TNA User Report

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Project title	**Chemical aging of ambient organic aerosol**
Name of the accessed chamber	FORTH-ASC
Number of users in the project	1
Project objectives (max 100 words)	The main objective of our experiments will be the study of the chemical aging of ambient organic aerosol as it is exposed to OH. The experiments will take place in FORTH taking advantage of the fact that the OA in that area is mostly the result of long range transport and is quite oxygenated already. The innovative aspects of the proposed project focuses in the ability to conduct smog chamber experiments using ambient air as starting point in the field. This approach advances smog chamber experiments from the use of simple components, closer to the complex interactions of ambient air where numerous organic species both in the gas and particulate phase coexist.
Description of work (max 100 words):	The ambient OA is characterized and then introduced to the dual chamber system. In one of the chambers HONO is introduced as a source of OH. UV lights are used for the HONO photolysis. The evolution of the OA and the organic vapors in both chambers is followed by a HR-AMS and a PTR-MS. Additional instrumentation is used (SMPS, NOx and ozone monitors, etc.). The procedure includes initially the installation of the chamber system indoors to validate the check/performance on how clean the chambers are, if there are any leaks, the wall losses profile, pump losses during the filling process etc. Finally, the system is set outdoors and experiments are conducted using artificial sunlight (wind conditions did not permit the use of natural sunlight).

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User 2 Information	
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Family name	
Nationality	
Activity domain	
Home institution	
Institution legal status	
Email	
Gender	
User status	
New user	

[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: Christos Kaltsonoudis
Chamber name and location: FORTH-ASC
Campaign name and period: 6/3/2018 – 5/4/2018
Text:

Introduction and motivation

Smog chamber experiments using as a starting point ambient air can improve our understanding of the evolution of atmospheric particulate matter at timescales longer than those achieved by traditional laboratory experiments. These types of studies can also take place under more realistic environmental conditions addressing the interactions among multiple pollutants. The use of two identical smog chambers, with the first serving as the baseline chamber and the second the perturbation chamber (in which addition or removal of pollutants, addition of oxidants, change in the relative humidity, etc., can facilitate the interpretation of the results in such inherently complex chemical systems. The differences of the measurements in the two chambers can be used as the basis for the analysis of the corresponding chemical or physical processes.

Scientific objectives

The main objective of our experiments is to study of the chemical aging of ambient organic aerosol as it is exposed to OH. The experiments took place in FORTH where the OA in that area is mostly the result of long range transport and is quite oxygenated already. The innovative aspects of the proposed project focuses in the ability to conduct smog chamber experiments using ambient air as starting point. This approach advances smog chamber experiments from the use of simple components, closer to the complex interactions of ambient air where numerous organic species both in the gas and particulate phase coexist. We aim to estimate the potential in forming additional SOA of already aged air masses. Additionally, we try to identify the precursors responsible for this OA enhancement.

Reason for choosing the simulation chamber/ calibration facility

The FORTH-ASC facility has produced significant results in respect to the OA levels and composition of ambient origin over the past (Pikridas et al., 2010; Kostenidou et al., 2015; Florou et al., 2017). Moreover, the chamber facility operating for the last 6+ years yielded a number of important publications including the emission of several sources such as biomass burning and meet cooking (Kostenidou et al., 2013; Kaltsonoudis et al., 2016). The Facility is well equipped (HR-tof-AMS, PT-RMS, SMPS, gas monitors etc) for ambient measurements and smog chamber experiments.

Method and experimental set-up

An HR-ToF-AMS (Aerodyne Research Inc.), a PTR-MS (Ionicon Analytik), a Scanning Mobility Particle Sizer (SMPS, classifier model 3080, DMA model 3081, CPC model 3787, TSI), an ozone monitor (API Teledyne, model 400E) and a NO_x monitor (API Teledyne, model T201) were used to measure the ambient and chamber composition. Details on the instrumentation used can be found elsewhere (Kostenidou et al., 2013; Kaltsonoudis et al., 2016). Sampling between the two chambers was alternated every three minutes by an automated three-way valve synchronized with the operation of the corresponding instrumentation. For the initial experiments the dual chambers were stationed inside the FORTH chamber facility in order to evaluate their performance in a regulated enviroment. After this they were deployed outside to simulate experiments on the field. In both cases artificial lights were used (windy conditions inhibited the use of natural sunlight).

The instrumentation was first used to characterize the ambient conditions for at least a couple of hours. After filling of the chambers was completed, sampling was switched from ambient measurements to the chambers where the initial characterization of the sampled air inside the chambers takes place. Then a perturbation (addition of HONO to produce OH radicals) is implemented in one of the chambers while the other is used as a reference. Following the completion of the experiment ammonium sulfate seeds are introduced into both chambers to measure their loss rate on the walls over time. In this step the chambers are refilled with particle free air. This last stage is used to quantify the particle size dependent wall loss rate constants in order to make corrections to the rest of the data. Finally, the instrumentation is switched back to ambient observation mode and the chambers are flushed with ambient air clean air in preparation for the next experiment.

Data description

A total of 5 experiments were conducted, 3 inside the FORTH chamber facilities and 2 outdoors (Not including the chamber preparation and evaluation tests). From the ambient collected data collected, we examined the particulate mass and number concentrations, as well as their size distributions that were obtained from the SMPS instrument. Additionally, the AMS mass spectra and O:C ratio of the OA were considered. For the gas phase species, the VOC levels and the NO_x and O_3 time-series were also measured. The same species/values were also measured from inside the two chambers to point out differences between the ambient, the reference chamber (due to the filling procedures and the chamber wall interactions) and the perturbation chamber (due to the addition of OH).

Preliminary results and conclusions

Preliminary results from the dual-chamber perturbation experiments show that the ambient air components have the potential to form additional SOA upon OH oxidation. Upon OH oxidation of the ambient air components in the perturbed chamber, nucleation was observed in most experiments. From the AMS measurements, 1-3 μg m^{-3} additional SOA (including organonitrates) was formed on average after an OH exposure equivalent to 12 h in the ambient. An additional 0.2 μg m^{-3} sulfate and 0.06 μg m^{-3} ammonium formed, probably in the form of a mixture of ammonium bisulfate and ammonium sulfate. No chemistry was observed in the control chamber due to the low level of OH.. The O:C for the ambient OA was on average 0.5, indicating that the ambient OA was moderately

oxygenated. Before UV illumination, the O:C of the OA in both the perturbed and the control chambers was also around 0.5, consistent with the fact that the OA in the chambers was aproximatelly the same as the ambient OA. After the OH introduction, the O:C of the OA in the control chamber remained practically the same at 0.5, while that in the perturbed chamber gradually decreased to 0.3 until the end of the experiment. An O:C of 0.3 indicates that the additional SOA formed in the perturbed chamber had much lower O:C than the ambient OA.

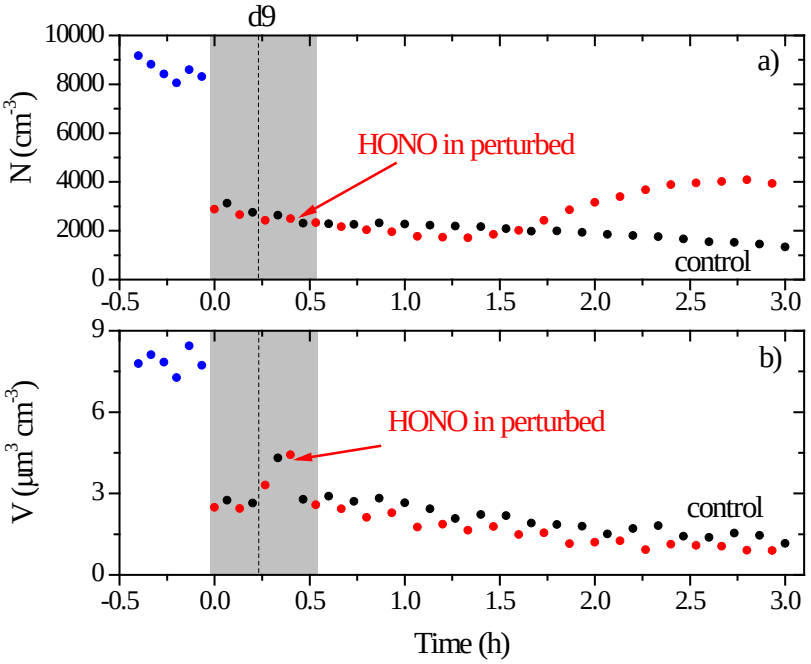

Figure 1: The SMPS-measured **a)** aerosol number concentration evolution and **b)** aerosol volume concentration evolution during Exp. 1 for ambient (blue symbols), the perturbed chamber (red symbols) and the control chamber (black symbols). At time zero, the instruments switched from measuring ambient to the chambers. Butanol-d9 was added to both chambers at *t*=0.25 h. At *t*=0.4 h, HONO was added only to the perturbed chamber to produce OH under UV illumination. The shaded area indicates that the chambers were dark.

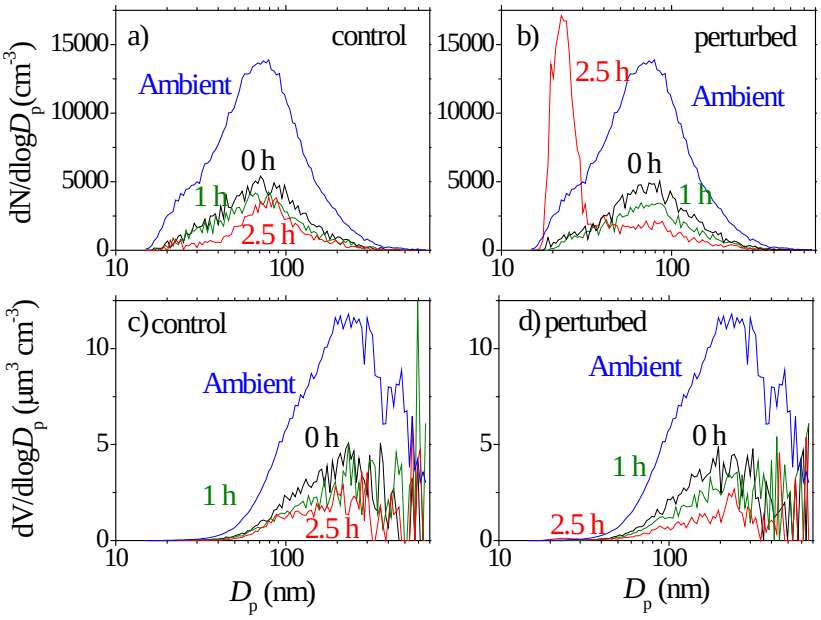

Figure 2: The SMPS-measured aerosol number and volume size distributions for the control and the perturbed chamber during Exp. 1.

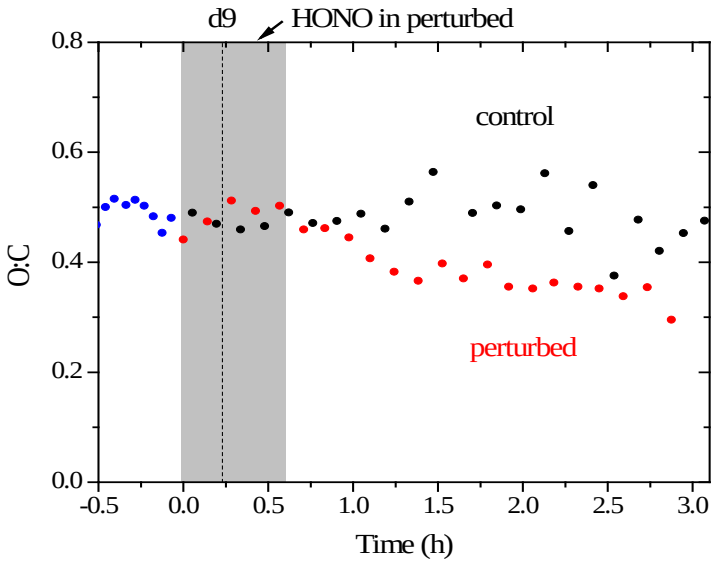

Figure 3: The atomic oxygen to carbon ratio (O:C) evolution of the AMS-measured organics during Exp. 1. At time zero, the instruments switched from measuring ambient (blue symbols) to the chambers. Butanol-d9 was added to both chambers at *t*=0.25 h. At *t*=0.4 h, HONO was added only to the perturbed chamber to produce OH under UV illumination. The shaded area indicates that the chambers were dark.

Outcome and future studies

The preliminary results indicate new mass formation of OA in these relativelly oxygenated air masses due to oxidation. A further evaluation of the VOC and IVOC potential to produce this extra mass is needed. The PTRMS data do not justify this formation since there was no noticible decrase in the VOC species measured. IVOC concentrations were not measured during these experiments. Future chamber experiments incorporating ambient air oxidation, coupled with IVOC measurments may produce solid results on the oxidative potential of relative aged air masses.

References

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