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Atmospheric
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Discussions

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

J. E. Shilling et al.

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Thanks to Neil Donahue for his helpful comments and suggestions. We have made changes in the final ACP paper based on his comments as described below.

Reviewer Comment: 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

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experiments were conducted at higher mass loadings (700 μg m^{-3} to 30 μg m^{-3}, 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.

Response: We apologize for the omission of the Grieshop et al. work. We have added a discussion of this work in the revised text.

Updated Text: A complication for the interpretation of the data, however, is that the gas-phase chemistry was simultaneously changing rapidly (cf. Figure 6 of Shilling et al. (2008)), and consequently the mass spectra were evolving in time and gas-particle equilibrium may not have been fully established. To overcome this difficulty in a batch chamber, Grieshop et al. (2007) first waited for the initial gas-phase chemistry to come to completion for the dark ozonolysis of alpha-pinene and then performed isothermal dilution experiments with clean air. Their results showed both that the gas-particle relaxation times from evaporation-condensation were longer than previously anticipated (e.g., tens of minutes rather than tens of seconds) and that the relative contribution 44/org measured at unit resolution by an AMS increased from ca. 4% to 6% as SOA particle loading decreased for the range 500 to 100 μg m^{-3}.

Response: We would also like to clear up slight confusion about the fragmentation table used. It is true that we used the CU fragmentation table for the many of the organic peaks. However, for peaks with air interferences we have modified the fragmentation table on an experiment-by-experiment basis. Specifically, we use the PToF mode to make minor ($<$ 10% variance from CU) adjustments to the fragmentation table at m/z

29 and 40. We have used our own estimate of the CO+ signal at m/z 28 as noted at lines 17 to 19, p15349. In addition, we found the AADCO pure air generator depleted CO2 in the pure air by a variable factor of 5 to 10 (relative to an atmospheric concentration of ca. 380 ppmv) and the fragmentation table was adjusted accordingly for m/z 44 on an experiment-by-experiment basis. We have emphasized these differences in the revised text.

Updated Text: Several changes were made to the standard fragmentation table (Allan et al, 2004; Aiken et al., 2008) to ensure accurate analysis of the organic particle mass. Specifically, the fragmentation table at m/z 29, 40, and 44 was adjusted on an experiment-by-experiment basis to account for the variability of gas-phase contributions.

Reviewer Comment: 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 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 $\bar{0}$.1 μg m^{-3}, one would then need to explain the observation of An et al., who reported complete evaporation of alpha-pinene SOA (from photo-oxidation) at 70C and 16sec 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.

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Response: We have no direct evidence that either supports or refutes the literature observations of oligomers (Gao et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004) (or organic peroxides and Criegee adducts for that matter) in SOA produced from alpha-pinene ozonolysis. In the manuscript, we are careful to point out that formation of organic peroxides and other adducts of stabilized Criegee intermediates, also reported in the literature (Docherty et al., 2005), is an alternative and equally valid interpretation of our basis-set fitting and of the composition measurements. Based on current literature studies, which report both organic peroxides and oligomers in the condensed phase, we feel that oligomers as well as organic peroxides are both plausible components of the low-volatility material. In addition, it is possible that the low-volatility material is composed of as-yet unidentified product. While we do not disagree with any of the points the reviewer presents, because we do not have any direct evidence for the presence of any of these species, we do not feel it is appropriate for us to further comment on these species in the manuscript. In our opinion, omission of the possibility of oligomer formation in the manuscript would constitute too strong a statement. In response to the reviewers concerns, we have made small revisions to our statements about oligomers as highlighted below.

Updated Text: An explanation could be the formation of longer carbon-chain products, such as oligomers (Gao et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004), organic peroxides and adducts of stabilized Criegee intermediates (Docherty et al., 2005), or other unidentified products that shift the H/C ratio without greatly affecting the O/C ratio.

Some possible products could include organic peroxides and adducts of stabilized Criegee intermediates, multimers (e.g., dimmers and longer chain oligomers, or other as-yet unidentified products (Gao et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004; Docherty et al., 2005). Formation of these species through routes not involving elimination of oxygen is consistent with the observed O/C atomic ratios (vida supra).

Reviewer Comment: 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 semilog 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.

Response: We feel that the use of linear axes supports out point that the chemical composition is most sensitive to changes in loading over the range of 0.5 to 15 μg m^{-3} and prefer to keep the figures on a linear scale. One of our main points is indeed that there is a large range of mass loadings over which changes in chemical composition are relatively minor. This loading range is the region over which many previous literature experiments were focused. For example, our in Figure 1B, the 44/org signal varies from 6% at 138 μg m^{-3} to 7% at 36 μg m^{-3}, an insignificant change in light of experimental errors. Extrapolation of the three highest loading points (ca. 36 to 138 μg m^{-3}) to low loadings of ca. 1 μg m^{-3} would predict a 44/org signal of 7 to 8%. Experiments showed a value of 12%. Thus, extrapolations of measurements made a high loading to low loading would be in error. We also point out that Figure 4 is presented on a semi-log axis and summarizes the composition information for those readers who prefer semi-log plots.

Reviewer Comment: 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

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chamber experiments 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 μg m^{-3}. 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 to 200 TgC/yr.

Response: We have revised our conclusion in this part of the manuscript in response to this question and the concerns of Reviewer 2. We are not arguing that low loading SOA from the ozonolysis of alpha-pinene is identical to ambient OOA. We are arguing that the relative distribution of functional groups among the samples is very similar based on the observation that chamber SOA produced under atmospherically representative conditions from biogenic SOA closely resembles the AMS mass spectrum of ambient OOA.

Updated Text: The implication is that the electron-impact fragmentation patterns of the organic material in the two types of particles are similar, suggesting that the relative distributions of the organic functional groups are also similar. Nevertheless, within this similarity there are undoubtedly important differences that are not revealed by the comparison shown in Figure 6 because of the myriad molecular assemblies possible from similar distributions of functional groups. Such different assemblies can be expected on the basis of the large number of VOC precursors involved in atmospheric SOA production compared to the single precursor employed in this study.

Reviewer Comment: 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.

Response: We have placed the literature data on the figure as the reviewer suggests.

Reviewer Comment: 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 dont 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.

Response: The information the reviewer is asking for is contained in Figure 2. For example, Figure 2 shows that m/z 57 is composed almost entirely of the C3H5O fragment the reviewer mentions. From Figure 2, and the elemental analysis it is clear that the material partitioning into the condensed phase at higher loadings contains some oxygen, albeit a lesser amount than material found in the condensed phase at lower loading. We have added text further discussing some of these issues.

Updated Text: Examination of Figure 2A shows that, although the relative contribution of the CxHyOz+ family at many m/z values decreases for higher loadings as expected, some exceptions are apparent (e.g., m/z 43, 55, and 57).The relative increases and decreases of specific peaks are complicated and reflect the integrated effects of the individual fragmentation patterns of the changing mix of molecules in the particles as organic mass loading changes. Nevertheless, the sum across all species (as reflected in the CxHy+ and CxHyOz+ families) provides overall insight into the changing oxidation state of the particles.

Reviewer Comment: p15355 l 22 "vapor pressure" should read "saturation concentration".

Response: Our understanding is that vapor pressure and saturation concentration are essentially identical terms (differing primarily in units) so no change is made to the manuscript in an effort to avoid confusing the reader by introducing new terms within

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the same paragraph.

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

Response: We have corrected this error.

Updated Text: Figure 5 shows that the effective organic density

Reviewer Comment: 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.

Response: We have changed the text as the reviewer suggests.

Updated Text: The increase in the O/C atomic ratio for lower mass loadings and the corresponding decrease in the H/C ratio can be explained in large part by the variable partitioning of semivolatile molecules into the particle phase.

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