Preliminary Findings from 2009 SHARP Campaign

SHARP Study of Houston Atmospheric Radical Precursors

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SHARP Objectives & Basic Chemical Conditions

I. Introduction
II. SHARP Goals
III. Moody Tower Project (including HINT)
IV. SHARP/FLAIR supporting studies
V. Preliminary Conclusions

SHARP Study of Houston Atmospheric Radical Precursors

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2006 TexAQS II & TRAMP

Instruments recorded large pulses of HCHO > 25 ppb (Insitu aircraft, HSC, Moody Tower, LP-DOAS)

Analysis indicated that portion of HCHO is “primary” associated with excess CO (combustion) and smaller fraction with SO_2

HONO in Houston can exceed 2 ppbv close to sunrise then remain at hundreds of pptv during day.

Strong vertical gradients indicate ground-level source of HONO (e.g. traffic)

Possible new heterogeneous mechanism: $HNO_3 \rightarrow$ HONO on HOA

$ClNO_2$ present at ppbv levels in GOM, formed via N_2O_5 and $HCl_{(g)}$

2006 TRAMP and O_3 production

Ozone production often greater than 40 ppbv/hr between 0800-1200 LT.

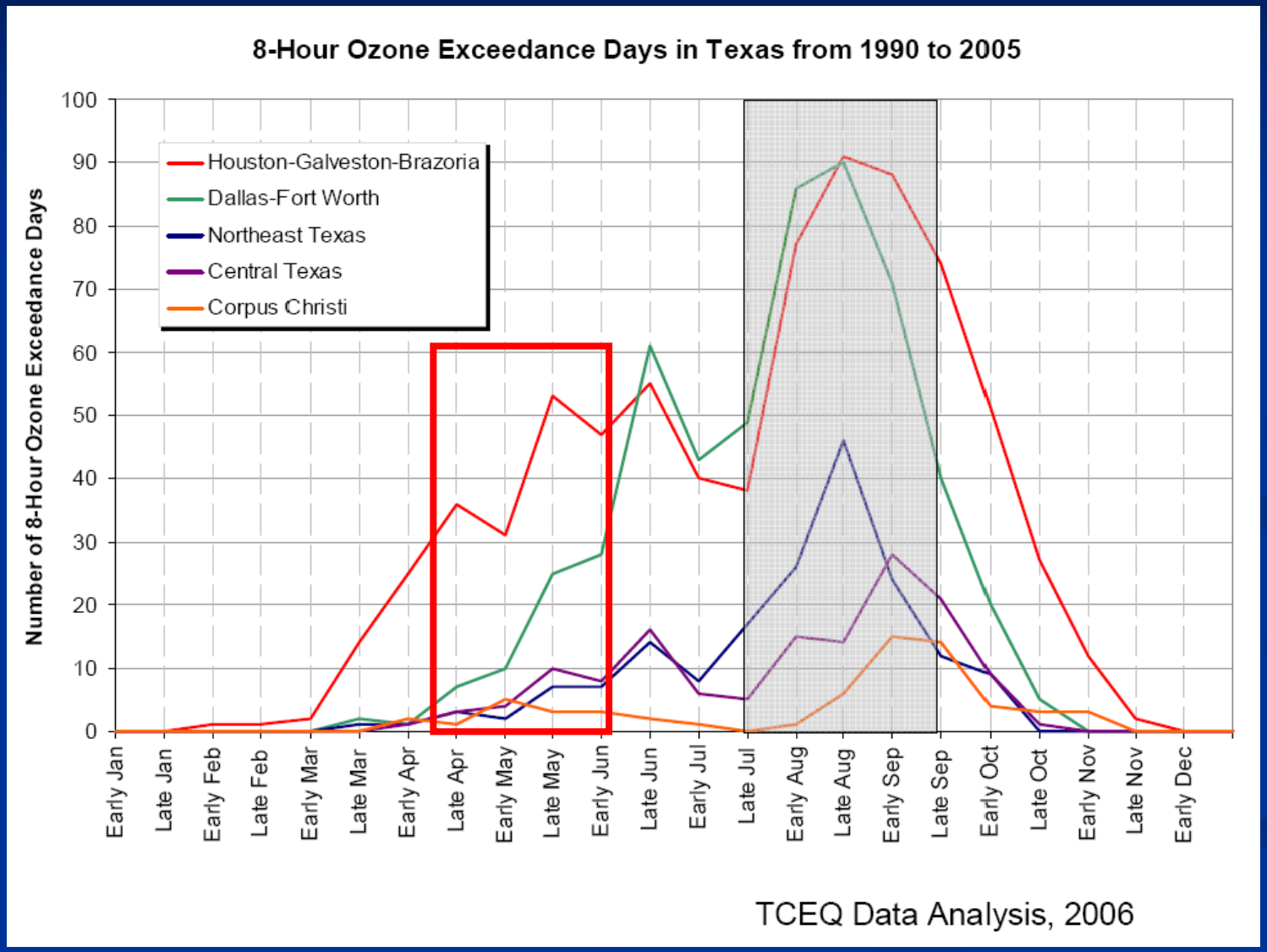
O_3 production is both NOx and VOC sensitive (NOx sensitive for 7 hours during the day).

OH chain length (10-20) during TRAMP was much greater than other North American cities.

Primary reason for enhanced Houston photochemistry were the high VOC abundances.

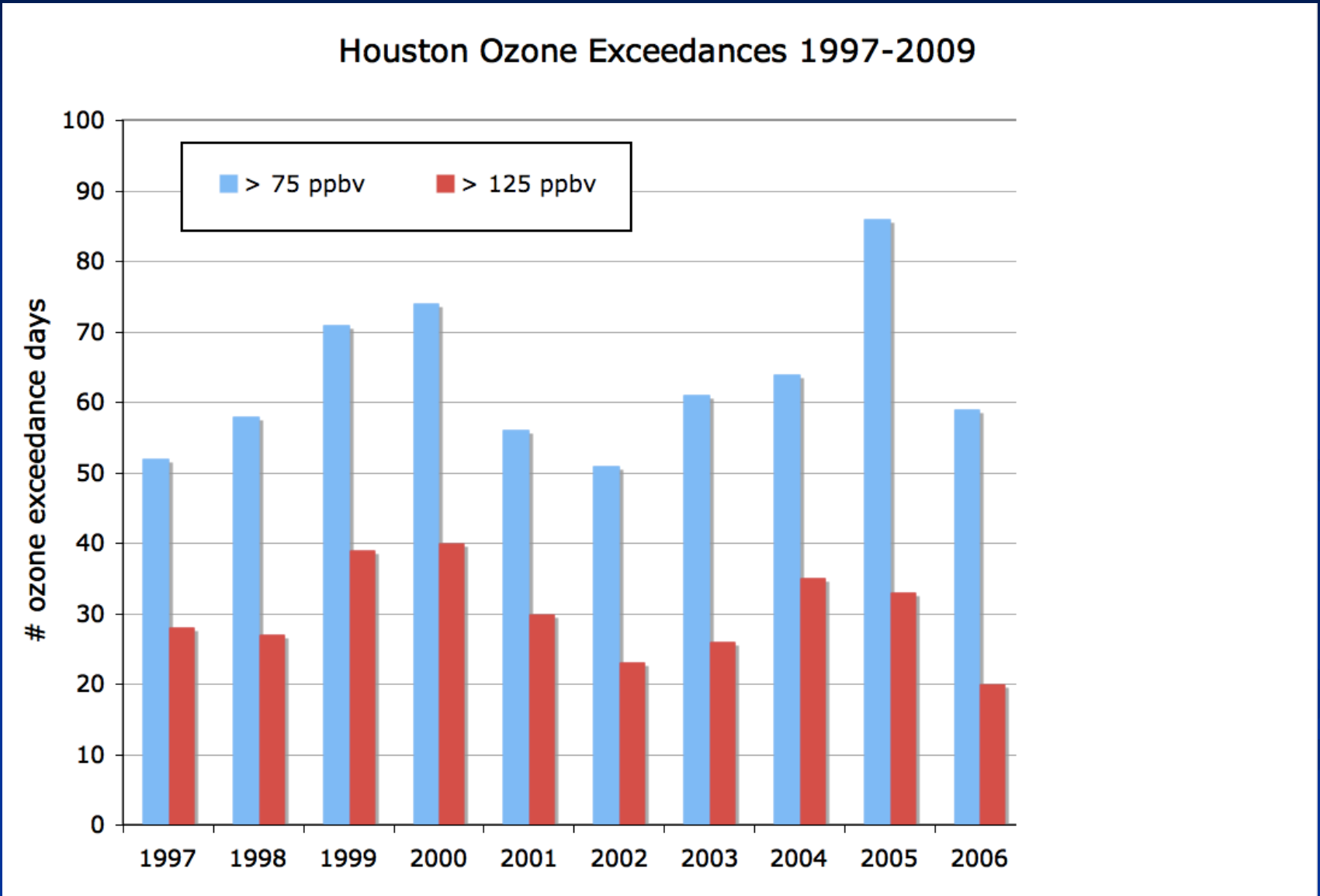
SHARP Time Period

15 April – 31 May 2009



Source: TCEQ

Houston Ozone Trends



Source: TCEQ

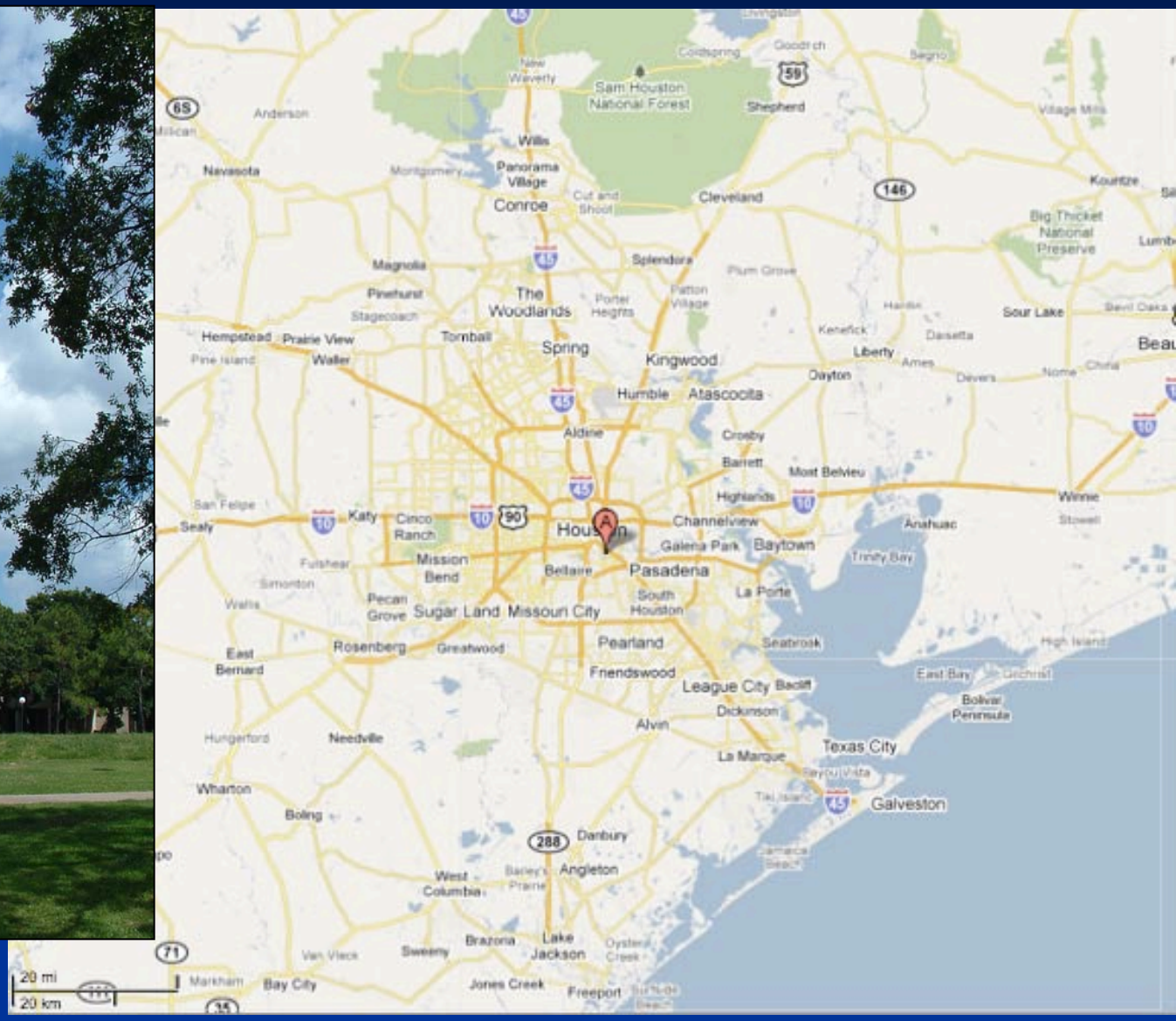
SHARP Goals

Based on the TexAQS-II and TRAMP findings concerning radical processes in the Houston atmosphere, the SHARP project intends to investigate the following:

1) The contribution of direct emissions of OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources and mobile sources.
2) The importance of secondary HCHO formation from ozonolysis of olefins.
3) Identification of formation pathways of HONO (Day/Night, surface, heterogeneous, homogeneous).
4) Impact of soot (fresh and coated) on chemistry, radiation (photochemistry and climate), and dynamics.
5) The ambient levels of $ClNO_2$ in Houston and potential as a radical source.
6) Intercomparison of ambient HONO measurement techniques in urban atmosphere.
7) Relative importance of springtime ozone formation mechanisms in Houston.

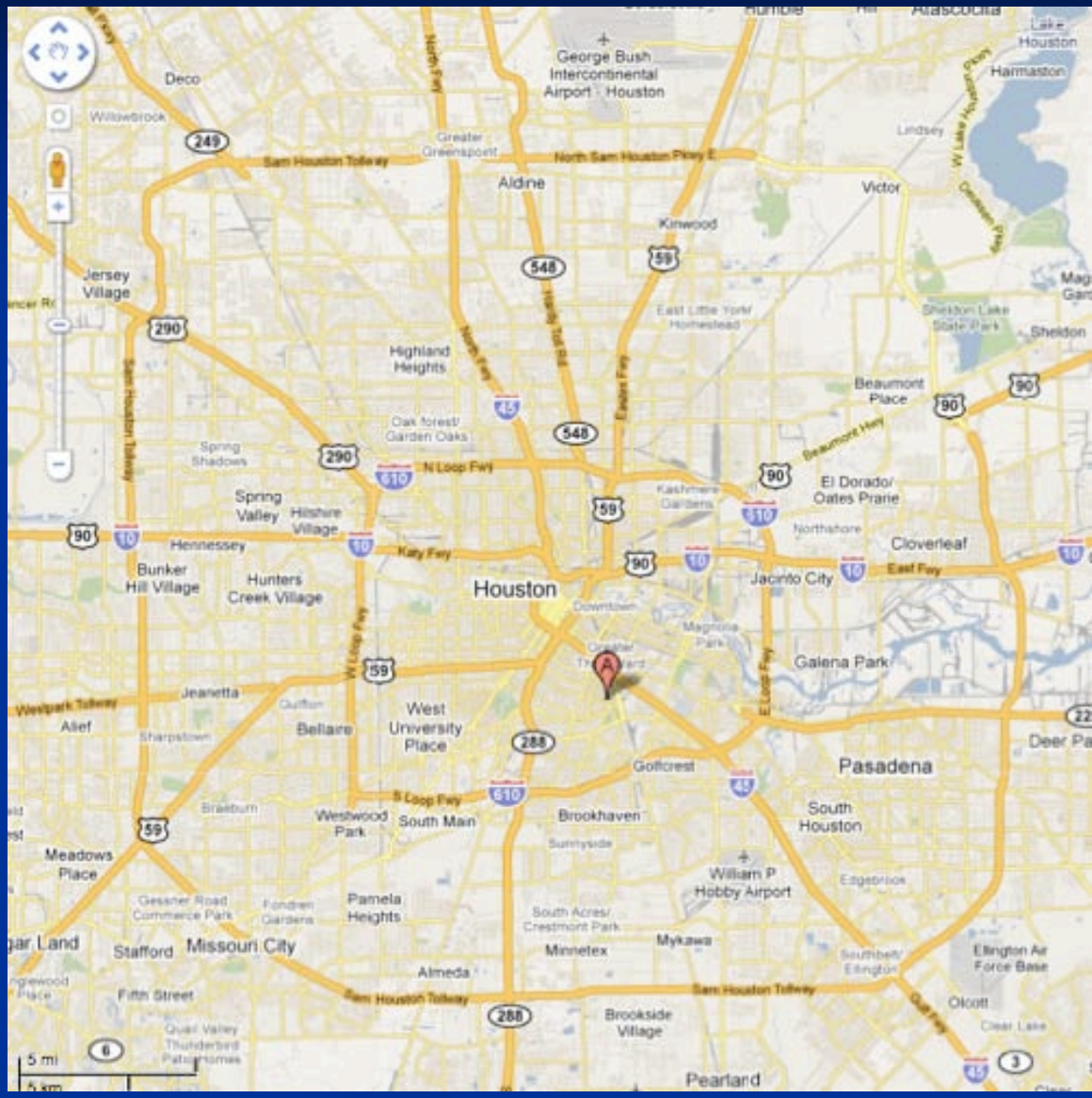
Reducing uncertainties surrounding these processes will improve our ability to model radicals and ozone formation.

Moody Tower



Sam Houston National Forest
Shepherd
Anderson
Navasota
Willis
Panorama Village
Conroe
Cleveland
Big Thicket National Preserve
Magnolia
Splendora
Pinehurst
The Woodlands
Hempstead
Prairie View
Waller
Tomball
Spring
Kingwood
Liberty
Sour Lake
Humble
Atascocita
Aldine
Crosby
Barrett
Highlands
Mont Belvieu
Winnie
Sealy
Katy
Cinco Ranch
Channelview
Galena Park
Baytown
Anahuac
Mission Bend
Bellaire
Pasadena
Trinity Bay
Pecan Grove
Sugar Land
Missouri City
South Houston
La Porte
Rosenberg
Greatwood
Pearland
Seabrook
East Bernard
Friendswood
League City
Bacliff
Dickinson
Alvin
Needville
Texas City
La Marque
Wharton
Galveston
Boling
Danbury
Angleton
West Columbia
Brazoria
Lake Jackson
Sweeny
Bay City
Jones Creek
Freeport
20 mi
20 km

Moody Tower



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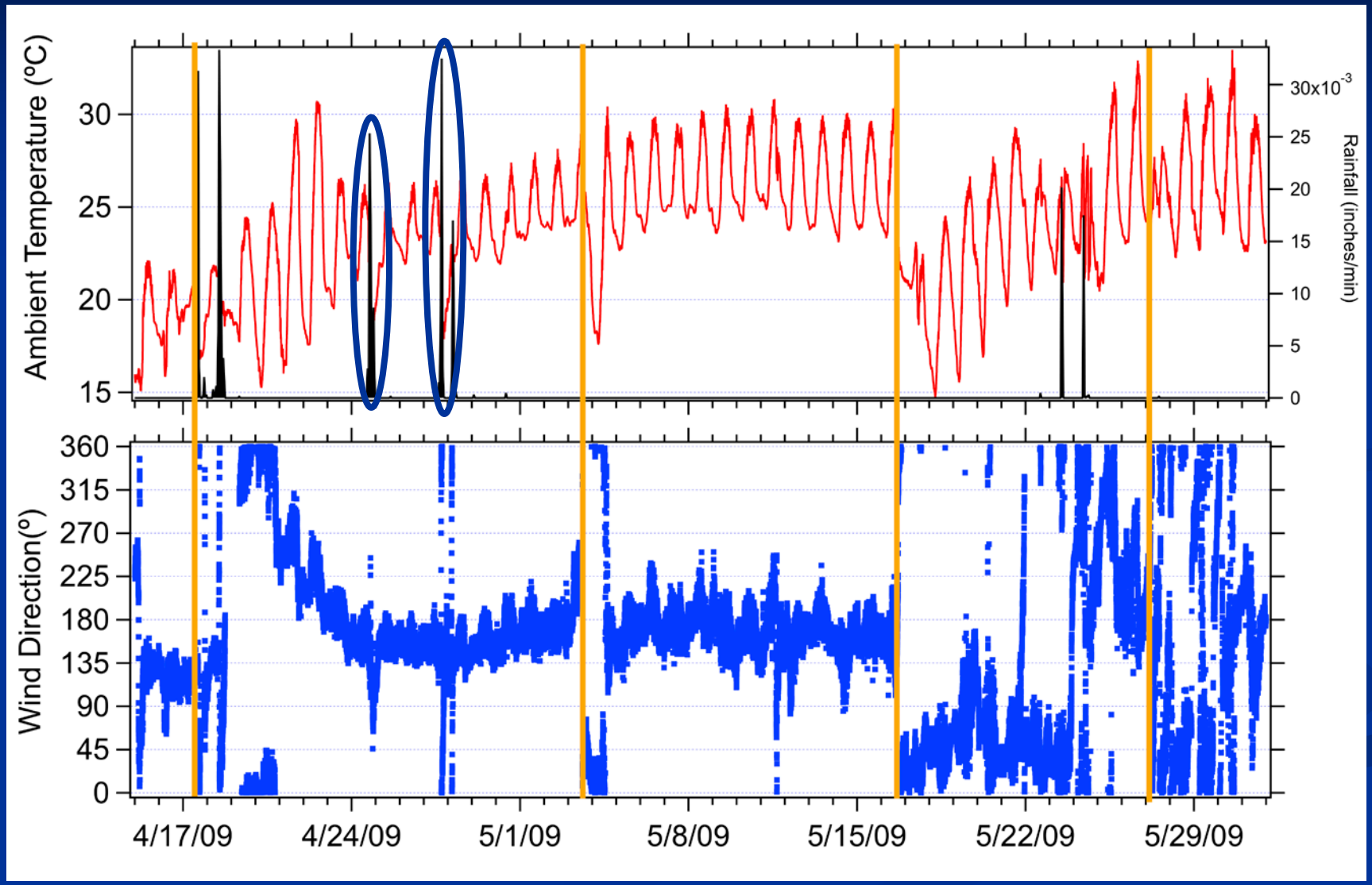
Moody Tower SHARP Measurements

Parameter	Instrument	PI
Meteorology (T, RH, P, ws, wdir, rain, cloud camera)	Campbell Research met system	Lefer (UH)
Basic Trace Gases (O_3, CO, SO_2, NO, NO_2, NO_Y)	Modified TECO Systems	Lefer (UH)
Photolysis Rates (jO_3, jNO_2, jHONO, jHCHO, etc)	Scanning actinic flux spectroradiometer (NCAR)	Lefer (UH)
Ozone Column, UV/VIS AOD	Brewer, CIMEL, UV-MFR	Lefer (UH)
Mixed Layer Height	Vaisala CL-31 LIDAR	Lefer (UH)
Vertical Profiles - O_3, T, P, RH, ws, wdir	Radiosonde/Ozonesonde Balloon	Lefer (UH)/Morris (Valpo)
VOCs (C2-C10 NMHCs)	Realtime GC-FID (Perkin-Elmer)	Rappenglüeck (UH)
HOOH, HONO	Aerolaser/QUMA-LOPAP	Rappenglüeck (UH)
Speciated PANs	Metcon GC-ECD	Rappenglüeck (UH)
HNO_3, HONO, HCl	Mist Chamber/IC	Dibb (UNH)
OH, HO_2, RO_2, OH Reactivity	Laser Induced Flouresence	Brune (Penn State)
Oxy-VOCs, HCHO	PTr-MS	Jobson (WSU)

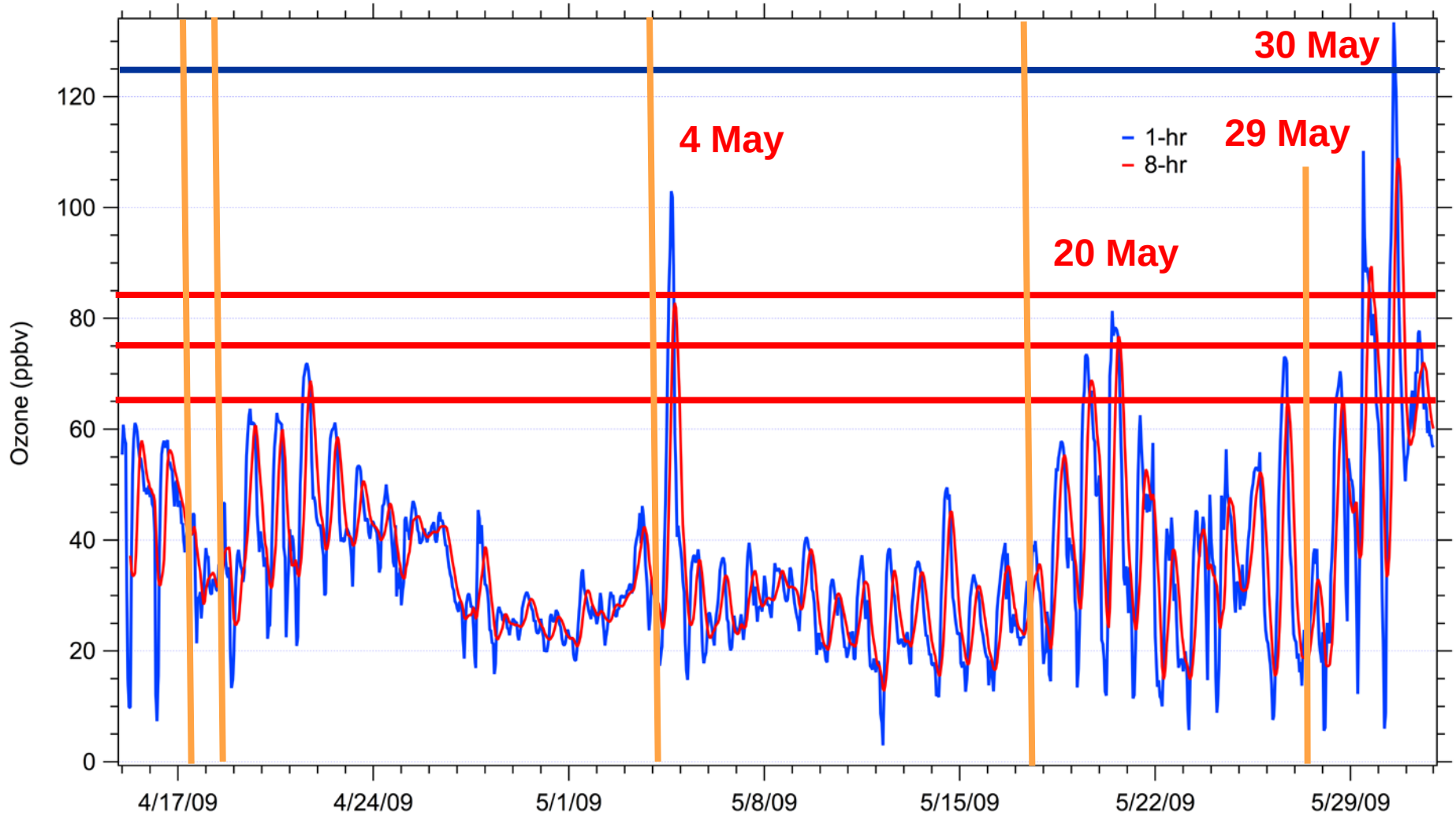
Moody Tower SHARP Measurements

Parameter	Instrument	PI
$ClNO_2$, N_2O_5, PAN, PPN, APAN	CIMS	Huey (Ga Tech)
Aerosol Composition	Aerosol Mass Spectrometer (AMS)	Herndon (Aerodyne)
HONO, HONO Flux, HONO Calibration Source	LOPAP	Ren (U. Miami)
Water Soluble Aerosol Composition	PILS/IC	Griffin (Rice)
Aerosol Size Distribution	DMA	Griffin (Rice)
Ozone Production Rate	MOPS	Brune (Penn State)
Nitrophenols	IC coupled to ESI Tandem MS	Dasqupta (UT-Arlington)
Aerosol Elemental and Organic Carbon	Sunset Labs EC/OC	Yu (PNNL)
Aerosol morphology, size, mixing state	TRAC-SEM	Yu (PNNL)
Potential Aerosol Mass	AMS with pre-reactor	Jimenez (Colorado)
3 Levels Profiles (40m, 150m, 300m) of O_3, NO_2, SO_2, HCHO, HONO, NO_3	Long-Path DOAS	Stutz (UCLA)

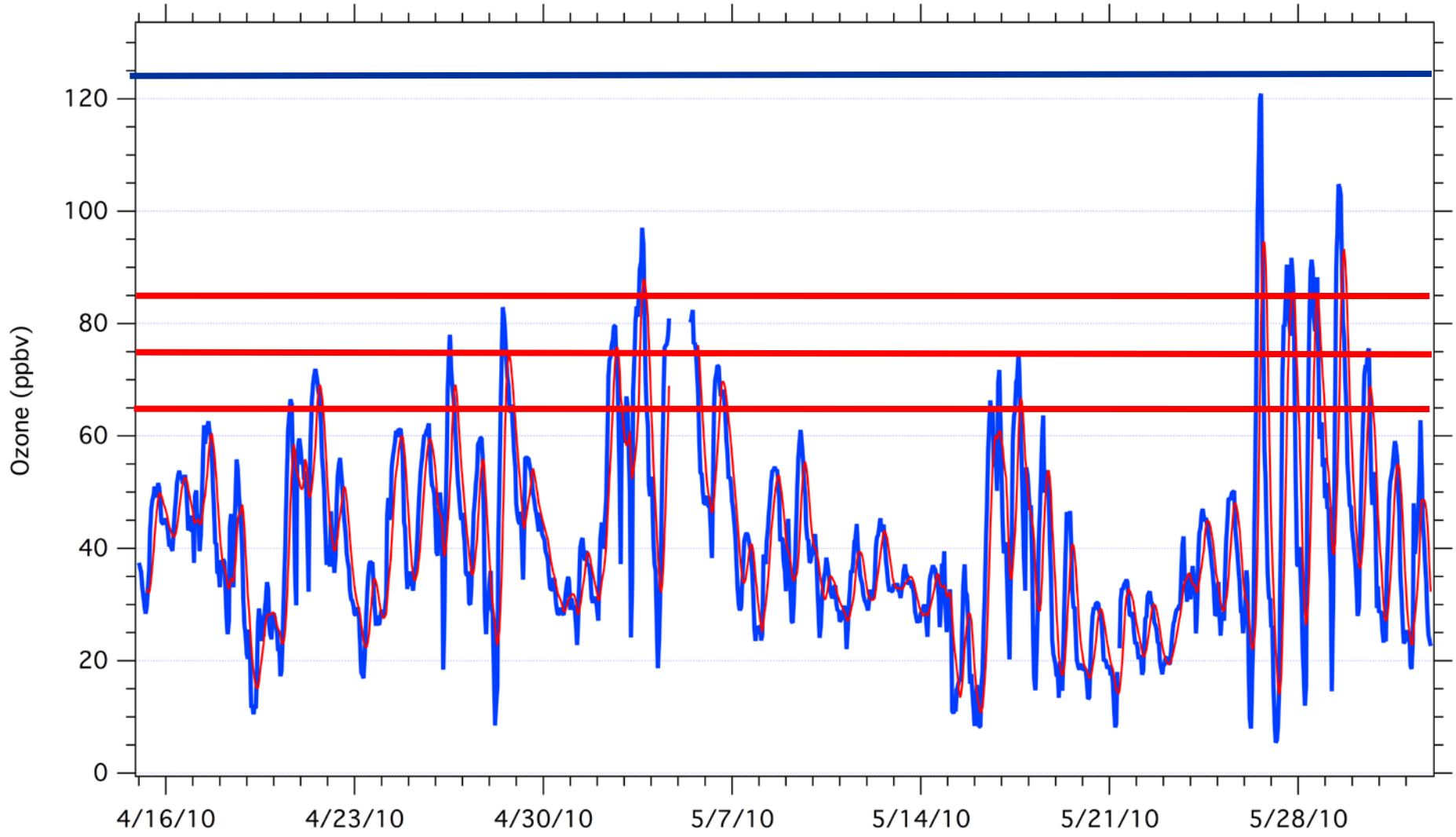
Meteorological Conditions



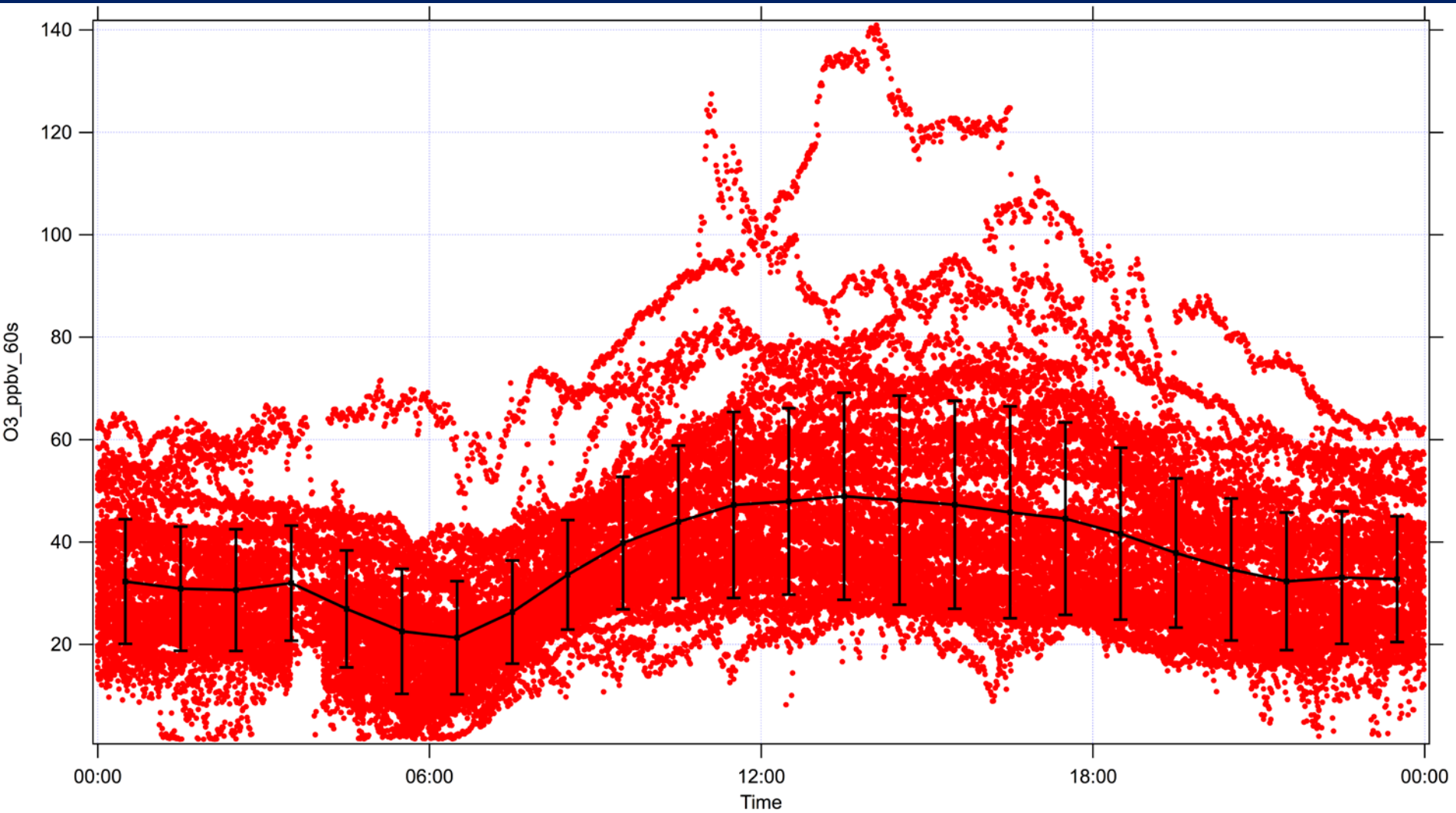
Ozone


30 May
4 May
29 May
20 May
1-hr
8-hr
Ozone (ppbv)
0
20
40
60
80
100
120
4/17/09
4/24/09
5/1/09
5/8/09
5/15/09
5/22/09
5/29/09

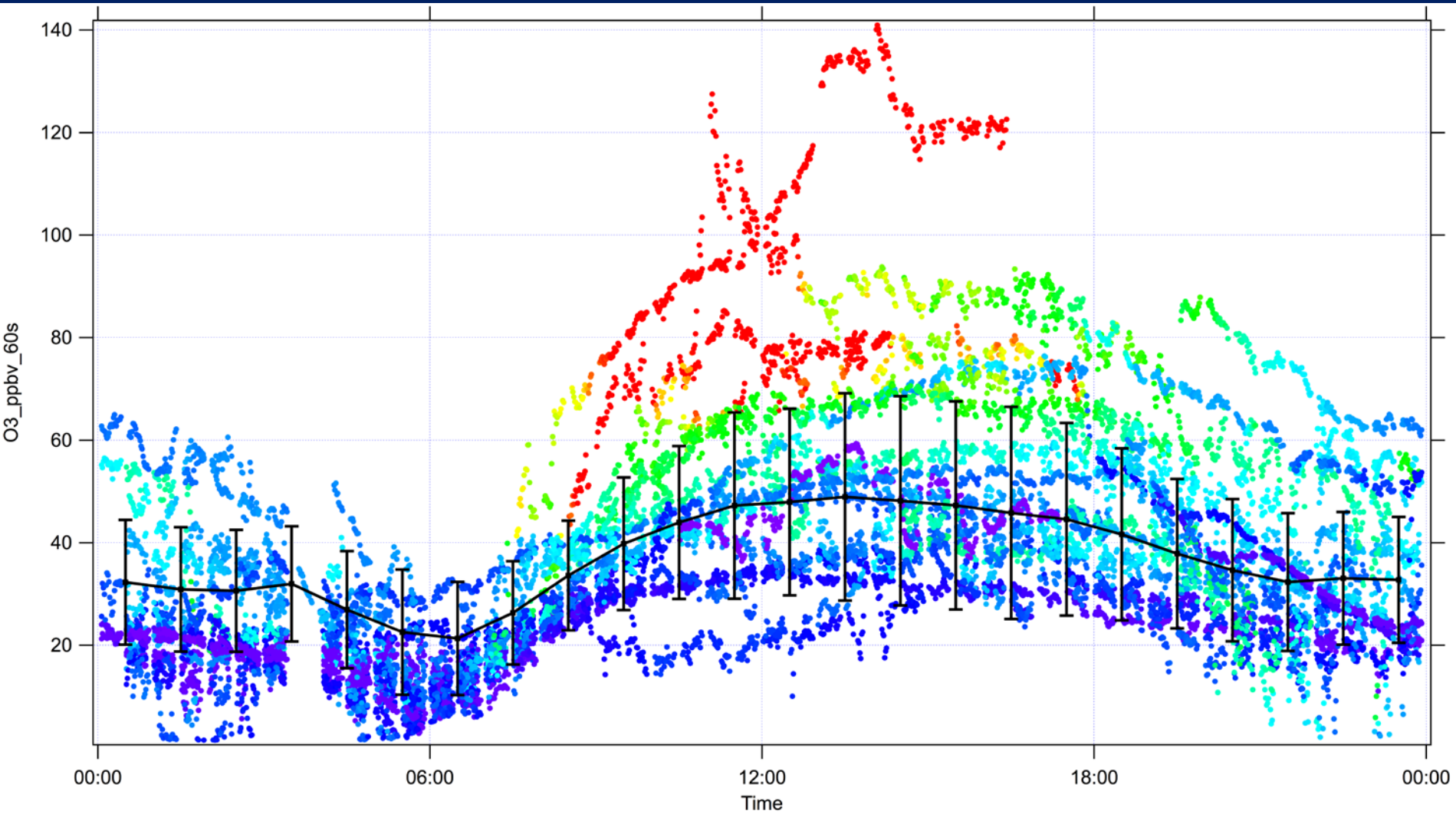
Ozone at Moody Tower 2010



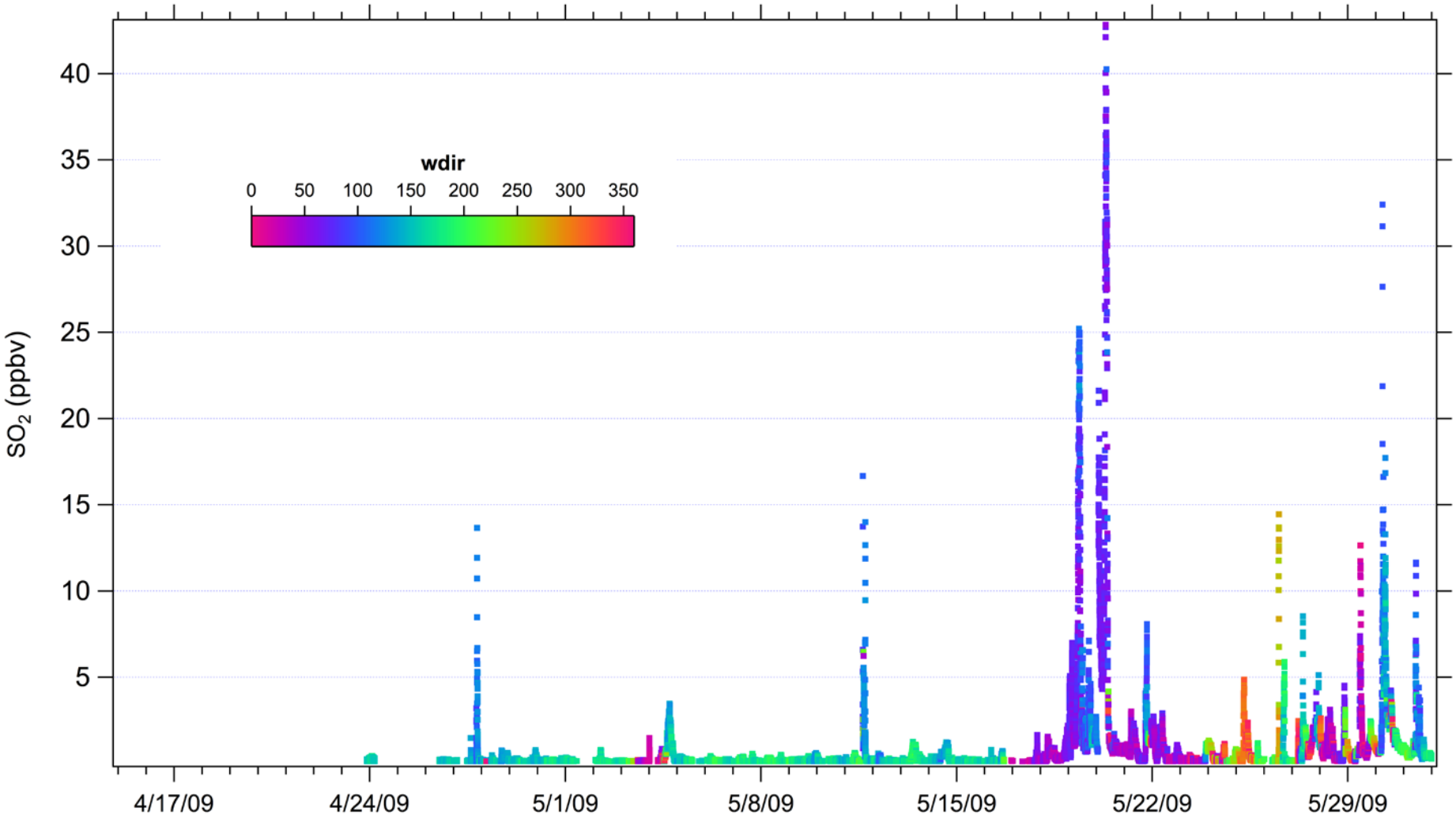
Ozone Diurnal (1 min data)



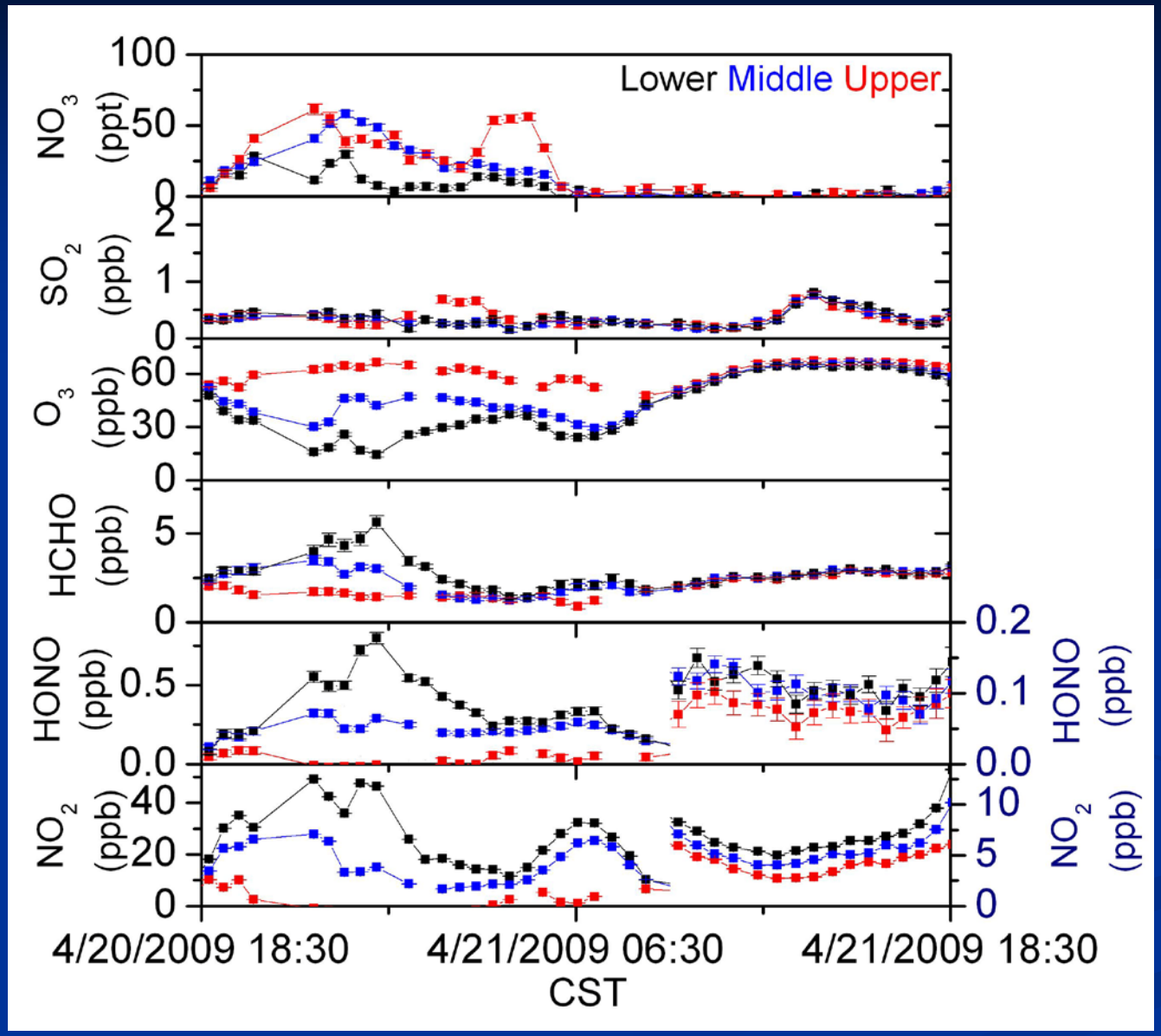
Ozone Diurnal (1 min data) with PAN



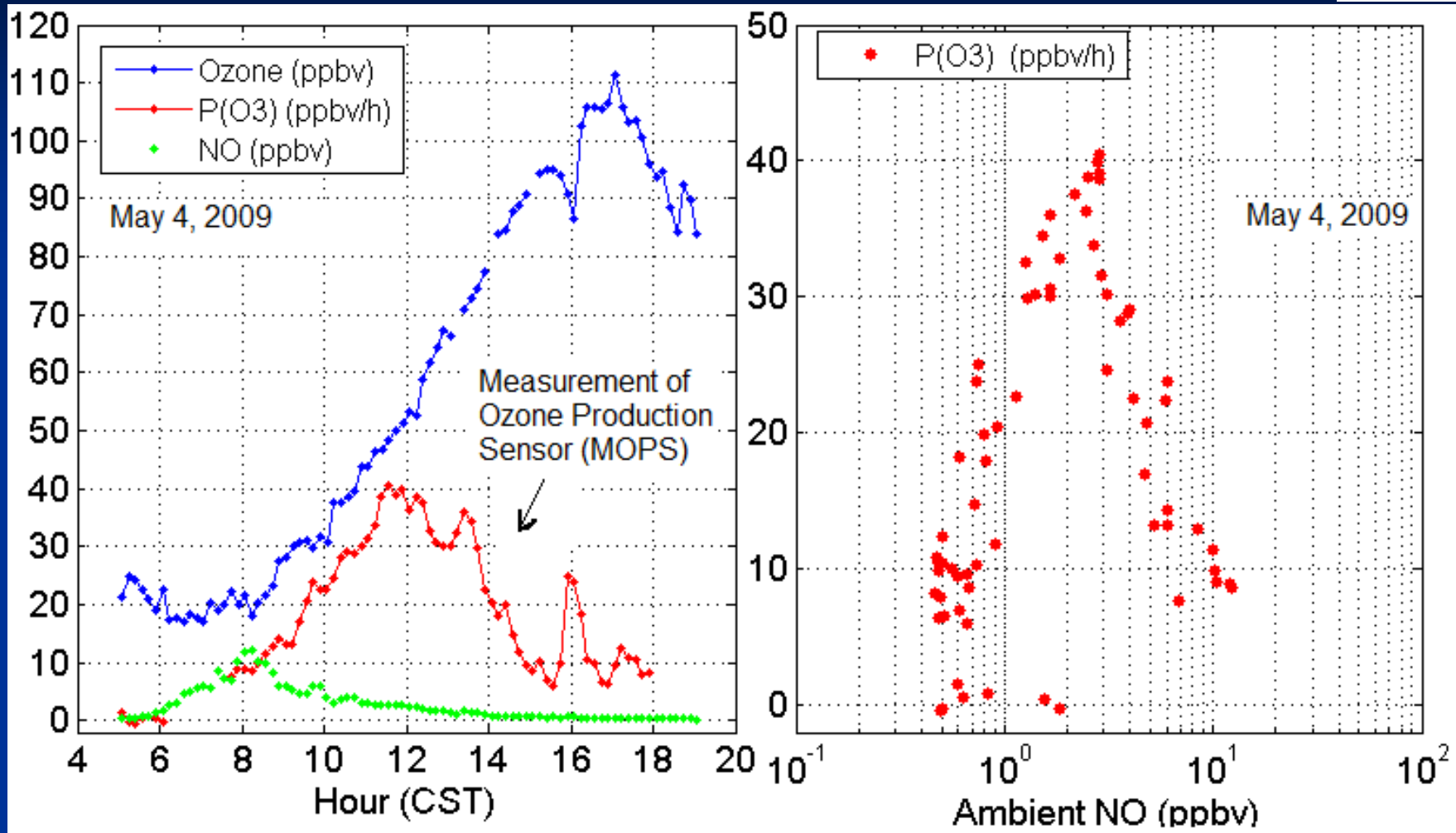
SO_2 time series (wdir)



Long Path DOAS (UCLA)

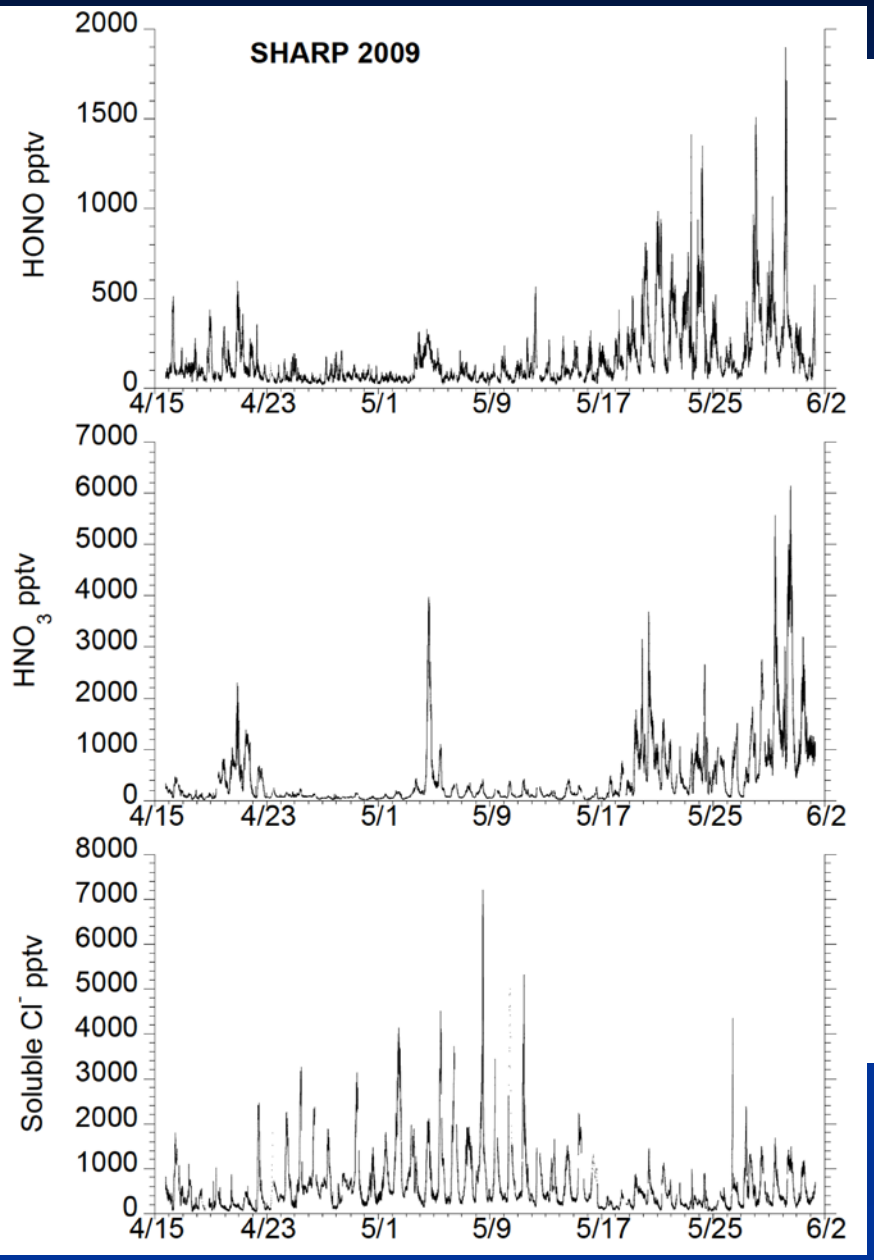


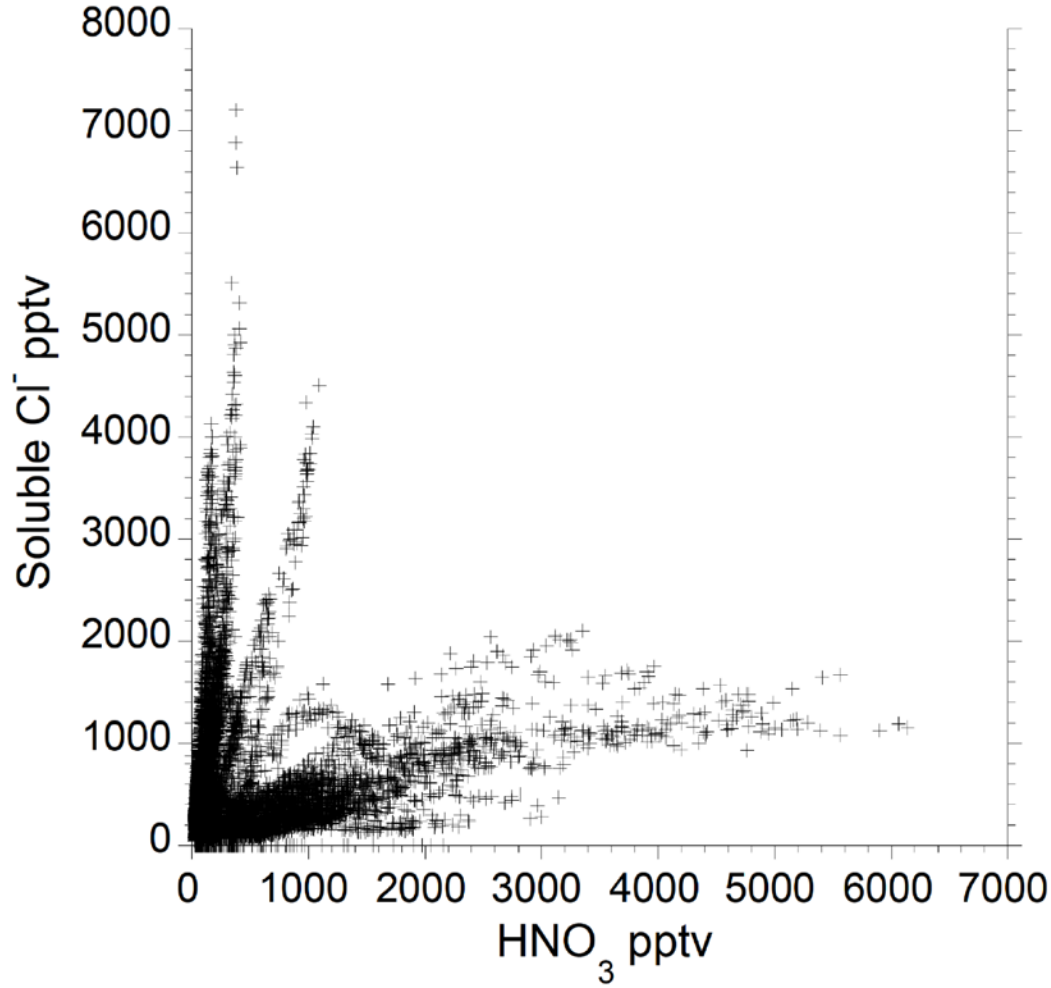
Ozone Production Sensor (PSU)



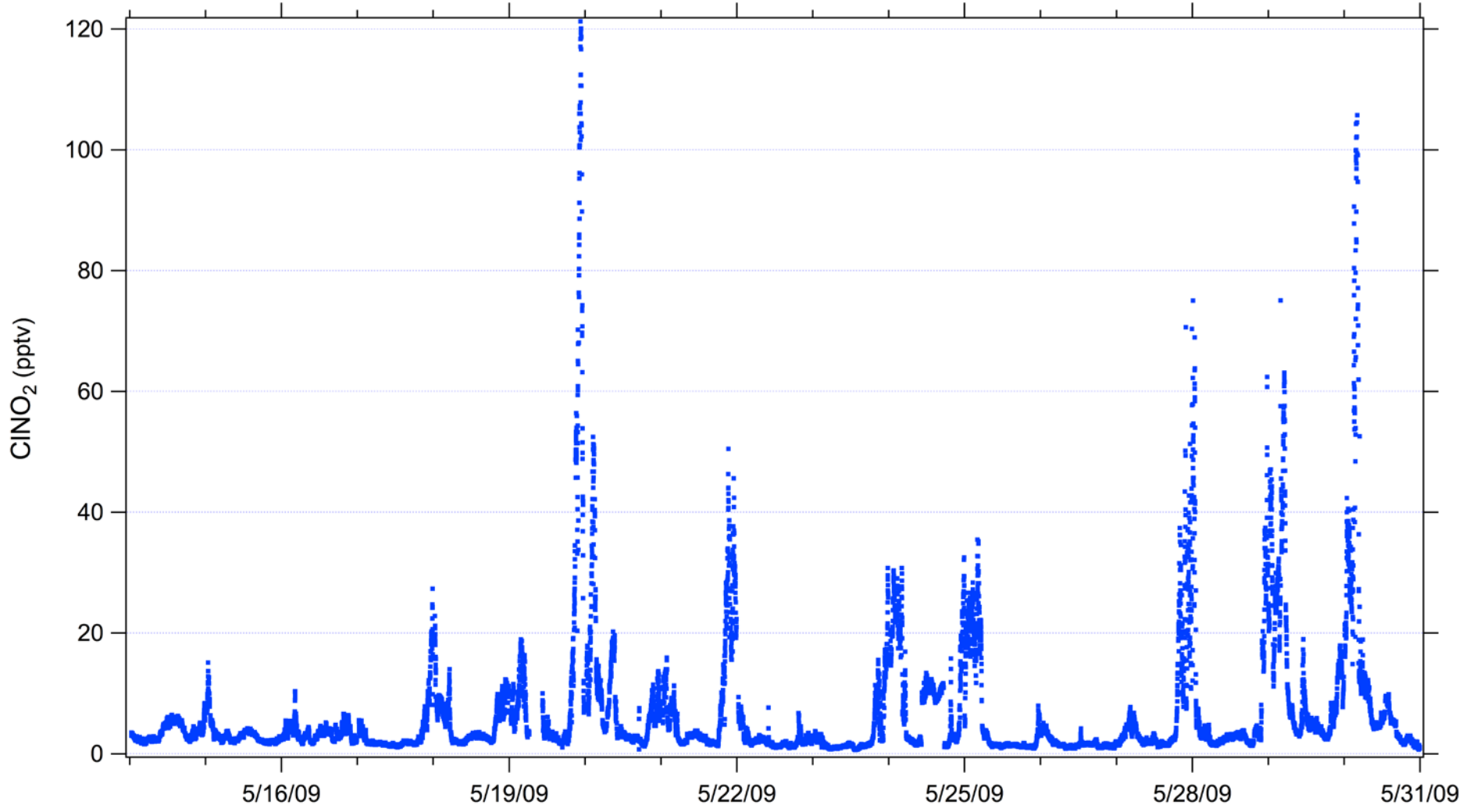
Direct measurement of ozone production in Houston and correlation with ambient NO. May 4, 2009. Measured P(O3) will be compared with modeled P(O3) to test mechanisms. Measured P(O3) also can be compared with calculated P(O3) from peroxy radicals and NO. Cazorla, M. and Brune, W.

HONO, HNO_3, soluble Cl^- (UNH)

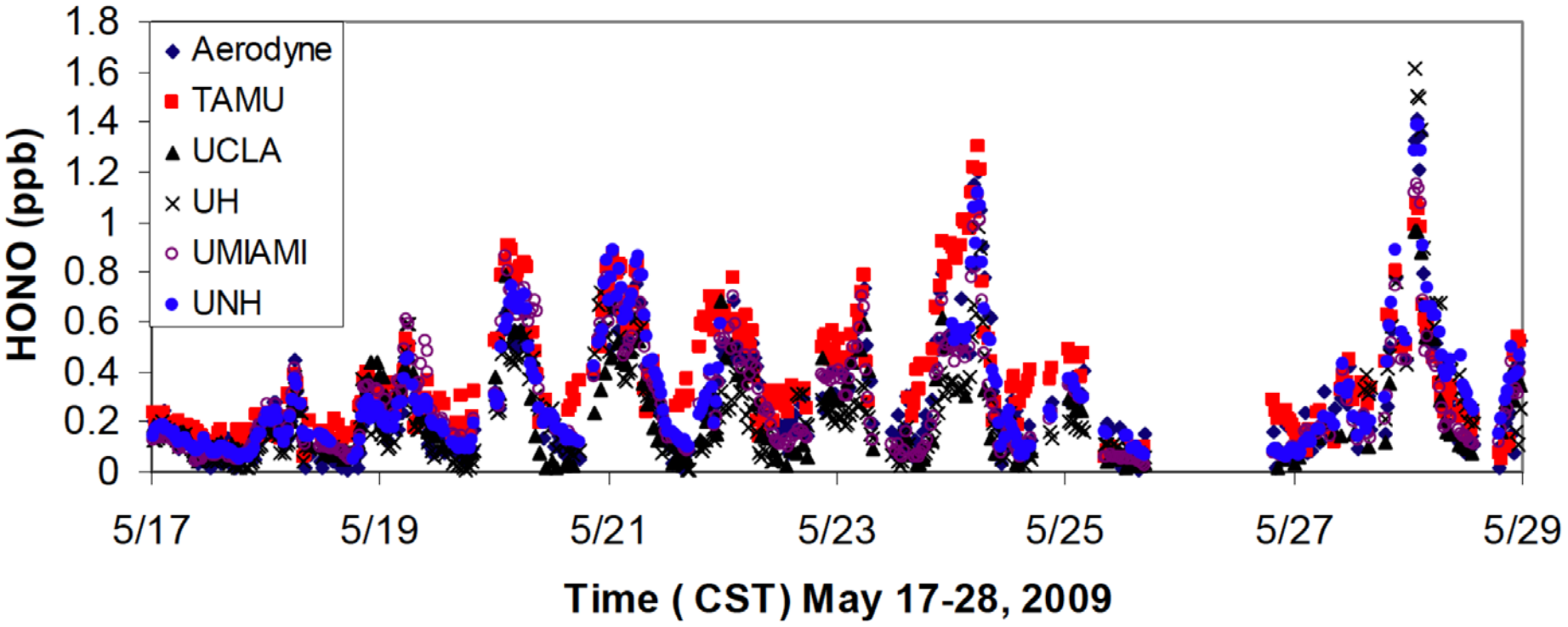




$ClNO_2$ (GaTech)



HONO Intercomparison (HINT)



SHARP Related Projects

Moody Tower SHARP Intensive UH & many other groups

- HONO Intercomparison Study (HINT) UH, UNH, UCLA, UMiami, Aerodyne, TAMU

Surface-induced Oxidation of Organics in the Troposphere (SOOT) TAMU

Traffic Related Emissions of HONO and HCHO (TRENF) UH

Study of HONO Surface Fluxes (HONO-FLUX) UH

Houston Urban Boundary Layer Study UH

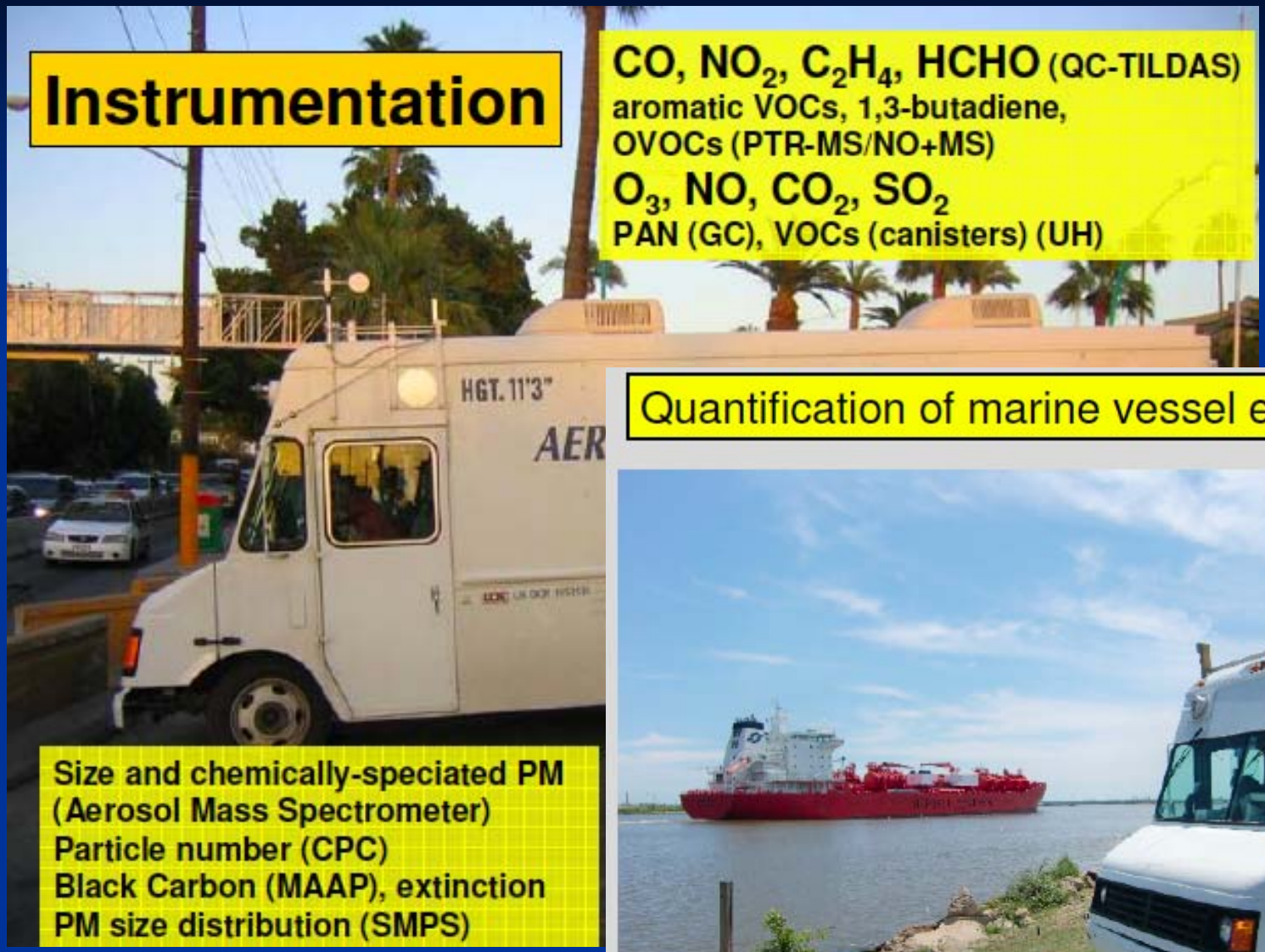
Measurements of HCHO, PAN, and CO in HSC UH

Nitrylphenols in Houston Atmosphere UT-Arlington

Formaldehyde and Olefins from Large Industrial Releases (FLAIR)

- Dual MAX-DOAS WSU & UCLA
- Imaging-DOAS UCLA
- Solar Occultation Flux (SOF) Chalmers University
- Aztec SHARP Flights UH
- Aerodyne Mobile Lab Aerodyne
- Plume Inversion Modeling Aerodyne

Aerodyne Mobile Lab



Quantification of marine vessel emission factors

Aerodyne Mobile Lab

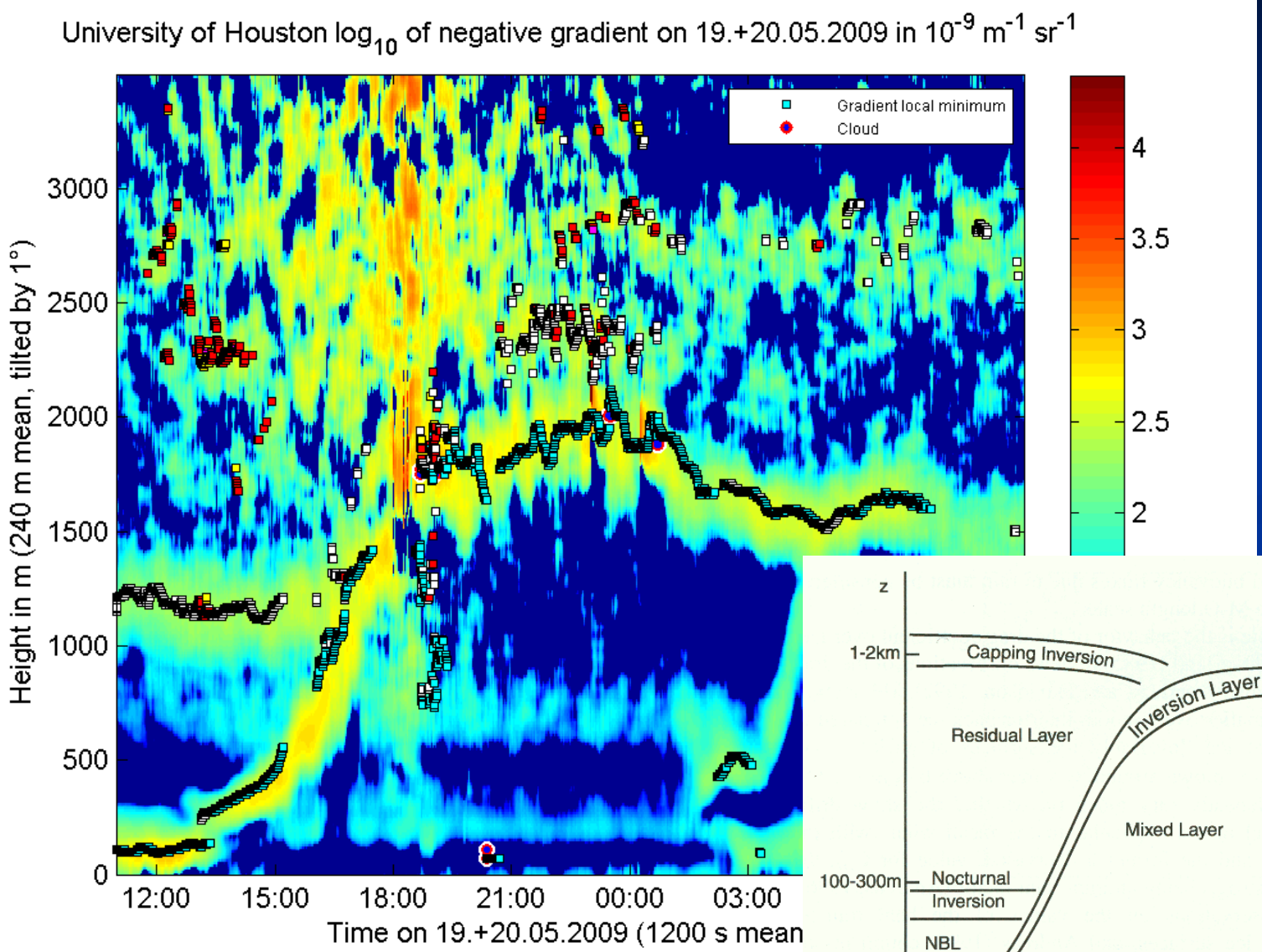
On-road emission factors

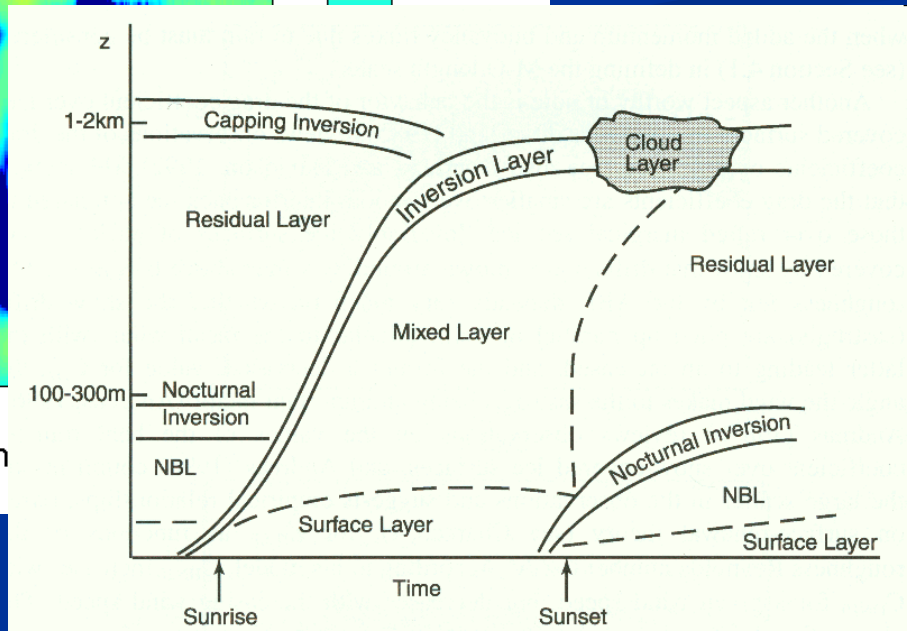
	Houston 2000 (McGaughey et al., 2002)	Houston 2009 This study
	Fl (gasc die	
CO (g/kg fuel)	6	
NO_x	1	
HCHO	N	
C_2H_4	N	
Particle number (#/kg fuel)	N	

Gasol

Overview of industrial emissions

UH Aerosol LIDAR for Boundary Layer Height Measurements





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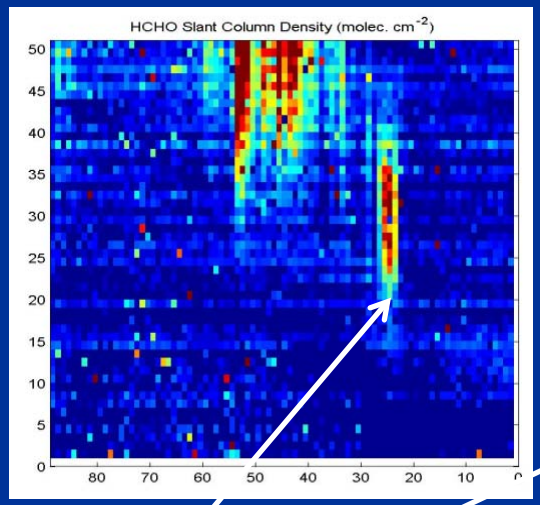
Preliminary Conclusions

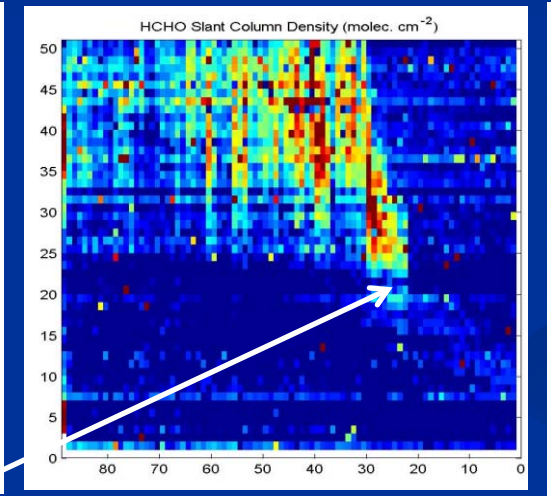
1) The contribution of direct emissions of OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources and mobile sources.

Yes. Some "pseudo-primary" HCHO observed from some flares.

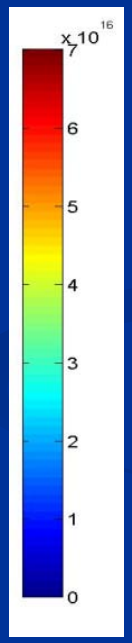
Maybe. HCHO and HONO in automobile exhaust plumes.

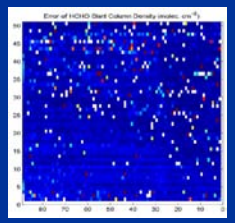


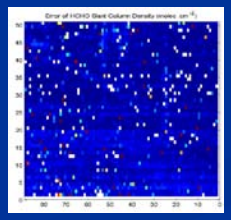
14:54 – 15:06



15:12 – 15:24







Uncertainty

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Yes. Some "pseudo-primary" HCHO observed from some flares.

Maybe. HONO enhanced in automobile exhaust plumes.

2) The importance of secondary HCHO formation from ozonolysis of olefins.

May be significant. TBD.

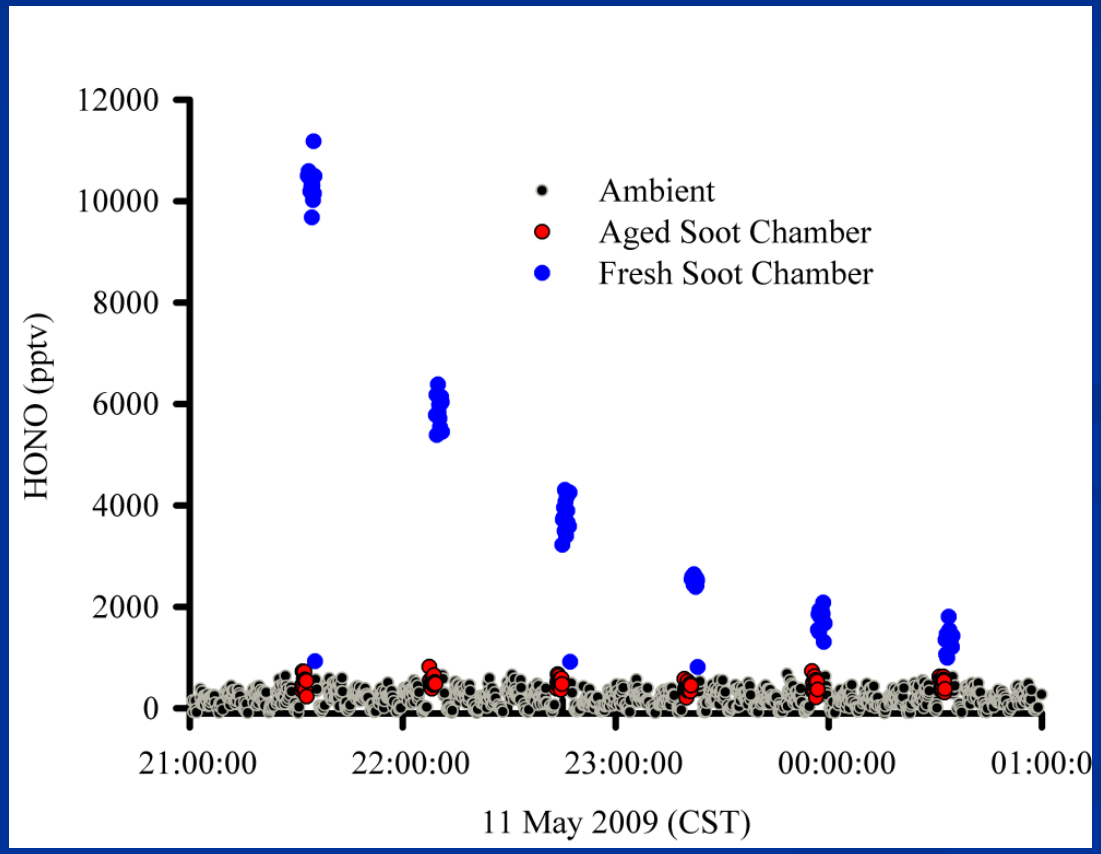
3) Identification of formation pathways of HONO (Day/Night, surface, heterogeneous, homogeneous).

Similar HONO - Rush hour - Aerosol Relationships. HONO-FLUX.

Preliminary Conclusions

4) Impact of soot (fresh and coated) on chemistry, radiation (photochemistry and climate), and dynamics.

HONO and SOA enhanced in SOOT Chambers.



Preliminary Conclusions

5) The ambient levels of $ClNO_2$ (and other halogens) in Houston and potential as a radical source.

Yes. GaTech found significant levels of $ClNO_2$ several nights. TAMU measured N_2O_5. UNH observed significant HCl levels, correlated with HNO_3.

6) Intercomparison of ambient HONO measurement techniques in urban atmosphere.

Various instruments all measuring "HONO", some calibration/interference issues found.

7) Relative importance of springtime ozone formation mechanisms in Houston.

Same mechanisms that produce ozone in Fall are active in the Spring. Post-frontal conditions, transport from North, re-circulation, entrainment of residual layer, etc.

Future Work

Dallas Measurements 2011

DISCOVER-AQ 2013

Texas Regional transport Experiment (T-REX)

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EPA

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