

Photo-Chemistry at T1: Secondary Organic Aerosol and the Influence of Biomass Burning

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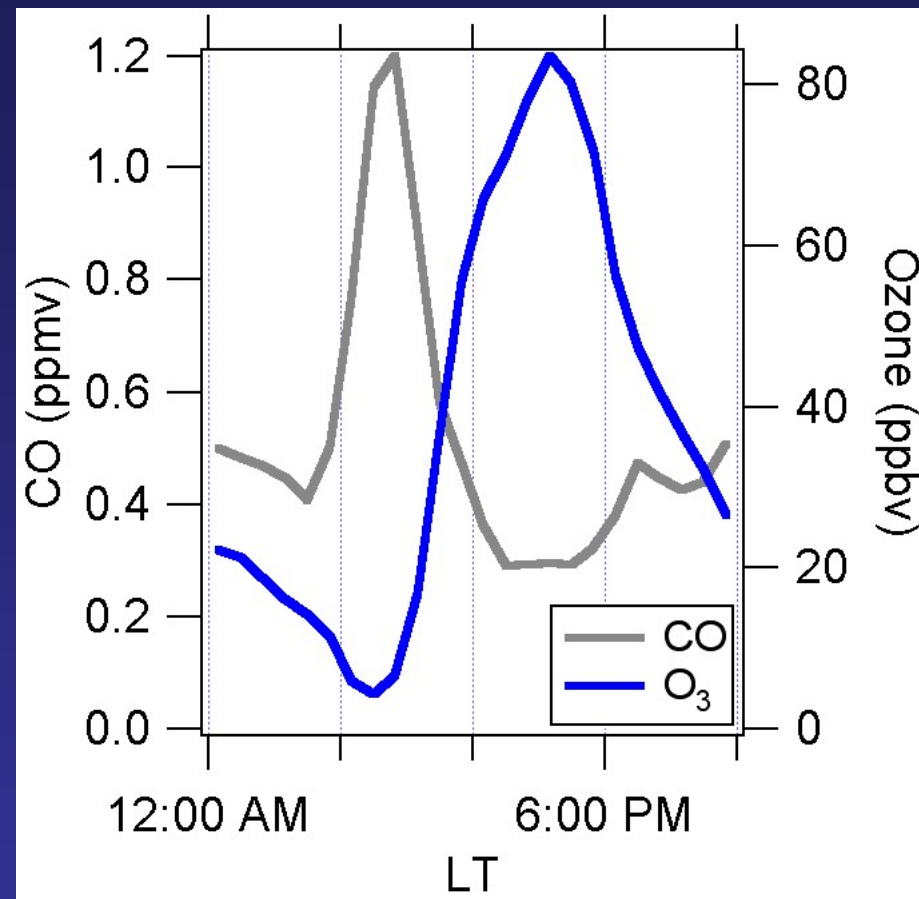
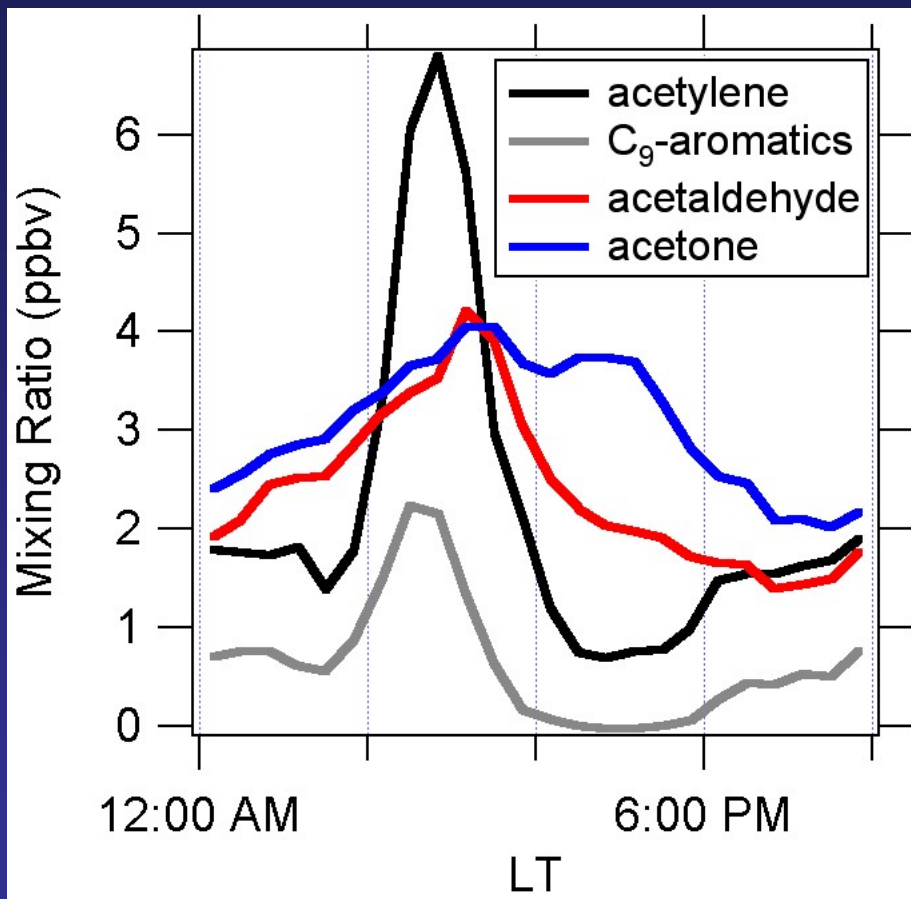
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<http://cires.colorado.edu/~gouw>



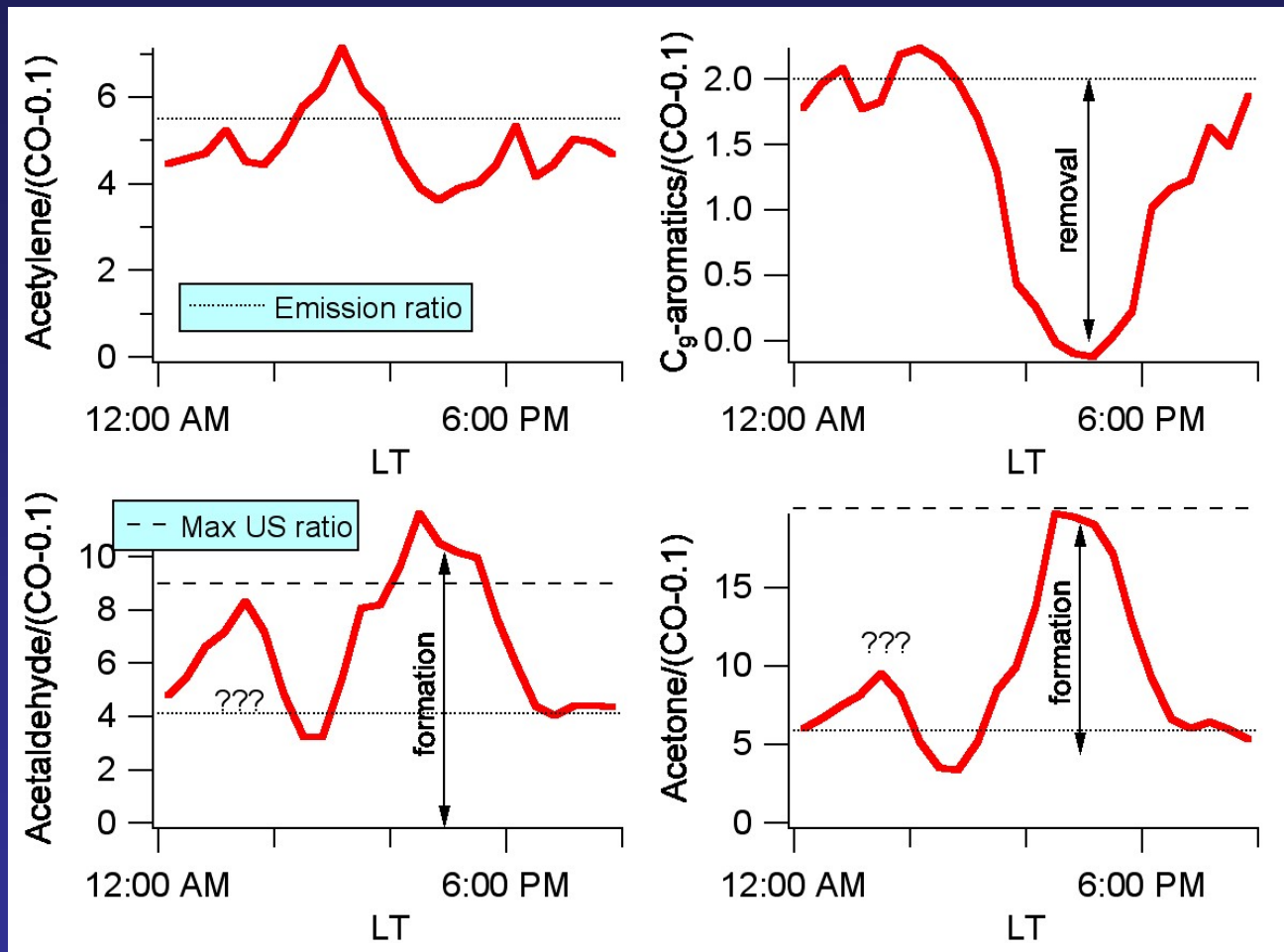
Photo-Chemical Formation of Oxygenated VOCs



CO, O₃: Huey et al.

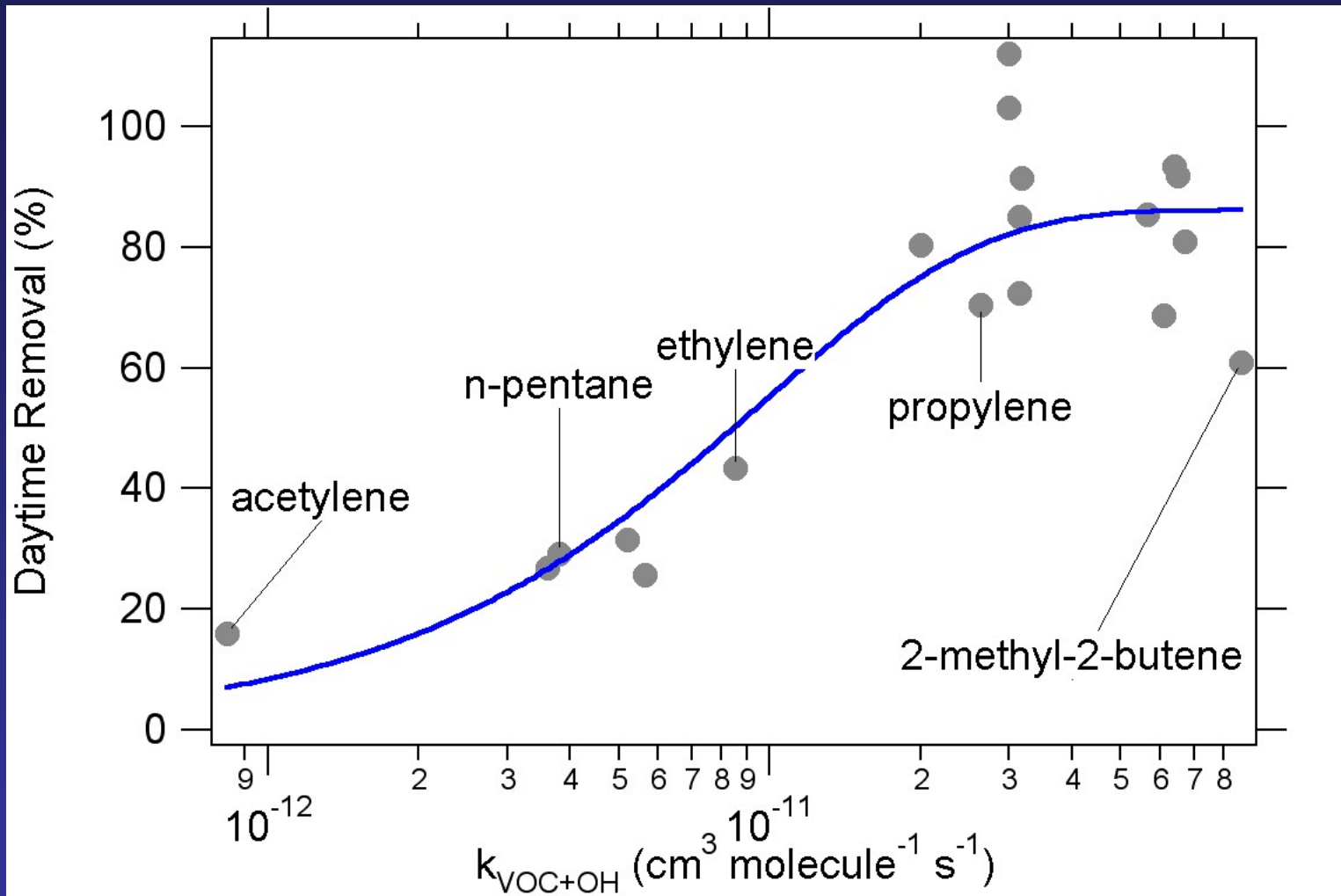
➤ Summary of diurnal variations

Photo-Chemical Formation of Oxygenated VOCs



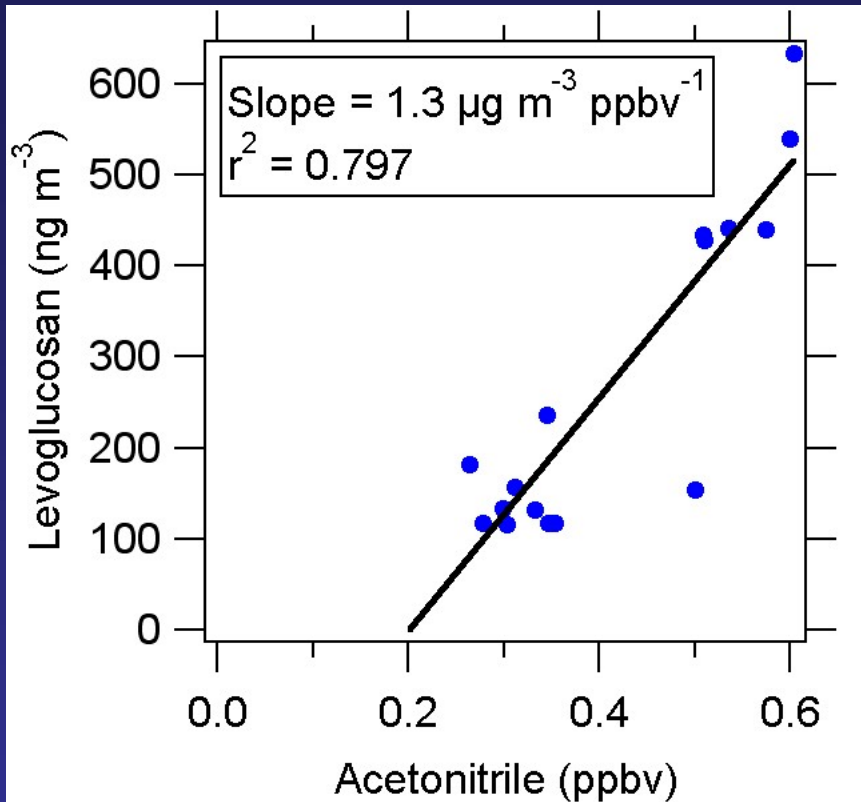
- Emission ratios of most VOCs vs. CO higher than in U.S.
- Secondary acetaldehyde and acetone comparable to U.S.
- Formation not complete at T1?

How Complete is VOC Removal During Day?

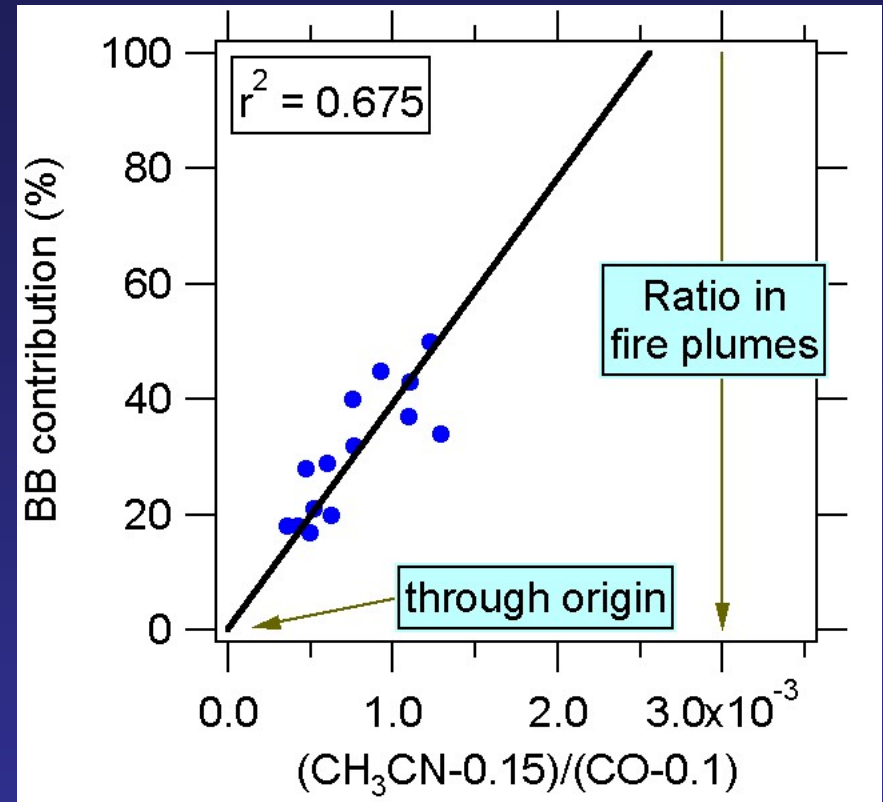


- Removal maximum 86% \Rightarrow 14% fresh, local emissions?
- $k = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \Rightarrow$ removal 50% of maximum
- From fit: $[\text{OH}]\Delta t = 10^{11} \Rightarrow \Delta t = 10 \text{ h} @ [\text{OH}] = 3 \times 10^6 \text{ cm}^{-3}$

Acetonitrile versus Levoglucosan

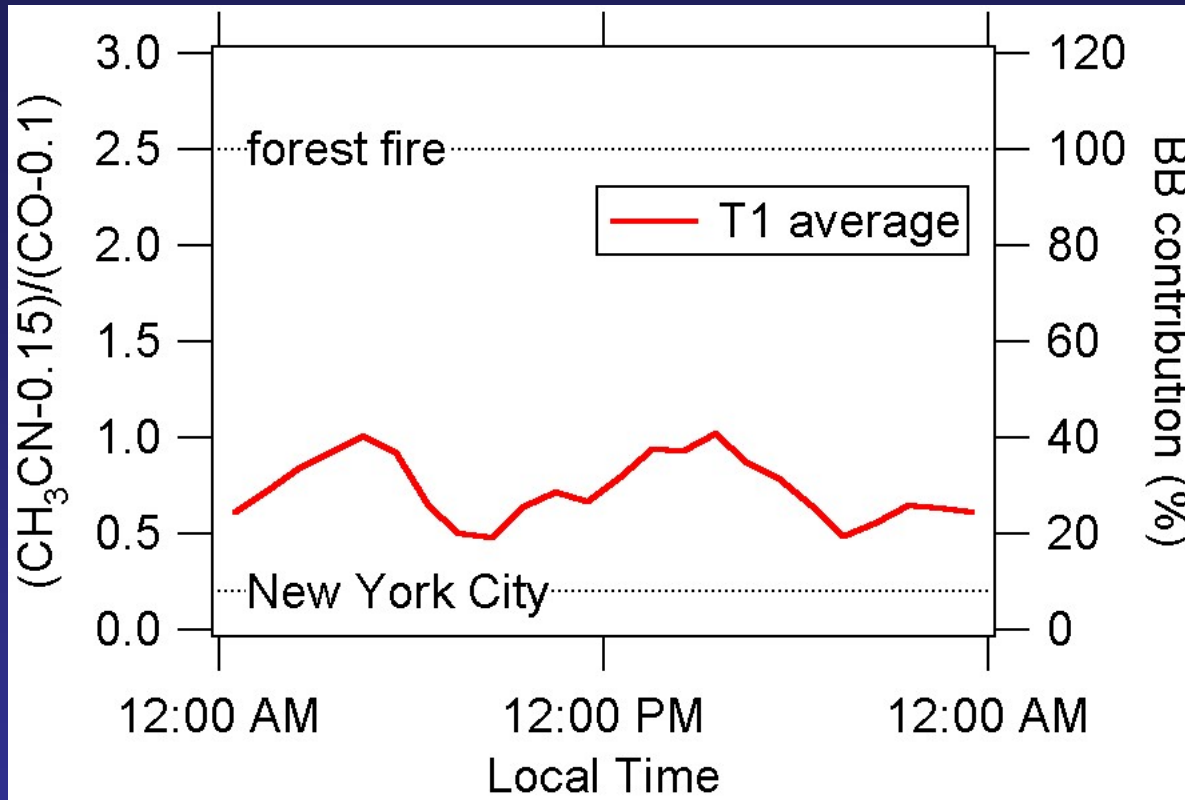


Levoglucosan: Schauer et al.



- Acetonitrile correlates with levoglucosan
- $\text{CH}_3\text{CN}/\text{CO}$ ratio correlates with BB contribution estimated using Chemical Mass Balance [Schauer et al., in prep.]

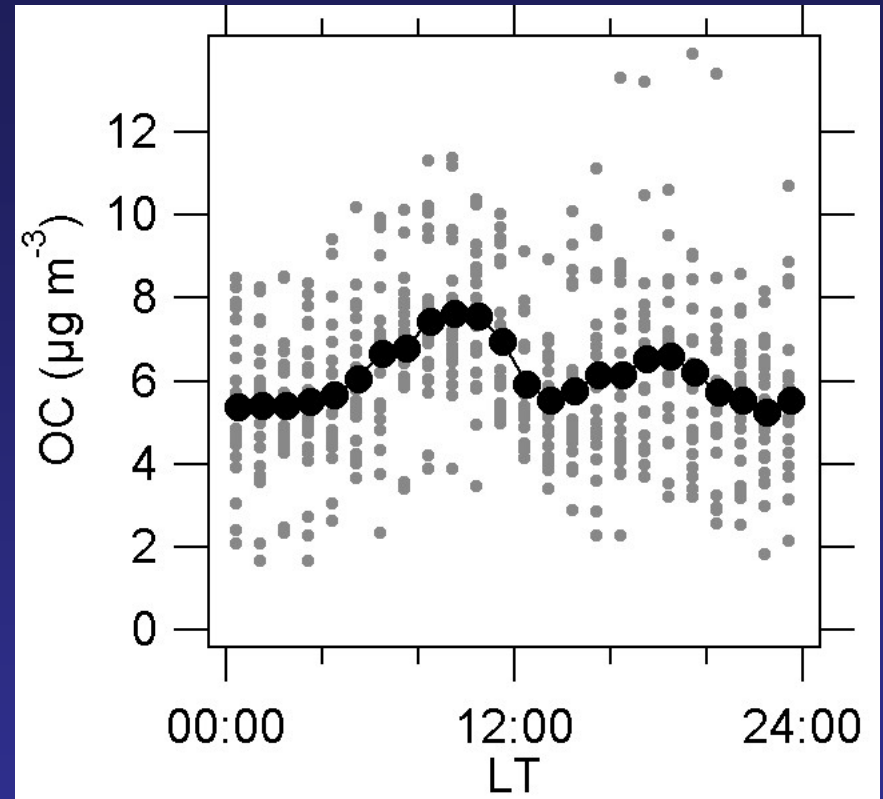
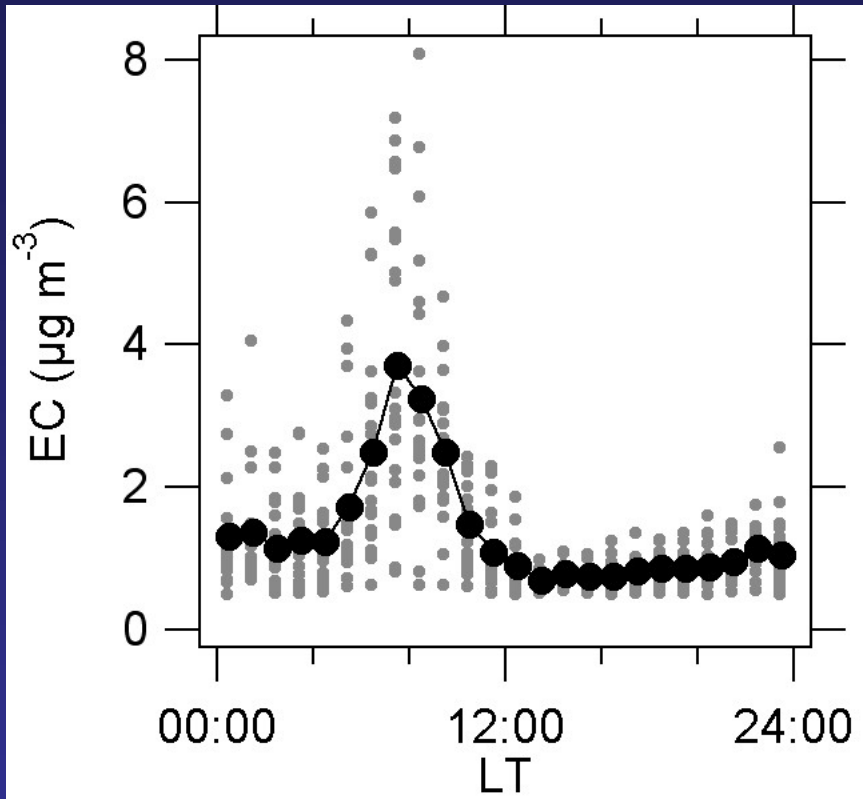
Diurnal Variation of BB Contribution to OC



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%

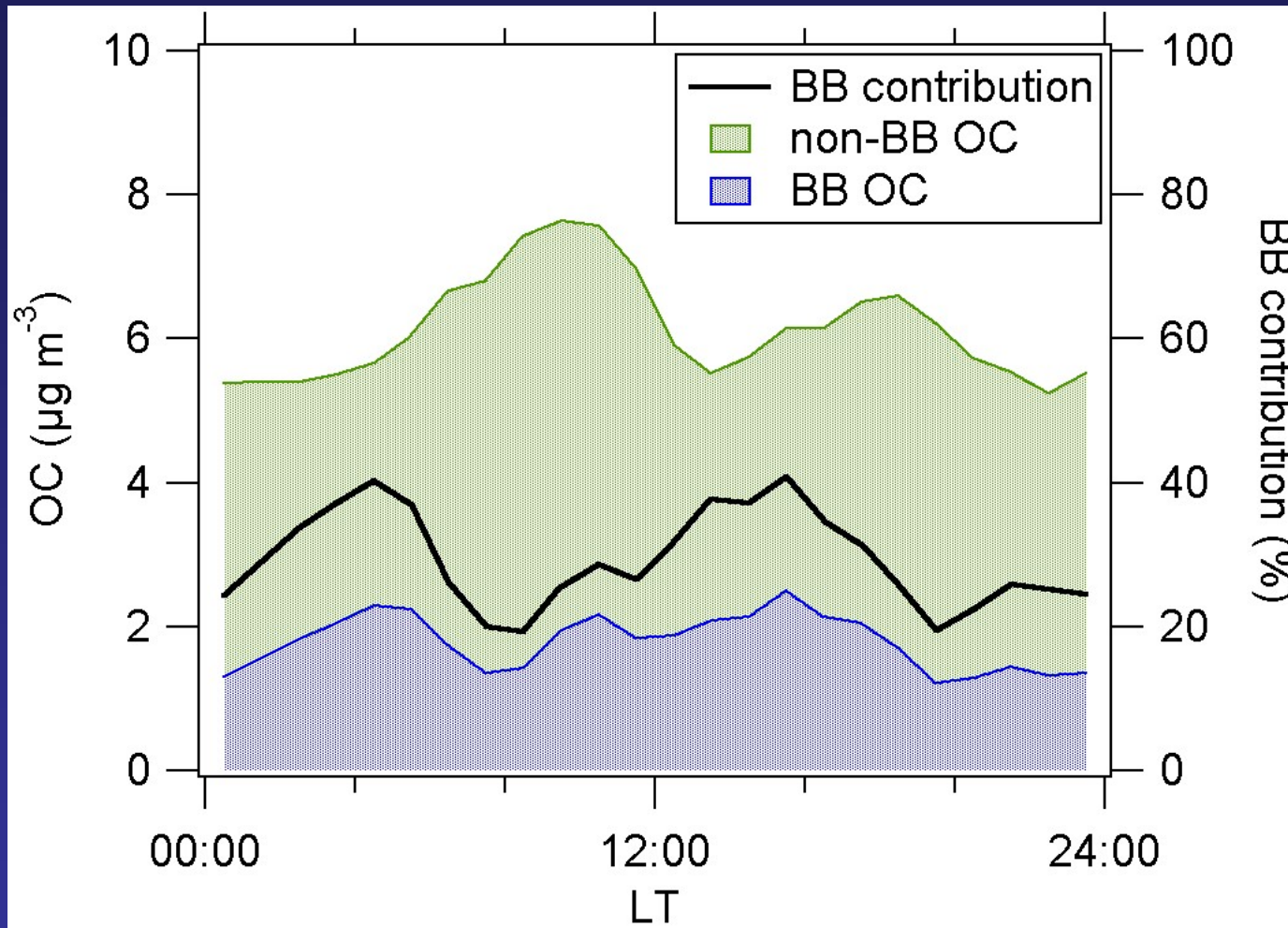
Diurnal Variation of Organic Aerosol



EC, OC: Weber et al.

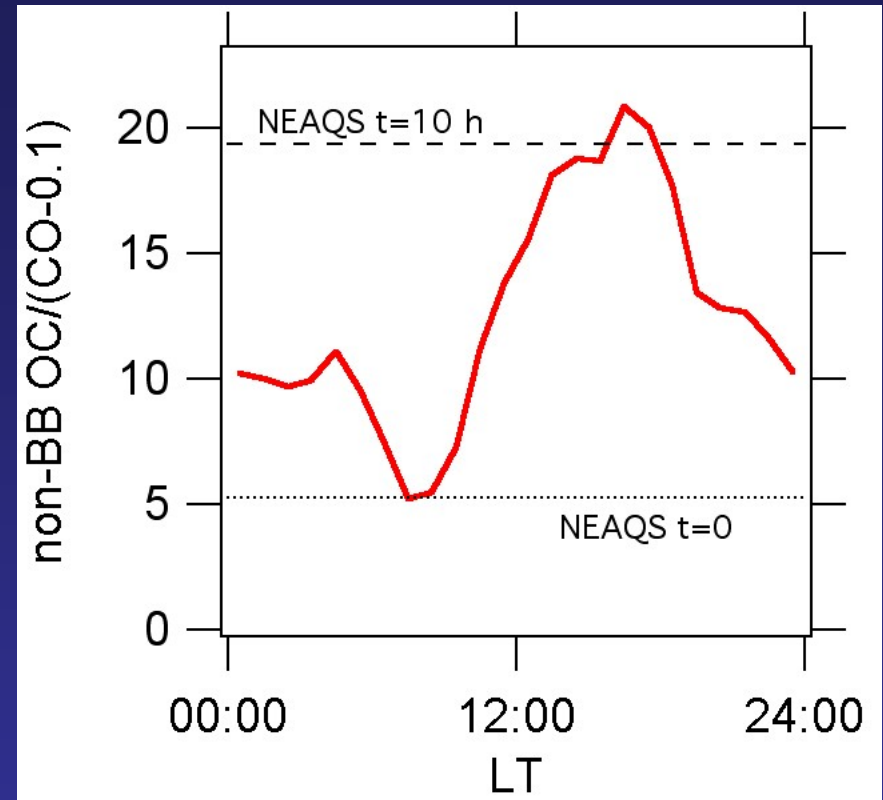
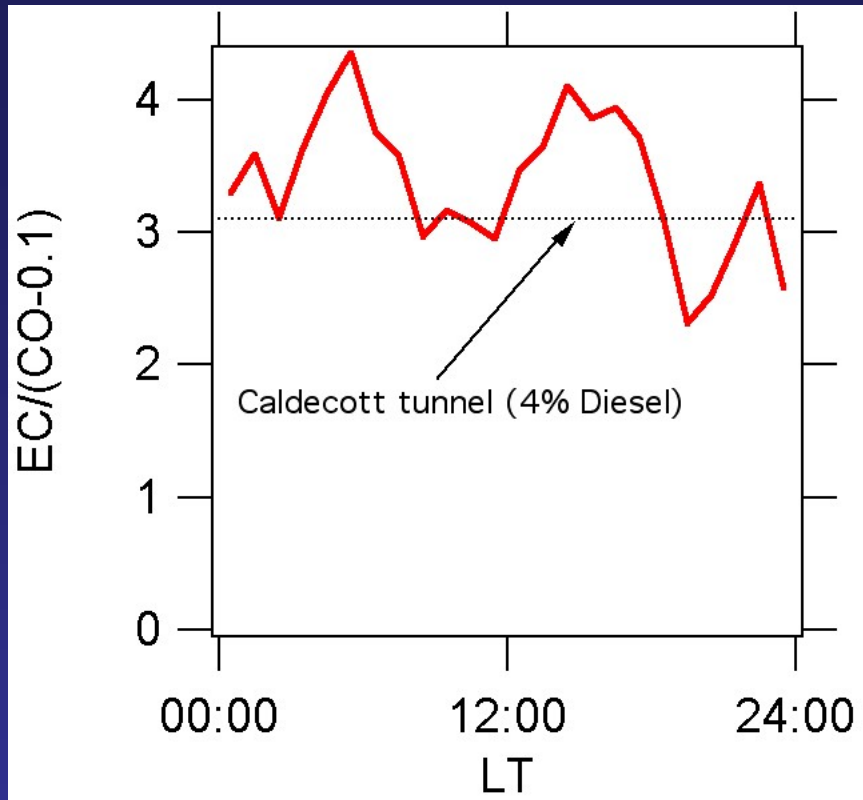
- EC follows CO and primary hydrocarbons
- OC follows secondary VOCs

BB and non-BB Sources of Organic Aerosol



- Acetonitrile data allow BB and non-BB sources of OC to be separated

Diurnal Variation of EC and non-BB OC



Caldecott data: Kirchstetter 1999

- Secondary formation of OC similar to U.S.
- EC/CO ratio constant \Rightarrow EC lifetime > 1 day
- EC/CO ratio constant \Rightarrow mix of vehicles constant

Summary

1. Secondary formation of oxygenated VOCs and organic aerosol comparable with the U.S. (within factor 2)
But: precursor emissions higher
Chemistry not complete at T1
2. Quantified BB contribution using acetonitrile data
Averages at 30%

Acknowledgments

CO, O₃

Levoglucosan

EC, OC

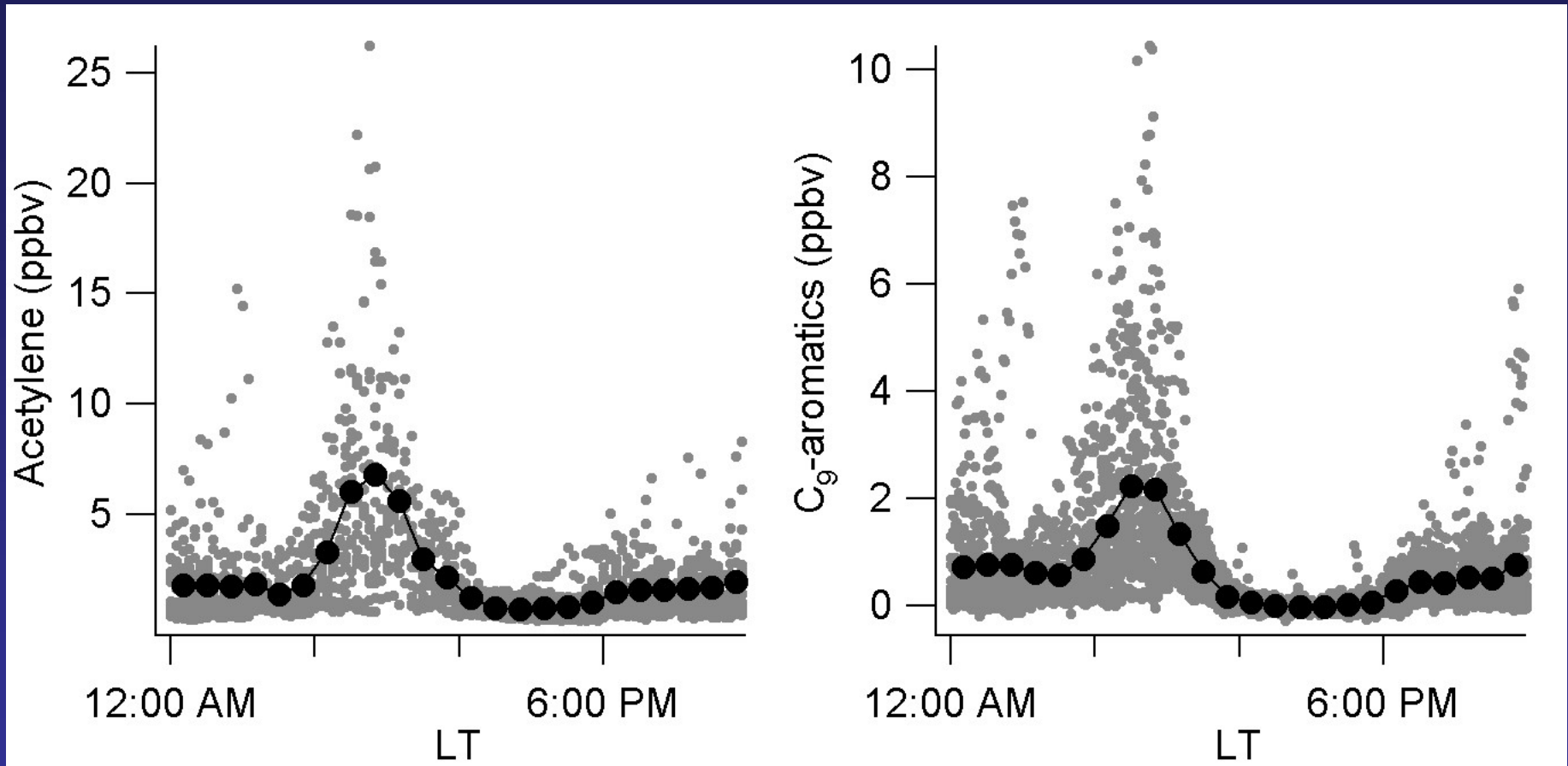
Oscar Vargas, Greg Huey

Betsy Stone, Jamie Schauer

Amy Sullivan, Chris Hennigan

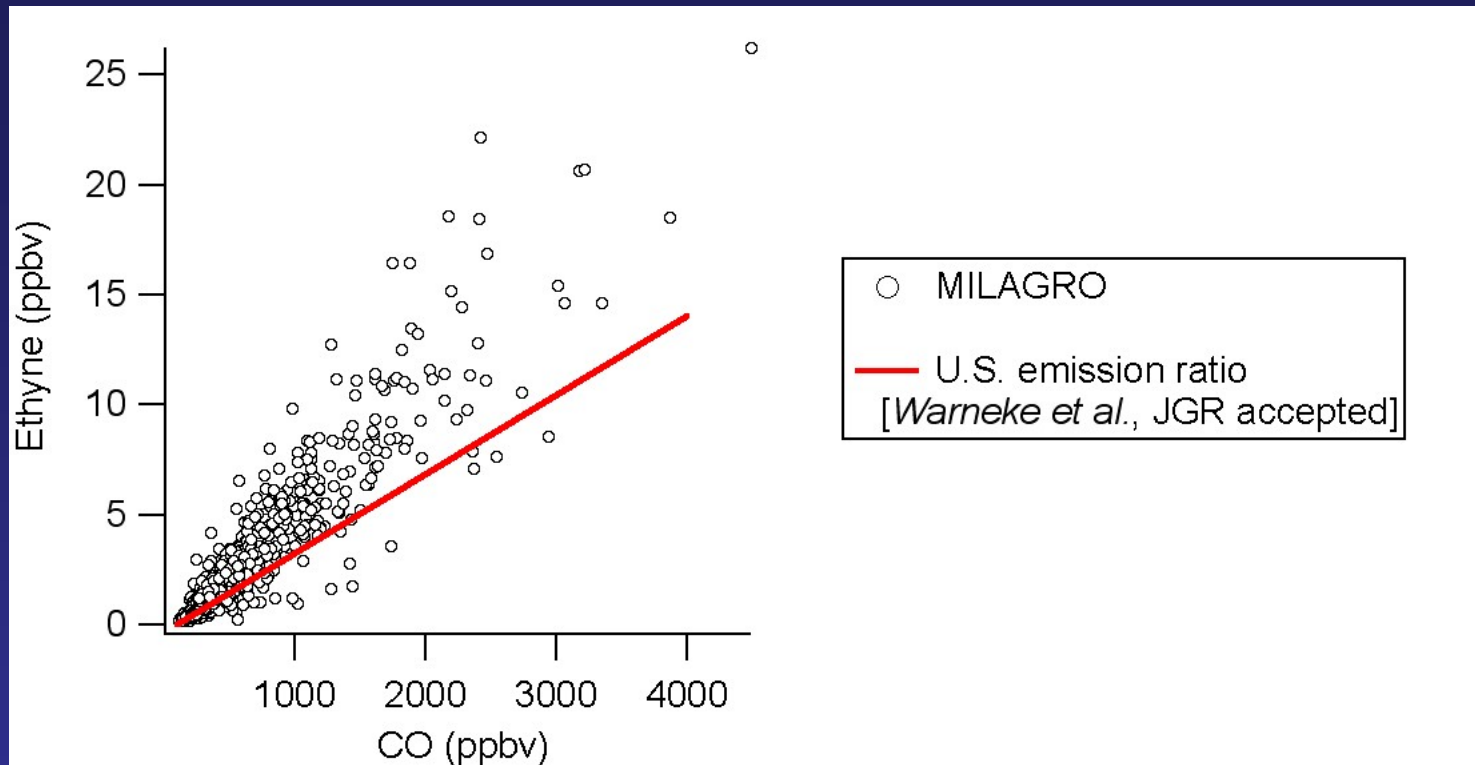
Rodney Weber

Diurnal Variations: Hydrocarbons



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

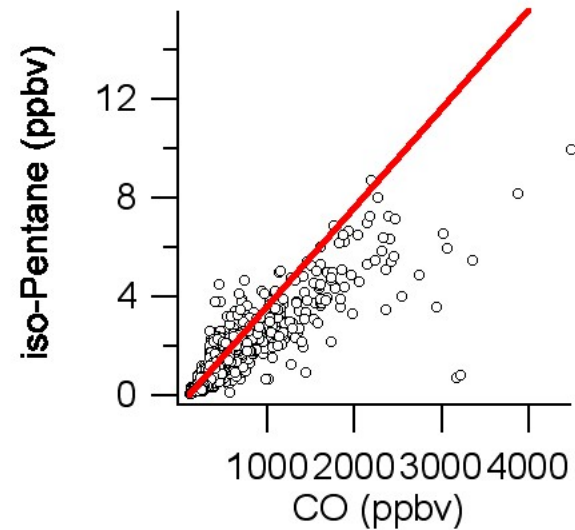
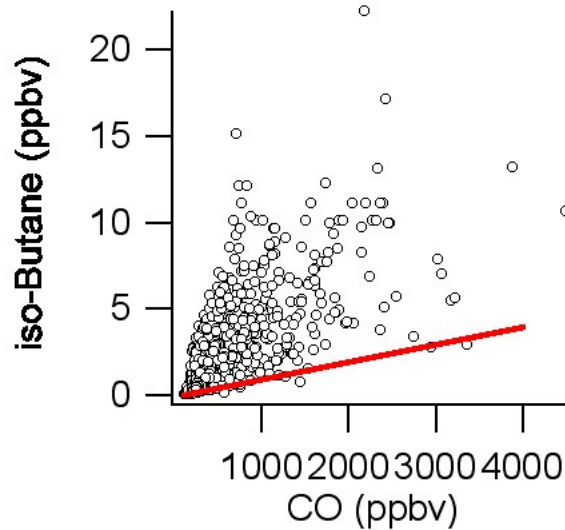
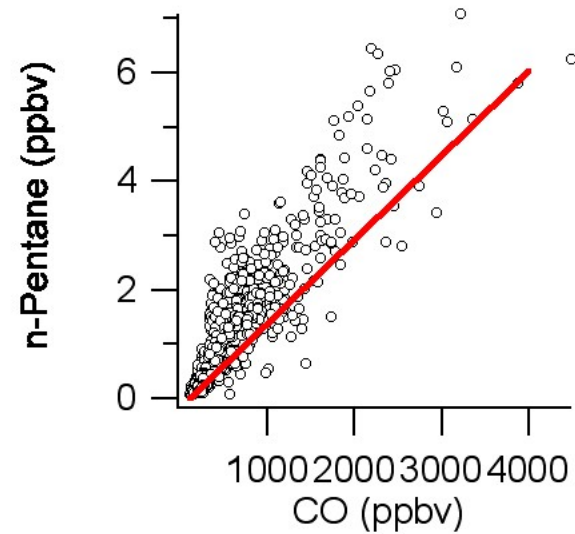
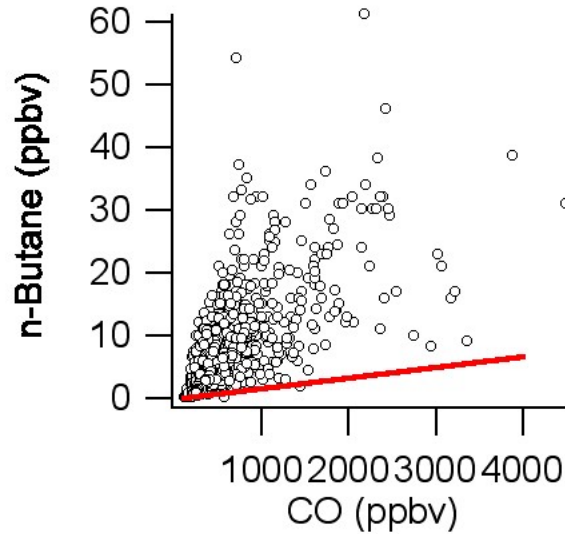
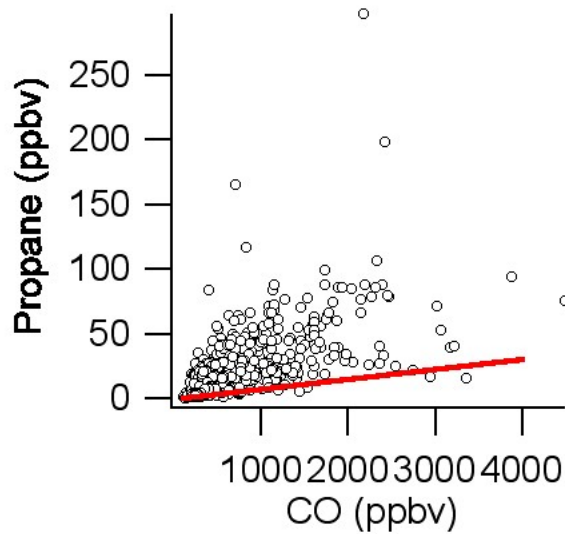
Comparison of Emissions with U.S.



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.

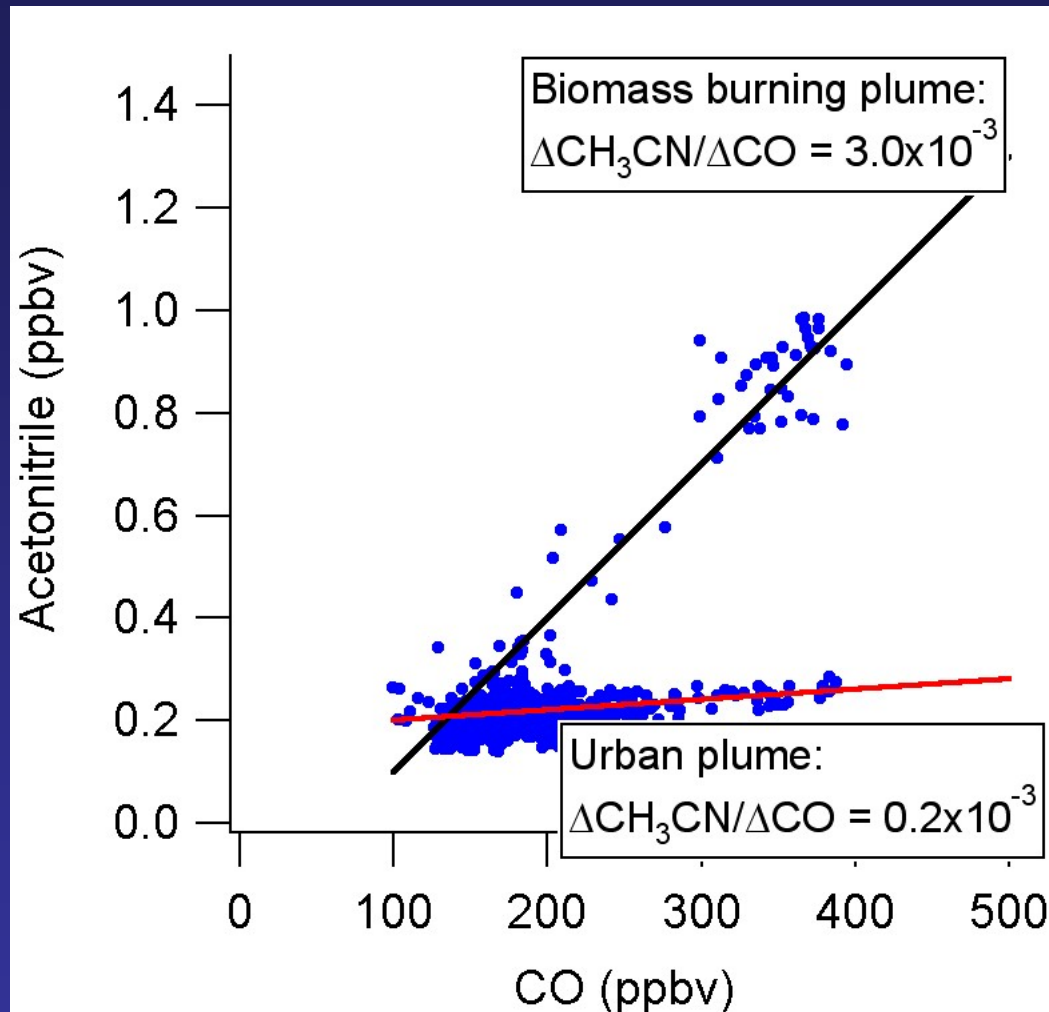
Comparison of Emissions with U.S.: Summary

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

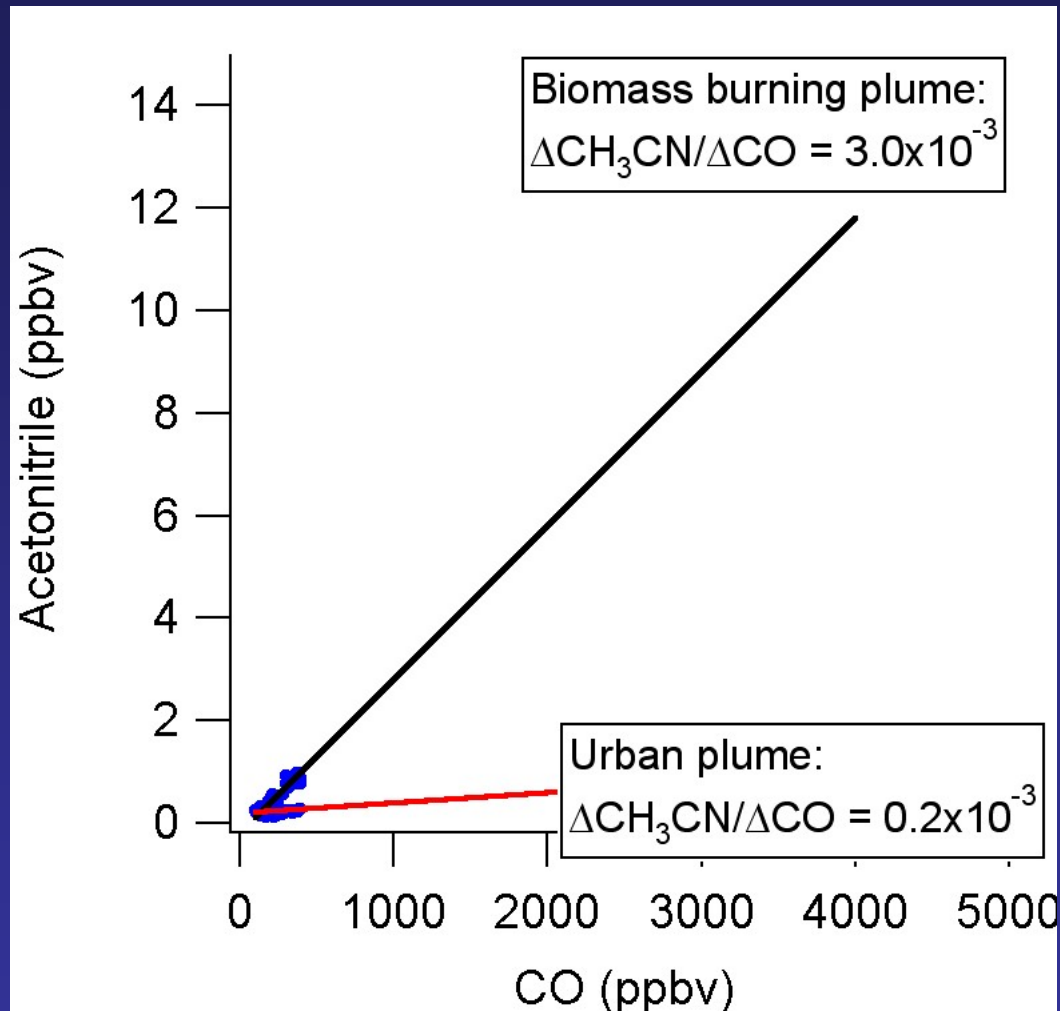
VOC signature = dirty vehicles + additional alkanes

What About Biomass Burning?



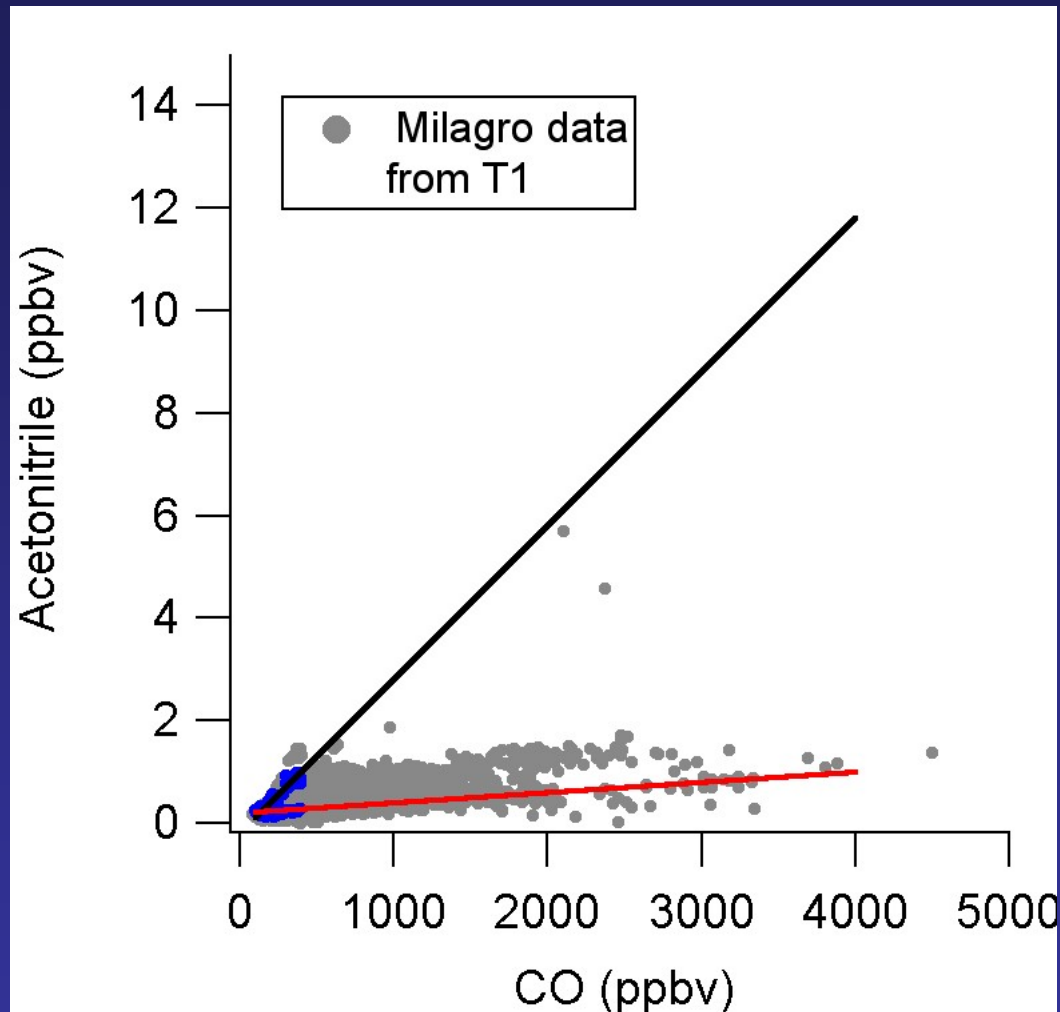
- Use of acetonitrile as a tracer
- Example from airborne data from ICARTT

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