Atmos. Chem. Phys. Discuss., 10, C8693–C8697, 2010
www.atmos-chem-phys-discuss.net/10/C8693/2010/

**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "An extended secondary organic aerosol formation model: effect of oxidation aging and implications" *by* F. Yu

Anonymous Referee #1

Received and published: 14 October 2010

General Comments As the title states, this manuscript describes a "new" model that attempts to improve the capability of simulating secondary organic aerosol on a global scale, a topic well within the purview of ACP. The text is generally clear and easy to follow, and the abstract is appropriate for the contents of the manuscript. However, based on the specific comments discussed subsequently, I am unable to recommend its publication. I do not find that previous work is cited adequately. There are several figures that could be removed or require clarification. Most importantly, I do not find the model approach to be terribly novel, and I believe that there may be some errors in the model formulation. Therefore, it is impossible to say whether the results (and therefore the interpretation of these results) are correct.

Specific Comments

Page 19814, Line 18. This statement is not exactly true. According to the Odum papers, the 2-product model has 2 products in it as a result of using least-squares fitting of experimental versus calculated yields in chamber experiments. Having an additional product showed no benefit with respect to the ability of the model to fit the data and therefore was superfluous mathematically.

Page 19815, Line 28, a reference is needed here (perhaps to Pankow or to the volatility basis set papers).

Page 19816, first paragraph. This introduction is woefully incomplete. The author gives the impression that the 2-product model developed by Odum ∼15 years ago is the only model used to simulate secondary organic aerosol. However, an incredible amount of work has been done to improve upon the original 2-product model (all described in USEPA documentation as well as in recent papers from that group). In addition, other model approaches are completely ignored. For example, the volatility basis set (VBS, from the CAPS group at Carnegie Mellon) is not mentioned beyond the relationship between a partitioning coefficient (Pankow) and a saturation concentration (Donahue). Pankow's new model is note mentioned at all either. Semi- explicit (CACM/MPMPO of Pun, Griffin, and co-workers) and completely explicit (based on the Master Chemical Mechanism or self-generating mechanisms such as that of Aumont) are not even mentioned. This is completely inappropriate given that the "novel" model described in this manuscript is very similar in some aspects to these other approaches. For example, the conversion of material into less volatile material is not a new idea, as it is one of the key features of the USEPA improvements to the 2-product model, the VBS, CACM/MPMPO, and the explicit approaches.

Page 19818, Line 14. I am troubled by the lack of inclusion of HV-SOG. If LV-SOG are not formed directly (perhaps they should be?), whatever material has been reacted goes to either SV, MV, or HV. With known alpha parameters for SV and MV and assumed molecular weights for these products, it is possible to calculate the yield of HV material. This is a feature in each of the SOA models described above yet not discussed in this manuscript. There are also examples in the literature of what would likely be considered HV material forming aerosol after an additional generation of oxidation. This model does not account for this at all. The author should also use caution in ascribing physical properties (SV or MV) to products that are completely hypothetical (or that are based solely on a fitting procedure; these products are not unique, and another different set of parameters would give only slightly different results in the fitting procedure).

I am not convinced that Equations (6) and (7) are exactly correct; they also raise several questions about the model formulation that are not addressed in the manuscript. These equations represent the time rates of change of the concentrations of MV and SV SOG. However, the reactive loss term only includes the fraction of the material that would be converted into the less volatile species upon reaction, yet in theory all of the material should react. Does this then mean that for each time step, the predicted concentration of MV or SV material is too large since the reactive loss term is too small? It is appropriate for this factor (ζ) to appear in the formation term for the products. What happens to the material that has reacted yet does not move down in volatility? Does it just float around in its volatility class ad infinitum or does it not react? If the same material were to be oxidized multiple times, should that material either move down (by addition of O) or up (by fragmentation) in volatility (as discussed recently by Kroll, Donahue, et al.). Additional model questions that are not addressed: How are the loss rates to partitioning and condensation calculated? Is it appropriate to use one aging rate constant when the molecular structure is very likely to change as you move from HV to MV to SV?

Page 19820, prior to section 3. There are no comparisons to controlled/chamber data for this model. Is it capable of matching chamber data? Has the model been evaluated? Because this is the first publication of this extended model, a model evaluation (besides a comparison to one site!) is required. On page 19825, it is stated that this will be done in a future publication using global AMS datasets. It is my opinion that this needs to be

done in the first paper describing this model.

Page 19823, top of the page. The author speculates that anthropogenic SOA could significantly affect the results shown. Alpha parameters and emissions inventories are available for many anthropogenic species; these could be included (as opposed to having speculations made about them) assuming that the model formulation is corrected.

Page 19823, Line 26. I would not say that is can be seen clearly in Figure 5 that the new model improves the capability to predict number concentrations. In fact, I would prefer a quantitative description of model performance (and improvement over the previous SOA model capabilities).

Page 19825, Line 17. It is nearly impossible to see the overlain values for the surface sites on Figure 7a.

Page 19826, Lines 6-8. I would argue that you need to validate modules used in global models before putting them into the global models (see earlier comment), not just use both aerosol mass and number.

Page 19826, second paragraph. No information at all is given in the manuscript regarding the CCN activity parameters of the SOA material. Because the LV material was not included in previous modeling efforts, it is imperative to include it here.

Page 19827, first paragraph. The calculations are admittedly crude. However, this end point seems to be a major conclusion of the paper – that this new model shows how important this SOA could be to the indirect effect of particles on climate. Without addressing the concerns previously raised, it is nearly impossible to put any credence in the result presented.

Figure 1 is not necessary. Saturation concentration increases with temperature. This is known. Figure 2 is also unnecessary. In Figure 3, mass concentrations are converted to particle number concentrations using an assumed molecular weight. Is molecular weight necessary for that? It would require diameter and density. In Figure 8, is this a statistically significant improvement? Can this be quantified as opposed to just shown as a scatter plot on a log scale?

Typographical Errors In general, the paper was well written, but there are several examples where greater care is necessary in the editing.

For example (and I believe this list is incomplete): Page 19812, Line 16, fact should be factor. Page 19812, Line 26, of should be to. Page 19813, Line 17, mass should be masses. Page 19813, Line 22, yielding should be yields. Page 19814, Line 3, phase should be plural. Page 19817, Line 21, the should be removed. Page 19827, Line 14, the should be inserted between of and major.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19811, 2010.