FINAL REPORT PROGRAM LEFE

Program LEFE/ CHAT	Project Title CHIMIE DES PARTICULES ATMOSPHERIQUES EN LEVITATION : INTERACTIONS AVEC L'EAU (LEVITEAU)	Years 2020– 2023

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Participating Laboratories :

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Contribution to

Other funding sources :

Context:- Atmospheric organic aerosol particles (SOA) have a recognised impact on climate change and human health. Biogenic SOA (BSOA), which make up 30 to 50% of the total SOA budget, can exist in a variety of physico-chemical states. The interactions between water vapour and BSOAs play a key role in air quality and climate, and need to be investigated.

Objectives / scientific questions*:* - The LEVITEAU project aims to gain a better understanding of BSOA-water interactions by determining the predominant physical and/or chemical factors that contribute to and/or influence the water-particle interaction during the atmospheric ageing process at the particle scale. This innovative project is based on a laboratory study of BSOA particles using an original experimental device, the levitation technique coupled with spectroscopic analysis techniques and mass spectrometry, dedicated to the study of processes on the scale of single particles.

Main results : The LEVITEAU project was divided in two main tasks. The first one was dedicated to the development of the experimental device based on acoustic levitation system coupled to a mass spectrometer for the gas phase analysis and a Raman microspectrometer for the particle characterization with in situ conditions. The device was validated and then used in a second task to study the evaporation and hygroscopicity properties of secondary organic particles formed from α-pinene oxidation pathways.

As mentioned above, we developed a novel coupling between an acoustic levitator (APOS BA 10, Tec5) and a proton transfer time-of-flight mass spectrometer (PTR-TOF-MS - Serie II, Kore Technologie). Validation of this coupling was essential for further work on the project. The composition of the gas phase within the levitator, as well as the relative humidity, are controlled using a Liquid Calibration Unit (LCU) and measured at the levitator outlet by the PTR-TOF-MS. A schematic diagram of the final setup is shown in Figure 1. Measurements were carried out with compounds selected for their molecular structures and atmospheric interest (i.e. ethanol, pinanediol, linalool, isopinocamphéol), in order to study (i) the instrument's sensitivity, linearity and repeatability with respect to the various compounds tested, (ii) the influence of the presence of the cell on the instrument's sensitivity, (iii) the influence of relative humidity (RH) on the instrument's sensitivity. The gas-phase study enabled us to gain a better understanding of the behavior of the gaseous compound in relation to the levitation cell and the PTR-TOF-MS, i.e. to assess adsorption on the walls of the levitation cell and potential losses in the analysis lines. The impact of the addition of the levitation cell on instrument sensitivity and quantification limits was also assessed. We demonstrated that semi-volatile compounds are not suitable for validating the device, as their low vapor pressure induces excessive losses on the cell walls. For the volatile compounds tested (linalool and ethanol), the results show good instrument sensitivity in the presence of the cell, and a linear instrument response for the concentration ranges tested. The sensitivity of the instrument is affected by the presence of humidity, and this should be taken into account during measurements.

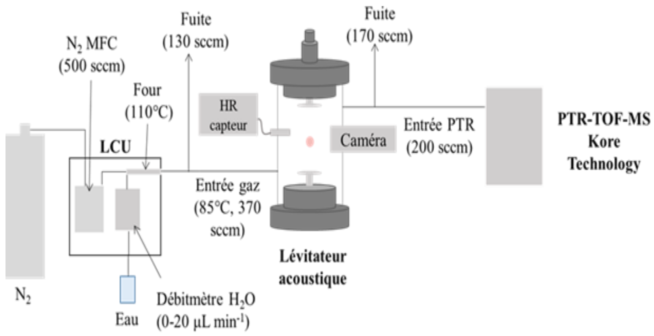

Figure 1 : Scheme of the coupling between an acoustic levitator and a proton transfer time-of-flight mass spectrometer.

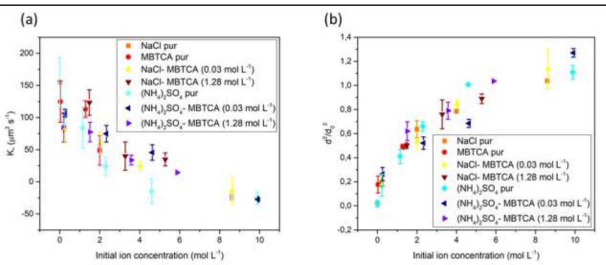

Figure 2: Evolution of evaporation rate (K) (a) and (d2/d02)eq (b) for MBTCA-NaCl or MBTCA-$(NH_4)_2SO_4$ mixed aqueous droplets, as a function of initial ion concentration. Error bars reflect experimental statistical dispersion of K* and (d2/d02)eq values.*

As a first application of the experimental set up we have investigated the droplet evaporation process by measuring the droplet size variation and analyzing the gas phase and/or the particle composition over time. The evaporation rate (K*) and particle size stabilization (d^2/d_0^2 - with d_0 the initial diameter of the particle and d the particle diameter at defined RH) can be determined and compare with theoretical calculations. Evaporation process at high humidity (RH > 90%) was determined for particles composed of volatile compounds (i.e. ethanol and linalool) and for non volatile components (i.e. cis pinonic acid (CPA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)). These two latter organics originate from the oxidation of α-pinene and are considered as markers of SOA. The influence of inorganic salts (i.e. NaCl or $(NH_4)_2SO_4$) on the process was evaluated. As an example of the results, the Figure 2 shows the behavior of droplets with various composition in salts and in organics. Evaporation and uptake of waters are governed by the water activity (aw) of the solution inside the droplets since that value governs the equilibrium water vapour concentration over the solution. The effect of aw can be approximated by using the number of dissolved entities (ions and molecules) in the solution as it is done using the van't Hoff factor approach to adjust to express Raoult's law (1-i*Zs). The important part is that it is not the concentration of, e.g., a salt but the concentration of dissolved entities that matter for both the evaporation rates and the equilibrium size. The mixtures have a very similar relationship of the equilibrium sizes with initial concentration of dissolved entities as the pure compound solutions. The presence of organic acids does not over-proportionally hinder the mass transfer of water at RH > 91%, but rather has the same influence on evaporation rates and equilibrium size as adding the comparable amount of $(NH_4)_2SO_4$ or NaCl ions would have.

A second application was exploring the hygroscopic properties of particles composed of non volatile compounds in mixture with salts described above. In this study, we demonstrated that the deliquescence process of mixed particles is a two-step process that depends on the MBTCA - inorganic salt ratio. We found that at low salt concentrations, and particularly in the case of a particle composed of a mixture with NaCl, the particle's behavior is very close to that of a pure MBTCA particle. However, at high salt concentrations, particle deliquescence is reduced from 95% to 90% RH. Considering that MBTCA concentrations in atmospheric particles may be similar to those in this study, the presence of particles composed of MBTCA and a small amount of salt, may decrease salt deliquescence and thus affect cloud condensation nuclei activity, optical properties and chemical activity of the particle.

Future of the project :
In the perspective of this project, we plan to focus on the main physical and/or chemical factors involved in the atmospheric ageing of aerosols during transport. The main scientific question we seek to answer is: what is the influence of chemical transformations (including photochemical reactions) on composition, chemical heterogeneities, molecular organization, hygroscopicity properties, water diffusion and, ultimately, particle viscosity at the single particle scale? We will pay particular attention to the role of particle surface and inter- and intra-molecular organization on the viscosity properties of organic aerosols. Model particles will be studied on a single particle scale under near-atmospheric conditions, using the levitation device developed as part of the LEVITEAU project, or deposited on different substrates. Molecular AOS-water processes will be studied using cryogenic matrix experiments. We aim to provide both original experimental set-ups dedicated to gas-particle interaction studies, and new multi-scale concepts, including the identification of physico-chemical markers linked to aerosol-water interaction processes, which will provide a better understanding of the direct impacts of aerosols on climate change and air quality.
- The LEVITEAU project enabled us to initiate collaborations with French laboratory and to obtain a collaborative project supported by ANR –SOAPHY Project – ANR-21-CE29-0031 – **01/04/2022-30/09/2025** – This project aim to study the influence of water on the physical chemical properties of Secondary Organice Aerosol – The laboratories involved in the project are ISM UMR5255 (Université de Bordeaux), EPOC UMR 5805 (Université de Bordeaux), ICCF UMR 6296 (Université Clermont Auvergne) and PIIM UMR 7345 (Aix Marseille Université).
- A doctoral student has been hired as a result of the LEVITEAU project supported by ANR SOAPHY – Gwendoline Bourdon – 2022-2025
- An additional support was obtained from the Région Nouvelle Aquitaine - LEVIAERO (convention n° AAPR2022-2021-17126210) – **2022-2027**
- A new collaboration with I2M UMR 5295 (Université de Bordeaux) – Dr Diego Baresh was initiated in 2023 and supported by funding from the University of Bordeaux - concerning the use of acoustic tweezers for the study of atmospheric aerosols.
- Internationally, as a follow-up to the LEFE-CHAT project, we have been awarded a JSPS Fellowship n°S20018 - 1-month visiting professorship at Hiroshima University - in collaboration with Professor Shoji Hishizaka - to develop the complementarity of optical tweezers and acoustic levitation for studying particle reactivity. A join international project will be proposed in 2024.

Number of publications, communications and theses

Publications

- Thèse Clara Becote – Etude de l'évolution de particules atmosphériques uniques en lévitation – Application à la qualité de l'air et au changement climatique – Université de Bordeaux – Soutenue le 14 décembre 2022.
- C. Becote, P.M. Flaud, E. Perraudin, E. Villenave, S. Sobanska Evaporation process under high relative humidity of mixed organic and inorganic levitated droplets as proxy for secondary organic aerosols, Environmental Science: Atmosphere, *in revision*.
- C. Becote, G. Bourdon, E. Perraudin, E. Villenave, S. Sobanska, Hygroscopicity of MBTCA particles and their mixture with inorganic salts - Comparison with E-AIM, *in preparation*

Communications

• **Oral Communications**

1- S. Sobanska – The chemistry of Levitated particles - The 2nd International Workshop for the FRIEND (Fine Particle Research Initiative in East Asia Considering National Differences) Project, 23 – 25 October, 2023; Busan, KOREA (conference invitée)
2- Becote C.; Bourdon G.; Flaud P.-M.; Perraudin E.; Villenave E.; Sobanska S. Interactions between SOA-like droplets and water vapor using acoustic levitation. Goldschmidt2023, Lyon, 9-14 July, 2023, France
3- Gwendoline Bourdon, Clara Becote, Pierre-Marie Flaud, Emilie Perraudin, Eric Villenave, and Sophie Sobanska - Hygroscopic properties of mixed organic and inorganic atmospheric single particles, SCF 2023, Nantes, 26-28 June 2023
4- S. Sobanska and E. Villenave - Etude des propriétés d'hygroscopicité de particules uniques en lévitation – Ateliers de Modélisation de l'Atmosphère 2023 – Toulouse, 9-11 mai 2023
5- Becote C.; Flaud P.-M.; Perraudin E.; Villenave E.; Sobanska S. Evaporation process of SOA-like droplets highlighted by an innovated experimental set up of atmospheric interest. Rencontres de Chimie Physique RCP21, Sète, September 20- 23, 2021, France.
6- Becote C.; Flaud P.-M.; Perraudin E.; Villenave E.; Sobanska S. Application of coupling between an acoustic levitator and mass spectrometry for investigating evaporation process of single secondary organic aerosol particle. EMLG/ JMLG Workshop – Molecular characterization of interfaces in atmospheric aerosol, September 13, 2021 – En ligne
7- Becote C.; Flaud P.-M.; Perraudin E.; Villenave E.; Sobanska S. Evaporation of biogenic organic particle using acoustic levitation. European aerosol conference, 30 August – 3rd September, 2021, En ligne
8- Becote C.; Flaud P.- M.; Perraudin E.; Villenave E.; Sobanska S. Evaporation process of linalool droplet at high relative humidity using acoustic levitation. Atelier commun GDR EMIE – GDR SpecMO, Fréjus – 25-27 mai 2021, France
9- Sophie Sobanska - Application of acoustic levitation for understanding atmospheric aerosol chemistry – workshop Trappists II – Bordeaux, 20 Juillet 2021, France.

• **Posters**

1- Becote C.; Hunel J.; Villenave E.; Sobanska S. Surface tension measurements of atmospheric particles using atomic force microscopy, Journée de la DCP, Paris, 2024
2- Becote C.; Hunel J.; Villenave E.; Sobanska S. Surface tension measurements of atmospheric particles using atomic force microscopy, Journées Grand Sud-Ouest de la Société Chimique de France, Bordeaux, 1-2 février 2024
3- Sophie Sobanska, David Talaga, Julien Hunel, Arnaud Desmedt, Diego Baresch, Christine Biateau, Pierre-Marie Flaud, Emilie Perraudin, Eric Villenave, LEVIAERO : Lévitation acoustique pour l'étude des propriétés des particules atmosphériques, Tremplin Futurs-ACT 2022, Anticipation du changement climatique dans les territoires en transition - Nouvelle Aquitaine, 16-17 juin 2022, Bordeaux (https://futurs-act.fr/tremplin-futurs-act-2022/)
4- Becote C.; Flaud P. –M.; Perraudin E.; Villenave E.; Sobanska S. Aging of atmospheric particles using acoustic levitation coupled with Raman spectroscopy, 24th French Neutron Diffusion Meeting, 14-17 novembre 2022, Biarritz.
5- Becote C.; Flaud P. –M.; Perraudin E.; Villenave E.; Sobanska S. Combining an acoustic levitator with a proton-transfer-reaction mass spectrometer and a Raman microspectrometer for studying single droplet reactivity of atmospheric interest. 3th day of the doctoral school of chemical sciences of Bordeaux, Bordeaux, 2021

International seminars

1- Sophie Sobanska - Reactivity of atmospheric particles: a single particle point of view – Séminaire pour l'Université d'Hiroshima, Japon, 15 juillet 2022

2- Sophie Sobanska - Reactivity of Secondary Organic Aerosol particles –Seminar of Materials-Measurement Hybrid Research Center, (The 8th Seminar on Nano-Micro Chemical Measurements), Tohoku University, Japan – 18 July, 2022.

Data availablility
Indiquer les liens où les données du projet sont stockées