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 emissions was used as the starting point of the aging experiments. Biomass burning organic aerosol (OA) was on average 70% of the total OA in the beginning of our 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 NO$_3$ 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. Organic nitrate represented approximately 10% of the mass of the secondary OA formed. The organic nitrate fraction to the total OA formed was on average 10%. 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; Jolleys 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 to the SOA formation during the chemical aging of biomass burning emissions (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 NO₃ (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 NO₃ 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 O₃ from the residual layer down to the nocturnal boundary layer can enhance the formation of NO₃ 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.

Usually smog chamber studies use fresh biomass burning emissions generated in the laboratory by a single source with many cases using clean air as a starting point of their experiments. The use of a dual chamber system with starting point ambient air rich in biomass burning emissions but also primary and secondary pollutants from other sources offers a bridge between the traditional laboratory studies and the ambient observations. Such a system offers the capability of aging realistic biomass burning emissions from multiple sources and fuels, diluted in the atmosphere and mixed with other pollutants (e.g., NOₓ from transportation). It therefore offers a bridge between laboratory experiments and ambient observations. 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 m\(^{3}\) 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 (Figure S1). The windows of the
labatory were kept open before and during the experiments, so the temperature of the dual
chamber system was in the range of 12-20°C range, while the outdoor temperature was on
average 5 degrees lower. The relative humidity (RH) in the chambers ranged from 35 to 45% 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 NO\(_x\) in the chamber formed NO\(_3\)
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: NO₃ radical (Orphal et al., 2003), NO₂ (Vandaele et al., 1998) and H₂O (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 black carbon (BC) levels. Using a series of gas monitors the concentration of nitrogen oxides (NO and NO₂) and ozone (O₃) 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. We did not use a dryer before the instruments and the RH of the samples was recorded. 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 v1.16I) 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 (θ) 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. The
theta angle is a useful metric for the comparison of OA mass spectra, similar to the often used $R^2$.
A $\theta$ theta-angle for the of two AMS spectra ranging from in the 0-5$^\circ$ range indicates an excellent
match between the compared spectra, which should be considered identical for all practical
purposes ($R^2$ ranging from 1 to ~0.99). For a $\theta$ angle of 6-10$^\circ$ there is a good match ($R^2$
approximately 0.98-0.96), but there are some small differences. A $\theta$ of 11-15$^\circ$ shows that the
spectra are quite similar, but they are not the same ($R^2$: 0.95-0.92), while for a $\theta$ in the 16-30$^\circ$ range
the spectra are coming from different sources, but there are some similarities ($R^2$: 0.91-0.73). A $\theta$
theta-angle higher than 30$^\circ$ suggests clearly different AMS spectra. We use the $\theta$ theta-angle in
this study due to its ability to better represent relatively smaller differences than the coefficient of
determination.

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. The ammonium sulfate seeds after the atomizer passed through
a diffusion dryer and then were injected in the chambers without passing through a neutralizer.
We did not use a neutralizer after the atomizer. 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 18:00-17:30-18:30 LT each evening
(approximately 30 min after the sunset which during the campaign was from 17:04 to 18:00 LT),
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
Our study has been designed so that the experiments would start when biomass burning was the major source of both organic aerosol and VOCs. In this section we first present in detail the results of one typical experiment (Exp. 1) and then we with more details before summarizing the results of the rest of the conducted experiments.

3.1 Results of a typical perturbation experiment

The average PM$_1$ concentration in the chambers during the filling process of Exp. 1 was approximately 50 $\mu$g m$^{-3}$. The concentration of OA during that period was 44 $\mu$g m$^{-3}$ with 2.4 $\mu$g 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 or COA (15%), oxygenated OA or OOA (10%) and hydrocarbon-like OA or HOA (5%). PMF was applied to the high resolution AMS organic mass spectra (m/z up to 300) at 3 min resolution from the month long field campaign. Using a 3 minute resolution PMF solutions with one to seven factors were investigated. The best solution included 4 factors corresponding to included one BBOA, factor an OOA, a COA and a HOA. The Figure S2 represents the time series of the four factors identified during the full field campaign are shown in Figure S2. The with detailed analysis of the field campaign, the determination of the PMF factors as well as particle and gas measurements will be included in a forthcoming publication.

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 $\mu$g m$^{-3}$ while the RH inside the both chambers was approximately 45%. 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 NO₃ (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 (Figure 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 high rate secondary OA production rate
of approximately 25 μg m⁻³ h⁻¹ is at least partially due to the result of the high ozone levels used in
these experiments to accelerate the corresponding chemistry and reduce the problems caused by
losses of both particles and vapors to the walls of the chamber. This roughly corresponds to an
initial OA formation rate of 25 μg m⁻³ h⁻¹. Although this formation rate is true under high ozone
levels, the absolute increase in the OA concentration result indicates 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 nitrate. 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 (a 90% increase of ammonium compared to its levels before the injection of
ozone) while in the control chamber its concentration remained within 8% of the initial value.
Most of this increase was due to the formation of ammonium nitrate. Approximately Almost 430%
of the total nitrate formed was inorganic nitrate, which requires approximately 1 μg m⁻³ of
ammonium to be neutralized. So the increase in ammonium is consistent with the increase in
inorganic assuming that ammonium nitrate was formed, suggesting that the increase in the
ammonium concentration is due to the formation of ammonium nitrate. The relative humidity (RH) during Exp. 1 inside the chambers was approximately 45%.

3.1-2 Organic aerosol spectra

Figure 2 represents the OA mass spectra in the two chambers at the start and end of Exp. 1. The comparison of 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 indicates that there was an increase in the fractional signal of m/z: 28 (CO⁺), 29 (CHO⁺), 30 (CH₂O⁺), 43 (C₂H₃O⁺), and 44 (CO₂⁺). The highest decrease was observed in 55 (C₄H₇⁺), 57 (C₄H₆⁺), 60 (C₂H₄O₂⁺), 69 (C₅H₉⁺), 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 remained practically the same constant during Exp. 1, with a value close to 0.4 increased slightly from 0.4 to 0.41 during the experiment (Fig. Figure 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 existing O₃ and any produced NO₃ in the control chamber, although the NO₃ would react away faster. 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 size-dependent particle rate loss rate constant measured at the end of each experiment, the concentration of the pre-existing OA as a function of time can be calculated. The pre-existing OA concentration in the perturbation chamber decreased from approximately 30 to 12 µg m⁻³ during Exp. 1 (Figure 4). Additional information about the particle
loss correction approach together with the size dependence of the particle loss rate constants for Exp. 1 (Figure S3)-4 can be found in the Check the SI for details on this correction approach along with the profile of the particle loss rate constants in Figure S3). The produced SOA that remains suspended in the chamber is then the difference between the total measured OA and the initial-pre-existing or “initial” OA (Figure 4). The maximum concentration of the produced SOA was 23 µg m⁻³, but it was gradually reduced to 15 µg m⁻³ due to the particle losses to the walls. With the concentrations of the pre-existing OA and the produced SOA both suspended in the chamber (these are the actual concentrations not corrected for wall losses) the AMS spectra that correspond to the sum of the two, the spectrum of the produced SOA can be estimated. Figure 4 and Figure 5 show the estimated produced OA and corresponding AMS mass spectrum in Exp. 1, respectively. Figure 4 is used to illustrate the concentrations of the OA components (primary and produced) during the corresponding experiment. Figure 5 shows the resulting spectra for the produced SOA both for Exp. 1 and the average SOA spectra for all the experiments. The similarity of the spectra supports our choice of Exp. 1 as representative of the rest. Figure 4 shows the estimated produced OA in Exp. 1 and Figure 5 the corresponding AMS spectrum.

Our estimation of the produced SOA levels is based on the mass balance approach of Jorga et al. (2020) and not on the yields and concentration reduction of the individual VOCs. Given the uncertainties in the concentrations and the yields of the various VOCs and IVOCs in this complexe system this is a more accurate estimate. We assume that the main process responsible for the reduction of the initial OA is loss of particles to the walls and that the loss of particle mass by evaporation and then loss of the vapors to the walls is negligible. The accuracy of this assumption can be confirmed by the change of the OA in the reference chamber (Figure 1a). The small change of the particle wall loss-corrected OA concentration (less than 7%) supports our assumption. If evaporation and vapor wall loss were important processes the corresponding concentration in the reference chamber would be decreasing significantly. —This is one of the advantages of our approach using ambient air. The evaporation of the bbOA after its emission has already taken place in the atmosphere. Therefore, the SOA production that we measure does account for the SVOCs that have moved to the gas-phase as the bbOA gets diluted in the atmosphere. The changes in the reference chamber illustrate well the changes that continue to happen in the system without our acceleration of the chemistry.
The produced OA mass spectra from the perturbed chamber were compared with the produced OA factor from the dark aging of biomass burning emissions in the laboratory (Kodros et al., 2020). Although the present study deals with ambient emissions from multiple biomass burning sources and fuels in a more-complex air mixture and varying conditions compared to 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 NO\textsubscript{2} and O\textsubscript{3} 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 \(\theta\) 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 (Figure 6). The comparison of our results with the work of Kodros et al. (2020) can also be viewed as an independent test of the validity of our assumption that most of the SOA formed in our experiments was indeed due to biomass burning. This previous study used only biomass burning emissions therefore there is no doubt that their results represent bbSOA. The good comparison of the produced SOA spectra in the two studies both strengthens our argument that we mainly observe bbSOA formation and also strengthens the argument of Kodros et al. (2020) that their laboratory results are a reasonable representation of realistic atmospheric processing of biomass burning emissions.

The produced OA was also compared with the ambient oxygenated organic aerosol (OOA) factor identified from the PMF analysis of the ambient data. The \(\theta\) 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 \(\theta\) 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). The contribution of biomass burning into the measured OA in the above field studies cities we compared ranged from 16\% (Fresno, California) up to 70\% (Patras and Athens, Greece) of the OA. The OOA as viewed by the PMF analysis of the AMS spectra has most of the time little information about its source. Therefore, this similarity
just strengthens our argument that the SOA produced in our experiments was rather realistic. We further compared the AMS spectrum of the SOA produced in this study with the spectra of the SOA produced during daytime oxidation of biomass burning emissions. There are notable differences in the two spectra, with theta angles approaching 30 degrees. This result is consistent with the findings of Kodros et al. (2020).

3.3 Results of other experiments

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. The injected ozone levels in the other experiments, excluding Exp. 1 ranged from 65 to 220 ppb. Figure 7 represents the produced OA (including organic nitrates) in all the perturbation experiments. In all experiments, the majority of secondary nitrate–aerosol nitrate was organonitrate, representing 55-85% of the total produced nitrate. Taking into account the organic nitrates, the initial SOA 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% (Table S3 summarizes the OA enhancement and the initial and final O:C in the perturbed chamber in the conducted experiments). At the same time, the O:C in the control chamber remained within 6% of the initial value. Table S3 summarizes the OA enhancement and the initial and final O:C in the perturbed chamber in the conducted experiments.

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 (Figure 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 thousands of fireplaces and heating stoves. Another possible explanation of the difference between the two studies works is the presence of non-biomass burning BB emissions in the urban ambient air that could contribute to the SOA formation.
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.

4.2.3.4 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. Given the sunlight in Greece even during the winter, these mentioned levels correspond to less than 10% of the daytime levels OH in the area during that wintertime period. Despite the relatively low OH in the perturbation chamber, its corresponding reactions with the various VOCs present do contribute to the observed chemical changes. Since the air we are using is a mixture of BB and non BB VOC
some organic vapors could possibly react with the OH radicals. The characteristic reaction times
with the OH of some of the VOCs present (toluene, xylenes, isoprene, monoterpenes and phenol)
that could contribute to SOA formation with OH at these levels for some of the VOCs (toluene,
xylenes, isoprene, monoterpenes and phenol) ranged from approximately 9 to 160 hours
suggesting that these reactions had a small contribution to the rapid SOA formation observed
during the first 30 min of a typical experiment (Figure 1). The corresponding OH concentrations
are practically negligible in the duration of a typical experiment (4.5 hours). The indirect
measurement of the OH levels in the chambers through the decay of d-butanol, showed that
through the experiment the OH levels were low and Instead in the control chamber the
corresponding OH concentrations were practically zero and below the detection levels of the d9-
butanol approach, since no additional ozone was added that could react with the organic vapors
and produce OH. Measurements of the OH levels were only possible when the PTR-MS was
available (Exps 9-11), but the results were pretty consistent. Some OH production is also expected
in the ambient atmosphere as the ozone mixes in the nighttime boundary layer from aloft, so these
reactions are also taking place, albeit slowly, in the ambient atmosphere too.

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 (Figure S4). 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.

4.3.3.5 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 (Table 1 Fig. Figure-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. We could identify not find a strong link between the small variations in the speciation of the initial VOCs and the SOA formed. This is probably due to the fact that we only quantified only a small fraction of the VOCs and IVOCs that serve as SOA precursors in the system.

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. This is due to the low NOₓ availability in the atmosphere during these experiments. These low NO₃ levels result in low NO₃ levels in the perturbed chamber and therefore together with the relatively low VOC levels, during the same days periods, lead to low SOA production. 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 NOₓ are affecting significantly the levels of SOA formed under these conditions. We estimated an R²=0.66 between the formed SOA and the levels of NO₃ in the perturbed chamber (Figure S5).

§ 4 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 NOₓ. The other chamber was used as a reference mainly as a safeguard against potential experimental artifacts. The novelty of this experimental approach is that it allowed the quantification of the nighttime chemical transformations of realistic biomass burning emissions from thousands of sources and multiple fuels after they had been diluted and mixed with ambient air, is that allows the further study of oxidation of realistic air. Our study has been designed so that the experiments took place
during periods in which biomass burning was responsible for 70% on average of the ambient OA and therefore the biomass burning emissions were the dominant source of VOCs and IVOCs. When biomass burning is the major source of both organic aerosol and VOCs.

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 organic nitrates, in some cases reaching up to 85% of the total aerosol nitrate. On average 10% of the total OA formed was organic 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. These results strongly suggest that significant secondary OA can be formed even during the nighttime of winter periods through the chemical processing of biomass burning emissions.

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, pointing towards the important role of biomass burning emissions in the OA formed in a winter urban environment. Furthermore, the produced SOA mass spectra were quite similar to those of ambient oxygenated OA factors found in urban areas during winter periods in which the fresh bbOA contributed 15-70% of the OA.

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 and steady levels of hydroxyl radical in the perturbed chamber along with the high characteristic reactions times of the measured VOCs with the OH compared to the duration of the experiments, 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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Table 1: Initial conditions for the dual chamber experiments.

| Exp. | Start Time (LT) | RH (%) | Temperature (°C) | BC (μg m⁻³) | OA (μg m⁻³) | % bbBB OA | O:C | NO (ppb) | NO₂ (ppb) | Total VOCs b (μg m⁻³) |
|------|----------------|--------|------------------|-------------|-------------|-----------|-----|---------|----------|----------------------|
| 1    | 17:45          | 45     | 17               | 2.4         | 44          | 70        | 0.4 | 17      | 24       | 150                  |
| 2    | 17:45          | 35     | 13               | 0.8         | 18          | 65        | 0.36| 4       | 22       | 50                   |
| 3    | 17:50          | 33     | 15               | 0.6         | 19          | 37        | 0.25| 3       | 20       | 38                   |
| 4    | 17:55          | 40     | 14               | 2.5         | 48          | 68        | 0.33| 90      | 20       | 160                  |
| 5    | 17:45          | 35     | 15               | 1.1         | 18          | 69        | 0.4 | 3       | 25       | 71                   |
| 6    | 17:50          | 40     | 17               | 2.6         | 50          | 72        | 0.36| 32      | 25       | 160                  |
| 7    | 18:00          | 45     | 20               | 1.0         | 16          | 78        | 0.36| 15      | 20       | 63                   |
|    | Time   | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | Value 7 | Value 8 | Value 9 | Value 10 |
|----|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|-----------|
| 8  | 17:55  | 42      | 22      | 1.2     | 22      | 77      | 0.45    | 22      | 22      | 75      |           |
| 9  | 18:15  | 40      | 19      | 0.7     | 16      | 75      | 0.44    | 3       | 14      | 46      |           |
| 10 | 18:15  | 45      | 21      | 1.6     | 25      | 50      | 0.33    | 32      | 21      | 100     |           |
| 11 | 18:30  | 45      | 24      | 0.6     | 6       | 48      | 0.41    | 1       | 5       | 38      |           |
| 12a| 18:00  | 32      | 21      | 2.1     | 6       | 65      | 0.37    | 3       | 15      | 131     |           |
| 13a| 18:20  | 30      | 19      | 3.0     | 33      | 67      | 0.35    | 31      | 23      | 188     |           |

a Blank experiment.
b Sum of the VOCs quantified by the PTR-MS.
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 NO$_3$ radicals with the organic nitrate formed in the perturbed chamber.