



Supplement of

Molecular-level characterization of urban aerosol analogues in controlled atmospheric simulations

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S1 Aerosols Density Estimation

Bulk aerosol density was determined from chemical composition data following the equation provided by (Salcedo et al., 2006):

$$\rho = \frac{[\text{SO}_4^{2-}] + [\text{NH}_4^+] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Organics}]}{\frac{[\text{SO}_4^{2-}] + [\text{NH}_4^+] + [\text{NO}_3^-]}{1.75} + \frac{[\text{Cl}^-]}{1.52} + \frac{[\text{Organics}]}{1.2}}$$

This approach gave aerosol densities of approximately 1.8 g.cm⁻³ for the standard urban scenario and 1.6 g.cm⁻³ for the biomass burning enhanced scenario. These values were used to convert the SMPS-derived volume distribution to mass and to compare it with the TOF-ACSM mass concentration.

S2 Quantification of VOCs Concentrations

The concentrations of the signals assigned to compounds from their *m/z* values in the PTR-TOF-MS data were calculated using the equation established by de Gouw and Warneke (2007) and Michoud et al. (2017).

$$[\text{X}] = \frac{i_{\text{X}_{\text{net}}}}{500 \cdot i_{\text{H}_3\text{O}^+} + 250 \cdot X_r \cdot i_{\text{H}_3\text{O}^+ (\text{H}_2\text{O})}} \times \frac{150\,000}{R_{f,X}}$$

Where:

[X] is the concentration of the detected mass (ppb).

$i_{\text{X}_{\text{net}}}$ is the net signal relative to the detected mass.

$i_{\text{H}_3\text{O}^+}$ and $i_{\text{H}_3\text{O}^+ (\text{H}_2\text{O})}$ are the relative signals at *m/z* = 21 and *m/z* = 39, respectively, to avoid detector saturation.

X_r is the sensitivity factor of the signal to relative humidity ($X_r = 0.5$). It is crucial to perform calibrations at different relative humidity values to determine the value of X_r . This ensures that the sensitivity X_r is independent of relative humidity.

$R_{f,X}$ is the response coefficient of the PTR-TOF-MS, experimentally determined for each compound.

S3 Supplementary Figures: SMPS Particle Size Distributions

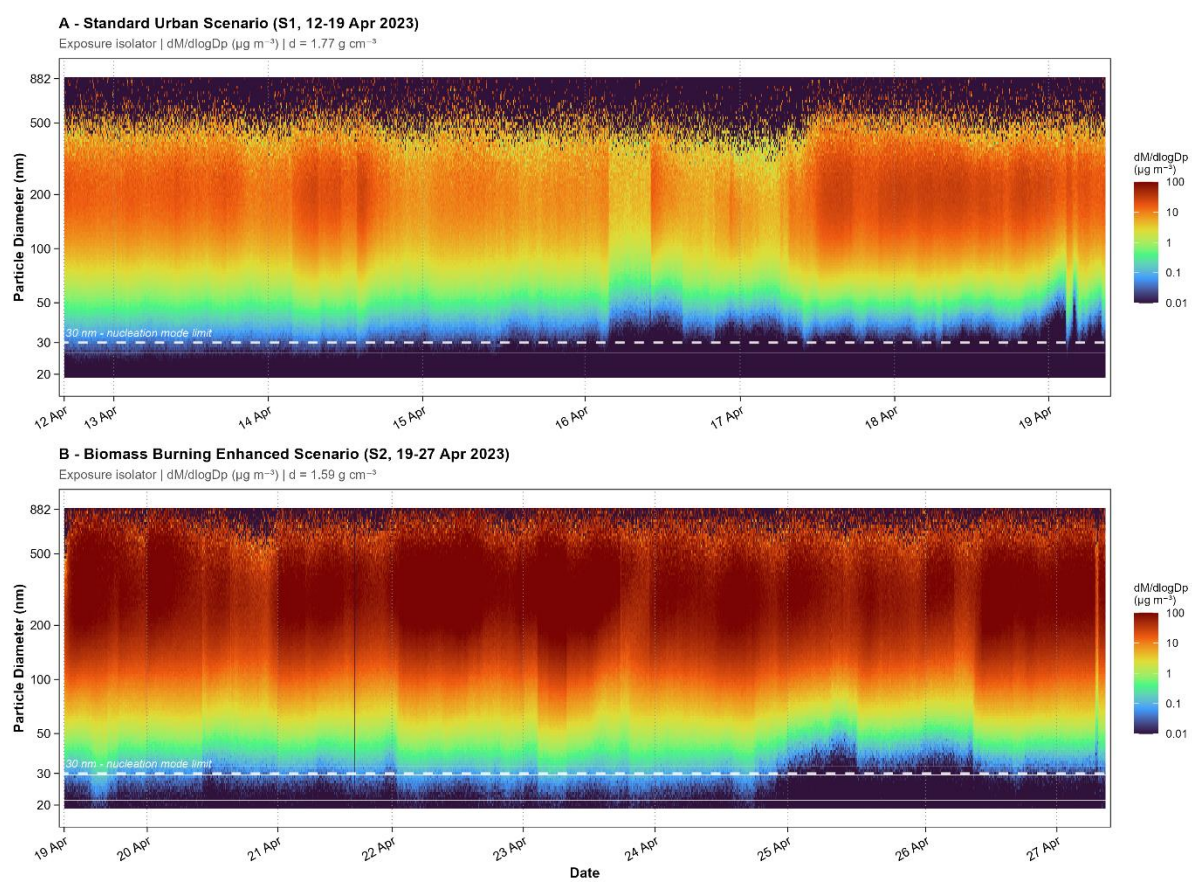


Figure S1a: SMPS particle size distribution time series in the exposure isolator, for both standard urban (A) and biomass burning enhanced (B) scenarios. The time axis shows only actual sampling timestamps (dotted lines mark day boundaries) and is not strictly linear. Colours are capped at $0.01\text{-}100 \mu\text{g m}^{-3}$. Values outside this range are shown at the nearest displayed colour. Zero readings mostly at the edges of the measured size range are shown at a fixed low value rather than left blank. No distinct nucleation mode ($<30 \text{ nm}$) is apparent in either scenario. The observed distributions are consistent with growth on pre-existing seed particles.

C - Mean Particle Size Distribution

Exposure isolator | mean $dM/d\log D_p \pm SD$ across full exposure period

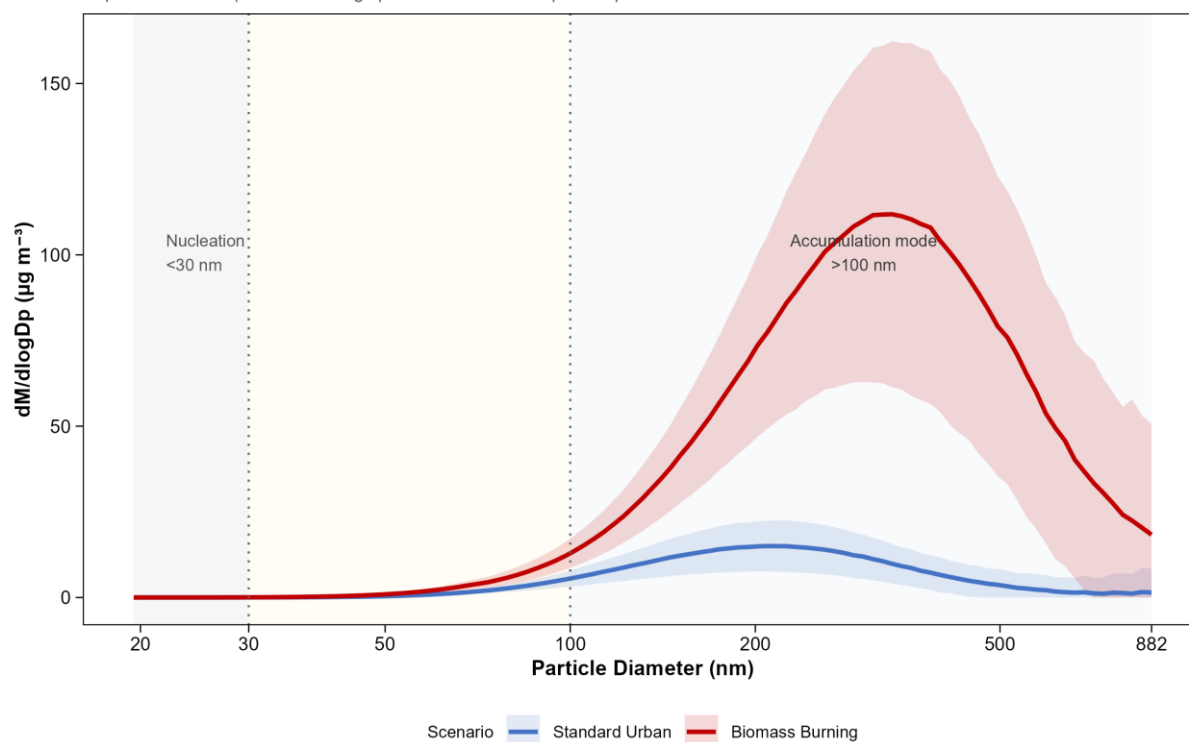


Figure S1b: Mean particle size distribution ($dM/d\log D_p \pm SD$) across the full exposure period for both scenarios. The modal diameters are 209 nm (standard urban) and 334 nm (biomass burning), both within the accumulation mode (>100 nm).

S4 Quantitative Analysis of Secondary Organic Aerosols (SOA)

S4.1 Internal Standard and Sample Preparation

To ensure robust quantification and account for potential analyte loss during extraction or matrix effects during ionization, an internal standard (IS) calibration method was used. All filter samples, blanks, and calibration standards were spiked with 5 μL of (1S)-(+)-camphor-10-sulfonic acid (1mg.L^{-1} in 50/50 acetonitrile/ultrapure water) prior to extraction. Filters were extracted in acetonitrile at room temperature under agitation (1000 rpm, 30 min), filtered at 0.2 μm , and evaporated under a nitrogen stream before being redissolved in 200 μL of a 50/50 acetonitrile/ultrapure water mixture (Pereira et al., 2026).

S4.2 Calibration and Linearity

Quantification was performed for five representative markers detected in both scenarios. Calibration curves were generated using a 5-point range (20 to 160 mg.L^{-1}), prepared by spiking pre-pyrolyzed quartz filters to replicate the sample matrix. All analyses were performed in triplicate.

Table S1: Calibration parameters for the quantified SOA markers.

Compound name	Regression equation	R^2
2-nitrophenol	$y=1.35\times10^{-4}x$	0.97
Cis-pinonic acid	$y=3.41\times10^{-5}x$	0.99
MBTCA	$y=3.14\times10^{-4}x$	0.94
Norpinic acid	$y=1.99\times10^{-4}x$	0.94
Pinic acid	$y=1.33\times10^{-4}x$	0.93

Note: x represents the mass in ng and y the ratio of compound/IS response area.

S4.3 Atmospheric Concentration Calculation

Atmospheric concentrations (ng.m^{-3}) were determined by dividing the mass quantified on the analysed filter portion by the corresponding volume of air sampled, corrected for the fraction of the total filter surface analysed (typically 1/3 or 1/2 of the filter). Average sampled volumes were $0.54 \pm 0.02 \text{ m}^3$ for CESAM and $2.85 \pm 0.10 \text{ m}^3$ for the exposure isolator. The concentration drop observed in the isolators is consistent with the 1:10 dilution ratio applied in the PolluRisk platform.

References

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