TNA User Report

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Project title	Impact of particle composition, morphology and aging on the direct radiative effect of Black Carbon aerosols
Name of the accessed chamber	CESAM
Number of users in the project	1
Project objectives (max 100 words)	The objective of this project is to perform laboratory chamber experiments with the aim to investigate the climatically-relevant spectral optical properties of black carbon (BC) aerosols. Specifically, the objectives of the projects are: 1. to determine the wavelength-dependent Complex refractive index of BC taking into account the complex morphology of the particles 2. to investigate the changes in the complex refractive index in link with atmospheric aging, in particular the impact of heterogeneous reactions of BC with atmospheric constituents inducing the formation of inorganic/organic coatings 3. to understand the role of chemical composition in light absorption efficiency of BC
Description of work (max 100 words):	Experiments were performed in the 4.2 m3 CESAM simulation chamber. BC aerosols generated form a commercial burner were injected in the chamber and subjected to different aging processes: 1/ BC were left to age without chemical forcing in order to investigate morphological restructuration; 2/ BC were made to react with SO2 and 3/ α–pinene in presence of ozone at 40% RH to form an inorganic/organic coating. The size distribution, spectral optical properties, BC content, and density of the aerosols were measured on-line. Aerosols were also collected on filters for additional chemical analyses and morphological characterization by transmission microscopy measurements.

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[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 EXP= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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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: Angela Marinoni
Chamber name and location: CESAM, CNRS-LISA, Cretèil, France
Campaign name and period: Impact of particle composition, morphology and aging on the direct radiative effect of Black Carbon aerosols, 8-19 July 2019
Text:

Introduction and motivation

Black Carbon (BC) aerosols, generated by the incomplete combustion of fuels and biomasses, strongly absorb shortwave (SW) radiation which induces a warming at the Top–Of–the–Atmosphere (Bond et al., 2013). By its direct radiative effect, BC is the main source of warming after carbon dioxide, both globally and regionally. Despite its recognized importance, the estimate of the BC direct radiative effect remains one of the largest uncertainties in the climate forcing assessment (Boucher et al., 2016).

At present the limiting factor remains our inability in representing the spectral optical properties of BC in models, in particular the complex refractive index (CRI=n–ik), i.e. the only intrinsic optical property of a particle describing its scattering/absorption capacity. Currently, little is known on the extent and spectral variability of the CRI and its possible modification as a function of different atmospheric aging processes, as well as its link to the particle composition and morphology (Samset et al., 2018; Liu et al., 2019).

Indeed, in the last decade a number of field studies have evidenced that the CRI of BC is highly variable (e.g., Cappa et al., 2012; Bond eta la., 2013). This depends on external/internal mixing with other compounds, and on the presence of organic/inorganic coatings resulting from heterogeneous reactions at the particle surface (Schnaiter et al., 2005; Zhang et al., 2008; Peng et al., 2016).

Particle morphology has been also identified as a key factor influencing the absorption/scattering properties of the particles and the ability to model their optical response (Soewono and Rogak, 2013). BC aerosols are fractal–like aggregates formed by quasi–spherical primary particles extremely difficult to represent in an optical model (Bescond et al., 2016). This complex structure is also continuously changing during atmospheric aging, because of the particle aggregation or restructuration due to coating formation, which can modify their morphology and their spectral optical properties. As of today reduced information exist on the complex refractive index of BC in particular due to this difficulty of modeling complex fractal–like aggregate structures and the impact of coatings on them.

Scientific objectives

The objective of this project is to perform laboratory chamber experiments with the aim to investigate the climatically–relevant spectral optical properties of BC. Specifically, the objectives are:

1. to determine the spectral CRI of BC taking into account the complex morphology of the particles
2. to investigate the changes in the CRI of BC in link with its atmospheric aging, in particular the impact of heterogeneous reactions with atmospheric constituents inducing the formation of inorganic/organic coatings on BC aerosols
3. to understand the role of chemical composition in the light absorption efficiency of BC aerosols

The results of this study will provide the data necessary to climate models to constrain the global and regional BC radiative effect, therefore helping to reduce the uncertainties in climate change prediction.

Reason for choosing the CESAM simulation chamber

To achieve the objectives of the project it is necessary to measure the spectral optical properties of the aerosols simultaneously with their physico-chemical properties in different conditions (fresh/aged aerosols) so that the two can be related via the CRI estimation. The CESAM chamber (Wang et al., 2011) provides the ideal and well–characterized environment to study aerosols and their aging in realistic and atmospheric–relevant conditions, as well to characterize simultaneously their spectral optical properties and physico–chemical state based on state–of–the–art instrumentation and established laboratory protocols. The LISA in particular offers the capability to measure the spectral optical properties of the particles by artefact–free “in situ” spectrometers working at ambient RH, that combine with classical “ex situ” instrumentation. At LISA it is also possible to investigate the composition of the particles, including the organic to elemental carbon fraction and soluble fraction by thermo-optical analysis and ion chromatography, and to characterize the morphological properties of the aerosols by transmission electron microscopy. The LISA group involved in CESAM experiments has also a long track of work on the retrieval of the CRI of different aerosol types (Denjean et al., 2015;

Di Biagio et al., 2014, 2017, 2019). In synthesis, the CESAM chamber at LISA enables to study the spectral optical properties of BC and provides the required complimentary competences to the project.

Method and experimental set-up

Chamber experiments targeted the generation and aging of BC aerosols with the objective of relating the spectral CRI to particle composition and morphology.

BC generation was performed by means of a commercial burner (the miniCAST JING model 5200, http://www.sootgenerator.com/), at present the most used soot generator in chamber laboratory experiments. The miniCAST was operated by using as input 60 ml min^{-1} of propane, 1.5 l min^{-1} of oxidation air, 20 l min^{-1} of dilution air, and 7 l min^{-1} of quench azote.

	DAY	Aerosol inital concentration (µg/m3)	RH (%)	O_3 (ppb)	SO_2 (ppb)	VOC α–pinene (ppb)	Timeline / Objective
Set up day	1	–	–	–	–	–	Instrument installation, calibrations
EXP1: BC aerosols restructuration	2–3	2000	0	0	0	0	BC aerosols injected in CESAM; BC left to age overnight; resuming measurements in the morning to see morphological restructuration
EXP2: BC aerosols restructuration	3–4	110	0	0	0	0	The same as previous experiment but at lower aerosol concentrations
Manual cleaning of the chamber	4	–	–	–	–	–	Manual cleaning of CESAM, check of instruments calibration
EXP3: ammonium sulfate aerosols, inorganic coating	5	150	35	485	80	–	Inorganic coating: control experiment with non–absorbing aerosols
EXP4: BC aerosols, inorganic coating	6	245	40	502	80	–	BC aerosols injected in CESAM; coating of sulfates simulated and the properties of the aged BC measured
EXP5: fullerene aerosols, inorganic coating	7	50	33	500	80	–	Inorganic coating: control experiment with absorbing aerosols
Manual cleaning of the chamber	8	–	–	–	–	–	Manual cleaning of CESAM, check of instruments calibrations
EXP6: BC aerosols, organic coating	9	190	31.5	485	–	60	BC aerosols injected in CESAM; coating of organic aerosols generated from the ozonolysis of α–pinene
EXP7: ammonium sulfate aerosols, organic coating	10	160	45	487	–	60	Organic coating: control experiment with non–absorbing aerosols

***Table 1**. List of experiments performed during the campaign*

Experimental protocol: the particles of BC generated by the miniCAST were suspended in CESAM and different aging processes were simulated during experiments, as summarized in Table 1. First experiments (EXP1, EXP2) focused on the BC “physical” aging (no chemical forcing, relative humidity (RH) at 0%) to see restructuration at high and low mass concentrations. The EXP4 investigated the change in BC spectral optical properties due to the formation of inorganic coating on the particles; this was obtained by the reaction of BC with sulfur dioxide (SO_2) at 40% RH in presence of ozone (O_3). The impact of organic coating (EXP6) was studied by making BC to interact with Secondary Organic Aerosols (SOA) produced in the chamber by the reaction between α–pinene, a natural Volatile Organic Compound (VOC), and with O_3 oxidant. Three control experiments were performed (EXP3, EXP5, EXP7) with non–absorbing (ammonium sulfate) and absorbing (fullerene) proxy aerosols. Chamber cleaning was performed to avoid any memory effect between experiments. Routine cleaning consisted of pumping down for few hours; manual cleaning was performed twice during the campaign.

Instrumentation: while suspended in CESAM, the physico-chemical and the spectral optical properties of the BC aerosols were measured by the ensemble of instruments listed in Table 2. The spectral optical properties (extinction, scattering and absorption coefficients) were measured by combining *ex situ* instrumentation (3–λ nephelometer, 7–λ aethalometer, 2–λ ring down extinction cavities, and 2–λ ring down extinction + scattering cavities) with the new in situ UV–Vis long path spectrometric pathway able to provide artefact–free measurement of aerosol extinction at high spectral resolution and ambient RH conditions (400 to 700 nm at 1 nm spectral resolution). In addition, the extinction spectrum between 2 and 16 µm was measured by means of an in situ spectrometer at 0.5 cm^{-1} resolution. The aerosol size distribution was measured in real time (6–sec 2–min resolution) from 20 nm to several µm from mobility and optical counters. The mass of the aerosols was measured by a combination of different techniques (2–min to 30–min resolution): (i) by size distribution measurements; (ii) by combining the measurement of the effective density from a CPMA (Centrifugal Particle Mass Analyzer) with those of the size, therefore taking into account BC non–sphericity.

The chemical composition of the particulate BC was studied by analysis on filters collected during the experiments to retrieve: the *total carbon fraction* and its distribution between *organic (OC) and elemental (EC) carbon* (by thermo–optical analysis; Sunset analyzer); the *aerosol soluble fraction* (by ion chromatography, IC); the *chemical surface state* (by X–ray induced photoelectron spectroscopy, XPS). In order to increase the chemical characterization capacity of BC aerosols, for this project a Single Particle Soot Photometer (SP2) measuring the refractory black carbon (rBC) content in single particles was added to the CESAM equipment during experiments. The SP2 provides the mass and number size distributions of BC cores in the SP2's size range (80-550 nm). Additionally, the SP2 provides optical sizing of particles. A secondary data product of the SP2 is a semi–quantitative measure of the coating thickness of non–refractory material on individual BC cores. The morphology of samples collected on filters was studies using transmission electron microscopy, MET, to retrieve the diameter of primary spheres, the radius of gyration, and the fractal dimension of the aggregate constituting the particles.

	Measurement	**Instrumentation**
Gas phase	Temperature, RH	PT100 gauge, hygrometer Vaisala HMP 234
	Pressure	Pressure gauge – Baratron
	SO_2 O_3 NO_x	On line analysers (HORIBA, APSA–APOA–APNA) In–situ long path (200 m) FTIR
	VOC	PTRMS, FTIR
Aerosol phase: chemistry	Carbon content	Filter sampling + thermo–optical analysis (SUNSET)
	Coating detection and mixing state	Filter sampling + Ion chromatography (IC) Transmission electron microscopye (MET)
	Surface state	Filter sampling + X–ray induced photoelectron spectroscopy (XPS)
	Refractory BC	Single Particle Soot Photometer (SP2)
Aerosol phase: physical properties	Size distribution	on–line SMPS (0.01–1 µm) + OPCs (0.2 to 32 µm; 0.2 to 10 µm)
	Mass aerosol concentration	From size distribution data Centrifugal Particle Mass Analyzer (CPMA) + DMA + CPC
	Morphology	Filter sampling + MET
Aerosol phase: spectral optical properties	Extinction coefficient	In situ Spectrometre, Ocean Optics (0.4–0.7 µm) In situ FTIR (2–16 µm) Ex situ Aerodyne CAPS PMex cavity ring–down spectrometer (0.45, 0.63 µm)
	Scattering coefficient	Ex situ TSI nephelometer (0.45, 0.55, 0.70 µm)
	Absorption coefficient	Ex situ Magee Sci. aethalometre (0.37 – 0.95 µm)
	Ext. & scat. Coefficients, SSA (scatt./ext.)	Ex situ Aerodyne CAPS PMSSA cavity ring–down spectrometer (0.45, 0.63 µm)

***Table 2**. List of instruments used during the campaign*

Preliminary results

Globally the experiments were successful. We were able to suspend, age and monitor simultaneously the physico–chemical and spectral optical properties of BC aerosols.

The analysis of microscopy images shows the formation of BC fractal–like aggregates of submicron size (Figure 1). The preliminary data analysis suggests that the BC size distribution is monomodal and centred at about 120 nm diameter at the beginning of the experiments (fresh BC aerosols) and it evolves with time due to coagulation that induces a shift towards larger diameters, as can be seen for example in the left panel of Fig. 1 for EXP2. The time evolution of the size distribution may also lead to a possible morphological restructuration; this is under investigation from the analysis of MET images / and CPMA measurements.

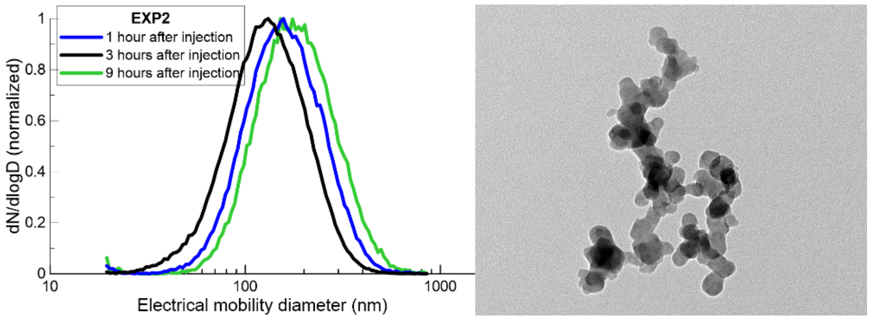

***Figure 1**. (Left) Size distribution measured during EXP2 after 1 hour from injection in CESAM and 3 and 9 hours later. (Right) MET image of the fresh soot aerosols (within one hour from injection) in CESAM for EXP2.*

The mass concentration of the aerosols in CESAM was between 110 µg m^{-3} to 2000 µg m^{-3} for the different experiments, as calculated from size data assuming a density of 1 kg m^{-3}. The CPMA–SMPS measurements suggest however that the effective density of the generated BC fractal aggregates is lower than 1 kg m^{-3}, in particular for mobility diameters larger than 100 nm. An example of the effective density vs mobility diameter obtained for EXP2 for fresh BC aerosols is shown in Figure 2.

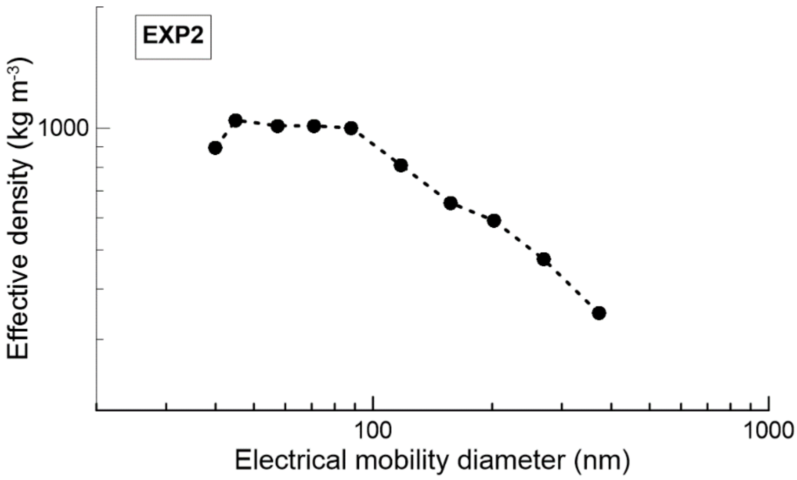

***Figure 2**. Effective density versus electrical mobility diameter for generated BC aerosols during EXP2.*

The optical signals show the dominance of absorption over scattering during all BC experiments. The single scattering albedo (SSA, ratio of scattering to extinction) retrieved from the CAPS SSA at 630 nm is within 0.30 to 0.35 for uncoated BC aerosols as shown in Figure 2; this range of values is in line with past literature estimates (Schnaiter et al., 2006; Forestieri et al., 2018). The SSA of BC aerosols does not seem to significantly change with time due to the changes of the size distribution owing to coagulation and the possible morphological restructuration, as seen for EXP2 data in Fig. 2.

Further analysis is ongoing for experiments involving coating formation on BC aerosols.

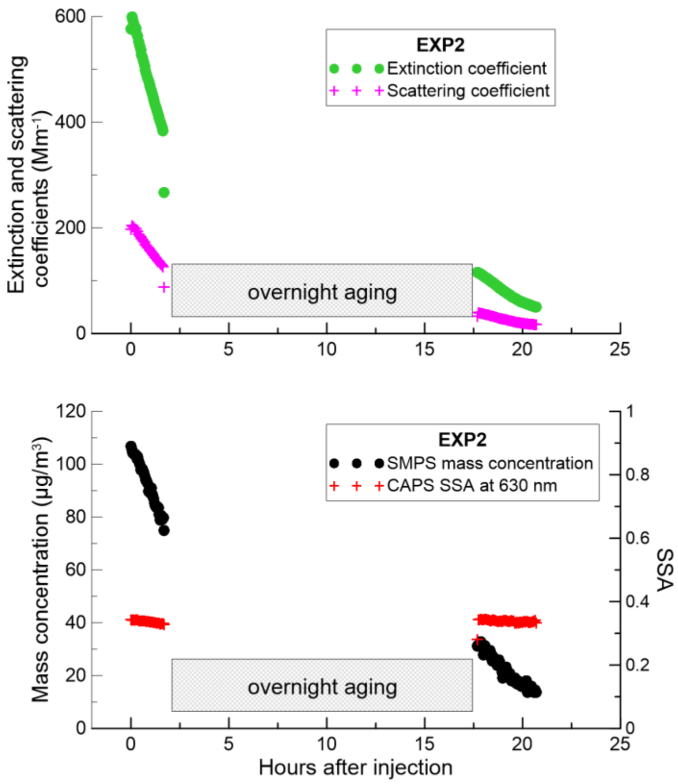

Figure 3*. (Top) Aerosol extinction and scattering coefficients and (bottom) aerosol mass concentration and single scattering albedo (SSA) versus time for EXP2. Optical data are at 630 nm. Data are not corrected for dilution*

Future studies

Data analysis on the CESAM measurements are being carried out. The spectral optical properties (mass absorption/scattering/extinction coefficients, SSA) of the BC and their change with aging for the different experiments are currently under investigation based on the data from the different ex situ and in situ optical instruments.

The BC chemical characterization from filter sampling is ongoing and will be completed by end of 2019 (thermo optical analysis – CNRS-LISA, measurements performed in August 2019; XPS measurements performed in October 2019 at the ITODYS laboratory in Paris; IC measurements– CNRS-LISA, to be performed in November–December 2019). The SP2 data analysis will be completed by spring 2020.

The characterization of the BC size distribution, effective density, and morphology will be completed by the beginning of 2020. The MET images for all samples were taken in September–October 2019; the automatic analysis to retrieve the morphological parameters necessary for optical modelling (radius of primary particles, gyration radius, fractal dimension) is ongoing.

The spectral CRI of the uncoated BC fractal–like aggregates will be estimated by optical calculations by the application of the RDG–FA (Rayleigh–Debye–Gans theory for Fractal–Aggregates) theory, whereas the RDG–CFA (Rayleigh–Debye–Gans theory for Coated Fractal–Aggregates) will be applied for coated BC (Yon et al., 2008). This study will be performed in collaboration with the Univ. of Rouen, Dr. J. Yon. For comparison, simulations will be also performed by means of the Mie theory for homogeneous spherical particles. The retrieved spectral CRI and its correlation to particle composition and morphology will be investigated both at selected wavelengths and broadband.

We plan to present first results at the International Radiation Symposium (6–10 July 2020) and/or at the European Aerosol Conference (30 August–4 September 2020).

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