Night-time chemistry of biomass burning emissions in urban areas: A dual mobile chamber study

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Abstract.

Residential biomass burning for heating purposes is an important source of air pollutants during winter. Here we test the hypothesis that significant secondary organic aerosol production can take place even during winter nights through oxidation of the emitted organic vapors by the nitrate (NO₃) radical produced during the reaction of ozone and nitrogen oxides. We use a mobile dual smog chamber system which allows the study of chemical aging of ambient air against a control reference. Ambient urban air sampled during a wintertime campaign during night-time periods with high concentrations of biomass burning organic aerosol was used as the starting point of the aging experiments. Ozone was added in the perturbed chamber to simulate mixing with background air (and subsequent NO₃ radical production and aging), while the second chamber was used as a reference. Following the injection of ozone rapid organic aerosol (OA) formation was observed in all experiments leading to increases of the OA concentration by 20-70%. The oxygen-to-carbon ratio of the OA increased on average by 50% and the mass spectra of the produced OA was quite similar to the oxidized OA mass spectra reported during winter in urban areas. Further, good correlation was found for the OA mass spectra between the ambient-derived emissions in this study and the nocturnal aged laboratory-derived biomass burning emissions from previous work. Concentrations of NO₃ radicals as high as 25 ppt were measured in the perturbed chamber.
with an accompanying production of 0.1-3.2 μg m\(^{-3}\) of organic nitrate in the aerosol phase. These results strongly indicate that the OA in biomass burning plumes can chemically evolve rapidly even during wintertime periods with low photochemical activity.

1 Introduction

Biomass burning from residential heating, agricultural fires, prescribed burning, and wildfires is a major source of atmospheric pollutants worldwide (Watson 2002, Bond et al. 2004, Robinson et al. 2006). Emissions from biomass burning contribute both primary organic aerosol (POA) and organic vapors that upon further reactions in the atmosphere can produce secondary organic aerosol (SOA) (Andreae & Merlet 2001, Akagi et al., 2011, Bruns et al., 2016, Akherati et al., 2020). The use of wood burning for domestic heating purposes is one of the major sources of OA in many countries and is a major contributor to the violation of daily PM standards in European cities (Alfarra et al., 2007, Favez et al., 2010, Fuller et al., 2014). Biomass burning emissions and their products have significant but still uncertain impacts on human health and climate (Ford et al., 2018; O’Dell et al., 2019).

The organic aerosol emitted during biomass burning undergoes extensive physical and chemical changes in the atmosphere. More volatile components evaporate as emissions dilute in the atmosphere (Tkacik et al., 2017); these semivolatile organic compounds (SVOCs) together with the other emitted intermediate volatility (IVOCs) and volatile organic compounds (VOCs) are subsequently oxidized leading to the production of SOA. Photochemical oxidation of biomass burning emissions and the resulting SOA production have been studied both in the laboratory (Hennigan et al., 2011; Ortega et al., 2013; Tkacik et al., 2017; Ahern et al.; 2019; Kodros et al., 2020) and in the field (Capes et al., 2008; Jolley et al., 2015; Vakkari et al., 2018). The reactions of VOCs, IVOCs and SVOCs with the OH radical are considered to be the dominant chemical pathway for oxidation, but reactions of emitted monoterpenes with ozone can also contribute (Yu et al., 1999, Zhao et al., 2015). Despite considerable uncertainties remaining on the amount of SOA that can be produced, and the net change of the biomass burning OA concentration when evaporation is considered, it is clear that this daytime processing is important for converting the fresh biomass burning OA to oxidized OA (OOA) (Bougiatioti et al., 2014).

Atmospheric processing of biomass burning OA during periods of low photochemical activity (such as in winter or at night), known also as “dark” aging, has received substantially less
attention than photochemical processing. Recent aircraft measurements during agricultural biomass burning periods indicated that nighttime oxidation of biomass burning VOCs is dominated by NO$_3$ (Decker et al., 2019). Hartikainen et al. (2018) reported high amounts of nitrogen-containing organic compounds both in the gas and particle phase after dark aging of residential wood combustion emissions. Kodros et al. (2020) reported significant and rapid OOA production in laboratory experiments in which fresh biomass burning emissions were exposed to NO$_3$ and suggested that dark oxidation may be an important process on regional scales. In the same study, ambient measurements in an urban area suggested that the mixing of O$_3$ from the residual layer down to the nocturnal boundary layer can enhance the formation of NO$_3$ and the nighttime oxidation of biomass burning emissions. The mixing of ozone from the residual layer and the importance to nighttime chemistry was also suggested in studies on nighttime oxidation of biogenic VOCs (Brown et al., 2009; Brown et al., 2013). Despite this important finding, the degree to which biomass burning plumes undergo night-time aging and produce significant amounts of SOA remains poorly understood. Lacking consideration of such nocturnal chemistry in transport models has been suggested as a possible source of the under prediction oxidized organic aerosol mass by a factor of 3-5 (Fountoukis et al., 2016; Tsimpidi et al., 2014) during wintertime in polluted areas with low photochemical activity.

In this study, we take advantage of the high levels of OA from residential biomass burning in Patras, Greece (the country’s third-largest city), to investigate the importance of night-time chemistry in the processing of biomass burning OA. Biomass burning leads to concentrations of OA exceeding 50 µg m$^{-3}$ in Patras in the early evening (Florou et al., 2017). A dual atmospheric simulation chamber system is used to elucidate the formation of SOA during winter periods in urban areas with high biomass burning organic aerosol concentrations. Usually chamber studies use fresh biomass burning emissions generated in the laboratory. The use of the dual chamber system offers the capability of aging realistic biomass burning emissions mixed with other pollutants. It therefore offers a bridge between laboratory experiments and ambient observations.

2 Experimental Methods

2.1 Dual chamber system

The dual chamber system developed by Kaltsonoudis et al. (2019) was used for experiments in early 2020 in Patras, Greece during the PyroTRACH-PANACEA Wintertime 2020
experiment. The system consists of two 1.5 m³ Teflon (PTFE) reactors attached to metallic frames. Use of the second reactor as a reference (control chamber) allows the identification and potential correction for any major experimental artifacts that could be due to the walls of the chamber and the other complexities of this experimental system. The dual chamber system was deployed from January 10 till February 15, 2020 in the city of Patras. The chambers along with the available instrumentation were located indoors, in the campus of the University of Peloponnese, approximately a few kilometers away from the center of the city. The windows of the laboratory were kept open before and during the experiments, so the temperature of the system was only a few degrees higher than that of the outdoor environment.

2.2 Experimental description

Both chambers were flushed with ambient air before each experiment using a metal bellows pump (Senior Aerospace, MB-602) for 1-2 h. This process is used to achieve higher sampling efficiency and brings the system (chamber walls, tubing) close to equilibrium with ambient air reducing losses of vapors to the sampling lines and walls of the chamber. Ambient air during nighttime cold periods was introduced inside both chambers. In one of the chambers, (perturbed chamber) ozone was added and upon reaction with the existing NOx in the chamber formed NO3 radicals. The second chamber (control chamber) was used as the reference in order to help us understand the unperturbed evolution of the system inside the chamber. During all experiments the chambers were under dark conditions. Ambient air was flushed through each of the chambers with a flow of 80 L min⁻¹. More than 70% of the ambient PM was transferred to the chambers and the concentrations of the measured VOCs were within 5% of their ambient values.

Using an automated valve switching between the two reactors, the particle and gas concentrations in both chambers were measured. Data were collected 1.5 min after the switching of the valve to avoid any memory effects related to the sampling lines. For the gas phase measurements PTFE tubing (0.25 in) was used, while for the particle phase the tubing was copper (0.25 in).

After filling the chambers with ambient air, the content of each chamber was characterized for approximately one hour. The ozone added in the perturbed chamber after the characterization period was in the range of 50-250 ppb. These values are higher than the 20 ppb measured during the nighttime in Patras in this campaign, but some acceleration of the corresponding chemical
processes is necessary to reduce the effects of the walls and to limit the duration of the experiments
in the relatively small chambers used.

In selected experiments, approximately 40 ppb of d9-butanol was added in both chambers
to measure the OH concentration. Following Barnet et al. (2012), the OH concentration in the
chambers was estimated with the measured decay of the butanol concentration assuming a reaction
rate constant with OH of 3.4×10^{12} cm^3 molecule^{-1} s^{-1}.

An incoherent broad-band cavity-enhanced absorption spectroscopy (IBB-CEAS) was
used to measure the NO_3 radical concentration. Detailed information about the technique can be
found elsewhere (Venables et al., 2006; Ventrillard-Courtillot et al., 2010; Chen and Venables,
2011; Fouqueau et al., 2020). Briefly the light from a LED source centered on the 662 nm
absorption cross section of NO_3 radical is focused and introduced into a high-finesse optical cavity
composed of two high reflectivity (-99.98\%) and 1 m curvature mirrors. The optical cavity has a
length of 0.61 m and allows up to 4.5 km (at 662 nm) optical path and a detection limit up to 3 ppt
(integration time of 10 seconds). Particle-free air is passed through the cavity at 2.5 L min^{-1}.
Spectra between 640 and 685 nm were recorded with an OceanOptics QE-65 Pro spectrometer. A
time resolution of one minute was selected for these experiments. Calibration with NO_2 (800 ppb
in dry nitrogen, Air Liquide) was performed daily in order to precisely determine the reflectivity
of the mirrors and estimate the optical path. The sample spectra were fitted against standard spectra
of gas species absorbing in the spectral region of the instrument: NO_3 radical (Orphal et al., 2003),
NO_2 (Vandaele et al., 1998) and H_2O (reference spectrum recorded with the instrument) using the
DOASIS software.

A quadrupole proton-transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik) was
used to measure the concentration of VOCs including d9-butanol. We calculated the initial VOC
levels in the chambers using the concentrations of m/z 42 (acetonitrile), 69 (isoprene), 71 (MVK
& MACR), 73 (MEK), 79 (benzene), 93 (toluene) and 107 (xylene). We used the above m/z peaks,
because the PTR-MS was calibrated for those values. For the experiments that the PTR-MS was
not available we scaled the initial VOCs concentration using the BC levels. Using a series of gas
monitors the concentration of nitrogen oxides (NO and NO_2) and ozone (O_3) were measured
(Teledyne models: T201 and 400E respectively).

A TSI scanning mobility particle sizer (SMPS, classifier model 3080; DMA model 3081
CPC model 3775) was used for measuring the particle number distribution in the 15-700 nm range.
An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was measuring the composition and mass spectrum of OA. For the analysis of the HR-ToF-AMS data we used the AMS software toolkit (SQUIRREL v1.57I) and for the high-resolution data the Peak Integration by Key Analysis (PIKA v1.6I) software. The elemental ratios were calculated using the improved method of Canagaratna et al. (2015). The mass concentration and particle distribution of black carbon (BC) were measured using a single-particle soot photometer (SP2, Droplet Measurement Techniques).

The collection efficiency (CE) of the AMS was calculated applying the algorithm of Kostenidou et al. (2007), comparing the SMPS volume distributions and the AMS mass distributions. The CE ranged between 0.40-0.45 depending on the experiment. Using the same algorithm, the density of the OA was calculated to be in the range of 1.25-1.4 g cm$^{-3}$.

Using the theta ($\theta$) angle (Kostenidou et al., 2009) a comparison between the OA spectra of the ambient and the chamber content after filling, we concluded that the OA composition injected in the chambers was the same as in the ambient air. The theta angle between the two chambers and the ambient OA spectra was always less than 4 degrees, suggesting excellent agreement. Also, the OA mass spectra in the two chambers right after their filling was in very good agreement ($\theta=3-4^\circ$), confirming that both chambers had the same OA composition initially.

Following the completion of each perturbation experiment, a wall-loss characterization experiment was conducted to measure the size-dependent particle wall-loss rate constant inside the two chambers (Wang et al., 2018). The particles were produced by the atomization (TSI, model 3076) of an aqueous solution of ammonium sulfate (5 g L$^{-1}$) and subsequent diffusion drying and were injected into both chambers. Using an ionizing fan, the chamber walls were swept before the start of each experiment to keep the particle loss rates low (Jorga et al., 2020).

The perturbation experiments started around 18:00 LT each evening, when the OA concentration was elevated from local nocturnal biomass burning emissions in the area for heating. The initial conditions in the experiments are summarized in Table 1. Thirteen experiments, eleven involving perturbation and two blank experiments, in which no ozone was injected in either chamber, were performed during January and February 2020 using ambient air from Patras.
3 Results of a Typical Perturbation Experiment

The average PM$_1$ concentration in the chambers during the filling process of Exp. 1 was approximately 50 μg m$^{-3}$. The concentration of OA during that period was 44 μg m$^{-3}$ with 2.4 μg m$^{-3}$ of BC. The positive matrix factorization (PMF) analysis of the full campaign ambient data set suggested that 70% of the OA at the time of filling originated from biomass burning. Other OA sources included cooking OA (15%), oxygenated OA (10%) and hydrocarbon-like OA (5%). The initial concentration of O$_3$ in the two chambers was 10 ppb, of NO 17 ppb and of NO$_2$ 24 ppb, values within 5% of their ambient concentrations. The measured initial VOC levels were approximately 150 μg m$^{-3}$. The rest of the conditions are summarized in Table 1.

In Exp.1 NO$_2$ increased to 30 ppb in the perturbed chamber in approximately 30 min after the ozone injection while at the same time NO levels dropped to close to zero. In the perturbed chamber 2 hours after the injection the mixing ratio of NO$_2$ was 18 ppb and of ozone 220 ppb. In the control chamber the concentrations of the above mentioned gases remained within 10% of their initial levels. Due to the time needed for mixing and the rapid reaction of NO and O$_3$ it is difficult to measure accurately the injected O$_3$ concentration. A zeroth order estimate can be made assuming that the injected amount of ozone is equal to the final (equilibrated) amount of ozone in the perturbed chamber plus the reacted NO$_x$ (Table S1). Based on this zeroth order estimate, the injected ozone in Exp. 1 was approximately 240 ppb.

Following the injection of ozone in the perturbed chamber (t=0 h) there was a rapid increase of OA (Fig. 1). Approximately 33 μg m$^{-3}$ of SOA was produced in 2.5 hours (70% increase from the initial injected OA levels). In just one hour after the injection of ozone, the OA concentration increased by approximately 25 μg m$^{-3}$. This roughly corresponds to an initial OA formation rate of 25 μg m$^{-3}$ h$^{-1}$, indicating the strong potential of the ambient air in an urban area with strong biomass burning emissions to form SOA even under dark conditions. The change of OA in the control chamber after the particle wall-loss corrections was less than 7% at all times. This strongly indicates that the OA changes in the perturbation chamber were not due to experimental artifacts.

The sulfate concentration remained practically the same (within 10%) in both the perturbed and the control chambers after accounting for particle wall-losses. The initial nitrate in the perturbed chamber was 1 μg m$^{-3}$ more than in the control. This small difference can be an artifact of the sampling system in this specific experiment. Production of approximately 6 μg m$^{-3}$ of aerosol nitrate was observed in the perturbed chamber with the majority of this increase in the form of...
organic nitrate. Using the method described in Farmer et al. (2010) using the NO+/NO2+ ratio from
the AMS, we estimate that close to 60% of the formed secondary aerosol nitrate in the perturbed
chamber was organic. Taking into account the organic nitrate, there was a 77% increase of the OA
compared to the initial concentration.

An increase of the ammonium concentration by close to 1 μg m⁻³ was observed in the
perturbed chamber while in the control its concentration remained within 8% of the initial value.
The relative humidity (RH) during Exp. 1 inside the chambers was approximately 45%.

3.1 Organic aerosol spectra

Comparing the OA mass spectra in the perturbed chamber at the beginning (after the air
injection) and at the end (2.5 hours after the ozone injection) of Exp. 1 there was an increase in the
fractional signal of m/z: 28 (CO⁺), 29 (CHO⁺), 30 (CH₂O⁺), 43 (C₂H₅O⁺), and 44 (CO₂⁺). The
highest decrease was observed in 55 (C₅H₇⁺), 57 (C₄H₅⁺), 60 (C₃H₅O₂⁺), 69 (C₆H₅⁺), 91 (C₇H₇⁺)
and 95 (C₇H₁₁⁺). The theta angle between the spectra was 19 degrees, indicating significant change.
The initial and final spectra in the control chamber had a θ angle of 8 degrees, with changes in m/z
28, 44, 57 and 60. Figure 2 represents the OA mass spectra in the two chambers at the start and
end of Exp. 1.

The O:C ratio during Exp. 1 in the control chamber increased slightly from 0.4 to 0.41
during the experiment (Fig. 3). This suggests that there was relatively low but probably non-zero
chemical activity in this chamber. This is consistent with the small change in the OA mass
spectrum. This activity is probably due to the O₃ that existed in this chamber. On the contrary in
the perturbed chamber after the injection of ozone the O:C ratio increased rapidly reaching 0.52
after 30 min. At the end of the experiment, the O:C ratio in the perturbed chamber reached a value
of 0.61, similar to the measured ambient value around 3:00 LT at night.

To calculate the mass spectrum of the produced OA in the perturbed chamber, we used a
simple mass balance approach. Details about this method can be found in Jorga et al. (2020).
Concisely, assuming that the main processes in the chamber are losses of particles to the chamber
walls and SOA formation, we estimate the initial (before the injection of ozone) and produced OA
mass spectra. Using the particle rate loss constant measured at the end of each experiment, the
concentration of the preexisting OA as a function of time can be calculated. The produced OA is
then the difference between the total measured OA and the initial OA. Figure 4 shows the estimated produced OA in Exp. 1 and Figure 5 the corresponding AMS spectrum.

The produced OA mass spectra from the perturbed chamber were compared with the produced OA factor from dark aging of biomass burning emissions in the laboratory (Kodros et al., 2020). Although the present study deals with ambient emissions with more complex air mixture and conditions than the laboratory work that we are comparing with, that used specific biomass burning emissions under idealized conditions, a comparison can provide us with information about the consistency of the two studies. Kodros et al. (2020) performed chamber experiments in which they exposed residential biomass burning emissions from a residential wood stove to NO₂ and O₃ under different RH conditions. Here we compare the produced OA from a medium RH (approximately 45%) experiment with those of the ambient perturbation experiments that had similar RH. The θ angle between the produced OA from perturbation Exp. 1 and the one from the laboratory chamber experiment was 11 degrees, indicating a considerable degree of similarity (Fig. 6).

The produced OA was also compared with the ambient oxygenated organic aerosol (OOA) factor identified from the PMF analysis of the ambient data. The θ angle between the ambient OOA in Patras from winter 2020 and the produced OA from Exp. 1 was 10 degrees. Similarities were also observed in the produced OA and OOA from cities around the world during winter periods. For Exp. 1 the θ angle was in the range of 9-18 degrees (Table S2) when compared with OOA factors from Fresno, US (Ge et al., 2012), Barcelona, Spain (Mohr et al., 2012), Paris, France (Crippa et al., 2013), Bologna, Italy (Gilardoni et al., 2016), Athens, Greece (Florou et al., 2017) and Xi’an/Beijing, China (Elser et al., 2016).

4 Results of Other Experiments
4.1 Secondary organic aerosol production

The rapid OA production observed during Exp. 1 was also observed in all the other experiments, with approximately 75% of the produced OA formed in the first hour after the ozone injection. Figure 7 represents the produced OA (including organic nitrates) in all the perturbation experiments. In all experiments, the majority of secondary nitrate aerosol were organonitrate, representing 55-85% of the total produced nitrate. Taking into account the organic nitrates, the
initial OA formation rate in the perturbed chamber in the conducted experiments was on average 10 μg m⁻³ h⁻¹ ranging from 1 to 30 μg m⁻³ h⁻¹.

An increase in the O:C in the perturbed chamber was observed in all experiments with an average increase from the initial O:C of 45%. At the same time the O:C in the control chamber remained within 6% of the initial value.

The mass spectra of the produced OA in the perturbed chamber were similar to that of Exp.1 with the major m/z values being 28, 29, 43, 44, 55 and 69 (Fig. 5). The θ angle between the different produced OA spectra in the perturbed experiments were less than 14 degrees, suggesting similarities between the produced OA from the different perturbation experiments. The θ angle between the produced OA mass spectra in the perturbed chamber and the one from Kodros et al. (2020) was in the range of 9-16 degrees, suggesting similarity of the results of the two studies, even if one relied on a single fuel burned in a single stove and the other in a mixture of emissions from hundreds of fireplaces and heating stoves.

4.2 NO₃ and OH radical levels

Based on the decay of d9-butanol after the injection of ozone, the OH concentration was in the range of 0.2-0.4×10⁶ molecules cm⁻³ in the perturbation chamber suggesting that the addition of ozone and reactions with organic vapors were not producing significant OH levels. In the control chamber the corresponding OH concentrations were practically zero.

Nitrate radical concentrations above the detection level of a few ppt were only measured in the perturbed chamber after the ozone injection. The maximum NO₃ radical concentrations in the perturbed chamber ranged from 3 to 25 ppt with the highest observed during Exp. 8 (Table S3). In this experiment before the ozone injection the NO₃ levels in both chambers were below the detection limit of the instrument, while after the injection (t=0 h) the concentration of NO₃ started to increase (Fig. S1). In Exp. 8 there were 44 ppb of NO₃ initially and 150 ppb of O₃ were injected. Approximately 15 μg m⁻³ of OA was formed in 2.5 h after the perturbation, with close to 2 μg m⁻³ of the OA formed being organic nitrate. The O:C reached a value of 0.6 at the end of this experiment.

The measured NO₃ concentrations along with the low concentrations of OH in the perturbed chamber suggests that the reactions of VOCs with NO₃ radicals and potentially ozone were the major source of SOA production.
4.3 Factors affecting the SOA production

The highest produced SOA was observed, as expected, in experiments that had high initial OA and VOC levels and therefore took place during polluted conditions. Experiments 1, 4 and 6 had the highest measured initial VOC levels among the conducted experiments, close to 150 μg m⁻³ (Fig. S2). Although, only a fraction of the VOCs present in the atmosphere were measured by the PTR-MS in this work, these measurements provide an indication of the SOA formation potential of the corresponding air masses.

The absolute concentration of SOA formed was also affected by the levels of NO present. Experiments with low initial NO, less than 5 ppb, (Experiments 2, 3, 5, 9 and 11) had the lowest SOA production. The lowest NO₃ radical concentrations were also observed in those experiments. Figure 8 shows the correlation between the concentration of NO₃ radicals and the produced organic nitrate levels in the perturbed chamber. The good correlation (R²=0.79) supports the strong link between the NO₃ chemistry occurring in the perturbed chamber and the corresponding SOA production. This suggests that the oxidants levels (mainly NO₃) produced after reactions of ozone with the pre-existing NO₃ are affecting significantly the levels of SOA formed under these conditions.

5 Conclusions

In this work, we studied the nighttime aging of urban wintertime air, strongly influenced by biomass burning emissions in Patras, Greece. Using a dual chamber system and ambient air as a starting point, we injected additional ozone in only one chamber to accelerate nitrate radical production via reactions with the pre-existing NO₃. The other chamber was used as a reference mainly as a safeguard against potential experimental artifacts.

After the addition of ozone, rapid SOA formation was observed in the perturbed chamber with the additional OA formed reaching up to 35 μg m⁻³. The SOA formed increased the pre-existing OA by 20-70%. Most of the secondary nitrate formed was attributed to organics, in some cases reaching up to 85% of the total aerosol nitrate. The organic aerosol formation was rapid, with 75% of the produced OA formed in the first hour after the ozone injection. The organic aerosol content in the control chamber remained within 10% of the initial injected levels, suggesting limited chemical oxidation without the addition of ozone in these timescales.
The O:C of organic aerosol increased rapidly in the perturbed chamber following the ozone injection. In 2-3 h of reactions a 40-50% increase of the O:C was observed while the OA O:C in the control chamber remained within approximately 5% of the initial value. The produced OA mass spectra showed similarities with the produced OA factor from a previous dark aging biomass burning experiments under laboratory conditions. Furthermore, the produced SOA mass spectra were quite similar to those of ambient oxygenated OA factors found in urban areas during winter periods.

Nitrate radicals were observed only in the perturbed chamber and only after the ozone injection. Their levels reached up to 25 ppt. Along with the low levels of hydroxyl radical in the perturbed chamber, indicates that reaction with nitrate radicals and ozone were responsible for the SOA formation and the change in the OA composition.

Author Contribution: S.D.J., K.F., C.K., J.K.K. and C.V. conducted the experiments, collected and analyzed the data. S.N.P and A.N. conceived and directed the study. M.C., A.F. and B.P.-V. provided the IBB-CEAS. S.D.J. and S.N.P. wrote the manuscript with inputs from all co-authors.

Data availability: Data related to this article are available upon request to the corresponding author. The data will be available in the EUROCHAMP-2020 website.

Competing interests: The authors declare that they have no conflict of interest.

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References


Table 1: Initial conditions for the dual chamber experiments.

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<th>Exp.</th>
<th>Start Time (LT)</th>
<th>RH (%)</th>
<th>Temperature (°C)</th>
<th>BC (μg m⁻³)</th>
<th>OA (μg m⁻³)</th>
<th>O:C</th>
<th>NO (ppb)</th>
<th>NO₂ (ppb)</th>
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<td>31</td>
<td>23</td>
</tr>
</tbody>
</table>

*Blank experiments.
Figure 1: Particle wall-loss corrected aerosol mass concentration (CE=0.4) for the AMS-measured (a) organics, (b) sulfate, (c) nitrates, and (d) ammonium in both the perturbed (red line) and the control chamber (blue line) during Exp. 1.
Figure 2: Mass spectra of OA during Exp. 1 in the (a) perturbed chamber and (b) control chamber at the start of the experiment (after the filling process) and at the end of the experiment.
Figure 3: Oxygen to carbon ratio of the OA in the perturbed (red line) and the control chamber (blue line) during Exp. 1.
Figure 4: Mass concentration of the measured OA (black points), the initial OA (red points) and the produced SOA (blue points) in the perturbed chamber in Exp. 1. All concentrations refer to the suspended aerosol in the chamber and do not include the material deposited on the chamber walls.
**Figure 5:** Mass spectrum of the produced SOA in the perturbed chamber for Exp. 1 (blue bars) and the average spectrum of the produced SOA in all experiments (black squares).
Figure 6: Comparison of the produced SOA mass spectra in the perturbed chamber during Exp. 1 (blue bars) and the produced SOA estimated during the chamber experiments of nocturnal aging of biomass burning emissions (Kodros et al. 2020) (black circles).
Figure 7: Produced OA (red bars) and the estimated organic nitrate (blue bars) in the perturbed chamber for the eleven perturbation experiments. All values have been corrected for wall losses and the AMS collection efficiency.
Figure 8: Correlation between NO₃ radicals with the organic nitrate formed in the perturbed chamber.