Quantification of Ethene Emissions from Petrochemical Industries in Houston, TX:

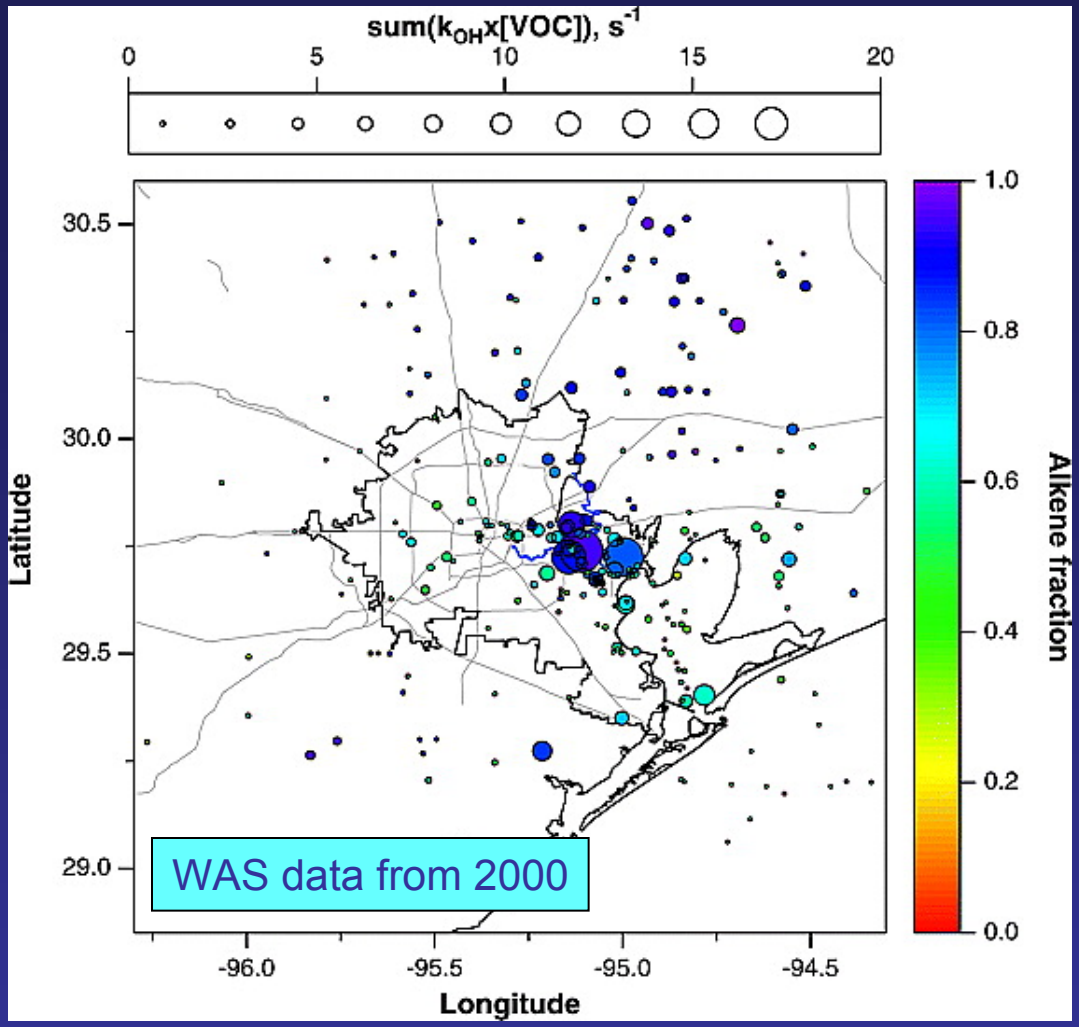
Large Disagreements with Emission Inventories

Joost de Gouw[1], C. Warneke[1], S. te Lintel Hekkert, J.S. Holloway[1], D.D. Parrish[1], J. Peischl[1], T.B. Ryerson[1], J. Mellqvist[2], E.L. Atlas[3], D. Richter[4], J. Walega[4], P. Weibring[4], A. Fried[4]

[1] NOAA ESRL & CIRES, University of Colorado, Boulder, CO
[2] Chalmers University, Gothenburg, Sweden
[3] University of Miami, Miami, FL
[4] NCAR, Boulder, CO

Outline:

1. Photo-acoustic measurement of ethene
2. Quantification of industrial emission fluxes
3. Ethene in Houston: 2006 vs. 2000



[*Ryerson*, JGR 2003; *Wert*, JGR 2003]

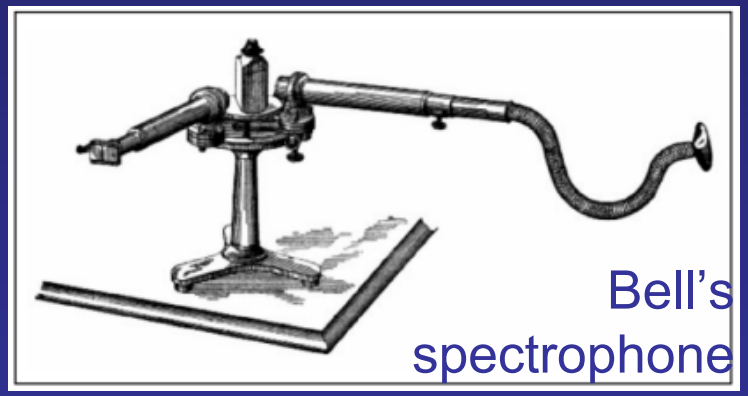
TexAQS 2000

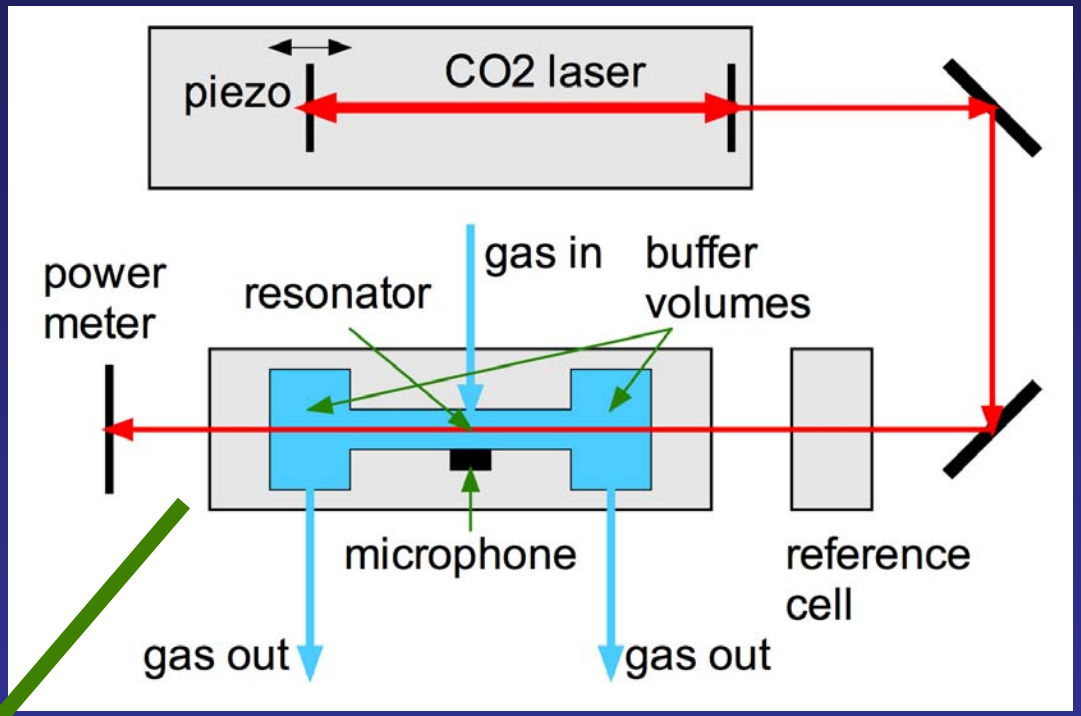
- Industrial emissions of alkenes are large
- Alkene emissions >> emission inventories (factor 10-100)
- Alkenes dominate the OH reactivity

Can we add fast-response, airborne measurements of alkenes for TexAQS 2006?

Fast-Response Measurements of Ethene Using Laser Photo-Acoustic Spectroscopy (LPAS)

Bell [1880]:
Absorption of modulated light source ⇒ acoustic signal (photo-acoustic effect)

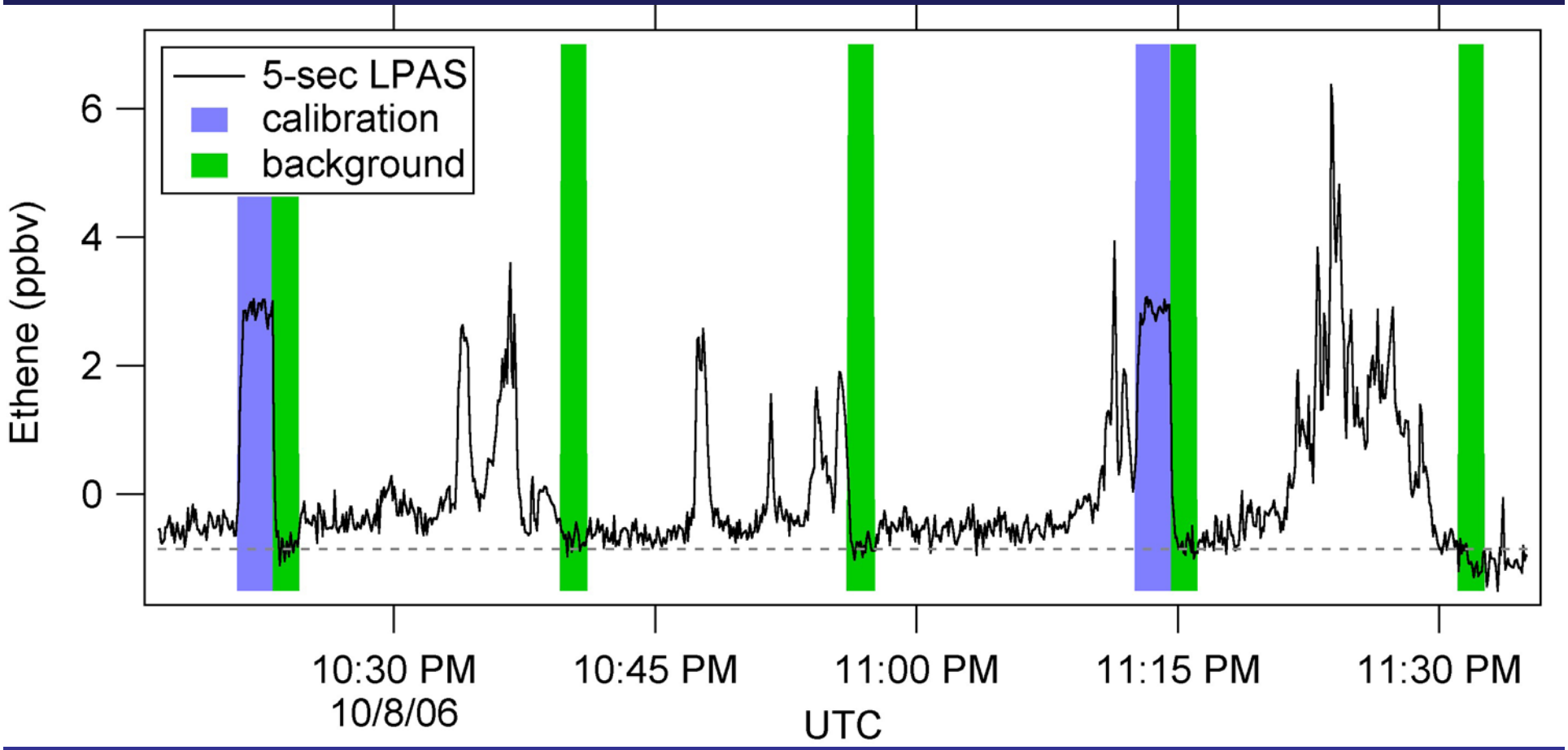




Best performance for ethene:

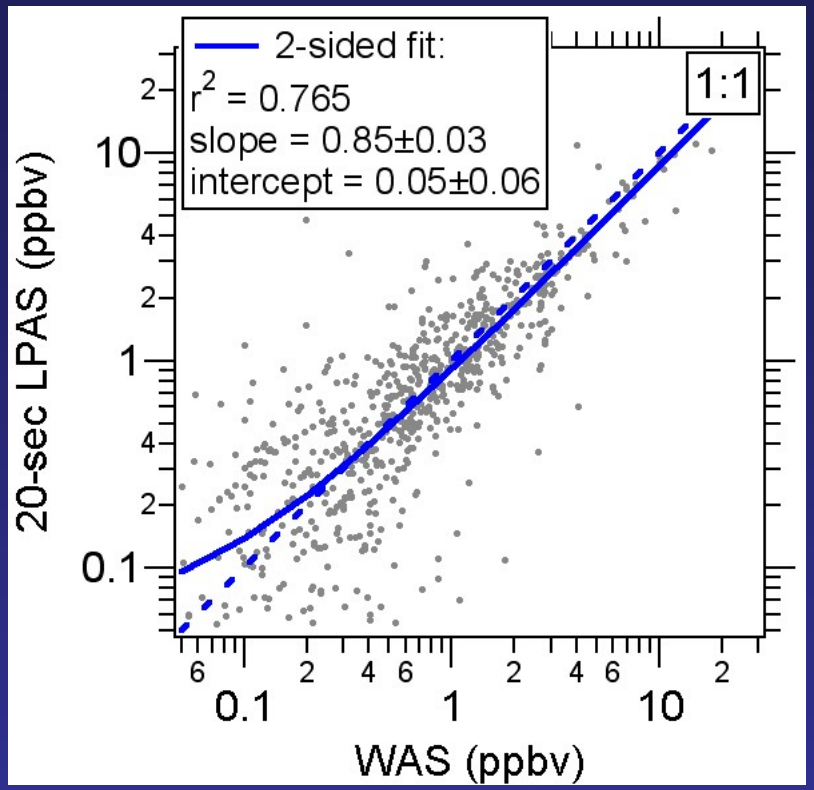
- 1-σ noise ≈ 70 pptv
- Time response 5 sec

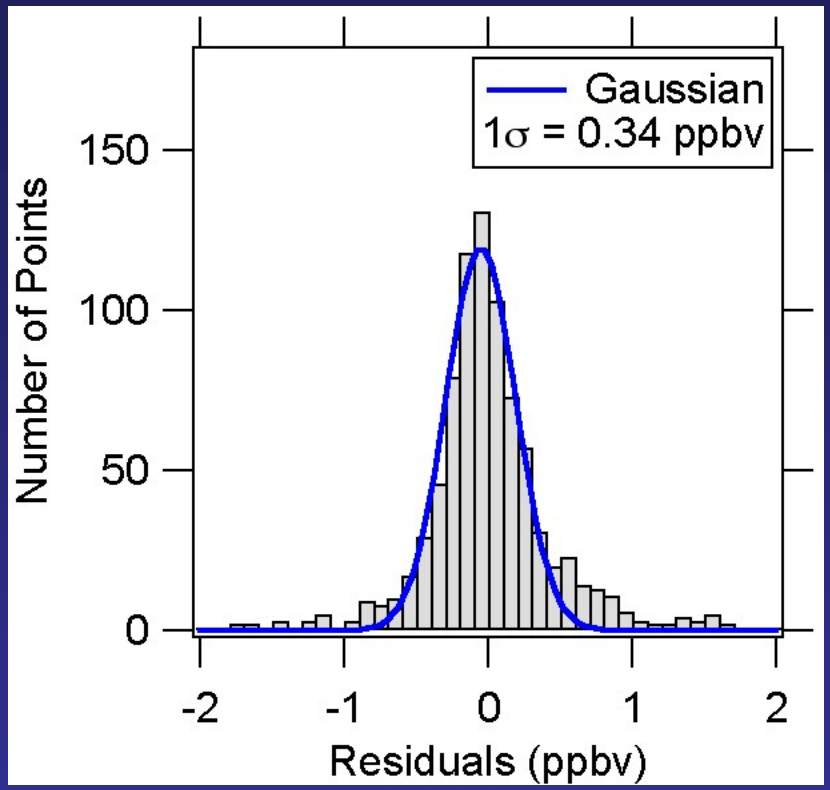
Raw Data Collected In-Flight During TexAQS II



- Backgrounds determined with catalyst
- In -flight calibrations with standard gas

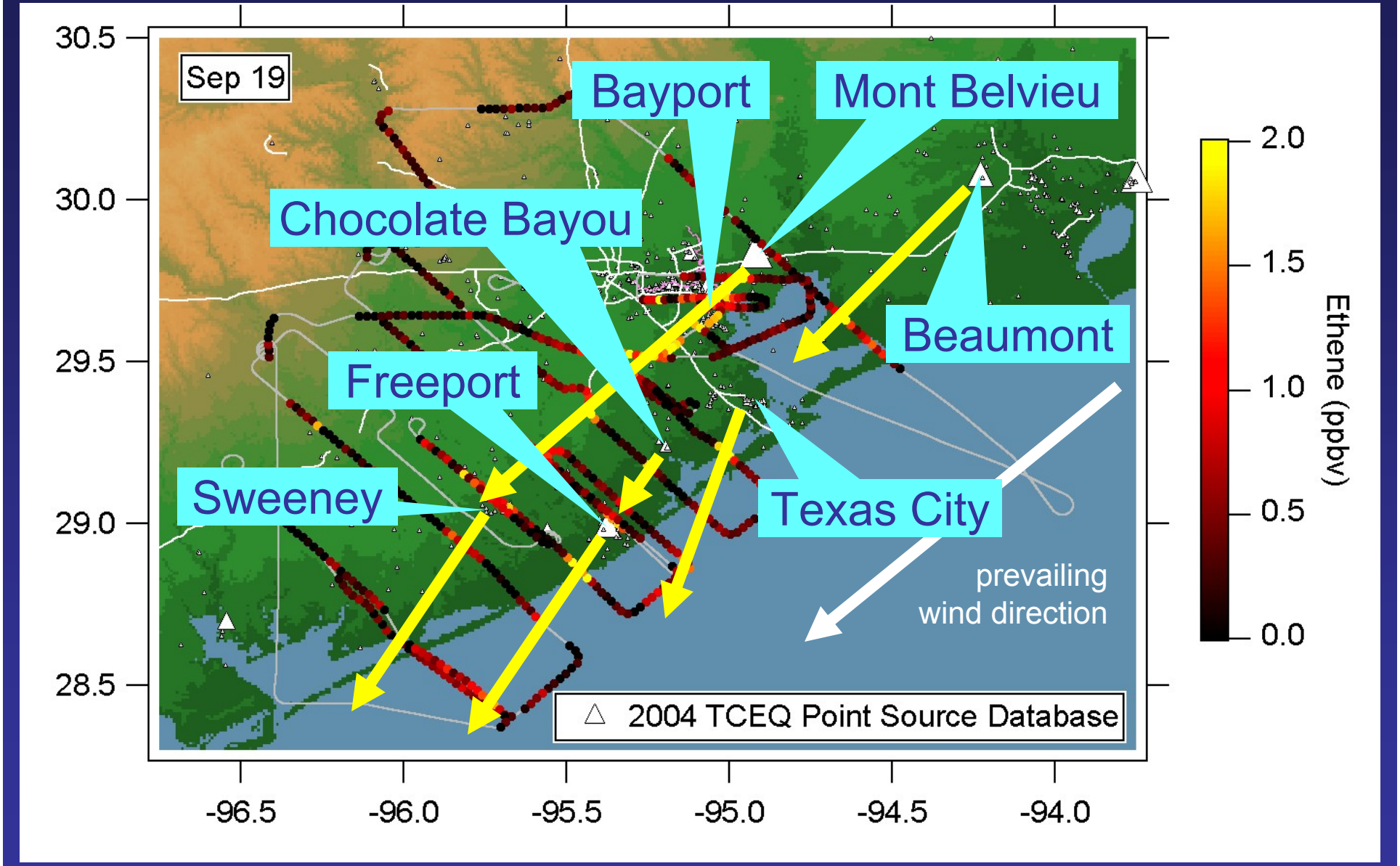
Inter-Comparison with Whole Air Sampler (WAS)





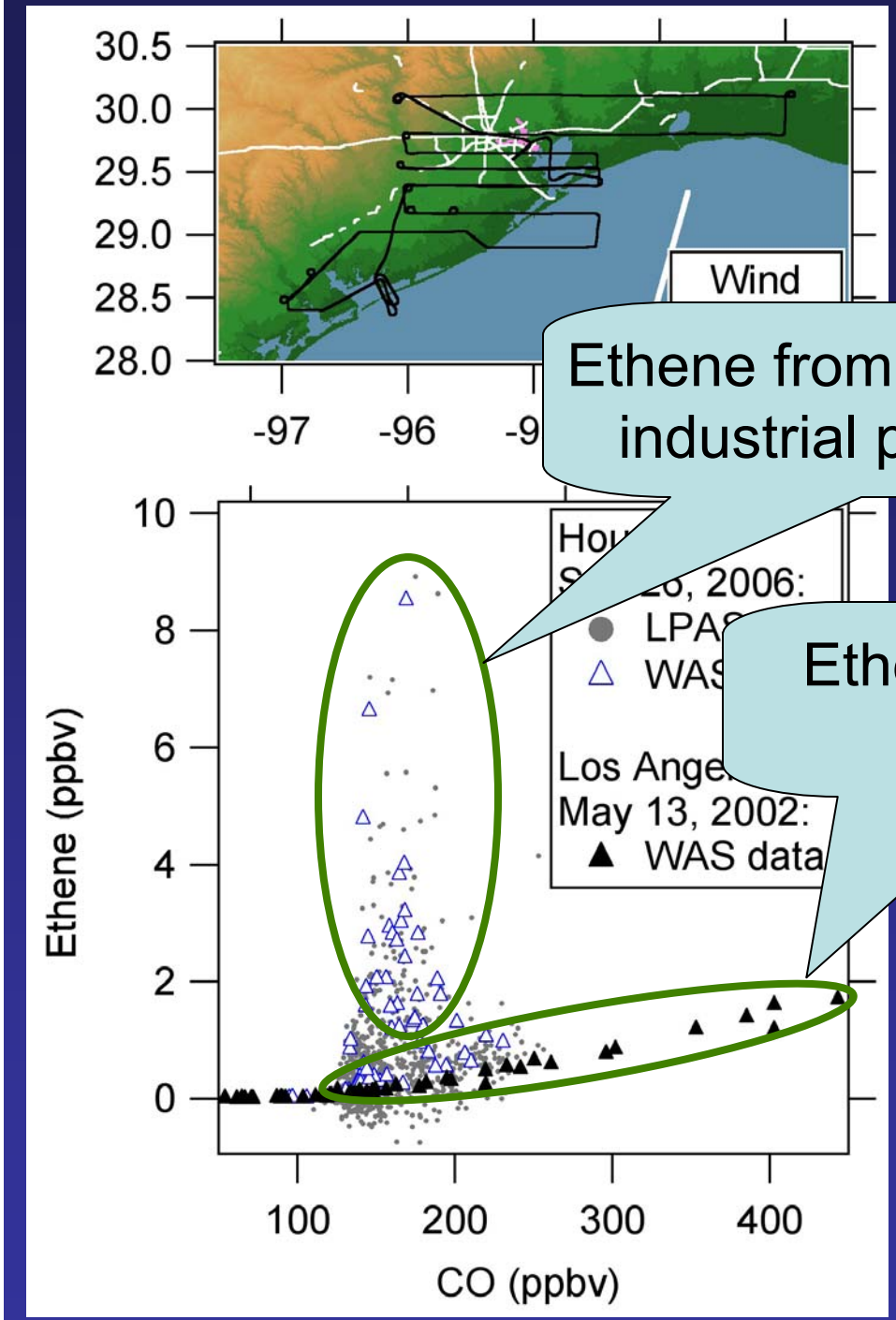
- LPAS 15% lower than WAS
- Scatter caused by rapid changes in ethene
- 20-sec LPAS detection limit <1 ppbv

Ethene Source Locations in Houston



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

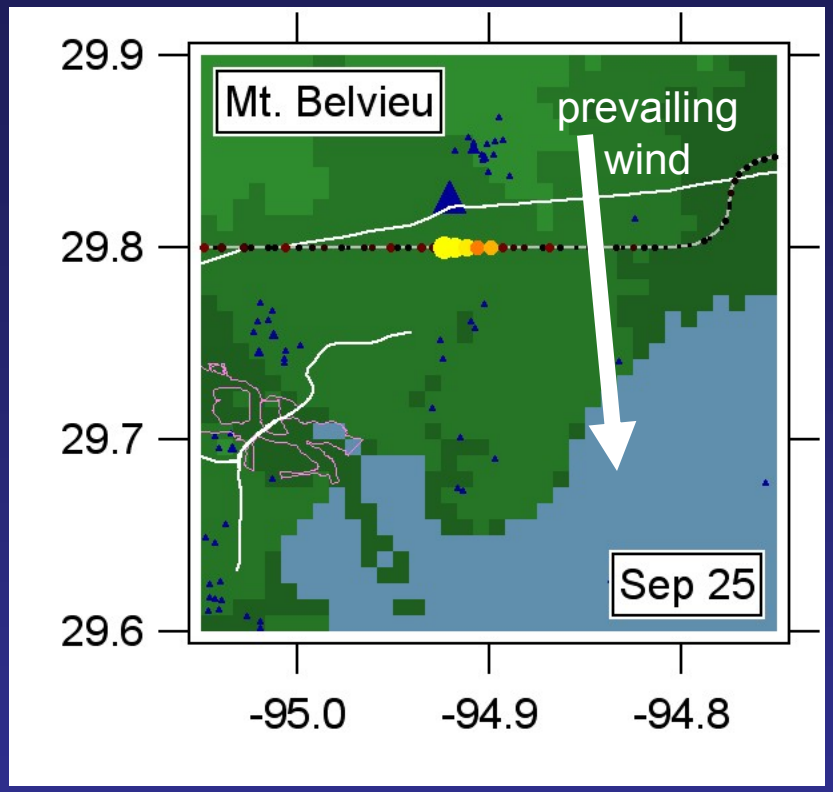
Ethene versus CO in Houston and Los Angeles

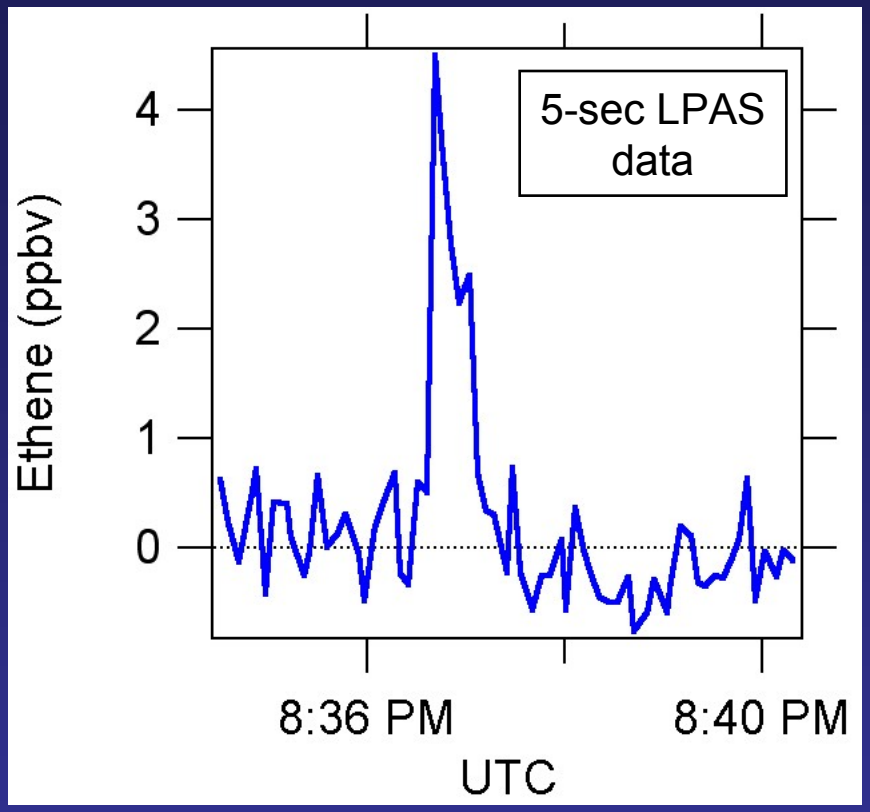


Ethene is strongly enhanced from petrochemical sources

- TexAQS 2000: ethene has key role in ozone formation [*Ryerson*, 2003]

Quantification of Emission Fluxes

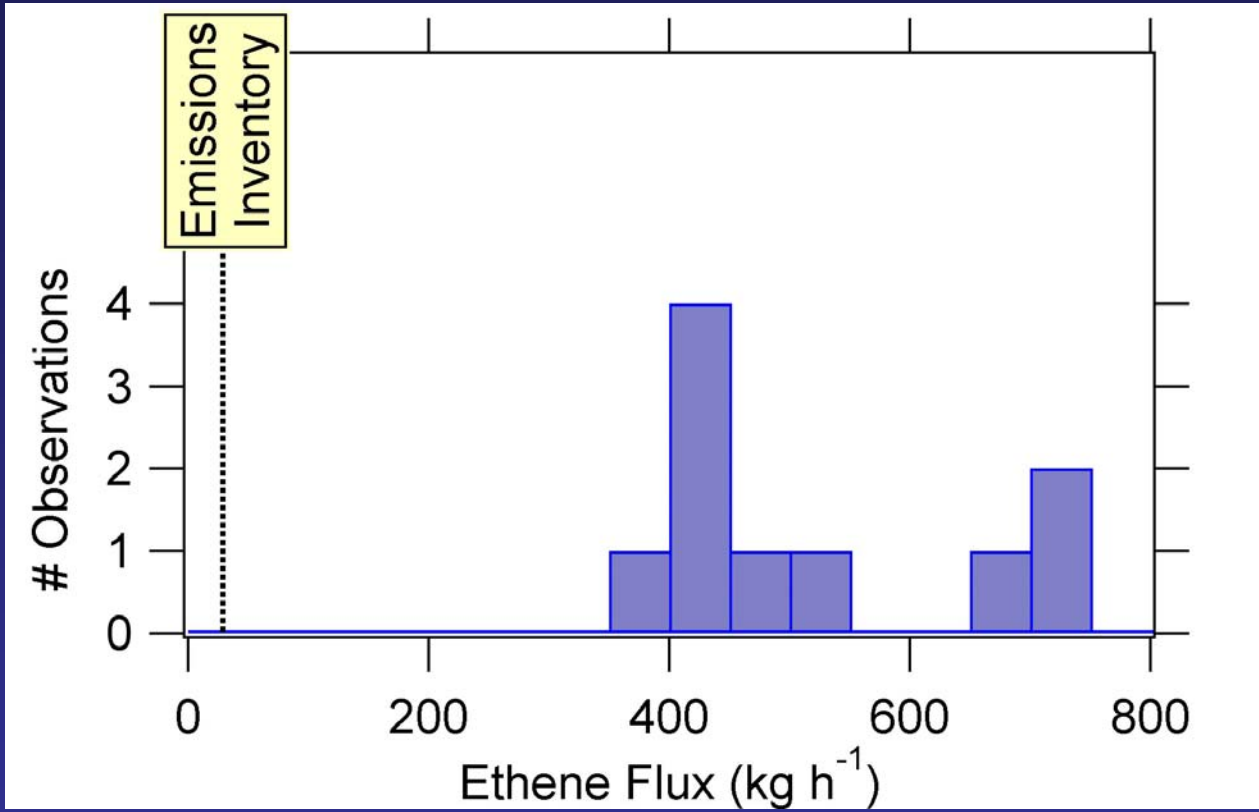




1. Integration over ethene peak
2. Multiplication by orthogonal wind
3. Assume uniform vertical mixing

$\Rightarrow$ flux $\approx$ 350 kg h^{-1}

Variability in Ethene Fluxes from Mt. Belvieu

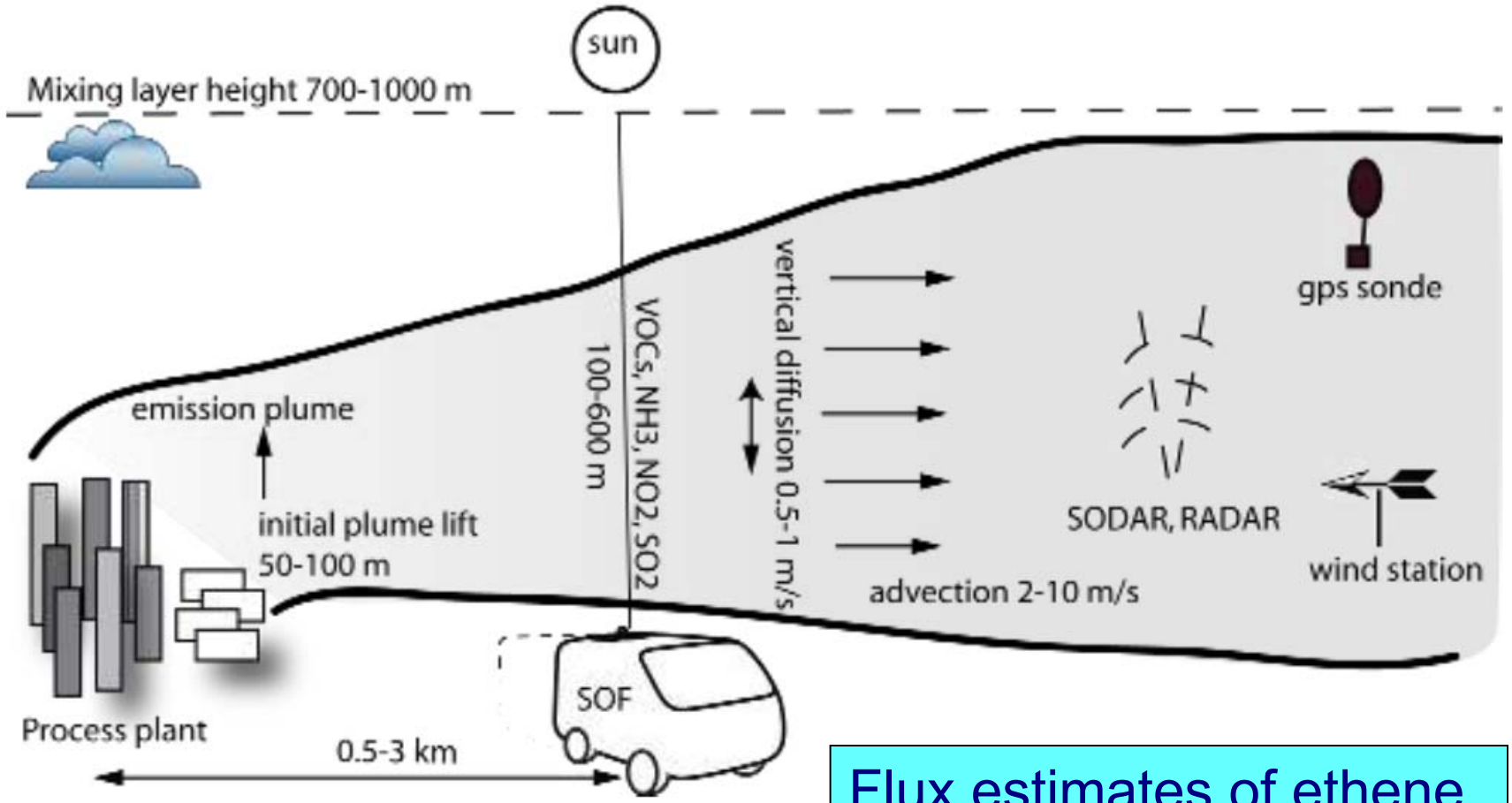


- Average ethene flux = 520±140 kg h^{-1}
- Uncertainty in the method = factor of 2

Measurements suggest that ethene emissions are underestimated by more than 1 order of magnitude

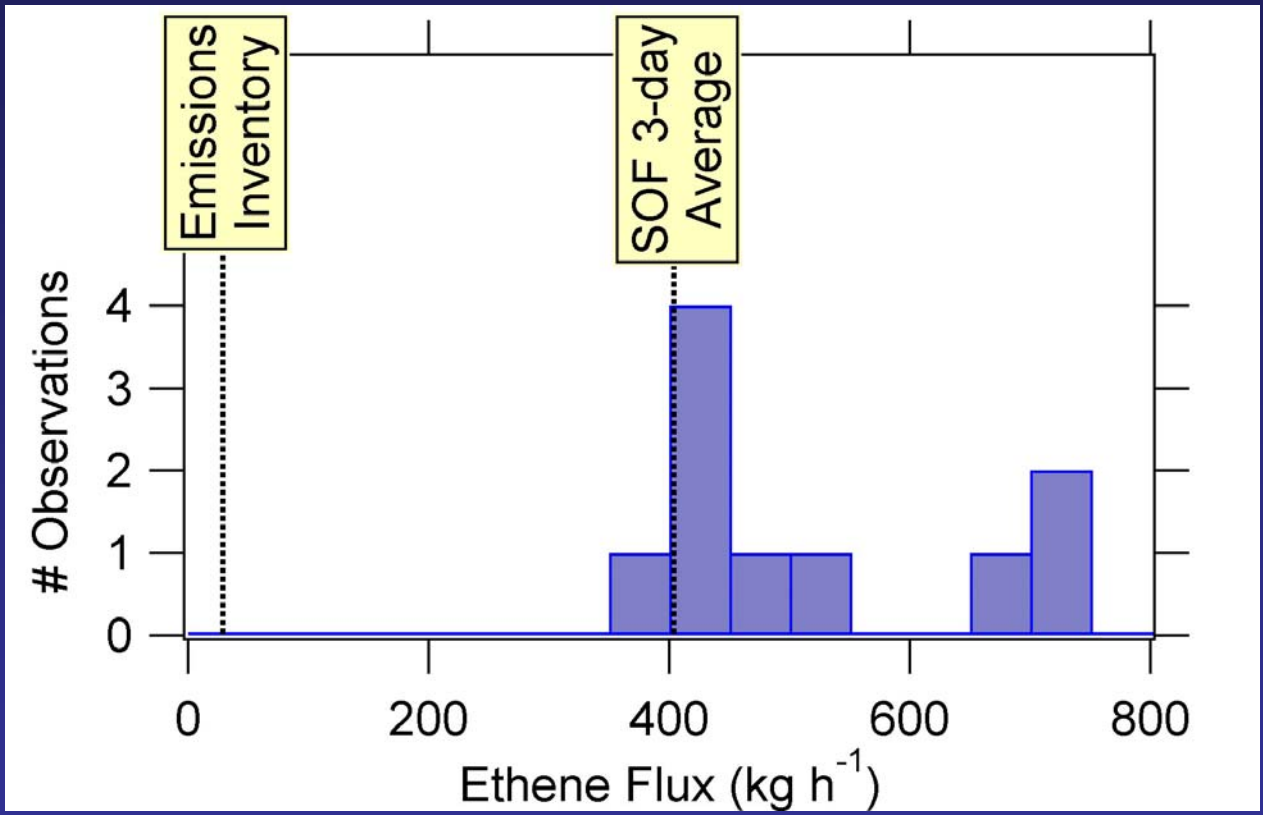
Additional Evidence:
Solar Occultation Flux (SOF) Measurements

Johan Mellqvist et al., Chalmers University, Sweden



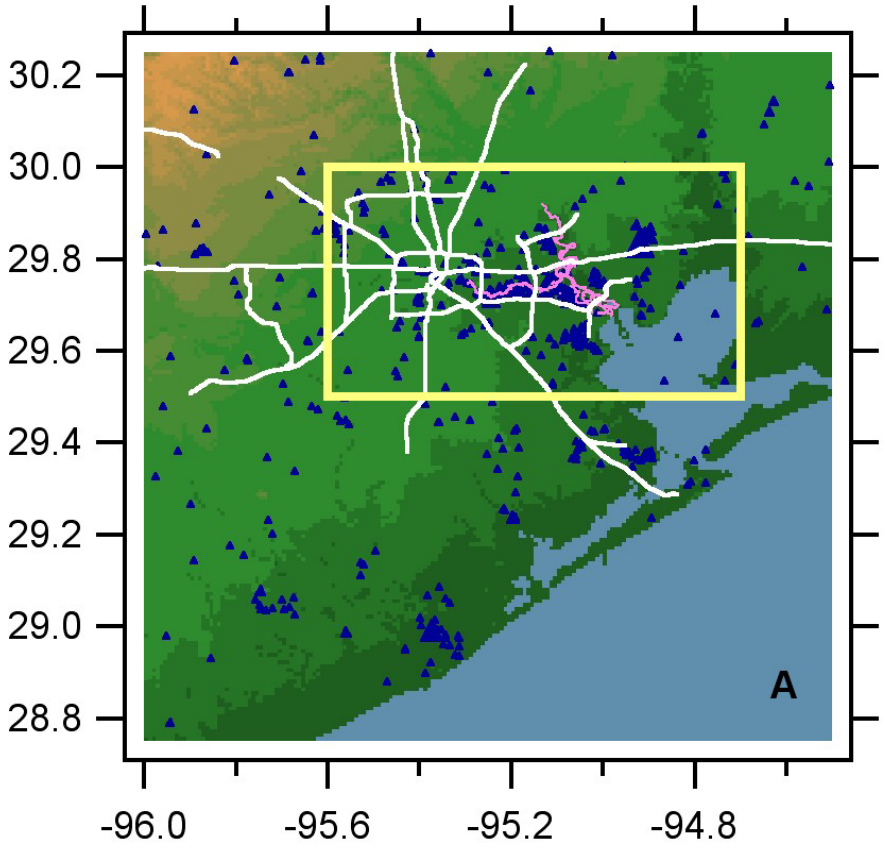
Flux estimates of ethene, propene, ammonium, etc.

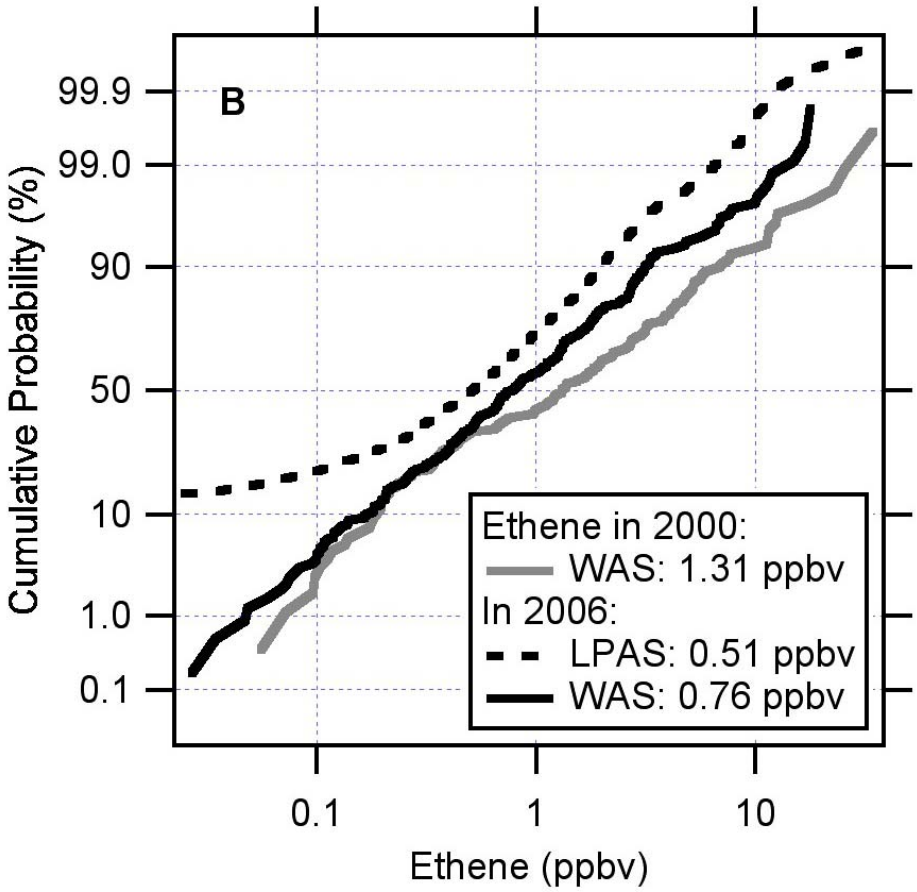
Additional Evidence:
Solar Occultation Flux (SOF) Measurements



Airborne and SOF measurements agree within uncertainty on the ethene flux from Mont Belvieu

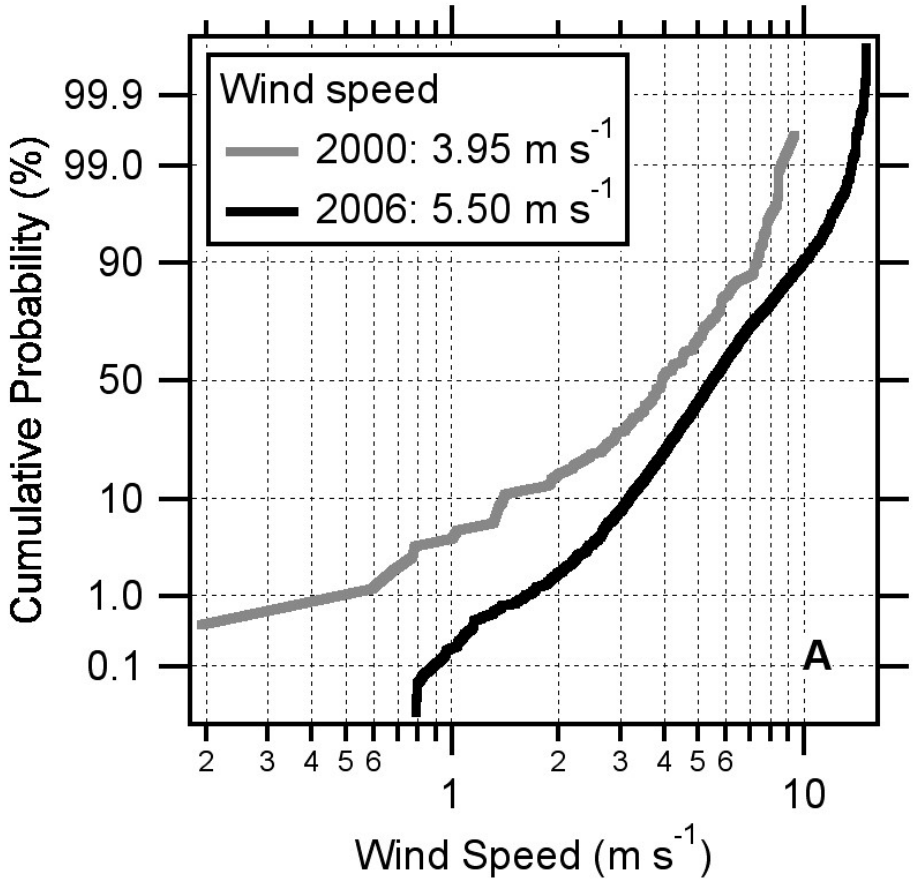
Comparison Between 2006 and 2000 Studies

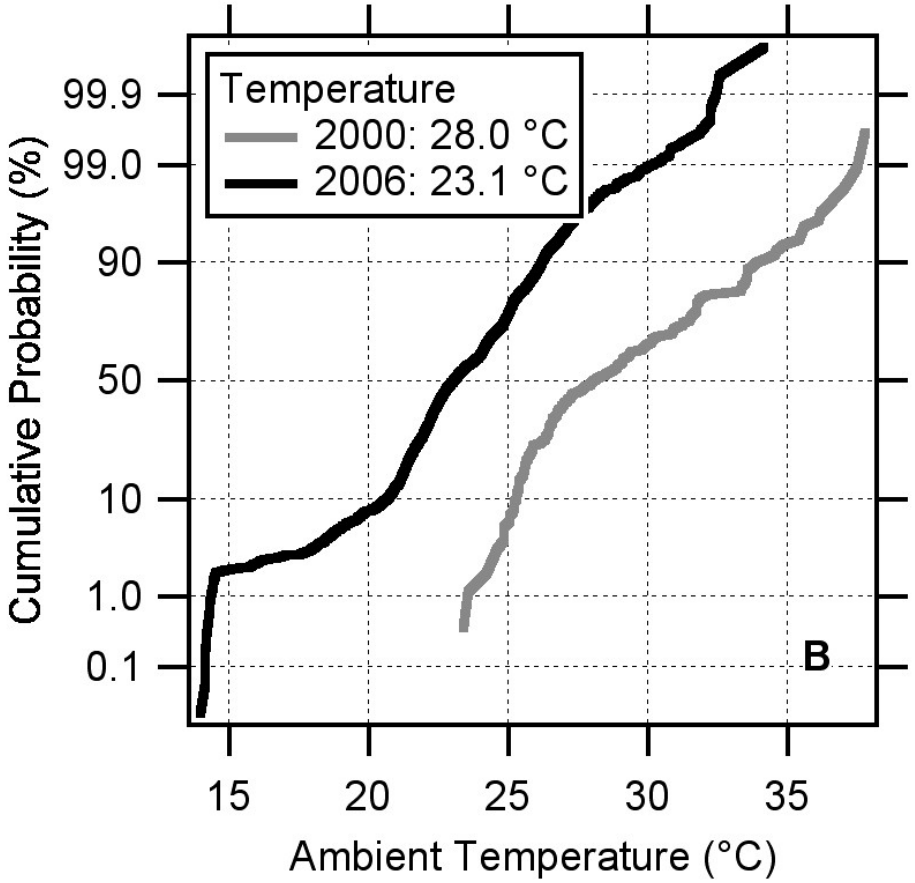




- Data averaged in box around Houston below 1000 m
- LPAS < WAS: sampling slightly biased towards plumes
- 2006 < 2000 (42%): Emissions lower, meteorology different?

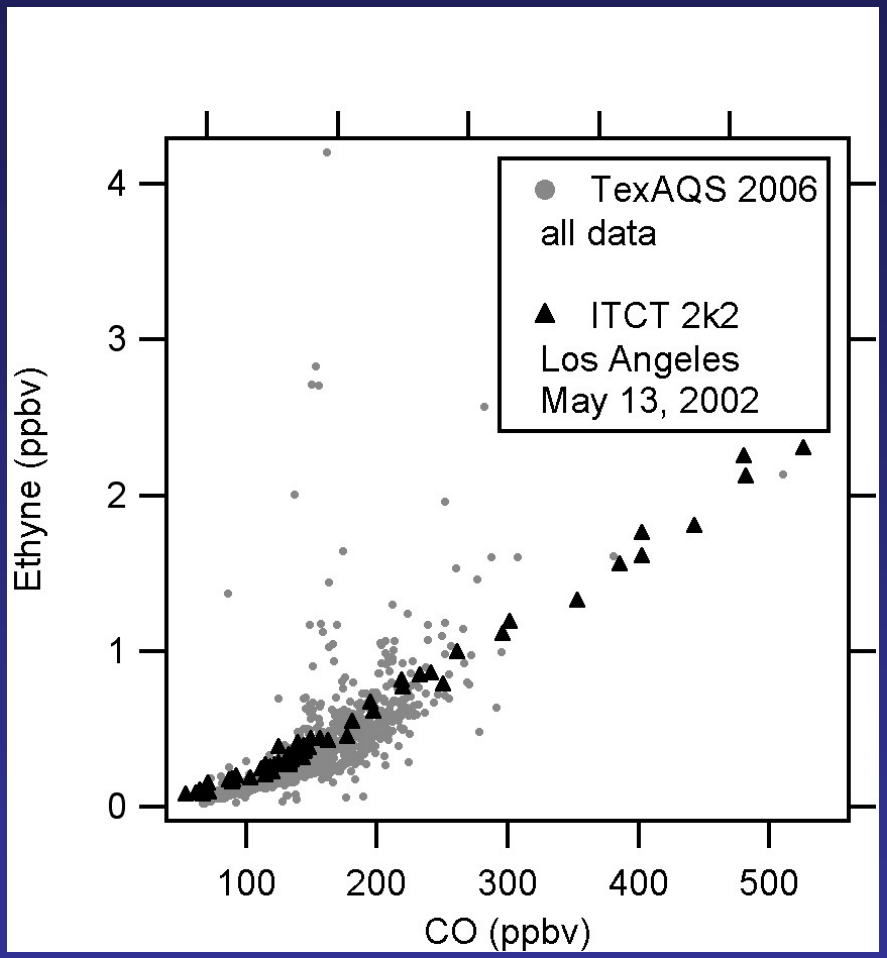
Difference in Meteorology

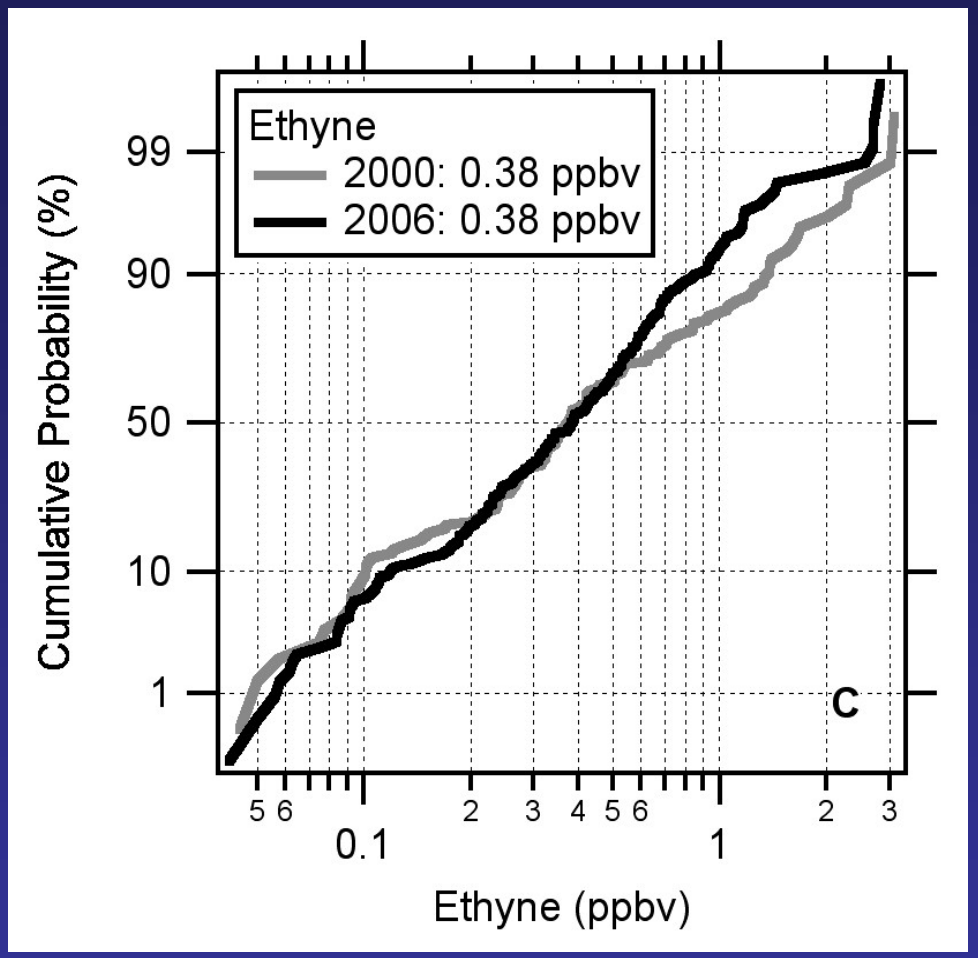




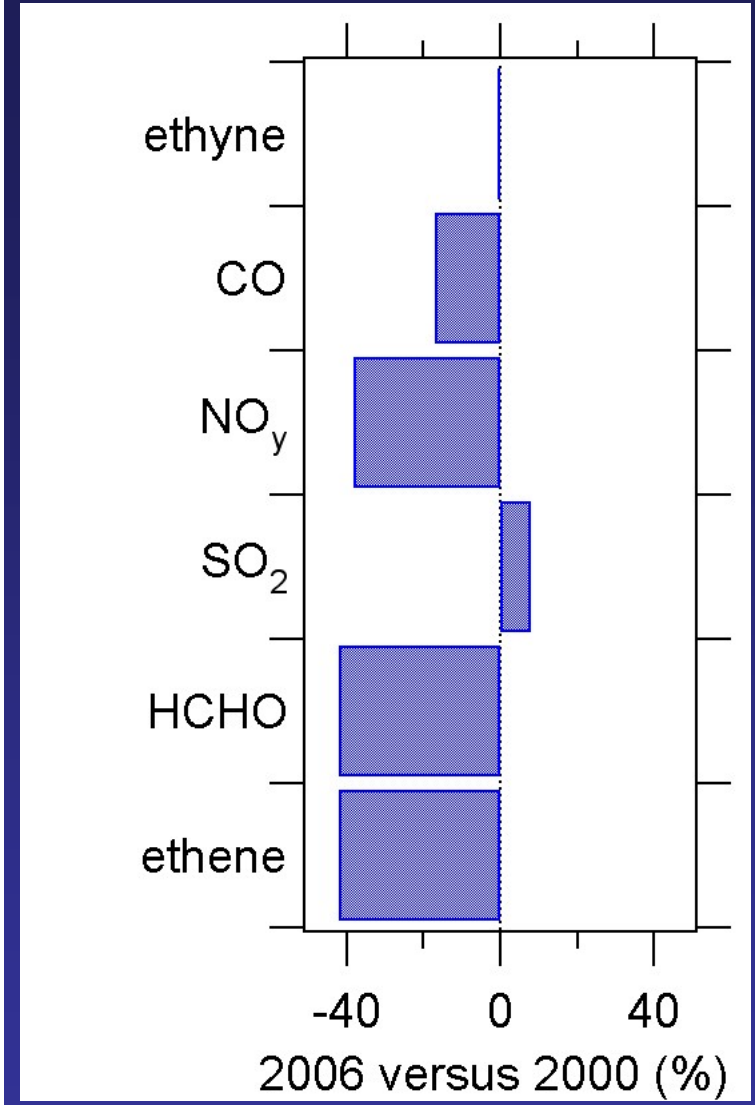
- Wind speed higher in 2006: more dilution
- Temperature lower in 2006: lower BL height, less dilution
- What about other chemical species?

Use of Ethyne as an Urban Tracer





- Ethyne mostly urban
- Not much difference between 2000 and 2006



Relative Differences Between 2006 and 2000

CO -17%: cleaner vehicles ⇒
expected = -6% year^{-1} [*Parrish*, 2006]
observed = -3% year^{-1}

NO_y -38%: power plant and ship channel emissions lower

SO_2 +8%: no emissions reductions

HCHO -42%: reduced formation from ethene

Weight of evidence suggests that ethene emissions in 2006 were lower than in 2000

Conclusions

1. Developed LPAS technique for fast-response measurements of ethene
2. Emission fluxes of ethene from petrochemical industries factor 13-23 larger than 2004 TCEQ point source database, in agreement with earlier work [*Ryerson*, 2003]
3. Weight of evidence suggests that ethene emissions in 2006 were lower than in 2000

Acknowledgments

Texas Commission on Environmental Quality

Ken Aikin, Fred Fehsenfeld, Gerd Hübler, Jim Meagher, Michael Trainer