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

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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
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?

[Ryerson et al., JGR 2003]
Laser Photo-Acoustic Spectroscopy (LPAS)

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

Inlet system
Constant pressure and flow
Calibrations
Instrument backgrounds

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

- Mont Belvieu
- Beaumont
- Texas City
- Freeport
- Chocolate Bayou
- Sweeney
- Bayport

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
- NCAR Electra
- Ground site at La Porte airport

Aug 31 - Oct 31, 2006
- WP-3D
- Ron Brown in Barbour’s Cut
Barbour’s Cut versus La Porte airport


Median decreased from 2 ppbv to 0.8 ppbv
Data averaged in box around Houston below 1000 m
LPAS < WAS \implies 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?  
   ⇒ more likely caused by different meteorology

3. Only certain trace gases lower in 2006?  
   ⇒ 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

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<th>Area</th>
<th>Contributors</th>
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<tr>
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<td>SOF</td>
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<td>Flight direction</td>
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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%