TNA User Report

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Project title	Molecular composition and volatility of secondary organic compounds from nitrate radical oxidation of biogenic and anthropogenic volatile organic compounds
Name of the accessed chamber	PACS-C3
Number of users in the project	3
Project objectives (max 100 words)	This project aims to provide fundamental data on nitrate radical (NO_3) initiated secondary organic aerosol (SOA) formation with representative biogenic and anthropogenic volatile organic compound (VOC) species. We focus on: 1) The molecular chemical composition of organic compounds in both gas and particle phases. 2) The volatility distribution of the oxidation products. 3) The potential impacts of night-day transition on SOA produced during night time.
Description of work (max 100 words):	During the project, we have conducted 22 chamber experiments of SOA formation via oxidation of isoprene, α-pinene, β-caryophyllene (biogenic VOCs), cresol (anthropogenic VOCs), as well as their mixtures (isoprene + α-pinene), with NO_3. The experiments were performed by first producing SOA under dark conditions and then switching to light conditions to simulate the night-day transition. By using state-of-the-art mass spectrometers and different methods for measuring volatility, we have obtained a comprehensive dataset of the chemical composition and volatility of the SOA formed.

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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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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Cheng Wu
Chamber name and location: PACS-C3, Paul Scherrer Institute
Campaign name and period: NARVE, March 25th – April 2nd, 2019
Text:

• Introduction and motivation

Nitrate radicals (NO_3) are effective nocturnal oxidants of a wide variety of volatile organic compounds (VOCs) from both biogenic and anthropogenic sources, including alkenes, aromatics, and oxygenates. Together with ozone (O_3) and hydroxyl radicals (OH) (which dominate during daytime), they are among the three major atmospheric oxidants and key species in secondary organic aerosol (SOA) formation. Field measurements using high time resolution instrumentation have shown significant day/night differences of SOA formation and properties, and significant contribution of nighttime chemistry, especially of NO_3 oxidizing biogenic VOCs, in different environments (Huang et al., 2019; Stefenelli et al., 2019; Lee et al., 2016). Overall, the number of chamber studies of NO_3 chemistry is much lower than that of O_3 and OH chemistry, and oxidation mechanisms as well as yields of NO_3 oxidation productions in the gas and particle phase have large uncertainties (Ng et al., 2017). This limits our understanding of formation and evolution of SOA and its health and climate impacts.

• Scientific objectives

In this project, we focused on investigating both the chemical composition and the volatility of NO_3 and O_3 oxidation products from biogenic and anthropogenic VOCs. Chemical composition and volatility are two important parameters for the determination of a compound´s lifetime in the atmosphere and thus its potential importance for aerosol formation.
This project has the following scientific objectives:

- Identification of the chemical composition of NO_3 initiated oxidation products in both gas and particle phases of purely biogenic VOCs isoprene, monoterpene (α-pinene), sesquiterpene (β-caryophyllene), an anthropogenic VOC (cresol), and mixed precursors (isoprene and α-pinene).
- Quantification of the potential impact of night-day transition on the SOA produced at night.
- Determination of the volatility distribution of SOA compounds formed both during night and during night-day transition.
- Long-term: improve the interpretation (e.g. source apportionment) of mass spectroscopic studies of ambient aerosols during nighttime and night-day transition.

• Reason for choosing the simulation chamber/calibration facility

The PSI chambers are well maintained and have many special state-of-the-art instruments. Further, the chamber used in this project can operate in a wide range of temperatures, and the emitted light spectrum captures the full range of atmospherically relevant photochemical reactions, which makes this chamber an ideal tool for our study.

• Method and experimental set-up

For most experiments, SOA was formed in the chamber by reaction of the precursor with NO_3 radicals (two experiments with O_3 for the comparison). Thermal decomposition of N_2O_5 served as a source of NO_3 radicals. Once the VOC concentrations in the chamber stabilized, reaction was initiated by vaporizing N_2O_5 into a glass bulb and then introducing it into the chamber. Most of the experiments were firstly performed under dark conditions to test NO_3 initiated SOA formation, and then the formed SOA was irradiated with UV lights to test the impacts of dark-to-light transition. The molecular composition of organic compounds in gas and particle phases was measured using a FIGAERO (filter inlet for gases and aerosols) coupled to a chemical ionization mass spectrometer (CIMS) with iodide as reagent ion, and an extractive electrospray ionization time-of-flight mass spectrometry (EESI-TOF). The volatile properties of particles were measured simultaneously with a volatility tandem differential mobility analyzer (VTDMA), and isothermal evaporation chambers.

• Data description

During this campaign, we conducted 22 experiments as summarized in Table 1. The data available include mass spectra on molecular level from gas phase oxidation products (from FIGAERO-CIMS) and particle phase oxidation products (from both FIGAERO-CIMS and EESI), the volatility information from both VTDMA and the evaporation chamber, as well as particle number concentration and size distribution.

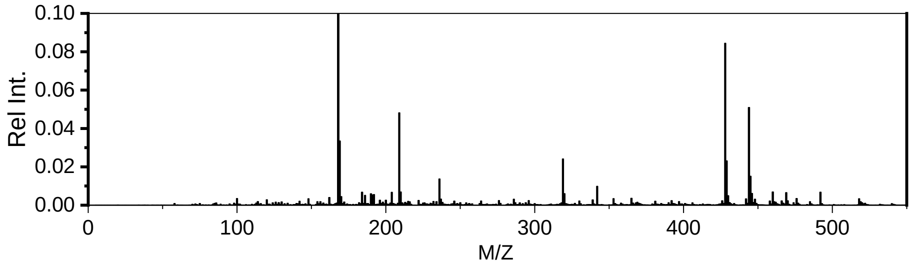
Table 1: Summary of experiments.

NO.	VOC	VOC Concentration (ppb)	Oxidant	Max OA Loading $(\mu g/m^3)$	RH (%)	T (°C)	Photolysis
With EESI, FIGAERO-CIM, VTDMA and evaporation chamber							
1	α-Pinene	100	NO3	18	58	21	x
2	α-Pinene	100	NO3	39	60	22	x
3	α-Pinene	100	NO3	53	58	18	
4	α-Pinene	40 - 50	NO3	4	65	25	
5	Cresol	50-60	NO3	3	75	22	x
5	Cresol	100	NO3	6	60	23	x
6	Cresol	200	NO3	43	63	23	x
7	Isoprene	100	NO3	9	58	20	x
8	Isoprene	100	NO3	24	58	23	x
9	Isoprene	100	NO3	11	58	23	x
10	α-Pinene + Isoprene	30 and 100	NO3	51	55	23	x
11	α-Pinene + Isoprene	30 and 100	NO3	10	60	23	x
12	β-caryophyllene	50	NO3	464	60	23	x
13	β-caryophyllene	5 - 10	NO3	60	60	23	x
14	α-Pinene	50	O3	47	58	23	
15	α-Pinene	40 - 50	O3	23	59	23	
With VTDMA and evaporation chamber							
16	α-Pinene	20	NO3	7	58	20	x
17	α-Pinene	20	NO3	8	65	20	x
18	α-Pinene	60	NO3	30	65	20	x
19	Cresol	40 - 50	NO3	24	62	20	x
20	Cresol	20 - 30	NO3	7	62	20	x
21	Cresol	70 - 80	NO3	1.6	59	20	x
22	Cresol	40 - 50	NO3	6	60	25	

• Preliminary results and conclusions

Preliminary results of the mass spectra from FIGAERO-CIMS and EESI showed a good agreement. As shown in Figure 1, for the NO_3 initiated SOA from α-pinene, the monomer region of the particle phase is dominated by $C_{8\text{-}10}H_yNO_z$, while the dimer region is made up of $C_{16\text{-}20}H_yN_{1\text{-}2}O_z$ for both instruments.

(a)



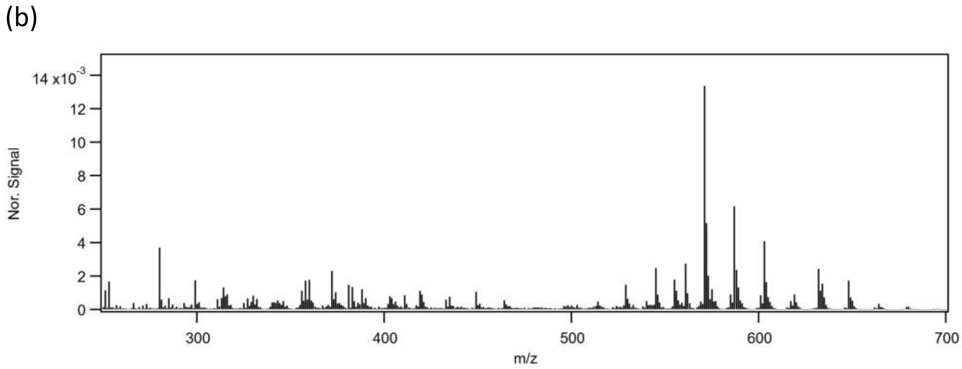


Figure 1 Example of particle phase mass spectra of NO_3 radical initiated oxidation of α-pinene from EESI (a) and FIGAERO-CIMS (b).

The mass spectra measured before and after photolysis clearly show that the chemical composition changes during the night-day transition (Figure 2). We find significant decrease of signals in the high mass regions (m/z > 500).

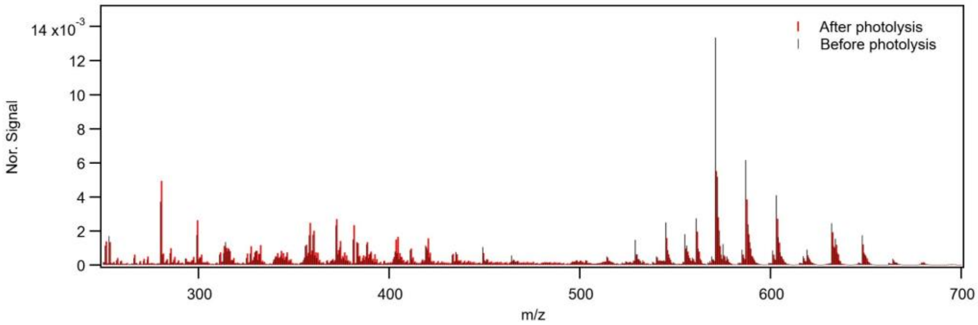


Figure 2. The FIGAERO-CIMS particle phase mass spectrum of α-pinene-NO_3 SOA before (black sticks) and after (red sticks) photolysis.

Figure 3 presents a comparison of the volatility (expressed as volume fraction remaining (VFR)) of NO_3 initiated SOA from different precursors. We observe different VFR at different heater temperatures for the different systems. Among them, the cresol- and β-caryophyllene SOA have the highest VFR values, i.e., lowest volatility, at 200°C, while isoprene and α-pinene SOA were almost completely evaporated at temperatures above 200°C, indicating a relative higher volatility. Preliminary results show that photolysis affects the volatility of SOA generated from NO_3 radicals, but this will be a focus of continued analysis.

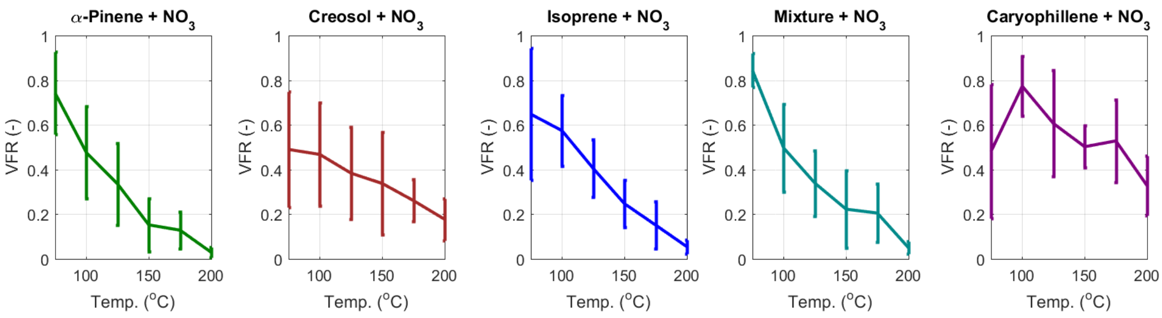


Figure 3. Thermograms, volume fraction remaining (VFR) plotted against the measured heater temperature, for SOA from different precursors.

• Outcome and future studies

This work performed at the Paul Scherrer Institute has provided a unique dataset with unprecedented detail of the molecular properties and volatility of the SOA formed from biogenic and anthropogenic precursors during the night, as well as during the night-to-day transition in a polluted (high NO_x) atmosphere. Data processing following the campaign is on-going and in a further analysis, we will combine the chemical composition and volatility information to improve our understanding of nighttime SOA formation from different precursors. Meanwhile, the mass spectrometric information will allow the assessment of the respective SOA fingerprints and enable us to improve the interpretation of mass spectrometric studies of ambient aerosols and to facilitate future source apportionment of this oxidation process.

• References

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