

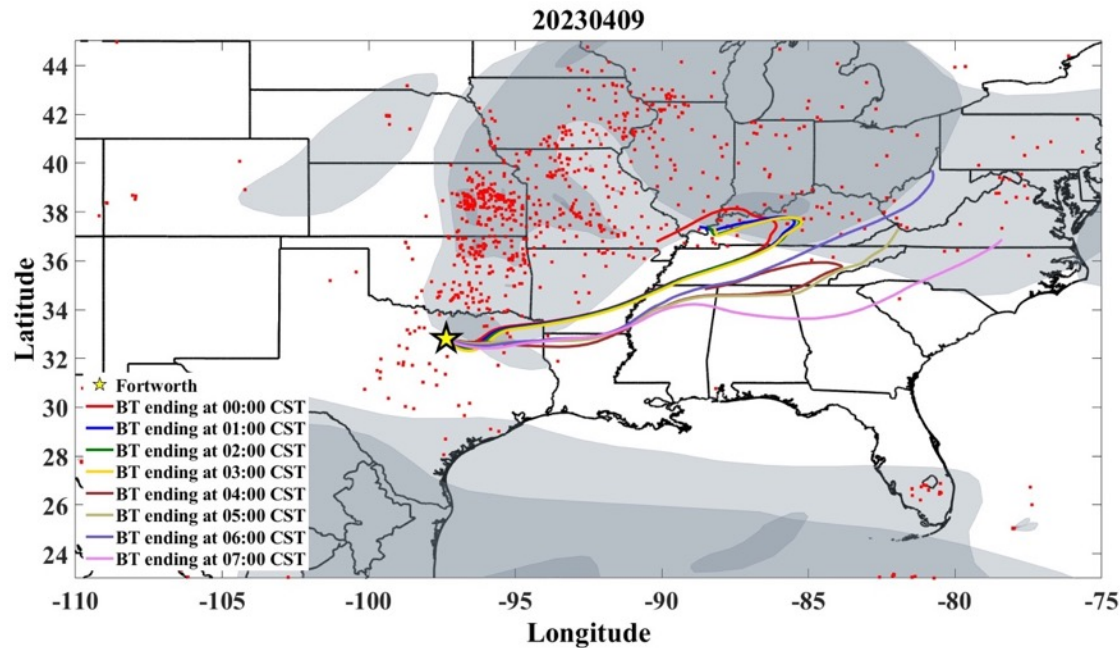
Hydrogen Cyanide for Improved Identification of Fire Plumes in the (BC)² Network

AQRP Project 22 – 006

Tara I. Yacovitch (PI) – Aerodyne Research

Dr. Rebecca Sheesley & Dr. Sascha Usenko (Co-PIs) – Baylor University

Texas Biomass Burning Emissions

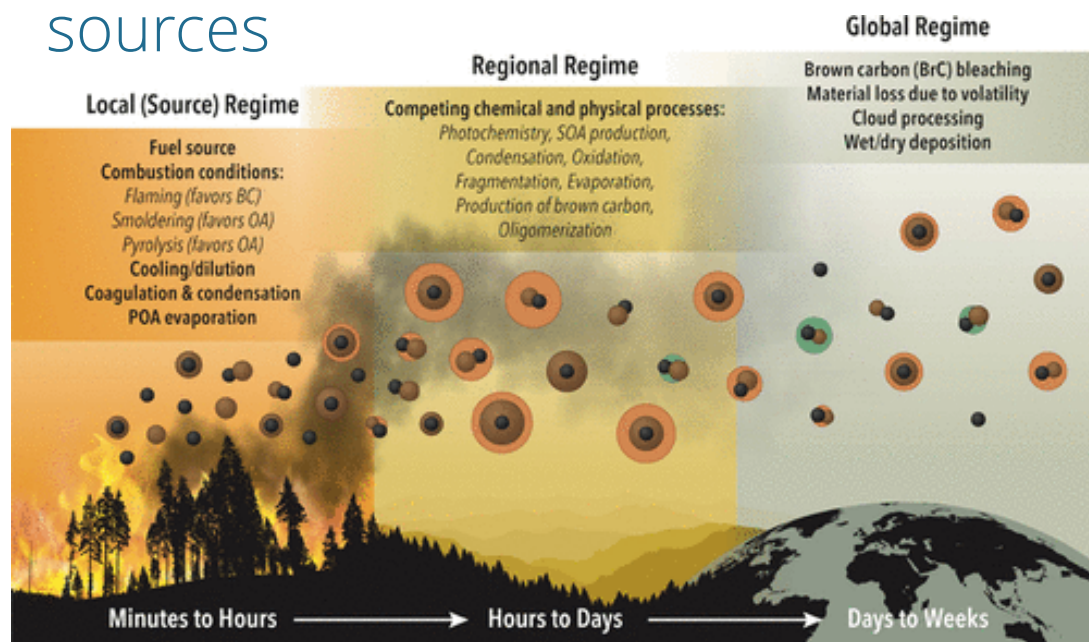


AQRP 2022-2023 research priorities

- “Domestic Fire Emissions” including transported emissions from wildfires (domestic, international) and their impacts on exceptional events in Texas.
- “Changing Emission Patterns in Texas” – additional research along the Interstate 35

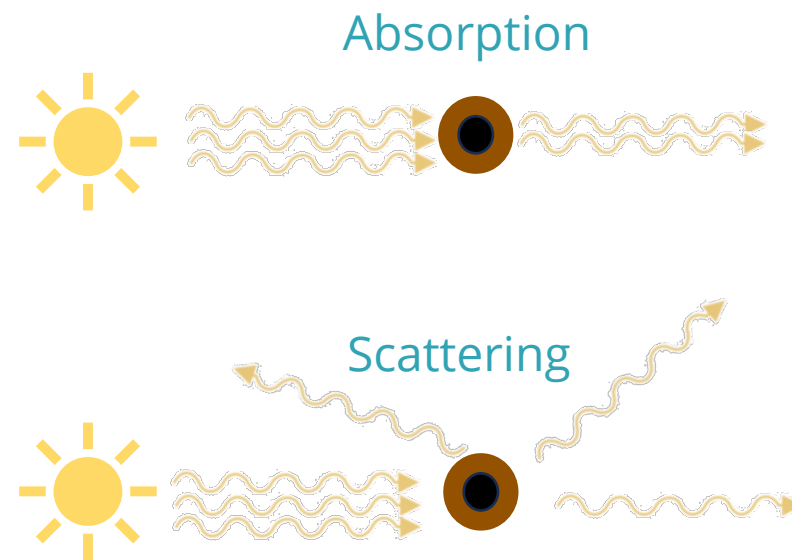
Black Carbon (BC) and Brown Carbon

- Particulate Matter (PM) is emitted from wildfires and many other sources



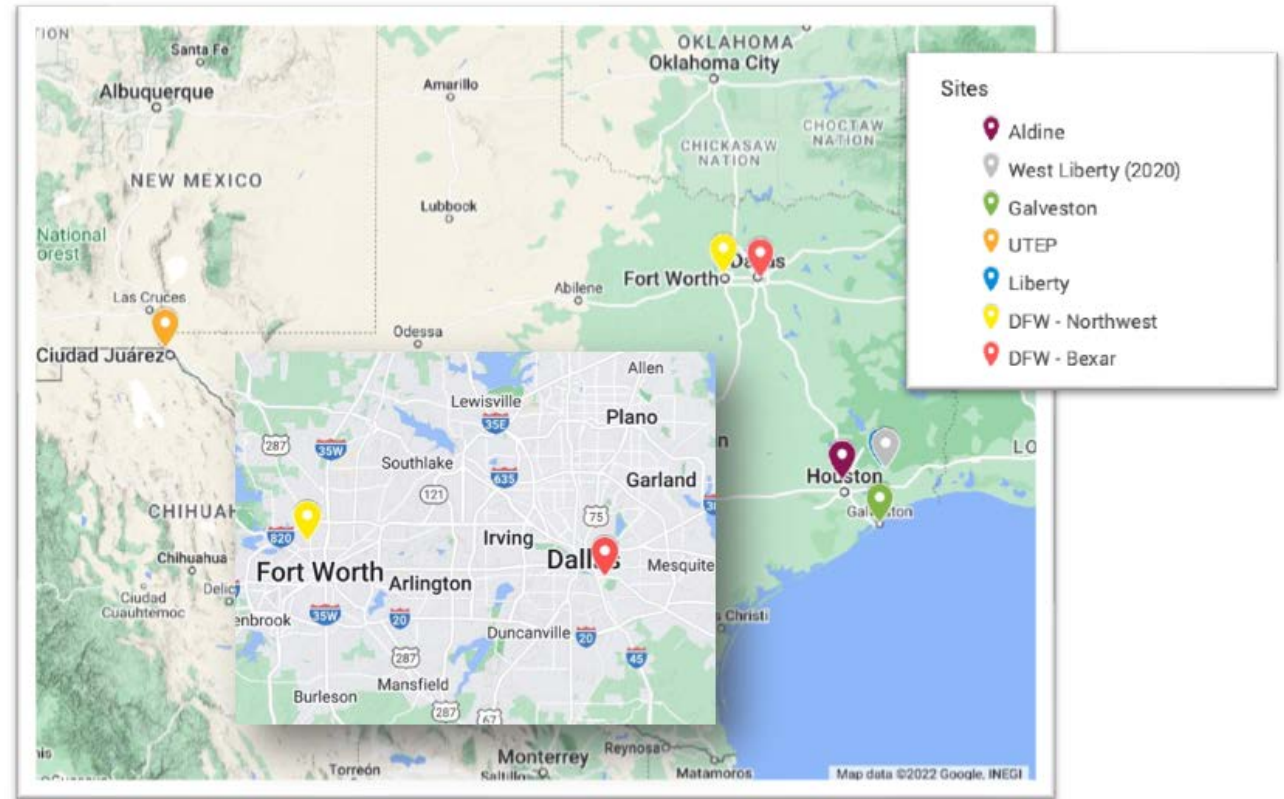
Sedlacek, A. J., III, E. R. Lewis, T. B. Onasch, P. Zuidema, J. Redemann, D. Jaffe, and L. I. Kleinman (2022), Using the Black Carbon Particle Mixing State to Characterize the Lifecycle of Biomass Burning Aerosols, *Environ. Sci. Technol.*, 56(20), 14315-14325, doi:10.1021/acs.est.2c03851.

- Optical properties = absorption or scattering with different colors of light
- Tell us about source of particulate matter
- Determine radiative forcing and climate impact



Black Carbon and Brown Carbon Network (BC)²

- Baylor University and University of Houston project
- Initial AQRP project 19-031
 - El Paso 2019
- Subsequent TCEQ funding 2020, 2021, 2022, and 2023
 - Houston, El Paso and Dallas-Fort Worth
- Serves as host site for related air quality projects in Texas
 - E.g. DOE-TRACER, HCN, ASCENT, PANDORA



Map of 2020-22 (BC)² network. Expansion to Dallas and Fort-Worth planned as part of that project. The HCN measurement and associated (BC)² measurements are at the DFW – Northwest site.

Hydrogen Cyanide



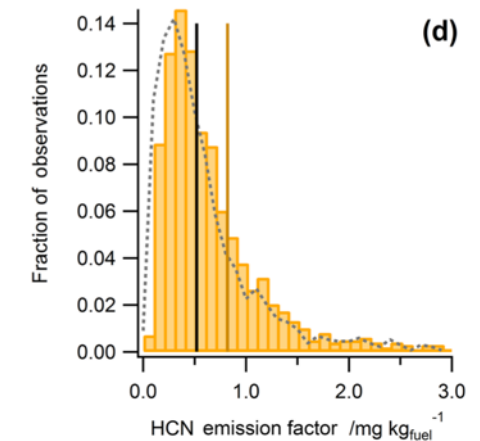
Biomass Burning

- Emission Factors:
 - EF: 0.29 – 1.52 g HCN/kg Fuel
 - (Akagi et al. 2011 DOI:10.5194/acp-11-4039-2011)
- Emission Ratios, HCN/CO:
 - ER: 0.43 to 12.8 ppt/ppb
 - (Le Breton et al., 10.5194/acp-13-9217-2013 and references within)



Vehicle Combustion

- Dynamometer tests:
 - EF ~0.000 3 – 0.077 g HCN/kg Fuel
 - (Moussa et al. 2016 DOI: 10.1016/j.atmosenv.2016.01.050)
 - ER ~2.4 ± 2.3 ppt/ppb*
- Fleet tests Emissions
 - EF: 0.000 32 – 0.000 88 g/kg Fuel (IQR, winter)
 - Higher in summer 0.002 3 g/kg Fuel
 - (Wren et al. 2018 DOI: 10.5194/acp-18-16979-2018)
 - No CO data published

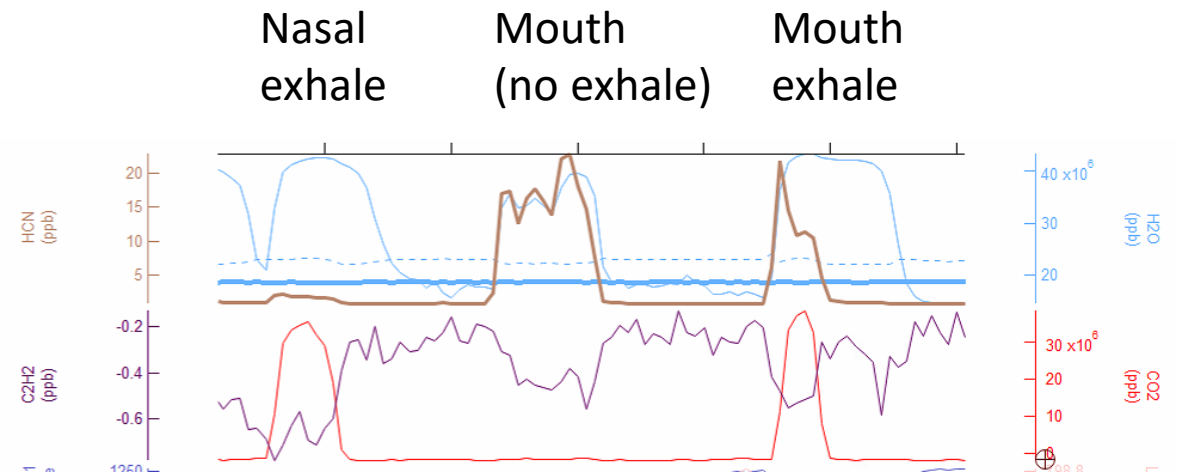


(Aside) Hydrogen Cyanide in Breath

Human Breath

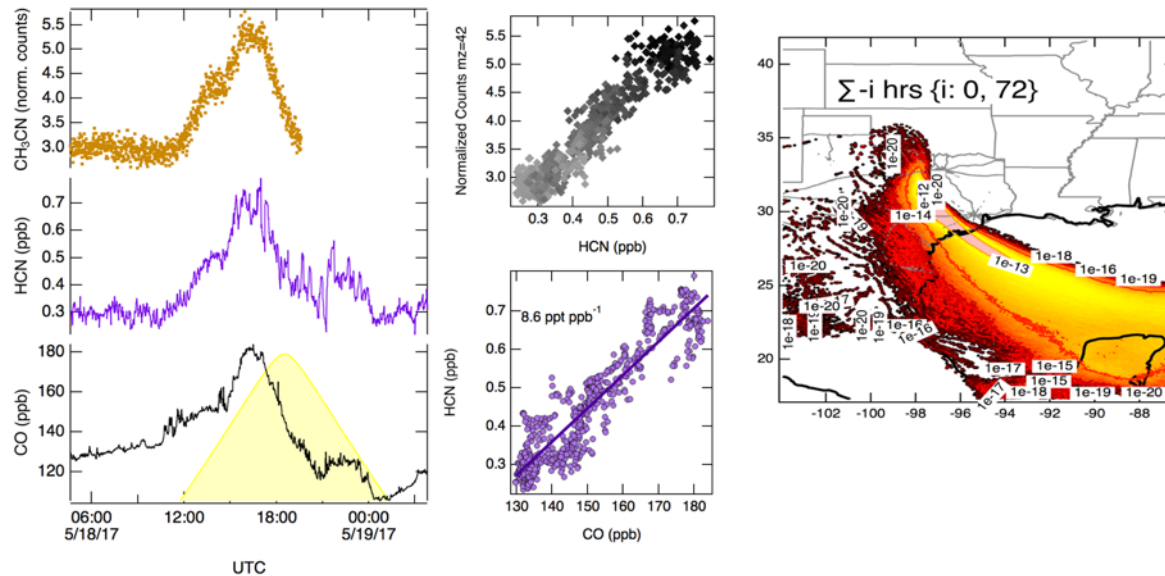
- HCN measured in breath of healthy volunteers both orally and nasally
- Produced by salivary peroxidase

Drummer et al, 2013 "Quantification of hydrogen cyanide (HCN) in breath using selected ion flow tube mass spectrometry—HCN is not a biomarker of *Pseudomonas* in chronic suppurative lung disease"
DOI: 10.1088/1752-7155/7/1/017105



Hydrogen Cyanide by Tunable IR Laser

2017 San Antonio Field Study



Imported fire emissions measured during the 2017 San Antonio Field Study. Time traces (left) of acetonitrile (CH_3CN , gold), hydrogen cyanide (HCN, purple) and CO are shown, overlaid with the solar elevation angle showing daylight hours (yellow triangle). The slope of HCN to CO (bottom middle) is shown. Acetonitrile (counts at $m/z=42$) is also well-correlated (top middle). Back-trajectory calculations show the predominant air mass originates from the Gulf of Mexico, with contributions from the Yucatan.

2019 FIREX

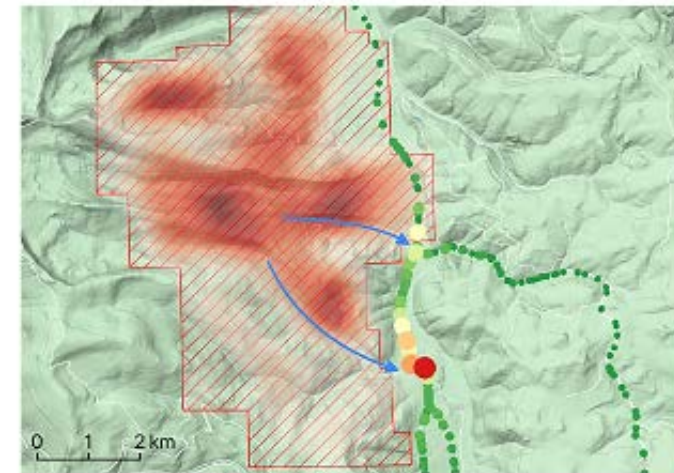
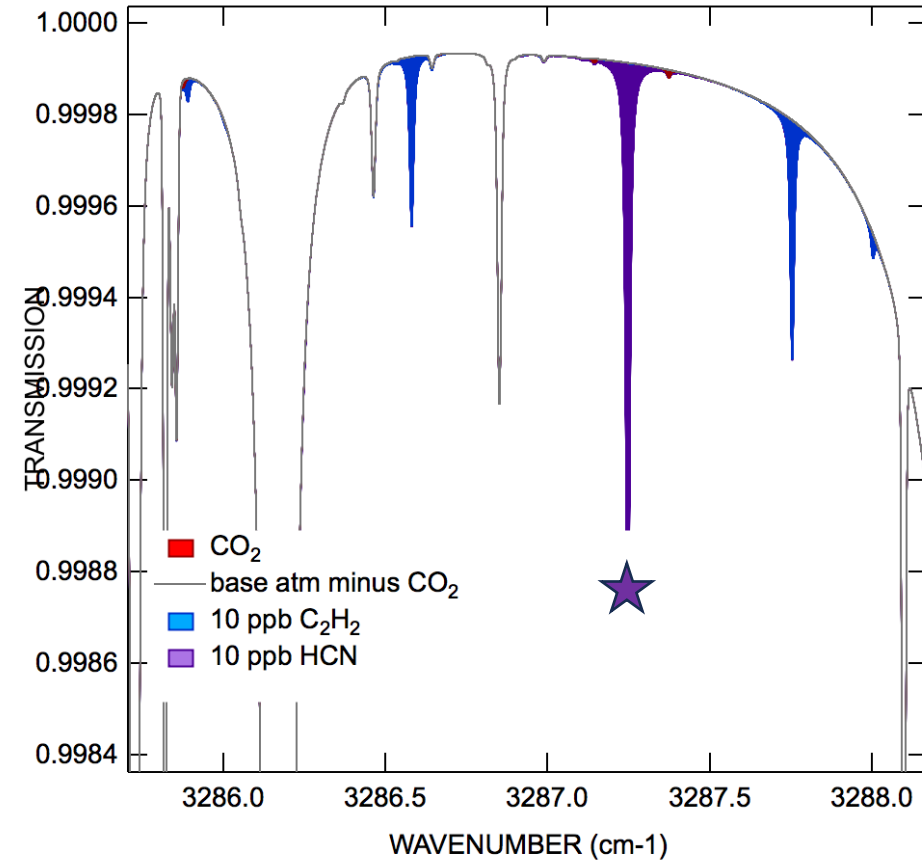


Figure 6. AML deployment at the 204 Cow fire on 26 August 2019. The HCN data are color (and size) coded in bins of 10 ppb from 0–10 ppb (green) to 60–70 ppb (red). The red area indicates the boundary of the fire during the month of August (VIIRS data (University of Maryland, 2020)). The red shaded heatmap shows fire observations as detected from satellite for the same time period. The blue arrows indicate outflow paths of fire tracers downhill through narrow valleys during the second half of the night. Topographical maps from [Google.com](https://www.google.com).

Warneke, C. et al. (2023), Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ), *J. Geophys. Res., [Atmos.]*, 128(2), e2022JD037758, doi:<https://doi.org/10.1029/2022JD037758>.

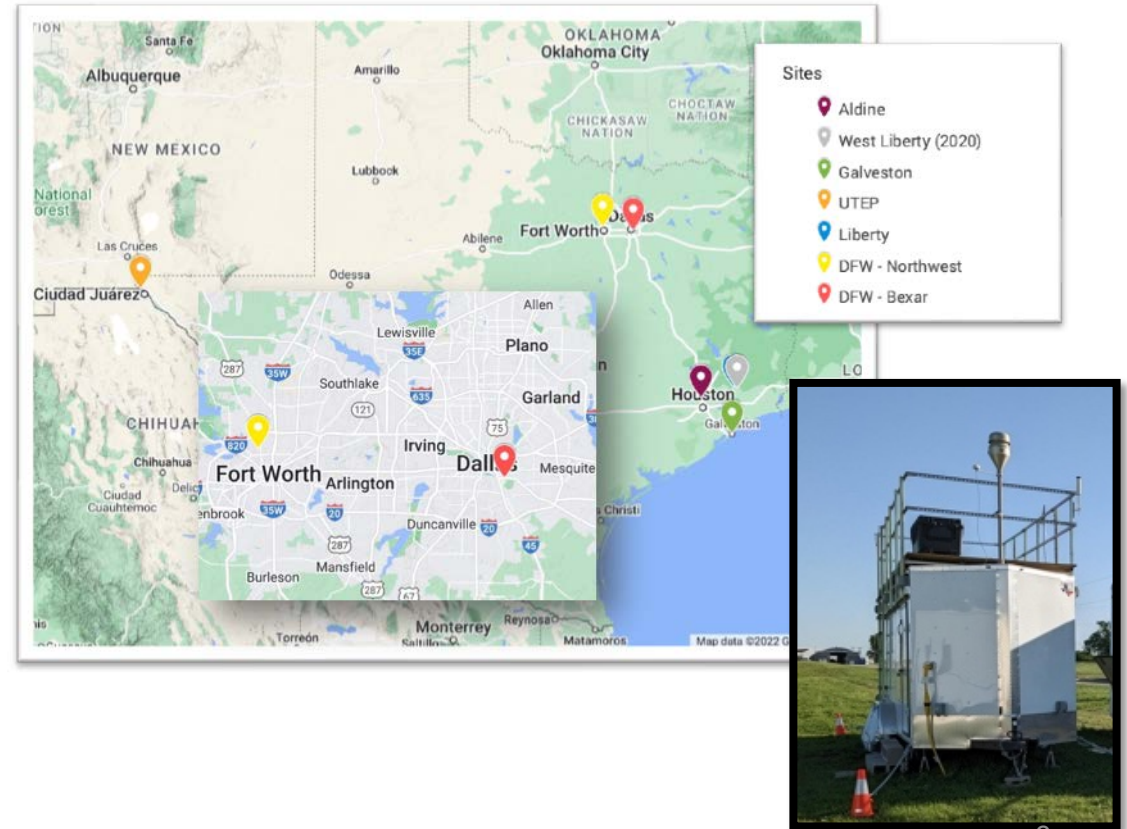
Tunable Infrared Direct Laser Spectrometer for Hydrogen Cyanide



AQRP 22-006 Project Tasks

1. Design Measurement Campaign: site choice, logistics, campaign planning
2. Execute Field Campaign: HCN measurements at the chosen Dallas Fort-Worth site
3. HCN Data Analysis: Quality assurance of the HCN dataset
4. Fire Plume Data Analysis: Enhanced identification of biomass burning plumes using HCN data to enhance existing (BC)² network data.

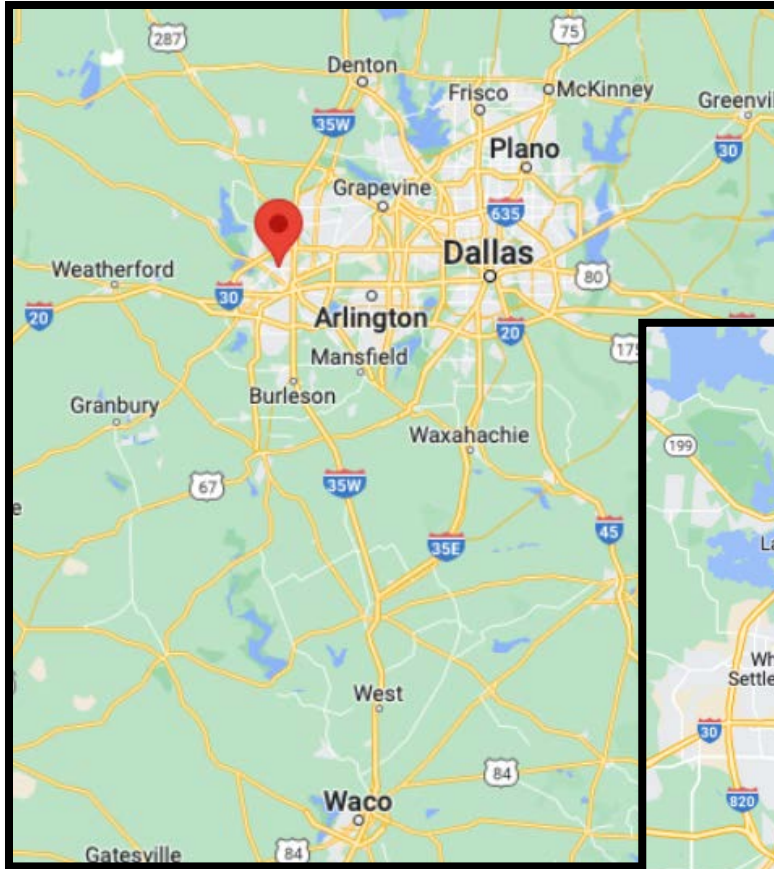
H—C≡N



TILDAS-HCN in the (BC)² Trailer



Campaign Overview

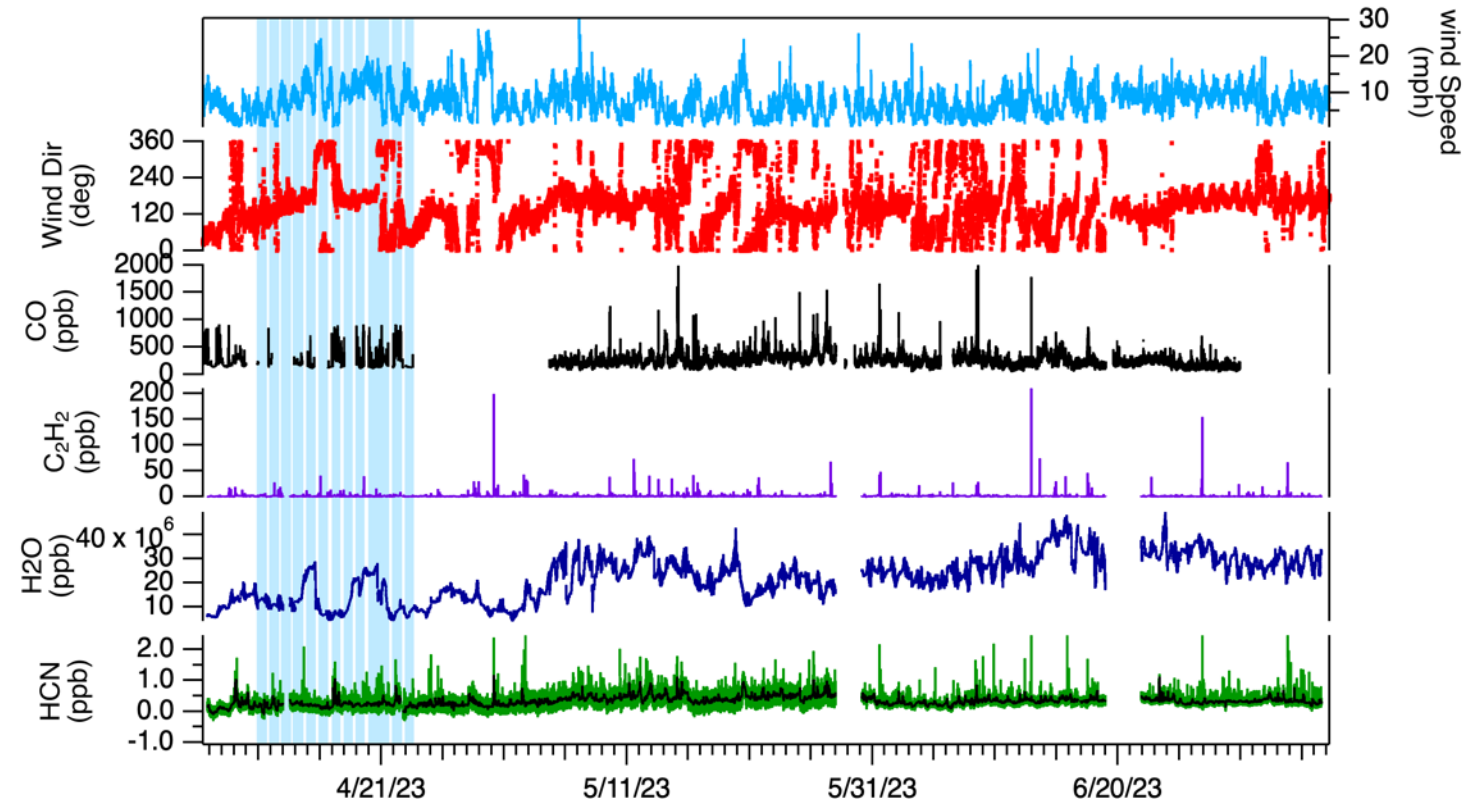


- Fort Worth Meachum Int'l Airport
- Co-located with TCEQ-operated CAMS site "Fort Worth Northwest" (32.8058182, -97.3565229)



HCN Measurement Overview

- 83 measurement days in Spring/Summer 2023
- Numerous co-located measurements available
 - (BC)² trailer
 - TCEQ site
 - Aerodyne Mobile Lab (AQRP 22-010)



Overview of HCN time series, with 1-second data shown in green, and a 5-minute average overlaid in black. Auxiliary tracers are also shown: acetylene, C₂H₂ and water, H₂O, from the HCN instrument; CO from the collocated mobile lab and the (BC)² network trailer; and wind speed (pale blue) and direction (red) from the TCEQ trailer at the Fort Worth Northwest site. Blue vertical shading indicates times when the mobile lab from project AQRP 22-010 was co-located with the site.

(BC)² Instrumentation

- Wavelength-dependent Aerosol Absorption Coefficient (σ_{abs}) →
 - Tricolor Absorption Photometer (TAP)
 - 365 nm (UV), 520 nm (green), 640 nm (red)
 - 2 instruments, alternating by hour
- Wavelength-dependent Aerosol Scattering Coefficient (σ_{scat}) →
 - Nephelometer (Ecotech Aurora 3000)
 - 450 nm (blue), 525 nm (green) and 635 nm (red)
- Thermo CO monitor →



Aerosol Optical Instrumentation matches NOAA Federated Aerosol Network (NFAN)
Mehra et al., 2023: <https://doi.org/10.1016/j.atmosenv.2023.119988>

Aerosol Optical Properties in (BC)²

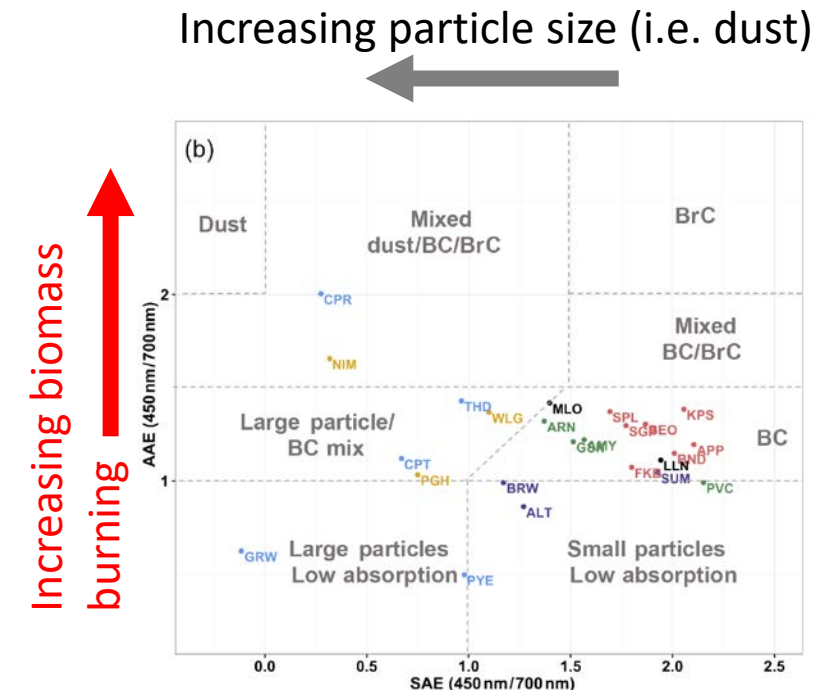
- Absorption Ångström Exponent (AAE)
 - Characterizes the wavelength dependency of aerosol absorption using the negative slope of the log-log plot of the absorption coefficient and the wavelength

$$\text{Absorption Ångström Exponent} = - \frac{\log(\sigma_{abs\lambda_1}, \sigma_{abs\lambda_2}, \sigma_{abs\lambda_3})}{\log(\lambda_1, \lambda_2, \lambda_3)}$$

- Scattering Ångström Exponent (SAE)
 - Wavelength dependency of aerosol scattering

$$\text{Scattering Ångström Exponent} = - \frac{\log(\sigma_{scat\lambda_1}, \sigma_{scat\lambda_2}, \sigma_{scat\lambda_3})}{\log(\lambda_1, \lambda_2, \lambda_3)}$$

- *Urban areas are often mixed sources (see fig)*



Schmeisser et al. 2017

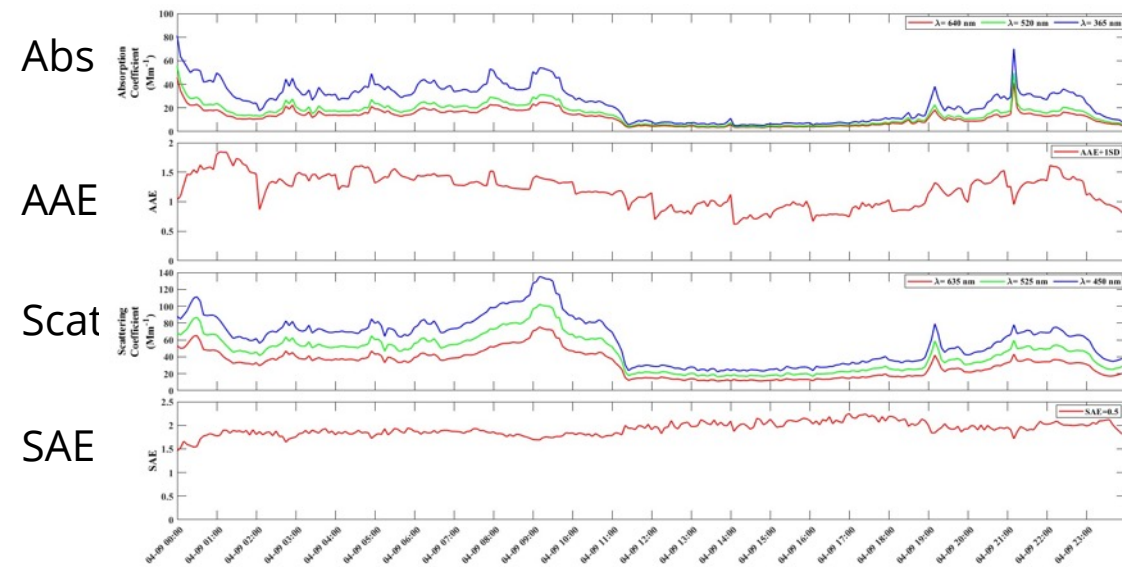
(BC)² Event Detection (*without HCN*)

Calculate average and standard deviation of the AAE at each site to establish a baseline.

Biomass burning events are identified as enhancements in the AAE above the normal baseline

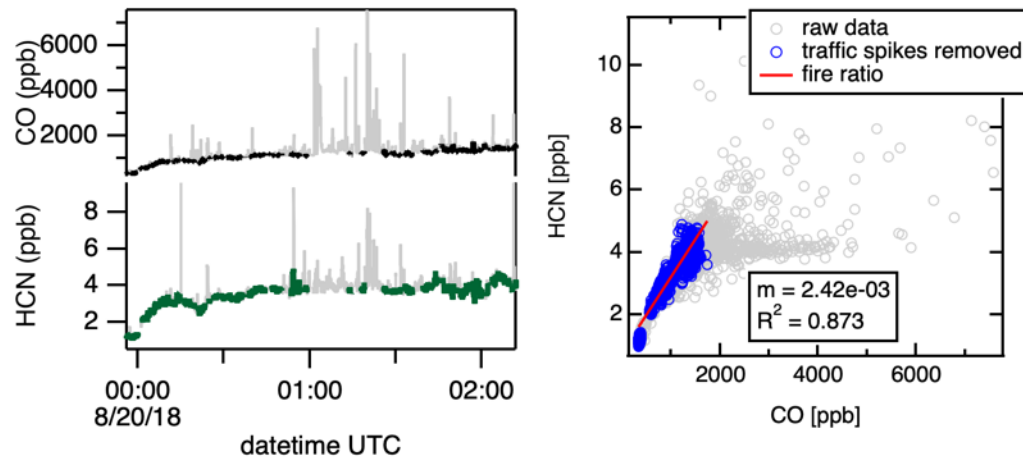
Biomass Burning Events defined when:

1. AAE > site average + 1 standard deviation
2. Duration of enhanced AAE
 - a. Long BB: > 4 hr enhanced AAE
 - b. Short BB: 1-4 hr enhanced AAE
 - c. Local plume: <1 hr enhanced AAE
3. SAE > 1
4. Absorption coefficients > ~2



HCN Traffic/Spike Filtering

Previous HCN Filtering



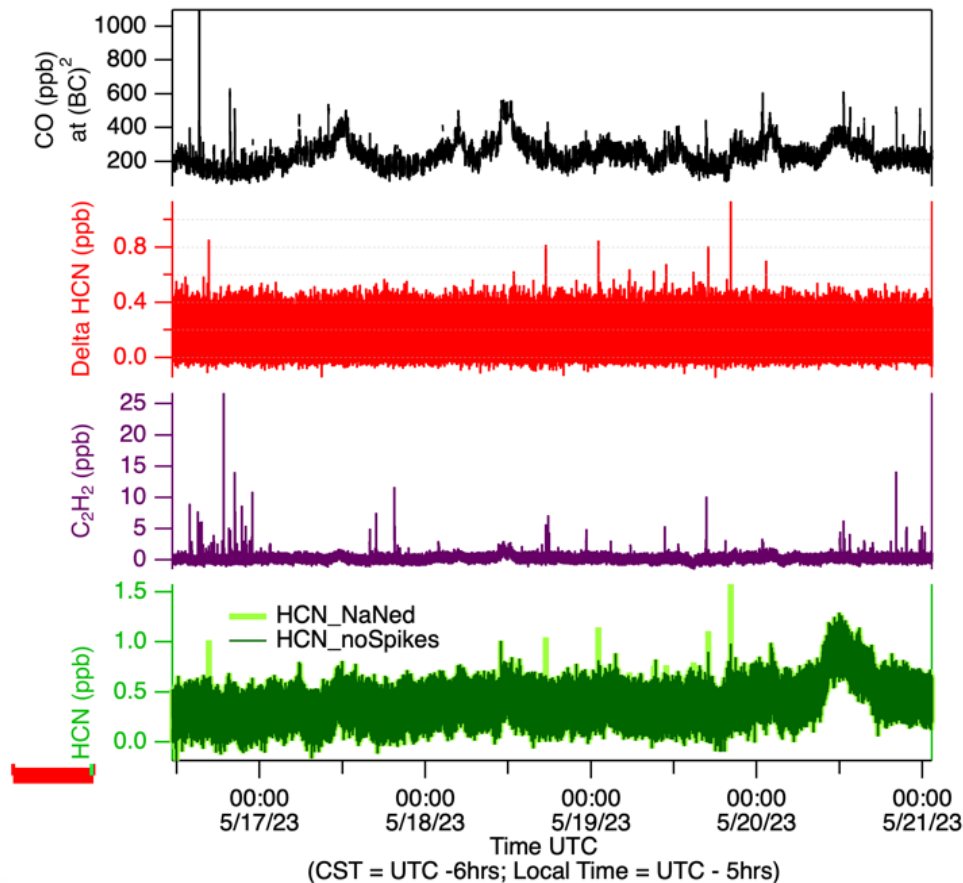
HCN and CO measurements during the 2018 FIREX campaign showing smoke-impacted enhancements along with spikes from traffic.

Traffic Plume Strategy

- Identify Short-Duration Spikes
- Correlation with acetylene (C_2H_2) and CO
 - C_2H_2 measured in same instrument
 - CO from AQRP 22-010 or $(BC)^2$

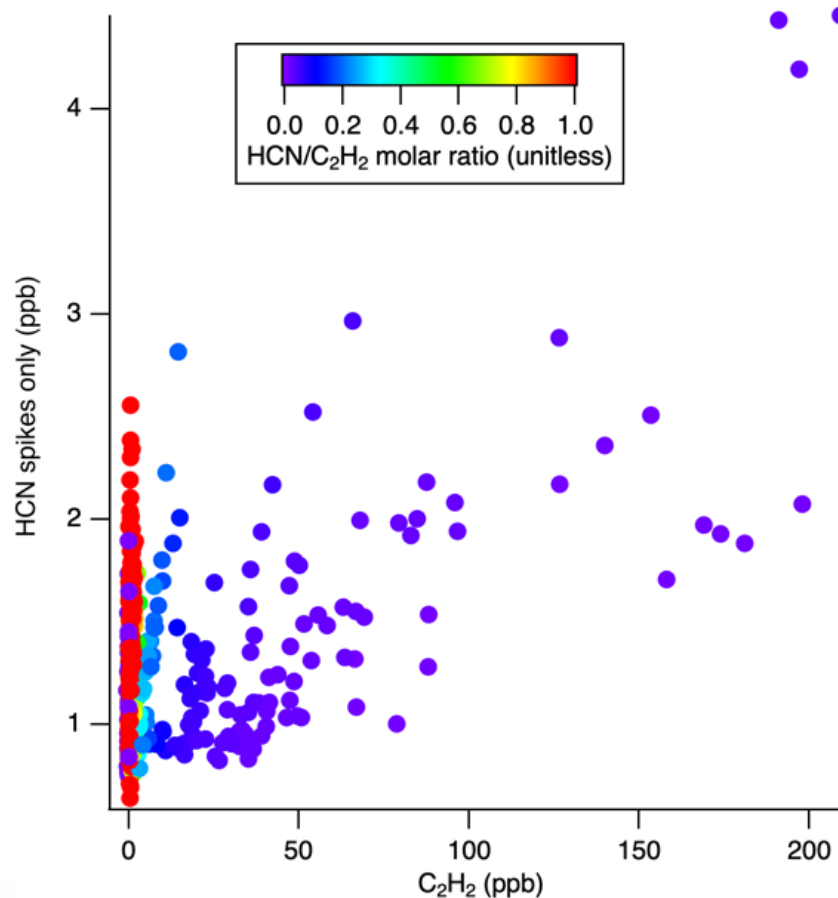
Literature BB HCN Emission Ratio:
HCN/CO ~ 0.43 to 12.8 ppt ppb^{-1}
(Le Breton et al., and references within)

Short Duration Spikes



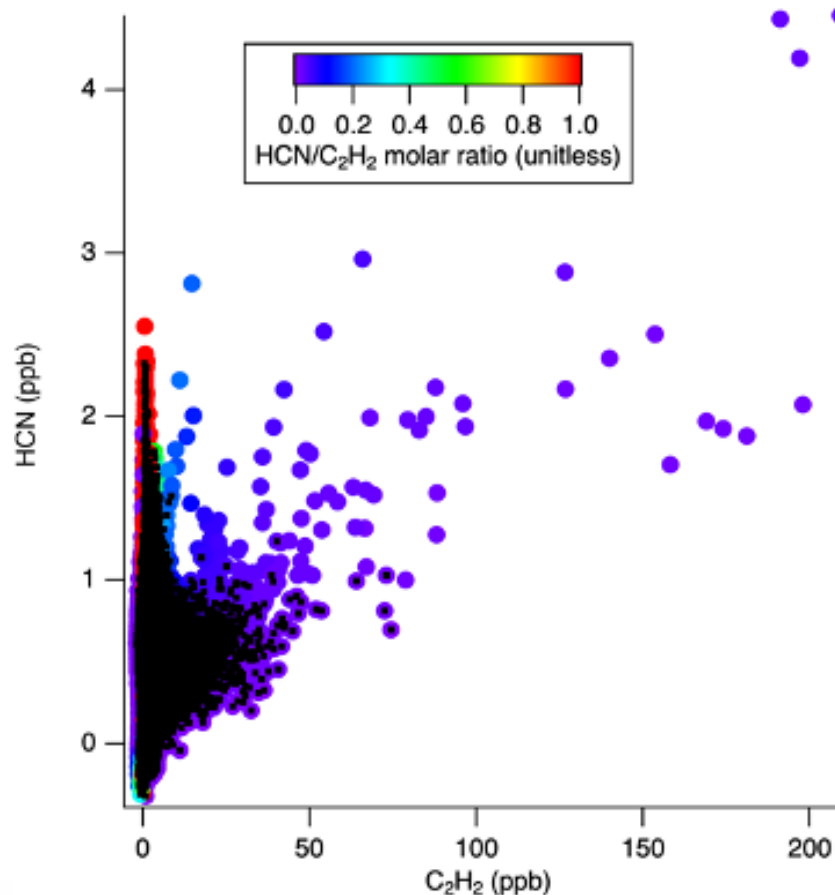
- Take 1-second HCN measurement
- Find minimum concentration in every 10-second window
- Deviations above 0.6 ppb from this minimum flagged.

Acetylene Tracer Ratios for Traffic Spikes



- HCN above ~ 3 ppb consistently has C₂H₂ (purple dots)
- Short duration spikes have a range of HCN/C₂H₂ ratios

Acetylene Tracer Ratios for Traffic Spikes

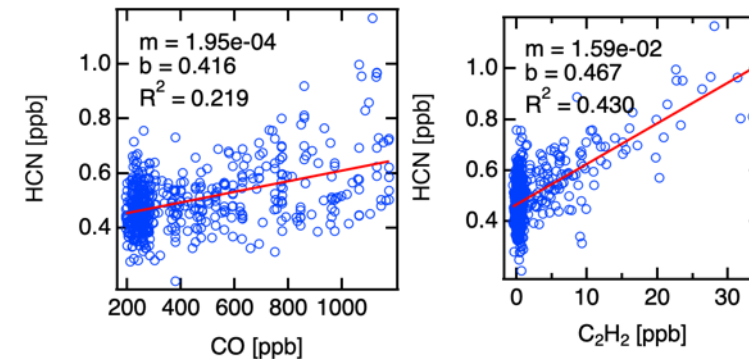
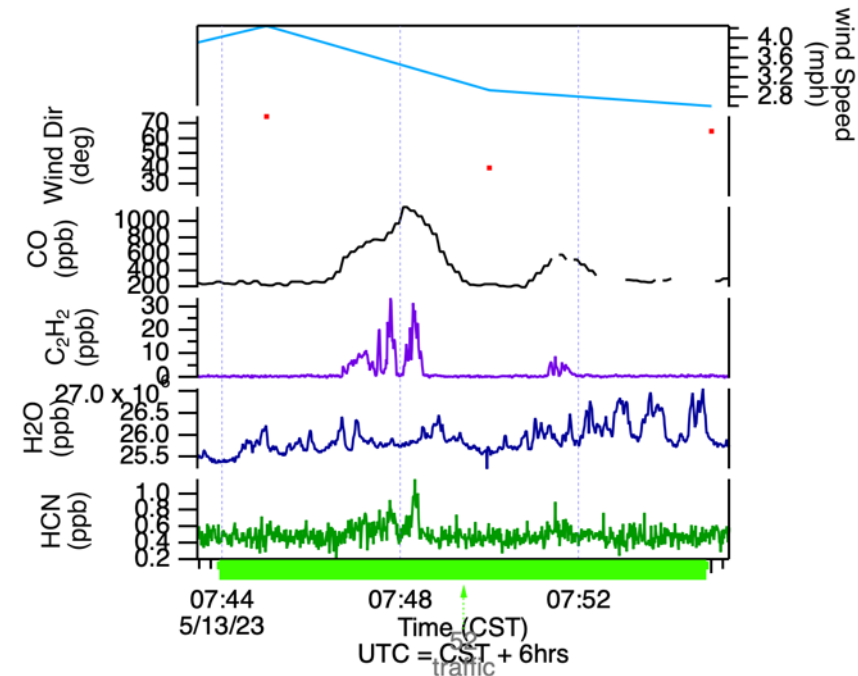


- HCN above ~ 3 ppb consistently has C₂H₂ (purple dots)
- Short duration spikes have a range of HCN/C₂H₂ ratios

Carbon Monoxide Ratios

- Ratios to CO need time base and time offset corrections
- slope of correlation plot
- Area under the curve may be better way to deal with these plumes.

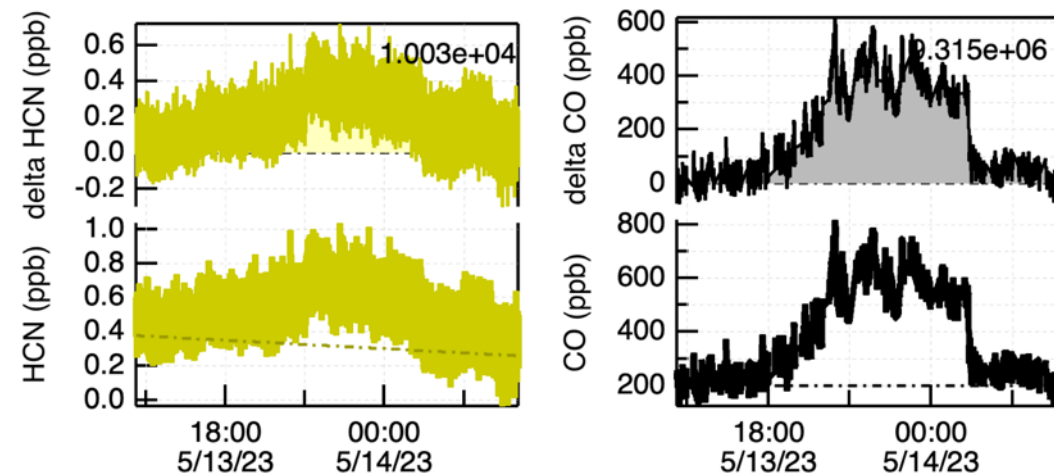
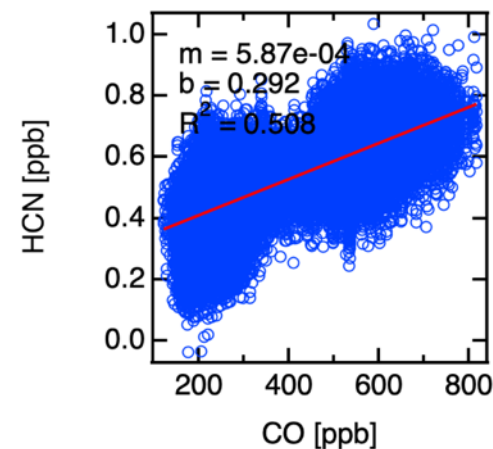
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Carbon Monoxide Ratios

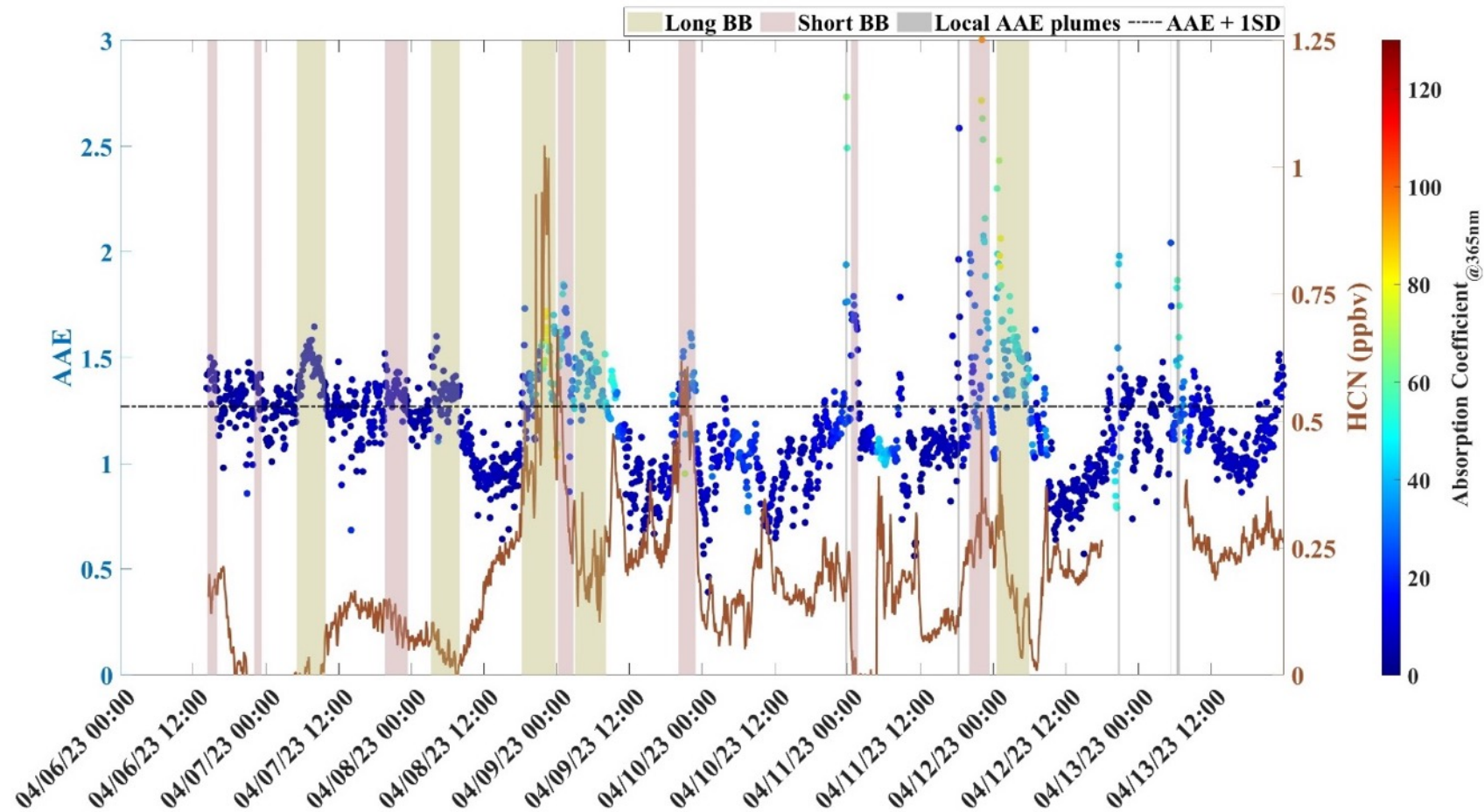
- Area under the curve can manage imperfectly correlated plumes

Literature BB HCN Emission Ratio:
HCN/CO \sim 0.43 to 12.8 ppt ppb⁻¹
(Le Breton et al., and references within)



HCN Area / CO Area = 1.08 ppt/ppb

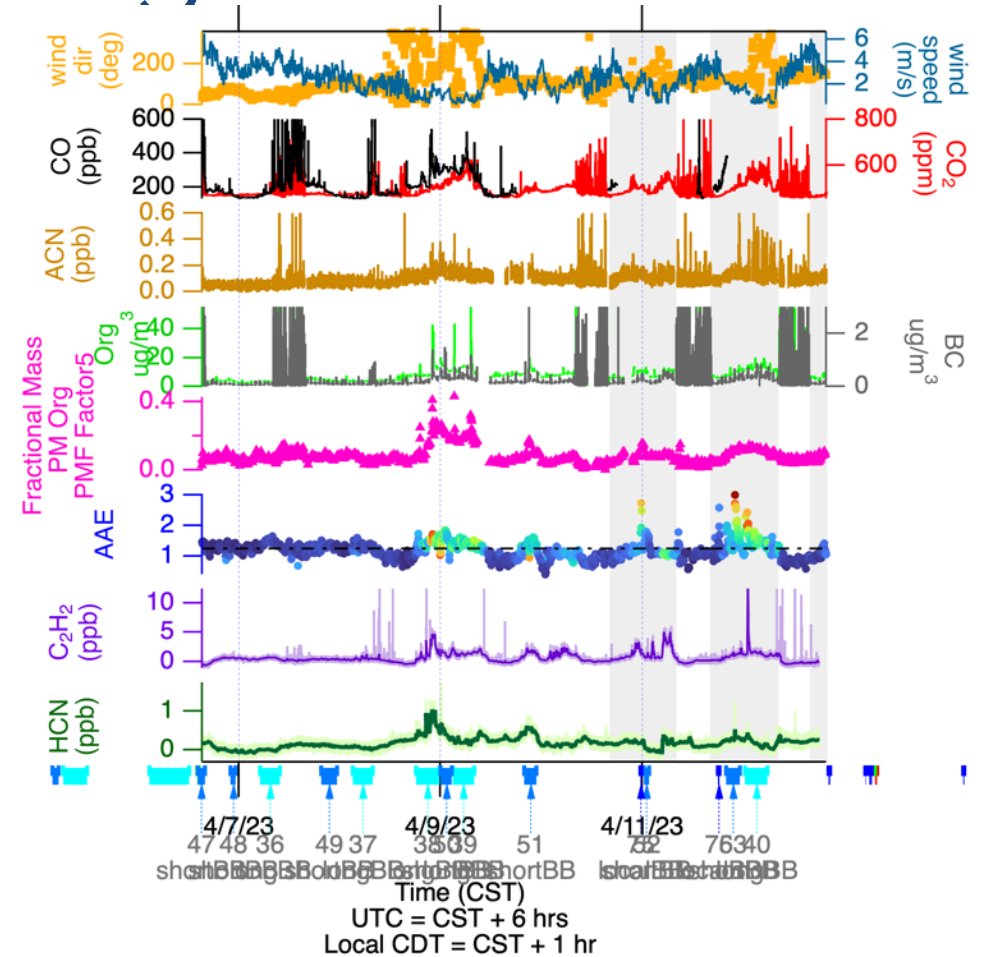
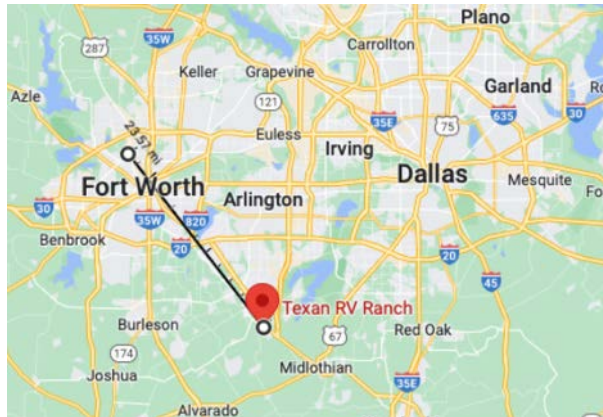
Case Study 1: Multiple Biomass Burning Events



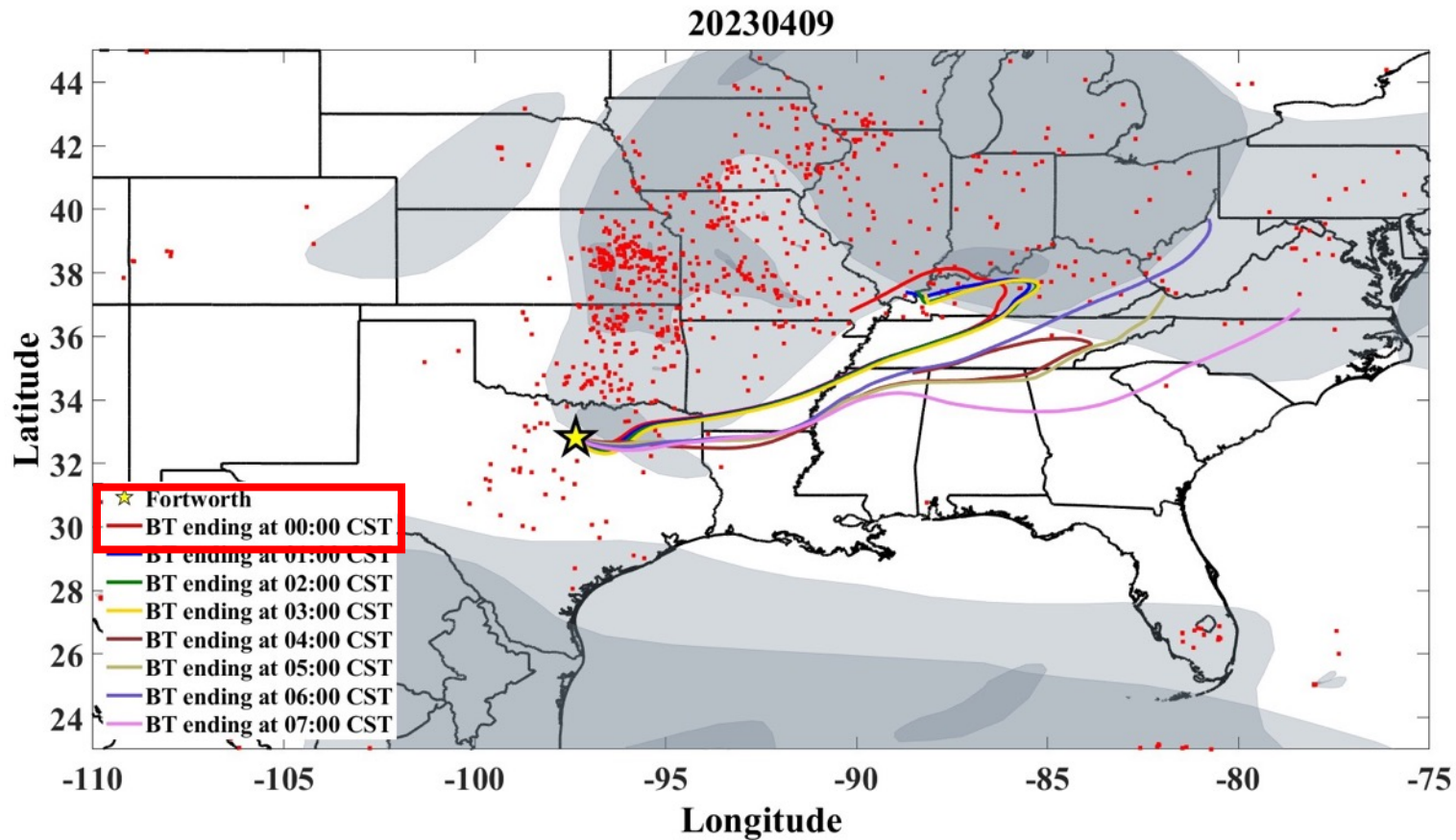
- Events with elevated HCN, AAE and Absorption Coefficient.
- Events of varying duration

Case Study 1: Multiple Biomass Burning Events

- BB tracers observed in Mobile Laboratory when collocated, *and in Mansfield*
- Confirms long-range BB designation and regional impact

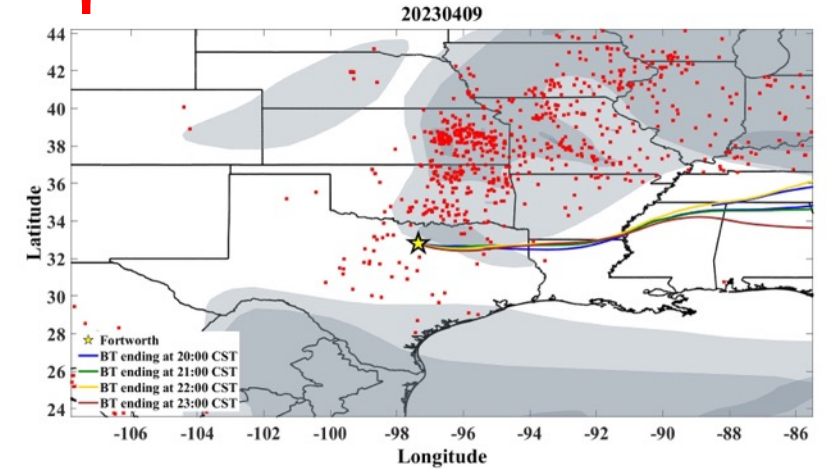
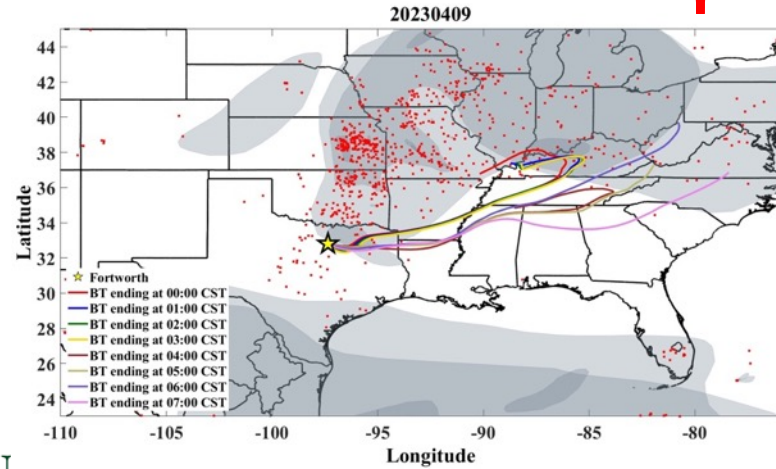
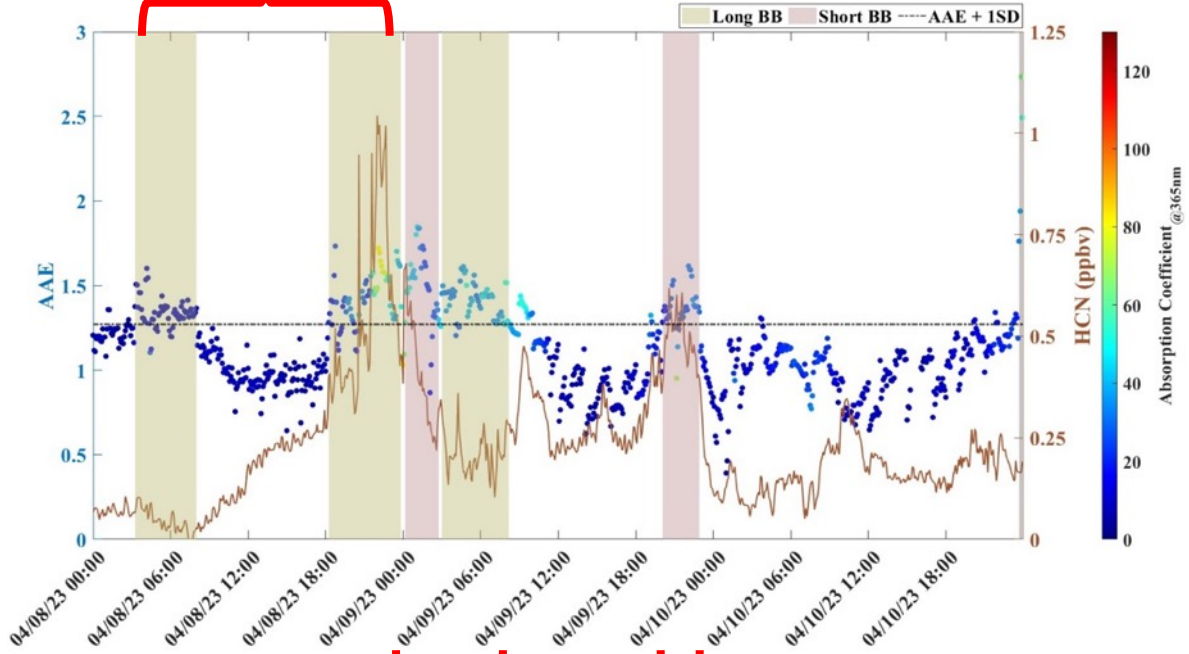
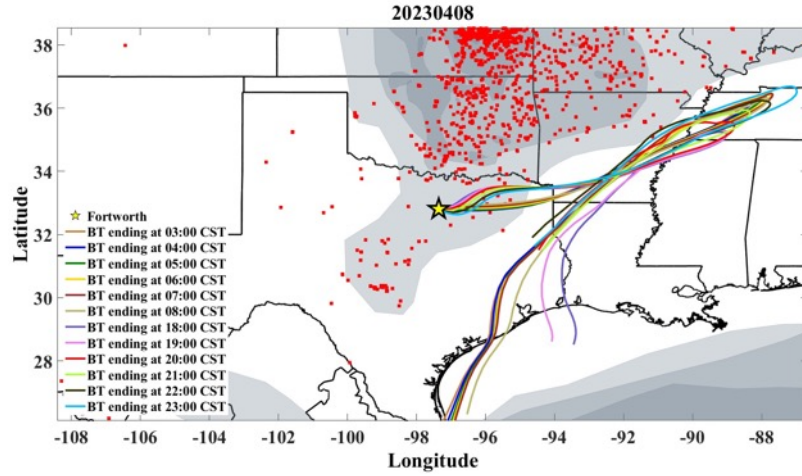


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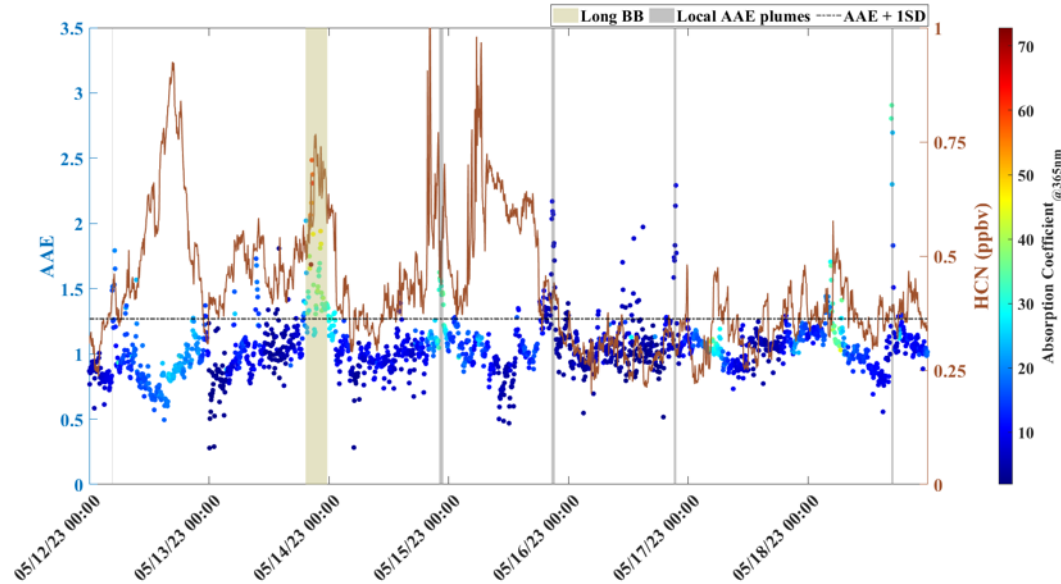


- Back trajectories help identify sources of smoke (in Texas; out of state; international)
- Fires (red dots) via NOAA HMS (Hazard mapping system)
 - VIIRS filtered to exclude flares
 - <https://www.ospo.noaa.gov/Products/land/hms.html#maps>
 - Texas A&M Forest Service Incident Viewer – no/fewer fires at this time.
- Grey indicates smoke overhead.
 - Satellite imagery – visible smoke
- 72-hour back trajectories for the Fort Worth Northwest site at 500m AGL height.
 - Trajectories from SE Missouri/Illinois during peak HCN

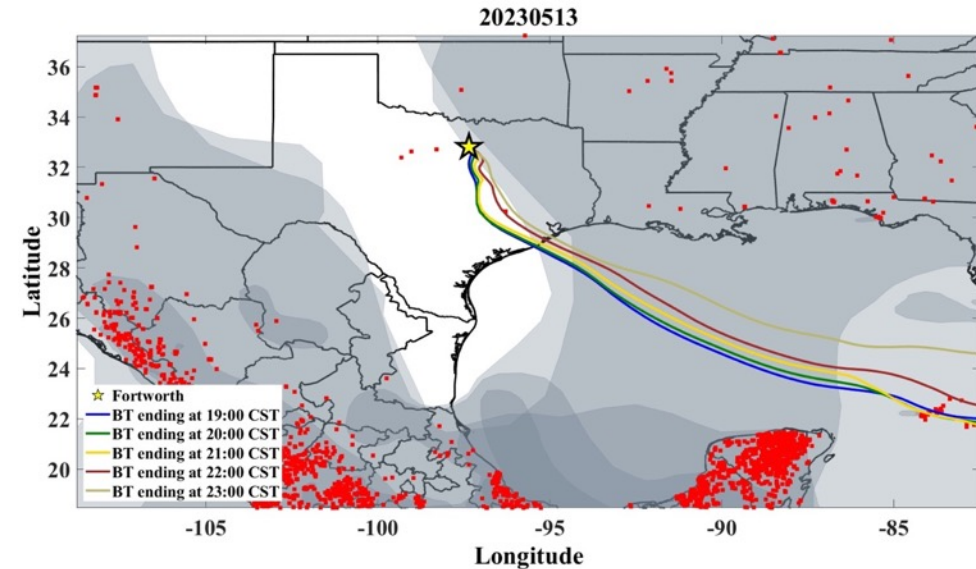
Case Study 1: Multiple Biomass Burning Events



Case Study 2: HCN peaks without a BB signal in the AAE

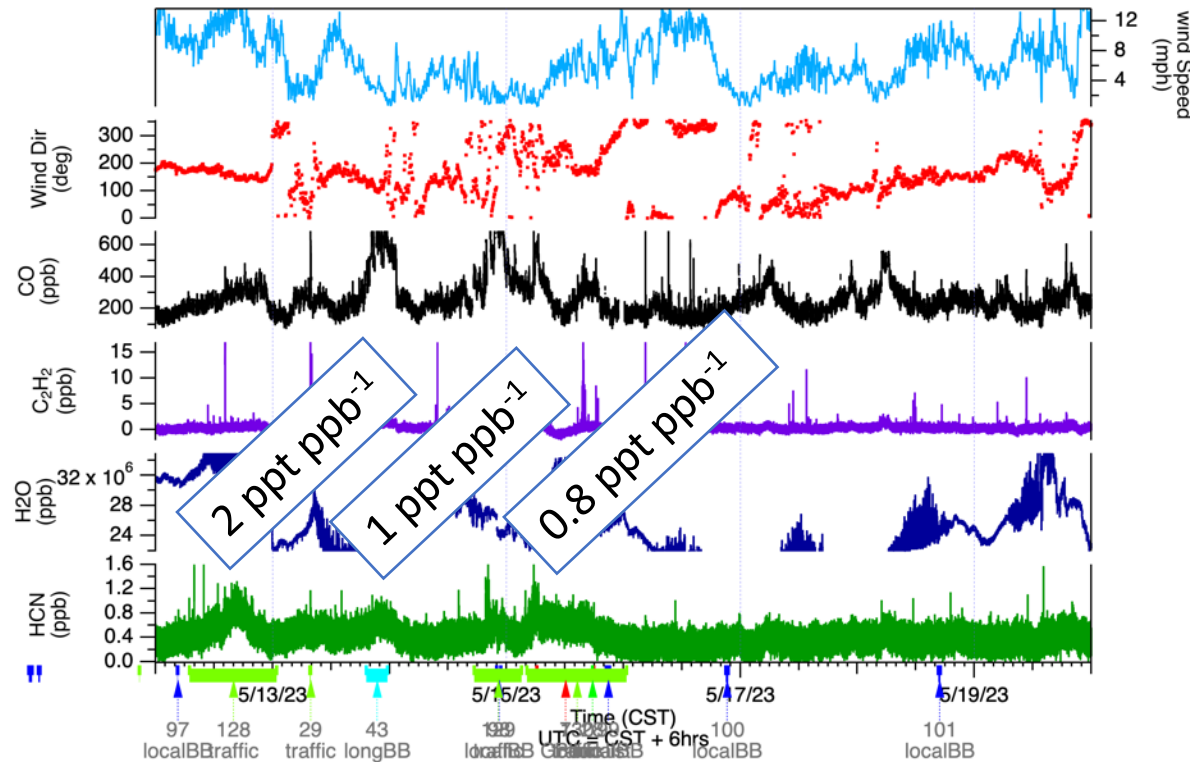


- Hypothesize traffic source
- AAE near 1
- Traffic has Black Carbon, which increases absorption coefficient
- CO suggests biomass burning

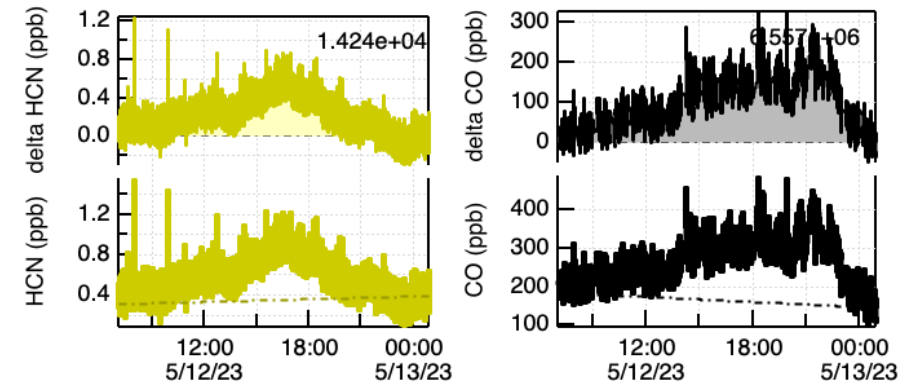


- Second HCN peak has high AAE and back trajectories through smoke regions

Case Study 2: HCN peaks without a BB signal in the AAE



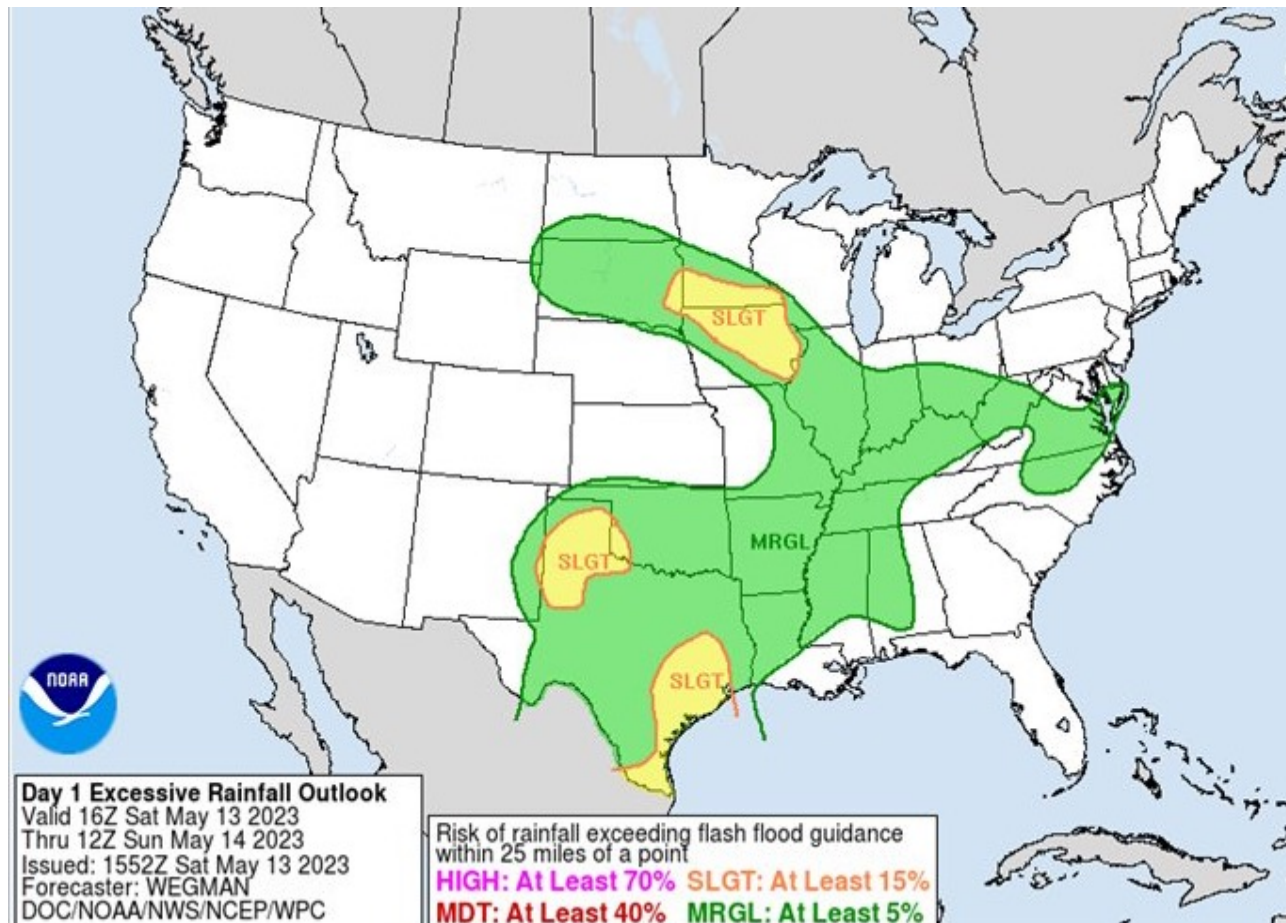
- Variable CO, within range of fire ratios.
- Imperfect correlation: mixed plume.



HCN Area / CO Area = 2.17 ppt/ppb

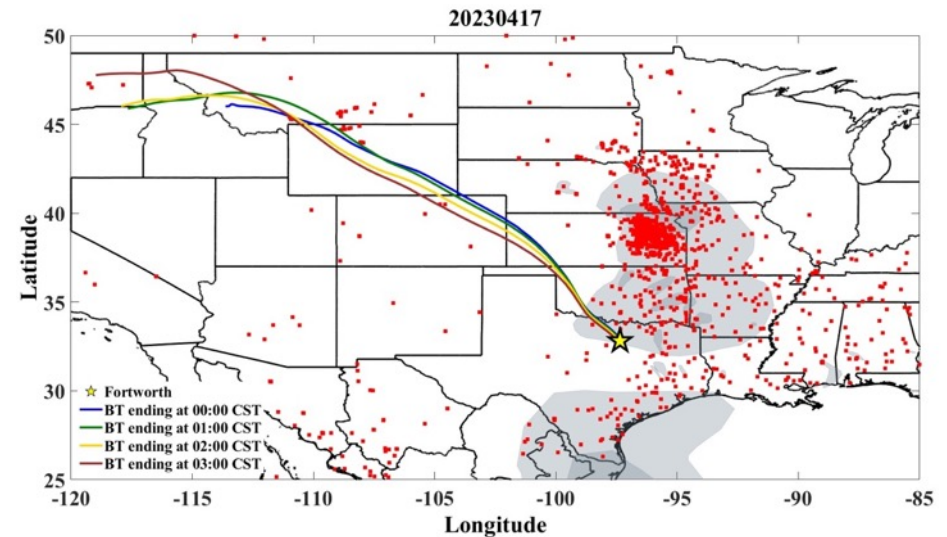
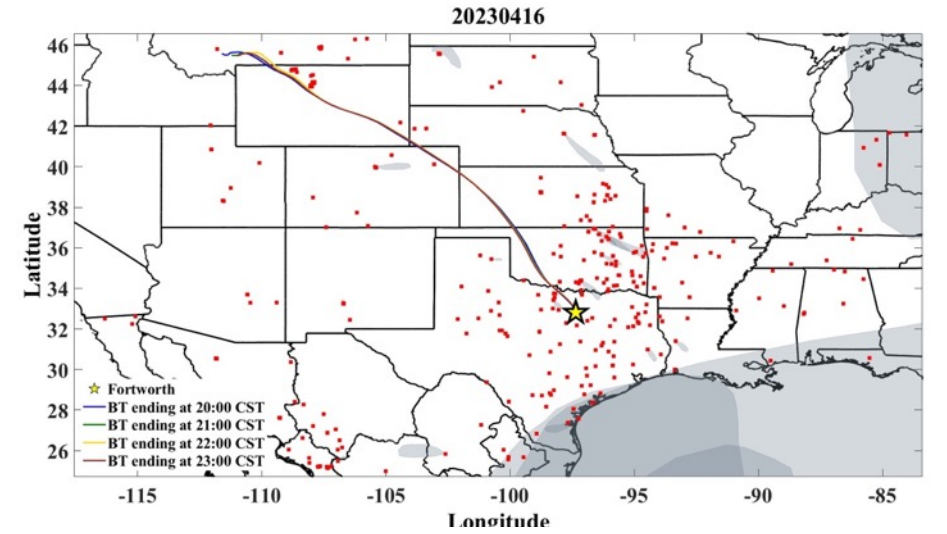
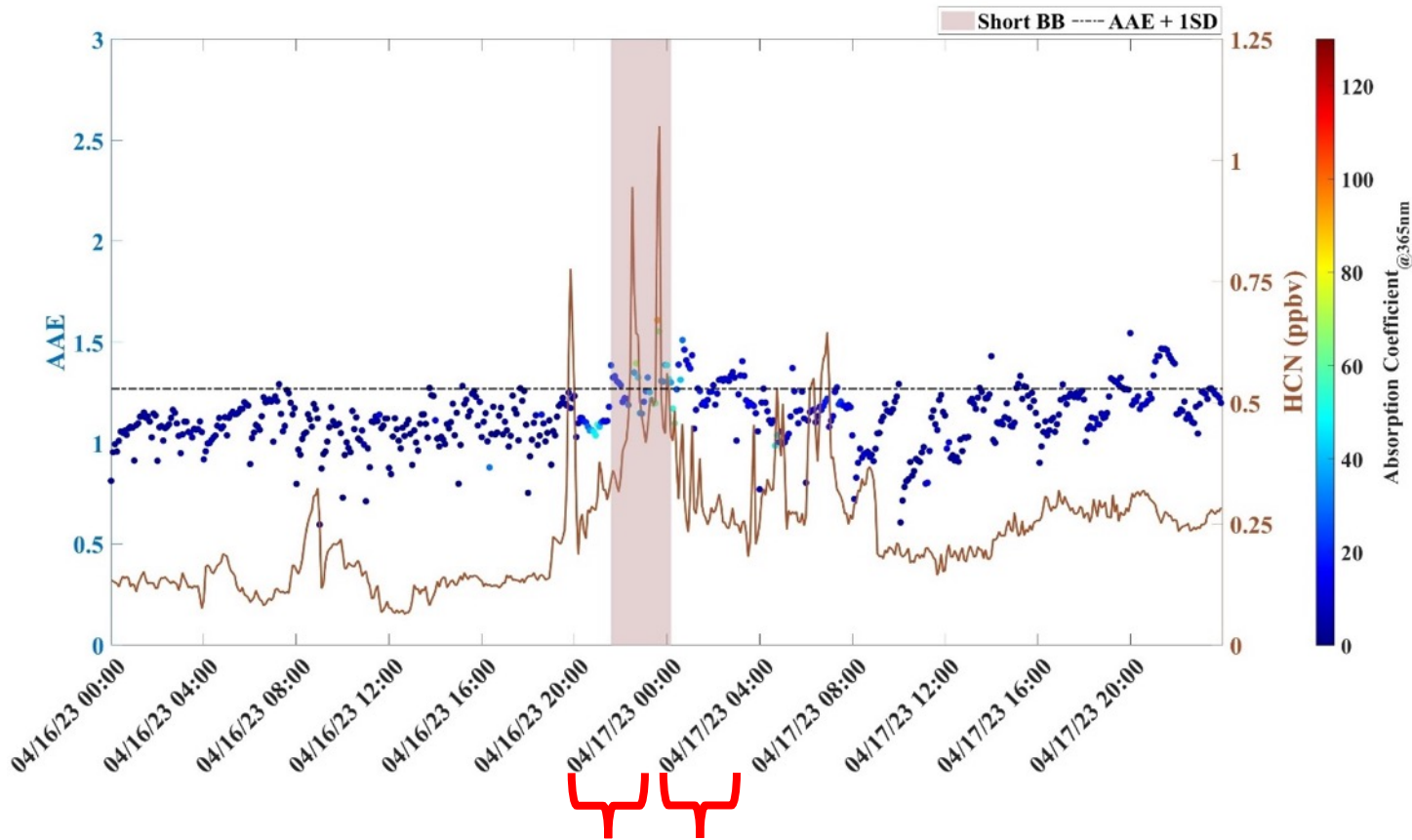
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Case Study 2: HCN peaks without a BB signal in the AAE

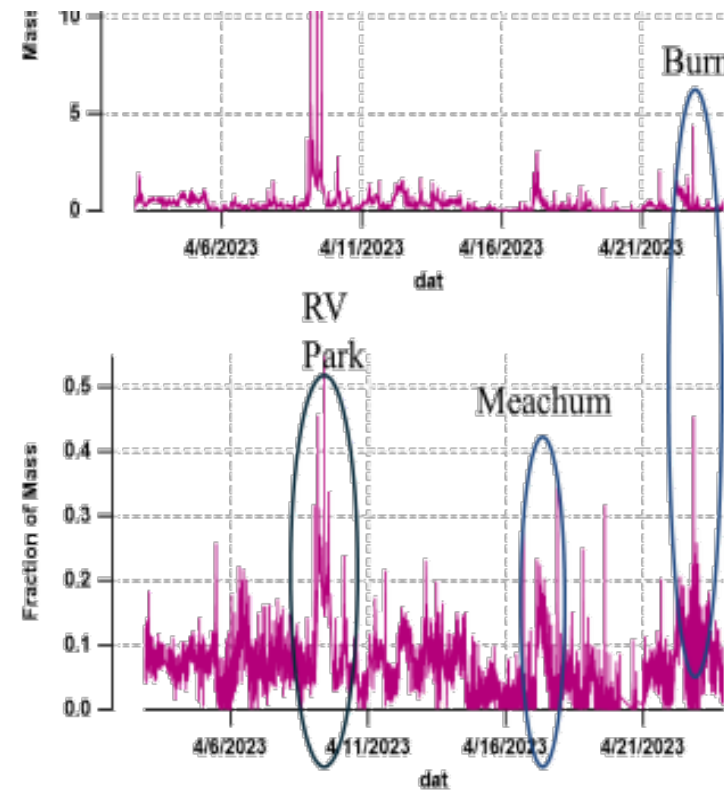
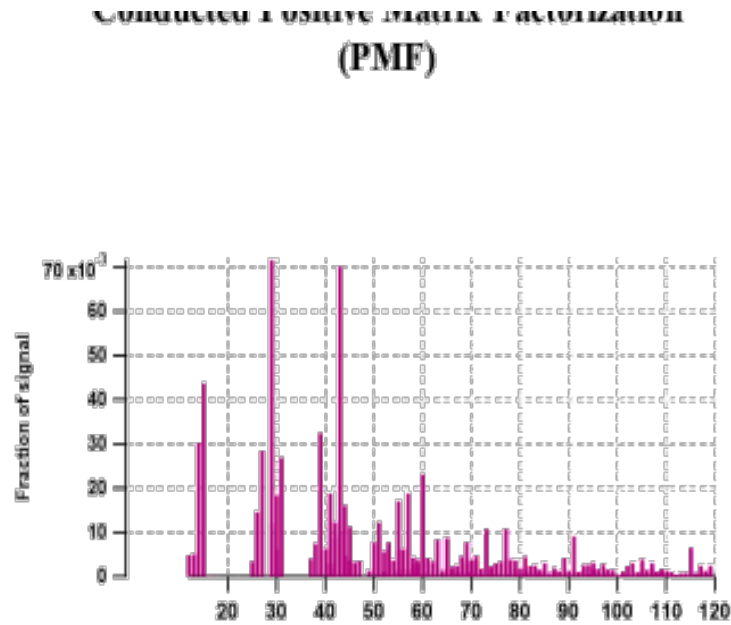


- Heavy rains were present in the back trajectory path for this period.
- Need to investigate potential rainout of aerosol in this week.
- CO and HCN have similar atmospheric lifetimes (months).
 - CO sink : OH oxidation
 - HCN sink: aqueous phase uptake
- These gas tracers may have more persistence when back trajectories go through precipitation regions.

Case Study 3: Biomass Burning with Enhanced Tracers

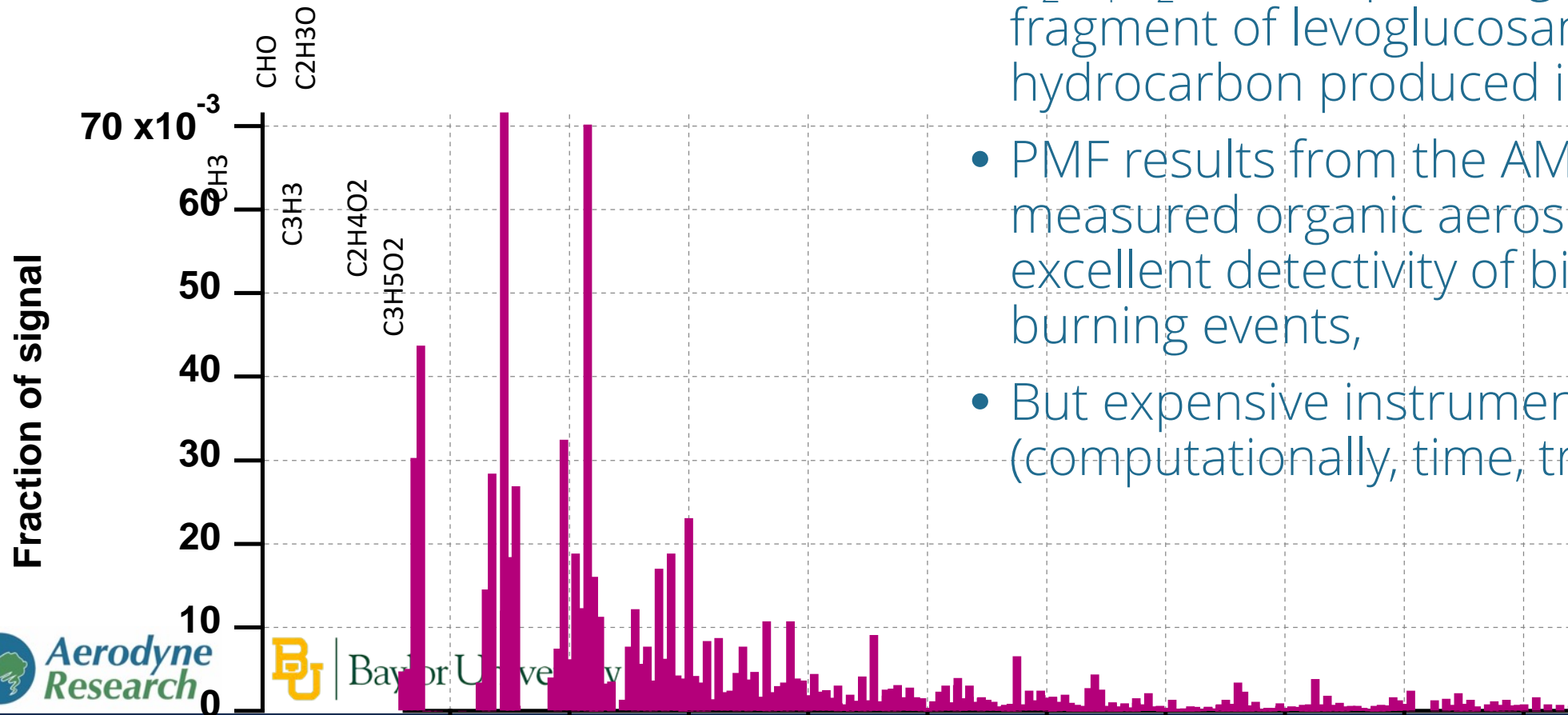


PMF interlude: Results from AQRP 22-010 (PI: Ed Fortner)



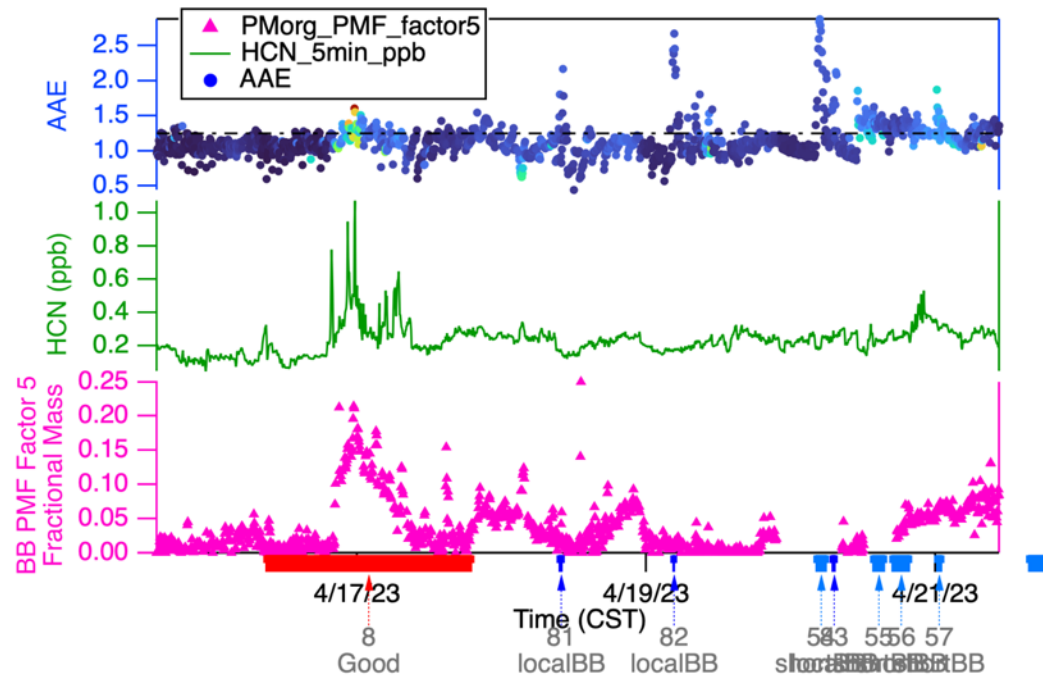
- Positive Matrix Factorization (PMF)
- Looks for species that vary together in time
- PMF of aerosol organics finds a group of ions that vary together and have the signature of biomass burning.

PMF Interlude



- BB factor has a characteristic ion at $C_2H_4O_2^+$, corresponding to a fragment of levoglucosan, a hydrocarbon produced in fires.
- PMF results from the AMS-measured organic aerosol provide excellent detectivity of biomass burning events,
- But expensive instrument & analysis (computationally, time, training)

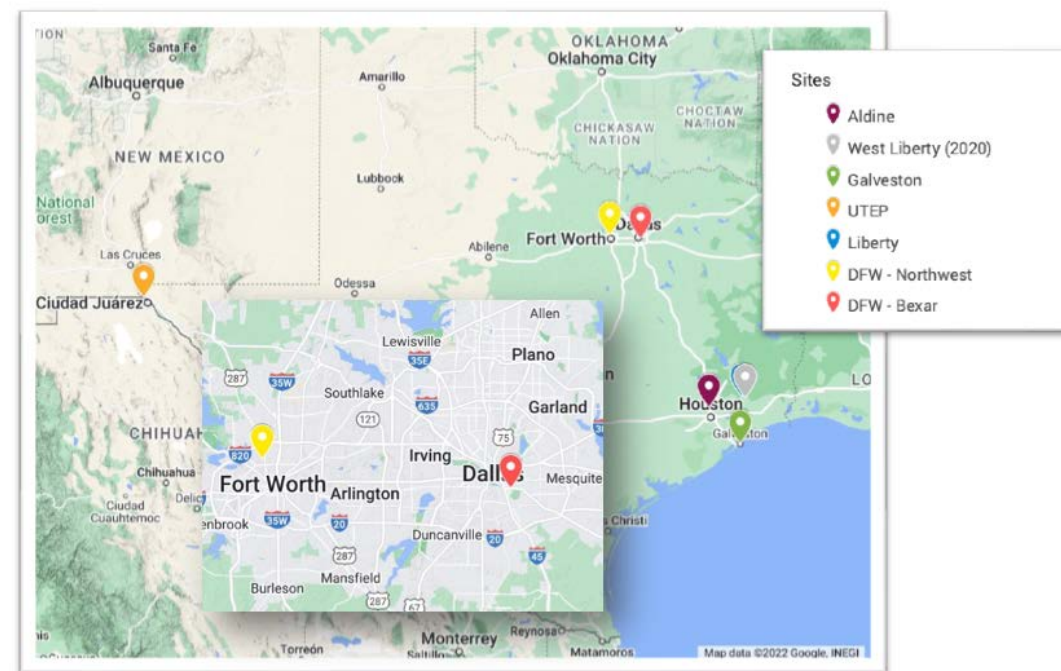
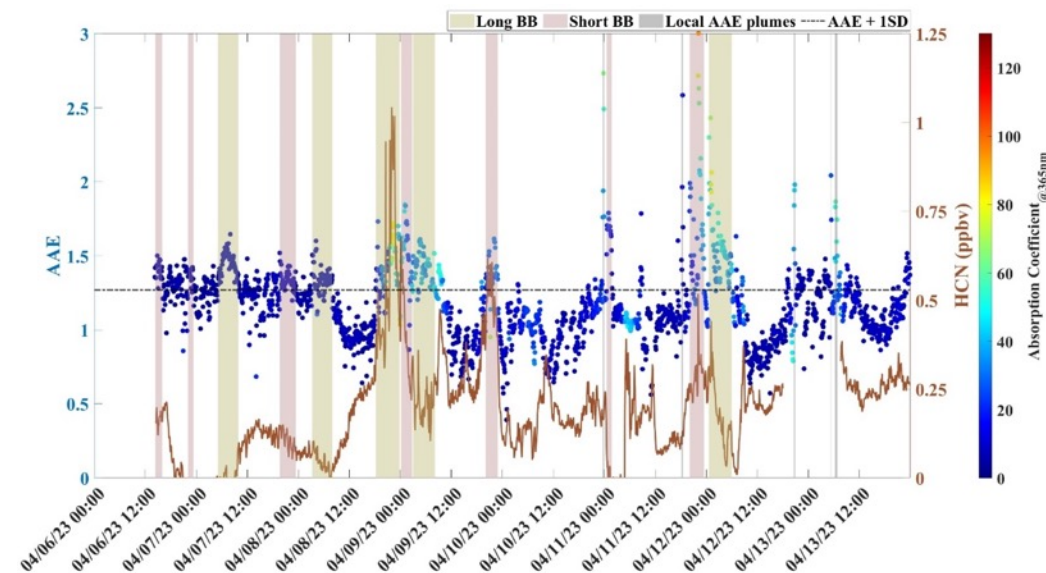
Case Study 3: Biomass Burning with Enhanced Tracers from AQRP 22-010



- PMF result indicates Organic PM has a clear fire signal, but it includes only 20% of mass.
- Remaining PMorg originates from other sources.
- HCN is a BB tracer capable of identifying BB even in mixed PM environments

Conclusions:

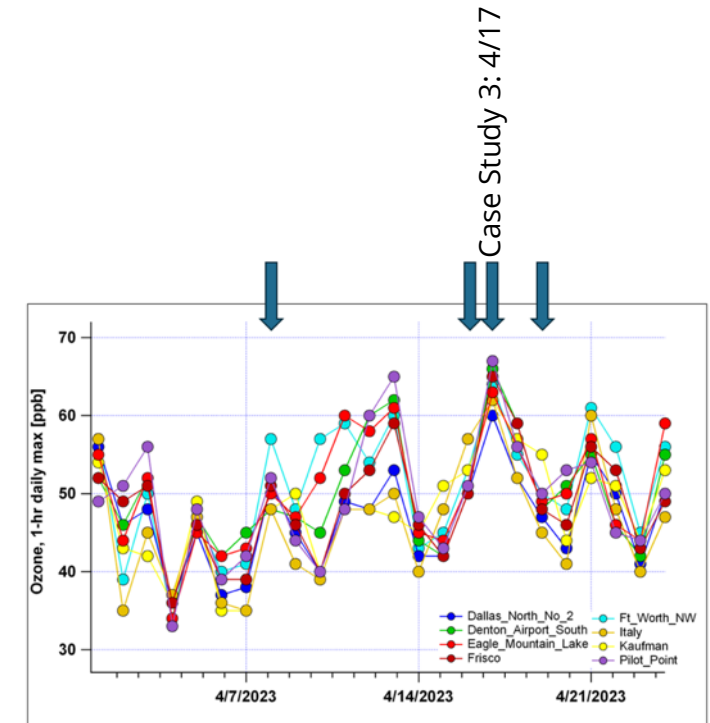
- When HCN and AAE (and absorption coefficient) are elevated, BB emissions more likely to impact local air quality
- Weight of evidence approach to identifying BB events.
- HCN is a sensitive fire tracer, even when BB impact is low
- Measurement of HCN via Tunable Infrared Laser Spectrometer is simple and robust.
 - Requires no filter changes
 - A good alternative to Chemical Ionization Mass Spectrometer techniques.
 - Agrees with PMF of PMorg via SP-AMS
 - Like AMS PMorg, HCN is composition-based



Future Work

- Monitoring for BB tracers in Texas
 - Monitoring at multiple sites: validate regional smoke impact.
 - (BC)² has 3 sites in Houston; 2 in DFW
 - Longer study: BB events seen outside of “fire season”
 - Add multiple chemical/PM indicators to increase confidence in smoke attribution.
 - HCN a good candidate
- Advanced analysis of field data
 - Ozone impact of smoke events.
 - Impact of precipitation on long-range transport
- Instrument development
 - Scrubber/zero air generator testing to eliminate UZA consumable for a truly unattended HCN instrument.
 - Improve recovery after power outages.

TCEQ daily
8-hr Max
Ozone
around
DFW



Data from TCEQ
(https://www.tceq.texas.gov/cgi-bin/compliance/monops/peak_monthly.pl)

Acknowledgements – Funding & Projects

- These HCN measurements were funded by AQRP Project 22-006

This project was made possible by:

- TCEQ's Fort Worth Northwest Data (CAMS Site 013)
- (BC)² Network Expansion – TCEQ
- Dallas Field Study – AQRP 22-010 – Aerodyne Mobile Laboratory

Acknowledgements - People

- Baylor University – Sascha Usenko, Rebecca Sheesley (Co-PIs),
 - Students Jeewan Poudel and Mackenzie Graham
 - Tate at Barrett Environmental
- Aerodyne Research –
 - Conner Daube (Interim PI), Ed Fortner, Matt Lund, and other scientists on AQRP 22-010
- University of Houston –
 - (BC)² Network collaborators
 - Provided CO measurement in (BC)² trailer

Questions

Supplementary Slides

Biomass Burning vs Traffic

Biomass Burning HCN/CO ratios

- HCN inversely correlated with MCE
 - Flaming = more HCN
 - Smoldering = less HCN
- Range includes variety of fuel types

Literature BB HCN Emission Ratio:
 HCN/CO ~ 0.43 to 12.8 ppt ppb⁻¹
 (Le Breton et al., and references within)

9222

M. Le Breton et al.: Airborne hydrogen cyanide measurements

Table 2. HCN : CO NEMRs as quoted in literature and the calculated NEMR for HCN from data collected throughout the BORTAS campaign, excluding flight B622. NEMR ratio units are ppt ppb⁻¹.

Lobert	Singh	Rinsland	Andreae	Sinha	Yokelson	Simpson	Hornbrook	This work
11.3 (lab)	0.001–0.011 (CA)	9.82 ± (AS)	0.43 ± 0.15 (Sv) 1.5 (TF) 1.4(TF)	9 ± 3 (Sv) 6 ± 2 (W) 9 ± 5 (G)	12.8 ± 9.5 (MC) 6.6 ± 4.8 (Yu) 7 ± 5.9 (TF)	8.2 ± 2 (Can)	8.8 ± 3.8 (As) 2.4 ± 0.9 (CA) 7.7 ± 3.2 (Can)	3.68 ± 0.149 (Can)

Sv: African savannas, TF: tropical forests, W: savanna woodland, G: savanna grassland, MC: Mexico City region, Yu: Yucatán, As: Asian, CA: California, Can: Canada, Lab: laboratory.

Traffic HCN: Dynamometer testing

S.G. Moussa et al. / Atmospheric Environment 131 (2016) 185–195

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- Moussa et al. 2016
- Individual tail pipe sensing by PTR-MS
- 3 gasoline vehicles, with different fuel injection, and use of an after-market particulate filter.
- More HCN during cold starts
- 2x more HCN for gasoline vs diesel

Table 1

Averages of the fuel-based emissions factors (^aEFs) for benzene, toluene, xylenes, acetonitrile and HCN from gasoline (PFI + GDI) vehicles for different transient cycles at different engine temperatures at the startup.

Vehicle type	Fuel injection	Exhaust treatment	Driving Mode	Engine temperature	CO (g/km)	CO ₂ (g/km)	Emission factor (mg/kg of fuel)					HCN (mg/km)
							Benzene	Toluene	^b xylenes	CH ₃ CN	HCN	
Sonata	GDI	GPF	LA4	Cold	0.4	233.9	3 × 3.3	527.6	177.7	7.4	5.5	0.6
Sonata	GDI	GPF	LA4	Hot	0.2	212.8	19.7	143.2	17.1	5.1	4.8	0.3
Sonata	GDI	OPF	SS mph50	Warm	0.1	106.0	77.3	262.8	42.3	6.0	5.8	0.2
Sonata	GDI	GPF	US06	Cold	0.8	179.0	314.9	5966	150.6	104	149	0.8
Sonata	GDI	GPF	US06	Hot	0.8	179.0	184.8	296.4	66.0	5.4	9.2	0.5
Volvo	PFI	No GPF	LA4	Cold	0.2	259.5	395.7	795.3	319.6	23.4	7.9	0.6
Volvo	PFI	So GPF	LA4	Hot	0.2	234.0	622	204.4	28.4	6.5	0.3	0.0
Volvo	GDI	No GPF	SS mph50	Warm	0.1	133.1	73.9	151.0	33.4	90	4.7	0.2
Volvo	GDI	No GPF	US06	Cold	0.3	217.2	91.2	217.6	63.2	5.3	16.0	1.0
Volvo	GDI	No GPF	US06	Hot	0.4	217.2	52.9	141.1	26.9	2.1	6.0	0.4
Sonata	GDI	No GPF	LAI	Cold	0.8	244.2	406.7	705.2	213.6	1.8	76.0	5.6
Sonata	GDI	No GPF	LAI	Hot	0.4	217.7	103.7	321.3	48.2	1.3	46.4	3.1
Sonata	OD3	No GPF	SS mph50	Warm	0.1	103.6	57.1	134.9	15.0	06	10.7	0.4
Sonata	GDI	No GPF	LS06	Cold	1.6	205.7	291.1	410.3	122.3	1.3	77.4	4.8
Sonata	GDI	No GPF	US06	Hot	1.6	205.7	117.6	191.3	41.5	1.3	39.7	2.5
silverado	PFI	No OPF	LA4	cold	3.0	341.6	691.0	643.7	726.5	27.7	15.9	1.8
silverado	PFI	No GPF	LA4	hot	3.0	381.6	165.7	382.9	370.2	15.2	6.9	0.8

^a Average of 22 min transient driving cycle.

^b Sum of o,m,p-xylene and ethyl benzene.

0.3 – 77.4 mg HCN/kg Fuel

Traffic HCN: Real-World Measurements

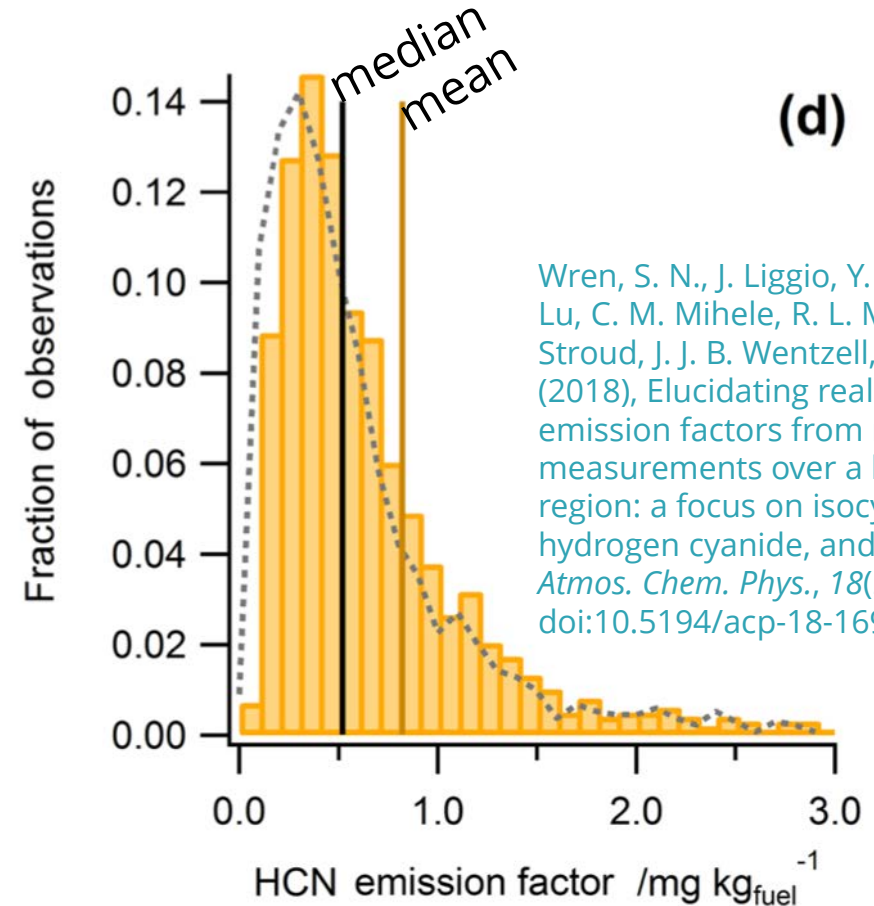
- Wren et al. 2018: fleet measurements in Toronto

Our work demonstrates that HCN emission factors obtained in outdated dynamometer studies for LDGVs equipped with first-generation three-way catalysts under abnormal operating conditions (Harvey et al., 1983) are not applicable to the present day. However, they indicate that the most recent dynamometer studies (Moussa et al., 2016; Karlsson, 2004) may also overestimate real-world HCN emissions. Overall, the relatively small vehicle emission factor obtained in this study suggests that vehicles are not likely a significant source of HCN on a regional and larger scale.

- 0.5 mg HCN/kg Fuel means 0.3 ppt HCN/ppb CO

- Assumptions:

- 81 ppb CO/ ppm CO₂
- 0.86 gC/kgFuel



Wren, S. N., J. Liggio, Y. Han, K. Hayden, G. Lu, C. M. Mihele, R. L. Mittermeier, C. Stroud, J. J. B. Wentzell, and J. R. Brook (2018), Elucidating real-world vehicle emission factors from mobile measurements over a large metropolitan region: a focus on isocyanic acid, hydrogen cyanide, and black carbon, *Atmos. Chem. Phys.*, 18(23), 16979-17001, doi:10.5194/acp-18-16979-2018.

IQR (0.32–0.88 mg kg_{fuel}⁻¹)

Unit conversions

$$\frac{50 \text{ mg HCN}}{1 \text{ kg Fuel}} \frac{1 \text{ mol HCN}}{31000 \text{ mg HCN}} \frac{1 \text{ kg Fuel}}{3153 \text{ g CO}_2} \frac{44 \text{ g CO}_2}{1 \text{ mol CO}_2} = 2.3 \times 10^{-5} \frac{\text{mol HCN}}{\text{mol CO}_2} = 23 \frac{\text{ppt HCN}}{\text{ppm CO}_2}$$

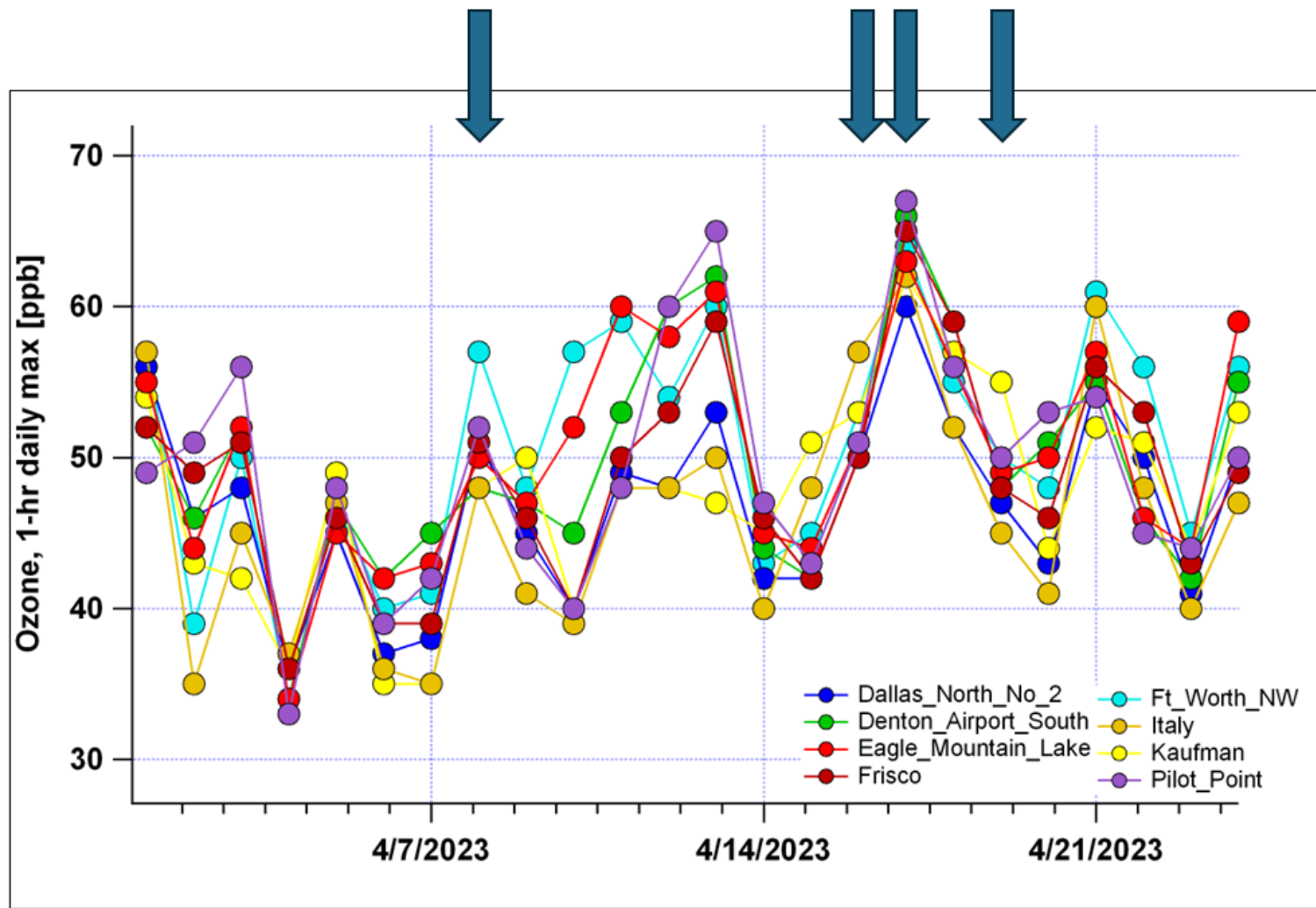
from 0.86 kgC/kgFuel
(weighted average
gasoline and diesel,
Wren et al. pub)

79 - 84 ppb CO per ppm CO₂, EPA
Average Annual Emissions and Fuel
Consumption for Passenger Cars and
Light Trucks, EPA420-F-00-013, 2000)

$$81 \frac{\text{ppb CO}}{\text{ppm CO}_2}$$

$$= 0.27 \frac{\text{ppt HCN}}{\text{ppb CO}}$$

Ozone



Daily maximum ozone in ppb, 1-hr average, from eight TCEQ monitoring sites around the DFW region.

Arrows indicate days where ARI conducted upwind / downwind studies (8-Apr, 16-Apr, 17-Apr, 19-Apr).

Note that 17-Apr was the day of highest maximum ozone across all monitoring sites for the campaign.

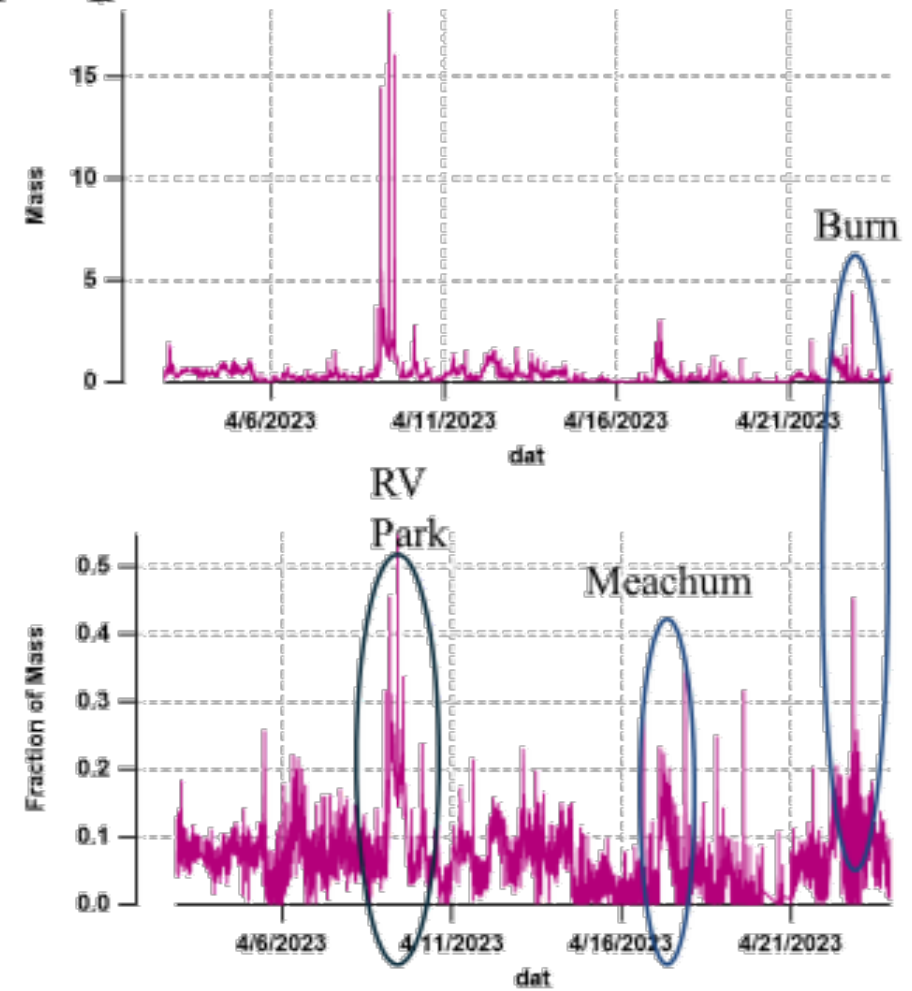
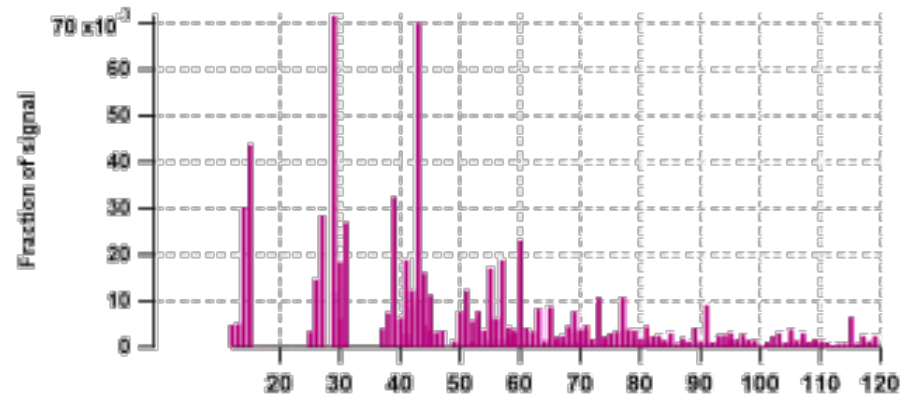
Data from TCEQ

(https://www.tceq.texas.gov/cgi-bin/compliance/monops/peak_monthly.pl)

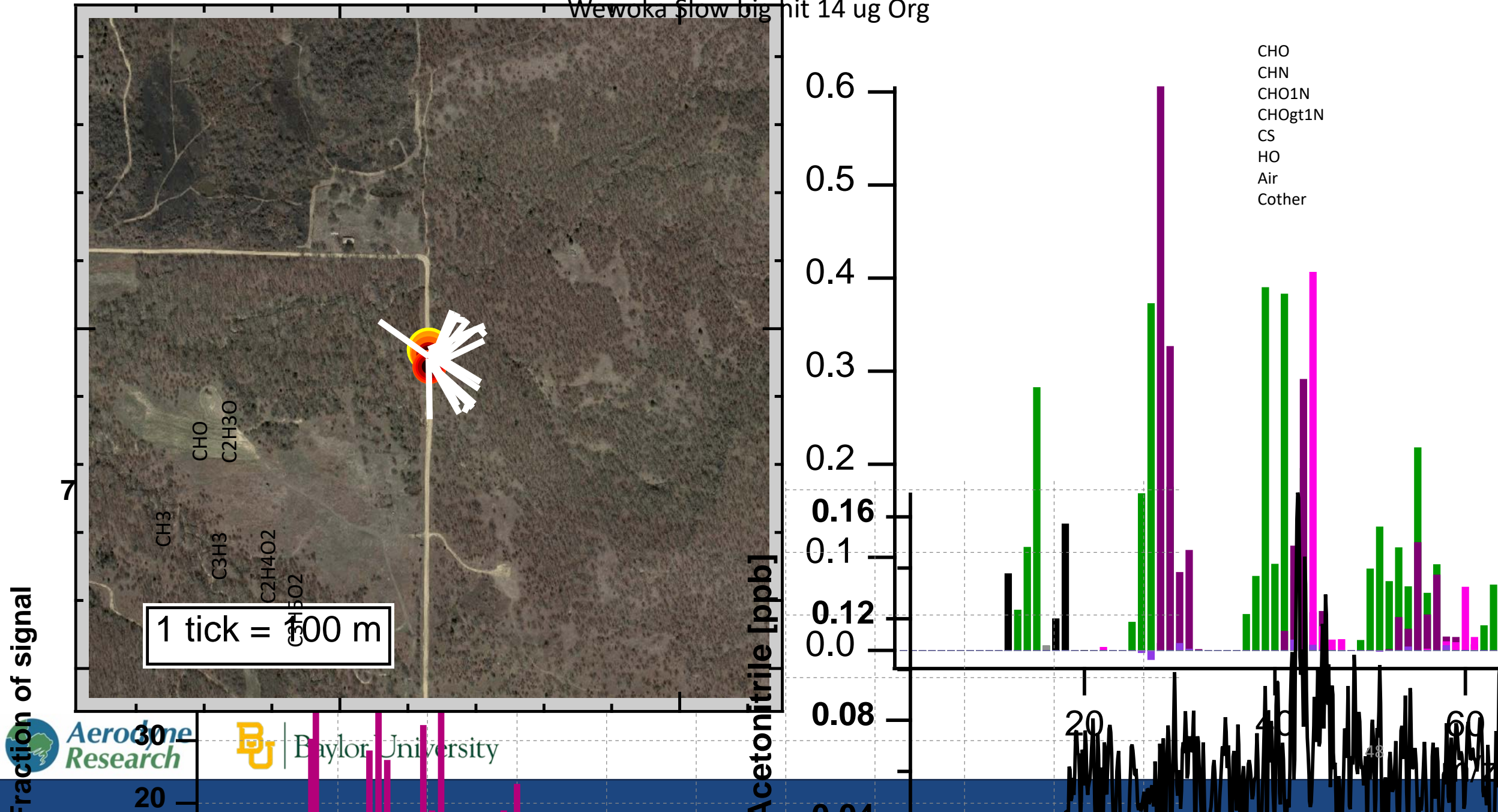
Positive Matrix Factorization

Signal Obtained at Burn Site Compared with Signal Throughout Campaign

Looking at SPAMS Organic Aerosol Signal
Conducted Positive Matrix Factorization
(PMF)



Wewoka slow big hit 14 ug Org



Fraction of signal

Acetonitrile [ppbb]

20

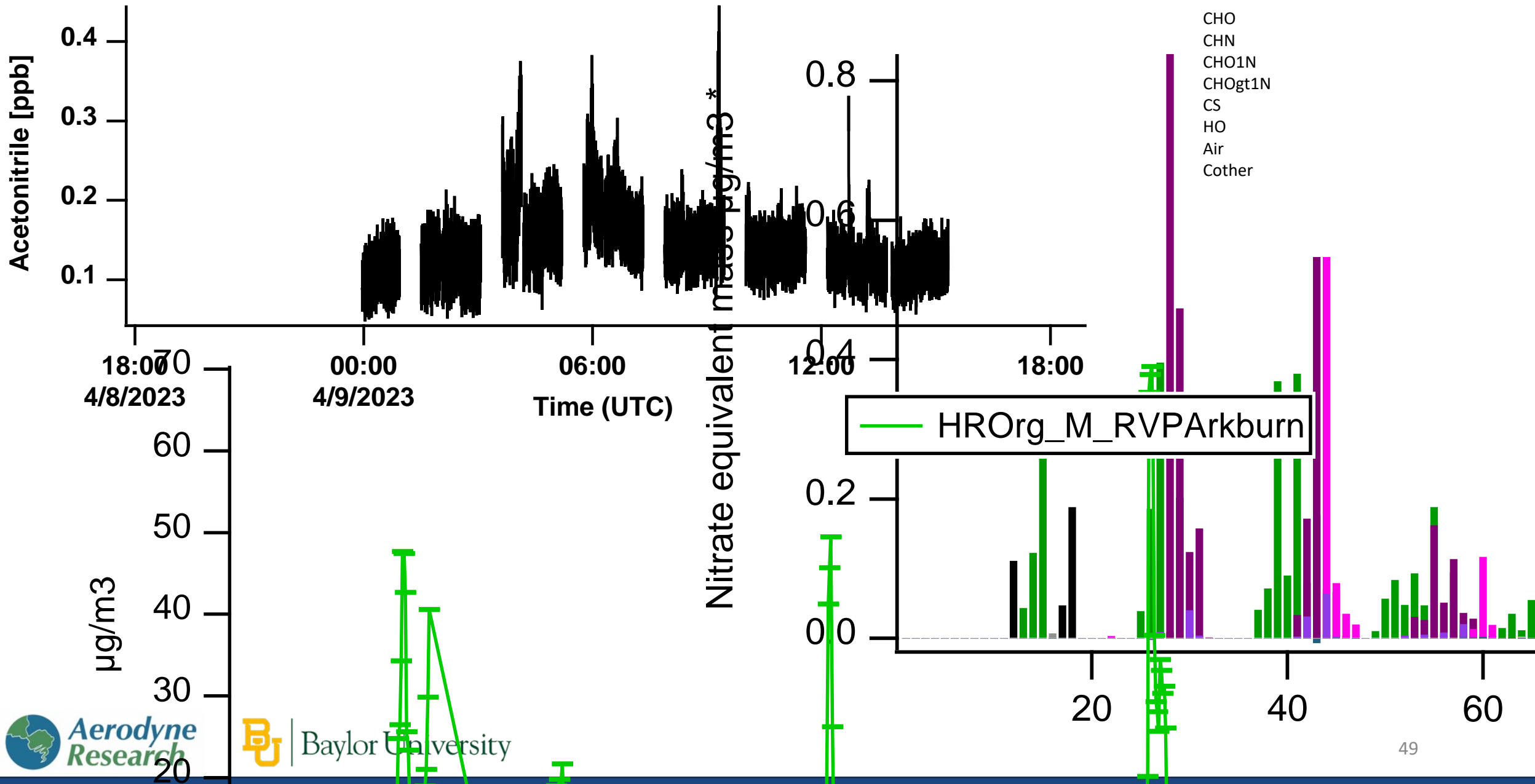
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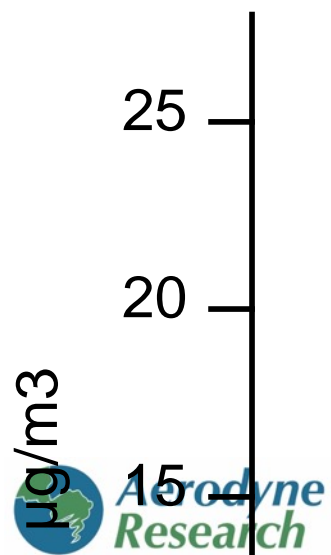
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RV Park





Aerodyne
Research

Baylor University

Meachum

Nitrate equivalent mass µg/m³ *

