FINAL REPORT PROGRAM LEFE

Program LEFE/ CHAT	Anthropogenic Secondary Organic Aerosol Tracers (Trac_AOS_A)	Years 2020– 2023

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IDEX program at the Université de Paris Cité (PhD thesis of D. Pereira (2020-2024)), ANR−17−MPGA−0002 of ACROSS project, LEFE CHAT ACROSS, CNRS INSU (CESAM chamber as a national facility), AERIS data center (for distributing and curing the data produced by the CESAM chamber and ACROSS campaign)

Context: Secondary organic aerosols (SOAs) can be formed *via* the oxidation of volatile organic compounds (VOCs) and contribute up to 90% of the organic aerosol (OA). However, their formation pathways and chemical composition are not well understood.

Objective: This work aims to determine the contribution of different VOCs precursors to the atmospheric SOA by combining field measurements and chamber experiments.

Main results: CESAM (Multiphase Atmospheric Experimental Simulation Chamber) experiments allow to retrieve the ratios of aerosol tracer to total SOA mass (fSOA) from different anthropogenic precursors. In particular, different f_{SOA} factors were determined during the OH oxidation of dodecane, toluene and naphthalene by a series of laboratory experiments (cf figure 1). To apply the tracer method, these results suggests to use f_{SOA} factors obtained in the simulation chamber, representative of field studies, i.e. taking into account the environmental parameters, the oxidation regime, daytime or nighttime chemistry... Field measurements allow to describe the chemical composition and to quantify the concentrations of tracers. During the ACROSS (Atmospheric Chemistry Of the Suburban forest) campaign from mid-June to the end of July 2022, filters were collected in the urban and peri-urban areas (Rambouillet forest) of Paris. Filters were analyzed by thermo-optical method, Orbitrap UPLC-QTOF-MS (Ultra-Performance-Liquid-Chromatography Time-of-Flight Mass-Spectrometry) and SFE-GC-MS (Supercritical fluid extraction – gas chromatography and mass spectrometry). The thermo-optical analysis shows similar organic carbon concentrations for Paris and Rambouillet although the environments are different, with mean values of 3.2 and 2.8 µgC/m^3, respectively. The aromaticity analysis by orbitrap shows the important contribution of polyaromatic compounds for Paris (between 22 to 30 %) and Rambouillet (from 16 to 36 %). Among the anthropogenic species identified with UPLC-QTOF-MS, 2-methyl-4-nitrophenol and 2-nitrophenol were detected in Paris (0.25 and 1.33 ng/m^3) and Rambouillet (0.07 and 0.34 ng/m^3) (cf. figure 2). The presence of nitro-phenol compounds and the contribution of aromatic compounds illustrate the influence of the urban plume in the forest area. Finally, combining the tracer concentrations observed in the field and the chamber experiments, the SOA tracer method was applied during the ACROSS campaign to estimate the SOAs from different VOC precursors. It is observed that nitro-aromatics (tracer 2-methyl-4-nitrophenol) can represent up to 36 % from the SOAs in Paris. On average, the presence of aromatic compounds (nitrophenol) from anthropogenic emissions influences the urban (11%) and peri-urban areas of Paris (4%). Biogenic compounds (monoterpenes) contribute to SOA formation in both environments at 3% and 11% for the urban and forested area of Paris during the summer 2022. In order to better constrain the SOA composition, other experiments are still in progress to identify tracers by SFE-GC-MS associated with isoprene, dodecane and toluene.

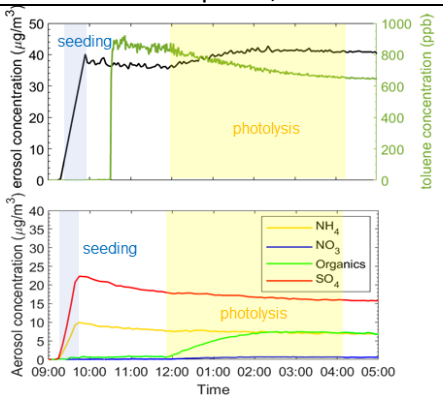

Figure 1: CESAM Experiment: toluene oxidation by OH in presence of NOx in dry conditions.

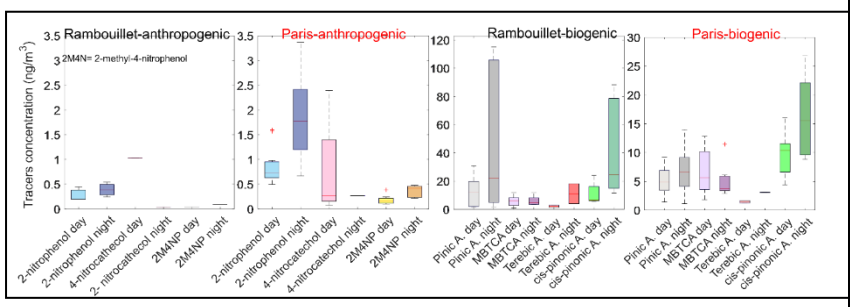

Figure 2: Biogenic and anthropogenic tracer concentrations determined by UPLC-QTOF-MS in Rambouillet and Paris during the ACROSS campaign (June-July 2022).

Figure 1: Typical experiments of oxidation of toluene by the OH radical in the presence of NOx (nitrogen oxides) at x% relative humidity and 20°C. These experiments use H_2O_2 as the OH source. VOCs (Volatile Organic Compounds) are measured using PTR-TOF-MS, and aerosol mass by SMPS and ACSM. Several experiments were performed for a single precursor in order to obtain an average estimate of the mass fractions of SOA and secondary organic carbon under different oxidation conditions. The f_{SOA} values for 2-methyl-4-nitrophenol and DHOPA are obtained from the oxidation of toluene. These are average factors obtained in the presence of NOx and with a relative humidity close to 10%. Other experiments on toluene were performed in January 2024 with the same VOC/NOx ratio but in the presence of 60% relative humidity to evaluate its influence on this factor.
Figure 2: The molecular-scale analysis by UPLC-QTOF-MS made possible to quantify different biogenic SOA tracers (pinic acid, pinonic acid, MBTCA and terebic acid) and anthropogenic (2-nitrophenol, 4-nitrocatechol and 2- methyl-4-nitrophenol) in the selected urban and rural sites. The oxidation products of α-pinene have a contribution in both environments, with higher concentrations in the Rambouillet forest area given the higher vegetation density. Species with higher concentrations of biogenic compounds (up to 110 ng/m^3) correspond to early oxidation products of α-pinene such as pinic acid and pinonic acid. The contributions from second oxidation products (MBTCA, terebic acid) also highlight the subsequent chemistry of these compounds. In the case of the urban environment, anthropogenic compounds, particularly nitroaromatics, appear in higher concentrations than in the forest. In particular, 2-methyl-4-nitrophenol and 2-nitrophenol were detected in Paris (0.25 and 1.33 ng/m^3) and Rambouillet (0.07 and 0.34 ng/m^3). Concerning nitrocatechol, it was only observed on the day of the fire (July 19) on the Rambouillet site with a lower concentration compared to the urban site. Most compounds exhibit different behavior during day and night at the two sites, probably associated with different oxidation processes and environmental parameters during day and night.

Future of the project :

ANR−17−MPGA−0002 of ACROSS project,

European REMEDIA project,

Future campaign on chamber and in field to study the SOA chemical composition at molecular scale

Publications

Lamkaddam Houssni, Aline Gratien, Edouard Pangui, Marc David, F. Peinado, Jean-Michel Polienor, Murielle Jerome, Mathieu Cazaunau, Cecile Gaimoz, Benedicte Picquet-Varrault, I. Kourtchev, M. Kalberer, Jean-Francois Doussin, Role of Relative Humidity in the Secondary Organic Aerosol Formation from High-NOx Photooxidation of Long-Chain Alkanes: n-Dodecane Case Study, ACS Earth Space Chem. 2020, 4, 2414−2425, 4, 2414−2425, https://doi.org/10.1021/acsearthspacechem.0c00265, 2020

Diana L. Pereira, Aline Gratien, Chiara Giorio, et al. Organic aerosol from an urban and suburban area of Paris during the summer 2022 Part 1: OC/EC description and non-target analysis, in preparation

Diana L. Pereira, Aline Gratien, Chiara Giorio, et al. Organic aerosol from an urban and suburban are of Paris during the summer 2022 Part 2: SOA approximation, in preparation

Diana L. Pereira, Aline Gratien, Chiara Giorio, et al. Secondary organic aerosol formation from toluene oxidation: an approximation of SOA factors, in preparation

Al Marj Elie, Coll Patrice, et al.. A novel/innovative approach to simulate “urban-like” aerosols and to study health impacts in murine models resulting from short-term exposures, in preparation

Communications

D.L. Pereira, A. Gratien, C. Giorio, et al. Organic aerosol from an urban and suburban area of Paris during the summer 2022, ACTRIS Science Conference 2024, Rennes, France, Mai 2024.

A. Gratien, D.L. Pereira, C. Giorio, et al. Molecular composition of secondary organic aerosol using chromatography and mass spectrometry, Molecular-Level Understanding of Atmospheric Aerosols MUOAA 2024, Cargèse, France, Avril 2024

Al Marj E., Coll P., Cazaunau M., et al. Experimental simulation at the laboratory of the exposome: presentation of the PolluRisk innovative platform, Fédération de Chimie d'Université Paris Cité (FedCup), Paris, France, Novembre 2023.

Al Marj E., Coll P et al. Experimental simulation at the laboratory of the exposome: presentation of the PolluRisk innovative platform, European Human Exposome Network (EHEN), Leuven, Belgique, Juin 2023.

Pereira, D. L., Gratien, A., Giorio, C., et al..: Addressing the chemical composition of secondary organic aerosol in the rural/ urban Paris area, EGU General Assembly 2023, Vienna, Autriche, 24–28 Apr 2023, EGU23-493, https://doi.org/10.5194/egusphere-egu23-493, 2023.

Diana L. Pereira*, Aline Gratien, Ouiza Boudaoud, et al. Chemical composition of SOA from anthropogenic precursors: using the tracer approach, 11th International Aerosol Conference (IAC 2022), Athènes, Grèce, September 4-9, 2022

Al Marj E., Coll P., et al., Impact of urban air quality on health studied at the laboratory: the Pollurisk platform, 13th International Conference on Air Quality, Science and Applications, Thessaloniki, Grèce, Juin 2022.

Al Marj E., Coll P., et al., Simulation d’atmosphères urbaines multiphasiques pour l’étude des effets sur la santé : analyse qualitative des aérosols organiques secondaires générés, Congrès Français sur les Aérosols(CFA), Paris, France, Mai 2022.

Gratien A., DL. Pereira, P. Besson-Magdelin, O. Boudaoud, et al., Chemical composition of secondary organic aerosol (SOA) from biogenic and anthropogenic precursors: tracer approach, workshop ACTRIS France, Ile d’Oleron, octobre 2021.

PhD thesis

Pereira D.L.., UPC PhD thesis (2021-2024) « *Composition chimique de l’aérosol organique secondaire à partir des précurseurs biogéniques et anthropiques.* »

Almarj E. UPC PhD thesis (2019-2023) *Effets de la pollution atmosphérique sur la santé : Développement de protocoles innovants de simulation d’atmosphères urbaines et d’exposition de modèles précliniques»*

Data availablility

upon request and at term in AERIS data center for CESAM experiment and ACROSS field campaign