TNA User Report

The completed and signed form below should be returned by email to

eurochamp2020@lisa.u-pec.fr

Project title	Investigation of the impact of nitryl chloride chemistry on the radical budget in ambient air – Part II
Name of the accessed chamber	SAPHIR
Number of users in the project	1
Project objectives (max 100 words)	Measurements of nitryl chloride (ClNO2) using the facilities provided by the SAPHIR chamber during summer. This is the second part of a study which aims to quantify ozone production from chlorine chemistry in air masses representative of continental Europe. The first part of the study took place in winter (February 2019).
1Description of work (max 100 words):	Deployment of a chemical ionization mass spectrometer (CIMS) at the SAPHIR chamber coupled with a 50m sampling tower to sample above the nocturnal boundary layer.

Principal Investigator's and group's information	
First name	Roberto
Family name	Sommariva
Nationality	Italy
Activity domain[1]	Earth Sciences & Environment
Home institution	University of Birmingham/University of Leicester
Institution legal status[2]	UNI
Email	rob.sommariva@gmail.com
Gender	MALE
User status[3]	RES
New user	NO

User 1 Information[4]	
First name	
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

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

Trans-National Access (TNA) Scientific Report

The completed and signed form below should be returned by email to

eurochamp2020@lisa.u-pec.fr

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: Roberto Sommariva
Chamber name and location: SAPHIR, Juelich, Germany
Campaign name and period: JULIAC-3, July-August 2019
Text:

Nitryl chloride ($ClNO_2$) has been shown in recent years to be present at a much larger extent than previously thought (e.g., Phillips et al., 2012; Bannan et al., 2015; Sommariva et al., 2018), even in regions that are not close to the coast, where sea salt can serve as a source for chloride.
Laboratory studies (Roberts et al., 2009) and field campaigns (Osthoff et al., 2008) have shown that the photolysis of $ClNO_2$, which is heterogeneously formed during nighttime, releases chlorine atoms which react with organic compounds to form organic peroxy radicals (RO_2).
This chemistry can have a large impact on the formation of tropospheric ozone (O_3), but only few measurements of $ClNO_2$ in ambient air have been performed in Europe and in none of these studies radical species were measured at the same time.

The main objectives of this project are: 1) to measure $ClNO_2$ contained in ambient air masses representative of continental Europe and 2) to quantify the additional ozone production caused by $ClNO_2$ chemistry using simultaneous measurements of photolysis rates, RO_2, O_3, NO_x and $ClNO_2$.
The SAPHIR chamber in Juelich has recently been coupled to an inlet that allows sampling ambient air from a 50m height, higher than the nocturnal surface layer, so that the sampled air masses are not directly influenced by local sources.
For this project, measurements of radicals (OH, HO_2, RO_2) and ancillary measurements (photolysis rates, NO_x, O_3, NO_3, N_2O_5, volatile organic compounds) were provided by the SAPHIR core instruments. The $ClNO_2$ measurements were taken with the University of Leicester Chemical Ionization Mass Spectrometer (CIMS), which was deployed at the SAPHIR chamber for the JULIAC-3 campaign (August 2019). The instrument was set up during the period July 22nd–26th, experiment as part of the TNA were done from August 5th to 9th and joint experiments were continued by remotely controlling the instrument for the rest of the campaign, with assistance from SAPHIR researchers.

The CIMS instrument operated continuously for 4 weeks, collecting data 24/7. Calibrations were carried out once a week. During the campaign two types of experiments were done:

1. Air masses were continuously flushed into the SAPHIR chamber at a high flow rate of 250 m^3/h (resulting in a residence time of air in the chamber of about 1 hour), while the instruments sampled from within the chamber. These experiments provided measurements of $ClNO_2$ and other chemical parameters which can be considered representative of continental Europe and not affected by local sources.
2. The SAPHIR chamber was filled with nocturnal air and the roof opened to allow the photochemical processes to take place. These experiments allowed the direct observations of the impact of $ClNO_2$ chemistry on ozone formation.

The experiments conducted during JULIAC-3 were similar to those conducted during JULIAC-1 in February 2019. Together, the winter and summer datasets allow a thorough investigation of $ClNO_2$

chemistry and its impact on the production of tropospheric ozone in different seasons and under a range of environmental conditions.

The data collected during the project (both in winter and in summer) are currently being processed and quality controlled. The preliminary results look very encouraging and show that $ClNO_2$ was present almost every night with concentrations of the order of tens to hundreds of parts-per-trillion. The dataset collected during this project is also been used to improve the characterization of the SAPHIR chamber, and understand the formation and loss of chlorine compounds on the chamber walls.

The preliminary results indicate that the project has been overall successful and has produced a valuable dataset which is now being analyzed. A first overview of the results will be presented at upcoming international conferences, such as the EGU and/or AGU Meetings, in 2020.

References

Bannan, T. J., A. M. Booth, A. Bacak, J. B. A. Muller, K. E. Leather, M. Le Breton, B. Jones, D. Young, H. Coe, J. Allan, S. Visser, J. G. Slowik, M. Furger, A. S. H. Prévôt, J. Lee, R. E. Dunmore, J. R. Hopkins, J. F. Hamilton, A. C. Lewis, L. K. Whalley, T. Sharp, D. Stone, D. E. Heard, Z. L. Fleming, R. Leigh, D. E. Shallcross, and C. J. Percival (2015), The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation, Journal of Geophysical Research: Atmospheres, 120(11), 5638–5657, doi:10.1002/2014JD022629.

Osthoff, H. D., J. M. Roberts, A. R. Ravishankara, E. J. Williams, B. M. Lerner, R. Sommariva, T. S. Bates, D. Coffman, P. K. Quinn, J. E. Dibb, H. Stark, J. B. Burkholder, R. K. Talukdar, J. Meagher, F. C. Fehsenfeld, and S. S. Brown (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, Nature Geoscience, 1(5), 324–328, doi:10.1038/ngeo177.

Phillips, G. J., M. J. Tang, J. Thieser, B. Brickwedde, G. Schuster, B. Bohn, J. Lelieveld, and J. N. Crowley (2012), Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, Geophysical Research Letters, 39(10), doi:10.1029/2012GL051912.

Roberts, J. M., H. D. Osthoff, S. S. Brown, A. R. Ravishankara, D. Coffman, P. Quinn, and T. Bates (2009), Laboratory studies of products of N2O5 uptake on Cl− containing substrates, Geophysical Research Letters, 36(20), L20,808, doi:10.1029/2009GL040448.

R. Sommariva, L. D. J. Hollis, T. Sherwen, A. R. Baker, S. M. Ball, B. J. Bandy, T. G. Bell, M. N. Chowdhury, R. L. Cordell, M. J. Evans, J. D. Lee, C. Reed, C. E. Reeves, J. M. Roberts, M. Yang, and P. S. Monks (2018). Seasonal and geographical variability of nitryl chloride and its precursors in Northern Europe. Atmospheric Science Letters, 19 (8):e844, 2018. doi: 10.1002/asl.844. 30.