Atmos. Chem. Phys. Discuss., 12, C9552–C9556, 2012
www.atmos-chem-phys-discuss.net/12/C9552/2012/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "The link between organic aerosol mass loading and degree of oxygenation: an α-pinene photooxidation study" *by* L. Pfaffenberger et al.

Anonymous Referee #2

Received and published: 19 November 2012

This manuscript describes chamber studies of the photooxidation of a-pinene, with the goal of elucidating the connection between aging and aerosol loading. Most importantly, the authors conclude that they have generated aerosol similar to the highly oxidized AMS factor "LV-OOA" measured in ambient studies. This is an important topic in SOA chemistry, given the challenges with generating highly oxidized aerosol in chamber studies (at least from a-pinene oxidation). However there are some aspects of the analysis – most importantly the consideration of the background aerosol, but also the wall loss correction and high-resolution mass spectrometric analysis – that are not carried out in sufficient detail to justify many of the conclusions reached. These must be addressed before this work can be published in ACP.

Most importantly, there seems to be no (quantitative) consideration of the role of background aerosol, which is a crucial aspect of any chamber study examining low SOA concentrations. On P. 24741 it is stated that organic aerosol mass concentrations of up to 1.7 ug/m3 can be formed when clean chamber air is oxidized in the presence of HONO and sulfate seed. This amount of background SOA is extremely problematic for the present study, which purports to examine SOA loadings below 2 ug/m3. Since the background SOA may make up a large fraction of this mass, it can have a large effect on final mass concentration, as well as on f44. Thus for low-concentration experiments the effects of such aerosol need to be subtracted out very carefully. However, this was not done, and more importantly no blank experiments were carried out under the same conditions of the individual SOA experiments, so it is not clear to me how it can be done. This is a potentially major problem for five of the nine experiments (the "low org mass" and "medium org mass" experiments), since the reported values of organic loading and f44 may be influenced considerably by the unmeasured background SOA.

Related to this, the authors state (p. 24741) that 1.7 ug/m3 represents an upper limit to the amount of background SOA. Even if this is the case, such background SOA could be very problematic. If the "correct" (for a given set of experimental conditions) level of background SOA is 1 ug/m3, this still accounts for 50% or more of the "low org mass" experiments. Additionally, the background aerosol may be continuously generated over the course of the whole experiment (for example, if its precursors are organics emitted from the walls). In that case, the mass fraction of background SOA may increase still further over the course of the experiment, since the background SOA may grow in importance at long reaction times. This could also have a large influence on the measured f44 over the course of the experiment.

Moreover, it's not clear that the 1.7 ug/m3 value truly represents an upper limit. Yes, the high RH may lead to more partitioning into the liquid water phase, but this is unlikely to be a large effect – the Henry's Law constant, or the total amount of condensable organics in the gas-phase, must be extremely large to lead to 1 ug/m3 partitioning into sulfate seed (assuming total sulfate loading of 10-100 ug/m3). The background SOA formed is instead likely to be a strong function of a number of reaction conditions (none of which are given for the blank experiment): HONO concentration, NOx levels, lights used, and previous use of the chamber (since the blank SOA may be from organic compounds from the previous days' experiments). Thus the background SOA could be higher or lower than 1.7 ug/m3, and really needs to be measured under the proper reaction conditions.

To summarize, the effect of degree of oxidation on organic loading, which is one of the main themes of this study, might not be from partitioning effects (as assumed in the manuscript) but instead from the influence of background aerosol, which is likely to be highest at low loadings and high reaction times. This unfortunately calls into question much of the conclusions made in the manuscript. Therefore either some new blank experiments – with experimental conditions that match those of the key experiments - need to be carried out, or the manuscript needs to be reworked extensively, to account for the very large uncertainties in the organic mass and f44 of experiments 1-5.

Other comments:

Throughout: it is highly unusual that no elemental ratios (O/C or H/C) are provided, given that the HR-AMS is used. While f44 and f43 can be useful metrics, O/C really should be the metric used to describe how oxidized the aerosol is.

P. 24747, line 28 - P. 24748, line 2 (and other discussions of changes to organic mass): it is stated that the organic mass levels off – but this is because it's constrained to do this (via the wall loss correction)! If at longer times (i.e., hours 4-8 in Fig S2), there was still some particle growth, but that growth was smaller than wall loss, it might still appear as an exponential decay, and so would be missed when the wall loss correction is applied. (The only way to know for sure is to carry out a different wall loss correction – such as the org/SO4 ratio – or to determine the correction when the UV lights are off and growth has definitely stopped.)

P. 24738 lines 17-19: It should be noted that several other precursors lead to higher O:C (or f44) than alpha-pinene oxidation. For example, even the very first AMS study of chamber SOA (Bahreini et al, ES&T 39:5674, 2005) showed that xylene photooxidation leads to f44 values of ~0.15.

P. 24741: Related to the discussion of background SOA above, a detailed discussion of the background SOA is needed. What is its time dependence? What is its f44, f43, O/C, and R2 vs the ambient LV-OOA factor?

P. 24742: How is aerosol mass concentration actually determined – with the AMS or the SMPS? In either case, how were the necessary corrections (collection efficiency or density, respectively) determined?

P. 24750, lines 1-4: Presumably the authors, when discussing 6 hours of transport time, are referring to the difference between the T0 and T2 sites in MILAGRO (Decarlo et al, ACP 10:5257, 2010). However by T2, SV-OOA still dominates over LV-OOA (see Figure 7c of that paper), which argues against the authors' assertion that SOA has mostly oxidized to LV-OOA. Thus the chamber and ambient timescales do not match up very well.

P. 24750: It appears that the comparisons were done with the unit mass resolution AMS spectral database, but the proper comparison is with the high-resolution database.

P. 24750: Moreover, it would be helpful to actually provide a visual comparison of the measured spectra with the LV-OOA factors, as side-by-side spectra, and/or the plots comparing the two spectra, so that the readers have a sense of what the R2 values actually mean.

P. 24751, lines 13-15: It is stated that "In this study, the aerosol products from a-pinene photooxidation are located within the f44-f43-space bounding the range of PMF factors previously identified in ambient SOA". This seems not to be the case, given that most of the data points (Figures 1 and 2) are located outside the triangle.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24735, 2012.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper