Fast Airborne Extractive Electrospray Mass Spectrometry (EESI) Measurements of the Chemical Composition of Biomass Burning Organic Aerosol

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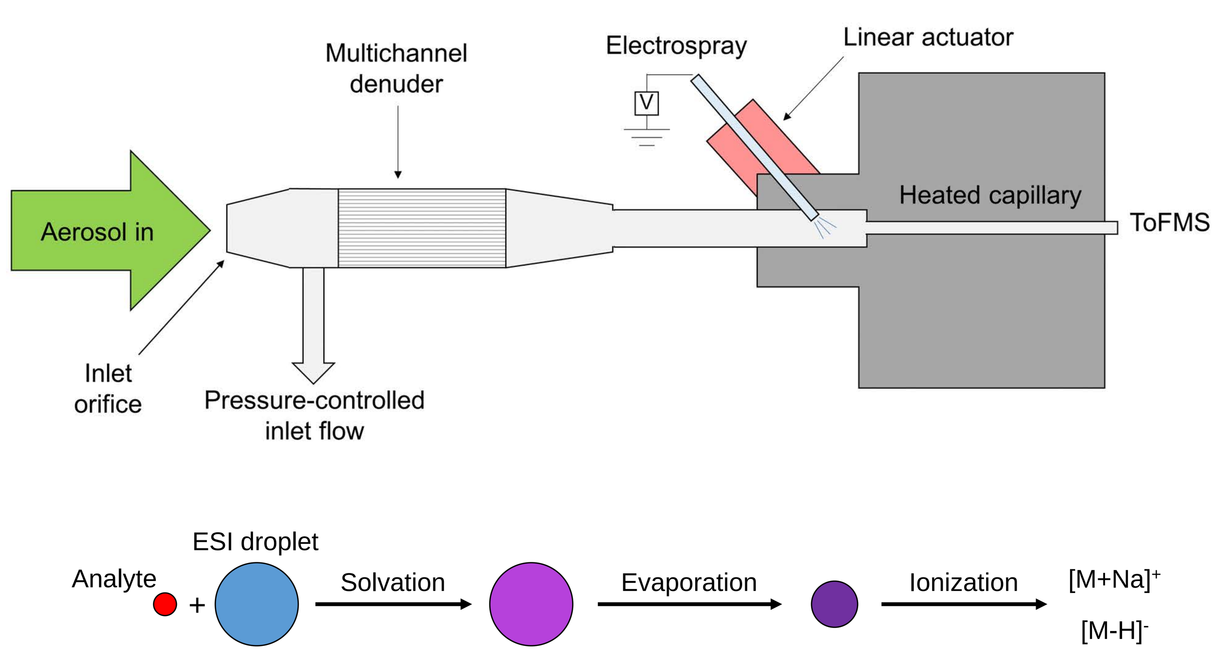
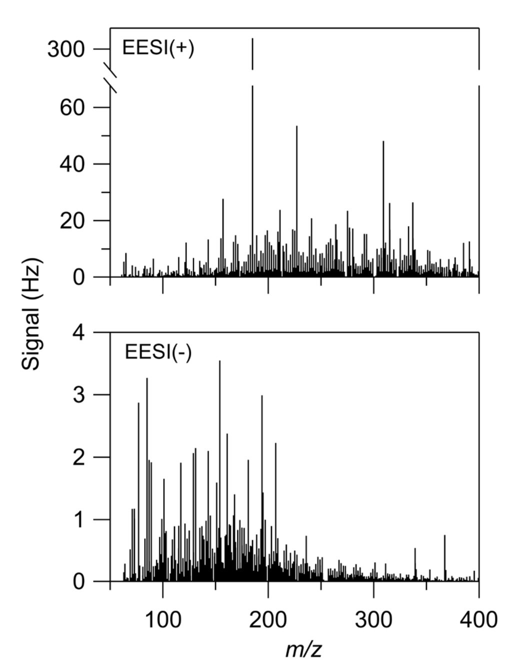
Principle of Operation



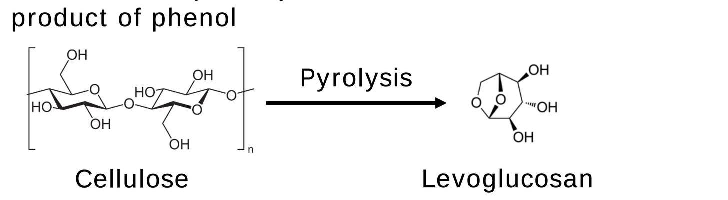
- Aerosol is sampled into pressure controlled inlet
- Gas-phase organics are removed by the activated carbon denuder
- Aerosol is dissolved in electrospray droplets and then ionized as the droplet evaporates inside the heated capillary
- EESI was operated with both positive (+) and negative (-) ion polarities during FIREX-AQ
- Electrospray working solution of 3:1 methanol:water
- EESI(+) electrospray solution is doped with sodium iodide and analytes are detected as adducts with sodium $[M+Na]^+$
- EESI(-) solution is doped with formic acid and analytes are deprotonated and detected as $[M-H]^-$
- Example EESI(+) and EESI(-) spectra are shown. Spectra correspond to 50 μg sm^{-3} of organic aerosol

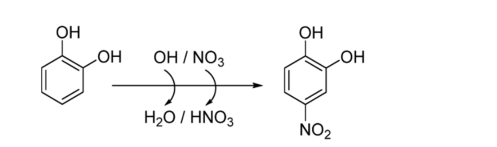


Lopez-Hilfiker et al. 2019, *AMT* 12, 4867-4886

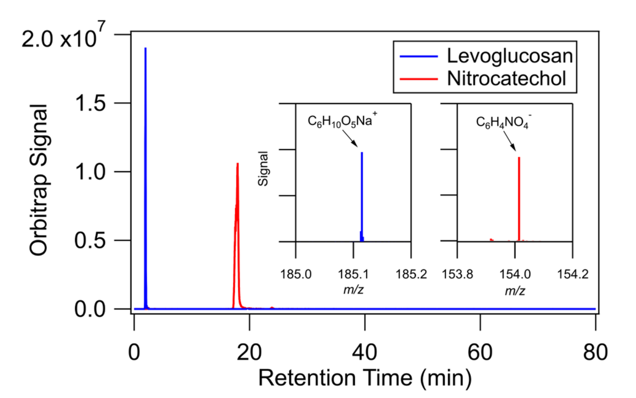
Quantified Organic Aerosol Components

- EESI(+): Aerosol $C_6H_{10}O_5Na^+$ as levoglucosan
  Aerosol $C_6H_5NO_4Na^+$ as nitrocatechol
- EESI(-): Aerosol $C_6H_4NO_4^-$ as nitrocatechol
- Levoglucosan (and isomers mannosan and galactosan) are a primary wildfire emissions from the pyrolysis of cellulose
- Nitrocatechol is the primary oxidation product of catechol (Finewax et al. 2018). Catechol is a primary emission from wildfires and is also an oxidation product of phenol





- Filter samples collected at FIREX-AQ were analyzed with HPLC coupled to electrospray ionization and orbitrap mass spectrometry (resolving power m/Δm = 100,000, Lin et al. 2018)
- Nitrocatechol and levoglucosan standards were analyzed to confirm that all signal for $C_6H_4NO_4^-$ and $C_6H_{10}O_5Na^+$ in FIREX-AQ filters (chromatograms below) is attributed to nitrocatechol and levoglucosan



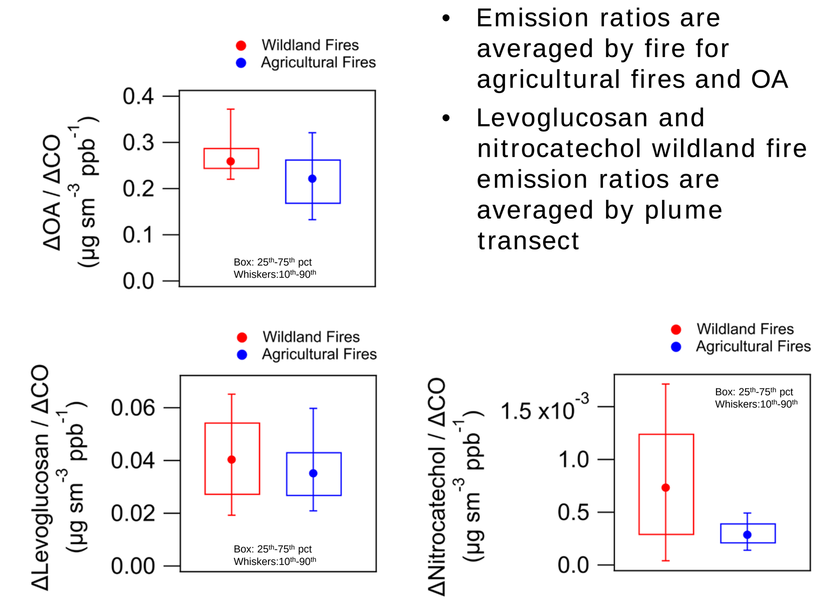
Finewax et al. 2018, *ES&T* 52, 1981-1989
Lin et al. 2018, *Anal. Chem.* 90, 12493-12502

FIREX-AQ Emission Ratios

Williams Flats fire
August 7th, 2019

Agricultural fire in Louisiana, August 26th, 2019

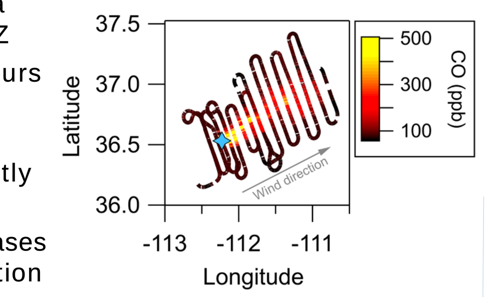
- Organic aerosol emission factors were higher for wildland fires
- Levoglucosan emission factors consistent across fire types
- Nitrocatechol emission factors are lower for agricultural fires because the smoke was typically sampled 300 m above the source (photo above), with very little time for catechol oxidation to occur. Indicates that downwind nitrocatechol concentrations are controlled by plume aging instead of emission ratios

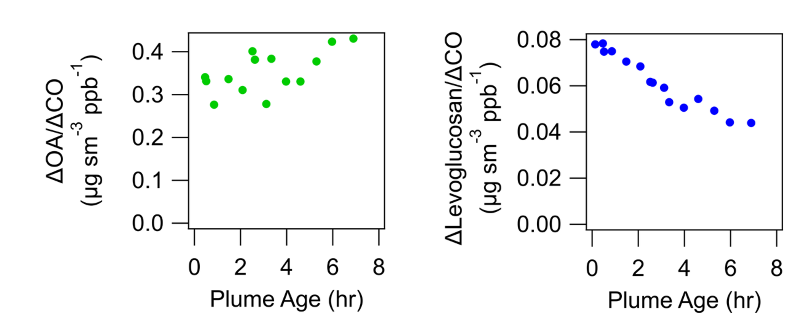


- Emission ratios are averaged by fire for agricultural fires and OA
- Levoglucosan and nitrocatechol wildland fire emission ratios are averaged by plume transect

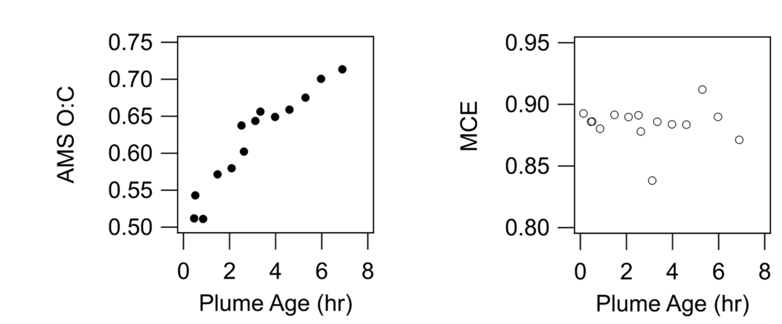
Smoke Aerosol Aging

- Using August 12th flight as a case study — Castle Fire, AZ
- Followed the plume for 7 hours of aging
- Dilution-corrected organic aerosol (OA) increases slightly as smoke travels downwind
- Aerosol levoglucosan decreases with plume age, due to dilution and gas-phase oxidation



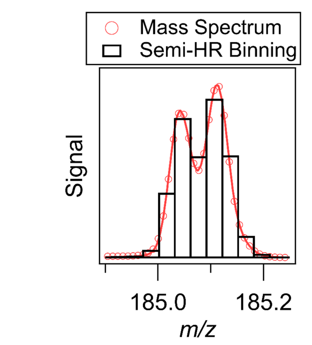


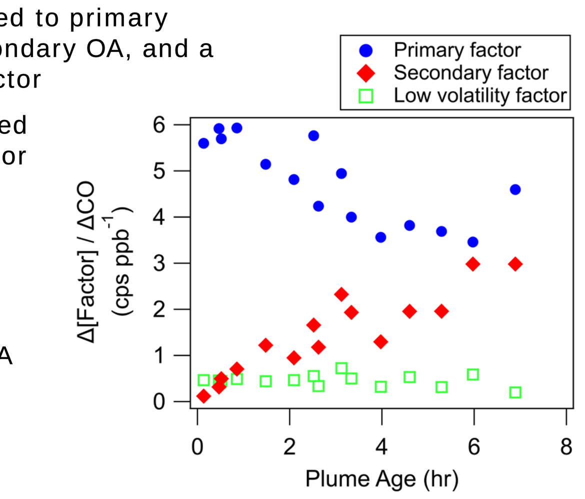
- Organic aerosol O:C measured by AMS increases significantly as the plume ages, indicating oxidation of OA
- BinPMF analysis shown at right indicates significant formation of secondary OA

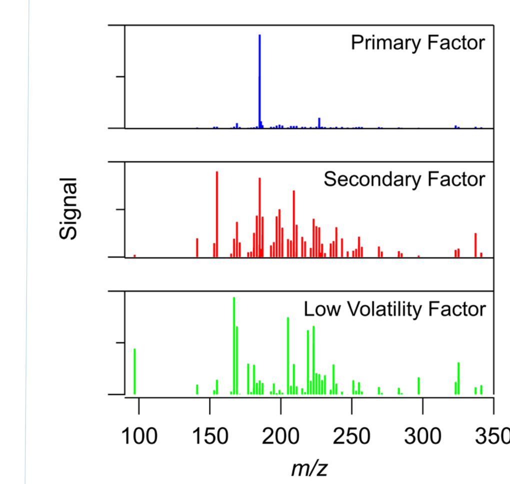


- No trend in fire MCE across each transect
- Indicates that fire phase wasn't driving the trends in aerosol composition shown above

- EESI mass spectra analyzed with binned positive matrix factorization, binPMF (Zhang et al. 2019)
- Five factor solution separated OA signal from spray variability
- Three factors were smoke OA, two factors were spray variability
- Factors attributed to primary smoke OA, secondary OA, and a low volatility factor
- Dilution-corrected primary OA factor decreases with plume age
- Secondary OA factor increases with plume age
- Low volatility OA factor signal is constant when corrected for dilution



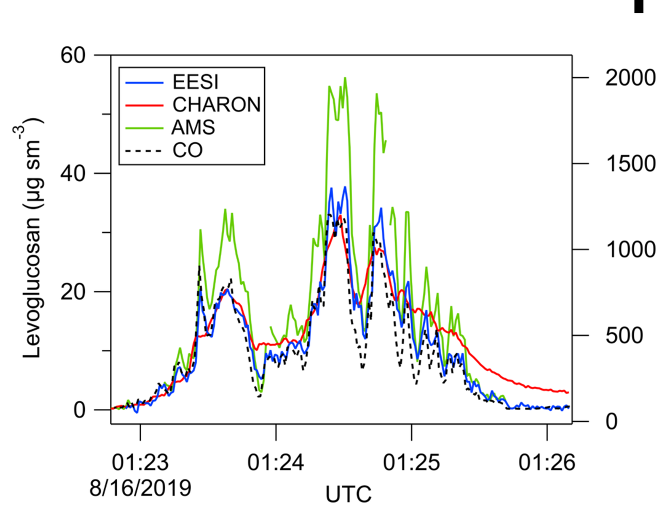


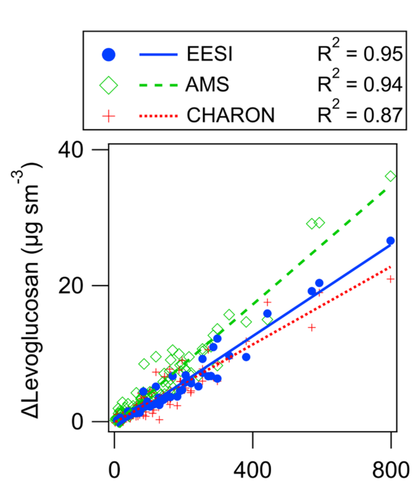


- Primary OA factor is dominated by levoglucosan
- Nitrocatechol is only a minor component of the secondary OA factor
- Identification of components in secondary OA factor is ongoing, along with box modeling of plume chemistry

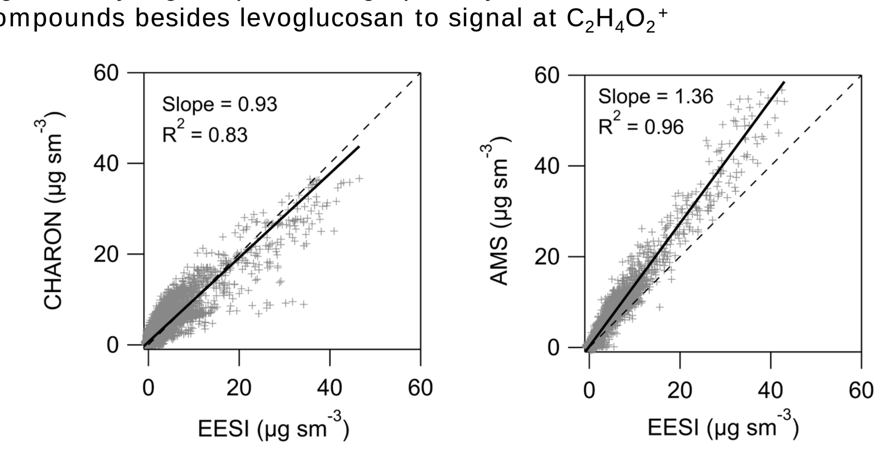
Zhang et al. 2019 *AMT*, 12, 3761–3776

EESI, CHARON, AMS Intercomparison



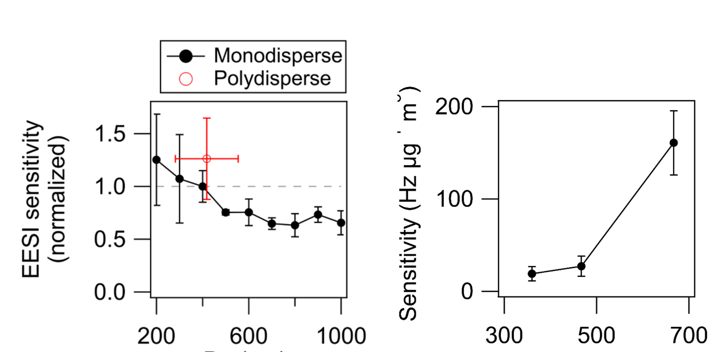


- A CHARON PTR-MS (chemical analysis of aerosol online proton transfer reaction mass spectrometer, Eichler et al. 2015, Piel et al. 2019) was flown with EESI during the August 12th research flight. CHARON data is preliminary
- Time response of each instrument is evaluated against carbon monoxide (top left)
- AMS equivalent levoglucosan derived from $C_2H_4O_2^+$ fragment (high-resolution fit at *m/z* 60) calibrated to a levoglucosan standard
- CHARON and EESI agree within 10% (bottom left), while AMS levoglucosan is significantly higher (bottom right), likely due to contribution of other compounds besides levoglucosan to signal at $C_2H_4O_2^+$



Eichler et al. 2015, *AMT* 8, 1353-1360
Piel et al. 2019, *AMT* 12, 5947-5958

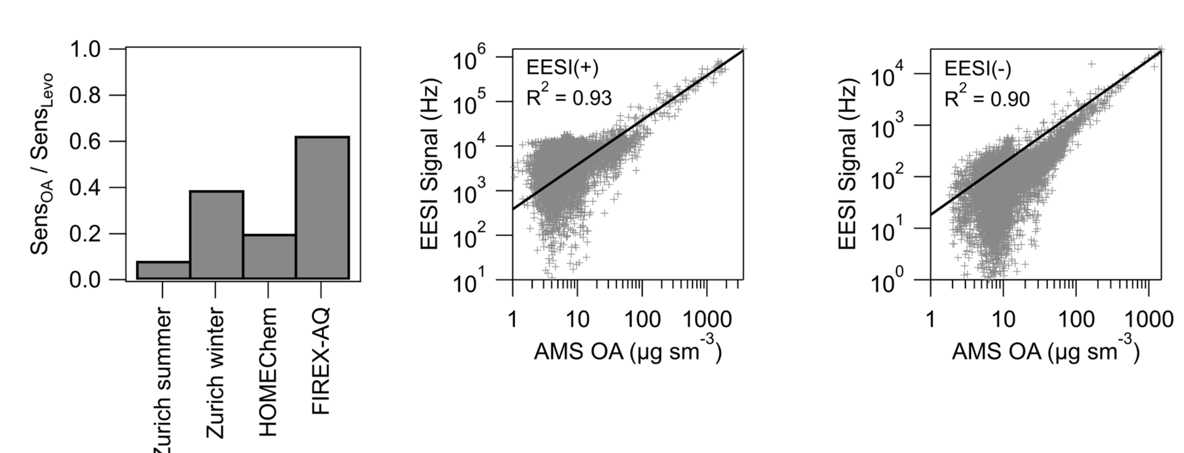
Calibration



- Pressure controlled inlet allows for calibration using monodisperse aerosols size-selected with a differential mobility analyzer
- No difference is seen between monodisperse and polydisperse calibrations
- Significant effect of PCI pressure on EESI sensitivity

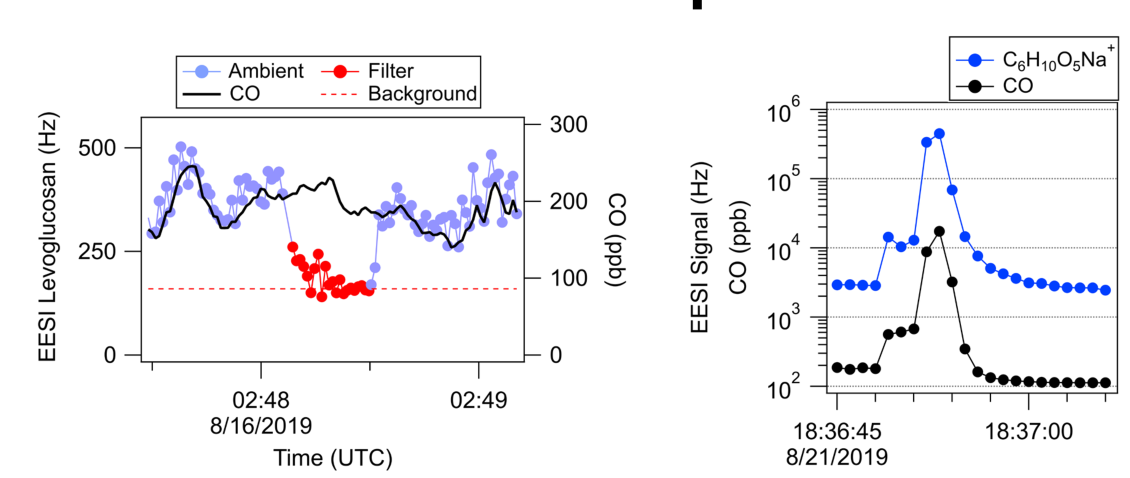
Bulk Sensitivity

- Total EESI signal correlates with AMS OA for both EESI(+) and EESI(-)
- All published EESI field measurements are EESI(+) and calibrated for levoglucosan. Bulk OA sensitivities are compared below at left (Qi et al. 2019, Stefenelli et al. 2019, Brown et al. Submitted)
- FIREX-AQ uses 3:1 methanol water working solution while other campaigns have used 1:1 acetonitrile:water. All use 100 ppm NaI electrospray dopant



Brown et al., *Submitted*
Qi et al. 2019, *ACP* 19, 8037-8062
Stefenelli et al. 2019, *ACP* 19, 14825-14848

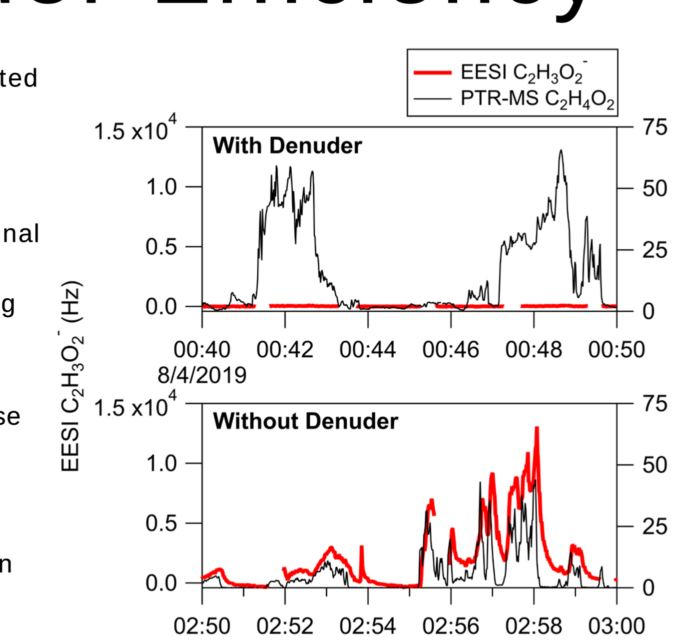
Time Response



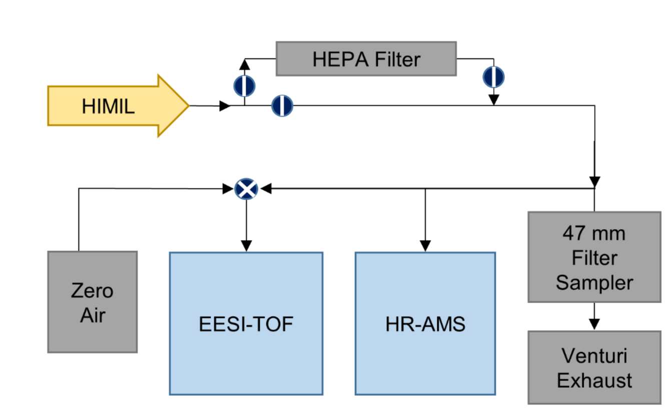
- EESI data recorded at 1 Hz
- Fast response to background measurements is shown at left, and fast recovery from agricultural fire plumes (>99% in 5 s) is shown at right

Denuder Efficiency

- Denuder efficiency is calculated to be >99.5%
- EESI was flown without a denuder July 25th-30th
- During those flights clear signal was observed for gas-phase organic compounds, including acetic acid
- When EESI is flown with the denuder in place, no response to acetic acid is observed
- EESI acetate signal is compared to acetic acid quantified by PTR-MS (proton transfer reaction mass spectrometer) at right

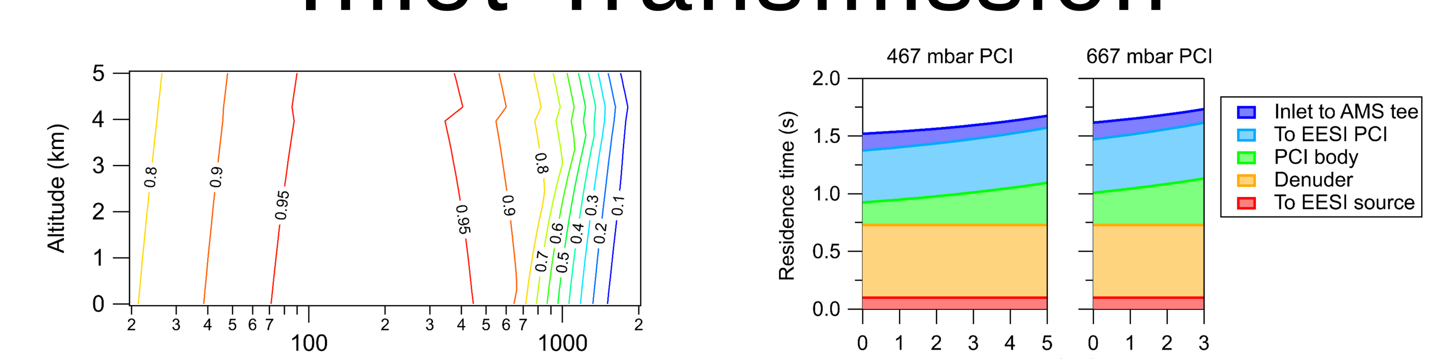


Instrument Configuration



- The University of Colorado EESI-ToF MS and HR-AMS sample from a shared HIMIL inlet and inlet HEPA filter
- The EESI-ToFMS can sample from the main inlet or from a zero air cylinder
- The EESI-ToFMS takes automated background measurements using zero air every 6 minutes
- Both instruments quantify detection limits using HEPA filter every 18 minutes
- The EESI-ToFMS samples zero air when the aircraft is above the instrument's altitude ceiling
- Filter samples were analyzed with ultra high resolution mass spectrometric analysis

Inlet Transmission



- Aerosol transmission in the EESI inlet across the altitude range sampled during FIREX-AQ
- Calculation includes losses from impaction, diffusion, aspiration, and settling
- EESI D_{50} is roughly 1 μm at all altitudes, with large particle losses dominated by losses at the PCI entrance orifice

- EESI inlet residence time as a function of sampling altitude for both PCI (pressure controlled inlet) settings used during FIREX-AQ
- Evaporative losses downstream of the denuder are calculated to be < 5% for compounds with C* < 100 μg m^{-3}