Study of Houston Atmospheric Radical Precursors
SHARP Science Plan

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Gary Morris	(Valparaiso University)
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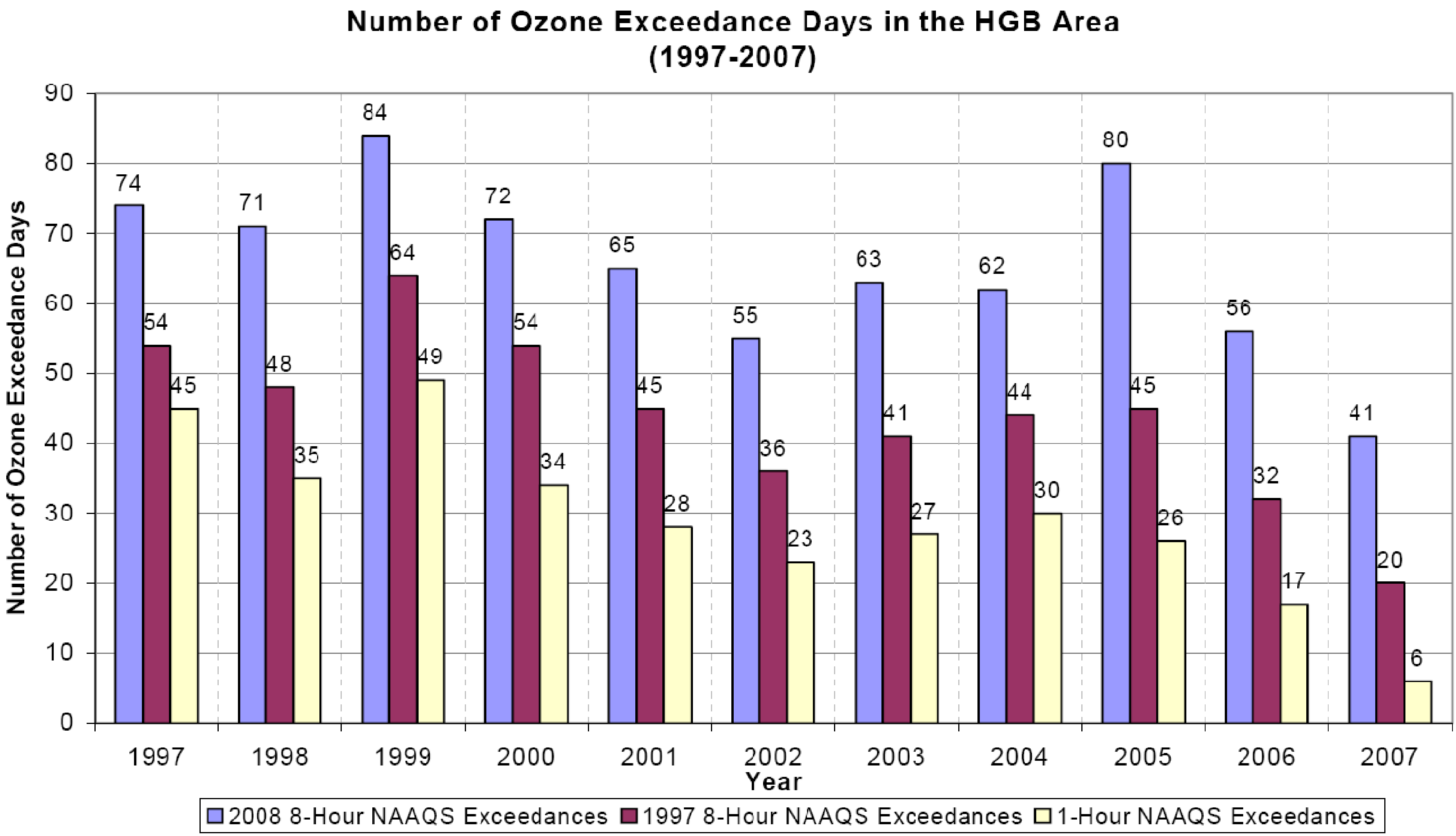
Sandy Dasgupta	(UT-Arlington

Outline

I. Introduction
II. SHARP Goals
III. Moody Tower Experiment Project (including HINT)
IV. FLAIR Goals and Description of FLAIR projects
V. SHARP/FLAIR supporting studies
- TRENF, Ship Channel, HONO-Flux, HBL, Aztec, SOOT, Ozonesonde

VI. Logistics and Flight plans
- Daily Meetings, Flares of Interest, Rapid Response, Sondes/BLH measurements, HINT

Houston Ozone Trend



*Source: Ozone - EPA's Air Quality System, May 23, 2008

**One-hour ozone values of 125 ppb or greater exceed the one-hour NAAQS. Eight-hour values of 85 ppb or greater exceed the 1997 eight hour NAAQS, and eight-hour values of 76 ppb or greater exceed the 2008 eight-hour NAAQS.

2008 (6 1-hr, 37 8-hr)

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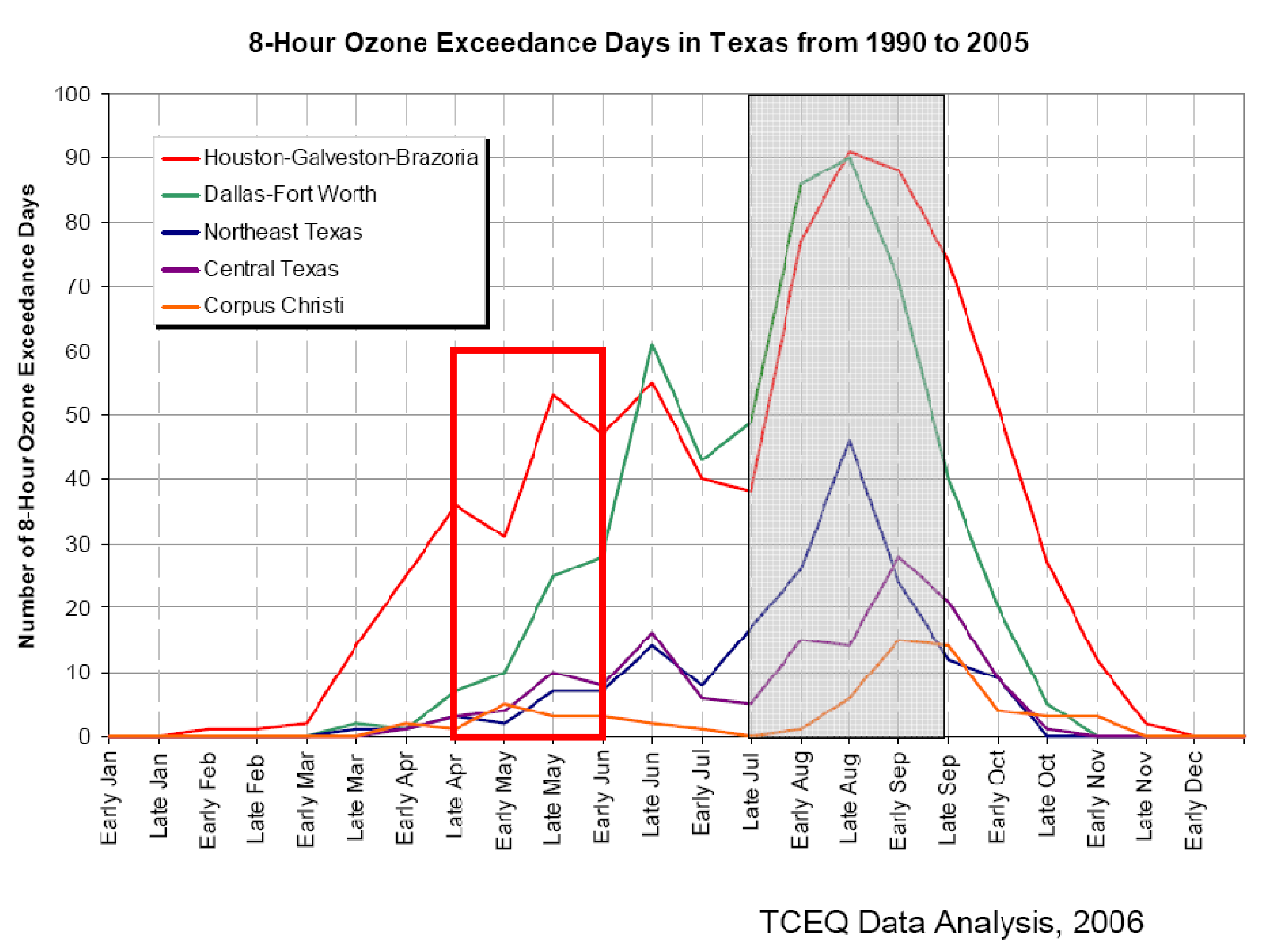
Dick Karp, TCEQ

SHARP Time Period

15 April – 31 May 2009



TexAQS II/TRAMP: Formaldehyde

Houston Ship Channel (HSC) instruments recorded large pulses of HCHO > 50 ppb

TRAMP data indicates significant portion of HCHO is primary associated with either CO (combustion) and smaller fraction with SO_2

Baylor Aztec saw a HSC flare with HCHO/CO = 2-4% (3-5x greater than for mobile sources) on Aug 31, 2006

Simultaneous mobile DOAS measurements detected HSC HCHO fluxes > 30x greater than reported in EI

Secondary HCHO formation from O_3+olefins may also be underestimated by SIP model

TRAMP/TexAQS II: HONO and NOz

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

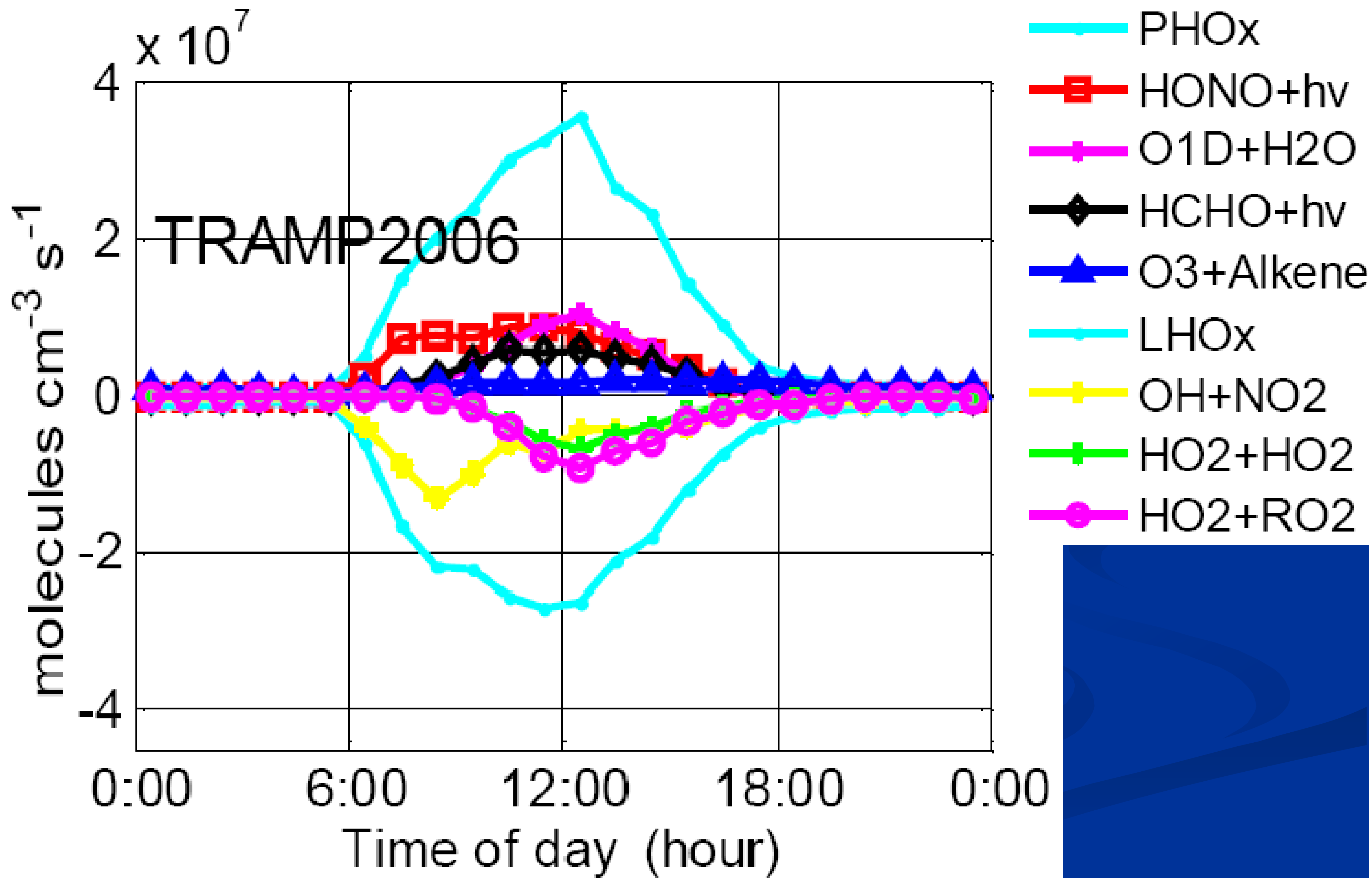
Strong vertical gradients indicate ground-level source of HONO (e.g. traffic)

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

Unknown NOz compound ubiquitous at night in Houston, possibly from NO_3 + VOC.

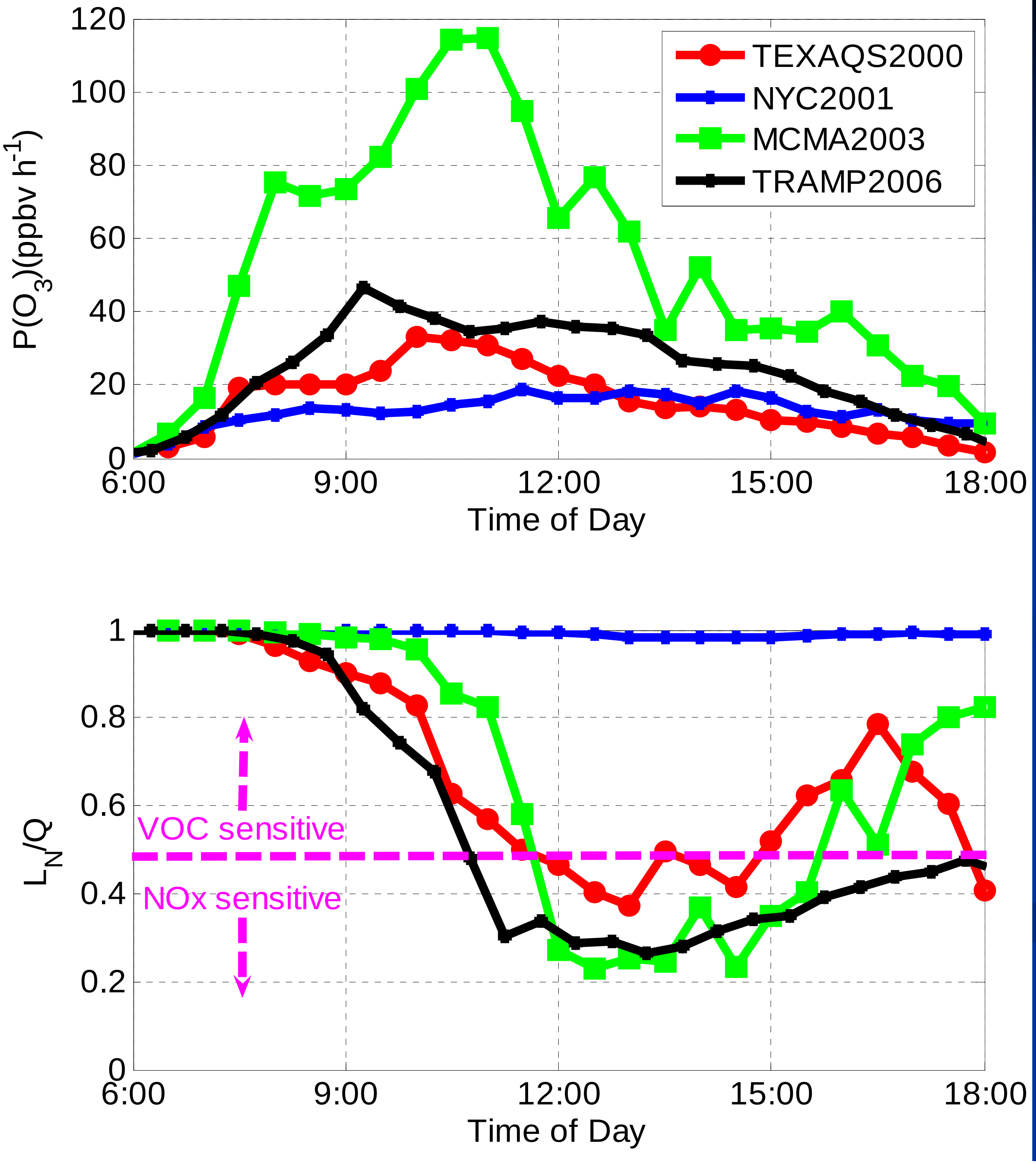
$ClNO_2$ present at ppbv level formed via N_2O_5 and $HCl_{(g)}$

HONO and HCHO important OH sources



Mao et al. (TRAMP AE Special Issue)

Ozone production



Mao et al. (TRAMP AE Special Issue)

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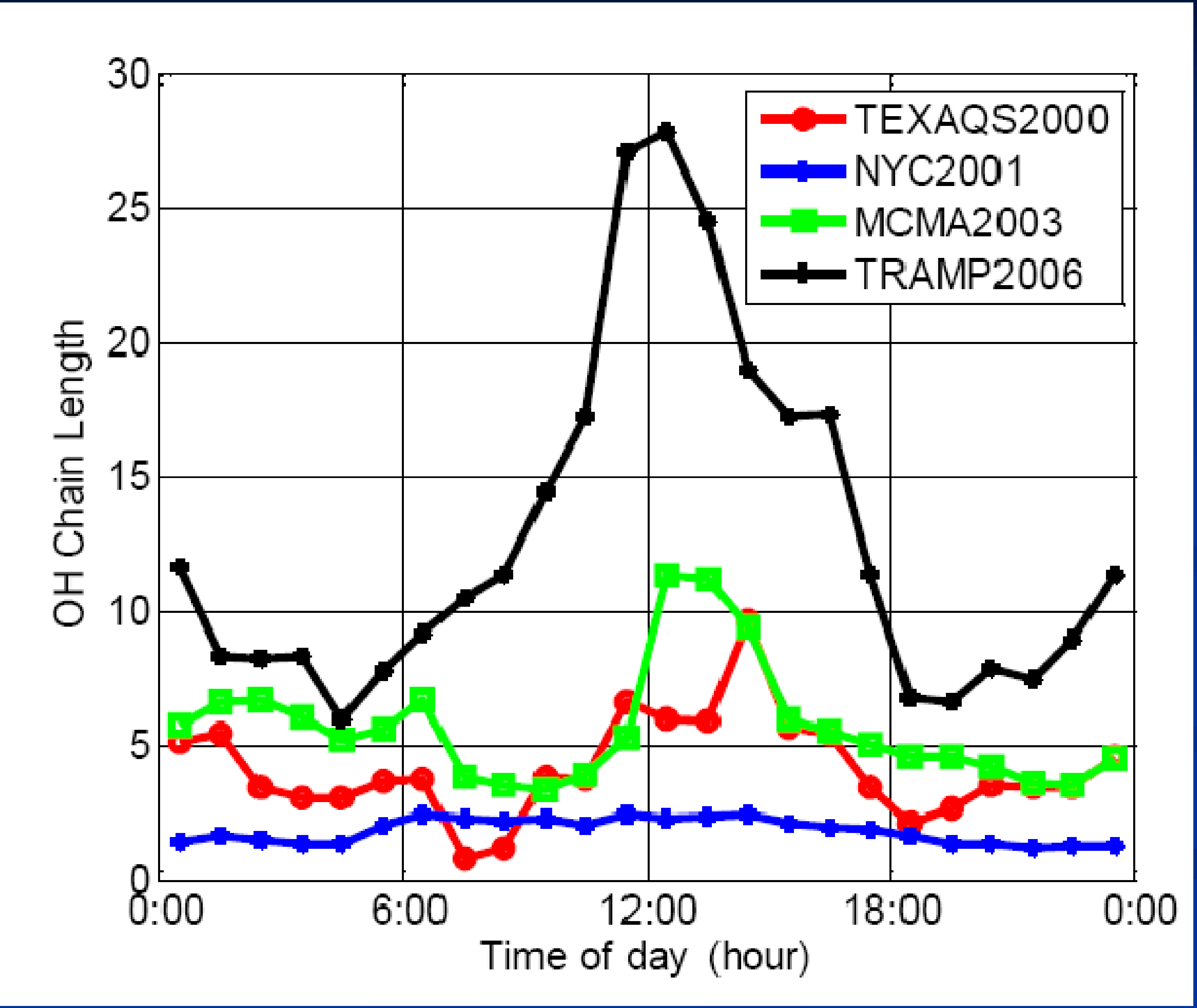
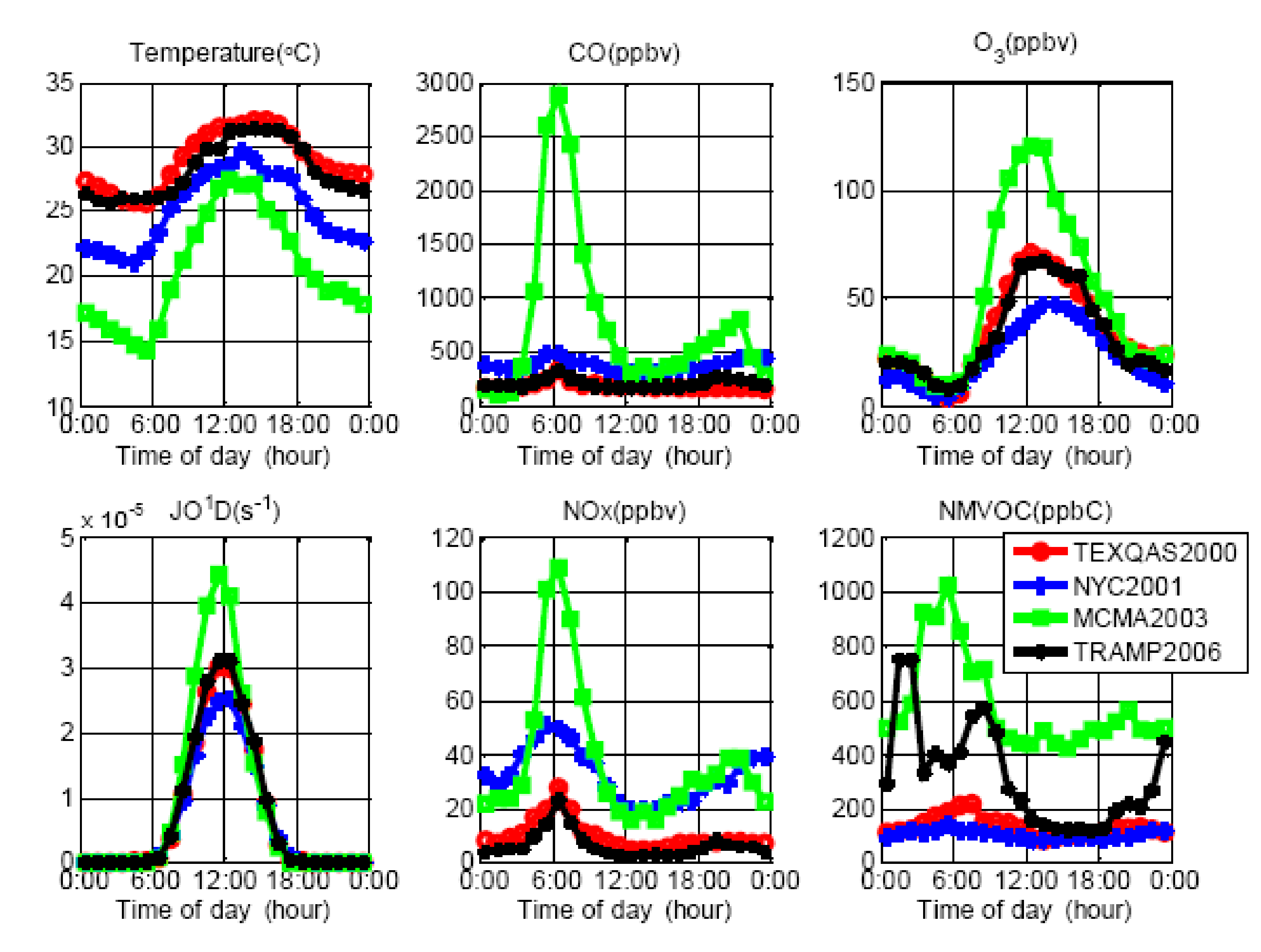
OH Chain Length



Mao et al. (TRAMP AE Special Issue)

Houston (and other) Chemical Environments



Mao et al. (TRAMP AE Special Issue)

TRAMP and O_3 production

- Calculated ozone production often greater than 40 ppbv/hr between 0800-1500 LT.
- O_3 production is both NOx and VOC sensitive (NOx sensitive for 7 hours during the day).
- OH chain length (10-20), which is much greater than other North American cities.
- Primary reason for enhanced Houston photochemistry is the VOC abundances in morning rush hour that approach those of Mexico City.

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 processes:

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) The importance of other "missing" radical sources.
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.

SHARP Related Projects

Moody Tower SHARP Intensive H100-UH & many other groups

HONO Intercomparison Study (HINT) H100-UH & many other groups

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

Traffic Related Emissions of HONO and HCHO (TRENF) H100-UH

Study of HONO Surface Fluxes (HONO-FLUX) H100-UH

Houston Urban Boundary Layer Study H100-UH

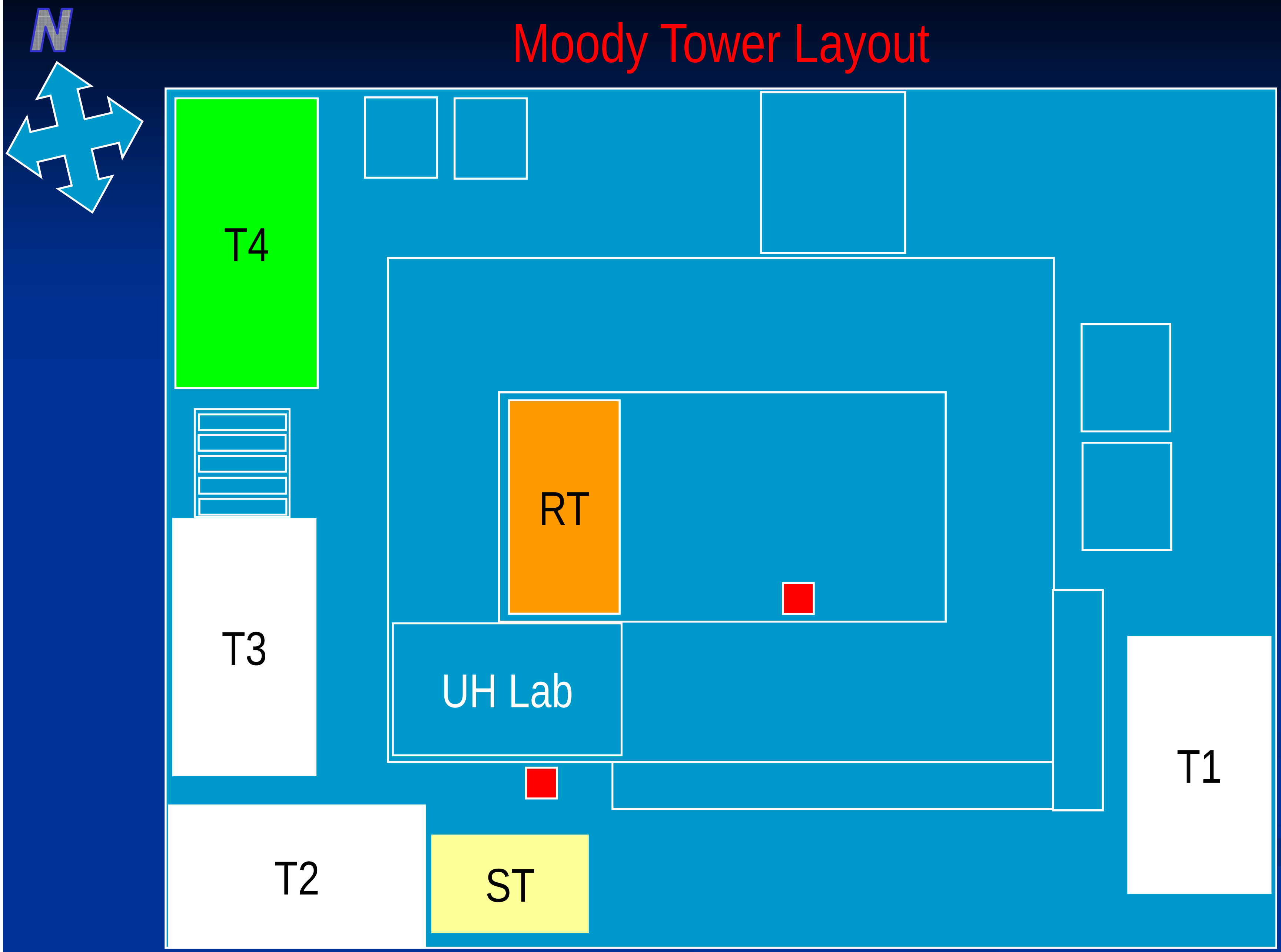
Measurements of HCHO, PAN, and CO in HSC H100-UH

Nitrylphenols in Houston Atmosphere UT-Arlington

Formaldehyde and Olefins from Large Industrial Releases (FLAIR)

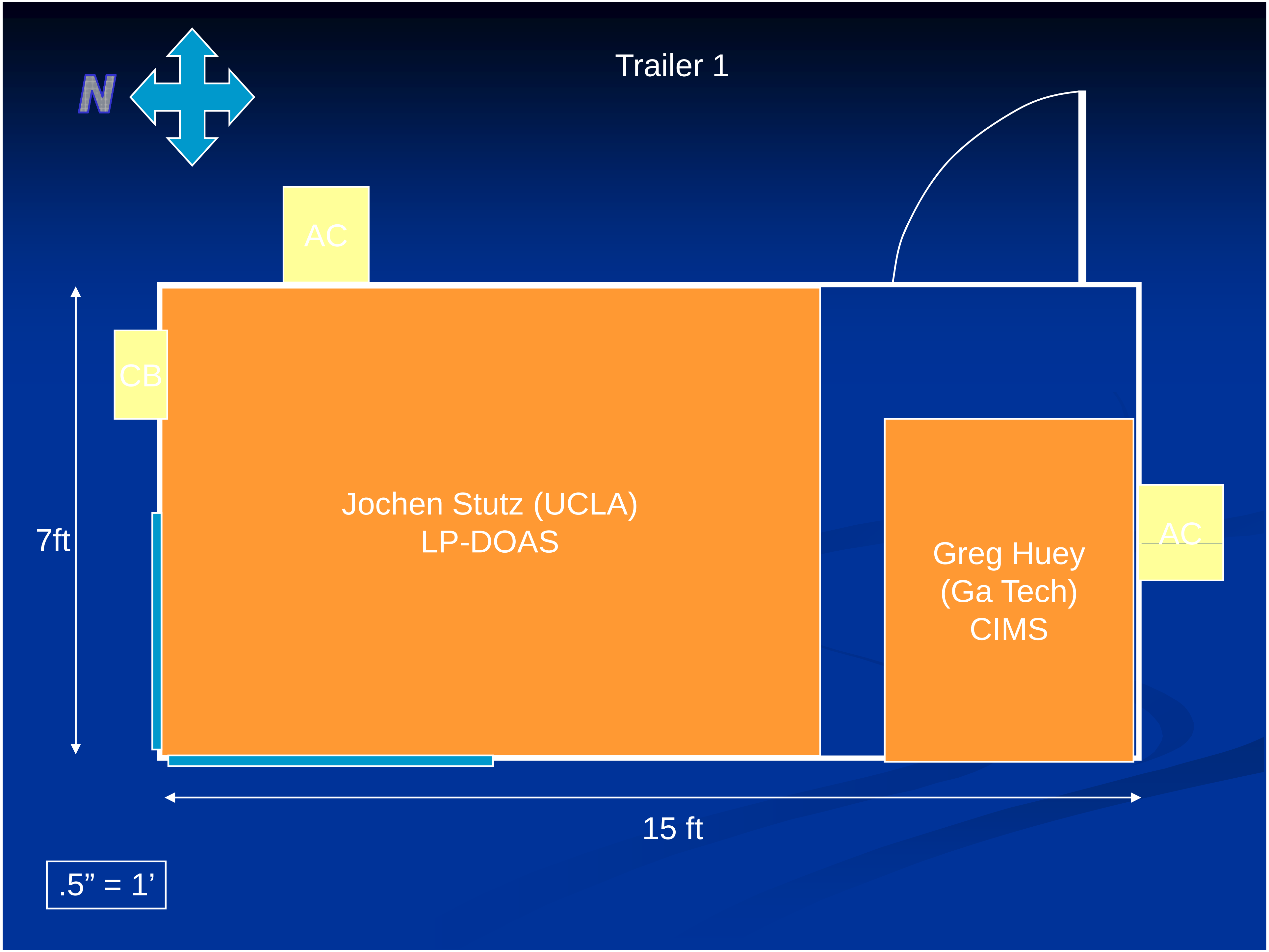
- Dual MAX-DOAS H104A-WSU & H104C-UCLA
- Imaging-DOAS H104C-UCLA & H100-UH
- Solar Occultation Flux (SOF) H102-Chalmers University
- Aztec SHARP Flights H103A-UH
- Aerodyne Mobile Lab H113-Aerodyne
- Plume Inversion Modeling H118-Aerodyne

Moody Tower Layout



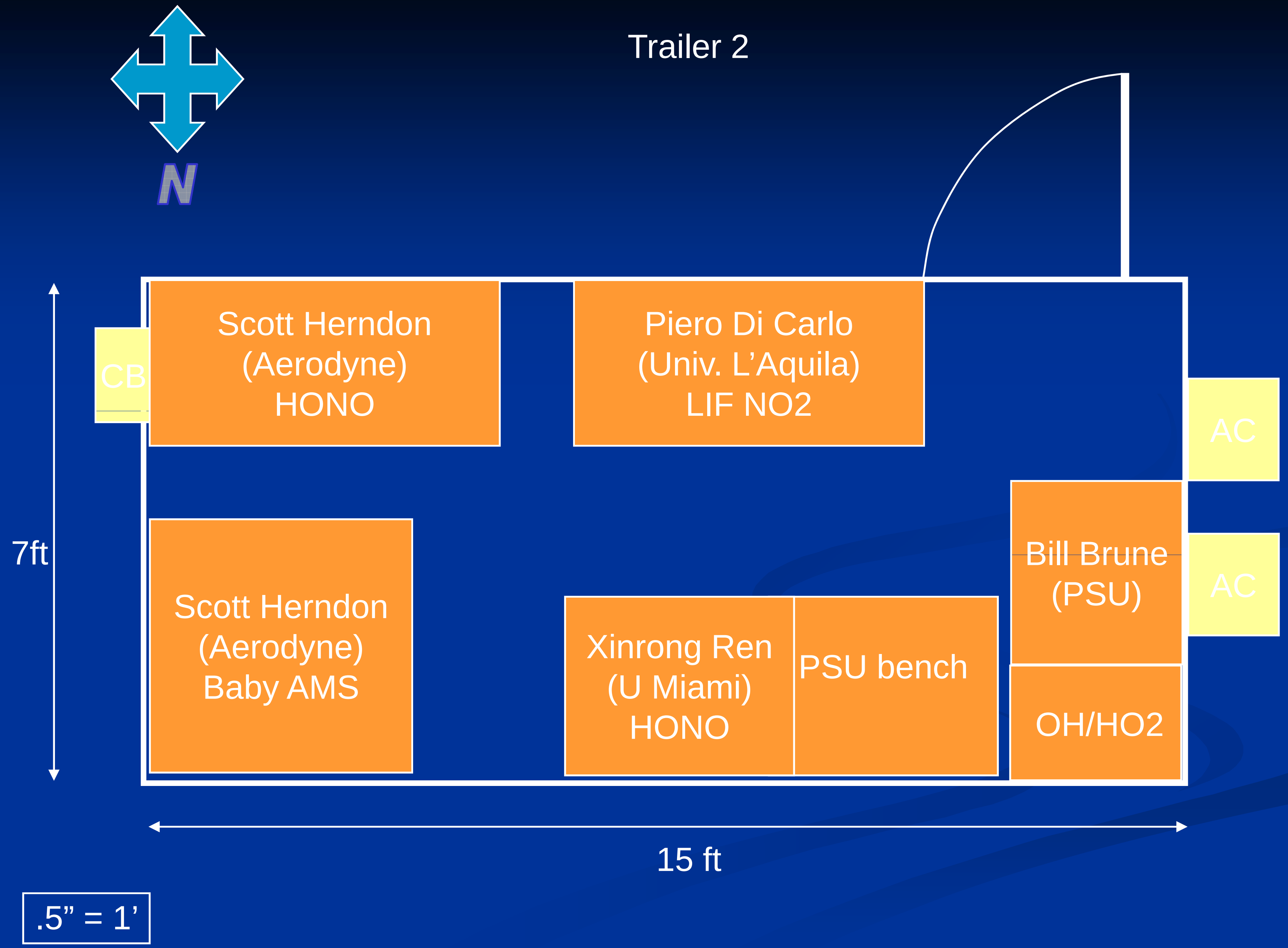
Live Moody Tower Axis Cam http://129.7.48.166/

Additional Walk Up Tower

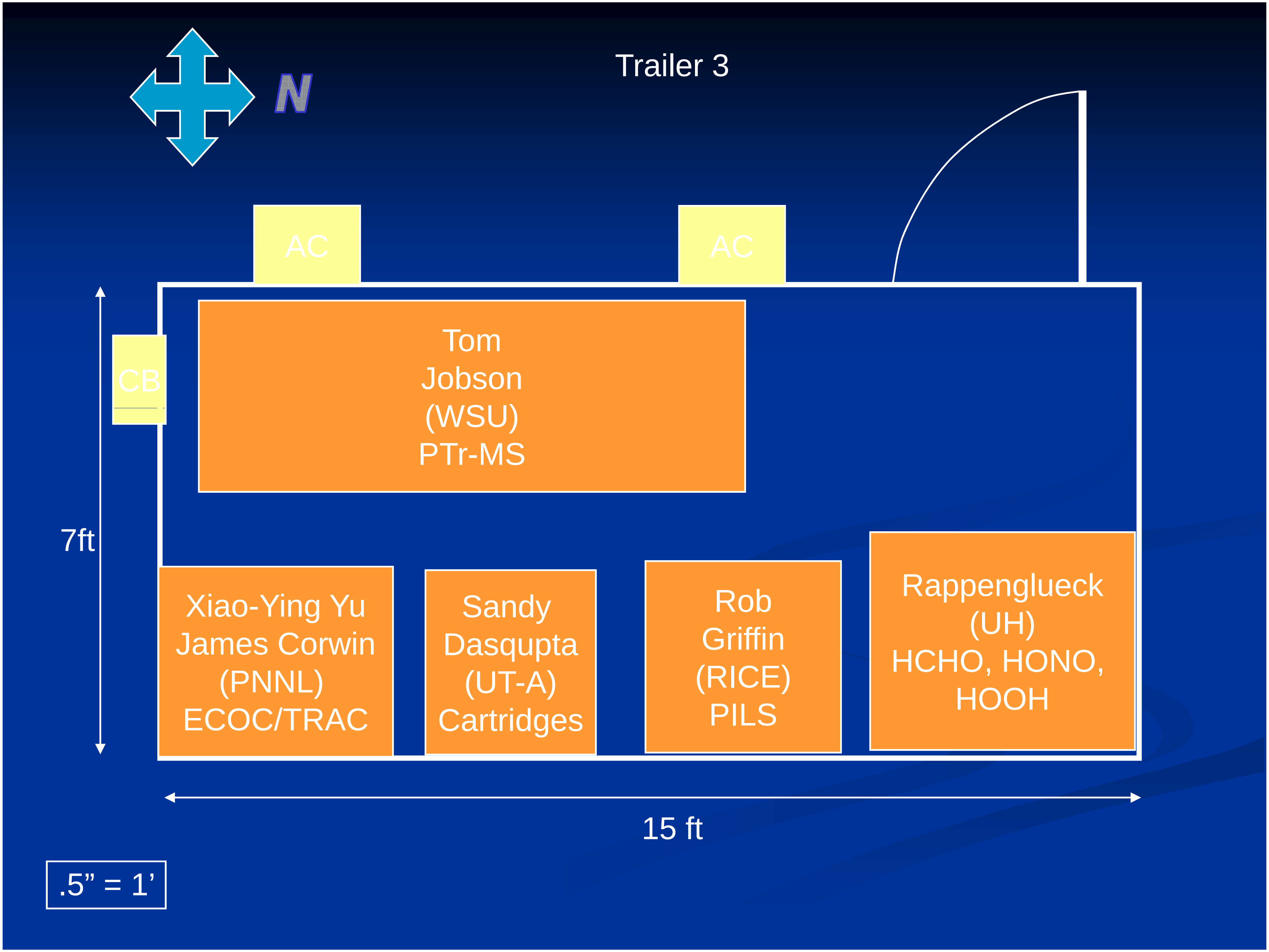


Trailer 1
N
AC
CB
Jochen Stutz (UCLA)
LP-DOAS
Greg Huey
(Ga Tech)
CIMS
AC
7ft
15 ft
.5” = 1’

Trailer 2

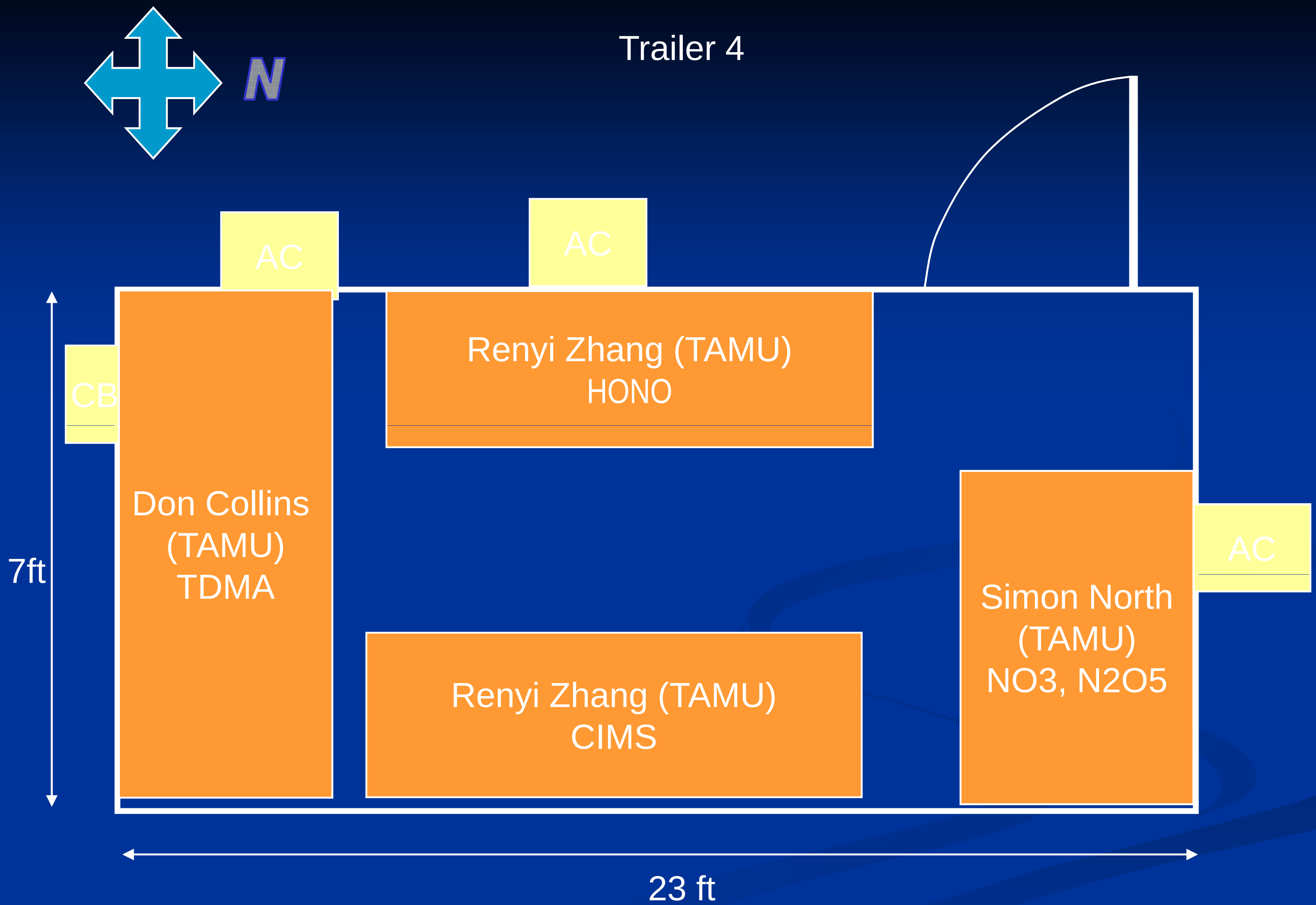


N
Scott Herndon
(Aerodyne)
HONO
Piero Di Carlo
(Univ. L'Aquila)
LIF NO2
CB
AC
AC
7ft
Bill Brune
(PSU)
Scott Herndon
(Aerodyne)
Baby AMS
Xinrong Ren
(U Miami)
HONO
PSU bench
OH/HO2
15 ft
.5" = 1'



N
Trailer 3
AC
AC
CB
Tom
Jobson
(WSU)
PTr-MS
7ft
Xiao-Ying Yu
James Corwin
(PNNL)
ECOC/TRAC
Sandy
Dasqupta
(UT-A)
Cartridges
Rob
Griffin
(RICE)
PILS
Rappenglueck
(UH)
HCHO, HONO,
HOOH
15 ft
.5" = 1'

Trailer 4


N
AC
AC
CB
Renyi Zhang (TAMU)
HONO
Don Collins
(TAMU)
TDMA
AC
Simon North
(TAMU)
NO3, N2O5
Renyi Zhang (TAMU)
CIMS
7ft
23 ft

SHARP/HINT Moody Tower Campaign

O_3, CO, NO/NO_2,/NO_Y, SO_2, T, P, RH, ws, wdir, precip (UH)
Actinic flux (photolysis frequencies), AOD, O_3 column, skycam (UH)
VOCs (AutoGC), PANs, HCHO, HOOH, HONO (UH)
OH, HO_2, OH reactivity, PAM, O_3 Production (Penn State)
Long Path DOAS at ~ 50 m, 150 m, and 300 m for path integrated O_3, NO_2, SO_2, HONO, HCHO, NO_3 (UCLA)
Speciated OVOCs (WSU)
TRAC, EC/OC, particle size distribution, actinic flux (PNNL)
HONO (UMiami)
Continuous boundary layer height (UH)
HNO_3, HONO*, HCl (UNH)
HONO*, baby-AMS, Mobile Supersite (Aerodyne)
SOOT Suite of measurements – t-DMA, HONO, N_2O_5, NO_3, particle size spectra, etc (TAMU)
$ClNO_2$, N_2O_5, PANs (GaTech)
Ozonesondes (Valpo/UH)

Moody Tower SHARP Campaign

New additions:

PILS [Rob Griffin – Rice, Jack Dibb - UNH]
Total peroxy nitrates (RO_2NO_2) & alkyl nitrates ($RONO_2$) [Piero Di Carlo – L'Aquila]
Additional NO, NO_2, SO_2, NO_Y [Winston Luke – NOAA]
Hg (GEM, RGM, FPM) [Steve Brooks – NOAA]*
Nitrophenols [Sandy Dasqupta – UT-Arlington]
Organic nitrate products from OH/NO_3 oxidation of VOC [Elliot Atlas – U. Miami]

http://sharp.hnet.uh.edu

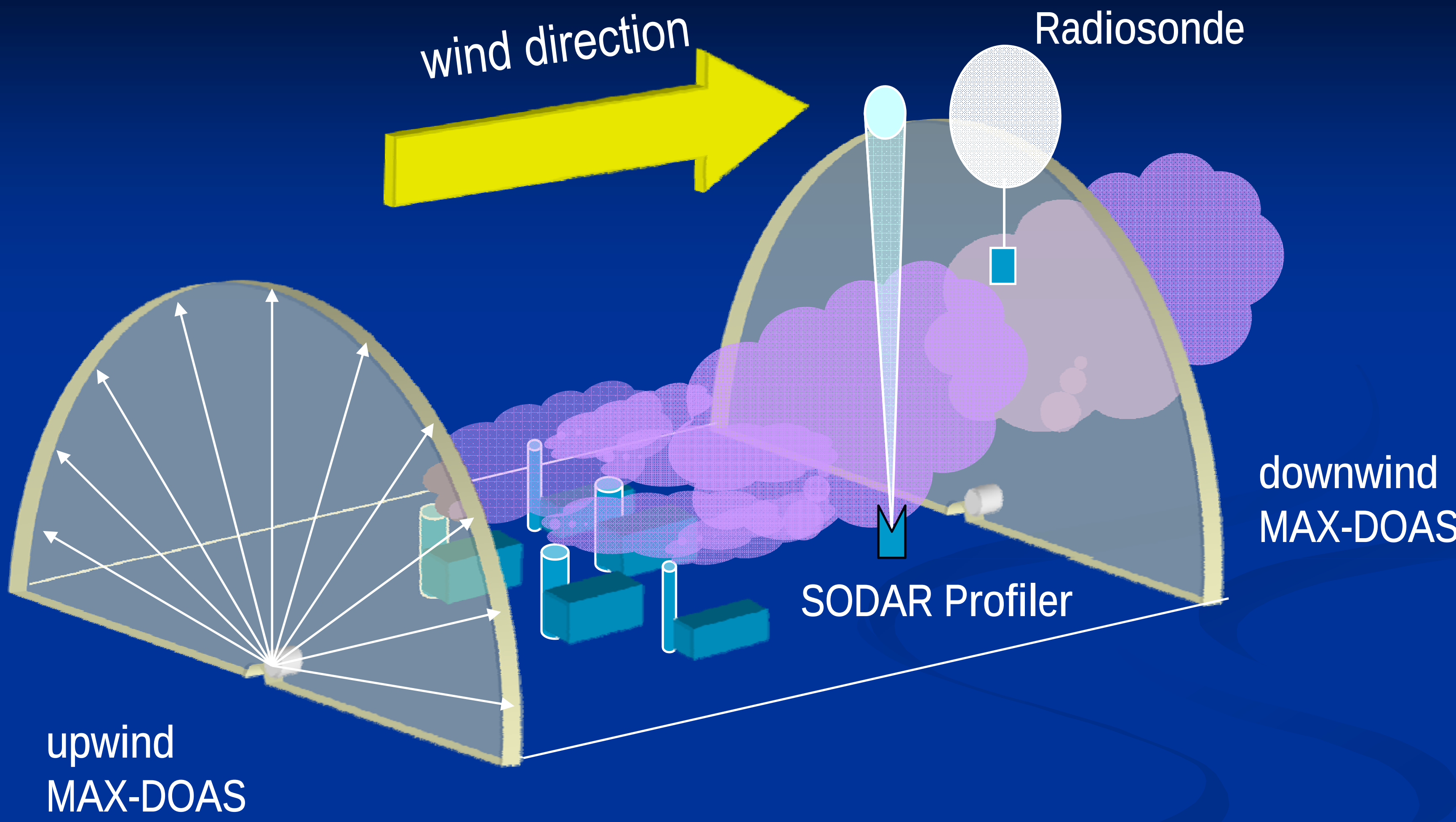
Formaldehyde and Olefins from Large Industrial Releases (FLAIR)

The FLAIR subproject will focus on the measurement of fluxes of HCHO from sources (e.g., flares, refineries, chemical facilities, etc) in southeastern Texas.

One goal is to improve Houston radical budget by providing accurate emission fluxes for HCHO. Another is to investigate the secondary formation of HCHO from ozone-olefin reactions. Several approaches will be pursed:

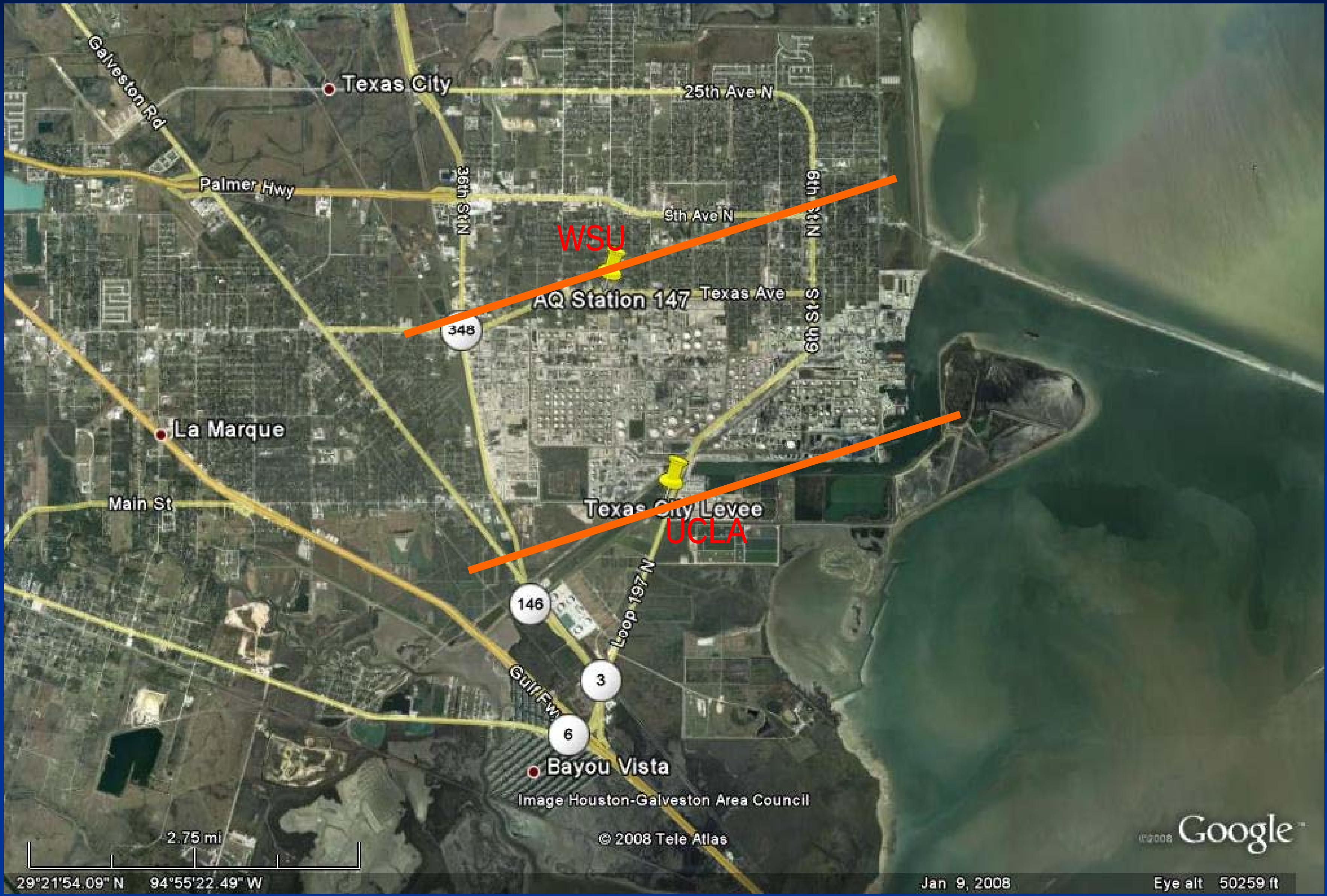
- Area-average flux from a number of facilities near Texas City (WSU, UCLA)
- Flux from individual flares and other point sources (UCLA, UH)
- Solar Occultation Flux (SOF) Method (Chalmers University, UH)
- Aerodyne Mobile Laboratory (Aerodyne)
- A plume inversion tool for indentifying and quantifying sources (Aerodyne)

Approach for Area-average Flux Measurements

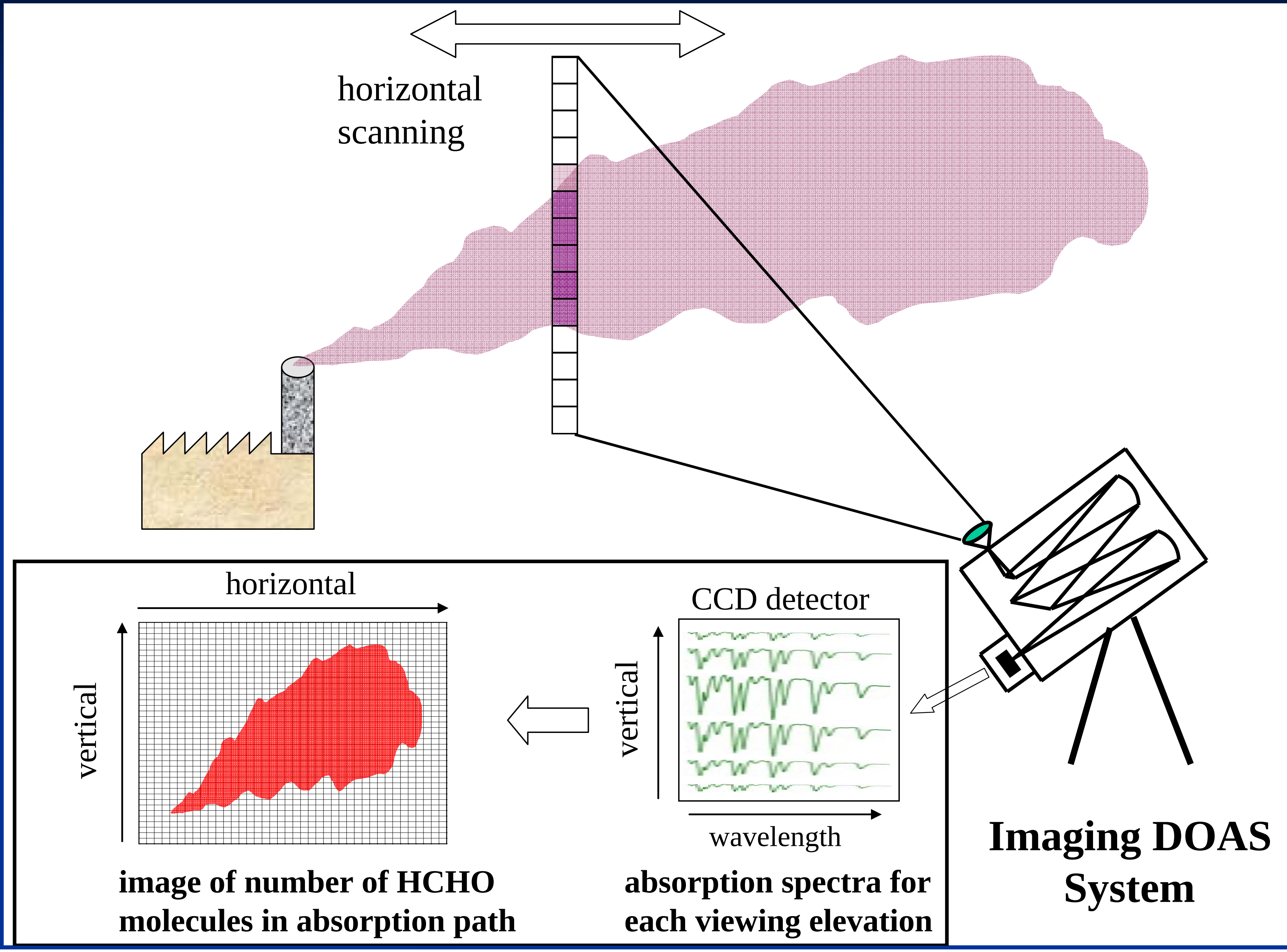


Setup of two stationary MAX-DOAS instruments, SODAR and GPS radiosondes to determine the area-averaged HCHO flux between the two vertical slices (~10km wide and ~5km high).

Max-DOAS Locations: Texas City



Approach for Single Source Flux Measurements: I-DOAS



Locations

Initial Targets

- Texas City
- Mont Belvieu Chevron Plant (K-Ranch)
- Channel View Plants / AQ Station

SOF