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Atmospheric
Chemistry
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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.

C. L. Heald et al.

heald@atmos.colostate.edu

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We thank the reviewer for their comments, which we found very helpful and have added clarity to the manuscript and implications. We quote specific comments below and respond beneath each point (marked by **). We also attach a "track changes" pdf of the manuscript for the reviewer and editor.

"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

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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."

**We agree with the reviewer (although sesquiterpenes are thought to have lower yields under low-NOx) and have added discussion of this to the text.

"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 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)?"

**This is a very good point. To address this question we performed a 2008 sensitivity simulation to examine the vertical distribution of the low NOx aromatic SOA and have added comments to the text based on this comparison.

"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?"

**We agree that these are excellent questions. It is difficult to estimate how the volatility of aromatic and alkane SOA would compare, as it would depend on the particular molecule (C chain length) and resulting product distribution. Similarly, the pattern of anthropogenically controlled BSOA would depend on the mechanism of anthropogenic control, which is not clearly understood (NO3 radical oxidation? Acidity? NOx dependent yields? Condensation on inorganics?). To begin to answer the reviewer's question (as well as some of the points raised in b) well it would be necessary to perform a suite of model simulations that compare the OA distribution as a function of emission patterns, reaction rates and volatilities. This is beyond the scope of this particular study, but we have indicated the need for such an investigation in the text.

"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?"

**We agree that overestimation of deposition could contribute to the model bias. To

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address this we performed a 2008 sensitivity experiment where we reduced SOA deposition efficiency by a factor of 2. Details of this result have been added to the text.

"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 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."

**This is a good point. We have examined the vertical profile from aerosol and cloud aqueous SOA as simulated in Fu et al. and find in fact that the vertical distributions are quite similar. Discussion on this has been added to the text.

"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?"

**First, we note that the enthalpies of vaporization needed for lumped two-product models need to be much lower than those for actual molecules, as discussed by Donahue

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et al. (2006) and Cappa and Jimenez (2010). The lower enthalpies in the lumped models are really fitting parameters that compensate the lack of a wide distribution of species vapor pressures in the SOA, to produce realistic evaporation curves for complex mixtures such as SOA. This difference in meaning between the pure species and the lumped species enthalpies of vaporization explains the differences with the pure-component values summarized by Epstein et al. (2010).

We agree that that a decrease in enthalpy of vaporization is not consistent with current understanding of aging (as we stated in the manuscript). We also agree that an overestimate in enthalpy of vaporization could compensate for an overestimate in initial volatility. However increasing the enthalpy of vaporization from a value of 42 kJ/mol to compensate for overly-volatile chamber measurements would increase OA aloft, exacerbating the discrepancies seen here. Thus while it is unclear what the “correct” enthalpy of vaporization should be, we simply present the result that a reduction in the value improved the comparison with ambient measurements, contrary to what might be expected.

"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?"

**A figure has been added to supplementary materials.

"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 “. . .anthropogenicallycontrolled SOA is increased to _100 Tg/yr accompanied by either a gas-phase fragmentation 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."

**Text modified as suggested.

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

**This was an ACPD formatting error and we apologize for not catching it earlier.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C12344/2011/acpd-11-C12344-2011-supplement.pdf

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