TNA User Report

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Project title	**Formation and properties of secondary organic aerosol from the photoxidation of α-pinene aged products**
Name of the accessed chamber	FORTH-ASC
Number of users in the project	3
Project objectives (max 100 words)	Monoterpenes are the second class of volatiles which significantly contribute to secondary organic aerosol (SOA) masses in the atmosphere. Monoterpene SOA may represent as much as 50% of the total organic aerosol in forested areas with α-pinene being one of the most important precursors. In contrast to first products of α-pinene oxidation, e.g., pinonaldehyde, there is a tremendous lack of data regarding the SOA formation from the OH oxidation of α-pinene SOA aged products that would explain underestimated global SOA loadings compared to the burden from field measurements. The project fills the gap and is concerned with the formation and properties of the aerosol particles formed through OH radical oxidation of selected α-pinene SOA aged products. For the study purposes the following compounds were selected: norpinic acid, terpenylic acid, terebic acid and diaterpenylic acid acetate, which are relevant components of aged monoterpene SOA.
Description of work (max 100 words):	During the realization of the project the following research tasks were conducted: i) Synthesis of norpinic, terpenylic, terebic acids and diaterpenylic acid acetate – as α-pinene SOA aged products. All products were isolated and then – purified; ii) Execution of a series of the OH radical-driven oxidation of the above mentioned oxygenates in a FORTH/ICE-HT smog chamber. The OH radicals were formed by HONO photolysis; iii) Determination of the properties of fresh α-pinene SOA aged products aerosol, including the product volatility as well as gas phase and aerosol mass concentrations. The former was determined using a thermodenuder, while the latter –using a Proton Transfer Reaction Mass Spectrometry (PTR-MS, Ionikon Analytik) and an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometry (HR-ToF-AMS), respectively. A Scanning Mobility Particle Sizer (SMPS, classifier model 3080) provided the size number distribution.

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[1] Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.
[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.
[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Name of the PI: Rafal Szmigielski
Chamber name and location: FORTH-ASC, University of Patras, Patras, Greece
Campaign name and period: 26/11/2017– 2/12/2017 and 27/05/2018 – 9/06/2018

A series of experiments were performed in the FORTH-ASC to characterize model aerosol consisting of biogenic SOA components that were synthesized by our group. The objectives were to obtain the AMS spectra of the corresponding organic compounds, to measure their volatility and density and to also investigate their chemical aging as these aerosols react with OH. The results of these experiments can also be used to estimate the loss rates of the corresponding vapors to the walls of the chamber. Some examples of the results of these experiments are presented below. We believe that these results will be used in one or more publications. The corresponding data will be added to the EUROCHAMP-2020 database.

1. Characterization of Norpinic Acid Aerosol

In the first set of experiments particles consisting of norpinic acid and ammonium sulfate were produced by atomization and were injected in the FORTH-ASC chamber. The concentration and composition of these particles were measured for 3-4 hr. A typical example of such an experiment is shown in Figure 1.

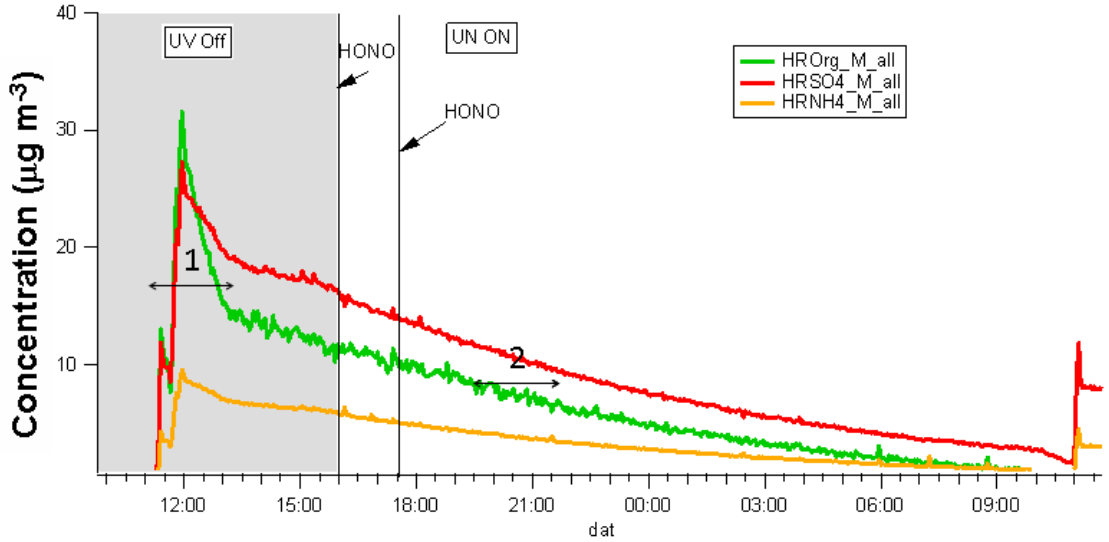

Figure 1. *AMS results of a typical experiment with Norpinic acid and ammonium sulfate particles. The first phase is the characterization of the particles in the dark. HONO was injected and the lights were turned on at 16:00 for the chemical aging phase.*

One of the interesting results of these experiments is that the ratio of OA/Sulfate changes rapidly during the experiment. During period 1 shown in Figure 1, the Norpinic acid partially evaporates trying to establish equilibrium with its surroundings. These measurements will be used to calculate the saturation concentration of Norpinic acid at room temperature, but also to quantify the evaporation rates. These results will be compared with theoretical predictions to investigate if there are any resistances to the mass transfer. The second interesting result is that after this initial equilibration period the ratio of the OA/Sulfate continues to decrease, more slowly this time. Our hypothesis is that this due to the loss of the Norpinic acid vapors to the walls of the chamber. These data will be analyzed and we may be able to develop a new method for the measurement of the rate of loss of semi-volatile vapors to the walls of chambers. This method could be useful in cases in which the gas-phase concentration of the semi-volatile organic vapor cannot be measured with the available instrumentation.

The change in the Norpinic acid/Sulfate ratio for another experiments performed in FORTH-ASC is shown in Figure 2. The ratio was initially equal to 6, dropped to approximately 2 due to the evaporation and then gradually dropped to 1 over 12 hours due to the losses of the vapors to the walls and then the evaporation of Norpinic acid from the particle phase in order to reestablish equilibrium with the gas phase.

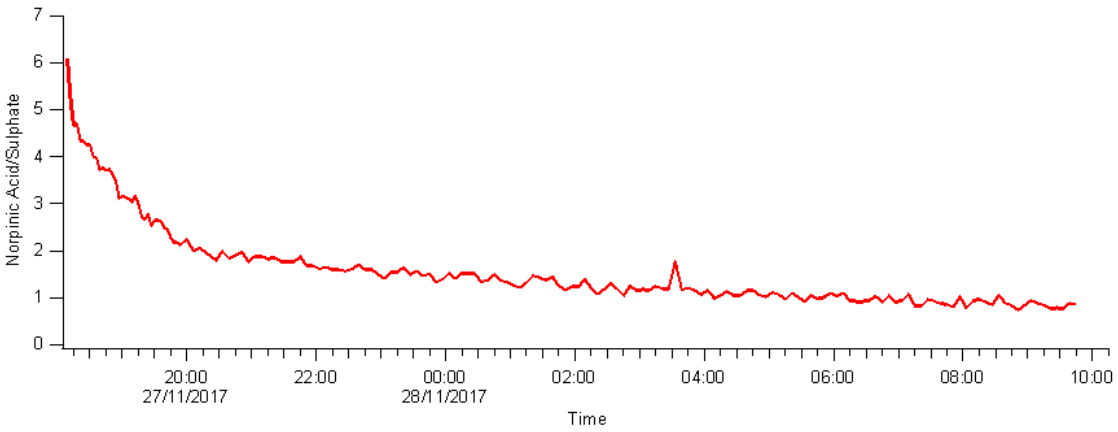

Figure 2. *Ratio of Norpinic acid to Sulfate during a typical experiment.*

The reaction of the Norpinic acid with OH during the second phase of our experiments resulted in the rapid production of a number of organic gas-phase compounds. These were measured by the PTR-MS. Examples of the production of secondary organic vapors can be seen in Figure 3. There is rapid increase of *m/z* 59 and *m/z* 81 after the production of OH in the chamber. These measurements together with the AMS measurements will be used to gain insights about the reactions taking place in the system and the fate of Norpinic acid in the atmosphere.

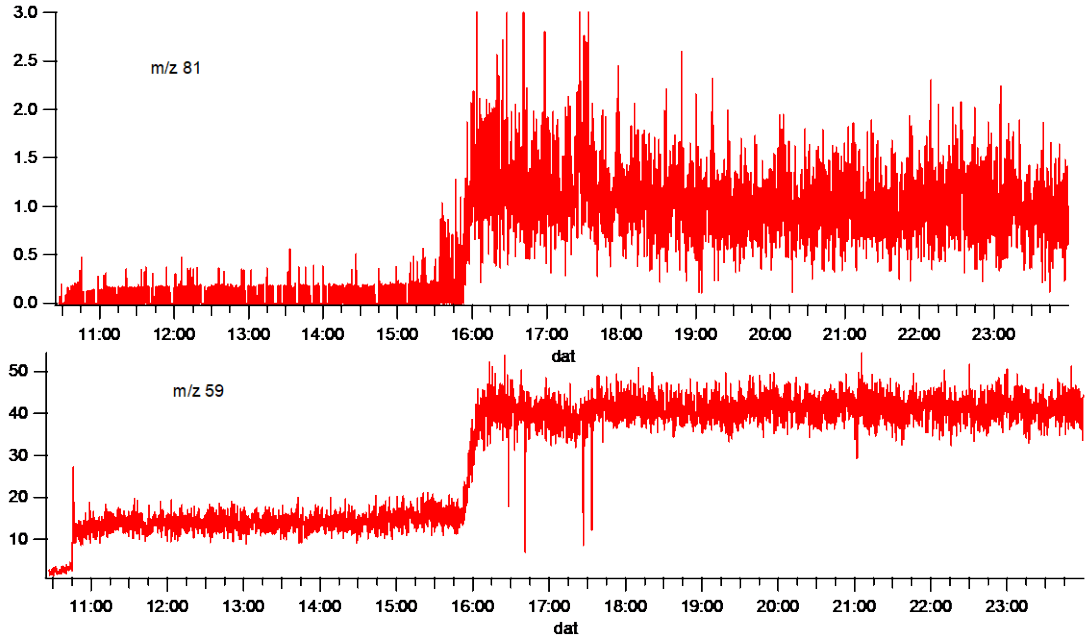

Figure 3. *PTR-MS measurements of organic vapors during a typical Norpinic acid production. HONO was introduced in the chamber and the lights were turned on at 15:45.*

2. Characterization of Diaterpenylic Acid Acetate (DTA)

The second set of experiments focused on the physical and chemical characterization of DTA aerosols. The same experimental procedure as in the Norpinic acid experiments was followed with a characterization state and then an oxidation with OH stage. Typical results of these experiments are shown in Figure 4.

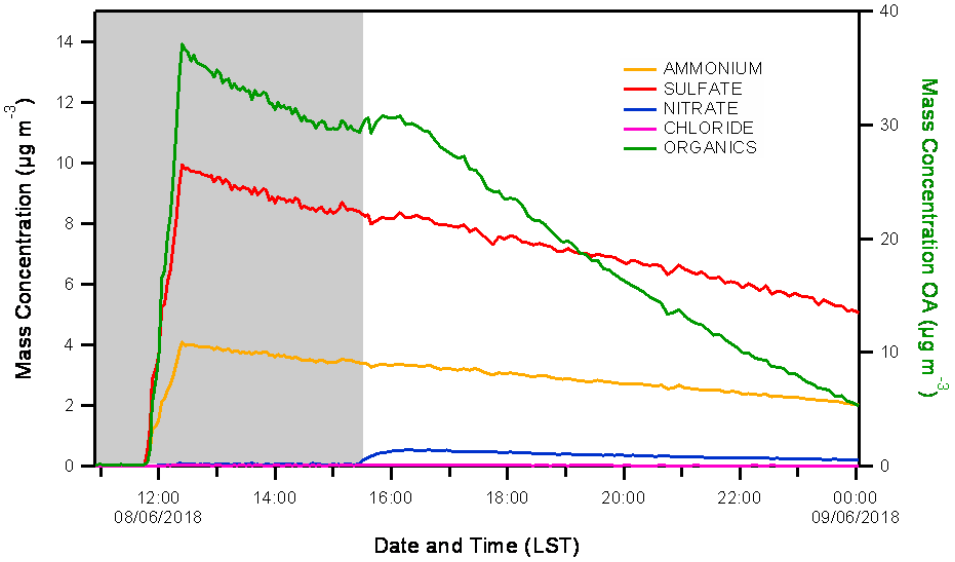

Figure 4. *Aerosol composition for typical DTA experiment. The shaded area corresponds to the characterization phase of the fresh aerosol (lights-off), while the white area to the chemical aging phase (lights-on). HONO was introduced into the chamber at the beginning of the aging phase.*

The most interesting result in this experiment is the decrease in the DTA aerosol concentration during the oxidation stage. These results will be valuable in understanding the fate of DTA in the atmosphere. The aerosol size distribution as measured by an SMPS is shown in Figure 5. No nucleation took place after the introduction of the OH.

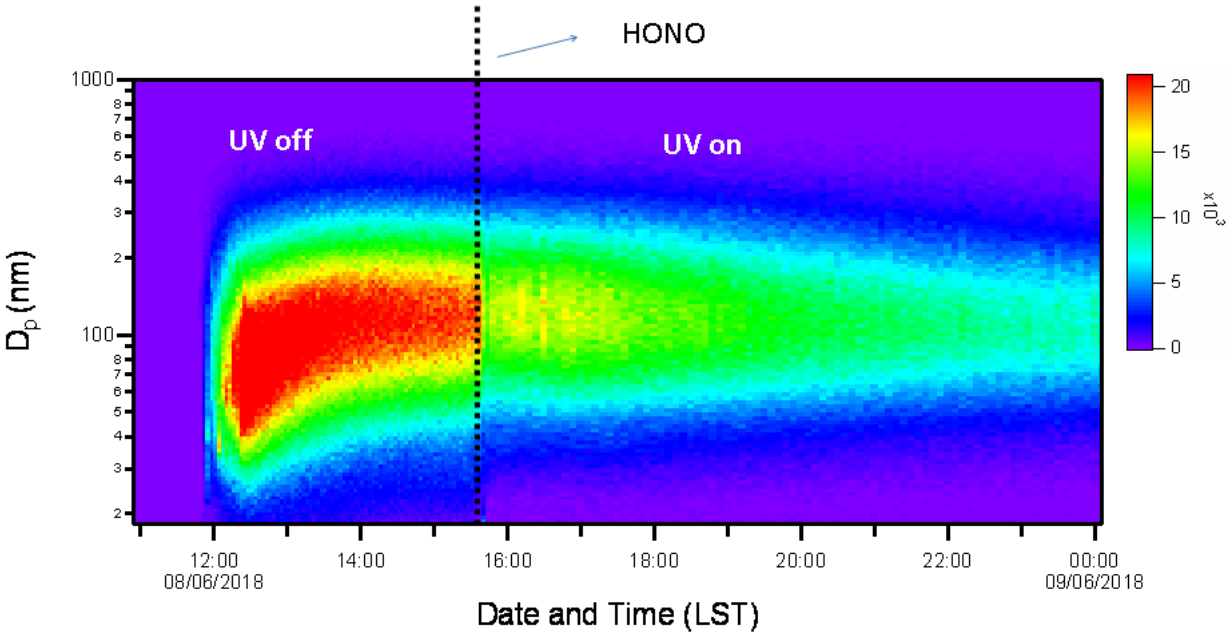

Figure 5. *Typical aerosol size distribution during a DTA experiment. The two phases (initial characterization and aging) are shown.*

One of the contributions of these experiments is the measurement, for the first time to the best of our knowledge, of the corresponding AMS spectrum of these biogenic SOA components. The corresponding mass spectrum of DTA is shown in Figure 6.

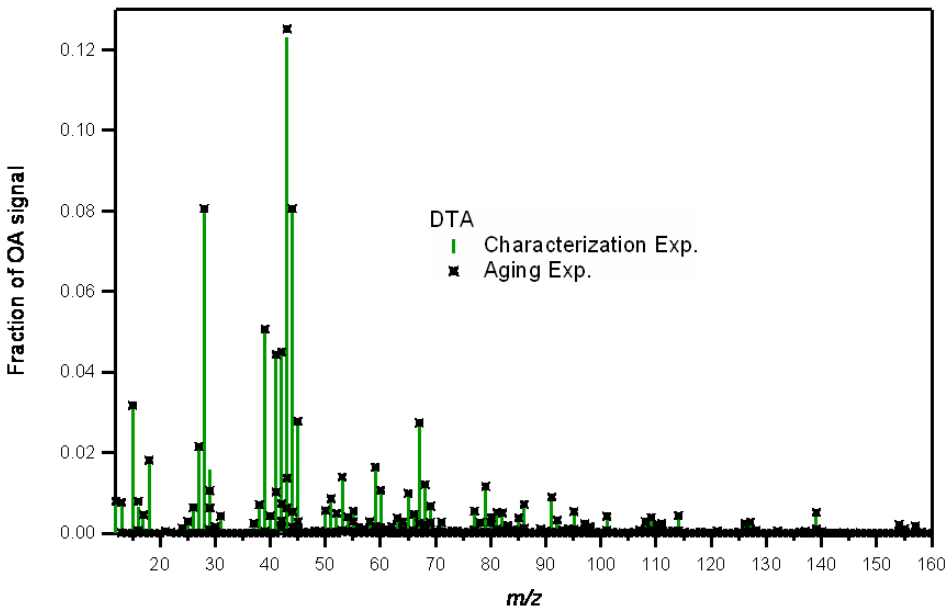

Figure 6. *AMS spectrum of fresh DTA and of DTA after exposure to OH for several hours. The changes were minor.*

3. Terebic acid characterization

The final set of experiments focused on the characterization of terebic acid/ammonium sulfate particles. The results of one of the experiments performed are shown in Figure 7. In the beginning ammonium sulfate particles were introduced in the chamber to quantify the particle wall loss rates in the particle. After six hours terebic acid/ammonium sulfate particles were introduced in the chamber and were characterized. Finally, HONO was introduced and the lights were turned on.

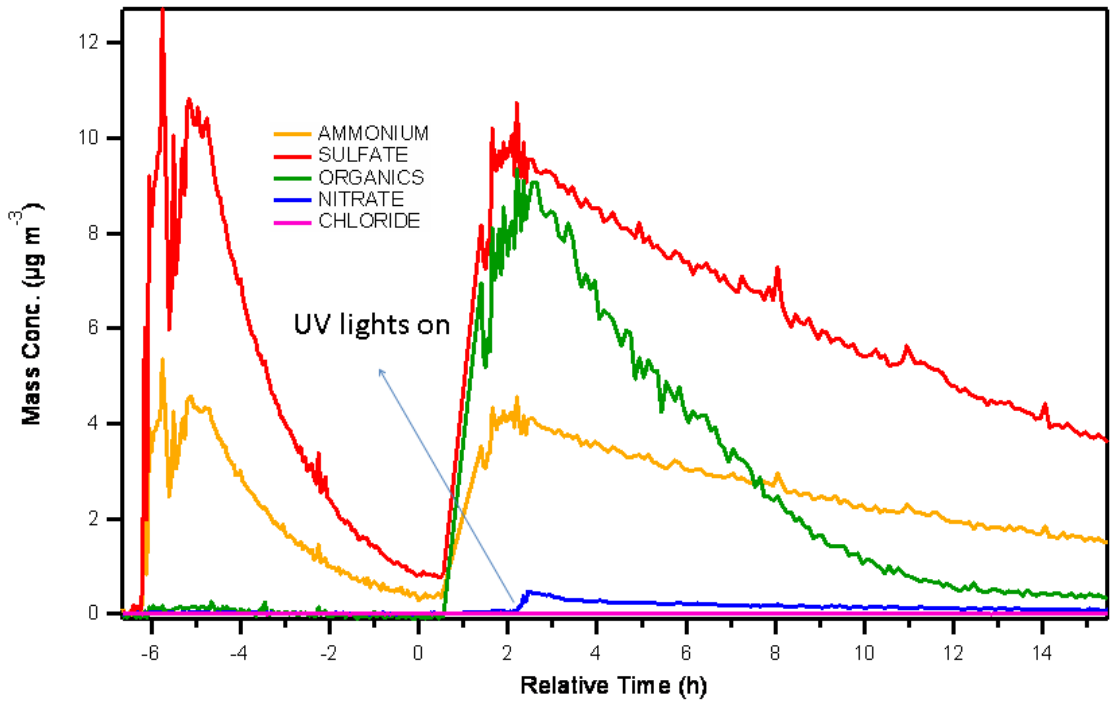

Figure 7. *Aerosol composition for typical terebic acid experiment. The shaded area corresponds to the characterization phase of the fresh aerosol (lights-off), while the white area to the chemical aging phase (lights-on). HONO was introduced into the chamber at the beginning of the aging phase.*

For this system too, the reaction of terebic acid with OH and the reduction of the organic aerosol concentrations is evident in Figure 7. The sulfate measurements will help in the data analysis because the corresponding reductions are due only to wall losses of the corresponding particles.