

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

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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.

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.

(2) Description of the air-quality model’s SOC formation processes, e.g. page 163/

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

(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?

Minor comments by page/line number:

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

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.

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?

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?

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.

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

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.

171/20-28: Labelling the model primary emitted "unexplained" here doesn't make

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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.

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

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.

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

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.

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