AMT-2019-406-Reviewer Comment 2

Specific comments:

One major question is what is the extent of reaction/derivatization between SOA and TPP? The residence time in the condenser/reaction volume is not given, but likely impacts the extent of derivatization. What tests were done to determine whether or not the aerosol was fully reacted with TPP? I do not see any mention of varying the reaction time and how this impacts the observed concentration of TPPO. At the very least, the diffusion of TPP in an organic matrix could be estimated to determine if the reaction time is long enough to get full mixing between a typical organic particle and the derivatization agent. In addition, it's possible that reaction of TPP with semisolid organic particles might be limited to the particle surface, thus limiting ability of the technique to give quantitative peroxide concentrations. Please comment on the potential effect of high viscosity/semisolid particles and their reaction with TPP.

The other major issue with the manuscript is the lack of experiments using organic peroxide standards to help determine the efficacy of the derivatization technique. While a suitable standard may be difficult to find, there are commercially available organic peroxides which could be used. Some combination of validation using standards or offline techniques to compare measured peroxide concentrations (from TPP/TPPO system) should be used to validate the technique.

Answer: The reviewer is right and actually using the same arguments as reviewer 1. Therefore the answer to reviewer 2 is identical:
The reviewer is right we admit that this is a weakness of the manuscript. In fact, however, we performed experiments with several commercially available organic peroxides, e.g. lauryl peroxide or benzoyl peroxide, and the qualitative results were as expected, i.e. peroxide compounds gave a clear signal, non-peroxide compounds did not (when background correction was applied). One of the problems with the peroxide standards studied is probably related to a substantial change in volatility after the reaction with TPP, which is likely a result of the breaking of the molecules into smaller units, e.g. the formation of benzoic acid from benzoyl peroxide. The changing aerosol mass also changed the partitioning of the analytes, which made it difficult to quantitatively determine the reference compounds. In fact, the same behaviour can be expected for structurally similar R-O-O-R peroxides in the atmosphere, and it can probably be said that the method developed is semi-quantitative for such compounds. Nevertheless, it can be assumed that most peroxides in the ambient atmosphere are hydroperoxides. Although there is certainly a vapour pressure difference between the hydroperoxides and the corresponding OH functionality after the reaction with TPP (R-O-O-H -> R-O-H) (Compernolle et al., 2010, Atmos. Chem. Phys.), the difference is not of several orders of magnitude as in the case of the standards used for this study. Therefore, we used the standards for the general proof of feasibility of the method and not for calibration. To make this limitation of the method clear, we have included an additional paragraph in the manuscript (section 3.1):
" Experiments with peroxides (R-O-O-R) as reference compounds were also performed, using commercially available organic peroxides. e.g. lauryl peroxide and benzoyl peroxide. While these experiments clearly showed the formation of TPPO from TPP, the use of these compounds for quantification was not possible, since the peroxide standards studied undergo a substantial change in volatility after the reaction with TPP. Therefore, lauryl peroxide and benzoyl peroxide were used to demonstrate the general proof of feasibility of the method, however, not for calibration. "

Reaction time and concentration ratios of analytes and reactants are now also discussed and mentioned in the revised manuscript text.

About the viscosity of OA: Here too the reviewer has a point. SOA is a complicated matrix, and several experimental/environmental parameters can affect the results. Therefore the phase state of SOA can also influence the peroxide measurements, as discussed in the manuscript. However, the main advantage of the presented method is the high time resolution, which to our knowledge is not achieved by other techniques. Therefore, we believe that the developed method should be made available to other researchers, although not all possible effects on the measurement results have been investigated in detail. It should also be mentioned that the relative humidity was always above 60% and the temperature between 22 and 25°C. Consequently, we expect the SOA to be liquid for all experiments performed. All aspects discussed here are now also discussed in the revised manuscript:

“Another aspect of SOA experiments which include chemistry, as in the case of peroxide-TPP reaction, that have to be considered is the question of the phase state of SOA. According to Koop et al. (2011) SOA is expected to be a liquid under the condition used for our experiments (22-25 °C, r.h. 60%). Also the AS seed particles can be expected to behave liquid-like (Matthew et al., 2008). As a consequence the diffusion time of TPP within the particles should be approximately one second (Koop et al., 2011), which is much shorter than the residence time of about 35 seconds of the aerosol in the ORD-setup (Figure 1). In conclusion, based on the agreement of the peroxide/SOA ratio at a later stage of the experiments measured in this work and the results of former studies, the estimated diffusion times and the excess of the reactant TPP to SOA, a quantitative reaction of TPP with the particle phase peroxides to TPPO can be assumed. However, in future investigations, the method should be revalidated using as aerosol particles composed of pure single component peroxides.”

“CSTR” needs to be defined in line 116.

Is defined now in the text: continuous flow tank reactor

How was the ozone concentration estimated (line 128)?

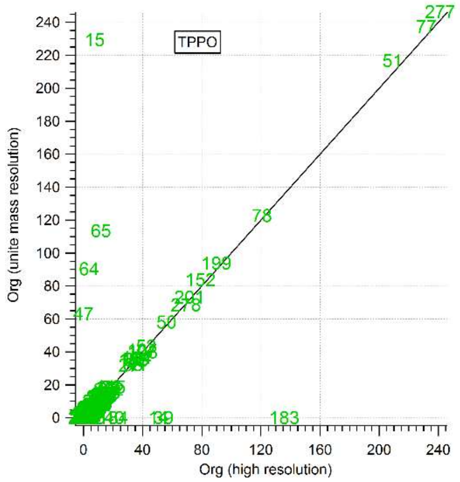
The ozone monitor is calibrated using wet chemical methods on a regular basis.

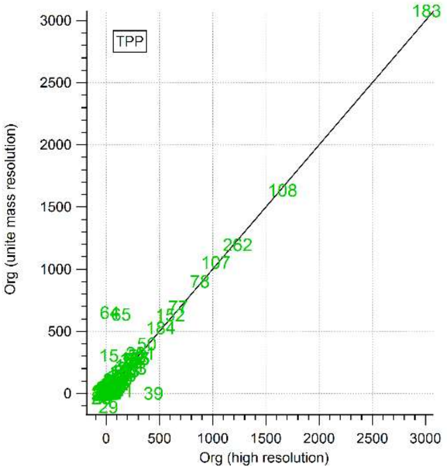
What is meant by “regular MS” (line 132)? Does this refer to EI-MS?

Regular MS refers to the ionization process in the AMS compared to a conventional EI mass spectrometer. Due to rapid evaporation, the compounds fragment more strongly in the AMS. The mass spectrum of the AMS shows the same fragments, but with a different intensity distribution than the reference spectra.

If a high resolution AMS was used, why use unit mass resolution peaks (e.g., m/z 277 for TPPO) rather than the high-resolution m/z values or identified ions?

No signals have been detected at mass 277 except for the [M-1]+ ion of TPPO. The signal of the UMR peak is therefore as high as that of the HR peak. At mass 262, only signals from TPP were detected, so HR is not necessary here either. Since the evaluation by UMR is easier and faster, HR peaks were omitted.





In section 3.3, it is stated that the experiments showed a constant background contribution of TPPO from TPP; however, these values vary in the SI. What is the impact on calculated peroxide concentrations when experiment specific corrections are used?

The background was 1.08% in the presented experiment for a-pinene and 1.33% for b-pinene. If one would take these values, the peroxide concentration would increase by 2% or decrease by 1 to 18%. The smaller the TPPO to TPP ratio, the greater the differences. Therefore, only data above the limit of determination of 2.25% were evaluated. As the origin of the background TPPO is unknown, the TPPO/TPP ratio was averaged.

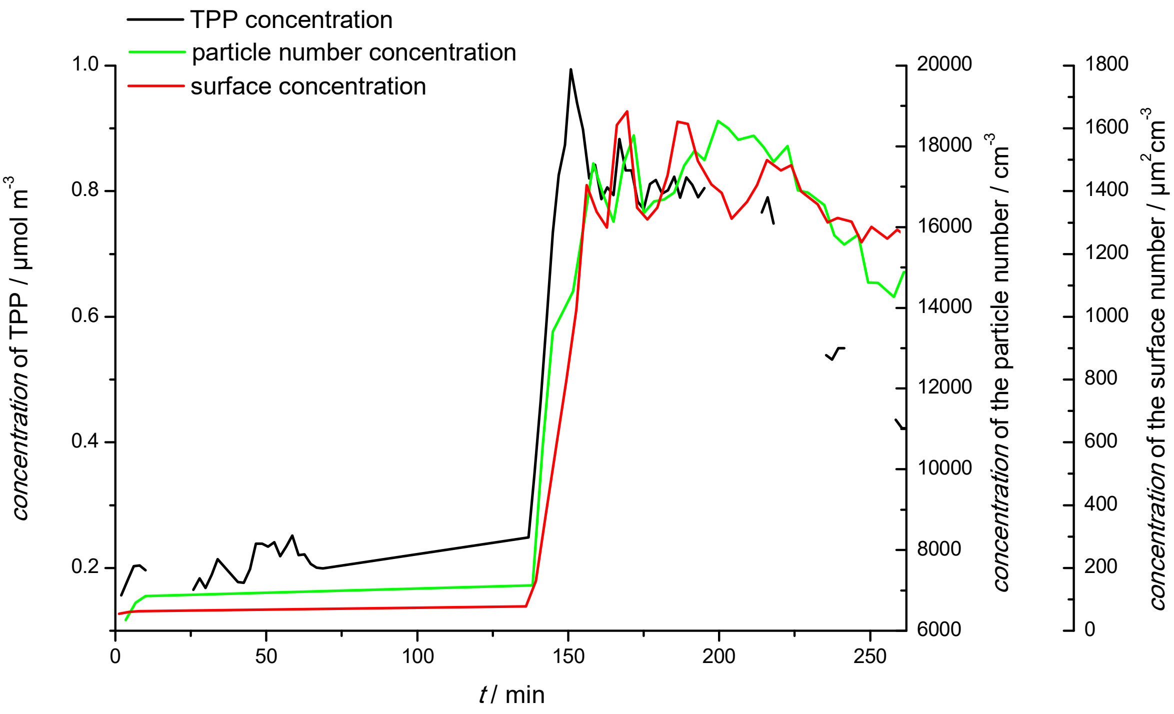
During SOA experiments, there are periods where TPP is not added. Please describe how this is accomplished? Also, in Figure 3 (a and b), why are there gaps in the data (excluding the grey bars)?

To measure SOA with the AMS, T-piece 1 was connected directly to T-piece 2 without the ORD setup. In order to determine the peroxide content again, the ORD setup was reconnected. During this phase, the data acquisition of the AMS and SMPS was interrupted and continued only after the particle concentrations at the CPC reach a constant value again. Therefore, there are the gaps in Fig 3.

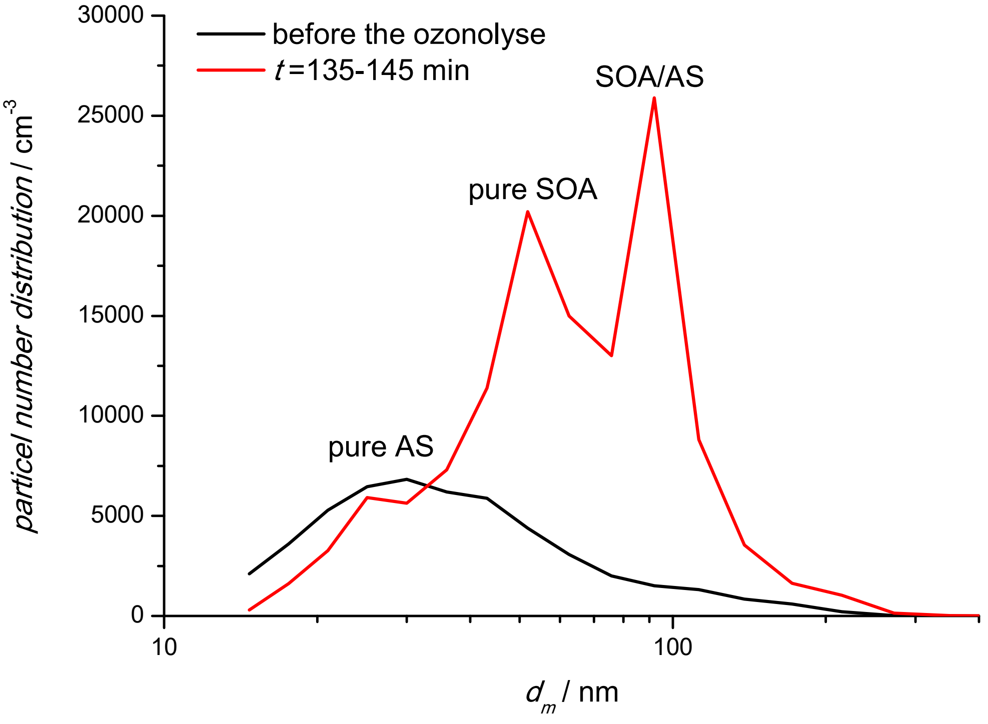
In Fig. 3b, why is the volume so variable?

Technical problems with the SMPS, probably because the scanning time per diameter was chosen very short in order to achieve the shortest possible total scanning time of 200 s.

In Figure 3a, what causes the increase in detected TPP when SOA is formed? Is it because there is additional surface area for the TPP to condense onto? Or is it due to some increase in collection efficiency?



TPP is only detected by AMS when it condenses onto particles. The more particles enter the condenser, the more TPP is detected. According to Figures 4 and 5. mainly new SOA particles are formed, but growth of the seed aerosol can also be observed. Since wall losses are size-dependent and for uncharged particles the minimum for the losses is about 150 nm, the enlargement of the pure AS particles from about 33 nm to over 100 nm should lead to less particle deposition in the chamber. The AMS ultimately only measures the particle concentration before the SMPS and ORD-AMS branches.



In the Fig. 3 caption, the time resolution is given as 10 minutes, but the abstract says 1-2 minutes.

The time resolutions for AMS and SMPS were 120 s and 200 s respectively. To compare the peroxide concentration with the volume concentration, the values were averaged to 600 s (10 min). It refers only to figure c).

Why use SMPS volume to quantify the SOA rather than the AMS? And why quantify peroxide concentrations in terms of volume at all, instead of mass?

In ORD-AMS mode, no SOA and AS concentrations can be determined because fragments of TPP and TPPO match SOA and AS fragments. Especially since TPP makes up a large part of the aerosol, its signals are very high compared to the signals of other compounds. The subtraction of TPP signals from the rest of the spectrum is therefore prone to errors. Correction: Molar SOA concentration is calculated assuming constant density.

It isn't clear what corrections are done to the data, if any. For example, is the data corrected for dilution in the chamber or AMS collection efficiency?

The addition of TPP in an N2 stream to the aerosol results in a dilution of the aerosol. The dilution and other particle losses during the transmission from T-piece 1 to T-piece 2 are corrected by the CPC. For this purpose, the particle concentration is measured when switching between ORD-AMS and normal AMS mode. The dilution can be corrected from the ratio. For a-pinene the dilution was 0.7 and for b-pinene 0.6. Particle losses in the chamber and the collection efficency of the AMS were not taken into account.

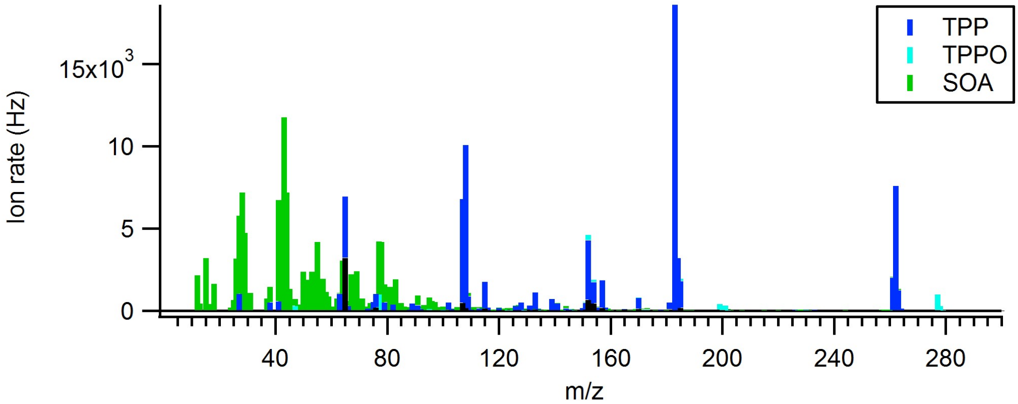
What systems were studied in the references given in lines 201 and 202 (Epstein et al. 2014, Li et al. 2016, Mertes et al. 2012)? It's not clear how these studies are related to the manuscript.

In the references the ozonolysis of a-pinene was also examined for peroxide content. The aerosol was collected on filters or impactors and the peroxide content was analysed iodometrically. However, several parameters such as the terpene/ozone ratio, temperature and humidity were different. Nevertheless, the peroxide content were observed to be between 34 and 12%. Our chamber conditions best match those of Li et al (2016). There, a yield of 21% was determined, which was also found in their own experiments. The effect of seed aerosol (5%) on the peroxide yield should be low for a-pinene.

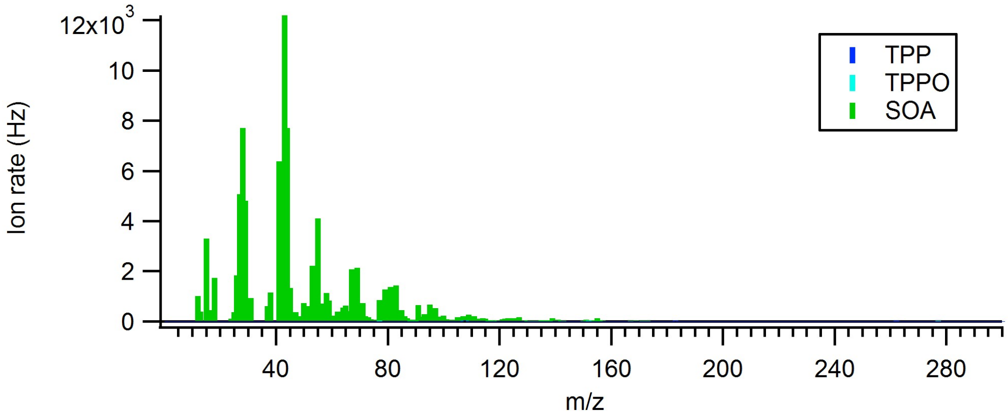
Does the formation of SOA interfere with the quantification of TPP/TPPO in the AMS mass spectra? AMS mass spectra of SOA + TPP/TPPO should be shown either in the main manuscript or the SI.

According to (DeCarlo et al. 2006) the ionization of the compounds after evaporation from the particles in high vacuum should take place independently. Thus, quantification should be independent of the aerosol matrix. As can be seen from the comparison of pure SOA to

SOA+TPP+TPPO, there is no significant overlap of the signal at m/z 262 and m/z 277 with SOA signals, therefore these signals can be used to quantify TPP and TPPO.



Pinene ozonolysis products with TPP



Pinene ozonolysis products without TPP

Does all of the TPPO that is formed from the SOA + TPP reaction stay in the particle phase? Any partitioning of TPPO to the gas phase would limit the quantification of peroxide.

A valid point. However, according to the manufacturer, the vapour pressure at 50 °C is less than 1 hPa and the boiling point is over 360 °C. Therefore, we assume a non-volatile substance although we cannot completely rule out this possibility.

In Figure 5, only m/z 277 looks to be bimodal, not the organic or sulfate as stated in the manuscript (line 217).I also don't find the inclusion of all of the size distribution data to be particularly useful. Some of these figures and discussion could be moved to the SI.

We prefer to have the figures in the manuscript.

In line 263, ozone is excluded as a direct oxidant for TPP. This should be mentioned much earlier in the manuscript given that it is an obvious question that clouds the interpretation of the preceding results.

Technical corrections:
Line 31, remove "however"
Line 73 should read "and use this"
Line 85 "carrier gas to deliver"
Line 99 "functions as a detector"
Line 100 "the beam passes"

Line 121 “was nebulized”
Line 140 “background signal has to be”
Line 191 “In any case, the”
Line 195 “As seen in”
Line 202 “Mertes and coworkers”
Line 240 “diameter depends on”
Line 253 “increased rapidly with the formation of SOA” or something to this effect
Line 258 “SOA concentration supports the concept”
Line 276 says only peroxides are detected during weekdays, but the weekend days are listed in parentheses

all done

Edited figures:

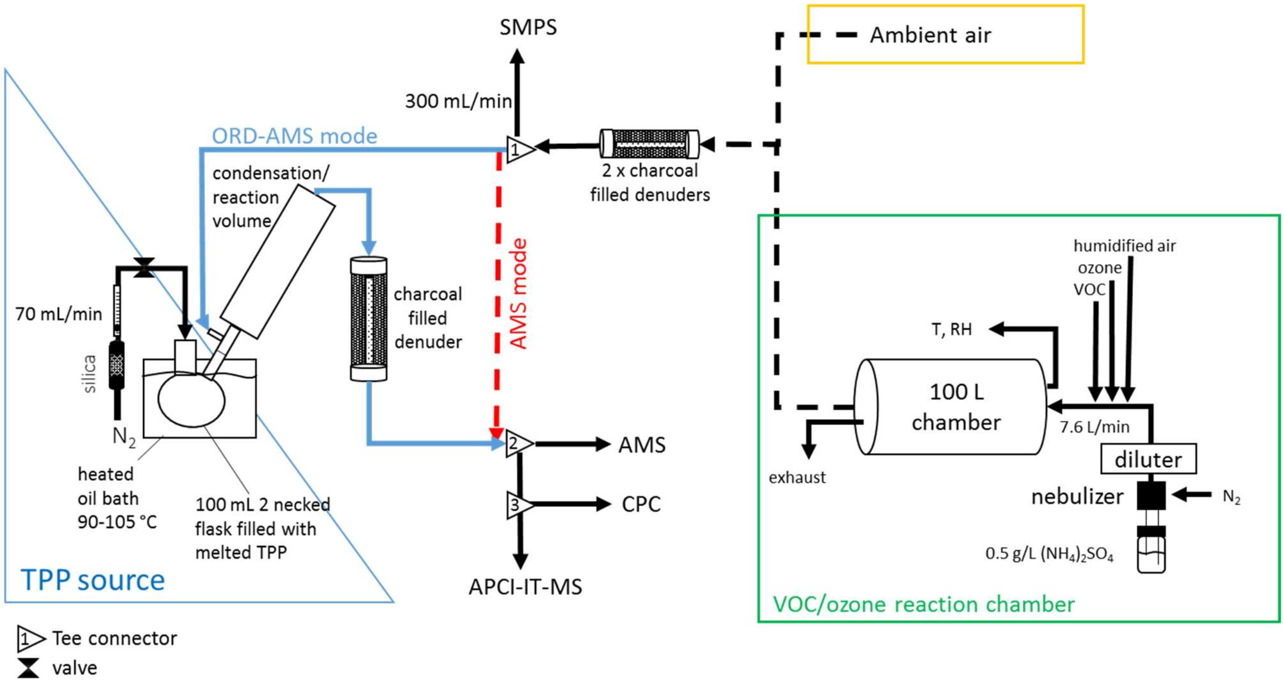


Figure 1

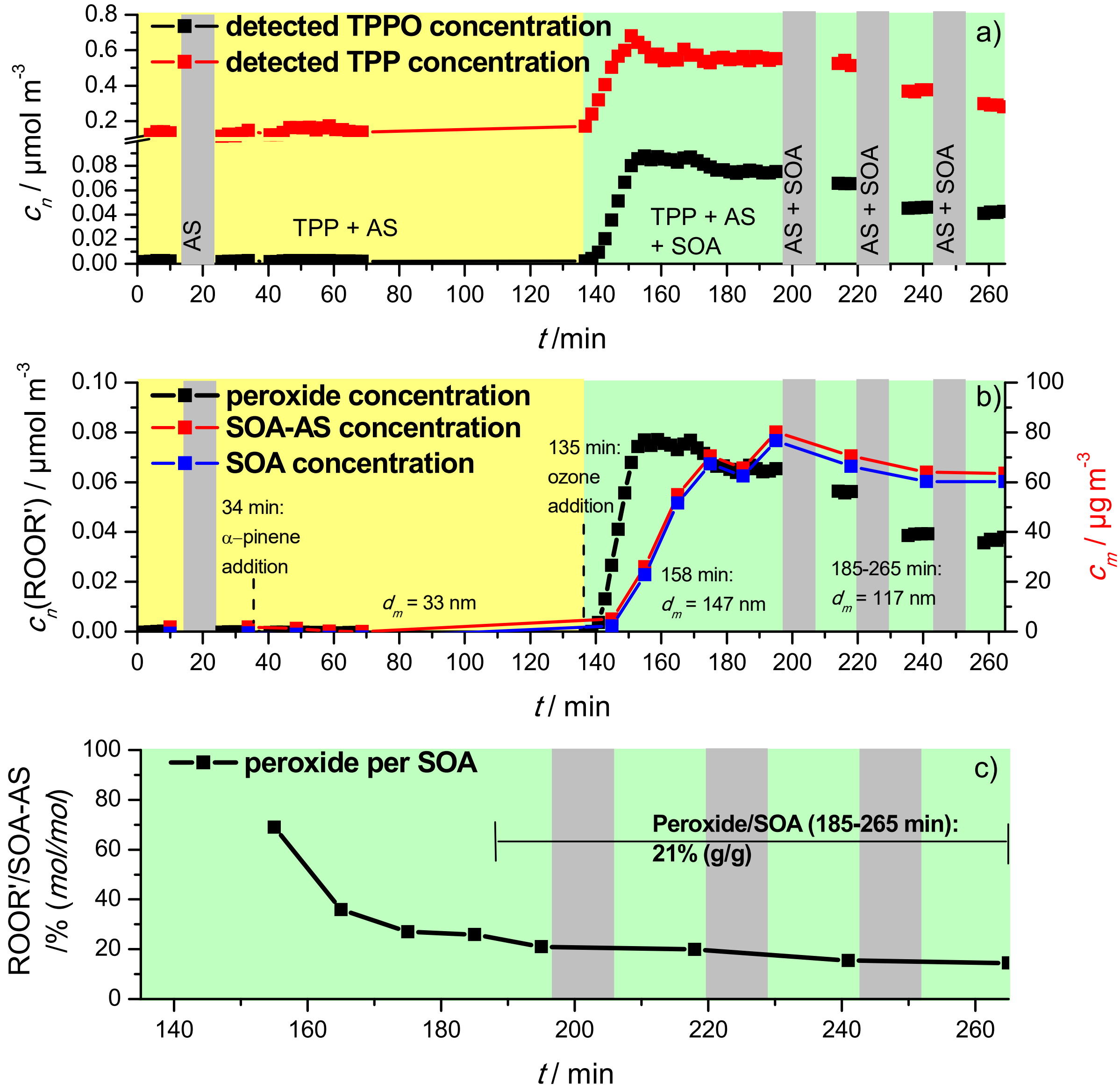

a)
detected TPPO concentration
detected TPP concentration
c_n / µmol m^{-3}
0.8
0.6
0.4
0.2
0.08
0.06
0.04
0.02
0.00
AS
TPP + AS
TPP + AS + SOA
AS + SOA
AS + SOA
AS + SOA
0
20
40
60
80
100
120
140
160
180
200
220
240
260
t /min
b)
peroxide concentration
SOA-AS concentration
SOA concentration
c_n(ROOR') / µmol m^{-3}
0.10
0.08
0.06
0.04
0.02
0.00
34 min: α–pinene addition
d_m = 33 nm
135 min: ozone addition
158 min: d_m = 147 nm
185-265 min: d_m = 117 nm
c_m / µg m^{-3}
100
80
60
40
20
0
t / min
c)
peroxide per SOA
ROOR'/SOA-AS /% (mol/mol)
Peroxide/SOA (185-265 min): 21% (g/g)
100
80
60
40
20
0
140
160
180
200
220
240
260
t / min

Figure 3

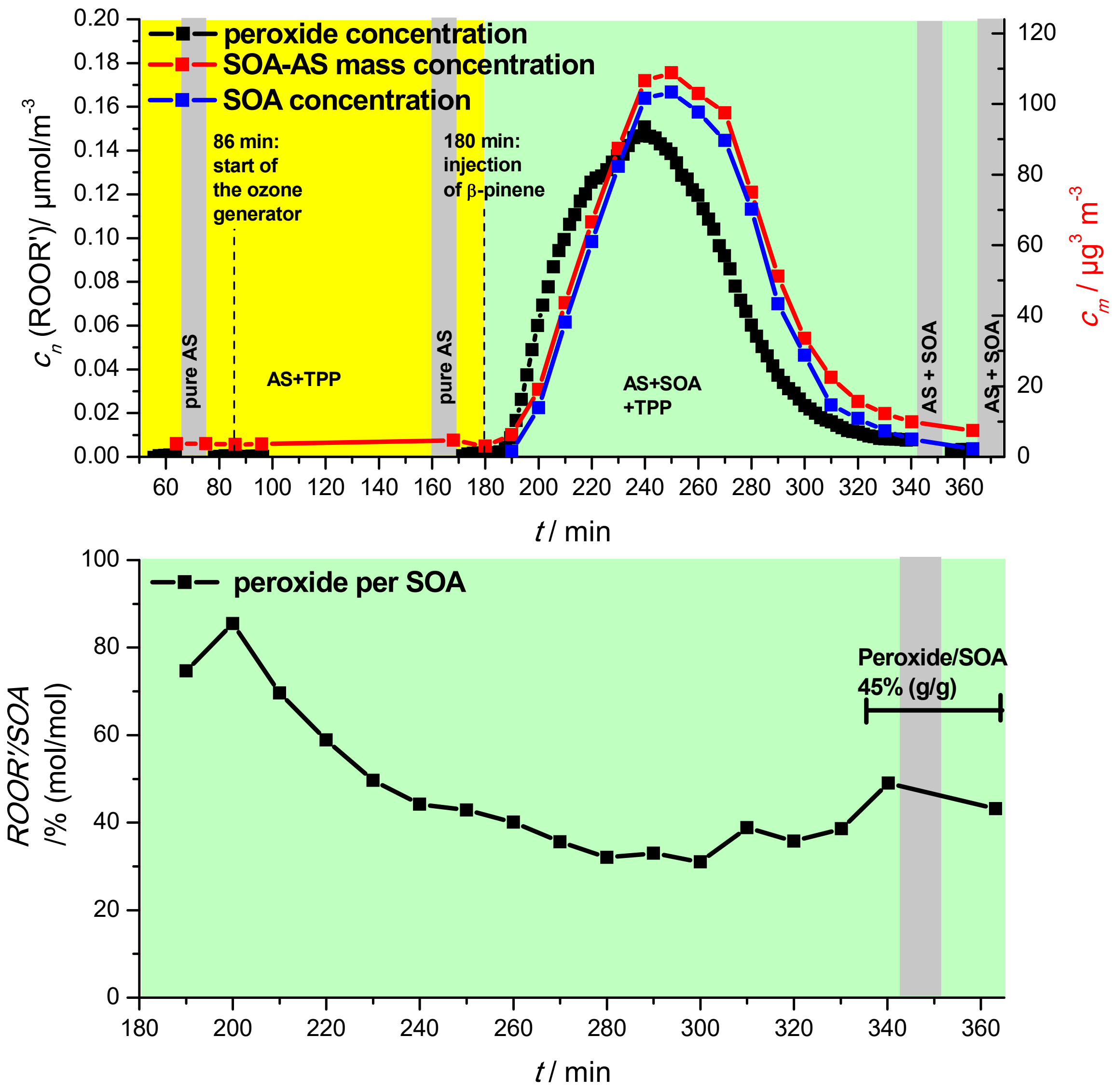

peroxide concentration
SOA-AS mass concentration
SOA concentration
86 min: start of the ozone generator
180 min: injection of β-pinene
pure AS
AS+TPP
pure AS
AS+SOA +TPP
AS + SOA
AS + SOA
c_n (ROOR')/ µmol/m^{-3}
c_m / µg^3 m^{-3}
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0
20
40
60
80
100
120
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
t / min
peroxide per SOA
Peroxide/SOA 45% (g/g)
ROOR'/SOA /% (mol/mol)
0
20
40
60
80
100
180
200
220
240
260
280
300
320
340
360
t / min

Figure 7