BECAS LEONARDO A INVESTIGADORES Y CREADORES CULTURALES 2018

Propuesta: *Química del carbón marrón: medidas y modelización de la absorción de amoníaco en los aerosoles secundarios orgánicos*

Investigador Principal: *Dr. Oriol Jorba Casellas*

1. Descripción

Organic aerosols (OA) affect climate forcing and human health, but still large uncertainties exist in their sources and evolution. OA makes up a large fraction of the submicron particulate matter, 20 to 90%. Recent studies have shown that secondary organic aerosols (SOA) accounts for a large fraction of the OA burden. Most OA efficiently scatter visible radiation and contribute to a cooling effect in the atmosphere. However, a significant fraction of OA absorbs radiation in the near-UV and visible ranges. Such fraction is known as "Brown Carbon" (BrC). BrC contributes together with Black Carbon and mineral dust to warming the atmosphere. Recent studies have identified that some initially scattering SOA undergoes browning during exposure to reduced nitrogen compounds such as ammonia, ammonium from dissolved ammonium sulfate or other salts, and amino acids (Figure 1). The contribution of such light-absorbing OA to the total warming effect of BrC is still highly uncertain and it may be significant in areas that have high emissions of ammonia or dissolved ammonium salts.

Figure 1. Colored appearance of SOA generated from different combinations of precursors mixed with variety of oxidants (Source: Jaoui et al. J. Geophys. Res. Atmos. 2008, 113, D09303)

We propose to conduct a specific field campaign in northeast Spain during July 2018 to study the relevance of this new chemistry in a region with high ammonia and ozone concentrations. Online and offline surface concentration measurements of ammonia, ozone and aerosol chemical composition will be conducted together with measurements of optical properties (absorption and scattering). Such a dataset will provide for the first time unique information on the light-absorbing contribution of secondary BrC in northeast Spain, and will contribute to disentangle the contribution of secondary BrC to the warming of the atmosphere-climate, which nowadays is a big uncertainty.

The main objective of the campaign is to gather experimental evidence at the field level of the reactive uptake of nitrogen-containing species by SOA and on the optical properties and burden of anthropogenic and biogenic SOA using both experimental and modeling approaches. We propose to use results from these field measurements to develop a new scheme to describe the uptake, chemistry and particle-phase diffusion involved in NH_3-SOA interactions, which will be implemented in a state-of-the-art atmospheric-chemistry model, the NMMB-MONARCHv1.0 model, to quantify the fraction of BrC from primary and secondary origin, and the contribution of this light-absorbing SOA on the radiative forcing of OA.

The campaign will be conducted in northeast Spain, in the countryside site—Village of Vic. A region characterized by recurrent exceedances of ozone concentrations (above 200 μg m^{-3}

average hourly concentration) during summertime where high concentrations of ammonia have been measured (40 μg m^{-3} daily mean concentrations). A measurement site located in a rural area where farming and agricultural activities are dominant, the Plana de Vic, will be the primary location used to conduct the field campaign.

The research groups involved in the project will be: **BSC** Modelling group: Oriol Jorba, Matthew L. Dawson - *Atmospheric Composition group, Barcelona Supercomputing Center (Spain).* **EGAR** Measurement group: Xavier Querol, Andrés Alastuey - *Institute of Environmental Assessment and Water Research CSIC (Spain).* **PNNL** Measurement group: Alla Zelenyuk-Imre - *Pacific Northwest National Laboratory (USA).* **UCI** Modelling group: Sergey Nizkorodov, Donald Dabdub - *University of California, Irvine (USA).*

The budget of the project will be devoted to sub-contract the measurements of the experimental campaign to EGAR and PNNL groups. Additionally, two scientific publications will be also covered.

2. Plan de trabajo:

In order to achieve the proposed objectives, we define the following methodology and working plan:

Work package 1: Experimental campaign
An experimental field campaign is planned to identify the role of the NH_3-SOA chemistry in the northeast Spain. Surface concentration of oxidants, reactants, OA and aerosol optical properties will be measured during July 2018. Considering the complexity of this objective, EGAR and PNNL will be in charge of the measurements. EGAR group has a wide experience conducting measurement campaigns oriented to study aerosol sources, chemistry, and optical properties, while PNNL group is expert on characterizing the composition of single organic particles.

Task 1.1 Design of the experimental campaign: measure of organic aerosol mass, NH3 concentration and aerosol optical properties
The browning transformation in some SOA (e.g., limonene/O_3 SOA) has been observed during exposure to high-concentration of reduced nitrogen compounds (NH_3, NH_4^+, and amino acids). This chemistry may contribute to aerosol absorption in ambient conditions where high concentration of reduced nitrogen compounds, frequent changes in relative humidity, and high photochemical activity are observed. Vic village is an excellent location where such conditions are present. The selected measurements to conduct during the campaign are:

- *Standard monitors* of NH_3, O_3, NO_2 and VOC concentrations.
- *Filters* to analyze offline the concentrations (PM10, PM2.5, PM1) of organic carbon, elemental carbon, sulfate, nitrate, ammonium, mineral fraction, trace elements like levoglucosan (tracer of organic mass from biomass burning), and pH. Filter measurements are planned to take place every 12 or 24 h.
- *Multi-Angle Absorption Photometer* (MAAP, model 5012,Thermo Scientific) to measure loading of black carbon (BC) in the atmosphere. The aerosol light absorption coefficient (σ_{ap}) at 637 nm will be obtained from BC mass concentrations assuming a constant mass absorption cross section (MAC) of 6.6 m^2 g^{-1} provided by the manufacturer.
- *Aethalometer* (model AE-33 Magee Scientific) to measure aerosol light absorption coefficients (σ_{ap}) at seven different wavelengths from the UV to near IR (370, 470, 520, 590, 660, 880 and 950 nm). From the multi-wavelength aethalometer measurements it will be possible to obtain the Absorption Angstrom Exponent (AAE), which is closely related to aerosol composition and type—BrC aerosols yield AAE over 2 while that of BC is closer to 1. Thus, AAE can provide an indication of the dominant absorbing aerosol type such as dust, black carbon, brown carbon, or mixtures.
- *LED-Based Integrated Nephelometer* (model Aurora 3000, ECOTECH Pty, Ltd, Knoxfield, Australia) to measure aerosol light scattering (σ_{sp}) and hemispheric backscattering (σ_{bsp})

coefficients measured at three different wavelengths (450, 525 and 635 nm). From the multi-wavelength nephelometer measurements it will be possible to obtain the Scattering Angstrom Exponent (SAE), which is closely related to the size of the sampled aerosols. From multi-wavelength scattering and absorption measurements it will be possible to estimate the Single Scattering Albedo (SSA) from the UV to the visible range.
- *Single-Channel CHM15K (CHM) Elastic Lidar* (ceilometer) to measure the vertical structure of atmospheric aerosols through the profiles of the lidar signals. The instrument is designed for continuous cloud base height determination and aerosol backscatter coefficient measurements during the day and night. Ceilometer data can be used to generate maps of aerosol loading in the atmosphere with high temporal and vertical resolution.
- *Aerosol Chemical Speciation Monitor* (ACSM) to provide quantitative measurements of the non-refractory components of submicron atmospheric aerosol: sulfate, nitrate, chloride, ammonium and organic aerosol (OA) with a time resolution of 15 min to 1 h. The instrument provides organic mass spectra, which can be analyzed by multivariate mathematical techniques, such as positive matrix factorization (PMF), to identify the OA origin or OA type. The most common OA sources/types are: hydrocarbon-like OA (HOA), related to primary engine emissions; biomass burning OA (BBOA), related to primary emissions from biomass combustion; and oxygenated OA (OOA), attributed to secondary OA (SOA).
- *SPLAT II/miniSPLAT* to provide real-time *in-situ* single-particle aerosol measurements. SPLAT II and miniSPLAT provide number concentrations and single-particle size and composition measurements, and can be used to determine several physical properties of single particles including density and morphology. miniSPLAT has recently been used to identify the effects of NH_3 reactions with laboratory-generated α-pinene SOA on particle chemical and physical properties, highlighting the complex effect of these reactions on particle morphology and coagulation.

Task 1.2 Summer campaign
The measurements will be conducted during July 2018 at Vic village (Northeast Spain). The research team of the proposal will support the EGAR group in the technical work required to perform the measurements. A key element for a successful campaign is the weather. The research group will analyze the seasonal forecasts and mid-term weather forecasts to identify which weeks of July will be the best ones to have high temperatures and high insolation in the area. Additionally, the CALIOPE forecasting system maintained by BSC will be consulted during the campaign to forecast when the polluted air masses from Barcelona will affect the area and when high ozone concentrations may be expected. To assure a proper success in the summer campaign, the technical work will be sub-contracted to EGAR and PNNL groups, with a wide experience in field campaigns. A database with the gathered data will be created and will represent Deliverable 1.1 of the project.

Task 1.3 Analysis of the data from the campaign
The results of the field campaign will be analyzed and used in Work package 2 for model simulations. A scientific paper will be prepared describing the objectives of the campaign, and the main findings of the measurements. This paper will be Deliverable 1.2 of the project.

Work package 2: BrC chemistry and role of the reactive uptake of NH3 by SOA: model development and simulations
The BrC chemistry will be implemented in the NMMB-MONARCHv1.0 model developed by Dr. Jorba and collaborators at BSC. Collaborators from University of California (UCI), Irvine, Prof. Donald Dabdub and Prof. Sergey Nizkorodov will contribute on the design of the related NH_3-SOA chemistry to be included in the model as experts on the chemistry of secondary organic aerosols.

Task 2.1 Implementation of new NH3-SOA aerosol chemistry in NMMB-MONARCHv1.0 model
Prof. Sergey Nizkorodov and Prof. Donald Dabdub fom UCI are currently performing chamber experiments designed to expand on their work to quantify the impact of NH_3 on SOA aging using a

variety of biogenic and anthropogenic SOA precursors under various atmospherically relevant temperature and relative humidity conditions (Figure 2). The work proposed in this task will collaboratively parameterize their published and on-going work on the formation of light-absorbing SOA from NH_3 processing for inclusion into the NMMB-MONARCHv1.0 model. Current version of the model includes a simplified treatment of SOA with a two-product scheme that contributes to the total OA (purely scattering) mass. Deliverable 2.1 will be the code of MONARCHv2.0 model with the new chemistry.

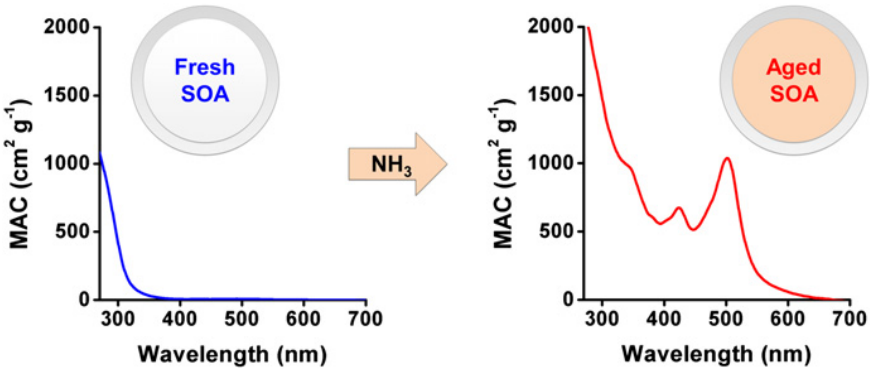

Figure 2. Absorption spectra of SOA extracts before and after exposure to gas phase NH_3 obtained in laboratory (Source: Updyke et al. Atmos. Environ. 2012, 63, 22-31).

Task 2.2 Modeling experiments

Several numerical simulations with the new chemistry implemented in NMMB-MONARCHv1.0 are planned. High-resolution simulations will be conducted to explore the role of BrC chemistry in the northeastern Spain at a resolution of 1 km x 1 km. Anthropogenic emissions will be provided by the HERMESv3 emission inventory developed by BSC at hourly temporal resolution. Biomass burning emissions will be obtained from the CAMS Global Fire Assimilation System GFASv1.2. Biogenic emissions will be calculated online within NMMB-MONARCHv1.0 with the MEGANv2.04 model. Ground-based observations gathered in WP1 will be used to evaluate model performance on surface concentration of organic aerosols and constrain the total AOD and the absorbing AOD. A scientific publication describing the new chemistry implemented in NMMB-MONARCHv1.0 and the modelling results obtained from the numerical experiments will be Deliverable 2.2.

3. Cronograma

Objectives	RRHH	2018												2019											
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
WP 1. Experimental campaign																									
Task 1.1 Design of the experimental campaign	PI, CSIC, PNLL																								
Task 1.2 Summer campaign	PI, CSIC, PNLL							D1.1																	
Task 1.3 Analysis of the data from the campaign	PI, CSIC, PNLL																	D1.2							
WP 2. BrC chemistry and role of NH3-SOA uptake: model developments and simulations																									
Task 2.1 Implementation of new NH3-SOA aerosol chemistry	PI																	D2.1							
Task 2.2 Modeling experiments	PI, UCI, PNLL, CSIC																								D2.2
Principal Investigator (PI): O. Jorba | Working groups: X. Querol and A. Alastuey (CSIC), A. Zelenyuk-Imre (PNLL), D. Dabdub and S. Nizkorodov (UCI)																									

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D1.1 Database with collected experimental data during the summer campaign
D1.2 Scientific publication about the summer campaign
D2.1 Code of the NMMB-MONARCHv2.0 with new chemistry
D2.2 Scientific publication about the modelling experiments conducted