



## TNA User Report

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Project title	Linking peroxides in the gas and particle phase of secondary organic aerosol
Name of the accessed chamber	LEAK-LACIS
Number of users in the project	3
Project objectives (max 100 words)	<p>Peroxides are abundant in the oxidation of VOCs and have gained significant attention in recent years as potentially key compounds in SOA formation. However, peroxides are challenging to characterize and quantify in the gas and particle phase.</p> <p>The overall aim of the present proposal is to comprehensively characterize the formation and concentration dynamics of peroxides (HOMs) in the gas phase and particle phase oxidation schemes of VOCs combining for the first time two unique online high time resolution instruments.</p>
Description of work (max 100 words):	<p>The large ensemble of online and offline instruments at this chamber, allows for a comprehensive characterization of gas- and particle phase peroxides formed in the oxidation schemes of VOCs.</p>

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<sup>1</sup> Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

<sup>2</sup> 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.

<sup>3</sup> UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

<sup>4</sup> 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](http://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:** Markus Kalberer

**Chamber name and location:** ACD, TROPOS Leipzig

**Campaign name and period:** Linking peroxides in the gas and particle phase of secondary organic aerosol, 19/02/2019-26/03/2019

### Introduction and motivation

A large, sometimes dominant aerosol fraction in the lower atmosphere is secondary organic aerosol (SOA), which is formed via oxidation of biogenic and anthropogenic volatile organic compounds (VOCs) by atmospheric oxidants such as ozone, nitrate, and hydroxyl radicals. It is often suggested, that SOA contains high concentrations of peroxides (e.g. Docherty, 2005). Peroxides and other so-called Reactive Oxygen Species (ROS), present in particles or generated by particle components upon deposition of particles in the human lung, could cause adverse health effects due to their oxidative capacity. Therefore, understanding the roles of organic and total peroxides in the gas and particle phase on governing the overall particle-bound ROS formation and components in SOA is of importance for a comprehensive evaluation of their influence on human health. While particle-phase peroxides are often related to peracids, hydroperoxides or dimers with a peroxide bond, gas-phase peroxides are rarely studied. Among all gas-phase compounds, highly oxidized organic molecules (HOMs) were intensively studied during the last few years. Despite this effort, little is known in particular about their fate after partitioning into aerosol particles as HOMs might not be stable and might decompose quickly in the particle phase.

We recently built a novel online instrument (OPROSI), which is the first of its kind allowing to quantify ROS, including peroxides, in the particle phase (Wragg, 2016). This instrument quantifies also very short-lived peroxides, thus having the potential to improve our understanding of HOMs after partitioning into the particle phase.

## Scientific objectives

The overall aim of the present proposal is to comprehensively characterize the formation and concentration dynamics of peroxides in the gas phase (HOMs) and in the particle phase oxidation schemes of VOCs combining for the first time two unique online high time resolution instruments. This will contribute to a better understanding of adverse health effects of SOA because peroxides are a significant fraction of particle-bound ROS. Furthermore, a detailed chemical characterization will provide further important hints about the fate of HOMs after partitioning. This study will significantly help to advance our understanding of peroxide production and their role in SOA formation.

## Reason for choosing the simulation chamber/ calibration facility

The aerosol chamber at TROPOS provides a large set of instrumentation. The chamber team at TROPOS has a significant expertise in the design of chamber experiments, the detection and quantification of HOMs using NO<sub>3</sub>-Cl-SPI-TOFMS and the quantification of organic peroxides offline from filter samples with iodometric and derivatisation HPLC-MS methods. Furthermore, the size of the chamber enables us to collect a number of samples to do several additional offline total reactive oxygen species (ROS) analysis.

## Method and experimental set-up

We carried out a series of experiments in the new ACD (Atmospheric Chemistry Department) chamber at TROPOS. The experimental setup is shown in Figure 1. Several online and offline techniques were applied for a comprehensive gas and particle-phase characterization. HOMs in the gas-phase were quantified by an NO<sub>3</sub>-Cl-API-TOFMS. Particulate HOMs (containing carbonyl groups) were characterized from filter samples after derivatisation with 2,4-dinitrophenylhydrazine (Mutzel, 2015). The peroxide fraction of ROS in the particle phase were quantified with our unique online ROS analyser (OPROSI, Wragg, 2016). The total organic peroxides in the particle phase were detected offline from filter samples applying an iodometric method modified by TROPOS (Mutzel, 2013). Besides that, the concentrations of gas- and particle-phase organic compounds were continuously measured using PTR-MS and AMS. The particle number and size, the concentrations of ozone and NO<sub>x</sub>, and Temperature (T) and relative humidity (RH) were also acquired during all these experiments.

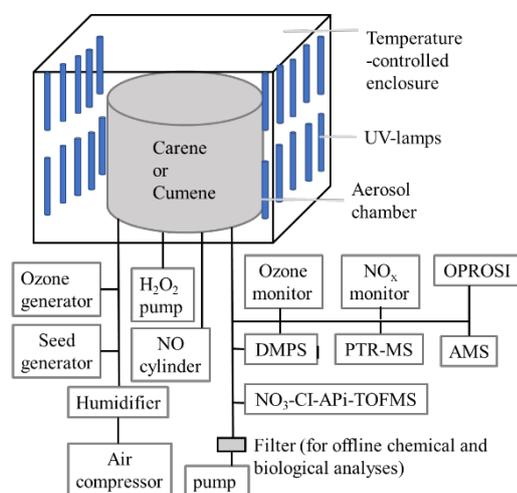


Figure 1 Experimental setup

Table 1 summary of experimental conditions and results

Experiments	Precursor conc. (ppb)	Seed Conc. (µg/m <sup>3</sup> )	NO (ppb)	T (K)	RH (%)	ΔHC (µg/m <sup>3</sup> )	ΔM (µg/m <sup>3</sup> )	SOA yield (%)
Cumene photooxidation	300	~ 15	0	298	~ 0	684-712	26.8-27.3	3.8-3.9
	300	~ 16.5	0	298	~ 55	667-673	12-16	1.8-2.4
	300	16-18	320-390	298	~ 0	918	13	1.4
Carene photooxidation	150	~ 15	0	298	~ 0	532-572	12.8-17.1	2.4-3.0
	150	~ 15	0	298	~ 55	499-512	19-21	3.8-4.1
	150	~ 15	180-200	298	~ 0	778	9	1.2
	300	12-15.8	310-400	298	~ 0	1347-1514	32-37	2.1-2.7
	300	15-17	320-390	298	~ 55	1470-1539	31-36	2.0-2.4
	300	15.2	0	298	~ 0	1040	89.9	8.6
	300	18.6	0	298	~ 55	1020	90	8.8
Carene ozonolysis	150	16-20	0	298	~ 0	601-730	218-268	36.2-36.7
	150		0	298	~ 55	748-794	267-310	35.7-39.0
Blank photooxidation	0	10-20	0 & 320-390	298	~ 55	-	-	-
Blank ozonolysis	0	20	0	298	~ 55	-	-	-

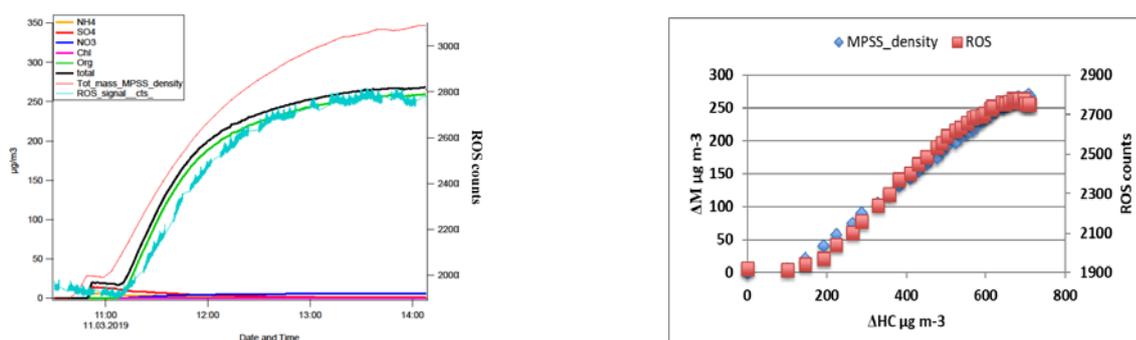
Within the project, carene and cumene were chosen to represent biogenic and anthropogenic SOA precursors, respectively. HOMs and peroxide formation during SOA formation from the two precursors under photolysis conditions were quantified and the role of NO<sub>x</sub> on ROS yield in these two SOA systems was investigated. ROS formation in carene SOA was in addition compared to ozonolysis experiment performed under dark conditions. The effects of relative humidity on the yield of ROS for all experiments were also evaluated. Table 1 summarises experimental conditions used in the study. As OH radical source, the photolysis of H<sub>2</sub>O<sub>2</sub> was used, whereby the amount of H<sub>2</sub>O<sub>2</sub> was kept as small as possible to exclude an influence on the online peroxide measurement. The online instrument has been carefully characterized for H<sub>2</sub>O<sub>2</sub> interference which was monitored through frequent blanks. Additionally, butanol-d<sub>9</sub> will be added as OH-clock to enable the quantification of OH radicals present in the system. Ozonolysis was carried out in the presence of carbon monoxide as OH scavenger. All experiments were performed for 3-4 hours in the presence of slightly acidic inorganic seed particles (pH=4-5) and up to 4 filter samples were collected at the end of the experiment for further offline analyses.

### Preliminary results and conclusions

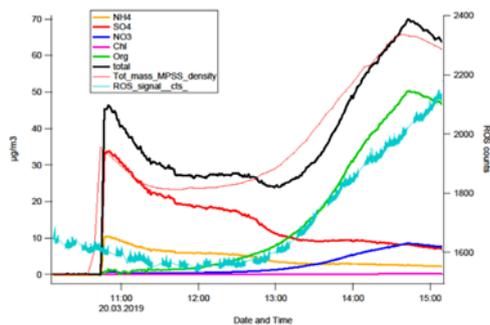
Figure 2 shows the typical reaction profiles from the ozonolysis of carene, and photooxidation of carene and cumene, respectively. From a preliminary analyse the following conclusions can be drawn:

- (1) there is a good correlation among the particle-phase organic compounds concentration, particles mass concentration (shown here as MPSS\_density), and ROS counts for all the experiments, indicating a constant content of ROS in SOA during SOA formation.
- (2) SOA generated from the photooxidation of cumene contains higher ROS/SOA compared to that from carene.
- (3) SOA produced from the photooxidation of carene has a higher ROS/SOA than that from the ozonolysis of carene.
- (4) The presence of NO<sub>x</sub> during the photooxidation of both biogenic and anthropogenic precursors inhibits particle-bound ROS formation, which can be explained by the formation routes of gas phase peroxides under high and low NO<sub>x</sub> conditions.
- (5) For both photooxidation and ozonolysis experiments, SOA formed under dry conditions has a higher particle-bound ROS yield and a higher ROS/SOA than those formed from wet conditions.

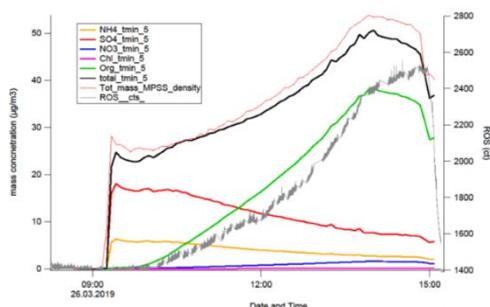
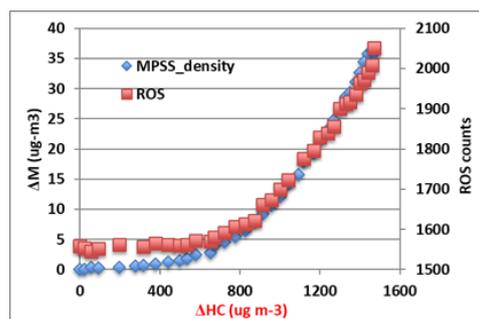
As for the particle-phase peroxide, as can be seen from Figure 3, (1) the total peroxide fraction (quantified with iodometry; Mutzel, 2013) from cumene photooxidation is much lower compared to that from carene photooxidation, and (2) peroxide for both cumene and carene photooxidation is much higher with NO<sub>x</sub> compared to than that with NO<sub>x</sub>.



(a) Carene (300 ppb) ozonolysis / RH=0% / NO=0 ppb



(b) Carene (300 ppb) photooxidation / RH~55% / NO=320-390 ppb



(c) Cumene (300 ppb) photooxidation / RH~0% / NO=0 ppb

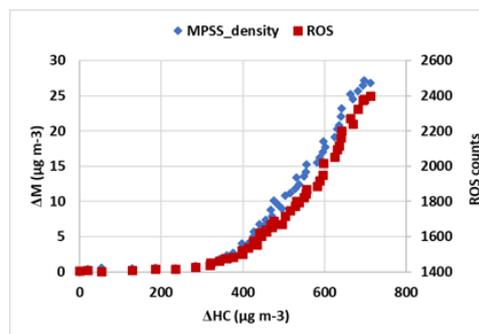


Figure 2 Reaction profile of (a) carene ozonolysis, (b) carene photooxidation, and (c) cumene photooxidation

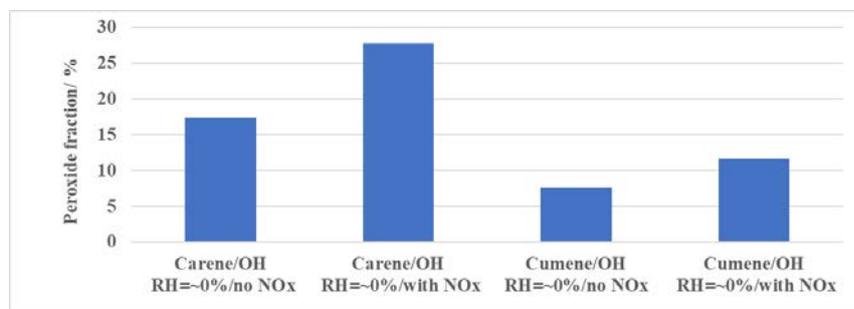


Figure 3 total peroxide fraction in SOA produced from carene (300 ppb) and cumene (300 ppb) photooxidation

## Future studies

(1) We are currently conducting chemical analysis from offline samples, and we started to prepare the results of the recently completed TNA experiments for publication in peer-reviewed journals.

(2) We have recently extended our study to examine the ability of the SOA to induce cell-based ROS production by using the same DCFH-HRP assay. We will further investigate the secretion of the (pro) inflammatory mediators and the expression of oxidative stress markers, and assess and compare gene expression after exposing human lung epithelial cell lines (A549) in organic extracts of SOA generated from different precursors and conditions during the TNA experiments.

Future chamber experiments will focus on refining the atmospheric parameter space influencing peroxide formation in the gas and particle phase and to translate the knowledge gained to field campaigns.

**References**

- Wragg et al., An Automated On-line Instrument to Quantify Aerosol-Bound Reactive Oxygen Species (ROS) for Ambient Measurement and Health Relevant Aerosol Studies, *Atmos. Meas. Tech.*, 9, 4891–4900, 2016.
- Mutzel et al., An improved method for the quantification of SOA bound peroxides, *Atmospheric Environment*, 67 (2013) 365-369.
- Mutzel et al., Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study, *Environmental Science & Technology*, 49 (2015) 7754-7761.