TNA User Report

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Project title	Aqueous Formation of Brown Carbon from Pyrogallol and Syringol Photo-oxidation.
Name of the accessed chamber	CESAM
Number of users in the project	10
Project objectives (max 100 words)	This project aims to quantify and to determine the chemistry behind the following multiphase processes: 1. the uptake of pyrogallol and syringol by aerosol particles and aqueous droplets, 2. the formation of brown carbon in aerosol by each compound during OH oxidation, and 3. the formation of secondary organic aerosol by each compound during OH oxidation. This project also aims to train students in advanced scientific methods in a multinational research environment. The achievement of these objectives will lead to better and more quantitative understanding of the sources of brown carbon aerosol in the atmosphere.
Description of work (max 100 words):	19 chamber experiments were conducted exploring the formation of brown carbon aerosol during the oxidation of gas-phase syringol, gas-phase pyrogallol, or particle-phase pyrogallol by OH radicals. Aerosol were sampled by AMS, SMPS, PILS-waveguide spectroscopy, and CAPS-ssa instruments operating at 405, 450, and 630 nm. Cloud size distribution were monitored by WELAS and SKY-GRIMM spectrometers. The gas-phase contents of the chamber were monitored by PTR-MS and long-path FTIR and UV/vis spectrometer systems. After 13 experiments where SOA formation was observed, chamber aerosol were collected overnight on a filter for off-line high-resolution LCMS analysis at IRCELYON.

Principal Investigator's and group's information	
First name	Mikael
Family name	Ehn
Nationality	Finland
Activity domain[1]	Chemistry
Home institution	University of Helsinki
Institution legal status[2]	UNI
Email	Mikael.ehn@helsinki.fi
Gender	M
User status[3]	ACA
New user	Yes

User 1 Information[4]	
First name	Liine
Family name	Heikkinen
Nationality	Finland
Activity domain	Chemistry
Home institution	University of Helsinki
Institution legal status	UNI
Email	Liine.heikkinen@helsinki.fi
Gender	F
User status	PGR
New user	Yes

User 2 Information	
First name	Frans
Family name	Graeffe
Nationality	Finland
Activity domain	Chemistry
Home institution	University of Helsinki
Institution legal status	UNI
Email	Frans.graeffe@helsinki.fi
Gender	M
User status	UND
New user	Yes

[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

User 3 Information	
First name	David
Family name	De Haan
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	University of San Diego
Institution legal status	UNI
Email	ddehaan@sandiego.edu
Gender	M
User status	ACA
New user	No

User 4 Information	
First name	Christian
Family name	Carmona
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	University of San Diego
Institution legal status	UNI
Email	ccarmona@sandiego.edu
Gender	M
User status	UND
New user	Yes

User 5 Information	
First name	Duncan
Family name	Ugland
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	University of San Diego
Institution legal status	UNI
Email	dugland@sandiego.edu
Gender	M
User status	UND
New user	Yes

User 6 Information	
First name	Matthew-Khoa
Family name	Tran
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	University of San Diego
Institution legal status	UNI
Email	matthewkhoatran@sandiego.edu
Gender	M
User status	UND
New user	Yes

User 7 Information	
First name	Lelia
Family name	Hawkins
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	Harvey Mudd College
Institution legal status	UNI
Email	lhawkins@g.hmc.edu
Gender	F
User status	ACA
New user	No

User 8 Information	
First name	Lindy
Family name	Conrad-Marut
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	Harvey Mudd College
Institution legal status	UNI
Email	lconradmarut@g.hmc.edu
Gender	F
User status	UND
New user	Yes

User 9 Information	
First name	Ellie
Family name	Smith
Nationality	U.S.A.
Activity domain	Chemistry
Home institution	Harvey Mudd College
Institution legal status	UNI
Email	ensmith@g.hmc.edu
Gender	F
User status	UND
New user	Yes

Trans-National Access (TNA) Scientific Report

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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

Instructions

Name of the PI: Mikael Ehn
Chamber name and location: CESAM, Université Est Paris – Créteil, France
Campaign name and period: Aqueous Formation of Brown Carbon from Pyrogallol and Syringol Photo-oxidation, 3 – 28 June 2019
Text:

Introduction and motivation. Identifying and limiting sources of brown carbon aerosol (light-absorbing organic aerosol) in the atmosphere will provide new, short-term pathways for combating climate change, buying time while the long-term project of decarbonization proceeds. The phenolic compounds pyrogallol and syringol form from lignin pyrolysis during biomass burning and from photooxidation of anthropogenically-emitted aromatic compounds.(1) They rapidly produce brown carbon in aqueous reactions with OH radicals,(2, 3) especially in the presence of Fe(III) (3, 4) or nitrogen oxides.(5-7) These species are leading suspects for generating brown carbon aerosol in the atmosphere, especially in urban areas.(1, 8) However, their aqueous chemistry has to date only been studied in bulk liquid experiments, which can often generate results that do not match more realistic experiments with aqueous nanodroplets.(*9*)

Scientific objectives. This project aims to quantify and to determine the chemistry behind the following multiphase processes:

1. the uptake of pyrogallol and syringol by aerosol particles and aqueous droplets,
2. the formation of brown carbon in aerosol by each compound during OH oxidation, and
3. the formation of secondary organic aerosol by each compound during OH oxidation.

This project also aims to train students in advanced scientific methods in a multinational research environment. The achievement of these objectives will lead to better and more quantitative understanding of the sources of brown carbon aerosol in the atmosphere, and more students in the atmospheric chemistry pipeline with international research experience.

Reason for choosing the chamber facility. The CESAM chamber at Université Paris Est – Créteil is designed for studying multi-phase chemical systems, including cloud processing and aqueous-phase chemistry in aerosol particles, which are primary scientific interests of the PIs. Chamber instrumentation allows continuous measurements of gas phase composition (long path FTIR and UV-vis, PTR-MS, ozone, NOx, CO, CO_2, RH) and aerosol physical properties (TSI scanning mobility particle sizing, WELAS cloud droplet sizing, CAPS-ssa albedo at 450 and 630 nm). This capability is complementary to instrumentation supplied by the participants – measuring aerosol optical properties (CAPS-ssa albedo at 405 nm, U. San Diego, and PILS/TOC/waveguide UV-vis absorption, Harvey Mudd College) and aerosol chemical components (high-resolution aerosol mass spectrometry (AMS) with a reactive flowtube inlet, U. Helsinki). Together, we have assembled a complete measurement suite to characterize chemistry happening in the aerosol aqueous phase, the gas phase, and even processes happening on the chamber walls.

Method and experiment set-up. Chamber instrumentation continuously monitored pressure, temperature, inlet flows, gas phase composition (long path FTIR, long-path UV/vis (new), PTR-MS, ozone, NO_x, CO, CO_2, SO_2, RH) and aerosol phase composition (high-resolution AMS with inlet decanal chemical reaction flow tube, U. Helsinki; high-resolution AMS with thermal denuder inlet, Drexel U.). Aerosol and cloud droplet physical properties (TSI scanning mobility particle sizing, WELAS cloud droplet sizing, SKY-GRIMM droplet sizing) and optical properties (Aerodyne cavity attenuated phase shift single scattering albedo (CAPS-ssa) at 405, 450, and 630 nm, U. San Diego and LISA; PILS/TOC/waveguide UV-vis absorption with 2 m pathlength, Harvey Mudd College) were also continuously monitored. Most experiments included overnight filter sampling of aerosol for offline characterization of aerosol chemical properties (high-resolution LC-MS analysis with diode array UV-vis absorption analysis, IRCELYON). In a typical experiment, dried aerosol was generated from 10 mM $(NH_4)_2SO_4$ solution. Syringol or pyrogallol gas were added in the large CESAM chamber under dry conditions (RH < 5%), and then the relative humidity was increased in several steps (50%, 85%, 92%) until a cloud event occurred. The solar simulator lights and a source of hydrogen peroxide gas were then turned on for a second cloud event in the presence of OH radical oxidants.

Completed experiments. The following experiments were completed at CESAM during the 2019 measurement campaign:

3-Jun-19	**Pyrogallol** (PG) detection in PTRMS and wall loss characterization (gas only)
4-Jun-19	PG detection in PTRMS and wall loss characterization (gas only)
5-Jun-19	AS seed control run (clouds, HOOH, lights, but no PG)
6-Jun-19	Testing role of oxidant (AS seeds, PG, cloud, lights, but no HOOH)
7-Jun-19	Full experiment with PG and peroxide in gas phase, AS seeds
11-Jun-19	Assess limiting factor of PG uptake (PG+ammonium sulfate (AS) atomized together)
12-Jun-19	Assess limiting factor of peroxide uptake (PG+AS+HOOH together in aerosol)

13-Jun-19	Assess sensitivity of BrC formation to the order (PG, deliq. AS, HOOH first, then lights)
14-Jun-19	Control to determine effects of wall off-gassing of leftover PG, SOA products
17-Jun-19	**Syringol** (Syr) detection in PTRMS, wall loss characterization, uptake by wet AS seeds
18-Jun-19	AS seed control run (clouds, HOOH, lights, but no Syr)
19-Jun-19	Testing role of oxidant (AS seeds, Syr, cloud, but no lights or HOOH)
20-Jun-19	Determine if BrC forms at 50% RH (vs cloud or deliq. AS aerosol)
21-Jun-19	Full experiment with AS seeds, Syr and peroxide in gas phase, lights, cloud
24-Jun-19	Testing role of photolysis (AS seeds, Syr, cloud, lights, but no HOOH)
25-Jun-19	Determine if BrC forms at 75% RH (vs cloud or deliq. aerosol)
26-Jun-19	Assess sensitivity of BrC formation to the order (Syr, deliq. AS, lights first, then HOOH)
27-Jun-19	Assess sensitivity of BrC formation to the order (Syr, deliq. AS, HOOH first, then lights)
28-Jun-19	Control to determine effects of wall off-gassing of leftover Syr, SOA products

Data description. At least 1 high-resolution aerosol mass spectrometer (AMS) was sampling the chamber for each experiment involving seed particles. Ten of the experiments were sampled by both AMS instruments, one with a thermal denuder inlet and the other with a switching chemical reaction flow tube inlet adding decanal or ammonia gas to the aerosol. A long path UV-vis spectrometer sampled the chamber's central volume in at least 15 experiments. All experiments were sampled by long path FTIR and proton transfer mass spectrometers. FTIR data was successfully utilized by Duncan Ugland to compute absolute water vapor concentrations throughout each experiment, and is currently being used to determine HOOH(g) concentrations. PTR-MS data was successfully utilized by Matt Tran to calculate aerosol uptake coefficients for syringol and pyrogallol, and is currently being used to determine OH radical concentrations. WELAS and a SKY-GRIMM cloud droplet spectrometers sampled 17 experiments starting with 4 June 2019. Overnight aerosol filter samples were collected after 13 experiments (whenever SOA or brown carbon formation was observed). Two seed particle filters and one blank filter were also collected. All 16 filters will be analyzed by Matthieu Riva's group at IRCELYON. Aerosol absorbance data was collected on 15 experimental days by the PILS / waveguide spectrometer, and on 17 days (all aerosol experiments) by CAPS-ssa instruments operating at 405, 450, and 630 nm.

Preliminary results and conclusions. Pyrogallol gas was added to the chamber using the vapor pressure of heated solid on a vacuum line to fill a glass bulb, the contents of which were swept into the chamber by a flow of dry N_2. Detection of pyrogallol in the gas phase was found to be difficult: no FTIR signals and no PTR-MS signals at $M+H^+$ (m/z 127) were observed when pyrogallol gas was introduced to the chamber. However, when aerosol was present in the chamber, aerosol-phase pyrogallol was detected at m/z 126 by AMS at each time it was added to the chamber in the gas phase, demonstrating that pyrogallol gas easily partitions to aerosol particles. Pyrogallol addition was, however, associated with rising PTR-MS signals at m/z 61 (HOCHCHOH) and 93 ($HOCH_2CH(OH)CH_2OH$), possible fragment ions of pyrogallol. Significant quantities of brown carbon were formed only when pyrogallol was added to the chamber in the seed aerosol, and then oxidized.

Syringol was easily detected in the gas phase by PTR-MS (at m/z 155) and FTIR (in the dry chamber). Syringol gas was added to the chamber by melting solid crystals in a ~5 mL vessel and flowing 2 L/min nitrogen over the liquid. Significant quantities of brown carbon were then produced upon oxidation. Different absorbing intermediates were detected in the aerosol phase by the PILS / waveguide spectrometer depending on whether photolysis or HOOH(g) was introduced first into the chamber.

Outcome and future studies. The following students participated in the experiments, with the following project mentors and research focus:

Liine Heikkinen (graduate student) and Frans Graeffe (undergraduate student) (U. Helsinki, mentored by Mikael Ehn, focus: AMS/flow tube operation & interpretation, objectives 2-3)

Matthew-Khoa Tran (undergraduate student, U. San Diego, mentored by Mathieu Cazaunau and David De Haan, focus: PTR-MS operation & interpretation, objective 1)

Duncan Ugland (undergraduate student, U. San Diego, mentored by Aline Gratien and Jean-François Doussin, focus: FTIR operation & interpretation, objective 1)

Lindy Conrad-Marut (undergraduate student, Harvey Mudd College, mentored by Michael Giordano and Liine Heikkinen, focus, AMS / thermal denuder operation & interpretation, objective 3)

Christian Carmona (undergraduate student, U. San Diego, mentored by Claudia Di Biagio and Paola Formenti, focus: CAPS-ssa calibration, operation, & interpretation, objective 2)

Ellie Smith (undergraduate student, Harvey Mudd College, mentored by Mathieu Cazaunau and Lelia Hawkins, focus, PILS waveguide operation & interpretation, objective 2)

We anticipate future studies will be conducted on additional phenolic compounds to determine if their chemistry is similar to that determined for pyrogallol and syringol in these experiments

References

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