

Supplement of

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

by Markus Leiminger et al.

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1 Discussion of reaction pathways in ILOx

Primary oxidants in ILOx include O_3 , OH, NO_3 and NO. They are produced via photolysis of precursors with ILOx's three irradiation wavelengths (185 nm, 275 nm and 365 nm) and additional radical - molecule reactions.

- O_3 :
 $O_2 + hv (185\text{ nm}) \rightarrow 2O(^3P)$
 $O(^3P) + O_2 + M \rightarrow O_3 + M$
- OH:
 $O_3 + hv (275\text{ nm}) \rightarrow O(^1D) + O_2$
 $O(^1D) + H_2O \rightarrow 2OH$
 $HONO + hv (365\text{ nm}) \rightarrow OH + NO$
 $(CH_3)_2CHONO + hv (365\text{ nm}) \rightarrow (CH_3)_2CHO^\bullet + NO$
 $(CH_3)_2CHO^\bullet + O_2 \rightarrow (CH_3)_2CO + HO_2^\bullet$
 $HO_2^\bullet + NO \rightarrow OH + NO_2$
- NO:
 $NO_2 + hv (275\text{ nm}, 365\text{ nm}) \rightarrow NO + O(^3P)$
- NO_3 :
 $O_3 + NO_2 \rightarrow NO_3 + O_2$

In the following, dominant reaction pathways including potential radical sinks are briefly summarized.

1.1 Ozonolysis

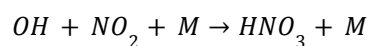
Ozone reacts preferentially with carbon-carbon double bonds. In addition to primary oxidation, O_3 plays a critical role in reactor background chemistry.

- Alkene Oxidation:
 $Alkene + O_3 \rightarrow \text{Primary Ozonide (PO)}$
- Criegee Intermediate (CI) formation:
 $PO \rightarrow \text{Carbonyl} + CI$
- CI stabilization: $CI + H_2O \rightarrow \alpha - \text{hydroxyhydroperoxide} \rightarrow \text{Carbonyl} + H_2O_2$ (or organic acids)
- Background radical sinks:
 $O_3 + OH \rightarrow HO_2 + O_2$
 $O_3 + HO_2 \rightarrow OH + 2O_2$

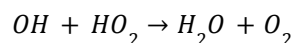
1.2 Hydroxyl radical

OH is the dominant, non-selective oxidant driving the decay of both saturated and unsaturated VOCs.

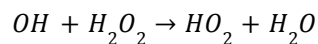
- H-Abstraction (e.g. Alkanes/Aromatics):
 $RH + OH \rightarrow R^\bullet + H_2O$
- OH-Addition (e.g. Alkenes):
 $>C=C< + OH \rightarrow >C(OH)-C^\bullet<$
- High NO_x background sink:



- HO_x self-reaction background sink:



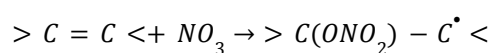
- Peroxide background sink:



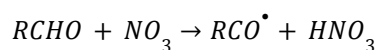
1.3 Nitrate radical

When NO_2 is introduced in the dark or alongside O_3 , NO_3 becomes an important nocturnal-like oxidant. Note that UVC illumination (275 nm) rapidly photolyzes NO_3 , making its chemistry most dominant in dark experiments.

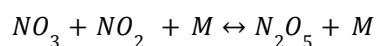
- NO_3 -addition (alkenes):



- H-abstraction (aldehydes):

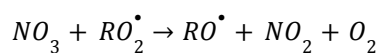


- N_2O_5 equilibrium:



- NO_3 photolysis: $NO_3 + h\nu \rightarrow NO_2 + O(^3P)$ (or) $NO + O_2$

- Cross-reaction with RO_2 :



2 Supplementary figures

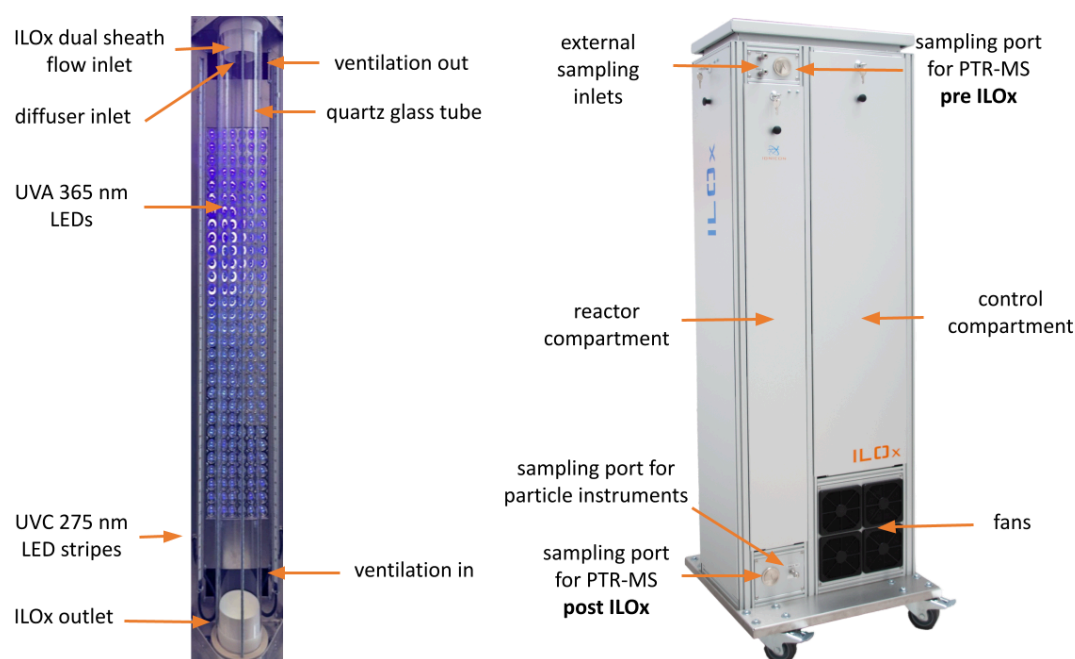


Figure S1: Main components of ILOx. The inside of the reactor compartment is shown on the left, consisting of the quartz-glass reactor, the UVA and UVC LEDs, the ventilation ducts, as well as the sample air inlets and outlets. The whole instrument is depicted on the right with the reactor compartment to the left and the control compartment, including e.g. the control unit, MFCs, the UVA lamp and the UVC 185 nm assembly, to the right. Highlighted are the PTR-MS sampling ports *pre* and *post* ILOx.

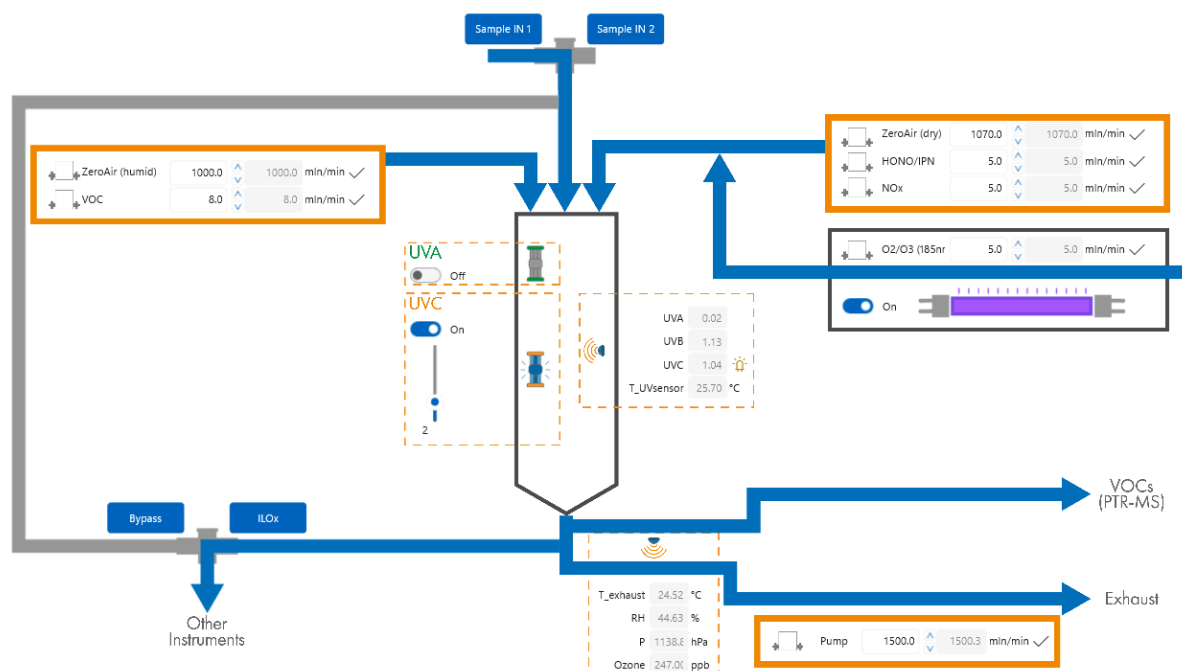


Figure S2: Screenshot of the Visual Interface of the ILOx control software.

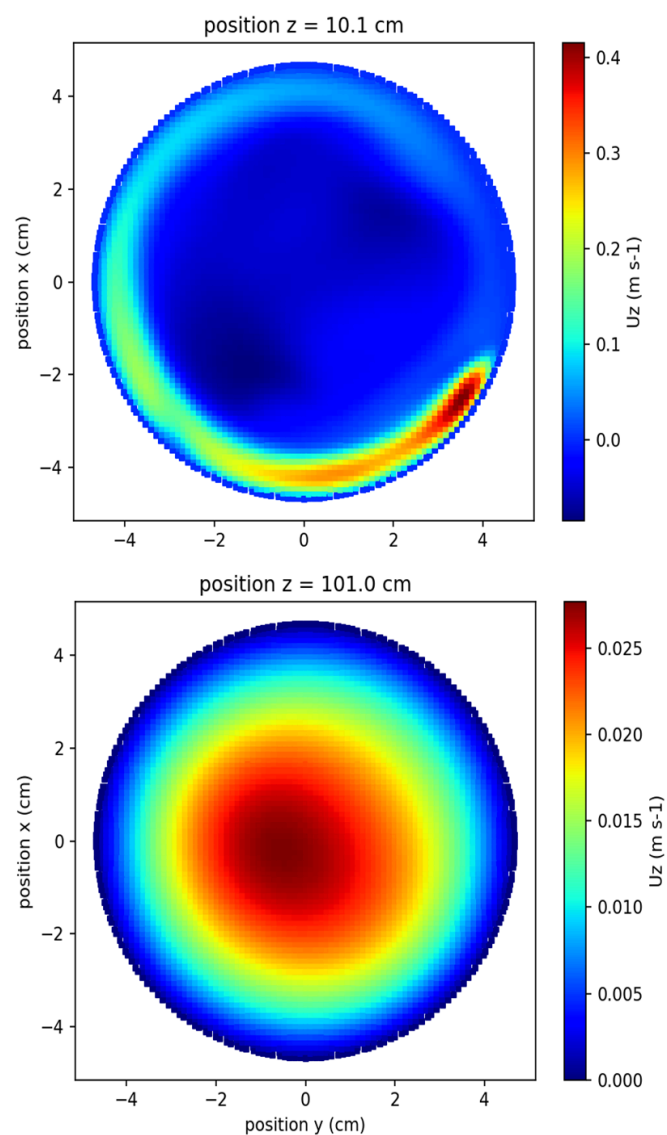


Figure S3: Vertical flow velocities as simulated by 3D Computational Fluid Dynamics (CFD) at the inlet ($z = 10.1$ cm) and towards the end of the laminar flow reactor ($z = 101$ cm).

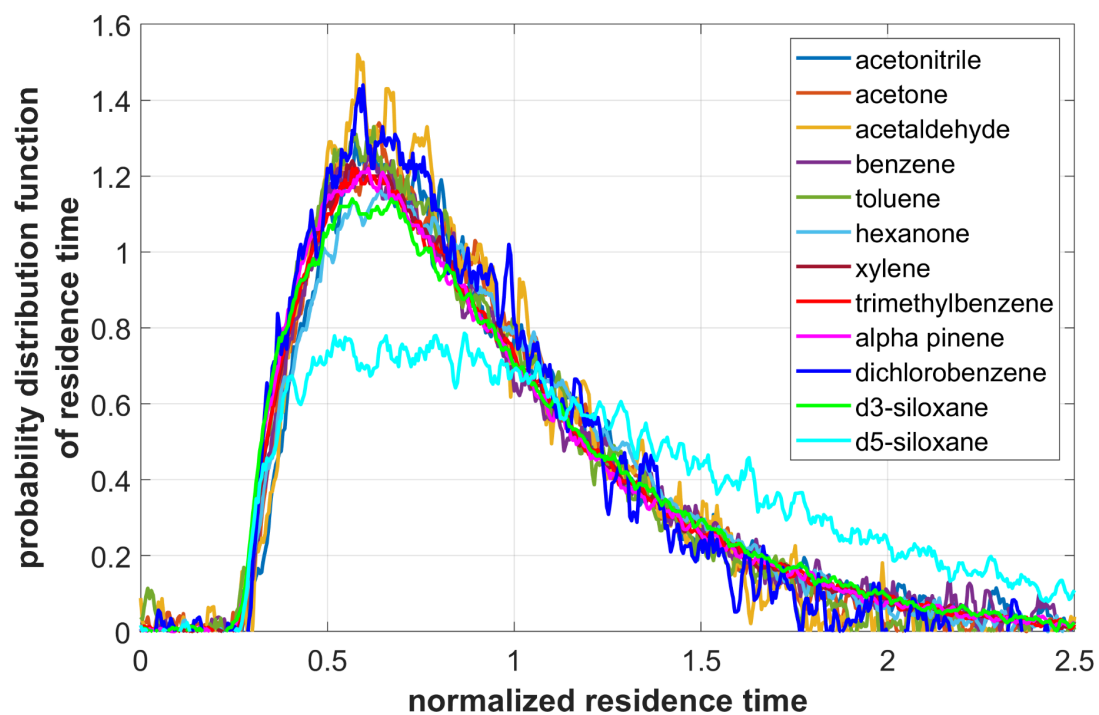


Figure S4: Response to a 5 s step function of a mix of VOC calibration gas standard at 2 l min^{-1} flow through ILOx.

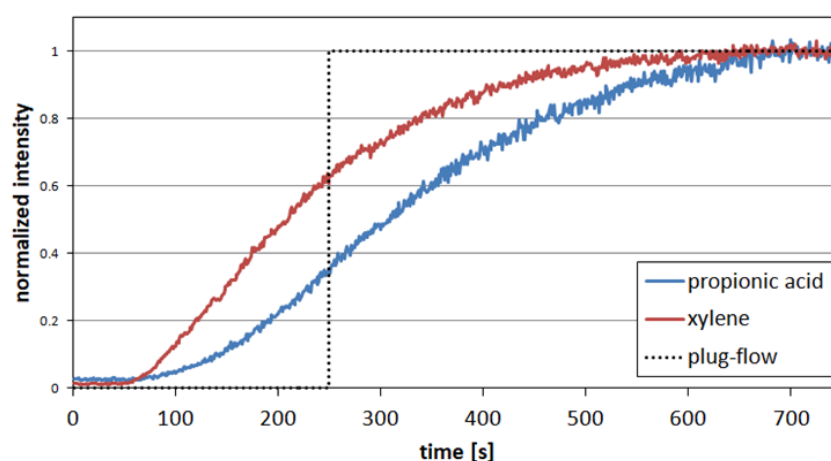


Figure S5: Response of the ILOx Reactor to propionic acid and xylene at 1.5 l min^{-1} carrier flow. The dotted line indicates a theoretical plug-flow response.

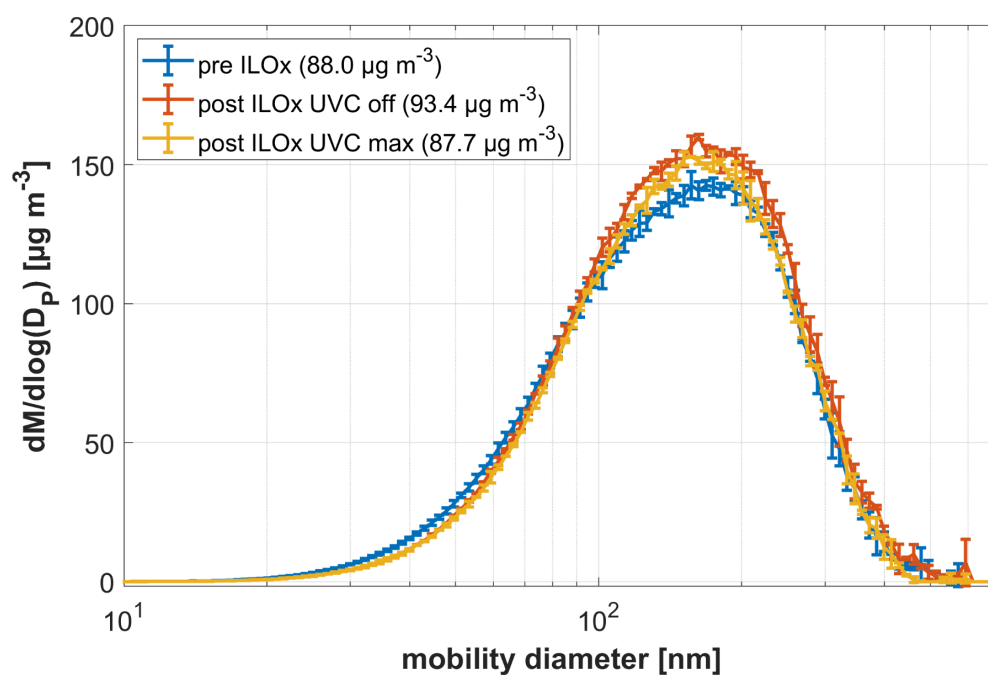


Figure S6: SMPS measurement of dry ammonium sulphate particles pre and post ILOx, with and without UVC 275 nm activated.