

FINAL REPORT PROGRAM LEFE

Program LEFE/ CHAT	Project Title Formation and characterization of low volatility organic compounds in the atmosphere: development of a flow reactor coupled to an Orbitrap mass spectrometer (CAROLA)	Years 2020 – 2022
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<p><i>Context</i></p> <p>Highly oxidized molecules (HOMS) produced by oxidation of volatile organic compounds (VOCs) play significant role in formation of atmospheric aerosols. However, due to analytical challenges in their identification and quantification, the mechanism of their formation and fate is not well understood.</p> <p><i>Objectives / scientific questions</i></p> <p>Performance evaluation and validation of an ultrahigh-resolution Orbitrap mass spectrometer coupled with a chemical ionisation interface for measurements of gas phase oxygenated organic molecules generated by oxidation of volatile organic compounds of biogenic origin.</p> <p><i>Main results</i></p> <p>The NO₃⁻ CIMS (Chemical Ionization Mass Spectrometry) Orbitrap mass spectrometer (ORBAS) developed in the LPC2E has been interfaced with a laminar flow tube chemical reactor (Figure 1a). This experimental setup has been used to test and characterize the ORBAS performance in relation to detection of oxidation products of a number of alkenes. In particular, oxidation of several monoterpenes (limonene, α-pinene, β-pinene, others) and of isoprene by OH and O₃ has been conducted at different conditions of reaction time and reactant concentrations. Highly oxidized molecules produced in these oxidation processes were monitored with the ORBAS. After optimization of various instrumental parameters of the ORBAS, the observed HOMs distributions were found to be in good agreement with results of previous studies and responded reasonably well to changes in experimental conditions in the flow tube. As a result, the ORBAS was optimized and validated for its implication in HOMs monitoring during field campaigns. Another outcome of these experiments with the flow tube is related to some results regarding the oxidation mechanism of some monoterpenes (in progress).</p> <p>The first implication of the ORBAS in field campaigns was during June-July of 2022 on a forest site in Rambouillet as a part of large scale campaign which took place in the frame of the ACROSS project (Atmospheric ChemistRy Of the Suburban foreSt). The ORBAS was mounted on a specially constructed platform and installed in a container (Figure 2a). Sampling at flow rate of 60 slm was performed through the wall of the container at about 1.5 m height. As illustrated in Figure 2, hundreds of oxidation products including HOMs and H₂SO₄ were successfully monitored with the ORBAS during about 1 month. Analysis of these data is presently in progress.</p>		

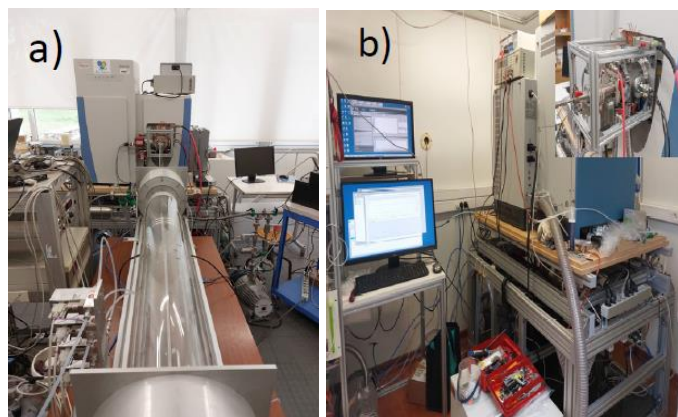


Figure 1

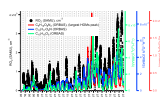


Figure 2

Figure 1. NO_3^- CIMS Orbitrap mass spectrometer (ORBAS) coupled to a laminar flow tube chemical reactor **(a)** or installed in a container for field measurements **(b)**.

Figure 2. Example of HOMs concentration profiles measured with ORBAS during ACROSS field campaign on a forest site in Rambouillet.

Future of the project :

1. Further development of the ORBAS:
 - a. Other ionisation schemes, e.g. using amines as reagent ions, with objective to extend the range of detected species (OVOCs and others) or make a methods selective for certain of them (e.g. organic hydroperoxides);
2. Extension to measurements of aerosol composition to allow quasi simultaneous analysis of organic composition of the gas and the particle phases ;
3. Kinetic studies with the ORBAS / flow tube setup (e.g. mechanism of organic hydroperoxides formation by oxidation of some alkenes);
4. Implication in future field measurements;
5. Exploitation of the ACROSS measurements in relation to OH and RO_2 radicals budget, formation of H_2SO_4 , oxidation of biogenic volatile organic compounds (BVOCs).

Number of publications, communications and theses

- 3 communications at EGU23, April 2023, Vienne, Austria :

Kukui, A., Xue, C., Houny, J., McGillen, M., Bachelier, F., Grosselin, B., Daële, V., and Mellouki, W.: Report on selected measurements in the canopy of a Rambouillet forest site during the ACROSS field campaign, EGU General Assembly 2023, Vienna, Austria, 24–28 Apr 2023, EGU23-3467, <https://doi.org/10.5194/egusphere-egu23-3467>, 2023.

Bachelier, F., Xue, C., Houny, J., McGillen, M., Kukui, A., Grosselin, B., Mellouki, A., and Daële, V.: Field measurements of organic and inorganic composition in the Rambouillet Forest during ACROSS campaign, EGU General Assembly 2023, Vienna, Austria, 24–28 Apr 2023, EGU23-3503, <https://doi.org/10.5194/egusphere-egu23-3503>, 2023.

Dusanter, S., de Brito, J., Lahib, A., Tomas, A., Jamar, M., Alhadj Moussa, E., Bauville, A., Cantrell, C., Michoud, V., Cazaunau, M., Formenti, P., Bachelier, F., Grosselin, B., McGillen, M., Daele, V., Mellouki, W., Xue, C., Houny, J., and Kukui, A.: Observations of trace gases above & below a forest canopy during ACROSS, EGU General Assembly 2023, Vienna, Austria, 23–28 Apr 2023, EGU23-17265, <https://doi.org/10.5194/egusphere-egu23-17265>, 2023.

- 3 publications in preparation (1 on writing stage and 2 others on writing/data analysis stage).

- 1 these (Jiao Yang, “Budget of OH and RO_2 radicals and their role in oxidation of BVOCs during ACROSS”, 2023-2026).

Data availability:

ACROSS database (<https://across.aeris-data.fr>)

