



Molecular-Level Characterization of Urban Aerosol Analogues in Controlled Atmospheric Simulations

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Abstract. Urban air pollution involves complex mixtures of gases and particulate matter whose molecular-level composition and gas-particle partitioning remain poorly characterized, limiting our understanding of secondary organic aerosol (SOA) formation. We address this gap using controlled atmospheric simulations combined with detailed molecular characterization. Two distinct urban atmospheric scenarios were simulated in the CESAM smog chamber: a standard urban (traffic emissions and biogenic precursors) and a biomass burning enhanced. Both scenarios were aged under controlled irradiation with NO_x to simulate tropospheric photochemistry.

PM₁ concentrations reached $15 \pm 7 \mu\text{g.m}^{-3}$ for the standard scenario and $63 \pm 24 \mu\text{g.m}^{-3}$ for the biomass burning scenario, with organic aerosol fractions of approximately 17 % and 40 %, respectively. Gas-phase analysis via proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) identified 23 volatile organic compounds (VOCs), dominated by oxygenated species (74-77 %). Particle-phase molecular analysis using ultrahigh-performance liquid chromatography electrospray ionization ion mobility quadrupole time-of-flight mass spectrometry (UPLC/ESI-IMS-QTOFMS) revealed 32 distinct compounds. The biomass burning scenario showed elevated source-specific tracers, including a levoglucosan isomer, nitrophenolic compounds (e.g., 3-methyl-4-nitrocatechol, 4-nitroguaiacol), and oxidized aromatics. Volatility distributions estimated via group contribution methods placed most compounds in the semi-volatile, low-volatility, and extremely low-volatility organic compound ranges ($C^* < 300 \mu\text{g m}^{-3}$), indicating substantial functionalization and partitioning.

These results demonstrate the capacity of simulation chambers to generate reproducible urban aerosol analogues with distinct source-specific molecular signatures and well-characterized volatility distributions. This detailed molecular speciation provides a robust basis for process-oriented model evaluation and opens perspectives for systematic investigations of SOA formation pathways under controlled urban photochemical conditions.



30 1 Introduction

Air pollution poses serious health risks worldwide, leading to millions of premature deaths each year (Slovic and Ribeiro, 2018). Without effective interventions, it is expected to become the major cause of early mortality by 2050 (Von Schneidmesser et al., 2015). Despite air quality measures by organizations like the World Health Organization (WHO), the rapid growth of cities and populations makes pollution issues in megacities even more challenging (Baudic et al., 2016; 35 Salameh et al., 2019). Pollution mitigation policies have been effective in reducing exposure to primary pollutants (SO₂, NO_x). However, they remain insufficient in reducing pollution due to secondary pollutants such as ozone and secondary aerosol. This highlights the need for deep understanding of complex atmospheric chemical processes.

Understanding urban air pollution complexity requires a detailed knowledge of the composition of particulate matter, especially at the molecular level. The molecular composition of PM₁ particles could play key roles in toxicological responses, 40 but these aspects remain poorly understood.

A major obstacle in atmospheric research is the instability and variability of ambient conditions. Variations in weather conditions, different emission patterns, and transport phenomena lead to constant fluctuations that complicate molecular characterization and limit the consistency of exposure studies (Finlayson-Pitts and Pitts, Jr., 2000; Seinfeld and Pandis, 2012). Traditional field studies capture real-world complexity but struggle to control temporal variations or isolate specific emission 45 sources. These uncontrolled factors make difficult the determination of clear connections between specific pollutant mixtures and health effects. Moreover, the long sampling periods needed for thorough molecular analysis are often incompatible with the rapid changes happening in the atmosphere. Atmospheric simulation chambers offer a complementary approach. By keeping reproducible conditions, these systems allow researchers isolate specific emission sources and conduct detailed chemical analyses that would be difficult in real-world studies. The stability of these chambers is especially beneficial for 50 molecular characterization techniques and for toxicological studies that require well-defined exposure scenarios.

Atmospheric simulation studies (e.g., (Hildebrandt Ruiz et al., 2015; Ng et al., 2007; Presto et al., 2009) have mainly focused on overall aerosol composition measurements or limited compound classes. However, few studies have combined controlled atmospheric simulation with detailed molecular characterization specifically designed for biological exposure assessment. This represents a significant gap because comprehensive identification of organic compounds is essential for linking specific 55 molecular components to biological responses under reproducible exposure conditions. Additionally, many chamber studies have focused on high-pollution scenarios, but these terms lack standardized definitions in the literature. To properly contextualize exposure studies, urban air pollution should be categorized based on European regulatory frameworks and WHO guidelines into three main scenarios. Highly polluted atmospheres are characterized by chronically degraded air quality that frequently exceeds regulatory health protection thresholds. These conditions typically show annual average concentrations of 60 PM_{2.5} > 35 µg.m⁻³, PM₁₀ > 70 µg.m⁻³, and NO₂ > 60 µg.m⁻³, with pollution episodes occurring several weeks per year. Such conditions are representative of dense city centres without low-emission zones, major enclosed traffic corridors, or poorly ventilated industrial basins. Moderately polluted atmospheres exhibit recurrently altered air quality without systematic daily



exceedances, with information or alert thresholds crossed occasionally. Annual average indicators typically range between $\text{PM}_{2.5}$: 15-35 $\mu\text{g.m}^{-3}$, PM_{10} : 40-70 $\mu\text{g.m}^{-3}$, and NO_2 : 30-60 $\mu\text{g.m}^{-3}$, with pollution peaks occurring a few days per month, particularly during winter (particles) or summer (ozone). These conditions are characteristic of large cities with partial traffic restrictions or peri-urban areas influenced by traffic emissions and heating. Lightly polluted atmospheres maintain good to very good air quality throughout most of the year, remaining below WHO guideline values. Annual averages typically show $\text{PM}_{2.5} < 10 \mu\text{g.m}^{-3}$ (ideally $< 5 \mu\text{g.m}^{-3}$), $\text{PM}_{10} < 20 \mu\text{g.m}^{-3}$, and $\text{NO}_2 < 20 \mu\text{g.m}^{-3}$, with very rare pollution episodes. These conditions represent medium-sized cities with limited traffic, extensive vegetation, clean heating systems, and distance from major industrial corridors (Official Journal of the European Union, 2024; World Health Organization, 2021). While previous chamber studies focusing on highly polluted conditions offer valuable insights into extreme events, they do not accurately reflect the moderate pollution levels that large urban populations are chronically exposed to. There has only been a few studies that have associated smog chamber atmosphere generation with health effect assessments (Krug et al., 2018; McGee Hargrove et al., 2018; Vernocchi et al., 2025).

To address these gaps, this study aims to simulate two different atmospheric scenarios representative of major emission sources in moderately polluted cities, to investigate the related health effects in mice. The first scenario mimics typical urban conditions dominated by traffic emissions and biogenic sources, which represents baseline urban exposure. The second scenario includes emissions from biomass burning to account for residential heating during colder months.

This paper presents the first part of this work, focusing on the detailed chemical analysis of PM_1 and their molecular composition, which remain poorly understood in current atmospheric studies. This work includes thorough chemical characterization of both gas and aerosol phases, featuring molecular-level organic aerosol analysis using UPLC/ESI-IMS-QTOFMS. This work addresses a gap in the literature on atmospheric simulations and enables the identification of specific molecular markers, transformation products, and volatility distributions. A subsequent paper examines the respiratory impacts of these simulated atmospheres on murine models.

2 Materials and methods

2.1 Pollurisk platform

The PolluRisk platform was developed at the Interuniversity Laboratory of Atmospheric Systems (LISA UMR CNRS 7583) in collaboration with the Mondor Institute for Biomedical Research (IMRB UMR U955 INSERM) located in Créteil, France. The fundamental concept of the PolluRisk platform (Fig. 1) is to simulate urban atmospheric pollution scenarios in a controlled environment, allowing researchers to expose biological models (e.g., mice) and study the resulting health effects. This platform has been previously described in several studies (Belgacemi et al., 2023; Blayac et al., 2024; Coll et al., 2018; Georgopoulou et al., 2024; Guilloteau et al., 2022).

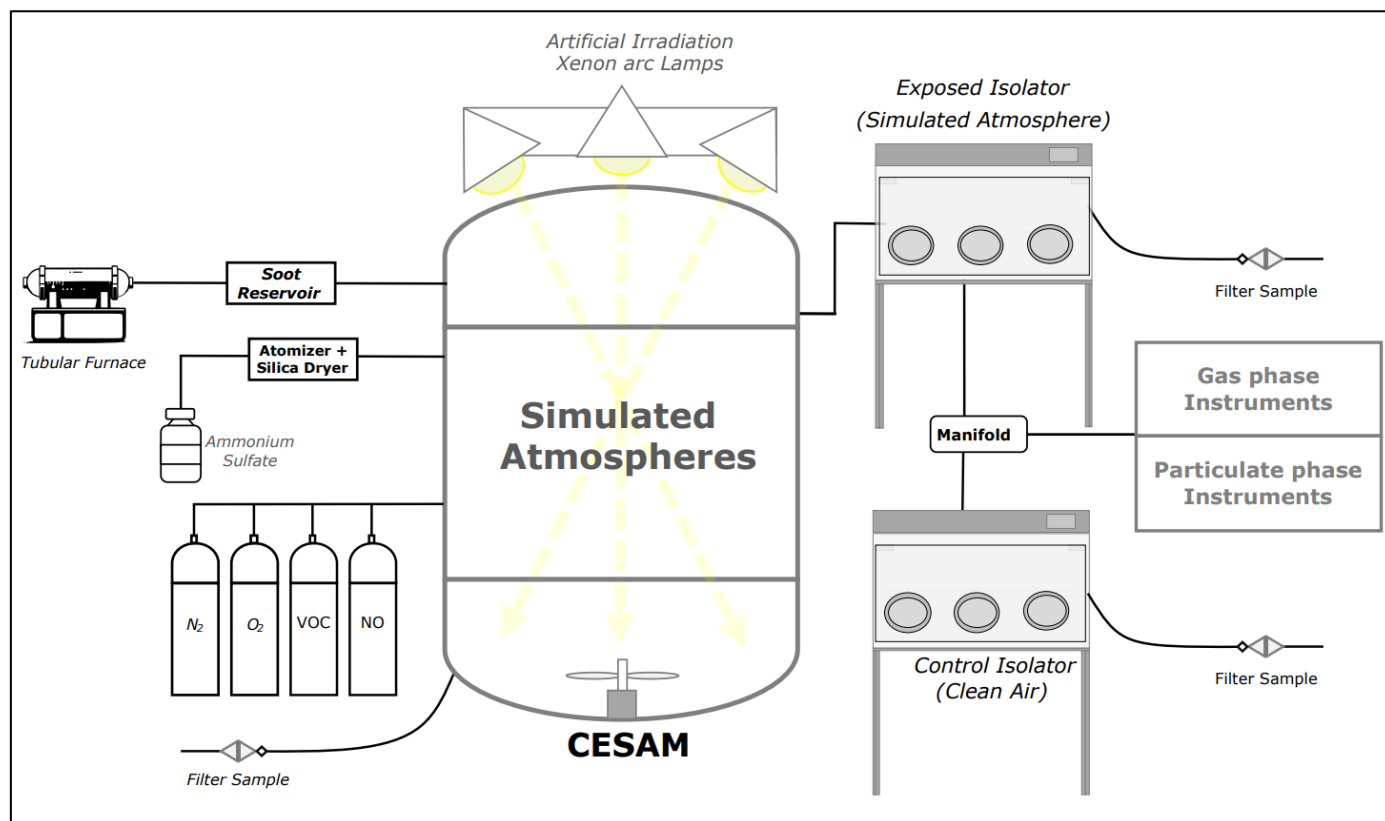


Figure 1: Schematic diagram of the PolluRisk experimental platform, illustrating the CESAM atmospheric simulation chamber equipped with a Xenon lamp irradiation system, two isolators for mice exposure (the exposure isolator receiving 90% filtered laboratory air using HEPA and activated carbon filters and 10% simulated air in CESAM, and the reference isolator receiving 100% of filtered room air), and the multi-instrument analytical set for pollutant characterization.

Central to the platform is the CESAM atmospheric simulation chamber (<http://cesam.cnrs.fr>), a 4.2 m³ stainless steel reactor designed to reproduce multiphasic oxidation processes. A detailed CESAM description is provided by (Wang et al., 2011). The chamber achieves controlled precursor concentrations, with mixing times of approximately one minute ensuring gaseous compound homogeneity. An artificial irradiation system powered by three 6.5 kW high-pressure Xenon arc lamps (IREM, EX170GM3) facilitates atmospheric photochemistry, achieving a JNO₂ value of 8.3×10⁻³ s⁻¹. Pyrex® filters reduce ultraviolet radiation intensity, especially below 300 nm, reproducing tropospheric solar radiation. The chamber maintains evacuable conditions (reaching 10⁻⁷ atm) with pumping systems capable of removing adsorbed compounds. Relative humidity (RH) was maintained at 30-50% to promote aerosol nucleation while avoiding water condensation interference with organic aerosol formation.

To study the induced health effects, the generated atmosphere is continuously transferred through a 3/8" copper line inside an isolator (I-Box+ Erlab, Noroit®), via an overpressure of 7 mbar applied in the smog chamber. This overpressure ensures continuous flow to the exposure isolator while preventing atmospheric contamination. The isolator houses experimental mice in individual cages (up to 19 cages) with controlled ventilation. The exposure isolator also receives filtered laboratory air



(HEPA- and activated carbon-filtered room air, removing particles $> 0.3 \mu\text{m}$ and gaseous compounds, respectively) with 90% filtered room air and 10% simulated smog atmospheres. This results in an atmosphere dilution ratio of 1:10 between CESAM
115 and the exposure isolator. In addition to the exposure isolator, another isolator receives only filtered laboratory air and serves to house the reference mice group. Using one-way valves, both isolators are connected to a manifold system. The latter is connected to analytical instruments for the analysis of gas and particulate pollutants. Measurements of particles and gases were performed via a manifold system alternating between the exposure isolator (4 hours) and the reference one (1 hour), across 7 consecutive days of experiment (days and nights). This paper presents the results of the measurements in the exposure isolator.
120 The resulting health impacts will be described in a subsequent paper.

2.2 Particulate and gaseous precursors

Following the PolluRisk platform methodology (Coll et al., 2018), we used a VOC mixture with concentrations determined by box modelling to achieve target urban pollution levels after photochemical processing in CESAM. Among the primary pollution sources affecting moderately polluted cities, road traffic represents a major VOC contributor. In Paris, for instance,
125 this source accounts for approximately 25% of annual VOC emissions, with toluene and m-xylene as major traffic-related aromatics, contributing for nearly 20% of this fraction, while long-chain alkanes (such as tridecane) result from diesel emissions (Gaimoz et al., 2011; Languille et al., 2020). Biogenic emissions such as α -pinene and isoprene can dominate during warmer periods, contributing up to 30% of oxygenated compounds (Ait-Helal et al., 2014; Baudic et al., 2016; Gaimoz et al., 2011). To replicate these urban environments, we selected representative anthropogenic VOCs including aromatic
130 hydrocarbons (toluene (P. Normapur®, PROLABO, puriss grade), m-xylene (Touzart & Matignon, 99% purity)) and an aliphatic hydrocarbon (tridecane (Sigma-Aldrich, CAS 629-50-5, 99% purity)), alongside biogenic VOCs (α -pinene (Sigma-Aldrich, CAS 80-56-8, $\geq 97.5\%$ purity), methylglyoxal (Sigma-Aldrich, CAS 78-98-8)) due to their atmospheric reactivity and SOA formation potential.

Ammonium sulphate particles (Sigma-Aldrich, CAS 7783-20-2, $\geq 99.9\%$ purity) were generated to simulate inorganic seed
135 aerosols and to allow the condensation of secondary organic products resulting from the oxidation of VOCs. For biomass burning simulation, commercially available pellets compliant with EN ISO 17225-2 standards (70% beech, 30% conifers, ash $< 0.6\%$, RH $< 8\%$) were used as the biomass source (0.5-1.0 g per combustion cycle).

2.3 Experimental simulation of atmospheric scenarios

This study simulated two atmospheric scenarios representative of moderately polluted urban environments for biological
140 exposure assessment. The target conditions were designed to reproduce PM_{10} concentrations ranging from background levels ($10\text{-}20 \mu\text{g.m}^{-3}$) to winter pollution episodes ($50\text{-}80 \mu\text{g.m}^{-3}$) recorded in the Paris region, with NO_2 levels typical of moderate urban traffic conditions (20-40 ppb) (AirParif, 2019; Petit et al., 2014; Von Der Weiden-Reinmüller et al., 2014). While the standard urban scenario falls within the moderately polluted range defined in the introduction, the biomass burning enhanced



scenario approaches the upper boundary between moderate and highly polluted conditions, representing winter pollution episodes affecting large urban populations.

To achieve these representative urban conditions, all particulate and gaseous precursors were continuously injected into the CESAM smog chamber, previously filled with synthetic air (nitrogen N₂ and oxygen O₂) in 80:20 proportions. Tanks of pressurized liquid nitrogen (Messer, ≥99.9% purity, H₂O content <5 ppm) and oxygen (Air Liquide, AlphagazTM Class 1, ≥99.9% purity) were used to generate the N₂ and O₂. A 10⁻² M ammonium sulphate solution was nebulized using a commercial atomizer (TSI Model 3075), followed by silica-gel dehumidification (TSI Model 3062). The biomass burning emissions were generated using a tubular furnace (CarboliteTM CTF Wire-Wound Tube Furnace) operated at 400°C under controlled airflow conditions (3 L.min⁻¹ synthetic air). Emissions were continuously transferred to an auxiliary chamber at 1 L.min⁻¹, then introduced into CESAM for atmospheric aging (Fig. 1). Combustion occurred twice daily while refilling the furnace every 10 to 12 hours, ensuring steady carbonaceous particle supply. A homemade VOC mixture (methylglyoxal (13 ppm), toluene (25 ppm), m-xylene (22 ppm), tridecane (33 ppm), and α-pinene (8 ppm)) was continuously injected into the smog chamber at a constant flowrate of 0.05 L.min⁻¹ following (Doussin et al., 2023) methodology for chamber protocols. After 20-30 hours, nitrogen monoxide (NO, Air Liquide, 99.5% purity) was introduced at 0.5 L.min⁻¹. Nitrogen monoxide was used to establish the NO-NO₂-O₃ photostationary cycle, promoting OH radical formation through NO₂ photolysis and enhancing VOC oxidation under high NO_x conditions representative of urban photochemical regimes. Irradiation began 11 hours before exposure initiation to reach a steady state and replicate tropospheric photochemistry. Irradiation was maintained continuously throughout the entire experimental period to ensure stable photochemical conditions.

This study simulated atmospheric scenarios characteristic of moderately polluted urban environments, focusing on two distinct scenarios representing different emission source contributions:

- (1) The standard urban scenario simulated baseline urban conditions dominated by traffic emissions and biogenic sources. This scenario used the VOC mixture (methylglyoxal, toluene, m-xylene, tridecane, α-pinene) with ammonium sulphate seed aerosols, representing typical urban atmospheric composition during moderate pollution episodes.
- (2) The biomass burning enhanced scenario included additional emissions from residential heating sources. In addition to the identical urban VOC mixture, biomass burning emissions were generated.

2.4 Analytical Instrumentation

A comprehensive analytical suite enabled detailed characterization of both gas-phase and aerosol-phase components, including concentration measurements, chemical composition analysis, and molecular-level identification.

2.4.1 Global investigation of particle and gas phases

Aerosol size distribution (19.5-881.7 nm) was measured using a scanning mobility particle sizer (SMPS) consisting of a differential mobility analyser (DMA, TSI 3080) and a condensation particle counter (CPC, TSI 3772) with 2-minute resolution.

Non-refractory submicron particle components (NR-PM₁, aerodynamic diameter between 40 nm and 1 μm) including



sulphates, nitrates, ammonium, organics, and chlorides were analysed using a time-of-flight aerosol chemical speciation monitor (TOF-ACSM, Aerodyne Research Inc.). This instrument operated with a 6-minute data acquisition and a collection efficiency (CE) of 0.5 for organics (Middlebrook et al., 2012). Particles were vaporized at 600°C and ionized by 70 eV electron impact before mass spectrometric separation and detection. Particle mass concentrations were calculated from measured particle number size distribution, assuming particles sphericity and a calculated density following (Salcedo et al., 2006). Nitrogen oxides (NO_x), ozone (O₃), and carbon monoxide (CO) were monitored using Horiba® APNA 370®, APOA 370®, and ProCeaS AP2e analysers. VOCs were measured using proton transfer reaction-time-of-flight-mass spectrometry (PTR-TOF-MS, Kore Technology LTD, Series II) at 1-minute resolution. The PTR-TOF-MS was operated using H₃O⁺ ions with a drift tube pressure of 1.3 mbar, temperature of 60 °C, and voltage of 400 V (E/N approximately 145 Td). Data were acquired in the *m/z* range from 20 to 130. Individual VOC concentrations were quantified following established quantification protocols by (De Gouw and Warneke, 2007) and reported by (Michoud et al., 2017). Systematic calibration was conducted before each experiment using gas calibration units (Ionicon®) containing VOC standards.

To complement overall aerosol composition measurements and achieve detailed molecular characterization of organic components, offline filter-based analytical techniques were used.

2.4.2 High-resolution investigation of particle phase at the molecular level

Secondary organic aerosols were characterized at the molecular level using ultrahigh performance liquid chromatography electrospray ionization coupled to ion mobility time of flight mass spectrometry (UPLC/ESI-IMS-QTOFMS, Waters), as described by (Pereira et al., 2026). Prior to analysis, filters were spiked with 5 µL of (1S)-(+)-camphor-10-sulfonic acid (Sigma Aldrich, 0.5 mg.L⁻¹) as internal standard. Filter extraction used acetonitrile (ULC/MS-CC/SFC grade, Biosolve) with room temperature shaking (Mini Shaker, VWR, 1000 rpm, 30 minutes), followed by 0.2 µm filtration (VWR Syringe Filter, hydrophobic PTFE) and nitrogen stream evaporation (N-Evap 12 positions, Organomation). Samples were redissolved in 200 µL of 50/50 acetonitrile/ultrapure water mixture and stored at -18°C until analysis. UPLC/ESI-IMS-QTOFMS analyses were performed using a Vion IMS-QTOF mass spectrometer (Waters) coupled to an Acquity UPLC system equipped with a BEH C18 column (1.7 µm, 2.1 × 100 mm). Analyses were performed in triplicate with 2 µL injection volume. Mobile phases consisted of ultrapure water (A) and acetonitrile (B), both acidified with 0.1% formic acid, with a 45-minute gradient at 0.4 mL.min⁻¹. The electrospray source was operated in negative ionization mode (desolvation temperature 250°C, *m/z* range 50-1000). Compound identification relied on two approaches: compounds matched against an existing database containing retention time, collision cross-section, and accurate mass for confirmed standards, and tentative identification based solely on accurate *m/z* matching for compounds without available standards.

To characterize volatility distribution, we applied the group contribution method developed by (Donahue et al., 2011). This approach estimates saturation mass concentrations (C*) (determined based on the web platform “UManSysProp”) from calculated vapor pressures at 298 K based on molecular structure and functional group contributions. Compounds were classified into volatility categories: volatile organic compounds (VOCs, C* > 3×10⁶ µg.m⁻³), intermediate-volatility



compounds (IVOC, $300 < C^* < 3 \times 10^6 \mu\text{g.m}^{-3}$), semi-volatile organic compounds (SVOCs, $0.3 < C^* < 300 \mu\text{g.m}^{-3}$), low-
volatility organic compounds (LVOCs, $3 \times 10^{-4} < C^* < 0.3 \mu\text{g.m}^{-3}$), and extremely low-volatility organic compounds (ELVOCs,
 $C^* < 3 \times 10^{-4} \mu\text{g.m}^{-3}$). This classification supports the assessment of gas-particle partitioning tendencies and secondary organic
aerosol formation potential for both injected precursors and detected transformation products (Donahue et al., 2006, 2011).

2.5 Summary of the experiment

The complete experimental workflow (Fig. 2) illustrates the five main methodological steps: (1) simulation setup with VOC
injection, seed aerosol generation, and optional biomass burning emissions; (2) atmospheric aging under controlled irradiation;
(3) controlled exposure in isolators with alternating sampling protocols; (4) extensive sampling and analysis using online
monitoring (PTR-TOF-MS, ACSM, SMPS), offline filter collection, and molecular characterization (UPLC/ESI-IMS-
QTOFMS); and (5) data processing yielding chemical composition profiles, molecular markers, volatility distributions, and
source-specific signatures for each exposure scenario.

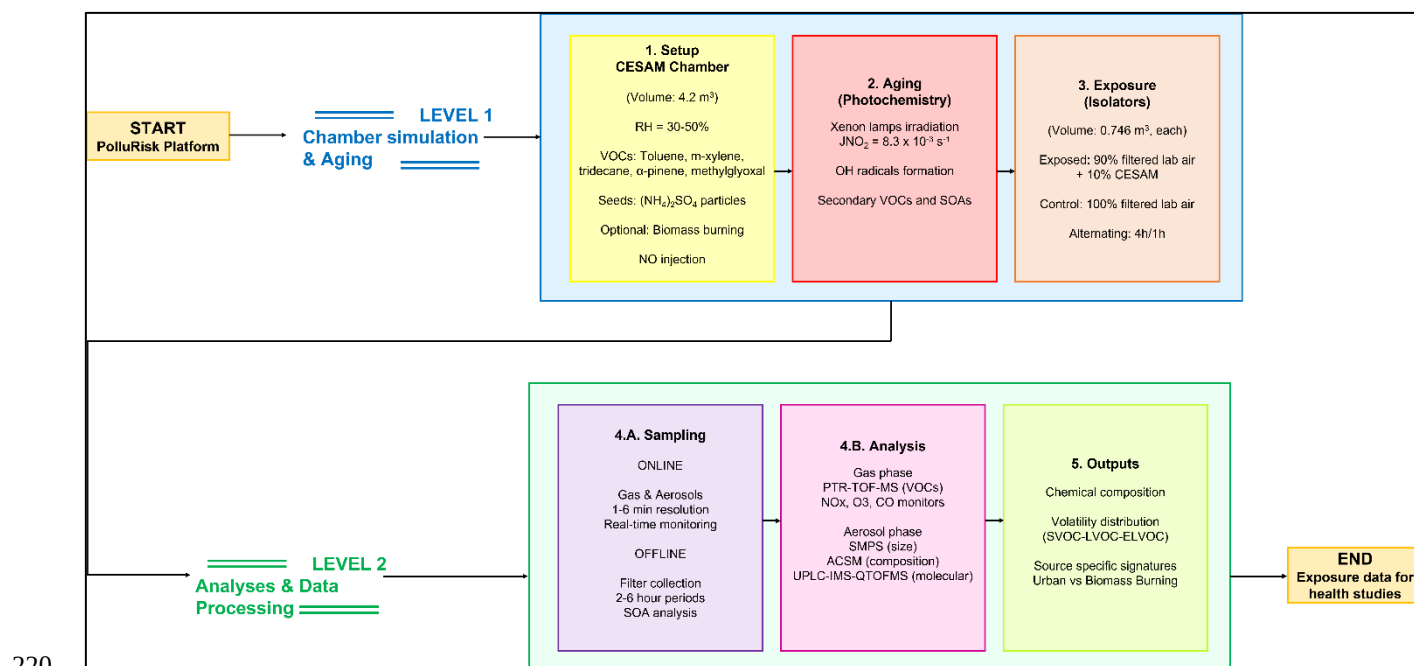


Figure 2: Complete experimental workflow. Two-sequence workflow: chamber simulation and aging processes, followed by analytical procedures and data processing. Colour coding: yellow = setup phase, red = photochemical aging, orange = exposure conditions, purple = sampling/analysis, green = final outputs. Flow direction: horizontal arrows indicate sequential progression, vertical arrow shows transition from chamber to analytical levels. END indicates completion of exposure protocol for health studies.

225 3 Results

The experimental design successfully maintained distinct atmospheric scenarios throughout the 7-day exposure periods in the exposure isolator (Fig. 3). Temporal profiles (exposure isolator) show characteristic variations reflecting controlled



photochemical processing and periodic biomass combustion cycles, while consistently maintaining scenario-specific concentration ranges. The biomass burning enhanced scenario exhibited elevated concentrations compared to the standard urban scenario across all measured parameters throughout the entire exposure duration.

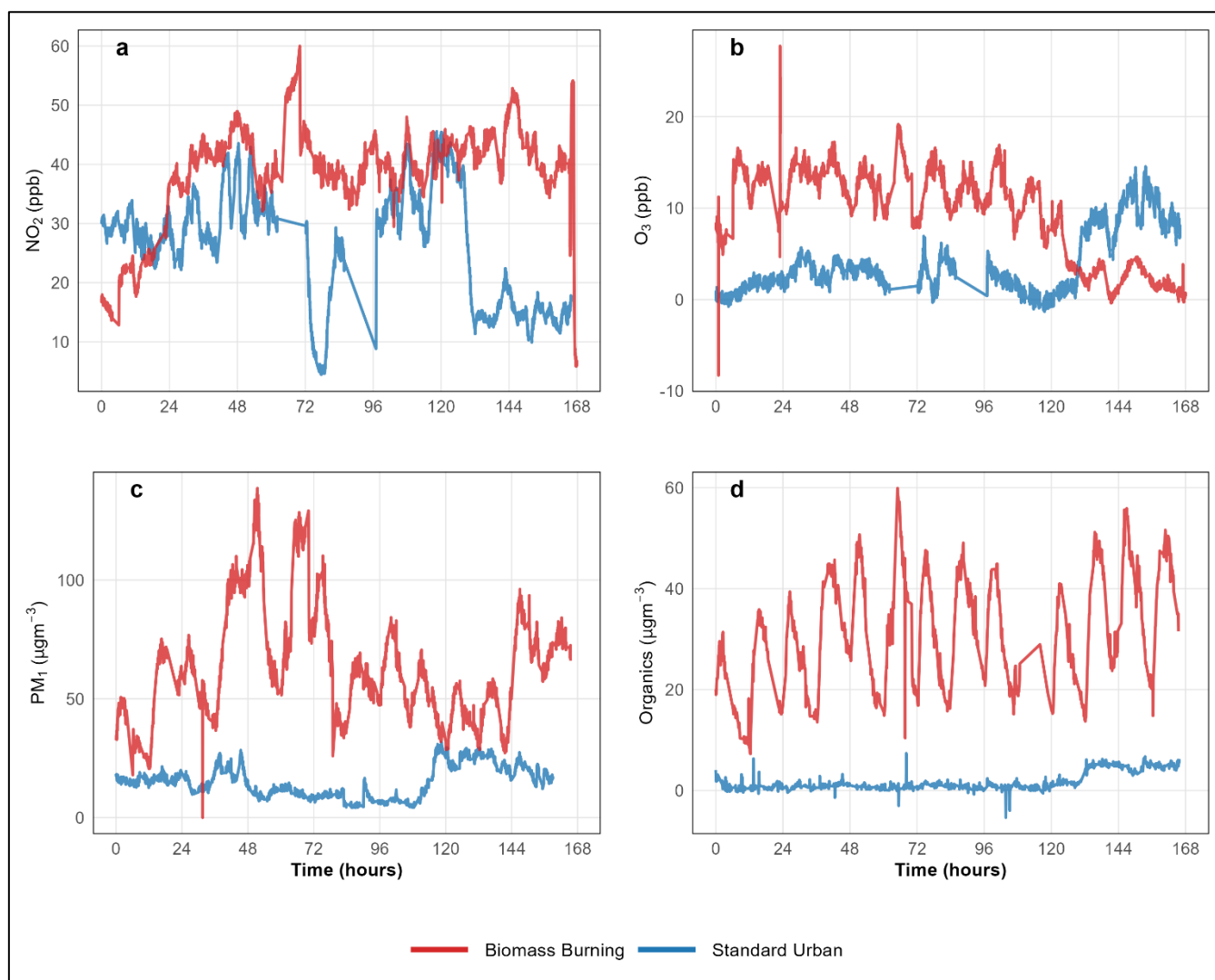


Figure 3: Temporal evolution of key pollutants during standard urban (blue) and biomass burning enhanced (red) exposure experiments: (a) NO₂, (b) O₃, (c) PM₁ concentrations, and (d) organic aerosol mass.

We characterized both scenarios in the exposure isolator through complementary analytical approaches, focusing on compositional differences. Hence, we based our analysis on two levels of investigation: PM and gas concentrations (Sect. 3.1), and the molecular composition of aerosols (Sect. 3.2). These analyses (exposure isolator) were then compared with regard to ambient air data and field studies results.



3.1 Global investigation of particle and gas phases

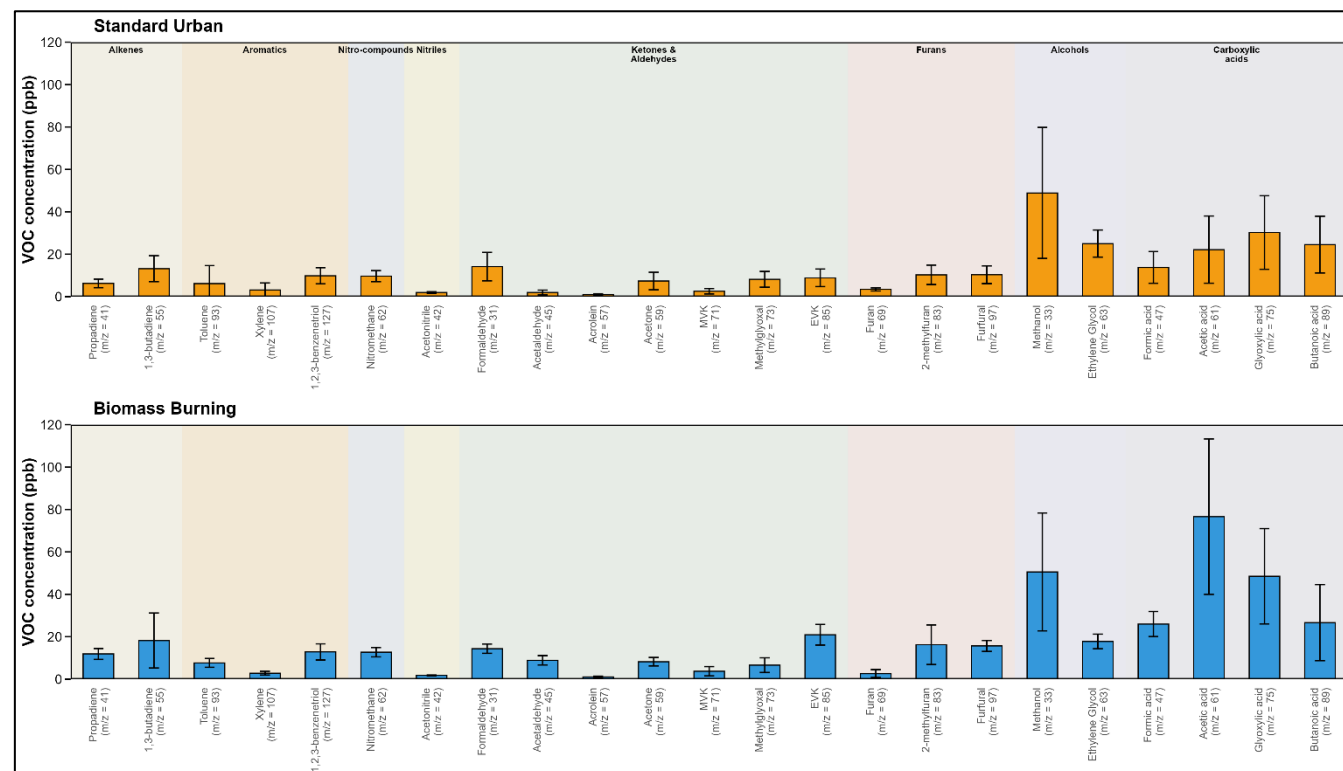
In the exposure isolator, PM₁ concentrations averaged $15 \pm 7 \mu\text{g.m}^{-3}$ for the standard urban scenario and $63 \pm 24 \mu\text{g.m}^{-3}$ for the biomass burning enhanced scenario. Non-refractory PM₁ chemical composition revealed distinct exposure profiles between scenarios (Table 1). Standard urban simulation showed sulphate dominance (approximately 42%), followed by ammonium (approximately 29%) and organics (approximately 17%). The biomass burning enhanced simulation showed that organics contributed approximately 40% of PM₁ mass, driven by carbonaceous particles and their atmospheric aging under controlled irradiation. Nitrates accounted for approximately 20%, reflecting secondary formation through NO₂ oxidation. The calculated aerosol densities were 1.6 g.cm^{-3} for the standard urban scenario and 1.48 g.cm^{-3} for the biomass burning-enhanced scenario.

Table 1: Non-refractory PM₁ chemical composition measured during standard urban and biomass burning enhanced atmospheric simulations. Values represent means $\pm$ standard deviations calculated from temporal variations throughout the 7-day exposure periods.

Scenario	SO ₄ ²⁻ ($\mu\text{g.m}^{-3}$)	NH ₄ ⁺ ($\mu\text{g.m}^{-3}$)	NO ₃ ⁻ ($\mu\text{g.m}^{-3}$)	Cl ⁻ ($\mu\text{g.m}^{-3}$)	Organics ($\mu\text{g.m}^{-3}$)
Standard urban	3.6 ± 2.3	2.5 ± 1.4	1.3 ± 1.4	< LOD	1.7 ± 1.8
Biomass burning enhanced	21.4 ± 11.2	13.8 ± 7.0	12.5 ± 5.6	< LOD	31.1 ± 11.3

Average NO₂ concentrations reached 27 ± 10 ppb for the standard urban scenario and 39 ± 4 ppb for the biomass burning enhanced scenario. Carbon monoxide concentrations increased from 171 ± 63 ppb (standard urban) to 472 ± 92 ppb (biomass burning enhanced). Ozone concentrations averaged 4 ± 3 ppb (standard urban) and 9 ± 5 ppb (biomass burning enhanced). PTR-TOF-MS allowed the identification and quantification of 23 distinct VOCs, including both primary emissions and secondary oxidation products. Complete compound list with *m/z* values, O:C ratios, volatility classifications, and calculated concentrations is provided in Table S1 (Supporting Information).

Figure 4 illustrates VOC classification by chemical families. Oxygenated compounds dominated both scenarios (74% standard urban, 77% biomass burning), with carboxylic acids predominant (31% standard, 42% biomass burning).



260 **Figure 4: Average concentrations of identified volatile organic compounds (VOCs) (including precursors toluene, xylene and methylglyoxal) in the exposure isolator measured by PTR-TOF-MS, organized by chemical families for standard urban scenario (orange bars) and biomass burning enhanced scenario (blue bars) (MVK: methyl-vinyl ketone, EVK: ethyl vinyl ketone).**

3.2 High-resolution investigation of particle phase at the molecular level

Building upon global composition measurements, molecular-level analysis reveals the specific organic compounds driving compositional differences between scenarios. After thorough peak selection and analysis using Waters UNIFI software, we identified 32 distinct organic compounds, offering detailed insights into secondary organic aerosol formation processes under stable conditions. Compound identification was classified into two confidence levels as reported by (Schymanski et al., 2014) level 1 when confirmed with authentic standards and level 2 when the identification is tentative based on accurate mass and fragmentation patterns. These compounds span multiple chemical families including nitrophenols, biogenic oxidation products, ring-opening products, anhydrosugars, and other oxidation products. Complete compound list with retention times, *m/z* values, O:C ratios, and volatility classifications is provided in Table S3 (Supporting Information).

Aromatic oxidation (toluene and m-xylene) produced both ring-retaining compounds including dihydroxyphenylacetic acid (DHOPA), 2-methyl-4-nitrophenol, 4-nitrophenol, dimethyl-nitrophenol and 3-methyl-6-nitrocatechol, as well as ring-opening products such as succinic acid and glycolic acid (GA), demonstrating multiple oxidation pathways for aromatic precursors under controlled conditions. We identified biogenic oxidation products including pinic acid, cis-pinonic acid, norpinonic acid, and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA).



We detected several compounds derived from biogenic and anthropogenic precursor oxidation in both scenarios, though we were able to achieve more comprehensive detection in biomass burning enhanced conditions due to higher organic aerosol concentrations. We confirmed compounds in both scenarios including 4,6-dinitro-o-cresol (from aromatic precursor oxidation under high NO_x), dimethyl-nitrophenol (from m-xylene oxidation), and cis-pinonic acid (from α-pinene ozonolysis and OH radical oxidation). The limited number of compounds detected in both scenarios likely reflects analytical detection limits rather than absence, as standard urban organic aerosol concentrations (1.7 µg.m⁻³) were substantially lower than biomass burning levels (31.1 µg.m⁻³). We also identified primary emission markers, including a levoglucosan isomer, using *m/z* matching without retention time confirmation, in biomass burning enhanced scenario.

Quantitative analysis was successfully achieved for five representative SOA markers (2-nitrophenol, cis-pinonic acid, MBTCA, norpinic acid, and pinic acid). To ensure the robustness of the results, all quantifications were normalized using camphor-10-sulfonic acid as an internal standard to compensate for matrix effects and potential losses during the extraction process. Atmospheric concentrations were calculated by reporting the mass identified on the filter to the specific surface area analysed and the total volume of air sampled. Sampled volumes ranged between 0.51 and 0.56 m³ for the CESAM chamber and 2.76 and 2.95 m³ for the exposure isolator. In the exposure isolator, these compounds reached concentrations ranging from 29 to 2374 ng/m³. Significant standard deviations were observed for some species, particularly in the isolator. These uncertainties primarily result from the temporal variability of the signals during the 7-day exposure periods and the proximity to analytical detection limits following the 1:10 dilution of the smog chamber atmosphere. Detailed information regarding the analytical methodology, internal standard normalization, calibration curves, and the calculation of atmospheric concentrations for these six markers is provided in Sect. S3 of the supporting information.

The volatility analysis (Fig. 5) revealed compound distributions predominantly within semi-volatile, low-volatility, and extremely low-volatility organic compound ranges (SVOCs, LVOCs, ELVOCs; *C** < 300 µg.m⁻³), indicating significant functionalization processes. Analysis of oxygen-to-carbon (O:C) ratios and estimated saturation mass concentrations (*C**) provides insights into atmospheric processing and gas-particle partitioning behaviour.

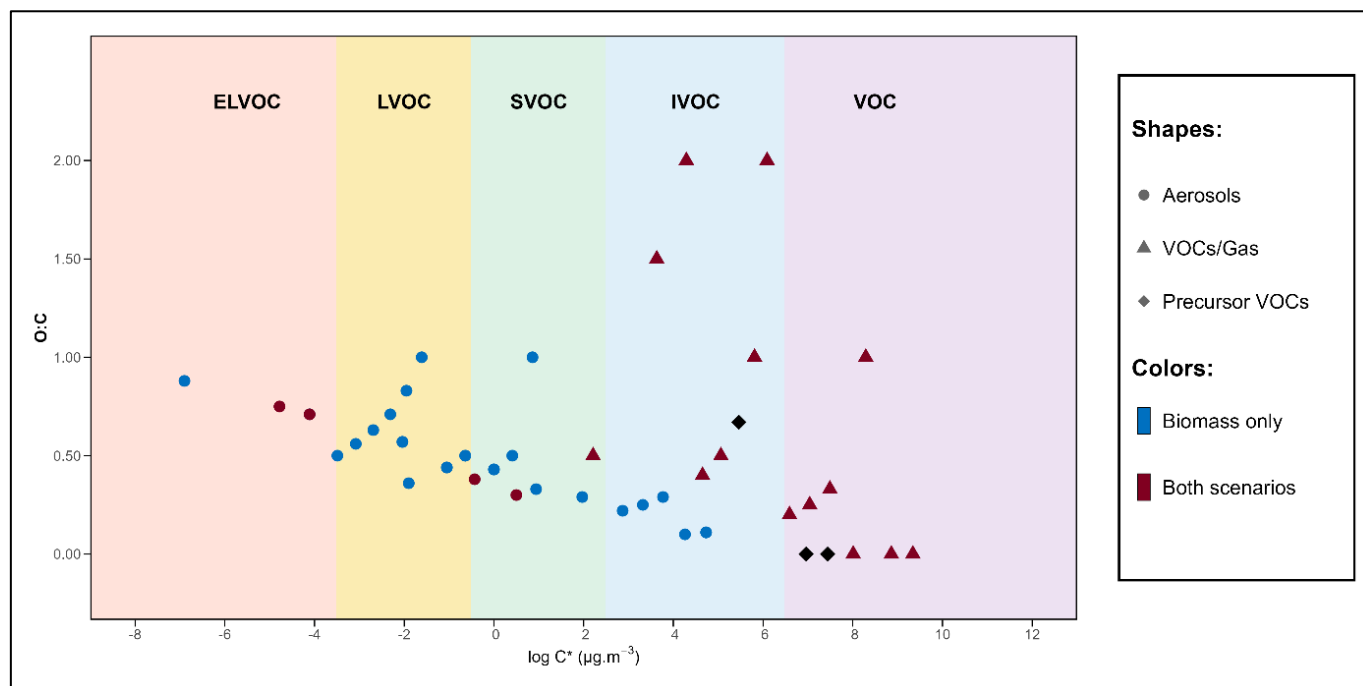


Figure 5: Molecular characterization of organic compounds identified in gas and aerosol phases, displayed as oxygen-to-carbon (O/C) ratios versus estimated volatilities (expressed as logarithm of saturation mass concentrations, C^*). Colour coding indicates compound volatilities, with blue symbols representing compounds detected in biomass burning enhanced scenario only and dark red symbols indicating compounds detected in both atmospheric scenarios. Diamond symbols (◆) indicate precursor VOCs initially injected into CESAM, circles (●) represent compounds detected by UPLC/ESI-IMS-QTOFMS, and triangles (▲) indicate compounds detected by PTR-TOF-MS.

The volatility distribution provides insights into atmospheric aging and gas-particle partitioning processes. The predominance of compounds in SVOC-LVOC-ELVOC ranges indicates substantial functionalization during photochemical aging. This volatility decrease drives partitioning from gas to particle phase, explaining the elevated organic aerosol fractions observed particularly in biomass burning scenarios.

4 Discussion and perspectives

4.1 Global investigation of particle and gas phases

The temporal variations observed throughout the 7-day exposure periods (Fig. 3) are characteristic of real urban environments, where pollutant concentrations naturally fluctuate due to emission cycles, photochemical processing, and meteorological influences. The ability to maintain distinct scenario-specific concentration ranges over extended periods demonstrates the robustness of the experimental protocol for chronic exposure studies.

PM₁ concentrations in standard urban and biomass burning enhanced scenarios are, respectively, similar to those of summer background (10-20 $\mu\text{g.m}^{-3}$) and winter pollution episodes (50-80 $\mu\text{g.m}^{-3}$) recorded in the Paris region (Petit et al., 2014; Von



Der Weiden-Reinmüller et al., 2014). Organic aerosol concentrations show contrasting patterns between scenarios: standard
320 urban levels ($1.7 \pm 1.8 \mu\text{g.m}^{-3}$) align with typical urban background measurements, while biomass burning enhanced
concentrations ($31.1 \pm 11.3 \mu\text{g.m}^{-3}$) represent wintertime pollution episodes characteristic of residential wood burning periods
in the Paris region (Languille et al., 2020; Petit et al., 2014; Von Der Weiden-Reinmüller et al., 2014)). However, VOC
concentrations in both scenarios exceed typical ambient levels observed in Paris, where individual aromatic compounds rarely
exceed 5-10 ppb (Gaimoz et al., 2011). The elevated VOC concentrations in our simulations (exceeding 20-50 ppb for several
325 compounds) were defined to ensure sufficient secondary aerosol formation within the experimental timeframe, while
maintaining realistic aerosol composition and mass concentrations for biological exposure studies. Though, NO_2
concentrations are also typical of urban levels observed in the Paris region. These fall within ranges reported for moderate
urban traffic conditions (20-40 ppb) and winter episodes (30-50 ppb), respectively (AirParif, 2019; Von Der Weiden-
Reinmüller et al., 2014). Quantitatively, the concentration of CO highlights the contribution of biomass combustion to exposure
330 profiles to urban pollution during winter (Baudic et al., 2016). O_3 concentrations in both cases were below WHO guidelines.
According to Sillman (1999), VOC-sensitive regimes are characterized by VOC/ NO_x ratios <4 , while NO_x -sensitive regimes
exhibit ratios >15 . In the urban photochemical regimes, high NO_x concentrations limit O_3 accumulation through ozone titration
reactions ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$), hence reproducing the chemical behaviour typical of urban centres where ozone levels are
suppressed despite high precursor concentrations (Seinfeld and Pandis, 2012).
335 Gas-phase characterization revealed scenario-specific VOCs. Biomass burning conditions had higher carboxylic acids (42%
vs. 31%) and combustion tracers (acetonitrile, furfural) contributions. The oxygenated compounds dominated both scenarios
(74% standard urban, 77% biomass burning), which is indicative of the photochemical transformations within CESAM. These
compounds are the products of distinct oxidation pathways: glyoxylic acid results primarily from toluene photooxidation under
high- NO_x conditions, while methylglyoxal originates from the oxidation of aromatics (toluene, xylene) and isoprene. Biomass
340 burning scenarios showed a notable increase in markers such as formic acid ($m/z = 47$), acetic acid ($m/z = 61$), ethyl vinyl
ketone (EVK, $m/z = 85$), and furfural ($m/z = 97$). For biogenic VOC transformations, the presence of MVK (methyl-vinyl
ketone) was also evident. The differences are in line with the source specificities shown by (Languille et al., 2020) in the Paris
region. The dominance of oxygenated compounds reflects photochemical aging of the precursor VOCs under controlled
conditions, consistent with atmospheric transformation studies (Li et al., 2019; Montero et al., 2001). The presence of glyoxylic
345 acid ($m/z = 75$), which has the highest ratio of oxygen-to-carbon ($\text{O:C}=1.5$), is indicative of highly oxidized products and has
been attributed to toluene photooxidation products (Jang and Kamens, 2001).
Aerosol analysis showed a significant difference in chemical composition, with an organic fraction of approximately 17% for
the standard urban scenario against 40% for the biomass burning scenario. The higher organic fraction highlights enhanced
carbonaceous particle emissions from biomass combustion alongside secondary organic aerosol arising from VOC oxidation.
350 The $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio shift from 0.36 to 0.58 reflects a secondary nitrate formation associated with biomass burning
emissions (Bressi et al., 2013; Crippa et al., 2013; Petit et al., 2014; Von Der Weiden-Reinmüller et al., 2014). The non-



refractory PM₁ composition indicates stability of the ammonium sulphate seed particles under the experimental conditions (RH ~40%), promoting nucleation processes involving sulfuric acid (Kulmala et al., 2013; Wollesen De Jonge et al., 2021).

4.2 High-resolution investigation of particle phase at the molecular level

355 Molecular-level characterization identified a total of 32 distinct organic compounds, with source-specific molecular markers such as a levoglucosan isomer (primary biomass burning tracer), nitrophenolic compounds (3-methyl-4-nitrocatechol, 4-nitroguaiacol) formed by oxidation of aromatic precursors, and biogenic oxidation products (pinic acid, norpinonic acid, MBTCA) of α -pinene. Volatility distribution analysis revealed compounds dominantly in the SVOC, LVOC, and ELVOC ranges ($C^* < 300 \mu\text{g.m}^{-3}$), indicating a significant contribution of functionalized and atmospherically aged compounds. The
360 presence of higher molecular weight compounds (up to m/z 220) suggested potential oligomerization mechanisms responsible for the low-volatility fraction. The highly oxidized product 5-nitrosalicylic acid (O:C ratio = 0.71) indicates ELVOC formation under stable conditions, thus demonstrating the ability of this platform to mimic complex atmospheric aging processes relevant for exposure characterization. These stable, controlled conditions allow for characterization of the aging process from highly volatile precursor molecules to low-volatility products. This process is practically impossible to trace in the ambient
365 atmosphere due to mixed source contributions and oxidation levels.

In both scenarios, SOA formation was the product of VOC oxidation and in the enhanced scenario, primary biomass burning emissions and their atmospheric processing had additional contributions. This dual formation pathway explains the enhanced organic mass fractions and distinct volatility distributions observed between scenarios. These oxidation processes demonstrate the capacity of the platform to reproduce specific atmospheric transformations under controlled conditions. The detection of
370 both ring-retaining and ring-opening products confirms the existence of multiple simultaneous oxidation mechanisms, providing molecular-level validation of urban atmospheric chemistry models.

These volatility distributions provide critical data for atmospheric model parameterization. Current secondary organic aerosol formation models are dependent on limited field observations wherein several sources interact continuously, hence isolating individual transformation processes becomes difficult. The molecular speciation and volatility distributions determined under
375 controlled conditions allow a systematic evaluation of atmospheric chemistry models and an improvement of mechanistic representations. Thus, source-specific transformation pathways known to be difficult to isolate in ambient measurements become available for evaluation through the use of atmospheric simulation chambers. This leads to stronger predictive capacities of regional air quality models.

Detection of primary emission markers (levoglucosan), and secondary products (pinic acid, norpinonic acid, MBTCA)
380 (Christoffersen et al., 1998; Jang, 1999; Mutzel et al., 2016; Yang et al., 2016), confirms the ability of the platform to reproduce direct emissions as well as atmospheric transformations (Ho et al., 2007; Kawamura and Kaplan, 1987; Yang et al., 2016). Nitrophenolic compounds, identified as abundant species in biomass burning aerosols (Lin et al., 2016), are specific molecular markers for residential heating emissions. They have not only been detected in biomass burning aerosols from biogenic sources but also in suburban and urban regions during wintertime, because of the widespread domestic wood burning for heating.



385 Detection of methyl-nitrocatechols and methyl-nitrophenols, as products of m-cresol photooxidation from wood combustion, provides molecular-level tracers for source apportionment in exposure studies. Several compounds that originated from biogenic and anthropogenic precursor oxidation were detected in both scenarios, although more comprehensive detections were achieved with the biomass burning enhanced conditions due to higher concentrations of organic aerosol. We identified compounds in both scenarios including 4,6-dinitro-o-cresol (a product of aromatic precursor oxidation under high NO_x),
390 dimethyl-nitrophenol (a product of m-xylene oxidation), and cis-pinonic acid (a product of α -pinene ozonolysis and OH radical oxidation).
(Hildebrandt Ruiz et al., 2015) emphasized the influence of photochemical aging on organic aerosols, highlighting the progressive oxidation of organic compounds which resulted to highly oxidized low-volatility aerosol species. Whereas, (Paciga et al., 2016) evaluated the dominance of organic nitrogen compounds in secondary organic aerosols, providing additional
395 insights into the distribution of semi-volatile, low-volatility, and extremely low-volatility organic aerosol compounds. The pyrolysis of lignin during biomass burning produces substituted phenols (i.e., alkylphenols, methoxyphenols), which undergo further oxidations with atmospheric radicals, primarily hydroxyl radicals (OH), or through NO₂ addition reactions, leading to the formation of nitrophenols (Haque et al., 2019; Simoneit et al., 1999; Yang et al., 2016). Beyond their utility as source tracers, these compounds have pro-oxidant and cytotoxic properties demonstrated in previous laboratory studies (Keith and
400 Telliard, 1979; Khan et al., 2022). This detailed chemical characterization facilitates mechanistic studies linking specific molecular components to biological responses under reproducible exposure conditions.

4.3 Limitations

Some aspects of the platform present limitations. Ozone concentrations did not exceed typical urban values due to rapid NO-O₃ reactions and chamber surface interactions. The molecular characterization was done based on on offline filter analysis,
405 without providing the temporal resolution of atmospheric transformation processes. Temporal exposure periods were limited to several hours, whereas health impacts research often evaluates chronic exposure scenarios. The molecular-level characterization, due to analytical constraints, successfully demonstrated the major transformation pathways, but did not reveal transient intermediates and radical chemistry products.

4.4 Perspectives

410 Nonetheless, promising developments can be achieved in the future. Ozone generation thus represents a priority to better reflect urban photochemical conditions. Extending the exposure durations while maintaining atmospheric stability presents technical challenges which will require systematic investigation. Mechanistic understanding would be enhanced through the integration of advanced analytical techniques. Chemical ionization mass spectrometry (CIMS) would allow real-time detection of highly reactive species, while derivatization methods would better capture reactive intermediates. Platform expansion should involve
415 a variety of scenarios, from low-polluted to high-polluted urban environments, enabling standardized exposure assessments across pollution levels. The inclusion of additional source-specific scenarios (e.g., industrial, agricultural, marine) would help



ensure full exposure characterization across different urban settings. Finally, the integration of real-time molecular analyses would offer a complementary temporal resolution for the transformation processes, linking controlled mechanistic laboratory studies with field observations.

420 **Conclusions**

This molecular-level characterization of urban aerosol analogues under controlled conditions offered detailed insights into source-specific chemical signatures. The identification of 32 distinct organic compounds, including nitrophenolic markers from biomass burning and oxidized aromatics from traffic emissions, contributes to understanding secondary organic aerosol formation under controlled conditions and gas-particle partitioning in urban environments.

425 This work presents atmospheric simulation chambers as complementary tools to field studies for urban air quality assessment. Thus, systematic investigation of emission source contributions under controlled atmospheric conditions facilitates the isolation of specific processes, which are otherwise difficult to conduct in complex ambient environments.

The capacity of the platform to generate reproducible atmospheric scenarios opens perspectives for toxicological investigations that may examine links between specific molecular components and biological responses. The potential to extend this approach
430 to cities with different levels of pollution will strengthen comparative studies across different urban contexts.

Data availability

All data presented in the study are included in the paper and Supplementary Materials. Raw mass spectrometry data (UPLC/ESI-IMS-QTOFMS and PTR-TOF-MS) are available at Zenodo: <https://doi.org/10.5281/zenodo.19546628> (Al Marj et al., 2026). Additional needs can be directed to the corresponding author.

435 **Author contributions**

EAM conducted the investigation and filter analysis, wrote the original draft, performed the data analysis and visualization. AD and JCMR reviewed the manuscript. AG provided the expertise on the filter analysis and reviewed the manuscript. MLT contributed to the filter analysis and data analysis. MC, EP, AB, CG, TB, and EM provided technical resources. BPV and JFD participated in the conceptualization and methodology of the study design. CB participated in the investigation. SL and PC are
440 the principal investigators of the study. All authors made contributions to this work and approved the final version of the manuscript.

Competing interests

The contact author has declared that none of the authors has any competing interests.



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