Quantifying the Influence of IVOC and SVOC on Ambient SOA Formation

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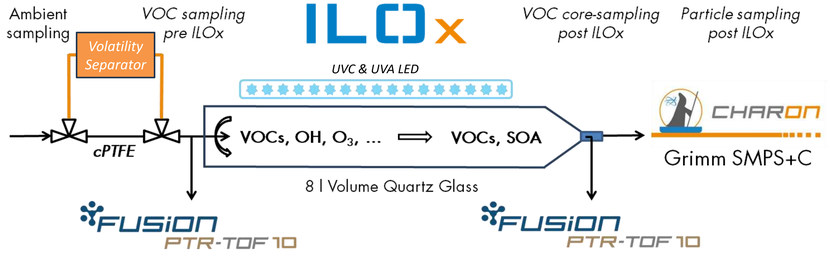
Introduction and Experimental Setup

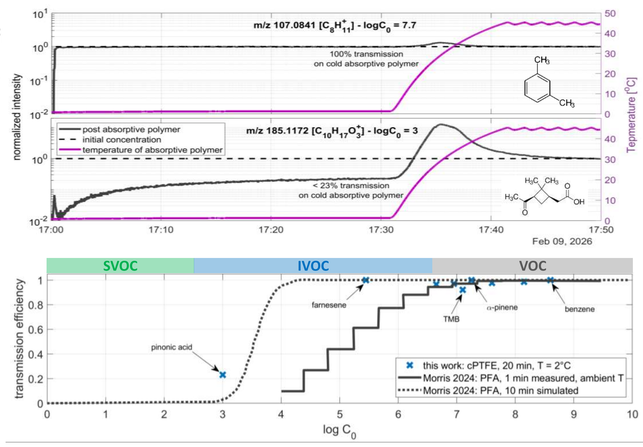
Quantifying the contribution of IVOC and SVOC to SOA formation remains challenging. To elucidate the atmospheric fate of IVOC and SVOC, the basic concept of gas-phase volatility separation based on aborptive polymers has recently been introduced [1]. This method utilizes absorption processes of low volatiles onto different polymer tubing to separate a complex gas mixture by volatility classes. We further improved this method by using an actively cooled conductive PTFE inlet as a Volatility Separator (VS) that allows to precisely adjust the volatility cutoff by temperature without the need to switch between different polymer lines.

To quantify the contribution of IVOC and SVOC to SOA formation, sample air is injected into the novel IONICON Laminar-flow Oxidation reactor (ILOx) for rapid photochemical ageing. By periodically removing and adding the volatility separator prior to the sample injection, the SOA yield of the sample with and without IVOC and SVOC can be studied and compared. Therefore, the ambient air pre and post ILOx is analyzed by two FUSION PTR-TOF [2], one equipped with a CHARON particle inlet [3], and an SMPS system (Grimm Aerosol Technik, Germany). Gas-phase measurements are covered from VOC to SVOC with limits of detection of <100 ppqV and condensed organics are detected on a molecular composition level with lowermost limits of detection (< 20 pg/m³).



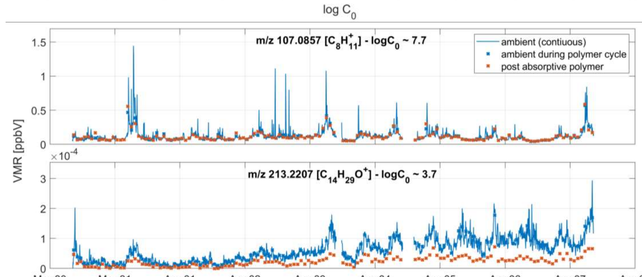
Characterization of the Volatility Separator

By adjusting the temperature of the volatility separator, the volatility cutoff can be precisely adjusted without the need to switch between different polymer lines



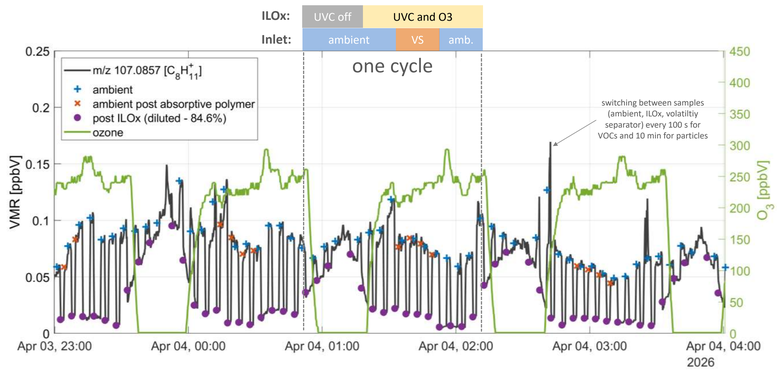
Measured transmission efficiency for different volatility classes at T = 2°C in comparison with previous work [1]

Ambient sampling with and without Volatility Separator:
- Xylene ($logC_0 \sim 7.7$) passes the volatility separator without losses
- $C_{14}H_{29}O^+$, presumably a secondary traffic emission compound ($logC_0 \sim 3.7$), is reduced to 36%

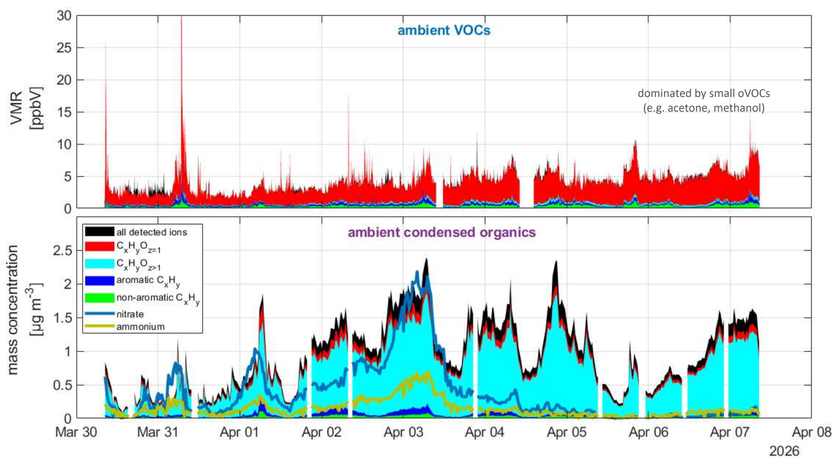


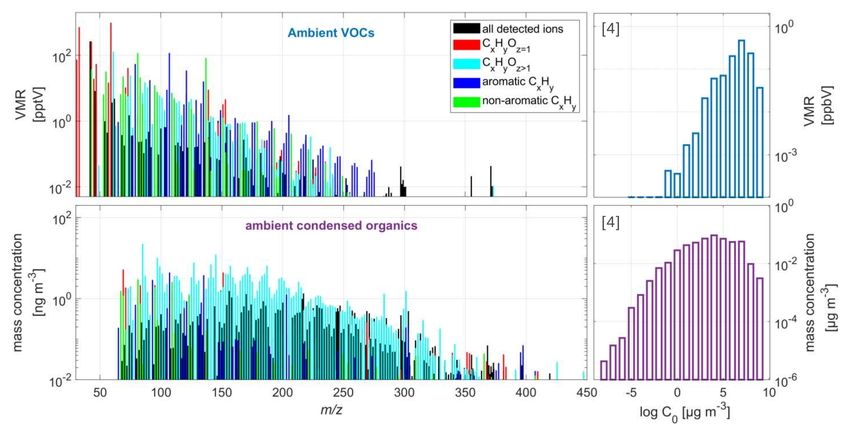
Measurement Sequence

One measurement cycle every 80 min covering VOCs and particles from three inlets (i.e. ambient, Volatility Separator and ILOx):



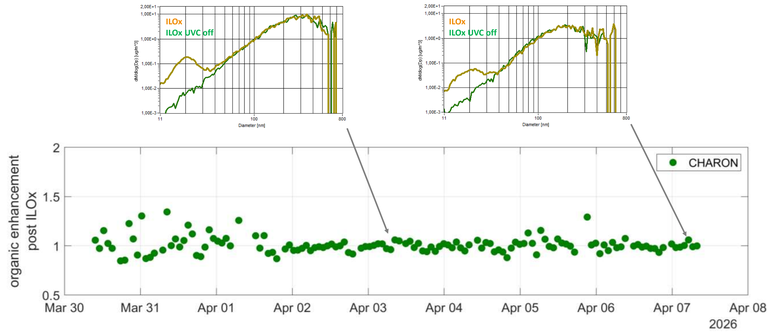
Ambient Composition, Innsbruck Austria





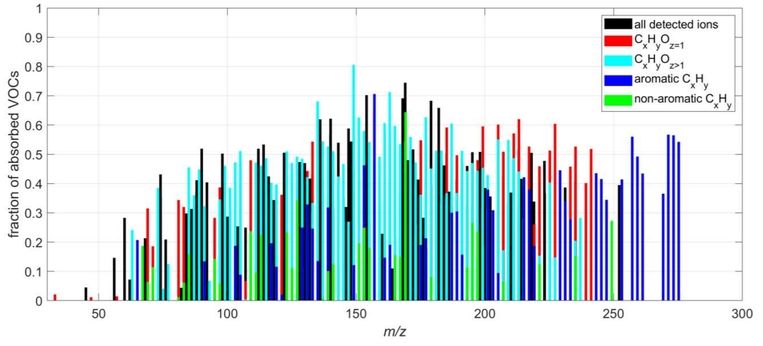
ILOx – Organic Enrichment

- CHARON and SMPS only show small organic enrichment after fast oxidation via ILOx – only very little concentration of reactive VOC is available
- CHARON mass spectra reveal a combination of production and loss (e.g. fragmentation of compounds)

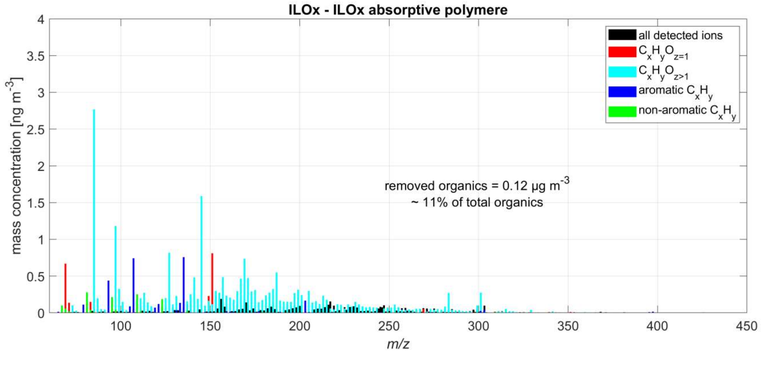


ILOx – Effects of the Volatility Separator

- On average, the Volatility Separator removes 0.14 ppbV of IVOC and SVOC
- Up to 80% of ambient concentrations are removed for specific compounds (e.g. $C_8H_5O_3^+$)



- Despite only 0.14 ppbV are removed, the mass concentration of organic aerosol after ILOx is reduced by 0.12 µg/m³
- This corresponds to a loss of **11%** of the total organics



References

[1] Morris et al.: Absorption of volatile organic compounds (VOCs) by polymer tubing: implications for indoor air and use as a simple gas-phase volatility separation technique (https://amt.copernicus.org/articles/17/1545/2024/)

[2] Reinecke et al.: Ultrahigh Sensitivity PTR-MS Instrument with a Well-Defined Ion Chemistry (https://doi.org/10.1021/acs.analchem.3c02669)

[3] Reinecke et al.: Direct detection of condensed particulate polycyclic aromatic hydrocarbons on a molecular composition level at low pg m-3 mass concentrations via proton-transfer-reaction mass-spectrometry (https://doi.org/10.5194/ar-2-225-2024)

[4] Li et al.: Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols (https://acp.copernicus.org/articles/16/3327/2016/)