

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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REVIEWER 2

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REVIEWER : 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.

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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.

AUTHORS : 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 PM_{2.5} organic carbon mass and the POA/SOA split. These are both substantial projects and build upon the work presented here.

REVIEWER : 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 aro-

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matics 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.

AUTHORS : 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).

REVIEWER : (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 sec-

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ondary 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 $\log_{10}(C^*)$ 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.

AUTHORS : 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.

REVIEWER : (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

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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?

AUTHORS : 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

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(MDL) for the SOC tracer species is 0.1 ng m⁻³. Additional details of this methodology are provided in the Supporting Information.

REVIEWER : 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”.

AUTHORS : 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.

REVIEWER : 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. AUTHORS : 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 PM_{2.5} 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.

REVIEWER : 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.

AUTHORS : 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.

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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.

REVIEWER : 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?

AUTHORS : 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.

REVIEWER : 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?

AUTHORS : 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.

REVIEWER : 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.

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AUTHORS : 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.

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

AUTHORS : 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.

REVIEWER : 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.

AUTHORS : 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

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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.

REVIEWER : 171/20-28: Labelling the model primary emitted “unexplained” here doesn’t make sense – it is the amount the model generates for primary PM_{2.5}, and the amount that the inventory has as primary PM_{2.5}. They shouldn’t be colored the same as the observations in Figure 4 either – they are not known to be the same.

AUTHORS : 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 PM_{2.5} 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.

Figure 4. Observed (top row) and modeled (middle and bottom rows) PM_{2.5} 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 PM_{2.5} that is both contemporary and fossil in origin. Middle row shows baseline model estimates and bottom row model sensitivity results with increased SOA yields.

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

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AUTHORS : 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).

REVIEWER : 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.

AUTHORS : 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.

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

AUTHORS : 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

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limonene has a much larger SOA yield than pinenes (Carlton et al., 2010).

REVIEWER : 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.

AUTHORS : 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

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low-NOX pathways dependent on hydroperoxyl concentrations and contribute to model under-estimates of SOC.

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