Measurements of Highly Reactive VOCs Onboard the NOAA WP-3D

Joost de Gouw, Carsten Warneke, Jessica Gilman, Dan Welsh-Bon, Bill Kuster, Paul Goldan, David Parrish
NOAA and CIRES, Boulder, CO

Sacco te Lintel Hekkert
SensorSense, Nijmegen, the Netherlands

Elliot Atlas
University of Miami, Miami, FL

Road Map for Next 3 Talks About VOCs

1. WAS
2. PTR-MS
3. LPAS

- ✓ Regional coverage
- ✓ Altitude profiles
- ✓ Plume evolution

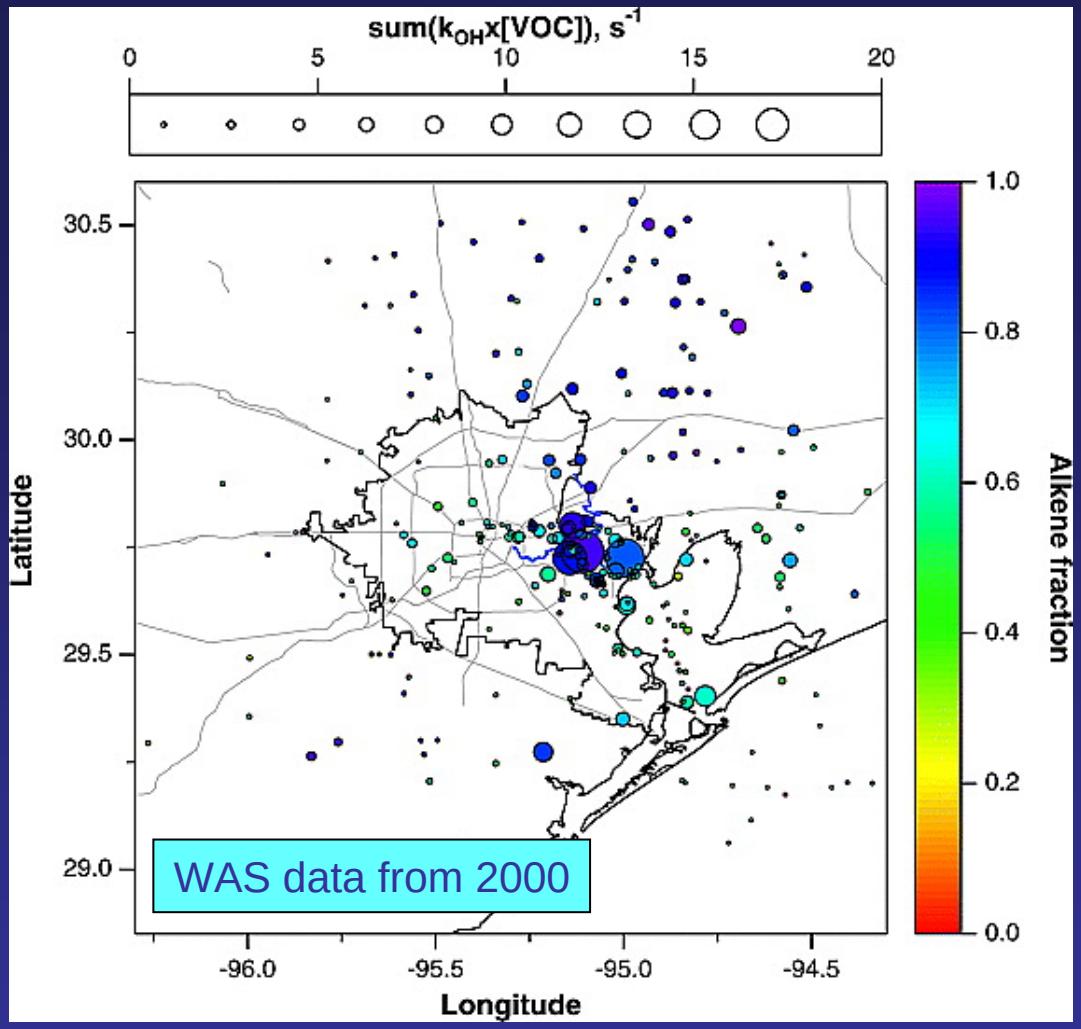
1. GC-FID/MS
2. PIT-MS

- ✓ High chemical detail
- ✓ Industrial influence

1. **This talk** Ethene by LPAS and WAS (WP-3D)
   Flux estimates, 2006 versus 2000

2. **Gilman** On-line GC-FID/MS (Ron Brown)
   Speciation and reactivity of industrial VOCs

3. **Warneke** PTR-MS and WAS (WP-3D)
   Biogenic VOCs, urban versus industrial emissions



[*Ryerson et al.*, JGR 2003]

TexAQS 2000

- Industrial emissions of alkenes are large
- Alkene emissions >> emission inventories (factor 10-100)
- Alkenes dominate the OH reactivity

Can we add fast-response measurements of alkenes?

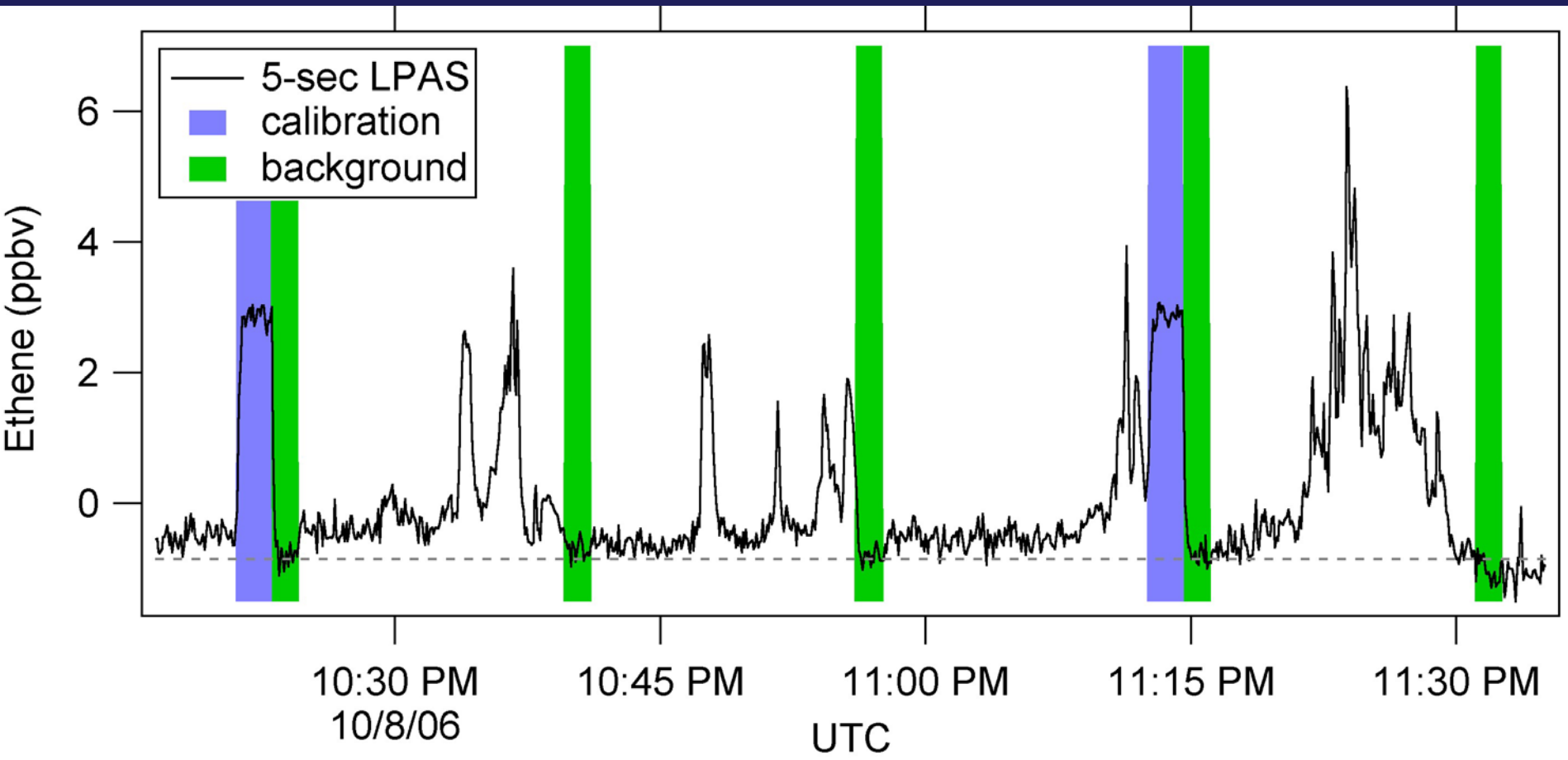
Laser Photo-Acoustic Spectroscopy (LPAS)

Inlet system
Constant pressure and flow
Calibrations
Instrument backgrounds

LPAS instrument for ethene
Sensor Sense, the Netherlands
5-sec measurement cycle
1σ noise = 100 pptv best case

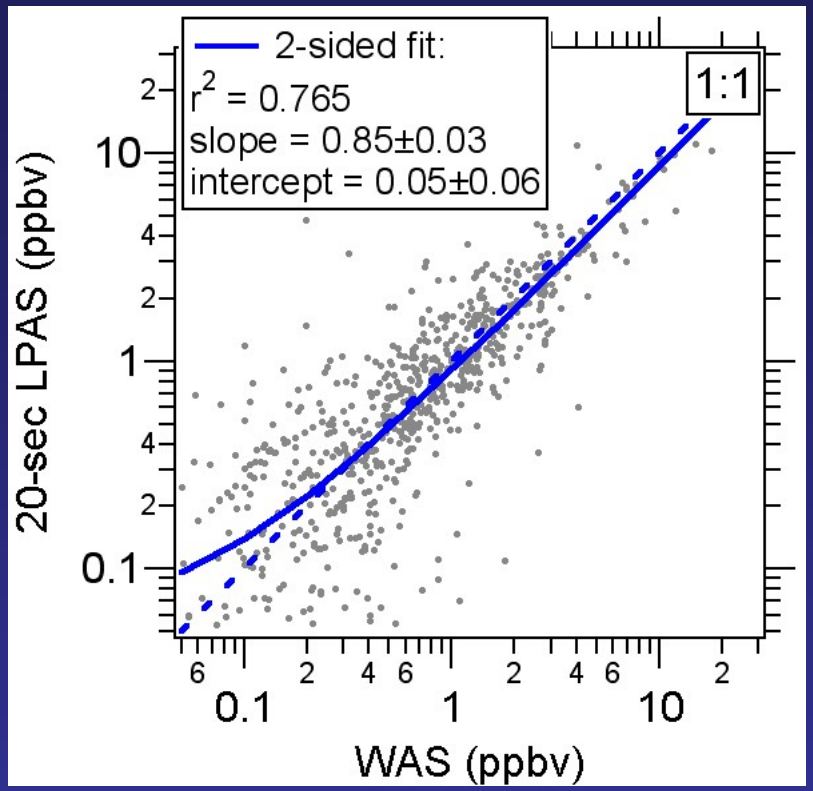
Fast-response measurement of ethene

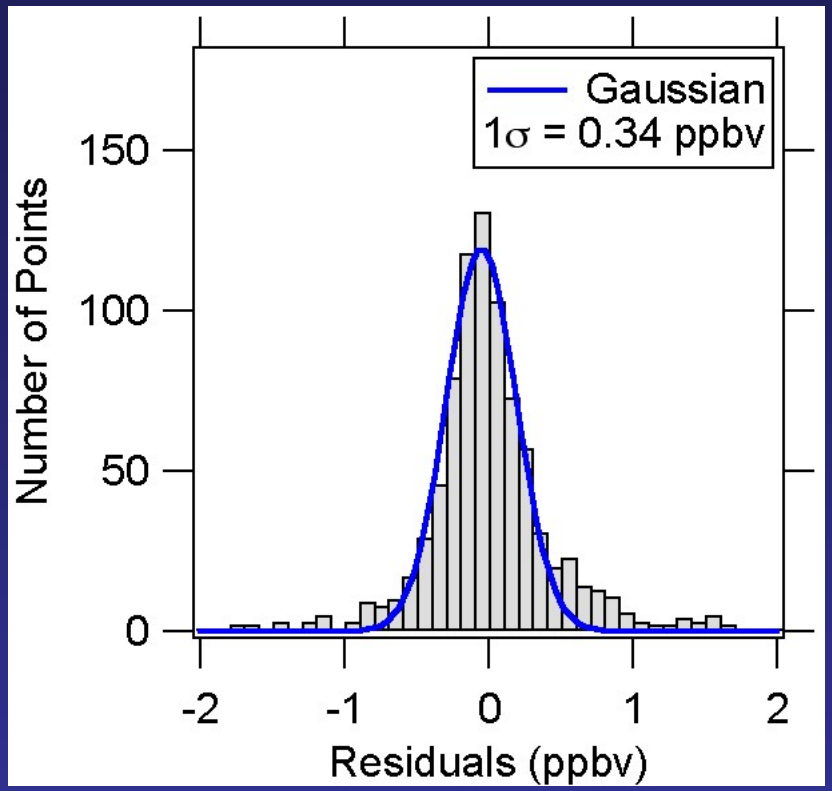
Example of Raw Data



- Measurement cycle steps between 2 laser lines
- Difference determines result ⇒ can be negative

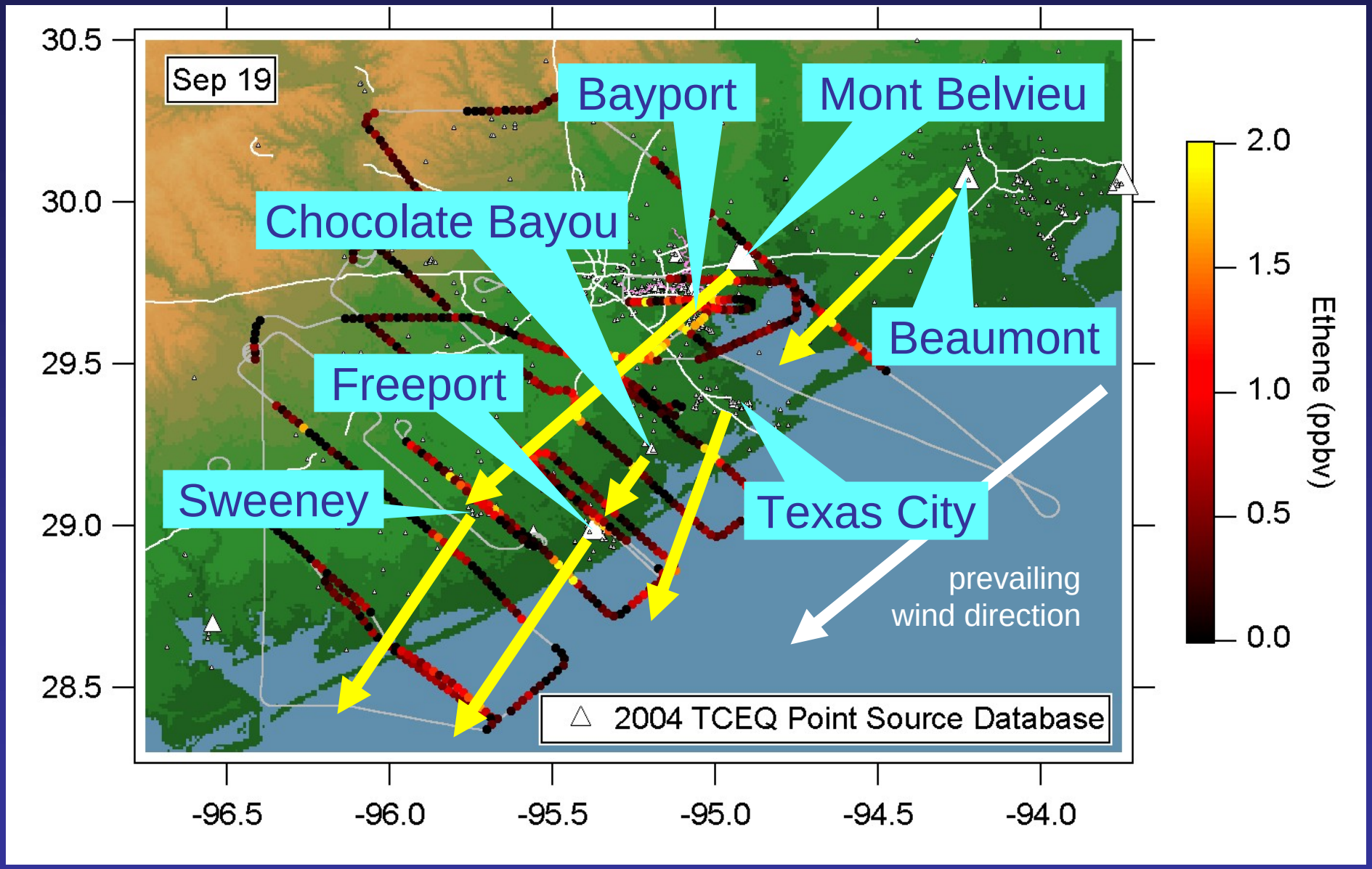
Inter-Comparison with WAS





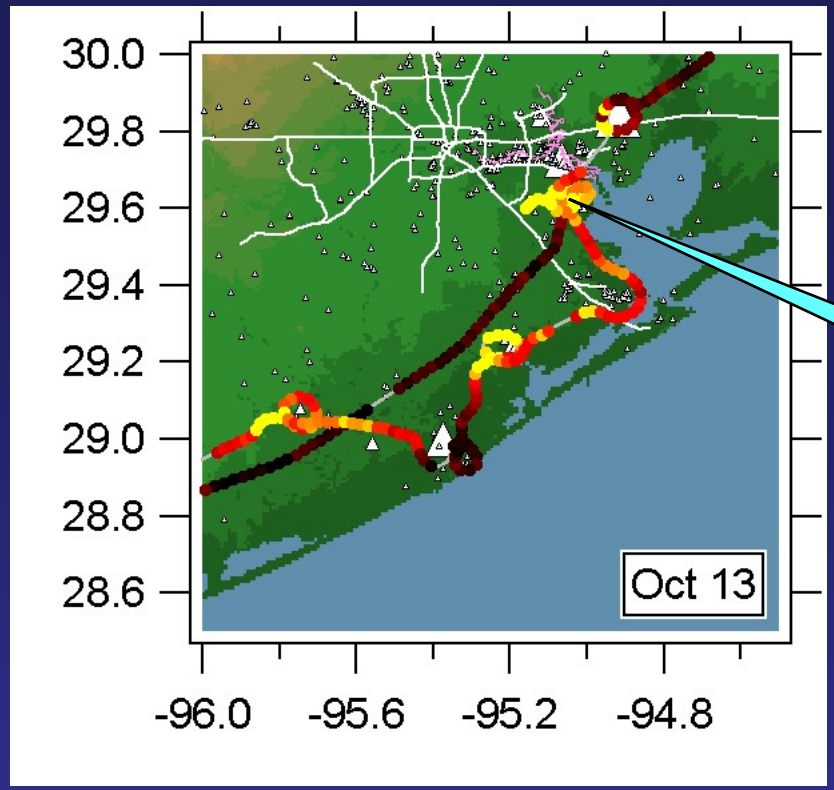
- LPAS 15% lower than WAS
- Scatter caused by extreme variability in plumes
- 20-sec LPAS detection limit <1 ppbv

Ethene Source Locations



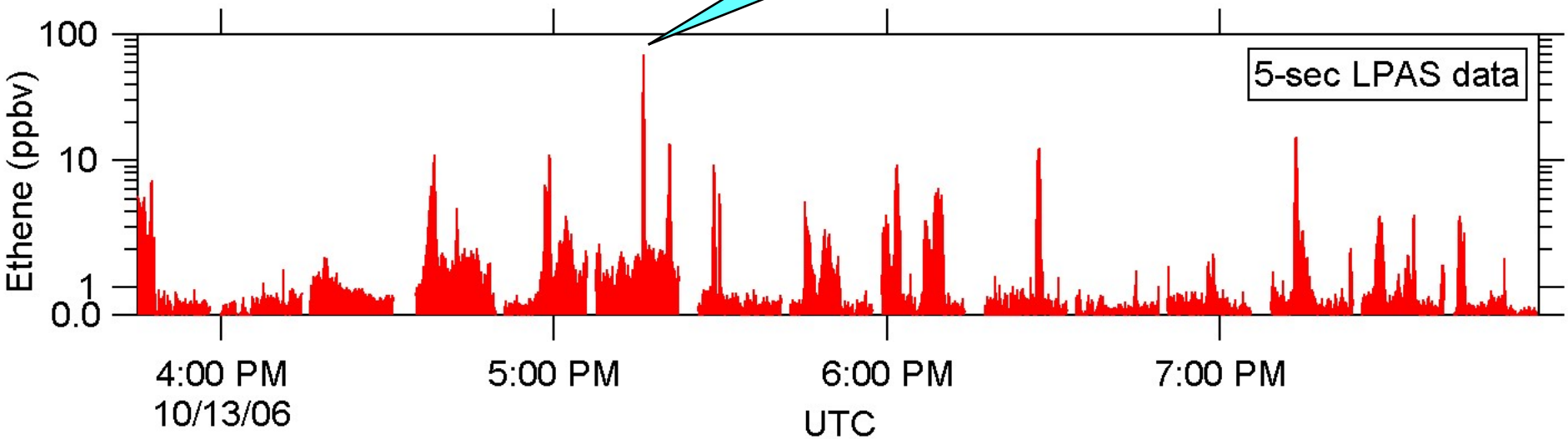
7 point sources ⇒ most of the ethene plumes in Houston area

And The Winner Is…

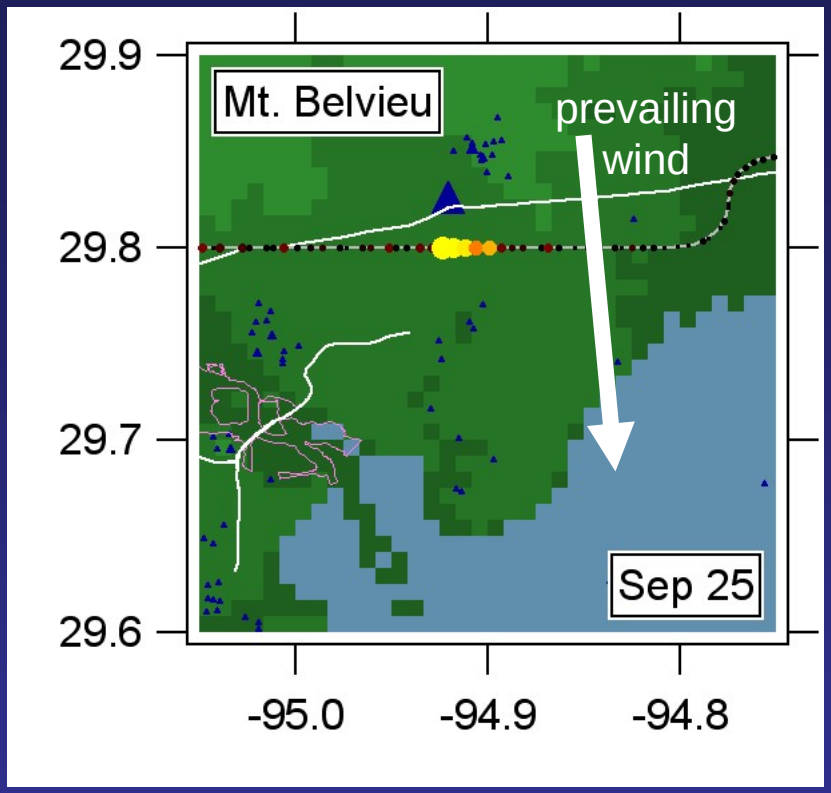


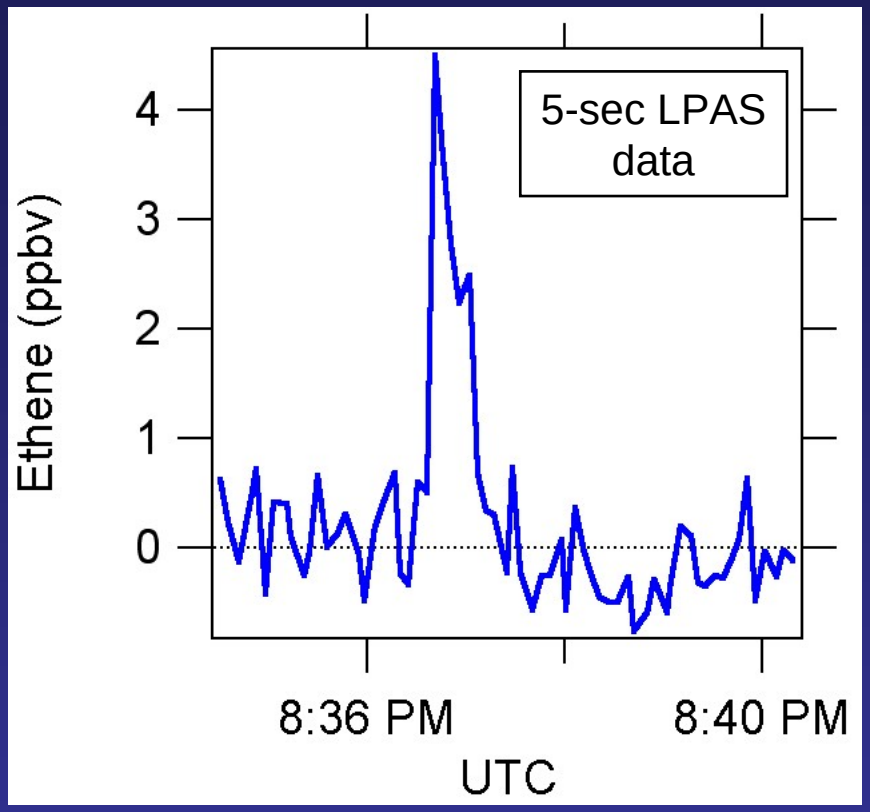
Bayport!

69 ppbv on
October 13
(last day of the study)



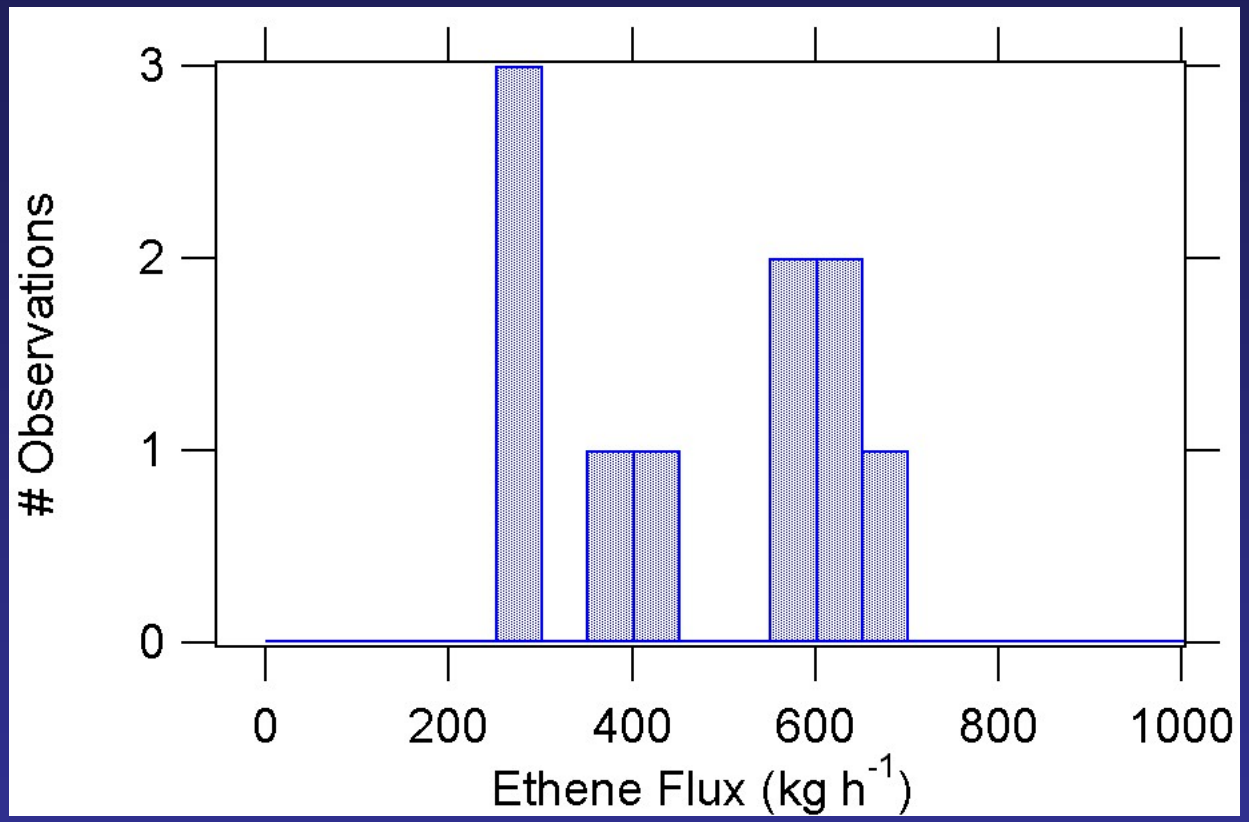
Quantification of Emission Fluxes





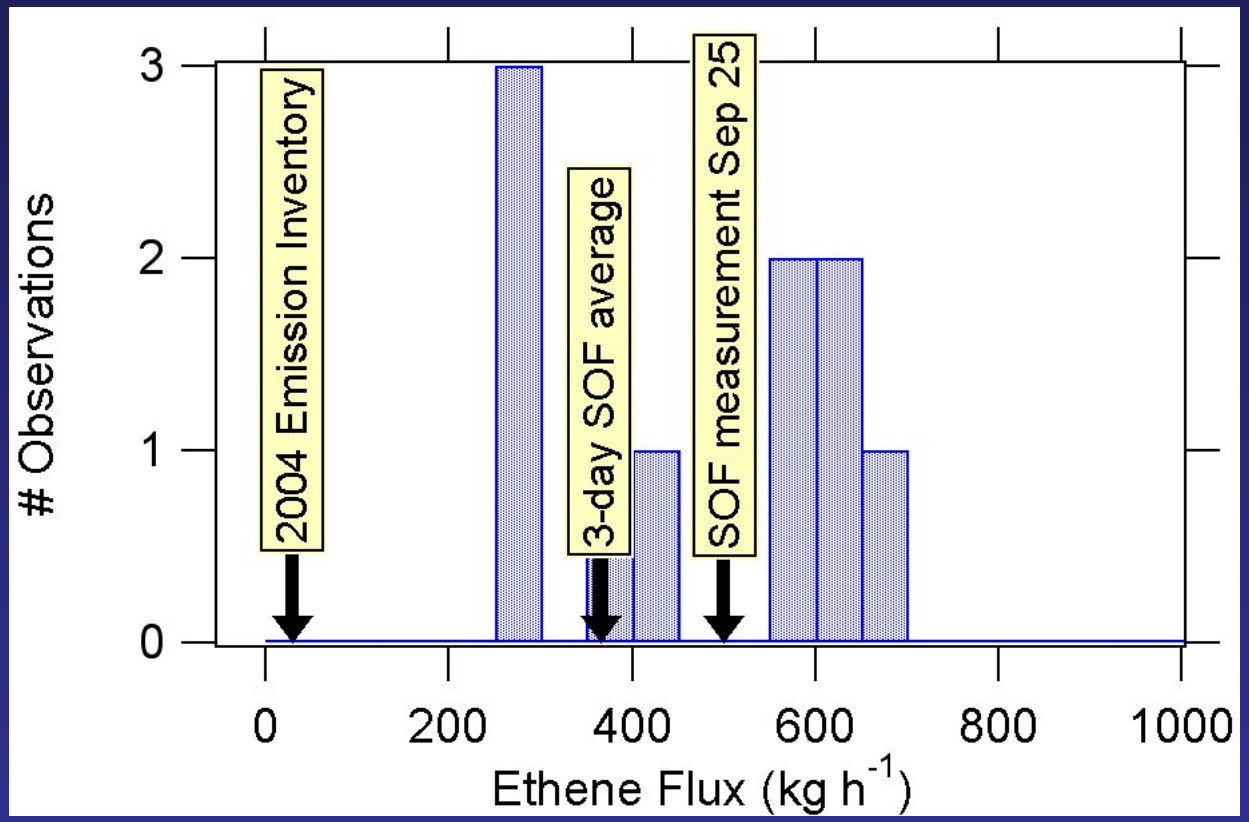
- Integration over ethene peak yields flux: 280 kg h^{-1}
- Solar Occultation Flux (SOF) on same day: 450 kg h^{-1}
- SOF and WP-3D fluxes agree within factor of 2
- Difference due to incomplete vertical mixing?

Variability in Ethene Fluxes from Mt. Belvieu



- Average ethene flux = 470 kg h^{-1}
- Standard deviation = 160 kg h^{-1}

Variability in Ethene Fluxes from Mt. Belvieu



- Good agreement with SOF measurements
- Measured fluxes >> 2004 TCEQ point source database (factor 10-40)

2000 versus 2006

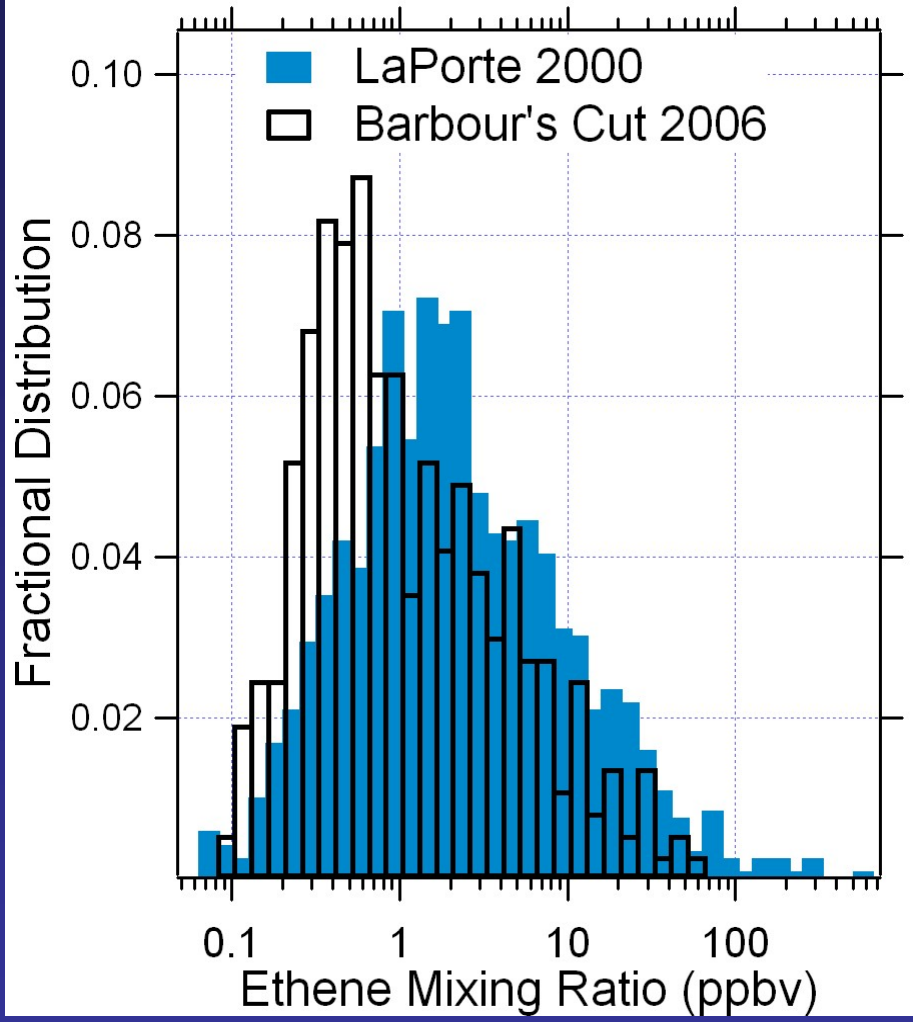
Aug 16 - Sep 13, 2000

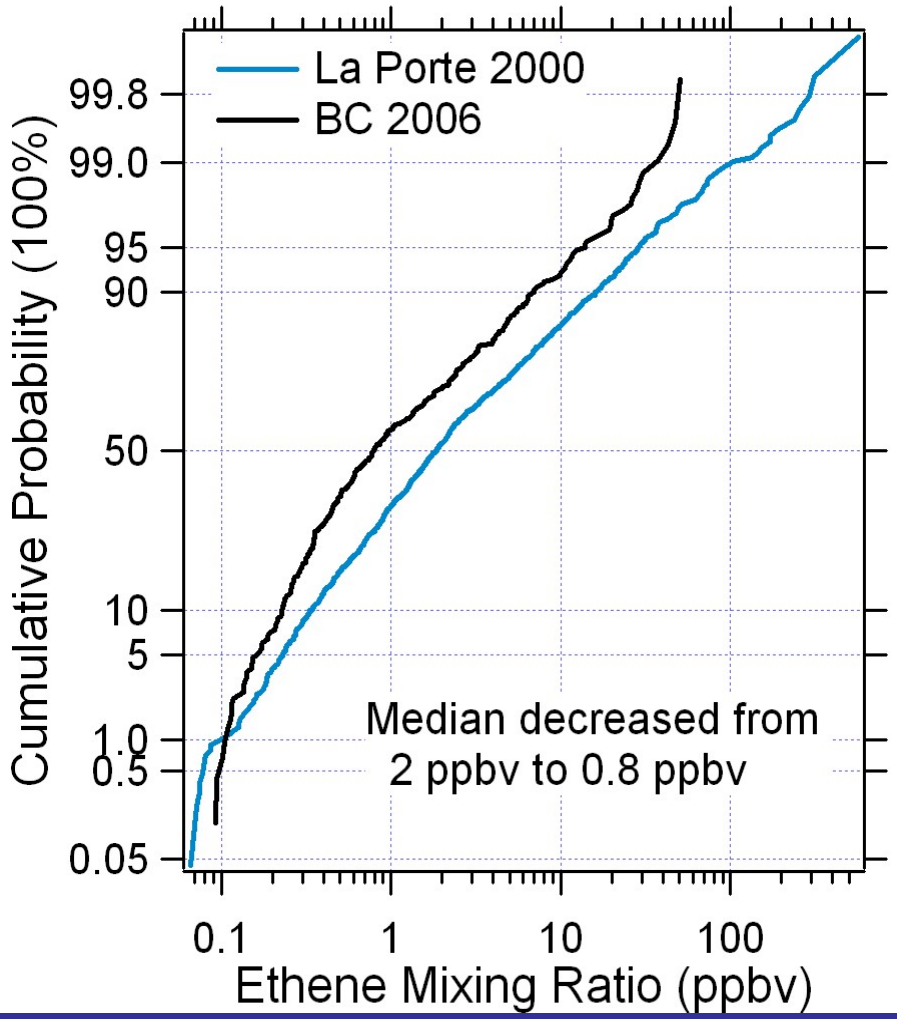
Aug 31 - Oct 31, 2006

2000:
Ground site at La Porte airport

2006:
Ron Brown in Barbour's Cut

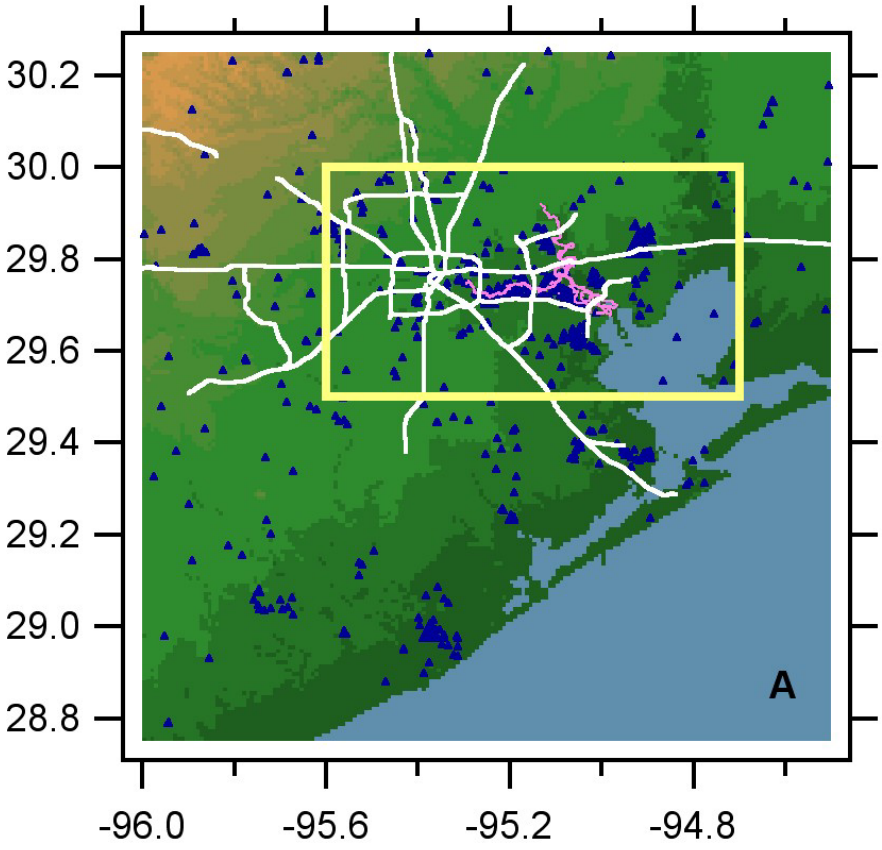
Barbour's Cut versus La Porte airport

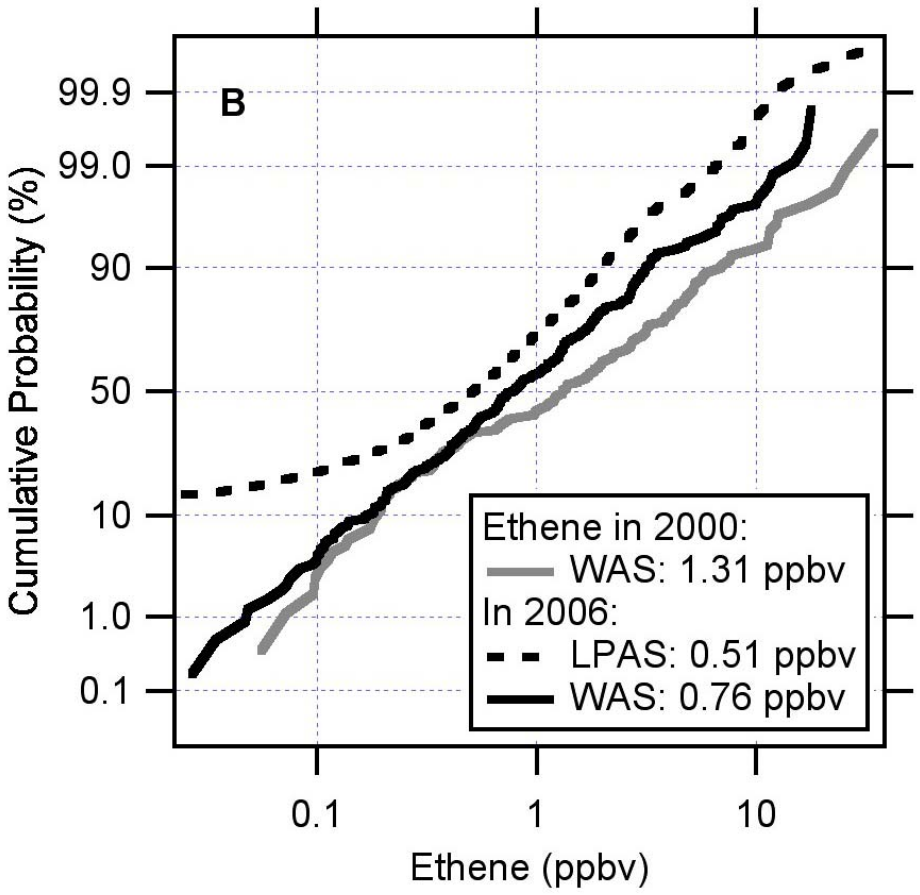




Ethene at Barbour's Cut (2006) 60% lower than at La Porte airport (2000)

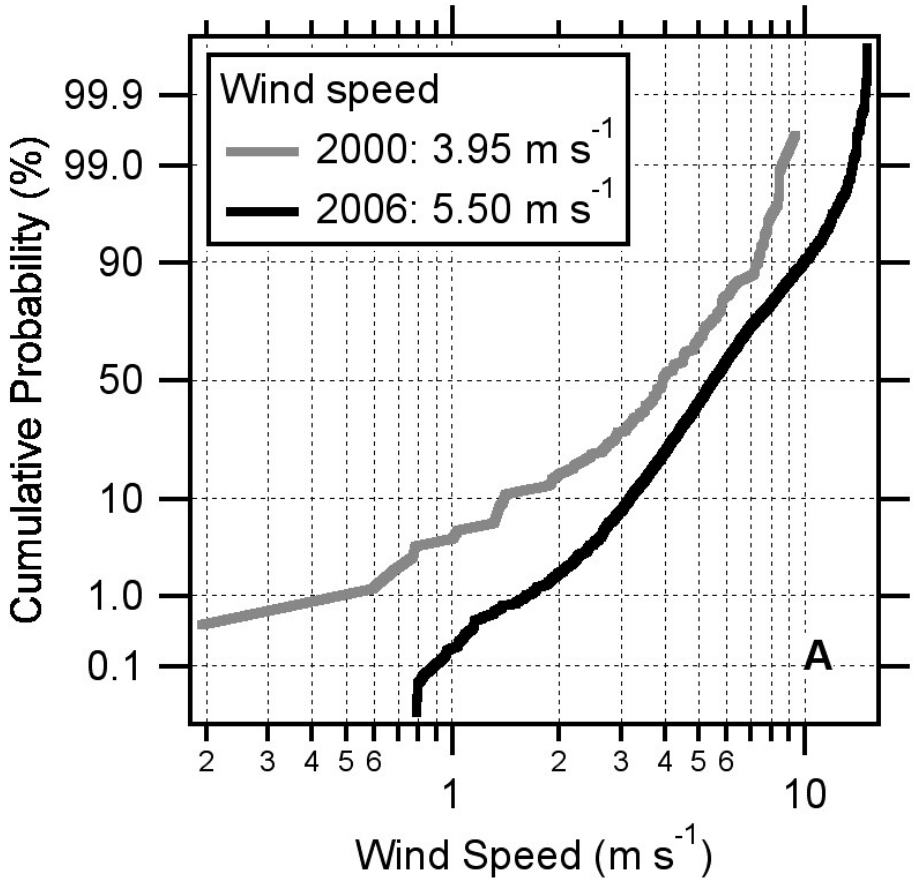
NOAA WP-3D versus NCAR Electra

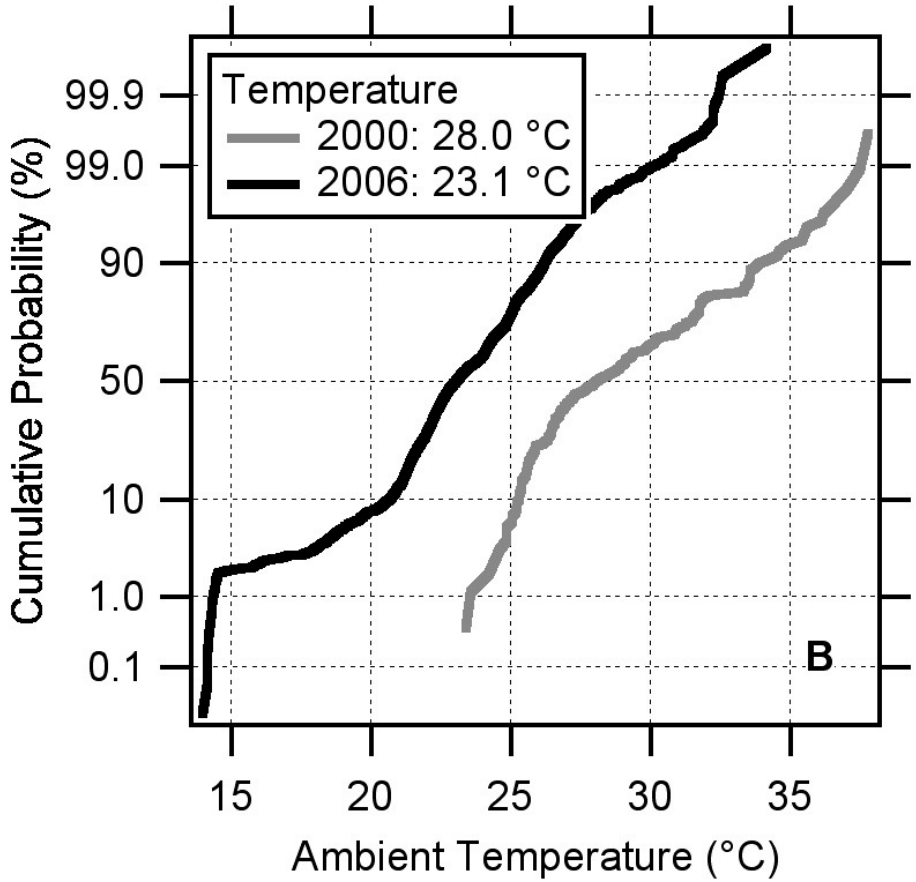




- Data averaged in box around Houston below 1000 m
- LPAS < WAS ⇒ sampling biased to plumes
- 2006 < 2000 (42%): Emissions lower, meteorology different?

Difference in Meteorology





- Meteorology was very different in 2006
- Higher wind speed, lower temperature
- 2006 study was 1 month later

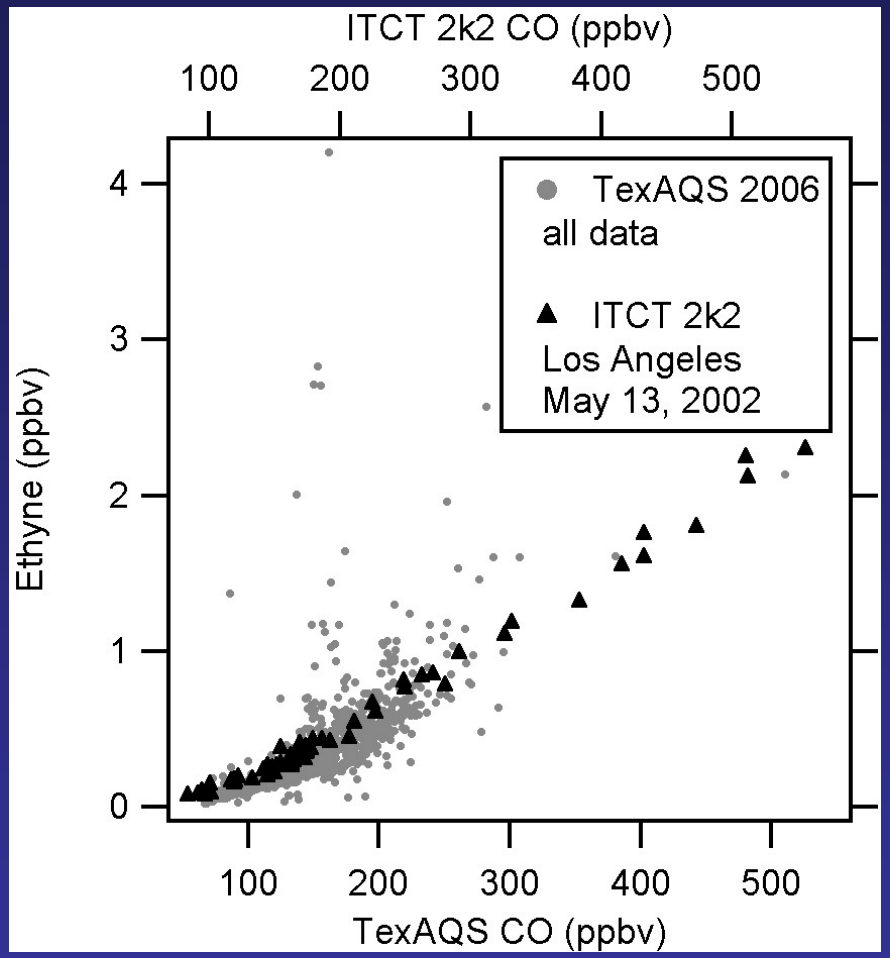
What About Other Trace Gases?

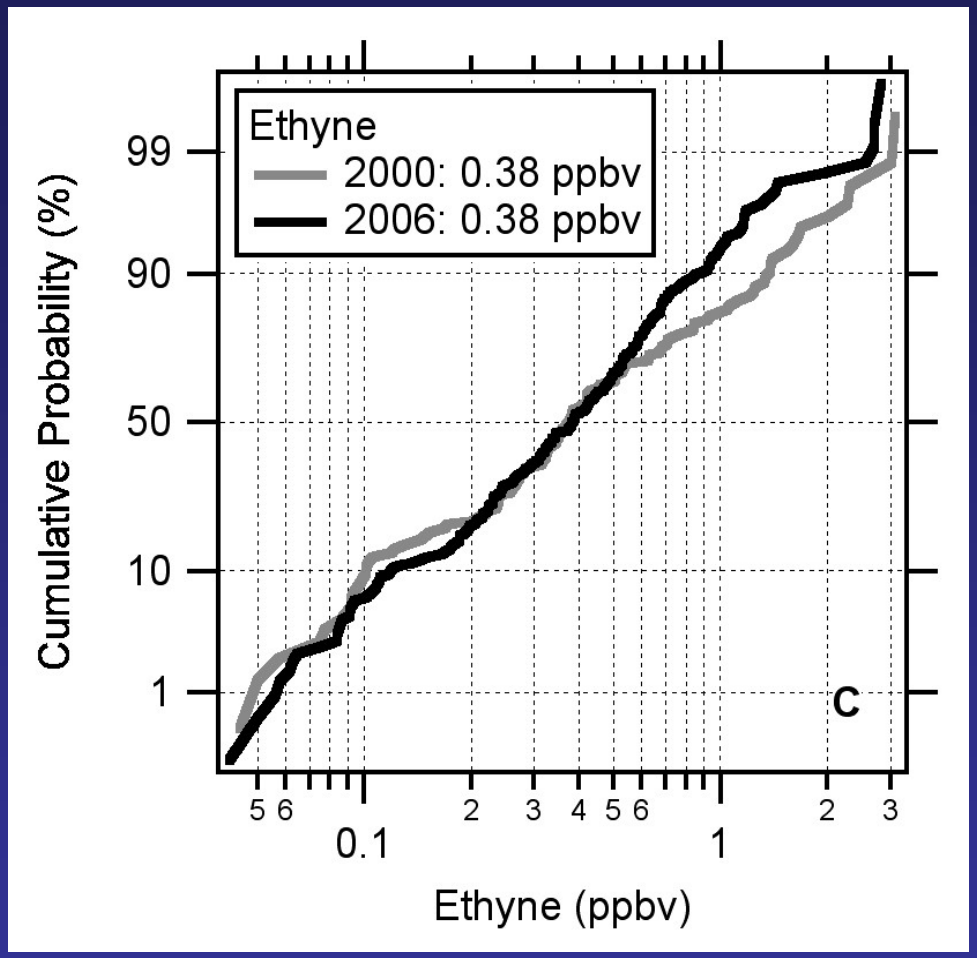
1. All trace gases are subject to same meteorology

2. All trace gases lower in 2006?
   $\Rightarrow$ more likely caused by different meteorology

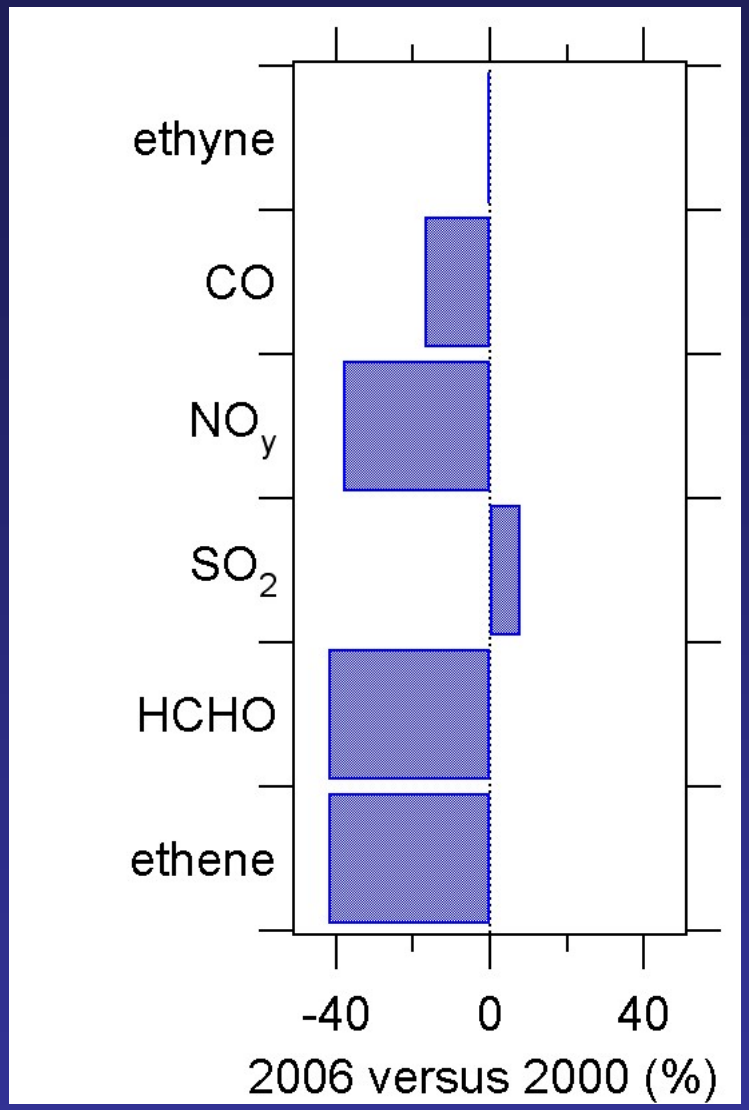
3. Only certain trace gases lower in 2006?
   $\Rightarrow$ more likely caused by different emissions

Use of Ethyne as an Urban Tracer





- Ethyne mostly urban
- Ethyne not much different between 2000 and 2006



Relative Differences Between 2006 and 2000

CO -17%: cleaner vehicles ⇒
expected = -6% year^{-1} [*Parrish*]
observed = -3% year^{-1}

NO_y -38%: power plant emissions lower [*Ryerson et al.*]

SO_2 +8%: no emissions reductions

HCHO -42%: reduced formation from ethene

Ethene -42% ⇒ *Weight of evidence suggests that emissions in 2006 were lower than in 2000*

Summary

1. Developed fast-response, airborne measurement of ethene
2. Located and quantified different ethene point sources
   - *Agreement with SOF data within factor of 2*
   - *Measured fluxes >> 2004 TCEQ point source database (factor 10-40 for Mt. Belvieu)*
3. Examined differences between 2000 and 2006
   - *Weight of evidence suggests that ethene emissions in 2006 were lower than in 2000 (factor 2 at most)*

Future Work

1. Extend flux estimates for other point sources and VOCs (WP-3D: aromatics; SOF: alkanes, propene)
2. Quantify the variability & compare with inventories

Acknowledgments

WAS	*Elliot Atlas, Stephen Donnelly, Rich Lueb, Sue Schauffler, Rebecca Washenfelder, Roger Hendershot*
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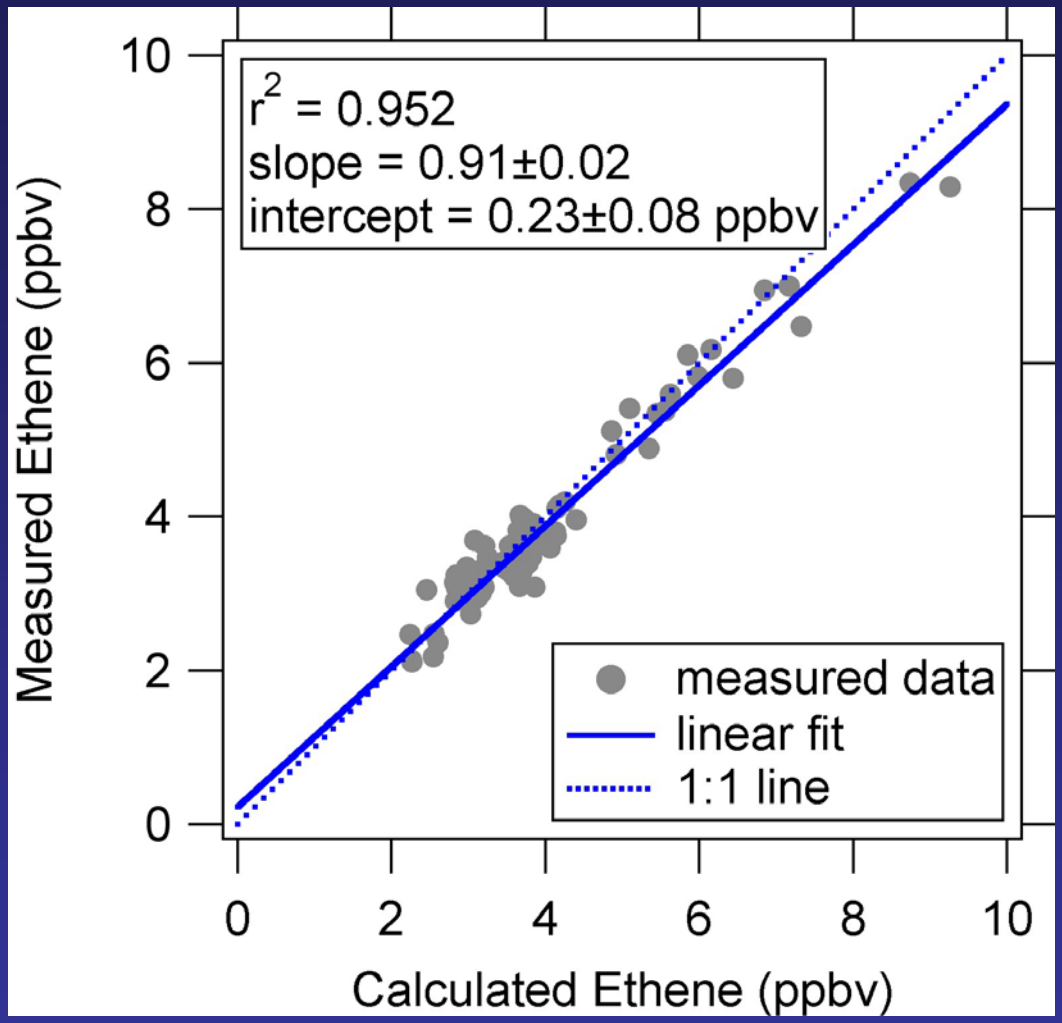
CO, SO_2	*John Holloway*
NO_y	*Tom Ryerson*
Flight direction	*Tom Ryerson, Chuck Brock*
Flight planning	*Michael Trainer*

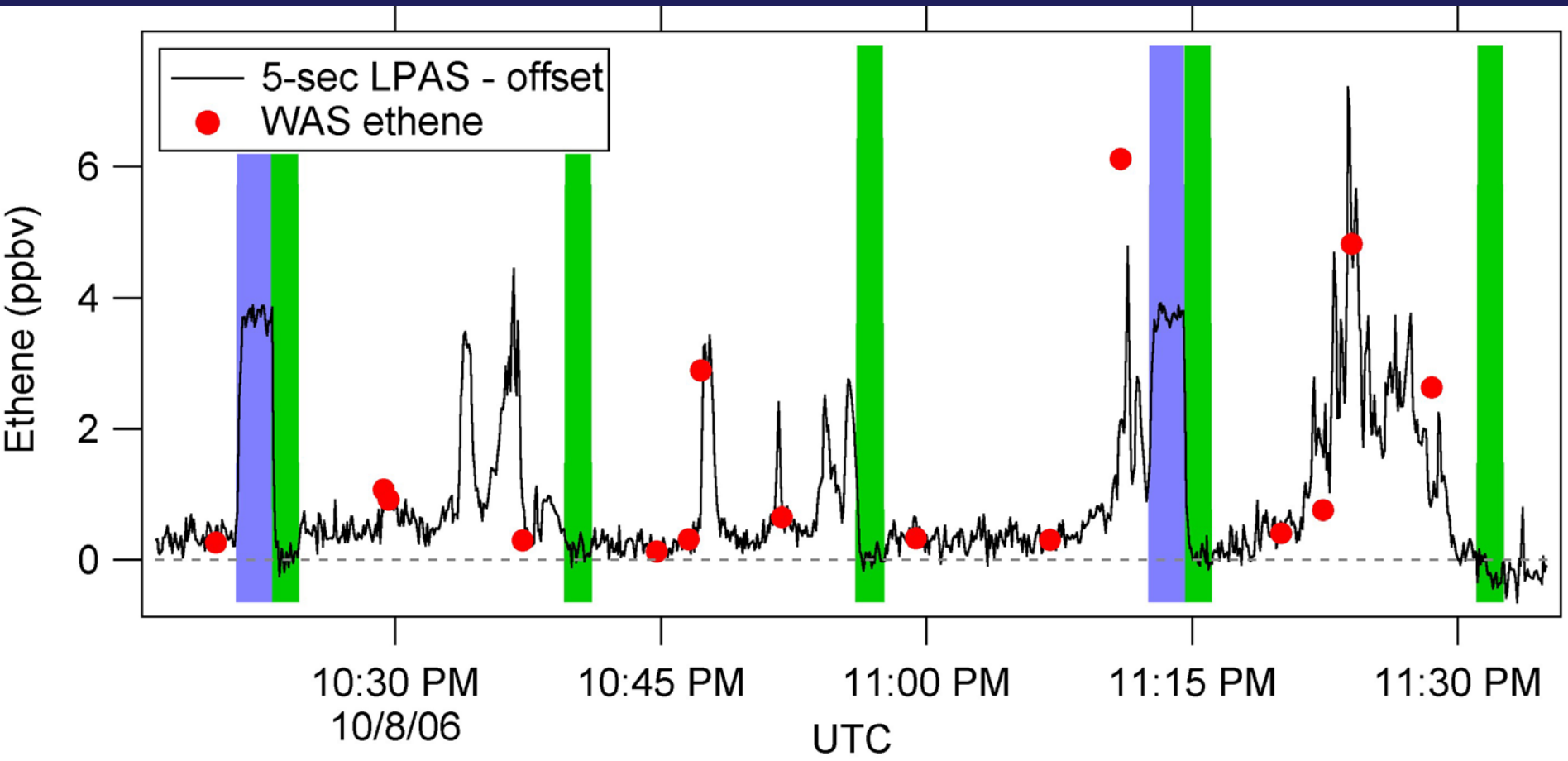
Jim Meagher, Fred Fehsenfeld, David Parrish

Summary of all Calibrations



- In-flight calibrations compared with pre-set calibration
- Final data adjusted by +9%

Example of Raw Data



- Correction for offset ⇒ good agreement with WAS
- Combined in-flight calibrations ⇒ final LPAS data corrected by +9%