Atmospheric
Measurement
Techniques

Supplement of

Application of time-of-flight aerosol mass spectrometry for the real-time measurement of particle-phase organic peroxides: an online redox derivatization–aerosol mass spectrometer (ORD-AMS)

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Supplement
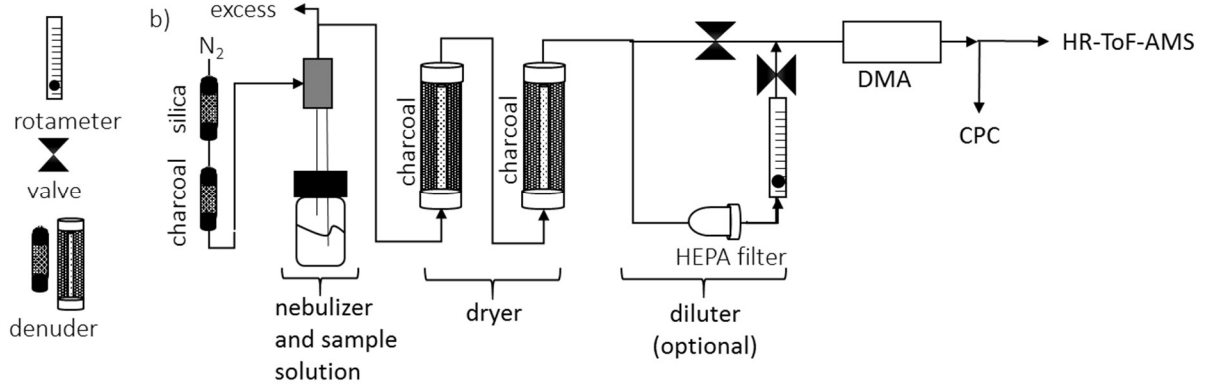
Calibration setup

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 selectingthe 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 µg/m³. $I(compound,i)$ 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/cm³ to be sure that only ions of single particles are detected in the BFSP mode of the AMS. *MPP* is calculated using equation Eq.4.

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

Eq. 4

S is the Jayne shape factor which corrects for the deviation from a sphere volume, ρ_d is the particle density which is identical to the material density ρ_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

ρ_0 is the standard density of spherical particles of 1 g/cm³ 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, the detected particles must contain only the compound to be calibrated.
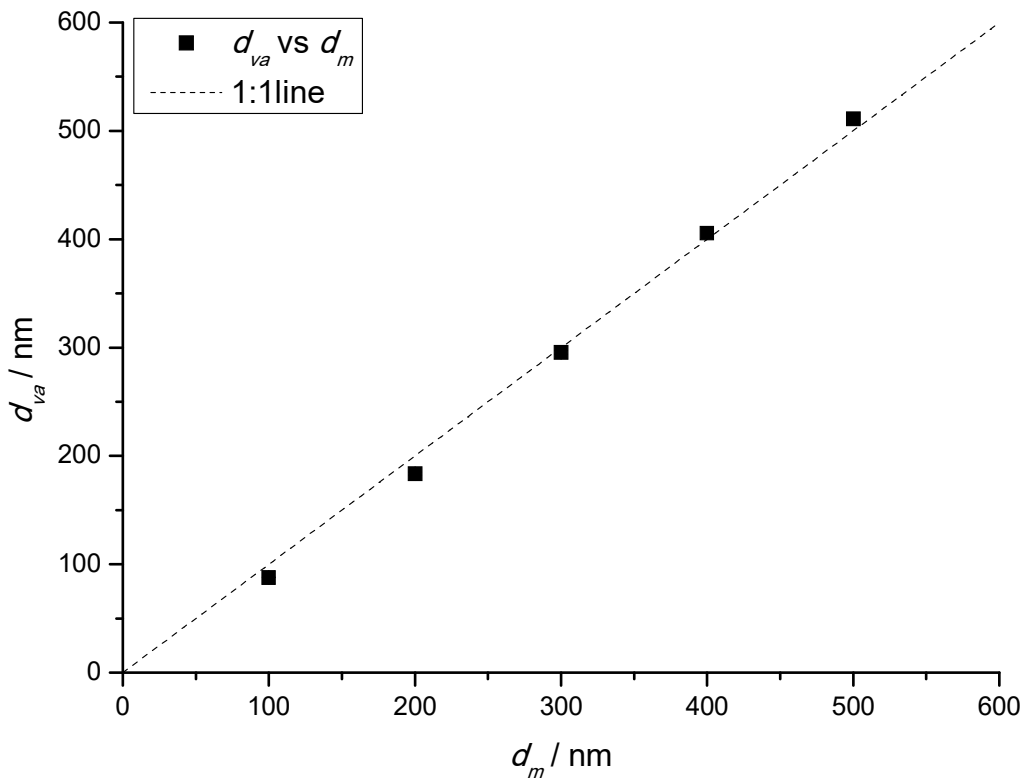
Result of the calibration

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 ρ_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) = $2.61 \cdot 10^{-13}$ hz^{-1}.

At the calibration of TPP, the Jayne shape factor is *S* = 0.72 and the *AB* normalized *IE* at *m/z* 262 is *IE/AB* (TPP, *m/z* 262) = $2.01 \cdot 10^{-13}$ hz^{-1}.
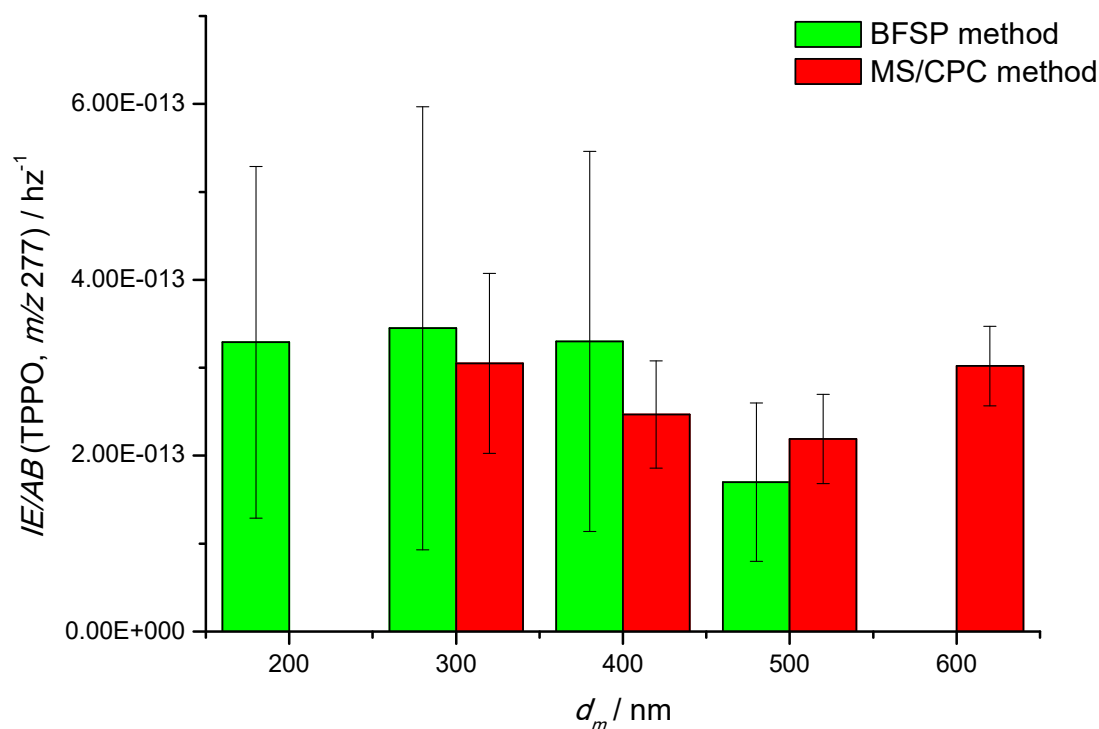

Figure S3: Results from the *IE* calibration of TPPO using the BFSP method (green) and MS/CPC method (red).

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 ORD-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.

Calculation of the SOA concentration

Since the mass concentration of SOA c_m(SOA) cannot be measured in the ORD-AMS mode, it was calculated from the particle mass concentration c_m(particle, SMPS), given by the SMPS, and the ammonium sulfate mass concentration using the following equation:

$$c_m(SOA) = c_m(particle, SMPS) - c_m(NH_4SO_4, AMS)$$

As the AMS measured at a time resolution of 120 s and the SMPS a resolution of 200 s, the data points were averaged to a resolution of 600 s (10 min).

Principally, the density ρ of the aerosol is needed to determine the particle mass concentration, given by the SMPS. The density was determined as follow:

The ozonolysis experiments can be divided into two periods. In the first one, only seed particles of ammonium sulfate and one of the reactants (terpene or ozone) were supplied into the chamber. Therefore, only ammonium sulfate particles were introduced into the ORD-setup, which why a density of 1.77 g/cm³ (material density of ammonium sulfate) was assumed for this period.

The second period started with the addition of the second reactants and the SOA formation. Here, a mixture of ammonium sulfate and SOA were expected and the density ρ was calculated using the parameterization from O/C and H/C ratios according to (Kuwata et al. 2012). $\rho = \left[12 + 1 \cdot \frac{H}{C} + 16 \cdot \frac{O}{C}\right] / \left[7.0 + 5.0 \cdot \frac{H}{C} + 4.15 \cdot \frac{O}{C}\right]$

The H/C and O/C ratios were calculated in the AMS mode at the end of the respective experiment. The results are given in table S2. The resulting density was applied for the whole period after the start of the ozonolysis.

Table S2.: Obtained H/C, O/C according to Kuwata et al. (2012) and resulting density for the period during the ozonolysis

Terpene	H/C	O/C	ρ / g cm^{-3}
α-pinene	1.64	0.41	1.19
β-pinene	1.47	0.40	1.24

In the end, the molar SOA concentration c_n(SOA) was calculated assuming a molar mass of 250 g/mol using:

$$c_n(SOA) = \frac{c_m(SOA)}{250 \text{ g/mol}}$$
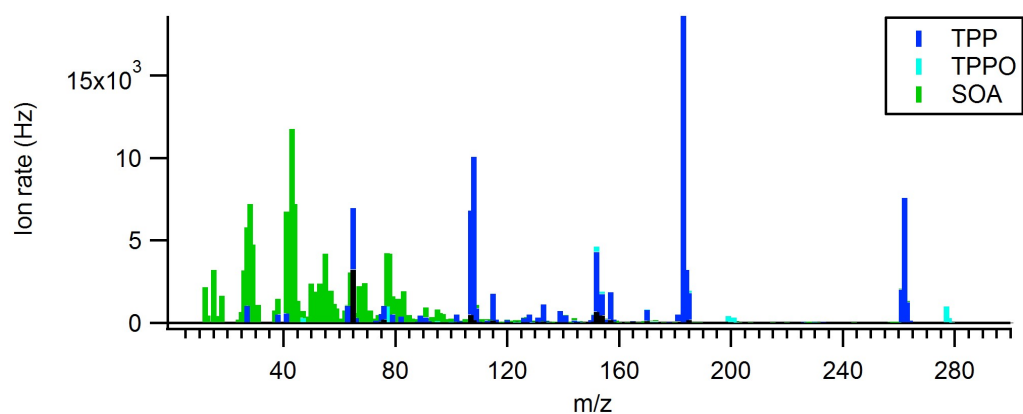
SOA mass spectra vs TPP and TPPO spectra

Figure S4: Mass spectra of SOA, TPP and TPPO at the ozonolysis of α-pinene, measured in the ORD-AMS mode.

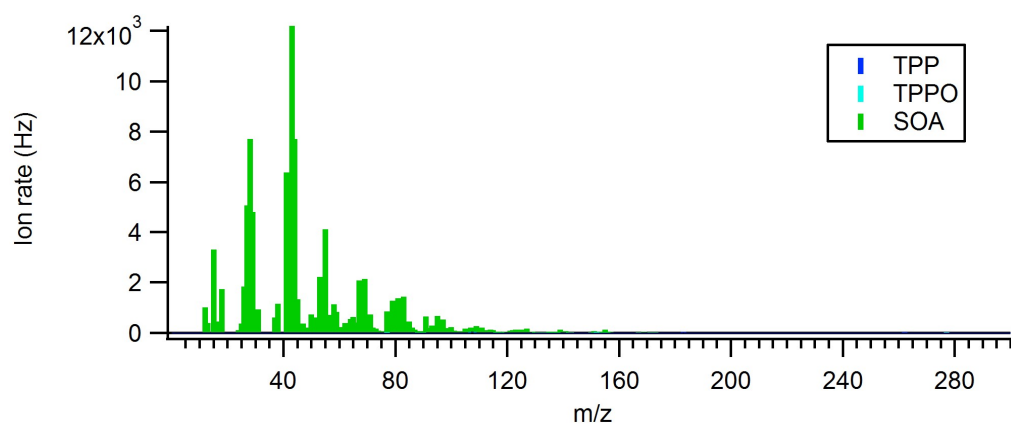

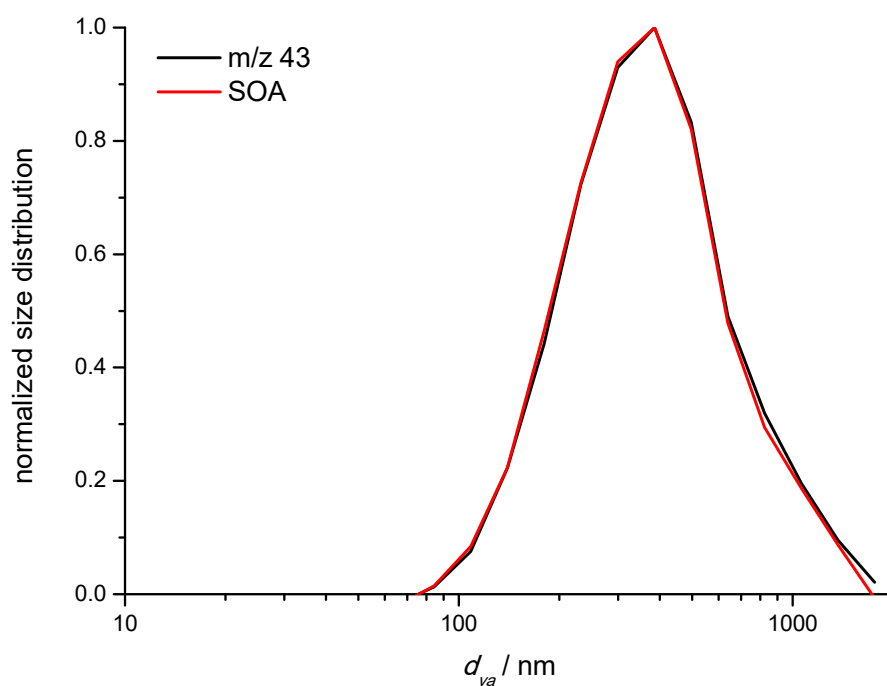Figure S5: Mass spectra of SOA, TPP and TPPO at the ozonolysis of α-pinene, measured in the AMS mode.

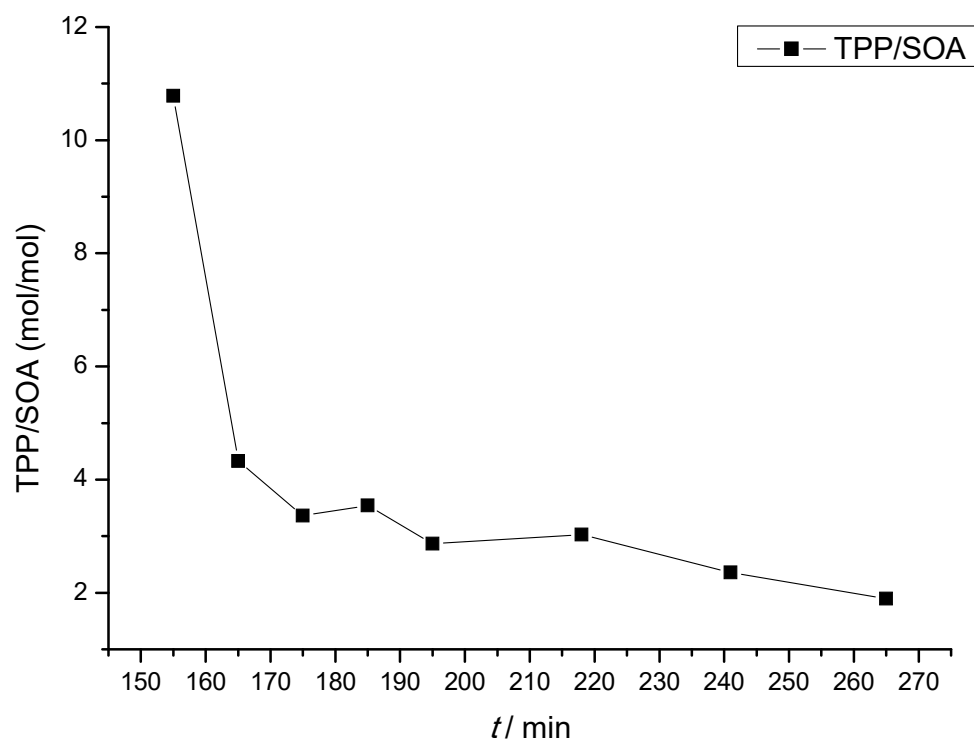Figure S6. The normalized size distribution of *m/z* 43 and SOA, measured in the AMS mode.

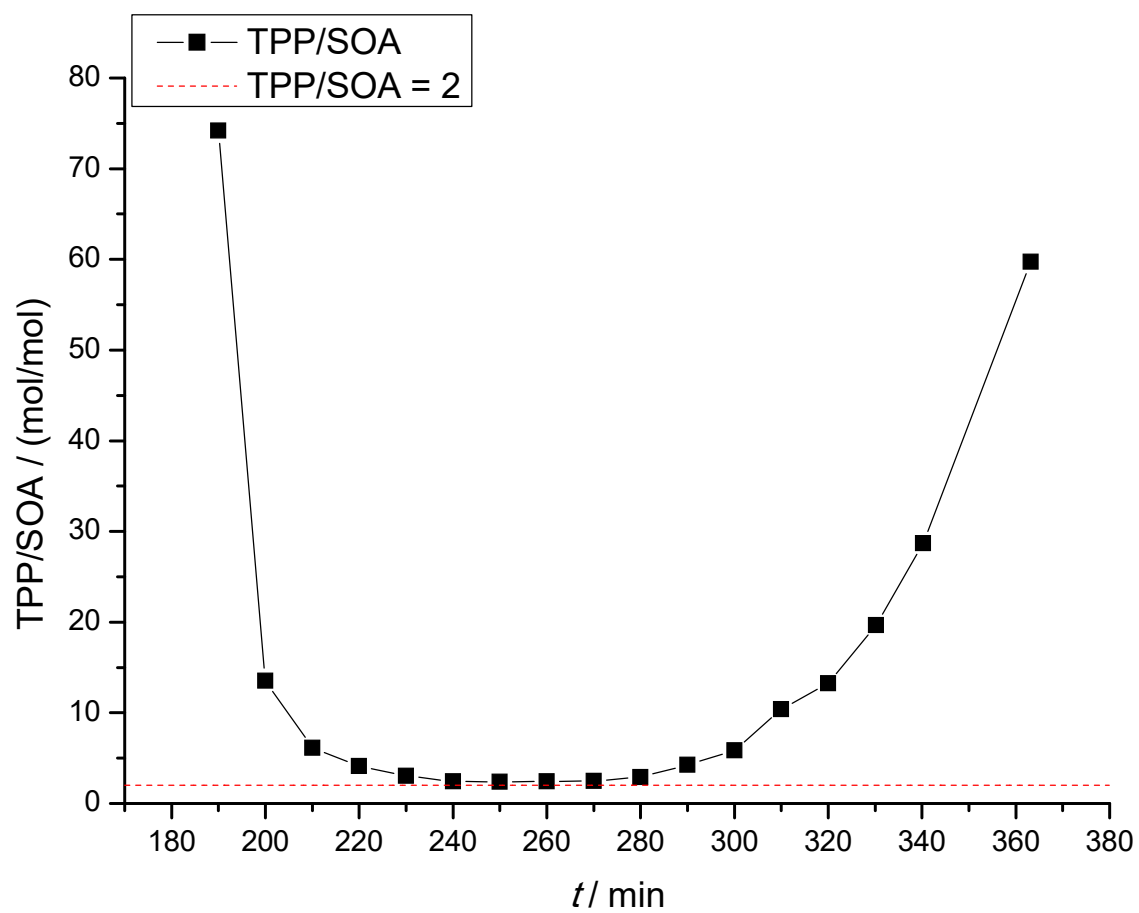Figure S7: Ratio of TPP (= detected TPP + detected TPPO) to SOA amount at the ozonolysis of α-pinene.

Figure S8: Ratio of TPP (= detected TPP + detected TPPO) to SOA amount at the ozonolysis of β-pinene.

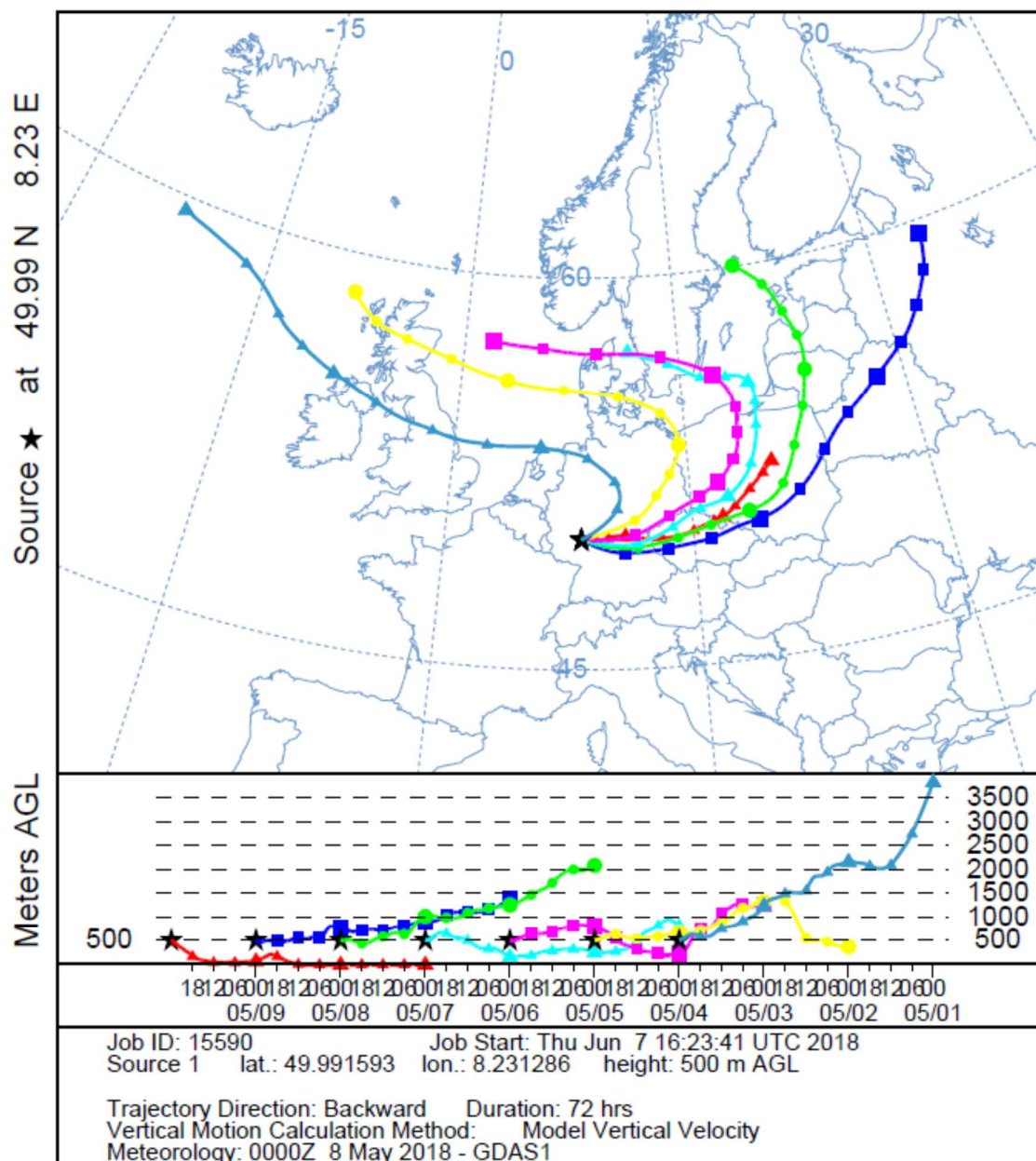Origins of the air masses between the 4 May to the 10 May 2018

Figure S9: 72h backward trajectories from 3.5 to 10.5 (every 24 hours)