

Responses to Referee #2

(Please note that a revised version of the manuscript with changes tracked and the supporting information appear below)

The manuscript by Murphy et al. reports on the revised treatment of organic aerosol (OA) in the Community Multiscale Air Quality Model (CMAQ) v5.2. The revised treatment of OA includes: 1. partitioning and gas-phase aging of primary OA (POA), and 2. a new model species “pc” (pcVOA, pcSOG, pcSOA) that represents the missing emissions and processes that may be associated with secondary OA (SOA) formation from urban combustion sources. Model simulations are performed at 4- and 12-km resolution and evaluated at different time periods, seasons, and US locations using surface network monitor data. The changes in the model representation of OA generally result in better correlation and improved bias; the average contribution of the new model species, pcSOA, to OA was 39% in winter and 24% in summer. The model evaluation is thorough and may contribute to elucidating the relative importance of emissions vs. processing in specific locations. The manuscript is generally well written and appropriate for publication in ACP. Specific comments and suggestions for revision are provided below.

We thank the reviewer for helpful suggestions in improving the depth and consistency of the manuscript. We have provided detailed responses to each individual point below.

In the abstract and introduction, the authors suggest that given the quality of the model predictions using the “simple” parameterization presented, caution should be exercised when using more complicated parameterizations (higher number of uncertain parameters). I do not see a fundamental difference with the approach presented here and others. SOA formation depends on the amount of precursor, the extent of oxidation, and volatility of the resultant oxidation/reaction products. The approach presented is a hybrid of existing approaches (including VBS for POA) and relies on arguably uncertain parameters for each of the factors controlling SOA from the new precursor (scaling factor for POA to determine pcVOC, reaction rate constant with KOH to obtain pcSOG, and c^* value to convert pcSOG to pcSOA). The net result of all of the current modeling approaches is that relative to the traditional two-product/non-volatile POA approach, they produce more oxidized OA with a temporal and spatial distribution that is more representative of observations. This is not to say that the changes in the model representation aren't warranted or needed; they are. As articulated by the authors, the changes represent the evolving knowledge of OA formation in the atmosphere. However, all of the current approaches face the same limitations regarding uncertainty in model parameters, a consequence of the complexity and likely variability of processes contributing to SOA formation.

We agree with the reviewer that there are uncertain parameters involved in each of the factors controlling SOA formation in the pcSOA approach. Our statement cautioning readers regarding complicated parameterizations was not meant to distinguish our approach from others in the literature or communicate superiority but rather to point out explicitly that our results indicate a model does not need an overly complicated approach in order to achieve arguably good performance when compared with existing configurations. This performance is not only satisfactory in urban areas where the simple approach has been parameterized before, but is also substantially useful for regional-scale predictions at routine monitoring sites. Although much can be learned from the complex approaches, including source attribution, phase distribution, and chemical evolution, it is very difficult to evaluate these findings with independent observations. For a policy-driven model like CMAQ that is used routinely to develop air quality policies, independent evaluation and justification is paramount. We look forward to improving the

representation of these important pathways in the future with bottom-up approaches, but with careful consideration of the balance between uncertainty and improvement to model skill, especially when potential improvements may dramatically affect source attribution.

The approach presented combines traditional model representation for VOCs, VBS model representation for POA, and a method based on Hodzic and Jimenez to represent missing sources and processes. It would be useful to see the relative contributions of these processes (by model species) to the total OA predicted. Were any simulations run with only the partitioning and aging of POA or only the consideration of pcSOA?

We have added figures to the supplement (Figs. S4 and S5) showing the separate contribution of pcSOA, POA, oxidation products of POA aging, SOA formed in the aqueous phase, and SOA from traditional VOC precursors to the total OA at each site. We have also rerun the model as the reviewer asks and added figures (Figs. S5-S7) showing the difference in OA predictions at the CONUS scale in January and July with the pcSOA pathway turned off.

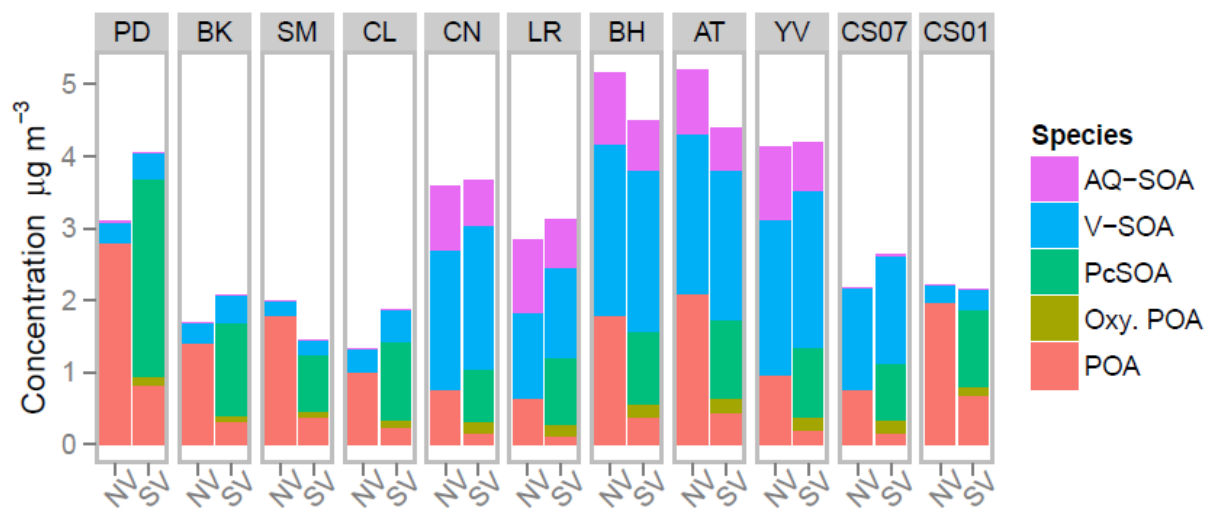


Figure S4. Composition of organic aerosol predicted by CMAQv5.2 run for both nonvolatile POA (NV) and semivolatile POA with pcSOA (SV). The species depicted include POA with very low O:C (POA), POA with high O:C (oxygenated POA or Oxy. POA), potential combustion SOA (pcSOA), SOA from traditional anthropogenic and biogenic VOCs (V-SOA), and SOA formed in the aqueous aerosol and cloud water phases (AQ-SOA). The sites shown in this figure include Pasadena (PD), Bakersfield (BK), Sacramento (SM), Cool (CL), Centreville (CN), Look Rock (LR), Birmingham (BH), Atlanta (AT), and Yorkville (YK). The rightmost two comparisons show the average contributions to OA for grid cells in the continental US from the CONUS11 simulation during July (CS07) and January (CS01). The higher contribution of AQ-SOA at the sites in the southeast US is a result of that simulation including isoprene and terpene aqueous-phase formation pathways that are not present in the California and CONUS-scale simulations.

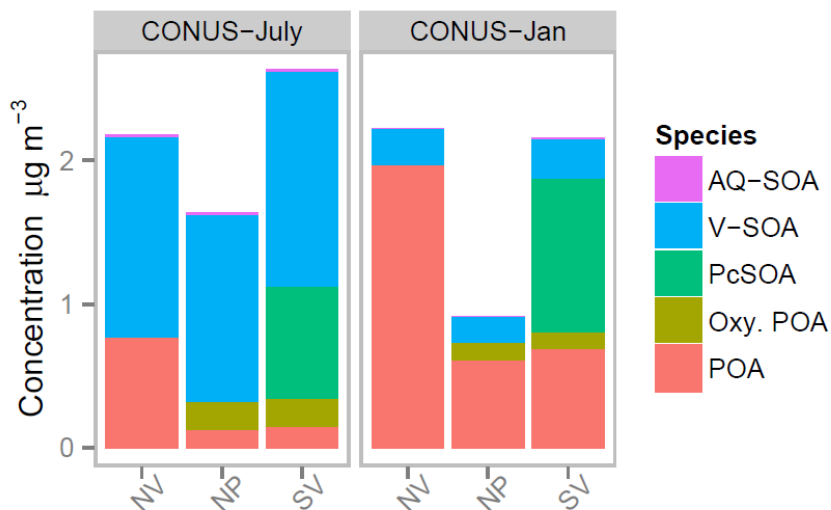


Figure S5. Composition of organic aerosol predicted by CMAQv5.2 run for both nonvolatile POA (NV), semivolatile POA with no pcSOA (NP), and semivolatile POA with pcSOA (SV). The species depicted include POA with very low O:C (POA), POA with high O:C (oxygenated POA or Oxy. POA), potential combustion SOA (pcSOA), SOA from traditional anthropogenic and biogenic VOCs (V-SOA), and SOA formed in the aqueous aerosol and cloud water phases (AQ-SOA). The concentrations are average contributions to OA for grid cells in the continental US from the CONUS11 simulation during July (CONUS-July) and January (CONUS-Jan).

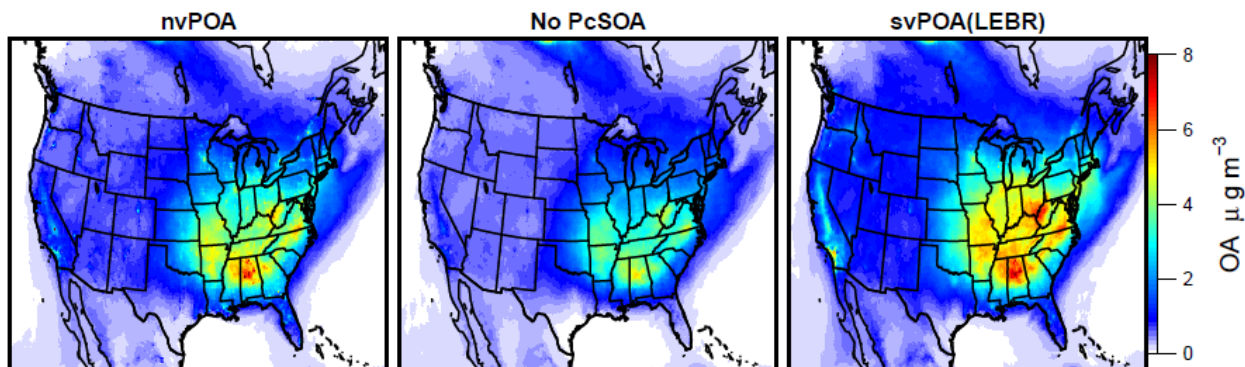


Figure S6. Average OA concentrations for nonvolatile POA (nvPOA), semivolatile POA with no pcSOA (No PcSOA), and semivolatile POA with pcSOA (svPOA(LEBR)). This simulation is for July, 2011.

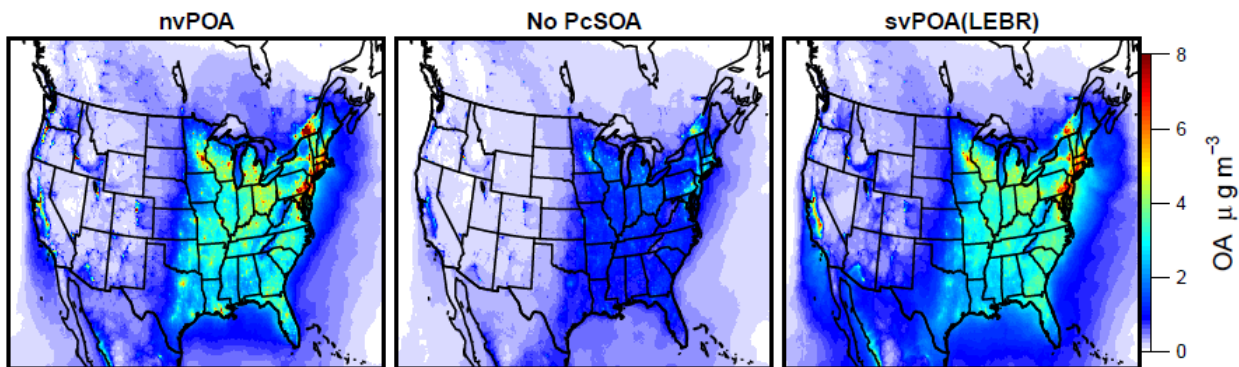


Figure S7. Average OA concentrations for nonvolatile POA (nvPOA), semivolatile POA with no pcSOA (No PcSOA), and semivolatile POA with pcSOA (svPOA(LEBR)). This simulation is for January, 2011.

On p. 5, line 34 the authors state that no POA emissions scaling was used to introduce SVOCs; however, that is effectively what is done using the pc surrogate species. If combustion source emissions inventories have been revised to reflect the knowledge of dynamic partitioning and missing IVOCs, then these emissions are being double counted by the combined use of a dynamic POA model and the scaling of pcVOC to POA emission rate.

Previous literature documenting implementation of POA volatility scaling address two quantities. First, the original POA emissions factor is distributed up to $C^* = 10^3$ or $10^4 \mu\text{g m}^{-3}$ depending on the model species available (Shrivastava et al., 2008; Murphy et al., 2009; Koo et al., 2014). When we discuss missing SVOCs and IVOCs, we are not referring to mass in this first quantity as, by definition, it was detected during characterization of the emission factors that informed the emission inventory. The second quantity addressed in the literature represents the missing SVOCs and IVOCs and is usually scaled between 150% and 750% of the original POA emission factor (Shrivastava et al. 2008, Matsui et al., 2014).

Currently, we are engaged in a parallel research effort to analyze the data in existing combustion inventories and estimate the amount of missing S- and IVOCs at a source level with emerging knowledge of source-specific volatility distributions. For the current study though, we choose not to add these emissions into the POA volatility-resolved species, and instead we have lumped them with the other uncertain pathways discussed in the manuscript in order to generate the emissions of pcVOC. We are not adding the missing IVOC emissions twice.

What is the rationale for maintaining the SOA formation pathway for traditional VOC precursors? Isn't this pathway essentially accounted for (or could be accounted for) using the surrogate?

The SOA formation pathways for traditional VOC precursors is maintained for compatibility with both past versions of CMAQ and as a benchmark for evaluating future improvements to bottom-up approaches. The traditional approach of applying SOA yields to the oxidation of specific precursors is a valuable one, especially for attributing bulk OA mass to specific emission sources, connecting laboratory experiments to ambient observations, and evaluating potential regulatory actions (e.g., fuel reformulation). This pathway could be partly accounted for with the surrogate, although there are some problems. First, there are evaporative, non-combustion, sources of some traditional VOCs that are also responsible for making SOA. Second, the oxidation products of

these VOC species are semivolatile and their yields are NO_x-dependent in the model, and these behaviors are important to take into account.

It is recommended that the products of POA evaporation and aging (“OO”) be listed in section 2.1, similarly to the directly emitted species, to improve the clarity of Table 1. How are the molecular weights assigned to the “OO” products?

The products of POA aging are listed in section 2.1 as the reviewer requests (original manuscript page 5, line 18). The molecular weights are assigned assuming each set of compounds comprises only carbon, oxygen, and hydrogen atoms. The O:C is calculated from the carbon number and volatility using Donahue et al. (2011). We further employ the oft-used parameterization of Heald et al. (2010) to calculate H:C from O:C. We have included these details in the manuscript as well.

“The molecular weights of these species are calculated using the given carbon number and OM:OC, while assuming each representative species comprises only carbon, oxygen and hydrogen atoms. The H:C is calculated from O:C using insights from Heald et al. (2010), a common assumption for deriving molecular weights of VBS species in chemical transport models.”

And to the Supporting information, we have added the following:

“The volatility of each surrogate species is calculated as a function of its given C* and O:C. Specifically, we use the following relationship:

$$\text{Log}_{10}C^* = 0.475 * (25 - n_C) + 2.3 * n_O + 0.6 * n_C * n_O / (n_C + n_O) \quad \text{Eq. S1}$$

where C* is the saturation concentration of the surrogate species in μg m⁻³, n_C is the number of carbon atoms in the species, and n_O is the number of oxygen atoms in the species (Donahue et al., 2012). “

On page 7, line 25 the authors note that no further reactions are considered for pc-SOG/pcSOA, but based on the very low c* and the rationale for including pcSOA, doesn't the conversion of pcSOG to pcSOA essentially represent these “other” reactions? Given that all of the pc is likely to end up (and stay) in the aerosol phase, it isn't clear what other reactions would be considered or why.

Some possible reactions would be particle-phase oxidation reactions or photolysis leading to degradation of the low volatility material (Hodzic et al., 2015). These reactions are not incorporated into CMAQ currently. If they were, they would increase the volatility of the OA species in the model and reduce aerosol-phase concentration. We have added these examples to the description of the methods.

“Although heterogeneous reactions are implemented for other SOA types in CMAQ, no further reactions are included for pcSOA. Additionally, photolysis leading to degradation of low volatility material is not considered in the model (Hodzic et al., 2015).”

It is suggested that the authors use naming conventions that have been presented previously. For example, “LO-OOA” is presented on pg 9, line 11. Is the same as AMS derived “OOA-II”?

The “LO-OOA” term is used often by the AMS community. Zhang et al. (2011) suggested using this term instead of terms like LV-OOA and SV-OOA when volatility information is not available. Xu et al. (2016) also argue that the correlations between oxygenation as observed by the AMS

and volatility are highly variable among lab and field studies. To our understanding, the terms OOA-I and OOA-II are less often used now.

On page 15, line 14: What is meant by wood burning area sources not emitting SOA precursors consistent with pcSOA formation?

This refers back to the distinction made between fossil-fuel and biomass-burning emissions described in the methods section. Recent studies have shown limited downwind OA formation from biomass-burning sources, and the current model configuration takes that into account by not emitting pcVOC from wildfire sources. However, our emission inputs, as is the case for most CTMs include gridded area fires (e.g. residential wood burning, prescribed fires, etc) lumped together with vehicle and other fossil-fuel emissions. For this reason, there may be a significant discrepancy introduced in the comparison to wintertime measurements when gridded area biomass burning sources are important. We have revised the sentence.

“Meanwhile in the wintertime cases, large wood burning area emissions may not result in substantial net OA formation downwind. Although the simulation results shown here take this possible feature into account for wildfire sources, residential and other smaller-scale wood combustion are assumed to produce pcSOA consistent with fossil-fuel sources. If these sources are significantly overpredicted, then lower pcSOA production rates would yield better agreement at the CONUS scale for the wrong reasons.”

The value of c^* for pc is 10^{-3} in the text and 10^{-5} in table 2.

Updated.

References for Response

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