# Response to Reviewer 2

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

We thank Reviewer 2 for the positive evaluation and the constructive technical suggestions. We respond point by point below and indicate, for each point, the exact text presented in the revised manuscript, together with its location.

## Comment 2.1 - Extended Wall Effects (7 days)

> *"The chamber experiments lasted for 7 days. Over such an extended period, the inner walls of the chamber are highly susceptible to organic adsorption saturation, potentially forming a film. Consequently, could heterogeneous secondary reactions on wall-adsorbed species interfere with the SOA composition? The effect of vapor and particle wall losses on the measured particle concentration and SOA composition needs to be addressed."*

We thank the reviewer for raising this important point, which was also highlighted by the other reviewers. We have therefore consolidated our response in a dedicated new section.

The reviewer is right to point to the effects of walls on losses and heterogeneous reactions.

We have substantially expanded the discussion of wall effects in Section 4.3 (p.20) as follows: "**Wall effects are an inherent consideration in extended chamber experiments. Particle wall losses have not been specifically investigated during these experiments but were characterized in previous work: polydisperse ammonium sulfate particles (submicronic) and dusts (supermicronic) were injected into CESAM, and the number size distribution was measured as a function of time to derive first-order decay rates for each size bin. These experimental loss rates were well reproduced using the parametrization of Lai and Nazaroff (2000). The aerosol lifetime in CESAM was determined to range from 10 h to 4 days depending on particle size distribution, which is therefore quite long, although not negligible for experiments lasting several days as in this study. These losses would need to be considered when performing numerical simulations, which was not the case here.**

**The loss of semi-volatile species has also been investigated in previous studies and found to be highly dependent on the wall state (Suarez-Bertoa et al., 2012). A passivation of the walls was observed when repeating the same experiment over several days, leading to a decreasing wall loss rate for the semi-volatile compounds injected. The impact of heterogeneous reactions occurring on the walls on gas-phase composition has also been investigated in CESAM; for example, the reduction of NO2 into HONO has been observed, and identified heterogeneous wall reactions are described in an "auxiliary mechanism" (Wang et al., 2011).**

**Taken together, these considerations confirm that particles and semi-volatile compounds may be lost on the walls, affecting the composition of the mixture. However, this study does not aim to investigate detailed chemical processes but to generate mixtures representative of urban atmospheres. What matters here is the composition of the mixture actually reaching the exposure isolator. Considering that experiments length for several days, we expect that chamber walls progressively passivates, leading to an equilibrium between emissions, losses, and partitioning between gas-particles and walls.**

**This is supported by the stability of the dilution ratio between CESAM and the exposure isolator throughout both experimental periods, consistent with the nominal 1:10 design specification, as well as by the day-by-day stability of the aerosol size distribution (Fig. S1a-b, Supporting Information). Such heterogeneous wall reactions have not been observed to lead to new compounds affecting SOA composition.**"

The full discussion is now centralized in Section 4.3, which combines the wall effects analysis with other experimental stability considerations.

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## Comment 2.2 - PAHs and GC Analysis

*"The experimental system involves biomass burning processes which typically generate PAHs. GC is more suitable for the characterization of these compounds."*

We agree. The analytical choice of UPLC/ESI-IMS-QTOFMS was driven by the objective of characterising polar, oxygenated secondary organic compounds, which are not efficiently ionized by GC-compatible techniques. We have added an acknowledgement of this limitation to Section 4.3 (p.21): "**Finally, polycyclic aromatic hydrocarbons (PAHs), a recognized class of biomass burning emission products, could not be characterized with the current UPLC/ESI-IMS-QTOFMS setup, as electrospray ionization is poorly suited to these non-polar compounds.**"

We have also added to Section 4.4 (Perspectives, p.22): "**Gas chromatography-mass spectrometry (GC-MS) would complement the current approach for the characterization of PAHs.**"

We recognize that GC-MS would be the method of choice for PAHs, and we have acknowledged this as a clear limitation of the current study, while also identifying it as a priority for future methodological development.

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## Comment 2.3 - OOMs and CIMS

*"The photooxidation of alpha-pinene readily generates OOMs. Due to their poor thermal stability, CIMS for real-time monitoring should be considered."*

Our offline UPLC/QTOFMS approach was supported by the successful detection of stable alpha-pinene oxidation products (cis-pinonic acid, norpinonic acid, MBTCA), demonstrating that our sample preservation protocol (immediate freezing at -18°C) is effective for these compound classes.

We have added to Section 4.4 (p.22): "**Recent developments in nitrate-ion CIMS instrumentation (Alage et al., 2024) represent a promising potential option for future integration of real-time monitoring with this platform.**"

We acknowledge that CIMS would provide complementary time-resolved information, and we have added this perspective to the manuscript.

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## Comment 2.4 - Transition Metals and ICP-MS

*"Actual biomass burning emissions typically contain trace amounts of transition metals that can trigger Fenton-like reactions generating ROS. ICP-MS characterization would be advisable."*

We agree that metals, particularly iron and copper, can drive oxidative stress through Fenton-like mechanisms. Our experimental design uses defined chemical precursors rather than real-world emissions, intentionally isolating the organic chemistry; metal characterization represents a complementary research direction.

We have added to Section 4.4 (p.22): "**Elemental and metal characterization by ICP-MS or real-time instrumentation (an Xact instrument has since been used in more recent PolluRisk campaigns) would provide additional insight into the oxidative potential of biomass burning aerosols.**"

We have also noted that an Xact instrument has already been used in more recent PolluRisk campaigns, indicating that metal characterization is being progressively implemented within the platform.

We believe these responses and the manuscript additions address all of Reviewer 2's technical concerns.