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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model" *by* C. L. Heald et al.

**Anonymous Referee #1**

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This article compares the global chemical transport model GEOS-Chem to organic aerosol data from 17 aircraft campaigns spanning a range of conditions and time. Assembling all this data into one comprehensive evaluation is a valuable exercise for the community and a follow-on article extending the analysis to additional species (aerosol- or gas-phase) could be useful. However, the suggested missing source of organic aerosol (as anthropogenic SOA, ASOA) could use additional investigation. It is unclear if ASOA, as parameterized in GEOS-Chem, is a good surrogate for all types of anthropogenic or anthropogenically controlled SOA. In addition, the model could be missing biogenic SOA formation dependencies that give a false importance to anthropogenic SOA in the scaling analysis. Given the significant effort required for this type of com-

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parison, the authors are ideally suited to provide more evidence and investigation for "missing" sources of organic aerosol. I recommend the work be published with some additional information and clarification provided as described below.

Comments:

1. Model representation of OA

The vertical distribution of organic aerosol in a model is governed by a limited number of factors compared to the actual atmosphere. In GEOS-Chem, the SOA components (excluding the aqueous pathways) differ in their spatial distribution of the parent hydrocarbon emissions, rate of reaction of the parent hydrocarbon, treatment (or lack thereof) of high- vs low-NOx pathways, yield of aerosol products, and the volatility of the SOA products, all of which contribute to a unique vertical profile for each existing SOA source in the model. This work indicates that the best agreement with observations is obtained when anthropogenic (aromatic) SOA is increased leading the reader to believe the missing SOA must be anthropogenic. Due to the limited number of dependencies captured, it might be more appropriate to provide the potential characteristics of the missing SOA (like volatility, NOx-dependence of volatility according to the model, etc) than to state that it is anthropogenic. The concerns are:

a. The aromatic SOA was the most recently updated SOA in GEOS-Chem and is the only SOA in the model with NOx dependent yields. Monoterpenes and sesquiterpenes have also been demonstrated to have NOx dependent yields. Including NOx dependent yields could alter the spatial distribution of biogenic SOA and the vertical distribution compared to the standard simulation. Like aromatics, monoterpenes are expected to have higher yields under low-NOx conditions.

b. The aromatic SOA is also the only SOA from VOCs (in the model) that is a combination of nonvolatile and semivolatile SOA. All biogenic SOA is modeled as semivolatile based on chamber experiments and chamber experiments tend to predict SOA that is more volatile than that observed in the atmosphere. Treating a fraction of the biogenic

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SOA as nonvolatile (and therefore independent of temperature) would significantly affect the vertical distribution. How does the vertical distribution of low-NOx and high-NOx aromatic SOA compare? Is the “missing” SOA more likely to be one of these volatilities? Can the importance of nonvolatile aromatic SOA be distinguished from the importance of nonvolatile POA (ie how does the low-NOx/nonvolatile aromatic SOA vertical profile compare to POA)?

c. It is hypothesized that the missing anthropogenic SOA may be due to alkane oxidation, S/IVOCs, anthropogenically controlled biogenic SOA, more aromatic SOA, all of these options, or none of these options. It is unclear whether ASOA as implemented would be representative of any of these or other anthropogenic SOA sources. For example although alkanes may have a similar spatial emission pattern as aromatics, is alkane oxidation predicted to produce nonvolatile SOA under any conditions? Would anthropogenically controlled biogenic SOA with a very different precursor emission pattern than aromatics have the same volatility as ASOA? Would an updated representation of biogenic SOA be a better surrogate for anthropogenically controlled biogenic SOA than SOA from benzene, toluene, and xylene?

d. Could a combination of decreasing wet deposition and adding a missing SOA pathway (for example fragmentation) also improve the vertical profile by increasing SOA near source and decreasing it aloft?

2. Aqueous production

Work by Tai et al., 2010 indicates that surface level OC over the US is negatively correlated with RH. Figure 10 right of this paper indicates that the model error might be correlated with RH with higher errors associated with higher RH. There seem to be many reasons why model error could be correlated with RH but not provide any information regarding whether or not aqueous production is important.

Vertical profiles in figure 9 include aqueous-phase SOA production from both clouds and aerosols with a dominant contribution (90%) from in-cloud production according

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to Fu et al. 2008. Could separating in-cloud vs aqueous aerosol production provide insight into whether or not there is a missing aqueous aerosol production pathway as opposed to an aqueous cloud production pathway? Perhaps the same information could be obtained from a profile of aerosol water content vs. altitude.

3. Sensitivity tests with enthalpy

The enthalpy of vaporization for semivolatile aerosol was changed from 42 kJ/mol to 25 kJ/mol as a sensitivity test. This is the opposite direction suggested by recent work regarding pure components [Epstein et al., 2010]. The work by Cappa and Jimenez, 2010 was based on ambient organic aerosol which is already lower in volatility than chamber experiments predict. Is it reasonable to use such a low enthalpy value as the default value in the model given that it is being used with an aerosol yield curve that produces aerosol that is too volatile compared to the ambient to start with? Is the low enthalpy compensating for the fact that the SOA parameterization itself is too volatile initially?

4. Additional information

In addition to the vertical profile plots, could something like figure 1 be produced in which flight tracks are colored by their agreement with the model or colored by altitude to give some more spatial information beyond what is displayed in a vertical profile for each campaign?

Additional minor comments:

1. volatility vs temperature dependence of volatility

In several places, the use of an enthalpy of 25 kJ/mol is referred to as a decrease in volatility away from source. Compared to the default value of 42 kJ/mol, this is generally true. However, it would be clearer to state that the 25 kJ/mol value is a reduction in the temperature dependence of the volatility. For example, pg 25373 "…anthropogenically-controlled SOA is increased to ∼100 Tg/yr accompanied by either a gas-phase frag-

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mentation process or an increase in volatility away from source. . .” could be rewritten as “. . . anthropogenically-controlled SOA is increased to ∼100 Tg/yr accompanied by either a gas-phase fragmentation process or a reduction in the temperature dependence of the organic aerosol partitioning. . .” Page 25395 “. . .via for example, the increase in volatility at lower temperatures (via the enthalpy of vaporization. . .” could read “. . .via for example, the decrease in temperature sensitivity (via the enthalpy of vaporization. . .” or similar.

2. Equation (1): reformat so that SOG2 does not appear to come from SOG1

References:

Epstein, S. A., I. Riipinen, and N. M. Donahue (2010), A Semiempirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosol, Environ. Sci. Technol., 44(2), 743-748.

Tai, A. P. K., L. J. Mickley, and D. J. Jacob (2010), Correlations between fine particulate matter (PM(2.5)) and meteorological variables in the United States: Implications for the sensitivity of PM(2.5) to climate change, Atmos. Environ., 44(32), 3976-3984.

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