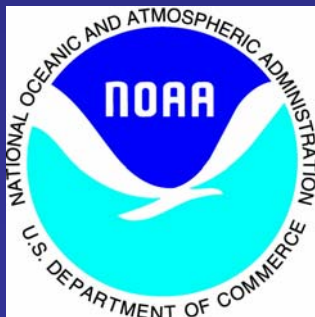


VOC Measurements at T1: Diurnal Variations, Emissions Fingerprint and Photochemical Production

Joost de Gouw, Dan Welsh-Bon, Carsten Warneke, Bill Kuster

*NOAA Earth System Research Laboratory
and*

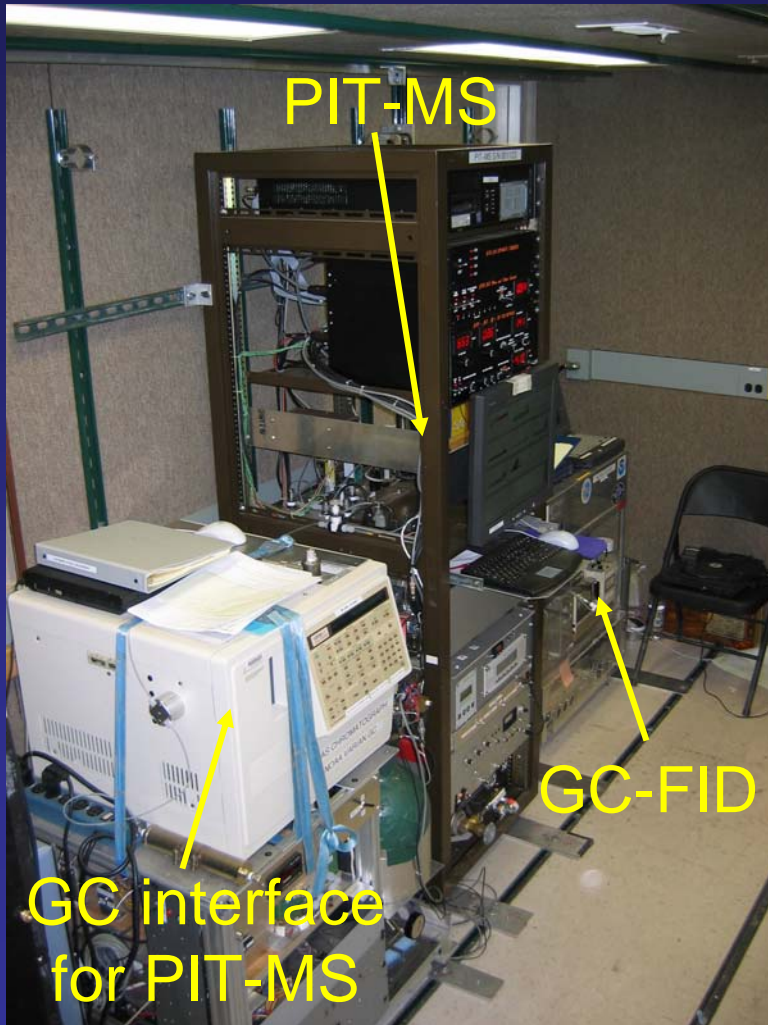
*CIRES, University of Colorado
Boulder, Colorado*



<http://cires.colorado.edu/~gouw>



NOAA VOC Instruments at T1



PIT-MS

“PTR-MS with an ion trap MS”

Aromatics

Oxygenates

Acetonitrile

5-min data

GC interface for VOC identification

On-line GC-FID

Alkanes

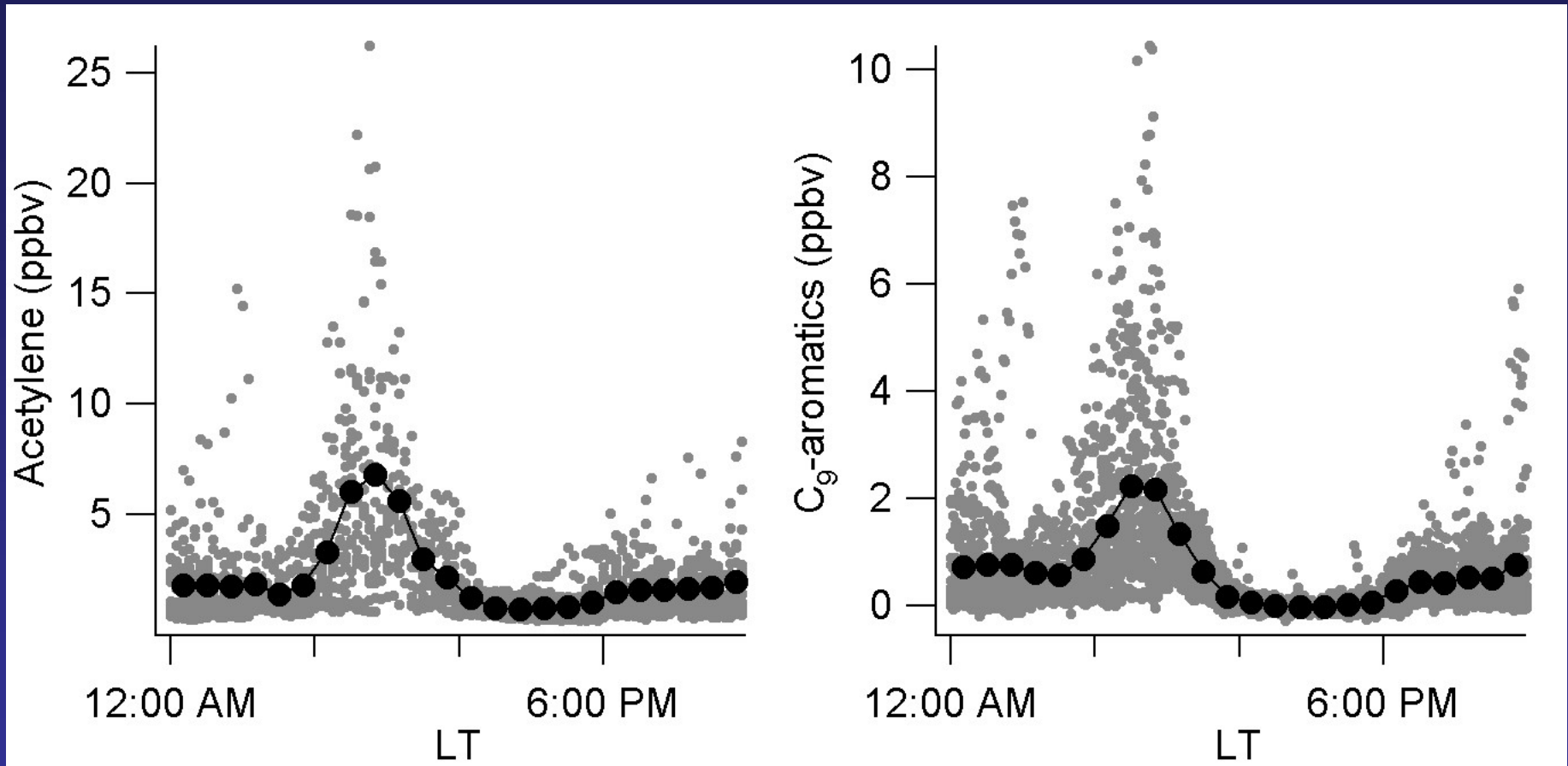
Alkenes

Acetylene

15-min data

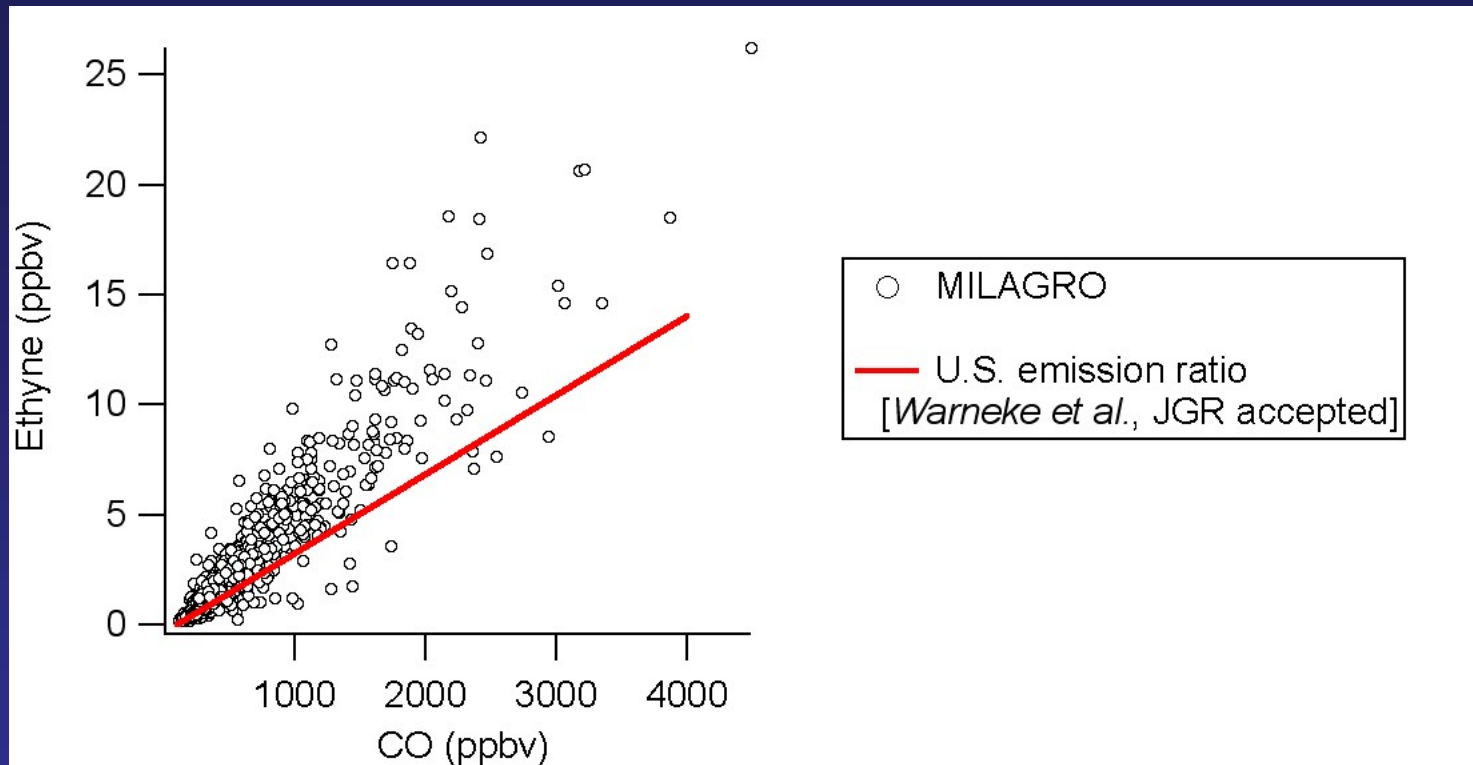
All data final, inter-compared
and @ NCAR CDP

Diurnal Variations: Hydrocarbons



- High in the morning: emissions, shallow BL, no chemistry
- Low during day: daytime BL much higher, chemistry

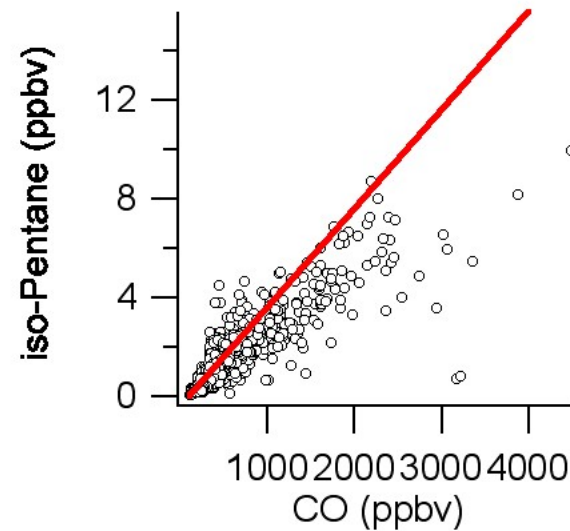
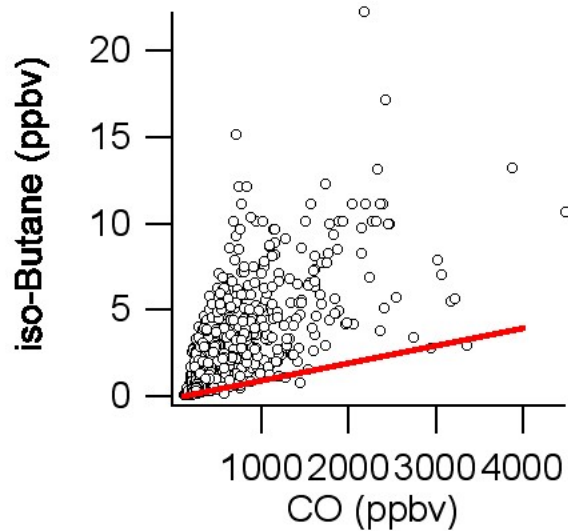
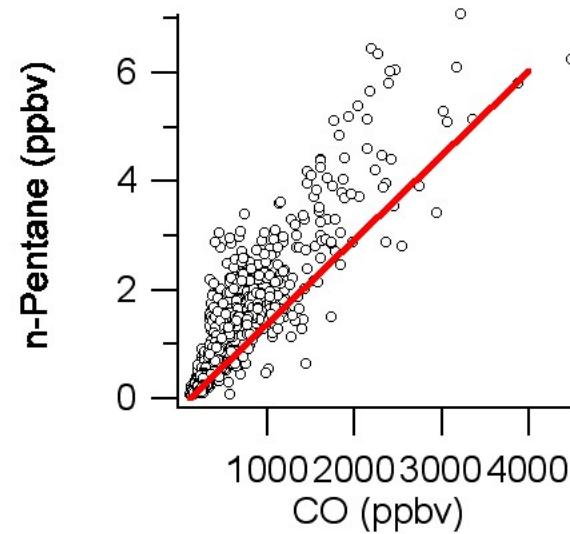
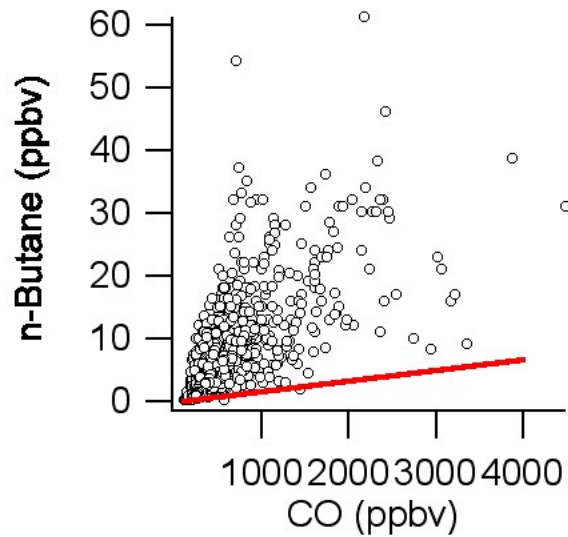
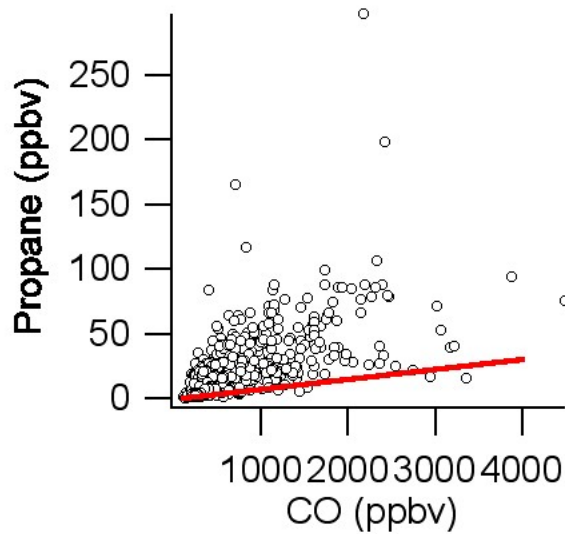
Comparison of Emissions with U.S.



CO: Huey et al.

- Scatter plots dominated by nighttime values (no chemistry)
- Well-suited for determining emission ratios
- Results compared with U.S.:
compilation of data from New York City, Boston and LA

Comparison of Emissions with U.S.: Alkanes



With few exceptions: emission ratios higher than in U.S.

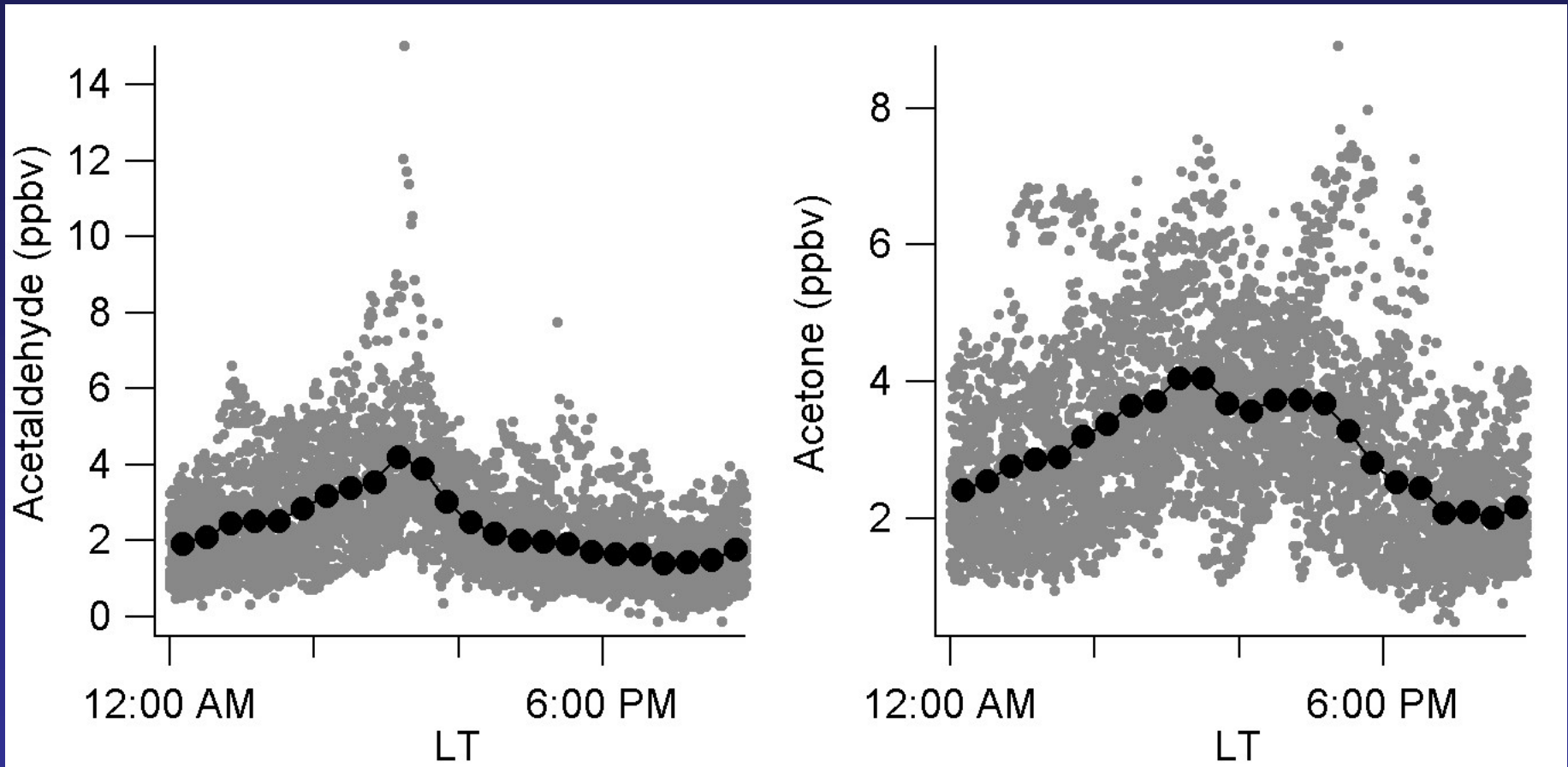
Comparison of Emissions with U.S.: Summary

Compound	OH reactivity (s^{-1} [ppmv CO] $^{-1}$)		Carbon mass (μg C m^{-3} [ppmv CO] $^{-1}$)	
	U.S.	Mex	U.S.	Mex
Alkanes	0.94 †	2.04	42 †	83
Alkenes	2.84	5.89	8.4	15
Aromatics	2.15	4.64	23	44

† for the alkanes measured during Milagro

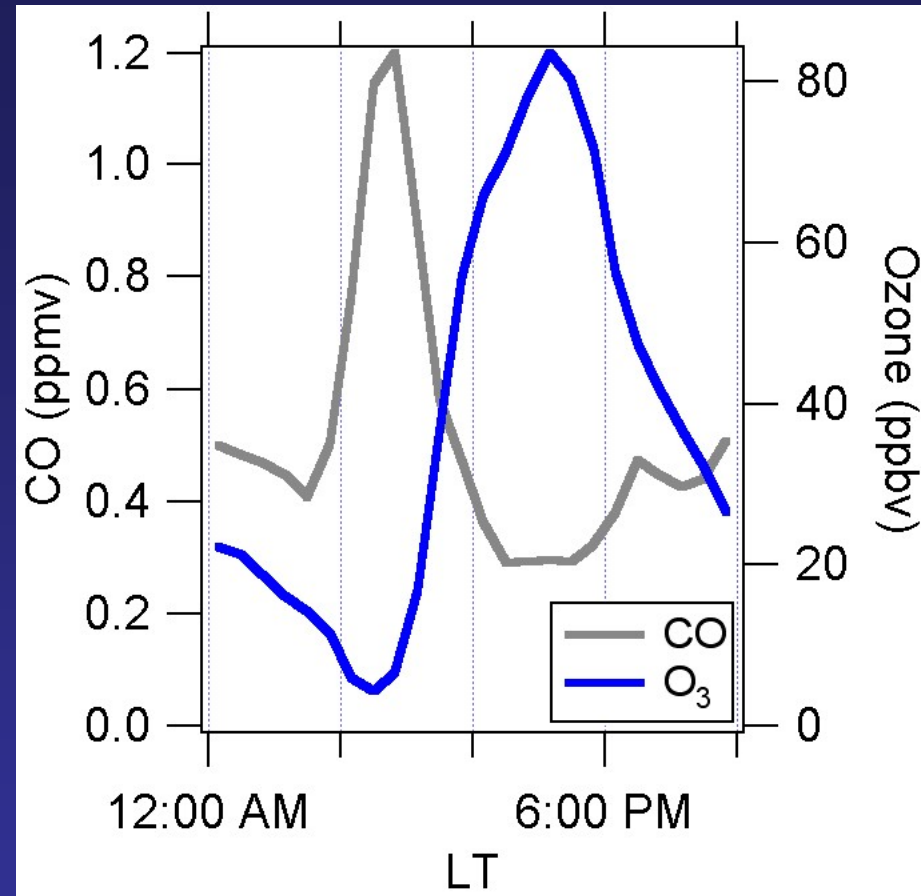
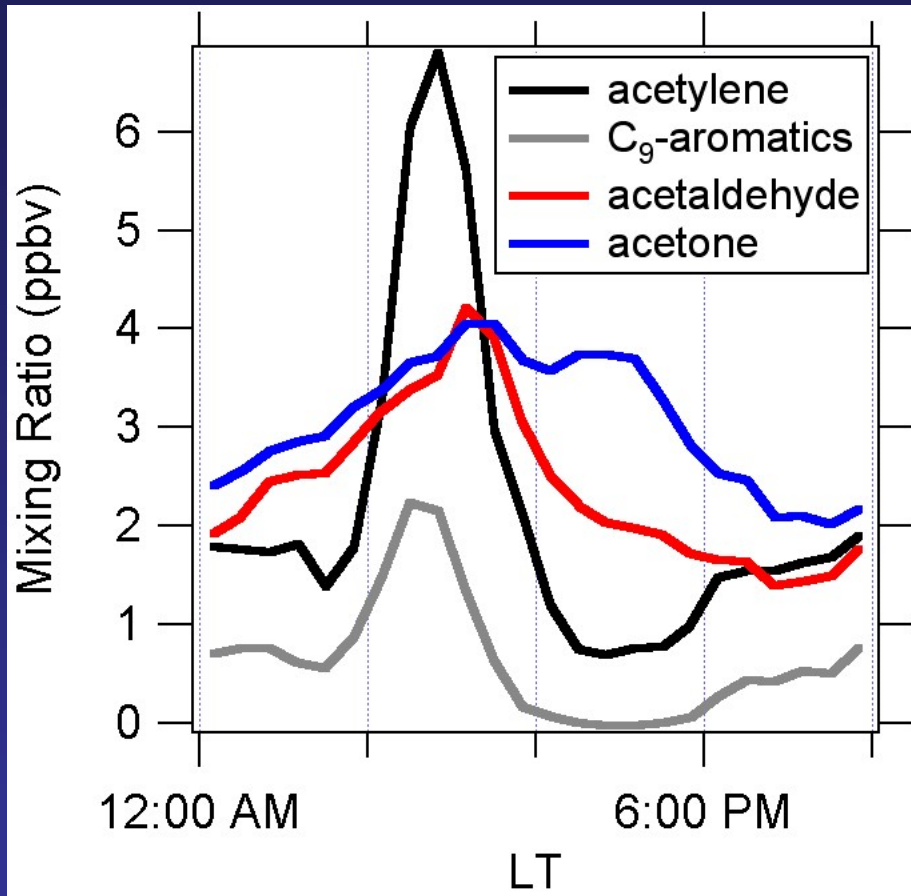
VOC signature = dirty vehicles + additional alkanes

Diurnal Variations: Oxygenates



- Direct emissions night and day
- Photochemical formation during the day

Photo-Chemical Formation of Oxygenated VOCs

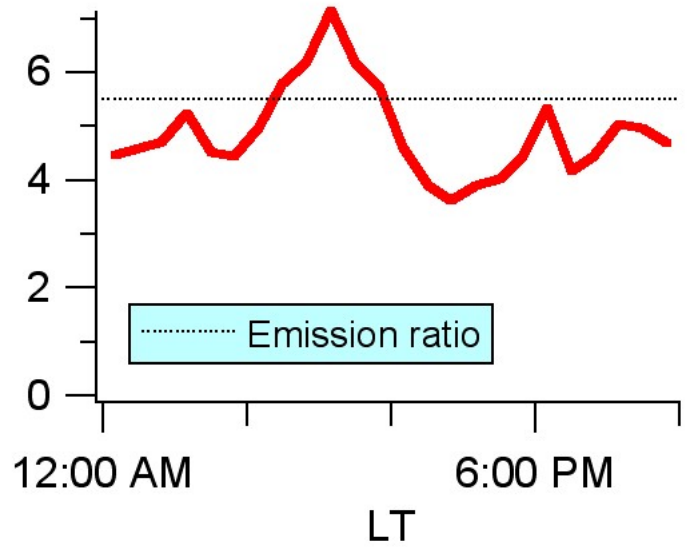


CO, O₃: Huey et al.

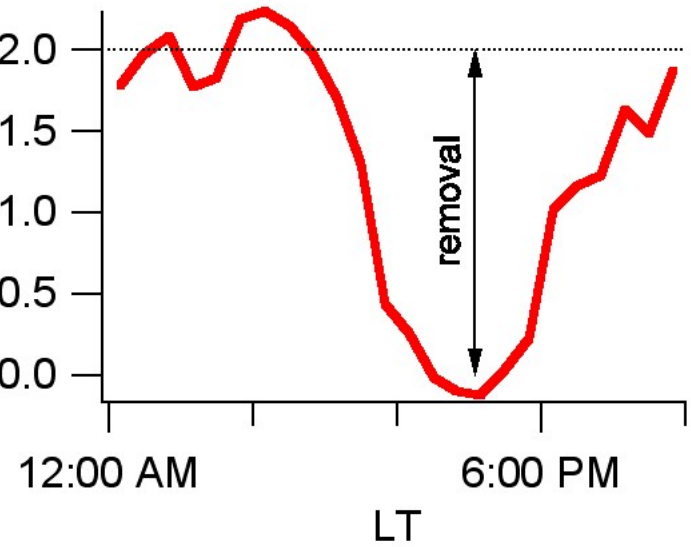
- Summary of diurnal variations
- Take ratio vs. CO minus a background (100 ppbv)

Photo-Chemical Formation of Oxygenated VOCs

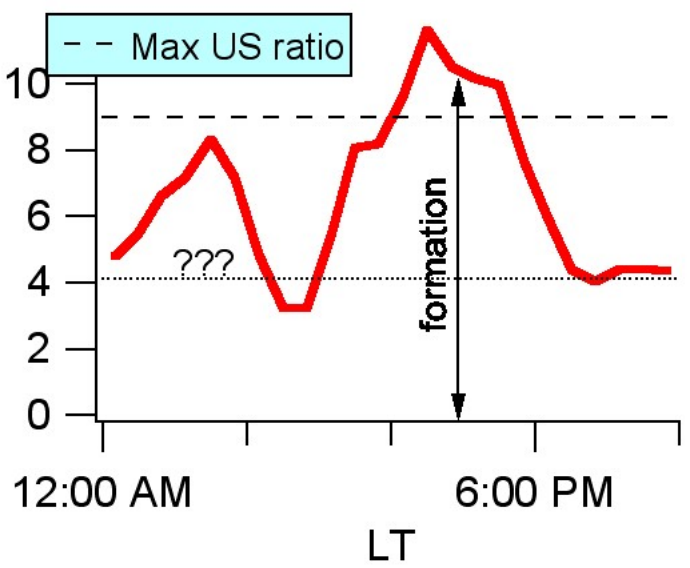
Acetylene/(CO-0.1)



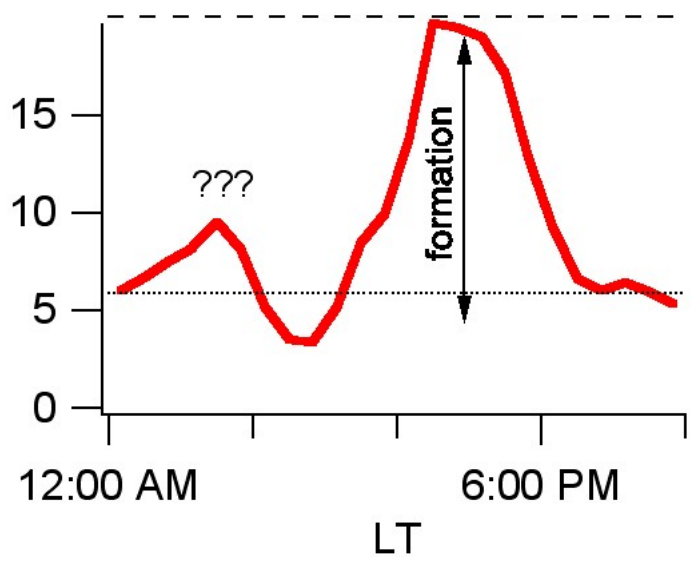
C₉-aromatics/(CO-0.1)



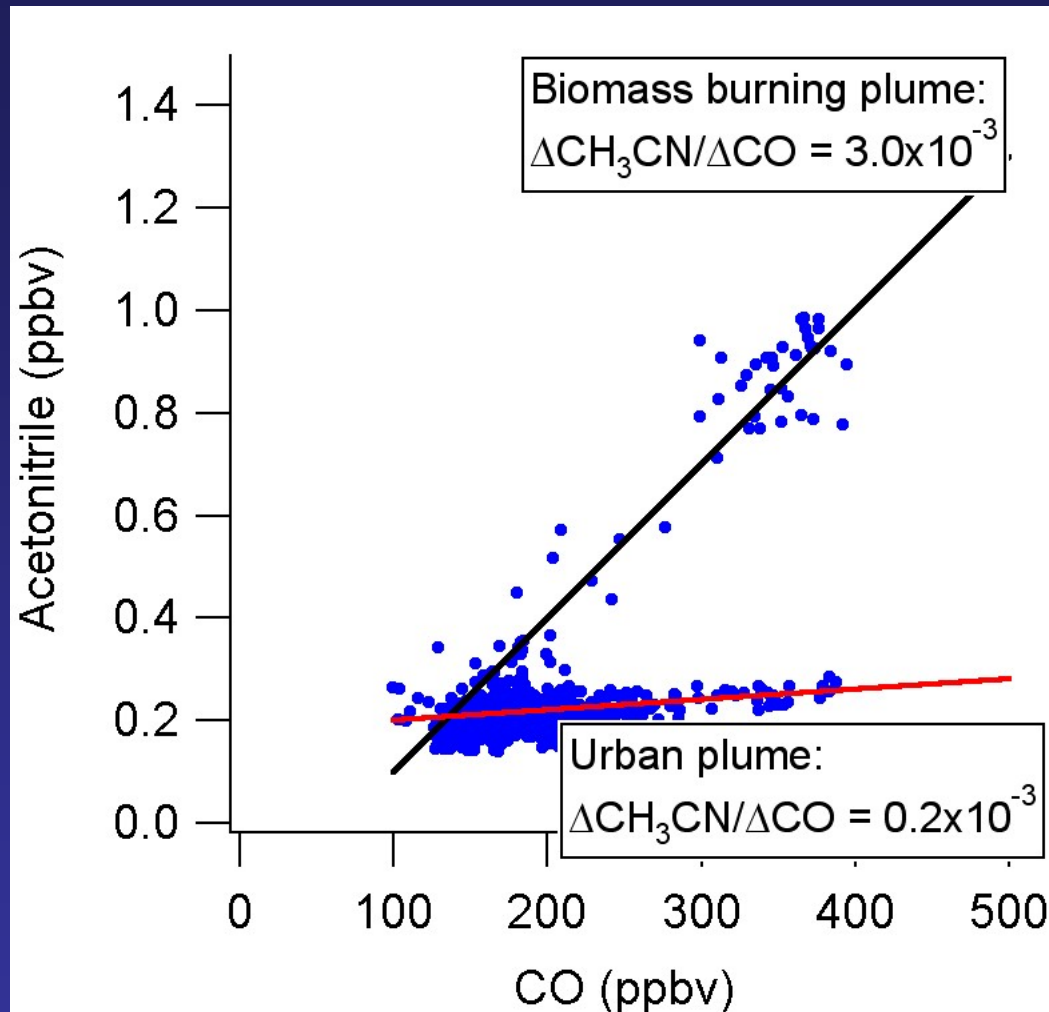
Acetaldehyde/(CO-0.1)



Acetone/(CO-0.1)

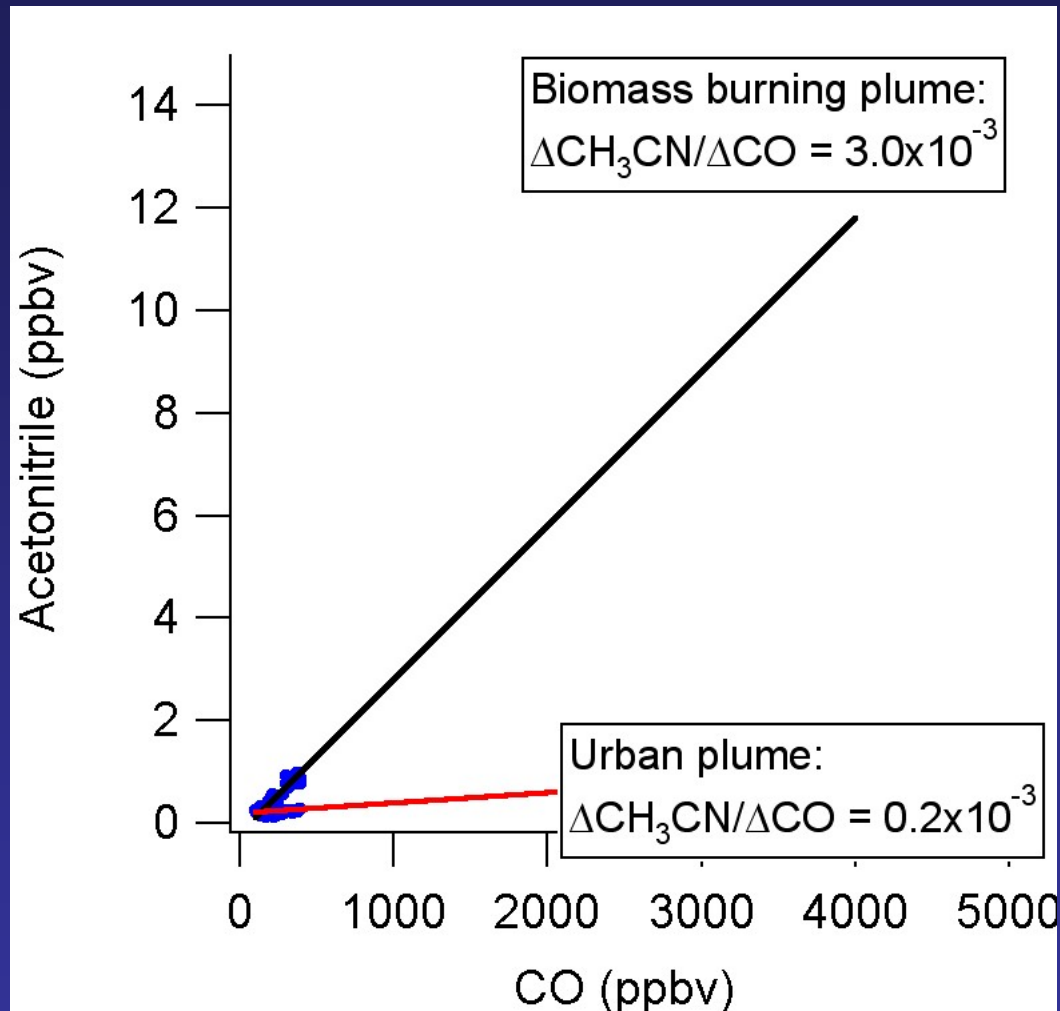


What About Biomass Burning?



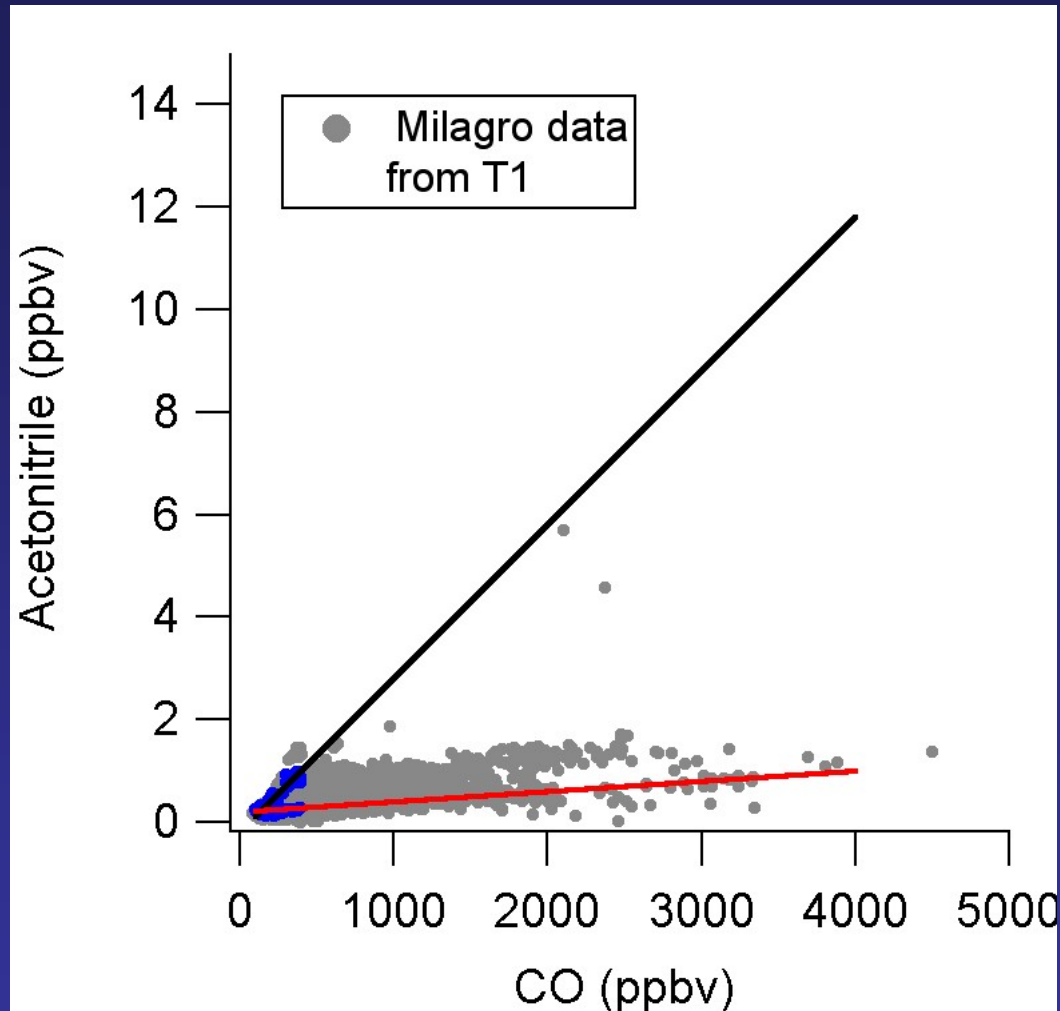
- Use of acetonitrile as a tracer
- Example from airborne data from ICARTT

What About Biomass Burning?



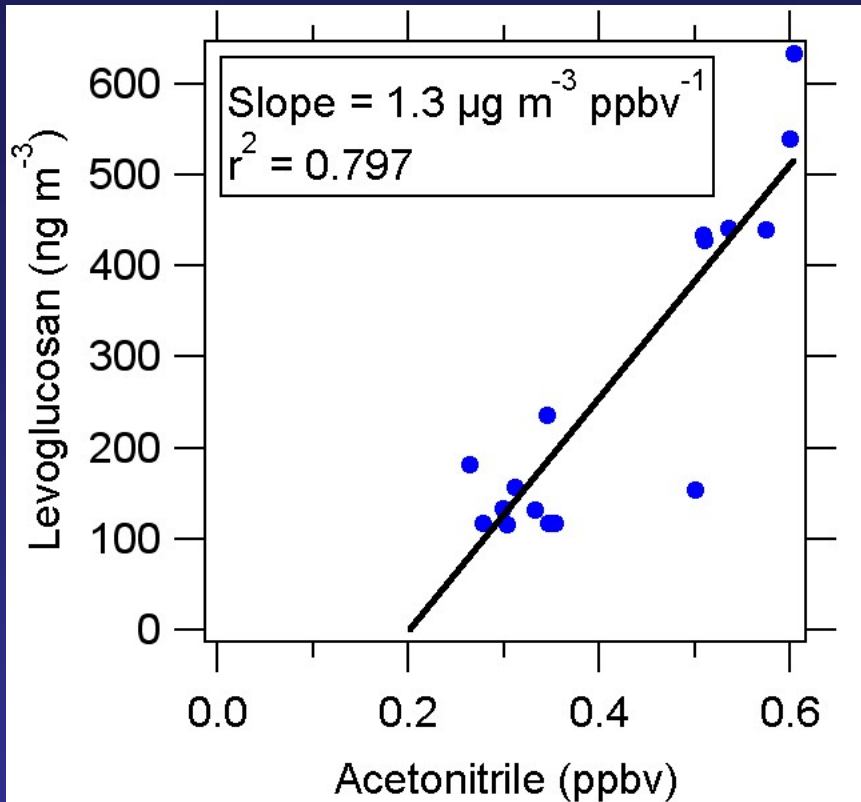
Zoom out by factor 10

What About Biomass Burning?

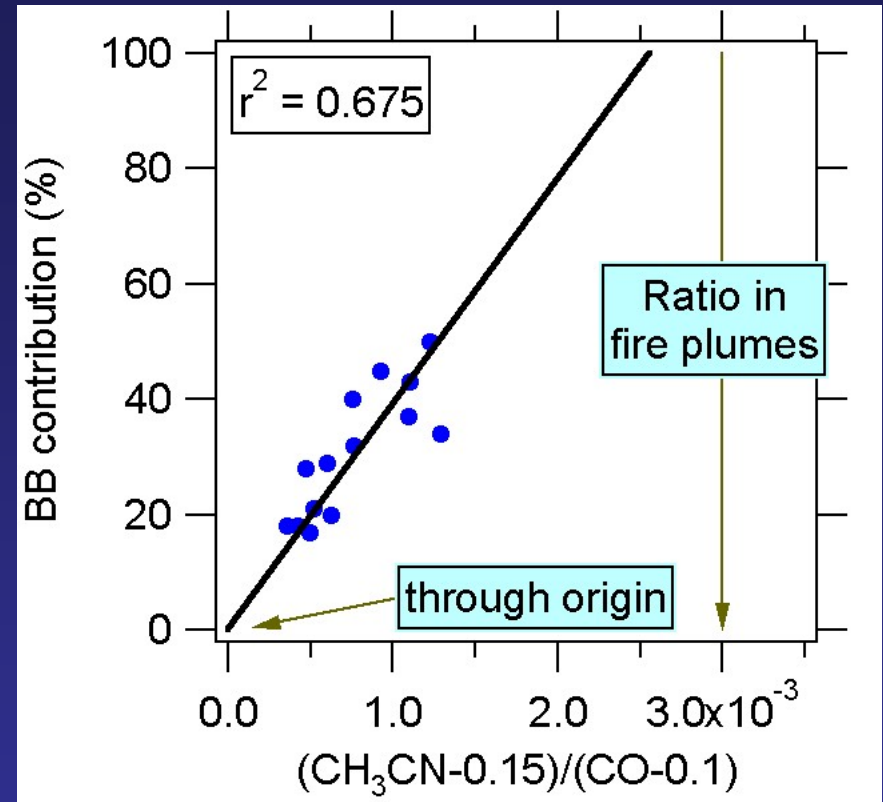


- Nighttime (high CO): Mexico City \approx New York City
- Daytime (low CO): more variability in $\text{CH}_3\text{CN}/\text{CO}$ ratio

Acetonitrile versus Levoglucosan

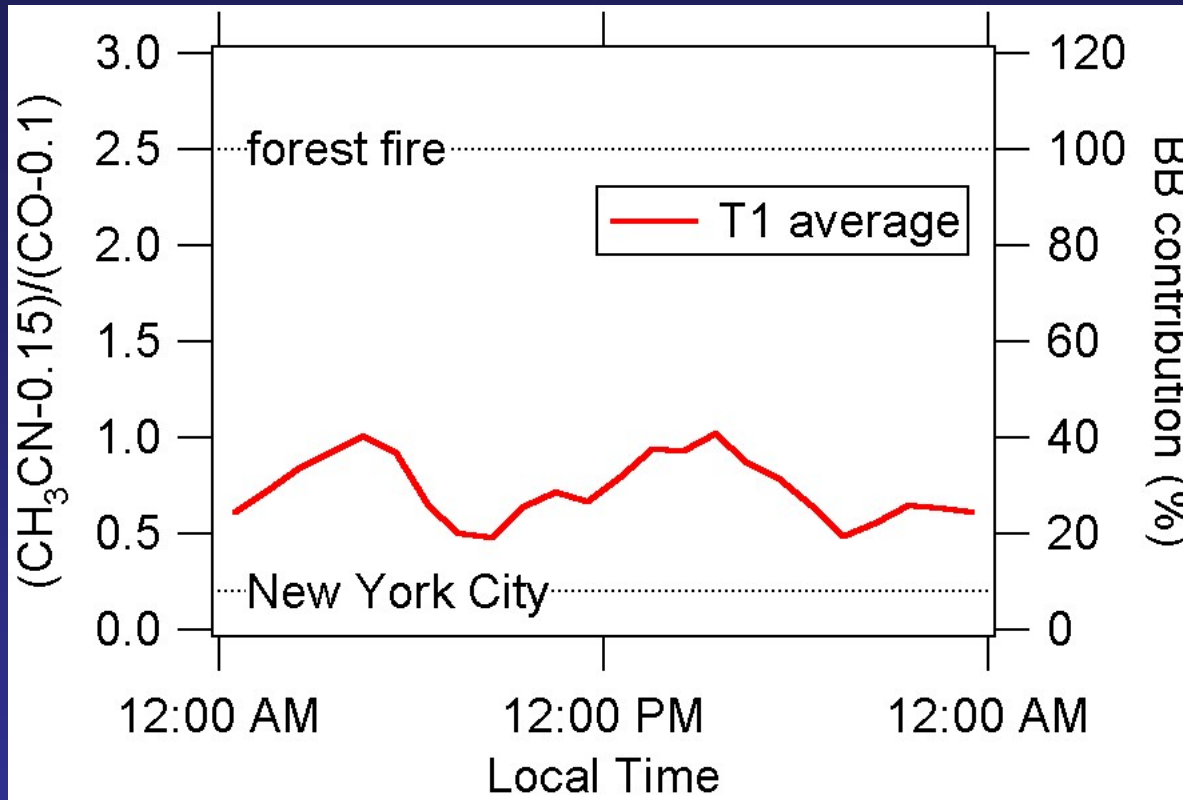


Levoglucosan: Schauer et al.



- Acetonitrile correlates with levoglucosan
- CH₃CN/CO ratio correlates with BB contribution estimated using Chemical Mass Balance [Schauer et al., in prep.]

Diurnal Variation of BB Contribution to OC



CO: Huey - BB contribution: Schauer

- Low in the early morning and similar to T0
- Higher in the afternoon: entrainment of regional fires?
- On average ~30%

Summary

1. $\Delta\text{VOC}/\Delta\text{CO}$ emission ratios factor ~ 2 higher than in U.S.
Higher VOC reactivity per CO emitted
More SOA precursors per CO emitted
2. Observed secondary formation of OVOCs and OC
How does formation differ quantitatively from U.S.?
3. Estimated BB influence at T1 using acetonitrile

Acknowledgments

CO, O₃ *Oscar Vargas, Greg Huey*
Levogluconan *Betsy Stone, Jamie Schauer*
WSOC *Amy Sullivan, Chris Hennigan, Rodney Weber*

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UCI Cans *Angela Baker, Don Blake*
Aerodyne *Berk Knighton, Scott Herndon, Chuck Kolb*
DOE G-1 *John Ortega, Liz Alexander*

Site:

*Andrew Turnipseed, Alex Guenther, Brian Lefer, Jim Smith,
Sasha Madronich, Luisa Molina*

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