

Anonymous Referee #3

In this chamber study (Denjean et al., Aging of secondary organic aerosol generated via the ozonolysis of alpha-pinene: effects of ozone, light and temperature), a series of experiments was conducted to study physical properties (e.g. optical properties, hygroscopicity, particle size) and chemical composition of secondary organic aerosol (SOA) at different aging conditions: 1) at elevated ozone concentrations, 2) under light (controlled temperature), and 3) under light and heat (6 °C temperature increase). SOA was generated via ozonolysis of alpha-pinene at dry conditions (i.e., RH < 1 %) and after 14 h of the start of SOA formation, the particles were exposed to forcing for 6 h. The aim of study was to investigate properties and aging of SOA particles over timescales of 20 h. The results showed that no change in SOA size, properties or chemical composition was observed during ozone and light exposure at constant temperature whereas the increase in temperature led to changes on SOA properties (particle size, optical properties, composition and hygroscopicity). The authors concluded that "SOA properties may be governed more by local temperature fluctuations than by oxidative processing and photochemistry".

The study presents novel and important results on aging of SOA particle produced by ozonolysis of alpha-pinene. In general, SOA have a significant impact on Earth's atmosphere and climate, and thus this study is an important increasing our knowledge of SOA. The methods have been described in detail in the manuscript (MS) as well as experiments have been well designed and conducted. Furthermore, the results were quite well reported and analyzed. The MS is well organized, written and in the scope of this journal, and thus MS is certainly suitable for publication in this journal. However, there are some comments, suggestions and technical corrections that should be considered before publication.

We would like to thank the Referee for his/her insightful and helpful comments on the manuscript. These comments have helped us to improve the manuscript. Hereafter we answer all the comments.

General comments

The experiments have been conducted at very dry conditions (RH < 1 %). It is known that humidity has an important effect on SOA formation, chemistry, reactions, properties of particles, etc. Please discuss in more detail the effect of RH on the results and conclusions in the MS.

Response: We thank Referee #3 for this suggestion. We added a discussion on the effect of RH in the Conclusion of the paper: "Since an increase in bulk diffusion coefficient would be expected to be accompanied by an increase in particle reactivity, we suggest that future studies examine the effect of ozone and light exposure on α -pinene-O₃ SOA properties under humidified conditions (i.e. RH > 30%). Beyond its effect on the physical state of the particles, the relative humidity may influence the chemical composition of SOA. Recently, Kristensen et al. (2014) observed for α -pinene-O₃ SOA increased concentrations of high-molecular weight compounds, such as dimer esters, at higher RH (>50%) relative to lower RH (<30%). An increase in high-molecular weight compounds with increase RH could lead to a change in hygroscopic and optical properties of α -pinene-O₃ SOA and in its sensitivity to aging processes."

The increase in temperature influences both evaporation of semi-/low volatile compounds and kinetics of chemical reactions. In current version of MS, the interpretation of results has mainly been done based on an influence of temperature on volatility of compounds, not kinetics of chemical reactions. What is the effect of temperature increase on the chemistry and chemical reactions of SOA formation?

Response: We agree with Referee #3 that the temperature changes may also affect the kinetics of reactions in both gaseous and condensed phases. However, the simulated atmospheric processing was performed after 14h of α -pinene ozonolysis and both oxidants and precursors were consumed when the

different forcing were applied. In addition, the SOA chemical and physical properties were stabilized for 5h when the aging process was started, suggesting that reactions in the condensed phase are also negligible at this time. Other reactions in the condensed phase initiated by the light may occur but we have no idea of the nature of these reactions, and therefore what is the temperature dependence of their kinetics. However, an increase of only 6°C should not strongly affect the rate constants of these possible reactions except if they have a strong activation energy. In addition, modeling studies allow to reproduce the evolution of the aerosol mass and O/C ratio by only taking into account evaporation of semi-volatile compounds. For these reasons, we expect that effect of the temperature on the kinetics is negligible here.

The increase in temperature has the most notable effect on SOA particles during aging mostly due to evaporation of low/semi volatile compounds. Was there any gas-phase component analysis during temperature aging (e.g. with FTIR or PTR-MS)? It would be very nice to know concentration of volatile compounds in gas-phase during experiments. The composition of gas-phase compounds may differ significantly particle phase compounds which might explain, e.g., why O:C and f44/f43 ratios changed with increasing temperature (Fig. 6a, 6b).

Response: During the experiments, α -pinene, ozone and gas-phase oxidation products were followed using FTIR. Despite the fact that formaldehyde, pinene oxide and pinonaldehyde were detected during SOA formation, the concentration of these volatile compounds was below the detection limit of FTIR during the aging time.

This information has been added p.6 l.22: “During the different forcing, the concentrations of gas-phase compounds were found to be below the detection limit.”

The aging at ozone of 700 ppb did not show any significant effect on SOA properties. SOA has been produced via ozonolysis of α -pinene. In generally, α -pinene easily reacts with ozone but reaction products of α -pinene do not (no more C-C double bonds, see e.g. Kroll and Seinfeld, 2008). Is this the main reason why no effect has been observed during ozone aging? What will the situation be if OH radicals have been used as oxidant instead of ozone, or α -pinene has been replaced with other terpene with more double bonds (e.g. myrcene)? Please discuss in more detail about ozone-terpene chemistry during particle formation and aging.

Response: The insensitivity of α -pinene- O_3 SOA to ozone-induced aging could be attributed to different reasons:

1/ As mentioned by Referee #3, the molecular structure of α -pinene, which contains only one double bond and thus one active site for ozone reaction, limits the gas-phase oxidation by ozone of reaction products of α -pinene. However, during the ozonolysis of α -pinene, OH-radicals are formed. Since no scavenger of OH radicals was added, SOA examined in this study is likely a mixture of OH and O_3 oxidation products of α -pinene. Therefore, some of the products may still contain unreacted C=C bonds, which can then react with O_3 during the forcing. The relative contribution of these reaction products may not be sufficient to significantly affect the chemical/physical properties of SOA.

If either OH radicals was used as oxidant instead of ozone or α -pinene was replaced by myrcene, the ozone-induced aging could have significant effect on SOA properties but for now, the results presented in this study can not be extended to other gaseous precursor or aging processes. This study represent a first attempt to explore the effect of aging processes on SOA properties and more work is clearly needed before SOA aging is well understood.

2/ In our companion paper (e.g. Denjean et al., 2014b), we observed that α -pinene- O_3 SOA is not composed of a homogeneous chemical mixture, but exhibits a core-shell structure. Since heterogeneous particle-phase reactions are predicted to occur mainly at the surface of the particles, this chemical structure could kinetically limit the reaction of SOA with O_3 .

3/ Recent studies have highlighted that α -pinene- O_3 SOA exhibits a glassy state under dry conditions (Saukko et al., 2012; Renbaum-Wolff et al., 2013; Denjean et al., 2014b). It is thus possible that the α -pinene- O_3 SOA viscosity limits the particle reactivity with O_3 .

The hypothesis 2/ and 3/ reported above were already discussed in the paper. We added the hypothesis 1/ in the paper as follows (p.15 l.6): “In addition, the molecular structure of α -pinene, which contains only one double bond and thus one active site for ozone reaction, limits the gas-phase oxidation by ozone of reaction products of α -pinene. Since no scavenger of OH radicals was added, α -pinene- O_3 SOA is likely a mixture of OH and O_3 oxidation products of α -pinene. Therefore, some of the products may still contain unreacted C=C bonds, which can then react with O_3 . Our results indicate that the relative contribution of these reaction products may not be sufficient to significantly affect the chemical properties of SOA during the ozone-induced forcing.”

SOA mass concentrations at the start time of forcing (Table 1, 14 h after the initiation of SOA formation) varied significantly from measurement to measurement (30 – 117 $\mu\text{g}/\text{m}^3$). It seems, however, that the initial VOC and ozone concentrations were practically identical in different experiments (ca. 250 ppb and 200 ppb, respectively). What is the reason for this mass concentration variation? Is a same amount of VOC injected to chamber in all experiments? How does this variation of SOA mass concentration affects aging and properties of SOA particles?

Response: Since α -pinene was introduced after ozone into the chamber, and due to the very fast consumption of α -pinene, its initial concentration could not be accurately measured by FTIR. The ozone concentration being practically identical in all experiments, the variation of the SOA mass concentration is likely to be due to different concentration of VOC injected to the chamber.

The [VOC]/[O_3] concentrations and the properties of SOA during its formation are discussed in details in our companion paper (e.g. Denjean et al., 2014b). Despite the variation of SOA mass concentration, the chemical, optical and hygroscopic properties of SOA were found to be very similar between the experiments.

We completed the paragraph p.6 l.8 as follows: “As discussed in our companion paper (Denjean et al., 2014b), the variation of SOA mass concentration between the experiments was attributed to different concentration of α -pinene injected to the chamber. Despite this, the chemical, optical and hygroscopic properties of SOA were found to be very similar between the experiments. Therefore, the experiments were considered to be comparable for studying the effect of forcing on SOA properties.”

The chamber illumination system provides a good reproduction of the solar energy distribution at the Earth's surface. What kind of atmospheric chemistry can this illumination produce? Are there any OH-radicals (i.e. OH chemistry) in the chamber during illumination experiments (especially when humidity is very low)?

Response: The concentration of OH-radicals have been estimated by simulating the SOA formation with the MCM and Gecko-A models. Both models show that OH-radicals were fully consumed after 3 hours of reaction. Aging experiments were carried out after 14 hours of α -pinene ozonolysis and thus no OH radicals are expected to remain in the chamber before irradiation. Once irradiation process is started, carbonyls and organic peroxides in the gas and particle phase can be photodissociated and thus cause a decrease of the SOA mass concentration. HOx radical may also be produced by these photolysis processes but since they were not measured during our experiments, we can not conclude on it.

Optical properties (CRI) changed when chamber temperature increased. At the same time particle size decreased due to evaporation of volatile compounds. How much does the decrease of particle size affect optical properties? Is this size-change-effect as significant as the change of particle composition?

Response: The effect of the change of particle size and chemical composition on the optical properties can be determined by calculating the mass extinction efficiency k_{ext} at 525nm using Mie scattering calculations for homogeneous spheres and the particles mass concentration. As stated in the Conclusion, we have estimated a value of $k_{ext} = 1.7 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ for unprocessed SOA. We estimate that the decrease of the SOA size from 286 nm to 249 nm leads to $k_{ext} = 1.3 \text{ m}^2 \text{ g}^{-1}$, while the increase of the SOA CRI from 1.35 to 1.49 (which represent the change of particle chemical composition for optical calculations) leads to $k_{ext} = 3.7 \text{ m}^2 \text{ g}^{-1}$. Overall, we estimate a value of $k_{ext} = 2.8 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ for the combination of these 2 effects. Although the change of particle size has less effect on optical properties than the change of CRI, it has a significant implication on the final mass extinction efficiency.

Heating of the chamber can increase evaporation of semi/low volatile VOC from walls. Can this have some effect on the gas-particle partitioning and thus composition of SOA particles?

Response: We agree with Referee #3 that some VOC could evaporate from the wall of the chamber during the heating of the chamber. However, we observed that the size of the particles decreased during the heating, which suggests that no condensation in the particle phase occurred.

Specific comments:

Abstract:

Please indicate already in abstract that the experiments have been conducted at very dry conditions.

Response: It has been added p1 l24: "SOA generated from the ozonolysis of α -pinene under dry condition (<1% relative humidity)."

Please also point out that the results and conclusions are probably valid only for apinene ozonolysis (see the final statement "SOA properties may be governed more by local temperature fluctuations than by oxidative processing and photochemistry").

Response: We want to thank the Referee to point out this oversight in the abstract. We completed the final sentence as follows: "These surprising results suggest that α -pinene- O_3 SOA properties may be governed more by local temperature fluctuations than by oxidative processing and photochemistry."

Please discuss in more detail whether the conclusions are also valid for other terpenes/ VOC or for different chemistry (e.g. OH radicals)? I am not very sure that the results of this study can be generalized to other terpenes or oxidants.

Response: The experiments presented in this study represent a first attempt to evaluate the effect of aging processes on the SOA properties. More laboratory studies will be needed to extrapolate these results to other terpene and aging processes.

Please also discuss in the abstract why the increase in temperature affects SOA properties (what are reasons). For instance, you have already stated at the end of chapter 3.4 (p. 22453) "These results suggest that the changes in SOA physical and chemical properties observed in these experiments resulted from the heating-induced evaporation of semi-volatile and less oxidized SOA species, which in turn modified the optical and hygroscopic properties of the condensed phase". Is this the main conclusion of this study?

Response: We completed the Abstract as follows: "The simulation of the experiments using the Master Chemical Mechanism (MCM) and the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) shows that these changes resulted from the evaporation of semi-volatile and less oxidized SOA species induced by the relatively minor increases in temperature (~6°C)."

Introduction:

Page 22441, line 12: Check brackets (before Lambe not needed).

Response: Done

Methods:

Page 22443, line 10: I think that the reference to the supplementary figure (Fig. S1) is not needed at all. Just refer to the original paper Wang et al., Atmos. Meas. Tech., 4, 2465–2494, 2011.

Response: The Supplementary Figure has been deleted.

2.4 Modeling SOA formation and aging (p. 22448, l. 10-12): The models "simulate gas/particle partitioning in terms of equilibria between the gas phase and an ideal liquid homogeneous condensed phase". As mentioned in the paper, recent studies have shown that SOA particles are like solid/semisolid, not liquid. How does the solidity of SOA particles affect model results?

Response: We thank the Referee for this suggestion. In highly viscous aerosol, heterogeneous chemistry and particle-phase reactions can be limited. The effect of viscosity on rate constants were not taken into account in the MCM and Gecko-A models.

We completed Section 2.4. as follows: "In addition, recent studies (Renbaum-Wolff et al., 2013; Saukko et al., 2012; Denjean et al., 2014b) suggest that α -pinene-O₃ SOA viscosity increases with aging. Due to possible kinetic limitations, heterogeneous chemistry and particle-phase reactions can be limited in highly viscous aerosol. The effect of viscosity on rate constants were not taken into account in the current MCM and Gecko-A models."

Results:

3.1 Changes in SOA size distribution during simulated atmospheric processing: Please plot also an average particles size (GMD) as a function of time for different experiments (as 3rd panel in Fig 2). This would help to compare different experiments.

Response: We completed Figure 2 with the temporal evolution of the median diameter observed during photochemical aging in the absence of temperature control and during a control experiment (panel c).

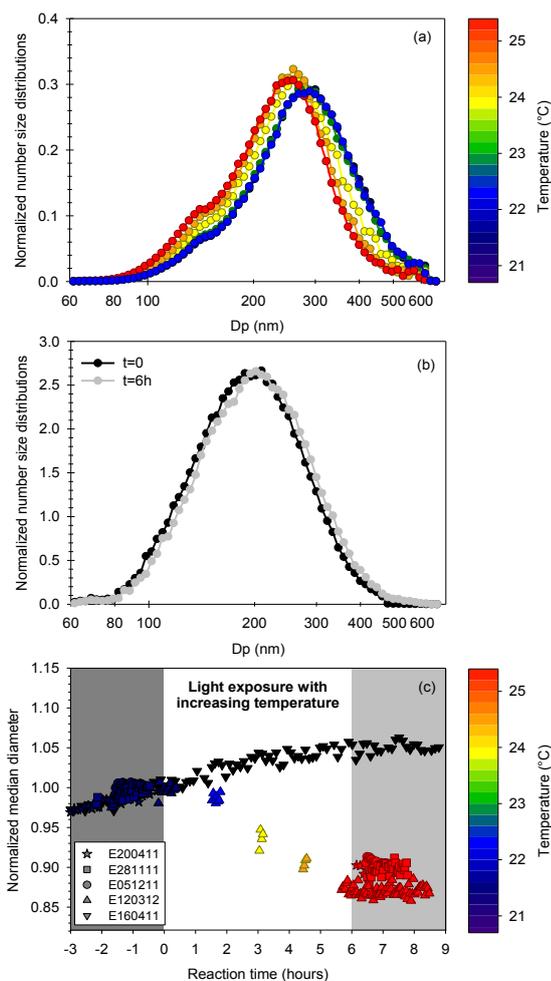


Figure A: Temporal evolution of SOA number size distribution (normalized to the total number concentration) a) during photochemical aging in the absence of temperature control (Experiment E120312) and b) during a control experiment (Experiment E160411). The temporal evolution of the median diameter during photochemical aging in the absence of temperature control (Experiments E201411, E281111, E051211 and E120312) and during a control experiment (Experiment E160411) is shown in c).

3.3 Changes in SOA chemical composition during simulated atmospheric processing: Page 22451, l. 5-7: Text "m/z 43 is associated to lower oxygenated groups, such as aldehydes and alcohols" is written two times.

Response: Corrected

Fig. 6a and 6b show an increase in O:C and f₄₄/f₄₃ ratios with increasing temperature. Does this only mean that particles with lower O:C and f₄₄/f₄₃ ratios evaporates easier?

Response: From Figure 6, it is not possible to conclude if the increase in O:C and f₄₄/f₄₃ are due to the evaporation of less oxidized compounds by heating or the fragmentation of less oxidized species in the condensed-phase by photolysis. The simulation of the experiments with the Gecko-A and MCM models indicate that the evaporation of semi-volatile and less oxidized SOA species by heating can explain both the decrease in particle mass concentration and the increase in O:C (Figure 8).

3.4 Effect of phase partitioning on SOA properties (p. 22451-22453): Recent studies have been shown that in the chamber experiments, the wall losses of very low volatile compounds might have significant implications on their partitioning between the gas and particle phase (see, e.g., Kokkola et al. Atmos. Chem. Phys., 14, 1689–1700, 2014). How do wall losses of low volatile VOC affect your result interpretation? Is the difference between measured and simulated SOA mass concentration caused (partially) by the wall losses of semi/low volatile compounds.

Response: An unavoidable consequence of simulation chamber measurements is the interaction of gases with the chamber wall surfaces during an experiment. The VOC-wall losses can affect the SOA mass concentration either by being a consumption pathway for SOA precursors in competition with oxidation or by being a sink for semi-volatile products preventing them from condensing on the aerosol phase.

Due to the large variability of chemical compounds involved, the quantification of the wall deposition of low volatile VOC involved in the reaction is very complex. A test experiment of α -pinene wall-loss was performed by injecting different concentrations of α -pinene in the chamber and following its concentration as a function of time. Figure B shows that the depletion of α -pinene to the chamber wall is negligible in CESAM. The depletion of gases to the chamber walls are strongly dependent on the nature and dimension of the chamber. It must be noted that the experiments presented here were performed in a chamber with a high surface-to-volume ratio (4.29, Wang et al., 2011), therefore minimizing the gas wall deposition. The overestimation of the simulated SOA mass concentration can partially be caused by this artefact, but it may not be the main reason of this result. As stated p.12 l.26, it might also be due to an underestimation of the vapor pressure with the Nannoolal method used in this study or some oxidation processes occurring in the aerosol phase and leading to fragmentation which may not be implemented in the model.

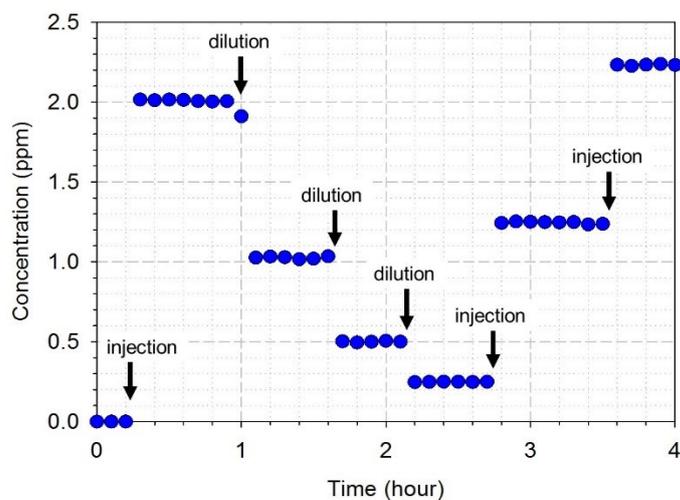


Figure B. Observed time-dependent concentrations of α -pinene during a wall-loss calibration experiment performed in the CESAM chamber. This experiment was conducted by adding N_2 and α -pinene in the chamber and by following the concentration of α -pinene. Injections of α -pinene were obtained by flushing into the chamber (in a N_2 flow) the entire volume of a glass bulb containing a known volume of pure gaseous α -pinene. Dilutions were performed by evacuating the chamber to 500 mbar and then filling it to ambient pressure with N_2 . Concentration of α -pinene being measured by FTIR, no instrument sampled from the chamber during the experiment. Measured concentrations of α -pinene were nearly constant over the measurement periods, indicating negligible wall loss of α -pinene in CESAM.

We completed section 3.1. as follows: "In addition, an unavoidable consequence of simulation chamber measurements is the interaction of gases with the chamber wall surfaces. It is plausible that the VOC-wall losses affect the SOA mass concentration by being a sink for semi-volatile products preventing them from condensing on the aerosol phase."

Conclusions:

Page 22456, line 8-10: "a-pinene-O₃ SOA is quite insensitive to light- and ozone induced aging under our experimental conditions, most likely as a result of kinetic limitations imposed by its physical state (semi-solid/glassy)." Please discuss also the effect of a-pinene - ozone chemistry on SOA properties. I suppose that the kinetic limitations due to SOA physical state is not main reason for observed insensitivity of light- and ozone-induced aging, rather the chemistry of a-pinene derived SOA.

Response: We thank Referee #3 to point out this oversight in the conclusion. We completed the Conclusion as follows: "Insensitivity to ozone-induced aging is most likely as a result of the molecular structure of α -pinene which limit the gas-phase oxidation by ozone of reaction products of α -pinene."

Supplement:

The supplementary figure (Fig. S1) is not needed. The figure is same as previously published: Wang et al., *Atmos. Meas. Tech.*, 4, 2465–2494, 2011.

Response: Deleted

References:

*Denjean, C., Formenti, P., Picquet-Varrault, B., Pangui, E., Zapf, P., Katrib, Y., Giorio, C., Tapparo, A., Monod, A., Temime-Roussel, B., Decorse, P., Mangeney, C., and Doussin, J. F.: Relating hygroscopicity and optical properties to chemical composition and structure of secondary organic aerosol particles generated from the ozonolysis of α -pinene, *Atmos. Chem. Phys. Discuss.*, 14, 10543-10596, 10.5194/acpd-14-10543-2014, 2014b.*

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*Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α -pinene secondary organic material and implications for particle growth and reactivity, *Proceedings of the National Academy of Sciences*, 110, 8014-8019, 10.1073/pnas.1219548110, 2013.*

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