Latest findings from the TexAQS II field study: Results presented at the Fall American Geophysical Union Meeting

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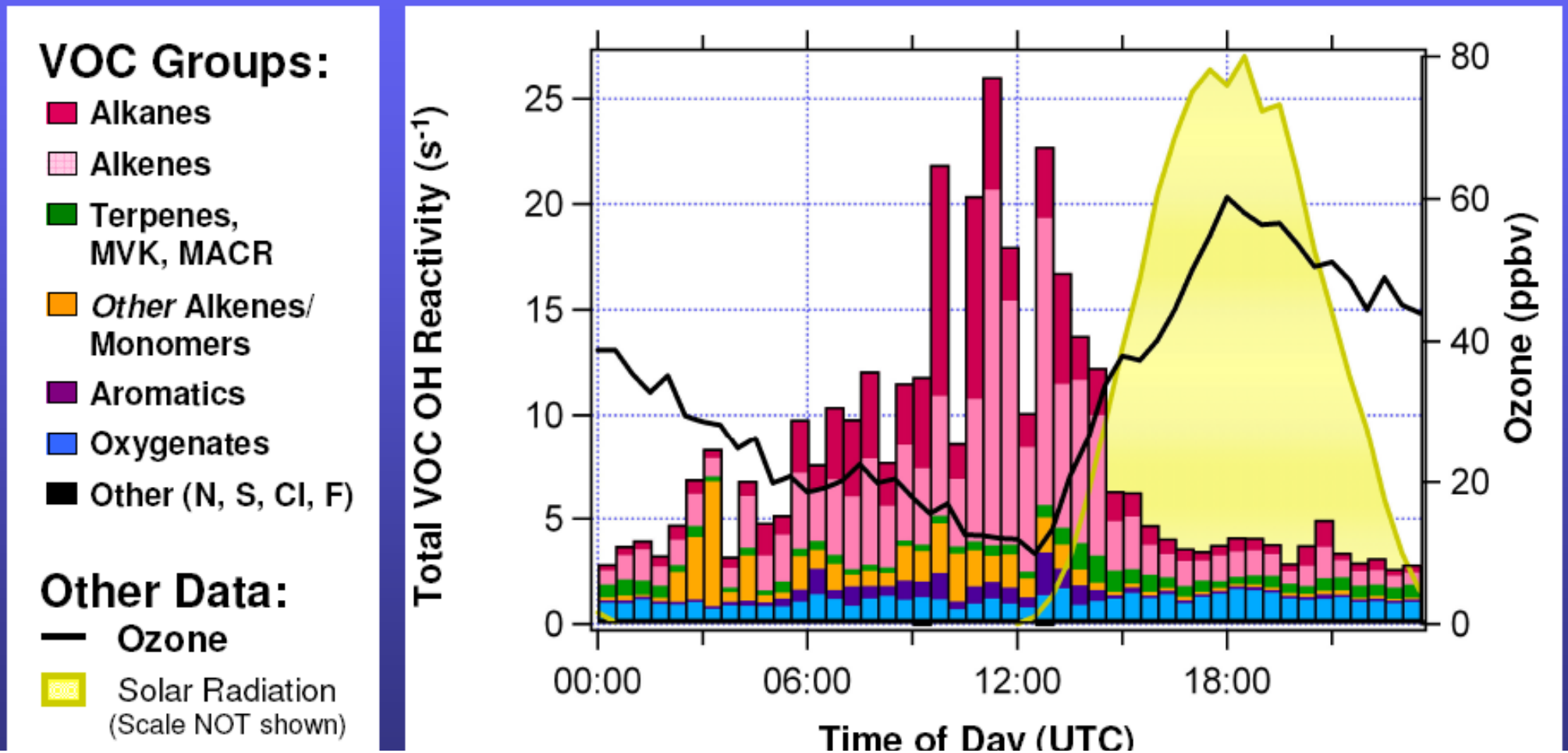
Fun with formaldehyde

Formaldehyde

- Emitted or created by chemical reaction?
- If emitted, is it in the inventory or not?
- If emitted, what kind of emissions: flares, shipping, diesel vehicles, other?
- These questions have SIP implications: control of alkenes (if 2°), control of aldehydes (if 1°).

3. Diurnal Variation in OH reactivity

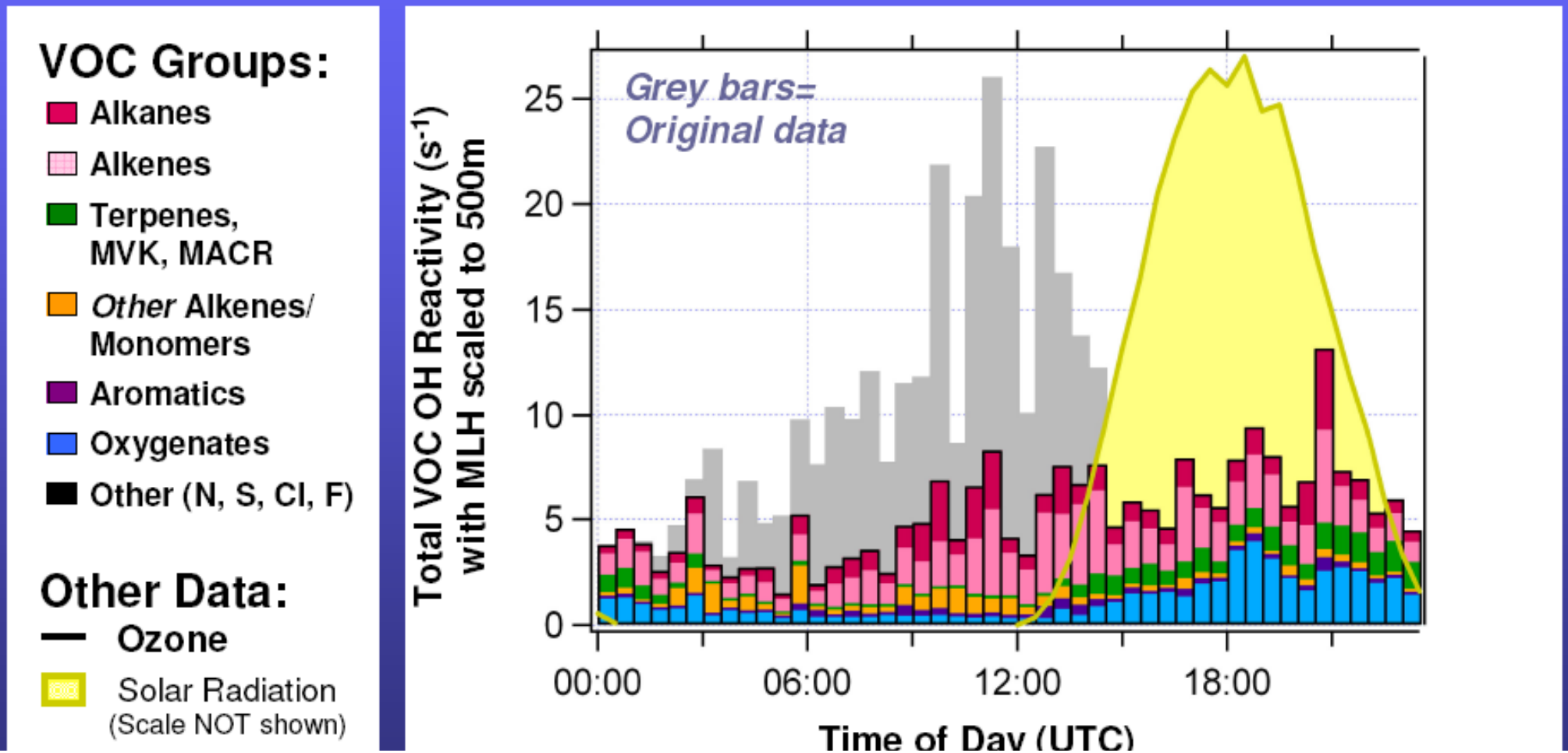
All of Galveston Bay & Houston Metropolitan Area



Gillman et al., 2007

3. Diurnal Variation in OH reactivity

Data has been scaled to a mixing layer height of 500m

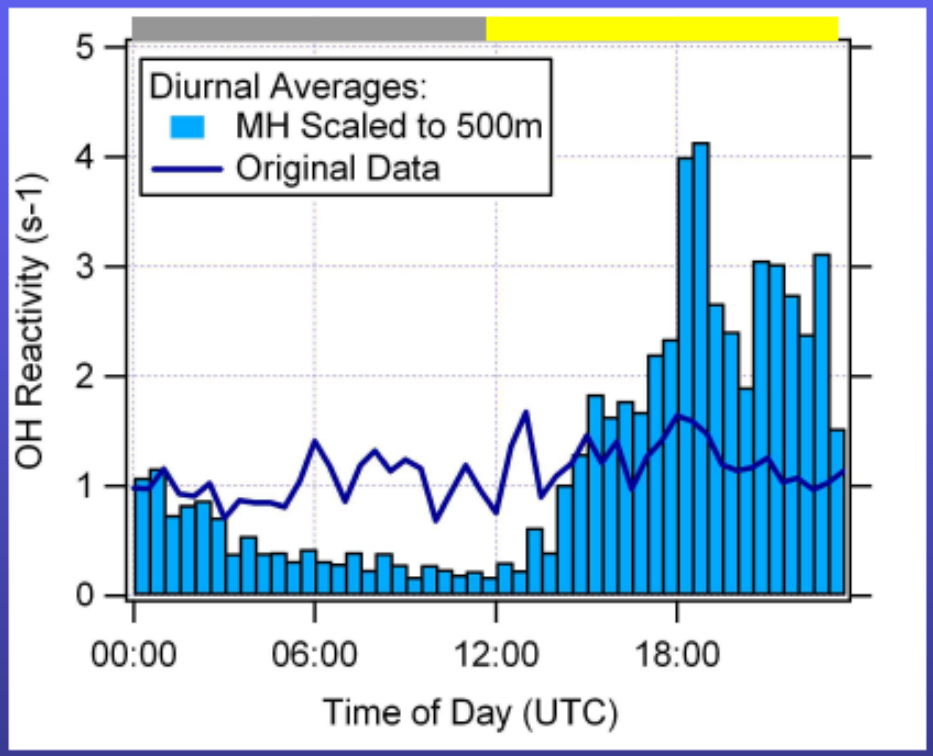


Gillman et al., 2007

3. Diurnal Variation in OH reactivity

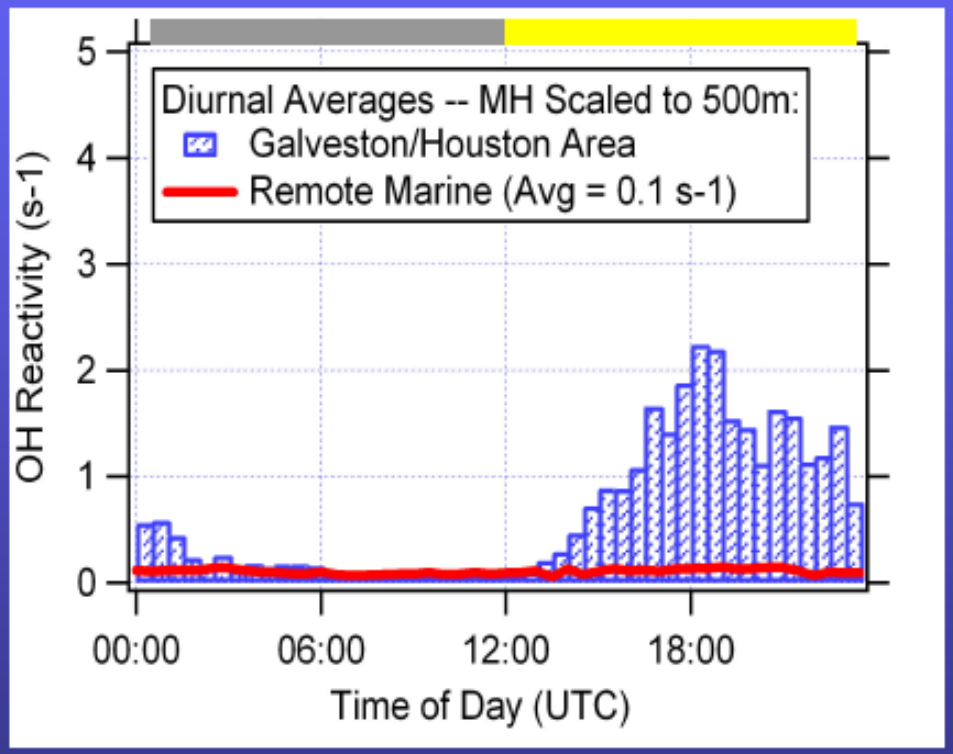
OH Loss to all Oxygenates

Galveston/Houston Area



OH Loss to Formaldehyde

G/H and Remote Marine

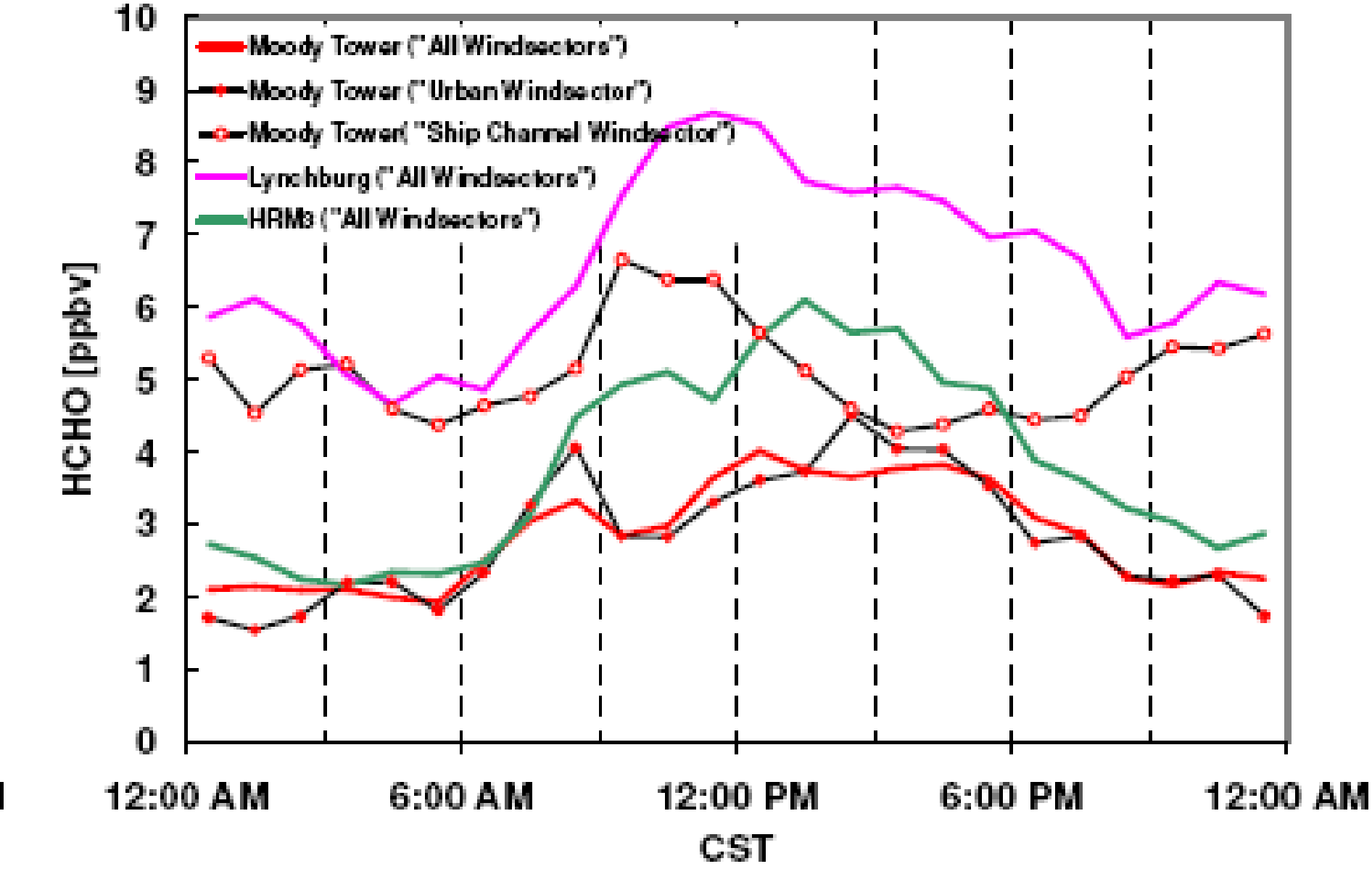


- Secondary production of oxygenated VOCs (esp. HCHO)

On average, nighttime HCHO is background; most of HCHO forms during the day.

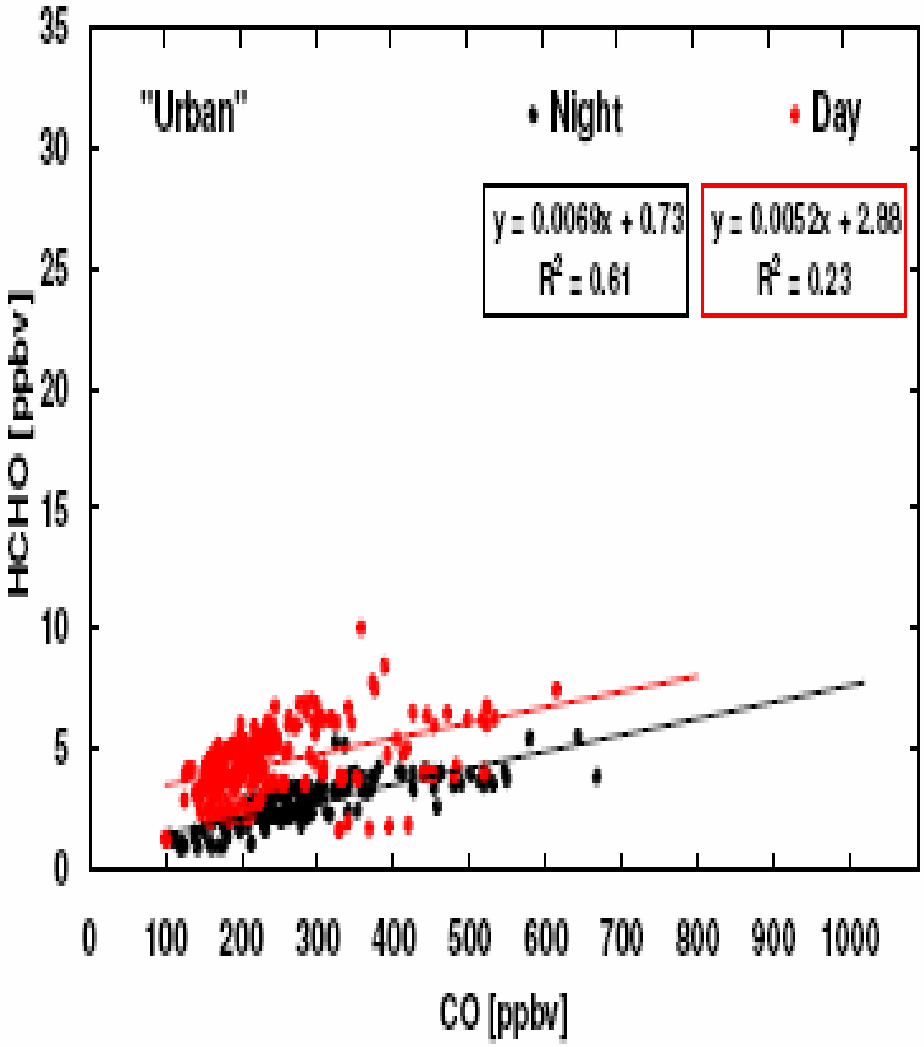
Gillman et al., 2007

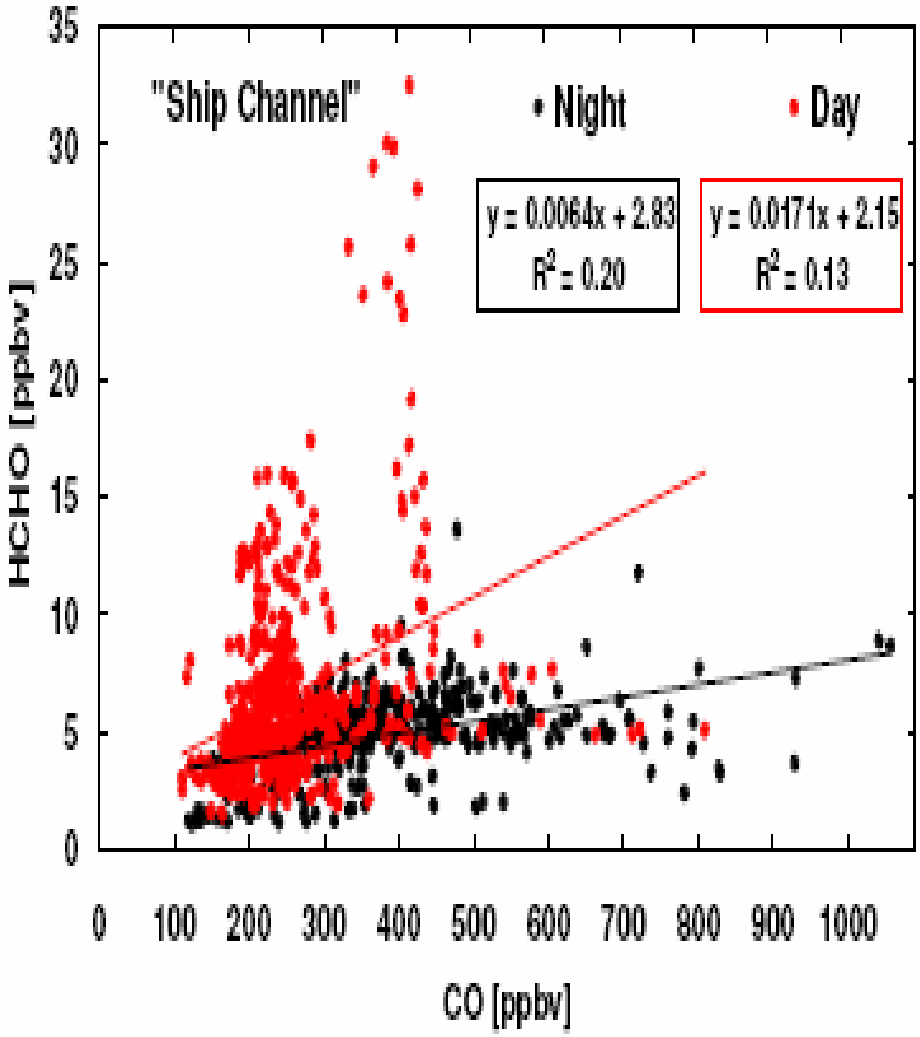
Rappenglueck et al., 2007



"Background" concentrations higher in Ship Channel, and HCHO peaks before noon.

Rappenglueck et al., 2007





HCHO behaves differently in Ship Channel plumes than in urban plumes.

De Gouw et al., 2007

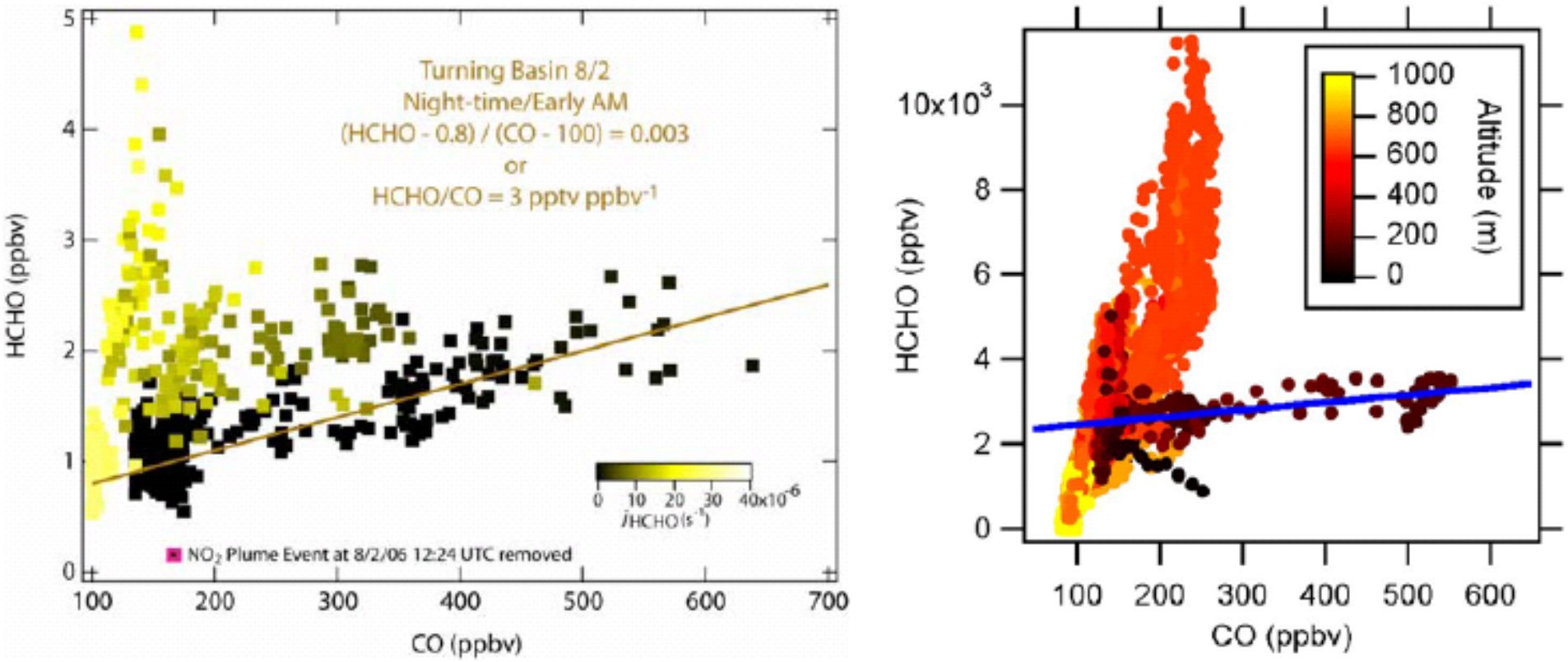
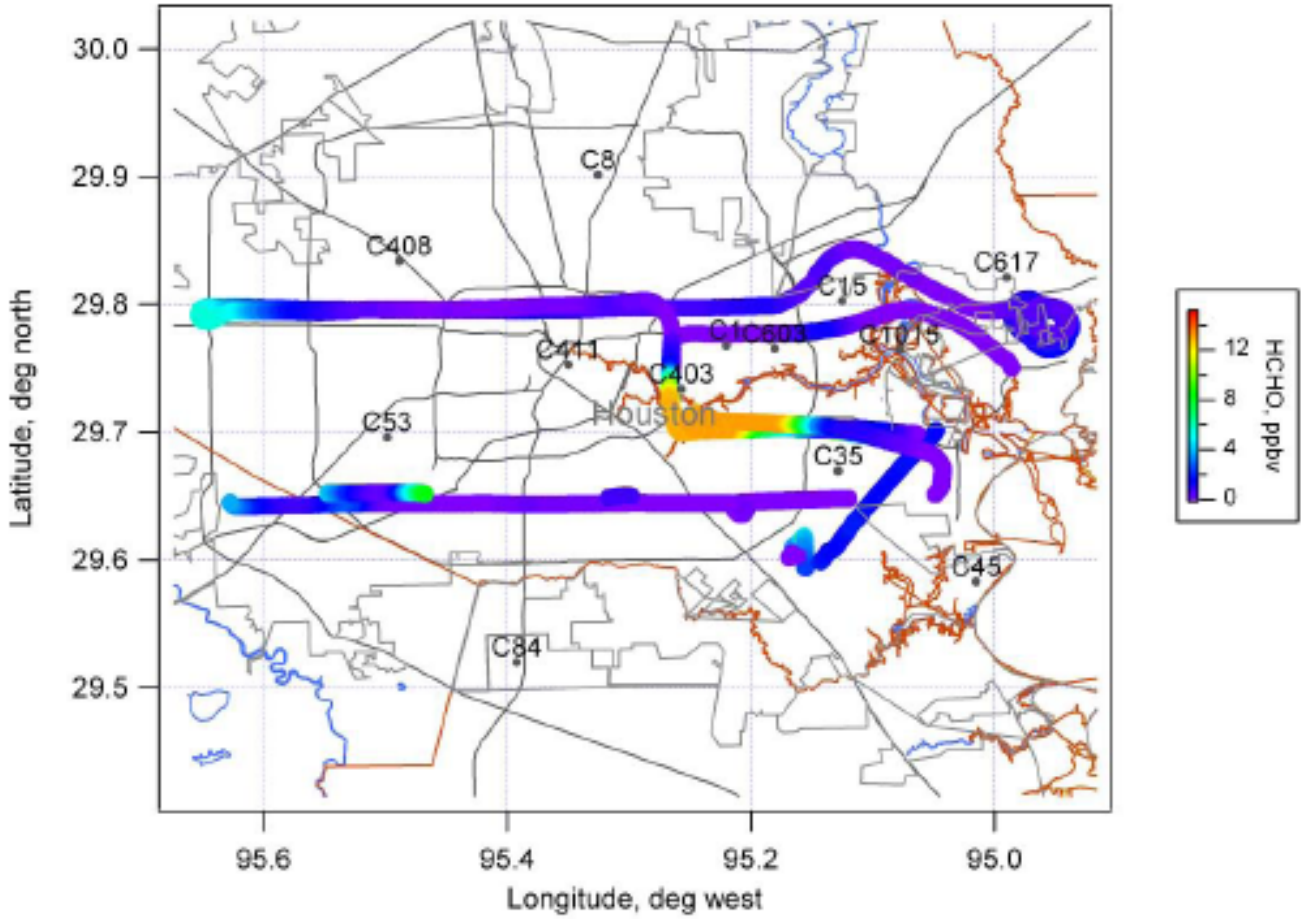
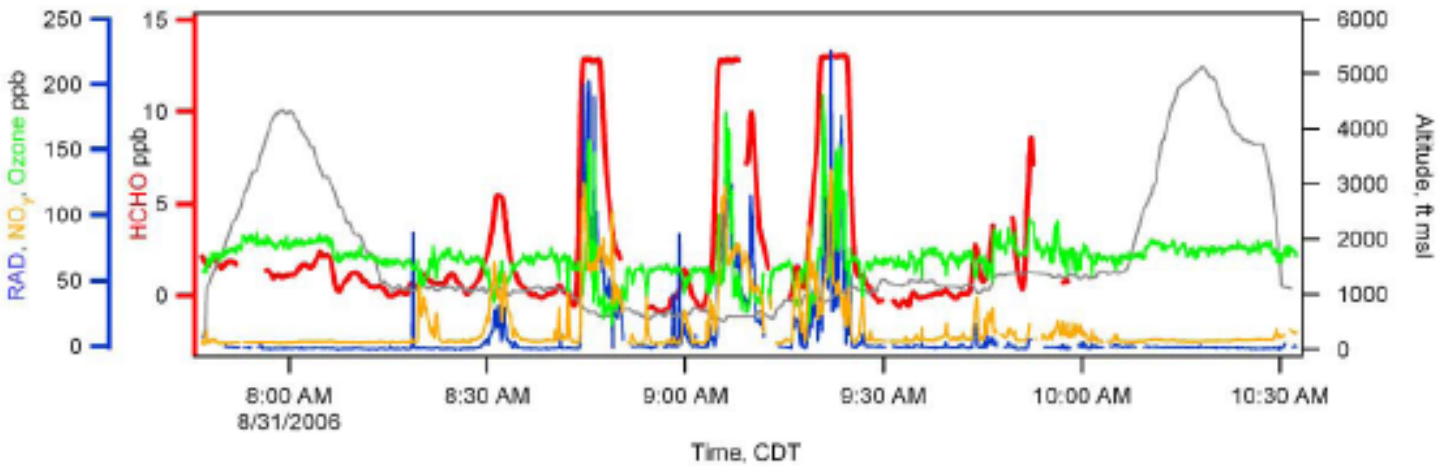


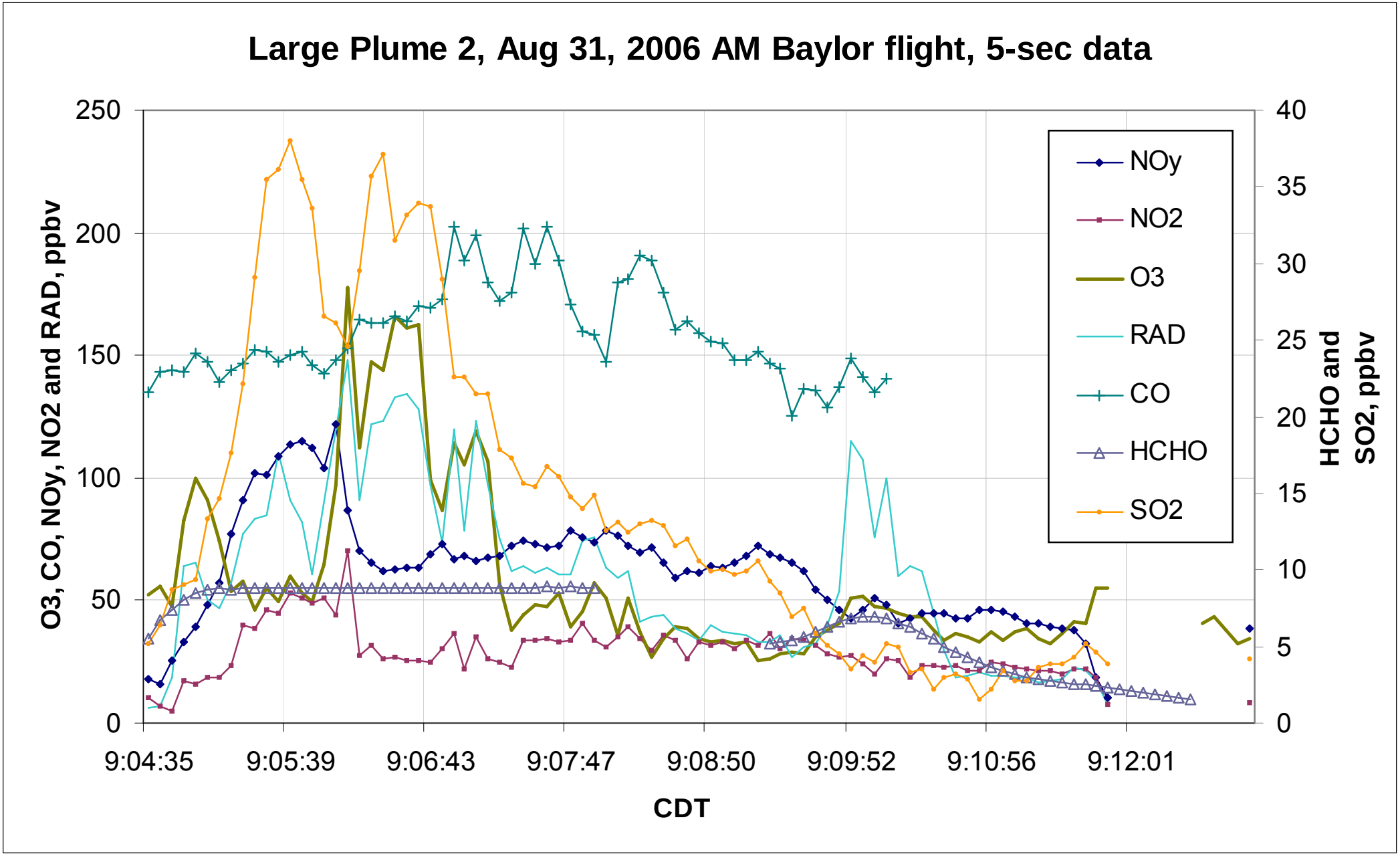
Figure E2. Relationships of HCHO to CO concentrations obtained onboard the *Ronald H. Brown* in the turning basin at the western end of the HSC (left panel), and from the WP-3D during a nighttime, missed approach at Montgomery County airport to the north of Houston.

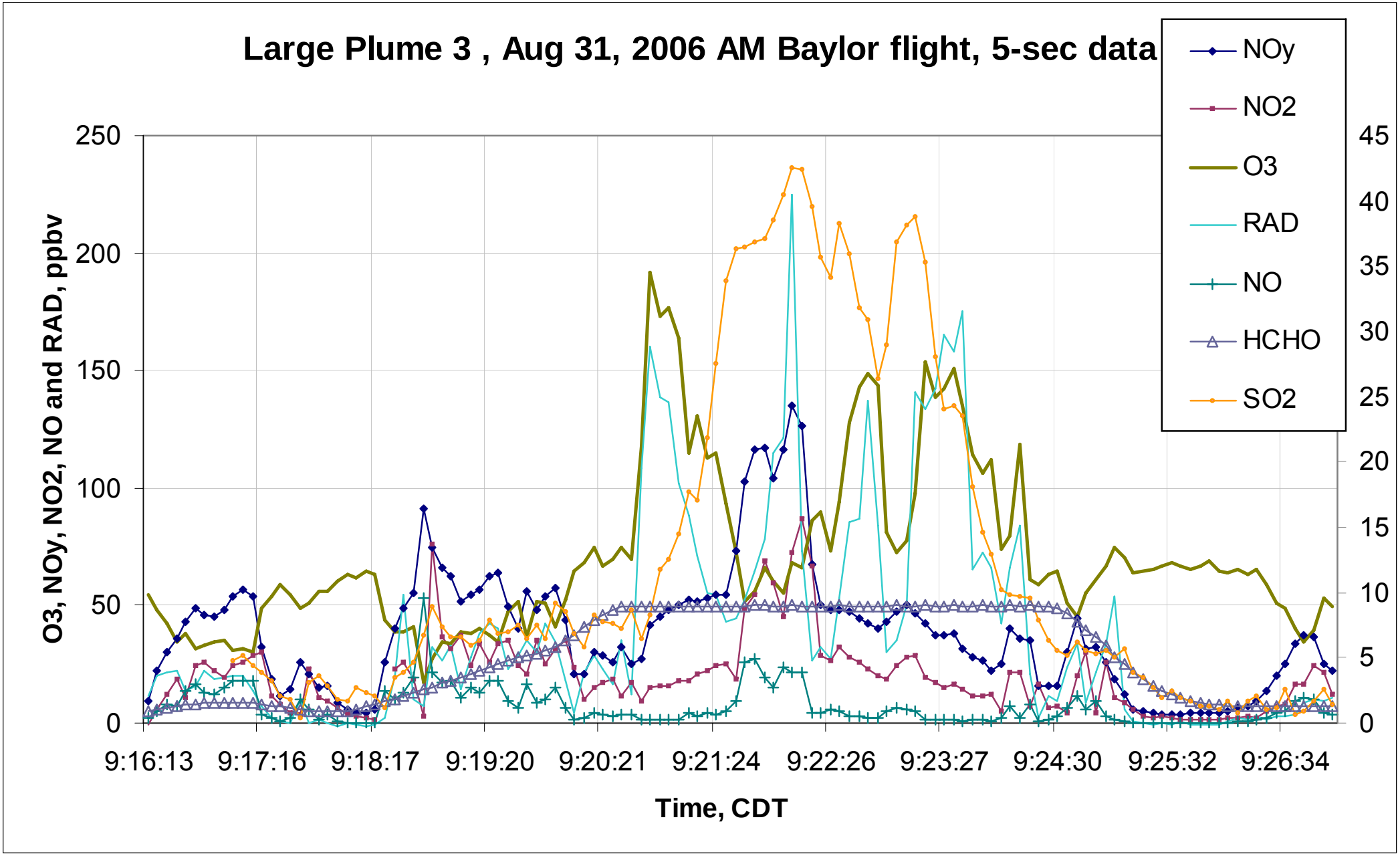
Alvarez et al., 2007

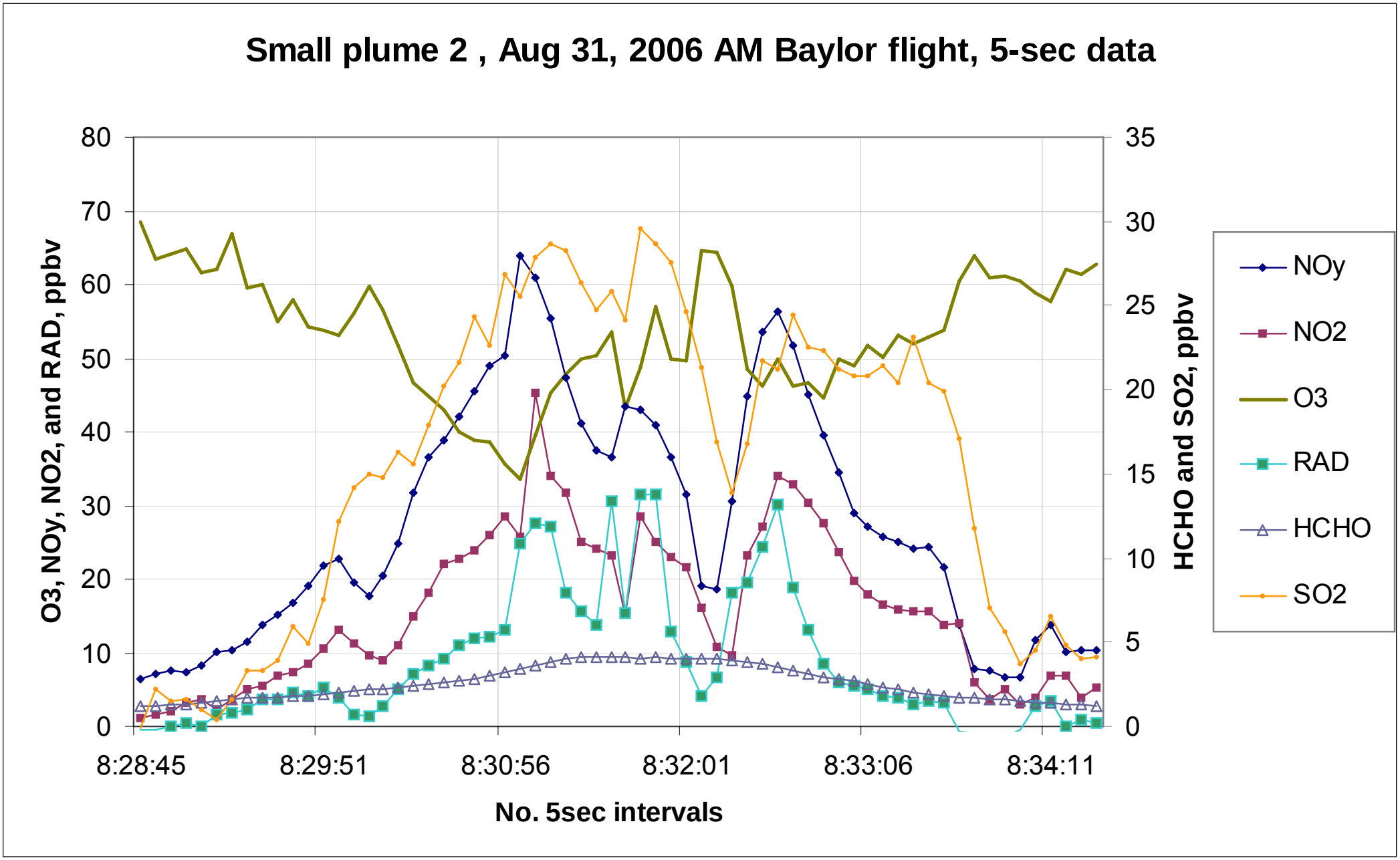


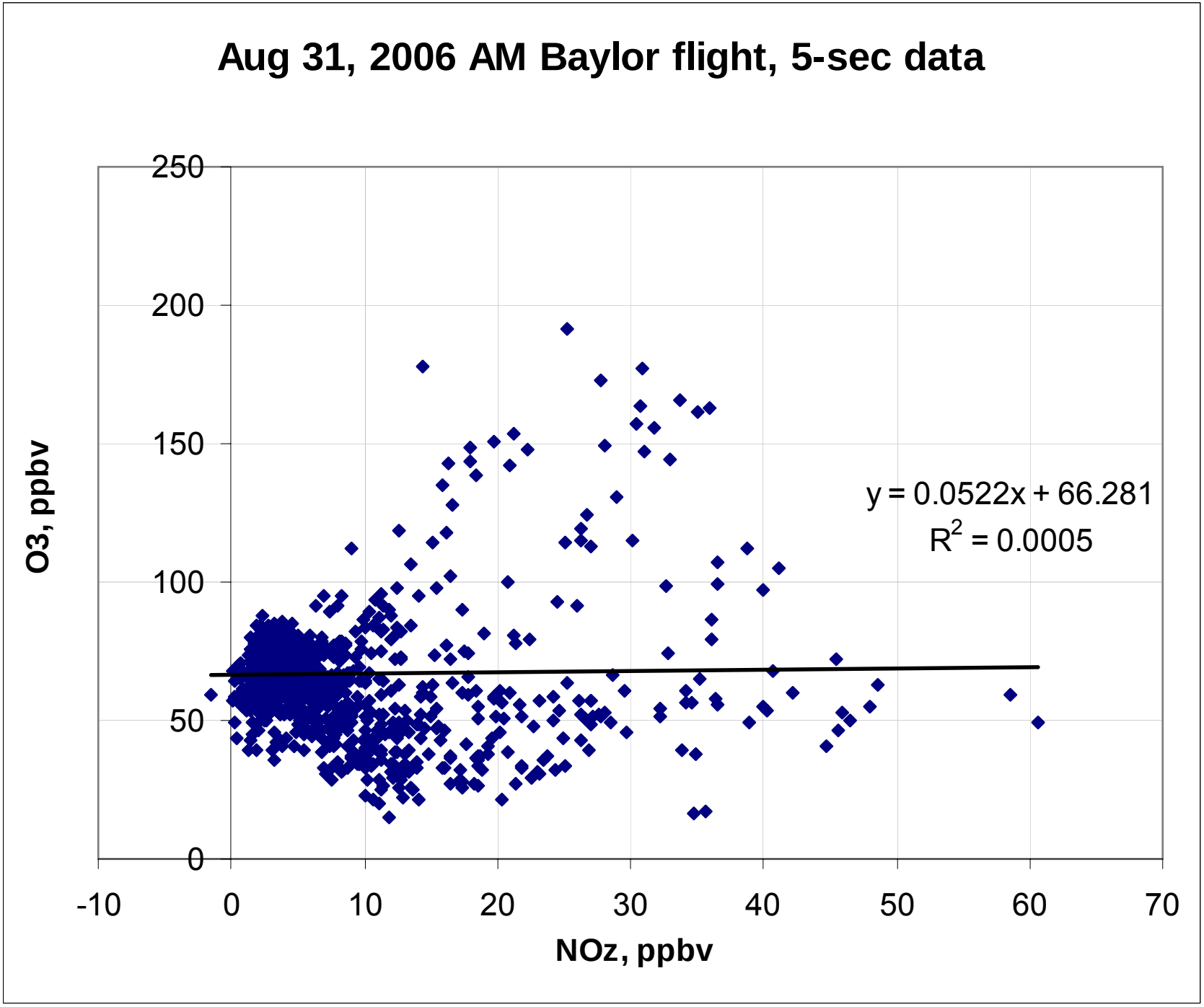
Aug 31, 2006: a very high ozone day in Houston

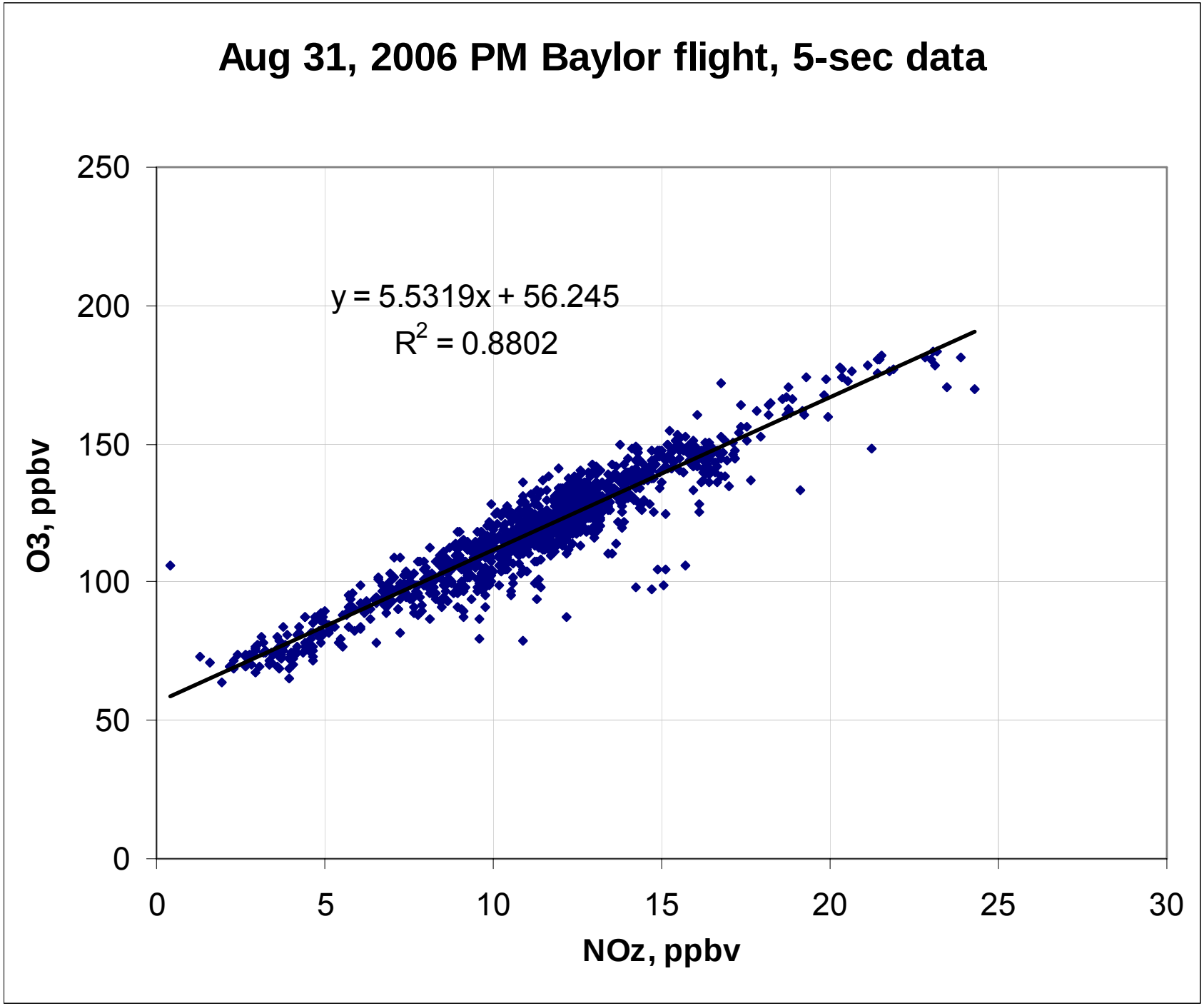



Large Plume 2, Aug 31, 2006 AM Baylor flight, 5-sec data
O3, CO, NOy, NO2 and RAD, ppbv
HCHO and SO2, ppbv
CDT
250
200
150
100
50
0
40
35
30
25
20
15
10
5
0
9:04:35
9:05:39
9:06:43
9:07:47
9:08:50
9:09:52
9:10:56
9:12:01
NOy
NO2
O3
RAD
CO
HCHO
SO2


Large Plume 3 , Aug 31, 2006 AM Baylor flight, 5-sec data
NOy
NO2
O3
RAD
NO
HCHO
SO2
O3, NOy, NO2, NO and RAD, ppbv
250
200
150
100
50
0
45
40
35
30
25
20
15
10
5
0
9:16:13
9:17:16
9:18:17
9:19:20
9:20:21
9:21:24
9:22:26
9:23:27
9:24:30
9:25:32
9:26:34
Time, CDT


Small plume 2 , Aug 31, 2006 AM Baylor flight, 5-sec data
O3, NOy, NO2, and RAD, ppbv
HCHO and SO2, ppbv
No. 5sec intervals
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25
30
35
8:28:45
8:29:51
8:30:56
8:32:01
8:33:06
8:34:11
NOy
NO2
O3
RAD
HCHO
SO2


Aug 31, 2006 AM Baylor flight, 5-sec data
O3, ppbv
NOz, ppbv
y = 0.0522x + 66.281
R2 = 0.0005
250
200
150
100
50
0
-10
0
10
20
30
40
50
60
70

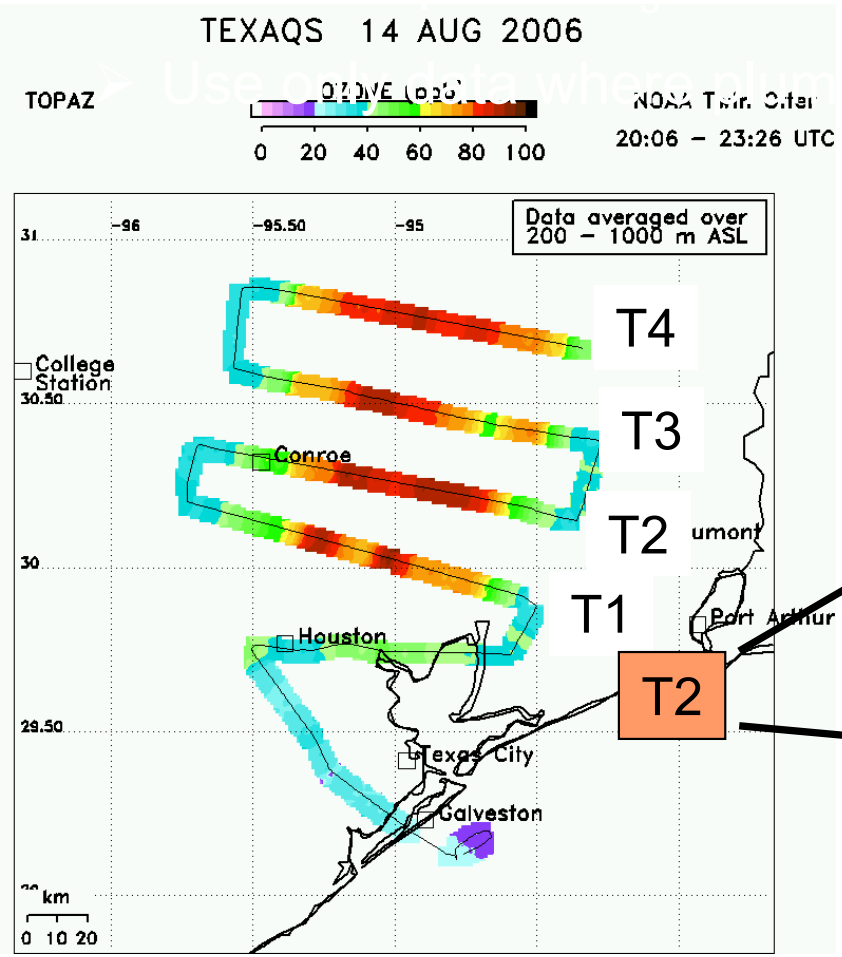

Aug 31, 2006 PM Baylor flight, 5-sec data
y = 5.5319x + 56.245
R2 = 0.8802
O3, ppbv
NOz, ppbv
250
200
150
100
50
0
0
5
10
15
20
25
30

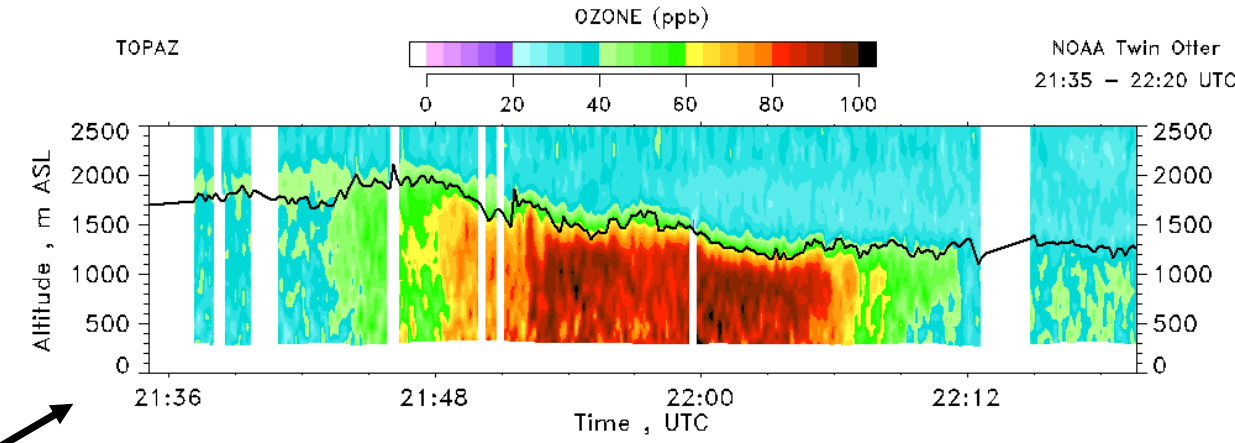
Fun with formaldehyde

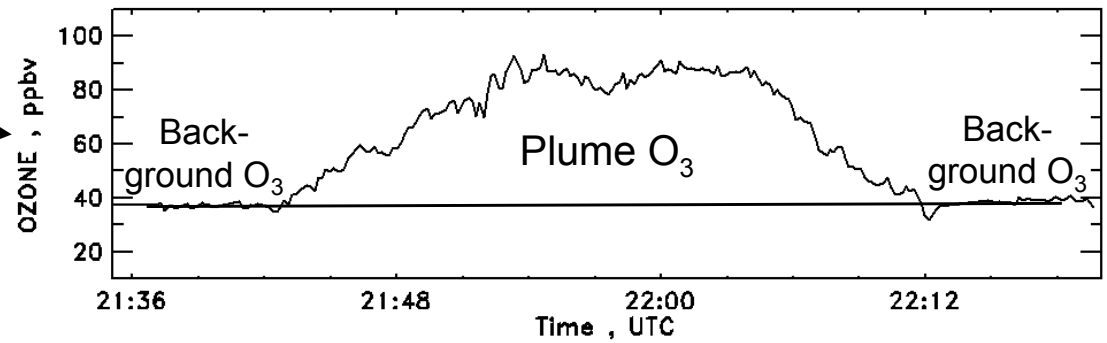
- HCHO concentrations are high downwind from the industrial region, in aged plumes where they are correlated with other reaction products such as ozone, NOz, and PAN.
- In a few plumes, formaldehyde is correlated with unreacted emissions such as NO, alkenes, CO, and SO2. These plumes have apparently not undergone much aging, and are associated with relatively fresh emissions, suggesting that the HCHO is either directly emitted or has formed very rapidly.
- On average, the ground-based nighttime HCHO concentrations are consistent with background concentrations, but background seems to vary with location.

Relationship between boundary layer depth and peak ozone

Hardesty et al., 2007





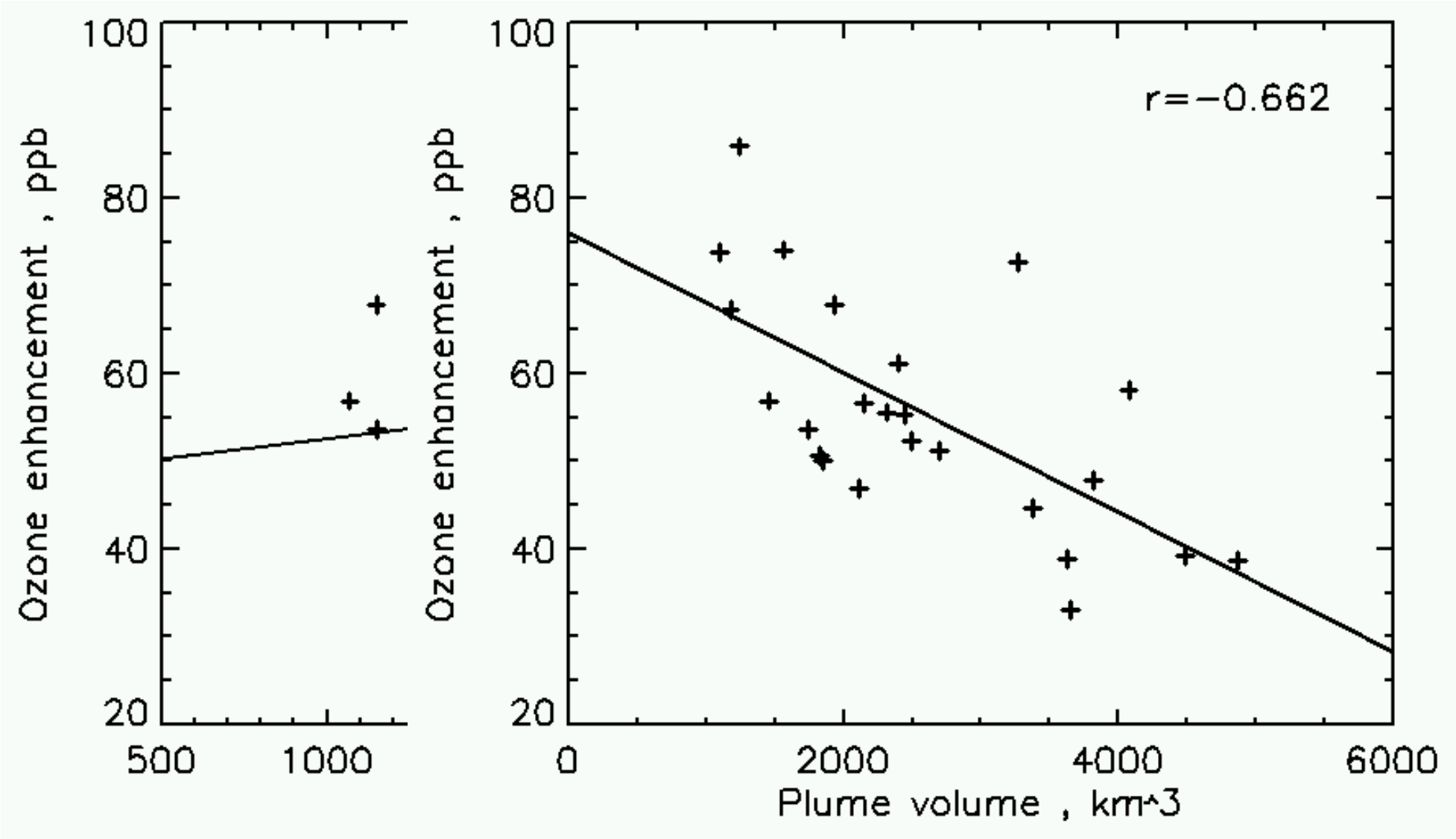


<u>For each transect >2 hours from source:</u>

- Ozone enhancement = 95 percentile O_3 in plume – background O_3
- Δz: Average BL height across plume
- Δx: Plume width
- Δy: Wind speed (at middle of transect) * Δt

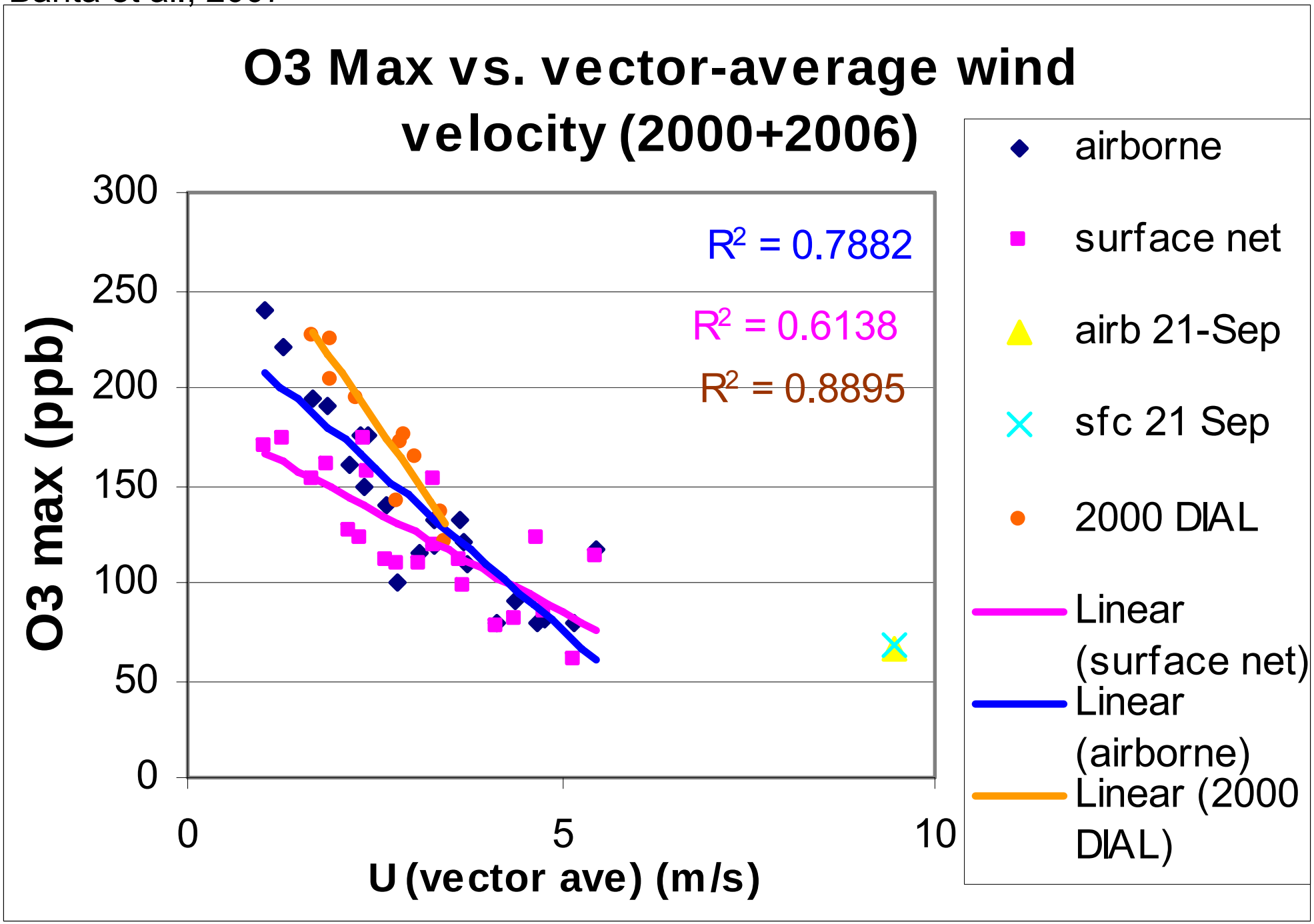
Hardesty et al., 2007

O3 vs BL height vs plume volume



24 transects from 7 flights from TexAQS 2006 and TexAQS 2000

Banta et al., 2007

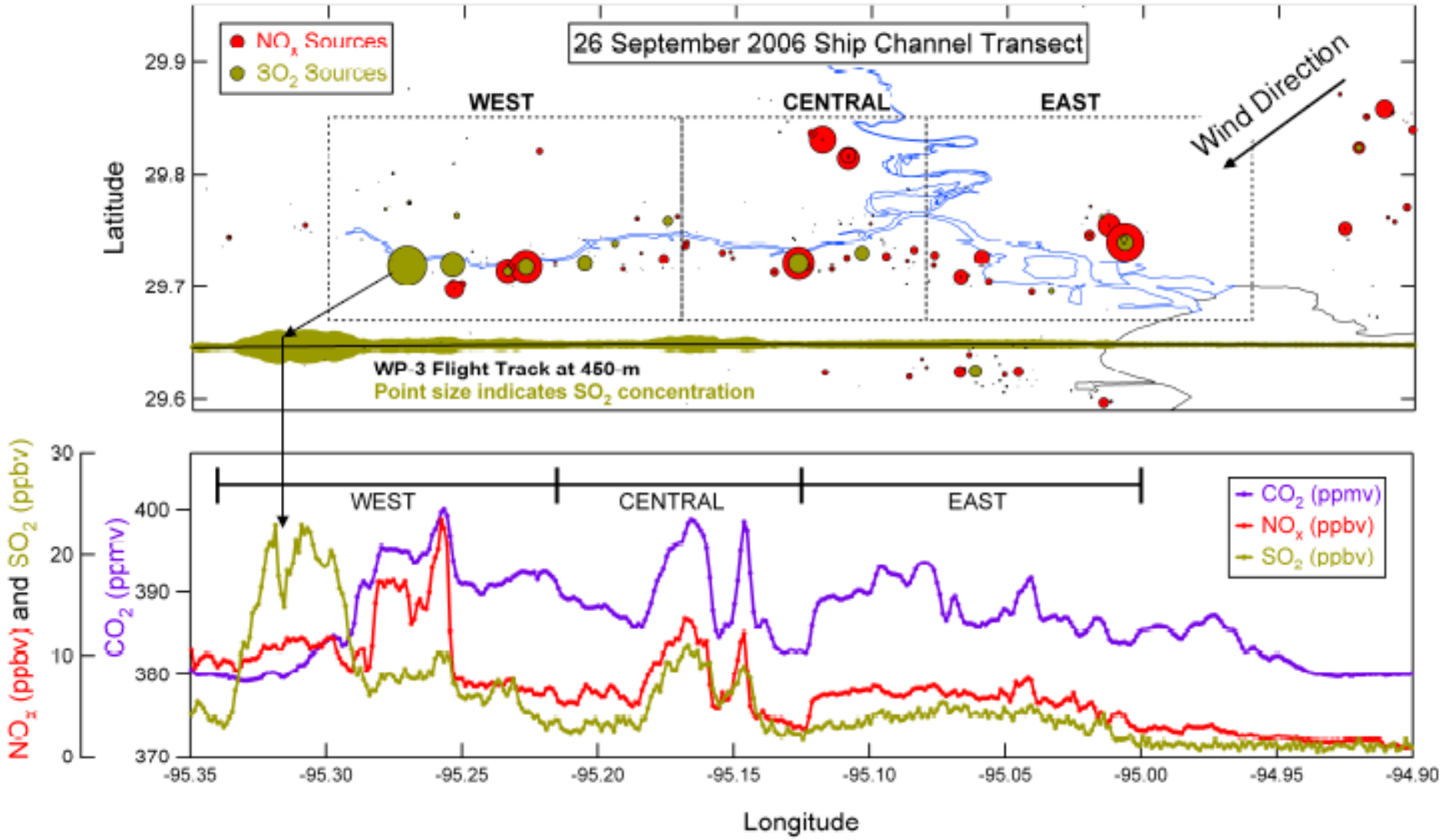


Relationship between boundary layer depth and maximum ozone

- Peak ozone observed is not very sensitive to the *afternoon* boundary layer depth *downwind of city*.
- Peak ozone is apparently much more sensitive to wind velocity.
- Note that this analysis doesn't investigate the role of nocturnal or morning boundary layer dynamics within the city.

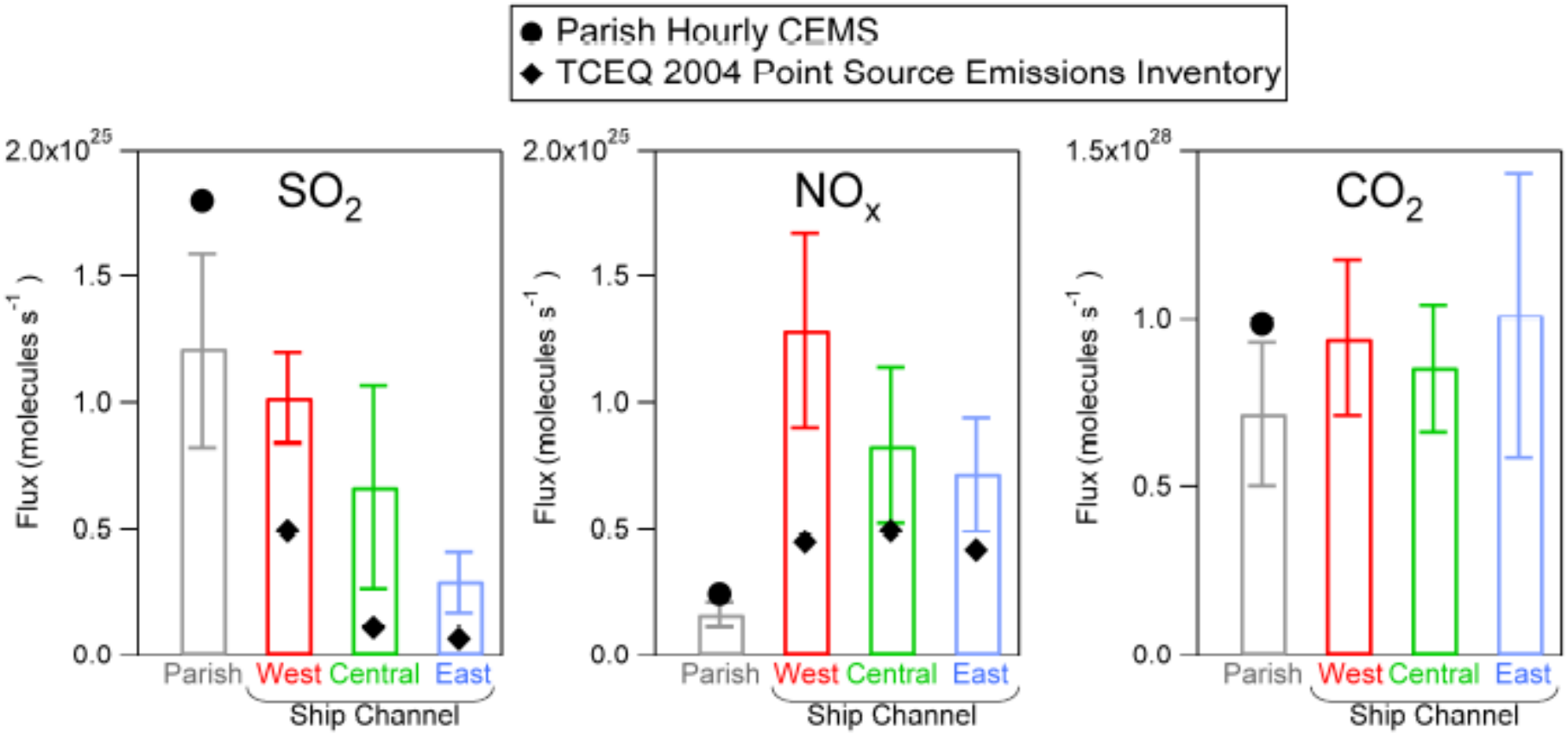
Emission changes between 2000 and 2006

Measurements Downwind of the Houston Ship Channel



Washenfelder et al., 2007

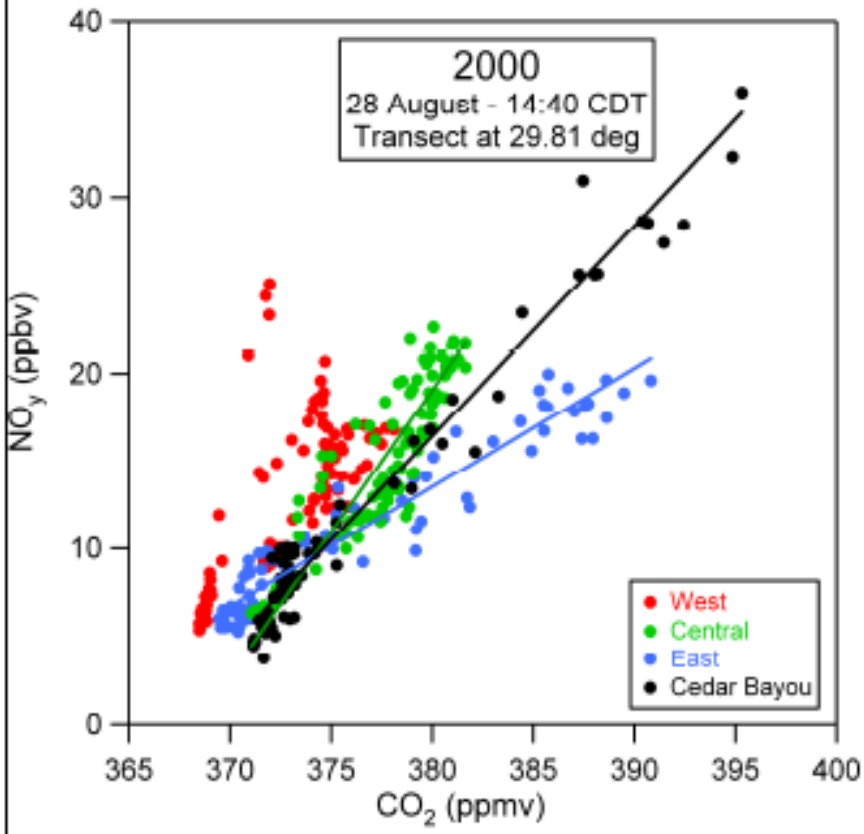
Absolute Fluxes From the Houston Ship Channel

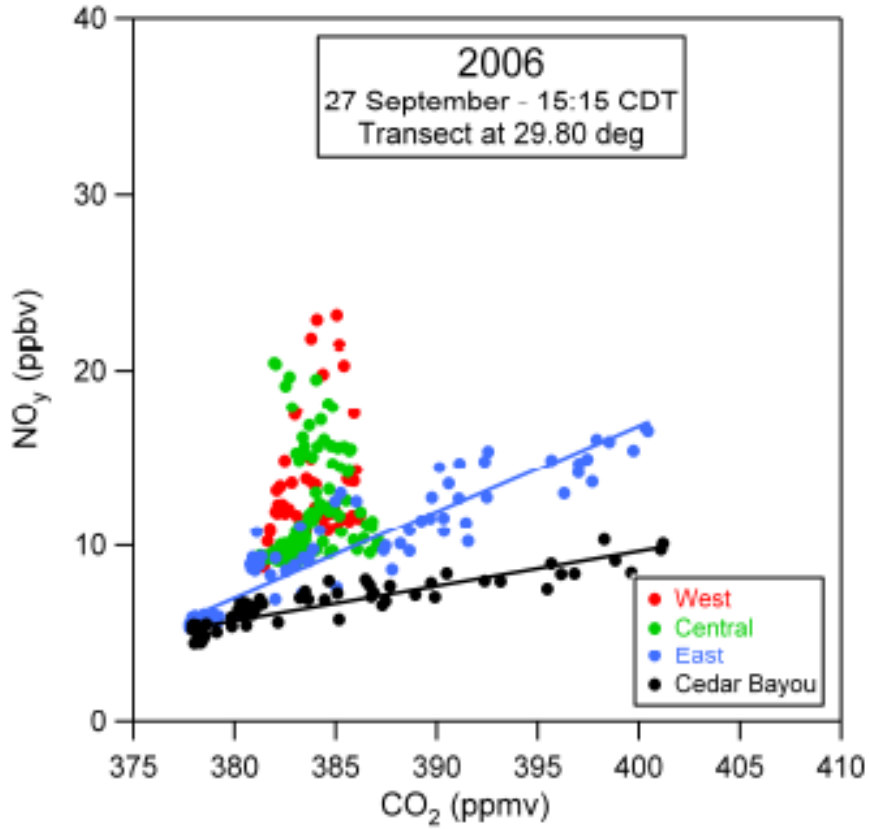


West Ship Channel has more non-point source emissions?

Washenfelder et al., 2007

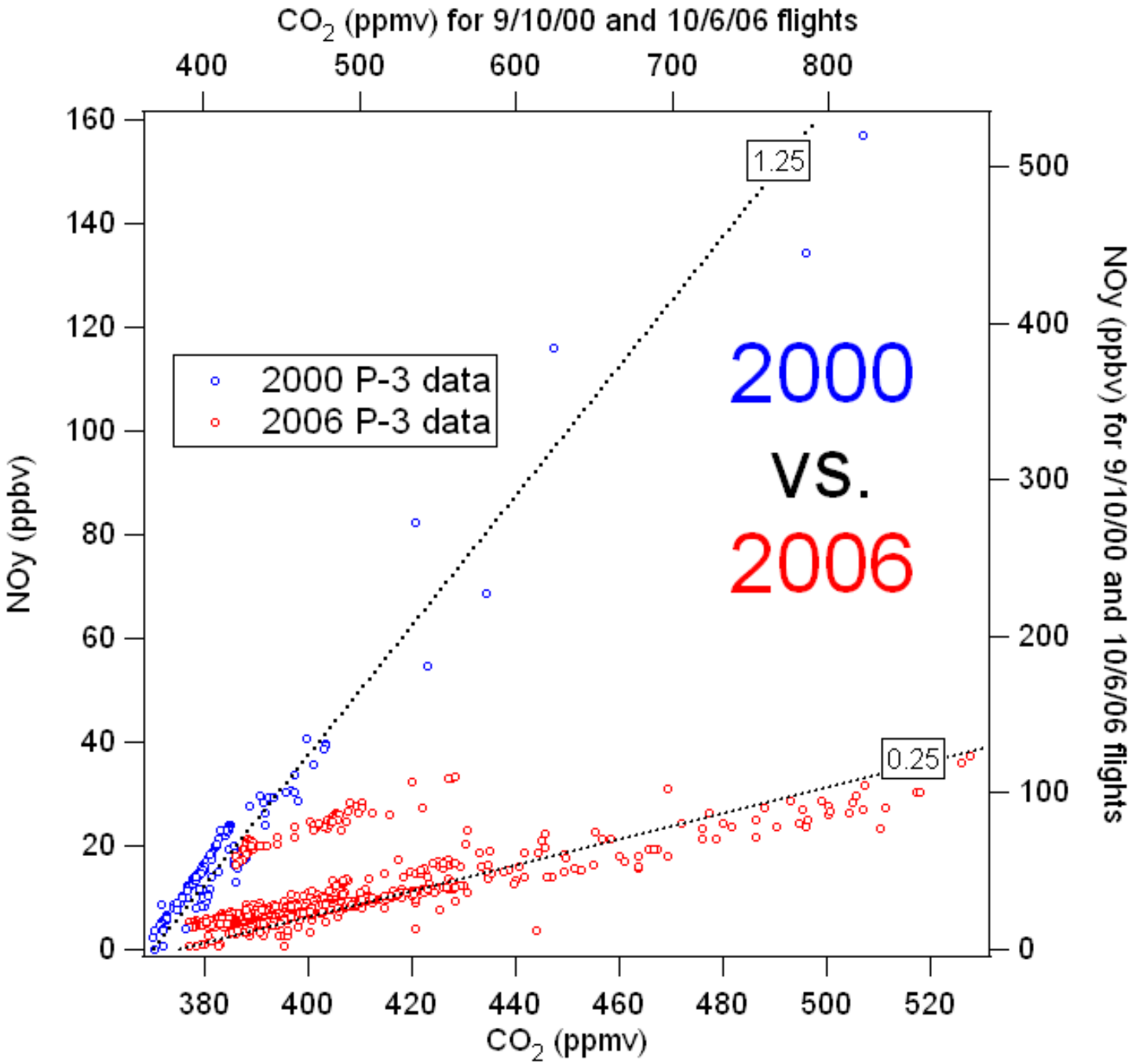
Evidence of NO_x Reductions





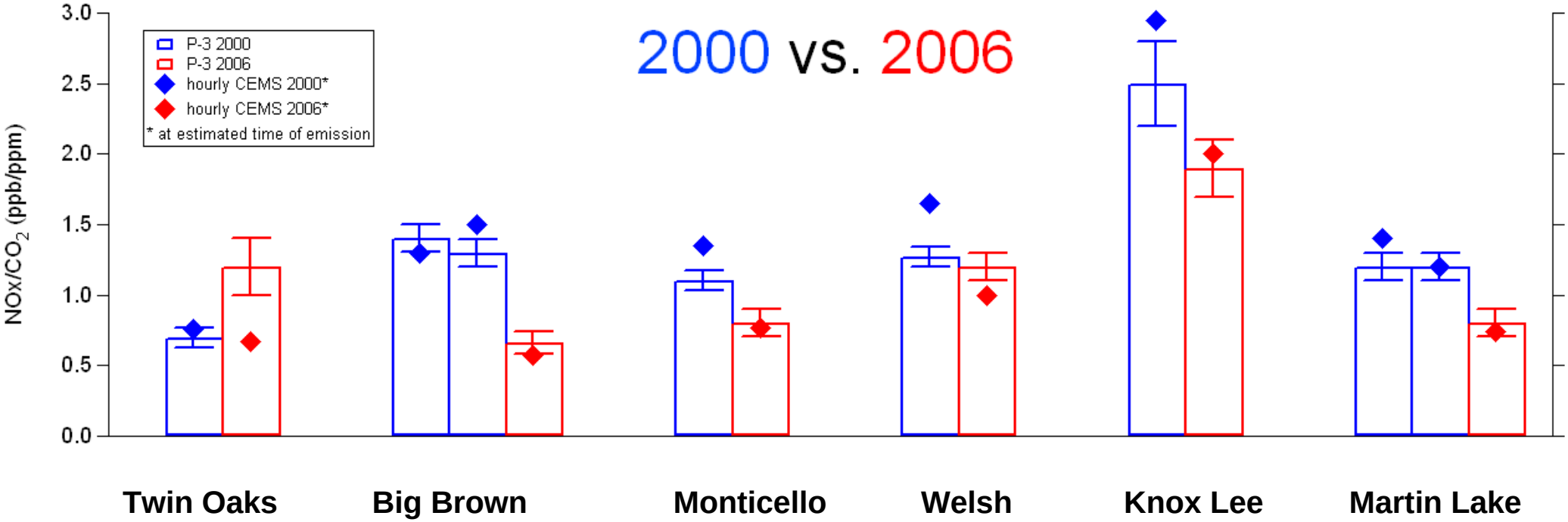
	NO_y / CO_2 Ratio	
	2000	2006
• Central Ship	1.62 ± 0.16	—
• East Ship	0.72 ± 0.07	0.49 ± 0.05
• Cedar Bayou	1.21 ± 0.12	0.20 ± 0.03

Washenfelder et al., 2007



Peischl et al., 2007

- 2000: 4 P-3 transects average 1.25
- 2006: 16 P-3 transects average 0.25
- NOx reduction measured by P-3: 80%
- NOx reduction according to annual CEMS: 79%



Peischl et al., 2007

Evidence of NOx emission reductions

- Apparent NOx reductions in eastern Ship Channel, Parish power plant, and perhaps Big Brown, Monticello, and Knox Lee power plants.
- Much of the NOx observed in the western Ship Channel area probably arises from other sources besides point sources.

Marine Vessel vs Stationary Source Emissions

1. Emission factor comparison.

Emission Source	Molecules / 1000 Molecules CO_2		
	NO_2	CO	SO_2
Ships (SSD; this work)	21 ± 8	5.6 ± 5.6	6.0 ± 3.5
Parish PP (Coal; NG)[a]	0.23	0.51	1.87
San Jacinto PP (NG)[a]	0.22	0.22	0.003

[a]Source: US EPA 1999 NEI; updates to 2004 from CEMS data by Greg Frost at NOAA/ESRL

2. Aggregate emissions comparison.

County (Texas)	2004 Point Source Emissions[1] (tons per day)		
	NO_2	CO	SO_2
Brazoria	53.77	16.81	138
Fort Bend	22.31	23.17	150
Galveston	24.62	11.95	16
Harris	113.23	53.08	72
Ships (this work)[2]	25	6.3	4.3

[1]Source: US EPA 1999 NEI; updates to 2004 from CEMS data by Greg Frost at NOAA/ESRL
[2]Ship activity data from Eastern Research Group, 2004 (Freeport & Texas City excluded)

Williams et al., 2007