

# Review comments and answers to Tritscher et al

## (Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber)

### 1. Anonymous Referee #1 (Received and published: 18 April 2011)

#### **Overall Assessment:**

*Tritscher et al. present measurements of the changes in hygroscopicity and volatility of laboratory secondary organic aerosol particles as they age in a chamber. I believe that this manuscript has a lot of potential, as the measurements are novel and cover a wide range of conditions. However, I find the paper overall includes insufficient analysis and discussion; it reads more as simply data presentation without consideration of the broader context and implications of these results. As one prime example, the authors refer fairly often to how composition must be playing a role, yet they never plot their kappa or VFR results vs. the particle O:C. And it is really only in the “Summary and Conclusions” that any real discussion gets going (and here it is very brief). Some of their results are quite intriguing, yet I don’t think sufficiently explained. Occasionally, hypotheses are given, but they tend to not be justified. Many of the figures I find to be difficult to read, due to the many different lines and points shown on individual plots. Given the wealth of data presented, I would like to see this manuscript published. But it is my opinion that significant revision will be required, with a focus on discussion and analysis, before this manuscript is acceptable for publication. Specific questions and comments are given below.*

- We thank the reviewer for the comments and suggestions. We explained and justified our hypotheses in more detail and improved the discussion of the results. “Summary and Conclusions” have been shortened accordingly. Details will be given below as answer to each comment or question. We would like to point out here that aging can have counteracting effects on some properties and thus the final result is not necessarily a clear trend. The emphasis of the paper is to highlight the processes occurring during aging.

#### **Comments and Questions:**

**Abstract, Line 11:** *I find the language “or by an exchange of molecules in the SOA by other molecules with different properties” to be a bit ambiguous. Does this mean that molecules react to turn into other molecules, or that individual molecules are replaced by other, distinct molecules?*

- What is meant by this process is described in the next sentence of the abstract. Since the wording seems to be misleading this sentence was changed to: “A change of VFR and/or  $\kappa$  during processing of atmospheric aerosols may occur either by addition of SOA mass (by condensation) or by a change of SOA composition leading to different aerosol properties.”

The abstract was completely improved and partly rewritten, please see new manuscript for the full abstract!

**Abstract, Line 15:** *What is meant by “a substantial change in the aerosol mass”? Many of the “exchange” processes indicated would lead to incorporation of oxygen, and thus mass increase.*

- The word “substantial” is not a quantitative term but it implies more than just an increase of a few percent. The latter would be the case by mere addition of one oxygen atom to all molecules in the aerosol phase. As not only functionalization but also fragmentation occurs, mass increase by these processes is not expected to be very large as also model calculations show. As we can not quantify the process we think the term is appropriate and expresses the observation.

**Abstract, Line 19:** Please use a different word than “phase.” This could be confused for the actual phase of the particles.

- We replace “phase of the experiment” by “period of the experiment” to avoid any confusion. Also everywhere else in the manuscript “phase” was replaced by “period”, thus phase is only used in the context of condensed/gas/aerosol phase.

**P. 7427, L. 6:** The authors state “Only a small increase, if at all, is expected for  $M_s$  and  $\rho_s$ , and thus changes of  $\rho_s/M_s$  will be small,” where  $\rho_s$  is density and  $M_s$  is molecular weight. This statement should be justified, as it can certainly be wrong. For example, fragmentation will clearly lead to a change in  $M_s$ . See, for example, Kröll et al. (2009). Also, fragmentation can certainly have an influence on solubility, in contrast to what is stated. Consider that for a homologous series of compounds solubility tends to vary with  $M_s$ .

The referee’s statements made here agree largely with Table 1 and our discussion of it. However, the referee misunderstood parts of our discussion, as the text parts belonging to different mechanisms were not split into separate paragraphs. This has been improved with slight modifications to the text and by introducing a separate paragraph for the discussion of each column of Table 1. The statement regarding solubility effects has also been adapted. This part of the manuscript reads now:

“[...]  $v_w$  is in good approximation constant across the water activity range of interest. This leaves  $i_s$  and  $\rho_s/M_s$  as the two key factors determining particle hygroscopicity ( $\kappa$ ). The expected effect of the three main chemical processes on  $i_s$  and  $\rho_s/M_s$  and thus  $\kappa$  is summarized in Table 1.

Functionalization typically increases  $i_s$  slightly due to positive interactions between polar functional groups and water (Petters et al., 2009). Additional dissociation effects would also increase  $i_s$ , though the degree of dissociation of carboxyl and hydroxyl groups is likely very small. Only a small increase, if at all, is expected for  $M_s$  and  $\rho_s$ , and thus changes of  $\rho_s/M_s$  will be small.  $\kappa$  is thus expected to increase slightly under the influence of functionalization.

Oligomerization strongly increases  $M_s$  with little effect on  $\rho_s$ , resulting in a decrease of  $\rho_s/M_s$ . Only small changes are expected for  $i_s$ . Overall a decrease of  $\kappa$  is expected under the influence of oligomerization, though the effect becomes smaller with increasing  $M_s$  (Petters et al., 2006).

Fragmentation strongly decreases  $M_s$  with little effect on  $\rho_s$ , resulting in an increase of  $\rho_s/M_s$ . Only small changes are expected for  $i_s$ . Overall an increase of  $\kappa$  is expected under the influence of fragmentation.

Equation 1 describes the hygroscopicity of completely dissolved solutes. Particle hygroscopicity would be reduced if the SOA was only partially soluble. Functionalization and fragmentation increase the solubility, while oligomerization decreases the solubility. The potential effects of functionalization, fragmentation or oligomerization on particle hygroscopicity caused by solubility changes have equal sign as the effects of changes of  $i_s$ ,  $\rho_s$  and  $M_s$ . Thus the summary of the effect of the three main chemical reactions on particle hygroscopicity as presented in Table 1 remains valid also under the influence of solubility limitations.”

**P. 7431, Line 5:** Although nucleation is a clear indicator of re-condensation, the absence of nucleation can by no means rule out the possibility of re-condensation on the suspended particles.

- This is by such a true statement, which simply means that the occurrence of nucleation indicates a considerable supersaturation of molecules, which then will not only form new particles but will also re-condense on the existing particles. The inversion is not necessarily true, however: Absence of nucleation just indicates that the supersaturation is not high enough for homogeneous nucleation; however, it does not mean that there is no re-condensation due to some lower supersaturation. We

believe that in our experimental set-up re-condensation on existing aerosols is unlikely as the surface area of the wall of the thermodenuder's cooling section is several orders of magnitude higher than the surface area of the aerosol particles.

**P. 7431, Line 22:** *The authors should state explicitly how the GF data were “corrected to 95.0%.”*

- The RH correction procedure is described in detail in equations 3 and 6 of Gysel et al. (2009). A single parameter growth curve parametrization is used to estimate the local shape of the growth curve (gradient and curvature in the RH range near the RH of the measurement) based on the measured growth factor. The RH correction is done in order to minimize systematic biases when reporting growth factors at a constant target RH from measurements acquired across a narrow range of RHs around the target RH (see Fig. 6 of Gysel et al., 2009). Such humidity corrections should only be applied for small RH differences, which was fulfilled in our case ( $\pm 2\%$ ).

We added the following details on the RH correction procedure to the manuscript:

“The GFs measured in the RH range between 93 - 97% were recalculated to 95.0% RH following Gysel et al. (2009), using a single-parameter growth curve parametrization for correcting small RH differences. The used RH correction in a small band of  $\pm 2\%$  RH minimizes systematic biases when reporting temporal evolution of GF at constant target RH. This is especially of importance when overall changes in the GF evolution are not large.”

**P. 7432, Line 13:** *The authors state that “A Kappa of 0 corresponds to GF=1. The use of Kappa allows for direct comparison with other studies or measurements e.g. from a cloud condensation nucleus counter.” However, it is well known that there are difficulties in connecting sub-saturated hygroscopicity measurements to super-saturated (e.g. CCN) hygroscopicity measurements, c.f. Prenni et al., 2007; Duplissy et al., 2008; Wex et al., 2009; Massoli et al., 2010. This statement should acknowledge this fact, as should any discussion to follow.*

It is correct that  $\kappa$  is a priori a water activity dependent quantity. Comparisons between H-TDMA and CCNC derived  $\kappa$  values can reveal the extent of this water activity dependence. The text has been reworded to clarify this point:

“A  $\kappa$  of 0 corresponds to  $GF = 1$ . The use of  $\kappa$  allows for direct comparison of hygroscopic growth factor measurements made at different dry diameters. It is also a convenient quantity to explore the water activity dependence of particle hygroscopicity by comparison of studies presenting  $\kappa$  values from H-TDMA or CCNC measurements made at different water activities.”

**P. 7432, Line 16:** *The authors state that the reason for testing the V-TDMA system with reference particles is for comparison to other systems. However, if this is the goal their choice of citric acid is strange, since it has not been the focus of any V-TDMA or thermodenuder studies that I am aware of, and thus does not serve as a good reference compound at all.*

- Already existing reference compounds like AS and NaCl were also used to compare with other systems (see discussion in text). However these salts are not really suitable as a reference for volatility studies focusing on organic compounds. Therefore citric acid was additionally selected as a more sensitive (i.e. more volatile) reference compound. We recommend that this should also be done in future studies applying thermodenuders or V-TDMAs to organic compounds.

**P7436, Line 2:** *Just wondering why the OH concentration was calculated from pinonaldehyde decay instead of from pentanol decay, which was supposedly added as a specific OH tracer.*

- We planned to use the pentanol decay to determine the OH concentration in the smog chamber. It turned out during the experiments that the  $m/z$  signal of this substance has an interference in the mass spectra of the PTR-MS with a product from alpha-pinene reactions. Therefore other possible OH tracers were tested and we found pinonaldehyde a good alternative to follow the OH concentration, especially during the first hours of aging. Due to its high reactivity pinonaldehyde can only be used for a relatively short reaction time. A discussion on different OH tracers is the topic of a specific paper which will be submitted soon (Barnet et al., in preparation).

We removed the “pentanol injection” label from the concept figure (Fig. 3) to avoid confusion and added the following remark: “Pinonaldehyde is a reaction product of AP ozonolysis and proved to be a better tracer than pentanol (Barnet et al., in preparation).”

*p. 7437, Line 12: Do the authors think that the erf function has any physical meaning, or is it simply used because it can represent the observations well?*

- We had a long discussion among the coauthors exactly on this question, because the erf function has no physical meaning here in our opinion. This empirical function was simply chosen as it represents clearly the observations in the most suitable way. We added the following to the manuscript: “This empirical function was simply chosen as it represents the observations in the most suitable way. It is helpful to extrapolate the volatility data from other experiments during this study...”

*Section 3.1: The authors may want to also include the alpha pinene VFRs from Meyer et al. (2009) and from Cappa and Wilson (2011). Also, it would be helpful to explicitly include the residence times for each of the literature experiments in the figure so that the reader can quickly know which experiments are/are not directly comparable.*

- We agree that those additional VFR from the studies can be included to the thermogram. Additional thermograms make the figure more busy, however, we included two SOA thermograms from the mentioned papers in the figure. The figure legend was also changed according to the reviewer’s suggestion.

*P. 7438, Line 2: It is, in my opinion, completely unrealistic to think that the slightly longer RT for the An et al. (2007) experiments explains the difference in the SOA thermograms between their study and this one [An et al., 2007]. Note that An et al. (2007) also presented a 3 second RT thermogram, which shows a VFR of around 50% at 100 C, which is in line with the observations here.*

- We believe that the RT is one important factor, which can explain part of the variation. The SOA thermogram from An et al. is indeed extreme and can not be explained solely by its longer (plug flow) RT. We agree completely with the reviewer (maybe in contrast to the An et al. paper) that the RT is not the only important factor for the differences between the instruments. Therefore, we also gave other explanations for the observed differences. To study and evaluate differences among the instruments/studies due to polydisperse sampling, aerosol conditioning, use of charcoal denuder etc. is challenging and extremely speculative (many missing details from other studies) and therefore the other options were not discussed in such detail as it was done for the RT.

Several sentences in this section were changed to meet this comment and also following (and previous) comments on this issue: “Comparison of our measurements with other AP SOA studies (squares in Fig. 4) shows the best agreement with the instrument and measurements from Meyer et al. (2009), from Cappa and Wilson (2011) and Jonsson et al. (2007) for low temperatures and Huffman et al. (2009) for higher temperatures. These and our SOA thermograms lie between the two other studies from An et al. (2007) and Paulsen et al. (2005). Different residence times (RT) in the heated zone are an important

cause among other instrumental differences for the disparate thermograms. The plug flow RT of all these studies are < 1 s (Baltensperger et al., 2005; Paulsen et al., 2005), 2.8 s (Jonsson et al., 2007), ~3 s (Meyer et al., 2009), ~15 s (Cappa and Wilson, 2011), 21.2 s (Huffman et al., 2008, 2009), 23 s (this study) and 31.6 s (An et al., 2007), respectively. If the above papers stated the centerline RT at laminar flow we converted it to plug flow RT (factor 2). Our instrument seems to have the second longest RT, at ambient temperature (see Sect. 2.2); only the RT from An et al. (2007) is longer. This could explain the stronger volatilization of SOA at relatively low temperatures in their study at least partly (as also seen in Fig. 3C). On the other hand shorter RT leads to higher VFR (Baltensperger et al., 2005; Paulsen et al., 2005; Jonsson et al., 2007). With our long RT we are able to use low temperatures in the heater and minimize kinetic limitations of evaporation and hope to be close to equilibrium, even though this is probably not the case as suggested recently (Riipinen et al., 2010).

The VFR of this comparison is generally following the RT, i.e. a shorter RT leads to higher VFR and vice versa. This is expected if the evaporation is kinetically limited and no equilibrium is reached in neither of these instruments (Riipinen et al., 2010). Further reasons for small differences in the SOA thermograms may be the type of AP SOA, its concentration, and experimental conditions. Recent studies by Vaden et al. (2011) as well as Cappa and Wilson (2011) postulate a glasslike modification of the AP SOA which would even inhibit effective evaporation within a reasonable RT. Other instrumental reasons e.g. initial particle size, monodisperse or polydisperse measurement, use of a charcoal denuder after the heating section or different experimental conditions may also lead to these variations. The latter is already reflected in the scatter of our data taken from different experiments like ozonolysis and/or OH exposure. Altogether, there are many indications that evaporation studies of SOA are quite challenging and need further attention.“

*P. 7438, Line 7: The authors state, “With our long RT we are able to use low temperatures in the heater and minimize kinetic limitations of evaporation and hope to be close to equilibrium, even though this might be not the case as suggested recently (Riipinen et al., 2010).” I recommend the authors look at the results from Vaden et al. (2011) and Cappa and Wilson (2011), which indicate that the alpha pinene system evaporates extremely slowly and is very far from equilibrium in a V-TDMA or thermodenuder system and likely would require excessively long RT’s to ever reach equilibrium. Also, I do not see how these results “show” the importance of residence time. Really only the An et al. (2007) results are quite different and, as pointed out above, are anomalous. Of course, RT is important, I’m just not sure that these measurements really show this.*

- We thank the reviewer for the suggestion of these two quite recently published papers that we did not consider for our manuscript, yet. We included both references in our manuscript and changed the section in a way to clarify that we (in agreement with the reviewer) do not believe residence time is the only and most important factor for the differences. We also say that equilibrium may not be reached according to these two studies. Corresponding answers are given in the reply above.

*Section 3.2: I find it particularly surprising that the VFR increases with time. Conventional wisdom tells us that low-volatility products will condense first, followed later by high-volatility products as the aerosol mass increases (or course, the conventional wisdom could be wrong). Further, it has been shown experimentally, both here and previously (e.g. [Shilling et al., 2009]) that O:C decreases as the particle mass increases. Again, I would think that O:C and volatility should be anti-correlated. Perhaps my assumption is incorrect, but I believe that an explanation for the observations needs to be put forward.*

- During ozonolysis not only more volatile compounds condense on the particles but also the low volatility compounds add further to the mass. The VFR depends on the volatility distribution of the compounds and their heat of vaporization. There is no general rule that the VFR should decrease. A modeling example is given by Riipinen et al. (2010) in their Figure 7 showing an increase in VFR with aerosol mass in agreement with our observation.

This will be addressed to some extent also in the paper of DeCarlo et al. in preparation on the dark ozonolysis. During ozonolysis (ripening period) increasing signal at high  $m/z$  in the AMS is indicating oligomerization with time. Over the full ozonolysis and ripening period the VFR increase is thus not surprising: if two monomers (or small molecules) oligomerize, they will lower their O:C ratio (water loss, for condensation reactions), but the product will have a significantly higher molar mass, which is lowering their vapor pressure.

Please see also changes in the manuscript due to other reviewer comments touching a similar topic.

**P. 7439, Line 13:** *The reference to Duplissy et al. (2008) is out of place [Duplissy et al., 2008]. Yes, Duplissy saw a “mass concentration dependence”, but their experiments were for photo-oxidation experiments, not ozonolysis experiments. The evolution of, e.g. O:C will likely be very different between these two types of experiments. Further, they find that the GF is lowest when mass is highest, exactly the opposite of what is seen here (although I suppose the Duplissy results are not wall-loss corrected, so perhaps my interpretation of the GF vs. mass relationship is off). Nonetheless, the photo-oxidation vs. ozonolysis difference remains, making these two experiments not particularly comparable. The authors do acknowledge this distinction, but it is my opinion that this distinction is key and makes the statement “Other studies found. . .” to be irrelevant.*

- We agree with the reviewer that the time evolutions of photooxidation and ozonolysis experiments are different. The decreased hygroscopicity at high mass found by Duplissy et al. was attributed to the volatile and less oxygenated vapor condensing at higher mass concentrations. Likewise, we expect a similar phenomenon during an ozonolysis experiment. This is what we discuss. Apparently this message was not clear enough. We also see a lower GF (albeit only slightly) at higher mass concentration similar to Duplissy et al. contrary to the statement of the reviewer. This issue will be addressed to some extent in another paper focusing on ripening during ozonolysis and AMS analysis by DeCarlo et al. (in preparation), where we found increasing signal at high  $m/z$  indicating oligomerization with time.

We rephrased the old section: “The split into low and high AP experiments is less clear [...] which can explain the differences in the findings”

In the following way: “The hygroscopicity of low and high AP experiments shows a similar evolution but separates slightly with time (Fig. 5A<sub>4</sub>, A<sub>5</sub>). Duplissy et al. (2008) found a distinct mass concentration dependence of GF for an  $\alpha$ -pinene photooxidation experiment, i.e. a lower GF at a higher particle concentration. This was attributed to volatile and less oxygenated vapor condensing at higher mass concentrations lowering the GF. Here we do observe only a slightly lower GF for the high concentration experiments after the SOA has evolved, but Duplissy et al. (2008) had higher AP concentrations (> 120 ppb) in their study and investigated a different system (photochemistry instead of ozonolysis), which can explain the differences in the findings.”

**P. 7440, line 4:** *It is not clear to what Figure this paragraph is referring. I think it should be “A1” not “A”. (I find the A1 to be confusing given all the panel A’s.) Also, not clear why this is in an appendix. I recommend making a two graph figure so Fig. 5 and A1 can be compared more easily.*

- The labeling of the appendix figure was done as the ACPD LaTeX template allows/suggests. We agree with the reviewer that this labeling is not well done and we were expecting an improvement from the final typesetting. As the data in both plots are almost identical, but on different time axis, we initially thought an appendix would make sense. We will follow the suggestion of the reviewer (in agreement with comments also from the other reviewers) and place both figures (Fig. 5 and A1) next to each other allowing for a direct comparison of both (new Fig. 5A and 5B). Thus the appendix will be removed completely.

The following section (last part of Sec. 3.2) was moved and rewritten as follows: “Figure 5B (panel B<sub>1</sub> - B<sub>4</sub>) shows the same experiments and parameters as Fig. 5A<sub>1</sub> - A<sub>4</sub> but as a function of the integrated O<sub>3</sub> exposure time (in ppb h). The trends of  $\kappa$  and VFR are split into low and high O<sub>3</sub> concentration experiments. After about 350 ppb h, 90% of  $\alpha$ -pinene has reacted in all experiments and we would expect a similar composition of the products. However, we see at this exposure time higher VFR and  $\kappa$  values for the low O<sub>3</sub> concentration experiments. The reason for this could be twofold. First, radical-radical reactions are decreased leading to a somewhat different product distribution (SOA mass is also decreased, see above). Second, at low O<sub>3</sub> concentrations it takes longer until 90% AP has reacted and the SOA had thus more time to evolve. It is clearly seen that after 350 ppb h the VFR keeps on increasing steadily although not much additional SOA mass is formed. On the other hand  $\kappa$  remains nearly constant. The increase of VFR could indicate an oligomerization process while this would imply a decrease of  $\kappa$ . Shilling et al. (2007) observed that O<sub>3</sub> can heterogeneously oxidize aldehydes to acids which would decrease VFR and increase  $\kappa$  (as dissociation of acids increases the van’t Hoff factor). A control experiment with an excess of AP during the ozonolysis shows in the AMS the same chemical changes as with an excess of O<sub>3</sub>. This does not support heterogeneous oxidation as the cause of this steady increase of VFR. At present we do not have an explanation for this evolution of the SOA. We call this unspecified process or processes ripening of the SOA.”

**Section 3.2:** *Why should there be any “ripening” during the O<sub>3</sub> experiments. Presumably, this has nothing to do with O<sub>3</sub>, since it is extremely unreactive towards compounds without double bonds. Calling this the “O<sub>3</sub> ripening” stage is a bit misleading. . . it is really just a “ripening” stage. In other words, had the experiments been done with excess alpha pinene instead of excess O<sub>3</sub>, the results may have been the same.*

- We fully agree with the reviewer that it is unlikely that the ripening is from O<sub>3</sub>. An experiment with excess of  $\alpha$ -pinene as suggested by the reviewer does indeed yield the same result. Based on this and the other reviewers comments we changed the terminology of the two ripening periods (during ozonolysis and during OH aging) to avoid confusion. As suggested by this reviewer only this stage of the experiment is called “ripening”.

New naming for the 4 periods:

Ozonolysis

- a) O<sub>3</sub> induced condensation
- b) Ripening

Reaction with OH = OH induced chemical aging

- a) ... with substantial mass gain
- b) ... without significant mass gain

The new names for the 4 periods were changed within the full manuscript including figures.

**P. 7441, Line 3:** *An explanation, or at least a hypothesis to explain the following statement is needed: “The O:C ratio is constant or slightly decreasing during the O<sub>3</sub> mediated phase, while it correlates*

well with Kappa during the OH mediated phase.” This seems to run counter to some recent observations, e.g. [Jimenez et al., 2009; Massoli et al., 2010].

- We do not agree that this is counter to Jimenez et al. and Massoli et al. These authors looked at the general trend during formation and aging. We also have a general increase of  $\kappa$  and O:C ratio from the beginning of our experiment until the aged aerosol. These variations during the course of the reaction are still in the scatter of the data in Jimenez et al. and Massoli et al.

**Section 3.3:** An attempt to explain the anti-correlation between O:C and volatility needs to be made.

- The volatile and semi-volatile oxidation products from the ozonolysis are further oxidized becoming less volatile and partition into the particles. The present conclusion “This calculation shows that the freshly added material is highly volatile. We hypothesize that the SOA formed after OH exposure consists of smaller molecules with slightly higher O:C atomic ratios than the original SOA, which condenses onto the particles during this period of the experiment” is modified and we added the following explanation: “A pathway of formation could be functionalization of volatile oxidation products reducing their volatility by one to two orders of magnitude such that they can partition now into the aerosol. This also increases the O:C ratio relative to the pre-existing SOA. However, since the increase of  $\kappa$  indicates the condensation of smaller compounds we conclude that most of the newly condensed volatile fraction occurs from fragmentation reactions. The breaking of the skeleton leads to radicals which react with molecular oxygen to form finally stable products. In this way small highly oxidized molecules of low volatility may be formed. This would be in agreement with a decrease of VFR and an increase in  $\kappa$  and O:C ratio.”

**Page 7441:** The connection between the ZSR equation and volatility is not clear. Instead, just state that a volume mixing assumption is being made. Also, I’m not convinced that a mixing rule can be used on VFR values. VFR is defined as the amount remaining divided by the total amount of “stuff”. Thus, the new VFR is (remaining\_old + remaining\_new)/(total\_old + total\_new), which does not separate easily.

- The volume mixing assumption easily separates to equation 5, which is mathematically equivalent to the ZSR mixing rule expressed in terms of hygroscopic volume growth factors. However, we removed the allusion to the ZSR mixing rule in the revised manuscript as it seems to confuse the readers (see also comment by the 2<sup>nd</sup> referee.

We believe it is justified to use a mixing rule and try to support this argument with the following calculations:

We can define the VFR as stated by the reviewer: 
$$\text{VFR}_{\text{tot}} = \frac{V_N}{V_V} = \frac{\sum V_{iN}}{\sum V_{iV}}$$
 with  $V_N$  the new volume

after heating (= amount remaining) and  $V_V$  the volume before heating (= total amount). The  $i$  denotes each element or component. We know:  $\text{VFR}_i = \frac{V_{iN}}{V_{iV}}$  and for the volume fraction (retrieved from AMS

mass data)  $\varepsilon_{Vi} = \frac{V_{iV}}{V_V}$ .

We can thus write 
$$\text{VFR}_{\text{tot}} = f(\varepsilon_{Vi}, \text{VFR}_i) = \frac{\sum V_{iN}}{\sum V_{iV}} = \frac{\sum V_{iN}}{V_V} = \frac{1}{V_V} \sum (\text{VFR}_i \varepsilon_{Vi} V_V) = \sum (\text{VFR}_i \varepsilon_{Vi})$$

For a 2-component mixture we can write:  $\text{VFR}_{\text{tot}} = \varepsilon_1 \text{VFR}_1 + (1 - \varepsilon_1) \text{VFR}_2$  and this is Eq. 5 in the manuscript.

We have modified the whole discussion of Fig. 6B in order to better address the assumptions and limitations of the simple volume mixing rule:

“Contrary to this the VFR (Fig. 6B) abruptly decreases after OH aging commences (turning lights on) and starts to stabilize after about one hour of aging with OH radicals. In the last period of the experiment, during the OH induced chemical aging without significant mass gain, the VFR tends to increase slightly. The newly added SOA mass after the onset of OH oxidation seems to have a higher volatility (lower VFR) than the previously existing SOA from the ozonolysis. The volatility of the newly added SOA was estimated by assuming simple volume mixing, i.e.

$$\text{VFR}_{\text{mixed}} = \varepsilon_{\text{old}} \text{VFR}_{\text{old}} + \varepsilon_{\text{new}} \text{VFR}_{\text{new}} \quad (5)$$

where the indices “old”, “new” and “mixed” stand for the SOA from the ozonolysis, the SOA added by OH-aging, and the mixed SOA particle, respectively, and  $\varepsilon$  denotes the volume fractions of the SOA components in the mixed particle. Solving Eq. 5 for  $\text{VFR}_{\text{new}}$  provides:

$$\text{VFR}_{\text{new}} = \frac{\text{VFR}_{\text{mixed}} - \varepsilon_{\text{old}} \text{VFR}_{\text{old}}}{1 - \varepsilon_{\text{old}}} \quad (6).$$

$\text{VFR}_{\text{mixed}}$  is directly measured by the V-TDMA.  $\varepsilon_{\text{old}}$  is derived from the organic aerosol mass measurements by the AMS before and after new material was added, thereby assuming the same density for the old and new mass.  $\text{VFR}_{\text{old}}$  is obtained by extrapolating a linear fit through the last 3 hours of ozonolysis data, as indicated by the dashed lines in Fig. 6B. In doing so we assume that the OH exposure does not cause additional oxidation of the old SOA within this short time span as heterogeneous OH uptake is much slower compared to SOA formation by OH oxidation of gaseous precursors. Fortunately, the calculations are anyway not very sensitive to the exact value assumed for  $\text{VFR}_{\text{old}}$ .

Based on Eq. 6 the VFR of the newly condensed material after one hour of exposure to OH,  $\text{VFR}_{\text{new}}$ , is calculated to be 0.24 and 0.04 for the low and high precursor experiment respectively. These numbers are to be taken with a grain of salt given that the simple volume mixing rule ignores e.g. the influence of absorptive partitioning and kinetic effects on  $\text{VFR}_{\text{mixed}}$ . Nevertheless, they confirm that the SOA mass added by OH aging is distinctly more volatile than the SOA mass resulting from the ozonolysis. A pathway of formation could be functionalization of volatile oxidation products reducing their volatility by one to two orders of magnitude such that they can now partition into the aerosol. This also increases the O:C ratio relative to the pre-existing SOA. However, since the increase of  $\kappa$  indicates the condensation of smaller compounds we conclude that most of the newly condensed volatile fraction occurs from fragmentation reactions. The breaking of the skeleton leads to radicals which react with molecular oxygen to form finally stable products. In this way small highly oxidized molecules of low volatility may be formed. This would be in agreement with a decrease of VFR and an increase in  $\kappa$  and O:C ratio.”

*Further, the extrapolation of the “O3 ripening” data into the OH oxidation region needs to be justified.*

- We assume here that the pre-existing SOA is not further oxidized by OH within this short time span as heterogeneous OH uptake is much slower compared to homogeneous oxidation. We added the following statement along with the changes made to address the previous comment: “In doing so we assume that the OH exposure does not cause additional oxidation of the old SOA within this short time span as heterogeneous OH uptake is much slower compared to SOA formation by OH-oxidation of gaseous precursors.”

Finally, I would like to see “VFR<sub>new</sub>” values for all of the experiments, not just the two selected here. Do they all give similarly highly volatile “new” material? From Figure 7, it would seem that e.g. experiment No. 11 is completely different.

- The following Table includes the VFR<sub>new</sub> calculations for experiments where it was possible to do so, other experiments had e.g. no AMS data, or large gaps due to thermodenuder measurements, etc. All show similar highly volatile fresh organic material. However, as stated above in other comments, this method is a simple assumption and should not be over-interpreted; there is quite some level of uncertainty.

| Exp. No. | AP input (ppb) / OH source | VFR <sub>new</sub> after 1 hour OH | comments             |
|----------|----------------------------|------------------------------------|----------------------|
| 3        | 40 / HONO + light          | 0.09                               |                      |
| 4        | 10 / HONO + light          | 0.24                               | presented in Fig. 6  |
| 5        | 10 / HONO + light          | 0.33                               |                      |
| 6        | 40 / HONO + light          | 0.03                               |                      |
| 7        | 40 / HONO + light          | 0.04                               | presented in Fig. 6  |
| 10       | 10 / HONO + light          | 0.09                               |                      |
| 11       | 40 / O <sub>3</sub> + TME  | 0.10                               | See comment below... |
| 13       | 10 / O <sub>3</sub> + TME  | 0.11                               |                      |
| 14       | 10 / O <sub>3</sub> + TME  | 0.08                               |                      |

Experiment No.11 shows in general the same behavior, however it is also a special case, because it has the highest aerosol mass concentration (see color code in Fig. 7 C+D) and therefore is e.g. more volatile and less hygroscopic than the other high concentration experiments.

The following sentence was added to section 3.3: “The calculated VFR<sub>new</sub> for all experiments is in a similar range from 0.03 to 0.33 (at 70°C) indicating highly volatile material.”

**Section 3.4:** *The meaning of the statement “The correlation is governed by the chemistry. . .” is unclear. By “chemistry”, do the authors mean “composition of the particles”? And if so, then shouldn’t O:C be an important parameter?*

- The correlation is determined by the strong trends in  $\kappa$  and VFR during the ozone induced condensation period which are related to changes in chemical composition. This does not necessarily lead to changes in the O:C ratio. We rewrote the sentence as follows: “The correlation is determined by the strong trends in  $\kappa$  and VFR during the O<sub>3</sub> induced condensation period which are related to changes in chemical composition (see Sect. 3.2).”

**Figure 8:** *I am confused by the differences between the two panels. A quick look at e.g. Figure 6 suggests that during the O<sub>3</sub> period(s) VFR and kappa are correlated, but during the OH period(s), they are anticorrelated (eventually both becoming flat, i.e. no correlation). Yet this doesn’t seem to be what is shown in Figure 8b? Am I missing something? Or is this what is meant by “It should be cautioned here that the opposing trends of VFR and kappa during the OH mediated condensing phase are buried in the scatter plot.” Also, why are only the TME experiments shown? Why not the HONO experiments? Are they the same? Different?*

- We decided to show the correlation for the ozonolysis and OH period separately. The HONO experiments show no clear trend in the scatter plot: volatility is first increasing with OH and then decreasing again, so no clear correlation is found for the full phase. We show the TME experiments, which were longer and therefore the trends are somewhat better visible. Especially with additional

lights on (=additional OH) in the TME experiments we see an interesting trend (stronger increase in hygroscopicity than in VFR) in the correlation plot.

We improved Figure 8 and added an additional panel to show the anti-correlation of  $\kappa$  and VFR (new Fig. 8B) for the beginning of the OH induced aging period (first hour for all HONO and TME experiments). We colored each experiment by time and added a linear fit to each experiment. This allows to see the anti-correlation as expected by the reviewer. Small details (e.g. symbols) were changed on the other panels in order to use a more consistent concept in the Figures, see also other reviewer comments on anti-correlation of  $\kappa$  – VFR and Fig. 8.

The sentence “It should be cautioned ...” was deleted.

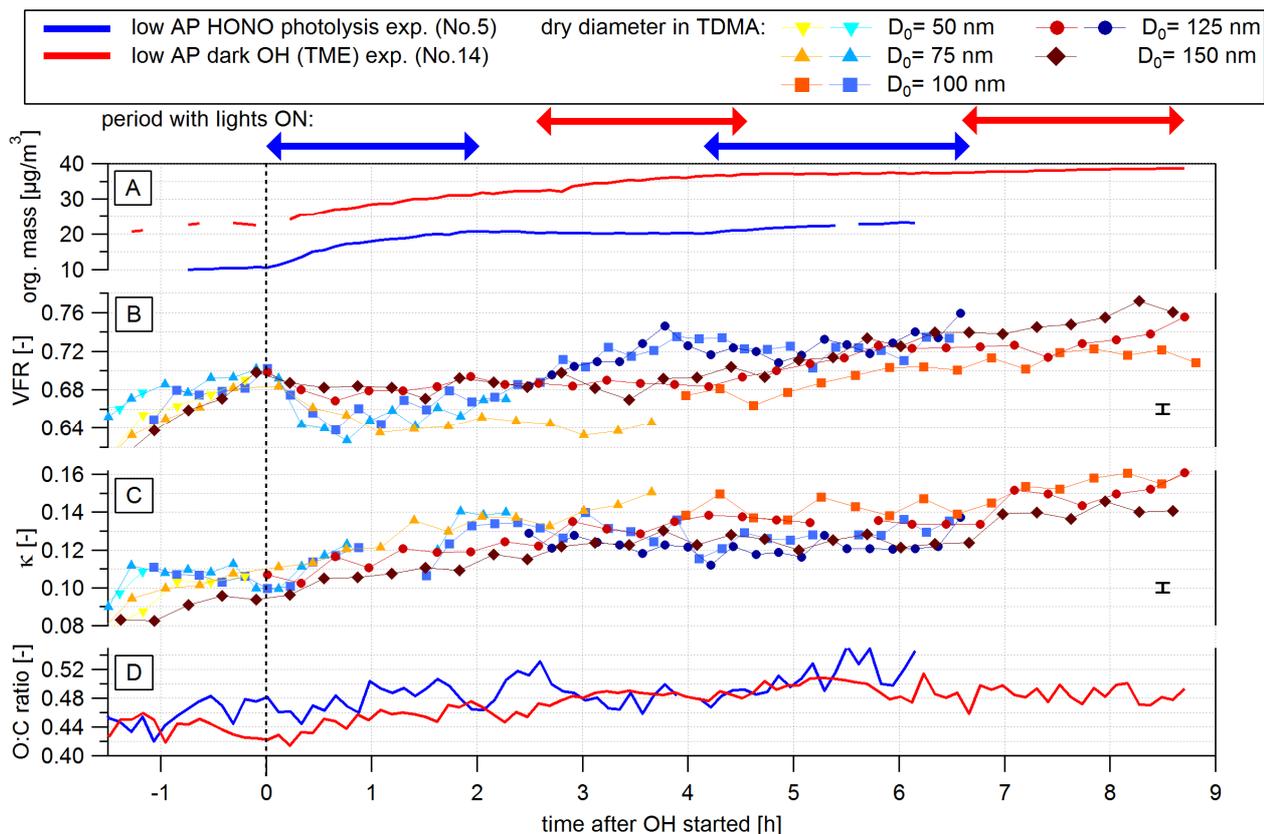
The text has been adapted and the following part was added: “The first hour of OH induced chemical aging is presented separately in Fig. 8B. In general an anti-correlation of  $\kappa$  and VFR is observed for all experiments although the magnitude and duration of this opposite trends for  $\kappa$  and VFR is varying.”

**Section 3.5:** *This section begins “In the following we present results from the second part of the experiments where OH mediated ripening was investigated.” However, ripening experiments have already been discussed in the previous sections. This section focuses on ripening and size, not ripening as a general phenomenon.*

- We discussed the “OH mediated condensation and ripening” already in the previous section 3.3, this is correct. However, the nomenclature of the different experimental periods was adapted and we changed the sentence to:” In the following we present results from the second part of the experiments with the focus on the sensitivity to OH exposure (lights on/off) and the dependence of  $\kappa$  and VFR on the particle diameter.”

**Figure 9:** *The authors need to figure out a different way to present this data. It is extremely difficult to see how, e.g. “In experiment No. 14 the smaller particles tend to have a higher Kappa and lower VFR (higher volatility); this is not observed in experiment No. 5.” The data need to be succinctly summarized, perhaps as a mean difference between the different sizes. However, the figure as is I do not find useful.*

- We agree the Figure 9 is quite complex to read. We do not see how a mean difference between the different sizes helps to simplify or clarify the Figure. There are up to 5 different sizes that need to be compared with each other. During the preparation of the manuscript we tried several versions of this Figure, especially how to present and indicate the different periods with lights on. We found vertical lines in this 4-panel plot disturbing and decided for the large arrows above the panels. We believe also in this case (with light on/off) an example for each HONO and TME is useful (a comparison of those experiments was asked before), because they behave somewhat different. This causes a certain complexity of the Figure. Therefore we tried to better work out the different sizes in the new version of the Figure using colors in addition to the symbols representing the sizes (see Figure below). This makes the differences between sizes better visible, but it still allows seeing the lights on/off periods. However, we believe this Figure is more confusing than the original to show our two messages in this plot: size dependence and light on/off effects. A further option, which we also discarded, is to split the Figure into two parts, one for each experiment, which would blow up the size of the paper unnecessary. Also a comparison between the two different experiments would be more difficult.



The best approach in our opinion is to leave the basic outline of the plot as it was. However, we increased the symbol sizes and labeling, and also added exemplary error bars (see new version of the manuscript for the improved Figure 9). We would like to stress again that the light on/off visibility is maybe even more important than the visibility of the exact size differences. These size differences are well discussed in the text with the conclusion that they are due to kinetic reasons and thus not so important in this context. See also other comments on this topic.

**P. 7445, Line 5:** *The assumption made here is poor. A single component aerosol will not give robust or correct results. Also, reporting the saturation concentration without reporting the enthalpy of vaporization is not useful to the interpretation of thermodenuder results; these are coupled parameters in a thermodenuder model [Riipinen et al., 2010; Saleh et al., 2010; Cappa, 2010]. The mass accommodation coefficient for alpha pinene SOA has been shown to be far from unity [Vaden et al., 2011; Cappa and Wilson, 2011], thus making this a bad assumption because this affects the kinetics, and thus the inferred size dependence and conclusions. Finally, I don't see how "The SOA was assumed otherwise to have similar properties as the theoretical AP SOA modeled in Riipinen et al. (2010)" since the important properties (saturation concentration, number of compounds, mass accommodation coefficient) have all been chosen here. Finally, the authors are only explaining one experiment here; the other one mentioned in this section does not show the same behavior. The authors need to explain this discrepancy.*

- We agree with the reviewer that the model runs do not represent the actual composition of the aerosol in detail. However, the purpose of the model runs was not to present a detailed analysis of the evaporation kinetics of the aerosol - as pointed out it would be impossible without knowing the exact

internal molecular composition as a function of particle size - but rather demonstrate that the size-dependence observed in the paper is similar to what one would expect based on the standard mass transport equations. Regarding the properties of the aerosol: We found that for a single component aerosol changing the saturation concentration is practically equivalent to changing accommodation coefficient within the experimental uncertainty - let alone the uncertainty in the surface tension, which was now just assumed to be the same as in Riipinen et al. (2010).

Therefore we think that presenting additional runs with a different accommodation coefficient would not really add anything meaningful to the paper (rather distract the reader from the main messages) - since we do not know the exact composition of the aerosol. However, we performed test runs with different accommodation coefficient  $\alpha$  and  $C^*$ , but results were very similar.

Furthermore, we would like to point out that the potential size dependence of the mass accommodation coefficient of SOA is at the moment still far from clear, even accounting for the recent developments in the field, so we feel that speculating on its effects on the V-TDMA results is far beyond the scope of this paper. We would therefore prefer keeping the simple analysis as it is at the moment. "The other properties of the SOA" that are referred to in the paper and parameters like molecular mass, vaporization enthalpy and diffusion coefficients have been clarified in the revised manuscript.

#### **References:**

- An, W. J., R. K. Pathak, B. H. Lee, and S. N. Pandis (2007), *Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol*, *J Aerosol Sci*, 38(3), 305-314, doi: 10.1016/j.jaerosci.2006.12.002.
- Cappa, C. D. (2010), *A model of aerosol evaporation kinetics in a thermodenuder*, *Atmos. Meas. Technol.*, 3, 579-592, doi: doi:10.5194/amt-3-579-2010.
- Cappa, C. D., and K. R. Wilson (2011), *Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior*, *Atmospheric Chemistry and Physics*, 11, 1895-2011, doi: 10.5194/acp-11-1895-2011.
- Duplissy, J., et al. (2008), *Cloud forming potential of secondary organic aerosol under near atmospheric conditions*, *Geophys. Res. Lett.*, 35(3), L03818
- Jimenez, J. L., et al. (2009), *Evolution of Organic Aerosols in the Atmosphere*, *Science*, 326(5959), 1525-1529, doi: 10.1126/science.1180353.
- Kroll, J. H., J. D. Smith, D. L. Che, S. H. Kessler, D. R. Worsnop, and K. R. Wilson (2009), *Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol*, *Physical Chemistry Chemical Physics*, 11(36), 8005-8014, doi: doi:10.1039/b905289e.
- Massoli, P., et al. (2010), *Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles*, *Geophys. Res. Lett.*, 37, L24801, doi: 10.1029/2010GL045258.
- Meyer, N. K., et al. (2009), *Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles*, *Atmospheric Chemistry and Physics*, 9(2), 721-732
- Prezzi, A. J., M. D. Petters, S. M. Kreidenweis, P. J. DeMott, and P. J. Ziemann (2007), *Cloud droplet activation of secondary organic aerosol*, *J. Geophys. Res.*, 112(D10), D10223, doi: 10.1029/2006jd007963.
- Riipinen, I., J. R. Pierce, N. M. Donahue, and S. N. Pandis (2010), *Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics*, *Atmospheric Environment*, 44(5), 597-607, doi: 10.1016/j.atmosenv.2009.11.022.

Saleh, R., A. Shihadeh, and A. Khlystov (2010), *On transport phenomena and equilibration time scales in thermodenuders*, *Atmos. Meas. Tech.*, 4, 571-581, doi:10.5194/amt-4-571-2011.

Shilling, J. E., et al. (2009), *Loading-dependent elemental composition of alpha-pinene SOA particles*, *Atmospheric Chemistry and Physics*, 9(3), 771-782

Vaden, T. D., D. Imre, J. Beránek, M. Shrivastava, and A. Zelenyuk (2011), *Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol*, *Proceedings of the National Academy of Sciences*, 108(6), 2190-2195, doi: 10.1073/pnas.1013391108.

Wex, H., M. D. Petters, C. M. Carrico, E. Hallbauer, A. Massling, G. R. McMeeking, L. Poulain, Z. Wu, S. M. Kreidenweis, and F. Stratmann (2009), *Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol: Part 1 – Evidence from measurements*, *Atmos. Chem. Phys.*, 9(12), 3987-3997, doi: 10.5194/acp-9-3987-2009.

## **Anonymous Referee #2** (Received and published: 28 April 2011)

*Copernicus: Referee #2 just informed us that the line and page numbering in his/her referee comment erroneously refer to the latest version before publication (**different page numbers!**) in the discussion forum. Since the writing of the report was quite time-consuming, this referee kindly asks you to compare the comment with your older version, and to ignore comments that you might already have improved in the discussion paper.*

### **General:**

*The manuscript reports results of a smog chamber study on formation and ageing of SOA generated from  $\alpha$ -Pinene under various conditions. The ageing is induced by OH radicals either formed as a side product of ozonolysis in the dark and or by a photolytical source. Besides total mass and O:C ratio derived from AMS data, volatility and hygroscopicity are the parameters chosen as diagnostic quantities to follow the chemical evolution of the SOA particles. These measurements were taken by tandem DMA setups, where the Volatility TDMA was newly developed. The VTDMA and its performance is also described in the paper. The manuscript clearly reports interesting and important results, however the presentation has some weakness. In my opinion this is owed to the fact that either the chemical changes are subtle themselves or are represented rather in a subtle than a in an obvious fashion in the diagnostic quantities. Figure 7 is indicative for that. Exception is the distinct decrease of the volatility during the OH induced condensation phase, which is an important finding. To summarize my impression, the authors in many case observe small effects, which are pointing in the expected direction, but the changes are subtle, often at the edge of significance and difficult to grab. This is actually in contrast to the summary statement of diagnosis value of  $\kappa$  and VFR for complex processes, which is a bit optimistic. Nevertheless, hygroscopicity and volatility together support classification of formation and ripening processes as described by the authors. The question arises if the observation and categorization have predictive power. Since the effects are often subtle it is important to have a good structured manuscript with quantified statements including errors. The latter are often missing and instead only qualitative statements are used of the type "similar but somewhat higher". Moreover, the manuscript is difficult to read and formulations are unclear. Despite the good experimental work, the extensive studies and interesting results, I cannot suggest to publish this manuscript in ACP as it is. The manuscript needs mayor revisions.*

- We thank the reviewer for the detailed comments, questions and suggestions which will help to improve the quality of the paper. We agree with the reviewer that the found chemical and physical changes are often small and difficult to grab as in many case 2 or 3 observed parameters are not enough to show and describe the behavior or even explaining it. We do not claim that changes were huge, but they could be identified with V/H-TDMA and AMS. We believe that the absolute quantities are often less important than the temporal qualitative changes during a reaction period (e.g. VFR is a quantitative measure, but we show in our instrumental section that this is depended on the instrument, therefore we focus more on the volatility trend than the absolute numbers in many cases). However, we quantified the trends wherever it was possible. We will address all the mentioned issues by answering to the specific comments in detail below.

### **Mayor comments:**

*page 2, line 8 "possible mechanism of chemical changes": I find the notation mechanism misleading, since you don't discuss chemical mechanisms. Essentially you observed and classified gross processes, which comprehend several types of chemical mechanisms. This should clarified throughout the manuscript. Moreover, there is unclearness about two processes of chemical composition change:*

*chemical reactions like oligomerization or (heterogeneous) oxidation and replacing or condensing molecules. The latter are physical processes.*

- The word mechanism does not necessarily mean chemical mechanism. We investigate the process of aging which has several causes. All these phenomena form the mechanism of aging. This may include specific chemical reactions occurring as simplified chemical processes like functionalization/fragmentation as well as physical processes which ultimately can be parameterized in a model (Donahue et al. submitted manuscript). We keep this terminology.

It is correct that we observed and classified “gross processes” as a result of chemical mechanisms. Often this is quite difficult as several chemical mechanisms are going on at the same time. However, due to the various setups and settings in the chamber experiments we are able in some cases to identify/derive the possible main dominating chemical mechanisms such as oligomerization, fragmentation and functionalization. These three main mechanisms are discussed in several places in the manuscript and one important goal of this study was to identify (if possible) such chemical mechanisms indirectly with the physical properties volatility and hygroscopicity.

**page 9, line 1** *The authors claim that the walls of the thermodenuder are sufficient to remove the vapors. Is that effect quantitative? Is there experimental data on the efficiency of the thermodenuder? In the setup, especially, if the temperature sensor in the center of the inner tube (see Fig. 1) controls the heater temperature, walls must be warmer than the center line. This should reduce the absorbing effect of the walls. The absence of nucleation is no proof, since the supersaturation that would be needed for nucleation may not be achieved, especially if the walls have some absorbing effect. Moreover, the residual particles may act as condensational sink. In this context: is it possible that HTDMA and VTDMA do not see the same aerosols, because vapors are lost differentially in the two branches of the TDMA?*

- Please, see also the answer to a similar previous question by reviewer 1.

The surface of the wall is much larger than the surface of the particles, so it is much more likely that gaseous organics condense on the wall than back on the particles. We believe that in our experimental set-up re-condensation on existing aerosols is unlikely as the surface area of the thermodenuder’s cooling section is several orders of magnitude higher than the surface area of the aerosol particles. This is especially the case as we have just very small particle number concentrations in the heater (monodisperse particles!). We performed a CFD calculation showing that the wall temperature is almost equal to the center temperature after a few cm.

The characterization of the thermodenuder with test aerosols is shown in Fig. 2. The diameter becomes smaller and with enough heating (strongly dependent on the substance) also number counts are reduced. However, all those arguments and indications can not totally rule out re-condensation, but it can be assumed due to the above discussion that it is negligible or only a minor effect.

We do not claim that absence of nucleation is a proof for non-existence of re-condensation. The occurrence of nucleation indicates a considerable supersaturation of molecules, which then will not only form new particles but will also re-condense on the existing particles. The inversion is not necessarily true, however: Absence of nucleation just indicates that the supersaturation is not high enough for homogeneous nucleation; however, it does not mean that there is no re-condensation due to some lower supersaturation. This can not be ruled out.

The branches in the TDMA are equal until the treatment (humidification and heating, respectively). We see no reason why the aerosols are not the same up to this point, they are dried, charged and monodisperse size selected and then divided into two flows. During and after the “treatment” of course particles undergo different processes, so the final aerosols are different.

**page 12, 2nd paragraph** *This paragraph should not be here. It describes in the same way what you claim as findings in the abstract and in the summary section. Here you mix hypothesis/concept with discussion and interpretation. In any case none of this should be in the experimental section. This regards also Figure 3. Here the legend describes already what you are going to show by your results. This introduces circularity in your manuscript. The way how conduct your experiments, formation by ozonolysis and ageing with OH in a second step is self-evident. You don't need to justify this here. Alternatively you could introduce a section like "concept of the study" where you formulate your concept. But this became sufficiently clear in the introduction section.*

- We agree with the referee that the section about the concept figure was not ideal placed here. The first and the second section about the concept plot: "The typical design of the MUCHACHAS experiments is shown as schematic in Fig. 3. [...] while ripening refers to chemical transformation of the SOA without significant change of the mass." were moved to the end of the introduction. As a consequence also the Figure numbers 1-3 were changed.

**page 13, line 23ff** *This paragraph about the clocks looks complicated too me. What is the sense of physical time? Is there any other time (in natural science)? I guess what you want to say is: The progress of the experiment is described by either "time since SOA formation" or "time since OH initiation". In addition two chemical clocks are introduced, O<sub>3</sub> exposure and OH exposure, which are defined as time x concentration(time) of the oxidant. Please change the manuscript accordingly.*

- We remove the word "physical time", which was supposed to stress the difference to the chemical clocks and replace "chemical time clock" by "chemical clock" everywhere in the manuscript. We changed the manuscript in the following way: "Different time axes as shown in the concept figure (Fig. 3) are used in the following. The progress of the experiment is described by either "time after AP injection" (relating to the start of the ozonolysis reaction) or "time after OH started" (relating to the time when OH production commences) in units of hours (h). In addition two "chemical clocks" are used to represent the experiments with respect to their exposure to O<sub>3</sub> or OH, respectively."

**page 14, line 2** *Above you mentioned addition of Pentanol as OH tracer, now you use Pinonealdehyde. This must be commented. Why didn't you use the Pentanol ? Could show in one of the figures an OH curve?*

- We planned to use the pentanol decay to determine the OH concentration in the smog chamber. It turned out during the experiments that the *m/z* signal of this substance has an interference in the mass spectra of the PTR-MS with a by-product from alpha-pinene reactions. Therefore other possible OH tracers were tested and we found that pinonaldehyde is a good alternative to follow the OH concentration, especially during the first hours of aging. Due to its high reactivity pinonaldehyde can only be used for a relatively short reaction time. A discussion on different OH tracers is the topic of a specific paper which will be submitted soon (Barnet et al., in preparation). We added a remark to the manuscript, see also answer to same question from reviewer 1.

**page 14f, section 3.1 and Figure 4** *The first two paragraphs of section 3.1 are confusing. Throughout the manuscript you claim that volatility is a good parameter to detect progress of processes. Here you state the data are "similar within these uncertainties", but not comparable in detail. What does this mean ? Then you fit a common curve to your data. If I take your approach here serious, you show that all thermograms look the same and you can fit it with one mathematical expression. The variability within an experiment (multiple measurements) is about the same as the variability from experiment*

*to experiment (for different conditions !). In my opinion multiple measurements (how many per experiment ? 2, 5, 10?) automatically mean that you were looking at particles with different chemical evolution. Why averaging them then? Because they are similar enough? But then thermograms are NOT a good diagnostics for processes, because everything seems to look about the same.*

*The comparison to VTDMA results of other groups is also not a real comparison, because you eventually argue with non-comparable experimental conditions or thermodenuder performance to explain the differences to your observations. Actually I trust your thermodenuder performance from what you presented in Sect. 2.2, although it maybe imperfect as all others in the sense that you are not reaching thermodynamic equilibrium but are limited by kinetic effects. The proof of performance via comparison to other VTDMA cannot performed with SOA systems which are so variable in themselves. Here it would be more helpful if you could compare your thermograms for the reference compounds to thermograms for the same compounds measured by other groups.*

- This section refers exclusively to thermograms, which are a totally different approach than the volatility measurements at one single temperature to observe (small) changes in volatility due to aging/changes of the SOA. This is a separate section and is therefore not to be mixed with the other results as the reviewer seems to do. The mentioned "similar within these uncertainties" for the thermograms refers to the variation due to the changes with aging time. The previous sentence says: "Large vertical error bars are due to real volatility changes of the chamber aerosol during the course of the experiment and do not reflect the V-TDMA accuracy." This means the error bars indicate somehow the range that we will show later with the time series. The thermodenuder data give rather an insight in the SOA behavior at different temperatures and allow also to compare the V-TDMA to other thermodenuder/V-TDMA systems.

We agree that these thermograms disregard the chemical evolution. If thermograms were the main topic they need to be done very fast (quick stepping through the temperatures) and always at exactly the same "reaction time" during an experiment. Subtle differences of VFR at constant temperature as observed between different experiments or as a function of aging become unimportant when it comes to the strong temperature dependence of the VFR shown in thermograms.

We never claimed that thermograms could be used in any case to diagnose chemical processes and therefore agree fully with the comment of the reviewer. Instead, we used volatility measurements at one constant temperature as diagnostics for processes. Our reasons for this SOA thermogram Figure are 1) to give an impression of the volatility behavior of the studied SOA with the new V-TDMA at different temperatures to characterize roughly the SOA from our chamber and to show the characteristics of the instrument and 2) to relate this to SOA thermograms from other instruments/studies. From 2) it can be seen that discrepancies between different instruments are higher than differences due to different SOA types.

We did a comparison with test substances (Fig. 2) and mention also values from other studies, but for many salts there is a steep decay/sudden volatility change. That is one reason why we did also thermograms with citric acid, which might be a useful substance for characterization and comparison in future studies. We showed in Fig. 2 only our data, but relate it to other studies in the text (end of section 2.2). In the revised version of the manuscript Fig. 2 becomes Fig. 3 and shows also thermograms of other studies for ammonium sulfate (see also other related comments). We agree that thermograms with SOA are more difficult to compare and several additional aspects need to be taken into account concerning the SOA (SOA type, concentration, SOA formation history etc.). However, we believe this SOA thermogram comparison is still helpful for the above mentioned reasons.

**page 17, line 25 and Figure 5** *One reason to use kappa was to compare particles selected at different diameters, thus to unify results. Why GF (Figure 5E) has a smaller variability than kappa (Figure 5D). Please, comment on that in the manuscript.*

- The mathematical function that relates  $\kappa$  to GF is dependent on the particle dry diameter. The variability of GF and  $\kappa$  can not be directly compared as the selected dry diameter differs between different data points. There are probably compensating effects: Particles with smaller diameter are slightly more hygroscopic and as the Kelvin effect underestimates the hygroscopicity of the small particles the GF measurement point fall rather on top of each other.

**page 21, line 27 and Figure 8** *The increase of volatility during the OH induced condensation phase is an interesting and important finding. This should be worked out nicely and not lapidary kept buried in the scatter plot. You need to mark the (anti-)correlation of VFR and kappa during the OH condensation phase, as this is the most significant finding.*

- We improved Figure 8 and added an additional panel to show the anti-correlation of  $\kappa$  and VFR (new Fig. 8B). This is just possible for the beginning of the OH induced aging period, so we selected just the first hour for all HONO and TME experiments.

**page 26, Conclusions** *Does your finding implicate there is not much ageing by OH in the atmosphere, since the volatile would evaporate as soon as the chemical source stops ? Can you comment on implications of your findings for the atmospheric aerosols?*

- No. The findings do not implicate this. We see a large mass increase by aging on atmospheric OH time scales. This fraction is fairly volatile but there are processes going on making the aerosol less volatile. Long-term evaporation studies of  $\alpha$ -pinene SOA at room temperature made by Vaden et al. show a very slow evaporation. It is also important to keep in mind that our measured volatility at 70°C, which is not ambient temperature, can not be easily extrapolated to a volatility of particles under ambient conditions.

### **Figures**

**Figure 10 and Table 2** *give a very good overview.*

- We happily agree on that.

*In Figure 5 and Figure 7 it is probably better to reduce the data to one or two typical or extreme cases, but then with error bars to show the significance of the changes. (The symbols of same color are difficult to distinguish.) In the text changes of VFR, GF (and O:C) over the four phases should always stated quantitatively with errors bars. A table with average / median of distinguished VFR and GF, which describe the time evolution, over all experiments with standard deviations, percentiles etc. could serve to show the variability from experiment to experiment.*

- Two typical cases are shown in Figure 6 while Figures 5 and 7 should give an impression of the variability of data due to different experimental conditions. We added a measure of the reproducibility of the measurement in the Figures to indicate the significance of the trends of VFR and  $\kappa$ . Averaging the data would lead to large standard deviations due to the variations between different experiments and thus smearing out trends.

### **Minor Comments:**

**page 2, line 7** *"sensitive physical parameters" what means sensitive in this context ?*

- We use “sensitive” in the sense that at constant conditions (RH and temperature) very small changes in the SOA (due to chemical processes) can be observed with these physical parameters. These parameters can be measured with great precision to follow subtle changes in the SOA properties. A non-sensitive parameter is not able to detect the small changes. We clarified this sentence in the abstract as: “These measurements were used as sensitive parameters to reveal the mechanisms possibly responsible for the changes in the SOA composition during aging.”

**page 4, line 11** *Jimenez et al. (2009) do not treat oligomers, they are mentioned only in conceptual context. Please, remove or replace reference.*

The sentence “During oligomerization the volatility decreases while the O:C ratio may be increased or reduced, depending on the process (Reinhardt et al., 2007; Jimenez et al., 2009).” refers to the conceptual figure 4C in the Jimenez paper, which shows the relation between oligomerization (or other mechanisms) and the O:C ratio as well as C\* as volatility measure. However, as the paper does not treat oligomers specifically, the reference was removed and the sentence reads now: “Functionalization and fragmentation lead to an increase in the O:C ratio while oligomerization may increase or decrease it depending on the process (Reinhardt et al., 2007).”

**page 4, line 14** *The phrase "Aerosols, including SOA but also inorganic and other organic substances, have an influence on global climate ..." sounds strange to me. The qualifier "but also inorganic and other organic substances" is misleading. Are you referring to SOA mixed with other substances or are referring to aerosols in general which are composed of inorganic and organic substances, including SOA components?*

- We refer to the latter, aerosols in general. The sentence was changed in the manuscript: “Atmospheric aerosols are composed of inorganic and organic substances, including SOA components. They have an influence on global climate via the direct aerosol effect ... “

**page 4, eq 1** *This equation for kappa is not from Petters and Kreidenweis 2007.*

- We did not take the equation from there but it can be derived/deduced from other equations in that paper. We wrote “The following equation for the hygroscopicity parameter  $\kappa$  can be derived from Petters and Kreidenweis (2007) to represent the hygroscopicity of an aerosol”. From Petters and Kreidenweis 2007 the equations 2 and 8 can be used to derive our equation, when the volume of solute is replaced by an expression of density and mass. We have no reference that presents the formula exactly as we do. Also Duplissy et al. (2008) (supplementary material) and Kreidenweis et al. (2005) deal with a similar equation, but not exactly this one.

**page 6, line 18** *What is exactly meant by "chemical quantification"? AMS does allow for chemical quantification of inorganic components, but not of organics mixtures, like SOA.*

- We wrote “The AMS detects inorganic species and the aerosol organic fraction quantitatively and is described elsewhere in detail (DeCarlo et al., 2006). It allows the chemical quantification and characterization of several types of fragments of the SOA with a time resolution of a few seconds (e.g. Alfarra et al. 2006).”

**page 7, line 7** *AP for  $\alpha$ -Pinene is not correctly introduced.*

- We explain it when we mention it for the first time (Last sentence of the introduction): “The main emphasis for the MUCHACHAS experiments at the PSI smog chamber was the aging of  $\alpha$ -pinene (AP) SOA with OH under dark and light conditions.” And it is repeated in the second sentence of section 2.3

to remind the reader: “The typical design of the MUCHACHAS experiments is shown as schematic in Fig. 3. The precursor in all experiments described here was  $\alpha$ -pinene (AP).” We think this is correctly done.

**page 9, line 20** *What do mean here with "very stable" ? What are the typical RH fluctuations ? You obviously had data outside the range 93-97% RH, which you discarded. How many data points you had to discard?*

- Very stable means that RH was typically less than +/- 0.5% off. On average less than 1-2 points of a full experiment were discarded from the data due to RH fluctuations. This was only the case when the instrument was disturbed in flow or in temperature by opening it. The main reason for stating the range 93-97% RH is that we do the correction of RH only in a very narrow range. See also answers to other reviewers on RH stability and RH correction procedure.

**page 9, line 24** *You probably mean "optimized" not "minimized"*

- This was changed.

**page 10, line 3** *You probably mean "selected" not "measured"*

- We measured a certain  $D_0$ , which was selected; it has the same meaning here. The word was changed.

**page 10, line 4** *"...and high AP precursor concentrations range from 75 to 250 nm." Here is something wrong.*

- The section including this sentence was changed to: “Typically particles are small in the beginning of an SOA experiment, but grow very rapidly during the ozonolysis and stabilize at a diameter of a few hundred nanometers. Several  $D_0$  in the diameter range cross the mode of the size distribution were selected for the H-TDMA and V-TDMA measurements at a time and the diameter range covered was gradually increased to follow the temporal evolution of the mode. For low AP experiments  $D_0$  ranged from 50 to 150 nm and for high AP precursor concentrations the  $D_0$  range was from 75 to 250 nm.”

**page 10, line 5** *"D0 had to be changed if the number size distribution in the smog chamber changed in a way that the D0 of the V/H-TDMA was out of the range or had too few counts." This sounds complicated: D0 was adjusted to have sufficient particles, thus signal.*

- See previous comment.

**page 10, line 23f** *Is 3% volume loss a very small effect? Very small compared to what? What is meant by reorientation? Is NaCl able to form needle-like structures ? 3% impurities seems to be quite a bit; how pure was your NaCl substrate, how pure was the water used for the solution? Could it be that the shrinkage was due to imperfect drying ?*

- We believe 3% change in volume between 25°C and 200°C is a relative small effect. Other substances (see ammonium sulfate, citric acid and SOA) are fully evaporated at 200°C in our system. This means we compare 100% with 3% change and this means 3% is in this context a small effect. The word “reorientation” was deleted, it has a similar meaning as restructuring (which is still there) and refers to the non-spherical crystal structure of NaCl which might be influenced by the higher temperature. It is known from hygroscopicity TDMA measurements that NaCl can show such size-effects due to non-sphericity.

The used NaCl was of good quality: Sodium chloride ultra  $\geq 99.5\%$ (AT) from Fluka, Sigma-Aldrich. The used water was MilliQ water. The RH of the selected particles in DMA1 was  $<10\%$ , we do not

think a shrinkage process due to drying would start to happen at 80/100°C and not below at lower temperatures (see thermogram). It is however possible that impurities are introduced during the nebulizer process, which was going on for several hours. Even clean NaCl solution get somewhat contaminated with impurities available in the gas phase.

**page 11, line 11** *The sentence starting with "Compared..." does not sound grammatically right.*

- The sentence "Compared to literature data the thermogram of the mass fraction remaining from AMS for polydisperse AS in Wu et al. (2009) looks similar as ours, with a rapid decrease of the mass fraction remaining between 120°C and 160°C." was changed to "The mass fraction remaining from AMS measurements for polydisperse AS in Wu et al. (2009) looks similar to our VFR thermogram of AS. It is characterized by a rapid decrease of the mass fraction remaining between 120°C and 160°C."

**page 11, line 18f** *The sentence starting with "In contrast..." sounds odd.*

- The sentence "In contrast to other studies and our V-TDMA there is a thermodenuder study where the diameter of AS decreases at lower temperatures around 75°C, but 150°C is needed to volatilize the particles completely ( $D_0 = 100$  and  $200$  nm) (An et al., 2007)" was changed to "..., where VFR of AS decreases at temperatures around 75°C in our V-TDMA system, 150°C is needed to volatilize the particles with  $D_0 = 100$  and  $200$  nm completely, which is in contrast to other studies (An et al., 2007)."

**page 11, last paragraph** *This whole paragraph sounds complicated. I guess you wanted to say that your instrument works well and comparable to other VTDMA in high temperatures ranges, but you also tested it with citric acid in the temperature range you are going to apply.*

- Yes, this is more or less what we want to say: Our instrument works well and we need relatively low temperatures. However, the curves in Fig. 2 (new Fig. 3) show also the characteristics of the instrument. Due to other reviewer comments we added some other studies to panel C (ammonium sulfate). This illustrates the comparison better than before, where we discussed and compared our results only in the text.

**page 12, line 25** *Neither 40 nor 10 ppb  $\alpha$ -Pinene are atmospheric relevant concentrations.*

*Nevertheless it is a merit to approach low concentrations as close as possible within the experimental abilities. Please, change the text accordingly.*

- The atmospheric relevance refers mainly to the produced organic mass, and thus those AP concentrations produce atmospherically relevant organic aerosol mass loadings in the chamber. The sentence was changed to "We conducted experiments at two precursor concentrations of 40 ppb ("high") and 10 ppb ("low")  $\alpha$ -pinene concentration, resulting in atmospherically relevant organic aerosol mass concentrations."

**page 13, line 2** *Unprecise formulation. Ozonolysis proceeds also with the residual 10%  $\alpha$ -Pinene, thus last as long as there is precursor.*

- This sentence refers to the duration of the ozonolysis period in our experiments. We changed the sentence to: "The ozonolysis period lasted a few hours until at least 90% of the AP precursor had reacted before OH exposure was started (Fig. 3)."

**page 13, line 6** *Too many brackets in this sentence. Please split.*

- The sentence was simplified and brackets reduced as follows: "SOA was exposed to OH aging by either photolysis of HONO or ozonolysis of tetramethylethylene (TME = 2,3-dimethyl-2-butene). The

former method is called "HONO photolysis experiment" throughout this study and the latter "dark OH (TME) experiment" (Epstein and Donahue, 2008)."

**page 13, line 13** *I think you wanted to say that are using the same setup as described by Taira and Kanda, (1990)? Or did you describe your setup elsewhere ?*

- Both the vessel construction and the setup of the HONO system are described by Taira and Kanda, (1990), we added "setup" to the sentence: "The vessel and the setup of the HONO system we used are described elsewhere (Taira and Kanda, 1990)."

**page 15, line 6,** *Do you want to say that thermograms of the single reference compounds are steeper than thermograms of SOA?*

- No, we do not want to say it so generally, because it strongly depends on the single reference compound and we do not mean at all that AS and citric acid are suitable compounds to simulate the volatility behavior of a SOA mixture. It is just seen from these few reference compounds that the AP-SOA volatilization range is much broader than for citric acid and AS and we speculate that the multiple compounds of SOA (which very likely do not all have the same volatility) might be one reason. There are additional possible reasons e.g. decomposition processes or glassy-like SOA that just takes much longer to evaporate (see also references and comments from reviewer 1). We believe the mentioned sentence did state this clearly: "This is a much wider temperature range than for pure citric acid or ammonium sulfate and is explained with different compounds in the chamber SOA possessing volatilities ranging from rather semi-volatile to low-volatile."

**page 15, line 8** *"The SOA produced purely by ozonolysis tends to be slightly more volatile than after aging with OH." What do want to say: it is the same or it is different. Maybe you (always) give numbers and errors with such statements (see comment above). This statement is symptomatic for many others in the manuscript.*

- The SOA thermogram given in Figure 4 presents a broader overview on the SOA behavior at different temperatures. It includes different experiments and data has been obtained during different periods of experiments. Therefore, the VFR's at a certain temperature setting show a relatively large variability. This was the reason for the vague formulation. We deleted this sentence and changed the following two sentences to: "Although the three experiment types (ozonolysis, HONO photolysis and dark OH (TME) experiments) cannot be compared directly as the data were acquired at different stages of the experiments, we fitted our thermograms with an error function. The fitted error function (erf) (Fig. 4, black line), is only valid above 50°C. It is set to 1 as maximum and has the following equation with  $T$  as the heater temperature".

As stated above (see answers to reviewer 1) the thermogram is not the method of choice to compare the detailed temporal evolution and processes of the experiments. The SOA thermogram gives a broader overview on the SOA behavior at different temperature and for different instruments. A more detailed analysis of this SOA thermodenuder data is not intended and would complicate and blow up the paper unnecessary.

**page 15, line 18** *Does this comparison really helps? Huffmann et al. have about the same residence time as you have. So if at all you should match Huffmann et al. data. The simultaneous agreement with Jonsson et al. could indicate that some other parameters are important. E.g. what happens to the vapors in the selecting DMA? Is it possible that some of the vapors are lost here. The same argument which you used for not-needing a charcoal denuder could apply here?!*

- The comparison helps to put our new instrument into relation to other instruments, and shows for instance that differences between the different measurement systems are larger than the differences due to the used "SOA type" (e.g. AP SOA from photolysis or ozonolysis). This implies that absolute values for volatility can only very carefully be compared to other studies and the absolute values should not be over-interpreted. Because of this we focus on temporal, reproducible, qualitative trends rather than absolute values with sophisticated error propagation, which can not be compared in this detail due to individual instrumental characteristics....

There are certainly several reasons for the "mismatch" of different instruments and residence time is just a prominent one (easy to compare and given in the instrument description). Finding and studying all the possible parameters (such as geometry of the heater, employment of charcoal, vapor conditioning/losses in the DMA and/or drier, etc) that lead to these differences is far beyond the scope of this study, therefore we just state some other reasons but do not further discuss them.

**page 17, line 19f and Figure 5** "plotting GF and kappa allows for better comparison" ... of what.

- Please, see answer to the previous reviewer on the GF-kappa comment. The next sentence (after the mentioned one) gives more details about the comparison of hygroscopicity of  $\kappa$  and GF. We write there why we present the hygroscopicity here in a "double" way. We simplified the first sentence to: "The hygroscopicity is presented in Fig.5 (panel D-E) in terms of  $\kappa$  and GF."

**page 18, line 4ff and Figure 10** If this is an important information, why do place it in the appendix?

- The appendix text and figure is moved up (to sect. 3.2/Fig.5) as suggested also by other reviewers (see comments above); there is no appendix in the final version.

**page 18, line 22** In which sense is the wall loss estimate conservative ?

- As noted in the manuscript, the estimated rate of wall loss represents a lower limit, as it assumes no further mass addition when calculating the rate of mass loss to the walls. If there is further mass addition during the period in which wall losses are calculated, then the actual wall loss rate would be higher, and the resulting wall loss correction would result in more OA mass.

**page 18, line 24** On which basis you defined the cut between the regimes?

- The cut in the OH aging period is not sharply defined. The nomenclature of the periods has changed now, which explains the "cut" a bit better. See comments to periods above. It is done based on three criteria, which are discussed in the following section of the manuscript: 1) change from substantial mass increase to non-significant mass change which is the most important one; 2) changes in the trend of volatility; 3) changes in the evolution of the hygroscopicity. This is seen in the concept figure (Fig. 3) and Fig. 6.

**page 18, line 27** What do mean by GF increases slightly? It increase by about 20%?! Isn't that in significant?

- We agree with the reviewer and quantify now the increase of hygroscopicity. The paragraph was changed to: "The hygroscopicity parameter  $\kappa$  (Fig. 6C) increases significantly by more than 30% during the OH induced chemical aging period with substantial mass gain. This indicates the condensation of smaller molecules than the average of previous condensed phase species. The trend of  $\kappa$  levels then off and stays constant during the OH induced chemical aging period. The O:C ratio is constant or slightly decreasing during the ozonolysis, while it correlates well with  $\kappa$  during the OH induced chemical aging period. Thus OH exposure leads to condensation of higher oxidized species

onto the existing SOA. During the period without significant mass gain the O:C ratio remains constant.”

**page 19, line 8** You quote ZSR. In my understanding, the idea of ZSR is to explain e.g. a non-ideal ternary mixture, by an ideal mixture of non-ideal binary sub-systems, wherein the non-ideality of the binary systems is considered at the total ionic strength of the ternary solution. I guess you did not try to estimate activities for your systems. So I think what you did apply is a simple, linear mixing rule. This is fully ok, but has not much to do with the ZSR approach.

- We agree that our approach has nothing to do with estimating activities etc. Thus we removed the “ZSR” as suggested and talk just about “mixing approach”. See answers to comment from reviewer 1 on the same issue (with changes in the manuscript).

**page 19, line 22ff** This is a highly speculative approach with large uncertainties. Therefore the statement “The results are very similar if we assume a constant VFR (0.72, 0.69)” is not enough. Please, give the numbers and discuss the errors.

- The bigger uncertainty comes from the fact that the volume mixing rule is also just a crude approximation. This fact has been addressed in the modified text (see comment of previous referee). We answered already several comments from other reviewers on this issue, please see also the Table with calculated  $VFR_{\text{new}}$  for many experiments in this document.

**page 20, line 4** If this statement is true, wouldn't the presence of a new class of smaller molecules be reflected in the steepness or the shape of the thermograms? Did you see such an effect?

- This effect was not observed during the thermograms simply for the reason that during this time of interest (the first few hours of OH exposure) no thermograms were done. Thermograms were typically done at the end of the ozonolysis or at the end of the entire experiment to avoid large data gaps in the temporal evolution data at one temperature, which was the primary focus of these experiments.

**page 20, line 21** “During the second phase, the OH mediated ripening  $\kappa$  increases just slightly but stays almost constant.” This is an unclear statements. Does it mean a small but significant increase or no change? If the first, how much increase?

- The statement was clarified as: “The  $\kappa$  values start at 0.07 - 0.12 and increase to 0.10 - 0.15 during the OH induced chemical aging with substantial mass gain. During the second period (after about  $8 \times 10^6 \text{ cm}^{-3} \text{ h}$ )  $\kappa$  stays more or less constant.”

**page 21, line 11** This first sentence of the paragraph signals to me not to expect too much from these correlations of VFR and GF. Was that the intention? Does the correlation analysis help to understand the evolution of the aerosols or not?

- No, it was not our specific intention to lower the expectations. As shown until this point we observe correlations and anti-correlations between VFR and  $\kappa$  depending on the dominating aging mechanism. Therefore, we asked ourselves if an overall trend might still be seen. It is interesting to see that overall a general correlation between VFR and  $\kappa$  is observed when the aging is pushed very far. However, the subtle variations are then buried in the bulk (see next question of the reviewer).

We modified the first two sentences: “Here we present  $\kappa$  and VFR in direct relationship to each other. We do it separately for the different periods as there can be a correlation or anti-correlation depending on the period. Figure 8A shows for all available ozonolysis experiments (14 in total) a good ( $R^2 = 0.80$ ) correlation of  $\kappa$  and VFR. The observed scatter is attributed to different experimental conditions and

periods. The correlation is determined by the strong trends in  $\kappa$  and VFR during the O<sub>3</sub> induced condensation period.”

**page 21, line 14** *Where can I see this anti-correlation in Figure 8 ?*

- Please see also the answer to the same issue of reviewer 1. We mentioned earlier that the anti-correlation is buried in the scatter plot. With the improved Figure 8 (specifically Fig. 8B), we show the anti-correlation of VFR and  $\kappa$ . A small section about Fig. 8B was added to the manuscript (see previous comments).

**page 21, line 17** *What is meant with "the correlation with R<sup>2</sup> = 0.8 is fair" ? Do you a priory expect the same functional change of VFR and kappa when the particles are formed or ageing ? Does your result imply that with exception of the OH condensation phase, kappa and VFR are linearly correlated. What would that mean?*

- “Fair” relates to the correlation coefficient R<sup>2</sup>, where >0.9 means very good, <0.4 rather bad and therefore 0.8 is quite ok, good or fair. We changed the sentence to: “The correlation is good (R<sup>2</sup> = 0.80) and the observed scatter is attributed to different experimental conditions and periods.”

We do not expect a priory that VFR and  $\kappa$  are linearly correlated. The relation depends on which mechanism dominates aging. The expected effect of each mechanism like functionalization, oligomerization or fragmentation on this relation is summarized in Table 1. Many parts in the manuscript have been changed due to other comments, which address also this question.

**page 21, line 22** *"Lights on" experiments were not introduced in the experimental section. Please, do so.*

This is true. The following section was added to the experimental section (2.3): “TME ozonolysis is the OH source in dark OH (TME) experiments, however in some of these experiments we turned the lights on in the smog chamber to increase the OH source from photolysis of ozone during a part of the experiment. We introduced also additional experimental conditions with turning lights on and off during some experiments; one TME experiment was partly performed with UV lights on. All experiments with these special light conditions are commented in Table 2.”

We also added the following sentences to the manuscript, where those experiments are discussed in the result section (3.4): “In some dark OH (TME) experiments we turned the lights on (and off) in the smog chamber to have an additional OH source. The idea was to check the influence of light and higher OH exposure on the aging process.”

**page 22, section 3.4.1** *This experiment was not introduced in the experimental section. Please do so. How did you determine the increased OH production? Could photolytic processes cause the changes observed in the gas phase or the particulate phase?*

- The experiment was added to the experimental section (see previous comment). UV light also photolyses ozone and in this way produces additional OH radicals. The principle of OH determination remains the same. The OH tracer 3-pentanol showed a strongly enhanced rate of consumption. According to 3-pentanol the OH concentration increased by a factor of 35. We do not think photolytic processes caused the observed changes, but we do not think a deeper analysis and discussion of this special case experiment is helpful.

**page 22, line 27** *What do you mean with "Usually several DO, not too different from each other, are selected in.."?*

- The “usually” means in most of the experiments. For just few experiments the increase of mass was so rapid (resulting in rapid changes of the size distribution) that these overlapping of several diameters could not be performed. The TDMA can not measure several diameters at the same time, but only sequentially. See also changes and answers to previous comments (also from reviewer 1) about the selected  $D_0$ .

**page23, line 23** *Did you detect the increased OH levels? How much was the increase?*

- From the three experiments with TME + lights, we used once the strong UV lights (Xe lamps without filter) and once the lights were turned on 18.5 hours after the OH production started. At that stage no OH tracer could be used anymore. For the remaining experiment we find an increase in the OH exposure of about 15 to 55% when turning the lights on. This increase in the OH concentration was expected, since the excited oxygen (from the photolysis of ozone) reacts with  $H_2O$  and forms OH radicals.

**page 23, line 24** *"Thus, VFR stays constant." Probably you wanted to say something different. Increase of OH induced SOA production should decrease VFR, does it?*

- VFR does not decrease but the increasing trend is stopped. We rewrote this part to read: “In case of the TME experiment (No. 14) turning lights on enhances the OH exposure and more SOA mass is produced. VFR does not decrease as expected but the increasing trend is stopped and VFR remains constant (best seen for small particles).”

**page 23, line 29** *typo "as"*

- Corrected, but sentences before changed as well to: “Since further condensation is small now and SOA mass gain is not significant anymore, the non-condensational chemical aging processes become dominant again. Another lights on period after 6.6 h does somewhat slow down the increasing trend. This may be expected because at this time not much additional condensation was observed.”

**page 24, line 3** *kappa decreased by more than 10%. Is that "slightly"?*

- We agree that the decrease in the mentioned experiment No.5 is clear and significant. We removed the sentence before “The effects on  $\kappa$  are less pronounced” and quantified the decrease. The sentence reads now: “In general  $\kappa$  (panel C) increased with OH exposure while without OH exposure, when lights were off (experiment No. 5, 2 - 4 h)  $\kappa$  decreased by about 10%.”

**page 25, line 13** *There is no thermogram of Qi et al. 2010 in Figure 4. What do you mean by slightly lower VFR ? The same within the errors ?*

- Conclusions were changed, the sentence reads now: “We conclude that the organic aerosol is continuously evolving once the SOA mass has been formed. Qi et al. (2010) also observed a steady change of hygroscopicity, volatility and chemical signature in photooxidation experiments of AP and xylene over many hours.”

**page 26, line 9f** *A lot of weak qualitative statements in this sentence, as mentioned several times above. Please, be precise. Does e.g. "more or less stable" means constant with in the errors of +/-xy?*

- The “more or less constant” was removed and the “summary and conclusions” section was significantly changed and rewritten.

**page 26, line 17** *NO<sub>x</sub> independence is a result not a conclusion. It was neither shown nor discussed in the result section.*

- The NO<sub>x</sub> independence is actually shown in all plots where we do not see any general differences between HONO high/low NO<sub>x</sub> experiments. Maybe we mentioned this not very clearly, but it was already in the manuscript in the context of Fig. 7 (Sect. 3.3): “The type of OH source, dark OH (TME) and HONO photolysis does not show differences in the particles’ hygroscopicity or volatility behavior. This also indicates that high or low NO<sub>x</sub> conditions during HONO photolysis experiments have no clear influence on  $\kappa$  and VFR (see Table 2).” The fact of non-existing systematic differences between the high or low NO<sub>x</sub> conditions experiments in Fig. 7 is probably the best illustration. However, this “NO<sub>x</sub> independence” is an interesting finding, but not the major focus of this study.

**page 34, Table 1** *hygroscopicity "/"  $\kappa$  ?*

- Was changed to “hygroscopicity ( $\kappa$ )”.

**page 37, Figure 2** *"[-]" in axis label? Can you compare with VTDMA results of other groups for these compounds ?*

- The [-] just stresses that this axis/parameter has no unit. We did that consequently in all our axis labels of all figures.

A comparison to the results of other groups concerning AS was already done in the text. We mentioned several other studies and temperatures ranges. To illustrate this comparison better we added AS thermograms from some other studies (we use the same studies later for a SOA comparison in Fig. 4) to the panel C of Fig. 2 (former Fig 2, now Fig 3). This allows a direct comparison with our AS thermogram. Thus we now show the comparison to other groups in the Figure and discuss it in more detail in the text.

**page 38, Figure 3** *Does O<sub>3</sub> also drops in case of photolytical OH production ?*

- The O<sub>3</sub> is clearly decreasing in the TME experiments because it is reacting with the TME. For the HONO experiments O<sub>3</sub> is not decreasing that strongly, but slowly. It depends somewhat on the experiment conditions and duration.

**page 39, Figure 4 caption** *Shift "(circles)" to the end of the first sentence*

- Done.

**page 40, Figure 5 Legend:** *Please, omit to name the colors. Captions: What is meant by "The vertical lines indicate roughly the 90%-AP-reacted value..." ? Please, give a range like e.g. 85-95%?*

- Colors “blue” and “orange” were deleted from the caption. The vertical line help to guide the eye where the 90%-AP-reacted value for the 4 different experiment types is. The data of AP reacted in % are given for each experiment in the upper panel (A or new A1). A range is now given in the legend as follows: “The vertical lines in panel (A) indicate roughly ( $\pm 5\%$ ) the 90%-AP-reacted value for the four main experiment conditions:...”.

**page 41, Figure 6** *According table 2 the experiments 4 and 7 are also different in NO. Could that have an effect ?*

- The low AP HONO experiment No.4 has no additional NO in contrast to the high AP HONO concentration (No.7) experiment (both in Fig. 6). Both experiments behave very similarly. Experiment 7 also compares well with the other high concentration experiment to other experiments with high AP

concentration, experiments without additional NO. Experiment 3 would also support this, but we excluded this experiment completely from Fig. 7 due to some experimental issues in the course of the experiment.

**page 42, Figure 7** *This figure signals me that the variation from experiment to experiment is about the same as the variation within the experiments, but overall the effects on VFR and kappa are small. How significant are the changes. It would be helpful to indicators the errors of measurements.*

- We added error bars to Fig. 7 showing the reproducibility of the measured parameters, which show that the observed changes are significant in most cases. The variability from experiment to experiment is relatively high due to several conditions and small changes within the smog chamber experiment. For further details see also answers to comments above and from reviewer 1.

**page 44, Figure 9** *I suggest to skip the size dependence in the Figure. The analysis in section 3.5 shows that it is a kinetic effect. The different symbols are difficult to distinguish, anyhow. Then the "light on" effects will become clearer. The O:C ratio in panel D for this Figure is not discussed in the text. It looks constant within the errors for both cases. How comes that the processing does not reflect in in the O:C ratio.*

- We believe it is also interesting to visualize the size dependence. Several comments and questions deal with the error bars and uncertainty we have on the measurements. Here it is seen that the VFR would look much noisier (with more scattering) if we combined the different measured diameters in one trace and hide the size information. Exactly this is the case for many Figures and indeed had to be done in order to have a complete temporal evolution and not totally confusing the plot with size information (see also details on sequential measured different  $D_0$ ); examples are Fig. 4-7. This kinetic effect on the VFR data is for most experiments less visible (due to chosen  $D_0$ ) than in Fig. 9. See also other comments on Fig. 9.

We agree that the O:C ratio in Fig. 9 D was not properly discussed. The following section was added to the discussion of  $\kappa$  and reads now: "The effects on  $\kappa$  are less pronounced. In general  $\kappa$  (Fig. 9C) increased with OH exposure while without OH, when lights were off (experiment No. 5, 2 - 4 h)  $\kappa$  decreased significantly by about 10%. The O:C ratio correlates well with  $\kappa$  and shows for the dark OH (TME) experiment an almost constant and slow increase to values of 0.48 - 0.5 (Fig. 9D). The increasing trend for the HONO photolysis experiment (from about 0.46 to 0.52) is less visible due to relatively high noise caused by the small organic mass concentration in this experiment. The O:C ratio seems to be less sensitive to the lights on/off effects compared to VFR and  $\kappa$ . This has partly to do with the large noise of this parameter due to the low particle mass concentration in this low AP experiments."

**page 45, Figure 10** *I think this is an important Figure and should not appear in the appendix. It gives the most clear overview about your experiments (see comment above).*

- Yes, we agree. Figure 10 is moved and the appendix removed; see other comment above.

#### ***Typos and Corrections:***

*Equations should be indented.*

- The manuscript was written with the official Copernicus ACPD style in LaTeX and we assume this will be either changed for the final version or is wanted like that by the publisher.

*Units are given in smaller font size ?!*

- The manuscript is written with the Copernicus template and all units are written as follows in the LaTeX code: e.g. “ $8 \times 10^6 \text{ cm}^{-3} \text{ h}$ ”; we suppose this is the correct way for this journal.

### **Anonymous Referee #3** (Received and published: 29 April 2011)

*This manuscript describes laboratory experiments aimed at understanding the “aging” (chemistry that lead to changes in physical properties) of secondary organic aerosol (SOA). In a very nice set of chamber experiments,  $\alpha$ -pinene is oxidized by ozone, and after some time the resulting reaction mixture is then oxidized further by OH radicals. The data (including volatility, hygroscopicity, aerosol growth, and O:C ratio) are interpreted in terms of both condensation (SOA-forming) processes and “ripening” reactions. The overall goal of this work (understanding OA aging) is very important, the experimental approach is quite nice, and the data seem to have been very carefully collected and analyzed. However I have several concerns about the interpretation of the data – the authors make many assertions about the underlying chemistry that either are not explained well or do not appear to be supported by the experiments. Additionally, I had difficulty following the various arguments made; a large number of experiments with several variables (pinene concentration, O<sub>3</sub> concentration, light, OH source. . .) are described, but without enough organization to make the key points of the work clear. (The Summary and Conclusions section certainly helped with this, but many of the previous sections, like 3.1, 3.4.1, and the first part of 3.5 still seem tangential.) This paper thus needs major revision (possibly with additional experiments) before it can be published.*

- We thank the reviewer for the comments and evaluation of the paper. We agree with the reviewer that the presented experiments have a large number of variables which cause a certain degree of complexity. In addition, several chemical and physical parameters are presented in a combined way. As the reviewer stated the number of experiments is large and we believe there are no additional experiments needed. We will work out more clearly the key points but the complexity of the finding can not be completely avoided. We will address each comment in detail below and apply the corresponding changes to the manuscript.

#### ***Specific comments follow.***

*1) Throughout the paper, the authors assert that observed physical/chemical changes are related to the presence of oxidants, but no control experiments (studies of what happens in the absence of these oxidants) are ever described. For example, references are made to “O<sub>3</sub> mediated ripening”, but with no evidence that ozone has anything to do with it – possible processes that come to mind include oligomerization, or loss of certain species to the chamber walls. The authors provide no evidence that O<sub>3</sub> is in any way involved, so I don’t see why this can be called “O<sub>3</sub> mediated”. The proper control experiment would be to run the experiment in an excess of  $\alpha$ -pinene, so that SOA in the absence of O<sub>3</sub> can be studied.*

*Similarly, for OH: what happens when the lights are turned on, with no HONO added? How are the authors sure that the extra organics added to the chamber (pentanol and TME) are playing no role in the observed physical/chemical changes?*

- In agreement with both other reviewers the name “O<sub>3</sub> mediated ripening” was changed, actually all 4 reaction periods were renamed (see manuscript and Fig. 3 (new Fig. 1)). It was never intended to claim that O<sub>3</sub> is responsible for the ripening process; it was rather used to contrast it to the OH chemical aging period (which follows after the ozonolysis). Please, see also the detailed answers to the similar reviewer comment (1+2).

We did a control experiment in an excess of  $\alpha$ -pinene and did see a similar ripening in the AMS (unfortunately only AMS data were available, but no V/H-TDMA) as for the normal ozonolysis experiments.

Experiments without HONO were also done (e.g. No. 9+10) and no significant differences in hygroscopicity and volatility compared to the HONO experiments were seen. There was still some OH production from ozone photolysis but at a lower level. However those experiments are presented only partly due to instrumental restrictions (lower RH in one experiment or additional light on/off conditions). We also did not want to add another category to blow things up more. We restricted our results mainly to the HONO and TME experiments.

Pentanol and TME have been used in chamber studies for years and they have no substantial aerosol yield. Dark OH (TME) and light OH experiments behave quite similar indicating that TME oxidation products have a negligible effect.

*2) I don't understand the need for introducing the new term "ripening" to the SOA lexicon. In addition to it being a rather silly word, it's unclear how it is in any way different from "aging" (which is in the title of the paper). If the authors insist on using this term, its definition needs to be laid out in detail, and the differences between "ripening" and "aging" need to be explicitly discussed.*

- We believe that the introduction of this new term is useful because the processes during "ripening" and "OH induced chemical aging" are different (as presented in this paper). Calling all processes simply "aging" does not help to distinguish the different complex mechanisms and reactions involved in SOA aging. The different naming is in this sense helpful and clarifying. One main feature of ripening is the nearly constant SOA mass after some hours in the dark period (ozonolysis) and a steadily evolving mass spectrum (in the AMS) and decreasing volatility while no further oxidation by ozone is expected (as was also shown in the control experiment, see below). See also the detailed answers to the comments on ripening from the other reviewers.

*3) Based on the data presented it's not clear to me that "ripening" (from O<sub>3</sub>, OH, oligomerization, etc) ever actually occurs. It's defined (p. 7424, lines 17-18) as changes in the properties of the aerosol that are not accompanied by changes to particle mass. But given that the authors feel their wall loss estimates are "conservative" (p. 7740, line 3), is this criterion ever actually met? Might the flat mass loading in the ozonolysis reactions actually be increases in aerosol mass? Even without an increase in the wall loss correction, for OH aging, mass very clearly goes up continuously (top right corner of Fig 6). Why is this interpreted as ripening?*

- The new term "ripening" is now only used for the second period of the ozonolysis and not anymore for the second part of the OH aging. The wall-loss correction during ozonolysis is quite good and easier than during the OH aging period. Since we did some fairly long ozonolysis experiments the reaction has gone to completion and any further mass gain is not expected. Further details on the chemical processes during ozonolysis and specifically the ripening will be presented in DeCarlo et al. (in preparation). See also other answers to comments on ripening.

*4) The figures are very busy and hard to read/interpret. Part of this arises from the differences in y-axes, x-axes, and symbol/color conventions, even when the figures were quite similar (e.g., Figures 5-9). Standardization of these would help a lot. Additionally, many of the changes in the various parameters measured (O:C, kappa, VFR, loading, etc) are quite subtle, and are very hard to make out given the highly condensed y axes and overlain datasets. Multiple side-by-side plots with aspect ratios of 1:1 would be far easier to read and interpret; some data averaging could help as well.*

- We worked on most Figures with the specific comments given also by the other reviewers. We discuss the harmonization, averaging etc. in several comments in detail (please, see answers to other reviewers). Briefly, we disclaim averaging our data because the variability between the experiments is

too large (see different experimental conditions) and would smear out trends. The focus is on the relative changes with aging. We believe showing single (temporal evolutions of) experiments with the same or very similar trends is the best support for our hypothesis and the deduced chemical mechanisms and processes. The summarizing Figures 5 and 7 should merely support Figure 6 in that trends are basically similar everywhere. We do not think this is better achieved with multiple small Figures.

The colors and symbols have to be used in a different way in many cases as too many variables and parameters are involved: e.g. color represents O<sub>3</sub> conc. (Fig.5), different experiments (Fig. 6, 7A+B, 9), mass loading (Fig. C+D) and temporal evolution (Fig.8). We are convinced it is impossible to use a simple convention on symbols and colors and present the same information.

***Other comments:***

*Ozone has previously been shown to cause physical/chemical changes to organics with no C=C double bonds, presumably due to additional oxidation reactions [Shilling et al., JPCA 111:3358, 2007]. That earlier work seems highly relevant to the present studies, and should be discussed here*

- Apparently ozone can oxidize aldehydes to acids. The reaction rate is 1000 times slower than with alkenes in the bulk phase. This could be a mechanism for ripening, but a control experiment is not favouring this mechanism (see answer to other comments for details).

The following sentences were added to the end of section 3.2: “Shilling et al. (2007) observed that O<sub>3</sub> can heterogeneously oxidize aldehydes to acids which would decrease VFR and increase κ (as dissociation of acids increases the van’t Hoff factor). A control experiment with excess of AP during the ozonolysis shows in the AMS the same chemical changes as with an excess of O<sub>3</sub>. This does not support heterogeneous oxidation as the cause of this steady increase of VFR. At present we do not have an explanation for this evolution of the SOA. We call this unspecified process or processes ripening of the SOA.”

***P. 7425, line 14:*** Volkamer et al 2006 utilizes a box model, not a chemical transport model.

- We added “box model” to this sentence. It reads now: “State-of-the-art chemical transport and box models cannot reproduce the measured ambient organic aerosol concentrations (i.e. directly emitted primary organic aerosol (POA) and SOA formed from various precursors) with currently known chemical and physical mechanisms (Volkamer et al., 2006; Hodzic et al., 2010).”

***P. 7426, lines 7-8 and P. 7427, lines 15-16 (and Table 1):*** for aging/ripening, an important set of reactions involve conversion of one functional group to another. Assuming this is considered a “functionalization” reaction, changes to volatility, hygroscopicity, etc are not always fixed: for example, the oxidation of an alcohol group to a carbonyl group involves an increase in vapor pressure and a decrease in hygroscopicity. Also, fragmentation reactions will generally increase solubility (consider acetaldehyde fragmenting to form formaldehyde), whereas oligomerization reactions will generally decrease it.

- Such a process would only be the conversion of an alcohol group to a carbonyl group. Both, the conversion of an alcohol or carbonyl group to an acid group would increase the O:C ratio and lower the volatility. The alcohol/carbonyl conversion is minor in the gas phase. Thus, overall functionalization and fragmentation are the dominant processes.

Please, see also comments on this topic from the other reviewers, we modified this section in the introduction about the processes and volatility as follows:

“Formation of SOA involves oxidation of semi-volatile vapors from primary emissions to less volatile species which partition into the organic aerosol. In a simplified picture we start with a pure volatile hydrocarbon species which is oxidized to different first generation oxidized products of a large range of volatilities. From the low volatility species a secondary organic aerosol is formed while the volatile and semi-volatile species form a large pool of organic mass in the gas phase in equilibrium with the particle phase. This aerosol can be further processed which is called aging and includes various processes changing the properties of the particles. Most of the oxidation will take place in the gas phase and generate more SOA via further functionalization (adding more oxygen to the carbon backbone) or fragmentation upon oxidation of the semi-volatile gases. Heterogeneous oxidation is much slower than gas phase oxidation due to mass-transfer limitations. Heterogeneous reactions include functionalization and fragmentation as well as some transformation reactions of functional groups (alcohol to carbonyl). Additional reactions in the condensed phase such as oligomerization have also been observed (Kalberer et al., 2004). Functionalization and fragmentation lead to an increase in the O:C ratio while oligomerization may increase or decrease it depending on the process (Reinhardt et al., 2007). Functionalization always decreases volatility while fragmentation forms species in a wide range of volatilities albeit mostly at lower volatilities. Oligomerization converts monomers to larger, less volatile compounds. The expected effects of the three main processes on particle volatility are summarized in Table 1.”

**Table 1:** *what does the last column mean?*

- The last column in Table 1 is named “fragmentation”. Fragmentation reactions are chemical processes that “break” larger molecules and lead to smaller species (more volatile molecules which are less likely to partition to the particle phase). For illustration of the fragmentation process (and oligomerization and functionalization) see e.g. Fig. 4 C in Jimenez et al. (2009).

**P. 7427, line 27:** *these three processes are different than the three discussed in the previous several paragraphs.*

- Besides functionalization, oligomerization and fragmentation also condensation occurs during aging. We do not specify all possible processes anymore and changed the section, see above comments.

**P. 7428, lines 22-24:** *of what magnitude was the wall-loss correction? (20%? 100%? 300?)*

- The wall loss correction is highly time dependent and the ratio of measured organics to wall loss corrected organics increases throughout the course of our experiments. As a point of reference after ~8 hours after the initial input of alpha pinene, the wall loss corrected organics concentration is approximately 2-3 times higher than the measured concentration of organic aerosol.

**P. 7428, lines 24-25:** *how was the collection efficiency (CE) of the AMS computed? Was the possibility of changes to the CE upon aging investigated?*

- Collection efficiency in the context of this study is of minor importance since the analysis deals with the bulk properties (O:C ratio and mass spectral features) and relative concentrations, but not the absolute concentration. However, the collection efficiency of the AMS was investigated by comparison of the AMS mass converted to an approximate volume using a density of  $1.25 \text{ g cm}^{-3}$ . The resulting AMS calculated volume compared well with the volume calculated by integration of the SMPS number distributions assuming spherical particles, indicating a collection efficiency of 1. No attempt was made to investigate changes in CE with aging of the aerosol.

**Section 2.3:** *what are the temperature and RH of the chamber? Do these change with reaction time, lights, etc?*

- In section 2.3 (p.7434 line 23) “In all experiments, the clean smog chamber was humidified to ~50% RH and in a first step O<sub>3</sub> was added.” Both temperature and RH stay stable during the experiment. Turning on the lights can be seen due to a small temperature change (+1°C) which affects of course also the measured RH. Otherwise the RH is constant at the initial conditions because there is no dilution or anything else added to the chamber, which could decrease RH. The sentence was changed and additional information are given: “In all experiments, the clean smog chamber was humidified to ~50% RH at a temperature of 21+/-1°C and these conditions stayed stable during the course of experiments. In a first step O<sub>3</sub> was added to the chamber.”

**Fig. 3:** *The OH trace is misleading, as OH is not zero during the ozonolysis phase – it almost certainly plays an important role then.*

- We are aware of an OH contribution also during the ozonolysis and this was mentioned in the text e.g. “The OH formed by the ozonolysis will mainly react with the AP, as long as this is still present in excess.” The OH during the ozonolysis was not included in the OH trace of the concept figure, because this is based on our OH data based on the PTR-MS measurements.

According to model runs with the Master Chemical Mechanism v3.1 (MCMv3.1) the OH concentration is highest in the very beginning, right after the AP injection. In this stage AP is still available in excess. Already after 30 minutes the OH concentration becomes a fractional amount of its peak concentration.

A model run with 40 ppb AP and 500 ppb ozone reveals that the OH exposure for the two hours ozonolysis period is about  $2.8 \cdot 10^6 \text{ cm}^{-3} \text{ h}$ . This corresponds to less than 1 hour of lights on.

Model runs with MCMv3.1 show that OH reacts with about 30% of the  $\alpha$ -pinene during the ozonolysis phase. Thus OH does not play an important role during the ozonolysis period.

In the new manuscript the OH concentration was added in the concept figure to the ozonolysis period. The above sentence was replaced by: “As no OH scavenger was used about 30% of AP will react with OH radicals based on model calculations.”

**P. 7434, line 11:** *The authors mention two mechanisms of “ripening”, but several more seem possible. Slow oligomerization, photolysis, thermal decomposition, etc.*

- Yes, there are additional possible reactions. We do not make an exhaustive list of all possibilities. We changed the sentence by mentioning generally “condensed phase reactions like oligomerization”. It reads now: “The former process increases the SOA mass by definition, while the latter keeps the SOA mass roughly constant and may occur either by heterogeneous reactions on the surface of the SOA particles, condensed phase reactions like oligomerization or by an evaporation – gas-phase oxidation – recondensation cycle.” The similar sentence was also adapted in the abstract.

**P. 7435, line 1:** *After a couple hours, pinene is no longer in excess, so OH will start reacting with other species. (OH+ $\alpha$ -pinene is not terribly fast, with  $k=5e-11 \text{ cm}^3/\text{molec}/\text{s}$ , so OH+aldehydes will be able to compete). As a result, the assertions that there are only first-generation products around at the end of the “ozonolysis phase” of the reactions (e.g., p. 7440, line 14; p. 7447, line 20) is quite misleading.*

- This is true, there is a certain small fraction of secondary oxidation products. We do not say that there are exclusively first generation products. After a couple of hours the AP is depleted completely and this means as well that there are no more OH radicals from the AP ozonolysis. See also comments above to OH traces and exposure.

We changed the first sentence in chapter 3.3 (on former p. 7440) to mention that there are not exclusively first generation products: “During the first period of the experiment the precursor was removed by ozonolysis, forming mainly first generation and a fraction of second generation gaseous oxidation products, as well as a certain mass of SOA.”

p. 7447 has been rewritten because of other comments.

**P. 7435, line 18:** *what was the initial concentration of the TME?*

- During ozonolysis no TME was in the chamber. For OH aging TME was continuously added to maintain a concentration of 0.5 to 1.5 ppb depending on the ozone level. The sentence reads now: “TME was continuously injected from a gas cylinder (Messer, TME 1000 mol ppm in N<sub>2</sub> 5.0) at a flow of 10mL/min to maintain a TME concentration between 0.5 – 1.5 ppb. “

**P. 7435, lines 22+:** *the use of four separate metrics to describe reaction time is very confusing, and makes the reading of the plots (which use all four as x axes!) quite difficult to intercompare. Can these be simplified in any way?*

- According to the other reviewer’s suggestions we moved Fig. 5 and Fig. 10 from the Appendix next to each other. This allows a direct comparison of the two time axes “time after AP injection” and “O<sub>3</sub> exposure”. The section where we introduce the different time axes was changed. We see the difficulty of using several time axes, but there is in our opinion no way to avoid this complexity (see also comments above). Each time axis was chosen in a way to present the data best and while trying different normal/”physical” time axes we realized that there is also the need to show data on a “chemical clock” axis as e.g. OH exposure.

We introduced this “complexity of time axes” already in the concept figure to make the reader somewhat familiar with it in order to help and support the understanding of the results presented later. Here it seems maybe extra load, but later for the results it is really helpful and necessary.

**P. 7436, line 2+:** *why was pinonaldehyde decay and not pentanol decay used? Were the data corrected for possible photolysis or wall loss of pinonaldehyde?*

- The pentanol was finally not used as OH tracer due to interferences in the mass spectra, while pinonaldehyde could serve as suitable OH tracer. Details and plots to this OH tracer are the topic of another paper (Barnet et al., in preparation). The data of pinonaldehyde were not corrected for photolysis or wall losses. We consider the photolysis of pinonaldehyde as negligible. For further details and explanations see answers to reviewer 1, the manuscript was adapted as well.

**P. 7436:** *the units h/cm<sup>3</sup> seem a little strange. I would recommend h molecules/cm<sup>3</sup>.*

- The units h/cm<sup>3</sup>, h molecules/cm<sup>3</sup> or h #/cm<sup>3</sup> have exactly the same meaning we choose cm<sup>-3</sup> h. Accordingly, particle number concentrations are given in cm<sup>-3</sup> (and not in particles/cm<sup>3</sup>).

**Section 3.1 and Figure 4:** *I would suggest removing this section, as it seems only tangentially related to the overall paper (which is about aging). The key to this work is how the aerosol properties change in a given experiment (the “large vertical error bars”), not how they compare to each other or to results from other studies.*

- It is somewhat true that Fig. 4 is not the core of the paper. But in the same way as Fig. 2 it helps to characterize the V-TDMA properties and behavior not only for salts, but also for SOA, which is more complex. The volatility/VFR is just a relative measure which can not be transferred easily to an absolute value like vapor pressure. We believe it is also essential to present the characteristics of the

instrument (it was not described anywhere else before). The thermogram of the SOA gives little information on the processes (which are the main topic of this paper) but it shows the important characteristic of the analyzed SOA at different temperatures (in our and in other instruments). One reviewer asked to add more studies for comparison to Fig.4 showing that it is not at all irrelevant. We need the thermogram of SOA also to justify the choice of 70°C for the presentation of the temporal volatility measurements. All this information is presented and discussed in Section 3.1 and Fig. 4. See also answers and comments for other reviewers on the same topic above.

**Fig. 6:** *why are similar plots for TME+O<sub>3</sub> not shown?*

- The experiments show the same trends and it does not matter if the OH source is HONO photolysis or TME ozonolysis. In order to show only the necessary things and not too many data and details (as asked by all reviewers) we believe it is not necessary to show TME experiments. Again, within the HONO and TME experiments might be differences in the magnitude of the effects due to different reasons/experimental conditions, but the trend is the same.

**Fig. 6:** *the grey dotted lines seem a bit misleading, as they don't always go through the data terribly well. Linear fits for the different regions are needed.*

- We agree that these lines are not fitting very well. This was the reason why we decided not to use linear fits (for the grey dotted lines in Fig. 6 C) but simply trend lines to guide the eye. The linear fits were extremely depending on the selected range. We adapted the trend lines to fit the data better and have less overlapping.

**P. 7442-3, lines 28+, and P. 7448, lines 16-18:** *I simply don't agree with the authors' assertions that the OH source doesn't make a difference. From Table 2, the drop in VFR for the TME data is far less pronounced than for HONO. (This would be more obvious if a version of Figure 6 for the TME+O<sub>3</sub> experiments was presented.)*

- The VFR<sub>new</sub> for all experiments was calculated as suggested by the other reviewers and it shows no difference due to the OH source (see Table in this file). A comparison of the data in Table 2 should be done carefully because the data are presented for certain hours (not averages) and they have different "chemical reaction stages". Please see the discussion above about different time axes. The correct way to compare the different experiments is done with the "chemical clocks" O<sub>3</sub> exposure (see Fig. 5/old Fig. 10) and OH exposure (see Fig. 7). By doing so, we observe no distinct differences in the HONO and TME experiments. Again, the temporal evolution of each experiment is important, and variability between the "same kind" of experiments and "other" experiments exists due to the variable experimental conditions.

**Figure 8:** *why are no HONO data shown?*

- Please, see also answers to reviewer 1+2 on Fig. 8 and the  $\kappa$  – VFR anti-correlation. Within comparable experiment times HONO and TME experiments look similar. But we decided to show the TME experiments, because they were (by chance) longer and therefore the trends are somewhat better visible. Especially with additional lights on (=additional OH) in the TME experiments we see an interesting trend (stronger increase in hygroscopicity than in VFR) in the correlation plot. We improved Figure 8 and added an additional panel to show the anti-correlation of  $\kappa$  and VFR (new Fig. 8B). This is just possible for the beginning of the OH induced aging period, so we selected just the first hour for all HONO and TME experiments. Thus HONO data are now included in Fig. 8.

**P. 7445, lines 16+:** *This paragraph seems unrelated to the title of the section it is in (“Ripening and size dependence”).*

- The section title was changed to “SOA aging - a closer look”. The term “ripening” is not anymore used for the OH induced aging period (see other comments on renaming the 4 periods).

**P. 7445, lines 23-24:** *I don’t understand the chemistry here; to my knowledge there is no evidence that  $O_3 + TME$  generates more OH in the presence of light. Was there an inferred increase in OH from pinonaldehyde decay? If so, could this have arisen from pinonaldehyde photolysis? (If this is the case, it would suggest that light, and not necessarily OH, is responsible for the observed changes.)*

- Ozone and TME produces OH and the light produces additional OH. Pinonaldehyde photolysis produces  $HO_2$  radicals which will react with  $O_3$  to produce OH. This is also the case for methylglyoxal, for example, which is a product of TME ozonolysis. To some extent OH is also produced from  $O_3$  photolysis by subsequent reaction of excited oxygen ( $O^1D$ ) with  $H_2O$ . There might be other possibilities; however, this chemistry is not in the focus of the paper, we see the “additional OH effect” clearly in VFR and  $\kappa$ . See also comments above where we discuss this issue, and state that we find an increase in the OH exposure of about 15 to 55% in TME experiments when turning the lights on.

**P. 7447, lines 26-27:** *increased OA mass will lead to more volatile compounds partitioning into the aerosol, not necessarily “smaller” compounds. While the higher volatility can arise from smaller size, it can also be from lower polarity, which would imply a lower kappa value.*

- We agree with this comment. The “smaller compounds”-hypothesis is motivated by the observations of the volatility and hygroscopicity behavior. As the reviewer state, lower polarity can cause higher volatility, but also lower  $\kappa$ , which would be exactly in contradiction with the reported observations presented in Fig. 6, for example: we see volatility increasing (decreasing VFR in 6B) and  $\kappa$  increasing as well (6C). From both we concluded that most likely “smaller” compounds are a reasonable explanation.

**P. 7448, lines 4-5:** *the O:C changes are rather subtle, when compared to the changes in particle mass, so I think it’s not accurate to call the newly condensed organics highly oxidized.*

- As the reviewer states just in the above comment at higher mass concentrations compounds with a lower oxidation degree could partition to the aerosol phase. The fact that the O:C however increases shows that these compounds must be more oxidized. The “highly oxidized” has to be seen in this context. During this OH induced condensation period both the hygroscopicity and the O:C ratio increase. All this indicates that fairly volatile, small and highly oxidized compounds, which are produced by functionalization and fragmentation are condensing during this phase.

*The Summary and Conclusions section could be strengthened further with a “cartoon” that illustrates the key processes involved.*

- The Summary and Conclusions section was completely rewritten. We believe that the processes should now be understandable from the text and a “cartoon” is not necessary.

*Additional changes to the manuscript:*

- As mentioned already above, the “abstract” section and the “summary and conclusions” section were significantly changed and rewritten. To save space here, please see new version of the manuscript.

- Several comments of the reviewers dealt with the error calculation and error bars on the Figures. We changed this part in the instrumental section and added several details, it reads now: “The calibration measurements presented in Fig. 3 show also the high precision of the V/H-TDMA instrument. The variance of precision at a constant temperature (same substance and  $D_0$ ) is about 0.005 in VFR, which means clearly below 1%. This demonstrates the high reproducibility of the VFR data and the same is true for the GF and  $\kappa$  measurements (not shown here). The important factor is the precise sizing of the particles, which can be done very well with DMA systems. The absolute accuracy of the volatility and hygroscopicity data is influenced by further parameters e.g. temperature and RH measurements leading to higher absolute uncertainties. The absolute quantification is less important in this study than the temporal changes. Therefore we report the results with errors showing the reproducibility of the observations during the temporal evolution in the chamber.”

- In addition to the referee comments we added also the following reference to the summary and conclusions section:

Salo, K., Hallquist, M., Jonsson, A. M., Saathoff, H., Naumann, K. H., Spindler, C., Tillmann, R., Fuchs, H., Bohn, B., Rubach, F., Mentel, T. F., Müller, L., Reinnig, M. C., Hoffmann, T., and Donahue, N. M.: Volatility of secondary organic aerosol during OH radical induced ageing, *Atmos. Chem. Phys. Discuss.*, 11, 19507-19543, doi:10.5194/acpd-11-19507-2011, 2011.

- The language was changed, by combining two sentences in the introduction in a slightly different way: “Recently the volatility basis set (VBS) approach was introduced (Donahue et al., 2006; Robinson et al., 2007; Jimenez et al., 2009), lumping the various organic compounds together according to their effective saturation mass concentration ( $C^*$ ) in order to describe the semi-volatile nature of the SOA particles including their gas-particle partitioning behavior.”

- In section 2.3 the sentence “The reaction started immediately forming particles (first-generation SOA) from the ozonolysis of the C=C double bond in AP.” was changed to “The reaction resulted in immediate particle formation (first-generation SOA) from the reaction products of ozonolysis of the C=C double bond in AP.”