Atmos. Chem. Phys. Discuss., 8, S9098–S9101, 2008
www.atmos-chem-phys-discuss.net/8/S9098/2008/

Atmospheric
Chemistry
and Physics
Discussions

ACPD

8, S9098–S9101, 2008

Interactive comment on “Loading-dependent elemental composition of α-pinene SOA particles” *by* J. E. Shilling et al.

N. Donahue (Referee)

nmd@andrew.cmu.edu

Received and published: 14 November 2008

I need to start by offering a public apology to the authors for taking a shamefully long time to submit this review. In the spirit of full public humiliation I shall not remain anonymous.

The subject of this paper is the composition of a-pinene + ozone secondary organic aerosol (SOA) observed as a function of OA mass concentration (C_OA) in the Harvard smog chamber. The chamber was operated in "CSTR" (flow-through steady state) mode for these experiments. The big-picture point of the paper is that the composition of the OA changes with C_OA, favoring more oxygenated material at lower C_OA. This point by itself is not new. However, the authors extend the topic considerably with a quantitative and coherent analysis buttressed by high-resolution mass spectrometer

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

data.

The paper should be published essentially as is after a few minor issues have been addressed. These are listed in order of significance.

First, in placing the work in context the authors omit the work of Grieshop et al. (GRL 34, L14810, doi:10.1029/2007GL029987, 2007), which is highly relevant to the topic at hand. In the paragraph near p 15351, line 25, as well as in the conclusion section, the authors place their work in the context of previous "batch" chamber experiments and correctly state that the steady state approach removes several ambiguities from the experimental interpretation. However, the isothermal dilution method described by Grieshop et al is orthogonal to both the steady-state method described here and the previous batch experiments because the dilution is carried out in a single batch run after the gas-phase chemistry has run to completion. The Grieshop experiments were conducted at higher mass loadings (700 –> 30 ug/m3, see for example Figure 1 and Figure 3 in Grieshop et al.), and the general trend observed in f(m/z = ...) vs C_OA is quite consistent with the trend described in this paper (one has to be a little careful about the fragmentation table used in the analysis, as Grieshop et al used the Manchester fragmentation table and the present authors use the CU fragmentation table). In addition to reporting the same general unit mass resolution behavior, Grieshop et al. also showed that a basis-set parameterization of the dilution experiments (using the Presto et al. parameters) was consistent with observed mass changes. However, they did not present any interpretation of the mass spectra associated with the various basis vectors.

First and a half, I question the discussion of "oligomers". This is such a wonderfully vague term in our field, but it is not obvious to me how the data presented here are consistent with substantial oligomer contributions to the total mass loadings. The discussion of volatility with regard to the nominal chemical formulas as well as general oxidation state is quite strong and well reasoned in the manuscript, but the authors then go on to point out that the C* value for the lowest volatility basis vector is about a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

factor of 25 lower than pinic acid. The authors seem to suggest that oligomerization is a plausible explanation for this difference (if the difference between a basis vector and a single molecule, albeit the lowest C* product commonly identified, can be regarded as significant). However, if these "oligomers" were indeed association products of C8O4 compounds, for example, one would expect enormous reductions in vapor pressure. If one were to argue that the C* for the lowest volatility product described here is really $<=$ 0.1 ug/m3, one would then need to explain the observation of An et al., who reported complete evaporation of a-pinene SOA (from photo-oxidation) at 70C and 16 sec residence time in a thermo denuder. It seems to me that the data are rather more consistent with monomeric products, or in the very least condensation products with only a few (say 2) added carbons.

Second, I am a fan of logarithmic x axes when the particle mass loading (C_OA) is on the x axis. The authors use a log axis for Figure 4 (the basis-set figure), but a linear axis for the other figures. While this is to some extent a matter of taste, I will make my case for using log axes in all the figures. For one thing, there is a lot of interesting stuff going on at the left-hand limit of each graph, and a big, boring flatland over much of the rest of the range. So, just in terms of information content the log axis spreads the wealth (yes we can). Second, the authors repeatedly make the point that the behavior of various quantities – density, O:C, etc – is nonlinear and thus difficult to extrapolate. As Figure 4 shows, this behavior is much more linear when viewed in a semi-log space. There are good physical reasons for this based on partitioning theory, which is the original motivation behind the decadally separated basis vectors for the volatility basis set. Thus, I believe that presenting the information on a semilog(x) plot is more directly tied to the physics that are in many ways the major subject of this paper. To do so would potentially force a revision in the statements about extrapolation. I believe this is warranted.

Third, the authors assert that the relationship between O:C and C_OA described here can in part explain the differences between AMS spectra from chamber experiments

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

and ambient observations. However, as Reviewer 2 also points out, the high O:C observed here at ambient mass loadings comes at the expense of quite low mass yields. Even though the mass yields from these authors are larger than others in the literature, they are still quite low – essentially 0.10 below a couple of ug/m3. For a global flux of about 100 Tg of terpenes, modeled with this yield (yes, this is an unjustified leap of faith, but it is what most models do), one would get an SOA flux of about 10 Tg/yr (really about 6 TgC/yr). This is nothing to sneeze at, but one has to be a "low counter" for this to be a really major part of the SOA budget if it is 100-200 TgC/yr.

Fourth, is it possible to put the literature data in Figure 5 (the density figure)? At least indicating the range of the data on the right-hand y axis would be a good use of white space.

Fifth, there are a few places where a more careful discussion of the mass spectrometry might be in order. For example, the authors state that m/z=57 is correlated with C_OA and typically associated with less oxidized products. While this is all factual, I would be quite interested in the high-resolution results for m/z=57. I don't know how to make a C4H9 fragment from a-pinene SOA. I do know how to make a C3H5O, however. It might be nice to present one of the atomically resolved mass spectra (with colors for C, H, O, etc) as a 3rd part of Figure 1.

Finally, minor edits:

p15355 l 22 "vapor pressure" should read "saturation concentration".

p15356 l 13 should be Figure 5 (reads Figure 6).

p15357 l 15 I am no fan of this use of "rationalized". To me (and to the dictionary) "rationalize" means to make up and explanation for some observation or action after the fact, typically one shaky ethical or scientific ground. I vastly prefer "explained", which does not carry the negative connotation.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15343, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper