

Based these comments from the reviewer, manuscript text has been updated to be clearer that radical representation is most likely not a large contributor to poor SOC representation and as the reviewer suggests other factors are likely more responsible. The revised manuscript text follows.

> One potential explanation for an underestimation of SOC despite well characterized precursors (e.g. toluene and xylenes) could be lack of available oxidants. As shown in Figure 7, the model tends to overestimate the hydroxyl radical compared with measurement estimates at Pasadena. Hydroperoxyl+peroxy radical measurements are underestimated at Pasadena by a factor of 2 on average. The model overestimates preliminary measurements of both hydroxyl (by nearly a factor of 2 on average) and hydroperoxyl+peroxy radicals at Bakersfield. Model representation of

hydroxyl radical at these locations during this time period does not seem to be limiting VOC oxidation to semi-volatile products. Better agreement between radical ambient and modeled estimates could result in less SOC produced by the model and exacerbate model SOC underestimates. This suggests deficiencies other than radical representation by the modeling system are more influential in SOC performance for these areas. However, hydroperoxyl underestimates at Pasadena could lead to muted SOA formation through low-NOX pathways dependent on hydroperoxyl concentrations and contribute to model under-estimates of SOC.

REVIEWER 3

The Baker et al. manuscript presents a comparison of gaseous and particulate organic carbon measurements and model predictions for the 2010 CalNex campaign. Simulation results from specific time periods and grid cells are analyzed to facilitate comparison with measurements.

The presentation quality of the paper could be improved. There: omissions of important/relevant literature, poorly organized sections, and many grammatical errors. Specific examples follow under the technical and editorial comments.

Technical:
The authors do not present sufficient evidence to support the assertion that reasonable predictions of VOCs and OH radical and underpredictions of SOC suggest error in parameterization of semi-volatile gases. The sensitivity simulation in which the concentrations of lumped oxidation products are increased by a factor of 4 only addresses one of the many limitations/uncertainties in the CMAQ model approach. While the sensitivity study is instructive, its importance should not be overstated. A more comprehensive sensitivity analysis of other limitations/uncertainties (likely beyond the scope of this manuscript) would be required to make such a statement. The authors refer to other limitations briefly throughout the manuscript.

We agree with the reviewer that we only explore some of the many possible uncertainties with OA model performance in California. We also agree other notable uncertainties that need to be explored require a large amount of detail and work and are best as follow-up projects. We plan to submit a manuscript to ACP in the near future that examines treating POA as semi volatile with the VBS approach and a second follow up manuscript examining uncertainties in IVOC emissions on SOA production in this area. We feel these manuscripts in totality will still not be able to fully address the range of issues that could be contributing to model performance but provide a strong basis for understanding the best future directions for future CMAQ and emission inventory improvements.

I am somewhat surprised that the authors did not further discuss the likely modeling implications of treating POA as non-volatile, particularly when comparing primary and secondary OC fractions. There have been several published studies suggesting that allowing evaporation and subsequent oxidation/partitioning of POA produces modeled primary to secondary OC ratios that are in better agreement with AMS measurements. I think this is a significant oversight/omission given the focus on underprediction of SOC. In the conclusions the authors do suggest this possibility, but it is not satisfactorily addressed in section 2.2.

The reviewer is correct that treatment of POA as semi-volatile would result in more SOA and thus a relative mix of SOA/POA in this area that better matched AMS estimates of SOA/POA. We do not explore semi-volatile treatment of POA in this manuscript because we have a follow-up manuscript in preparation that should be submitted to ACP in the near future where we apply CMAQ with semi-volatile treatment for POA for this same period and area and compare with AMS based measurements. A great deal of complexity is involved with treating POA as semi-volatile, which includes some estimate of IVOC emissions. We felt the scope of that work is complex enough to necessitate an entire subsequent manuscript. This issue will be addressed in detail in a separate ACP submission.

How do the modeling results compare with those presented by Fast et al. (ACP, 2014), in which aerosol precursors over California were modeling during CalNex using WRF-Chem)?

We appreciate the reviewer noting the (Fast et al., 2014) manuscript describing modeling of the CALNEX period using a different modeling system that includes WRF-CHEM and an episodic emission inventory developed by California Air Resources Board for the ARCTAS field campaign in 2008. (Fast et al., 2014) show large under predictions of SOA mass at both Pasadena and Bakersfield. Primary OC is overestimated at Bakersfield and both over and underestimated at Pasadena depending on the time of day. Modeled total OA at Bakersfield is comparable to AMS measurements and largely under predicted at Pasadena compared to AMS measurements. The under prediction at Pasadena is most notable during peak events that are not captured by the modeling system. Text has been added to the manuscript providing results from (Fast et al., 2014) as context for some of the model performance features shown in this work. Revised manuscript text follows.

> A modeling study for the same time period using different emissions, photochemical transport model, and SOA treatment also show underestimated OA and SOA at Pasadena and underestimated SOA but comparable OA at the Bakersfield location (Fast et al., 2014).

Editorial:
Throughout the paper there are grammatical errors. It is recommended that the authors read carefully for such errors, some examples are noted below. It is suggested that the authors consider introducing the CMAQ model (2.2 Model Background) prior to discussing model application (2.1).

We agree with the reviewer and have moved the section describing the model itself to be before the section describing the model application in the revised version of the manuscript. We have also carefully reviewed the manuscript for grammatical errors and made revisions where appropriate.

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