

RC1:

The paper "Exploring biogenic secondary organic aerosol using a PTRMS-CHARON in laboratory experiments: characterization and fingerprint analysis" applies the PTRMS-CHARON instrument to investigate the chemical composition of SOA obtained from the oxidation of well-known biogenic reactive organic precursors i.e. isoprene, limonene and beta-caryophyllene. The study employed the DouAir atmospheric simulation chamber to simulate ambient aerosol formation. The CHARON data is also supported by additional gas- and particle-phase measurements. The paper is well-written and research discussion is appropriately supported with citations of relevant previous measurements. However, I felt the study is a bit lacking in casting a proper scope to justify the work. It can be considered for publication after the following concerns are resolved:

1. The scope of the study is not clear. The introduction section is quite large and the authors use only the last paragraph of the section to show that PTRMS-CHARON has been in existence for nearly 10 years already and used in ambient as well as chamber/lab measurements. Several studies are cited to support this. However, the nuances of its use in these studies are not properly laid out. It'd be good to provide some more detail on how was the CHARON instrument used in previous work that leaves open a gap for a systematic investigation of BVOC oxidation products. If the paper is about the application of PTRMS-CHARON, then it should somehow be the focus element of the introduction, especially since the oxidation of BVOCs in itself is not a new thought.

We thank the reviewer for this insightful comment regarding the scope and structure of the introduction. We agree that the initial focus was too heavily weighted towards general BVOC oxidation. We have restructured the introduction to better define the scope. Instead of a general overview of BVOC oxidation, we now focus more specifically on the application of the PTR-MS/CHARON. We have enhanced the references to highlight why a systematic investigation of BSOA formation pathways was necessary to fill the current knowledge gap.

"Globally, organic aerosol (OA) particles account for an average of ~50 % of the submicron particulate matter (PM₁), however, with values ranging from 10 to 90 %, depending on the nature of the site (forested, urbanized, etc.) and atmospheric conditions (de Gouw and Jimenez, 2009; Tsimpidi et al., 2025). PM largely affects radiative forcing, climate, air quality, and public health, and has therefore been the subject of intense research (Hallquist et al., 2009; Shrivastava et al., 2017; Nault et al., 2021; Pye et al., 2021). While primary sources contribute to this burden, a dominant fraction originates from the atmospheric oxidation of volatile organic compounds (VOC), with biogenic VOC (BVOC) being widely accepted as the most significant precursors globally (Yáñez-Serrano et al., 2020; Dada et al., 2023). The chemical complexity of biogenic secondary organic aerosol (BSOA) formation is high. Terpenoids such as monoterpenes and sesquiterpenes are key precursors in boreal environments due to their rapid reactivity (Hakola et al., 2012; Zhou

et al., 2017; Roldin et al., 2019). Conversely, in tropical regions like the Amazon, isoprene dominates emissions, where its oxidation pathways, varying drastically between low-NO and high-NO conditions, dictate the resulting aerosol composition (Martin et al., 2010; Leppla et al., 2025). Unraveling these distinct chemical pathways requires precise identification of the oxidation products, which serve as unique tracers for source apportionment.

Mass spectrometric techniques such as Aerosol Mass Spectrometers (AMS) have been extensively used in the scientific community to understand OA loadings and dynamics (Hu et al., 2015; Kristensen et al., 2017). However, the high fragmentation associated with electron impact ionization hinders molecular characterization and reduces the source/process identification capabilities. In recent years, new soft ionization techniques have been implemented in mass spectrometry techniques to reduce fragmentation, allowing the identification of low-volatility compounds at the molecular level, such as chemical ionization mass spectrometry (CI-MS) (Lopez-Hilfiker et al., 2014; Eichler et al., 2015). Molecular ionization is achieved by the transfer of an electron/proton/adduct of various reagent ions (e.g., Br^- , H_3O^+ , NH_4^+ , I^- , Huang et al., 2021). CI-MS equipped with a H_3O^+ source (Proton-Transfer-Reaction Mass Spectrometry, PTR-MS) has been the main tool for fast and precise quantification of small organic gaseous compounds for several decades (de Gouw and Warneke, 2007). More recently, the system has been coupled with thermo-desorption (TD) aerosol inlets, termed CHEMical Analysis of aeRosol ONline (CHARON-PTRMS, Eichler et al., 2015).

However, the application of CHARON to date has left specific gaps regarding BSOA. Previous field deployments have successfully quantified bulk OA or identified specific tracers in urban and biomass burning plumes (Müller et al., 2017; Piel et al., 2019; Song et al., 2024). Similarly, laboratory applications have largely focused on anthropogenic precursors like toluene (Lannuque et al., 2023) or vehicle emissions (Kostenidou et al., 2024). While isolated studies have touched upon biogenic precursors (Gkatzelis et al., 2018a, b), a comprehensive spectral library covering the major isoprene and terpene oxidation pathways is lacking.

To address this gap, we characterized the formation of SOA from the most relevant biogenic precursors in the new Teflon DouAir atmospheric chamber. We systematically investigated five distinct SOA formation pathways, namely monoterpene (limonene) and sesquiterpene (β -caryophyllene) ozonolysis, the isoprene-OH oxidation via the HO_2 route, favoring or suppressing the epoxidiol route (IEPOX-SOA and non-IEPOX-SOA) under low-NO conditions, and the isoprene-NO oxidation promoting the isoprene-NO-SOA in high polluted environments.”

2. Lines 104-115: No citation is provided for previous characterization tests of the DouAir chamber in section 2.1. Is this a new chamber? If so, it should be stated as such since this may introduce uncertainties in measurements. Is the chamber mixed mechanically? The schematic in figure 1 does not show the mixer.

The DouAir chamber is indeed a new facility described here in its first peer-reviewed publication, though preliminary characterization results have been presented at international conferences (e.g., Bouzidi et al., EGU 2021). We have updated Section 2.1 to explicitly state this status.

Line 81: *“The experiments were conducted in the new 9 m³ mobile DouAir Teflon chamber (Fig. 1), housed at IMT Nord Europe, Douai, France.”*

Regarding mixing, the chamber operates without a mechanical stirrer to minimize wall losses. However, characterization tests for both gaseous and liquid species (the latter injected via rapid vaporization in a heated injector) confirmed that homogeneity is reached in less than 4 minutes via airflow dynamics.

The following sentence has been added to the SI:

“The DouAir chamber operates without a mechanical stirrer to minimize wall losses. Characterization tests for both gaseous and liquid species (the latter injected via rapid vaporization in a heated injector) confirmed that homogeneity is reached in less than 4 minutes via airflow dynamics, as indicated in Figure S2.”

3. Line 123: The thermodesorption unit of the CHARON was operated at 140°C. How was this operating temperature set for your instrument and up to what volatility range is evaporated from the particle-phase at this setting?

The more recent Fusion-CHARON instrument from Ionicon Analytik operates at around 170°C to evaporate up to ELVOCs.

The temperature of 140°C was selected based on manufacturer recommendations for our specific model. Our own optimization tests confirmed that higher temperatures did not increase OA mass recovery but indicated potential increased fragmentation. Importantly, at the low operating pressure (~8 mbar), 140°C is considered sufficient to evaporate species down to 10⁻¹⁴ Pa (ELVOCs) (Peng et al., 2023), which is consistent with previous deployments in the literature (e.g., Leglise et al., 2019; Tan et al., 2018)

4. Line 144-145; 152-153: EF was determined as a ratio of the flows before and after the ADL. It is not clear what the term "flow" here means. Is it the particle count or the volumetric flow rate? In line 152, it is unclear what the authors mean by "PTRMS-CHARON measurements". The CHARON provides chemical speciation of the incoming aerosol sample. CPC on the other hand provides particle number/ mass count for monodispersed particles. The authors should specify

what CHARON measurement is being ratioed with the CPC data. Citations are provided in lines 145-146 but there should be a brief description to help the reader.

Yes, it is the volumetric flow rate. Theoretical EF can be calculated using the following equation:

$$EF = \frac{F_{DT}}{F_{ADL}}$$

Where, F_{DT} is the flow into the drift tube and the F_{ADL} is the flow before the aerodynamic lens.

The text was modified accordingly:

Line 125: “The theoretical EF is defined as the ratio of the volumetric sampling flow rate entering the Aerosol Dynamic Lens (ADL) to the volumetric flow rate entering the drift tube. However, to account for transmission efficiency and wall losses, the experimental size-dependent EF was determined by introducing a known number concentration of monodispersed particles, as described in Eichler et al. (2015) and Peng et al. (2023).”

Line132: “The monodisperse particles were sampled by a condensation particle counter (CPC; TSI 3750) and the PTRMS-CHARON. The mass concentration of size-selected particles measured by the CPC was determined assuming a shape factor of 0.8 and 1 for ammonium nitrate and levoglucosan, respectively. This mass concentration was subsequently converted into a Volume Mixing Ratio (VMR, in ppbv). Finally, the size-dependent EF was calculated as the ratio between the VMR measured by the PTRMS-CHARON and the equivalent VMR derived from the CPC data.”

5. I could not find information about the accuracy of mass calibrations in this study. It should be stated to ascertain confidence in peak identifications/molecular formulas.

We agree that stating the mass accuracy is essential for confidence in our peak identification. We have revised the manuscript to specify the internal calibration method. The following text has been added:

Line 113: “To ensure high mass accuracy and confidence in molecular formula identification, mass calibration was performed internally using four ubiquitous peaks spanning the measured mass range. These included the hydronium water isotope (H_3O^+ at m/z 21.022), the second water cluster (at m/z 55.039), and the diiodobenzene peaks ($C_6H_5IH^+$ at m/z 203.943 and $C_6H_4I_2H^+$ at m/z 330.848). This continuous internal calibration resulted in a mass accuracy of better than 5 ppm across the detection range”.

6. Line 242: A maximum of 5 ppb for a total injection of 60 ppb is interesting. The half life of SQT with ozone would be a few seconds following pseudo first order kinetics. In order to say that the loss is primarily due to high reactivity, the timescale of mixing of the precursor inside the chamber should also be stated.

We agree with the reviewer's analysis. The characteristic mixing time in the chamber is < 4 minutes (now stated in the text). Since the chemical lifetime of SQT with ozone is on the order of seconds, the reaction timescale is indeed significantly shorter than the mixing timescale. This rapid consumption - occurring faster than the chamber can become well-mixed - explains why the measured concentration never reaches the theoretical injected values. It is also important to clarify that the total amount introduced was not 60 ppb, but 70 ppb (this value was corrected based on the number of injections shown in Figure 2). The SQT was added in seven separate injections of ~10 ppb each to maintain low concentrations.

7. Figure 2: Since the paper is CHARON focused, the PTR-CHARON data in this figure should be made clearer visually. I also raise the following points:

We have revised Figure 2 to enhance the visual distinction of the PTR-CHARON data as requested.

(a) Why the OA exhibits two modes while the isoprene injection occurred only once. (b) Isoprene injection occurred twice but three modes appear in OA.

Response to (a) & (b): The stepwise increase (or "modes") in OA concentration is driven by oxidant availability rather than the precursor injection. In these experiments, OH radicals were generated via TME ozonolysis. Since the precursor (Isoprene) was already present in the chamber, SOA formation occurred in bursts triggered by each discrete injection of Ozone (added to maintain O₃ levels for TME reaction).

For (a): Two Ozone injections were performed, resulting in two distinct periods of rapid SOA formation.

For (b): Three Ozone injections were performed, resulting in the three observed steps. We have clarified this oxidant generation strategy in the revised manuscript.

The text has been revised to clarify the interpretation of these results.

Line 227: "It is important to mention the stepwise increases ("modes") in OA concentration during ISOP-IEPOX-SOA and ISOP-non-IEPOX-SOA reflect bursts of SOA formation driven by oxidant availability rather than the number of isoprene injections. Because OH radicals were generated through discrete O₃ injections for TME ozonolysis, each addition of O₃ triggered a new period of rapid SOA formation, producing the observed modes in the OA time series."

We also described the ozone injections used to maintain the concentration between 100 and 110 ppbv

Line 182: "To maintain ozone concentrations between 100–110 ppbv, additional ozone was injected as needed, and TME was injected every 5 minutes for approximately 4 hours."

(c) Three injections of monoterpene but a smooth enhancement in the OA signal.

The "smooth" appearance of the OA signal during the MT experiment, despite three distinct injections, is due to the timescale of mixing relative to the reaction kinetics. The injections occurred all within the first hour. The chamber mixing time (~4 minutes) acts to smooth out the instantaneous effect of each injection. Unlike the Isoprene experiment (where OH bursts caused sharp steps), the MT oxidation proceeded more steadily, resulting in a gradual cumulative increase in OA rather than sharp steps.

(d) SQT-SOA and the precursor SQT signal are positively correlated. Should the precursor not reduce over time as OA grows? Or am I not understanding this correctly.

The reviewer is correct that in a single-pulse decay experiment, precursor and product should be anti-correlated. However, in this experiment, SQT was introduced via sequential injections over time (up to minute ~350). Consequently, the total SQT burden in the chamber was increasing (positive slope in gas signal) while simultaneously reacting to form SOA (positive slope in OA signal). The expected decay of the precursor is indeed observed, but only after the injections stopped (after minute 400). The alternation between Gas and Particle measurement cycles in the instrument may also contribute to the visual fragmentation of this trend.

8. Is C₄H₈O a real peak or a fragment in figure 5c? Similarly for the C₅H₆O trace in the CHARON measurements in figure 4a. In AMS measurements, C₅H₆O is a fragment produced from electron ionization of parent species, which should be interpreted differently than a C₅H₆O trace signal in PTRMS-CHARON measurements. These compounds appear prominently in the CHARON mass spectra in figures 5a and c and therefore should be carefully discussed. I am not sure whether such oxidation products partition enough to the particle phase to appear so strongly in the aerosol spectra.

We agree with the reviewer that these signals likely arise from fragmentation or thermal decomposition within the instrument, rather than from parent compounds partitioning directly into the particle phase.

Regarding C₄H₈O: We attribute this signal to ionic fragmentation. As demonstrated by Gkatzelis et al. (2018) using separation techniques for parent and fragment ions in CHARON-PTR-ToF-MS, C₄H₈O in the particle phase is a characteristic fragment observed in Isoprene-NO experiments, distinct from its gas-phase isomer (MEK).

Regarding C₅H₆O: We interpret this signal (attributed to methylfuran) as a product of thermal decomposition occurring during the desorption process. As described by the reviewer, this mechanism is well-documented in AMS studies (e.g., Allan et al., 2014; Lin et al., 2012) and filter-based GC-MS analysis (Robinson et al., 2011), where it forms from the decomposition of IEPOX-SOA. However, a key finding in our study is that the CHARON inlet detected this ion in both the IEPOX-SOA and the non-IEPOX-SOA (both low-NO_x) experiments. This contrasts with AMS

results where it is strictly an IEPOX tracer. Consequently, we suggest that for CHARON measurements, C_5H_6O acts as a broader potential tracer for low- NO_x isoprene SOA, rather than being specific to the IEPOX pathway. We have added a cautionary note in the text regarding the robustness of this tracer.

9. Figure 3 caption should clearly note whether this is AMS data. Add units/ (e.g. # or fraction) to the y-axis label in figure 3 if there is one on the x-axis. The x-axis unit ‰ is a bit confusing. Is it a percentage?

Both axes are now expressed in percentages. For improved clarity now the figure caption now reads as:

“Figure 3: AMS scatter plot of f_{CO_2} vs. $f_{C_5H_6O}$ (expressed in percentage, %) for ISOP-SOA experiments conducted in the DouAir atmospheric chamber. The successful production of IEPOX-SOA was achieved by increasing relative humidity (from 20% to 50%) and using acidic seed particles. For comparison, data from literature laboratory experiments characterizing IEPOX uptake and isoprene oxidation pathways are also included.”

10. Figure 4: (b) "AMS/SMPS" can be confused as a ratio. A comma or "and" would be more appropriate.

It has been corrected.

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