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Atmospheric
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Discussions

Interactive comment on "Model evaluation of NO₃ secondary organic aerosol (SOA) source and heterogeneous organic aerosol (OA) sink in the Western United States" *by* J. L. Fry and K. Sackinger

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We wish to extend our sincere thanks to the reviewers for the time spent evaluating this manuscript. Thank you for the helpful comments, which we have carefully considered and used to inform several revisions to the manuscript. Below we address each comment individually.

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1 Responses to reviewer 1

1.1 Reviewer 1 Comment #1

1. Some simplifications do not seem necessary.

a. For example, equation (2) and Table 1 indicate a fixed yield of aerosol is used for each lumped parent hydrocarbon. What conditions (organic aerosol concentration, temperature) is this yield valid for? Could you use a yield curve and calculate the yield for the organic aerosol concentration predicted by WRF? The mass yield of 5% might be more realistic given nighttime aerosol loadings.

1.1.1 Response #1-1

The fixed aerosol yields used are from low-concentration ($\approx$ 10 ppb VOC, $<$ 40 μg/m3) chamber experiments. To our knowledge, the only published NO_3 yield curve data available is one for β-pinene based on Griffin et al 1999 (interpreted in volatility basis set formalism by Pye et al 2010 and Farina, Adams & Seinfeld 2011). As is apparent in Fig. 1, these two interpretations disagree the mass dependence of SOA yields. (Note: the +P simulations add an additional low-volatility product) Recent unpublished work from new chamber experiments at the NCAR community lab (labeled “Fry” in Fig. 1) suggests higher yields at the lowest mass loadings. With these remaining large uncertainties in the mass dependence of SOA yield, we decided that using a constant mass yield and conducting the sensitivity tests would be most appropriate.

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1.2 Reviewer 1 Comment #1b

b. For equation (7), could the fraction of the semivolatile in the gas and aerosol phases be calculated instead of using a cutoff?

1.2.1 Response #1-1b

In response to this reviewer comment, and a similar one from Reviewer 2, we have modified our offline modeling code to calculate the fraction of volatilization of each semivolatile species, rather than a 50% cutoff, and the manuscript has been updated accordingly. This alteration resulted in only minor numerical changes, but all affected figures have been updated.

1.3 Reviewer 1 Comment #2

Can you clarify how OLI and OLT were used? It is my understanding that the olefinic bonds are mapped to OLI and OLT and the rest of the carbon is mapped to another species. How do you assemble back the parent hydrocarbon that serves as the SOA precursor? What is the molecular weight? Are there significant amounts of compounds other than monoterpenes that make up OLI and OLT?

1.3.1 Response #1-2

The calculation of OA source operates as if every OLI double bond belongs to a molecule of α-pinene and every OLT double bonds belongs to a molecule of β-pinene, with corresponding molecular weights. Since the geographic domain we are considering contains many coniferous forests, we expect monoterpenes to be the major contribution to total gaseous alkenes. Although cities contain more anthropogenic VOCs as well, the alkenes are still expected to have a dominant contribution from biogenic monoterpenes. We have added the following text to the section “Modeling NO_3 SOA source" to explain this more fully in the manuscript: “This calculation assumes that all OLI are α-pinene and all OLT are β-pinene, a simplification that we expect represents the bulk of the VOCs in the west coast domain reasonably well, as these are the dominantly emitted monoterpenes from coniferous forests. Even in urban areas, where this NO_x chemistry is most important, biogenic alkenes emitted from managed gardens, modeled as OLT and OLI, are expected to contribute substantially to NO_3 reactive loss."

1.4 Reviewer 1 Comment #3

Figure 3. Do colors also have meaning?

1.4.1 Response #1-3

Each functionalization of products has a unique color. In cases where the same color occurs in two boxes, it indicates that the reaction pathways produce the same type of product, for example, all alkene scission pathways result in a short-chain ketone (aqua), as well as a short-chain bifunctionalized product the functionalization of which varies with the starting molecule. The following sentence was added to the caption of Fig. 3: “Colors indicate the functional groups of the products, so that reactions producing similarly functionalized products can be easily identified – *e.g.*, every scission pathway produces a short-chain ketone (aqua); hydroxyketonitrates are shown as mauve."

1.5 Reviewer 1 Comment #4

Page 5196-5198: Additional clarification is needed on the conversion between functional groups of bulk aerosol vs whole molecules of individual species (for use in vapor pressure calculations, mechanism species, etc.)

1.5.1 Response #1-4

We assume there's a normal curve of carbon number, functional group percentages are independent of carbon number, and reaction type is independent of initial functionalization. This gives us the carbon chain length and functional groups of individual aerosol-phase molecules to analyze for volatility and total mass. The aerosol species taken at hourly intervals from WRF/Chem model runs have no information about chemical functionalization, so we use the total organic aerosol mass simply to determine the total OA surface area for calculation of uptake reaction rates, and then impose our assumed functional group contribution to understand the chemistry. We added the following sentence to the section introducing the calculation of NO_3-initiated OA sink to help clarify this: “Because the organic aerosol taken at hourly intervals from the WRF/Chem simulation contains no information about functionalization, we use the reported organic mass to constrain the total surface area, but then apply estimates from the literature to determine an assumed carbon number distribution and functional group composition of this organic aerosol and it's reaction products, which can be interpreted as individual molecules for calculation of vapor pressures."

1.6 Reviewer 1 Comment #4a

Each starting molecule is assumed to have only one functional group. Given that organic aerosol tends to have OM/OC of 1.4-2.1, is this a realistic assumption?

1.6.1 Response #1-4a

This is an excellent point. Many oxidation products in atmospheric SOA must contain multiple functional groups to explain observed O:C ratios. But with the lack of knowledge of individual compounds in SOA, we felt the simplification was necessary. It was also spurred by the fact that our SOA composition reference (Alves et al., 2001) had percentages of molecules containing individual functional groups that added up to 100 %, suggesting that their empirical numbers were based on an assumption of one functional group per molecule. Finally, this renders our calculation a conservative estimate, since greater functionalization would create products of lower volatility.

1.7 Reviewer 1 Comment #4b

The average carbon number of 27 seems high. That seems valid for primary organic aerosol, but given the ubiquity of multifunctional organic aerosol and SOA/OOA, it seems high. Alves et al. carbon numbers are based on PM10 measurements and they attributed the >C20 compounds to vascular plants. Does that match up with the aerosol WRF predicts? Following the previous comment, given how oxidized ambient aerosol is, would you not expect a much shorter carbon backbone?

1.7.1 Response #1-4b

We had previously done a sensitivity test on the effect of this carbon chain length by conducting additional model runs started with a 15-C backbone. This resulted in a change in revolatilization rate of only approximately a factor of 2. Nevertheless, to help address this question we have added an additional test case starting with a 9-carbon backbone, so the reader can see how this would affect our conclusions comparing the source and sink rates.

1.8 Reviewer 1 Comment #4c

Given the functional group composition on the bottom of page 5196, the assumption that each starting molecule has only one functional group, and the specification of the carbon number distribution, is the composition of aerosol over specified?

1.8.1 Response #1-4c

We certainly don’t wish to imply that this represents a definitive characterization of organic aerosol composition over the western U.S., however, in order to calculate vapor pressures to assess gas/aerosol partitioning of products of uptake reactions, we need specific molecular structures to use in the group contribution method. So perhaps this over-specification is a necessary evil for our calculations . We have added the following sentence to the section describing the revolatlilization calculation to emphasize this point: “While the generation of this specified product matrix is required for calculation of gas/aerosol partitioning of the species and thus to determine an OA revolatilization rate, we wish to be clear that the assumptions invoked about initial composition and mechanism result in significant uncertainty in these products. The molecular structures represent our best guess, and the sensitivity calculations shown below are intended to help the reader evaluate the robustness of our conclusions."

1.9 Reviewer 1 Comment #5

Table 3: The assumption of 100% unsaturated aerosol and 97% aliphatic aerosol both increase the aerosol loss rate relative to the base sink. Why is that?

1.9.1 Response #1-5

We suspect this confusion arose from our use of the word “aliphatic" to refer to unfunctionalized carbon of any saturation (i.e., alkene or alkane). Apologies for the confusion. We have changed all instances of “aliphatic" in the paper to “unfunctionalized" to clarify.

1.10 Reviewer 1 Comment #6

Is there any reasonable combination of parameters (ie low aerosol yield, shorter carbon backbone, more functional groups, higher uptake coefficient for aliphatic sites, etc) that would make the source and sink within an order of magnitude of each other?

1.10.1 Response #1-6

In August, using the highest uptake coefficients found in our literature search for both saturated (4.1×10^{-3}) and unsaturated (0.62) aerosol, assuming 20% unsaturation, using either 50% unfunctionalized or average C9 aerosol, and using 1% mass yields for the source, the sink indeed reaches the same order of magnitude as the source, although it is still less. This suggests that under limited conditions, the two processes may become competitive, and that important new directions in understanding this system are determining the quantity and activity of double bonds in aerosol. The manuscript has been updated to discuss this result, and an additional sensitivity test using high uptake coefficients has been added.

1.11 Reviewer 1 Comment #7

Page 5192, line 2: ‘(51)’ seems out of place.

1.11.1 Response #1-7

Thank you, reference fixed.

1.12 Reviewer 1 Comment #8

Page 5196: insert definition of variables for equation 4 in text.

1.12.1 Response #1-8

Done, thank you.

1.13 Reviewer 1 Comment #9

Page 5196, line 17, is there a reference for the 2 g/cm3 density?

1.13.1 Response #1-9

Just a round number chosen. Perhaps a lower number (e.g. 1.2) would have been justified, but for example aliphatic dicarboxylic acids have average densities of 1.5 g/cm^3 and up to 1.9 g/cm^3 (Pang, et al, LBNL-57273, http://escholarship.org/uc/item/8f59q044).

1.14 Reviewer 1 Comment #10

Title should be revised. “Model evaluation..” implies that a model has been evaluated. What about “Model investigation. . ..”

1.14.1 Response #1-10

Good point. Change made. Thanks for the suggestion.

2 Responses to reviewer 2

2.1 Reviewer 2 Comment #1

Page 5194: Why was the model run for January May and August of 2008, but October 2004? How different were emissions during these 2 years?

2.1.1 Response #2-1

This was simply because we had already run Oct. 2004 previously and did not have the computing time to re-run for 2008 after we had done the remainder of the seasonal comparisons for 2008. Anthropogenic emissions would be identical for either year, and biogenic emissions are always calculated based on local temperature, which may have been slightly different in these two years. However, we don't anticipate this would substantially affect our conclusions. Nevertheless, we do now have additional computation time available and could re-run the calculations for Oct. 2008 if the reviewers feel this is essential. This would take a few weeks time.

2.2 Reviewer 2 Comment #2

Did SOA yield from NO3 get added to WRF-Chem variables oc-a01, oc-a02, oc-a03 and oc-a04? This needs to be mentioned.

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2.2.1 Response #2-2

No. We are here predicting the instantaneous *rates* of production and loss - because this is an offline calculation, there is no feedback into the model such that e.g. NO_3-initiated aerosol would build up overnight. We aim exclusively to compare the source and sink rates and determine which process is likely more important. We have added the following text to the manuscript at the end of the explanation of the source calculation to clarify this: “At each WRF/Chem model timestep, we predict the magnitude of this rate and the corresponding NO_3 OA sink (described below). As an offline calculation aimed only at comparing the instantaneous rates of these processes, the OA produced by this source term in not added in to the model for the sink calculation."

2.3 Reviewer 2 Comment #3

The yields in Table 1 for SOA from NO3 are chosen for 10s of ppb of reactants which could be an upper bound. The calculations in Table 3 for mass yield of 5% may be relevant under most atmospheric conditions. However, the 95% mass yield is clearly unrealistic, not supported by measurements. There should be some discussions about atmospheric relevance of mass yields used in this study.

2.3.1 Response #2-3

In Table 3 we present the conditions employed for sensitivity tests purposely conducted at very extreme values of e.g. SOA mass yield, to see the full range of possible results. As this reviewer rightly points out, there is likely to be significant asymmetry in the range of possible yield values - it is more likely that SOA yield at atmospheric conditions would be towards the lower end of this range than towards the higher end. In acknowledgment of this, we have run an additional sensitivity test at 1% and added this to Table 3. To address the concern about atmospheric relevance, we have also added the following text: “We note that because these yield data are taken from experiments conducted at ≈10 ppb of starting VOC, they may be higher than many ambient locations. Sensitivity studies are conducted (see section on Sensitivity Tests) to assess the effect a lower yield would have, and we have added an additional lower-SOA-yield data point to that section. See also the added text on testing at the “extremes" of these assumptions for additional relevant discussion.

2.4 Reviewer 2 Comment #4

Page 5197: To determine products of heterogenous reaction sink of OA due to NO3 radical, the authors assumed composition of starting aerosol material as 35% aliphatic. But in Table 3 97% aliphatic aerosol gives higher sink rate than their unmodified sink. Why?

2.4.1 Response #2-4

See response 1-5 above. We have changed our use of “aliphatic" to “unfunctionalized" to clarify this confusion.

2.5 Reviewer 2 Comment #5

Equation 7: I agree that using partitioning theory to determine the gas-particle distribution of products is much better and far less confusing to readers than using a 50% cutoff approach.

2.5.1 Response #2-5

Done. See response 1-1b above.

2.6 Reviewer 2 Comment #6

Page 5198: The reaction products are divided into bins with similar vapor pressures reported in Torr. It would be better to give the vapor pressure range in ug/m3. Also what was the bin spacing used?. On page 5201 there is an indication of using 1.5 orders of magnitude bins. But then this should be mentioned here.

2.6.1 Response #2-6

Because products vary in molecular weight, vapor pressure cannot be converted in general to mass concentration. However, the manuscript section on the sink calculation has been edited to clarify bin spacing, and a table presenting this information has been added to the supplement.

2.7 Reviewer 2 Comment #7

Page 5198: It is also confusing that if the authors use very high carbon number of 27 carbon atoms and standard deviation of 9 carbons for all products. Is there any support for this assumption either from laboratory studies or from Master Chemical Mechanism? If so, it should be explicitly described.

2.7.1 Response #2-7

No, because the MCM only includes VOC precursors up to C10, it does not have high carbon numbers. We used these values because they were reported in the empirical study of SOA functionalization that we used to determine an initial functional group distribution. As mentioned in the section on sensitivity studies, we don't believe this changes the major conclusions of the manuscript, however, because of the relatively small sensitivity to changing this carbon number.

2.8 Reviewer 2 Comment #8

Page 5202 and Table 3: OA sink rates are shown to be several orders of magnitude lower than formation rates. But given that all these calculations are done offline without consuming ROG, NO3 radical or OA in the model at each time step, would this reasoning still hold? There has to be some discussion on the relevance of these calculations done offline.

2.8.1 Response #2-8

Agreed. We added more discussion of the offline nature of these calculations already earlier in the manuscript (see response 2-2) To emphasize this further, we have also added the following to the Atmospheric Relevance section, at the end of the first paragraph: "We note again, however, that our modeling is based strictly on offline calculations of source and sink rates of $\mathrm{NO_3}$, not allowing products of these reactions to accumulate or interract with the chemistry in the regional model. As such we can base comparisons only on the instantaneous rates of these processes."

2.9 Reviewer 2 Comment #9

Page 5204: The calculated peak night-time OA prediction from NO3 are shown to be 23-46 ug/m3. The authors mention that it is an overestimate, due to the crude lifetime analysis, mainly because the model does not consume NO3 radical, ROG or OA at each time step. But, at the beginning of page 5205, the authors suggest that large magnitude of SOA source due to reaction with NO3 radical is likely to be significant both in terms of OA production and NO3 radical sink. These 2 statements are contradictory.

If OA is overpredicted, how can it be a large magnitude of SOA source due to reaction with NO3? The only way to asses this nitrate SOA source is through online WRF-Chem calculations. If the authors wish to make any statement about importance of NO3 initiated SOA source during night-time, they should show it through online WRF-Chem predictions using relevant yields from literature.

Secondly, they have argued on page 5202 that NO3 radical sink due to heterogeneous reaction with OA is insignificant, because NO3 rapidly photolyzes after sunrise. Also, the homogenous sink of NO3 radical due to reaction with gas phase organic species such as alkenes is already included in current photochemical mechanisms such as SAPRC. So their argument here needs to be revised and clarified.

2.9.1 Response #2-9

Points well taken! We have revised the text to be clear that online calculations with this process are required to truly assess the importance of these process in terms of total OA budgets and NO_3 loss. The final sentences before the Conclusions, where the statements this reviewer identified as contradictory, have been replaced with the following: “Furthermore, the large magnitude of the predicted SOA source relative to global estimates suggests that this process should be included online in models. Only with such direct inclusion will it be possible to definitively assess the importance of this process in terms of OA production and as a NO_3 radical sink." Also, the final sentence of the conclusions has been modified to read: “Comparison of the average modeled NO_3 + alkene source for the western United States to other regional and global predictions of total organic aerosol loading suggests that this process may be an important contributor to both OA and nitrate radical budgets; online calculations including this NO_3 chemistry are required to determine the quantitative importance of both source and sink processes."