The first field intercomparison of chemical ionization mass spectrometers

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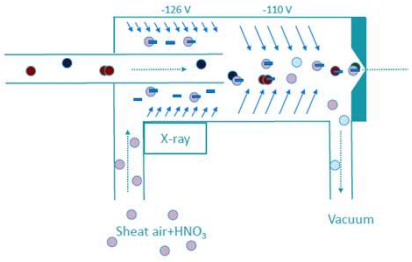
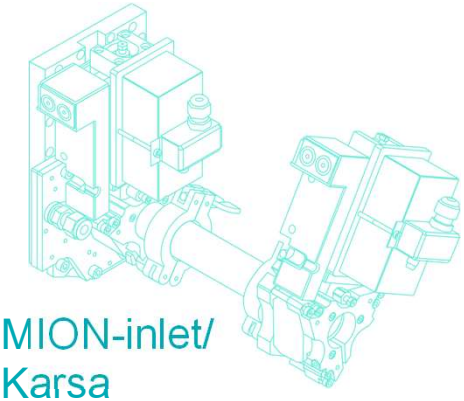
Measurements of condensable vapours

- **Condensable vapours & direct aerosol precursors**: such as sulfuric acid (SA) and highly oxygenated organic molecules (HOM) can be measured with online techniques, such as CI-APi-TOF MS, *chemical ionization atmospheric pressure interface time-of-flight mass spectrometer*



"Eisele-type" inlet/ Aerodyne



MION-inlet/ Karsa

APi-TOF/ Tofwerk

Orbitrap/ Thermo Fisher

Intercomparison campaign 2024

Program:

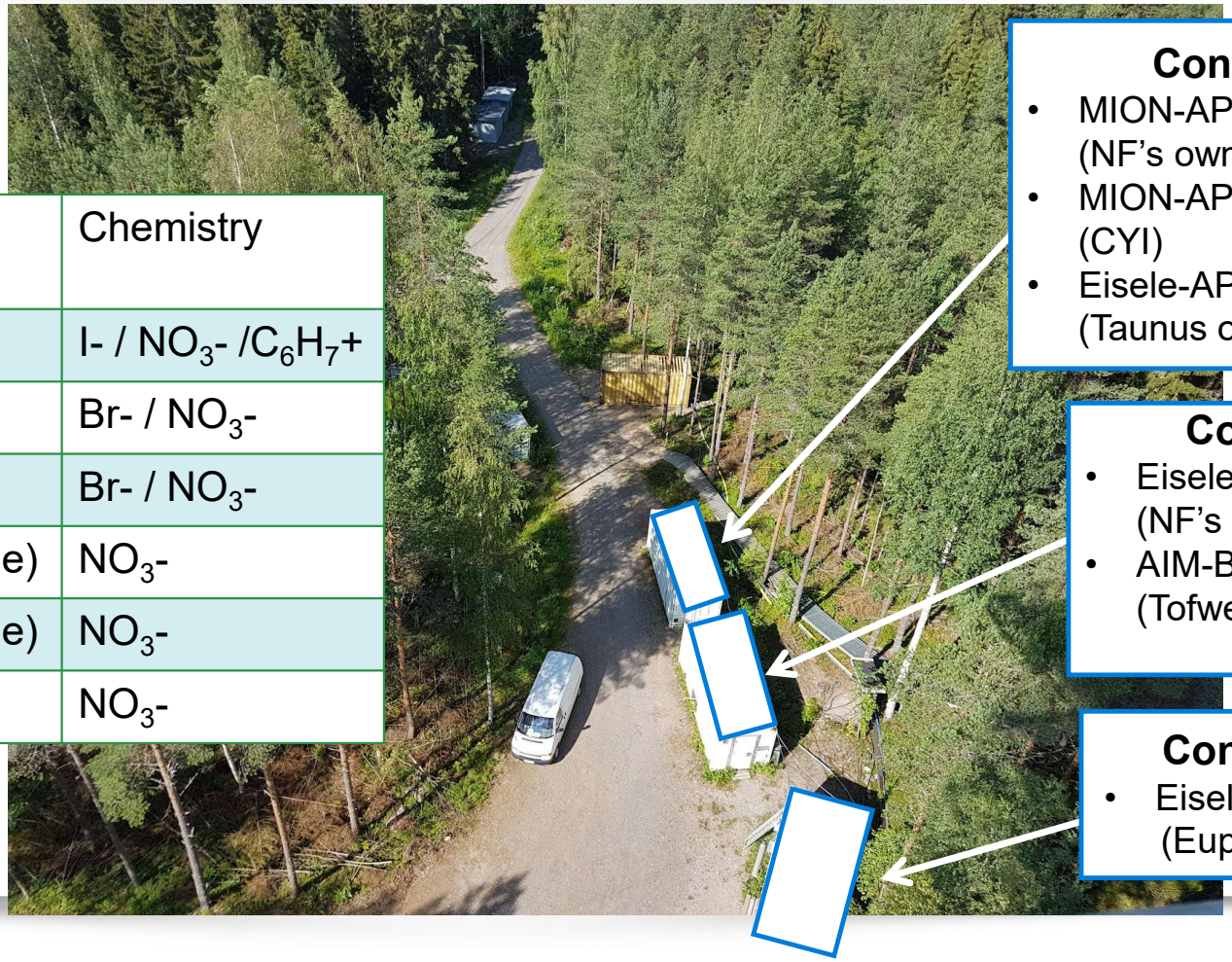
- Ambient measurements (~1 week)
- SA calibrations
- Transmission calibrations with PFAS
- Tutorials and discussions on measurements (2 days)

- 2 weeks in July-August

SMEAR II station in Hyytiälä, Finland (Boreal forest)

Intercomparison campaign 2024

Mass spectrometer	Inlet	Chemistry
B-TOF	AIM (Tofwerk)	I- / NO_3- /C_6H_7+
L-TOF	MION1 (Karsa)	Br- / NO_3-
L-TOF	MION2 (Karsa)	Br- / NO_3-
L-TOF	Eisele (Aerodyne)	NO_3-
H-TOF	Eisele (Aerodyne)	NO_3-
H-TOF	Eisele (UHEL)	NO_3-



Container 1
- MION-APi-L-TOF (NF's own instrument)
- MION-APi-L-TOF (CYI)
- Eisele-APi-L-TOF (Taunus observatory)

Container 2
- Eisele-APi-H-TOF (NF's own instrument)
- AIM-B-TOF (Tofwerk)

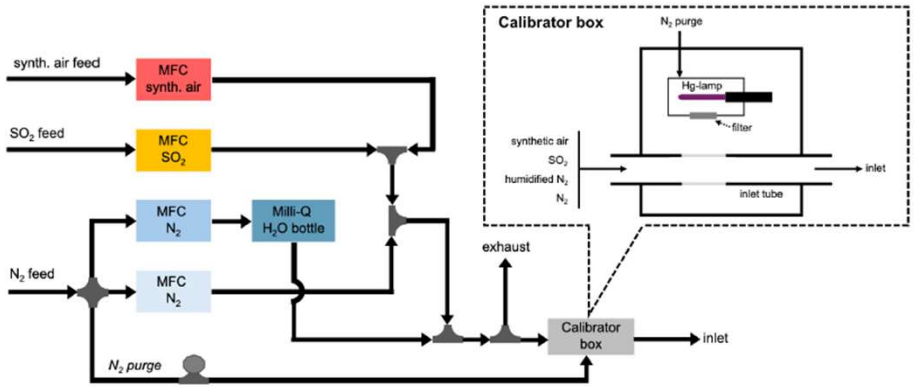
Container 3
- Eisele-APi-H-TOF (Euphore-CEAM)

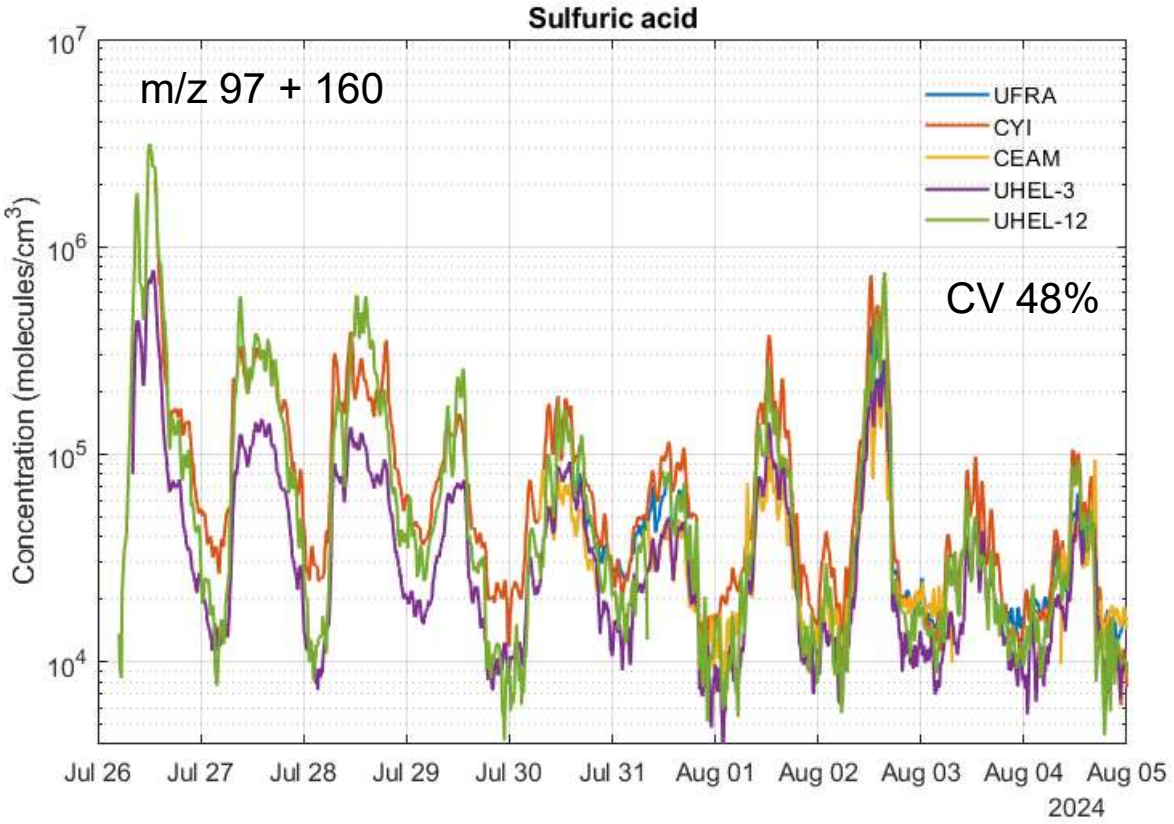
Agreed target compounds

- Inorganic acids: sulfuric acid H_2SO_4, methanesulfonic acid CH_4SO_3, iodic acid HIO_3
- Malonic acid $C_3H_4O_4$, nitrophenol $C_6H_5NO_3$
- Organic peroxy radicals: $C_{10}H_{\mathbf{15}}O_{4,6,8,10...}$ ($C_{10}H_{\mathbf{17}}O_{3,5,7}$, $C_{10}H_{\mathbf{16}}NO_{5,...}$)
  - Nitrate CIMS: O_8 and O_{10}, 325 and 357
- Closed shell non-nitrate monomers: $C_{10}H_{\mathbf{14/16(/18)}}O_{3\text{-}12}$
  - Nitrate CIMS: starting from O_7, **308**, **310**, 324, 326, **340**, **342**, 356, 358, **372**, 374
- Closed shell organonitrate monomers: $C_{10}H_{\mathbf{15}}O_{2\text{-}8}NO_3$
  - Nitrate CIMS: $O_{5,6,8}$, 339, 355, 387
- Dimers: $C_{20}H_{30}O_{6\text{-}18}$, $C_{19}H_{28}O_{5\text{-}13}{}^{*}$, $C_{20}H_{32}O_{5\text{-}15}$, $C_{20}H_{34}O_{4\text{-}12}$, $C_{20}H_{31}O_{7\text{-}15}NO_3$
  - Nitrate CIMS: 524, 556, 588, 620, 494, 510, 542, 574, 555

Sulfuric acid

Calibrations done to each instrument with the same setup (producing sulfuric acid from SO_2)





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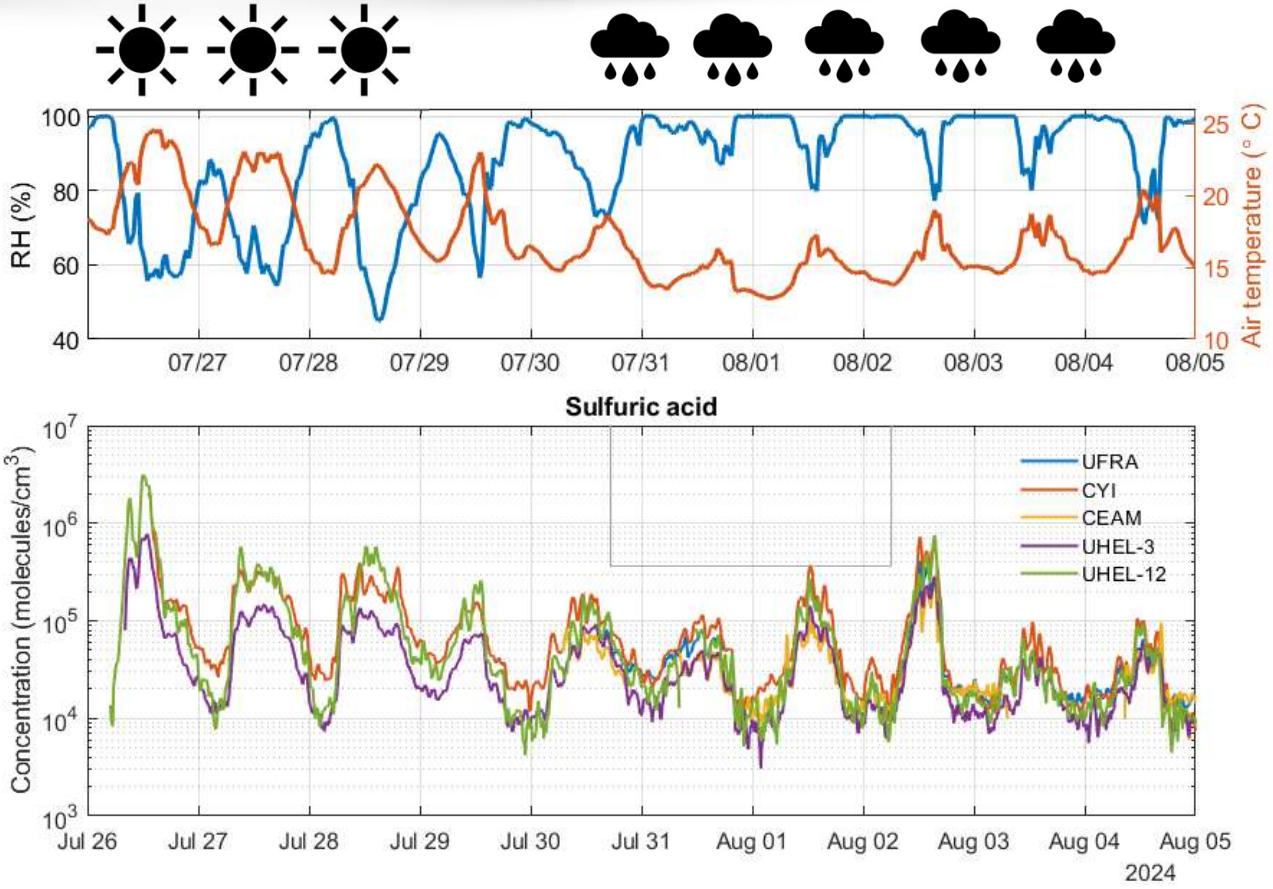
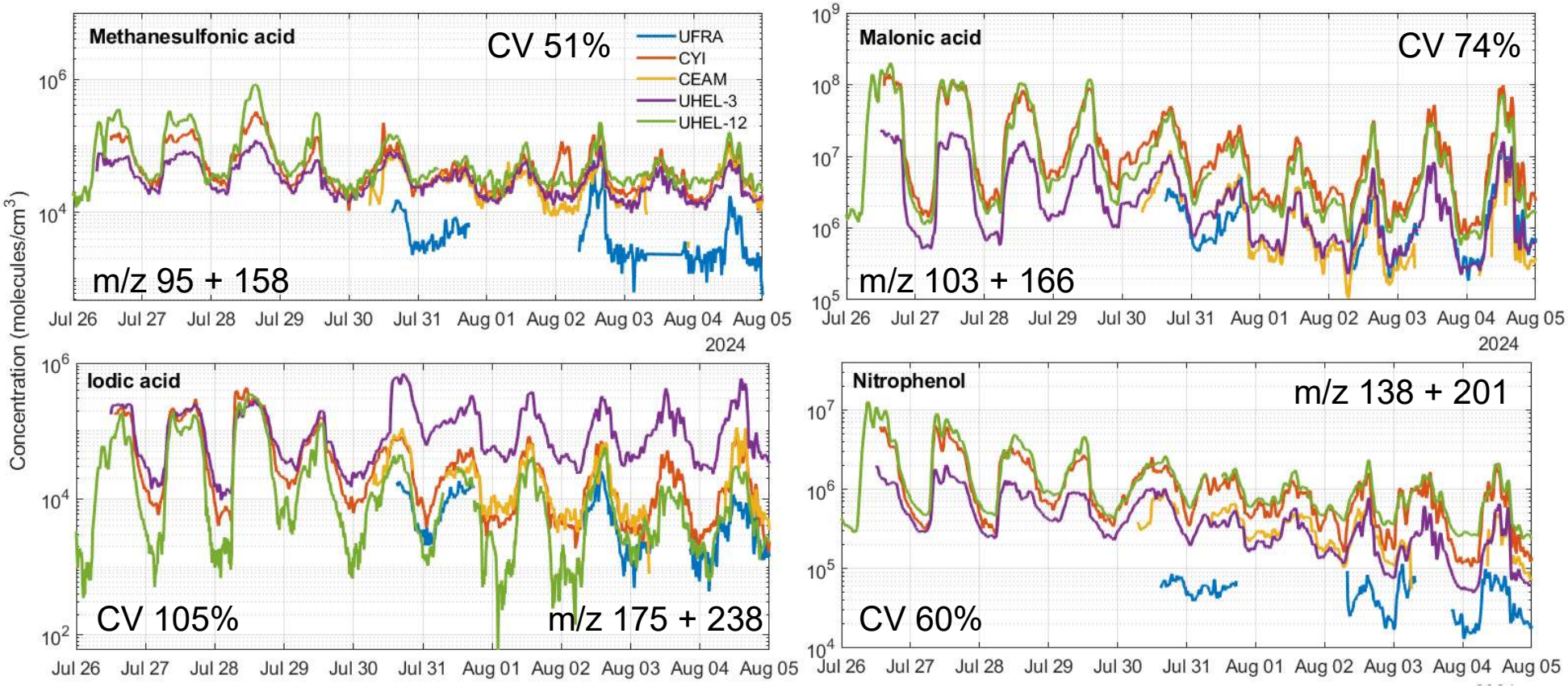


Different sensitivities towards small acids

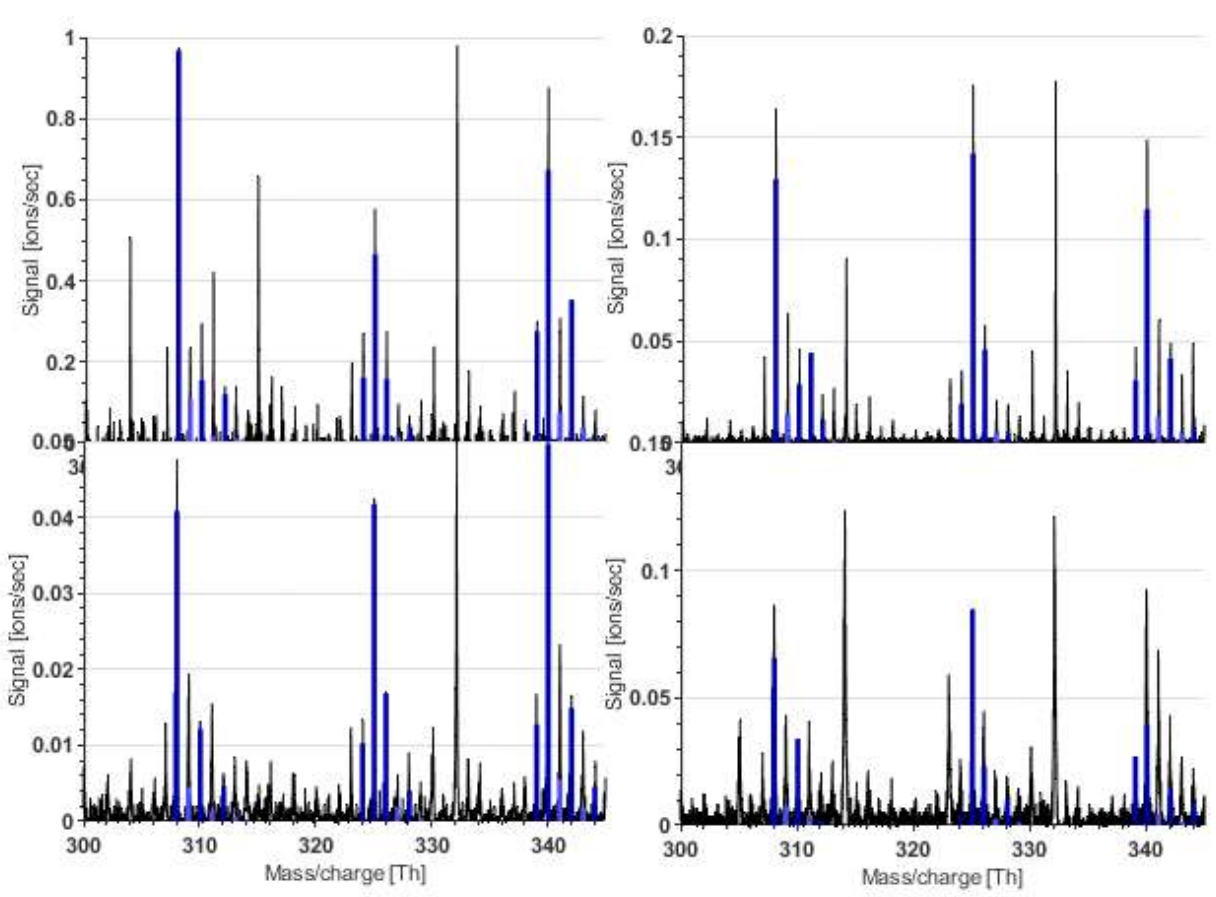
Concentration calculated with SA calibration coefficient



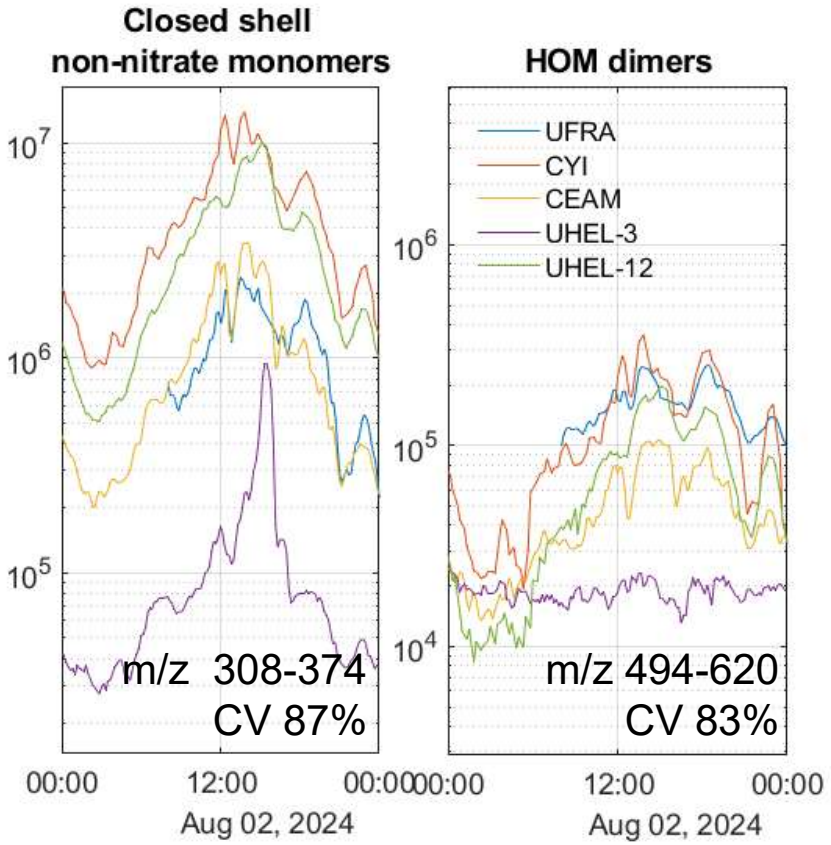
Highly oxidized organic molecules

MION-
L-TOF:

Eisele-
H-TOF:

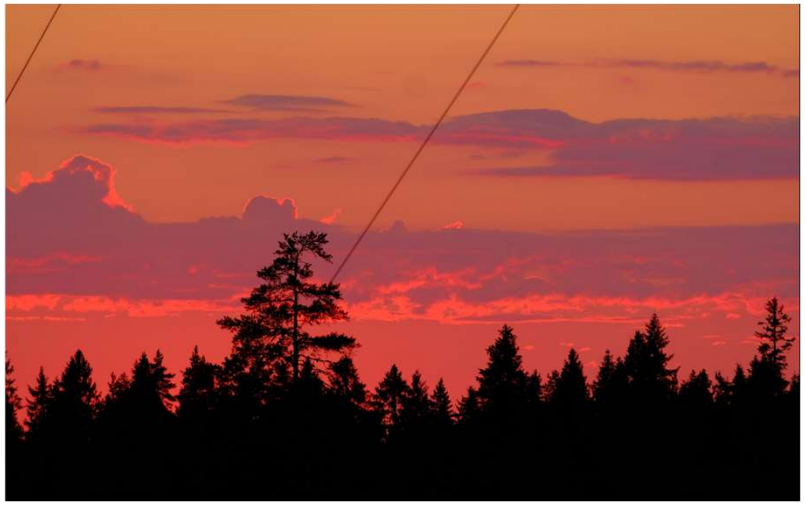


Next tasks with the analysis



This campaign data:

- Transmission calibration (to this data set)
- AIM data (with Tofwerk)



Current work of CiGas-UHEL

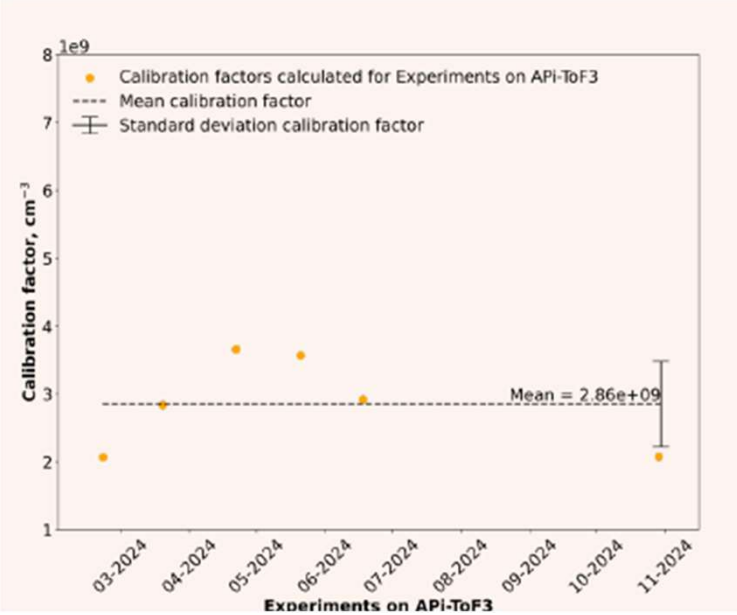
Laboratory and field studies on SA calibration

→ measurement guidelines

Next:

- Calibration studies for other compounds (a lot to do!)
- Tuning studies -> instead of reference instrument finding a “reference” tuning

Monthly calibration experiments on two additional instruments at SMEAR II yielded calibration factors with uncertainties of 24% and 27%.



Thanks for all the participants!

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