

The author thanks Dr. Napelenok for the careful reviewing of the manuscript and constructive comments. My point-to-point replies to the comments are given below (the original comments are copied here in *Italic*). The manuscript has been revised accordingly.

This is an interesting and well written manuscript on an enhancement to the $n \times 2p$ model for SOA formation and its implementation in the GEOS-Chem model. Some comparisons with observations are provided at a boreal site in Finland and several implications for climate forcing calculations are discussed.

I have reviewed this manuscript with several colleagues at EPA and we came to a consensus at offering the following questions and recommendations centered mainly on model formulation:

The author appreciates the constructive comments by Dr. Napelenok and his colleagues at EPA.

The majority of new SOA papers coming out currently are some kind of an extension to existing models, so it may be beneficial to come up with a title that uniquely distinguishes your work from other “extended SOA models.” In the text, perhaps you can build upon Jim Pankow’s $n \times 2p$ nomenclature (e.g., use “ $n \times 2p$ + SOG” aging instead of just the word “extended”).

Agree. To distinguish the work from others and reflect the content of the extended SOA formation model in the title, we have changed the title to:

“A secondary organic aerosol formation model considering successive oxidation aging and kinetic condensation of organic compounds: Global scale implications”.

We have also modified the text to use “ $n \times 2p$ + A/C” nomenclature with “A/C” refers to oxidation aging/kinetic condensation.

When the terms SV-SOG and MV-SOG are introduced in the Abstract, it would be helpful to provide the range of c^ values that these two groups span at 290K.*

Good suggestion. We have provided the range of C^* values for SV-, MV-, and LV- SOGs when these terms are introduced in the abstract.

It may be beneficial to clarify your reasoning on why particle growth should be modeled kinetically rather than thermodynamically (page 19815, line 16).

We have added the following clarification after the sentence:

“The equilibrium approach assumes that the secondary organics in the particle phase and gas phase are always in instantaneous equilibrium which is a good approximation for organics with relatively high saturation vapor pressure. Based on equilibrium, the gas concentrations of low volatile species (such as H_2SO_4 and well aged SOGs with very low C^*) are very low. In the real atmosphere, it takes time for low volatile condensable vapors produced in-situ to get into particles (i.e., diffusion limited) and thus substantial concentrations of low volatile condensable species can build up in the atmosphere.”

How appropriate is it to age an Odum 2-product model given that the Odum 2-product model may overpredict the amount of gas-phase SOG? For example, Cappa and Jimenez (2010, ACP) found that the amount of semivolatile gas-phase organic in equilibrium with OA could range from 20% to 400% of the OA mass with smaller values generally corresponding to higher (and perhaps more reasonable (Epstein 2010 ES&T)) enthalpies of vaporization.

The parameters used in 2-product model are based on laboratory measurements which generally last for several hours. Aging is known to occur in the atmosphere where secondary organics can float around for days. Actually, the aging reduces the amount of gas-phase SOG. Our simulations indicate that the value of SOG/(SOG+SOA) increases as C^* decreases (and thus ΔH increases) which is generally consistent with the results of Cappa and Jimenez (2010, ACP).

Donahue's parameterization of the enthalpy of vaporization (page 19817, line 10 – 11) was recently updated (see Epstein et al., ES&T 44:743-748, 2010). Perhaps a column of H_{vap} values can be added to Table 1.

Thanks for the useful tip. Enthalpy of vaporization (ΔH) is an important parameter and incomplete knowledge of ΔH is a significant source of uncertainty in global modeling of SOA formation. In the revised manuscript, we have expanded the discussion on the values of ΔH reported or used in the literature and how we calculate ΔH for different SOGs in our study. We have updated our ΔH parameterization with new information given in Epstein et al. (2010), re-run all simulations, and updated all related figures. The updated parameterization leads to some differences in the simulated results but the main conclusions of the paper remain unchanged. We have added a column of the ΔH values in Table 1.

The standard distribution of compound vapor pressures was likely chosen as a mathematical convenience, but is there any evidence to support this assumption? From the caption of Figure 3, it seems that the standard deviation of 2 was used in the analysis. It would be helpful if this was stated in the text along with some explanation of how was this parameter was determined and under what conditions it might be different.

The vapor pressures depend on temperature and thus have significant diurnal and seasonally variations. The standard distribution is introduced so that the values of ξ can change smoothly with temperature. In the 2-product model, only one mean vapor pressure is given for each SOG group. Each SOG group may contain hundreds of different organic species with vapor pressures distributed around the mean value. Log-normal distribution is a logical one but to evaluate how good is such an approximation needs laboratory data. Yes, we assume a standard deviation of 2. These have been pointed out in the revised manuscript.

Are equations (6) – (8) solved by operator splitting? If so, in what order are the processes of partitioning, nucleation, and oxidation solved?

Yes. In the model, we first solve partitioning, then oxidation, and then condensation. This has been pointed out in the revised manuscript.

Do the new and existing aging/oxidation reactions consume radicals in the chemical mechanism?

Not included yet. This is expected to be relatively small compared to other loss processes of radicals. This has been pointed out in the revised manuscript.

What deposition and scavenging parameters are assumed for each SOG species? It seems that only 6 additional tracers were added to the model to accommodate the mechanism enhancements (page 19821, line 27). I understand that the different size bins were tracked as an aggregate and split when necessary based on surface area. However, it is not really clear how it was possible to track the first generation products for all the species coating the several listed surfaces (dust, poc, etc.)

Yes, only 6 additional tracers are added (one gas phase LV-SOG, SP-LV, BC-LV, POC-LV, and salt-LV). The amount of SV-SOAs and MV-SOAs on particles is calculated through equilibrium partitioning and is lumped into SOA1-SOA4 in GEOS-Chem. We assume that LV-SOG has similar deposition and scavenging parameters as H₂SO₄. The deposition and scavenging parameters for SP-LV, BC-LV, POC-LV, and salt-LV follow those of sulfate in these different types of particles. The deposition and scavenging parameters for SV-SOGs and MV-SOGs follow the original GEOS-Chem scheme for these species (Chung and Seinfeld, 2002; Liao et al., 2007). This has been clarified in the revised manuscript.

In the manuscript you frequently use the term “vapor pressure.” You probably really mean “saturation vapor pressure.” If that is the case, it should be changed for clarity.

Yes, we have changed all “vapor pressure” to “saturation vapor pressure”.

In equation (8), why is only condensation but not partitioning included for a loss pathway of LV-SOG (i.e. why is there no L_{par} term)?

LV-SOG vapor pressure is low enough for explicit condensation (i.e., solving the diffusion equation), similar to H₂SO₄ gas. We can't calculate both kinetic condensation and equilibrium partitioning at the same time as it will lead to double count. In addition, equilibrium partitioning will not allow the buildup or accumulation of LV-SOG concentration in the atmosphere as their saturation vapor concentration is very low ($\sim 0.001 \mu\text{g}/\text{m}^3$).

Page 19818, lines 14-18: The authors use a new term HV-SOG without defining it. Based on their C^* values (10 ppb – 10 ppm), does HV-SOG include VOC1-6? Or are the HV-SOG analogous to Robinson's IVOC? It might be useful to make this connection.

I apologize for forgetting to define clearly the HV-SOG in the manuscript. As detailed in the text, SV-SOG and MV-SOG correspond to the “two products” in the widely used 2p SOA model. HV-SOG refers to those high volatile oxidation products of VOCs (i.e, products other than those SOGs indicated in Equations 3 and 4 which experimental yielding information are available). Many HV-SOGs may be further oxidized to CO₂ (or other volatile carbon species) but some unknown fractions may be end up as SOA. As I understand, the widely used 2-product model (at least the one implemented in GEOS-Chem) does not track HV-SOG. To avoid confusion, I have deleted the discussion of HV-SOG in the revised manuscript.

Page 19820: What is the C^*_{upp} for LV-SOG based on?

Based on the observed contribution of low volatile organics to the growth rates of nucleated particles (and hence the typical concentration of LV-SOG) and Kelvin effect. This has been pointed out in the revised manuscript.

Page 19821: It would be helpful to give a few details about the PM sectional size distribution. How many bins are used?

The details have been reported in Yu and Luo (ACP, 2009). We use 40 bins for secondary particles with variable bin resolution. This has been pointed out in the revised manuscript.

Figure 5: The text states several times that this figure "clearly" shows improvement from the no oxidation case to the oxidative aging case when comparinnig to observations.

To me, this figure is not very clear at all. Is there a better way to present this? Perhaps show "difference" plots between the two cases and observations?

Good point. Comparison of simulated evolution of particle size spectrum with that of observations is challenging but is necessary to assess and improve the representation of key aerosol processes in global aerosol models. To our knowledge, this study represents the first attempt to compare the simulated month-long diurnal variations of particle size spectrum detailing particle formation and growth processes with those of observations.

When we stated in the text that this figure "clearly" shows improvement, we referred to the similarity in the time-dependent shapes of particle size spectrums for the two cases to those of observations. We have tried and found that the "difference" plots are not clear either. To address the referee's concern and to show the improvement more clearly and quantitatively, we have added an additional figure which give a comparison of monthly mean size distributions along with the size-dependent correlation coefficients and normalized mean bias. This additional figure shows clearly the improvement in the GEOS-Chem's ability in capturing the particle formation and growth processes when the $N \times 2p + A/C$ SOA formation scheme is used.

Figure 8: Reporting NME and NMB values for the data in this figure would help to quantify the improvement. It would be helpful if the results of this model application were placed in context with other recent efforts to extend the SOA treatment in GEOS-Chem (e.g., Pye & Seinfeld) and regional scale models (e.g., biogenic SOG is not aged in PMCAMx). On line 1 of page 19815, please replace the reference to Schell et al. with (Carlton et al., ES&T in press).

In the revised manuscript, we have reported the NME and NMB values for the two cases. A review of other efforts to extend the SOA treatment in different models has been added. The reference to Schell et al. has been updated.