## Supplement

## Calibration setup



Figure S1: Schematic setup for the calibration of the AMS.

Figure S1 illustrates the typical setup for the calibration of the AMS for a compound using tandem DMA-AMS/CPC (Slowik et al. 2004). A binary solution of the compounds is nebulized to a polydisperse aerosol. The solvent is removed by charcoal denuders and the aerosol concentration is set using a diluter. A monodisperse aerosol is obtained by selecting of mobility diameter using the DMA and supplied to the HR-ToF-AMS and CPC.

## Calibration method

The mass concentration  $c_m$  of a single compound is calculated by the AMS according to (Canagaratna et al. 2007):

$$c_m = \frac{10^{12} \cdot MW(compound)}{IE(compound) \cdot Q \cdot N_A} \cdot \sum_{all,i} I(compound, i),$$
 Eq. 1

where *MW* and *IE* are the molar weight and the ionization efficiency of a compound, respectively. The ionization efficiency is defined as the total ion rate of all detected ions per vaporized and ionized molecules of one compound. *Q* is the AMS flow rate,  $N_A$  Avogadro's number and  $10^{12}$  a conversion factor to  $\mu g/m^3$ . *I(compound,i)* is the ion rate of an ion i formed at the ionization and fragmentation of a compound. Since the fragmentation pattern can be assumed to be robust, it is possible to use the ion yield of a single ion to calculate the concentration. The concentration of TPPO can be calculated as:

$$c_n(detected TPPO) = \frac{10^{12}}{\frac{IE}{AB} \left( TPPO, \frac{m}{z} 277 \right) \cdot AB \cdot Q \cdot N_A} \cdot I(\frac{m}{z} 277)$$
Eq. 2

IE is calculated by equation 3:

$$IE = \frac{IPP}{MPP}$$
 Eq. 3

*IPP* is the number of detected ions per particle and *MPP* the number of molecules per particle. To obtain *IPP*, it is important to adjust the particle concentration, measured by the AMS below

500 particles/cm<sup>3</sup> to be sure that only ions of single particles are detected in the BFSP mode of the AMS. *MPP* is calculated by equation:

$$MPP = \frac{S \cdot \rho_d \cdot \frac{4}{3} \cdot \pi \cdot \left(\frac{d_m}{2}\right)^3}{MW}$$
 Eq. 4

*S* is the Jayne shape factor which corrects for the deviation from a sphere volume,  $\rho_d$  is the particle density which is identical to the material density  $\rho_m$  for a full sphere,  $d_m$  is the electrical mobility diameter which can be set by the DMA and *MW* is the molecular weight. *S* can be obtained by equation 5:

$$S = \frac{\rho_m \cdot d_{va}}{\rho_0 \cdot d_m}$$
 Eq. 5

 $\rho_0$  is the standard density of spherical particles of 1 g/cm<sup>3</sup> and  $d_{va}$  the vacuum aerodynamic diameter, obtained by the PToF mode of the AMS. (DeCarlo et al. 2004)

Alternatively, *IE* can be determined by the MS/CPC method. Here, the particle concentration measured by the CPC has to be included. For the *IE* determination, it is important that the detected particles contain only the compound to be calibrated.



Result of the calibration

Figure S2: Determination of Jayne shape factor S for TPPO.

In Figure S2, the vacuum aerodynamic diameter  $d_{va}$  is plotted against the electrical mobility diameter  $d_m$ . The nearly 1:1 relation of the two diameters indicates spherical particle shape. With a material density  $\rho_m$  of 1.2 g/mL, the Jayne shape factor S is 0.80 +/- 0.05 according to Eq 5.

Figure S3 illustrates the results from the *IE* calibration of TPPO using the BFSP and the MS/CPC method. The average ionization efficiency *IE*, normalized to the airbeam *AB at the calibration*, of the ion rate at m/z 277 of TPPO is *IE/AB* (TPPO, m/z 277) = 2.61·10<sup>-13</sup> hz<sup>-1</sup>.





Figure S3: Results from the IE calibration of TPPO using the BFSP method (green) and MS/CPC method (red).

## TPPO background

Table S1. Background contribution of TPPO on detected TPP, obtained at several SOA-seed aerosol experiments.

	Background value BV = c(detected TPPO)/c(detected TPP)/%	
Experiment	Average	Standard deviation
1	1.307	0.121
2	1.076	0.071
3	1.124	0.012
4	1.269	0.094
5	1.337	0.036
Average	1.222	
Standard deviation	0.103	
Detection limit	1.530	
Quantification limit	2.250	

Table S1 shows the TPPO background per detected TPP from several SOA seed experiments. Therefore, ammonium sulfate (AS) seed particles were introduced into the chamber and further supplied to the OD-AMS setup, where TPP condensed on the AS particles. The ratio of the TPPO background concentration to the detected TPP concentration was determined for the periods before the ozonolysis had been started, when either the terpene or ozone was added to the chamber. An average value and standard deviation were obtained from the results of several experiments and used for background correction. Limits of detection and quantification were obtained from this average value.

Origins of the air masses between the 4 May to the 10 May 2018



Figure S4: 72h backwards trajectories from 3.5 to 10.5 (every 24 hours)