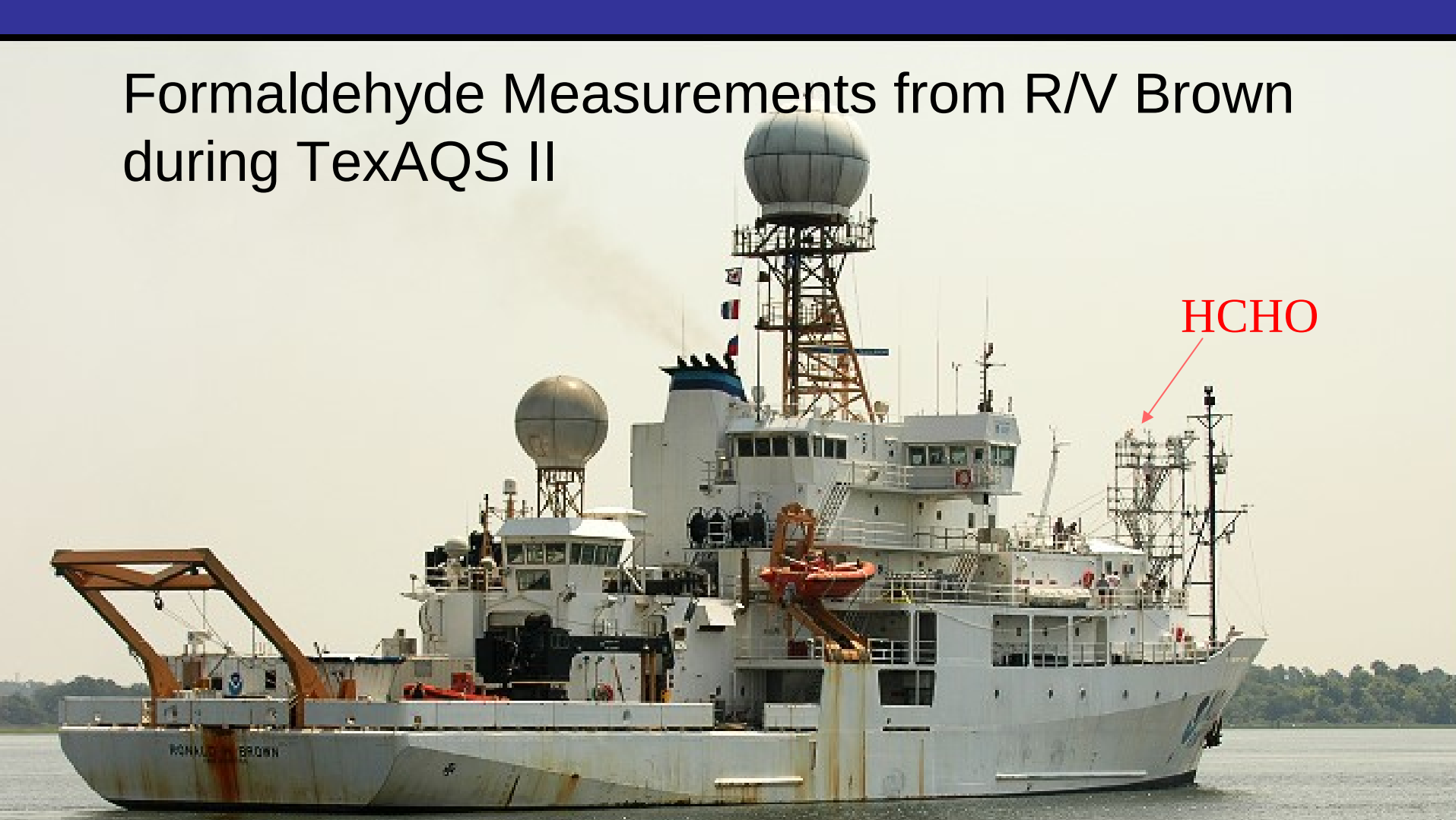
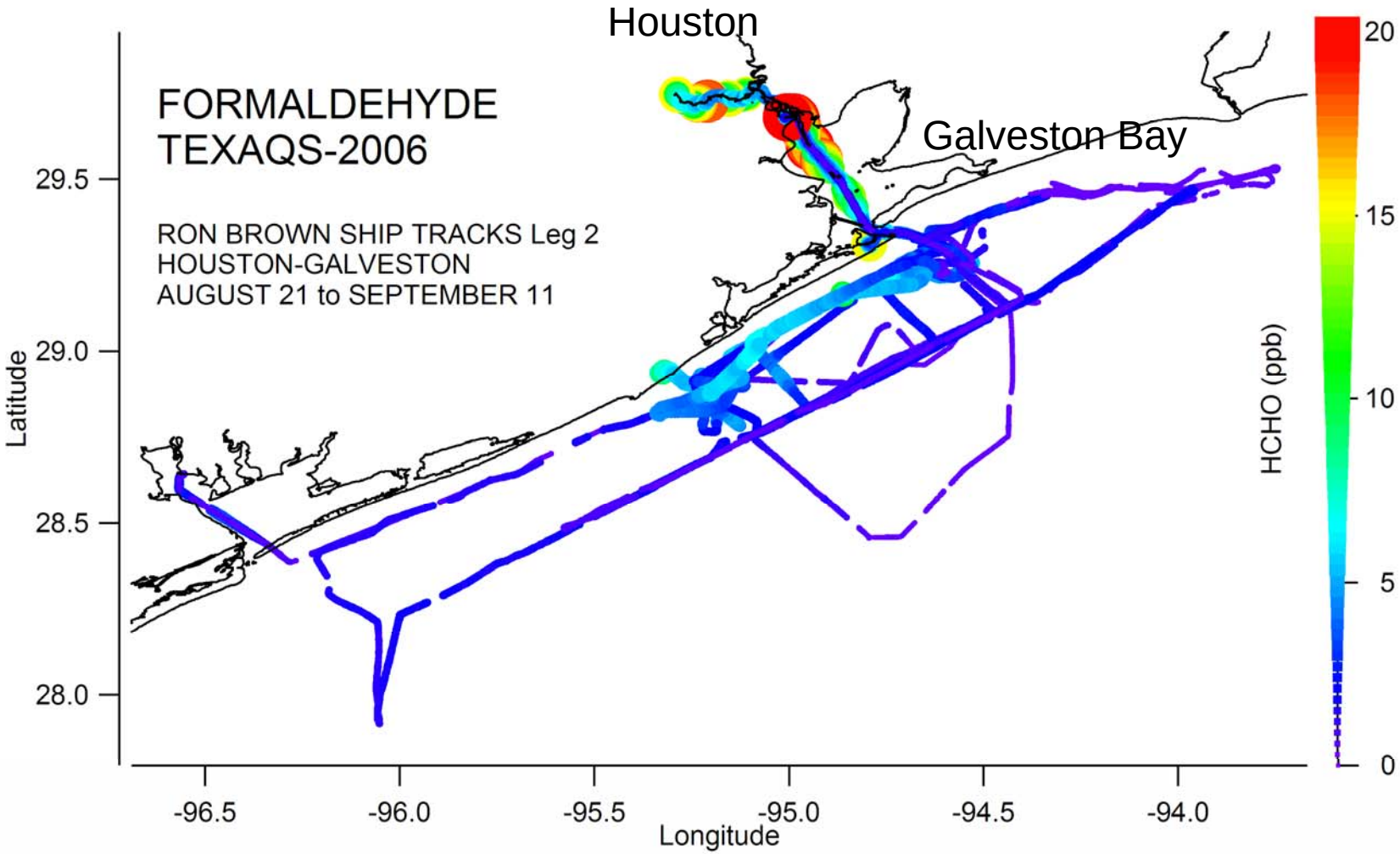
Formaldehyde Measurements from R/V Brown during TexAQS II



Scott C. Herndon, Mark S. Zahniser, Timothy Onasch, Hans Osthoff, Brian Lerner, Dan Welsh-Bon, Jessica Gilman, Roberto Sommariva, Jim Roberts, Ken Aikin, Alan Brewer, Sara Tucker, Tim Bates, Patricia Quinn, Bill Kuster and Eric Williams

Photos by Richard Marchbanks and Dan Welshbon

Formaldehyde (HCHO) Measurement Overview



Outline

Introduction

- HCHO in the urban atmosphere
- Why HCHO emissions are important in Urban Air Quality

Analytical Approach

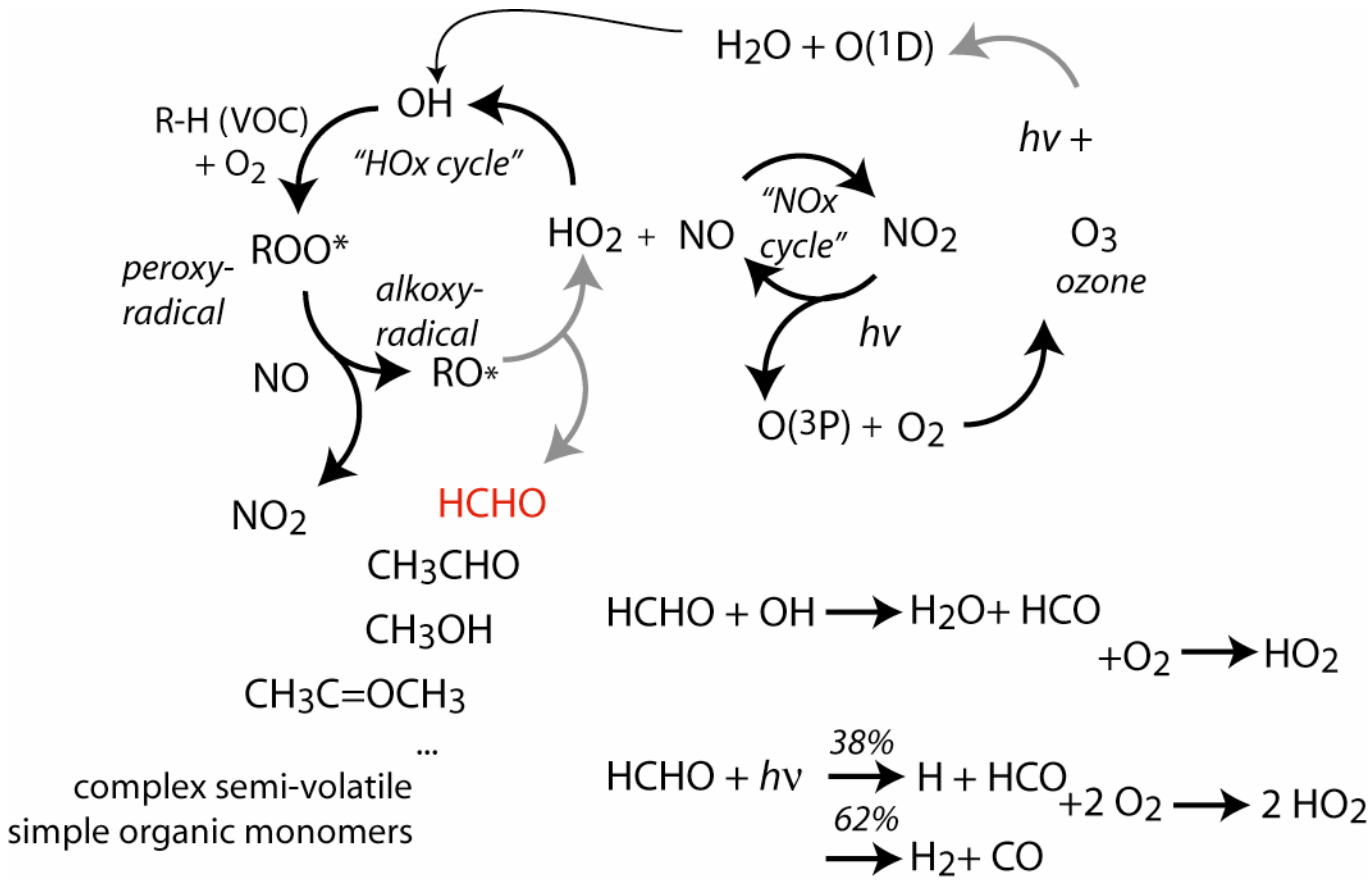
- Tunable Infrared Differential Absorption Spectroscopy
- Inlet Schematic, Characterization, Performance

Comparison with P3 overflight

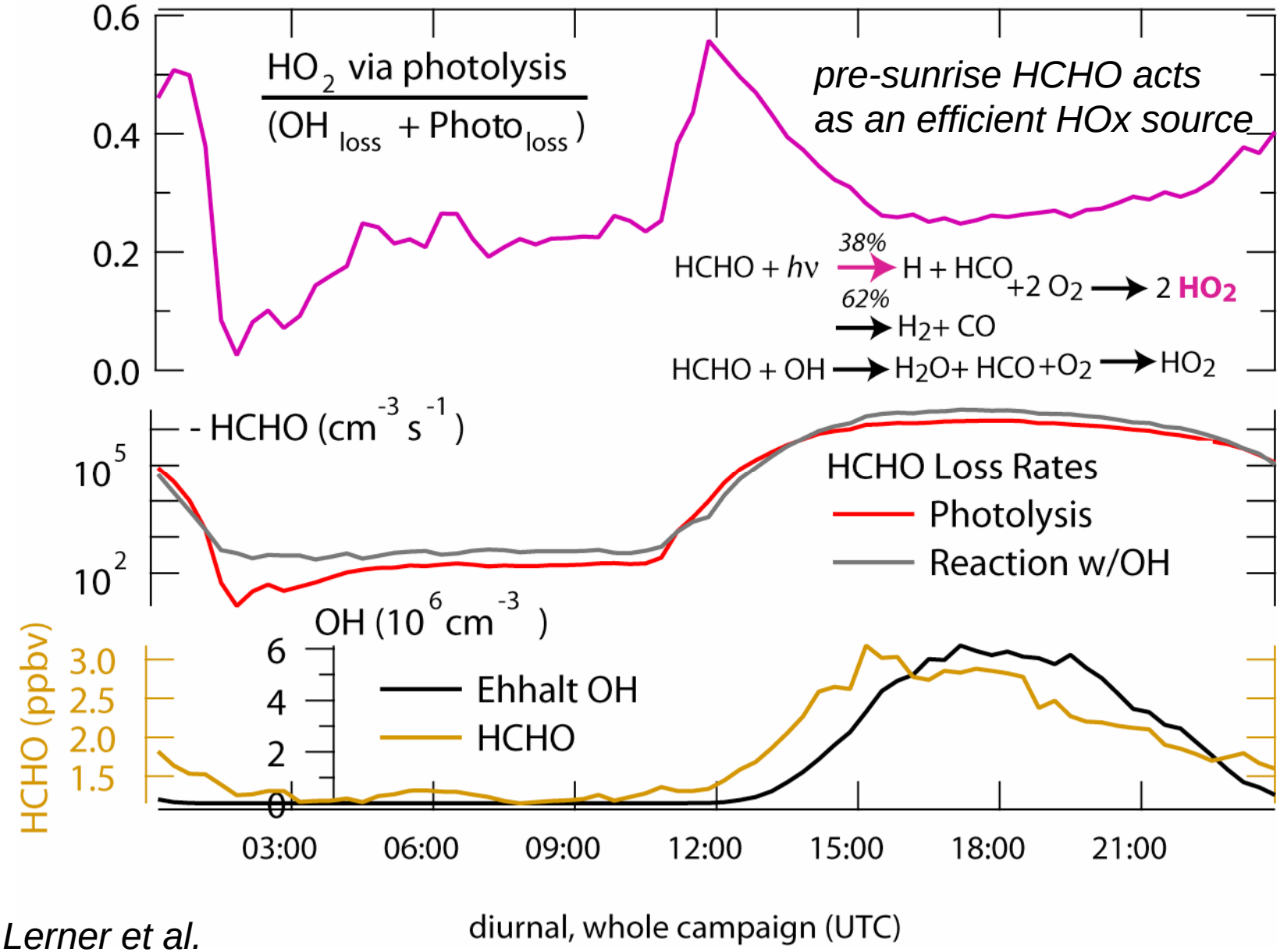
Primary & Secondary HCHO

- Time Series Analysis
- Direct Emissions

HCHO in the Urban Atmosphere



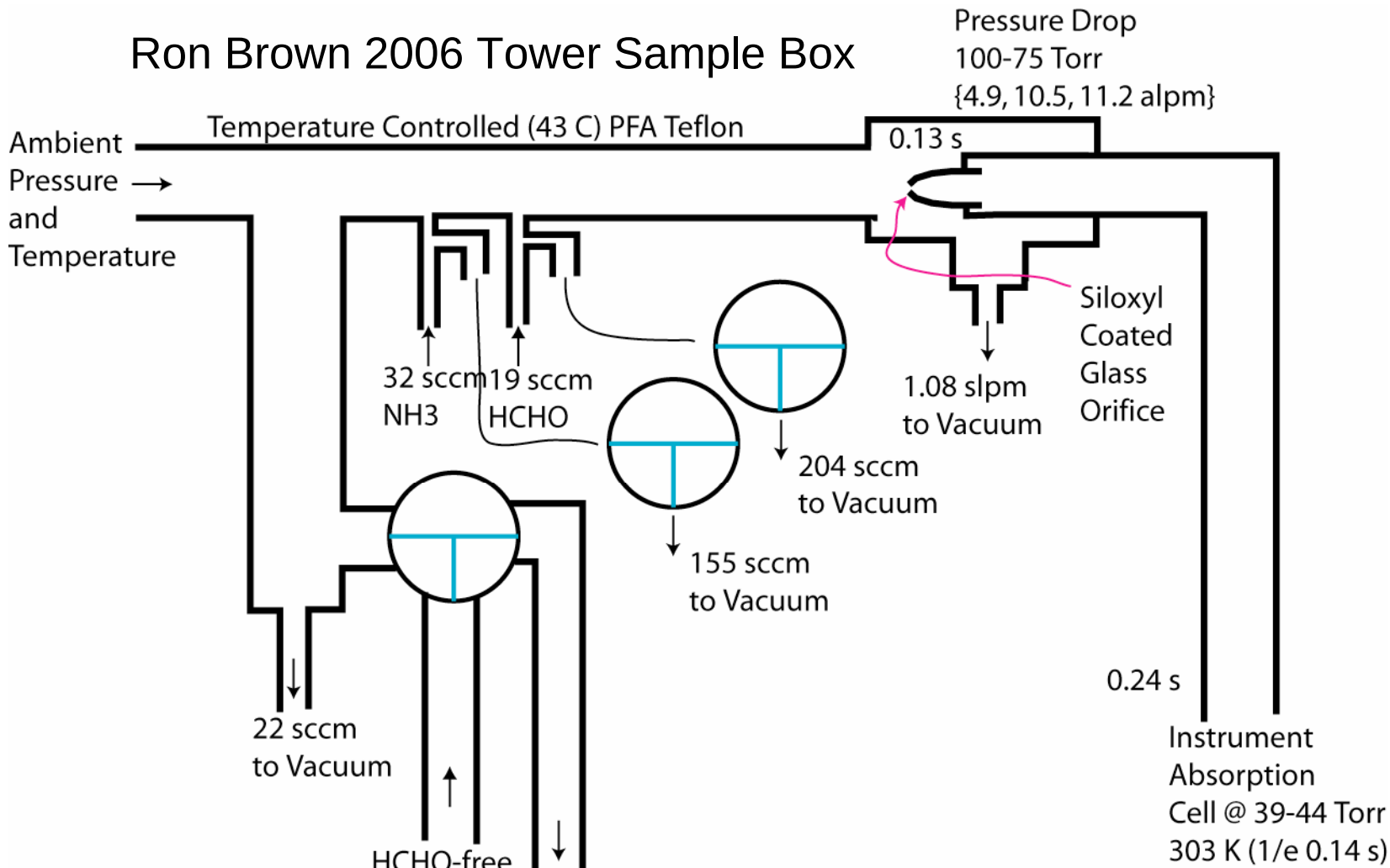
HCHO Emission and Influence on O_3



Lerner et al.

Inlet Sampling Schematic

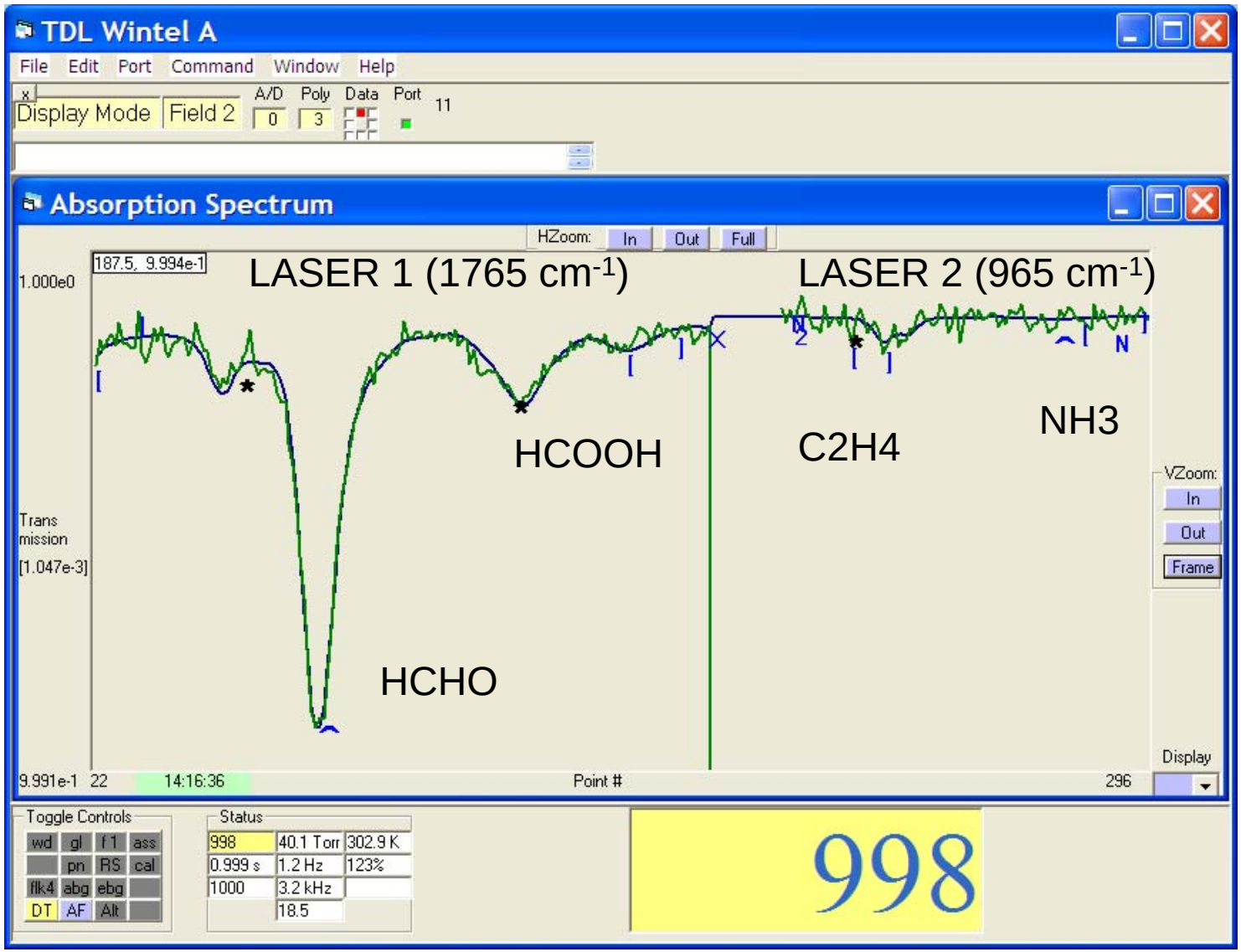
Ron Brown 2006 Tower Sample Box



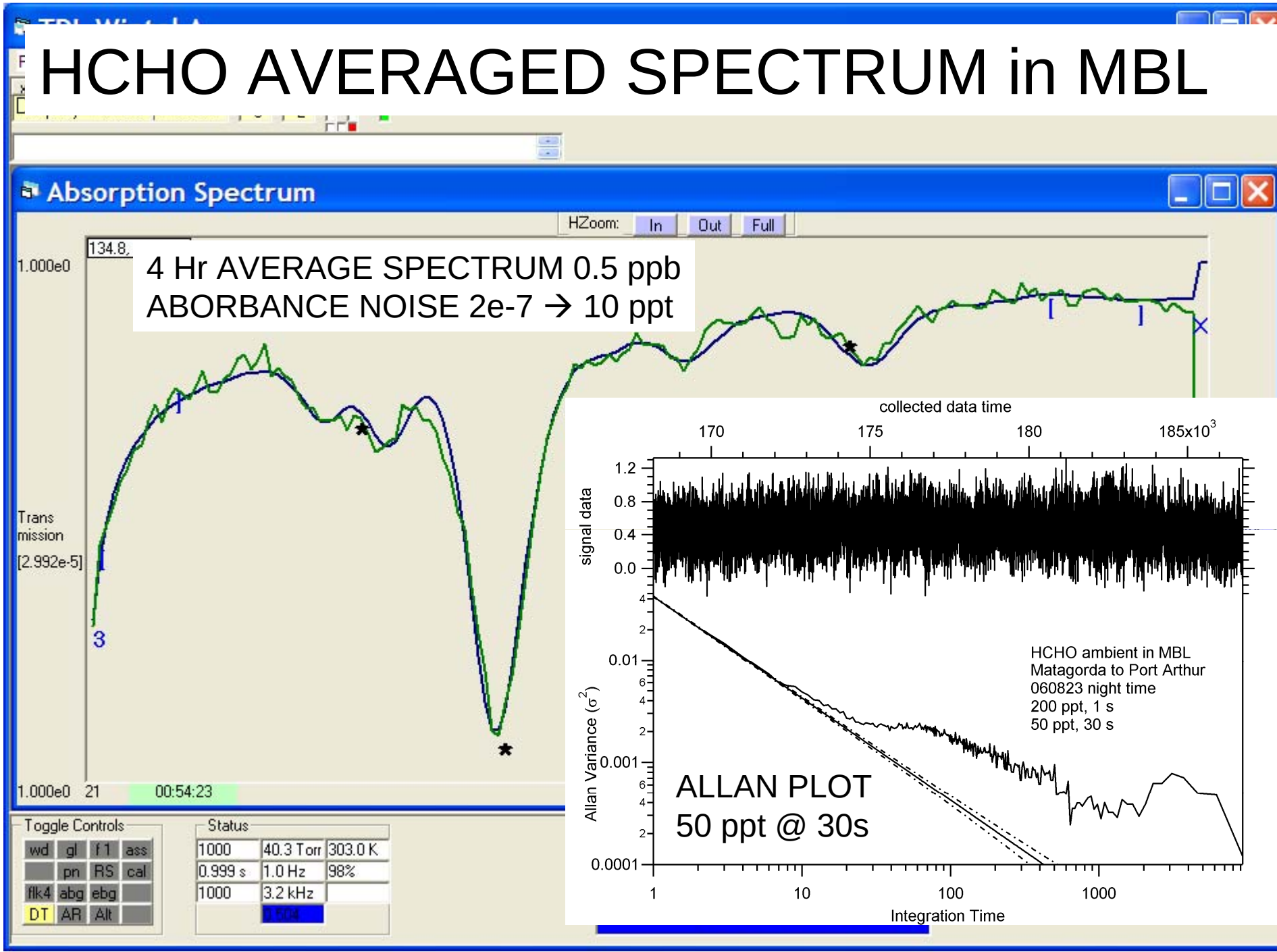
Instrument in Deck Trailer
Tunable Infrared Laser-
Differential Absorption Spectroscopy

Dual Quantum Cascade Lasers

Two Wavelength Regions contain 4 decent absorbers



HCHO AVERAGED SPECTRUM in MBL



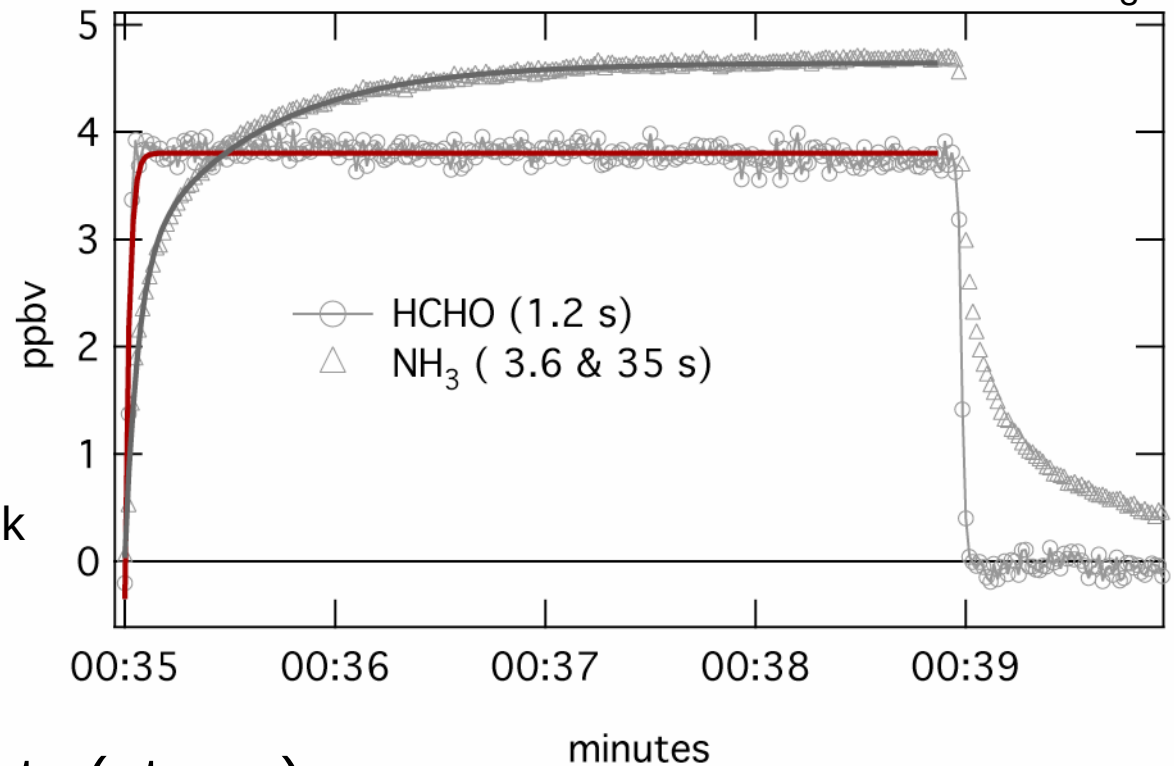
Inlet Characterization Results

Advice from Osthoff, Roberts, Kuster

At-Sea
Inlet Characterization
(5 mins. of each hour)
Even hours:
  Perm + Zero Air
Odd hours:
  Standard Addition

HCHO: inlet transmission
  complete and quick
NH_3: inlet transmission
  ok but slow

Permeation sources of HCHO and NH_3

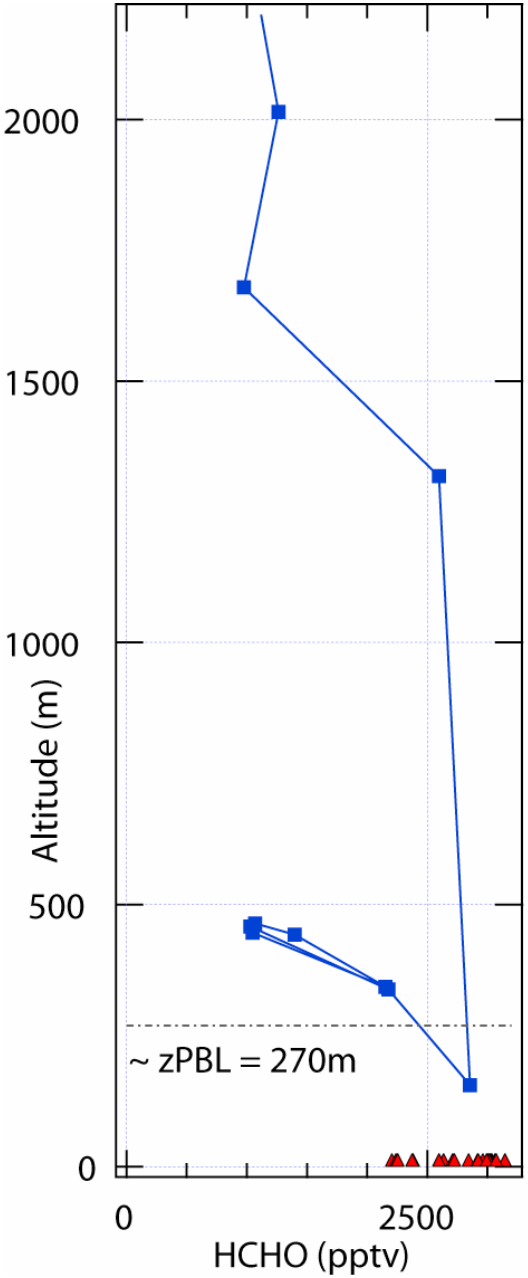


Additional Inlet Tests (at sea)

Total Flow Variations
  different residence times
  by factor of 5, saw
  no difference
  in diurnal MBL HCHO

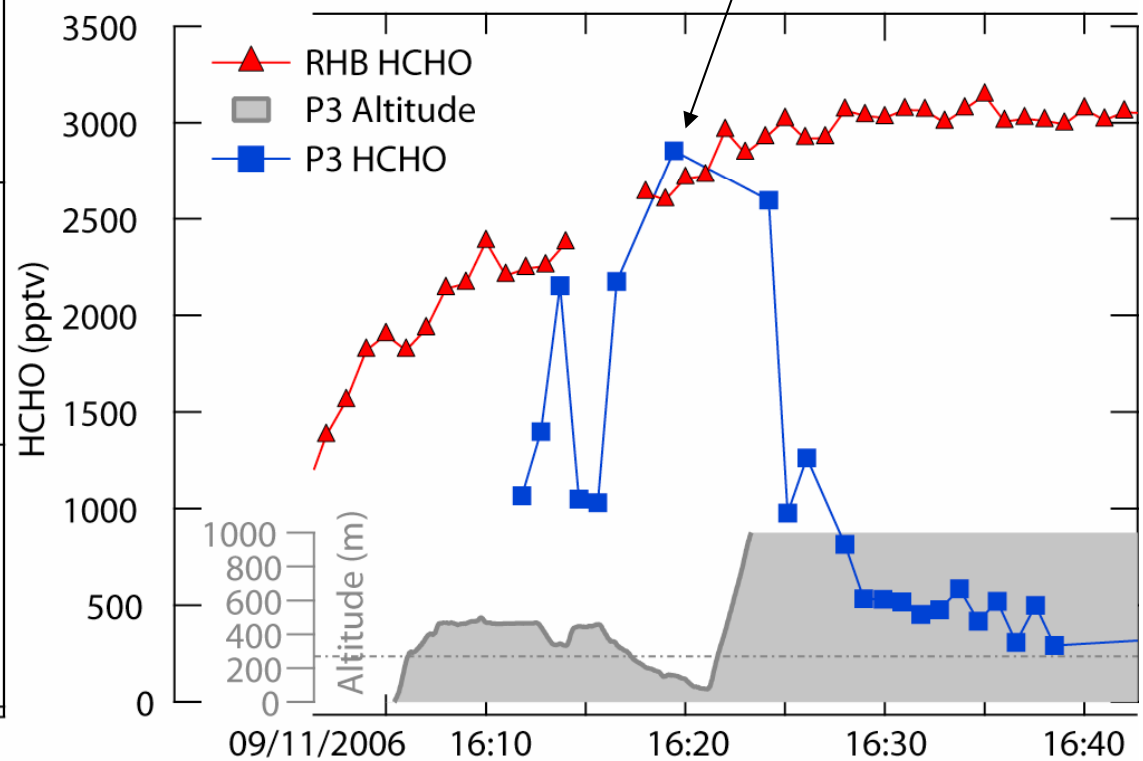
With O_3 Addition
Alternate ambient O_3
and enhanced (120 ppbv) O_3

No change in measured HCHO in MBL



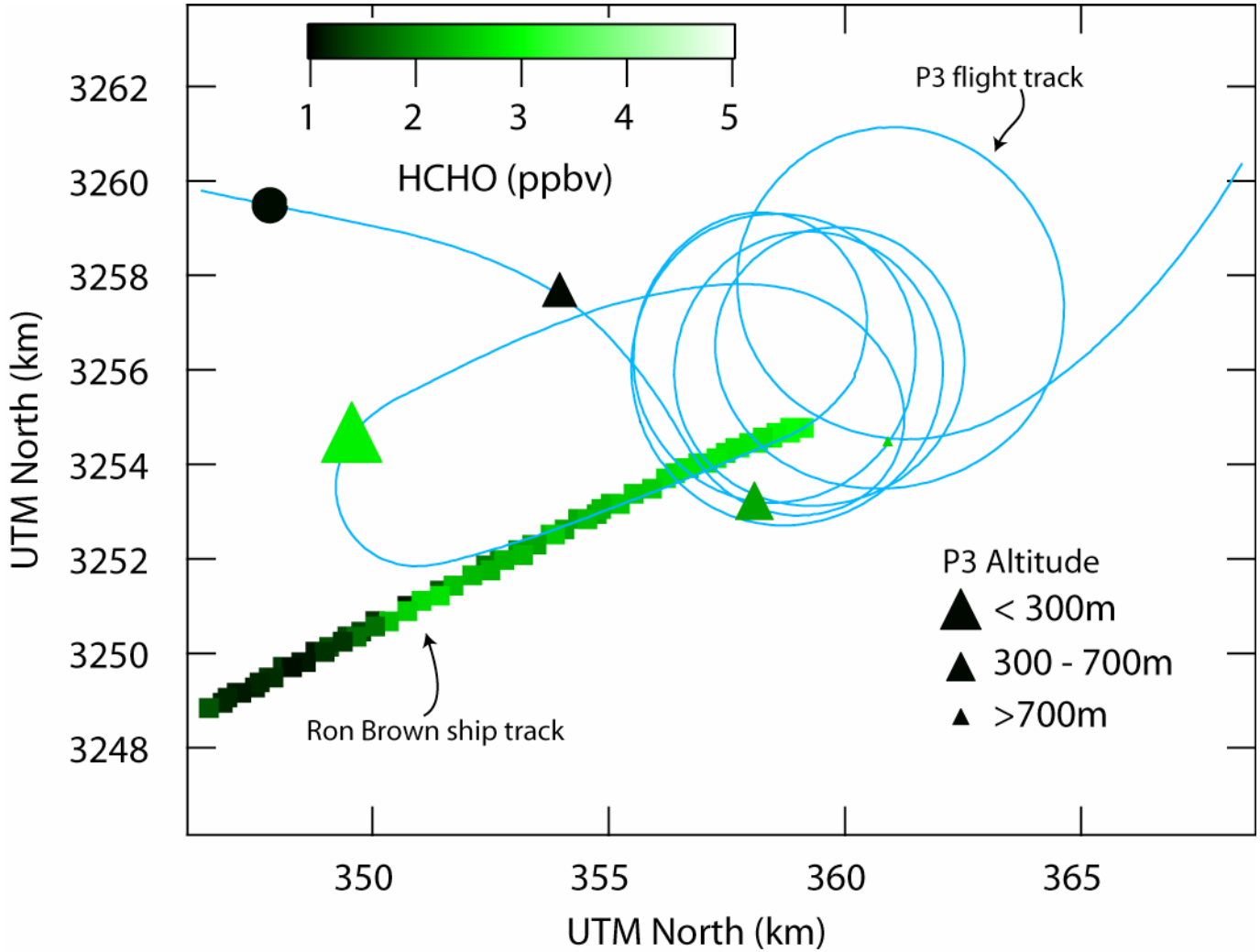
Ron Brown comparison with P3 overflight

Below PBL raw difference is 7.5%



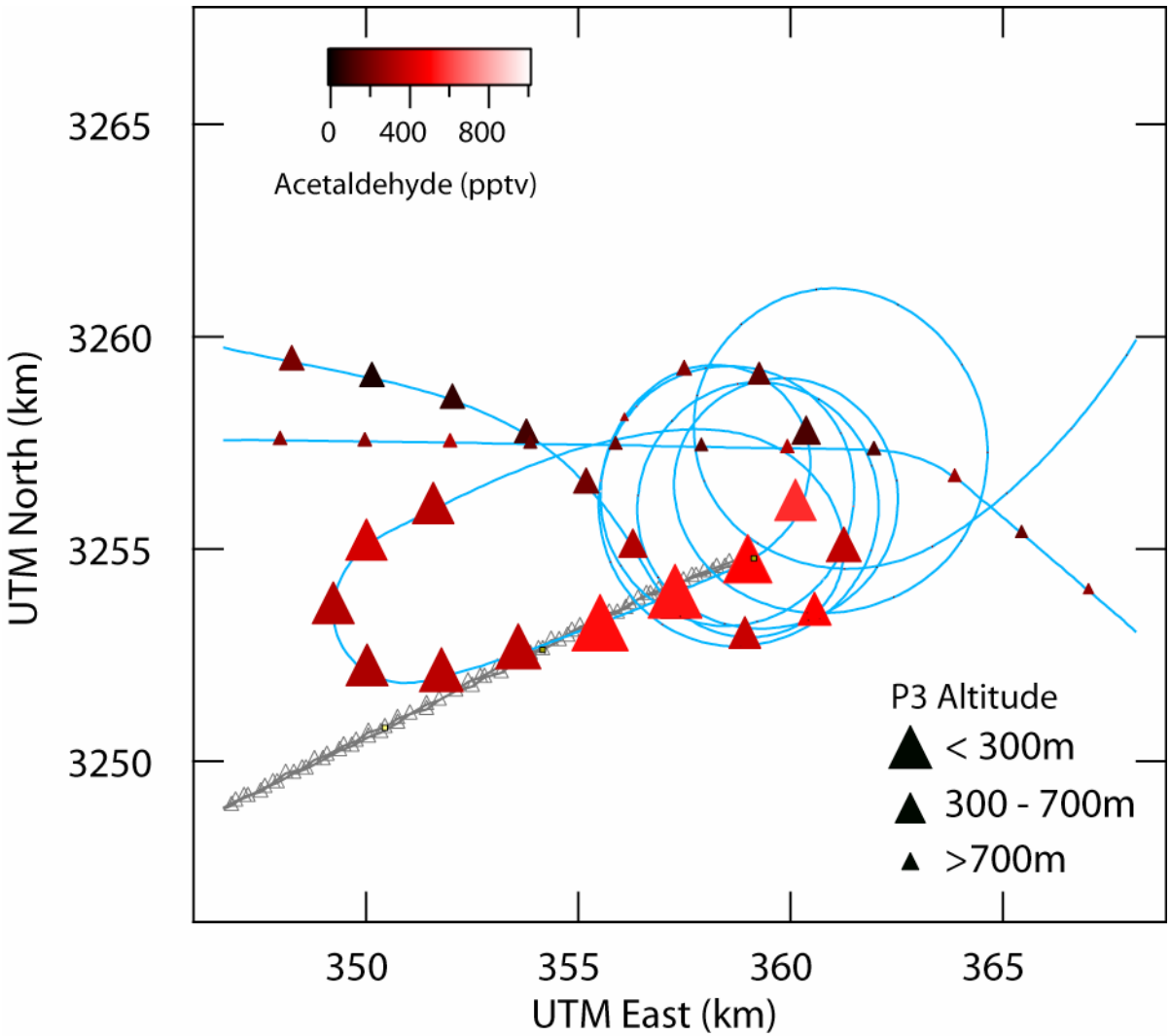
P3 HCHO - Richter, Fried et al.

HCHO comparison - North vs East



Overflight comparison is short -
spatial overlap - amounts to one point comparison

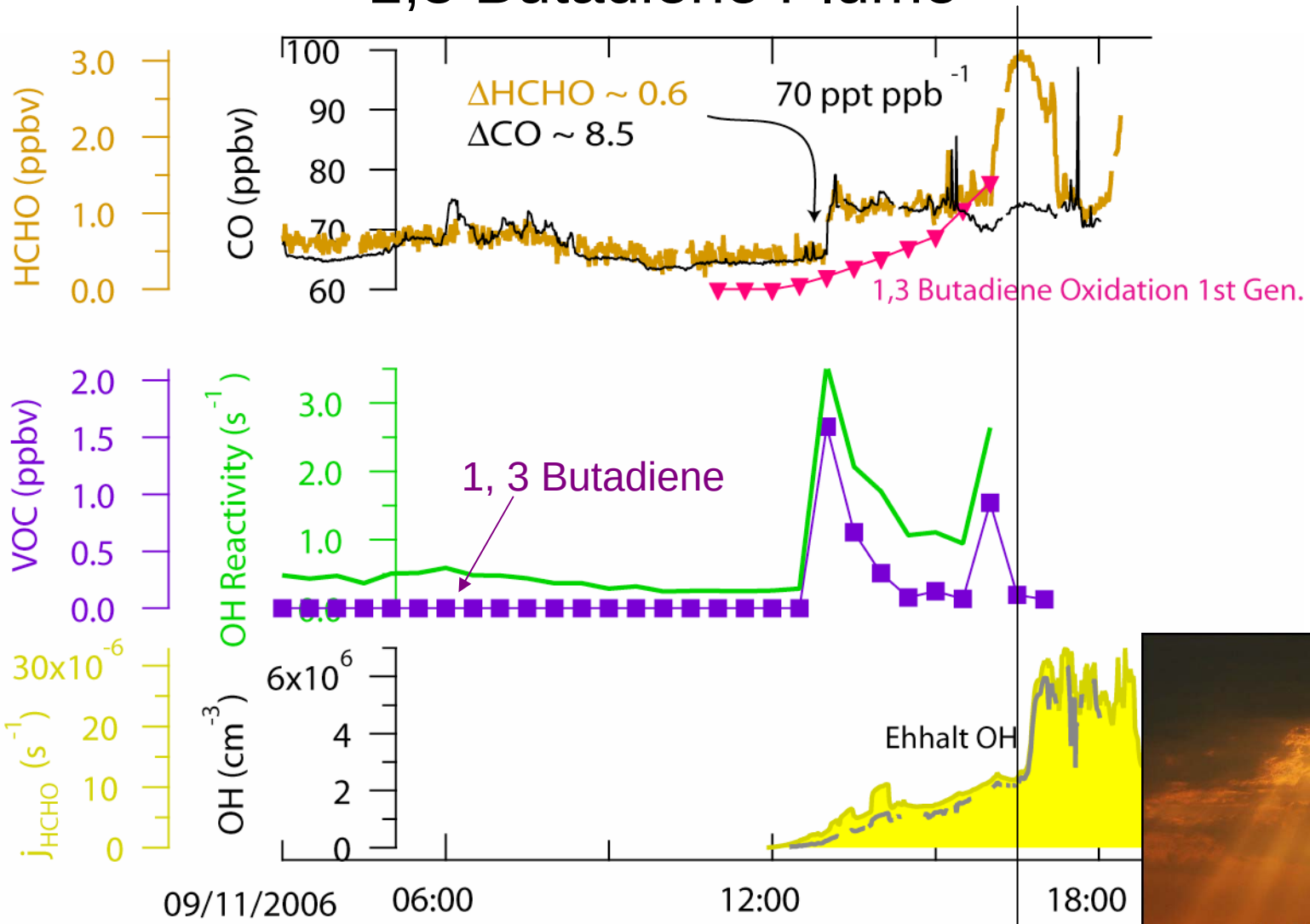
Acetaldehyde - North vs East



Airmass below PBL where HCHO was elevated also has high CH_3CHO

de Gouw, Warneke, Welshbon

1,3 Butadiene Plume



1,3 Butadiene oxidation yeilds, Sprengnether et al. & Tuazon et al.

Lerner, Gilman, Kuster et al.

overflight

Primary, Secondary HCHO

'Primary' = directly emitted from various sources
'Secondary' = produced in the atmosphere

HOx source
costs an OH, O_3 et al.

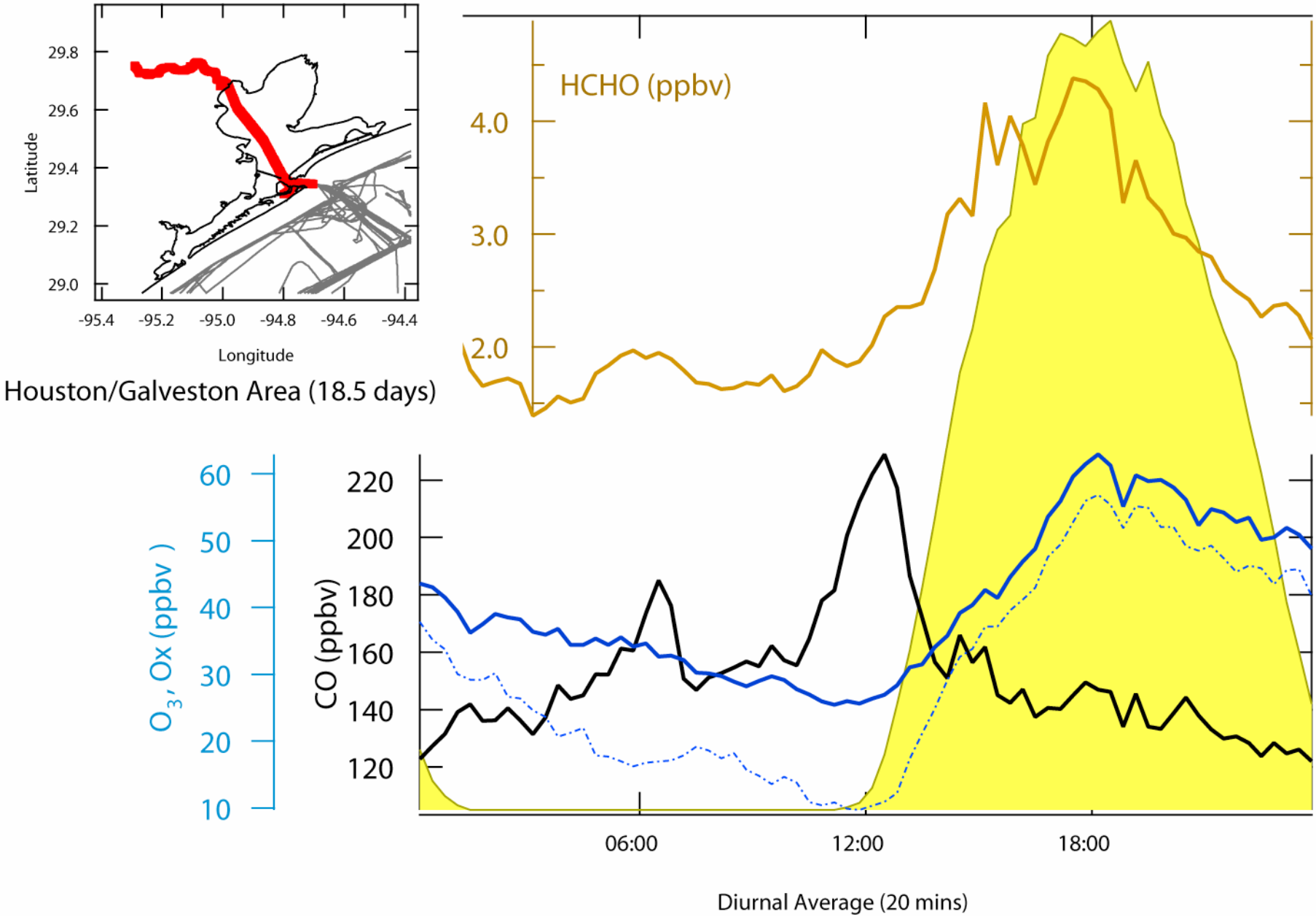
Part 1: Time-series analysis
untangle directly emitted HCHO from atmospheric production

Houston/Galveston Bay Area
diurnal average & median
Tracer Pair Correlation, CO and O_3

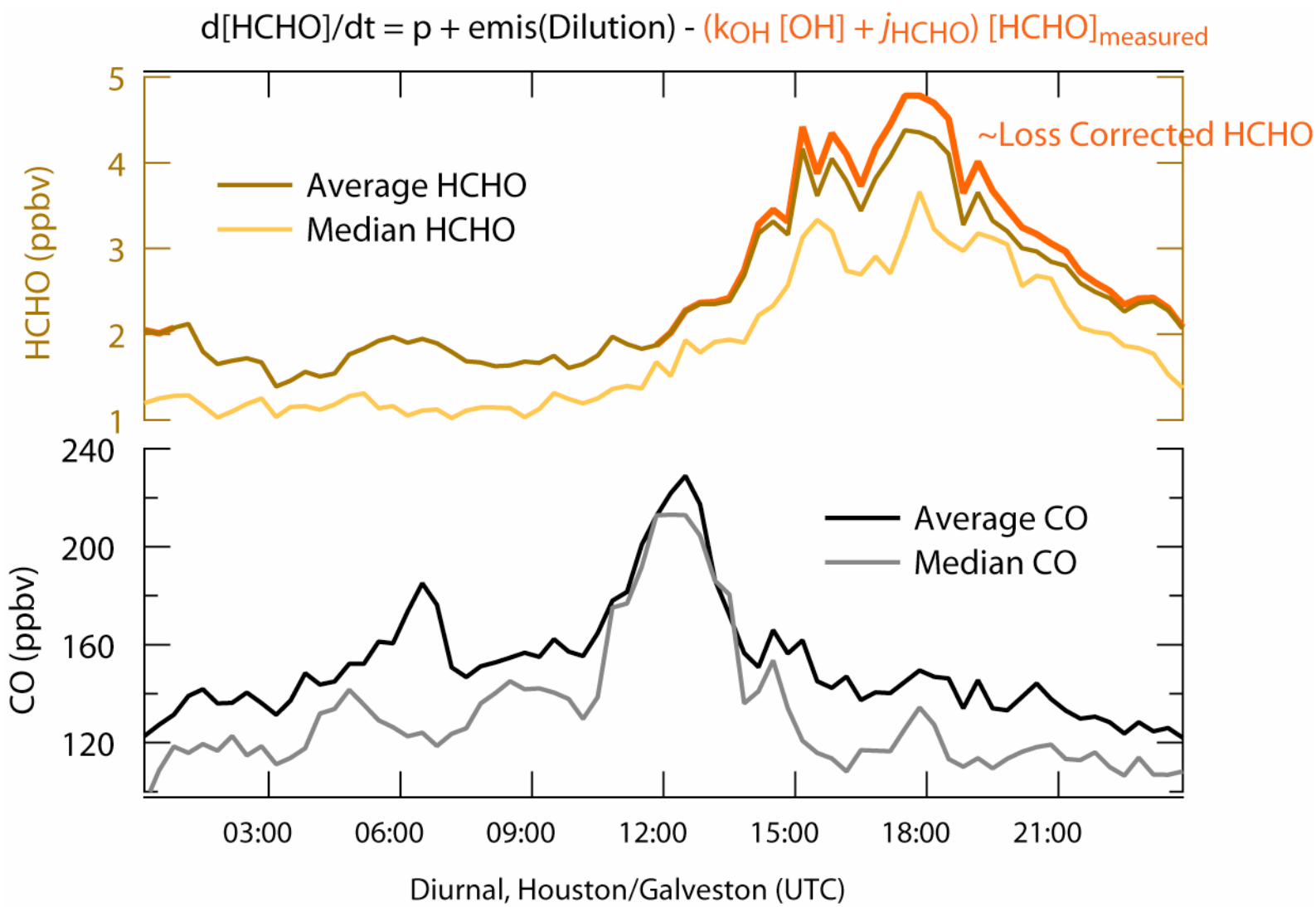
Part 2: Exhaust Plume Analysis (w/source attribution)
Measure directly emitted HCHO, ratio by dilution tracer CO_2

Ship Channel Plume Encounters (Williams et al.)
Anchored Ship Emissions
Drilling Platform (gas-flare vs diesel generator)

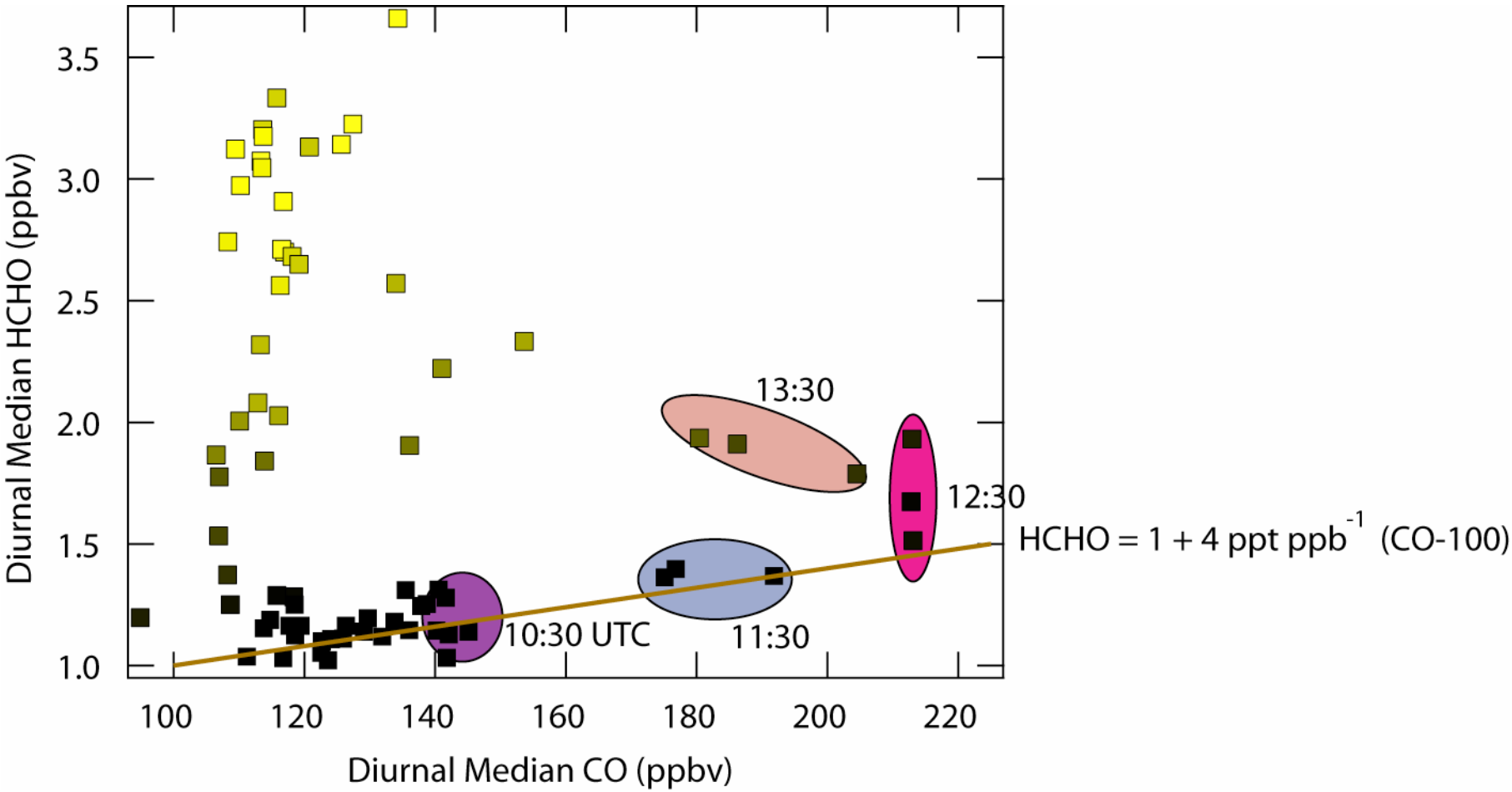
Houston/Galveston Bay - Diurnal HCHO



Diurnal Median vs Average

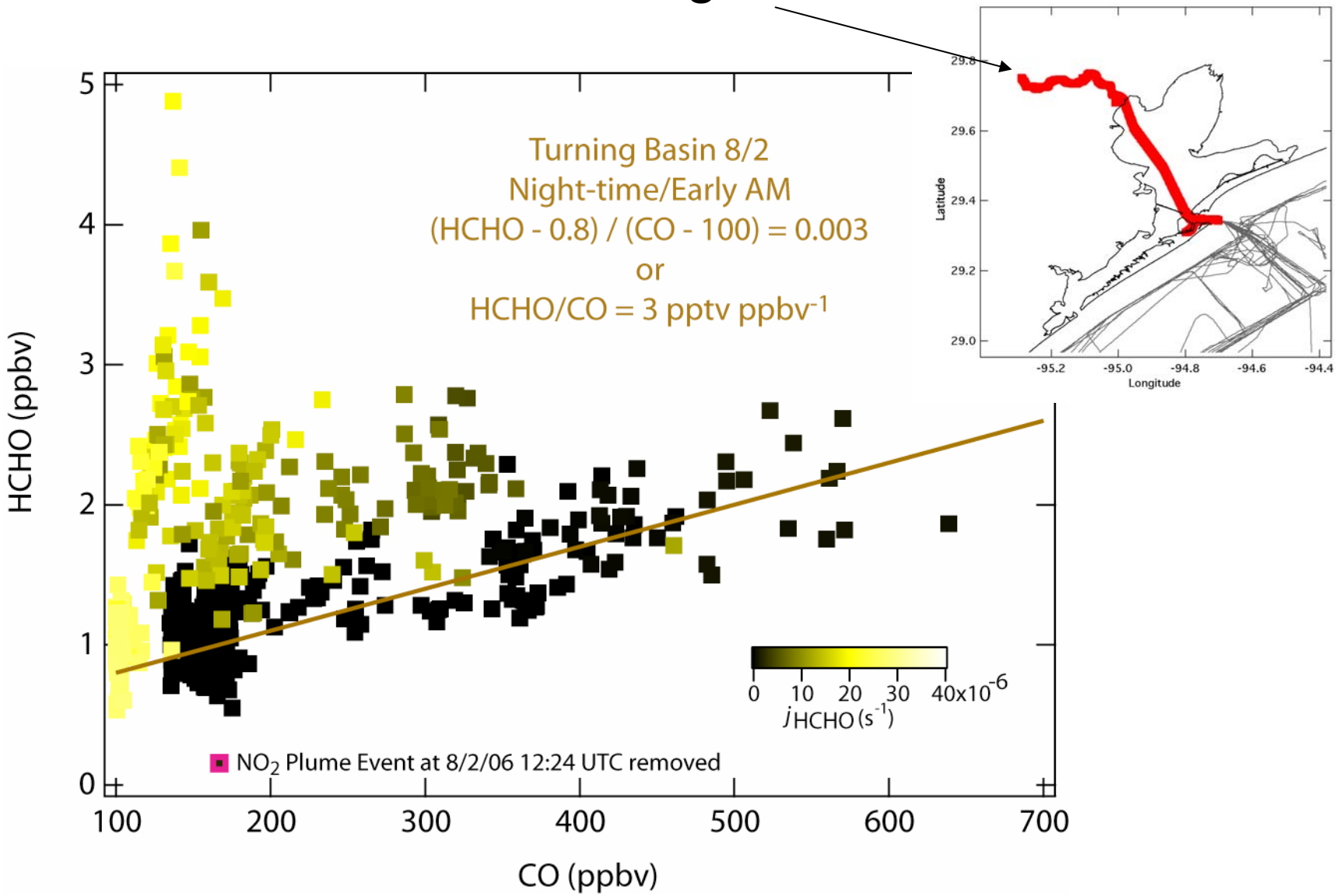


Simple HCHO vs CO correlation



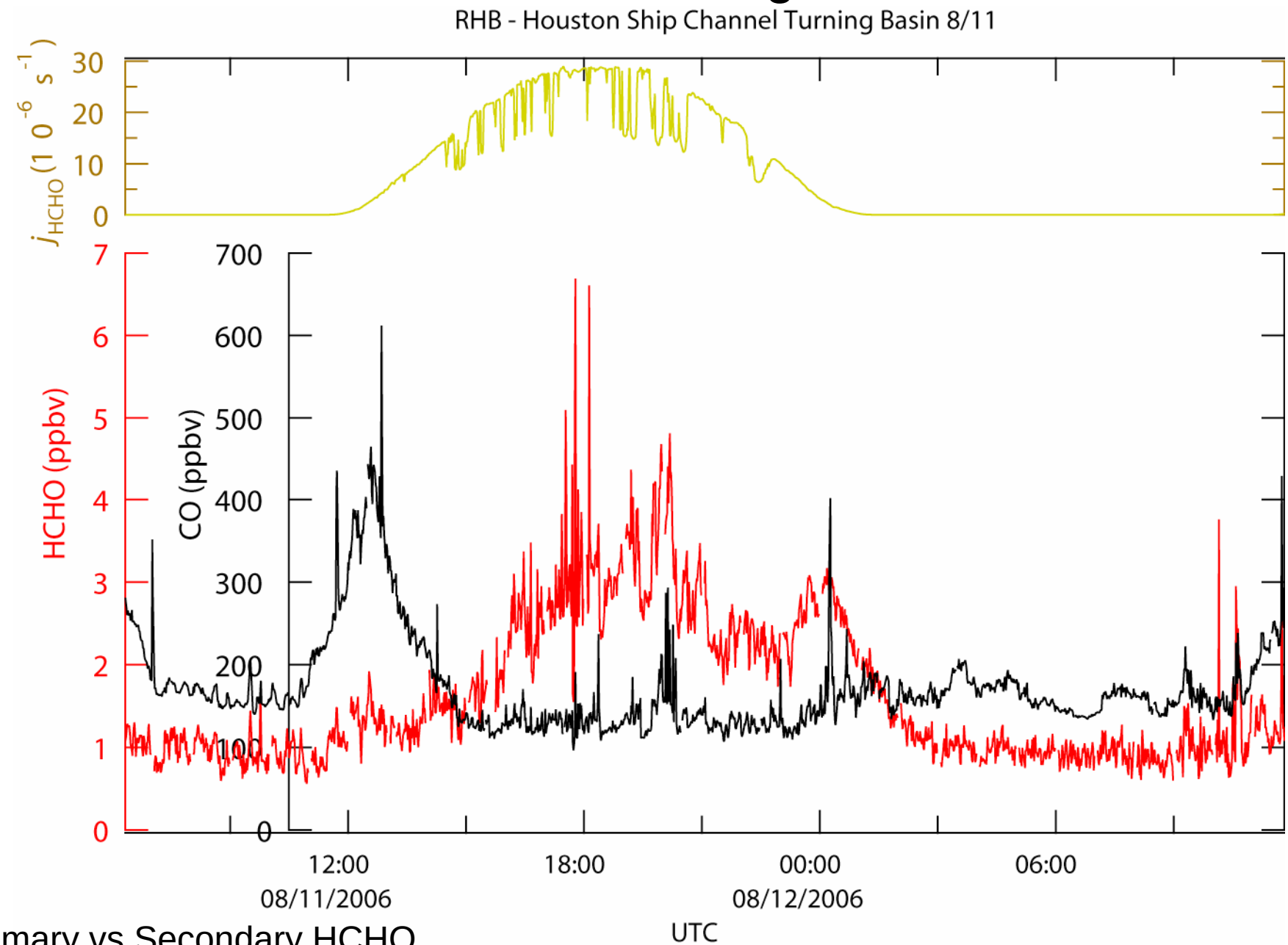
How representative is median correlation plot of Houston Ensemble Emissions?

First Visit to Turning Basin 8/2



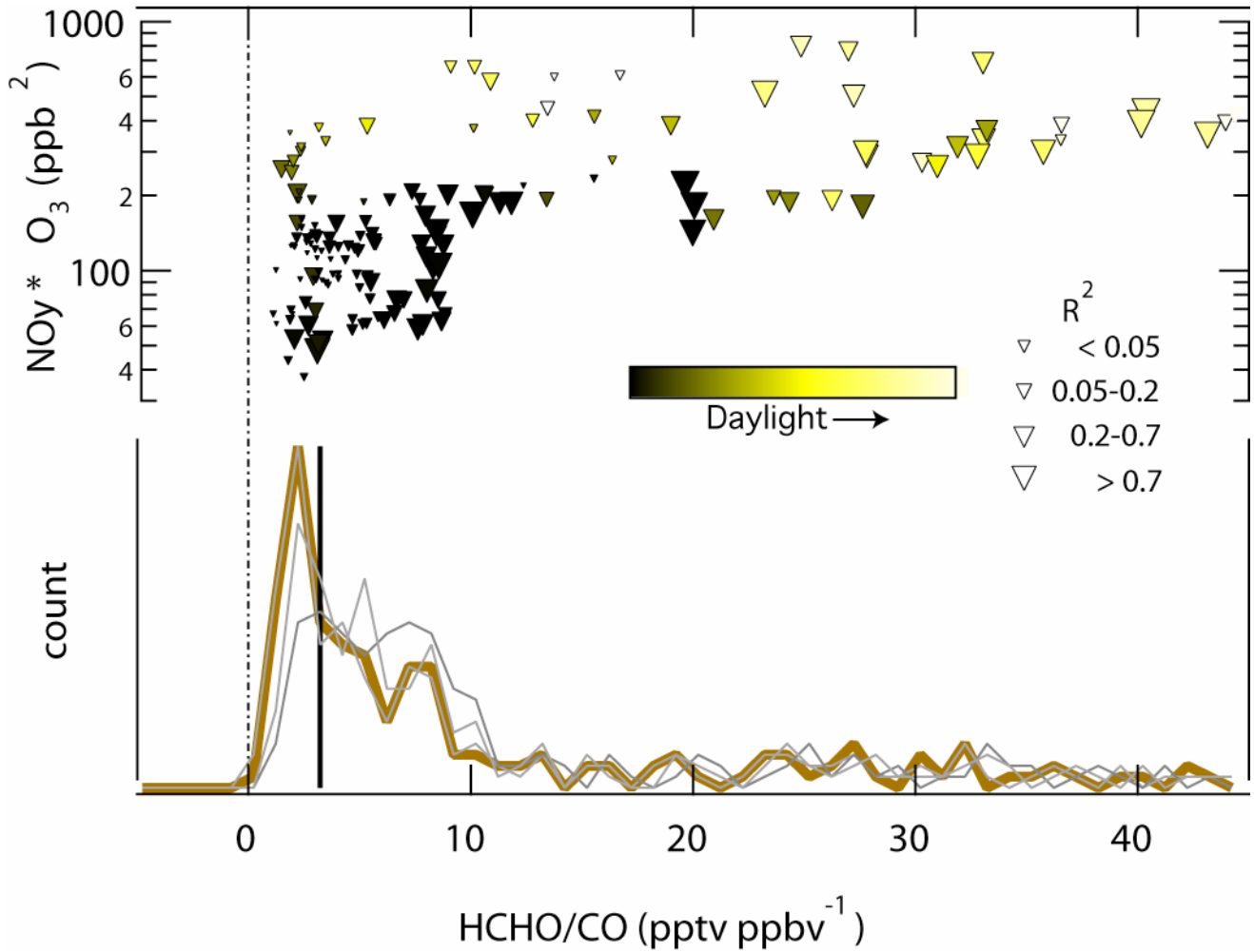
Primary vs Secondary HCHO

Second Visit to Turning Basin 8/11



Primary vs Secondary HCHO

Plume by Plume Analysis HCHO/CO



30 minute segments in the turning basin analyzed for primary HCHO/CO plume content; 2 - 10 ppt/ppb

Primary vs Secondary HCHO

Primary vs Secondary HCHO

Friedfeld et al. - Tracer Pair (CO w/time lag; O_3)

Houston Area: **Primary HCHO 37%**

Possanzini et al. HCHO/Toluene

Rome, Italy: Primary **less than 20%** in summer

Li et al. - Principal Component Analysis

Vancouver: **Primary~ 20%**

Jimenez et al. Tracer Pair (NOx; O_3)

Grenoble, France: **Primary <20%**

Garcia et al. - Tracer Pair (CO; glyoxal & CO; O_3)

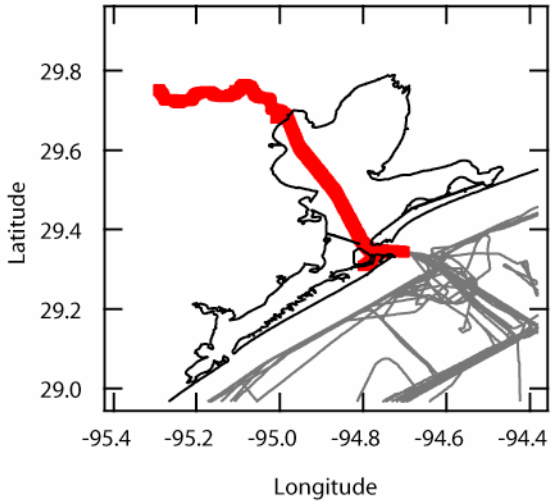
Mexico City Metro. Area: **Primary 40%**

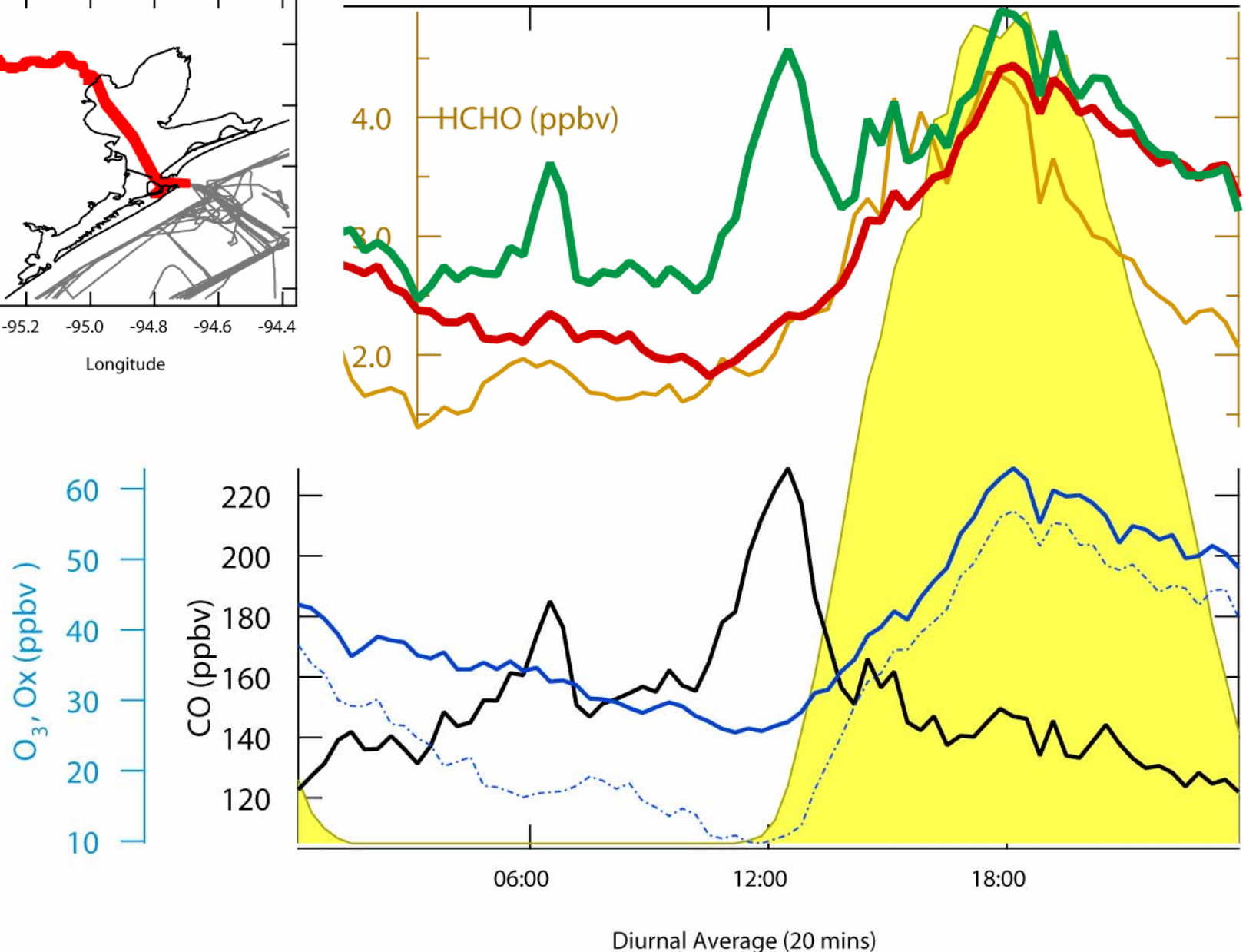
(allowing for ~20% as point source, or area bg.)

Return to Diurnal - CO, O_3

Scenario #1 HCHO = 1.25 + 0.03 * (CO - 120) + 0.06 * (O_3 - 10)

Scenario #2 HCHO = 1.25 + 0.008 * (CO - 100) + 0.06 * (O_3 - 10)





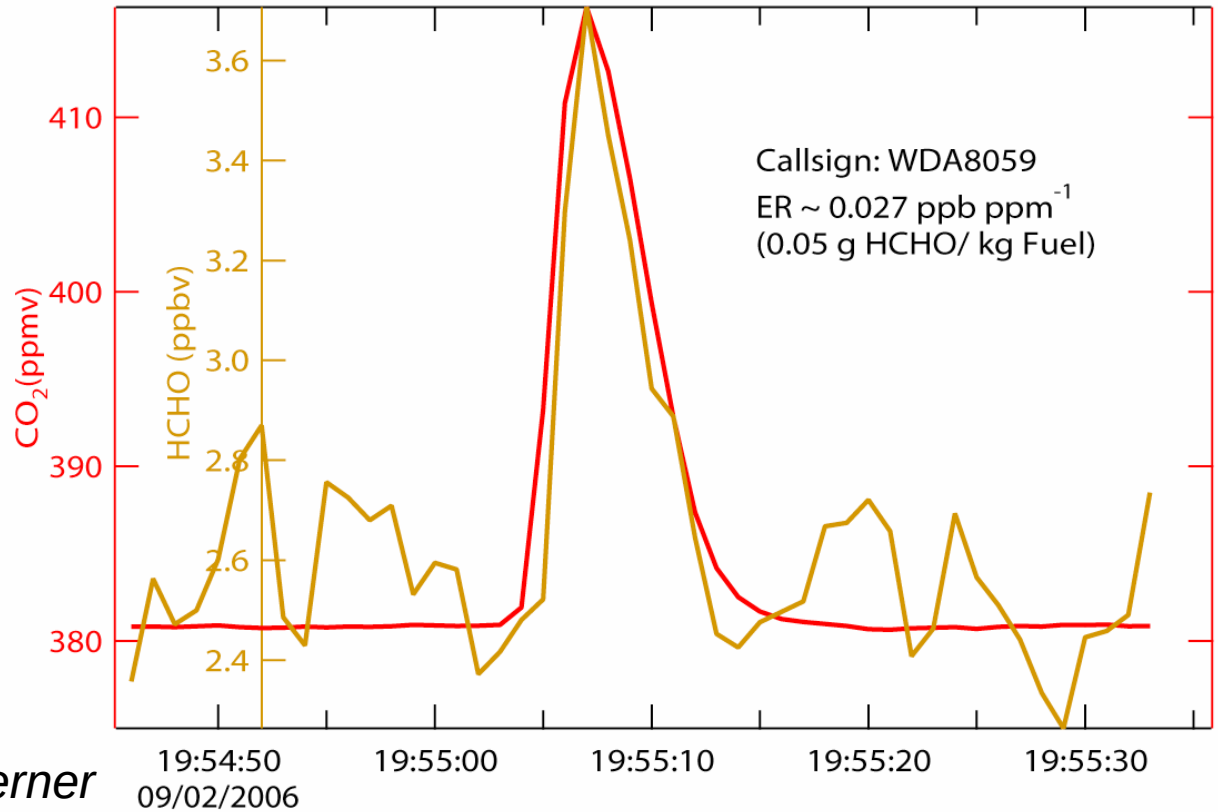
H_2CO Loadings by Combustion Sources

		ppb H_2CO / ppm CO_2
Automobiles with functioning Catalytic Converter		<0.05
Gasoline "Engine Out"		0.2-0.4
Diesel Heavy Duty		<0.03-0.1
Compressed Natural Gas		~0.5
high bypass turbine engine (aircraft engines)	low throttle	0.9-2.2
	take-off	<0.02
Ships in HSC		?

Ship Emissions

Time Series of HCHO and CO_2

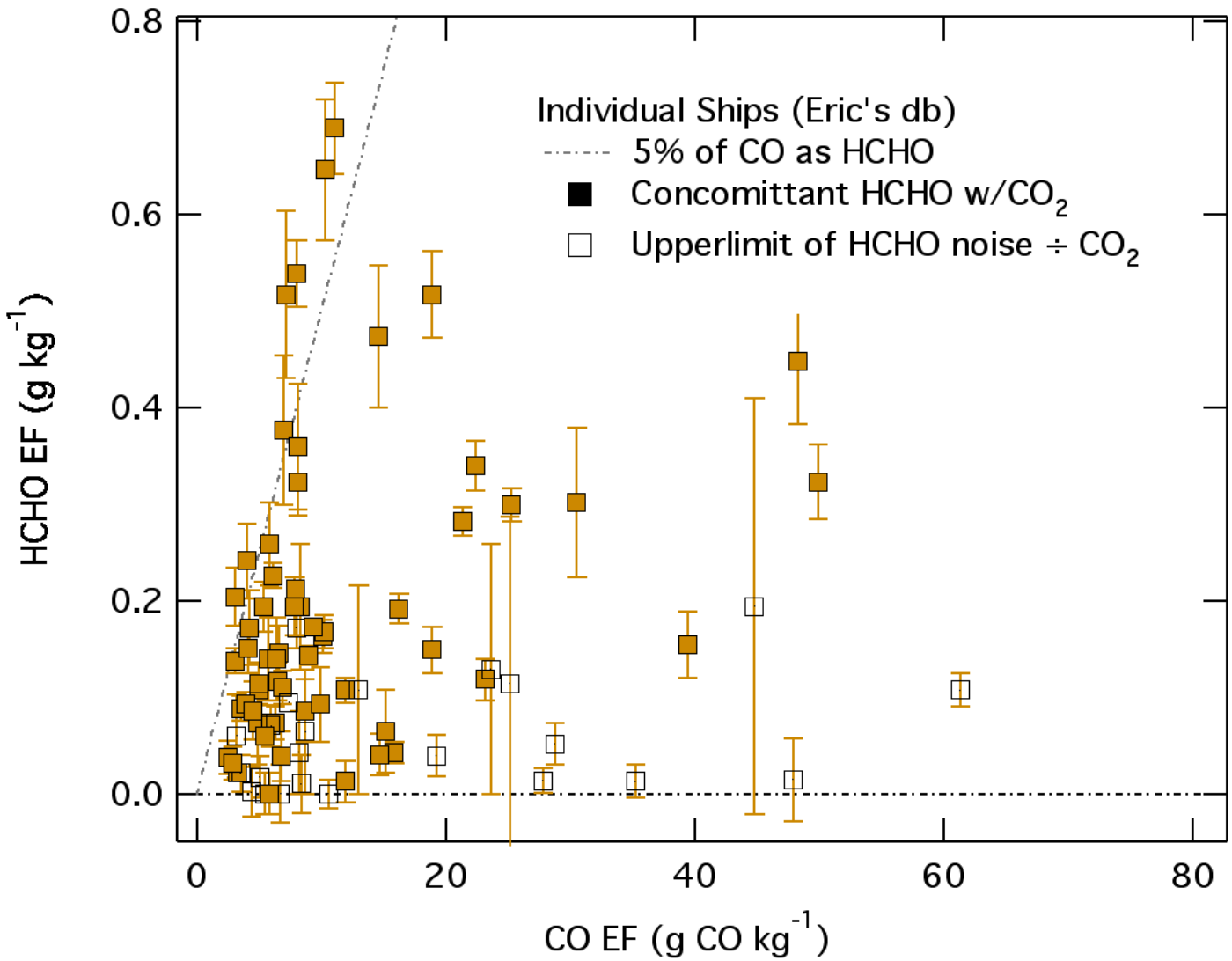
despite different inlets, and different computer times plume attribution is possible (Δt = 3.7s)



Primary HCHO Direct Measurement

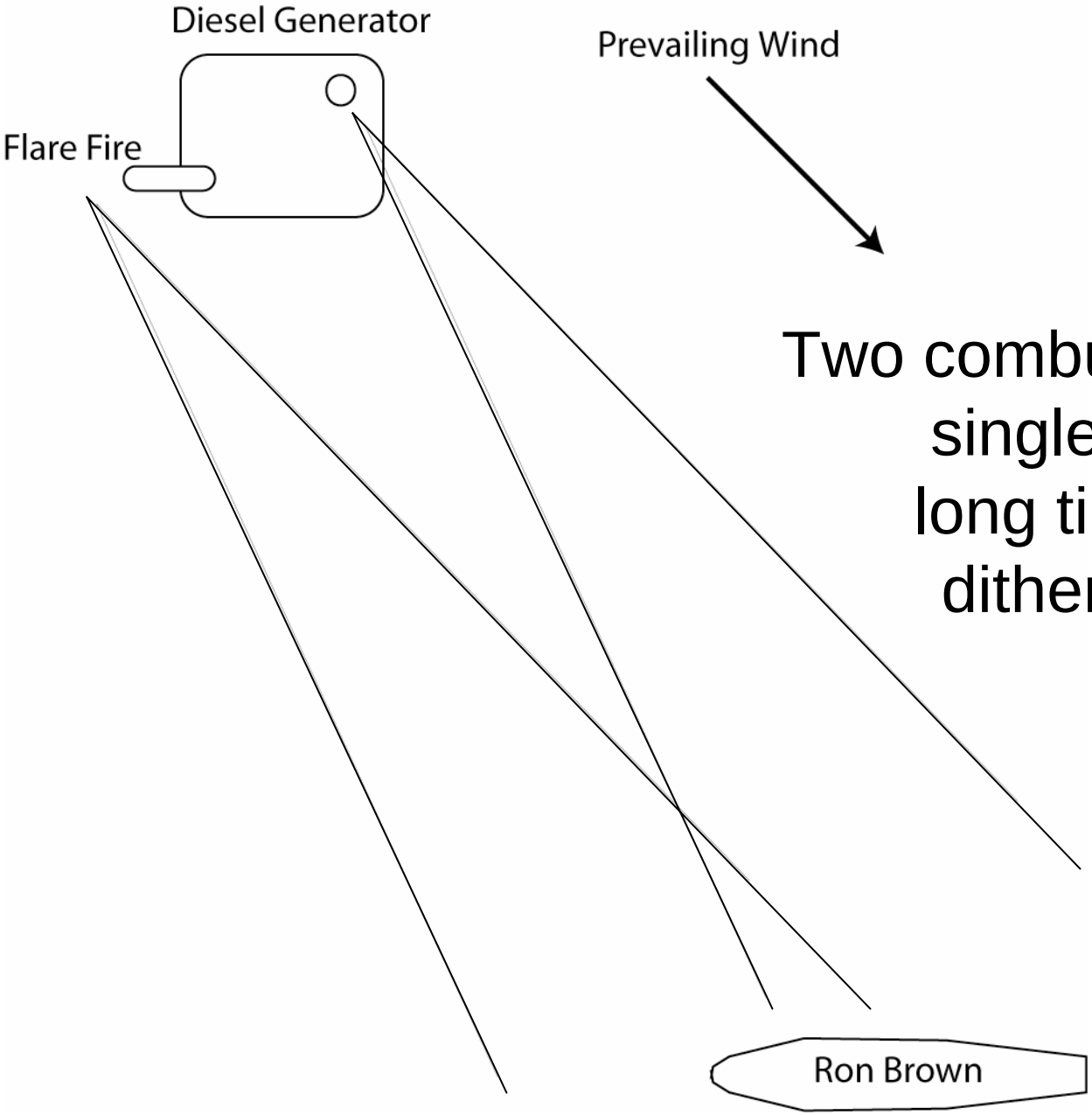
Williams and Lerner

Despite challenges, can limits be set for direct HCHO emissions?



tentative anticorrelation with target speed

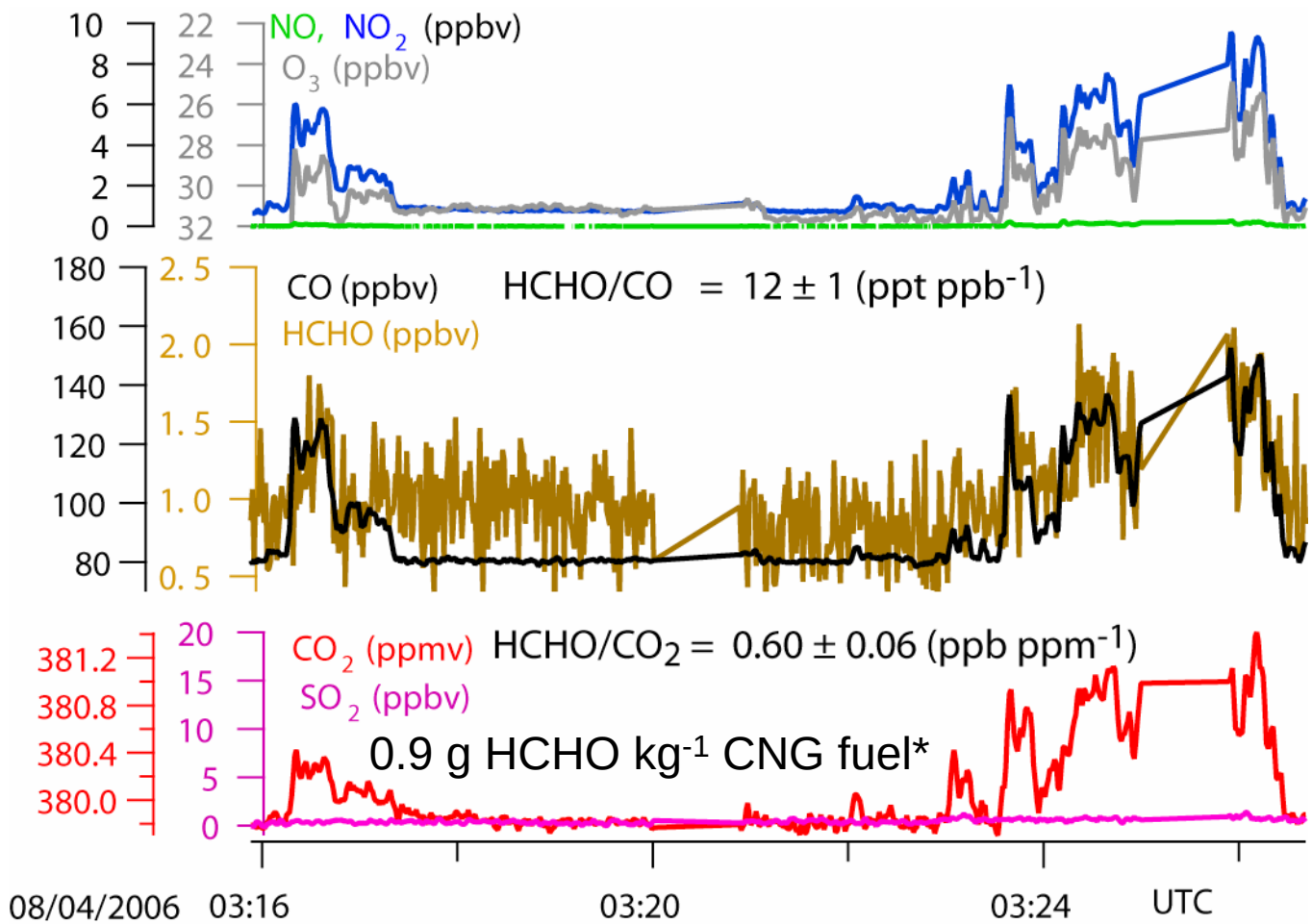
Primary HCHO Direct Measurement



Two combustion sources
single platform
long time series
dithering wind

Primary HCHO Direct Measurement

Drilling Platform Flare Fire vs Diesel Generator



Dan Lack Photoacoustic Black Carbon ⇒ER(BC) flare ~ 1/2 diesel

Diesel Generator contained Fuel Sulfur Content ~2%

Primary HCHO Direct Measurement

H_2CO Loadings by Combustion Sources

		ppb H_2CO / ppm CO_2
Automobiles		
with functioning Catalytic Converter		<0.05
Boston Fleet Traffic		0.03
Mexico City Fleet (2002)		0.14
Mexico City Fleet (2006)		0.11
Gasoline "Engine Out"		0.2-0.4
Diesel Heavy Duty		<0.03-0.1
Compressed Natural Gas		~0.5
high bypass turbine engine		
(aircraft engines)	low throttle	0.9-2.2
	take-off	<0.02
Ships in HSC		0.02-0.15
1 Flare in Gulf of Mexico		prelim analysis ~ 0.6

Summary and Conclusions

Dual QCL TILDAS Performance

- HCHO 1s rms < 250 pptv; 2σ D.L. (1 minute) 75 pptv

- Systematic Error Est. 7% linestrength, 9% total

- No evidence of Inlet effects for marine BL HCHO

- Instrument also measured HCOOH, C_2H_4, sharp NH_3 plumes*

Analysis

-Diurnal time-series suggest substantial photochemical production

- Turning Basin ER (HCHO) 30 min dist. (2-10) **3** ppt ppb^{-1} CO

-CO, O_3 tracer pairs indicate <u>upper limit</u> for HCHO/CO

ER (HCHO) 0.008; (8 ppt ppb^{-1} CO)

CO, O_3 do not capture HCHO temporal profile (poor pair)

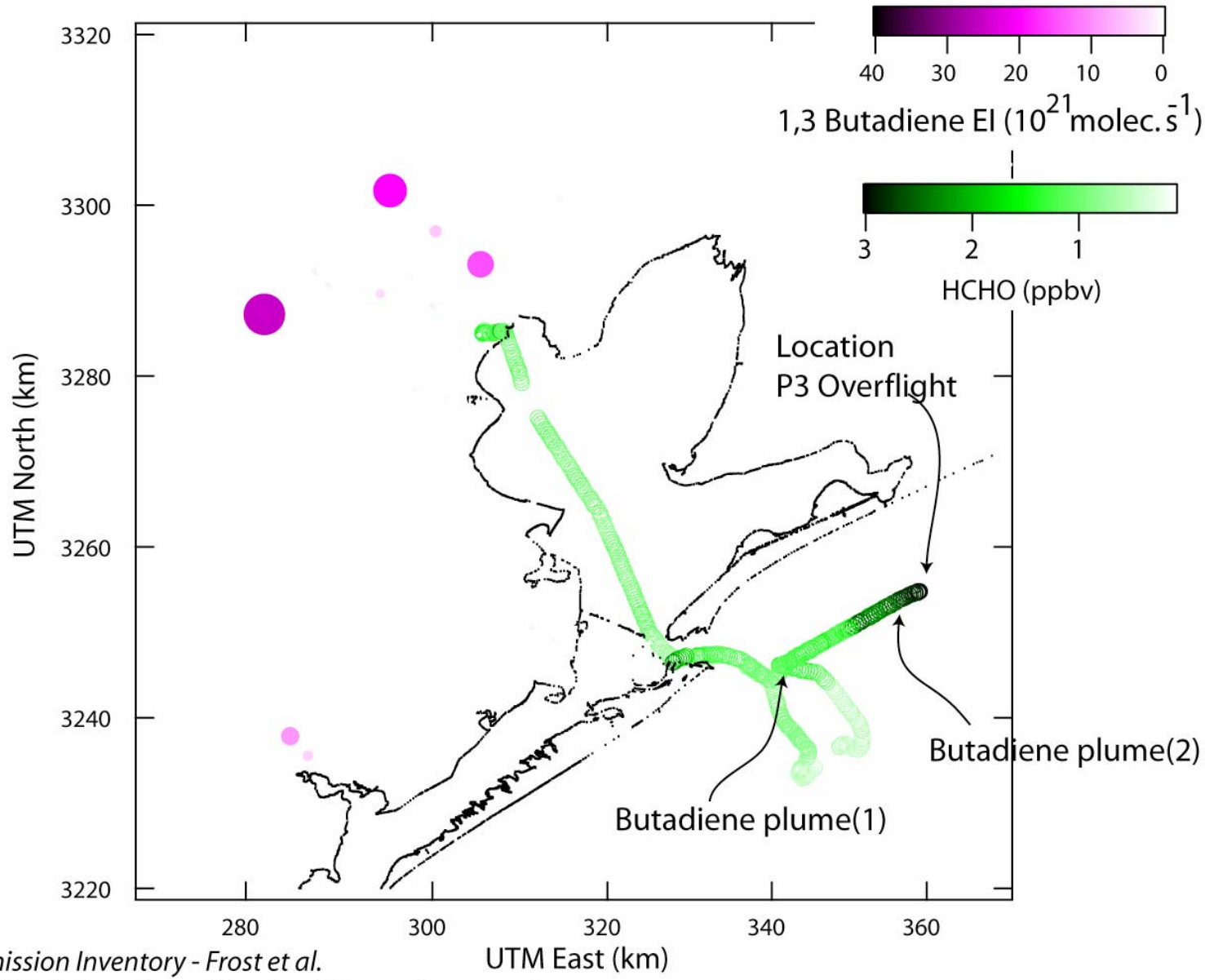
- Direct HCHO EF from working ships in HSC/Galv. (g HCHO kg^{-1} fuel)

- Ship EF is greater than anticipated, more like on-road category

‘diesel working hard’ -- EF < 0.05 * EF(CO)

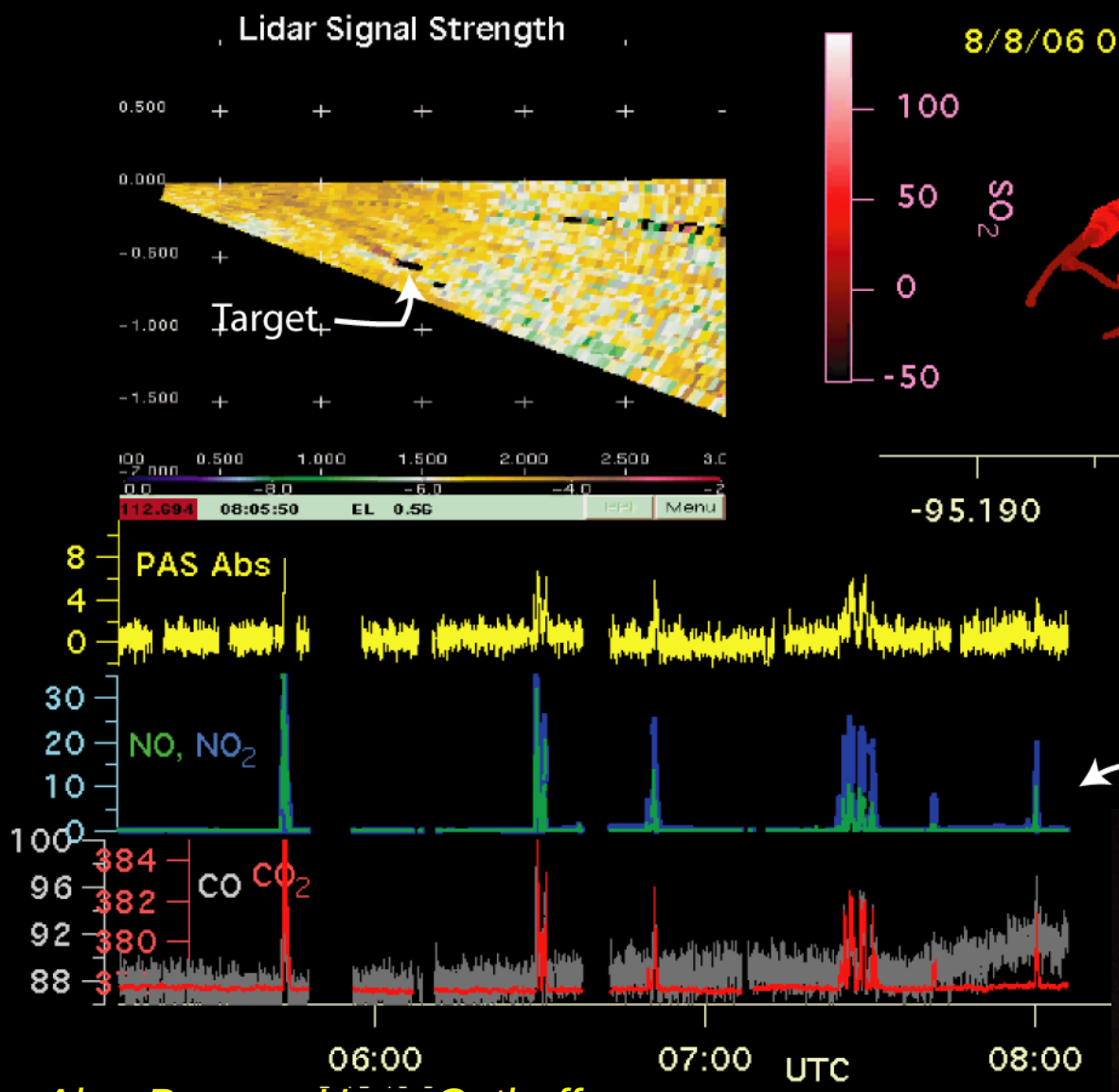
Backup Slides

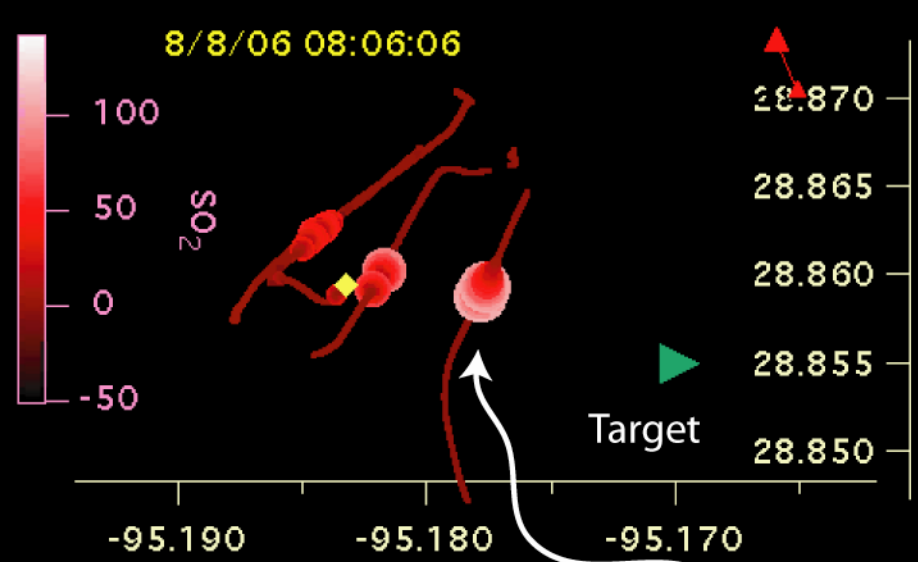
1,3 Butadiene Emission Inventory



Emission Inventory - Frost et al.
HCHO & Butadiene - Herndon, Gilman, Kuster et al.

Anchored Ship Upwind Plume Encounters



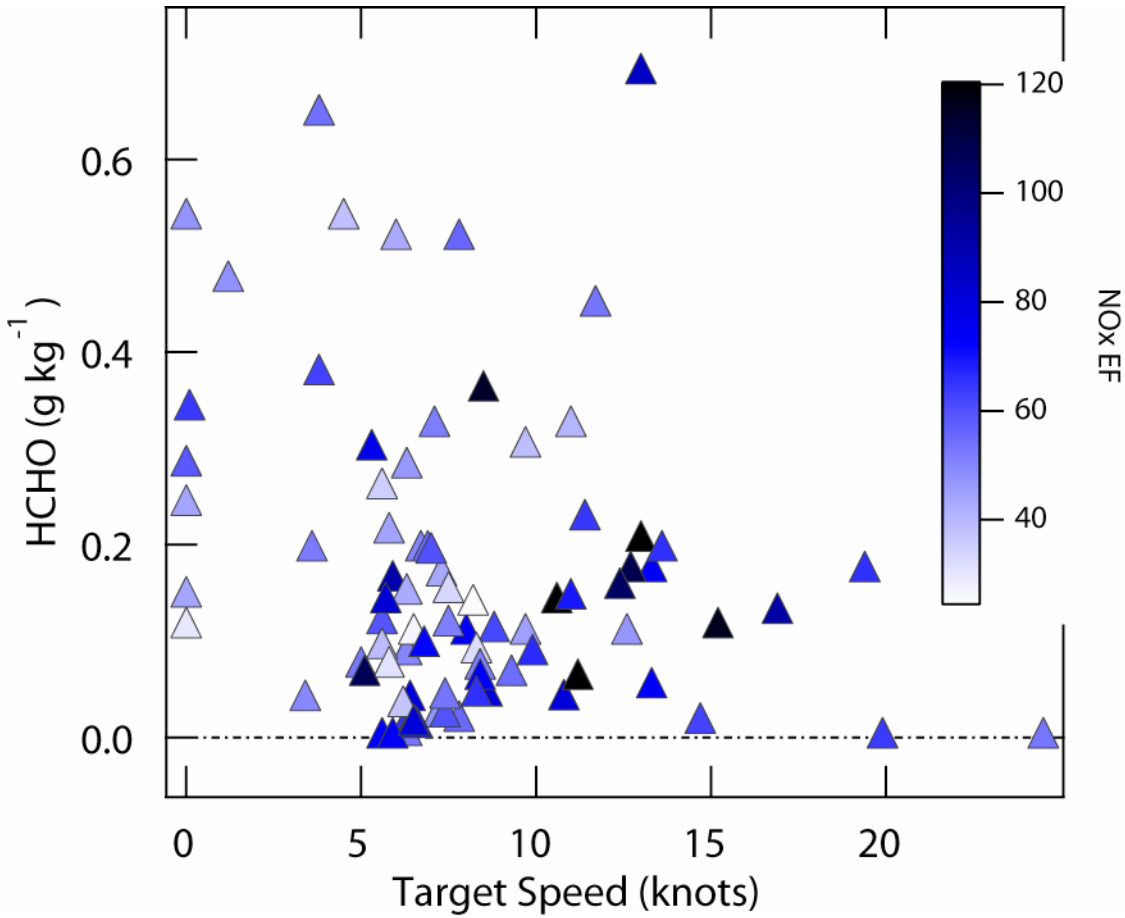


Spatial Plumes
time-series Plumes

Alan Brewer, Hans Osthoff

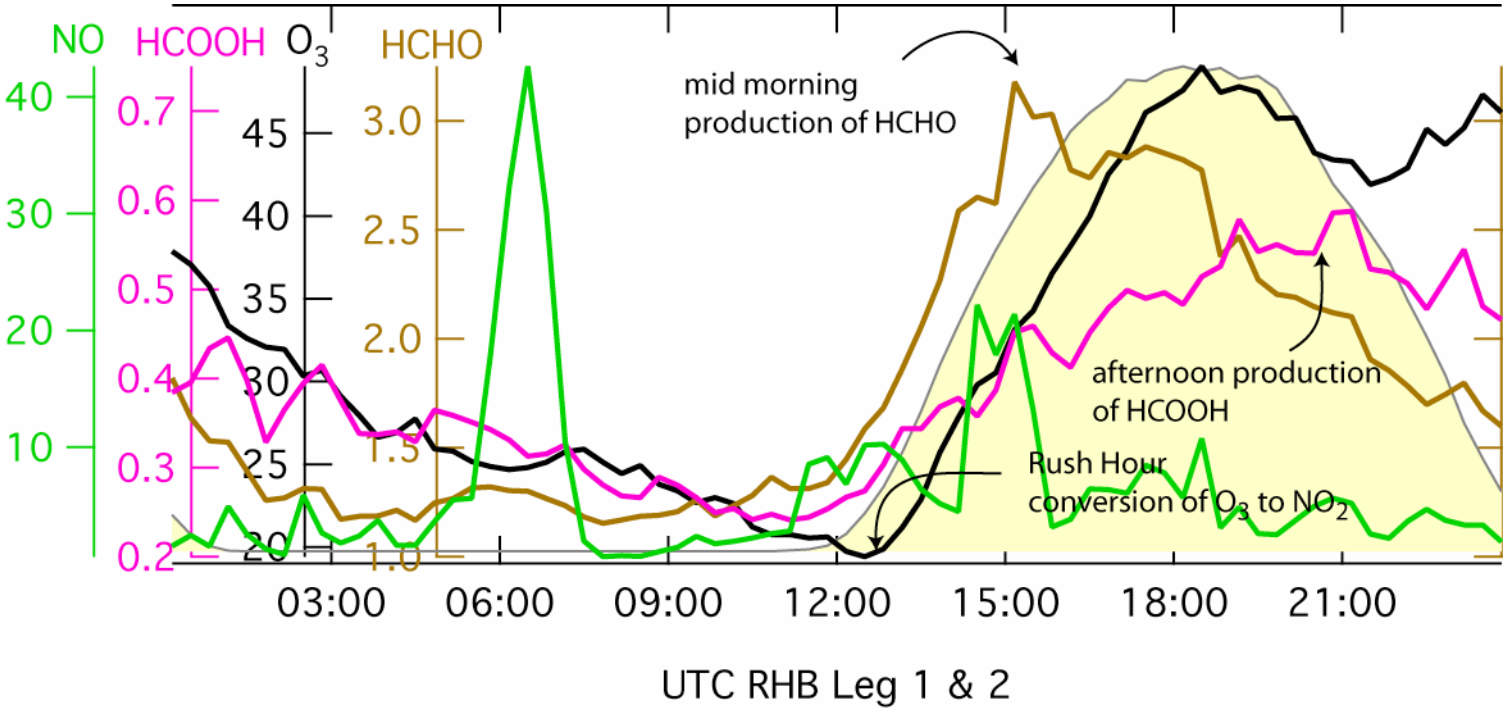
available as a movie

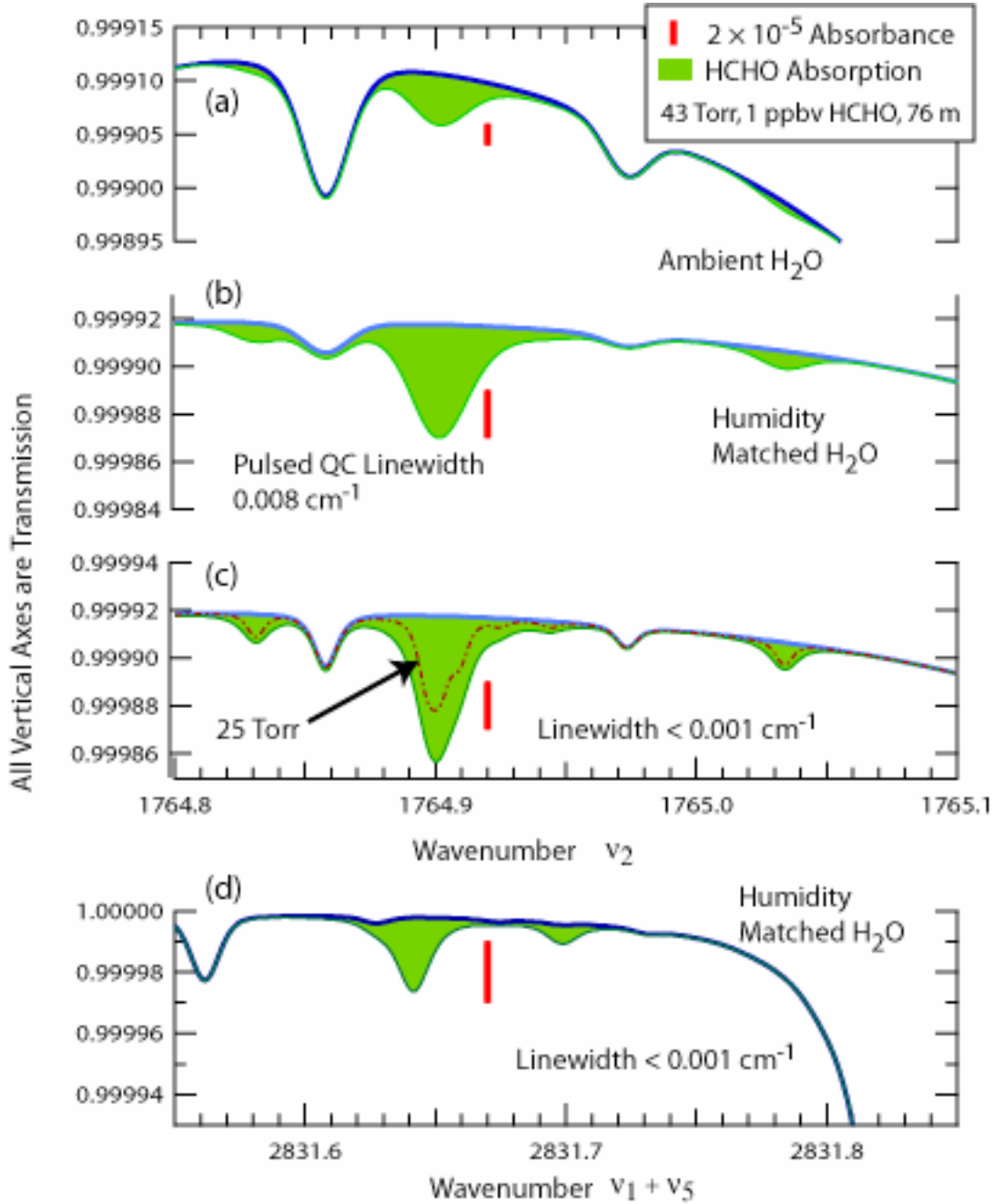
Tentative Inverse Correlation: HCHO with Target Speed

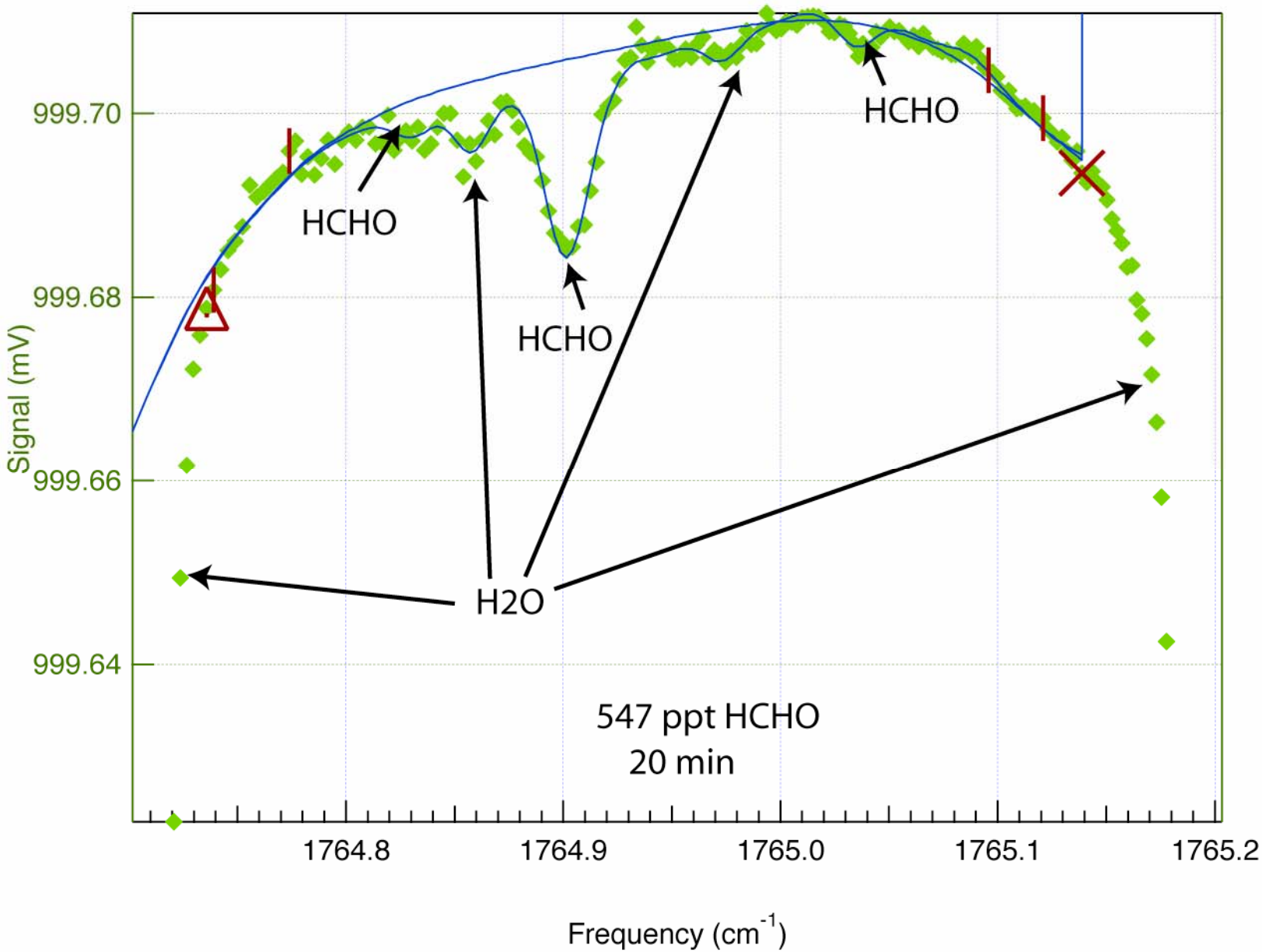


Primary HCHO Direct Measurement

Diurnal Day in Houston-Galveston Area

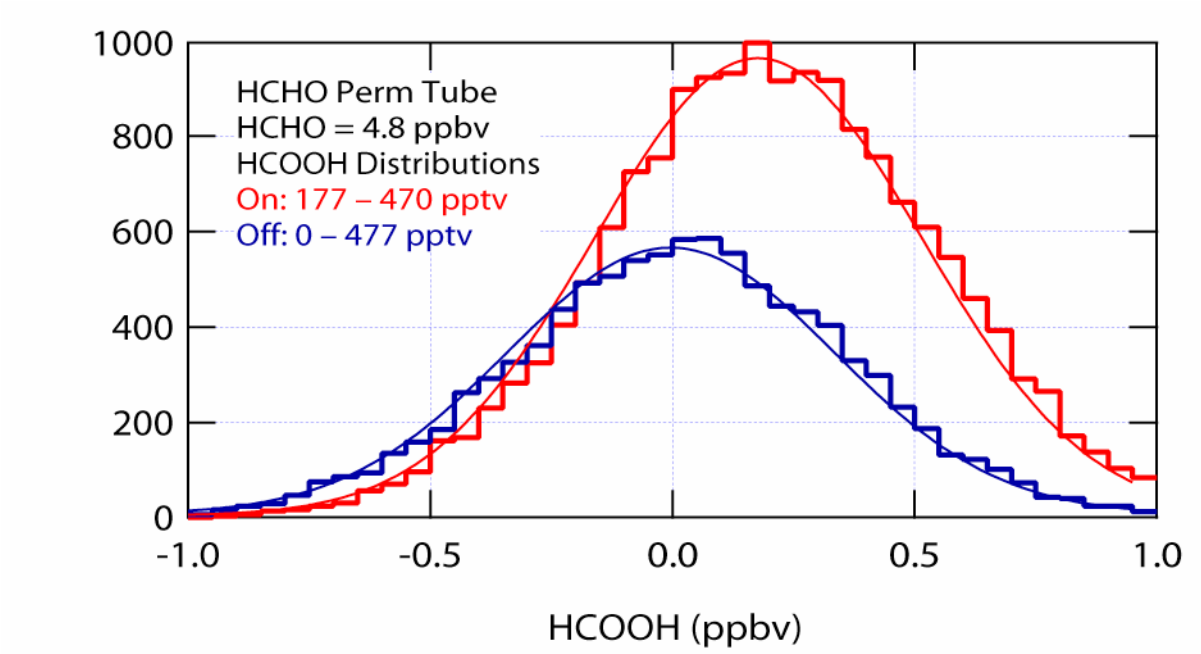



2 × 10-5 Absorbance
HCHO Absorption
43 Torr, 1 ppbv HCHO, 76 m
(a)
Ambient H2O
(b)
Pulsed QC Linewidth
0.008 cm-1
Humidity
Matched H2O
(c)
25 Torr
Linewidth < 0.001 cm-1
All Vertical Axes are Transmission
Wavenumber ν2
(d)
Humidity
Matched H2O
Linewidth < 0.001 cm-1
Wavenumber ν1 + ν5


999.70
999.68
999.66
999.64
Signal (mV)
HCHO
HCHO
HCHO
H2O
547 ppt HCHO
20 min
1764.8
1764.9
1765.0
1765.1
1765.2
Frequency (cm-1)

HCHO and HCOOH Spectroscopic Purity

- Limit on cross talk; orthogonal retreivals; first figure of this type; only limit because no measure of HCOOH



Additional Inlet Tests (at sea)

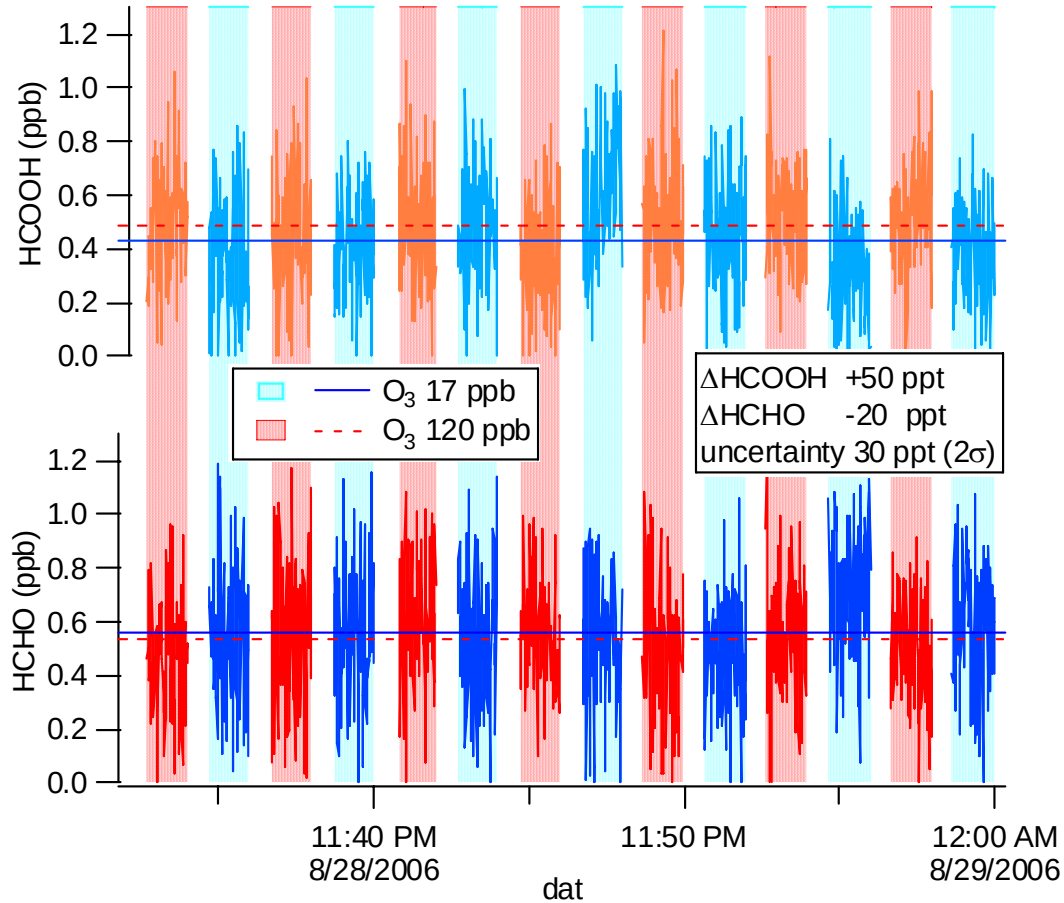
Total Flow Variations
different residence times
by factor of 5, saw
no difference
in diurnal MBL HCHO

With O_3 Addition

Alternate ambient O_3
and enhanced O_3

No significant change
with 120 ppb of added O_3

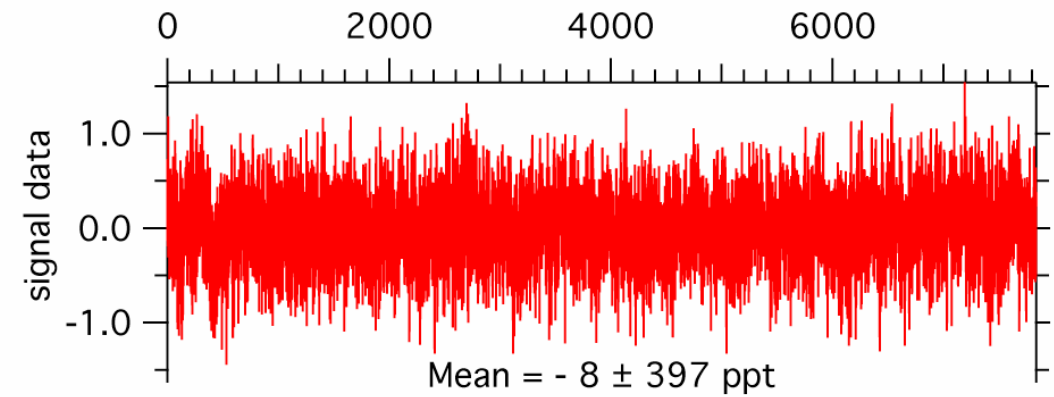
Measured HCHO in MBL
is not due to O_3
inlet effects

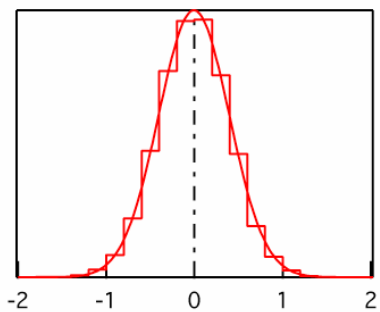


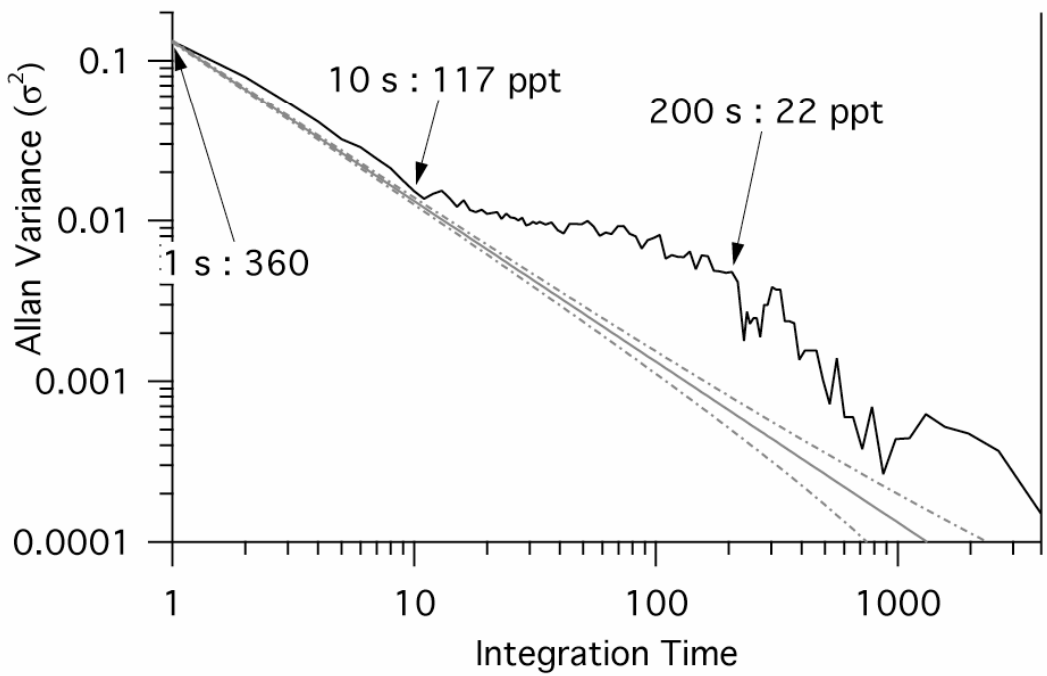
Advice from Ostoff, Roberts, Kuster

Instrument Performance

- Allan plot and systematic error estimates



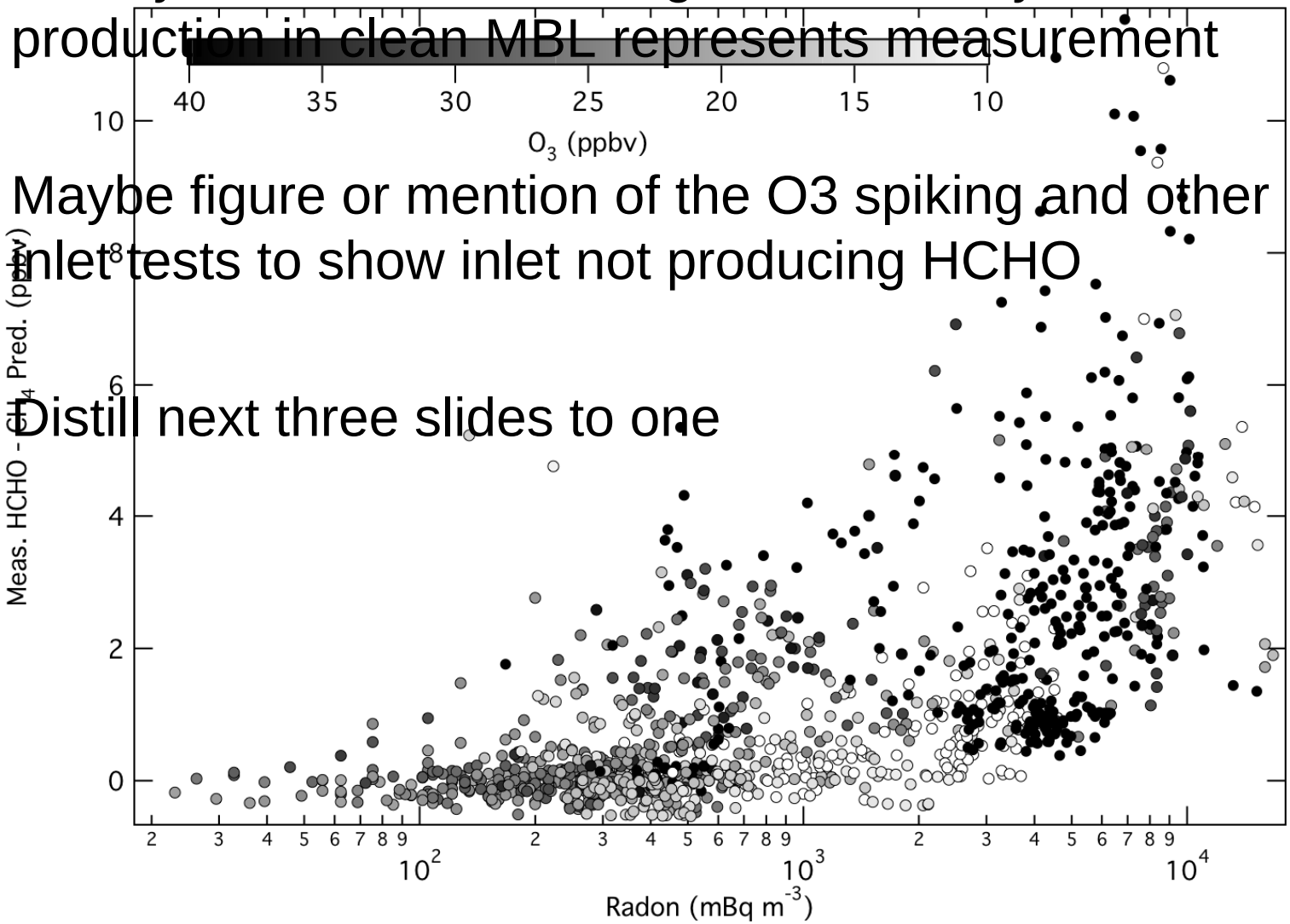




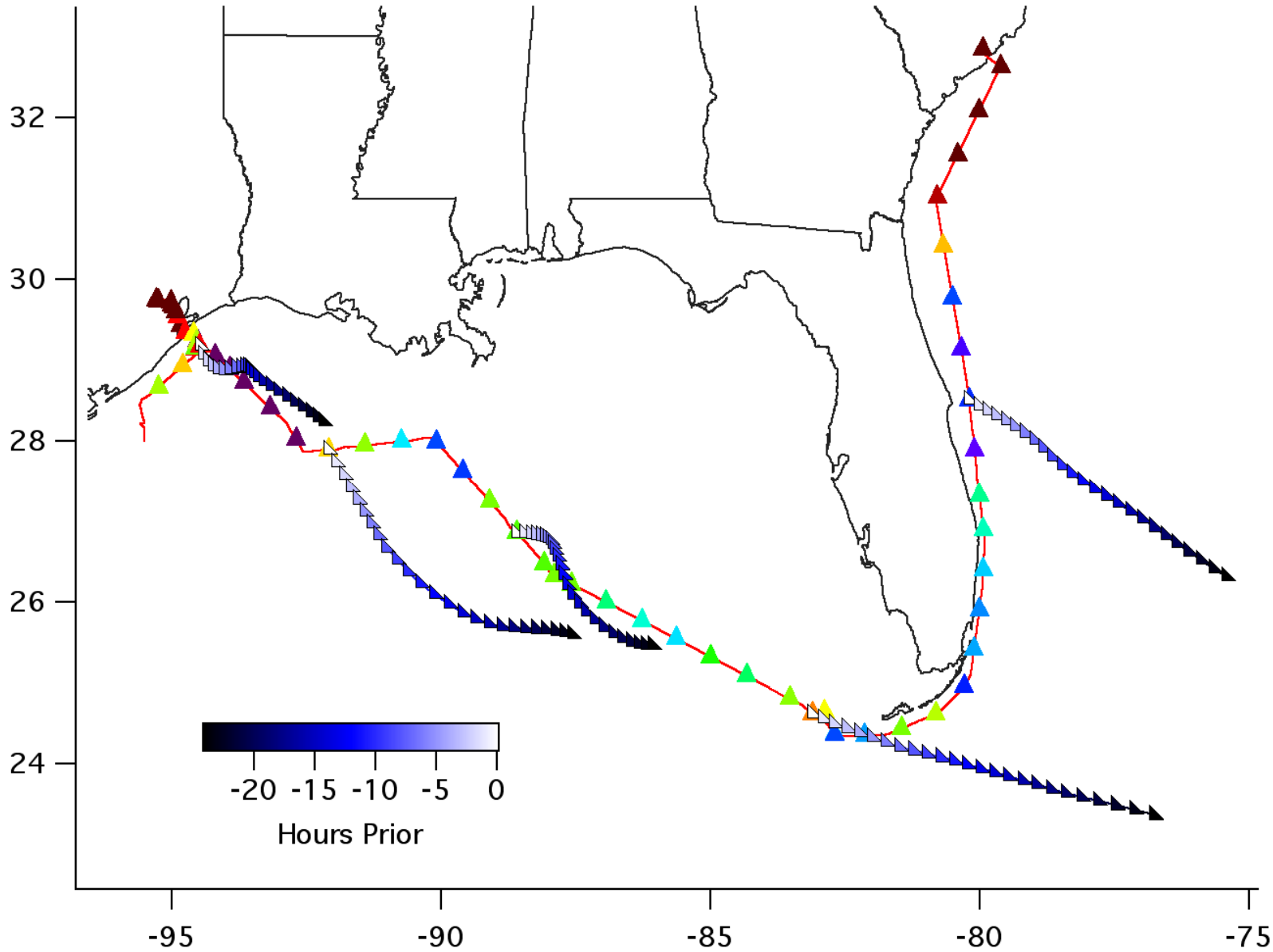
detection limits
10 s = 360 pptv
200 s = 66 pptv

HCHO in MBL

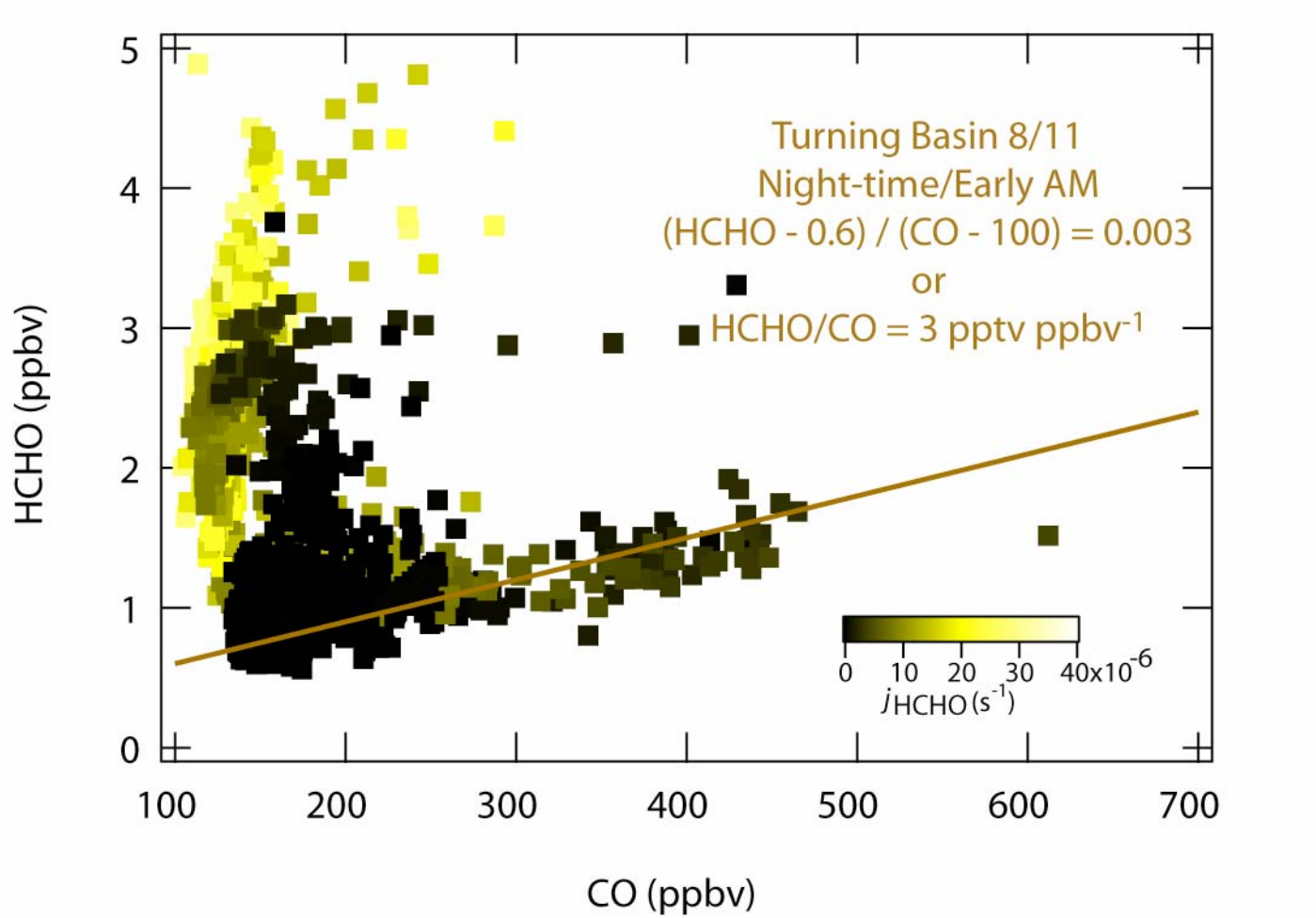
- Steady state model showing methane-only production in clean MBL represents measurement
- Maybe figure or mention of the O3 spiking and other inlet tests to show inlet not producing HCHO
- Distill next three slides to one



Back Trajectories all from the South

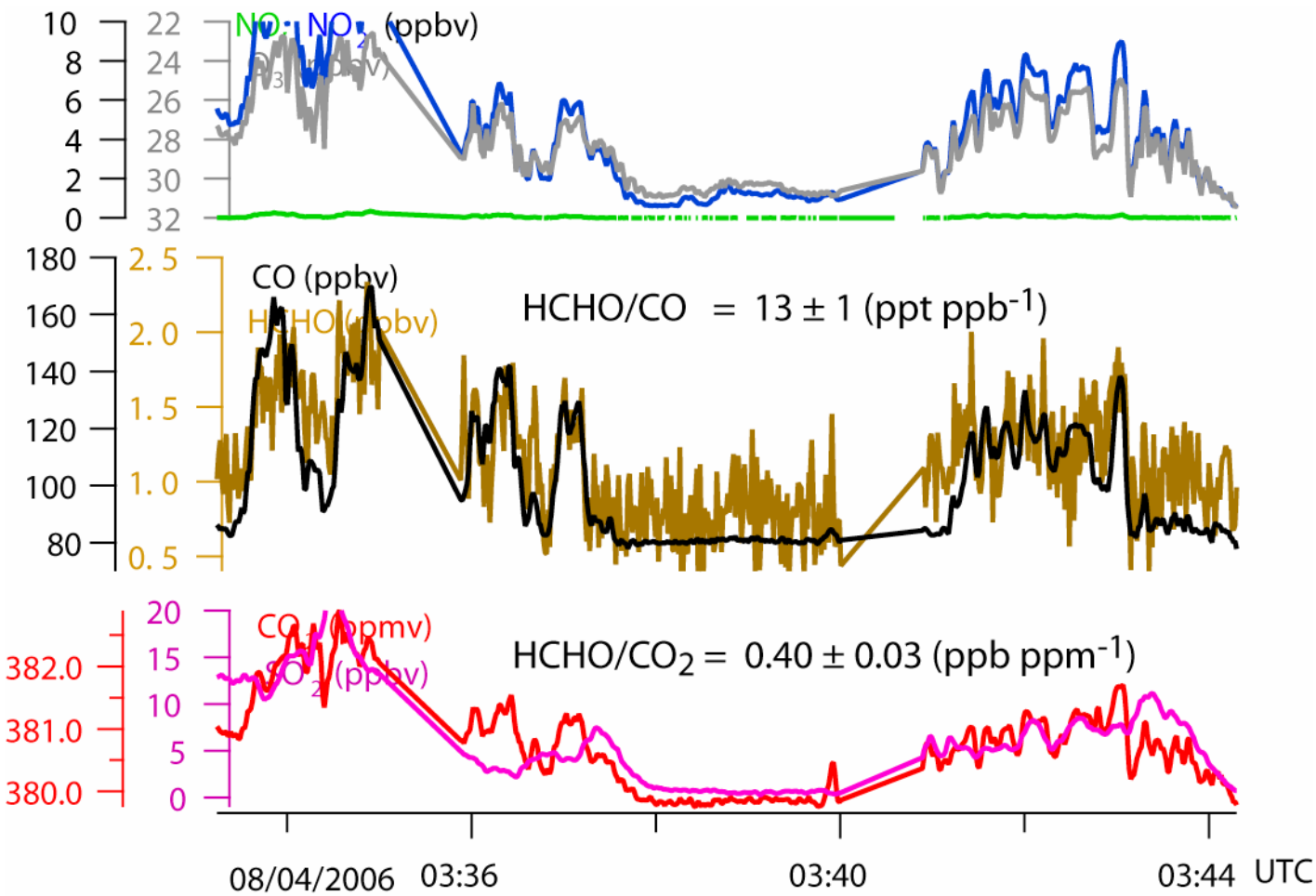


HCHO vs CO in Houston Turning Basin



Primary vs Secondary HCHO

Drilling Platform Flare Fire vs Diesel Generator



Primary HCHO Direct Measurement