Initial Report on Preliminary TexAQS II Results

Rapid Science Synthesis Team

November 8, 2006

TexAQS II major deployments

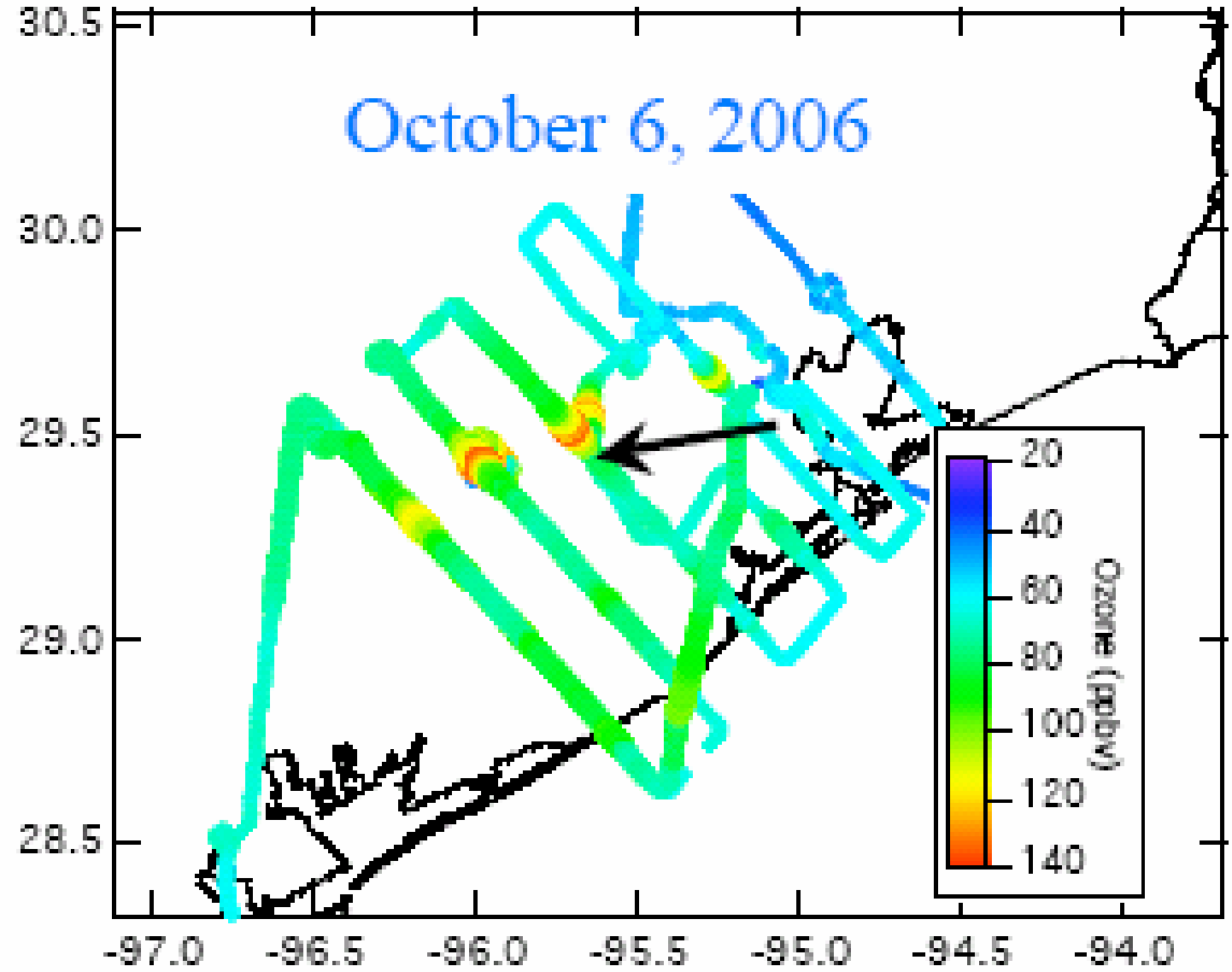
• NOAA ship Ronald H. Brown	• Aug 1 – Sept 12
• NOAA Twin Otter	• Aug 2 – Sept 15
• NOAA WP3	• Aug 31 – Oct 15
• CIRPAS Twin Otter	• Aug 18 – Sept 15
• NASA King Air	• Aug 27 – Sept 29
• Baylor Aztec	• Aug 21 – Aug 31
• UH Moody Tower	• Aug 14 – Sept 29
• UH Ozonesondes	• July 23 – Oct 12
• UH Rawinsondes and tethersonde	• July 15 – Oct 12
• Solar occultation flux	• Aug 25 – Sept 25
• TERC Vertical Mixing Experiment	• Sept 27, Oct 5
• TERC/DOE Houston Triangle Experiment	• Sept 9 – Sept 28
• UT/TCEQ surface monitoring network	• July 2005 – Oct 2006
• NOAA profiler network	• May 2005 – Oct 2006

Question A.

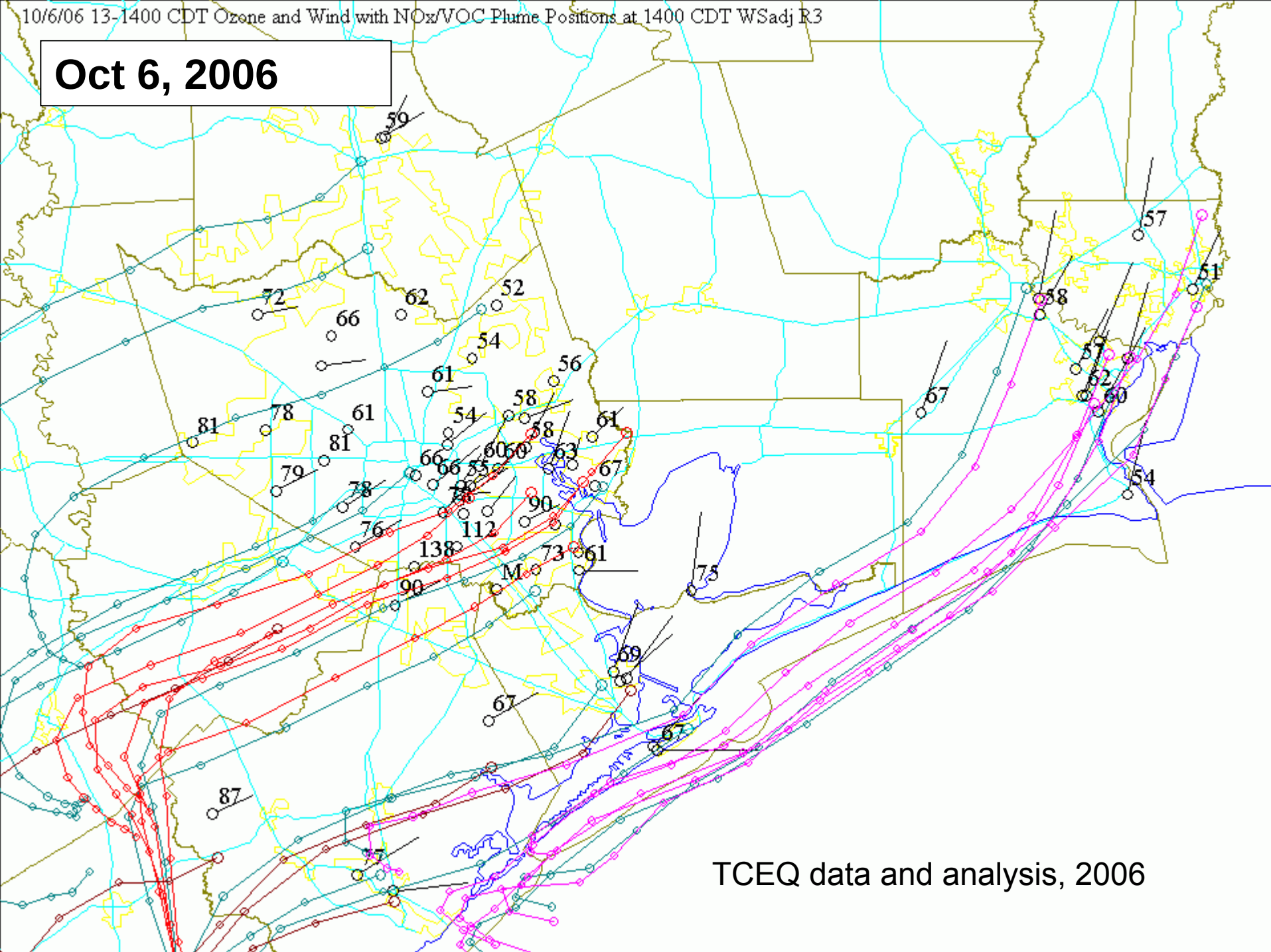
- Which local emissions are responsible for the production of high ozone in Houston?
- Are different kinds of emissions responsible for transient high ozone and 8-hour-average high ozone?

Preliminary Results

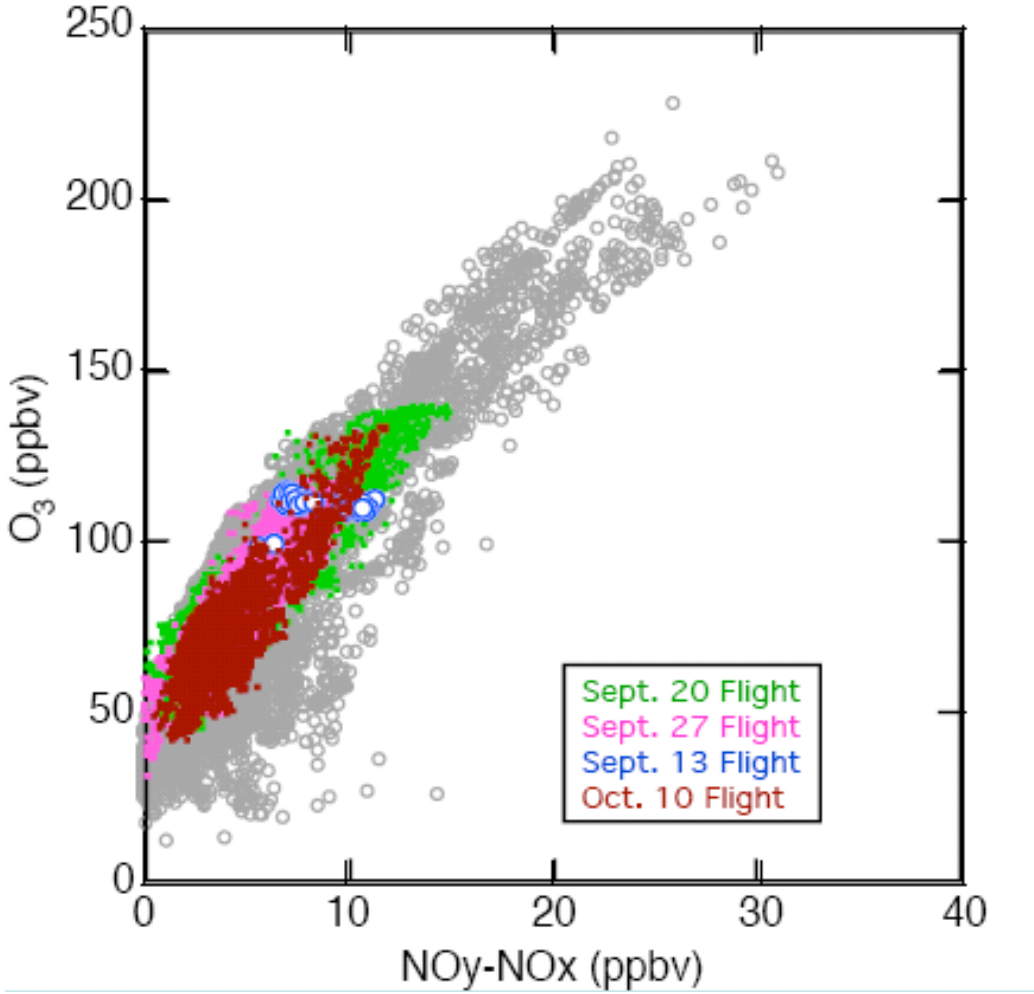
- The highest ozone in Houston occurs downwind of the industrial areas, just as in 2000. Ozone production efficiency in the industrial plumes in 2006 is about the same as in 2000, but the peak ozone on episode days was lower. It's too early to say why the ozone was lower.



NOAA P3 data from Parrish, 2006


10/6/06 13-1400 CDT Ozone and Wind with NOx/VOC Plume Positions at 1400 CDT WSadj R3
Oct 6, 2006
TCEQ data and analysis, 2006

Aircraft data from four 2006 flights (colors) overlaid on aircraft data from 2000 (grey)



NOAA P3 data from Parrish, 2006

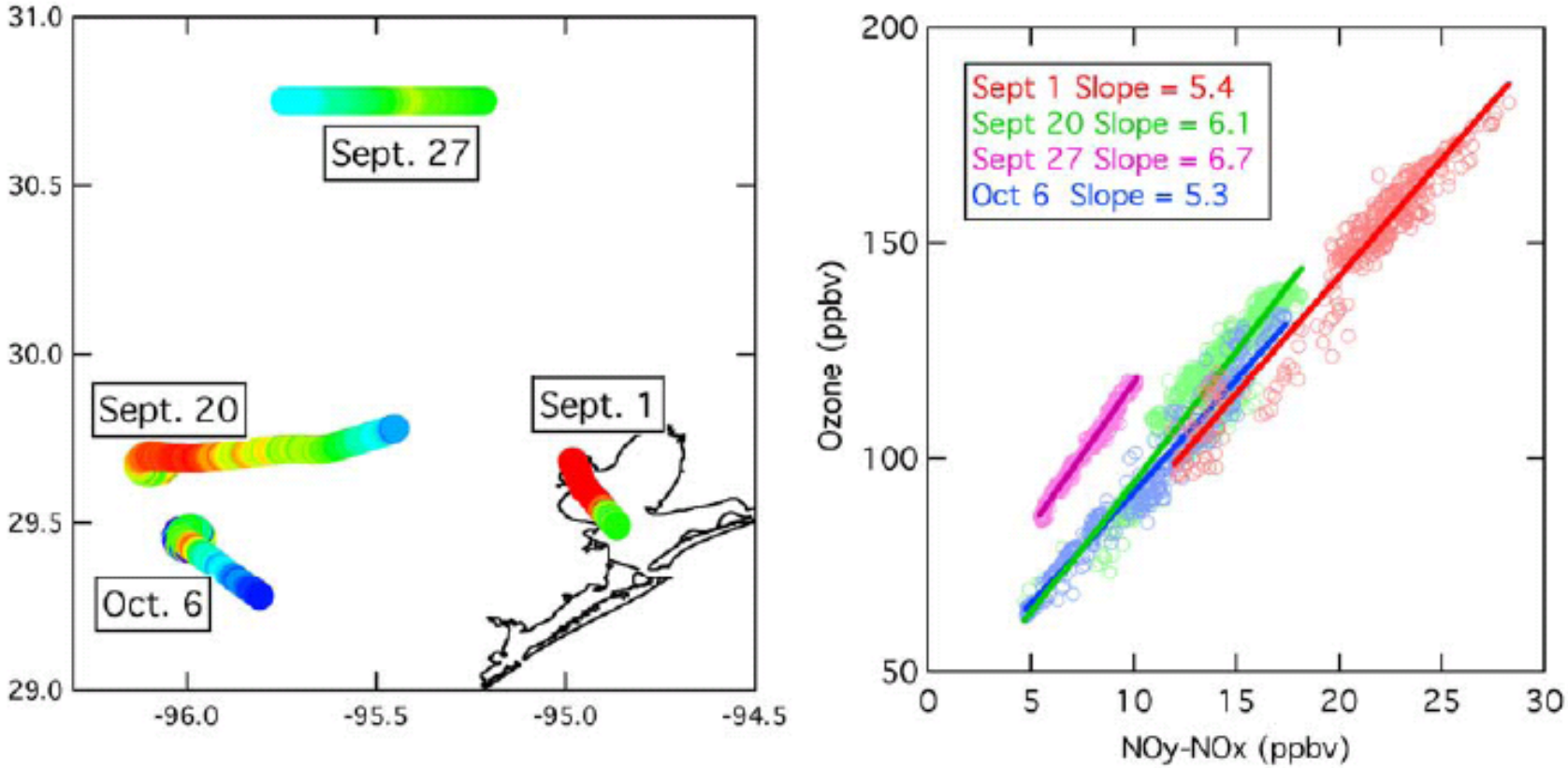


Figure A3. Highest ozone observed by the WP-3D aircraft and RHB research vessel during TexAQS 2006. The figure is in the same format as Figure A2, but with different ranges on axes.

NOAA data, from Ryerson et al., 2006

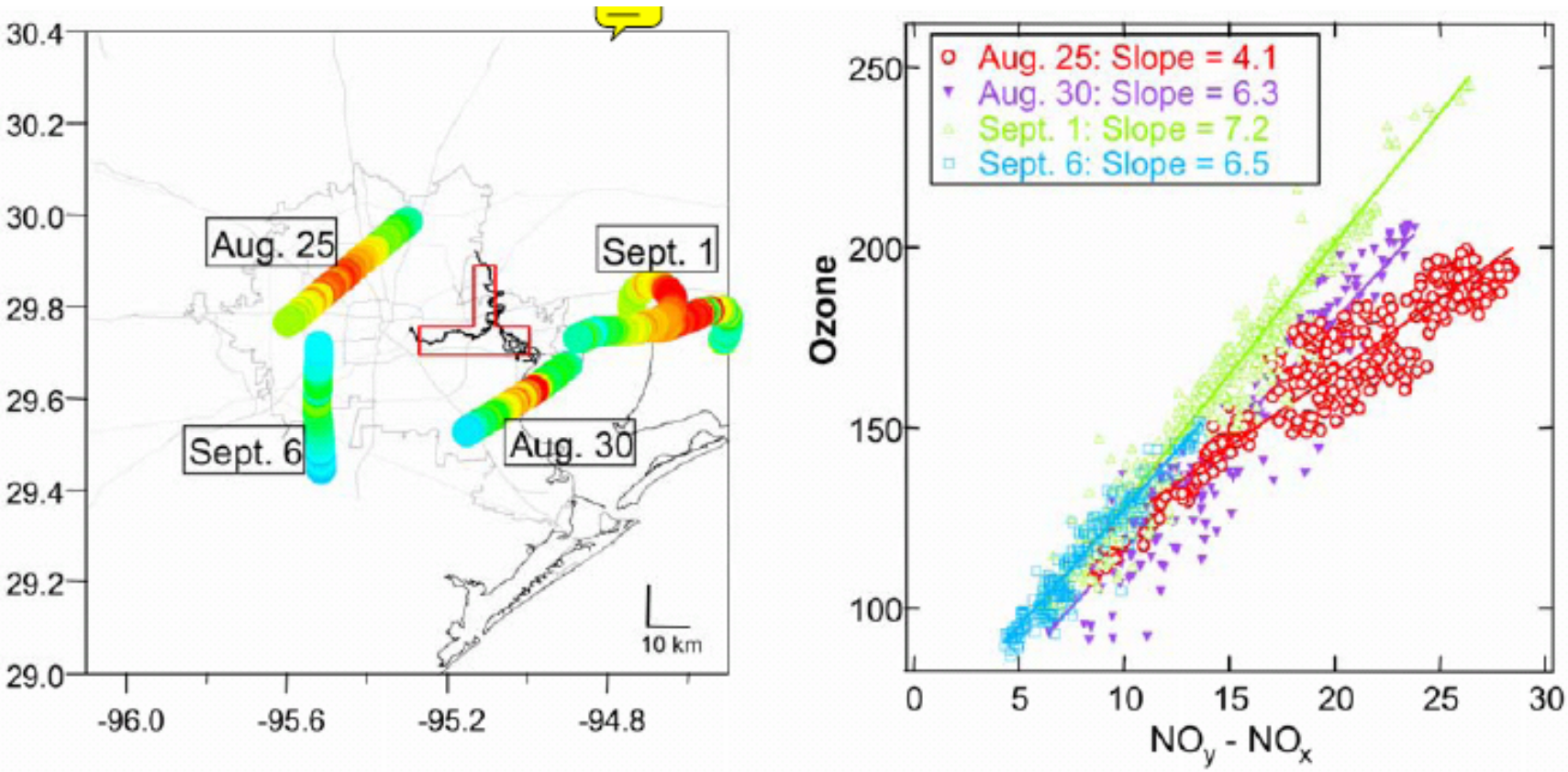


Figure A2. Highest ozone (red points) observed by the Electra aircraft during four flights in TexAQS 2000. In the left panel flight track segments are color-coded by observed ozone, and in the right panel the dependence of ozone on the products of NO_x oxidation are shown with approximate ozone production efficiencies estimated from fitted slopes.

From Ryerson et al., 2006 report to TCEQ

Question B

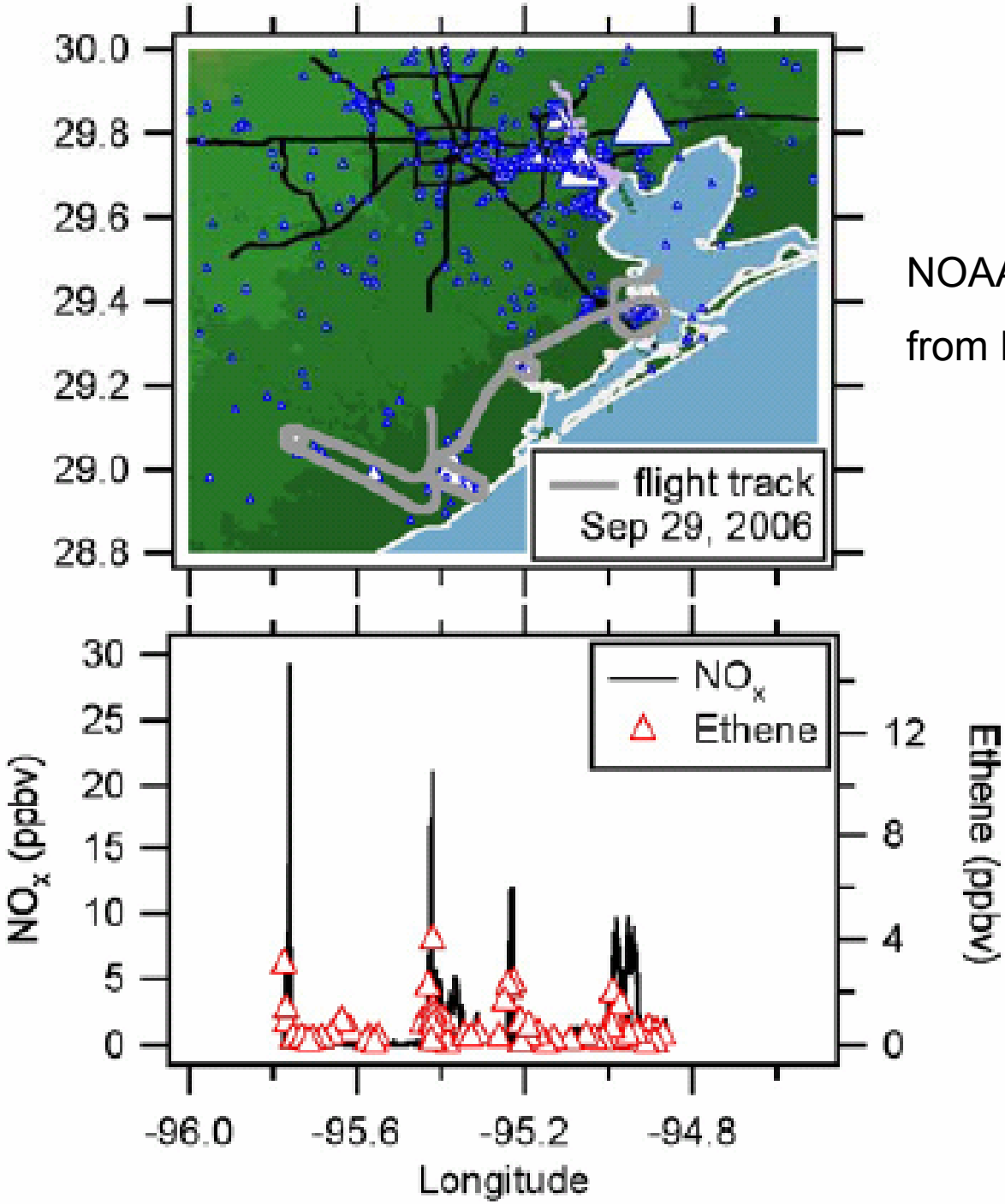
- How do the structure and dynamics of the planetary boundary layer and lower troposphere affect the ozone and aerosol concentrations in Houston?
- PBL behavior over Galveston Bay and vicinity is very complex; will require further analysis to answer this question.

Question C

- Are HRVOC and NOx emissions still at same levels as 2000? If not, how have they changed? How well do the reported emissions inventories explain the observed concentrations?

Preliminary Results

- There are indications that HRVOC emissions from industrial sources have decreased by as much as a factor of two since 2000.
- The latest available reported EIs still underestimate ethene emissions by approximately an order of magnitude.
- For NOx results, see the next question…



NOAA data,

from De Gouw et al., 2006

Table C1. Ethene/NO_x emission ratios determined from measurements in 2000, 2002 and 2006, compared with emission inventories.

	Ethene/NO_x Emission Ratios				
	Inventories		Measured		
	1999 [a]	2004 [b]	2000 [c]	2002 [c]	2006
Sweeny	0.05	0.019	3.6	1.7	0.5
Freeport	0.05	0.030	1.5	0.62	0.32
Choc. Bayou	0.08	0.048	2.0	1.2	0.62

[a] TNRCC emission inventory.
[b] TCEQ point source emission inventory with 1999 VOC speciation.
[c] Ryerson et al., 2003.

NOAA data, from De Gouw et al., 2006

Question D

- What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?

Preliminary Results

- Concentrations of NOx in power plant plumes seem to be lower in 2006 than in 2000 by as much as a factor of 4.

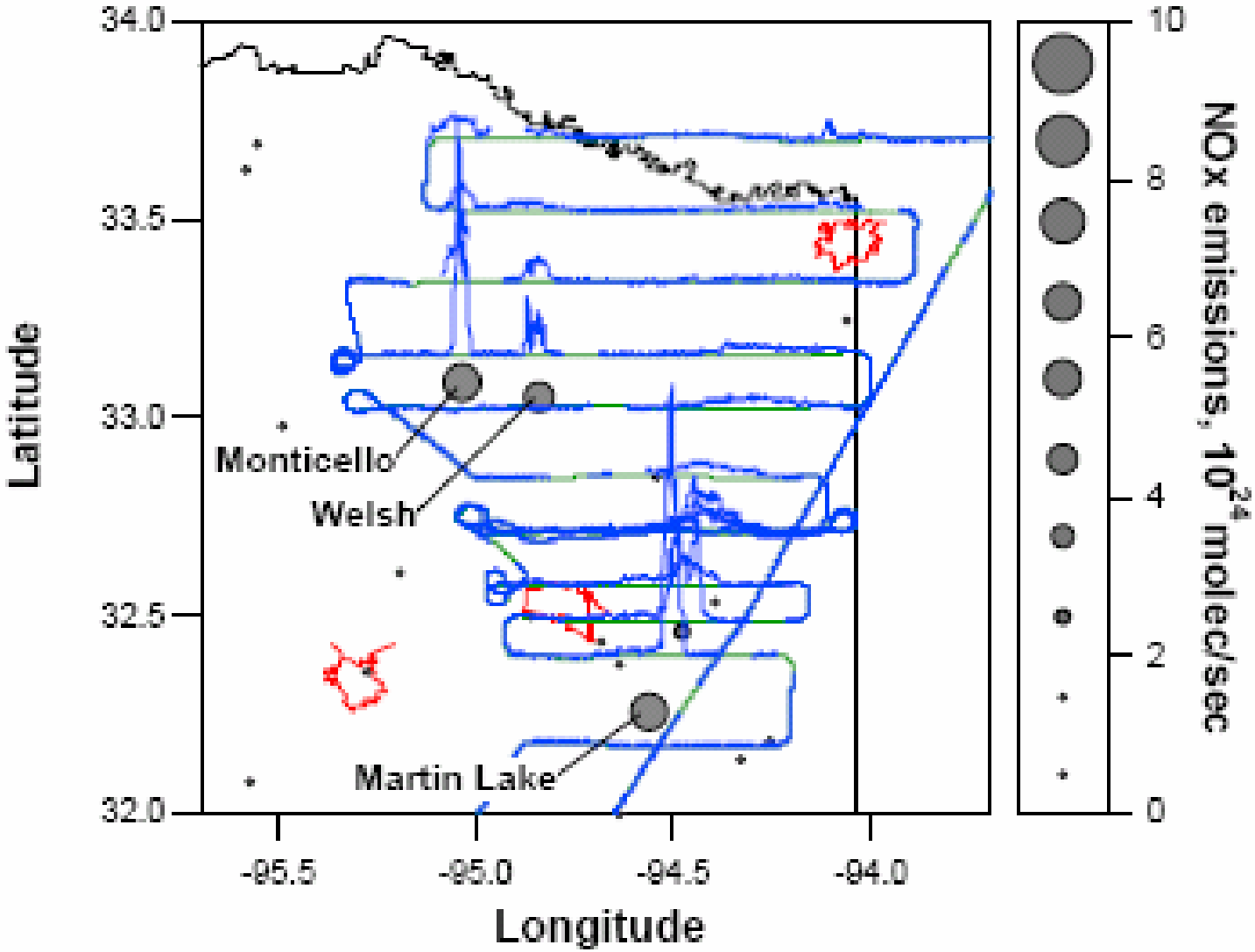
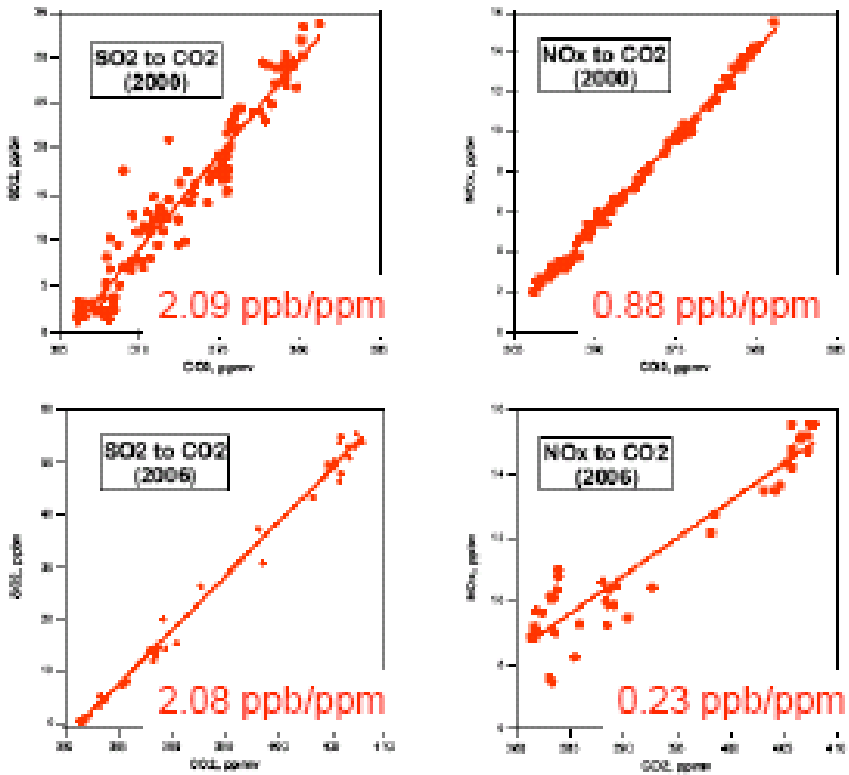


Figure D1a. Sept. 16, 2006 WP-3D ground track (green) with observed SO2 enhancements (blue) plotted along the track.

NOAA data, from Peischl and Ryerson, 2006

W.A Parish NOx emissions have been reduced by a factor of ≈4 since 2000

W.A. Parish: changes since 2000



TexAQS
08/28/2000

TexAQS II
09/19/2006

SO_2/NOy ratio
2004 (CEMS): 8.8
2006 (P-3): 7.8

CEMS give excellent results; emission inventories based on them are very accurate

NOAA data, from Peischl and Ryerson, 2006

Table D1. Measured emissions relative to CO_2 for EGUs in East Texas.

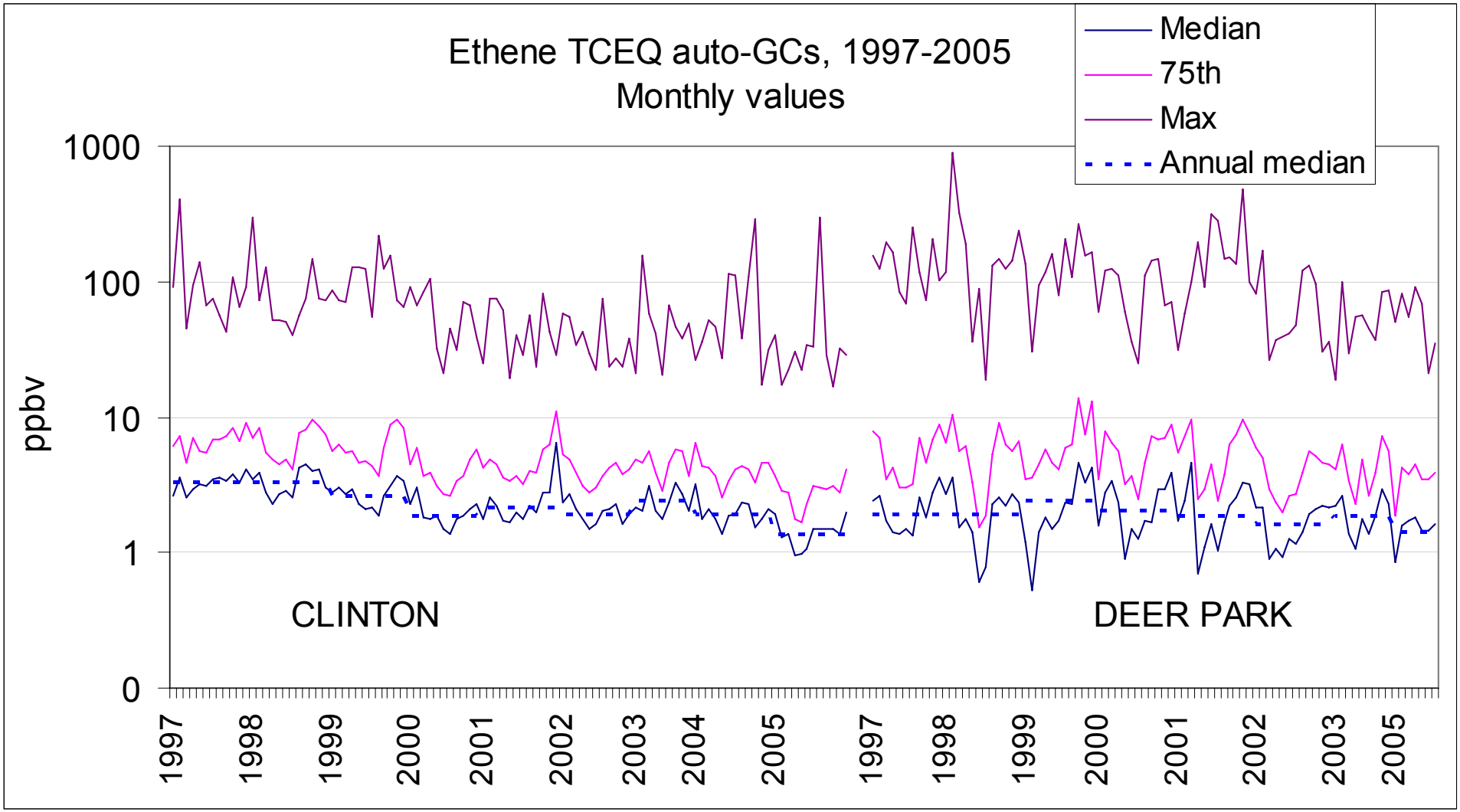
	NCAR Electra aircraft data **2000**			NOAA WP-3D aircraft data **2006**			NOx emissions decreased by factor of:
EGU name	**SO_2**	**CO**	**NOx**	**SO_2**	**CO**	**NOx**	
Monticello	3.5	6.4	1.0	2.7	5.4	0.71	(minor decrease)
Welsh	1.5	1.7	0.80	1.5	1.7	0.98	(minor increase)
Martin Lake	1.4	4.0	1.3	2.8	6.0	0.70	**1.9**
Big Brown	4.8	2.9	1.5	6.9	6.0	0.65	**2.3**
W.A. Parish	2.1	(variable)	0.88	2.1	(variable)	0.23	**3.8**

Emissions values presented as molecules per 1000 molecules of CO_2 emitted

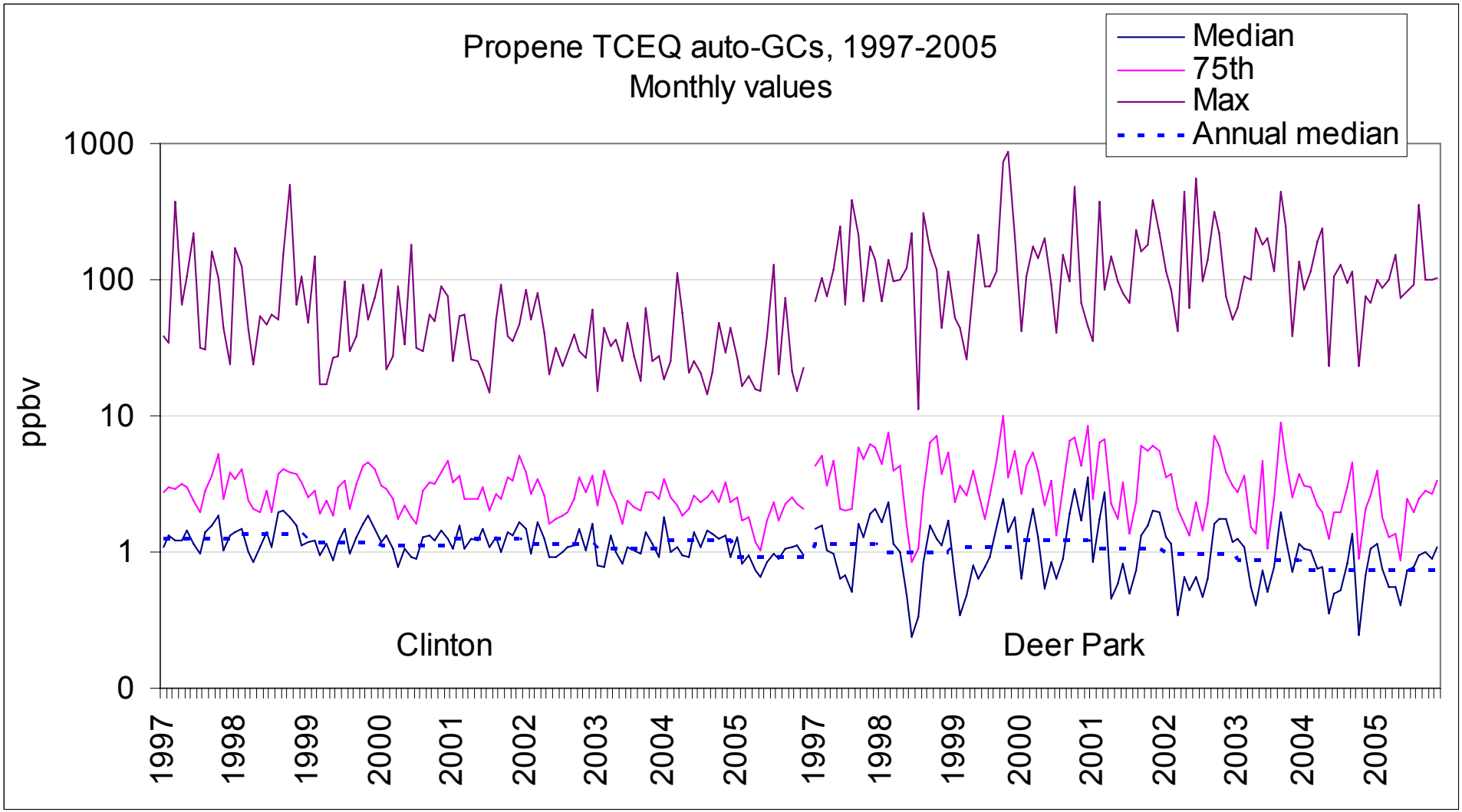
From Peischl and Ryerson, 2006

Preliminary Results

- Concentrations of ethene in the industrial areas of Houston and Brazoria County seem to be substantially lower than in 2000.
- Concentrations of propene downwind of Houston industrial areas have not decreased as much as ethene.



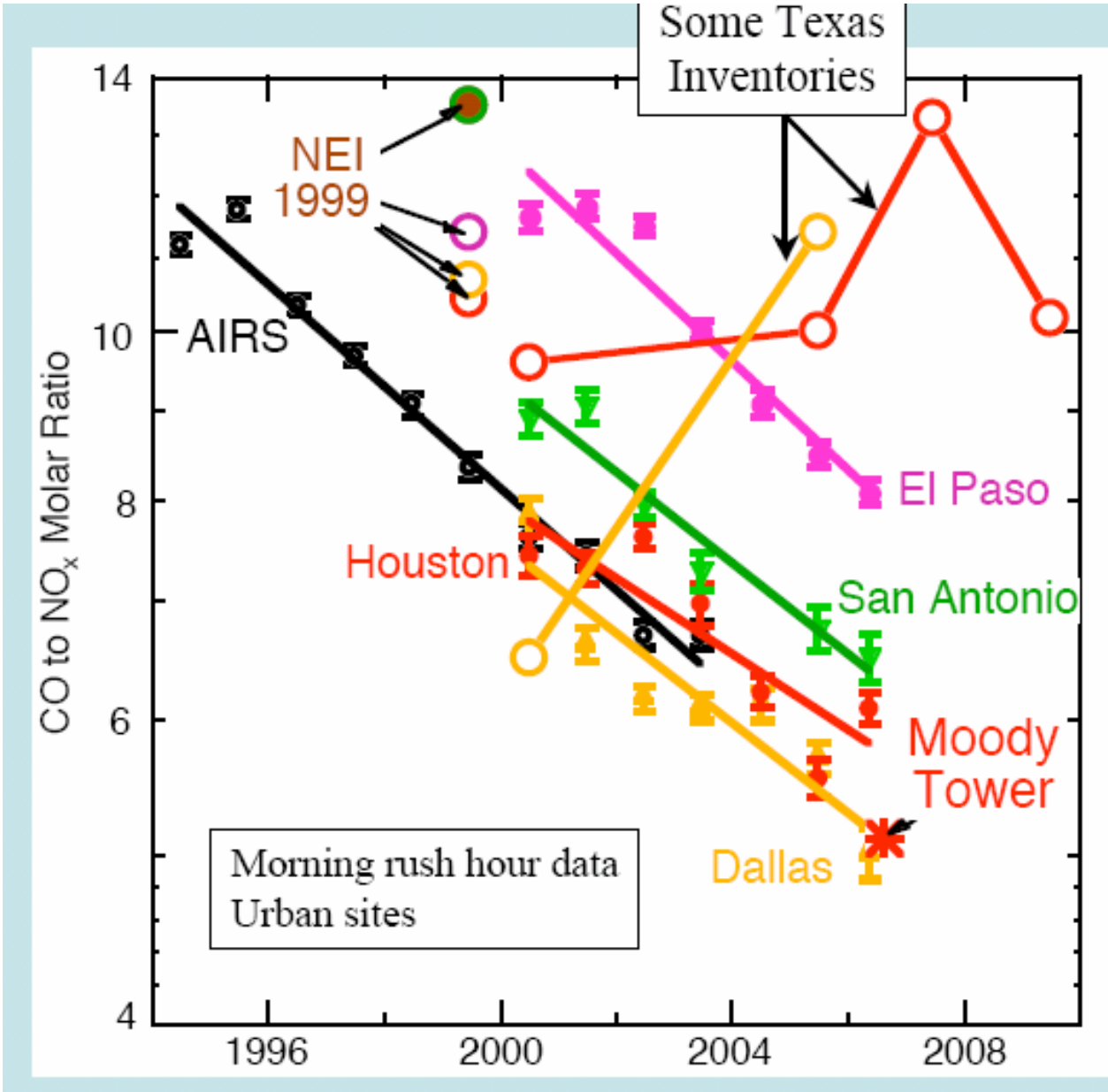
TCEQ data and analysis, 2006



TCEQ data and analysis, 2006

Preliminary Results

- Measurements of the ratios of CO to NOx seem to indicate a discrepancy between the Mobile 6 emissions model and the observations.

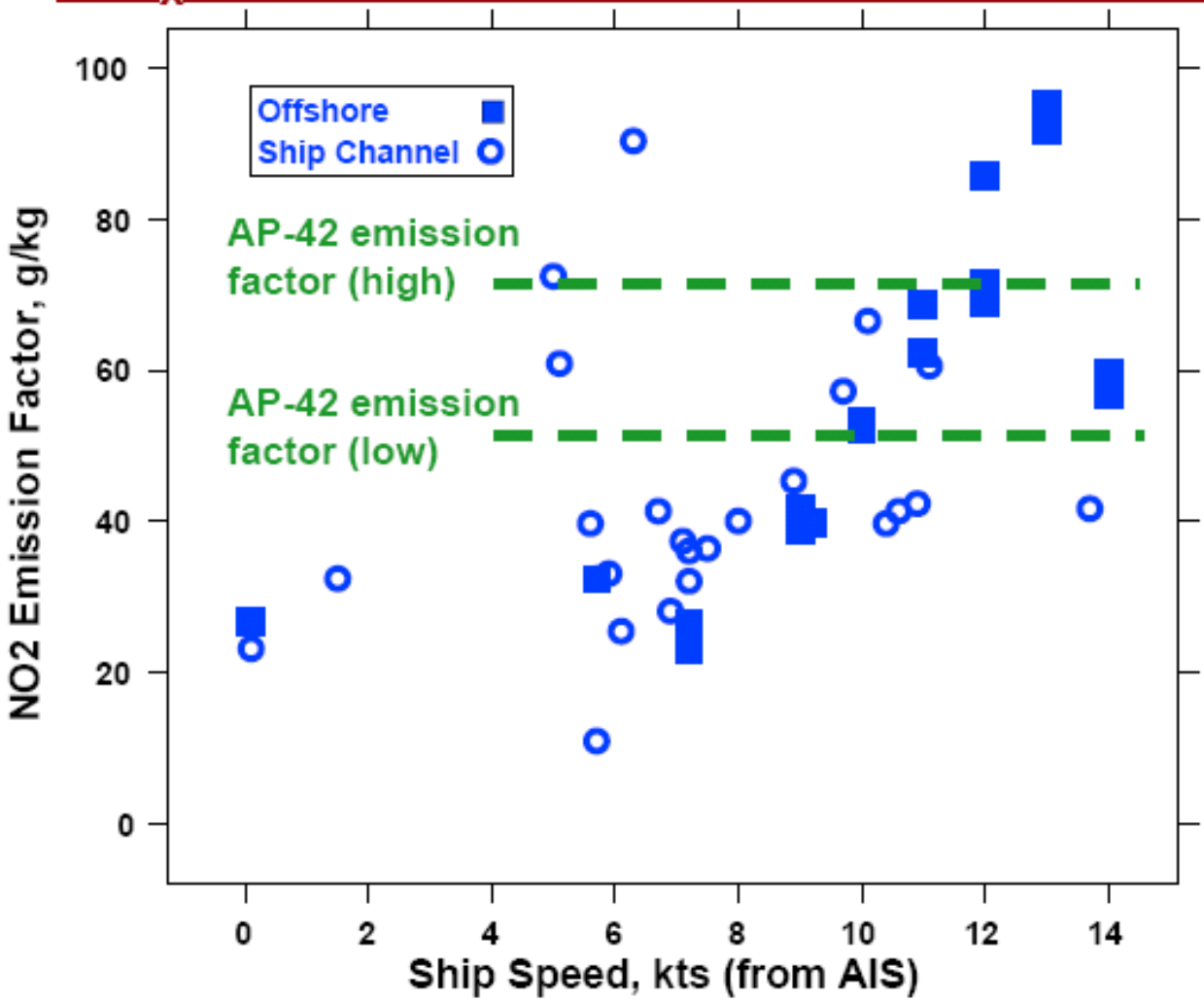


From Parrish et al., 2006; UH data from Lefer and Rappenglueck, 2006

Preliminary results

- NOx emissions from ships are a strong function of vessel speed, and inventories based upon AP-42 emission factors will overestimate NOx emissions, especially for ships at rest.

NO_x Emission Factor vs Vessel Speed



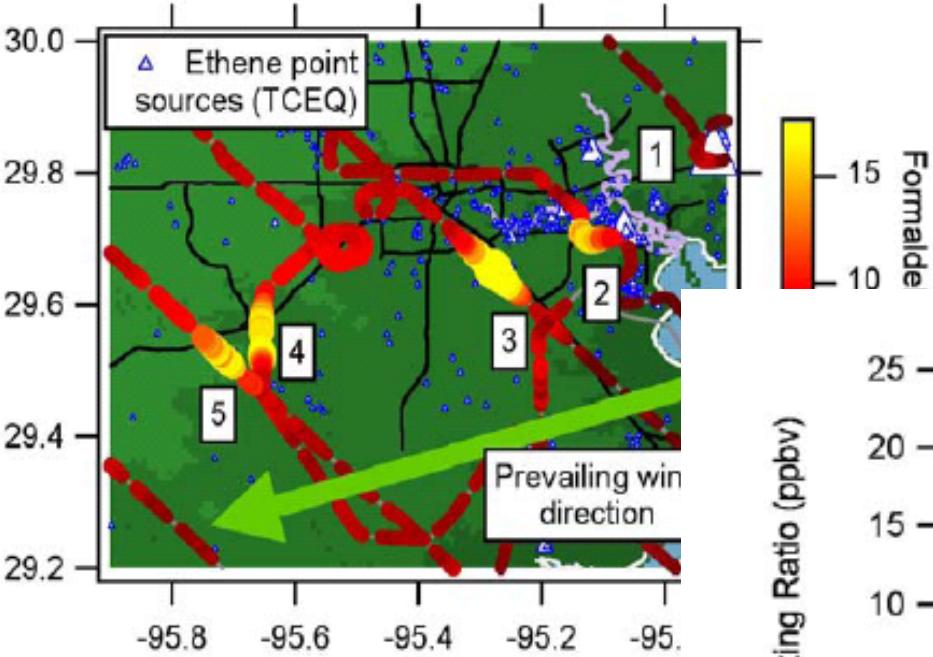
NOAA data, from Williams et al., 2006

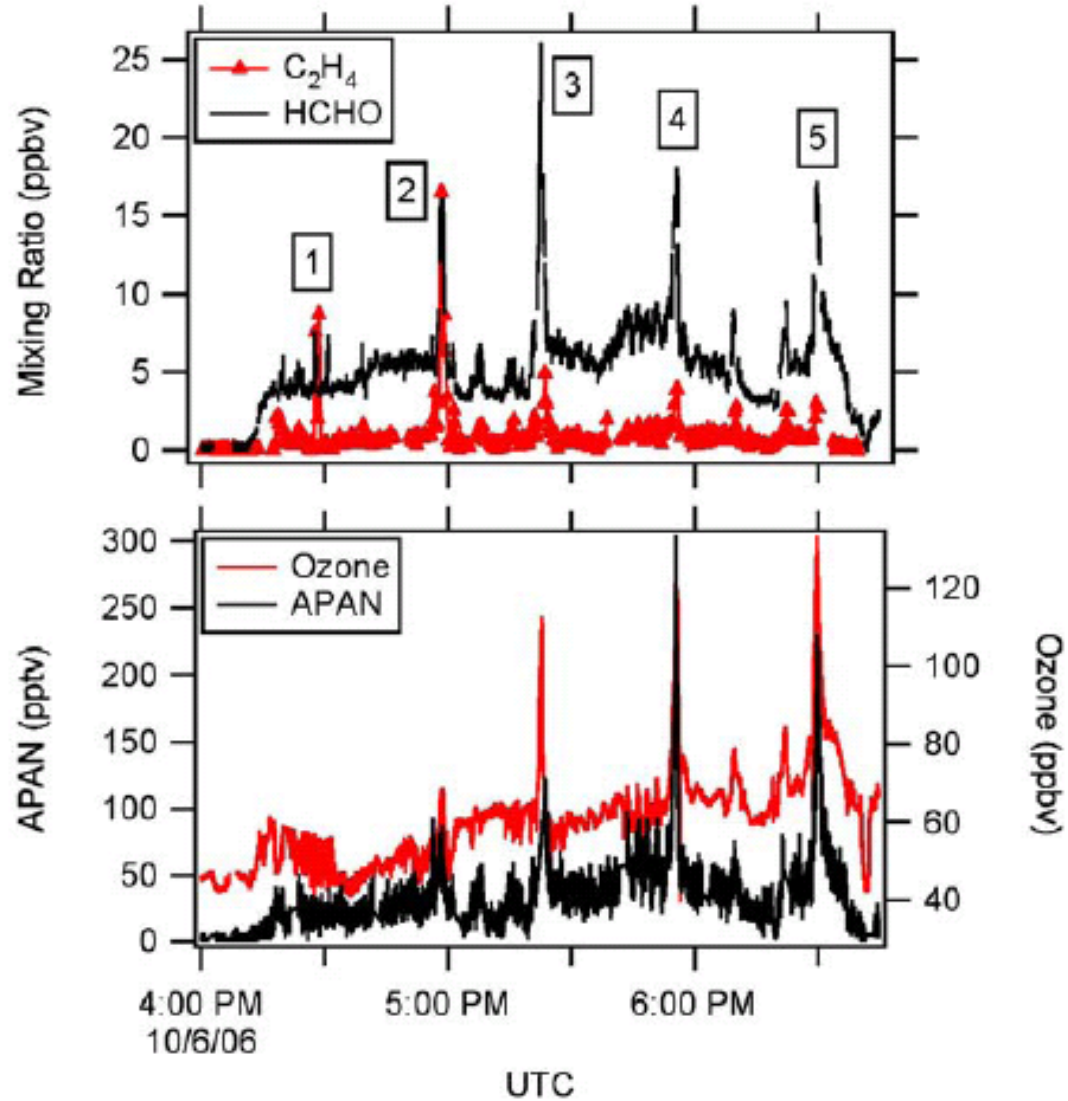
Question E

- Are there sources of ozone and aerosol precursors that are not represented in the reported emissions inventories?

Preliminary Results

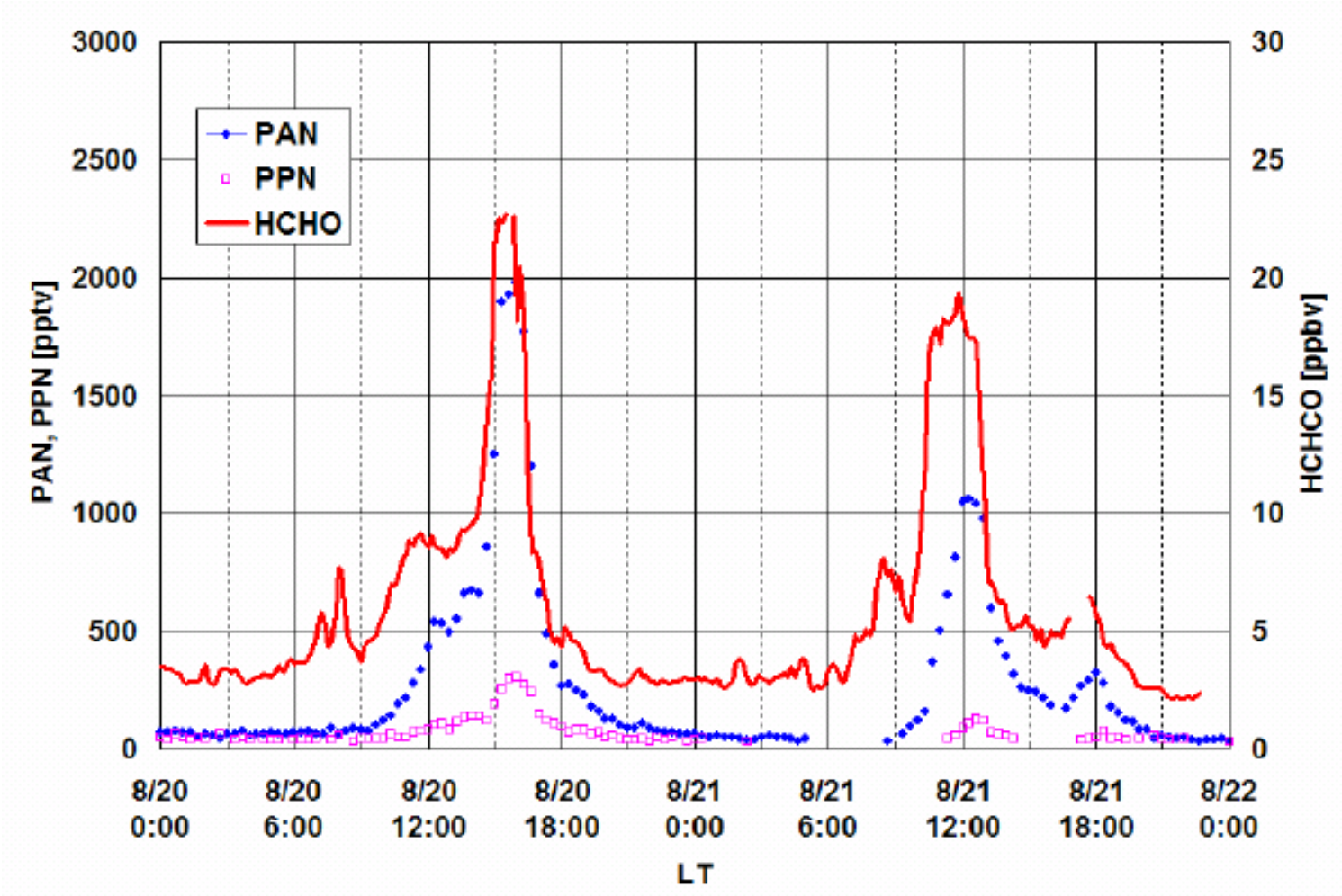
- The observed concentrations and distributions of ambient formaldehyde are broadly consistent with daytime photochemical production associated with olefin emissions.
- Primary formaldehyde emissions appear to be significantly less important, with more precise quantification awaiting additional analyses.





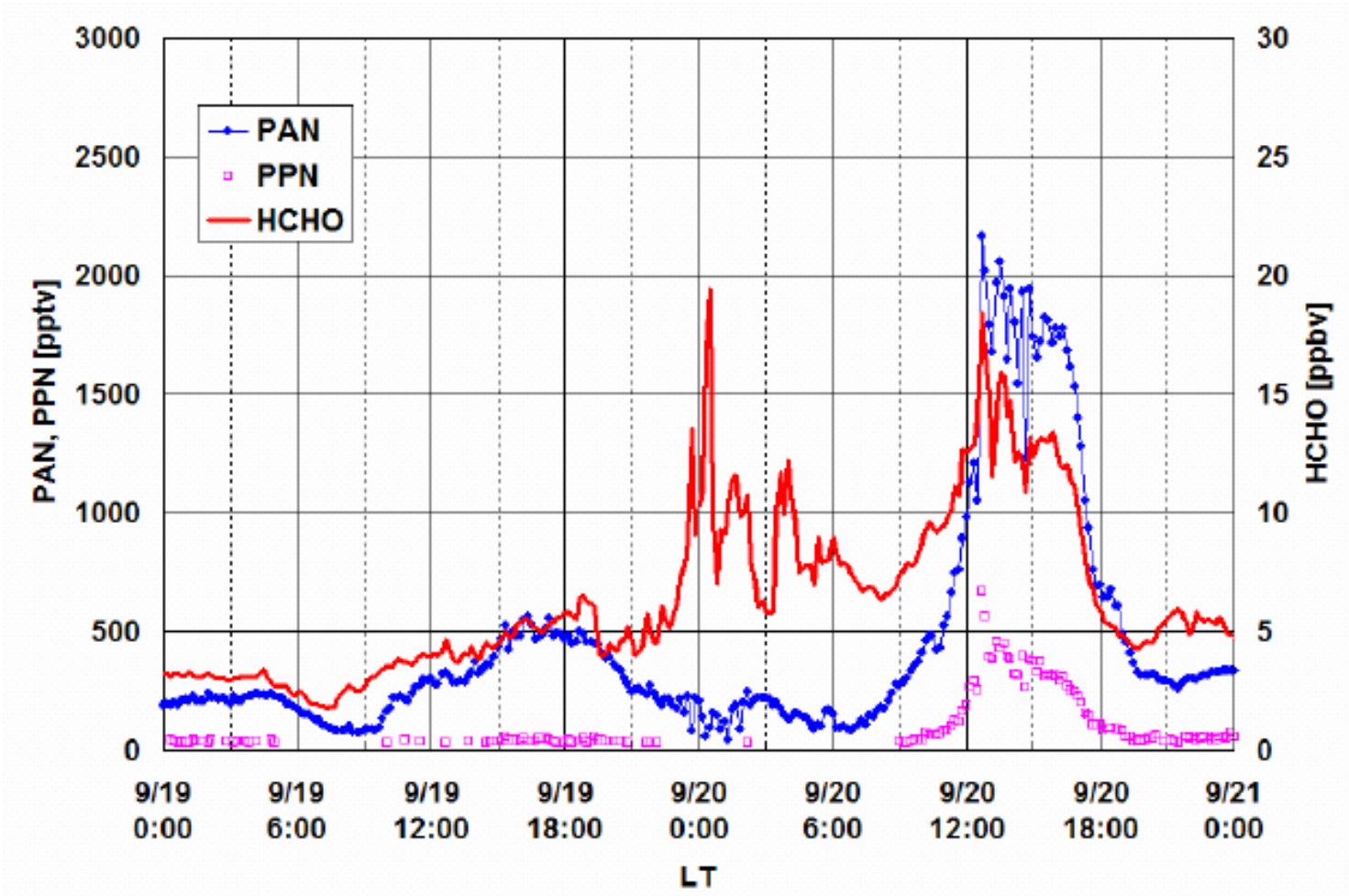
NOAA data from De Gouw et al. 2006

Formaldehyde measurements at Moody Tower: Aug 20-21

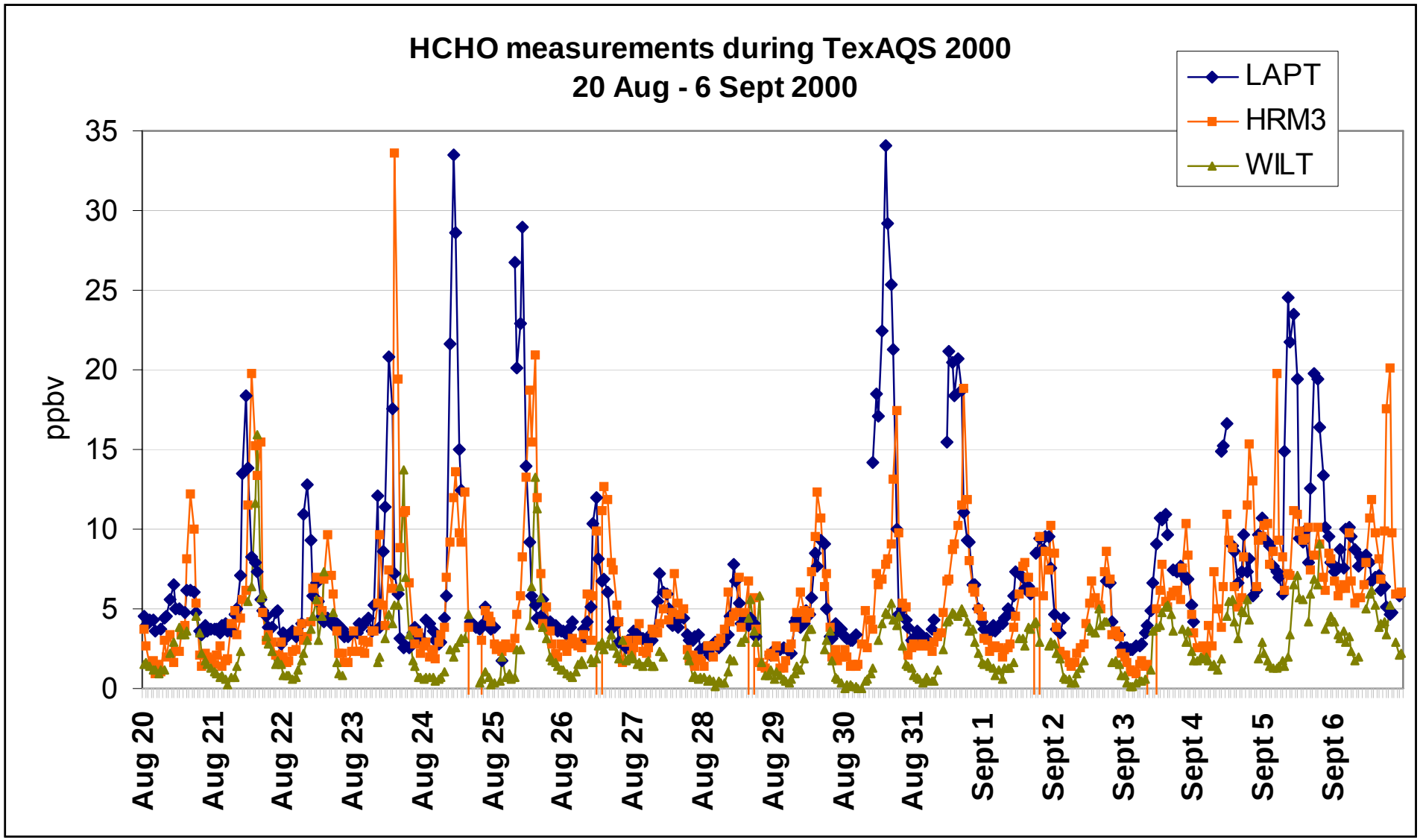


From Leuchner and Rappenglueck, 2006

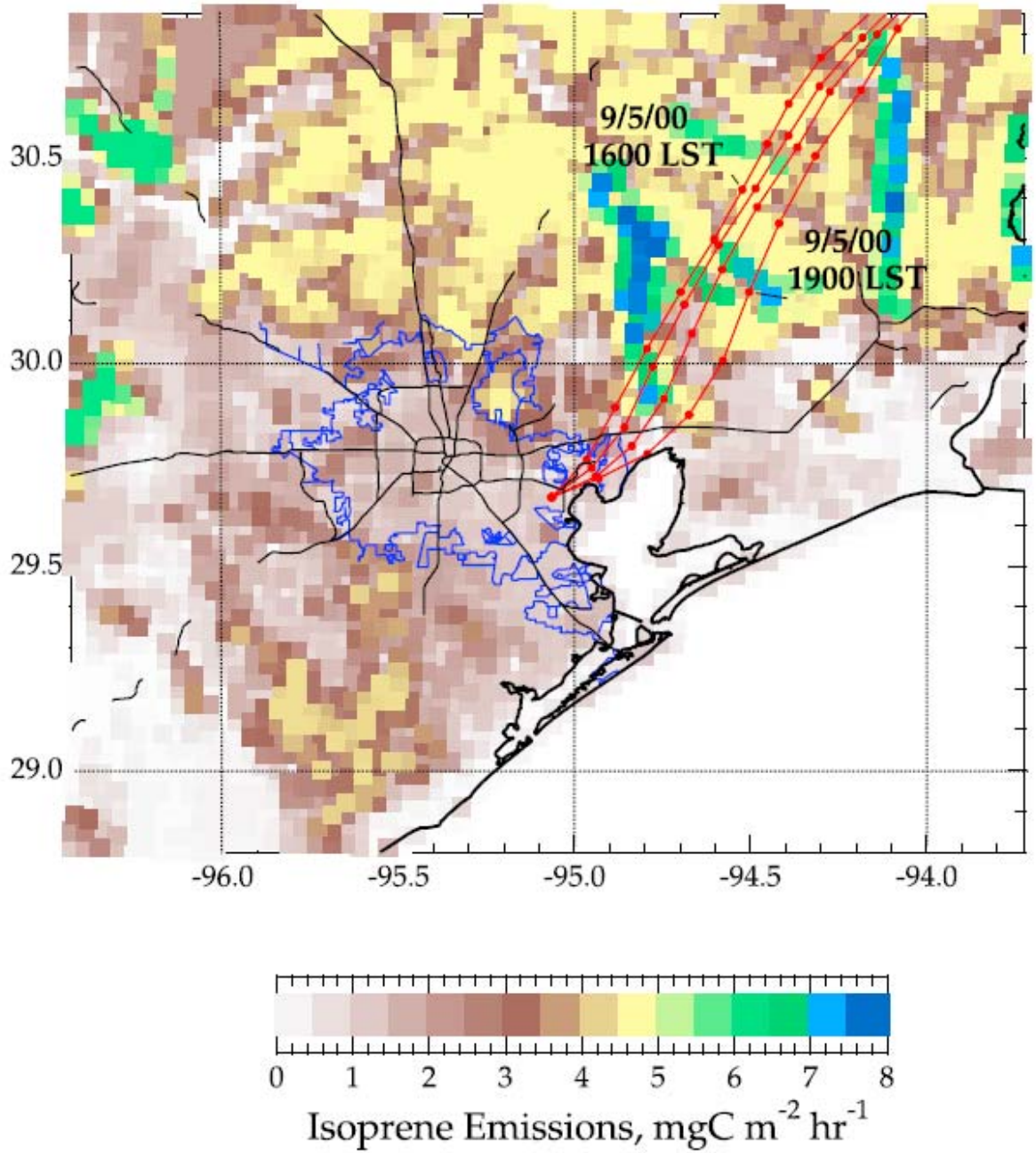
Formaldehyde measurements at Moody Tower: Sept 19-20



From Leuchner and Rappenglueck, 2006



Measurements from TexAQS 2000 scientists



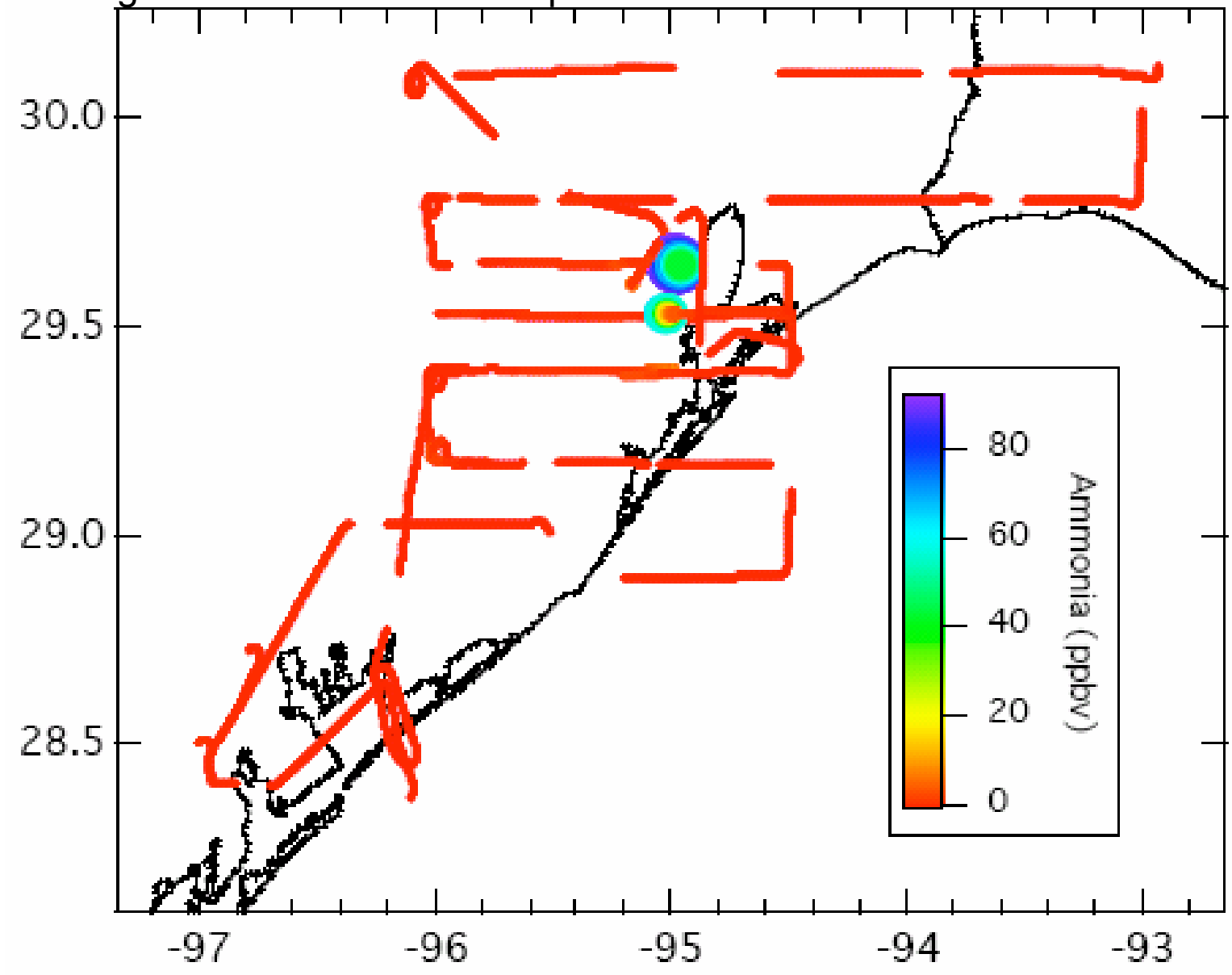
From Roberts et al., 2003

Figure 10. Isentropic backtrajectories for air masses that arrived at the La Porte site between the hours of 1600 and 1900 LST on 5 September, plotted on a map of the Houston-Galveston are. Also shown are the biogenic isoprene area emissions estimated according to the method of *Wiedinmyer et al.* [2001].

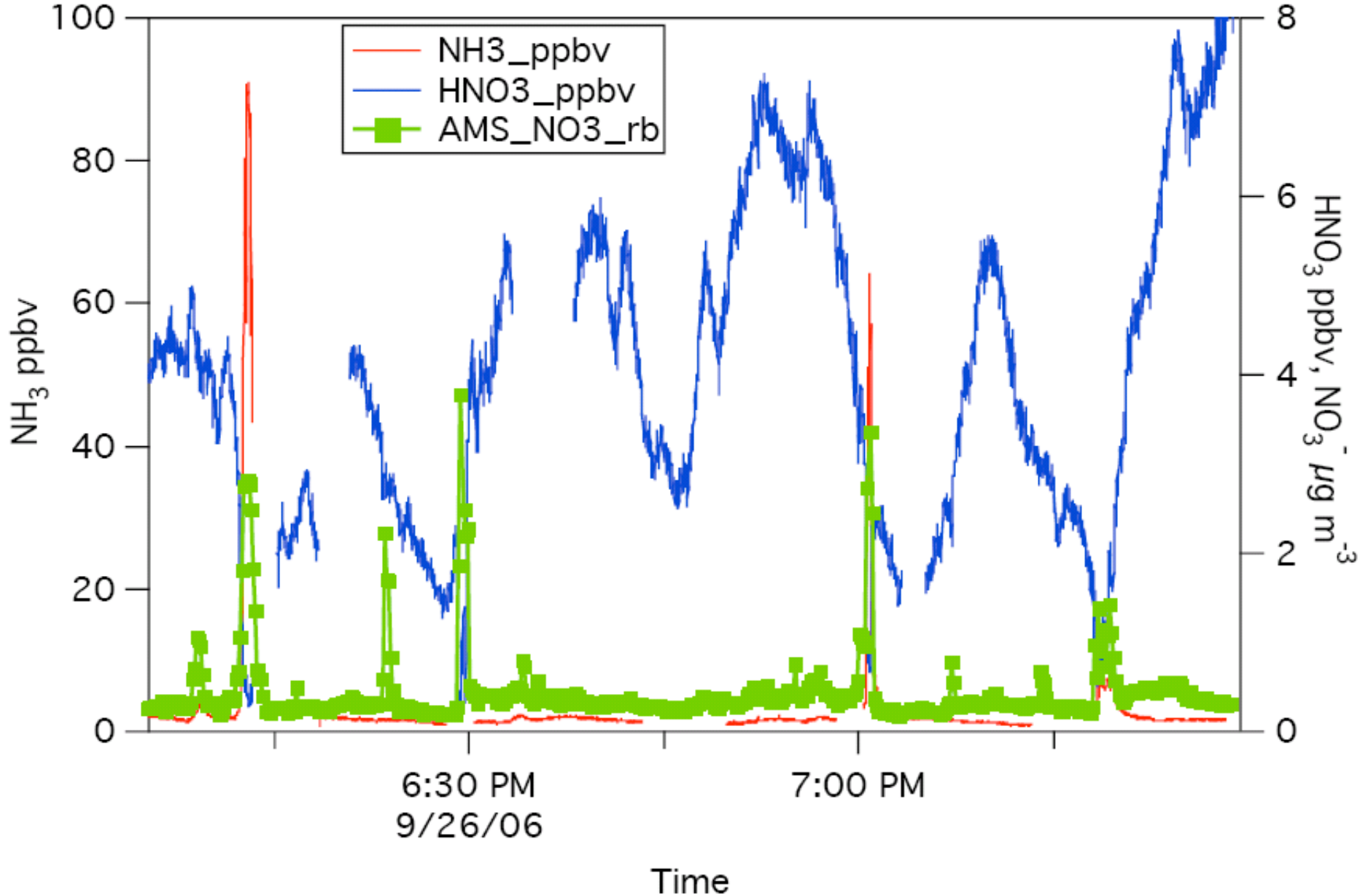
Preliminary Results

- Concentrated plumes of ammonia were observed occasionally in the Houston Ship Channel area.

WP3 flight observations from Sept 26



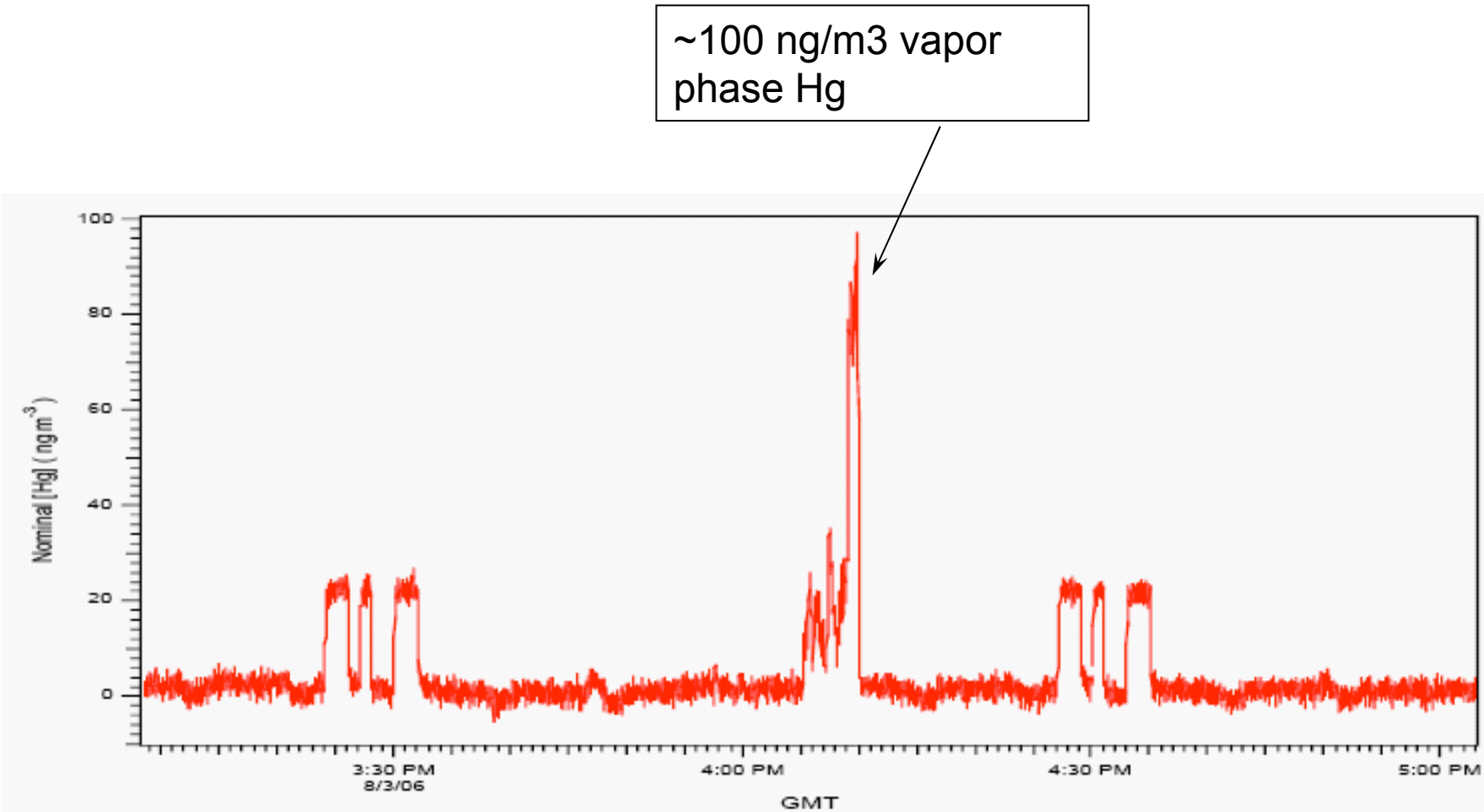
From Nowak and Herndon, 2006



From Nowak and Herndon, 2006

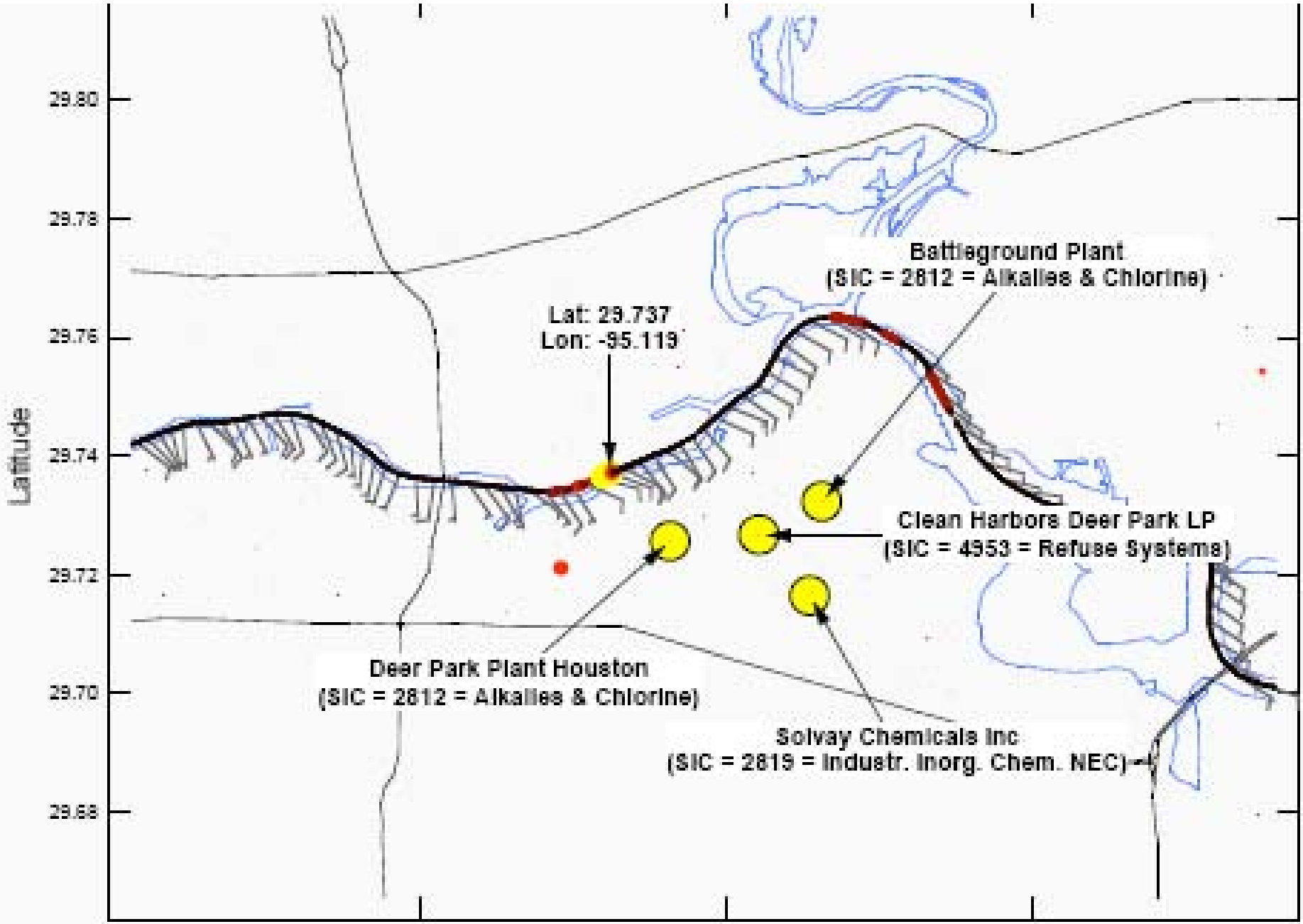
Preliminary Results

- Concentrated plumes of gaseous mercury from at least one point source were observed in the Houston Ship Channel area.



Measurements from the NOAA vessel Ronald H. Brown, 3 Aug 2006

From Fortin and Ryerson, 2006



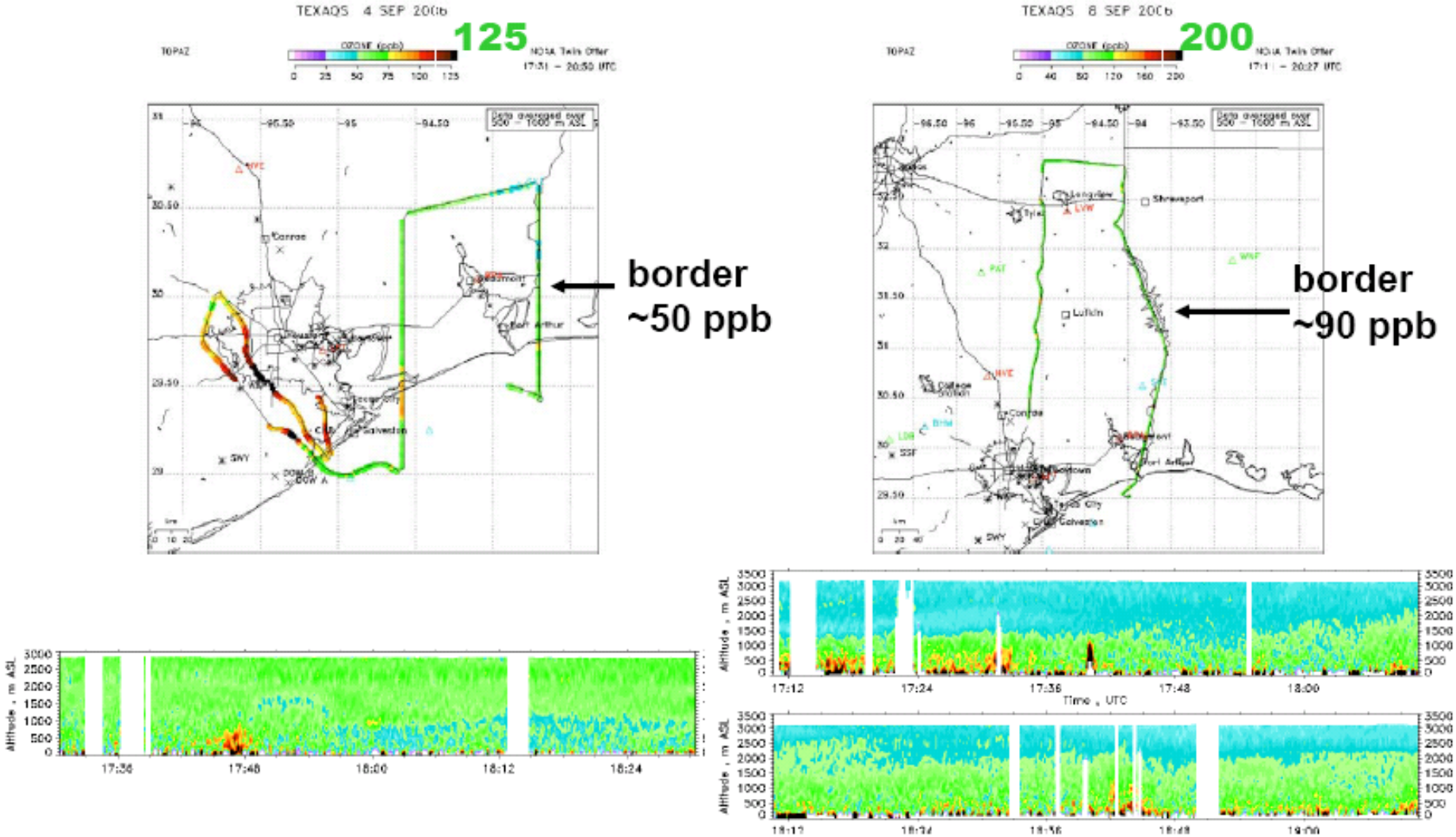
From Fortin and Ryerson, 2006

Question G

- How do emissions from local and distant sources interact to determine the air quality in Texas?
- What meteorological and chemical conditions exist when elevated background ozone and aerosol from distant regions affect Texas?
- How high are background concentrations of ozone and aerosol, and how do they vary spatially and temporally?

Preliminary results

- Background ozone varied between 15 ppb and >85 ppb in Houston during TexAQS II. The highest background ozone concentrations observed were greater than 85 ppbv. On average, air of continental origin had higher background concentrations than marine air.



High background days—other days flown in east Texas had lower background concentrations. NOAA data from Banta et al., 2006.

Preliminary Results

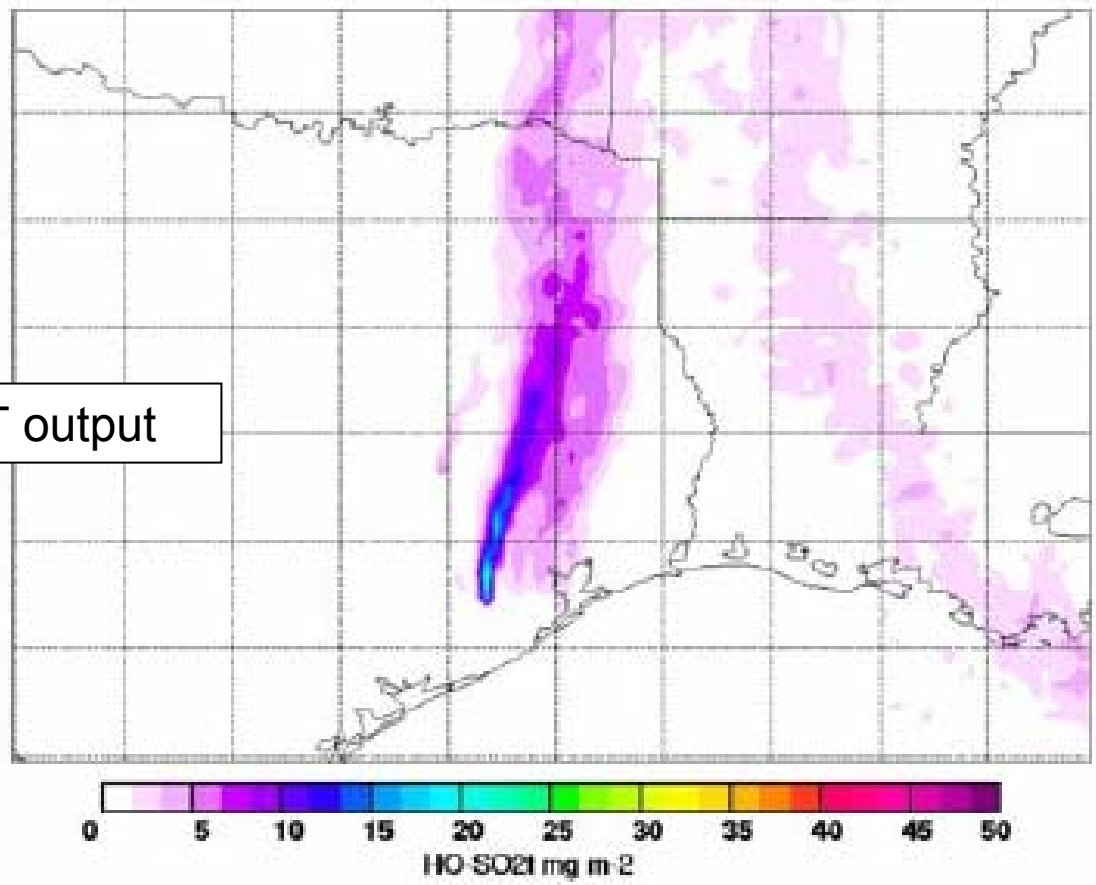
- Plumes from Texas urban areas make substantial contributions to the ozone, aerosol, and precursor concentrations in the rural regions of eastern Texas.
- Dust of African origin and sulfate aerosol advected into the region make substantial contributions to background aerosol in southeast Texas, even under southerly flow from the Gulf.

Contributions estimated with the FLEXPART Lagrangian model.

Table G1. Summary of impact of Parish and Houston plume on northeast Texas.

	background	Parish	Houston/Ship Channel
Total mass ($\mu g\ m^{-3}$)	4.9	7.3	6.4
Sulfate ($\mu g\ m^{-3}$)	1.6	5.6	2.1
Organic ($\mu g\ m^{-3}$)	1.3	2.02	2.08
Black Carbon ($\mu g\ m^{-3}$)	0.11	0.13	0.17

FLEXPART output



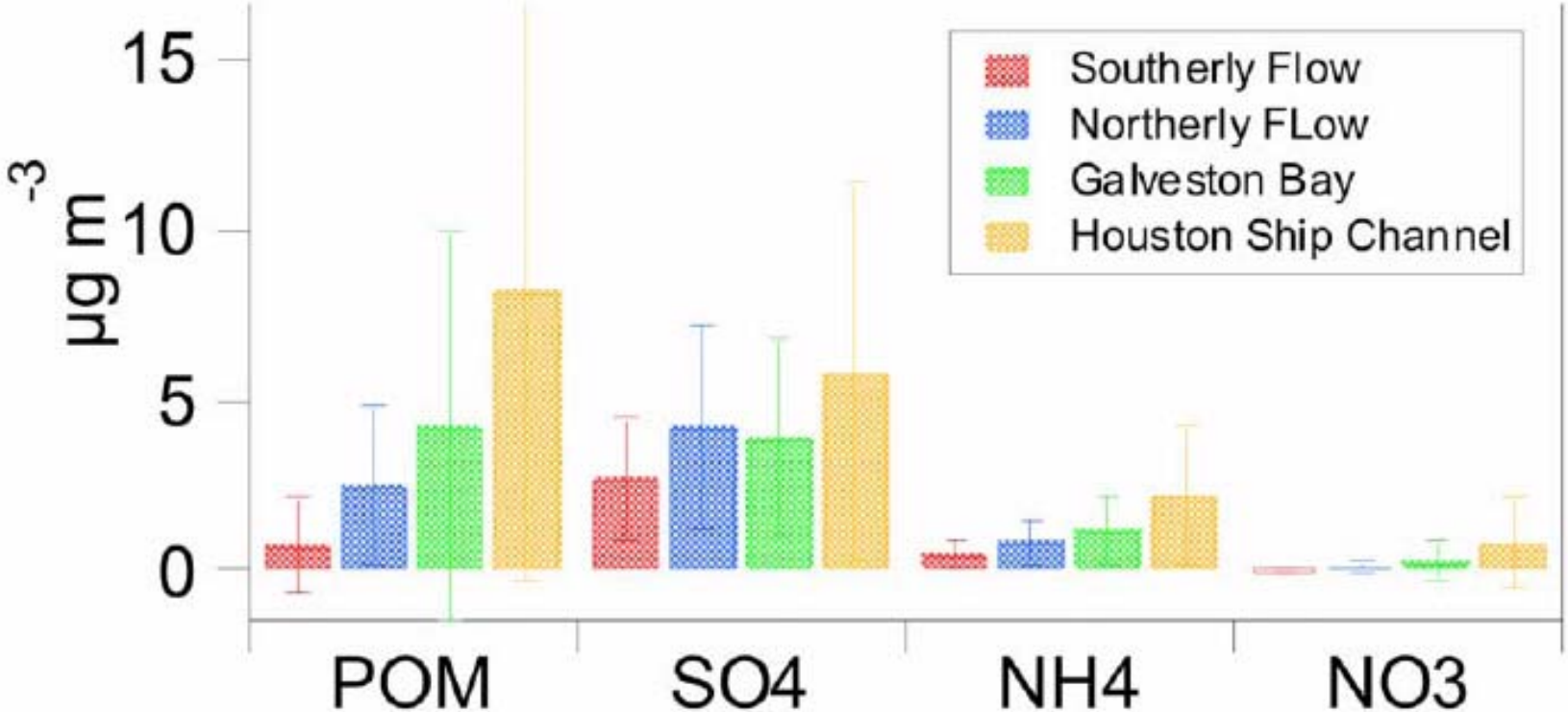


Figure G4. Average aerosol composition measured from the NOAA R/V *Ronald H. Brown* during 2006 (Figure from Bates and Quinn -NOAA).

African dust was a major component of PM2.5 on four high PM days, when concentrations averaged >15 ± 1.7 µg/m3.

Question H

- Which areas ***within Texas*** adversely affect the air quality of non-attainment areas in Texas?
- Which areas ***outside of Texas*** adversely affect the air quality of non-attainment areas in Texas?

Preliminary Results

- Ozone can be transported from Houston to Dallas.

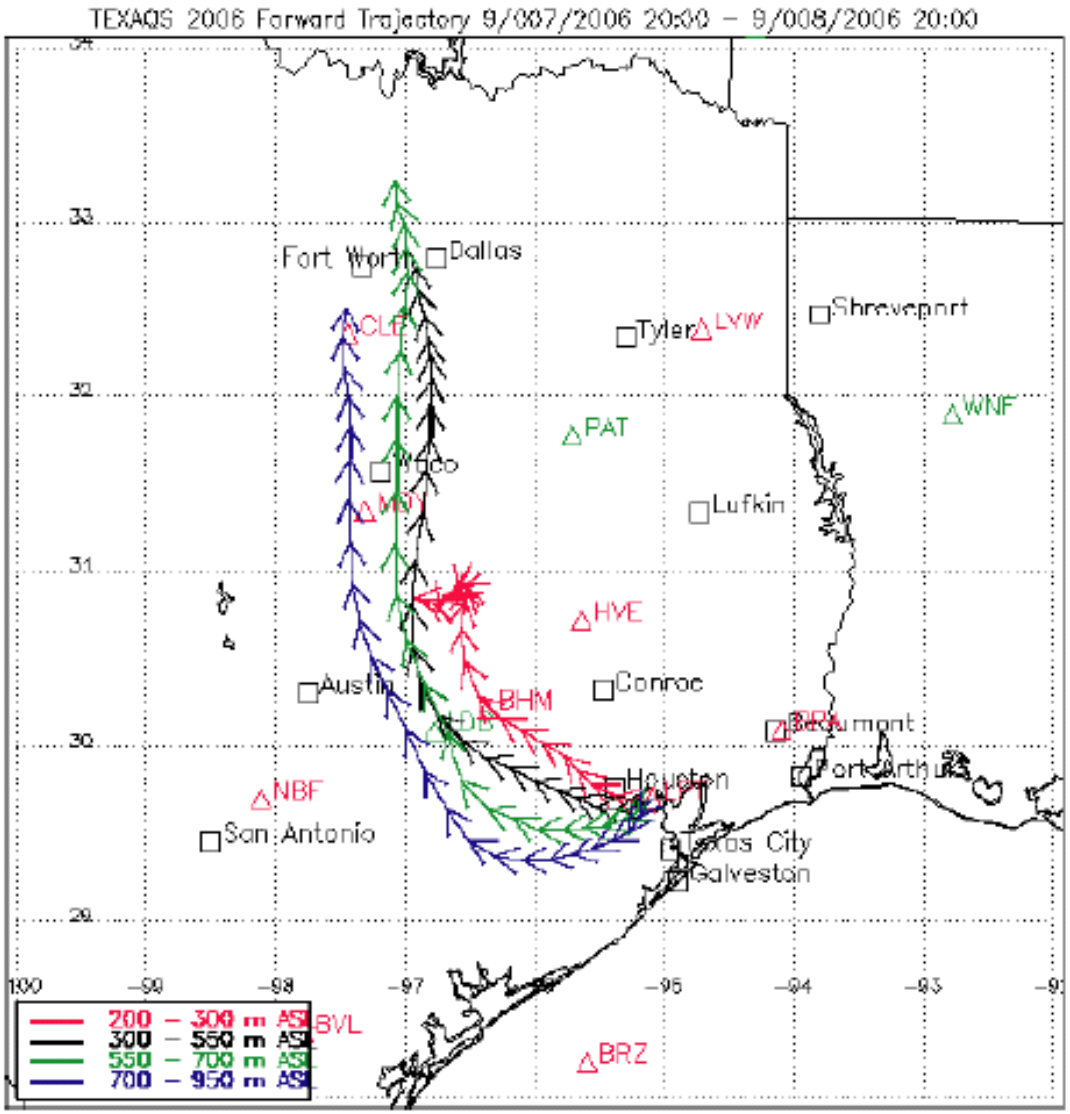


Figure H2. Forward trajectories starting at 3 pm local time in Houston, 7 September, and ending at 3 pm local time on 8 September 2006. The trajectories show direct transport from Houston to Dallas. 7 September was an exceedance day in Houston, 8 September was an exceedance day in Dallas. (The trajectory map was created using the NOAA Physical Science Division (PSD) upper air back-trajectory tool [http://www.etl.noaa.gov/programs/2006/texaqs/traj/]).

Preliminary Results

- High ozone in eastern Texas result from both in-state sources and transport of continental air from the east and northeast.

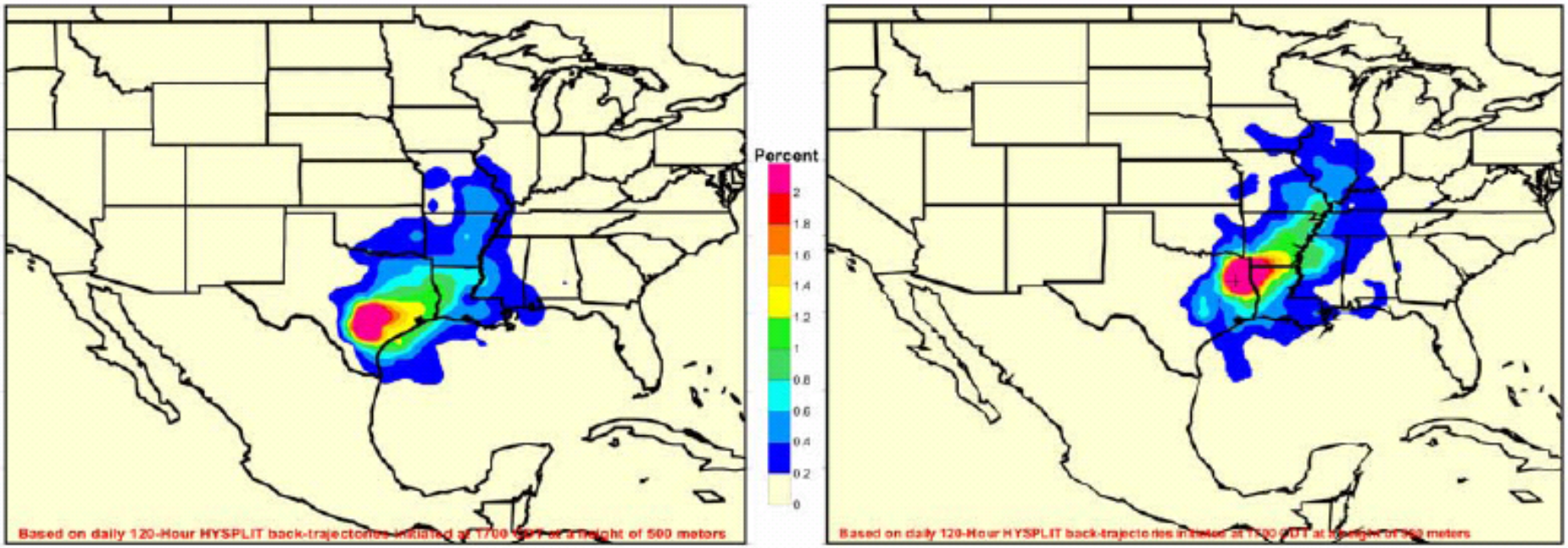


Figure H3. Contouring of Hysplit 500 meter 5-day back-trajectories on moderate and worse O_3 days in San Antonio (left) and Tyler/Longview/Marshall (right), color coded by density of end point frequency (analysis Sullivan et al.-U. Texas).

Question I

- Why does the SAPRC99 chemical mechanism give different results from the Carbon Bond IV mechanism? Which replicates the actual chemistry better?

Preliminary Results

- Differences in SAPRC and CBIV occur because of differences in (1) aromatic chemistry, (2) nitric acid formation rates, and (3) availability of free radicals.
- *Preliminary* results cannot answer which mechanism replicates reality better.

Question J

- How well do air quality *forecast* models predict the ozone?
- Not very well, unless they are combined into an ensemble. Daewon Byun's MM5-CMAQ model was used most frequently in the briefings, because it usually gave decent results.
- Reanalysis is needed, including assimilation of observational data.

Question K

- How can observation and modeling approaches be used for determining (i) the sensitivities of high ozone to the precursor VOC and NOx emissions, and (ii) the spatial/temporal variation of these sensitivities?
- Require sophisticated analyses that haven’t been completed yet.
- Consensus has not been reached about the optimal approach to reach answers.