

Measurements of secondary organic aerosol formation by aerosol mass spectrometry during ozonolysis of terpenes

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Introduction

Aerosol plays a key role in atmospheric processes. They can directly or indirectly influence the radiative forcing, decrease the visibility, and affect the human health. Secondary organic aerosol (SOA) is formed from atmospheric reactions of both anthropogenic and biogenic volatile organic compounds. Among these biogenic SOA precursors, it is known that gas phase reactions of monoterpenes represent an important source of biogenic SOA. However, knowledge on mechanisms of formation and the variation of the chemical composition of monoterpene SOA is still relatively sparse. Thus, the formation of SOA during the ozonolysis of three different monoterpenes (limonene, α -pinene and β -pinene) was investigated in an aerosol chamber. Formation of SOA was followed by measuring vacuum aerodynamic size distribution and chemical composition using an Aerodyne Aerosol Mass Spectrometer.

Aerosol Chamber

A series of monoterpene ozonolysis experiments was carried out in the LEAK chamber (Leipzig Aerosol Kammer). This chamber has a volume of 17 m³ and a surface to volume ratio (S/V) of 2.1. Temperature, ozone concentration and relative humidity were monitored during the course of experiment.

Ozone was produced by a UV-lamp. Seed particles were generated by atomizing an acidic solution of ammonium sulfate (0.03M/0.05M (NH₄)₂SO₄/H₂SO₄). Parallel to the AMS measurements, the particle size distribution was monitored by a SMPS system.



Figure 1: LEAK aerosol chamber at the IFT

AMS

Formation of SOA was followed by an Aerosol High Resolution Time of Flight Mass Spectrometer (HR-ToF-AMS) that provides real-time size resolved aerosol chemical composition (Jayne et al. 2000, Canagaratna et al. 2007).

Particles are focused into a narrow beam by aerodynamic lens. A chopper wheel is used to cut the particles beam for "Time of Flight" mode measurements (i.e. P-ToF mass distribution measurement mode) or to block/clear the particle beam for "mass spectrum" mode measurement (MS mode). The non-refractory components of the particles are flash vaporized on a heated surface (600°C) at the end of the P-ToF chamber. The evaporated particles are ionized by electron impact source (70eV). Positive ions are then extracted into the time of flight mass spectrometer with a frequency of 80Hz for their mass-to-charge-ratio (m/z) determination. During this work, the mass spectrometer was only used in V-mode.



Figure 2: Aerodyne Aerosol High Resolution Time of Flight Mass Spectrometer (HR-ToF-AMS)

Experimental conditions

Initial conditions are summarized in Table 1. In all cases the ratio between the reactant and ozone was chosen in relation with the rate constant of each monoterpene. Before each experiment, chamber is flushed by clean air at the corresponding relative humidity for 16h. Subsequently chamber is closed and ozone is introduced. Seed particles are added into the chamber when ozone concentration is reached at the set level.

| Reactant | Ozone | RH |
|------------------|-------|-----|
| ppb | ppb | % |
| Limonene | 300 | 35 |
| Limonene | 300 | <10 |
| α -pinene | 70 | 35 |
| β -pinene | 300 | 37 |

Table 1: Summary of the initial experimental conditions.

The concentration of seed particles was measured for 10-15 min. This allowed us to obtain an accurate initial seed particle concentration. At last, the reactant is introduced into the chamber by vaporizing a pure solution. In all experiments, AMS measurements started during the ozone injection. This period is totally free from organic compounds and these measurements are considered as blank for the AMS signals.

Results

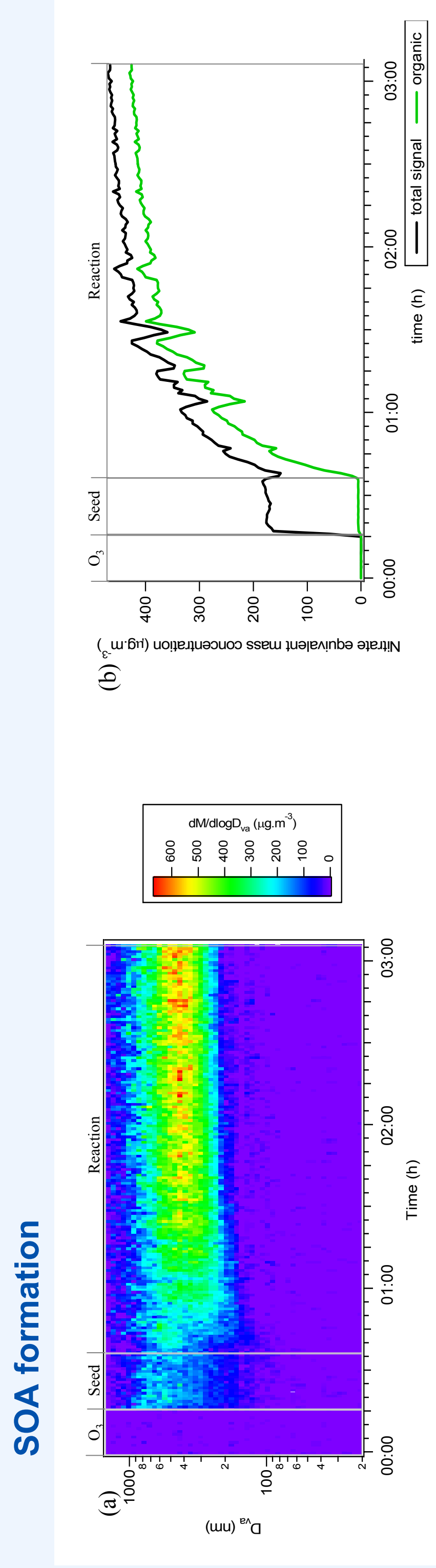


Figure 3: Ozonolysis of limonene at RH=35%. (a) Evolution of particle mass size distribution during the experiment in PToF mode and (b) time profile concentration of total signal and organics in MS mode.

Figure 3 shows (a) a particle mass size distribution and (b) organic mass time profile observed during ozonolysis of limonene. Directly after the introduction of the reactant, we observe a quick increase in organic signal. The size distribution shows the formation of smaller particles compared to the initial seed particles. The same kinds of profiles were also obtained during ozonolysis of α - and β -pinene.

Impact of relative humidity

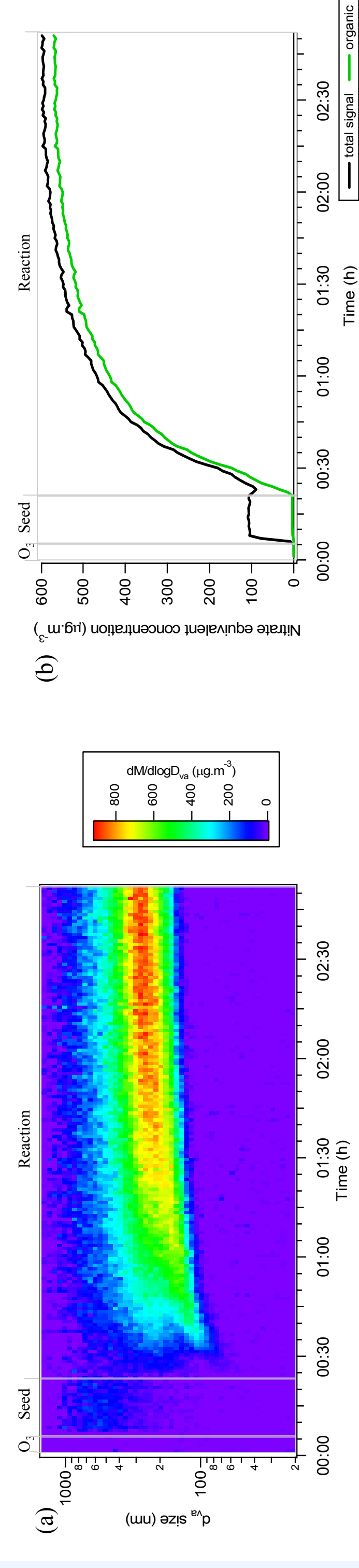


Figure 4: Ozonolysis of limonene at RH<10%. (a) Evolution of particle mass size distribution during the experiment in PToF mode and (b) time profile concentration of total signal and organics in MS mode.

Impact of the relative humidity on SOA formation can be evaluated by comparing the results with RH=35% (Figure 3) and with RH<10% (Figure 4). Time profiles at RH<10% look very similar to those at RH=35%. However, a much higher increase in the total SOA mass was observed in dry conditions. Similar to the RH=35% case, the formation of small particle in the first step of the reaction was observed but with smaller aerodynamic diameters.

It is not clear at his moment how the RH and the initial seed particle size distribution influenced the total SOA mass shown in Figure 3 and 4. This warrants further investigation in the future.

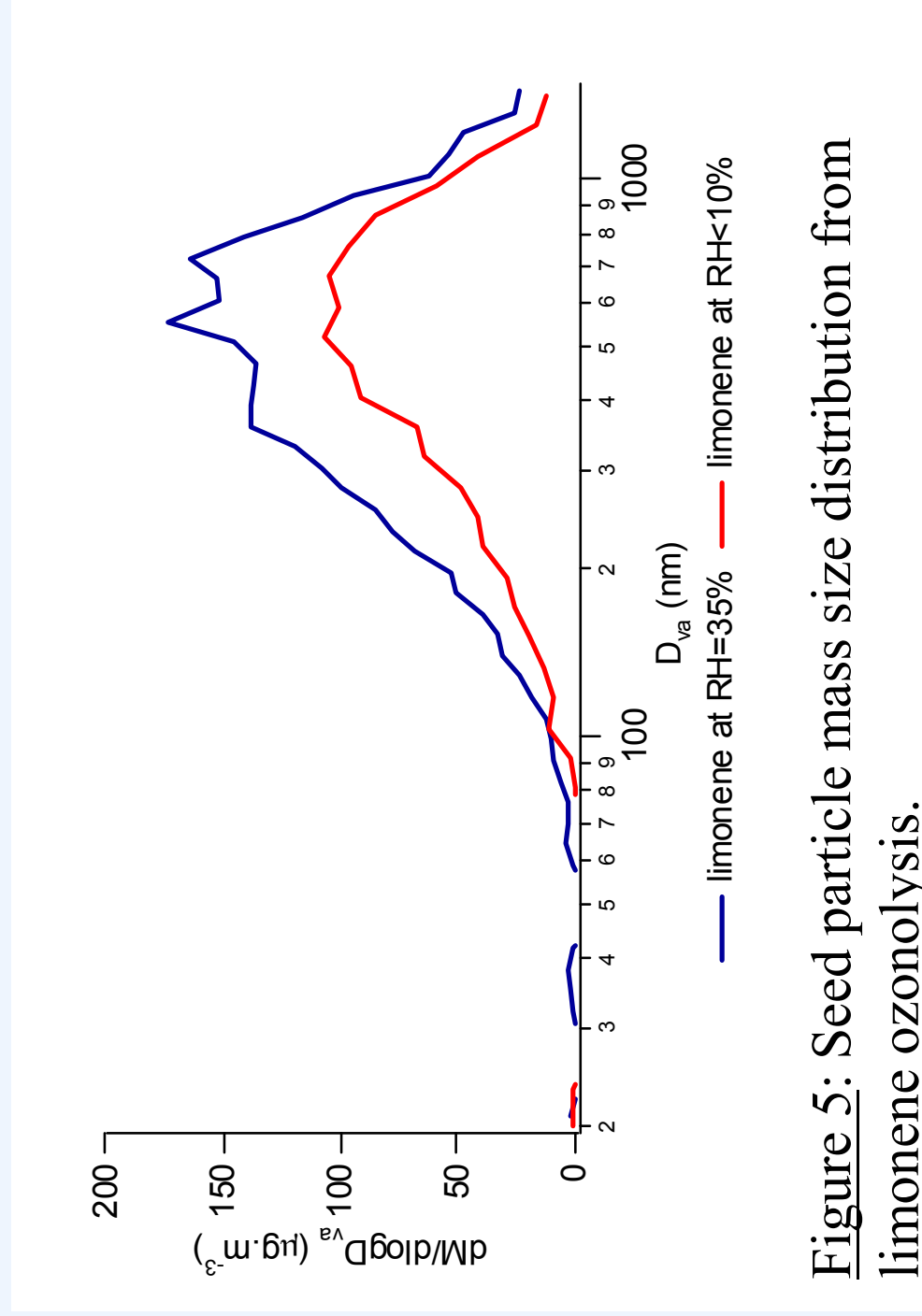


Figure 5: Seed particle mass size distribution from limonene ozonolysis.

References

- Alfarra M.R., Paulsen D., Gysel M., Garforth A.A., Dommen J., Prevôt A.S.H., Worsnop D.R., Baltensperger U. and Coe H., Atmospheric Chemistry and Physics, 6, 5279-5293 (2006)
- Bahreini R., Keywood M.D., Ng N.L., Varutbangkul V., Gao S., Flagan R.C., Seinfeld J.H., Worsnop D.R. and Jimenez J.L., Environmental Science and Technology, 39, 5674 (2005)
- Canagaratna M.R., et al., Mass Spectroscopy Reviews, 26, 185 (2007)
- DeCarlos P.F., Slowik J.G., Worsnop D.R., Jimenez J.L., Aerosol Science and Technology, 38 (12), 1185 (2004)
- Jayne J.T., Lear D.C., Zhang X., Davidovits P., Smith K.A., Kolb C.E. and Worsnop D.R., Aerosol Science and Technology, 33, 49 (2000)
- Takegawa N., Miyakawa T., Kawamura K., Kondo Y., Aerosol Science and Technology, in press.

SOA density

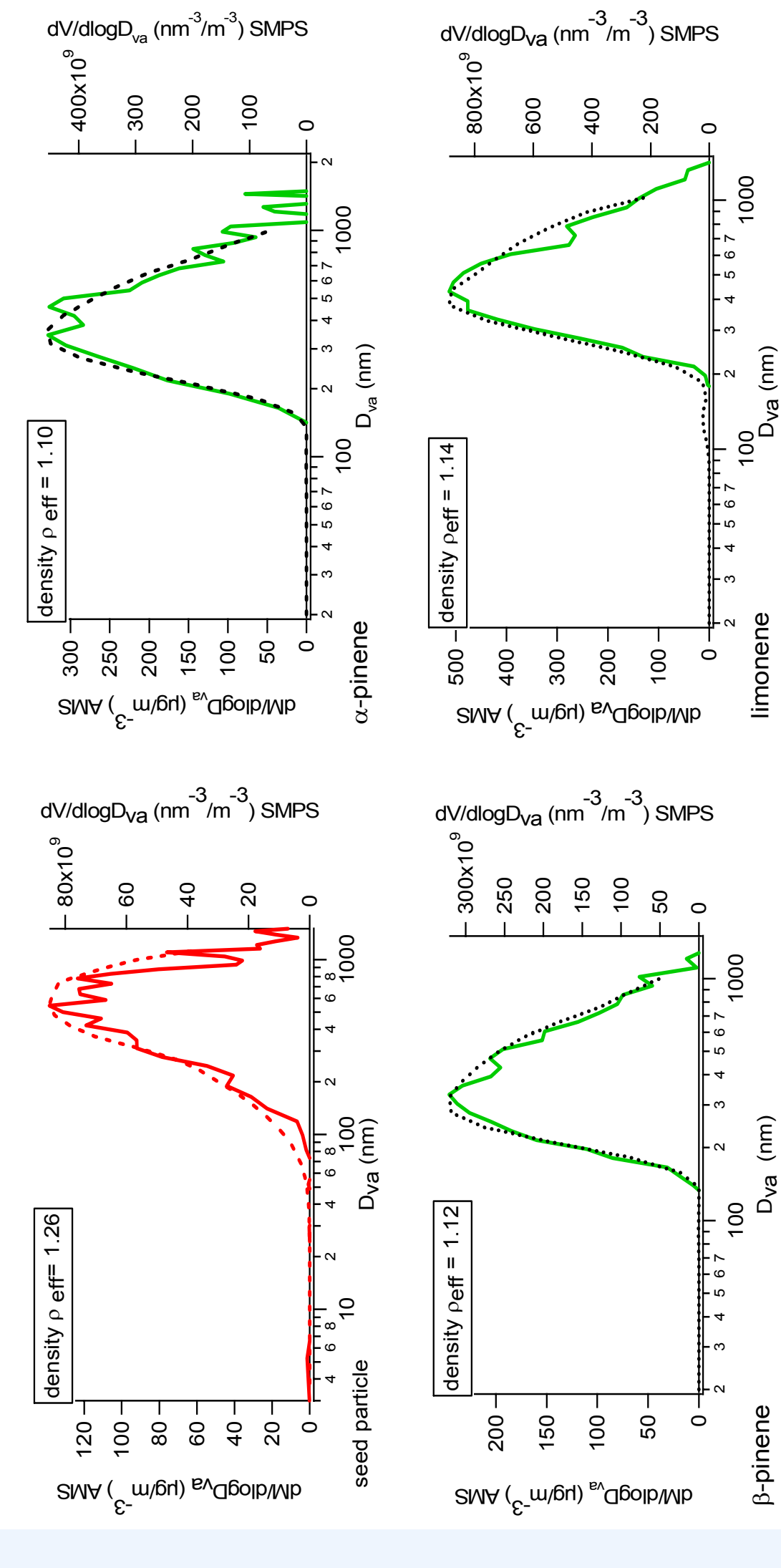


Figure 6: Comparison of particle size distribution giving by AMS and SMPS to estimate the effective density of SOA.

In Figure 6, the mobility diameter of SMPS ($d_{m,SMPS}$) was adjusted to align with the vacuum aerodynamic diameter ($d_{m,AMS}$) of AMS. For all studied compounds the effective densities of SOA at the end of experiment were smaller than the effective densities of seed particles. The effective density obtained for α - and β -pinene were somewhat lower than ones obtained by Bahreini et al. (2005) with RH = 55% (1.19 and 1.20 g cm⁻³, respectively).

$$\rho_{eff} = \frac{D_{m,AMS}}{D_{m,SMPS}} \cdot \rho_0$$

where ρ_0 is unit density, 1g/cm³ (DeCarlos et al., 2004).

Simultaneous measurements of particle size by AMS and SMPS allow us to access to the variation of the effective density (ρ_{eff}) of SOA which is an indication of the modification of the particle composition (e.g. oligomerization). The effective density is a direct function of the vacuum aerodynamic diameter ($D_{v,AMS}$) and the mobility diameter ($D_{m,SMPS}$) as follows:

Mass spectra

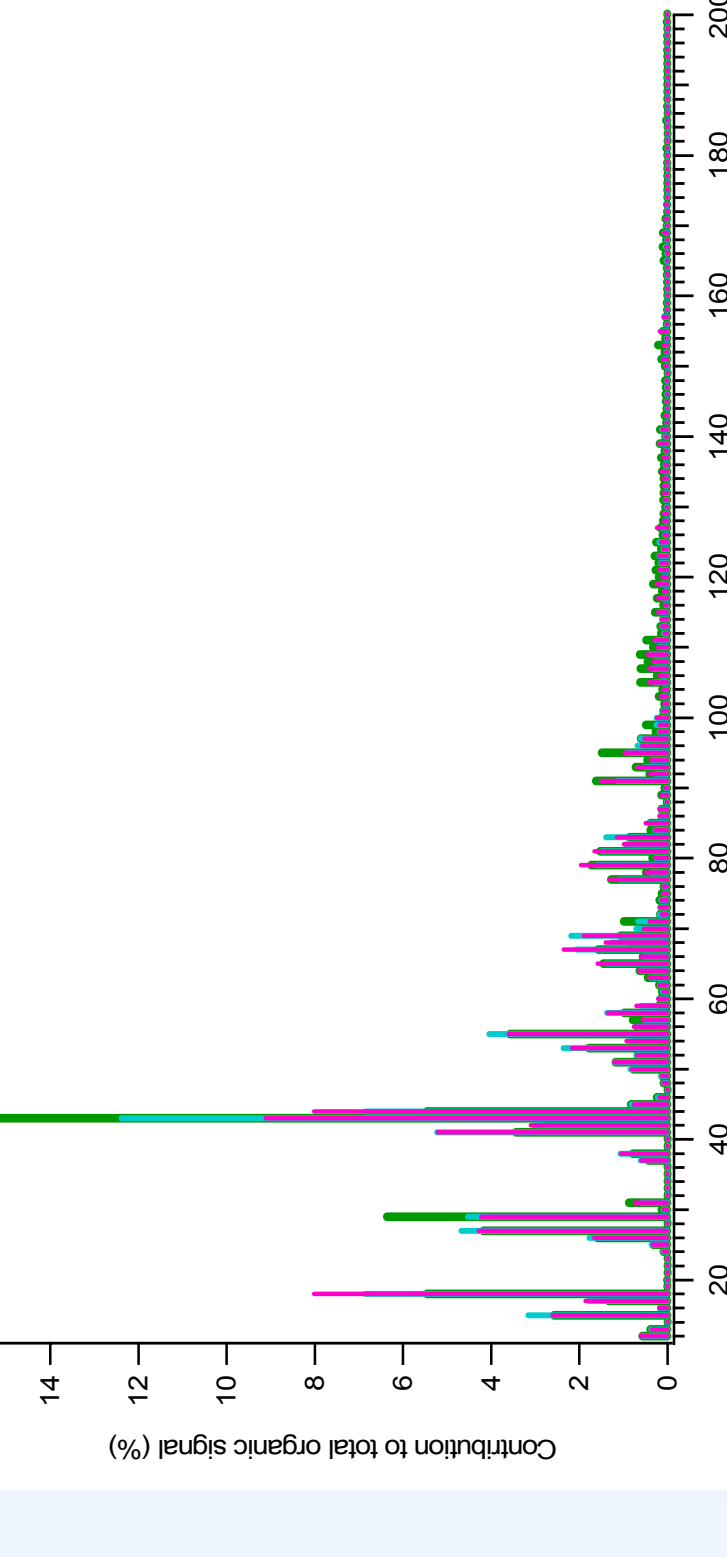


Figure 7: MS comparison at the end of experiment

Due to the electron impact ionization source of the AMS, organic compounds are highly fragmented. However, the presence of characteristic fragments can be observed. The comparison of the MS of the three studied compounds (Figure 7) shows the presence of similar fragments that are the indicators for monoterpene ozonolysis products. In all cases, the most important fragment is m/z 43 which corresponds to C₃H₃O⁺ (characteristic fragment of carbonyl functions) (see Table 2). Only for β -pinene this fragment (m/z 43) is at the same order of magnitude to m/z 44 (CO₂⁺ characteristic of decarboxylation of oxo- and dicarboxylic acids). The good correlation with m/z 18 (H₂O⁺) confirms the presence of carboxylic acid (Takegawa et al., in press). These fragments are characteristic for the formation of highly oxidised compounds. Moreover, contribution of m/z 43 and m/z 44 and 18 for α -pinene are in good agreement with results of Alfara et al. (2006).

| | m/z 43 | m/z 29 | m/z 44 | m/z 18 |
|------------------|--------|--------|--------|--------|
| Limonene | 15 % | 6 % | 5 % | 5 % |
| α -Pinene | 12 % | 4 % | 7 % | 7 % |
| β -Pinene | 9 % | 4 % | 8 % | 8 % |

Table 2: Comparison of the percentage of relative intensity of the main organic fragments.

Summary

The formation of SOA during ozonolysis of limonene, α -pinene and β -pinene was followed by AMS in presence of acidic ammonium sulfate seed particles. In all cases, the organic fraction of the particle rapidly increased after the beginning of the reaction. Impact of the relative humidity was investigated for limonene. The formation of smaller particles in the first steps of the reaction and the presence of more organic compounds at the end of experiment than at RH=35% were observed. The initial concentration of seed particles was slightly lower in the dry condition that might have also contributed to this differences.

The MS mode showed that the carbonyl (m/z 43) and oxo- and dicarboxylic acids (m/z 44) functions represented the most important component of organic fragments in all cases. These indicate that the SOAs are composed of highly oxidized compounds. The presence of higher molecular weight compounds was also observed.

Acknowledgement

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