

Interactive comment on “Global modeling of organic aerosol: the importance of reactive nitrogen” by H. O. T. Pye et al.

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The authors would like to thank the referees for their comments. Feedback from the reviews has been used to improve the manuscript. Minor revisions have been made to improve the clarity of the manuscript. The individual reviewer comments are addressed below. Original referee comments are *italicized*.

C10036

1 Responses to anonymous referee 1

1.1

Suggest calling out NO_x and NO₃ specifically in title, e.g., “. . . reactive nitrogen (NO_x and NO₃)”.

NO_x and NO₃ have been added to the title.

1.2

End of section 2.2 (p. 21265 lines 6-11): Would be informative to cite approximate aerosol yields of various compounds here to give reader a sense of relative importance.

Yields at a loading of 10 $\mu\text{g}/\text{m}^3$ are shown in Table 1. In order to keep section 2.2 focused on how the emissions were implemented in the model, some example yields have been added to the Introduction section based on the values in Table 1. Specifically, the following values were added:

- light aromatics (aerosol yield about 5 to 40% at an organic aerosol loading of 10 $\mu\text{g}/\text{m}^3$, see Table 1)
- naphthalene (yield about 20 to 70 %)
- alkanes (yields ranging from a few percent to 50 %)
- isoprene (aerosol yield about 4 to 10% depending on oxidant)
- monoterpenes (yield generally about 10 to 20%)
- sesquiterpenes (yield generally higher than 40%)

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1.3

SOA parameterization (section 2.3): General comment: Your two-way arrows emphasize that gas/aerosol partitioning of all these species responds instantaneously to changes in overall aerosol loading. Yet some recent chamber studies (e.g. Leungsakul, et al. 2005) show that aerosol-phase species must have significantly (2 orders of magnitude!) lower effective vapor pressure than would be predicted for those structures. This seems to argue for oligomerization/polymerization. Is there any way to parameterize this in your model, or is it not well enough experimentally constrained? Perhaps just a comment on how this might affect ultimate SOA loading estimates.

While it is often convenient to think about the different volatility species from an Odum 2-product or limited volatility basis set fit (with only a few products, like those used here) as real products they are in fact fitted surrogate products and could span a large range of volatilities. As a result, effective vapor pressures may appear "too low" and enthalpies of vaporization may also appear "too low." In a chamber experiment, like the ones used to obtain the fits in this paper, high molecular weight products like oligomers or other very low volatility products likely do form as mentioned by Leungsakul et al. 2005. Oligomers that form in the chamber experiments are already included (although to a poor degree) in the fits used in these paper as part of the lumped volatility species. In this work, fits are limited to what was "observed" in the chamber. Since chamber loadings do not go very low ($0.1 \mu\text{g}/\text{m}^3$ at the lowest and usually more than $1\text{-}10 \mu\text{g}/\text{m}^3$), the low volatility products cannot be separately identified in the yield curves. Fits tend to produce fitted volatilities (C^*) (or constrain yields of specified volatilities) equivalent to the loadings (M_0) measured in the chamber. Work by Cappa and Jimenez (2010) has indicated that coarse volatility lumping likely does obscure the presence of low volatility species, and that replacing coarse fits with fits that better resolve the very low volatility products may allow us to use more reasonable enthalpies of vaporization in addition to better capturing species like oligomers. Providing data to support better

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model parameterizations should be a future priority. In addition to the volatility, the kinetics of oligomerization are not well understood

The lack of very low volatility products in the model likely results in underpredictions of aerosol in remote regions where loadings are lower and the semivolatile products evaporate. The fits are less reliable as temperatures and loadings get farther away from the values at which the chamber data was available.

1.4

p. 21267 line 5 "ozonolysis"

Corrected

1.5

Section 2.3.1: I don't find text in here describing how NO_3 + terpenes yield (seemingly a pivotal parameter in your modeling) is fit using a single b-pinene measurement from Griffin 1999. Please discuss. For example, another recent measurement of NO_3 bpinene yield was much higher (Fry et al 2009, 50% at $< 10 \mu\text{g m}^{-3}$) . . . how uncertain is this yield parameter? Are there other measurements in the literature suggesting it might be higher/lower?

The Griffin et al. 1999 experiments are mentioned on page 21268, lines 1-3. Table 1 also mentions the data upon which the fit was based. The fit is based on one experiment that has 4 (yield, loading) data points. The raw data (Y vs. M_0) can be found in the supplement. Yields start at around 50% for loadings around $40\text{-}60 \mu\text{g}/\text{m}^3$ and exceed 100% for higher loadings (yields and loadings were corrected using a density of $1.3 \mu\text{g}/\text{m}^3$ as mentioned in Table 1). Fry et al. reports a yield at $41\text{-}48 \mu\text{g}/\text{m}^3$ of 46 to 53% which is consistent with the density corrected Griffin data. The Griffin et al. 1999

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data does not constrain the yields at low loadings which may be higher or lower than the fit in Table 1 predicts.

1.6

p. 21268 lines 10-12. Is this because the “high-NO_x” limit was completely unrealistically high?

For reference, these lines state: “Although high-NO_x conditions have traditionally been thought to suppress isoprene aerosol, recent work shows high-NO_x isoprene aerosol yields can be similar to the low-NO_x yields at atmospherically relevant NO₂/NO ratios.”

The older “high-NO_x” limit likely did not produce the right behavior because the importance of the NO₂/NO ratio, which influences PAN chemistry, had not been identified and was not carefully controlled. The role of the NO₂/NO ratio in SOA yields has only recently been identified (by Surratt et al. and Chan et al. 2010). The NO₂/NO ratio is a proxy, and recent work indicates that SOA from high-NO_x isoprene oxidation is likely from MPAN.

1.7

Fig 2: (discussed section 3.2). Could you redo this figure so that rather than each hydrocarbon summing to 1, the entire plot sums to 1? Or something similar to ease comparison of relative importance of different HC classes as well as oxidants?

Panel (b) of Figure 2 has been revised to show the contribution of each parent hydrocarbon-oxidant pair to total biogenic aerosol. The effect is essentially to scale down the monoterpene and sesquiterpenes (compared to the previous plot) since isoprene photooxidation is such an important source of organic aerosol. Note that normalizing by total biogenic OA instead of each individual parent hydrocarbon introduces

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additional uncertainty (we use assumed yields at a specified loading) since the different biogenic emissions are not necessarily collocated and partition under different ambient loadings. For example, isoprene aerosol (on a global average) seems to exist in areas with slightly lower loadings than terpene aerosol. The revised figure has been uploaded as a supplement to this author response.

The following was also added to the manuscript:

The bottom of Fig. 2 shows the predicted contribution of each reaction pathway to net biogenic aerosol production (all pathways shown sum to one).

On a global, annually averaged basis, isoprene photooxidation is the largest single parent hydrocarbon-oxidant contributor to biogenic organic aerosol. The second largest source of biogenic OA is low-NO_x oxidation of monoterpenes.

1.8

p. 21271, line 5: You use a global avg OA loading of 1.5 ug m⁻³. Might be worth re-emphasizing here that this is highly regionally variable (maybe mention something about how different this would look if you took a high or low background OA number?) More generally, there are some interesting “hot spots” on the August 2000 plots (e.g., Idaho?!) Please comment briefly on this in the text. Is this forest fires?

The globally average OA loading of 1.5 μg/m³ was only used to estimate the numbers in Figure 2(b) (which are global numbers), since all the aerosol from MTPA, LIMO, MTPO, and SESQ is lumped based on volatility, not parent hydrocarbon. If the yield at a loading of 1.5 μg/m³ is used to calculate SOA production, the global OA production rate from GEOS-Chem using all the semivolatile species with their individual yields and volatilities, can be approximately reproduced. Using a much higher or lower loading than about 1 to 1.5 μg/m³ does not reproduce the global budget. The model calculates the OA loading and yield as a function of all the species concentrations and

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saturation concentrations which does lead to a regionally variable OA level. This has been clarified in the manuscript. The August 2000 hot spots are forest fires (biomass burning events) which is now mentioned in the figure caption and the text.

The revised/new sentences in the manuscript are:

Section 3.2: These global values were calculated using the aerosol yield at an organic loading of $1.5 \mu\text{g}/\text{m}^3$ which was found to approximately reproduce the lumped global net aerosol production rate in GEOS-Chem which considers the partitioning of all individual semivolatile species based on their yields and saturation concentrations. The loading of $1.5 \mu\text{g}/\text{m}^3$ is thus a fitted value used for illustration purposes since all monoterpene and sesquiterpene aerosol is lumped by volatility instead of parent hydrocarbon, and aerosol yields are regionally variable as a result of the semivolatile nature of most SOA.

Section 3.3.1: High loadings occur in areas such as Idaho as a result of biomass burning.

1.9

p. 21271, lines 15-17: This is completely dependent on your assumptions about the volatility of nitrate products. If e.g. oligomerization is occurring, this could look dramatically different. How would this conclusion change if you lowered the volatility a couple orders of magnitude?

Yes, the model prediction is dependent upon the assumptions of the volatility predicted by the fit. Oligomerization could be occurring, but might be poorly represented by the fit (see earlier discussion, oligomerization is not specifically excluded). If the terpene + NO_3 reactions did produce lower volatility products, the yield of the current $\text{C}^* = 10$ and $100 \mu\text{g}/\text{m}^3$ products would have to be decreased which would lead to less global OA production from $\text{C}^* = 10$ and 100 products, but more OA from the new lower volatility products. The global OA production from terpenes+ NO_3 would probably increase due

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to the dominance of low loadings on a global basis, but could also decrease if the current fit is overestimating yields at low loadings. Section 4.4 mentions that the yields for terpenes+ NO_3 are relatively unconstrained at low loadings. The reader is now directed to Section 4 for a discussion on biases in the model.

Added: A discussion on possible model biases is presented in Section 4.

1.10

p. 21275, lines 16-21. Again, some caveats might be worth mentioning here. How well-constrained do you consider the 4% / 26% yield numbers to be?

The yields mentioned correspond to loadings of 1 and $10 \mu\text{g}/\text{m}^3$. Both loadings mentioned (1 and $10 \mu\text{g}/\text{m}^3$) are below the loadings observed in the chamber experiments upon which the fit is based. The 4% yield is thus very unconstrained and the 26% is moderately unconstrained.

The following has been added (revised) to the manuscript: Since the terpene + NO_3 aerosol yield data upon which the fit is based contains information at relatively high loadings, aerosol loadings must be significant for organic nitrate aerosol to contribute to surface level OA.

1.11

p. 21278 line 27: "levels, even"

Corrected.

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1.12

Fig 1 caption: "Schematic"

Corrected.

1.13

Fig 2: please see comment above for a suggested alternative presentation of this data

See above.

1.14

Fig 4: cite Tref in caption?

Added: T_{ref} is 298 K for all semivolatile species except primary SVOCs and oxidized SVOCs which use 300 K.

2 Responses to anonymous referee 2

2.1

Does the coarse spatial resolution of the model influence the results and conclusions? NOx / VOC ratios have large variability within single grid cells (e.g. Atlanta versus rural north Georgia).

The spatial resolution of the model will influence results to some degree and our resolution will not be able to resolve small scale gradients. For reference, in preparation for

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the 2x2.5 degree simulations, simulations were performed at 4x5 degrees with GCM meteorology. The 2x2.5 and 4x5 results were qualitatively consistent. In particular, that they both predicted a significant role of terpene + NO₃ aerosol, a relatively small effect of NO + RO₂ branching ratio, and qualitatively the same partitioning shown in Figure 4. There were differences due to the fact that the meteorology was different which lead to different biogenic emissions. The 2x2.5 resolution for a global model was found to be a good compromise between resolution and computational efficiency.

2.2

Equation 5 could use additional discussion to clarify what is being calculated here. It was not clear what was "forcing" primary SVOCs out of particles (presumably preferentially to secondary SVOCs). Is this not just due to the thermodynamic assumptions in the model about these respective species. And how are gas phase reactions not in the fit. It is not clear how gas phase reactions would be included in the fit.

The following:

SVOCs are forced out of the particle phase to a greater degree than the other semivolatiles as a result of gas-phase reaction and are not included in the fit.

Has been replaced by this:

Transfer of mass between the gas and aerosol phases is driven by deviations from equilibrium. The semivolatile organic species are always assumed to be at equilibrium during the partitioning routine. Deviations from equilibrium occur as species are dry deposited, wet deposited, and gas-phase chemical reactions produce more (or less) of the semivolatile species. For all secondary semivolatiles, the only gas-phase removal process is dry and wet deposition. For the primary semivolatiles, reaction in the gas-phase to produce lower volatility species is an additional removal process that will tend to force primary semivolatiles out of the particle phase. Since secondary semivolatiles

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do not experience this same loss process, the primary semivolatiles were not included in the secondary semivolatile fit of Fig. 4.

2.3

In section 2.3.1 it was unclear how the enthalpy of vaporization was used. It seems it was used to adjust experimental yields to yields at the reference temperature. But was 42 kJ per mol also used to represent the temperature dependence of vapor pressures or saturation concentrations for all semivolatile species? Assuming saturation concentrations were adjusted in this way during the model runs, what is the sensitivity of concentrations to the enthalpy of vaporization?

The enthalpy of vaporization was used to adjust the saturation concentration, C^* (or partitioning coefficient) to the actual temperature of the data based on the fact that C^* is a function of vapor pressure. The procedure for fitting the chamber data to yield curves is described by Stanier et al. 2008 and essentially determines the mass-based stoichiometric coefficients for a given parent hydrocarbon/oxidant system by minimizing the difference between the modeled and observed yields at a given loading. The modeled yield is a function of C^* . The C^* for the fit/modeled yields are generally fixed at a reference temperature (298 K used here) so that different systems may be easily combined. If the chamber experiment was conducted at a temperature other than the reference temperature, the C^* used in the fit (to calculate the "modeled" yield) is adjusted from 298 K to the actual experiment temperature using an enthalpy of vaporization of 42 kJ/mol and the Clausius-Clapeyron relationship (see eqn 8 of Stanier et al.). During GEOS-Chem model runs, 42 kJ/mol was also used to adjust C^* at the reference temperature to the actual grid-box temperature. Previous work (Henze and Seinfeld 2006, Pye and Seinfeld 2010) has examined the effect of enthalpy of vaporization on global SOA budgets. In short, the parameter is very influential, but 42 kJ/mol is likely the appropriate value to use given the coarse saturation concentration lumping

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used here.

The following has been updated in the manuscript: If yields are not available at the reference temperature, an enthalpy of vaporization of 42 kJ/mol is used in the fitting procedure to adjust C^* (Chung and Seinfeld 2002). The same enthalpy is also used for temperature adjustments online in GEOS-Chem.

2.4

Line 371 – the term nitrate aerosol is usually used to refer to ammonium nitrate. Can this be reworded to clarify this is meant for SOA from the nitrate radical pathway? Similar confusion may occur in other places in the manuscript, for example line 411.

Instances of 'nitrate aerosol' in the manuscript were replaced with 'organic nitrate aerosol.'

2.5

Line 430 – This paragraph could be rewritten for improved clarity. For example, the term offline oxidation is perhaps inferior to offline calculation of oxidation rates; also a reference to where in the text the offline oxidation scheme is described (presumably in a previous section) would be helpful. However, at line 434, the offline oxidation scheme is described, a few lines after it is mentioned for the first time in section 4.2. Overall, more effort to explain separately the issues of knowing what is happening in the real reacting system, versus how it is simulated, would seem appropriate.

The offline oxidation was mentioned in section 2.3 but not described. Readers are now directed to section 4.2 for more information about the offline calculation.

Section 4.2, line 430 (old) had been revised to read: As mentioned previously, the oxidation of monoterpenes and sesquiterpenes by OH, O₃, and NO₃ is an offline

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calculation. For each timestep, the gas-phase OH, O₃, and NO₃ levels are saved from the chemistry solver and used offline in the aerosol routines to determine how much of a given terpene should react with the oxidant during that timestep. Thus, monoterpene and sesquiterpene chemistry does not directly affect OH, O₃, and NO₃ levels. As a consequence of this offline oxidation calculation, the current version of GEOS-Chem essentially assumes oxidants such as OH, NO, HO₂, O₃, and NO₃ are 100% recycled when they react with monoterpenes and sesquiterpenes. Recycling of the oxidants is recommended when only a limited amount of the parent hydrocarbon gas-phase oxidation is represented and later generation products may release oxidants, but this approach may cause the model to overestimate the potential importance of aerosol from nitrate pathways since NO₃ levels may be artificially high.

2.6

Line 454 – can a quantitative statement be used in place of fairly aggressive recycling levels.

The analysis on the following page indicates that recycling as high as 75% might not be high enough to prevent depletion of nitrate radicals due to reaction with monoterpenes. (perhaps >75%) was added after aggressive recycling in the line mentioned.

3 References

Cappa, C. D. and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, *Atmos. Chem. Phys.*, 10, 5409-5424, doi:10.5194/acp-10-5409-2010, 2010.

Please also note the supplement to this comment:

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<http://www.atmos-chem-phys-discuss.net/10/C10036/2010/acpd-10-C10036-2010-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 21259, 2010.

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