Extractive Electrospray Ionization Mass Spectrometry (EESI-MS) and AMS Measurements of Biomass Burning Organic Aerosol

AMS Users' Meeting
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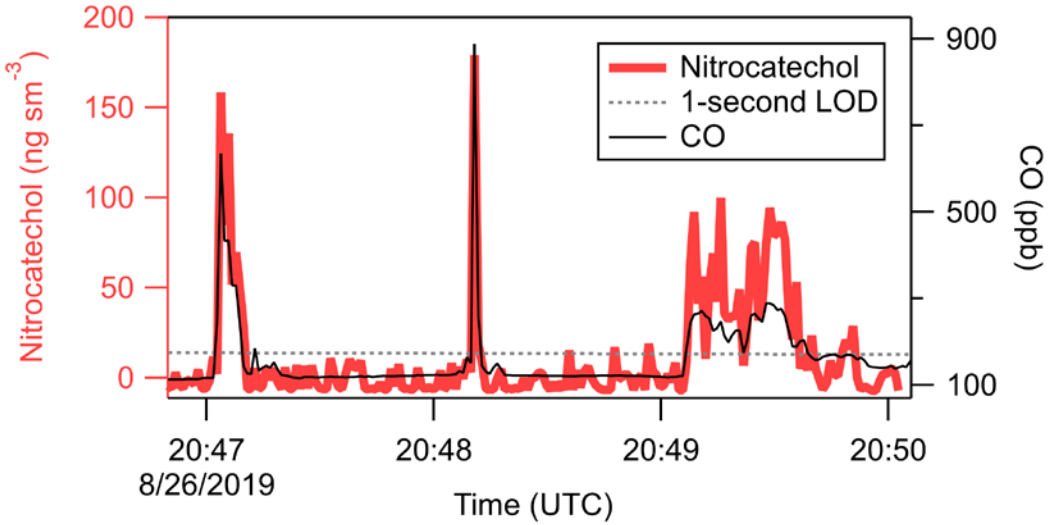
D. Pagonis, P. Campuzano-Jost, H. Guo, D. Day, M. Schueneman, W. Brown, B. Nault, H. Stark, K. Siemens, A. Laskin, F. Piel, L. Tomsche, T. Mikoviny, A. Wisthaler, M. Coggon, J. DiGangi, G. Diskin, G. Gkatzelis, H. Halliday, J. Krechmer, J. Nowak, D. Thomson, C. Warneke, and J. L. Jimenez

- Introduce EESI-MS
- Airborne Deployment FIREX-AQ
- Complementary to AMS

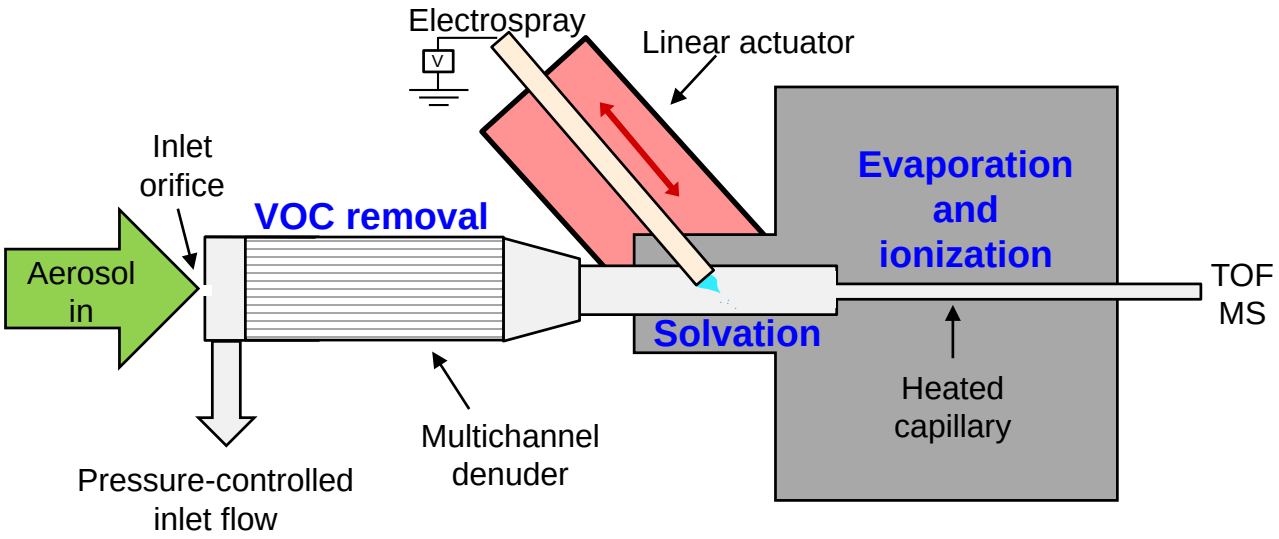
Extractive Electrospray Ionization Time-of-Flight Mass Spectrometry



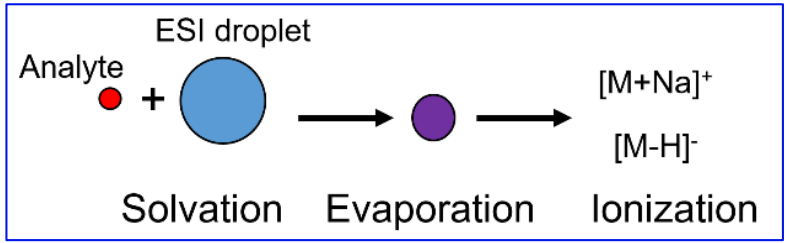
- Quantitative 1 Hz measurements of individual components of organic aerosol
- 1 Hz detection limits of ng sm^{-3}
- Highly complementary to AMS

sm^{-3} = standard conditions: 273.15 K; 1013 mbar

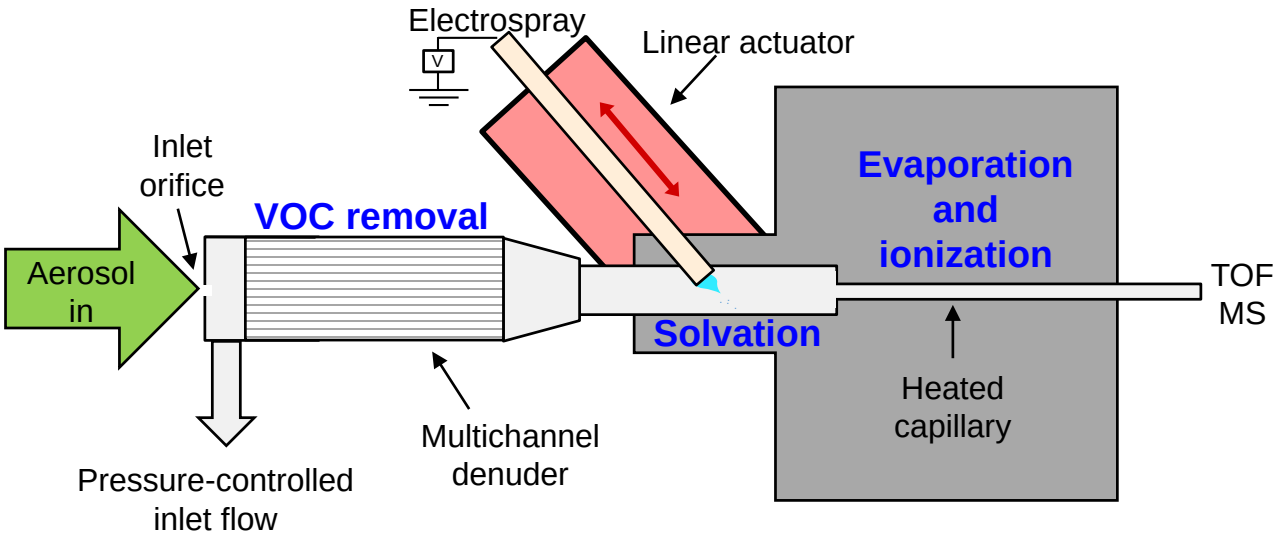
Extractive Electrospray Time-of-Flight Mass Spectrometry



- Strip out VOCs to prevent SESI
- Flow particles through the electrospray
- ESI drops evaporate, ionize, then enter API-ToF



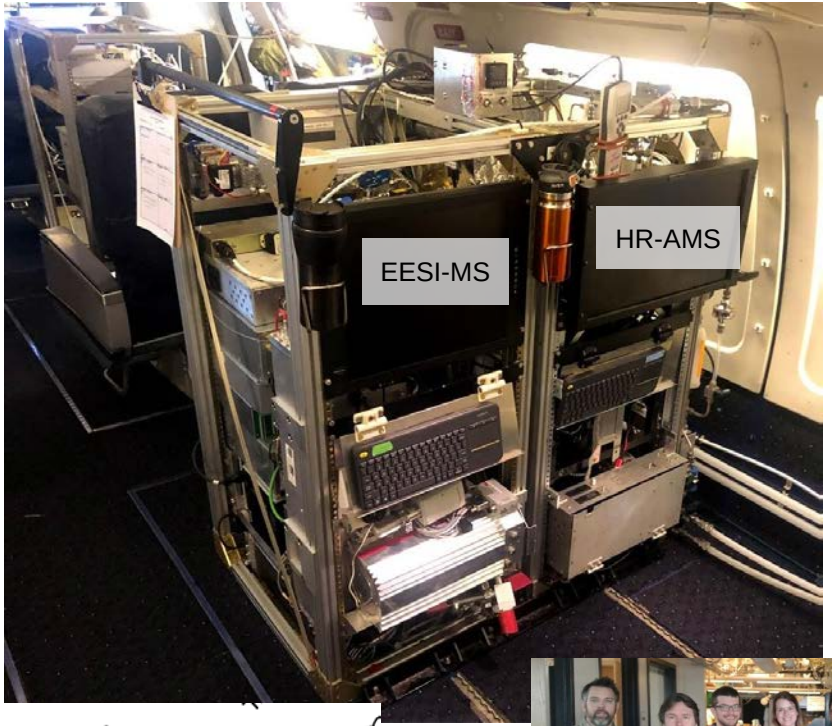
Extractive Electrospray Time-of-Flight Mass Spectrometry

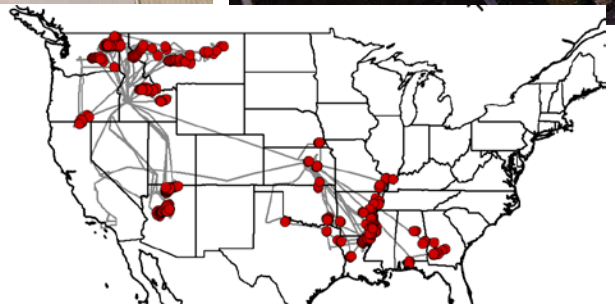


- Optimization of electrospray working solution
- Precise control of electrospray position
- Pressure control within ±1 mbar
- Flight-day and in-flight calibrations with AMS
- Pagonis et al. *AMT* 2021, In press

FIREX-AQ

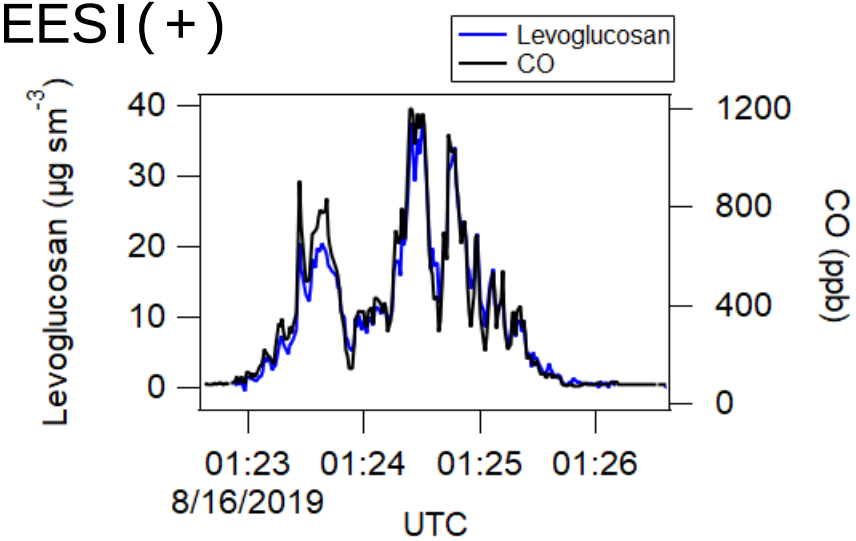
- Summer 2019
- 21 research flights
- Deployed EESI-MS and HR-AMS



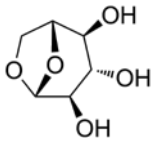


Targeted analysis at FIREX-AQ

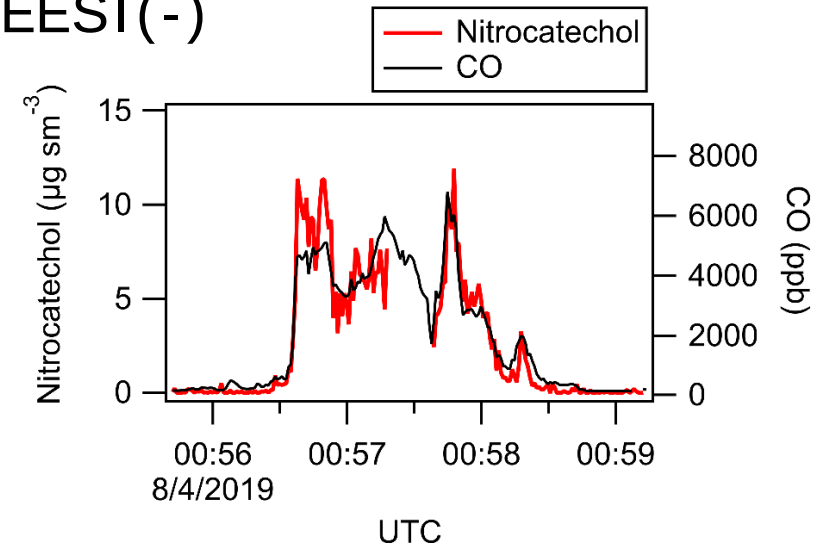
EESI(+)



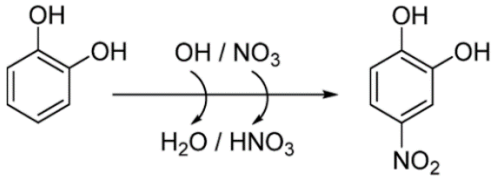
- $C_6H_{10}O_5Na^+$ calibrated as levoglucosan
- Primary emission from cellulose pyrolysis
- LC-MS confirmation of peak assignments



EESI(-)

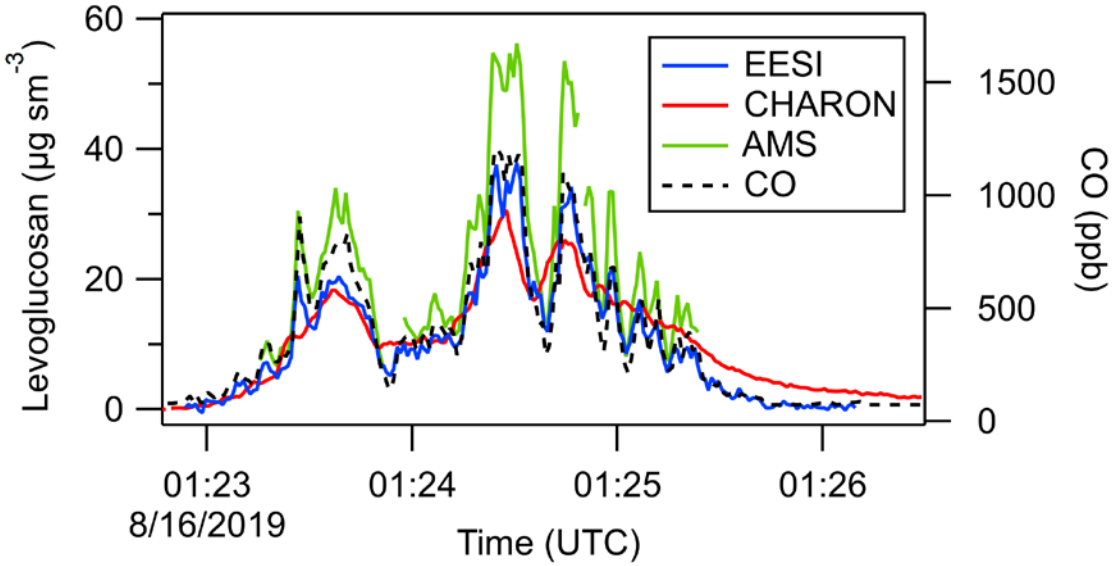


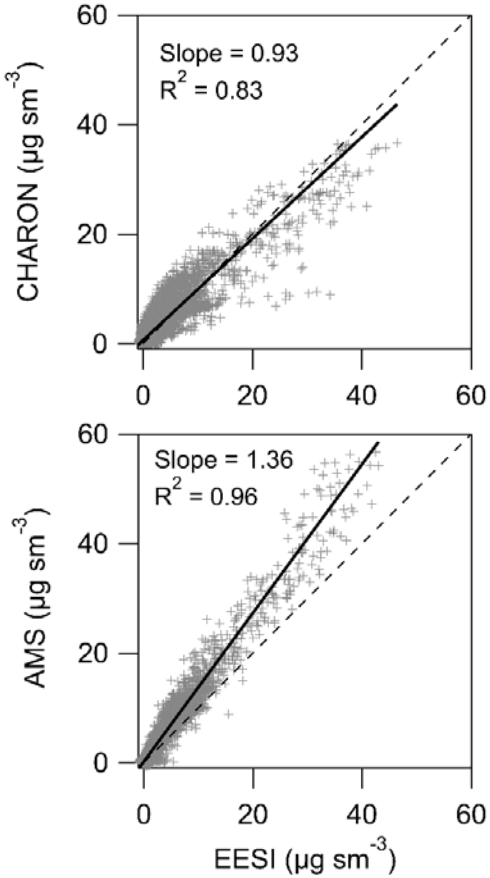
- $C_6H_4NO_4^-$ calibrated as 4-nitrocatechol



Finewax et al., *ES&T 2018*

CHARON–EESI–AMS Intercomparison



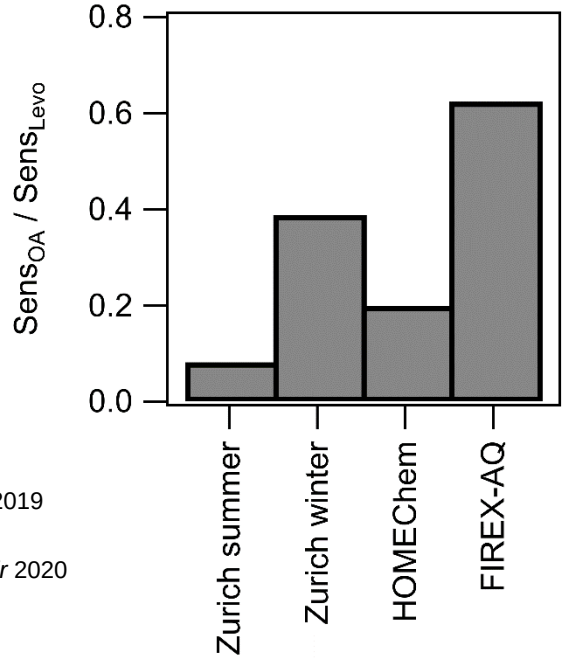


- Flew EESI(+) alongside CHARON for one flight
- Compared levoglucosan measured by EESI, CHARON, and AMS
- AMS equivalent levoglucosan calculated from $f_{C2H4O2+}$ calibrated with levoglucosan standards

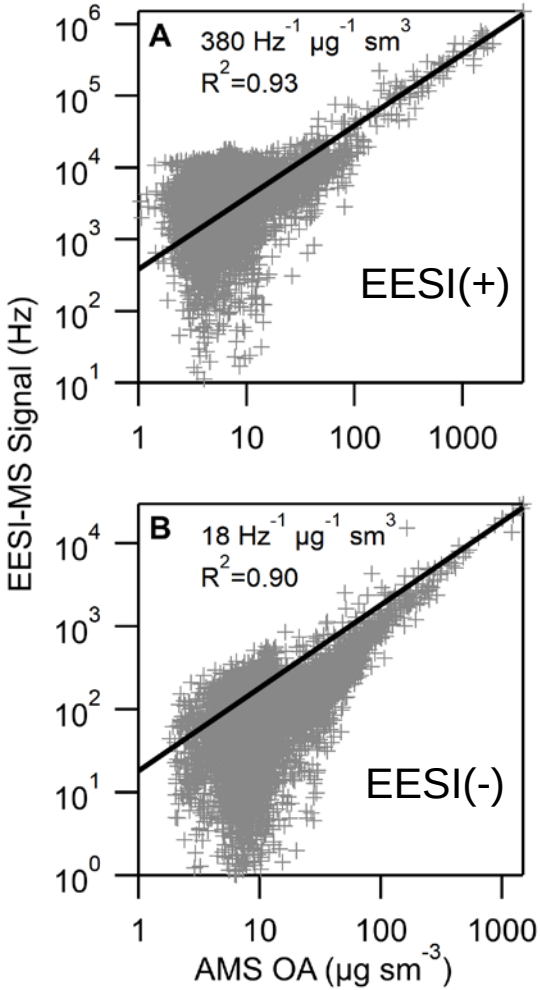
Bulk OA Sensitivity

- Total EESI-MS signal correlates well with AMS OA
- Normalize to levoglucosan sensitivity to compare across campaigns

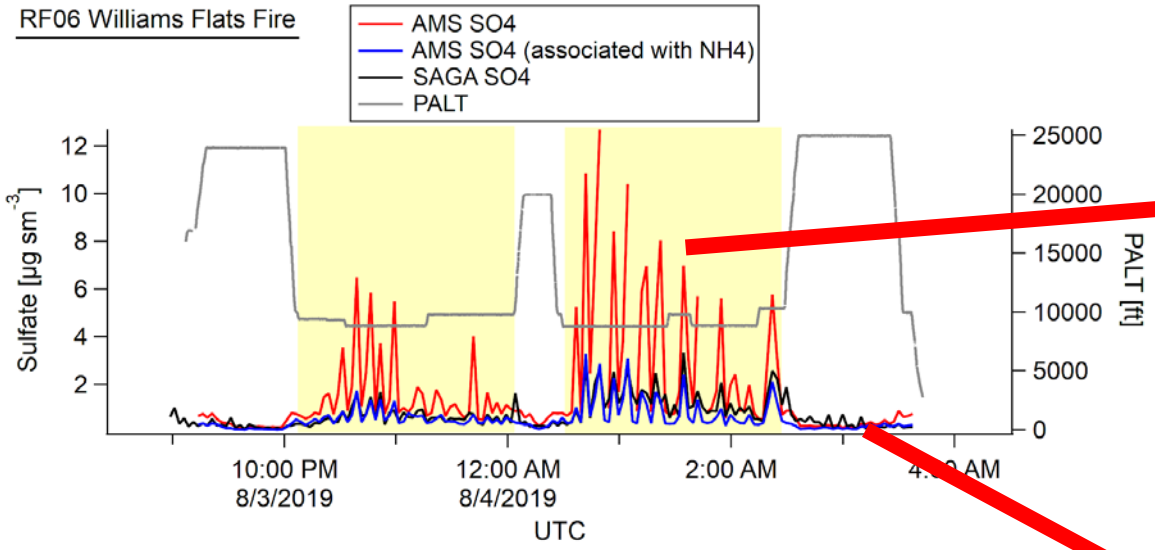
- Bulk EESI-MS sensitivity varies with OA composition
- Published studies are blind to HOA, highly sensitive to BBOA
- Future work planned using different EESI solvents

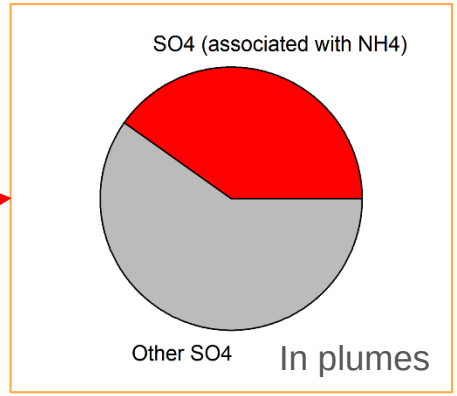


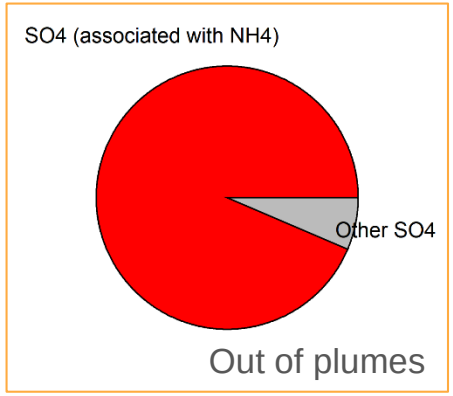
Stefenelli et al. ACP 2019
Qi et al. *ACP* 2019
Brown et al. *Indoor Air* 2020



Organosulfur emissions at FIREX-AQ



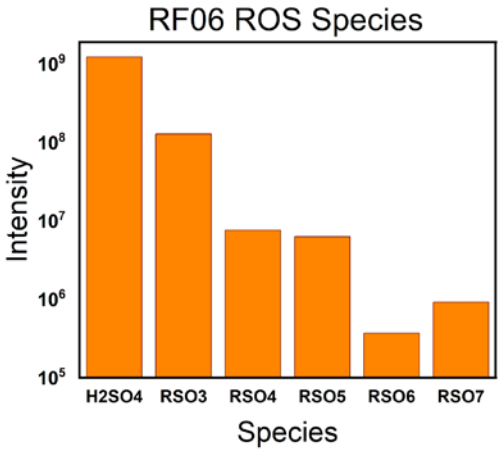


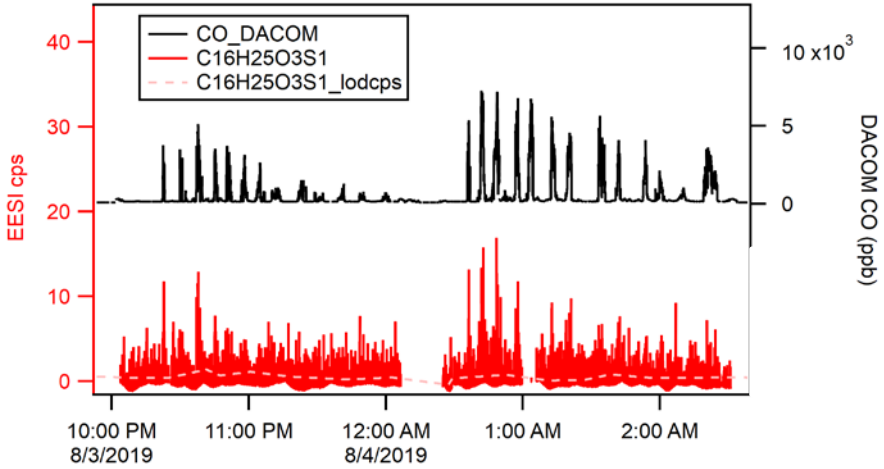


- Discrepancy between AMS sulfate and sulfate on SAGA filters
- AMS SO_4 > SAGA SO_4
- Evidence pointing towards organosulfur

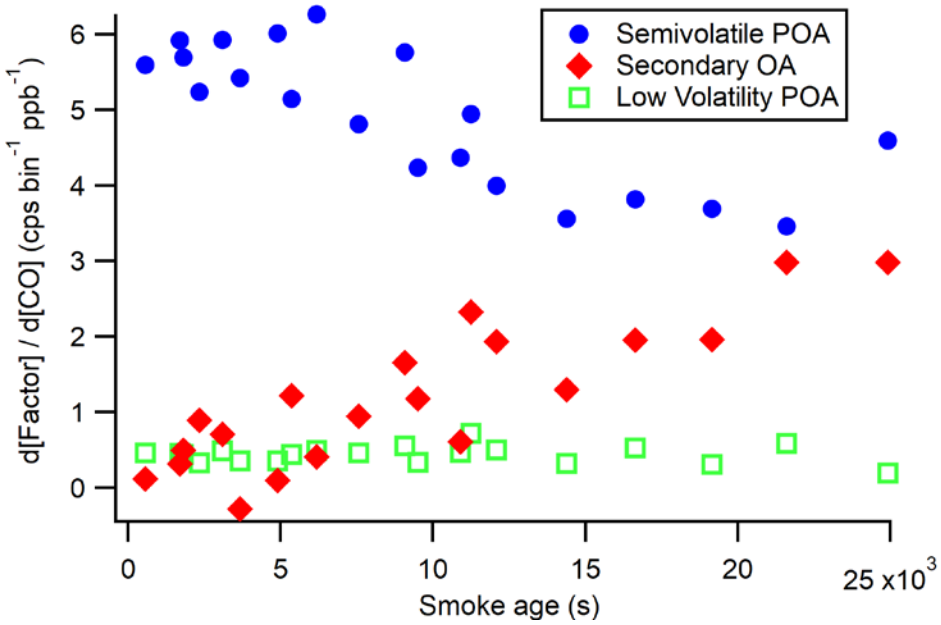
Support from filter samples and EESI-MS

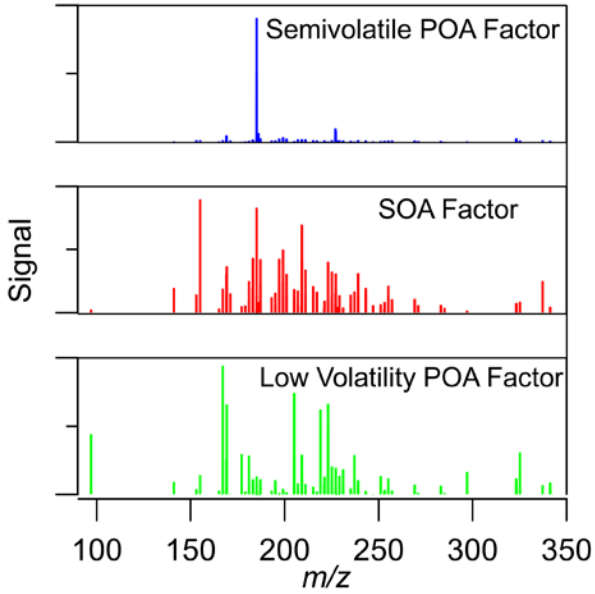
- Collected filter samples throughout FIREX-AQ
- Collaboration with Alex Laskin at Purdue, HPLC-ESI-OrbitrapMS
- Identify abundant sulfonates (RSO_3)





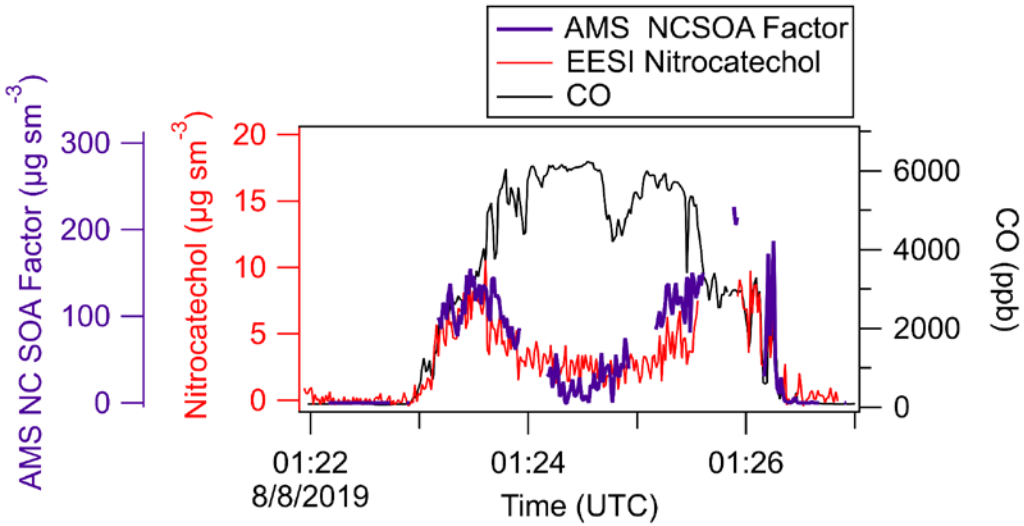
EESI-MS PMF Analysis

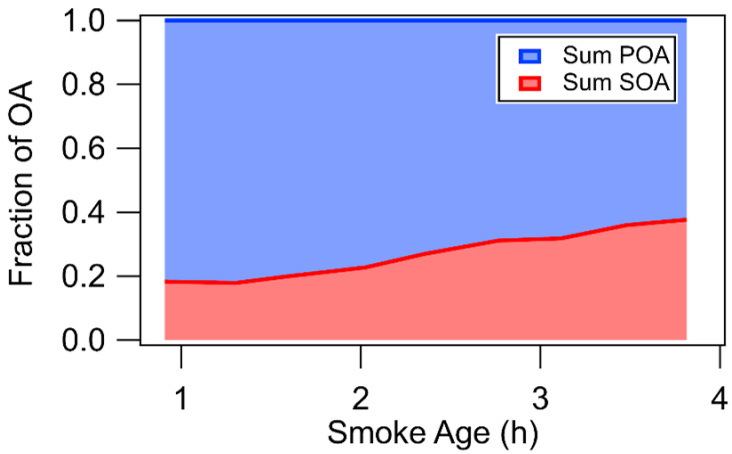




- Balance between SOA formation and POA loss in EESI-MS PMF

Connecting EESI-MS Tracers to AMS Factors

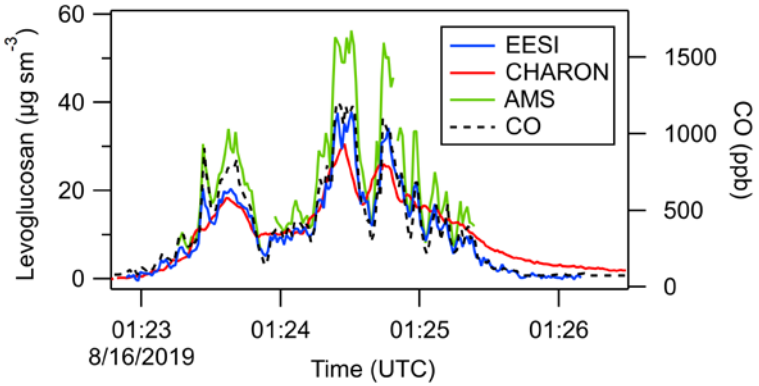




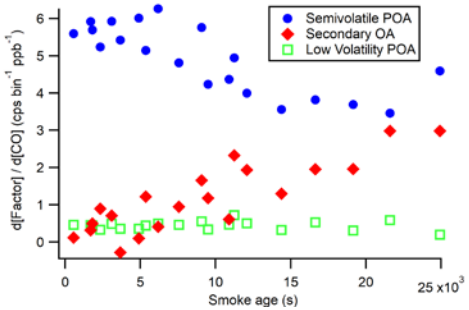
- Unique cross-plume gradients match EESI-MS nitrocatechol to an AMS factor
- Can quantify the contribution of this chemical process (oxidation of phenols) to SOA production
- EESI-MS gives a level of chemical specificity that is not accessible by AMS alone

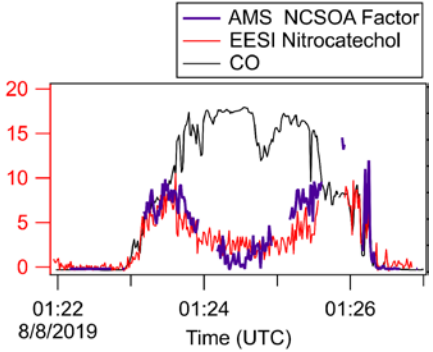
FIREX-AQ Deployment

Intercomparison of EESI-MS, AMS, CHARON PTR-MS



Chemical Specificity in PMF Analysis





Molecular composition