



A versatile laminar-flow oxidation reactor for studying multi-day oxidation of atmospheric organics

Markus Leiminger¹, Tobias Reinecke¹, Martin Graus¹, Johannes Brecher¹, Tobias Fügenschuh¹, Daniel Gunsch¹, Gernot Hanel¹, Andreas Klinger¹, Nicholas Tovazzi¹, Markus Müller¹

¹IONICON Analytik GmbH., Innsbruck, 6020, Austria

Correspondence to: Markus Müller (markus.mueller@ionicon.com)

Abstract

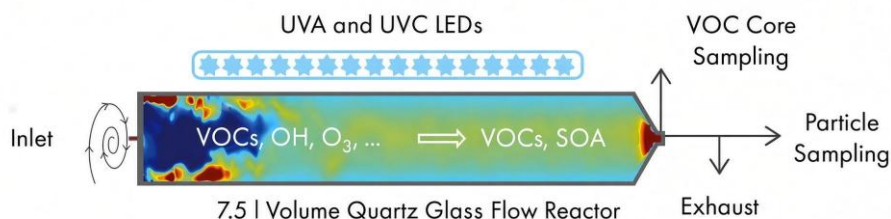
We present the fully automated IONICON Laminar-flow Oxidation reactor (ILOx), a versatile oxidation flow reactor designed for photochemical aging of atmospheric organics. ILOx enables the simulation of multi-day atmospheric oxidation processes within minutes under controlled conditions. The reactor consists of a 110 cm long quartz-glass tube with a usable internal volume of 7.5 l that is irradiated by arrays of UVA and UVC light-emitting diodes (LEDs). Oxidants and precursors are introduced through multiple customizable inlet ports. Computational fluid dynamics (CFD) optimized sample injection suppresses jet formation and quickly establishes near-laminar flow. The reactor outlet permits simultaneous sampling of particles and volatile organic compounds (VOCs). Particle transmission efficiency was verified with dried ammonium sulphate particles, showing only small changes in the size distribution before and after the reactor. VOC core-sampling minimizes wall interactions and potential artefact formation; all wetted surfaces are restricted to inert materials to ensure rapid response even for lower-volatility gas-phase organics.

Herein we characterize ILOx with three distinct oxidation modes: ozonolysis, OH induced oxidation via the photolysis of isopropyl nitrite (UVA 365 nm), and OH induced oxidation via the photolysis of O₃ (UVC 275 nm). The ozonolysis of limonene forms reasonable amounts of secondary organic aerosol (SOA) with 25% of SOA mass yield. NH₄⁺ soft adduct ionization mass spectra of this particulate phase show well distributed products ranging from monomer to trimer fractions. OH induced oxidation of o-xylene via the photolysis of isopropyl nitrite at 365 nm was studied in detail. Box model simulations reveal an OH exposure of 10¹¹ cm⁻³ s that is equivalent to approximately 30 h of ambient ageing. We also apply this oxidation scheme to ambient air and study the compounds reacted and formed by proton transfer reaction mass spectrometry in high chemical detail. Finally, with the OH induced oxidation via the photolysis of O₃ we evaluate the limonene SOA mass yield without seed for a series of initial concentrations (5 - 48 ppbV) and a large range of OH exposure (0.016 to 10.1 x 10¹¹ cm⁻³ s) and ozone levels (60 - 2500 ppbV); optimal SOA mass yields were found at an OH_{exp} of around 0.5 to 2 x 10¹¹ cm⁻³ s.

Based on the findings we discuss the advantages of LED irradiation, the decoupling of oxidants or precursor production and injection, and the effects of the applied materials on the condensation of reduced volatiles on chamber walls.



30 Graphical abstract



31

32 Short summary

33 We introduce the IONICON Laminar-flow Oxidation reactor (ILOx), a 7.5 l quartz-glass reactor for rapid photochemical aging
 34 of atmospheric organics. ILOx features CFD-optimized near-laminar flow, decoupled oxidant generation using narrow-band
 35 UVA/UVC LEDs and automated operation. Characterized via ozonolysis and OH-induced oxidation, ILOx demonstrates
 36 minimized wall interactions, reasonable SOA mass yields and robust simulation of multiple days of atmospheric aging.

37



1 Introduction

Photochemical oxidation of volatile and intermediate-volatility organic compounds is a central process in the troposphere. It governs the formation of secondary organic aerosol (SOA), tropospheric ozone and a wide range of oxygenated gas- and particle-phase products that influence air quality, human health and climate (Cohen et al., 2017; Hallquist et al., 2009; IPCC, 2023; Jimenez et al., 2009; Shrivastava et al., 2017). Quantification of oxidation rates, product distributions and secondary-aerosol yields is therefore essential for atmospheric models, emission inventories and policy-relevant assessments (Kanakidou et al., 2005; WHO global air quality guidelines, 2021). Because ambient air contains complex, rapidly changing mixtures of precursors, laboratory and field studies that can simulate multi-day oxidative aging under controlled yet atmospherically relevant conditions remain indispensable (Peng and Jimenez, 2020).

Oxidation flow reactors (OFRs) have become established tools for rapidly simulating several days of atmospheric oxidative aging in minutes. The Potential Aerosol Mass (PAM) OFR (Aerodyne Research Inc, USA) remains the most widely used and commercialized design (Kang et al., 2007; Lambe et al., 2011). Subsequent systems have refined fluid dynamics, reduced wall losses and expanded experimental flexibility, including the CPOT (Huang et al., 2017), PFA-OFR (Xu and Collins, 2021), RAAD-OFR (Wu et al., 2023), APPA (Xu et al., 2024) and AC-OFR (Xu et al., 2024). Recent reviews comprehensively compare these reactors and their applications to SOA studies (Ma et al., 2025).

Herein we introduce the IONICON laminar-flow oxidation reactor (ILOx). ILOx is a fully automated, vertically oriented quartz-glass flow reactor (110 cm length, 7.5 l volume) designed for rapid photochemical aging of atmospheric organics under near-laminar conditions. Sheath-air injection is CFD (computational fluid dynamics)-optimized to suppress jets, while multiple mass-flow controllers deliver oxidants and precursors. Complementary UVA and UVC LED arrays, together with an external 185 nm Pen-Ray source, enable generation of OH, O₃ and NO₃ radicals. All wetted surfaces are restricted to inert materials to minimise wall losses and memory effects. Dual over- and under-pressure modes allow pure-compound studies as well as continuous sampling of ambient air, with simultaneous gas- and particle-phase detection.

2 Instrumental

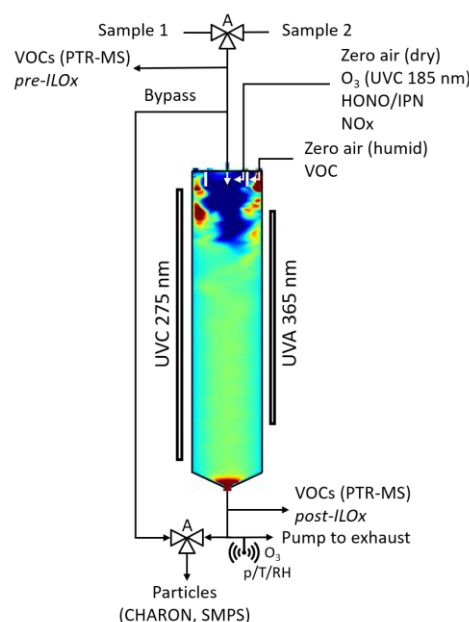
2.1 ILOx

ILOx is a versatile oxidation flow reactor designed for laboratory and ambient studies of atmospheric oxidation processes, including the photochemical aging of volatile organic compounds (VOCs) and the formation of secondary organic aerosol. It enables controlled generation of oxidants such as OH, O₃ and NO₃ under near-laminar flow conditions and is particularly suited to investigating the atmospheric oxidation potential of complex samples, including ambient air. A schematic of ILOx is shown in Figure 1.

The core of the reactor is a vertically oriented quartz-glass tube of 110 cm length and approximately 7.5 l internal volume. Near-laminar flow is established by injecting sheath air in a circular motion, which suppresses jet formation at the inlet and



promotes a well-defined flow regime. CFD simulations and experimental characterisation confirm the laminar character of the flow. All wetted surfaces are restricted to quartz glass, Teflon and passivated materials in order to minimise wall losses, memory effects and chemical artefacts, thereby ensuring rapid response and high purity of the experimental matrix. Sampling ports in front and after ILOx, labeled pre- and post-ILOx, respectively, are specifically designed to interface with proton-transfer-reaction mass spectrometry (PTR-MS) instruments.



74

Figure 1: Schematic of the ILOx laminar-flow oxidation reactor that includes 7 MFCs, two automated three-way valves, dedicated sampling ports for VOCs and particles, three UV light sources, a series of chip-based sensors and a 7.5 l quartz-glass reactor with CFD optimized in- and outlets. The colored patched area inside the reactor represents the vertical flow velocity derived from 3D-CFD simulations (blue indicates a low velocity, red a high velocity).

Photooxidation is driven by three complementary ultraviolet sources. An external Pen-Ray UVC lamp (185 nm, Analytik Jena US LLC, USA) generates O_3 from pure oxygen without direct contact with the sample gas; concentrations of up to 3 ppmV can be produced in a 1 l min^{-1} carrier gas flow and are adjusted manually. Arrays of UVC LEDs at 275 nm (maximum electrical power 40 W, software-dimmable) photolyse the generated O_3 to produce OH radicals inside the reactor. An array of UVA LEDs (365 nm, maximum electrical power 450 W, manually dimmable) enables photolysis of OH precursors such as nitrous acid (HONO) or isopropyl nitrite (IPN) and supports NO_x cycling. A brief overview on the supported reaction pathways can be found in the supplement.

The reactor is mounted vertically in a dedicated rack that is divided into a reactor compartment and a control compartment (Figure S1). Side panels permit ready access and fully shield dangerous UV irradiation. Cooling air is drawn from below, forced through the reactor compartment and exhausted at the top. Active fan cooling maintains near-ambient temperatures inside the reactor under typical irradiation conditions. A water bubbler humidifies the zero-air supply. Integrated I^2C sensors



continuously monitor temperature, pressure, relative humidity and ozone concentration at the reactor exhaust; a three-channel UV irradiance sensor is mounted on the UV reflector. These sensors support routine operation and monitoring; their absolute accuracy may depend on the sample matrix (for example, the ozone sensor responds to humidity and pressure changes). A software multiplier allows empirical correction, and cross-calibration against a research-grade ozone monitor is recommended. The ozone sensor's resolution is approximately 10 ppbV with a lower detection limit of 20 ppbV. Seven mass-flow controllers (MFCs) provide flexible delivery of carrier gases, oxidants and precursors. Dry zero air (up to 3 l min⁻¹) and humidified zero air (up to 3 l min⁻¹) are introduced through separated concentric circular injection cylinders. VOCs from standards or pressurised vessels (recommended 1 - 10 ppmV) can be injected at flows up to 20 ml min⁻¹ using the humidified zero air as carrier gas. Separate MFCs supply oxygen for external O₃ generation (up to 20 ml min⁻¹ of grade 5.0 O₂), HONO or IPN (up to 20 ml min⁻¹ from a pressurised vessel), and NO₂ (up to 20 ml min⁻¹ of ~10 ppmV in N₂). The latter, in combination with O₃, permits generation of NO₃ for simulation of night-time chemistry. To pull sample air through ILOx, a seventh MFC (up to 10 l min⁻¹) can be connected to an external pump; the practical upper limit of the total flow is set by the pressure drop of the inlet tubing and the acceptable over- or under-pressure inside the reactor. With the described MFC-setup, ILOx can be operated in two complementary modes: In over-pressure mode the carrier gas is actively pushed through the reactor; this configuration is optimal for pure-compound oxidation studies in zero air. In under-pressure mode, the MFC connected to the external pump at the exhaust draws the sample of interest through the reactor, enabling oxidation of ambient air or other sample matrices. Two servo valve controlled external sampling inlets allow for automatic switching between two sources, for example ambient air and zero air. Dedicated sampling ports are provided for connecting PTR-MS both upstream (pre-ILOx) and downstream (post-ILOx) of the reactor; sequential sampling is achieved via a multiport valve located inside of the heated inlet of the PTR-MS. An additional optimised port accommodates particle instrumentation (e.g. CHARON particle inlet for PTR-MS or scanning mobility particle sizer systems) with the option to bypass ILOx. ILOx is controlled via a dedicated software. The main visual interface (Fig. S2) displays set-points for all flows, lamp states, UVC-LED intensity, servo-valve positions and real-time sensor read-outs, with active flow paths highlighted. Sequences of set-points can be automated through the sequencer module of the data acquisition software (IoniTOF, IONICON Analytik GmbH, Austria). All commanded parameters and measured diagnostics are recorded in real-time within the IoniTOF HDF5 data file, ensuring complete experimental documentation.

2.2 Analytical instrumentation

Herein, ILOx is coupled to state-of-the-art analytical instrumentation for simultaneous characterization of gas- and particle-phase organics. Volatile organic compounds (VOCs) are measured with a FUSION PTR-TOF 10 (IONICON Analytik GmbH, Austria) that is further interfaced to a CHARON particle inlet for the direct analysis of non-refractory particle-condensed organics. Particle number size distributions and mass concentrations are recorded in parallel with a scanning mobility particle sizer (SMPS+C, Grimm Aerosol Technik GmbH, Germany). For the characterization of particle transmission, an ammonium



123 sulphate solution is nebulized with a 3D printed nebulizer (Rösch and Cziczko, 2020) operated at 2 l min^{-1} flow and dried by a
124 diffusion drier (Grimm Aerosol Technik GmbH, Germany).

125 The FUSION PTR-TOF 10 has been described in detail by (Reinecke et al., 2023). Briefly, it is a proton-transfer-reaction
126 time-of-flight mass spectrometer that employs ion-molecule reactions of H_3O^+ primary reagent ions with VOCs inside a radio-
127 frequency-enhanced chemical ionization reactor. The instrument achieves sensitivities of up to $80\,000\text{ cps ppbV}^{-1}$ and detection
128 limits below 100 ppqV (1 min integration), while retaining the established advantages of conventional PTR-MS systems - wide
129 linearity range, robust ion chemistry and predictable sensitivities spanning from non-polar hydrocarbons to highly oxygenated
130 molecules. Dissociative proton-transfer-reactions of H_3O^+ , most commonly resulting in the loss of a neutral water molecule,
131 can be mitigated by rapid switching (within seconds) to NH_4^+ reagent ions, which enable soft, nearly fragmentation-free adduct
132 ionization of oxygenated species (Müller et al., 2020; Piel et al., 2021; Xu et al., 2022). Ions are then detected by a time-of-
133 flight mass spectrometer offering a mass resolution greater than 10 000 (FWHM), sufficient to resolve and assign the majority
134 of atmospherically relevant chemical compositions.

135 When interfaced with the CHARON (CHemical Analysis of aeRosol ONline) inlet, the FUSION PTR-TOF 10 extends its
136 analytical range from gas-phase VOCs to particle-condensed organics (Eichler et al., 2015; Müller et al., 2017). CHARON
137 employs a multi-channel charcoal denuder that removes $> 99.999\%$ of gas-phase organics, followed by an aerodynamic lens
138 system that collimates particles for sub-sampling into a thermodesorber. The thermodesorber is operated at pressures $< 8\text{ mbar}$
139 and a moderate temperature of 150°C , sufficient to evaporate organics across the intermediate- to low-volatility range (and
140 fractions of the extremely low-volatility range). Particle enrichment is essentially constant for diameters between 100 and 2500
141 nm; transmission declines for particles smaller than 100 nm. The combined CHARON FUSION PTR-TOF 10 system has been
142 shown to quantify individual chemical compositions at 1 min time resolution down to approximately 20 pg m^{-3} (Reinecke et
143 al., 2024).

144 All FUSION PTR-TOF 10 data is processed with the IONICON Data Analyzer software suite (IDA v2.2.2.2) for peak
145 identification and quantification (Müller et al., 2013). Additional visualization and advanced analyses are performed with
146 custom MATLAB scripts (The MathWorks Inc., USA). For chemical simulations, the FOAM box model (Wolfe et al., 2016)
147 in version 4.4 is deployed utilizing the master chemical mechanism (MCM) in version 3.3.1 (Bloss et al., 2005; Jenkin et al.,
148 1997, 2003; Saunders et al., 2003). The geometries for optimal sample injection and extraction are optimized via 3D
149 computational fluid dynamics (CFD) simulations using OpenFOAM version 12 (OpenFOAM, The OpenFOAM Foundation).

150 3 Results

151 3.1 Characterization of flow-conditions and transmission efficiencies

152 Three-dimensional CFD simulations are performed to identify an inlet geometry that maximises initial mixing while rapidly
153 establishing optimal laminar-flow conditions. The selected design employs dual radial injection of buffer gas and oxidants (or
154 precursors) together with a diffuser-based injection of, for example, ambient sample air. Humidified air and VOCs are



introduced orthogonally to the main flow axis in an outer annular cylinder, while dry air, oxidants and precursors can be injected separately through an inner cylinder. The radial injection jets of the buffer gases rapidly homogenise to form two initial sheath-air layers (Fig. S3, top panel). Mixing of the two gas streams is essentially complete within the first ~ 25% of the reactor length (Fig. 1). The diffuser inlet for the ambient sample is positioned precisely in this mixing zone. The arrangement suppresses jet formation along the reactor centreline, provides spatial pre-separation of oxidants from the sample, and reduces wall losses of volatile and particulate material in the first few centimetres of the reactor. After approximately 30 - 40% of the reactor length the flow becomes fully laminar (Fig. 1 and Fig. S3, bottom panel). Sample is extracted from the quartz-glass tube through a conical outlet followed by core sampling of VOCs; this configuration minimises losses of low-volatility compounds while maximising particle transmission efficiency.

To verify the CFD predictions, a series of characterisation experiments was performed. A 10 s pulse of limonene is injected into the ILOx reactor while buffer gas flows continuously at 1, 2 or 4 l min⁻¹. The post-reactor response is monitored with a FUSION PTR-TOF 10. Figure 2a shows the resulting limonene time series. For all three flow rates a sharp rise is observed, with maximum signals reached at approximately 60% of the geometric residence time (reactor volume/flow rate). A slower decay follows. Despite the expected broadening of the pulse response with decreasing flow rate, the overall shape remains remarkably similar, confirming the wide operational flow range of the ILOx reactor.

Figure 2b presents the probability distribution function (PDF) of the residence time normalised to the geometric residence time for ILOx and compares it with gas-phase responses reported for several other OFRs. These OFRs employed CO₂, O₃ or SO₂ as tracers. An ideal laminar-flow PDF is included for reference. The AC-OFR exhibits the earliest initial response (O₃ tracer), indicative of a residual jet; its maximum, however, also occurs near 60% of the normalised residence time, similar to ILOx. The PAM-OFR shows a near-laminar response for CO₂, yet the maximum is reached below 30% of the normalised residence time, implying under-utilised volume near the walls; the mean residence time corresponds to only 69% of the geometric value. In contrast, ILOx yields a mean residence time for limonene of 92% of the geometric value. RAAD-OFR (CO₂) and CPOT (O₃) produce similar PDFs; CPOT reaches its maximum at 80% of the geometric residence time and has a mean residence time of 96%. For the PFA-OFR the maximum appears at 90% (SO₂) and 70% (CO₂) of the normalised residence time; the earlier onset of the SO₂ signal relative to CO₂ raises the question of possible compound-dependent residence-time distributions.

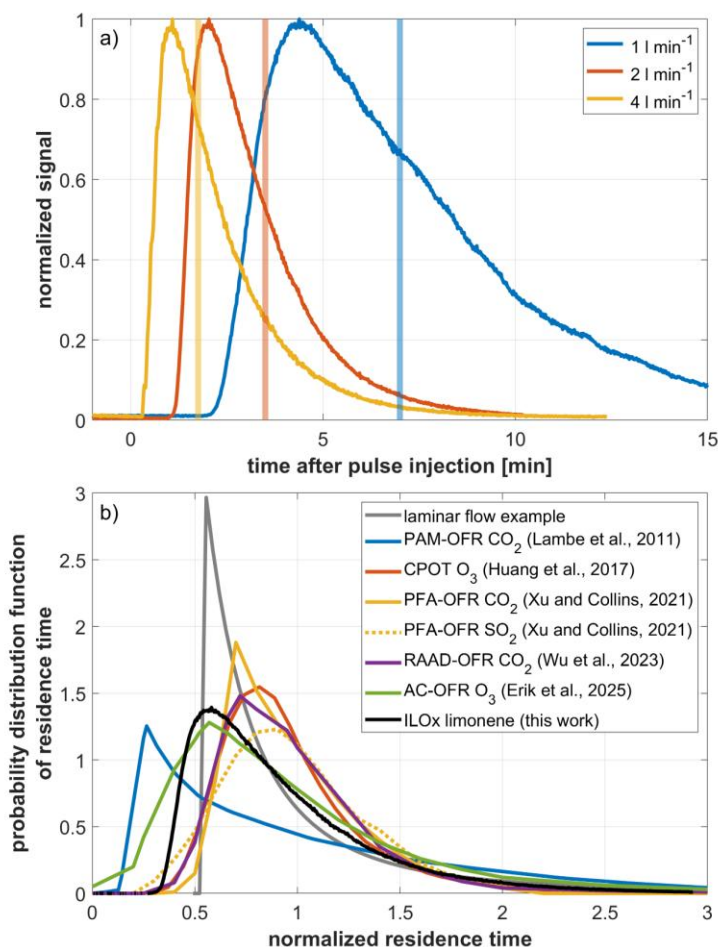


Figure 2: a) Response to a 10 s pulse of limonene at buffer-gas flow rates of 1, 2 and 4 l min⁻¹ through ILOx. Vertical lines indicate the respective geometric residence times (i.e. reactor volume/flow). b) Probability distribution functions of the normalised residence time for ILOx and a selection of other oxidation flow reactors; an ideal laminar-flow distribution is shown for comparison.

To examine this possibility, a 5 s pulse of a multi-component calibration standard is injected into a 2 l min⁻¹ flow through ILOx at 24°C and 50% relative humidity. The standard includes compounds of saturation mass concentrations (log C_0 at room temperature) from 6.5 (d5-siloxane) to 9.3 (acetaldehyde). All compounds except d5-siloxane produce indistinguishable response curves within measurement uncertainty (Fig. S4). D5-siloxane, whose volatility lies at the upper edge of the intermediate-volatility organic compound (IVOC) range, exhibits a comparable initial rise but reaches only ~ 60% of the maximum intensity of the more volatile species and shows a longer tail. Nevertheless, quantitative recovery of the entire injected d5-siloxane mass is achieved. We have also tested the response to a step function for propionic acid (log C_0 = 7.1) as a proxy for polar VOCs. Here ILOx shows a delayed transmission but a stable intensity is reached well within 3 times of the exchange time (Fig. S5).



To quantify the particle transmission efficiency of ILOx, dried polydisperse ammonium sulphate particles are introduced through the diffuser inlet fabricated from antistatic PTFE. Experiments are conducted at a total flow rate of 2 l min^{-1} , a temperature of 24°C and a relative humidity of 17%. Particle generation is stable, with mass concentrations varying only between 87 and $94 \mu\text{g m}^{-3}$. To minimise temporal drift, SMPS sampling alternates between the inlet and outlet of the reactor. Post-reactor measurements also include a 20 min interval during which the 275 nm UVC LEDs are operated at maximum intensity. Figure S6 presents the average particle mass size distributions ($\pm 1\sigma$) under the three conditions (pre-ILOx, post-ILOx without UVC, and post-ILOx with UVC).

Figure 3 shows the resulting particle transmission efficiency, defined as the ratio of the post- to pre-reactor size distributions, over the mobility-diameter range of 15 to 300 nm. Transmission efficiencies obtained with and without UVC irradiation are indistinguishable within measurement uncertainty - an expected outcome given that the maximum UVC irradiance raises the reactor's reflector temperature by only 0.2°C . At 50 nm, 84% of the inlet signal is recovered downstream of ILOx, while recovery increases to 108% at 150 nm. This modest size dependence may reflect limited coagulation within the accumulation mode during the ~ 3.5 min of mean residence time. Figure 3 also depicts the particle transmission efficiencies for a series of selected other OFRs.

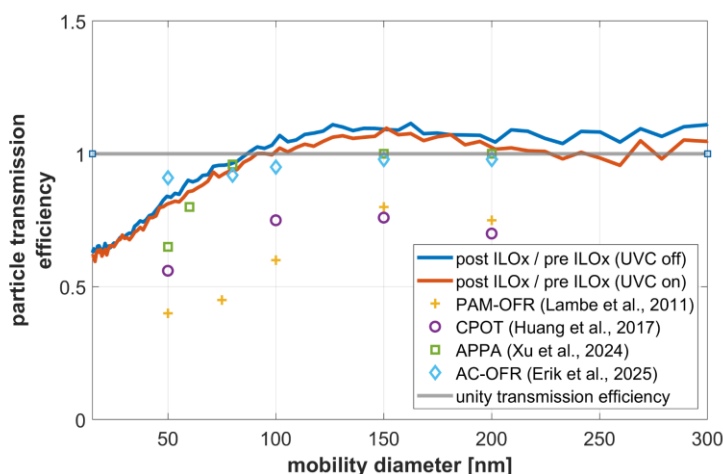


Figure 3: Solid lines depict the particle transmission efficiencies of ILOx for polydisperse ammonium sulphate particles with and without UVC. Symbols represent a selection of reported transmission efficiencies for other OFRs. PAM-OFR, CPOT and APPA also used ammonium sulphate, whereas AC-OFR used cetyl trimethyl ammonium chloride particles.

3.2 Characterization of the oxidative performance

ILOx offers a series of options for the generation of radicals of interest (see supplement for more information). Herein we report results utilizing three distinct modes: ozonolysis, OH induced oxidation via the photolysis of IPN (UVA 365 nm) and OH induced oxidation via the photolysis of O_3 (UVC 275 nm).



3.2.1 Ozonolysis of limonene

Ozone is produced in the external Pen-Ray UVC 185 nm quartz-glass assembly that is flushed with 5-10 sccm of pure O₂. The assembly allows to manually shade the Pen-Ray light-source and hence adjust the photolysis rate. Concentrations of clean O₃ inside ILOx range up to 3000 ppbV for 1 l min⁻¹ of total flow (reduced if the flows are higher). During our characterization experiments, stable O₃ levels as low as 30 ppbVs could be manually set resulting in a dynamic O₃ concentration covering two orders of magnitude ranging from typical ambient levels to highly enhanced concentrations.

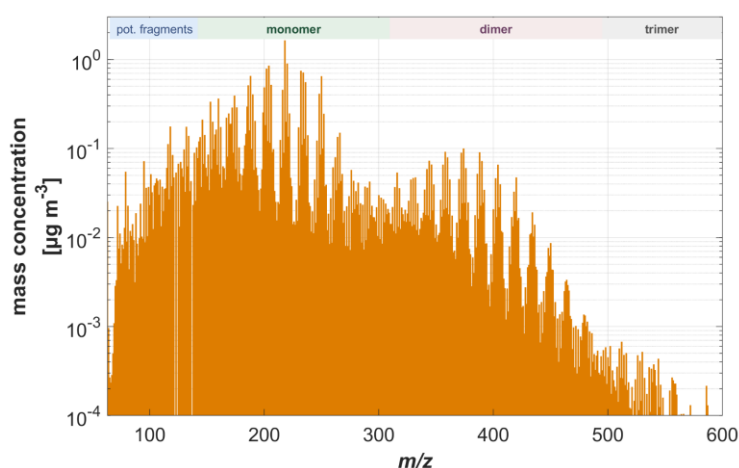


Figure 4: Chemical composition of the particle phase during a limonene ozonolysis experiment as measured by CHARON FUSION PTR-TOF 10 in soft chemical A.NH₄⁺ adduct ionization mode. Clearly distinctive monomer, dimer and trimer ranges are visible.

Ozonolysis of monoterpenes like limonene are well reported chemical systems. Herein we oxidize 120 ppbV of initial limonene with 250 ppbV of O₃ in 1 l min⁻¹ zero air at room temperature and 50% relative humidity. High concentrations are chosen to produce large enough SOA for quantitative chemical analysis via CHARON FUSION PTR-TOF 10 without seed. Approximately 65 ppbV of limonene are oxidized and produce 90 μg m⁻³ of SOA (assumed particle density of 1.4 g cm⁻³) at a size mode of 100 nm. This corresponds to a SOA mass yield (i.e. ΔM_{SOA} / ΔVOC, with ΔM_{SOA} representing the mass concentration of organic aerosol produced, and ΔVOC being the mass concentration of VOC reacted) at the given conditions of 25%. The chemical composition of this SOA is analyzed in almost fragmentation free A.NH₄⁺ adduct ionization mode to conserve the chemical composition of the particulate sample molecules. A 5 min averaged resulting mass spectrum is depicted in Figure 4. Clearly distinctive monomer, dimer and even trimer sections are visible, the latter at sub-ng m⁻³ mass concentrations.

3.2.2 OH via photolysis of IPN

IPN is synthesized on-site and a gas-phase standard containing approximately 15 ppmV of IPN in 3 bar N₂ inside a 10 l SilcoCan (Restec Corporation, USA) is prepared and connected to the dedicated IPN/HONO port of ILOx. Hence,



concentrations of IPN in the sample gas can be adjusted from a low ppbV level up to hundreds of ppbV. UVA irradiation at 365 nm will photolyze the IPN to form OH, NO₂ and acetone (see supplement for detailed information).

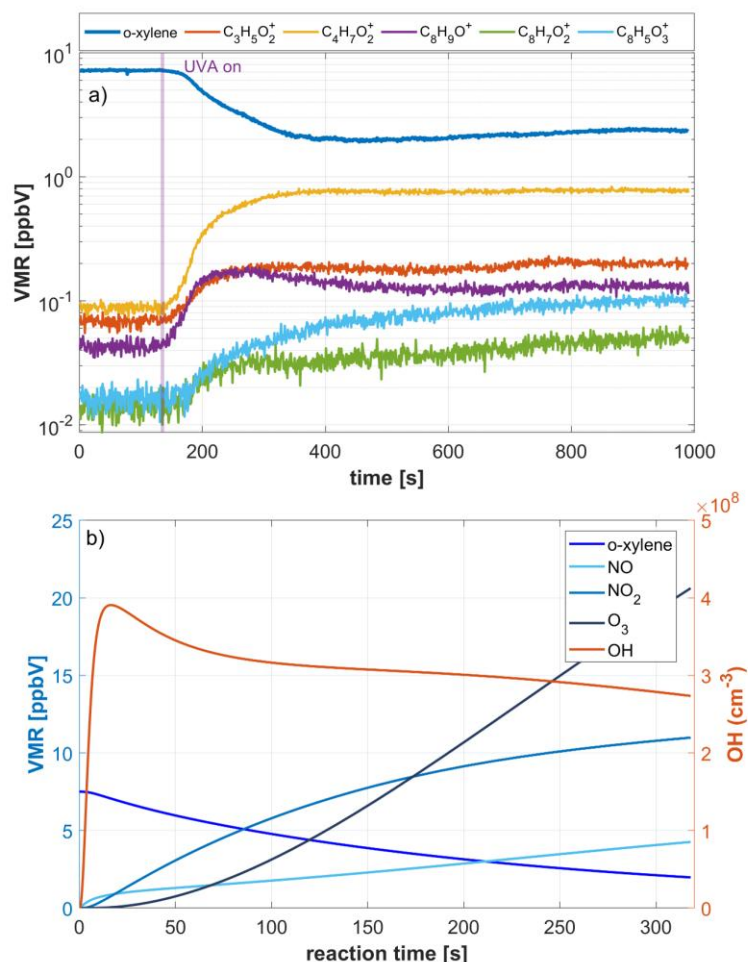


Figure 5: a) Oxidation of 7.5 ppbV of o-xylene via the photolysis of 200 ppbV of IPN by UVA 365 nm LED irradiation as measured post-ILOx. The transparent line shows when the irradiation was activated. The decaying o-xylene is depicted together with a selection of prominent oxidation products. b) FOAM-4.4 simulation of the radical regime mirroring the experimental conditions.

A simplified system of o-xylene mixed in 1.3 l min⁻¹ of humidified synthetic air (RH = 50%) is chosen to characterize the oxidation potential of ILOx via the photolysis of IPN. About 8 ppbV of o-xylene and 200 ppbV of IPN are injected into ILOx until the signals post-ILOx stabilise. With the activation of the UVA LED lamp, photolysis of IPN is initiated and o-xylene is reacted by OH. Figure 5a depicts the time-series of o-xylene and of a series of reaction products ranging from methylglyoxal (C₃H₅O₂⁺) to C₆H₅O₃⁺ (e.g. phthalic anhydride) as measured in H₃O⁺ ionization mode with a FUSION PTR-TOF 10. A custom FOAM-4.4 box model based on the Master Chemical Mechanism in version 3.3.1 is updated with the photolysis of IPN (Raff and Finlayson-Pitts, 2010) and applied to simulate the oxidation of o-xylene. The results for this simulation experiment are shown in Figure 5b. Average OH concentrations reach 3 x 10⁸ cm⁻³, which equals to an OH exposure OH_{exp} of 10¹¹ cm⁻³s. This



is equivalent to a typical atmospheric oxidation of around 30 h. Hence the ILOx reactor is very well capable of mimicking such conditions even without the need of potentially ionizing UVC irradiation (e.g. 185 nm UVC is able to ionize polycyclic aromatic hydrocarbons (PAHs) emitted e.g. by biomass burning).

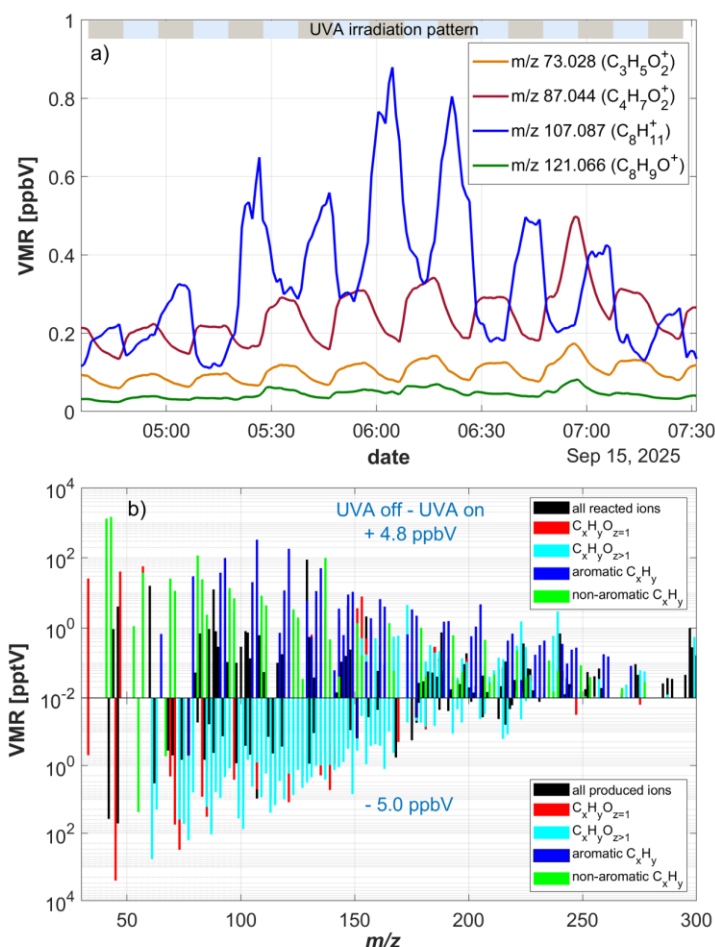


Figure 6: Example of atmospheric multi-day oxidation via the photolysis of IPN during a rush-hour event in Innsbruck, Austria. a) displays the time-series of xylene plus three well reported gas-phase oxidation products. UVA irradiation was periodically activated and deactivated every 10 min. b) shows the difference spectra (UVA off - UVA on) as measured by FUSION PTR-TOF 10 - the upper panel equals ions of molecules being reacted away while the lower panel shows products being produced.

To test this capability for the real-world, 1.7 l min^{-1} of ambient air is actively pulled through ILOx together with 0.3 l min^{-1} of buffer gas (equally distributed to humid sheath air and IPN carrier gas). UVA is activated and deactivated every 10 min; this equals to roughly 3 times of the residence time in ILOx. Figure 6a shows ambient concentrations of xylenes ($C_8H_{11}^+$) plus prominent oxidation products as measured post-ILOx with and without irradiation during a morning rush-hour event in Innsbruck, Austria. Similar to the test experiment, up to 65% of xylene is consumed - but of course, not only xylene is consumed. Figure 6b shows two difference-spectra during the displayed rush-hour event (i.e. UVA off minus UVA on) - the



top panel displays compounds being consumed by photooxidation, the inverted bottom panel depicts compounds that are produced. Looking at the chemical information, mostly non-aromatic hydrocarbons (e.g. monoterpenes, measured on m/z 81 and 137, and isoprene measured on m/z 69) and aromatic hydrocarbons (e.g. toluene, xylene and trimethylbenzene measured on m/z 93, 107 and 121, respectively) are consumed. On the other hand, produced compounds include ions with one or multiple oxygens. Most prominent volatile products are protonated acetaldehyde (m/z 45) and acetic acid (m/z 61). Interestingly, 4.8 ppbV of VOCs are reacted away and 5 ppbV of products are produced. Although no carbon closure can be reached by those PTR-MS based measurements, this agreement illustrates the good transmission capabilities of ILOx that are not only shown during the initial characterization experiments.

3.2.3 OH via photolysis of ozone

The photolysis of ozone is the simplest way to generate OH inside the ILOx reactor. O_3 is photolysed by 275 nm LED irradiation to form O_2 and $O(^1D)$ and $O(^1D)$ reacts with H_2O to form 2 OH radicals (see supplementary information). One drawback of this formation pathway is its direct dependency on the humidity of the sample gas. However, in ILOx humidity and UVC 275 nm irradiation are both measured; hence the UVC 275 nm intensity can be adjusted accordingly.

As a first proof-of-principle experiment we have studied the SOA mass yields for limonene. A wide range of initial concentrations of limonene (5 - 48 ppbV) and O_3 (60 to 2500 ppbV) in zero air are tested to identify optimal SOA formation conditions. Total ILOx flow is 1.2 l min^{-1} operated at room temperature ($T = 26^\circ\text{C}$) and a relative humidity of 50%. The SOA mass concentration is measured via SMPS; no seed is added. OH exposure (OH_{exp}) is estimated via FOAM 4.4 simulations. Respective OH_{exp} range from 0.016 to $10.1 \times 10^{11} \text{ cm}^{-3} \text{ s}$. Figure 7 shows the results of these tests.

The data reveals that maximum limonene SOA mass yields can be reached for OH_{exp} around 0.5 to $2 \times 10^{11} \text{ cm}^{-3} \text{ s}$. This roughly corresponds to 0.5 to two days of typical atmospheric ageing. This result is in agreement with the findings of other OFRs (Palm et al., 2016). The results also clearly visualize that individual VOC consumptions can show a wide range of SOA yields depending on the O_3 concentration and OH exposure. Too high OH_{exp} and O_3 concentrations lead to enhanced fragmentation reactions reducing the SOA formation potential whereas too little exposure hinders the formation of low volatiles that can cause new particle formation.

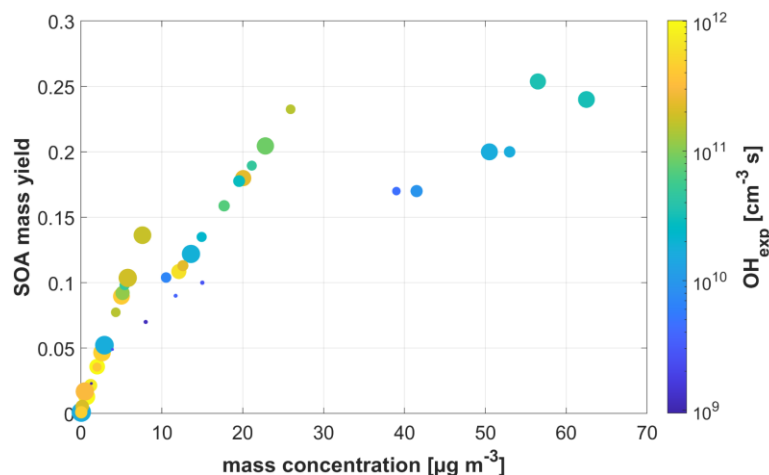


Figure 7: SOA mass yield of limonene (5 to 48 ppbV), oxidized without seed under various oxidation conditions via the photolysis of ozone. The colorbar displays the OH exposure OH_{exp} derived via FOAM simulations. Marker sizes indicate the range of O_3 (60 to 2500 ppbV, linear relationship).

Parts of these experiments apply radical concentrations at or slightly above ambient conditions. Such concentrations seem to be optimal for studying the initial generations of gas-phase oxidation. Figure 8 illustrates an example mass spectrum for limonene as measured by FUSION PTR-TOF 10 in almost fragmentation-free $A.NH_4^+$ adduct ionization mode. 16 ppbV of limonene are injected in synthetic air at a flow rate of 1.2 l min^{-1} ($RH = 50\%$). The simulated OH exposure equals to $6.4 \times 10^9 \text{ cm}^{-3} \text{ s}$ and 124 ppbV of O_3 are measured. $60.7 \mu\text{g m}^{-3}$ of limonene are reacted away at these conditions whereas less than $2 \mu\text{g m}^{-3}$ of SOA is being formed (SOA mass yield $\sim 3\%$). The mass spectrum displays limonene oxidation products in repetitive groups with variable oxygen numbers ranging from 1 to 6 and higher (please note: the residual 5.1 ppbV of the limonene signal is removed for better visibility of the formed products). The highest signal is $C_7H_{10}O_3$ (m/z 142.063) followed by $C_5H_8O_2$ (m/z 100.052), $C_6H_{10}O_2$ (m/z 114.068) and $C_5H_8O_3$ (m/z 116.044) - all those products represent fragmentation products of the oxidation in ILOx. According to the MCM 3.3.1, $C_7H_{10}O_3$ (*C626CHO* in MCM nomenclature) likely represents an ozonolysis product via the dominant *LIMOOA* ozonolysis pathway whereas $C_5H_8O_2$ is a dicarbonyl fragment formed during extensive photochemical aging (e.g. *CO24C5*). In addition, a large number of oxidation products with carbon numbers of 9 or 10 are measured. $C_{10}H_{16}O_2$ (m/z 168.115) represents the ion with the largest signal. According to the MCM this could be *LIMAL*, an OH induced product via *LIMAO2* and *LAMBO2*. Visually prominent products also include $C_9H_{12}O_4$ (m/z 184.074), $C_9H_{12}O_5$ (m/z 200.068), and $C_9H_{12}O_6$ (m/z 214.047) - i.e. a series of first generation $C_9H_{12}O_x$ highly oxidized molecule (HOM) monomers - likely formed through the *LIMKET* pathway of the limonene OH oxidation.

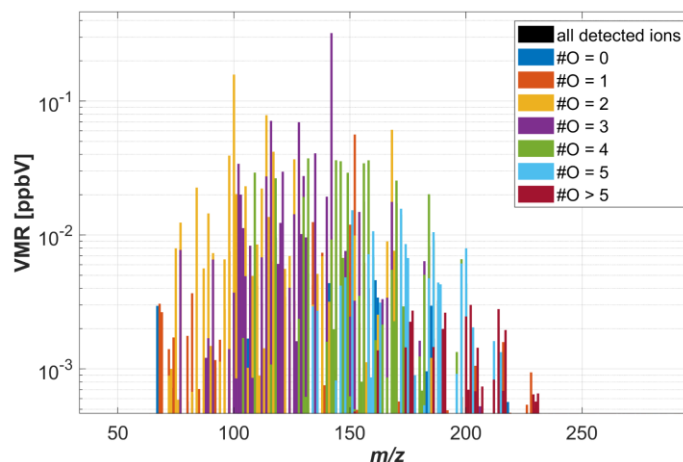


Figure 8: Gasphase oxidation products of limonene as measured in soft A.NH₄⁺ adduct ionization mode. The NH₄⁺ adduct is subtracted from the measured exact mass for clarity. The color code represents the number of oxygen per detected ion.

4 Discussion

4.1 LED irradiation

Replacing traditional discharge lamps (e.g., low-pressure mercury lamps or UV fluorescent tubes) with solid-state LEDs at 275 nm and 365 nm provides critical operational and scientific advantages.

Standard mercury lamps emit fixed, multi-line spectra (e.g. strong 254 nm alongside parasitic 185 nm VUV light), while fluorescent lamps exhibit broad spectral tails. UV LEDs feature narrow emission bands (FWHM ~ 10 - 15 nm). Therefore a 275 nm LED selectively targets the peak absorption of the O₃ Hartley band for O(¹D) production while eliminating high-energy 185 nm light and thus no additional shielding may be necessary. Similarly, 365 nm LEDs cleanly drive the photolysis of HONO, NO₂ or alkyl nitrites without unintentionally photolyzing secondary organic aerosol (SOA) components or background intermediates.

In addition, discharge lamps generate significant convective heat and infrared (IR) radiation, warming the reactor tube walls and sample gas. Temperature shifts alter temperature-sensitive kinetic rate constants, disrupt laminar flow via thermal flows, and artificially shift the gas-to-particle partitioning of semi-volatile organic compounds. LEDs emit directional "cold light" into the reactor volume, conducting most of their heat out the back of the printed circuit board into dedicated heat sinks. This helps to maintain isothermal conditions within the sample stream.

Instantaneous response and linear dimming are additional advantages of LEDs. Mercury lamps require lengthy warm-up times, suffer from temperature-dependent drift of the photon yield, and exhibit an unstable plasma discharge when dimmed. In contrast, LEDs respond instantaneously to current tuning or pulse-width modulation (PWM). This allows linear, reproducible



adjustments of photon flux across a large magnitude, facilitating precise step-changes in radical exposure (e.g. OH_{exp}) without lamp drift.

The flexible geometry of LED arrays allows for an axially almost uniform photon field along the ILOx reactor, which does not inherently suffer from intensity drop-offs near the lamp ends or directional shadowing. Additionally, life times of LEDs may reach tens of thousands of hours whereas mercury lamps might degrade far quicker.

4.2 Decoupled oxidant generation

In the application of OFRs to simulate atmospheric aging, the choice of UV irradiation scheme dictates not only the primary radical generation but also the extent of non-ambient chemical artifacts. Conventional OFR operation often utilizes simultaneous 185 nm and 254 nm irradiation (the "OFR185" mode, as characterized in PAM-OFR studies) to generate both O_3 and OH radicals directly from the sample flow containing O_2 and H_2O . While highly efficient for producing massive OH exposures, a well-documented drawback of 185 nm irradiation is the introduction of non-tropospheric chemistry (Peng et al., 2016). The high-energy 185 nm photons (~ 6.47 eV) are capable of directly photolyzing and, in some cases, photoionizing highly light-absorbing volatile organic compounds (VOCs) such as PAHs. These direct photolytic pathways compete with radical-driven oxidation, artificially skewing degradation kinetics, product distributions, and secondary organic aerosol (SOA) yields away from true ambient atmospheric behavior.

The decoupled irradiation approach utilized in the ILOx reactor (or the PAM-OFR utilising the so-called "OFR254" mode) effectively circumvents these limitations. By spatially or temporally separating the 185 nm generation of O_3 (from O_2) from the sample exposure, the target VOCs are shielded from more energetic UV. Instead, the sample flow - now mixed with the pre-generated O_3 and humidified air - is irradiated exclusively at 275 nm.

This decoupled strategy provides three distinct advantages for simulating tropospheric chemistry:

- *Suppression of Non-Ambient Photolysis:* Photons at 275 nm lack the energy required to widely ionize or directly photolyze many complex VOCs and PAHs. Consequently, the loss of these precursors is driven almost entirely by genuine OH or O_3 oxidation rather than non-tropospheric photolysis artifacts.
- *Mechanistic Fidelity:* At 275 nm, O_3 is efficiently photolyzed to produce $\text{O}(^1\text{D})$, which subsequently reacts with water vapor to yield OH radicals. This mimics the primary daytime mechanism of ambient OH formation, ensuring the chemical regime inside the flow tube remains highly representative of the troposphere.
- *Independent Oxidant Control:* Separating the 185 nm and 275 nm stages decouples the initial O_3 production from the subsequent OH generation. This provides independent control over the ratio of O_3 to OH, allowing for targeted studies that isolate pure ozonolysis regimes from OH-dominated regimes, or allowing for the precise tuning of the HO_2/OH ratio.

By eliminating 185 nm light from the primary reaction zone, the reactor minimizes non-OH chemistry artifacts, ensuring that the derived physicochemical aerosol parameters and VOC decay rates are robust and atmospherically relevant.



4.3 Wall interactions

Wall interactions remain an important consideration for the quantitative interpretation of OFR experiments, including those performed with ILOx. SVOCs and LVOCs formed during photo-oxidation can be lost by irreversible or quasi-irreversible uptake onto reactor surfaces. These losses compete directly with condensation onto aerosol particles and with further gas-phase oxidation, and therefore tend to reduce observed secondary organic aerosol (SOA) mass yields relative to the atmosphere. Models developed for PAM-OFR type reactors (Palm et al., 2016, 2017) quantify the fractional fate of condensable vapours as a function of residence time, condensational sink and volatility. Under typical PAM-OFR conditions (residence times of ~100–200 s and modest aerosol surface areas), 20 - 70% of LVOCs may be lost to the walls or to downstream sampling lines rather than condensing to particles. Wall-loss timescales of several hundred seconds have been reported, comparable to the reactor residence time, so that the effect cannot be neglected for low-volatility products.

Heterogeneous reactions on the walls constitute a second type of artefact. Surfaces can act as sinks for reactive intermediates (e.g. N_2O_5) or, in the case of metal walls, may catalyse additional oxidation pathways that are not representative of gas-phase atmospheric chemistry. Quartz and PTFE or PFA surfaces that are used in ILOx minimise these effects but do not fully eliminate such processes.

Despite all considerations including the laminar-flow design, inert materials and sub-sampling strategy deployed in ILOx, residual wall interactions should still be evaluated for each experimental configuration. Accurate quantification of SOA yields and product distributions requires either experimental correction (seed-surface-area dependence, transmission efficiencies) or model-based accounting for the competing fates of condensable vapours.

5 Conclusion

We have characterised the new laminar-flow oxidation reactor ILOx, which is optimised for simultaneous sampling of gas- and particle-phase species. Photochemistry is driven by irradiation at three wavelengths: an external 185 nm Pen-Ray lamp for O_3 generation, 275 nm LEDs for O_3 photolysis, and 365 nm LEDs for photolysis of isopropyl nitrite (IPN) or nitrous acid (HONO). Irradiation, the suite of mass-flow controllers, and all valves are controlled via software permitting automated operation.

Three-dimensional computational fluid dynamics simulations were used to optimise the inlet and outlet geometries, ensuring rapid mixing of injected gases, the rapid establishment of laminar flow within the quartz tube, and efficient core sampling of reaction products. Pulse-response experiments with a range of volatile organic compounds confirmed the near-laminar residence-time distribution. Sequential measurements with ammonium sulphate particles demonstrated high transmission and low wall losses across the accumulation-mode size range.

ILOx was operated successfully in three complementary modes - ozonolysis, OH production via IPN photolysis, and OH production via O_3 photolysis - thereby spanning a wide range of radical exposures. These modes enabled experiments from the oxidation of individual VOCs in synthetic air to multi-day equivalent ageing of ambient air. When interfaced with a



CHARON inlet and a FUSION PTR-TOF 10, the ILOx reactor provides molecular-level chemical insight into the observed oxidation chemistry.

Code and data availability

Code and data are available upon request.

Supplement link

The link to the supplement will be included by Copernicus, if applicable.

Author contributions

ML, TR and MM designed the setup, ML conducted the CFD simulation, MM the box modelling, ML, TR, MG and MM conducted the experiments. Data analysis was done by ML and MM. TF led the electrical engineering, DG and AK the mechanical engineering. JB, GH and NT were responsible for software control and automation. MM wrote the manuscript with inputs from all authors. Note: Large Language Models (LLMs) were used for language editing and refinement of author-provided text and notes. The revised text was reviewed and verified by the authors.

Competing interests

The authors work for IONICON Analytik GmbH, which commercializes ILOx.

Disclaimer

Copernicus Publications remains neutral with regard to jurisdictional claims made in the text, published maps, institutional affiliations, or any other geographical representation in this paper. While Copernicus Publications makes every effort to include appropriate place names, the final responsibility lies with the authors. Views expressed in the text are those of the authors and do not necessarily reflect the views of the publisher.

Review statement

The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.



References

- Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, *Atmospheric Chemistry and Physics*, 5, 641–664, <https://doi.org/10.5194/acp-5-641-2005>, 2005.
- Cohen, A. J., Brauer, M., Burnett, R., Anderson, H. R., Frostad, J., Estep, K., Balakrishnan, K., Brunekreef, B., Dandona, L., Dandona, R., Feigin, V., Freedman, G., Hubbell, B., Jobling, A., Kan, H., Knibbs, L., Liu, Y., Martin, R., Morawska, L., Pope, C. A., Shin, H., Straif, K., Shaddick, G., Thomas, M., van Dingenen, R., van Donkelaar, A., Vos, T., Murray, C. J. L., and Forouzanfar, M. H.: Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015, *Lancet*, 389, 1907–1918, [https://doi.org/10.1016/S0140-6736\(17\)30505-6](https://doi.org/10.1016/S0140-6736(17)30505-6), 2017.
- Eichler, P., Müller, M., D’Anna, B., and Wisthaler, A.: A novel inlet system for online chemical analysis of semi-volatile submicron particulate matter, *Atmos. Meas. Tech.*, 8, 1353–1360, <https://doi.org/10.5194/amt-8-1353-2015>, 2015.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmospheric Chemistry and Physics*, 9, 5155–5236, <https://doi.org/10.5194/acp-9-5155-2009>, 2009.
- Huang, Y., Coggon, M. M., Zhao, R., Lignell, H., Bauer, M. U., Flagan, R. C., and Seinfeld, J. H.: The Caltech Photooxidation Flow Tube reactor: design, fluid dynamics and characterization, *Atmospheric Measurement Techniques*, 10, 839–867, <https://doi.org/10.5194/amt-10-839-2017>, 2017.
- Intergovernmental Panel on Climate Change (IPCC) (Ed.): Short-lived Climate Forcers, in: *Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, 817–922, <https://doi.org/10.1017/9781009157896.008>, 2023.
- Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, *Atmospheric Environment*, 31, 81–104, [https://doi.org/10.1016/S1352-2310\(96\)00105-7](https://doi.org/10.1016/S1352-2310(96)00105-7), 1997.
- Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, *Atmospheric Chemistry and Physics*, 3, 181–193, <https://doi.org/10.5194/acp-3-181-2003>, 2003.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimojo, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, *Science*, 326, 1525–1529, <https://doi.org/10.1126/science.1180353>, 2009.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre,



- 455 C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review,
456 Atmospheric Chemistry and Physics, 5, 1053–1123, <https://doi.org/10.5194/acp-5-1053-2005>, 2005.
- 457 Kang, E., Root, M. J., Toohey, D. W., and Brune, W. H.: Introducing the concept of Potential Aerosol Mass (PAM),
458 Atmospheric Chemistry and Physics, 7, 5727–5744, <https://doi.org/10.5194/acp-7-5727-2007>, 2007.
- 459 Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N. L., Wright,
460 J. P., Croasdale, D. R., Worsnop, D. R., Davidovits, P., and Onasch, T. B.: Characterization of aerosol photooxidation flow
461 reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements,
462 Atmospheric Measurement Techniques, 4, 445–461, <https://doi.org/10.5194/amt-4-445-2011>, 2011.
- 463 Ma, X., Li, K., Zhang, S., Yang, Z., Xu, L., Tsona Tchinda, N., and Du, L.: Oxidation Flow Reactor and Its Application in
464 Secondary Organic Aerosol Formation in Laboratory Studies, ACS EST Air, 2, 1394–1410,
465 <https://doi.org/10.1021/acsestair.5c00047>, 2025.
- 466 Müller, M., Mikoviny, T., Jud, W., D’Anna, B., and Wisthaler, A.: A new software tool for the analysis of high resolution
467 PTR-TOF mass spectra, Chemometrics and Intelligent Laboratory Systems, 127, 158–165,
468 <https://doi.org/10.1016/j.chemolab.2013.06.011>, 2013.
- 469 Müller, M., Eichler, P., D’Anna, B., Tan, W., and Wisthaler, A.: Direct Sampling and Analysis of Atmospheric Particulate
470 Organic Matter by Proton-Transfer-Reaction Mass Spectrometry, Anal. Chem., 89, 10889–10897,
471 <https://doi.org/10.1021/acs.analchem.7b02582>, 2017.
- 472 Müller, M., Piel, F., Gutmann, R., Sulzer, P., Hartungen, E., and Wisthaler, A.: A novel method for producing NH₄⁺ reagent
473 ions in the hollow cathode glow discharge ion source of PTR-MS instruments, International Journal of Mass Spectrometry,
474 447, 116254, <https://doi.org/10.1016/j.ijms.2019.116254>, 2020.
- 475 OpenFOAM | Free CFD Software | The OpenFOAM Foundation, <https://openfoam.org/> (last access: 14 September 2026).
- 476 Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., Cross, E.
477 S., Kroll, J. H., Peng, Z., Brune, W. H., and Jimenez, J. L.: In situ secondary organic aerosol formation from ambient pine
478 forest air using an oxidation flow reactor, Atmospheric Chemistry and Physics, 16, 2943–2970, <https://doi.org/10.5194/acp-16-2943-2016>, 2016.
- 480 Palm, B. B., Campuzano-Jost, P., Day, D. A., Ortega, A. M., Fry, J. L., Brown, S. S., Zarzana, K. J., Dube, W., Wagner, N.
481 L., Draper, D. C., Kaser, L., Jud, W., Karl, T., Hansel, A., Gutiérrez-Montes, C., and Jimenez, J. L.: Secondary organic aerosol
482 formation from in situ OH, O₃, and NO₃ oxidation of ambient forest air in an oxidation flow reactor, Atmospheric Chemistry
483 and Physics, 17, 5331–5354, <https://doi.org/10.5194/acp-17-5331-2017>, 2017.
- 484 Peng, Z. and Jimenez, J. L.: Radical chemistry in oxidation flow reactors for atmospheric chemistry research, Chem. Soc. Rev.,
485 49, 2570–2616, <https://doi.org/10.1039/c9cs00766k>, 2020.
- 486 Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H., and Jimenez, J. L.:
487 Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling,
488 Atmospheric Chemistry and Physics, 16, 4283–4305, <https://doi.org/10.5194/acp-16-4283-2016>, 2016.
- 489 Piel, F., Müller, M., Winkler, K., Skytte af Sättra, J., and Wisthaler, A.: Introducing the extended volatility range proton-
490 transfer-reaction mass spectrometer (EVR PTR-MS), Atmospheric Measurement Techniques, 14, 1355–1363,
491 <https://doi.org/https://doi.org/10.5194/amt-14-1355-2021>, 2021.



- 492 Raff, J. and Finlayson-Pitts, B.: Hydroxyl Radical Quantum Yields from Isopropyl Nitrite Photolysis in Air, *Environmental*
493 *science & technology*, 44, 8150–5, <https://doi.org/10.1021/es102218d>, 2010.
- 494 Reinecke, T., Leiminger, M., Jordan, A., Wisthaler, A., and Müller, M.: Ultrahigh Sensitivity PTR-MS Instrument with a Well-
495 Defined Ion Chemistry, *Anal. Chem.*, 95, 11879–11884, <https://doi.org/10.1021/acs.analchem.3c02669>, 2023.
- 496 Reinecke, T., Leiminger, M., Klinger, A., and Müller, M.: Direct detection of polycyclic aromatic hydrocarbons on a molecular
497 composition level in summertime ambient aerosol via proton transfer reaction mass spectrometry, *Aerosol Research*, 2, 225–
498 233, <https://doi.org/10.5194/ar-2-225-2024>, 2024.
- 499 Rösch, M. and Cziczo, D. J.: Aqueous particle generation with a 3D printed nebulizer, *Atmospheric Measurement Techniques*,
500 13, 6807–6812, <https://doi.org/10.5194/amt-13-6807-2020>, 2020.
- 501 Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical
502 Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmospheric Chemistry*
503 *and Physics*, 3, 161–180, <https://doi.org/10.5194/acp-3-161-2003>, 2003.
- 504 Shrivastava, M., Cappa, C. D., Fan, J., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T.,
505 Ng, N. L., Petaja, T., Pierce, J. R., Rasch, P. J., Roldin, P., Seinfeld, J. H., Shilling, J., Smith, J. N., Thornton, J. A., Volkamer,
506 R., Wang, J., Worsnop, D. R., Zaveri, R. A., Zelenyuk, A., and Zhang, Q.: Recent advances in understanding secondary organic
507 aerosol: Implications for global climate forcing, *Reviews of Geophysics*, 55, 509–559,
508 <https://doi.org/10.1002/2016RG000540>, 2017.
- 509 WHO global air quality guidelines: particulate matter (PM_{2.5} and PM₁₀), ozone, nitrogen dioxide, sulfur dioxide and carbon
510 monoxide, <https://iris.who.int/items/5b0ca7ab-830a-44b8-b99f-4ee743b4d7b2>, last access: 16 July 2026., 2021.
- 511 Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R., and Liao, J.: The Framework for 0-D Atmospheric Modeling
512 (F0AM) v3.1, *Geoscientific Model Development*, 9, 3309–3319, <https://doi.org/10.5194/gmd-9-3309-2016>, 2016.
- 513 Wu, C., Brown, R. A., Brown, Z. E., Trounce, H., Horchler, E. J., Wang, L., Miljevic, B., Zhang, C., Wang, H., Wang, B.,
514 Ristovski, Z., and Stevanovic, S.: A new oxidation flow reactor for the measurements of secondary aerosol formation:
515 Characterisation and a case study, *Atmospheric Environment*, 309, 119886, <https://doi.org/10.1016/j.atmosenv.2023.119886>,
516 2023.
- 517 Xu, L., Coggon, M. M., Stockwell, C. E., Gilman, J. B., Robinson, M. A., Breitenlechner, M., Lamplugh, A., Crounse, J. D.,
518 Wennberg, P. O., Neuman, J. A., Novak, G. A., Veres, P. R., Brown, S. S., and Warneke, C.: Chemical ionization mass
519 spectrometry utilizing ammonium ions (NH₄⁺ CIMS) for measurements of organic compounds in the atmosphere, *Atmospheric*
520 *Measurement Techniques*, 15, 7353–7373, <https://doi.org/10.5194/amt-15-7353-2022>, 2022.
- 521 Xu, N. and Collins, D. R.: Design and characterization of a new oxidation flow reactor for laboratory and long-term ambient
522 studies, *Atmospheric Measurement Techniques*, 14, 2891–2906, <https://doi.org/10.5194/amt-14-2891-2021>, 2021.
- 523 Xu, N., Le, C., Cocker, D. R., Chen, K., Lin, Y.-H., and Collins, D. R.: An oxidation flow reactor for simulating and
524 accelerating secondary aerosol formation in aerosol liquid water and cloud droplets, *Atmospheric Measurement Techniques*,
525 17, 4227–4243, <https://doi.org/10.5194/amt-17-4227-2024>, 2024.