

## ***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 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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REVIEWER : 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.

AUTHORS : 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.

REVIEWER : Introduction Pg 4. Line 15. "Given the direct relationship between precursor VOC and OH radical abundance and SOA formation,...." Can you rephrase 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.

AUTHORS : 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.

REVIEWER: 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.

AUTHORS : 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

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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.

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

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

REVIEWER : 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?

AUTHORS : 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.

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

AUTHORS : The SAPRC07TB condensed mechanism was applied for these simulations. Text in the methods section has been updated to add this specificity about the

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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).

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

AUTHORS : 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).

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

AUTHORS : 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.

REVIEWER : Results and Discussion

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

AUTHORS : 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 HO<sub>2</sub> directly as opposed to less direct methods to assess performance. This suggestion certainly has merit and will be kept in mind for future assessments.

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

AUTHORS: 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.

REVIEWER : Pg 21. Line 12. At Pasadena, I would think that SOA formation would be in the high NO<sub>x</sub> limit, so the SOA formation would be less dependent on HO<sub>2</sub> than NO<sub>x</sub>.

AUTHORS : 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<sub>x</sub> 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<sub>x</sub> emissions. In general we agree with the reviewer that SOA at Pasadena during this time of year would be less dependent on HO<sub>2</sub>. 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.

REVIEWER : 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.

AUTHORS : 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.

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

AUTHORS : 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 PM<sub>2.5</sub> 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.

REVIEWER : Figure 1. What are the blue colored species above MGLY and GLY that

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have the same names? Can you put an explanation in caption?

AUTHORS : 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.

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

AUTHORS : 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.

REVIEWER : Figure S2. NO<sub>3</sub>-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 NO<sub>3</sub> and SOA yields?

AUTHORS : The reviewer raises a good point that the NO<sub>3</sub> isoprene oxidation pathway is not included in this version of CMAQ and would contribute some amount of SOA.

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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.

#### REFERENCES

Kwok, R., Baker, K., Napelenok, S., and Tonnesen, G.: Photochemical grid model implementation of VOC, NO<sub>x</sub>, and O<sub>3</sub> source apportionment, *Geoscientific Model Development*, 8, 99-114, doi:10.5194/gmd-8-99-2015, 2015.

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