



TNA User Report

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Project title	Aqueous Formation of Brown Carbon: Effects of Photooxidation, Clouds, and SO ₂
Name of the accessed chamber	CESAM (Universite Paris – Est Creteil)
Number of users in the project	4
Project objectives (max 100 words)	<p>This project will explore new pathways of atmospheric brown carbon formation, following up promising experimental results obtained in simple bulk-phase studies with more realistic aerosol and cloud-phase experiments. It has two objectives:</p> <ol style="list-style-type: none"> 1) Determine the effects of SO₂ oxidation on brown carbon formation by glyoxal and methylglyoxal. 2) Quantify aerosol and cloud-phase browning by the reactions of hydroxyacetone.
Description of work (max 100 words):	<p>We performed 10 experiments exploring the interactions of glyoxal and SO₂ with aerosol and clouds. In three experiments, the SO₂ was dissolved in water (as the sulfite ion) and added to the chamber in the aerosol phase; these experiments showed the largest aerosol light absorbance. SO₂ gas reacted extremely rapidly with hydrogen peroxide causing new particle formation, and so we alternated between cloud processing in the dark, in the light, and in light with HOOH present.</p> <p>We performed 4 cloud experiments with hydroxyacetone, including one where hydroxyacetone was added to the chamber in the aerosol phase. Little aerosol browning was observed in these experiments.</p>

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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; EXP= Expert; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

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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: David De Haan

Chamber name and location: CESAM, Université Paris Est - Creteil

Campaign name and period: Aqueous Formation of Brown Carbon: Effects of Photooxidation, Clouds, and SO₂, 04/07/17 – 24/07/17

Text:

Introduction and motivation. SO₂, emitted primarily from burning ‘dirty’ fossil fuels such as coal, is oxidized in clouds to form sulfate aerosol. These aerosol particles tend to cool the planet by reflecting light and altering cloud structure. SO₂ also reacts with aldehyde species in clouds, of which the two most common are formaldehyde and glyoxal. In the atmospheric chemistry literature, reversible SO₂ + aldehyde reactions are treated as mechanistic “dead ends,” and the products are seen as reservoir species that merely break apart into SO₂ and aldehyde again. However, preliminary work in our lab shows that the oxidation of the combined glyoxal-SO₂ species causes the formation of light-absorbing hydroxy quinone products at liquid surfaces at pH as low as 5, and this browning can occur even in sunlight. Hydroxy quinones are highly redox active, and thus their formation in the atmosphere would be a likely contributor to the adverse health effects caused by inhaling submicron aerosol particles. Organic chemists have used the glyoxal + SO₂ reaction to synthesize hydroxyl quinones under basic conditions (1), but its importance to the atmosphere has never been examined.

Scientific objectives. This project followed up promising experimental results obtained in simple bulk-phase studies with more realistic aerosol and cloud-phase experiments (2, 3). It had two objectives:

- 1) Determine the effects of SO₂ oxidation on brown carbon formation by glyoxal and methylglyoxal.
- 2) Quantify aerosol and cloud-phase browning by the reactions of hydroxyacetone.

Reason for choosing the simulation chamber. The CESAM chamber at Universite Paris Est – Creteil is designed for studying multi-phase chemical systems and cloud processing of aerosol particles under dark or simulated sunlit conditions. The chemical systems the PI studies are multi-phase and driven by cloud processing and photolysis.

Method and experiment setup. Chamber instrumentation continuously monitored gas phase composition (long path FTIR, PTR-MS, ozone, NO_x, CO, CO₂, SO₂, RH) and aerosol physical properties (TSI scanning mobility particle sizing, WELAS cloud droplet sizing). The American partners supplied analytical capability for online measurements of aerosol optical properties (Aerodyne cavity attenuated phase shift single scattering albedo from the University of San Diego, PILS/TOC/waveguide UV-vis absorption from Harvey Mudd College, California) and offline characterization of aerosol chemical properties (high-resolution LC-MS analysis with diode array UV-vis absorption analysis, University of North Carolina, Chapel Hill, USA). In a typical experiments (4-11 July), dried aerosol was generated from Na₂SO₄ solution. SO₂ and glyoxal gas were added in the large CESAM chamber under dry conditions (RH < 5%), and then the relative humidity was increased in several steps until a cloud event occurred. The solar simulator lights were then turned on for a second cloud event, in some cases with addition of HOOH gas. In later experiments (12-17 July), S(IV) was added via Na₂SO₃ aerosol buffered to pH 5.5 with sulfuric acid, resulting in aerosol consisting of mixed, effloresced NaHSO₃ and NaHSO₄, and a background concentration of ~20 ppb SO₂ (Figure 1).

Data description. The following experiments were conducted at CESAM during the 2017 campaign:

- | | |
|--------|---|
| 4 July | No glyoxal control run: SO ₂ (g) + isobutanol (g) + NaCl (aerosol) + HOOH(g) + lights, dry |
| 5 July | SO ₂ (g) + 3-pentanol (g) + Na ₂ SO ₄ (aerosol) + negligible glyoxal (g), dry |
| 6 July | SO ₂ (g) + 3-pentanol (g) Na ₂ SO ₄ (aerosol) + HOOH (g) + light + glyoxal (g) + clouds |
| 7 July | glyoxal (g) + SO ₂ (g) + 3-pentanol (g) + Na ₂ SO ₄ (aerosol) + cloud + photolytic cloud |
| 10 Jul | continuous glyoxal (g) + SO ₂ (g) + Na ₂ SO ₄ (aerosol) + cloud + photolytic cloud with HOOH(g) |
| 11 Jul | 3-pentanol (g) + Na ₂ SO ₄ (aerosol) + glyoxal (g) + cloud + continuous glyoxal (g) + SO ₂ + cloud + photolytic HOOH cloud |

12 Jul	3-pentanol (g) + Na ₂ SO ₃ (aerosol) + glyoxal (g) + cloud + photolytic HOOH cloud
13 Jul	3-pentanol (g) + pH 5.5 Na ₂ SO ₃ (aerosol) + glyoxal (g) + cloud + photolytic cloud
17 Jul	N ₂ only + 3-pentanol (g) + pH 5.5 Na ₂ SO ₃ (aerosol) + glyoxal (g) + cloud + photolytic cloud + photolytic HOOH cloud
18 Jul	Clean chamber, run hydroxyacetone (g) + cloud + photolytic HOOH cloud no-seeds control
19 Jul	3-pentanol (g) + (NH ₄) ₂ SO ₄ (aerosol) control experiment
20 Jul	(NH ₄) ₂ SO ₄ (aerosol) + hydroxyacetone (g) + cloud + photolytic cloud + photolytic HOOH cloud
21 Jul	(NH ₄) ₂ SO ₄ / glycine (aerosol) + hydroxyacetone (g) + cloud + photolytic HOOH cloud
24 Jul	(NH ₄) ₂ SO ₄ / hydroxyacetone (aerosol) + methylamine (g) + cloud + photolytic HOOH cloud

Sample datasets from the first 9 experiments are summarized in Figures 1 and 3.

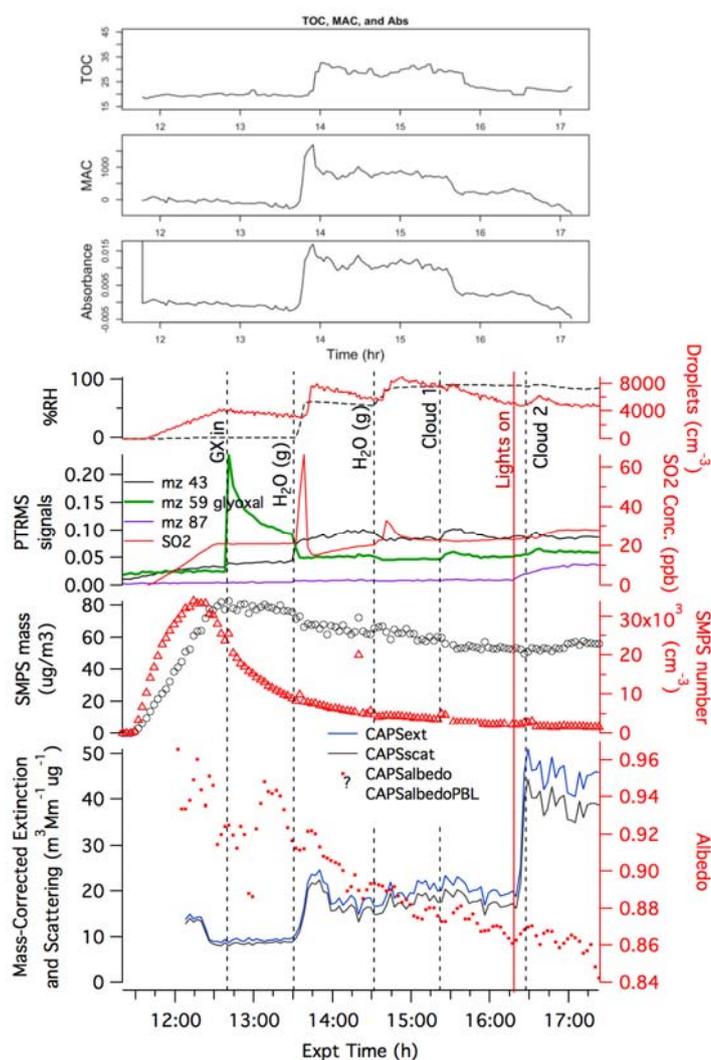
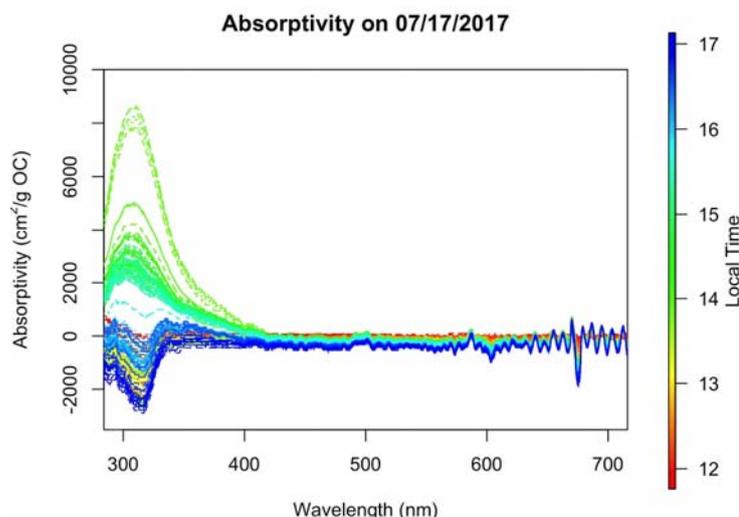


Figure 1: Gas-phase glyoxal uptake experiment with dried, then deliquesced NaHSO₃ aerosol in CESAM chamber. Top: total organic carbon and waveguide absorbance measurements at 365 nm (also expressed as mass absorption coefficients) of aerosol sampled by PILS. Chamber RH and droplet spectrometer counts are shown next, color-coded to axes. Middle: water- and dilution-corrected PTRMS data from chamber (m/z 43, black line; m/z 59 glyoxal, green line; m/z 87, purple line), and sensor SO₂ concentrations in ppb (red line). SMPS total mass (assuming density = 1 g/cm³) and counts shown next, color-coded to axes. Bottom: CAPS-ssa data at 450 nm (mass-corrected extinction, blue line; mass-corrected scattering black line; single-scattering albedo, red dots). Glyoxal addition, water vapor additions, two cloud events, and start of chamber illumination occurred at times marked by labeled vertical lines.

Preliminary results and conclusions. Glyoxal addition under dry conditions did not increase SMPS mass or decrease single-scattering albedo, consistent with exploratory small flowing chamber experiments conducted by the PI at the University of Colorado, Boulder, earlier in 2017. Over 45 min after its addition, glyoxal gas concentrations fell by around 60%, presumably due to wall uptake. At 1:31 pm, chamber RH was increased to 61%, causing NaHSO₃ to deliquesce. This change in conditions caused a rapid drop in gas-phase glyoxal concentrations (to < 15 ppb) and a pulse of SO₂ to be released to the gas phase. At the same time, a decline in aerosol mass was observed by SMPS, indicating that the loss of SO₂ from the aerosol is greater than the uptake of glyoxal in terms of volume. NaHSO₃

deliquescence also caused optical changes: the beginning of a long-term decline in albedo at 450 nm (observed by CAPS at 450 nm in aerosol sampled after drying), and an increase in absorbance measured at 365 nm (observed by waveguide spectrometer in wet-sampling PILS outflow) corresponding to an increase in MAC of 2000 cm²/g. The total organic carbon signal in the PILS outflow also increased at this point, further evidence that SO₂ loss from the particle was partially offset by uptake of glyoxal. The absorbance spectra of the PILS outflow (Figure 2) showed a clear increase at all wavelengths below 410 nm. These observations are strong evidence that glyoxal can form light-absorbing brown carbon in reactions with bisulfite ions in deliquesced aerosol, but not under dry conditions.

Figure 2: Time-dependent absorbance spectra measured by waveguide spectrometer in PILS outflow. Large increase in absorbance at $t = 13:30$ followed increase in CESAM chamber humidity from < 5% to 61% RH, which deliquesced the NaHSO₃ aerosol.



A chamber experiment where glyoxal and SO₂ were added in the gas phase to deliquesced sodium sulfate aerosol is summarized in Figure 3. Glyoxal addition was continuous after 14:03, while SO₂ was added in a single pulse. While a subsequent water vapor addition and cloud event after SO₂ addition each caused an increase in particle mass, the aerosol albedo at 450 nm does not change significantly, indicating that glyoxal and SO₂ are not taken up in large enough amounts by cloud droplets or deliquesced aerosol to produce brown carbon products. This is likely due to SO₂'s small Henry's law coefficient, 1.47 M/atm, which keeps dissolved SO₂ concentrations below 1 μM in the absence of base to produce HSO₃⁻ or SO₃²⁻ ions. These aerosol-phase S(IV) concentrations are much lower than in experiments on NaHSO₃ or Na₂SO₃ aerosol.

After the chamber solar simulator lights were turned on, HOOH (g) was added to the chamber (about a minute before cloud event 3). As soon as HOOH was added, particle counts increased more than 10-fold due to a nucleation event, likely caused by oxidation of SO_{2(g)} by OH radicals or HOOH. At the beginning of cloud event 3, [glyoxal_(g)] = 120 ppb and [SO_{2(g)}] = 70 ppb, but this cloud event caused a 40% drop in SO_{2(g)} concentrations, several times larger than dark cloud event 2. As cloud event 3 dissipated and the nucleated particles continued to coagulate ($t = 16:50$), single-scattering albedo measured at 450 nm began to decline from 0.90 to 0.75, stopping only when the lights were turned off 40 minutes later.

Outcome and future studies. The browning observed in the experiment with SO_{2(g)} (Figure 3) was apparently triggered by either new particle nucleation or the cloud event, but also required either photolysis or OH radical production to continue. This browning mechanism with gas-phase SO₂ is evidently different than with Na₂SO₃ or NaHSO₃ aerosol particles, since aerosol containing the S(IV) salts brown in the dark via glyoxal uptake as soon as deliquescence occurs. When glyoxal is taken up by deliquesced S(IV) salts, glyoxal – sulfite adduct molecules likely reach such high concentrations that brown carbon forms in the dark by non-radical mechanisms such as aldol condensation. However,

when SO₂ gas is the source of S(IV) in an experiment, brown carbon formation requires a radical-based mechanism.

It is hoped that, as was the case with 2015 experiments at CESAM, filter analysis at UNC-Chapel Hill will shed more light on the types of compounds responsible for the production of organic aerosol material, and for the observed light absorption in the two types of S(IV) experiments.

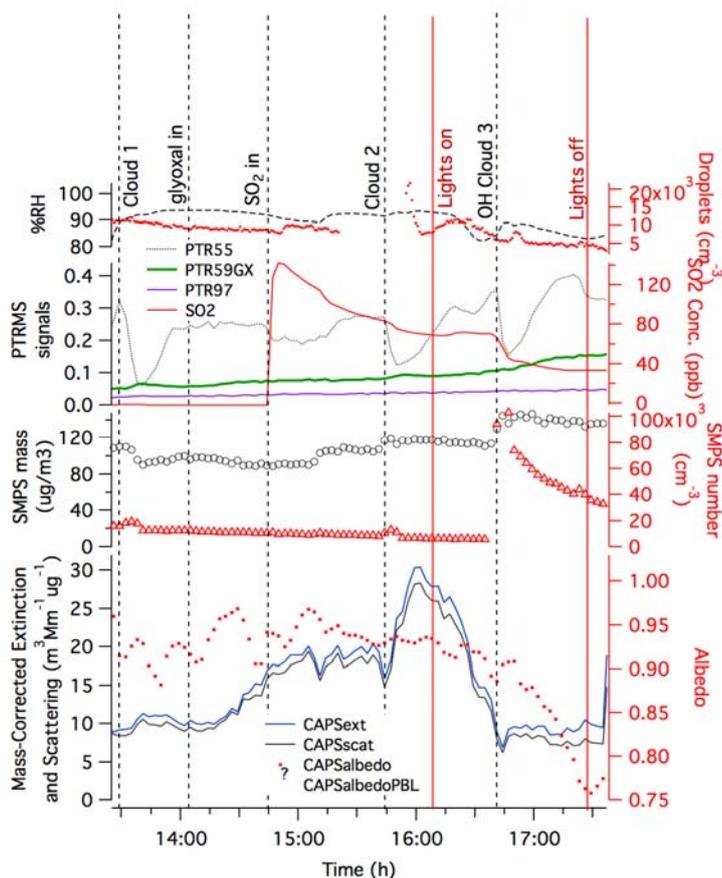


Figure 3: Gas-phase glyoxal and SO₂ uptake experiment with deliquesced Na₂SO₄ aerosol in CESAM chamber. Top: chamber RH and droplet spectrometer counts, color coded to axes. Middle: water- and dilution-corrected PTRMS data from chamber (m/z 55, black dotted line; m/z 59 glyoxal, green line; m/z 97, purple line), and SO₂ concentrations in ppb from dedicated sensor (red line). SMPS total mass (assuming density = 1 g/cm³) and counts shown next, color-coded to axes. Bottom: CAPS-ssa data at 450 nm (mass-corrected extinction, blue line; mass-corrected scattering black line; single-scattering albedo, red dots). Three cloud events, start of glyoxal addition, SO₂ addition, water vapor additions, and start and end of chamber illumination times are marked by labeled vertical lines.

References

1. Fatiadi, A. J.; Sanger, W. F., Tetrahydroquinone. *Organic Syntheses* **1962**, *42*, 90.
2. Galloway, M. M.; Powelson, M. H.; Sedehi, N.; Wood, S. E.; Millage, K. D.; Kononenko, J. A.; Rynaski, A. D.; De Haan, D. O., Secondary organic aerosol formation during evaporation of droplets containing atmospheric aldehydes, amines, and ammonium sulfate. *Environ Sci Technol* **2014**, *48*, 14417-14425.
3. Powelson, M. H.; Espelien, B. M.; Hawkins, L. N.; Galloway, M. M.; De Haan, D. O., Brown carbon formation by aqueous-phase aldehyde reactions with amines and ammonium sulfate. *Environ Sci Technol* **2014**, *48*, (2), 985-993.