**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "A global perspective on aerosol from low-volatility organic compounds" by H. O. T. Pye and J. H. Seinfeld

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The authors would like to thank the reviewers for their comments. The reviewers raise a number of important questions to which the answers are the subject of ongoing research. We hope readers will use this response as a companion to the main manuscript since additional details and more lengthy explanations are provided here. Responses to the reviews are below with original reviewer comments in *italics*. Changes to the manuscript are explicitly indicated.

1 Response to Anonymous Referee 1

1.1 Wintertime performance

The base version of the revised model underpredicts US wintertime OC levels. The paper investigated a number of sensitivities, but one that they did not consider was enthalpy of vaporization. The model uses a value of 42 kJ/mol for all organics based on the work of Offenberger, but a value this small is hard to physically justify (see, e.g., Epstein et al., EST 2009). The wintertime model predictions should be sensitive to this value and doubling it into the more physically realistic range might substantially improve model performance.

A simulation using an enthalpy of vaporization of 83 kJ/mol (double the baseline of 41.6 kJ/mol) has been performed. Changing the enthalpy of vaporization to a higher value reduces the discrepancy with the traditional model during both the winter and summer (the reference temperature for monoterpene SOA is 310K which is higher than even the summer average temperature). Note that the traditional value used in GEOS-Chem is 42 kJ/mol, and 30 kJ/mol is commonly used in other models (Lane et al., 2008, Farina et al., 2009).

The following has been added to the manuscript (section 2.6, some text removed): "However, a discrepancy exists in the predicted enthalpy of vaporization for semivolatile organic aerosol estimated for complex SOA systems (around 10-40 kJ/mol, Offenberg 2006) and based on theory or single component systems (around 100 kJ/mol, Epstein et al., 2010). See section 3.4.1 for an examination of this value."

The sensitivity test was added to table 6 and the new table 7 (mean bias and normalized mean bias, described later). The ΔH*2 simulation was added to section 3.4 and described: "ΔH*2 doubles the enthalpy of vaporization to 83 kJ/mol for all semivolatiles."

Section 3.4.1 and figure 9 addition: "Figure 9 shows the change in OC surface concentration for DJF relative to the traditional simulation for the ΔH^*2 simulation. The new enthalpy produces a result similar to that of doubling the POA inventory (*2*SVOC* simulation) in terms of reducing the discrepancy with the traditional simulation and observations. In conclusion, increasing the SVOC emissions, decreasing the SVOC emission volatility, or increasing the enthalpy of vaporization are very effective ways of reducing measurement/model discrepancy, although significant underestimates of the seasonal mean OC concentration persist (mean bias of -0.51 μgC/m^3 for *2*SVOC* , -0.44 μgC/m^3 for *SVOC K*10*, and -0.50 μgC/m^3 for ΔH^*2 compared to the IMPROVE observations)."

"Additional constraints as well as a correct treatment of SOA temperature dependence are needed to assess the optimal model parameters."

The simulation was also mentioned in the conclusions. The global net SOA production rate for the ΔH*2 simulation remains within the estimated range of 60 to 100 Tg/yr.

1.2   Summer performance

The paper discusses that doubling SVOC emissions essentially closes the wintertime model measurement comparison gap for OC. How does doubling the SVOC emissions affect the summertime performance?

The summertime performance of the model is an area of ongoing research. We are currently updating the traditional SOA formation and are seeing significant changes in the predicted surface level concentrations of OA. Therefore, a careful examination of summer OA levels is left to future work. However, both reviewers were interested in summertime OA levels, so we have added a figure to the supplement and a paragraph to the manuscript.

Paragraph added to manuscript (section 3.4.1: Winter US Concentrations):

"For reference, Fig. S2 (see supplement) shows the effects of the sensitivity simulations on surface level June-July-August OC concentrations. The summertime simulations also indicate that increasing the SVOC emissions or decreasing the SVOC emission volatility are effective ways of reducing the discrepancy with the traditional simulation. However, since the summer OA is dominated by contributions from biogenic SOA, future updates to this source of SOA will likely have significant effects on the summertime predictions."

Caption for figure in supplement:

"June-July-August 2000 surface total OC concentration relative to traditional (non-volatile POA) simulation using GISS meteorology at 4°x5° horizontal resolution. Tests are outlined in Table 6 (main manuscript)."

1.3   Model measurement comparisons

I was disappointed that the paper did not present more extensive model-measurement comparisons. The only comparisons were for the absolute OC levels in the US during the wintertime (Fig. 7). I understand that the authors focused their model evaluation on the winter period to reduce uncertainties associated with biogenic SOA, but more summertime comparisons would also be informative. For example, does a large model measurement gap also exist for total OC in the summertime? Furthermore, more extensive comparisons that consider parameters in addition to absolute OC levels would be useful too. For example, Shrivastava et al. (JGR 2008) compared their model predictions to OOA/HOA ratios inferred from measured AMS data. Fossil versus contemporary carbon would be another parameter to consider. Section 3.5 of the paper discusses C14 data but the discussion seemted qualitative.

Regarding summertime comparisons, see our response to the previous question as well. GEOS-Chem organic aerosol concentrations for the traditional non-volatile POA

simulation have been extensively compared to observations in the work of Liao et al., 2007 (comment added to section 3.4.1).

Since we are using a global model with relatively large grid boxes, localized urban areas are not resolved well and thus the urban to regional or very localized OOA/HOA comparisons, like those performed by Shrivastava et al. (2008) or Hodzic et al. (2010) would be difficult to replicate. The current predicted concentrations are representative of a more regionally distributed aerosol which should match well with the IMPROVE observations which are typically located in National Parks or other remote areas. A more extensive model-measurement comparison should be the topic of future work.

The fossil/contemporary comparison remains qualitative since fossil/modern OC is not separately tracked.

1.4   Scaling inventories

Using Schauer et al. emissions data to scale inventories (page 4088). The paper uses a scaling factor of 0.27 to scale up POA inventories to account for gas phase SVOCs. It appears that this value is based only on the speciated wood smoke SVOC measurements of Schauer? Is that correct? How representative is Schauer et al. fire place burning profile to the sources that dominate global sources of POA? The paper states that this is a conservative lower bound estimate. What fraction of the total SVOC vapor emissions were speciated in the Schauer study? Is there any reason to think that this estimate of missing SVOC vapor emissions might be biased low? Can the SVOC UCM be used to bound the range of missing SVOC?

Note that the Schauer et al. (2001) inventory does not specifically identify SVOCs or IVOCs. The 0.27 value used to scale up the POA inventories is from Schauer et al. (2001) for pine wood burning. This number was obtained by taking all the gas-phase emissions collected on the PUF sampling train/filter that also had a particle-

phase sample as well. This number may be biased low since (a) some SVOCs may not have been identified in the particle phase and therefore their gas-phase emissions were not counted as SVOCs, (b) some SVOCs may not have been captured by the PUF sampling train/filter, (c) some gas-phase SVOCs may be part of the UCM, or (d) POA inventories may represent a significantly different fraction of SVOCs than in the study by Schauer et al. (2001).

The following has been added to the manuscript, section 2.4.1 (some text was also rearranged): SVOC emissions: "Accounting for the all gas-phase species on the PUF/filter and the entire gas-phase UCM would increase the 0.27 estimate to 0.61. The possibility remains that POA inventories may represent a significantly different fraction of SVOCs than in the study by Schauer et al. (2001)."

Additional discussion: The Schauer et al. POA emission factors (4 to 7 mg/kg wood) are consistent with the global GFED2 inventory (factors 3.2 to 9.1, source: Global Fire Emissions Database version 2 (GFEDv2) (2005) readme file, available: http://ess1.ess.uci.edu/ jranders/data/GFED2/). The largest global source of POA is biomass burning, so the Schauer et al. inventory should be very applicable. Roughly 10% of the gas-phase emissions in Schauer et al. belonged to the UCM. If all of those gases were SVOCs, that would change the scaling factor from 0.27 to 0.45. However, there may still be additional gas-phase compounds that were misclassified as IVOCs. By taking that into account, the Schauer et al. 2001 inventory supports a scaling factor as high as 0.61 for the missing SVOCs which is still lower than the missing factor of 1 (for a total scaling of 2=1(captured SVOCs) + 1(missing SVOCs)) based on our top-down estimate. We have added a clarification to the description of the *2*SVOC* simulation (Section 3.4) that $G_R/POA_R = 1$. It is important to note that the global POA emission inventory has uncertainty. The GFED2 inventory cautions that there are uncertainties in fuel loads, combustion completeness, and burned area. Given the amount of uncertainty in the underlying POA emission inventory and the fact that the traditional POA inventory was not meant to capture low volatility gas-phase emissions, a factor of 2

scaling still seems plausible. Other studies have assumed that all SVOCs are captured by traditional POA inventories (Robinson et al., 2007) or that POA inventories need to be multiplied by 3 (Hodzic et al., 2010).

1.5   IVOC Emissions

I was confused on how the IVOC emissions were generated. The paper states that IVOC emissions are distributed like naphthalene (page 4091). However, my impression was that for biomass burning the emissions are scaled with CO, using naphthalene as an intermediate. For anthropogenic sources they are scaled with benzene. Is this correct? I was also confused with the derivation of the beta parameter (equation 9). It seems like you are linking the IVOC emissions to the traditional nonvolatile POA emissions? If one repeats this sort of analysis with a phenol or some other IVOCs (instead of naphthalene) in the Schauer emission profile how variable are the estimated IVOC emissions?

The reviewer is correct in stating that the emissions for biomass and biofuel burning are scaled to CO using naphthalene as an intermediate. Anthropogenic sources are spatially distributed like benzene, but their magnitude is that of naphthalene before the scaling takes place. To summarize, the IVOC emissions were created as follows:

1. create baseline naphthalene inventory from biomass burning, biofuel burning, and anthropogenic (fossil fuel burning, etc) sources

    (a) biomass burning: use an emission ratio relative to CO

    (b) biofuel burning: use an emission ratio relative to CO

    (c) anthropogenic sources: spatially distribute like benzene, but estimate the global emission magnitude based on the work by Zhang and Tao (2009)

2. scale the naphthalene emission inventory to represent all IVOCs using two pieces of information:

    (a) the globally averaged ratio of IVOCs to traditional (non-volatile) POA should be 0.34 based on Schauer et al. 2001 for biomass and biofuel burning (the 0.34 is the estimated ratio of all IVOCs to POA based on the work by Schauer et al. 2001 for wood burning)

    (b) the entire naphthalene emission inventory should be scaled with one factor (meaning that the ratio of biomass:biofuel:anthropogenic emissions for IVOCs should be the same as that of naphthalene)

The Beta parameter is just a mathematical representation of the items listed in step 2 above. If another species, like phenol, had been used in the same analysis, presumably there would be no difference in the magnitude or spatial distribution of IVOC emissions predicted for biomass or biofuel burning (unless the species was not well correlated with CO). However, the anthropogenic emissions could be different. The use of naphthalene produced emissions of IVOCs, that when ratioed to traditional POA, are consistent with other studies that indicate anthropogenic sources of POA likely produce relatively more IVOCs than wood burning.

Note that the following sentence has been revised in the manuscript (ACPD page 4093, line 10) from: "As a result of the separation of POA and IVOC emissions, the ratio of IVOC:traditional POA emissions is roughly 1.7 for anthropogenic sources and 0.34 for biomass and biofuel sources combined." to

"As a result of the separation of POA and IVOC emissions, the ratio of IVOC: traditional POA emissions is roughly 2.1 for anthropogenic sources and 0.34 for biomass and biofuel sources combined."

The ratio of IVOCs:SVOCs is 1.7 for anthropogenic sources. Note that Robinson et al., 2007 assumed IVOCs:traditional POA is 1.5 and traditional POA encompassed all

SVOCs.

The following has been added to section 2.5.1: IVOC emissons: "Thus, our scaling incorporates two ideas: IVOCs are spatially distributed like naphthalene and the ratio of IVOCs to traditional POA for wood burning sources is 0.34 as in the work of Schauer et al. (2001)."

1.6 C* of low volatility SVOC

The Shrivastava et al. wood smoke volatility distribution is not well constrained at atmospherically relevant concentrations. This issue was raised in section 4.2. For example, assigning the lower volatility component of the Shrivastava two product fit a C* of 10 as opposed to 20 ug /m3 (at 298 K) likely will not alter the fit over the range of the source test data but could have a significant impact on model performance?

The reviewer is correct in stating that since the volatility distribution is not well constrained, the lower volatility component could be different from 20 μg/m^3. This uncertainty should be encompassed by the sensitivity test *SVOC K*10* in which the emissions are made a factor of 10 less volatile than suggested by the Shrivastava et al. (2006) fit. The *SVOC K*10* test shows that wintertime OC concentrations are still slightly lower than the traditional simulation. A test in which K is doubled (leading to a C* of 10 μg/m^3 for the lower volatility component), should have a much smaller effect on surface OC concentrations in winter than the *SVOC K*10* test.

1.7 Relative importance of SVOCs vs IVOCs

Is the fact that anthropogenics account for half of the IVOC inventory an artifact of how the inventory was constructed (i.e. using napthalenes)? I am concerned that the argument in section 3.5 that "These observations lend support to the hypothesis that

SVOCs contribute significantly to ambient OA and that scaling up SVOC emissions may be more justified than scaling up IVOC emissions" seems circular.

Spatially distributing IVOCs like naphthalene appears to be a good approximation. The idea that fossil carbon sources (like diesel combustion) contribute relatively more IVOCs than modern carbon sources is supported by independent estimates of IVOC emissions and aerosol formation that are not based on naphthalene (Shrivastava et al., 2008, Grieshop et al., 2009a).

1.8 Need for additional information

At a number of points the paper mentions the need for additional information to constrain the model, but only briefly discusses what those might be in the final paragraph of the conclusion section. Given the challenges associated with simulating OA and the additional parameters introduced by this new approach, it would be good if the paper could discuss in more detail some directions that the community could head to help resolve these issues. For example, what types of ambient data (beyond absolute OC concentrations) could be used to help assess the performance of different models?

Replace the last sentence: "Information from improved SVOC and IVOC emission estimates and composition information (in the form, for example, of O:C ratios or ^{14}C fractions) over atmospheric time scales can help to constrain models." with

"Information in the form of improved SVOC and IVOC emission estimates or data (such as ^{14}C fractions, O:C ratios, AMS PMF components (OOA, HOA), correlation with gas-phase tracers (Weber et al., 2007, de Gouw et al., 2005), or identification of marker compounds (Bhave et al., 2007)) that allow for the determination of sources of OA can help to constrain models."

1.9 IVOC deposition

How was deposition of IVOC gases treated, i.e. hydrophobic or hydrophilic?

The IVOC gas (naphthalene-like surrogate) is not deposited. The oxidation products of the IVOC (the semivolatile species that partitions between the gas and aerosol phase) are wet and dry deposited in the gas and aerosol phases like traditional SOA (hydrophillic). See section 2.6 (Additional model parameters and specifications) for more information. The following sentence has been added to that section: "The IVOC surrogate gas is not deposited."

1.10 NAP as an IVOC surrogate

The authors argue that napthalene is a reasonable IVOC surrogate for biomass smoke, but it is less clear that is a good surrogate for mobile source dominated urban emissions which may be dominated alkanes.

In the manuscript, we highlighted the work by Chan et al. (2009) that indicated naphthalene is an important SOA precursor from both wood burning and diesel exhaust. Although alkanes are an important part of diesel combustion emissions, Chan et al. (2009) estimated that PAHs are actually more important when it came to SOA formation and produced 40 to 70% more aerosol than alkane oxidation. Models must balance the need for compound specific-information and treatments with computational efficiency. Just like the volatility basis set approach (Donahue et al., 2006), we treat all compounds of a certain volatility the same. Better representations of IVOC oxidation behavior are called for and should be incorporated in the future.

2 Response to Anonymous Referee 2

General comments

2.1 Summertime OA

The authors try to explain their results based on wintertime OA calculations over the USA, claiming that the absence of biogenic SOA makes the results easier to understand. Although this is true, summertime OA are also very interesting to study. The conclusions extracted from the wintertime discussion (present in several places in the manuscript) can be used in a discussion of the summertime OA, with special attention to the biogenic SOA.

Reviewer 1 raised a similar concern. Please see the response above.

2.2 Comparison to model/measurements

Most of the comparisons are being made using the traditional simulation as a basis. The reason given is that between the traditional and the revised simulations, the former was the one that compared the best with measurements (figure 7). Nevertheless, the traditional simulation is just another model result. The comparisons of the sensitivities should be made with the observations themselves, and not with the traditional simulation, which might have a better agreement with measurements, but is not the reality. In order to conclude that the 2*SVOC simulation is the best, this has to be extracted from its comparison against measurements, not against the traditional simulation.

We chose to compare to the traditional simulation since the traditional simulation has been extensively evaluated against observations (Liao et al., 2007), and the observations from year 2000 for the IMPROVE network are relatively sparse. In the Eastern

U.S., many grid boxes have 1 or fewer observations. Liao et al. (2007) indicate that wintertime OA levels in GEOS-Chem are generally underestimated (simulated vs. observed for DJF has a slope of 0.77 and R=0.72). Comparisons by Liao et al. (2007) indicate that GEOS-Chem underpredicts OA levels by about 0.56 μg/m^3 (mean bias) or 34% (normalized mean bias) on an annual basis with the bias being larger in magnitude in the western US and lower in magnitude in the eastern US. See next comment.

2.3 Quantitative comparison

In comparing simulations with measurements, some statistical analysis is necessary. The only part where model-measurements comparison was made is figure 7. In order to have comment 2 answered, a quantitative analysis is required, that is completely absent from the manuscript.

Calculations of the mean bias and normalized mean bias compared to the IMPROVE observations have been added as a table (see next page). The following text has also been added to the manuscript (Section 3.3):

"Comparisons to the IMPROVE network by Liao et al. (2007) indicate that GEOS-Chem underpredicts annual OA levels by about 0.56 μg/m^3 (mean bias) or 34% (normalized mean bias) with the bias being larger in magnitude in the western US and lower in magnitude in the eastern US. A comparison of simulated and observed OC levels for the US during DJF 2000 in this work, indicate that GEOS-Chem underestimates OC by 0.20 μgC/m^3 (21%) for the 2x2.5 simulations and 0.37 μgC/m^3 (39%) for the 4x5 simulation. The bias for the 4x5 simulation is likely larger as a result of the coarser model resolution and the fact that a climatological meteorology has been used as opposed to the assimilated, year-specific meteorology used by 2x2.5 simulations."

And section 3.4.1: "Table 7 shows the mean bias and normalized mean bias for the sensitivity simulations compared to the IMPROVE network. Panel (a) of Fig. 8 repre-

sents the difference..."

Table 1. Mean bias (MB) in μgC/m^3 and normalized mean bias (NMB) in percent for the sensitivity simulations for DJF 2000 ($MB = \frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)$, $NMB = 100\% * \sum_{i=1}^{N}(P_i - O_i)/\sum_{i=1}^{N}(O_i)$, where P$_i$ are the model predictions and O$_i$ are the IMPROVE observations at N locations). IMPROVE observations are shown in Figure 7. Sensitivity simulations are outlined in Table 6. 2x2.5 simulations use GEOS4 meteorology. 4x5 simulations use GISS GCM meteorology.

Simulation	MB [μg C/m^3]	NMB [%]
2x2.5 Traditional	-0.20	-22
2x2.5 Revised	-0.59	-63
4x5 Traditional	-0.37	-39
4x5 Revised	-0.70	-75
4x5 2*IVOC	-0.68	-73
4x5 2*SVOC	-0.51	-55
4x5 SVOC K*10	-0.44	-47
4x5 O-SVOC K*10	-0.60	-64
4x5 H-Law/100	-0.67	-71
4x5 ΔH*2	-0.50	-54

2.4 NAP vs. alkanes

A brief discussion on how the results are expected to change if alkanes were used as a surrogate for IVOC instead of naphthalene would be useful, expecially concerning the spatial distribution, the seasonality of emissions (if any) and the modern vs. fossil carbon discussion. My main concern is how the conclusion in page 4106, lines 24-25 would change.

IVOC emissions from biomass burning have pronounced seasonality and are specific to the year being simulated. Biofuel emissions of CO are aseasonal (the SVOC biofuel emissions, however, do have seasonality). Anthropogenic IVOC emissions (based on benzene) do not have seasonality in this work, but future versions of GEOS-Chem will incorporate seasonality into the benzene emissions. The same seasonality would likely be imposed for an alkane-like surrogate.

The conclusion on page 4106 states that "These observations [the dominance of modern C in aerosol observations, the large modern C component of SVOC emissions, and the large fossil C component of IVOC emissions] lend support to the hypothesis that SVOCs contribute significantly to ambient OA and that scaling up SVOC emissions may be more justified than scaling up IVOC emissions."

The following has been added to the manuscript (ACPD page 4106): "Using alkanes to obtain the spatial distribution of IVOC emissions would likely lead to large estimates of anthropogenic sources and small estimates of wood burning sources since wood burning is not a large source of intermediate volatility alkanes (approximately C17) (Schauer et al., 2001). Thus, the IVOC composition would be shifted even more toward fossil fuel sources than predicted by the naphthalene spatial distribution. Since ambient data indicate a large modern C component to aerosol, the alkane distribution would further diminish the expected role of IVOCs in ambient organic aerosol formation."

2.5 Specific comments

1. *Page 4091, line 11: Can you support this, as you did in the previous paragraph for the total emissions?*

   Line 11 states: "IVOC emissions are assumed to be spatially distributed like naphthalene." The preceding paragraph addresses the appropriateness of naphthalene as an IVOC surrogate. To add further emphasis, the sentence has been revised to (ACPD page 4091): "Since naphthalene is an important IVOC from

   many sources including wood combustion and vehicle exhaust (Chan et al., 2009, Schauer et al., 2001, Schauer et al., 2002), IVOC emissions are assumed to be spatially distributed like naphthalene."

2. *Page 4094, line 20: What kind of identity should be preserved, but is being lost? Which is the "artificial migration" you are referring to?*

   Each volatility component should ideally have its own tracer. Lumping different volatilities together means that a species of one volatility could be converted to a species of another volatility. A qualifier, "of mass," has been added: "Since the identity of each individual species is not preserved during transport, some artificial migration of mass between the volatilities may occur."

3. *Page 4095, lines 1-3: More information on the lumping is needed.*

   The following has been added (ACPD page 4095): "Each species with a saturation concentration below 10^5 μg/m^3 in Table 1 has a separate gas and aerosol phase tracer. The IVOC has a gas-phase tracer only, for a total of 15 additional tracers for the low-volatility organic aerosol simulation. A list of GEOS-Chem tracers for a standard full-chemistry SOA simulation can be found in Table 2 in the work of Liao et al. (2007)."

4. *Page 4099, line 1: Can you estimate an e-folding lifetime for the revised simulation?*

   The POA lifetime in this situation refers to the POA lifetime against deposition. Table A1 shows that the tropospheric lifetime against deposition for POA in the revised simulation is 17 days. The hydrophobic to hydrophilic conversion lifetime of SVOCs in the revised simulation can be estimated by

   $\tau = 1/(k_{OH}[OH]) = 1/(2 \cdot 10^{-11} * 1 \cdot 10^6)s = 0.6$ days

   Note that the mechanism for conversion is different in the revised model since the hydrophobic to hydrophilic conversion takes place in the gas phase by reaction

with OH instead of as an imposed particle-phase conversion like in the traditional simulation.

The sentence has been revised to include (17 days against deposition): "In the revised simulation, the hydrophobic nature of POA leads to a much longer POA lifetime (17 days against deposition)."

5. *Page 4104, middle paragraph: More numbers are needed in this discussion.*

   Absolute numbers were left out of this section because the absolute numbers are sensitive to the resolution and meteorology used in a given simulation. The relative change compared to the traditional simulation seems to be robust (within a few percent, verified for the *Revised* and *2*SVOC* simulations). The budget numbers (including production) for the traditional and revised simulations can be found in Table 5. The relative changes (from Figure 9, 4x5 resolution) have been added to the text. Change relative to the traditional simulation: Revised (-26%), 2*IVOC (-17%), 2*SVOC (+12%), SVOC K*10 (+3%), O-SVOC K*10 (+2%), H-law/100 (+12%). The relative change in OA lifetime as a result of sensitivity simulation depends on the resolution since the lifetime tends to be shorter in the 2x2.5 simulations (see Table A1.)

6. *Page 4106, lines 27-29: Why?*

   These lines state: "However, when scaling up the POA emission inventory to obtain SVOC emissions in this work, all sources were scaled up equally. SVOCs from anthropogenic sources could be underestimated to a greater extent by the traditional POA inventory than SVOCs from biomass or biofuel burning sources..."

   The following has been added: "Scaling up the POA emission inventories from all sources equally is supported by the work of Shrivastava et al. (2006) and others that indicate that diesel and wood combustion exhaust have very similar volatility profiles in the SVOC range. Thus, traditional POA inventories may represent the same fraction of SVOC emissions in each case. But, work by Shrivastava et

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   al. (2008) and Grieshop et al. (2009a) indicate that diesel combustion or other anthropogenic sources may produce relatively more IVOCs than wood burning. The volatility at which the wood burning and anthropogenic emission volatility profiles diverge is not known (this works assumes it is about 10^4 μg/m^3 based on sources that have been examined), and the fraction of SVOCs captured by diesel exhaust and wood burning POA inventories might differ leading to the need for source specific SVOC scaling factors."

7. *Page 4108, lines 4-6: This applies to all semi-volatile compounds, not just IVOC.*

   These lines state: "However, chamber aerosol studies typically do not access very low organic concentrations, and thus what appears nonvolatile in a chamber study may actually be semivolatile under atmospheric conditions."

   The reviewer is correct in stating that limited access to low organic aerosol concentrations in chamber experiments is a problem for all semivolatile compounds.

8. *Page 4108, lines 10-15: Robinson et al. (2007) is based on Donahue et al. (2006) that takes into account fragmentation, by assuming that 10% of the oxidized material from any volatility bin will produce compounds with C* = 1e6 ug/m3 (see Donahue et al. (2006) and the supporting material, matrix A).*

   Although the Donahue et al. (2006) work includes a fragmentation reaction, the fragmentation reaction has not been included in regional scale modeling studies such as Robinson et al. (2007). Robinson et al. (2007) assumes only functionalization. The discussion in this section focuses on the performance of current air quality models since their atmospheric implications (in terms of O:C ratios, ambient OA levels) are more easy to assess or are already available.

9. *Page 4110, line 9: Studying only two years does not give concrete results for the interannual variability. Now different is 2000 from 2001? Maybe including this comparison in the Appendix will provide this information.*

The sensitivity simulations were performed for year 2000 (main manuscript) and 2001 (supplement) to verify that the general conclusions are not highly sensitive to the choice of meteorological year. See next comment's response as well.

10. *Page 4110, lines 18-20: Since the results from different years, different meteorologies and different years are very similar, how can this conclusion be extracted? Why not a certain tuning for, say, year 2000, will not work for the year 2001?*

This statement was made based on the fact that doubling SVOC emissions for the 2x2.5 simulation could actually result in surface OA concentrations higher than the traditional simulation, while doubling SVOC emissions for the 4x5 simulation resulted in surface OA concentrations that are always lower than the traditional simulation (for DJF over the US). Thus, 2x2.5 and 4x5 simulations would yield slightly different tuning factors.

Updates to the original text (in bold): "Sensitivity tests performed indicate that **doubling SVOC emissions leads to more realistic surface-level OC concentrations for the US in winter.** This conclusion was reached using sensitivity tests for DJF in year 2000 with GISS meteorology at 4x5 horizontal grid resolution. The same tests were repeated for DJF in year 2001 with GISS meteorology at 4x5 **to confirm that this conclusion is not highly sensitive to the choice of meteorological year** (see Supplement Fig. S2). Three of the tests in Table 6 were also performed for year 2000 DJF using GEOS-4 meteorology at 2x2.5 horizontal grid resolution. Thus, the robustness of the conclusions with respect to **meteorological year** as well as horizontal grid resolution can be determined. GISS tests for year 2000 and 2001 both indicate that doubling SVOC emissions brings concentrations closer to those observed, but still leaves a slight underestimate that may be larger in 2001. Using the GEOS-4 meteorology at 2x2.5 indicates that concentrations might actually be higher compared to the traditional simulation in the northeast when SVOC emissions are doubled (Fig. S3). In con-

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clusion, years 2000 and 2001 are roughly similar in terms of the effects of the sensitivity simulations on DJF surface OC. The GEOS-4 2x2.5 simulation confirms that doubling SVOC emissions is reasonable. However, these tests **and the fact that the 2x2.5 and 4x5 simulations have different mean biases (Table 7)** illustrate that tuning a model based on one simulation may not produce the same result for other simulations **(like the Northeast at 2x2.5 vs 4x5)**. Any tuning of the model emissions should be based on multiple constraints and/or a large observational data set."

11. *Figure 6, top-left panel (DJF) and figure 7 bottom panel should be the same, but the colorscale has a factor of two difference. Is this just a mistake?*

The colorscales in Figure 6 and 7 are correct. Figure 6 is in $\mu g/m^3$ and Figure 7 is in $\mu gC/m^3$. Since all SOA species have an OM/OC of 2.1, the concentrations in $\mu gC/m^3$ will be about half of the concentrations expressed in $\mu g/m^3$. The model predicts SOA in $\mu g/m^3$, but IMPROVE observations are in $\mu gC/m^3$ so multiple units are used.

2.6 Technical comments

1. *The first paragraph of the abstract has too many parentheses, making it hard to follow.*

The abstract has been updated and some parentheses removed. Revised abstract:

"Global production of organic aerosol from primary emissions of semivolatile (SVOCs) and intermediate (IVOCs) volatility organic compounds is estimated using the global chemical transport model, GEOS-Chem. SVOC oxidation is predicted to be a larger global source of net aerosol production than oxidation of traditional parent hydrocarbons (terpenes, isoprene, and aromatics). Using

a prescribed rate constant and reduction in volatility for atmospheric oxidation, the yield of aerosol from SVOCs is predicted to be about 75% on a global, annually-averaged basis. For IVOCs, the use of a naphthalene-like surrogate with different high-NO$_x$ and low-NO$_x$ parameterizations produces a global aerosol yield of about 30%, or roughly 5 Tg/yr of aerosol. Estimates of the total global organic aerosol source presented here range between 60 and 100 Tg/yr. This range reflects uncertainty in the parameters for SVOC volatility, SVOC oxidation, SVOC emissions, and IVOC emissions, as well as wet deposition. The highest estimates result if SVOC emissions are significantly underestimated (by more than a factor of 2) or if wet deposition of the gas-phase semivolatile species is less effective than previous estimates. A significant increase in SVOC emissions, a reduction of the volatility of the SVOC emissions, or an increase in the enthalpy of vaporization of the organic aerosol all lead to an appreciable reduction of prediction/measurement discrepancy. In addition, if current primary organic aerosol (POA) inventories capture only about one-half of the SVOC emission and the enthalpy of vaporization of OA is on the order of 80-100 kJ/mol, a global estimate of OA production is not inconsistent with the top-down estimate of 140 Tg/yr by Goldstein and Galbally (2007). Additional information is needed to constrain the emissions and treatment of SVOCs and IVOCs, which have traditionally not been included in models."

2. *Units throughout the manuscript should be uniform, as much as possible. Using both TgC and Tg is not always necessary and is often confusing.*

   Although we recognize that using both Tg and TgC can be confusing, we use both units in order to preserve information from the model. For example, SVOC and O-SVOC species are transported in the model as mass of carbon. The POA inventory is also in mass of carbon, not mass of organic material. Thus converting them to Tg involves an approximation (an OM/OC). All other SOA species are transported as total mass since chamber experiments report yields

in terms of total mass and OM/OC ratios are not measured for each experiment. Thus converting SOA to TgC would involve an approximation. We have tried to provide the native units from our model (TgC for emissions, TgC for SVOC related aerosol, Tg for SOA related species) although we often convert them to present information in a unified table or section. By providing both units, our results could easily be adjusted if future estimates of the OM/OC differ from 2.1 or 1.4.

3. *Page 4084, line 18: "which in the" should be "which is the".*

   Corrected.

4. *Table 6, Kom columns: saturation concentration should be used, or discuss Kom in page 4102.*

   The first reference to saturation concentrations on page 4102 now contains $1/K_{OM}$ in parentheses as a reminder.

5. *Figure 1 should have SI units (m-2 instead of cm-2).*

   The colorbar has been appropriately adjusted.

3 Additional changes

1. The caption of figure S3 (ACPD figure S2) incorrectly stated year 2000 although it also stated that the meteorology was for year 2001. It has been relabeled with year 2001.

2. Some tables and figures have been renumbered.

3. The following was added to the conclusions (and replaces "Sensitivity tests .....observed organic aerosol concentrations." in the second paragraph):

"Sensitivity tests indicate that uncertainties in the IVOC emissions, the Henry's Law coefficient for scavenging of gas-phase semivolatiles, or the assumed 100x (or 1000x) decrease in volatility upon oxidation of the primary SVOCs are not especially influential in reducing the discrepancy between predictions and observations. However, a significant increase in SVOC emissions, a reduction of the volatility of the SVOC emissions, or an increase in the enthalpy of vaporization to 83 kJ/mol all lead to an appreciable reduction of the prediction/measurement discrepancy. The reduction in SVOC volatility examined is likely too extreme, but scaling up the SVOC emissions by a factor of 2 seems reasonable considering that traditional inventories do not necessarily captures SVOCs emitted in the gas phase. The higher enthalpy of vaporization is also supported by a recent study (Epstein 2010).

4. In the conclusions, replace "A prediction of 100 Tg/yr .....", with:

"If current traditional POA inventories capture only about one-half of the SVOC emissions and the enthalpy of vaporization for OA is on the order of 80-100 kJ/mol, this would lead to an estimate of global OA production that is not inconsistent with top-down calculations, such as those by Goldstein and Galbally (2007) who estimated SOA production ranging from 140 Tg/yr and up."

5. Other minor changes to the conclusions were made (rewording).

4 References

See Manuscript.