

## **Author comments to the manuscript: “The link between organic aerosol mass loading and degree of oxygenation: An $\alpha$ -pinene photooxidation study”**

L. Pfaffenberger et al.

The authors would like to thank all three anonymous reviewers and C. Cappa for their helpful and thoughtful comments and suggestions. Each specific point of the four comments is consecutively addressed below. Reviewer comments are in italics and our responses are in plain text. All references are listed in the end of the document.

***Short comment by C. Cappa***  
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*The authors present an interesting study of SOA formation from the OH oxidation of alpha-pinene at different precursor concentrations and different OH exposures. Studies such as this are important to understand how the intensive properties of SOA depend on reaction conditions*

*I have but one specific comment/request.*

*They use as their primary metric for interpreting the extent of oxidation the normalized relative intensity of the peak(s) observed at  $m/z = 44$  at unit mass resolution ( $f_{44}$ ) from an Aerodyne Aerosol Mass Spectrometer (AMS). They additionally use the equivalent signature at  $m/z = 43$  ( $f_{43}$ ). Both are uniquely instrument specific metrics. However, from the instrument description it appears that they were operating a "High Resolution Time-of-Flight" AMS (HR-ToF-AMS). With this instrument, it is possible to explicitly extract the oxygen:carbon and hydrogen:carbon atomic ratios, which are physically more meaningful than  $f_{44}$  and  $f_{43}$  (Aiken et al., 2008). Although there are empirical relationships (e.g. Aiken et al., 2008 and Ng et al. 2011) that relate  $f_{44}$  to O:C and  $f_{43}$  to H:C, these relationships can break down when SOA from individual compounds are considered (e.g. Chhabra et al., 2010). Thus, when data from an HR-ToF-AMS are available, I believe it is preferable to use the explicitly determined O:C and H:C and not O:C and H:C values that are simply calculated from  $f_{44}$  and  $f_{43}$ .*

*Although  $f_{44}$  and  $f_{43}$  are useful in their own right, I believe that the fact that they are instrument specific can limit their broader applicability and interpretation. Thus, I suggest it would be desirable if the authors were to additionally present their results using experimentally determined O:C and H:C unless there are specific reasons that this cannot be done. Providing information on the actual atomic composition, as opposed to only  $f_{44}$  and  $f_{43}$ , would make the results more relevant to modelers and to people (such as myself) who do not have an AMS in our lab.*

As suggested, a high resolution (HR) data analysis will be presented in the revised manuscript including:  $\text{CO}_2^+$  vs.  $\text{C}_2\text{H}_3\text{O}^+$  next to the  $f_{44}$ - $f_{43}$  figures, in addition a van-Krevelen diagram (O:C vs. H:C) and O:C as a function of wall loss corrected organic mass concentration. Two figures: O:C vs.  $f_{44}$  and H:C vs.  $f_{43}$  will be provided in the Supplement. HR mass spectra for all nine experiments will be presented.

**References:**

- Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol.*, 42, 4478-4485, doi: 10.1021/es703009q, 2008.
- Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, *Atmos. Chem. Phys.*, 10, 4111-4131, doi: 10.5194/acp-10-4111-2010, 2010.
- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys.*, 11, 6465-6474, doi: 10.5194/acp-11-6465-2011, 2011.

### ***Anonymous Referee #1***

*This manuscript describes chamber studies that have produced highly oxidized  $\alpha$ -pinene secondary organic aerosol (SOA) that is as oxidized as ambient aerosol. This is an interesting study because it is the first report of chamber SOA for this precursor with such a high level of oxidation and because the authors use it to address the roles that organic loading and OH exposure play in achieving this oxidation level. I think this work is useful from both experimental and modeling viewpoints and I recommend publication after the following issues are addressed:*

#### ***Main Comments***

*1) The current manuscript under-utilizes all the information that can be obtained with a high-resolution AMS. It is now typical for high-resolution AMS datasets from chamber data to be described not only in terms of their  $f_{44}$  and  $f_{43}$  values, but also in terms of their O/C and H/C ratios (see the Chhabra et al. article cited in this manuscript, for example). I recommend that the authors include Van Krevelen diagrams next to the  $f_{44}$ - $f_{43}$  diagrams and also add in O/C values in addition to  $f_{44}$  in figure 3. A supplementary figure showing the  $f_{44}$  vs. O/C (Aiken et al.) and  $f_{43}$  vs H/C (Ng et al. 2011a) would also be useful for reference to see how well the published empirical relationships work for this system.*

As suggested, a high resolution (HR) data analysis will be presented in the revised manuscript including:  $\text{CO}_2^+$  vs.  $\text{C}_2\text{H}_3\text{O}^+$  next to the  $f_{44}$ - $f_{43}$  figures, in addition a van-Krevelen diagram (O:C vs. H:C) and O:C as a function of wall loss corrected organic mass concentration. Two figures: O:C vs.  $f_{44}$  and H:C vs.  $f_{43}$  will be provided in the Supplement. HR mass spectra for all nine experiments will be presented.

*2) It would be helpful if the authors put this work in context of other chamber work. Previous manuscripts (Shilling et al., Chhabra et al. (2011), Ng et al (2010)) have already identified the importance of operating at lower loadings and there are several other chamber studies on this particular system. What have the authors done differently to allow for operation with lower loadings? Are the authors also achieving higher OH exposures than is typical in smog chamber operation? A short paragraph in the introduction outlining and stressing the differences/advances made in this work would be useful for the reader who is not fully aware of all the details of chamber studies.*

The Introduction will be extended with a more detailed comparison to previous experiments:

“Measurements of dark  $\alpha$ -pinene ozonolysis in a continuous flow chamber by Shilling et al. (2009) demonstrated that the aerosol chemical composition depends on the total organic mass concentration, however the generated aerosol was less oxygenated than ambient LV-OOA. For non-wall-loss-corrected organic mass loadings between  $> 140 \mu\text{g}\cdot\text{m}^{-3}$  and  $0.5 \mu\text{g}\cdot\text{m}^{-3}$ , O:C values increasing from 0.29 to 0.45 and H:C values decreasing from 1.51 to 1.38 were reported. Recently, LV-OOA-like aerosol was obtained in a smog chamber, but mostly by starting with oxygenated gas phase precursors



Ng et al. 2011b:

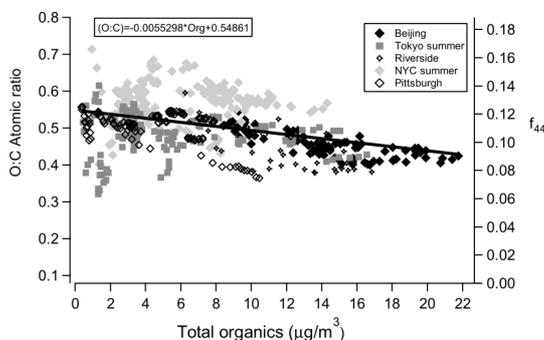


Figure S3. (a) Correlation of LV-OOA and SV-OOA components with nitrate and sulfate. In general, the LV-OOA components correlate better with sulfate and the SV-OOA components correlates better with nitrate. (b) The  $f_{44}$  of ambient OOA from several of the urban sites as a function of total organic loading. These ambient data overlap well with laboratory data with low organics loadings as shown in Ng et al. (2010) (1).

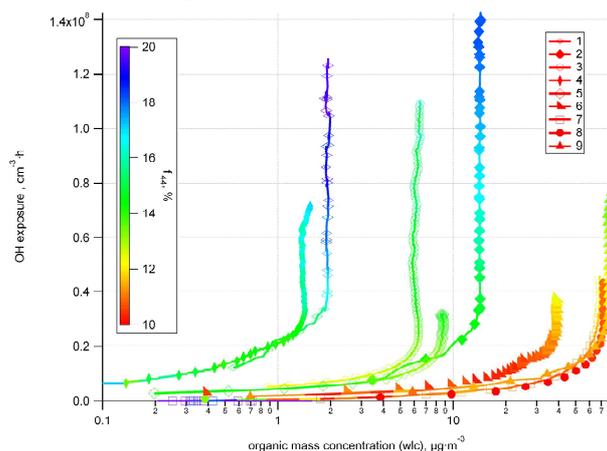
Fig. 7 in Ng et al. (2010) shows the maximum measured  $f_{44}$  for each experiment. The higher OH exposure in the Caltech chamber compared to the smaller CMU chamber is mentioned for toluene. Ng et al. (2010) state that the organic mass loading as well as the limited OH exposure is important in determining the different  $f_{44}$  levels reached. It is not clear whether the maximum  $f_{44}$  has already been reached during these experiments. One has to be careful in comparing Fig. 7 in Ng et al. (2010) to Fig. 3 in the present study, as the organic loadings are not wall loss corrected in Ng et al. (2010), which could add to a discrepancy in  $f_{44}$ . Another possible explanation for the lower  $f_{44}$  in Ng et al. (2010) compared to the  $f_{44}$  in this study could be differences in the vaporizer temperature, due to the fact that the  $\text{CO}_2^+$  ion is thought to result in large part from thermal decomposition of organic acids. This is especially the case because the thermocouple measurement of the vaporizer temperature is known to be unreliable and experimental verification is frequently not performed. This instrument specific fragmentation can be overcome with means of a high resolution analysis, as will be provided in the revised manuscript. The data in Fig. S3b of Ng et al. (2011b) shows considerable variability in the range of low mass concentrations and as a function of measurement site/instrument used. Nevertheless, the slope of  $-0.145 \text{ } \%/(\mu\text{g}/\text{m}^3)$  of  $f_{44}/\text{org}$  shown in Fig. S3b (Ng et al. 2011b), converted via the relationship between O:C and  $f_{44}$ , in Aiken et al. (2008), is within the range of slopes between low and medium organic mass loading found in Fig 3 of this study. A more precise comparison will be done using measured elemental ratios of O:C in the revised manuscript.

The description of Fig. 3 in the text has been changed in the following way:

“The slope is steeper for the lower organic mass range than for the higher mass range. Ng et al. (2010) see a similar trend and a levelling off of  $f_{44}$  at mass loadings higher than  $100 \mu\text{g}\cdot\text{m}^{-3}$ . This implies that at typical atmospheric concentration levels ( $\sim 1\text{-}30 \mu\text{g}\cdot\text{m}^{-3}$ ), partitioning effects on SOA oxygenation are even more sensitive to the organic mass concentration than for the higher-than-atmospheric concentrations used in most previous smog chamber studies.”

4) Table 2: Is there a way to graphically display so that it would be easier to digest? For example, could you plot an image plot of OH exposure vs. organic mass colored by  $f_{44}$ ? A plot like this would make it easier to figure out the operating parameters which would yield the desired  $f_{44}$ . The authors could also identify regions of this diagram which have been used in previously published  $\alpha$ -pinene chamber studies to underscore why they haven't been able to achieve the high oxidation levels.

The kind of figure that was asked for looks is similar to this:



However, we do not think that this figure provides more information. The values of Table 2 are displayed by the squared symbols (black frame, filling color corresponding to the OH exposure) in Figure 3 of the manuscript. We think that this illustration of the data is sufficient to follow the trend. In the revised manuscript, the O:C ratio instead of  $f_{44}$  will be displayed against the organic mass concentration.

### Minor comments

1) p. 24738, L17-20: *the authors should be more explicit that there are some non-oxygenated precursors like naphthalene and toluene, for example, that also produce highly oxygenated SOA that is at the very edge of the LV-OOA range.*

We are convinced that the compilation of degrees of oxygenation of smog chamber SOA in Ng et al. (2010) and Chhabra et al. (2011) represent a good overview of former studies and this will be mentioned in more detail.

Two changes in the Introduction of the revised manuscript will be done:

“The study of Ng et al. (2010) shows that SOA produced in smog chambers from various non-biogenic pure precursors can reach high degrees of oxygenation, although having higher or lower  $f_{43}$  values than ambient. In an  $\alpha$ -pinene oxidation flow reactor experiment  $f_{44}$  values as high as 0.25 were reached, however these required OH concentrations that are orders of magnitude higher than in smog chambers.”

“Recently, LV-OOA-like aerosol was obtained in a smog chamber, but mostly by starting with oxygenated gas phase precursors (Chhabra et al., 2011), whereas most primary volatile organic compound emissions are thought to be more hydrocarbon-like. However,

these results indicate that the location of SOA in the  $f_{44}$ - $f_{43}$  as well as in the Van-Krevelen space is affected by precursor identity. Chhabra et al. (2011) showed O:C ratios for  $\alpha$ -pinene photooxidation of approximately 0.3-0.5 for organic mass concentrations of 53.7 - 63.9  $\mu\text{g}\cdot\text{m}^{-3}$  and OH exposures of  $1.7$ - $3.3\cdot 10^7$   $\text{cm}^{-3}\cdot\text{h}$ .”

2) p. 24740, L7-9: *The authors should be more explicit as to what they mean by extensive aging?*

p. 24739, L7-9:

This sentence meant: What are the driving factors for a difference in chemical composition after SOA precursors were extensively oxidized and the dependence on OH exposure is cancelled out by comparing at the same OH exposure?

The sentence was changed to:

“The aim of this study is to find the main driving factors responsible for the inability of smog chamber studies to yield LV-OOA-like aerosol from the biogenic precursor  $\alpha$ -pinene, even after the equivalent of tens of hours of atmospheric aging.”

#### **References cited:**

- 1) Aiken, A.C., P.F. DeCarlo, J.H. Kroll, D.R. Worsnop, J.A. Huffman, K. Docherty, I.M. Ulbrich, C. Mohr, J.R. Kimmel, D. Sueper, Q. Zhang, Y. Sun, A. Trimborn, M. Northway, P.J. Ziemann, M.R. Canagaratna, T.B. Onasch, R. Alfarra, A.S.H. Prevot, J. Dommen, J. Duplissy, A. Metzger, U. Baltensperger, and J.L. Jimenez. *O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High Resolution Time-of-Flight Aerosol Mass Spectrometry Environmental Science & Technology*, 42, 4478-4485, doi: 10.1021/es703009q, 2008.
- 2) J.E. Shilling, Q. Chen, S.M. King, T. Rosenoern, J.H. Kroll, D.R. Worsnop, P.F. DeCarlo, A.C. Aiken, D. Sueper, J.L. Jimenez, and S.T. Martin. *Loading-Dependent Elemental Composition of  $\alpha$ -Pinene SOA Particles. Atmospheric Chemistry and Physics*, 9(3), 771-782, 2009.
- 3) Ng, N.L., M.R. Canagaratna, Q. Zhang, J.L. Jimenez, J. Tian, I.M. Ulbrich, J.H. Kroll, K.S. Docherty, P.S. Chhabra, R. Bahreini, S.M. Murphy, J.H. Seinfeld, L. Hildebrandt, N.M. Donahue, P.F. DeCarlo, V.A. Lanz, A.S.H. Prevot, E. Dinar, Y. Rudich, and D.R. Worsnop. *Organic Aerosol Components observed in Northern Hemispheric Datasets measured with Aerosol Mass Spectrometry. Atmospheric Chemistry and Physics*, 10, 4625-4641, 2010. DOI: 10.5194/acp-10-4625-2010
- 4) Chhabra, P.S., N.L. Ng, M.R. Canagaratna, A.L. Corrigan, L.M. Russell, D.R. Worsnop, R.C. Flagan, and J.H. Seinfeld. *Elemental Composition and Oxidation of Chamber Organic Aerosol. Atmospheric Chemistry and Physics*, 11(17), 8827-8845, 2011.
- 5) N.L. Ng, M.R. Canagaratna, J.L. Jimenez, P.S. Chhabra, J.H. Seinfeld, and D.R. Worsnop. *Changes in Organic Aerosol Composition with Aging Inferred from Aerosol Mass Spectra. Atmospheric Chemistry and Physics*, 11(13), 6465-6474, doi:10.5194/acp-11-6465-2011, 2011a.
- 6) N.L. Ng, M.R. Canagaratna, J. L. Jimenez, Q. Zhang, I.M. Ulbrich, and D.R. Worsnop. *Real-Time Methods for Estimating Organic Component Mass Concentrations*

*from Aerosol Mass Spectrometer Data. Environmental Science & Technology, 45, 910–916, 2011b.*

## ***Anonymous Referee #2***

*This manuscript describes chamber studies of the photooxidation of  $\alpha$ -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  $\alpha$ -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  $\mu\text{g}/\text{m}^3$  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  $\mu\text{g}/\text{m}^3$ . 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  $f_{44}$ . 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  $f_{44}$  may be influenced considerably by the unmeasured background SOA.*

*Related to this, the authors state (p. 24741) that 1.7  $\mu\text{g}/\text{m}^3$  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  $\mu\text{g}/\text{m}^3$ , 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  $f_{44}$  over the course of the experiment.*

*Moreover, it’s not clear that the 1.7  $\mu\text{g}/\text{m}^3$  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  $\mu\text{g}/\text{m}^3$  partitioning into sulfate seed (assuming total sulfate loading of 10-100  $\mu\text{g}/\text{m}^3$ ). 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, NO<sub>x</sub> 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  $1.7 \mu\text{g}/\text{m}^3$ , 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.

The authors agree that background aerosol has to be quantitatively studied in order to assess uncertainties in the measurement data. Three blank experiments were carried out during the campaign and two additional experiments shortly after its conclusion. Blank experiment conditions are listed in the table below. (The table will be added to the Supplement).

**Table S3:** Conditions of blank experiments B1-B5. The SMPS mass concentration is only given for blank experiments without seed. Detection limit is abbreviated with DL.

Blank No.	Maximum Organic mass $\mu\text{g}\cdot\text{m}^{-3}$	RH av(sd) %	T av(sd) $^{\circ}\text{C}$	NO av(sd) ppb	NO <sub>2</sub> av(sd) ppb	radiation source	added		Previous SC use
							ppb	seed $\mu\text{g}\cdot\text{m}^{-3}$	
08.12.10 (B1)	SMPS: 0.03 (Suspended) AMS: below DL	Ca. 50*	Ca. 22*	0.9(0.3)	no data	UV+xen	-	-	moped emissions (up to $100 \mu\text{g}/\text{m}^3$ )
02.03.11 (B2)	SMPS: 0.16 (Suspended) AMS: below DL	49(2)	21.8(0.6)	1.0(0.3)	Below det.lim.	UV+xen	-	-	$\alpha$ -pin photooxid. (2 - $73 \mu\text{g}/\text{m}^3$ ) moped emissions (up to $100 \mu\text{g}/\text{m}^3$ )
08.04.11 (B3)	AMS: 1.7 (Suspended)	61(6)**	25.2(1.4)	3.3(0.6)	Below det.lim.	UV+xen	HONO 10	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (6.6 $\pm$ 0.2)	$\alpha$ -pin photooxid. (1.4 - $80 \mu\text{g}/\text{m}^3$ )
27.04.11 (B4)	AMS: 0.16 (w/c)	80-85				UV+xen	NO 40***	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1.8)	$\alpha$ -pin photooxid. (1.4 - $80 \mu\text{g}/\text{m}^3$ )
29.04.11 (B5)	AMS: 0.11 (w/c)	80-85				UV+xen	HONO ~2	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1.2)	$\alpha$ -pin photooxid. (1.4 - $80 \mu\text{g}/\text{m}^3$ )

\* During blank experiment B1, no radiation shielded T/RH measurement existed. 55 % RH and  $19.5^{\circ}\text{C}$  were measured in darkness before lights were switched on. Assuming the temperature increases by  $3^{\circ}\text{C}$  after lights are switched on, leads to a RH of 50 %.

\*\* Before lights were switched on, 85 % RH and  $19.2^{\circ}\text{C}$  were measured. After lights were switched on, the temperature increased to  $25^{\circ}\text{C}$ , resulting in a decreased RH of 60.9 %.

\*\*\* 40 ppb of NO added to the blank before lights were switched on.

The aerosol mass concentration produced in blank experiments B1 and B2 was below the detection limit of the AMS also due to the mean diameter ( $\sim 30\text{nm}$ ) being below the measuring range of the AMS. The SMPS showed values between 0.03 and  $0.16 \mu\text{g}\cdot\text{m}^{-3}$ . The organic mass concentration measured by the AMS during blank experiment B3 reached  $1.7 \mu\text{g}\cdot\text{m}^{-3}$ . This significantly higher background concentration is likely due to

both, the contamination of the  $(\text{NH}_4)_2\text{SO}_4$  seed solution with organic compounds and an increase in the surface available for condensation compared to nucleation experiments. Evidence that primary organic aerosol was injected with the seed is seen in an increase of the organic aerosol with two later seed injections during blank experiment B3.

We are convinced that it is valid to compare background aerosol generated during the experiments without seed with the blank experiments B1 and B2, while only the single seeded experiment 7 during the study should be compared with blank experiment B3, B4 and B5.

The chemical composition of SOA in blank experiment B3 measured by the AMS differs from that measured during the low-concentration  $\alpha$ -pinene experiments. This will be demonstrated in the Supplement with a figure showing their location in the Van-Krevelen space (H:C vs. O:C).

We are convinced that the particle and gas phase history of the smog chamber is of low importance for the following experiments as the cleaning procedure after each experiment with 10 hours visible and UV light irradiation of the remaining gas and particle phase in the presence of several ppm of  $\text{O}_3$  (input 5 h) is very efficient. The chamber is flushed for at least 36 h with a flow of 9000 l/h, thus the chamber volume gets exchanged 12 times [36 h/(27000 l/9000 l/h)].

Neither  $\text{NO}_x$  nor OH concentrations are too low in blank B1 and B2 to react the available volatile organic compounds (VOCs) further to form SOA. As the remaining VOCs after the cleaning procedure are low in concentration, the  $\text{NO}_x$  required maintaining a relevant VOC/ $\text{NO}_x$  ratio for regenerating OH is low as well. The HONO concentration in blank B3 speeds up the oxidation process and equivalent HONO/VOC ratios were never reached during the experiments.

In general, it is difficult to quantify the contribution of contaminants in the smog chamber to the total organic aerosol mass over the course of an experiment. Nevertheless, we used the measured mass spectra (MS) at three different times of blank experiment B3 as input for the statistical tool ME-2 (multi-linear engine: model by Paatero et al. (1999), analysis interface by Canonaco (in prep.)) to estimate its contribution to the total mass concentration. For the ME-2 runs, the blank experiment mass spectrum was fixed and two more free components were allowed (similar to the approach of Lanz et al. (2008) for ambient measurements). 120 iterations (40 for each blank experiment MS) of the model using different randomly distributed initial values resulted in a contribution of the constrained blank MS between 6.6-9.9% in the first two hours to 10-20% in the last three hours of experiment 4 with the lowest organic mass concentration. A detailed description of the model runs and results can be found in the Supplement.

The quantification of background aerosol was described in more detail by changing the manuscript in the following way:

“To ensure that the organic matter (OM) formed during the experiments is not significantly influenced by background contamination in the smog chamber, blank experiments before, during and after the campaign were carried out. The conditions of the

five blank experiments are listed in Table S3 in the Supplement. During two blank experiments (B1 and B2) at  $RH \approx 50\%$  with neither HONO nor seed aerosol present, the maximum mass concentration measured by the SMPS was  $0.16 \mu\text{g}\cdot\text{m}^{-3}$  and  $0.03 \mu\text{g}\cdot\text{m}^{-3}$  after 5 h and 8 h exposure to UV and xenon lights, respectively. A blank experiment (B3) with  $6.6 (\pm 0.2) \mu\text{g}\cdot\text{m}^{-3}$  ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) seed, 10ppb HONO and a relative humidity of  $61 (\pm 6) \%$  yielded a peak organic mass concentration of  $1.7 (\pm 0.1) \mu\text{g}\cdot\text{m}^{-3}$  30 minutes after lights on. Two additional seeded blank experiments (B4 with NO and B5 with HONO) with a lower  $(\text{NH}_4)_2\text{SO}_4$  concentration yielded only  $0.1\text{-}0.16 \mu\text{g}\cdot\text{m}^{-3}$  organic mass concentration. The significantly higher background concentration in blank experiment B3 can be explained by the contamination of the  $(\text{NH}_4)_2\text{SO}_4$  seed solution with organic compounds. There is evidence that primary organic aerosol ( $\sim 0.3 \mu\text{g}\cdot\text{m}^{-3}$ ) was injected with the seed. In addition, it is likely that water soluble organic compounds are injected with the aqueous seed which are then oxidized in the gas phase and form additional SOA. Moreover, the yield of secondary organic mass is enhanced by the surface provided by the seed: Condensation is happening earlier than during the blank experiments without seed where higher vapor pressures are needed for nucleation. Experiment 7 (which is most similar to the seeded blank experiment) included a concentration of  $69.2 \mu\text{g}\cdot\text{m}^{-3}$  and thus an organic mass concentration well above the blank value. The organic mass concentration of the unseeded experiments is well above that of blank experiments B1, B2, B4 and B5.

In general, it is difficult to quantify the contribution of contaminants in the smog chamber to the total organic aerosol mass over the course of an experiment. Nevertheless, we used the measured mass spectra (MS) at three different times of blank experiment B3 as input for the statistical tool ME-2 (multi-linear engine: model by Paatero et al. (1999), analysis interface by Canonaco (in prep.)) to estimate its contribution to the total mass concentration. For the ME-2 runs, the blank experiment mass spectrum was fixed and two more free components were allowed (similar to the approach of Lanz et al. (2008) for ambient measurements). 120 iterations (40 for each blank experiment MS) of the model using different randomly distributed initial values resulted in a contribution of the constrained blank MS between 6.6-9.9% in the first two hours to 10-20% in the last three hours of experiment 4 with the lowest organic mass concentration. A detailed description of the model runs and results can be found in the Supplement.

Another indication that the low concentration experiments are surely not dominated by the background contamination is shown in Fig. S7 of the Supplement. The chemical composition of SOA in blank experiment B3 measured by the AMS differs from that measured during the low experiments of the study as shown by their different location in the Van-Krevelen space (H:C vs. O:C).”

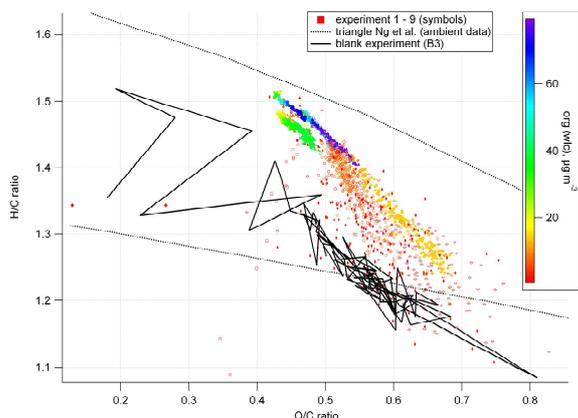


Fig. S7: (the traces for the low concentration experiments have to be averaged over a longer time)

**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  $f_{44}$  and  $f_{43}$  can be useful metrics, O/C really should be the metric used to describe how oxidized the aerosol is.*

As suggested, a high resolution (HR) data analysis will be presented in the revised manuscript including:  $\text{CO}_2^+$  vs.  $\text{C}_2\text{H}_3\text{O}^+$  next to the  $f_{44}$ - $f_{43}$  figures, in addition a van-Krevelen diagram (O:C vs. H:C) and O:C as a function of wall loss corrected organic mass concentration. Two figures: O:C vs.  $f_{44}$  and H:C vs.  $f_{43}$  will be provided in the Supplement. HR mass spectra for all nine experiments will be presented.

*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.)*

The wall loss correction method used in the study represents a minimum wall loss correction and was chosen because it is most representative of the actual experimental conditions. As nearly all experiments were conducted without sulfate seed, correction via the org/SO4 ratio is not possible. A calculation of wall loss under dark conditions would be subject to biases due to (1) increased condensation after lights are switched off caused by a temperature decrease due to the delayed reaction of the air conditioning systems after a heat source is switched off; and (2) reduced turbulence in the bag during darkness (due to the missing heat source) which in turn reduces the wall loss. The manuscript will be changed in the following way:

“Initially, there is a period of rapid mass increase with a slow increase in  $f_{44}$ , followed by a later period of a continuous  $f_{44}$  increase with only a slight further increase in mass. The

precise rate and termination point of the late-experiment mass increase are somewhat uncertain due to corresponding uncertainties in the applied minimum wall loss correction method.”

*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.*

A sentence will be added to the Introduction:

“SOA produced in smog chamber (SC) studies typically falls within the range of ambient SV-OOA, almost always showing lower degrees of oxygenation than ambient LV-OOA (Ng et al., 2010), while for individual precursors LV-OOA-like SOA was found (Bahreini et al., 2005;Chhabra et al., 2011).”

*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?*

The evolution of the chemical composition (time dependence) will be shown in the Supplement in a Van-Krevelen diagram (H:C vs. O:C) including the data of blank B3 and the nine experiments. Also the time series of organics, ammonium, nitrate and sulfate will be shown.

*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?*

The organic mass concentrations shown in the ACPD manuscript were derived from the AMS data. The ratio between SMPS and AMS volume has been investigated carefully, applying the following densities in g/cm<sup>3</sup> to the AMS species:  $\sigma_{\text{Org}}=1.4$ ;  $\sigma_{\text{SO}_4}=1.78$ ;  $\sigma_{\text{NO}_3}=1.72$ ;  $\sigma_{\text{NH}_4}=1.75$ ;  $\sigma_{\text{ChI}}=1.4$ . In the revised manuscript, the following correction factors (CF) based on the ratio  $\text{volume}_{\text{AMS}}/\text{volume}_{\text{SMPS}}$  will be applied to correct the AMS data for collection efficiency and transmission issues:

In brackets, the possible reasons for a disagreement between SMPS and AMS are given.

CF=0.4 for experiment 1 (volume weighted  $d_m = 60\text{-}70\text{nm}$ )

CF=0.85 for experiment 2 (volume weighted  $d_m = 70\text{nm}$ )

CF=1 for experiments 3, 4, 5, 6, 8, 9 (volume weighted  $d_m=150\text{-}200\text{nm}$ )

CF=0.8 for experiment 7 (bouncing of sulfate)

For experiments 1 and 2, the volume weighted mean diameter is on the lower edge of the AMS measurement range and therefore the AMS samples significantly less than the SMPS. As all experiments except expt. 7 were nucleation experiments, the chemical composition is not expected to vary substantially as a function of diameter, relevant for

experiment 1. The correction of experiment 1 influences the mass concentration substantially, but does not significantly affect the conclusions drawn.

*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.*

The SV-OOA factor in DeCarlo et al. (2010) is in comparison to other studies very oxidized, in fact as oxidized as some LV-OOA factors in other studies. Jimenez et al. (2009) define the O:C ranges of LV-OOA as 0.6-1.0 and of SV-OOA as 0.25-0.6, respectively. One could argue that the two OOA factors found in Mexico actually refer to two separate LV-OOAs. As the definitions of SV-OOA and LV-OOA are not universal it is better to compare the O:C ratios instead.

The manuscript will be changed in the following way:

“The OH exposure observed for oxidation of SOA to an O:C value of ~0.64 in the Mexico City plume ( $\sim 4\text{-}5\cdot 10^7 \text{ cm}^{-3}\cdot\text{h}$ , six hours air transport time) as estimated from aircraft measurements (DeCarlo et al., 2010; Dusanter et al., 2009) is on the lower edge of the range of OH exposures required in this study, despite different precursors.”

*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.*

We agree that comparison with the high-resolution database would be ideal, however this database presently contains measurements from only three different cities. Such comparisons are therefore subject to large uncertainties because LV-OOA and SV-OOA factors vary significantly from site to site. In contrast, the selected unit mass resolution spectra are averages of factors collected at more than 40 locations and represent a more robust description of the ambient variability in such spectra. Therefore we believe a comparison with the unit mass resolution spectra is more robust at the present time. However, the HR mass spectra obtained in the present study will be added to the high-resolution database to facilitate future comparisons.

*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.*

Figures of the mass spectra (measured/LV-OOA reference/SV-OOA reference) of all 9 experiments will be given in the Supplement for comparison.

*P. 24751, lines 13-15: It is stated that “In this study, the aerosol products from  $\alpha$ -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.*

The sentence will be changed to the following in the revised manuscript:

“In this study, the aerosol products from  $\alpha$ -pinene photooxidation are located on the right side of the  $f_{44}$ - $f_{43}$ -space bounding the range of PMF factors previously identified in ambient SOA (Ng et al., 2010).”.

**Anonymous Referee #3**

Received and published: 20 November 2012

*Synopsis of the paper: The paper describes a set of smog chamber experiments to test the concept of aerosol aging with the research question being “How can secondary organic aerosol produced in a smog chamber be more representative of ambient aerosol”. The main analytical tool for evaluating the aerosol in this way is specific masses produced in the Aerodyne Aerosol Mass Spectrometer (AMS)  $m/z$  43 and  $m/z$  44. The ratio is then compare to the work of Ng et al. (2010; 2011) to compare the degree of oxidation in the chamber produced aerosol to that of oxidized ambient aerosol.*

**General comments:**

*The paper appears to include carefully performed experiments using a unique experimental protocol. The authors have produced their aerosol from the OH-oxidation of HONO and subsequently by the standard NO<sub>x</sub>-cycling. One metric that they focus on is the so-called OH-exposure in molec cm<sup>-3</sup> h<sup>-1</sup>, which is related back to the level of oxidation in the atmosphere, thus, an OH concentration of 1x10<sup>6</sup> molec cm<sup>-3</sup> for 24 h is representative the same oxidation processes for an OH concentration of 2.4x10<sup>7</sup> molec cm<sup>-3</sup> for 1 h. In this work the assumption is not tested but relies on previous findings. A number of the findings appear to be dependent on the exact means of conducting the experiment and many of these will be considered below. However, a number of experimental aspects are poorly described and these flaws should be addressed before considering uncertainties in interpretation.*

*In general, I believe that there are an insufficient number of experiments with only a single precursor to come to the broad conclusions reached in the paper. The authors need to be more reserved in their statements about the role of organic mass in the aging of the aerosol. In addition, the manuscript uses a considerable amount of jargon (triangle, aging scale, etc.) that makes the writing suitable for only a small insider class of scientists.*

We agree that one could always add further experiments to increase the suitability of a study. However, we believe that this paper contains a very rich dataset, and is worth being published without further experiments. We specify in the title that this is an  $\alpha$ -pinene photooxidation study, and we look forward to other authors comparing their findings with ours. Also, we can not think of a better metric to compare the different experiments conducted with varying HONO, NO<sub>x</sub> and O<sub>3</sub> concentrations than the OH exposure.

The triangle introduced in Ng et al. (2010) will be explained in more detail in the Introduction. The authors will replace “jargon” with appropriate explanations or replace it with more commonly used terms.

**Specific comments:**

*Much of the interpretation relies on the work of Ng and coworkers (2010; 2011). I would suggest the Introduction as a place to discuss the background and findings of Ng et al.*

*(2010; 2011) and to provide the basis for the “triangle” frequently referred to in the Results section of the paper.*

The framework for representing OA composition developed by Ng et al. (2010), including the “triangle plot” and its relevance to the present study, will be discussed in more detail in the Introduction.

*With respect to the Experimental part of the paper, some topics are handled in far more detail than needed (p.24741, l.9-29; detail on flushing and other items in that paragraph). In the same paragraph, it seem quite incredible that one can get to 85% RH in a 27 m<sup>3</sup> bag. What was the chamber temperature in this test.*

The temperature and relative humidity data for the blank experiment were revisited. The blank experiment B3 was conducted at a lower RH than given in the ACPD manuscript. Before lights were switched on, 85% RH and 19.2°C were measured, afterwards, the temperature increased to 25°C, resulting in a decreased RH of 60.9%.

*Black carbon is injected into the chamber as part of the seed aerosol composition from a liquid suspension. Is there any information as to how reproducible this injection is?*

The volume measured by the SMPS (assuming spherical shape) accounted for  $0.75 \times 10^{-3}$  mm<sup>3</sup>/m<sup>3</sup>. The injection was never performed for the same duration and suspension concentration again. Thus we can not give information about the reproducibility. It should be mentioned that the injection of BC was motivated by a parallel single particle study where BC with its non-hygroscopic property was investigated. The mass and the chemical contribution of BC are negligible for the present study.

*The use of the word “chemical composition” (p24742, l. 5) is a bit of a misnomer with respect to the conventional use of the word chemical composition.*

The utilized HR-ToF AMS is able to speciate the chemical composition of non-refractory submicron particles in terms of organics, ammonium, nitrate, sulfate and chloride. The manuscript was changed in the following way:

“A high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc., Billerica, MA, USA) was operated online to measure the chemical composition (organics, ammonium, nitrate, sulfate, chloride) of non-refractory submicron particles (DeCarlo et al., 2006)”

*Give the diameter and length of the sampling lines as described on p.24742, l. 8. This is a factor of 30 dilution for wall-loss corrected aerosol.*

The supporting flow mentioned in the manuscript was not added to the measuring volume, but is maintained only to reduce the residence time in the sampling lines. A

pump connected to the AMS inlet sucks smog chamber air. There is no dilution taking place. The diameter of the sampling line is ¼ inch, the length is 3.85 m.

*As I understand the basic experimental method.  $\alpha$ -Pinene and NO, NO<sub>2</sub>, and HONO were added to the chamber a combination of Xe arc and blacklights photolyzed the mixture to create SOA. After 5 hours and accounting for the wall loss, ozone was added to the chamber. At that point, the Xe arc photolyzed ozone to give O(1D) which reacted at least partially with water to give high concentrations of OH which could then undergo heterogeneous reactions to age the particles thereby increasing the O:C ratio which is then reflected in the f43/f44 ratio. Perhaps this is correct, perhaps incorrect but it is clear that the description needs to be improved so that the reader know exactly the experiment being conducted.*

The manuscript will be extended by the following sentences:

“During all experiments, photooxidation of the biogenic precursor  $\alpha$ -pinene in the presence of nitrogen oxides (NO<sub>x</sub>) led to secondary aerosol formation and growth. In general, the experimental protocols were designed in the following way: Humidification of the chamber, addition of seed aerosol if applicable, introduction of SOA precursor, addition of OH precursor, addition of NO<sub>x</sub> if applicable, mixing period, turning-on of xenon and/or UV lights to generate OH radicals and a reaction time from 5h to 22h. The procedure for each individual experiment is described in Sect. 2.1.1. and summarized in Table 1.”

O<sub>3</sub> was only injected during experiment 6 and this took place eight hours after lights were switched on. This information will be added to Table 1 in the column “added”.

*One question that arises from the experimental method is the disposition of the OH radicals produced at high concentration. I'm curious about your evidence for whether the radicals are undergoing surface reactions in the particle or oxygenated products still in the gas phase.*

The increase in O:C can be due to higher oxygenated products partitioning into the aerosol phase as well as due to heterogeneous surface reactions. From the rate of OH collisions with the particle surface we calculated a possible increase in O atoms by heterogeneous reactions and compared this to the measured increase in O:C, to estimate how much of the O:C increase could be due to heterogeneous surface reactions. We used the same approach as DeCarlo et al. (2008):

“The uptake of oxygen by heterogeneous reaction can be estimated assuming an uptake coefficient ( $\gamma$ ) due to reaction with OH.  $\gamma = 1$  is used as an upper limit.”

We did the calculations by means of measured data in the beginning of experiment 2 with the highest OH concentration ( $5 \cdot 10^7 \text{ cm}^{-3}$ ) present. The volume weighted mean diameter was 70nm. The average molecular speed of OH,  $c$ , is approximately  $600 \text{ ms}^{-1}$ . A correction factor,  $\alpha$ , of 0.92 is taken from Seinfeld and Pandis (2006, Fig. 12.2). The number of OH collisions with the particle surface,  $N_{\text{OH}}$ , can then be estimated as:

$$N_{OH} = \alpha \frac{\gamma c}{4} \pi d_{ve}^2 [OH] \Delta t$$

where  $\Delta t$  is the aging time (DeCarlo et al., 2008).

The result of the calculation is  $4 \cdot 10^5$  collisions with OH. If each successful collision results in the addition of 1 or 2 oxygen atoms to the organic aerosol, then a  $\gamma$  of 1 implies the uptake of  $4\text{--}8 \cdot 10^5$  O atoms in a 1-h period.

O:C increases with  $2\% \cdot \text{h}^{-1}$  and the ratio of organic matter and organic carbon, OM:OC, with  $4\% \cdot \text{h}^{-1}$  during aerosol aging. Together with an assumed density of  $1.4 \text{ g} \cdot \text{cm}^{-3}$  and the measured volume weighted diameter of  $70 \text{ nm}$ , the increase in oxygen atoms is estimated as  $5 \cdot 10^4$  per hour. This suggests that heterogeneous OH reactions are relevant at high OH concentrations, while the chosen parameters represent an upper limit for the uptake coefficient  $\gamma$  and the number of added O atoms per collision which could in reality be much lower than assumed. A recent study of Donahue et al. (2012) suggests an at least 5 times lower heterogeneous OH reaction rate than the reaction rate in the gas phase due to gas-phase diffusion limitation.

*According to a simple calculation, the 4 Xe arcs and 80 blacklights produce 24 KW of energy that needed to be dissipated for seven of the nine experiments. Please say a word (more than just giving a reference) as to how this energy was removed without there being some increase in the chamber temperature. Was the reported temperature range of 21-24 C, the initial temperature, the temperature during the irradiation, or both? I find it hard to believe that the chamber could be operated at 85% RH with full lights and not have condensed water somewhere in the chambers (p.24741, l. 18-19). Presumably some level of air conditioning is used to keep the chamber between 21-24 C, which would generate local cold spots and sites for condensation.*

The four Xenon-arc lamps (16 kW in total) are a strong heat source and are therefore cooled by four fans, directed to the lamp. In addition, the smog chamber housing is air conditioned by two AC systems (with a total capacity of about 19.5 kW). The cool air is not directed to the bag, but put in parallel to it. To prevent cold spots from developing on the chamber walls, two fans are operated in the smog chamber housing to mix the air more effectively. During the high RH experiments, no condensation was observed while checking with the eye. A relative humidity of 85% is the maximum value that has been achieved in the PSI chamber for stable operation without condensation.

The temperature and relative humidity data for the blank experiment was revisited. The blank experiment B3 was conducted at a lower RH than given in the ACPD manuscript. Before lights were switched on, 85% RH and  $19.2^\circ\text{C}$  were measured, afterwards, the temperature increased to  $25^\circ\text{C}$ , resulting in a decreased RH of 60.9%.

Despite the AC systems, the smog chamber temperature is increasing by  $\sim 2\text{--}5^\circ\text{C}$  when all lights are switched on. This is measured with a radiation shielded temperature and RH sensor, flushed with smog chamber air. A table will be added to the Supplement summarizing these experimental conditions:

**Table S3:** Conditions of blank experiments B1-B5. The SMPS mass concentration is only given for blank experiments without seed. Detection limit is abbreviated with DL.

Blank No.	Maximum Organic mass $\mu\text{g}\cdot\text{m}^{-3}$	RH av(sd) %	T av(sd) $^{\circ}\text{C}$	NO av(sd) ppb	NO <sub>2</sub> av(sd) ppb	radiation source	added ppb	seed $\mu\text{g}\cdot\text{m}^{-3}$	Previous SC use
08.12.10 (B1)	SMPS: 0.03 (Suspended) AMS: below DL	Ca. 50*	Ca. 22*	0.9(0.3)	no data	UV+xen	-	-	moped emissions (up to 100 $\mu\text{g}/\text{m}^3$ )
02.03.11 (B2)	SMPS: 0.16 (Suspended) AMS: below DL	49(2)	21.8(0.6)	1.0(0.3)	Below det.lim.	UV+xen	-	-	$\alpha$ -pin photooxid. (2 - 73 $\mu\text{g}/\text{m}^3$ ) moped emissions (up to 100 $\mu\text{g}/\text{m}^3$ )
08.04.11 (B3)	AMS: 1.7 (Suspended)	61(6)**	25.2(1.4)	3.3(0.6)	Below det.lim.	UV+xen	HONO 10	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (6.6 $\pm$ 0.2)	$\alpha$ -pin photooxid. (1.4 - 80 $\mu\text{g}/\text{m}^3$ )
27.04.11 (B4)	AMS: 0.16 (w/c)	80-85				UV+xen	NO 40***	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1.8)	$\alpha$ -pin photooxid. (1.4 - 80 $\mu\text{g}/\text{m}^3$ )
29.04.11 (B5)	AMS: 0.11 (w/c)	80-85				UV+xen	HONO ~2	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1.2)	$\alpha$ -pin photooxid. (1.4 - 80 $\mu\text{g}/\text{m}^3$ )

\* During blank experiment B1, no radiation shielded T/RH measurement existed. 55 % RH and 19.5 $^{\circ}\text{C}$  were measured in darkness before lights were switched on. Assuming the temperature increases by 3 $^{\circ}\text{C}$  after lights are switched on, leads to a RH of 50 %.

\*\* Before lights were switched on, 85 % RH and 19.2 $^{\circ}\text{C}$  were measured. After lights were switched on, the temperature increased to 25 $^{\circ}\text{C}$ , resulting in a decreased RH of 60.9 %.

\*\*\* 40 ppb of NO added to the blank before lights were switched on.

*From the OH tracer method using the loss of butanol-d9, give the maximum absolute OH concentration determined during the individual experiments, needed for the OH exposure determination. Does the concentration ever get as high as  $1 \times 10^8$  molec.  $\text{cm}^{-3}$ ?*

The manuscript will be extended with the sentence:

“The mean OH concentration in the smog chamber is indirectly determined by dividing the OH exposure by the respective time period. The highest OH concentration was  $5 \cdot 10^7 \cdot \text{cm}^{-3}$  and occurred at the beginning of experiments 1 and 2. On average, the OH concentrations during the experiments were in the range of  $0.12$ - $2.7 \cdot 10^7 \cdot \text{cm}^{-3}$ .”

*Discuss the possibility that products of the butanol tracer could sufficiently oxidize to generate condensable products on the aerosol, especially after the addition of ozone and the generation of high levels of OH radicals.*

The products of butanol-d9 can be identified by their particular masses including deuterium atoms. The high resolution mass spectra measured by the AMS in experiment 4 did not show any contribution at the specific fragments: C<sub>2</sub>D<sub>3</sub>O (m/z 46.06), CDO (m/z 30.02), CD<sub>3</sub>O (m/z 34.05) and C<sub>3</sub>D<sub>5</sub>O (m/z 62.10). This confirms that there was no measurable contribution from butanol-d9 to SOA.

*Discuss the likelihood of the hydrocarbons present in the reaction mixture photolyzing due to the presence of short wavelength radiation from the Xe arc. What is the lowest wavelength UV likely in the chamber.*

The lowest wavelength emitted by the xenon lights used in this study is approximately 280nm due to a filter in front of the Xenon arc lamps. The spectrum of the black lights is centered at 350nm ranging from 300nm to 400nm. In this way, a spectrum very similar to the solar spectrum is reached, where photolysis at low wavelength compares to the natural photolysis. A graph of the measured light spectra will be added to the Supplement.

*What is the magnitude of the wall loss correction. What is the factor increase of the aerosol mass concentration due to the correction.*

The manuscript was changed in the following way:

“The measured (AMS) aerosol mass during this period was fitted with an exponential. The data were then corrected by dividing the measured organic mass concentration by the exponential decay. The estimated half-lives ranged between 2.8 and 10 h, the maximum derived from experiment 8, with a very short period to fit.”

The factor between measured and wall loss corrected organic mass concentration is time dependent and increasing over time, resulting in factors of 1.6 to 10 between measured and wall-loss-corrected organic mass concentration.

*Do both  $f_{43}$  and  $f_{44}$  use the same correction factor?*

Because  $f_{44}$  and  $f_{43}$  are the fraction of organic mass measured at  $m/z$  44 and  $m/z$  43, they are unaffected by the wall loss correction. The only corrections that must be applied are subtraction of air interferences from the mass spectrum; these air interferences are characterized by periodically sampling through a filter to remove all non-air components. This subtraction applies to the total AMS-measured signal, and is therefore also unaffected by the wall loss correction.

*At least a cursory explanation to the “triangle” (p24747, l. 2) needs to be given either in the Introduction or in the Results section itself.*

The triangle, originating from average ambient data as well as the high relevance of the study by Ng et al. (2010) to the presented work will be explained in more detail in the Introduction.

*Some definition for the “aging scale” (p.24747, l. 26) needs to be give. It is not self evident.*

Instead of the widely used “time after lights on”, referring to hours, this study uses the OH exposure to compare between experiments with very different OH concentrations present. The definition is given on p. 24742, line 26.

The manuscript was changed to: “For a comprehensive comparison of all experiments described in this study, the OH exposure was utilized as the aging scale, rather than the time after lights on.”

*What is the implication of the sentence starting on p.24747, l. 6. The authors imply that this is a significant scientific finding. What is the implication for chamber measurements conducted by other research groups.*

The present study represents the first time that LV-OOA-like aerosol has been produced from smog chamber photooxidation of alpha-pinene. The SOA produced in previous studies has had a significantly different composition (i.e. less oxygenated). The primary reason appears to be the combination of low mass concentration (i.e. similar to the atmosphere) together with enough oxidation time. Conducting experiments at such low concentrations is difficult and higher concentrations have thus been frequently used by the community. The present study clearly demonstrates the dangers in this approach, i.e. that the chemical composition is strongly concentration-dependent and that this dependence grows stronger as near-atmospheric concentrations are reached. Because particle composition governs other important properties and reflects the dominant reaction pathways, accurate simulation of the SOA system requires experiments to be performed at near-atmospheric concentrations, which constitutes a break with current practice.

*The authors need to be more specific in stating on p.24747, l. 22 that the data clearly shows. . .*

The manuscript was changed as follows:

“Seen by the differences in  $f_{44}$  for the three different mass loadings, the data clearly show that at the same OH exposure, the degree of oxygenation is dependent on the total organic mass concentration present in the chamber.”

*The conclusions of the authors on p.24751 at the present time pertain only to a single monoterpene and without additional precursor measurements should not be generalized presently.*

The results obtained for this single precursor are consistent with a generalized partitioning theory (Donahue et al. 2006) predicting increased aerosol yield for a higher organic aerosol mass concentration, with the particle phase containing a proportionally higher fraction of lower volatility (likely more oxygenated) species at low concentrations. Therefore the trends observed for the single precursor analyzed in this study are expected to hold regardless of precursor identity. The present study illustrates the potential magnitude of this effect for a single precursor (specified in the title of the paper), which already demonstrates the hazards of conducting SOA experiments at significantly higher-than-ambient concentrations and assuming the resulting aerosol is atmospherically relevant.

*Copy edits:*

*p24740, l. 14. A rogue question mark is present.*

The question mark will be deleted.

*p24740, l. 27. Some product information is needed for Tokai black printer ink.*

The manuscript was changed in the following way:

“Before switching on the lights during experiment 7, a suspension of  $50 \mu\text{l}\cdot\text{l}^{-1}$  black carbon (printer ink, Tokai carbon, Japan) containing black carbon and a solution of  $4 \text{ g}\cdot\text{l}^{-1}$  ammonium hydrogen sulfate ( $\text{NH}_4\text{HSO}_4$ ), both in water, were sequentially nebulized and introduced into the chamber with  $0.6 \text{ l}\cdot\text{min}^{-1}$  and a dilution flow of  $10 \text{ l}\cdot\text{min}^{-1}$  to act as seed particles.”

*p.24746, l. 16-20. This is a repetition of text presented earlier*

The authors believe that the repetition of the meaning of the two fragments  $f_{44}$  and  $f_{43}$  is important to understand most of the results Section.

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