TNA User Report

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eurochamp2020@lisa.u-pec.fr

Project title	Organic characterization of secondary biomass burning aerosol through advanced spectrometric (MS and NMR) techniques
Name of the accessed chamber	FORTH-ASC
Number of users in the project	2
Project objectives (max 100 words)	The project focuses on ageing experiments of biomass burning aerosol at the FORTH Atmospheric Simulation Chamber facility. Specific objectives are: 1- To assess the production of secondary organic aerosol (SOA) resulting from ageing by means of online aerosol mass spectrometers (AMS) and offline using proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy. 2- To simulate both diurnal and nocturnal chemical ageing (via OH and NO3 radical oxidation) and explore the effects of different chemical pathways on organic chemical composition. 3- To assess the effects of humidity and particulate water on SOA condensation and chemical transformation as measured by AMS and ^{1}H-NMR methods.
Description of work (max 100 words):	A total of twelve biomass burning experiments were carried out at the FORTH ACS: SOA formation was investigated under different experimental conditions in term of oxidants (OH or NO_3), photochemical conditions (illumination vs. dark), and relative humidity (up to 80%). The formation and evolution of organic aerosol was monitored using a HR-ToF-AMS, while aerosol samples were collected for offline chemical characterization. Filter samples of fresh and aged smoke were extracted in deionized water and analysed by ^{1}H-NMR spectroscopy at 600 MHz. Spectral fingerprints for biomass burning SOA were evaluated in relation to the different oxidation conditions employed in the chamber.

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Principal Investigator's and group's information	
First name	Stefano
Family name	Decesari
Nationality	Italian
Activity domain[1]	Earth Sciences & Environment
Home institution	National Research Council of Italy (CNR)
Institution legal status[2]	RES
Email	s.decesari@isac.cnr.it
Gender	M
User status[3]	RES
New user	yes

User 1 Information[4]	
First name	Marco
Family name	Paglione
Nationality	Italian
Activity domain	Earth Sciences & Environment
Home institution	National Research Council of Italy (CNR)
Institution legal status	RES
Email	m.paglione@isac.cnr.it
Gender	M
User status	RES
New user	yes

Trans-National Access (TNA) Scientific Report

[1] *PLEASE CHOOSE ONLY ONE DOMAIN* 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 ENG= Engineer; ACA= Academic; TEC= Technician.

[4] Reproduce the table for each user who accessed the infrastructure

Name of the PI: Stefano Decesari
Chamber name and location: FORTH-ASC, Patras (GR)
Campaign name and period: 15 May – 14 June 2019; 21 Oct – 31 Oct 2019.
Text:

1. Introduction and motivation

Biomass burning is one of the major sources of organic particulate matter both on a global scale and in Europe. In spite of the emerging evidence of secondary aerosol formation from biomass burning sources, there are still major knowledge gaps in quantifying such processes (Hodshire et al., 2019). The project focuses on the identification of formation pathways of biomass burning SOA using advanced spectrometric techniques, including aerosol mass spectrometry (AMS) and ^{1}H-NMR spectroscopy (Paglione et al., 2014). The outcomes of the project will contribute to current research in FORTH and ISAC-CNR on the chemical processes responsible for biomass burning SOA formation and, eventually, to the formulation of realistic representations of such processes into CTMs.

2. Scientific objectives

Specific objecti.es of the project include:

1. To assess the production of secondary organic aerosol (SOA) resulting from ageing of biomass burning aerosols by means of online aerosol mass spectrometers (AMS) and offline using proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy.
2. To simulate both diurnal and nocturnal chemical ageing (via OH and NO_3 radical oxidation) and explore the effects of different chemical pathways on organic chemical composition.
3. To assess the effects of humidity and particulate water on SOA condensation and chemical transformation as measured by AMS and ^{1}H-NMR methods.

3. Reason for choosing the simulation chamber/ calibration facility

The FORTH Atmospheric Simulation Chamber facility (FORTH-ASC) is equipped with a combustion facility allowing to inject directly primary emissions from biomass burning (BB) inside the chamber and to follow their ageing with state-of-the art on-line instruments.

FORTH is involved in other projects (like ERC PyroTRACH, Pyrogenic Transformations Affecting Climate and Health) investigating BB-aerosol and their regional and global impacts. These projects represent an ideal frame for the activities planned in the present TNA.

4. Method and experimental set-up

A total of twelve biomass burning experiments were carried out during the TNA.

The experiments were designed in order to explore different conditions in term of oxidants (OH or NO_3), photochemical conditions (illumination vs. dark), and relative humidity (up to 80%). The biofuels employed were the two most common types in Greece: olive tree logs (for a wood heater) and pellets made by residuals of pine.

For each experiment, the formation and evolution of organic aerosol was monitored using a HR-ToF-AMS (Kaltsonoudis et al., 2017), while two aerosol samples were collected on quartz-fiber filters for offline ^{1}H-NMR characterization: a first one immediately after the smoke injection ("Fresh BB"), and a second one upon aging ("Aged BB") (around 3-4 hours after the injection of oxidant precursors or the lights on). Filter collection was carried out using a dedicated pump equipped with a flow mass

controller and a cyclone for the size cut-off at PM1. During four experiments, an additional sample was collected directly from the injection pipe in order to investigate the composition of the undiluted fresh emissions. After the collection, the filters were stored at -20°C in aluminium foils and transferred (frozen) to the ISAC lab in Bologna for the chemical analysis. In the end of the project a total of 30 filters were moved to the ISAC lab: 28 filters from the experiments + 2 blanks.

A list of the experiments performed during the present TNA project together with the number and type of filters collected is summarized in the table here below (Table 1).

The filter samples were processed in the Bologna laboratories for WSOC characterization (Zanca et al., 2017). Upon extraction with milliQ water in a mechanical shaker, drying and recovery with deuterated water, each extract was transferred into a 5 mm NMR tube with a Shigemi microtube assembly and analysed at 600 MHz with a Varian Unity INOVA spectrometer at the Department of Industrial Chemistry of the University of Bologna. The employ of microtubes enabled for the first time to analyze sample extracts containing less than 10 µg of WSOC which is crucial for application to reaction chamber experiments. A PRESAT sequence was used for the saturation of the HDO signal and the spectra were acquired for 1024 transient (about 1h of acquisition for each spectrum).

Table 1. List of the performed experiments: a short description of the main ageing conditions explored in each experiment is reported together with the number, the type and the current status of the collected filters.

Exp. ID	Experiment type	Main Conditions	Filters collected	Status of the analyses
A	**Wood - Dark ozonolysis**	Ageing in dark with ONLY O3	A1 - Fresh BB	✓ completed
			A2 - Aged BB	✓ completed
B	**Wood - Dark O3+NOx (dry)**	Ageing in dark with NO2 + O3(low) - dry	B0 - Directly from the injection pipe	✓ completed
			B1 - Fresh BB	✓ completed
			B2 - Aged BB	✓ completed
C	**Wood - Photoxidation (dry)**	Ageing UV-lights without additional oxidants @RH=50%	C0 - Directly from the injection pipe	✓ completed
			C1 - Fresh BB	✓ completed
			C2 - Aged BB	✓ completed
D	**Wood - Dark O3+NOx (High RH)**	Ageing in dark with NO2 + O3(high) @RH=80%	D0 - Directly from the injection pipe	✓ completed
			D1 - Fresh BB	✓ completed
			D2 - Aged BB	✓ completed
E	**Wood - Reference Dark (Dark no oxidants)**	leaving in chamber without additional oxidants	E0 Directly from the injection pipe	✓ completed
			E1 - Fresh BB	✓ completed
			E2 - Aged BB	✓ completed
F	**Wood - Photoxidation + H2O2 (High RH)**	Ageing UV-lights +H2O2 @RH=80%	F1 - Fresh BB	✓ completed
			F2 - Aged BB	✓ completed
G	**Pellet - Dark ozonolysis**	Ageing in dark with ONLY O3	G1 - Fresh BB	...analysis in progress
			G2 - Aged BB	...analysis in progress
H	**Pellet - Dark O3+NOx (dry)**	Ageing in dark with NO2 + O3(low) - dry	H1 - Fresh BB	...analysis in progress
			H2 - Aged BB	...analysis in progress
I	**Pellet - Photoxidation (dry)**	Ageing UV-lights without additional oxidants @RH=20%	I1 - Fresh BB	...analysis in progress
			I2 - Aged BB	...analysis in progress
J	**Pellet - Dark O3+NOx (High RH)**	Ageing in dark with NO2 + O3(high) @RH=80%	J1 - Fresh BB	...analysis in progress
			J2 - Aged BB	...analysis in progress
K	**Pellet - Reference Dark (Dark no oxidants)**	leaving in chamber without additional oxidants	K1 - Fresh BB	...analysis in progress
			K2 - Aged BB	...analysis in progress
L	**Pellet - Photoxidation (High RH)**	Ageing UV-lights @RH=80%	L1 - Fresh BB	...analysis in progress
			L2 - Aged BB	...analysis in progress

5. Data description

During all the experiments, the HR-TOF-AMS provided measurements of mass and size-resolved chemical composition of non-refractory submicron aerosol (NR-PM1). All HR-ToF-AMS data were analyzed using the standard AMS software toolkit (SQUIRREL v1.53), while the high-resolution data were processed using the Peak Integration by Key Analysis (PIKA v1.10C; Sueper, 2011) software, within Igor Pro 6.34A (Wave Metrics). The HR-TOF-AMS collection efficiency (CE) was calculated based on a combination of HR-ToF-AMS mass distributions and the SMPS volume distributions (for particle diameters between 10 and 500 nm), according to Kostenidou et al. (2007).

The ^{1}H-NMR spectra were acquired and stored as FID (free induction decay) files. Postprocessing was performed in the following steps: a) automatic FT, b) manual phase correction, c) applying a line broadening parameters of 0.5 to 1 to decrease the baseline noise, d) integration of the main spectral region. Finally, the integrals were converted into concentrations of organic functionalities expressed as μmol H m^{-3} and merged with ancillary data from the chamber experiments to produce the final databases.

6. Preliminary results and conclusions

The analysis of the HR-TOF-AMS measurements provided information on the PM1 composition in terms of concentrations of the main chemical components and of elemental ratios of the organic fraction. The AMS results highlighted that primary biomass burning organic aerosol (BBOA) can rapidly age also in the dark to form secondary Oxidized Organic Aerosols (OOAs) both in dry and humid conditions. The AMS identification of spectral fingerprints for the various SOA formed under different oxidation conditions is under way.

The results of ^{1}H-NMR characterization of POA and SOA samples in the FORTH-ASC facility represent, in our knowledge, the very first data obtained using this technique in reaction chambers during biomass burning aerosol ageing experiments. Figure 1 shows the set of ^{1}H-NMR spectra of fresh and aged aerosols collected in the chamber before and after the oxidation is taken place. Exception is experiment E where no oxidant was added or generated although chemical transformations may still have occurred through the internal reactivity of aerosol and gases in the emission (in dark conditions). The spectra show considerable variability between experiments. The concentrations of compounds like levoglucosan, which are sensible to OH and NO$_3$ oxidation but not on O$_3$, decreased in the aged samples in experiments C and D, not in A and E in agreement with the expectations. Other compounds which were observed to be produced (and sometimes even consumed) during ageing include: phenols, dicarboxylic acids (maleic acid) and monoterpene SOA compounds. Noticeably, the evolution of spectral features in experiment E indicates that chemical composition may evolve spontaneously ("ripening") even without promoting radical chemistry.

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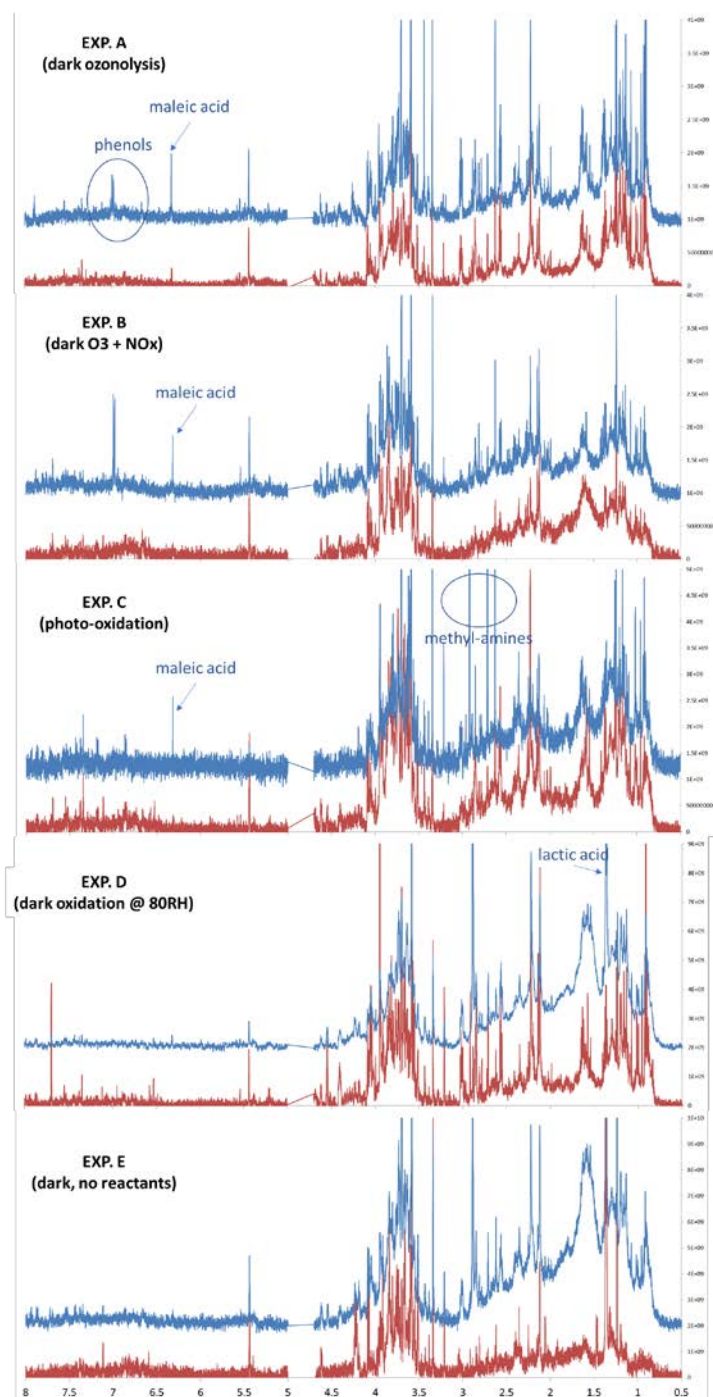
Figure 1: ^{1}H-NMR spectra @600 MHz of WSOC extracts of fresh (red) and aged (blue) organic particles in the FORTH-ASC facility during five biomass burning aerosol experiment. The x axis represents the chemical shift (ppm) with respect to the frequency of resonance of an internal standard.

7. Outcome and future studies

The on-line AMS analysis highlighted that BB-emissions can undergo rapid chemical ageing also in the dark to form secondary oxidized aerosol species (OOAs). So dark aging of BBOA may be an important source of OOA in urban environments not accounted for in models. Moreover the presence of water (linked with high relative humidity conditions) demonstrated to have an important role on the ageing of BB emissions (either not accounted for in models) leading to very oxidized components.

The offline chemical characterization showed that ^{1}H-NMR spectroscopic methodologies can be optimized for the analysis of small sample loads (sub- 10 µg) typically produced in reaction chambers when multiple steps of aerosol evolution must be probed. The preliminary analysis of the ^{1}H-NMR data from five aerosol ageing experiments illustrates a complex evolution resulting from both ripening (i.e. not induced by the injection of oxidants) and "genuine" ageing reactions. The identification of organic markers is under way. Future studies involve the analysis of specific SOA tracers for monoterpenes (co-emitted with biomass burning particles and contributing to biomass burning SOA).

8. References

Hodshire et al., Aging effects on biomass burning aerosol mass and composition: A critical review of field and laboratory studies, Environ. Sci. Technol. 2019, 53, 10007–10022, 2019.

Kostenidou et al., An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, Aerosol Sci. Technol., 41, 1002 - 1010, 2007.

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