12-13 October 2006
Rapid Science Synthesis Workshop
UT Pickle Campus, Austin, Texas

Presentations organized around:

(1) Near final figures that we will include in the October 31 report to TCEQ, and

(2) the preliminary conclusion statements that we wish to make in that report.

Details posted at:
http://esrl.noaa.gov/csd/2006/rss/

Questions:

Cari Furiness - cari_furiness@ncsu.edu
David Parrish - david.d.parrish@noaa.gov
Ellis Cowling - ellis_cowling@ncsu.edu

29 September Preview
Rapid Science Synthesis*

Questions A, C, D, E – Emissions: P-3 data

- **Onboard measurements of HRVOC (Joost de Gouw)**

Questions F, K – VOC- vs NOx-sensitive photochemistry

- **1-hr vs 8-hr SIP modeling and process analyses (Will Vizuete)**

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Questions A, C, D, E – Emissions: P-3 data

- **Onboard measurements of HRVOC (Joost de Gouw)**

Measurements of HRVOCs Onboard the NOAA WP-3D

Joost de Gouw, Carsten Warneke
NOAA & CIRES, Boulder, CO

Lori Del Negro
Lake Forest College, Lake Forest, IL

Today:
Proton-transfer-reaction mass spectrometry aromatics
Laser photo-acoustic spectroscopy ethylene

Later:
Whole air samples (Atlas et al.) alkanes, alkenes, aromatics

PTRMS-LPAS Instrument

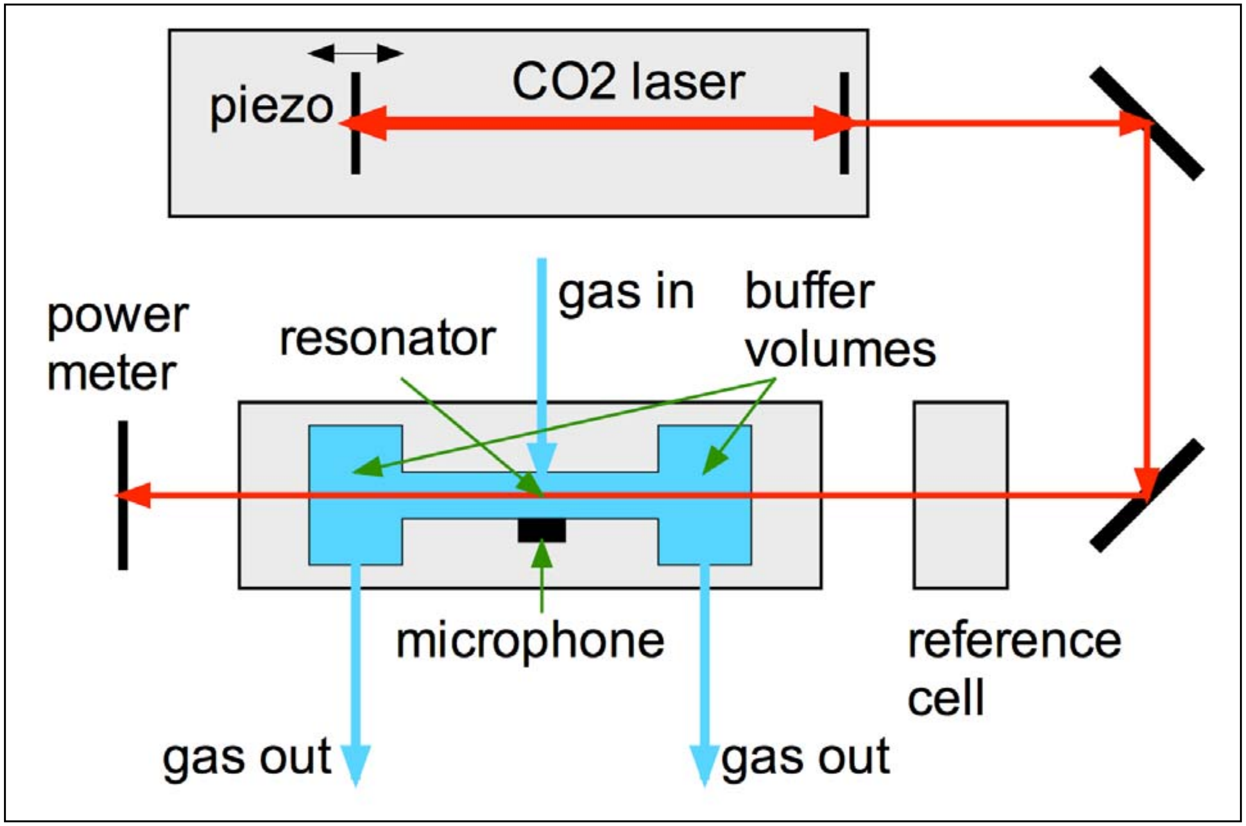
PTR-MS = proton-transfer-reaction mass spectrometry

benzene, toluene, C8-aromatics, C9-aromatics

LPAS = laser photo-acoustic spectroscopy

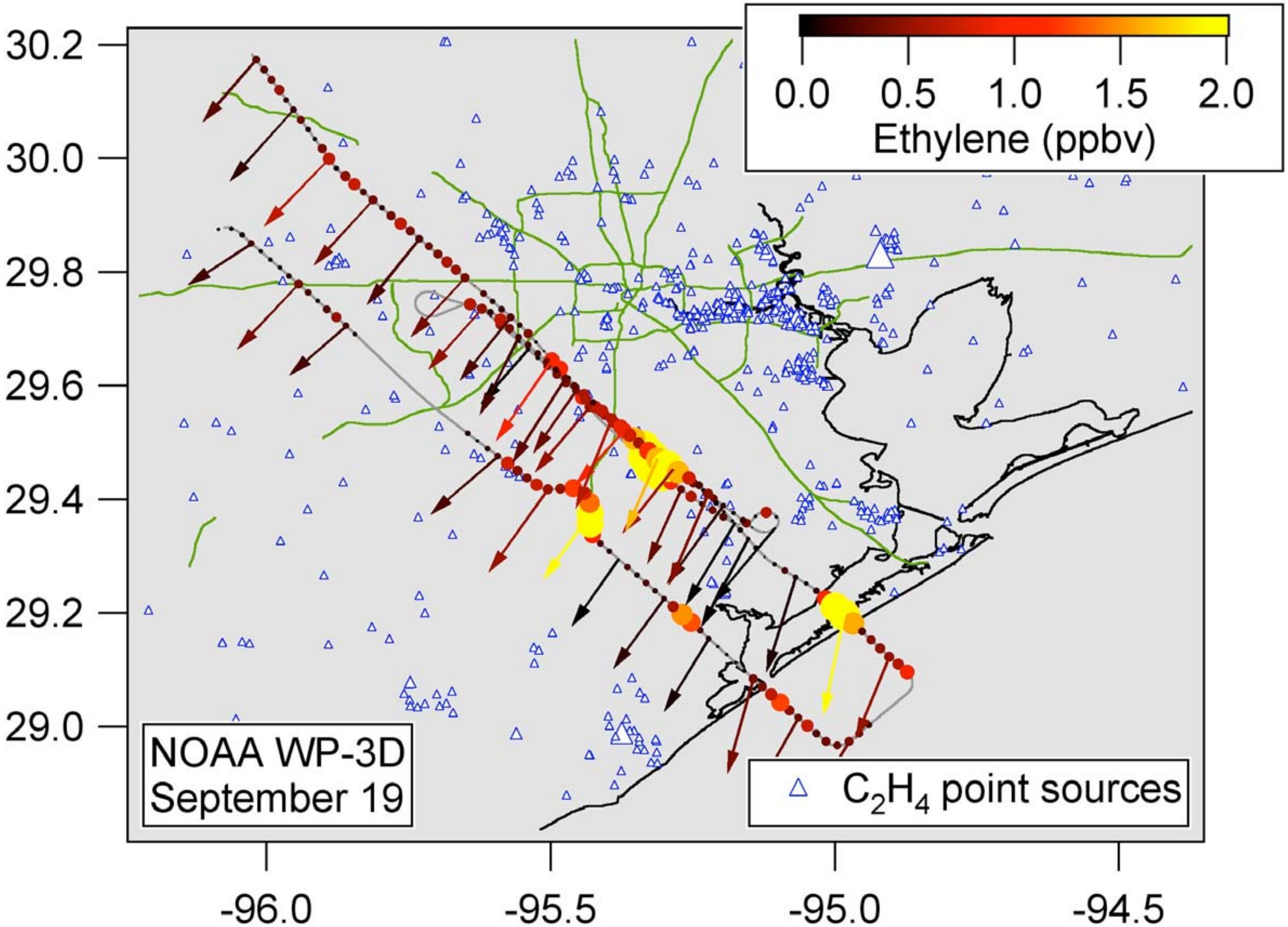
ethylene

Laser Photo-Acoustic Spectroscopy (LPAS)

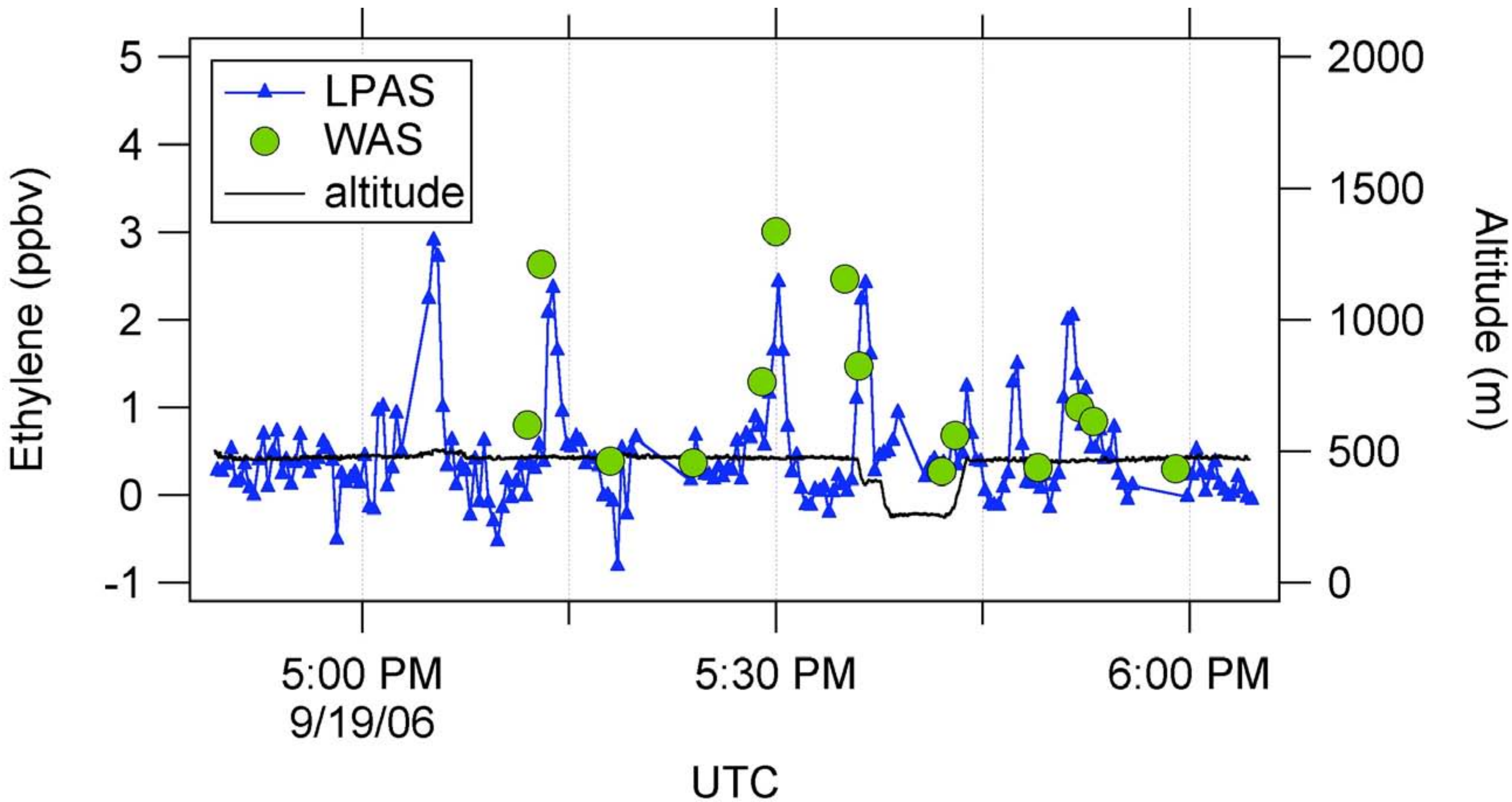


1. CO_2 laser excites ethylene
2. Ethylene is de-excited in collisions
3. Heating leads to pressure gradient (=sound)
4. Signal measured with a microphone

Comparison between LPAS and WAS

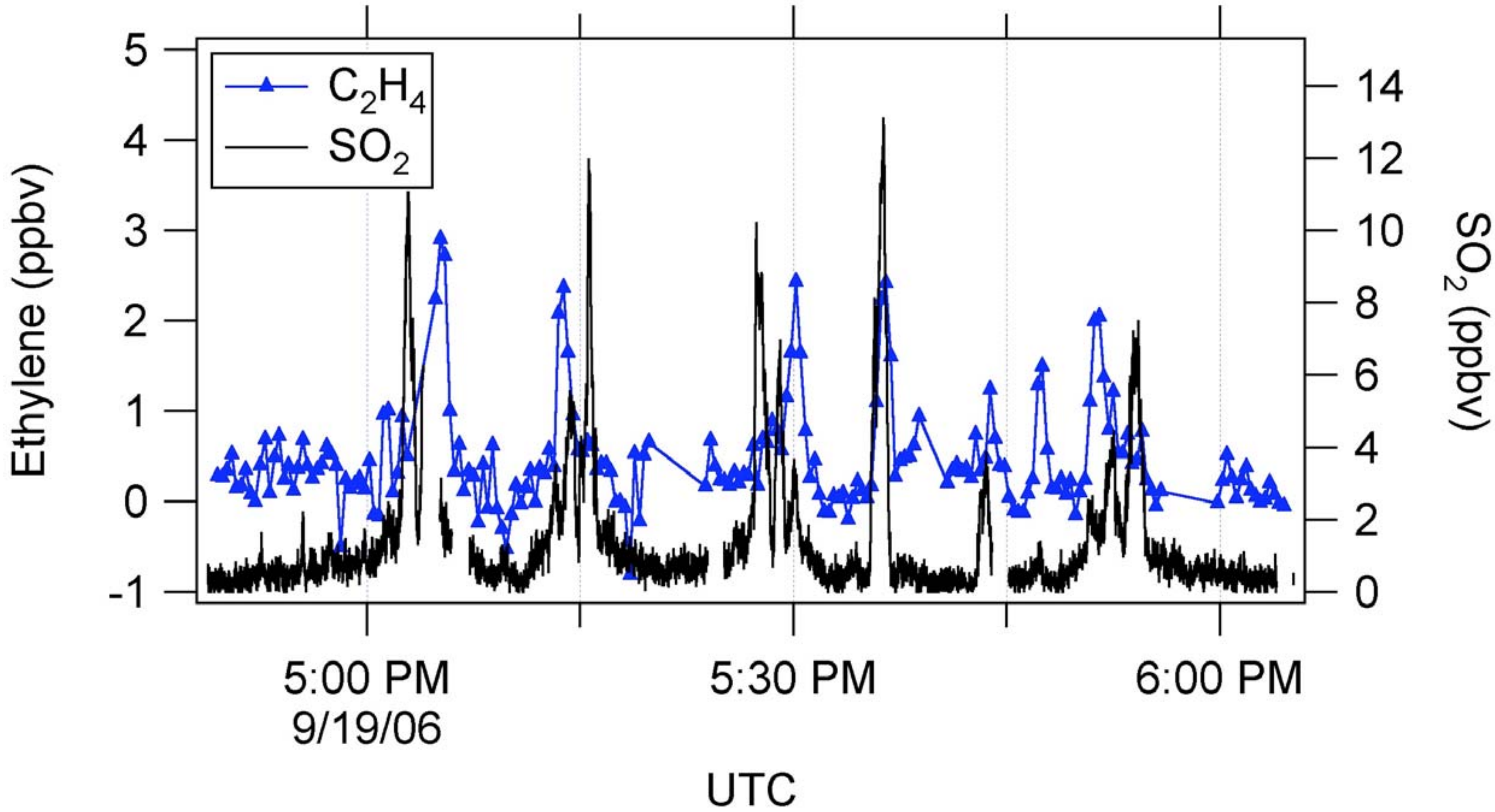


Comparison between LPAS and WAS



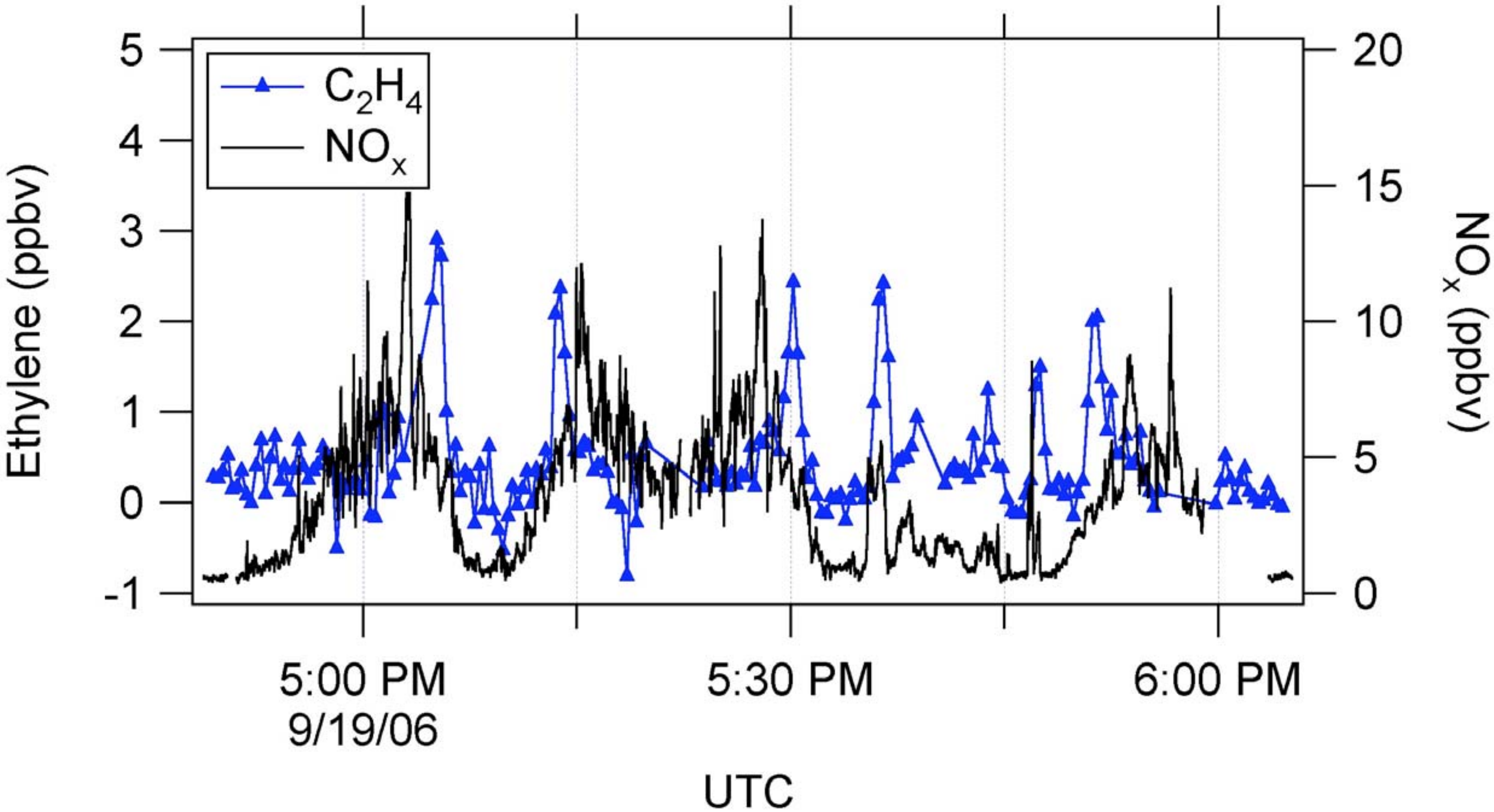
- ➢Initial results from LPAS and WAS compare well
- ➢LPAS more noisy in the turbulent PBL $\Rightarrow$ 20 sec averages

Ethylene and NO_x, SO_2 Sources Not Co-Located?



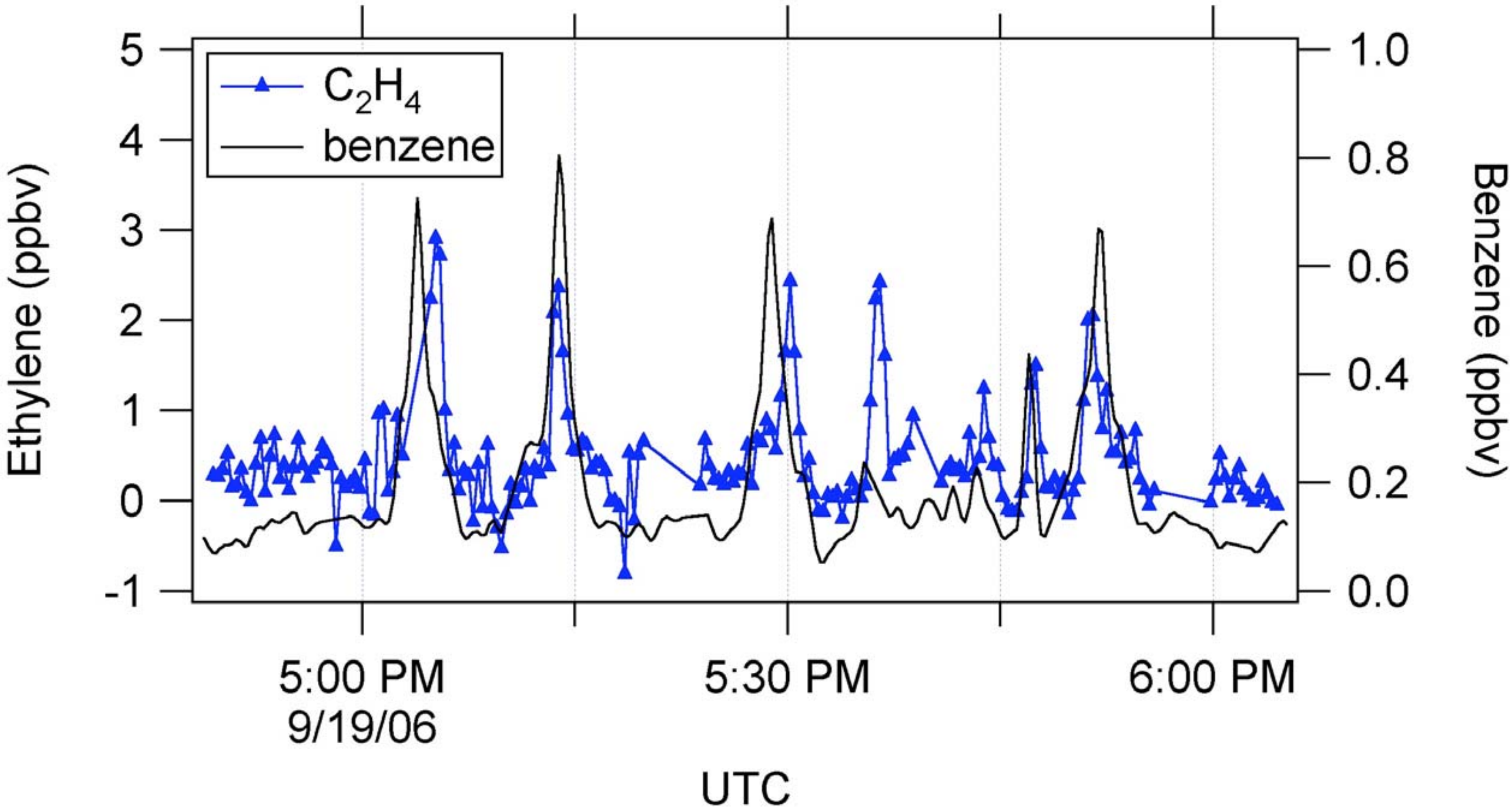
Ethylene and SO_2

Ethylene and NO_x, SO_2 Sources Not Co-Located?



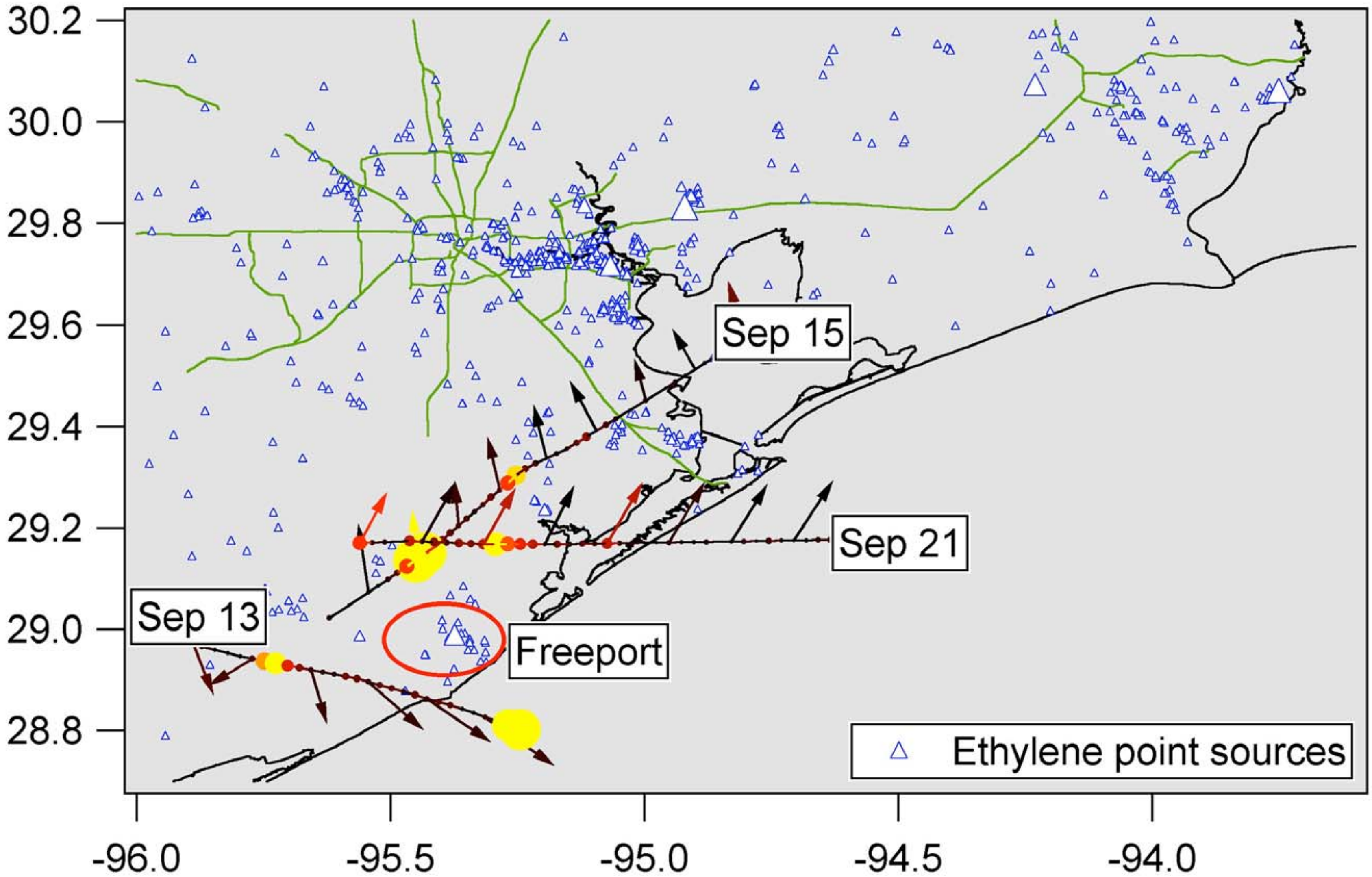
Ethylene and NO_x

Ethylene and NO_x, SO_2 Sources Not Co-Located?



Ethylene and Benzene

Where Have we Seen the Highest Ethylene?



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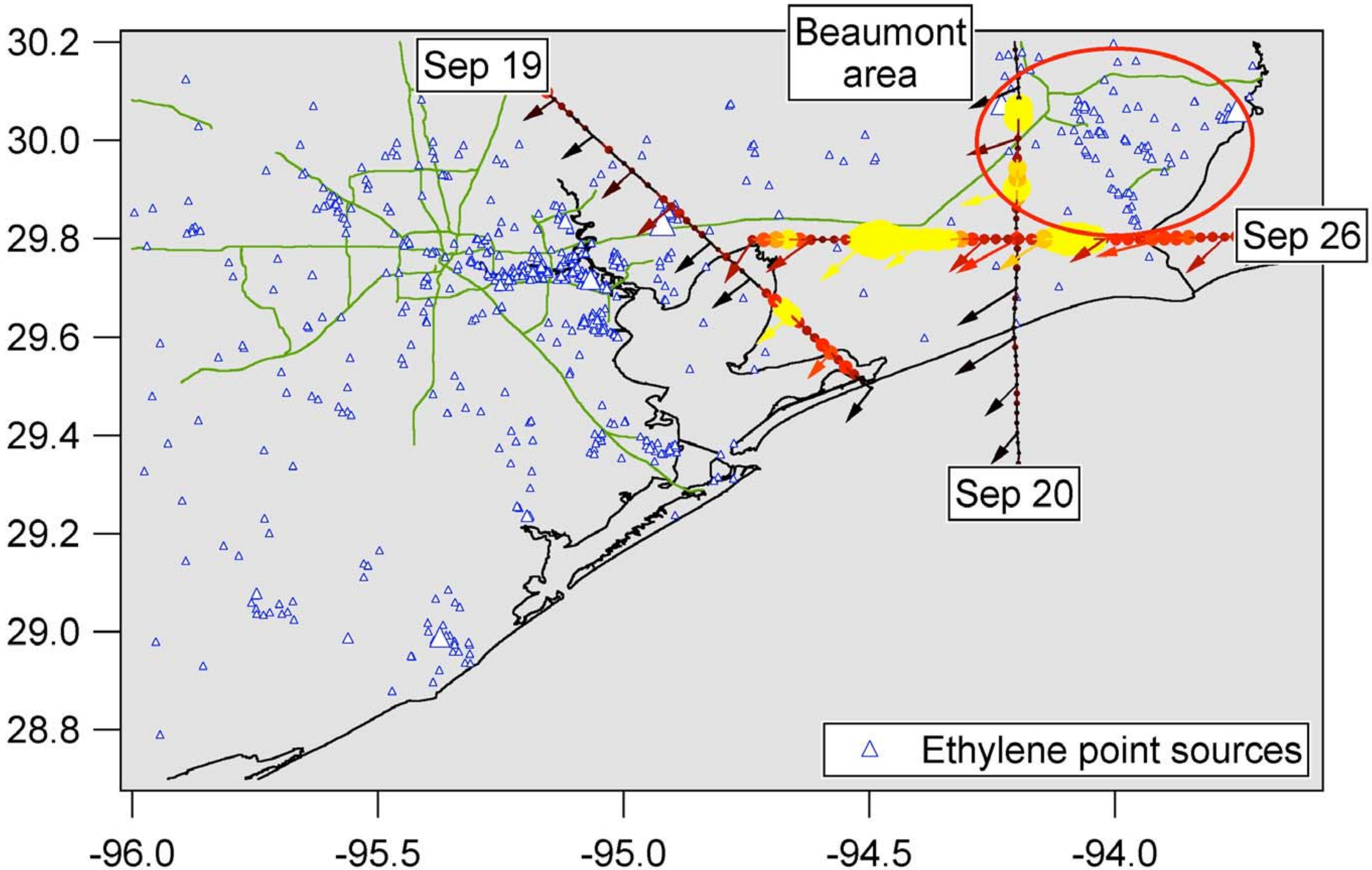

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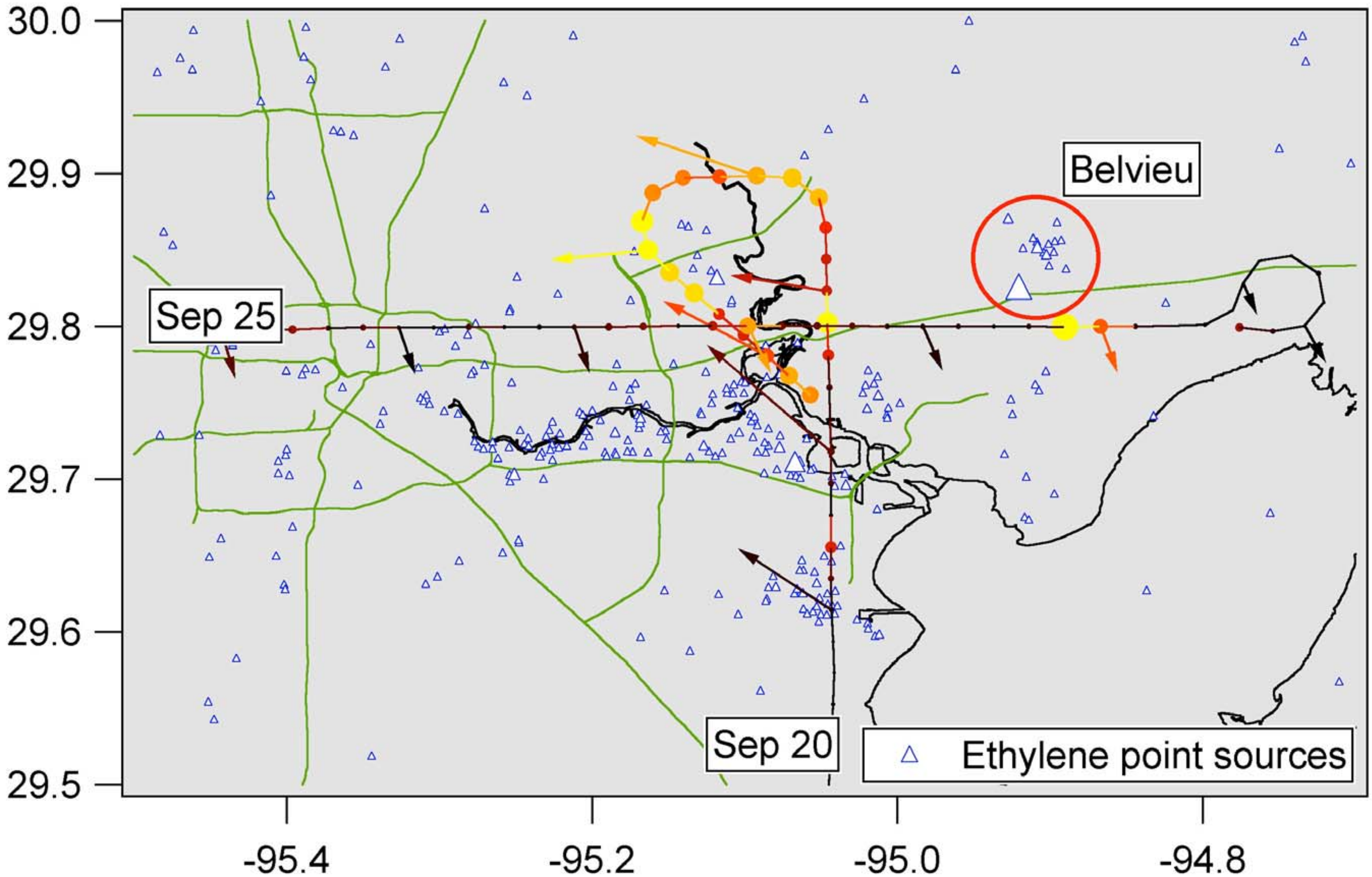

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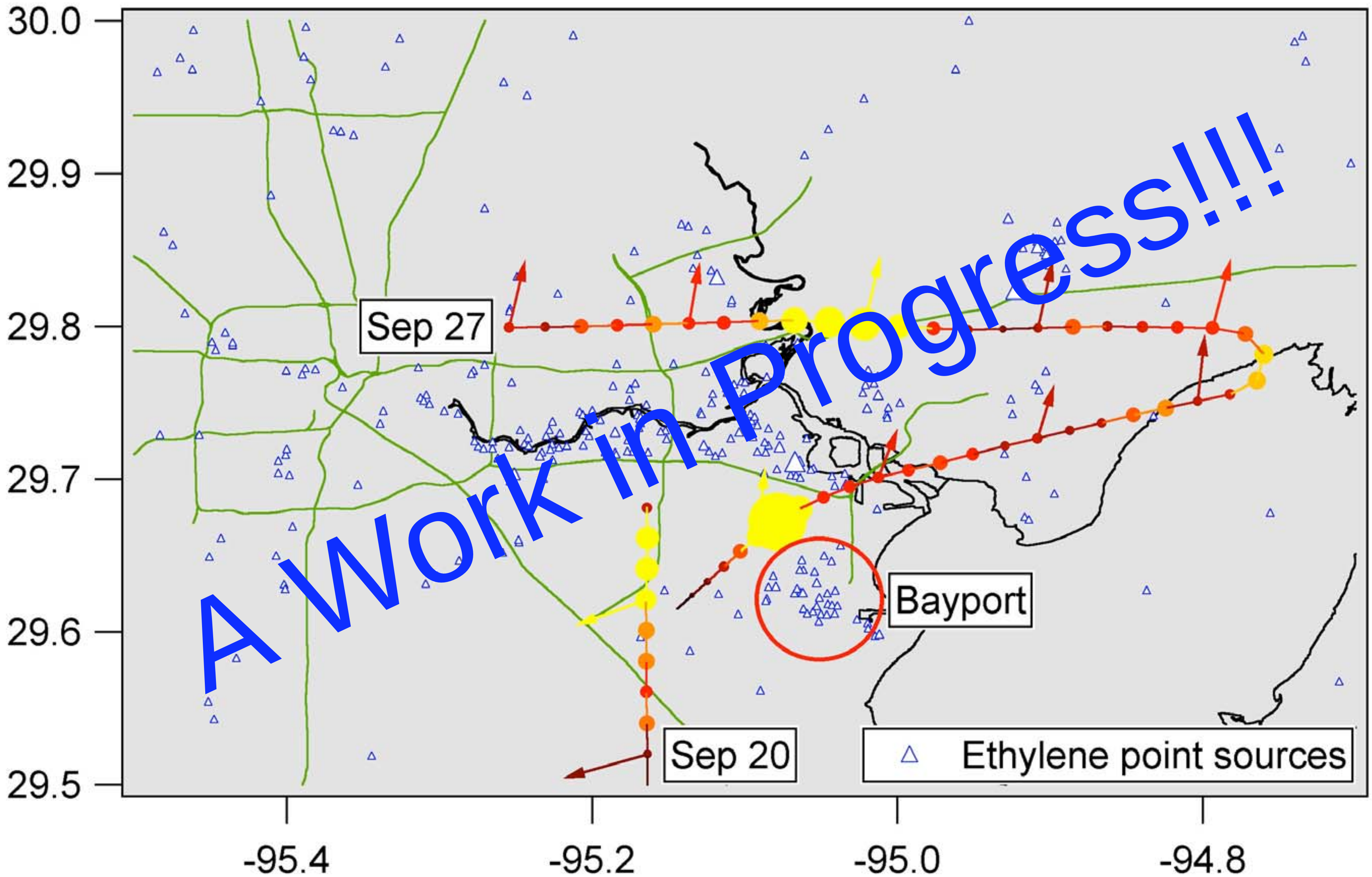
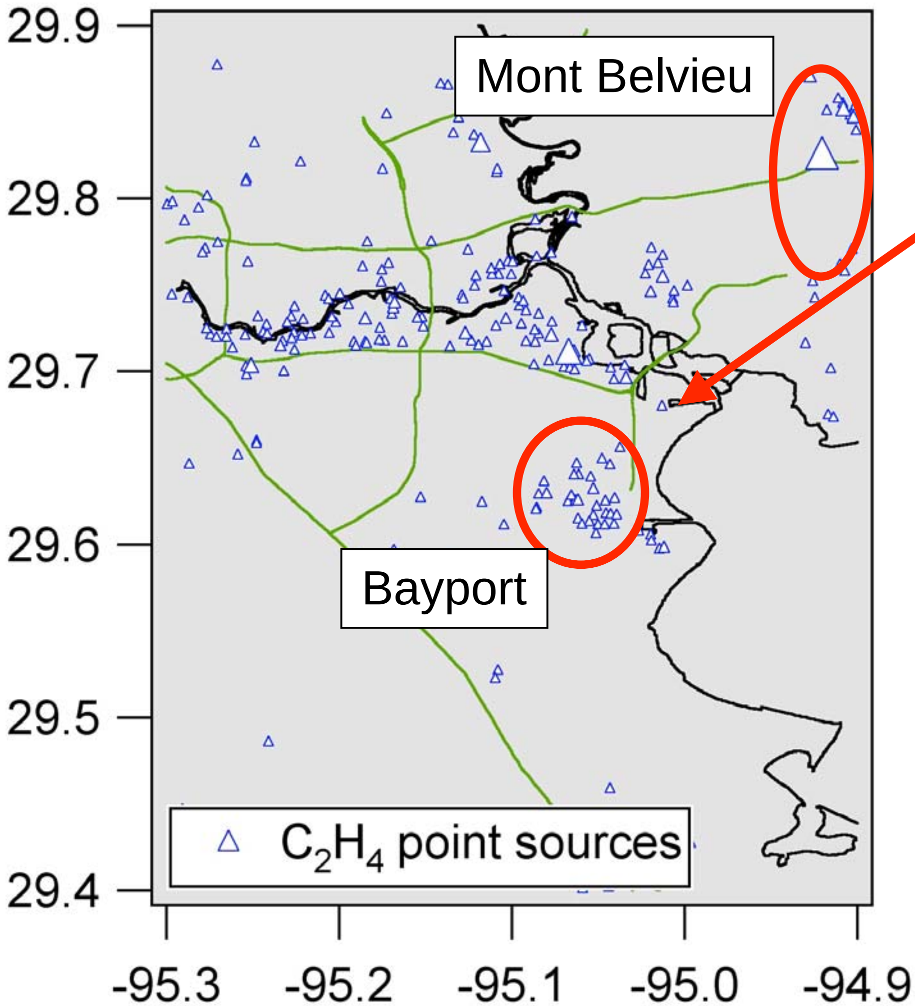
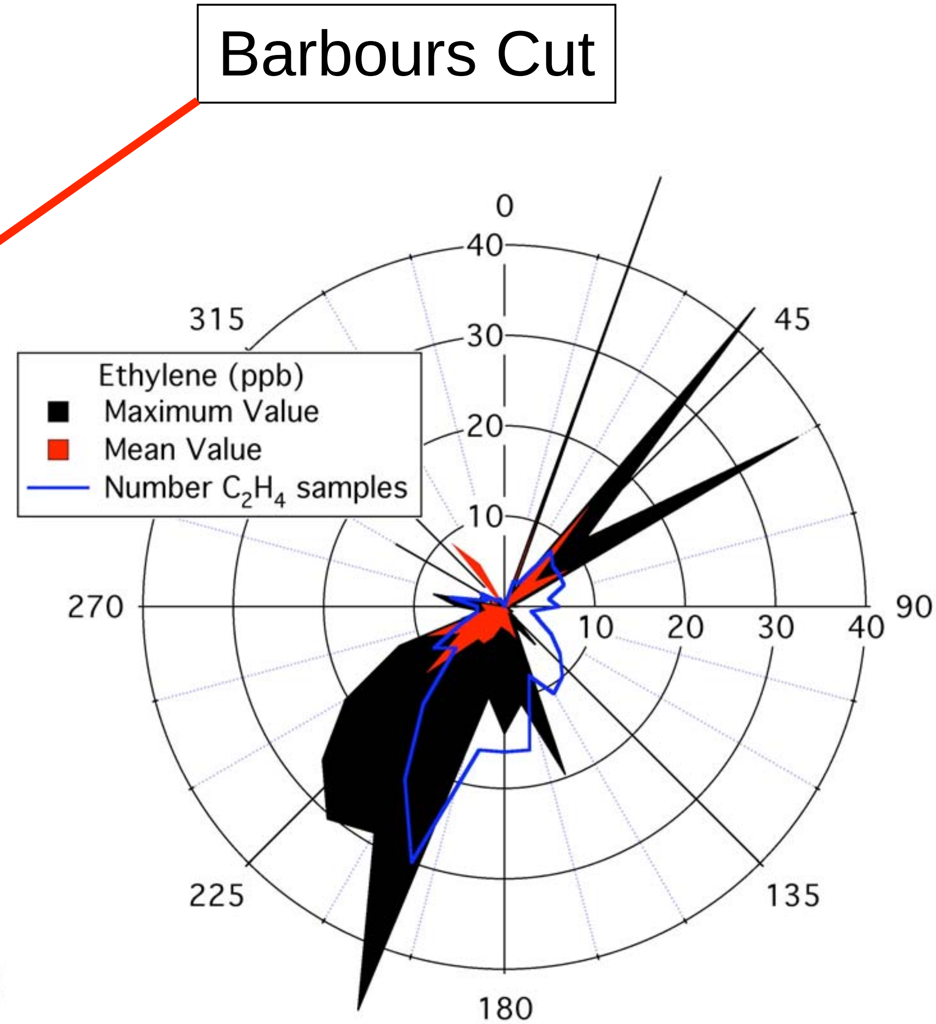


Observations from the Ron Brown in Barbours Cut

Jessica Gilman, Bill Kuster, Joost de Gouw

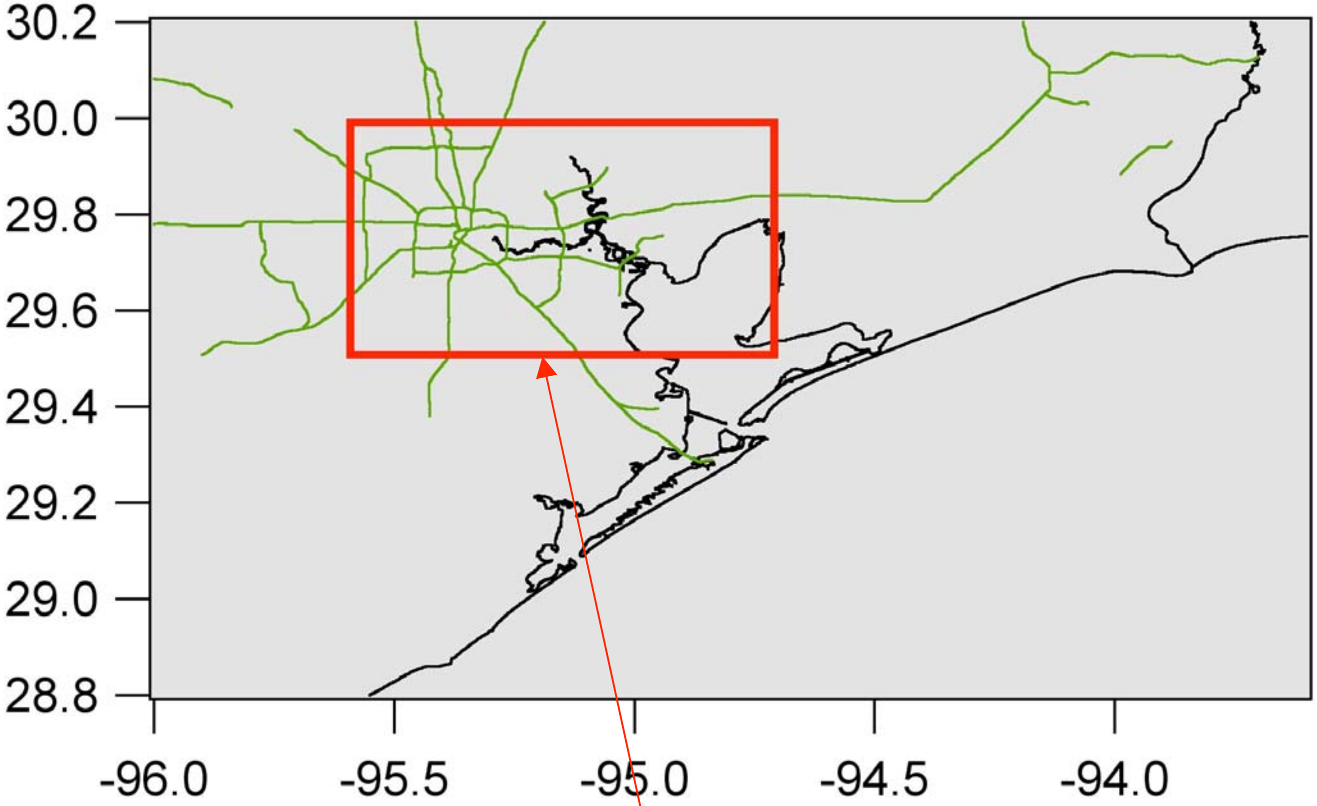




Consistent with C_2H_4 sources at Bayport and Mont Belvieu

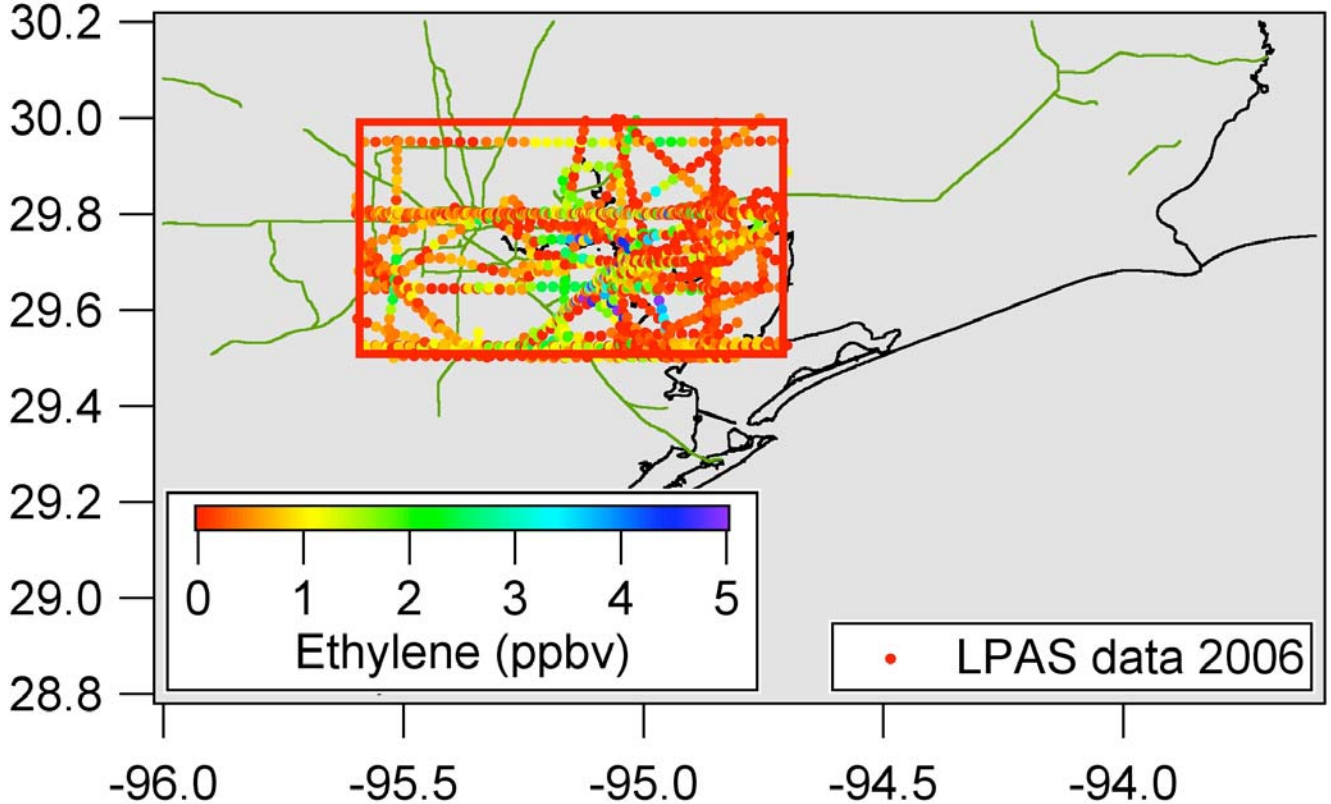
Ethylene in 2006 vs. 2000

Have ambient mixing ratios changed?



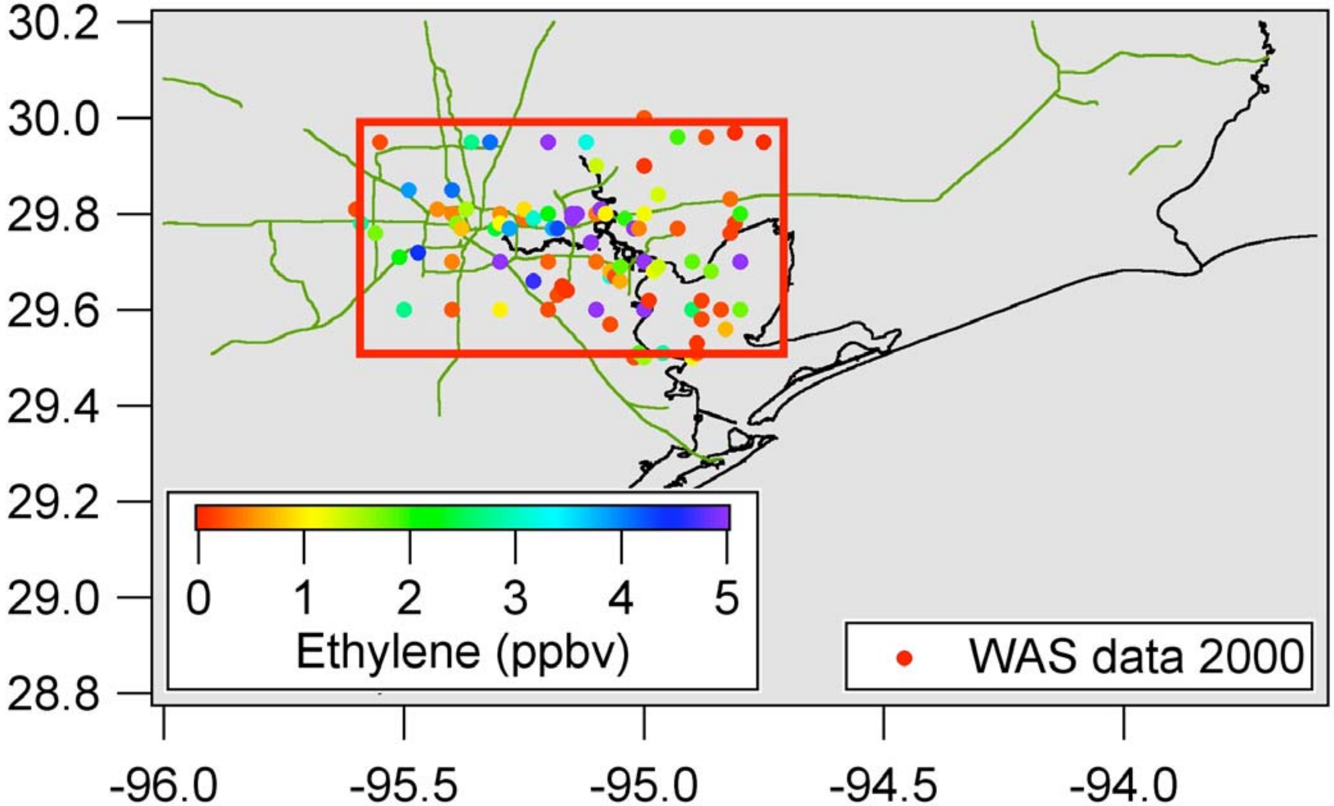
Compare 2000 WAS data with 2006 LPAS data below 1000 m in this box

Ethylene in 2006 vs. 2000



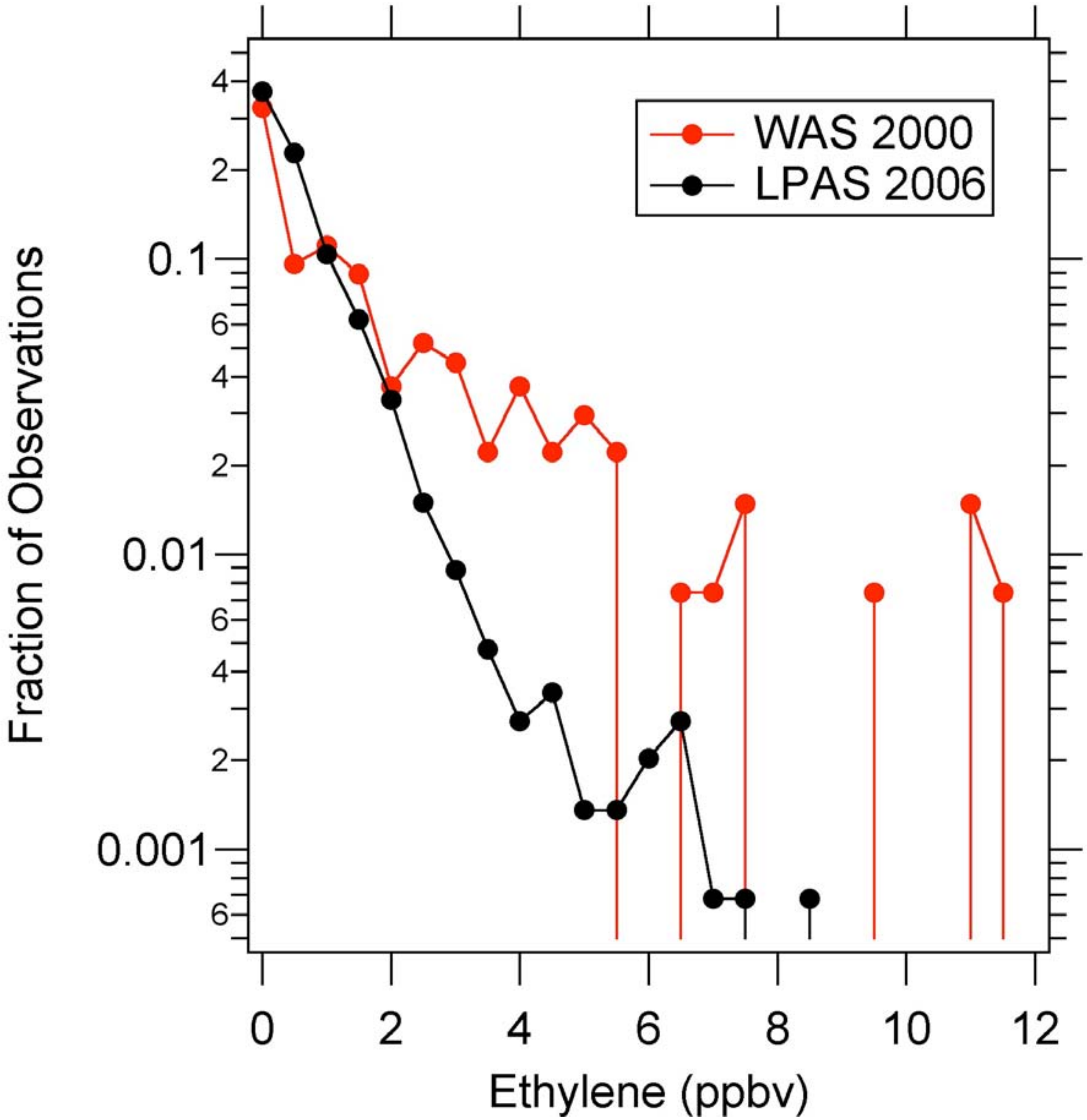
1472 samples average = 0.7 ppbv

Ethylene in 2006 vs. 2000



133 samples average = 2.9 ppbv

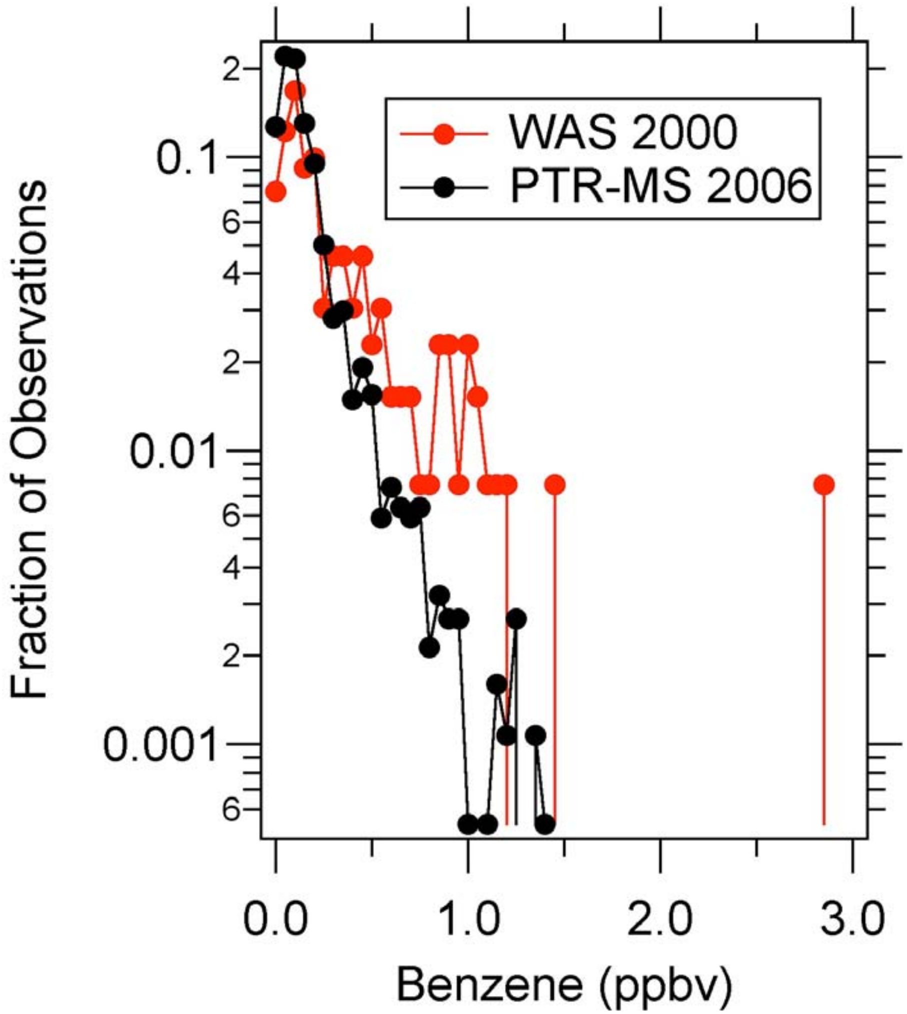
Ethylene in 2006 vs. 2000



- ➢Ethylene lower in 2006?
- ➢WAS are typically collected in plumes. WAS biased high?

Too early to tell!

Benzene in 2006 vs. 2000

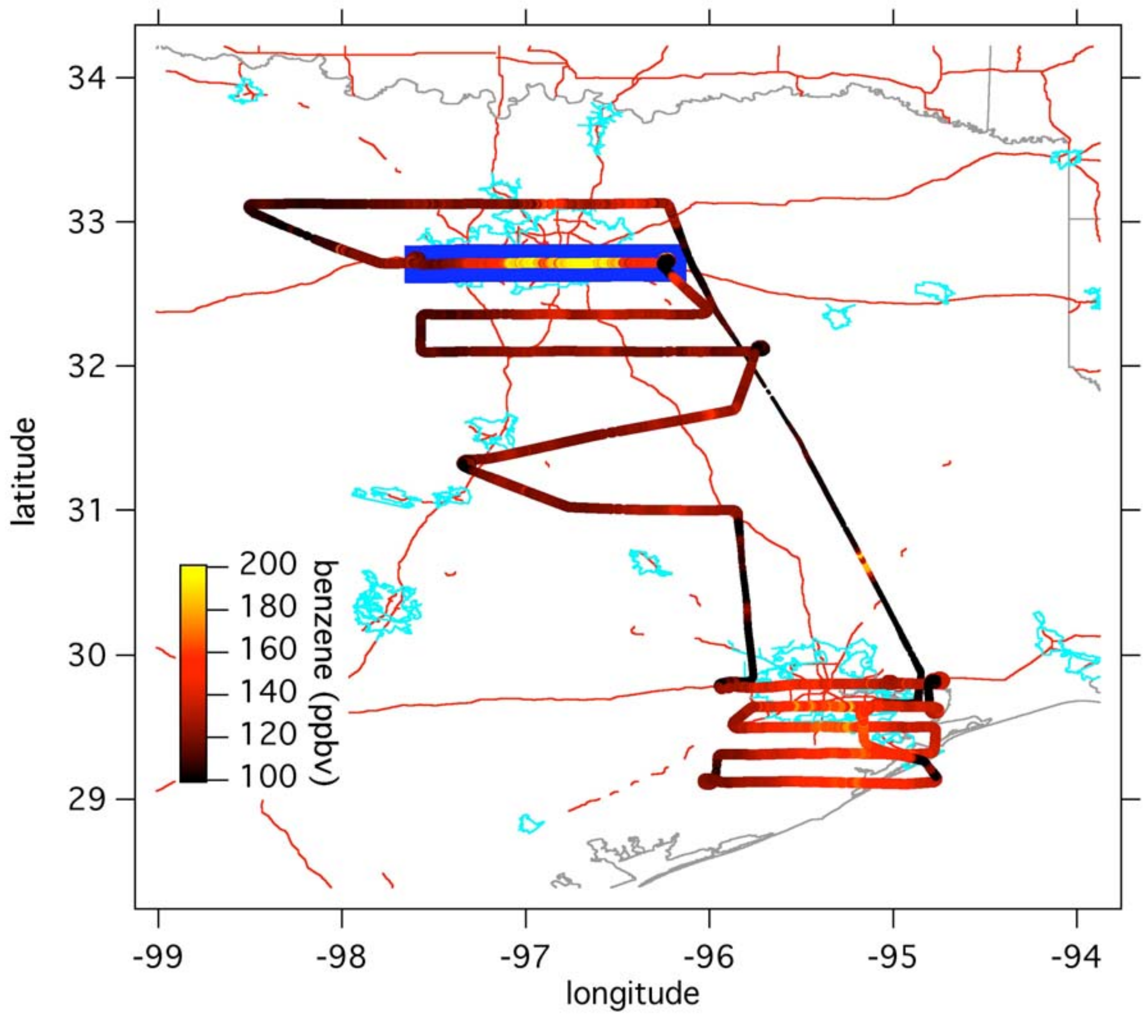


- ➢WAS in 2000:
131 samples
0.37 ppbv average

- ➢PTR-MS in 2006:
1874 samples
0.19 ppbv average

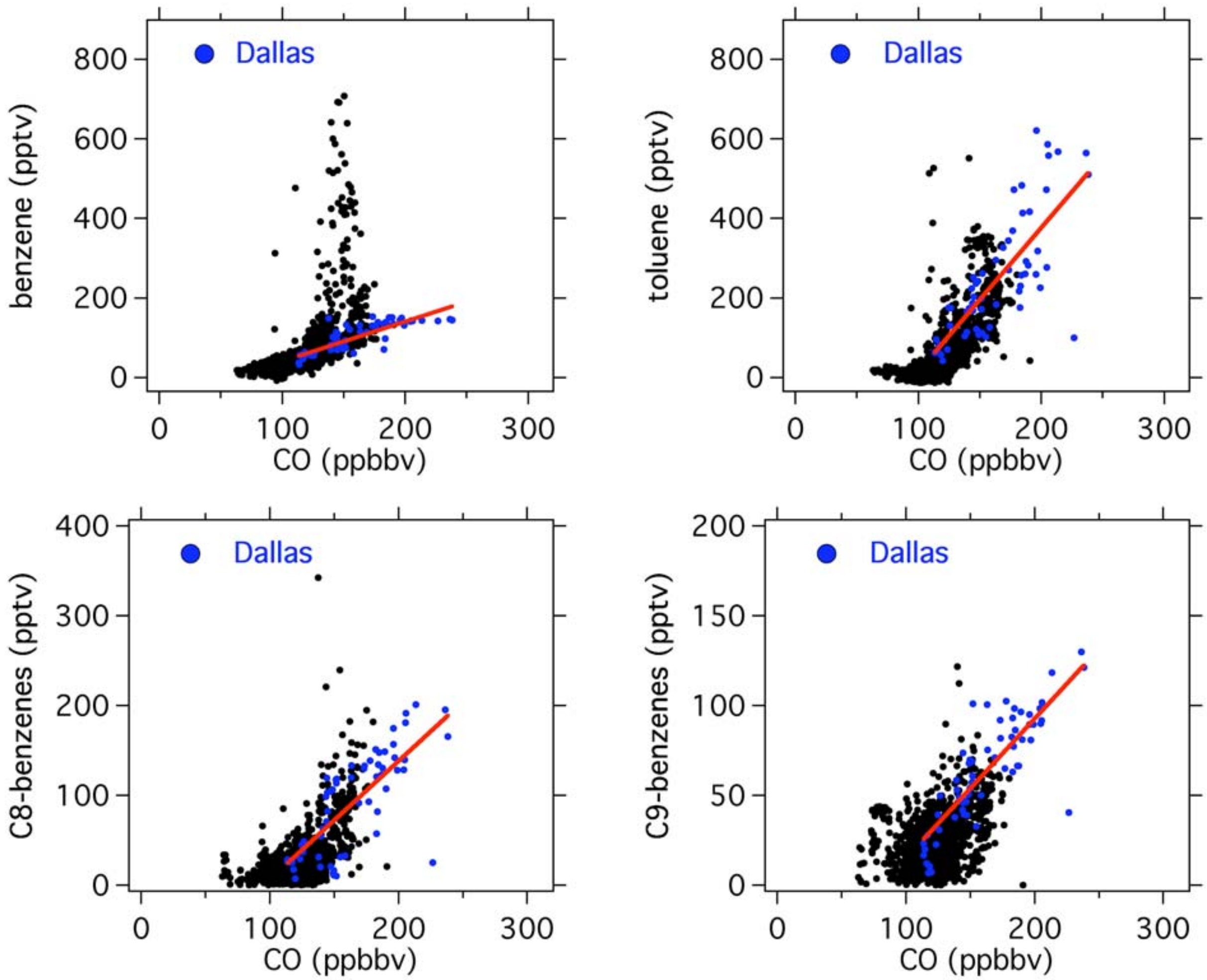
- ➢Lower in 2006 or WAS data biased high?

Urban vs. Petrochemical Emissions of Aromatics



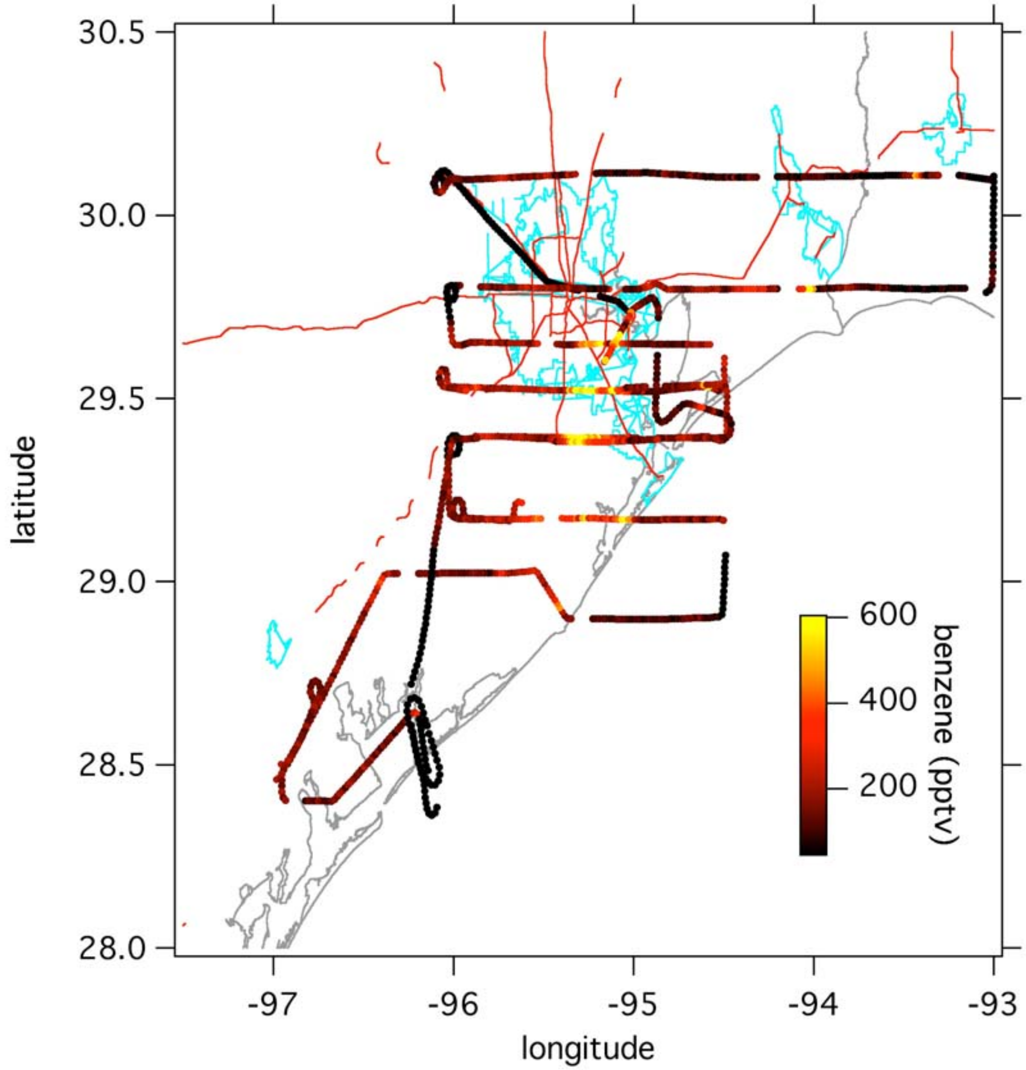
Flight 09/25/2006: Emissions from Dallas and Houston

Urban vs. Petrochemical Emissions of Aromatics



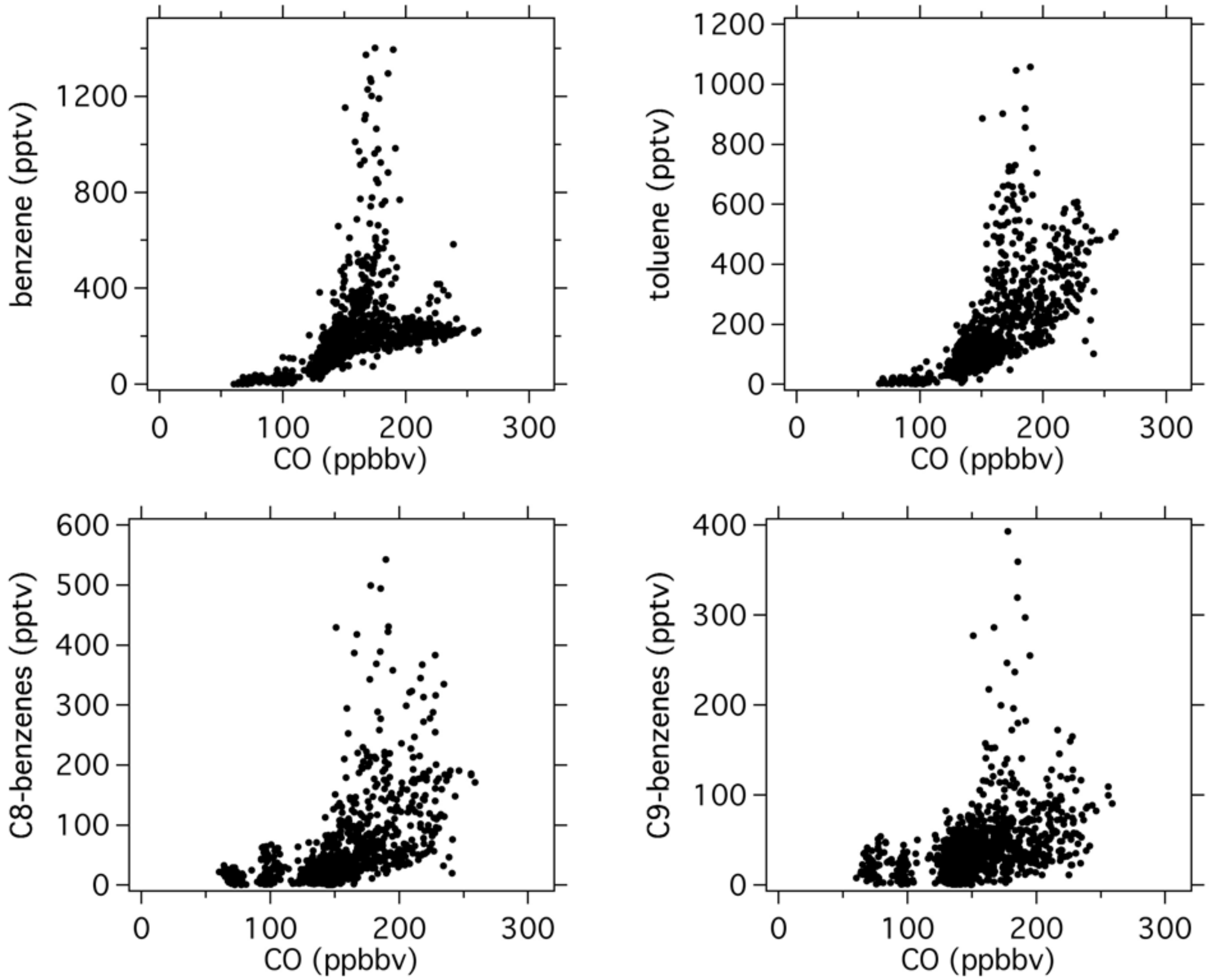
- Emissions in Dallas similar to other U.S. cities
- Additional emissions in Houston

Urban vs. Petrochemical Emissions of Aromatics



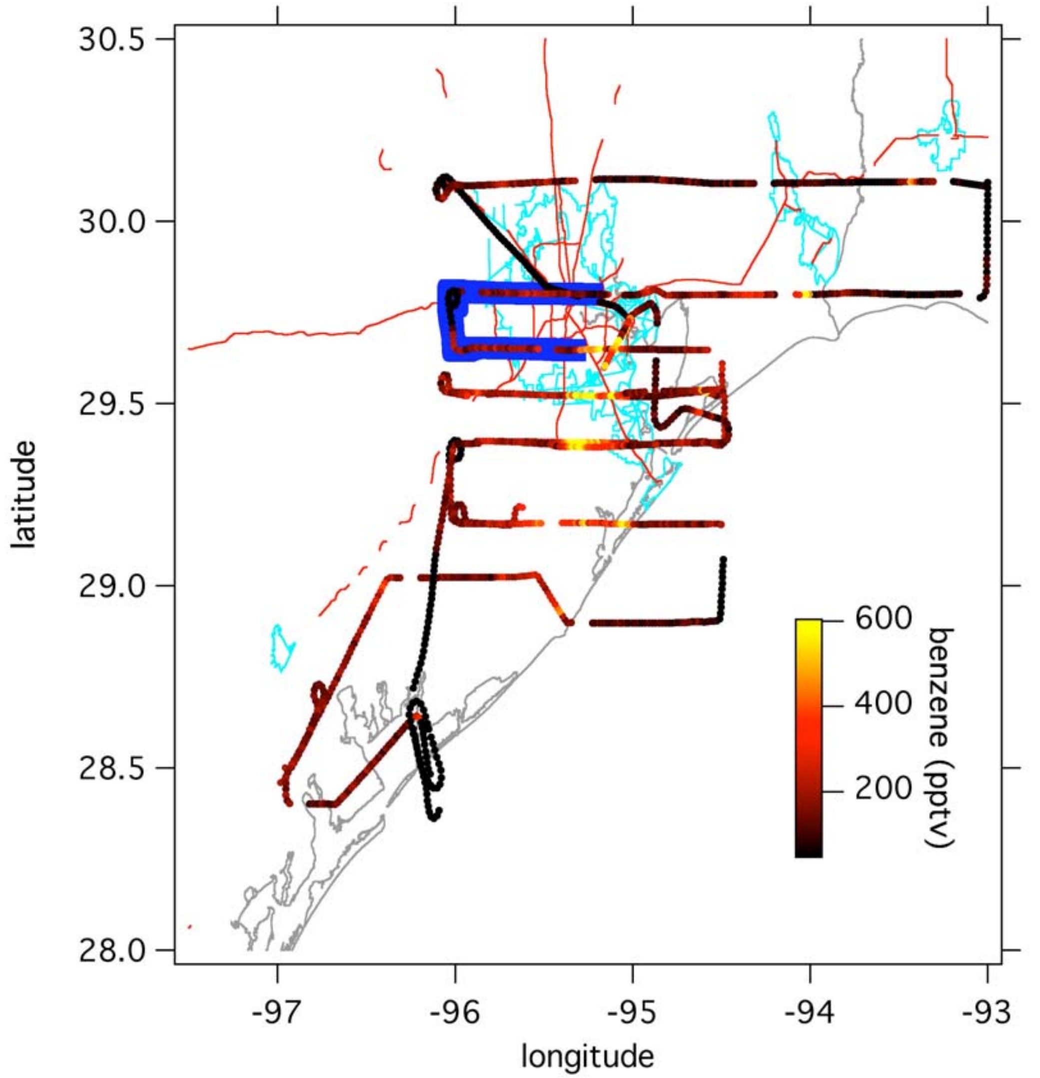
Flight 09/26/2006: Emissions from City and Ship Channel

Urban vs. Petrochemical Emissions of Aromatics

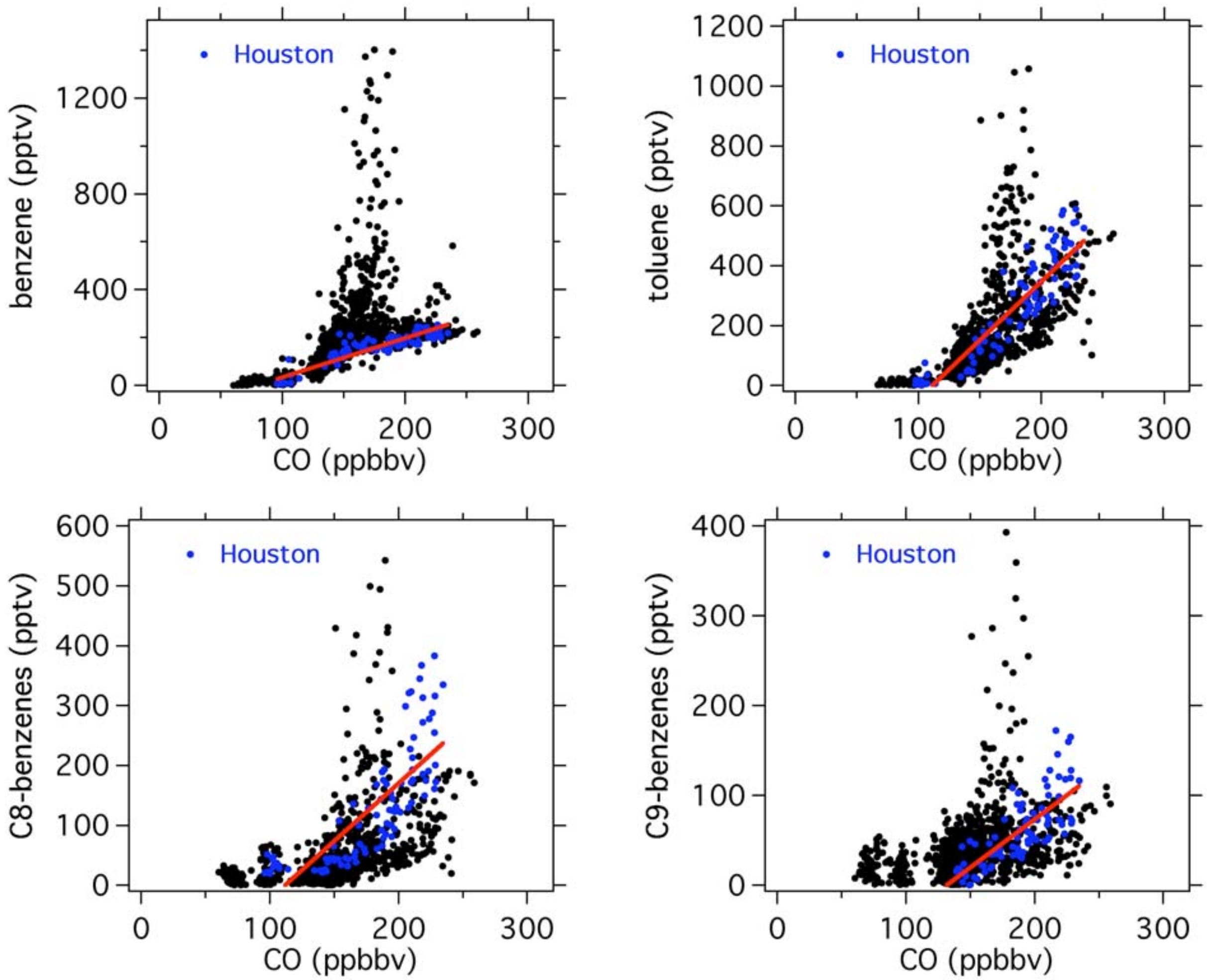


Urban vs. Petrochemical Emissions of Aromatics

HOUSTON



Urban vs. Petrochemical Emissions of Aromatics

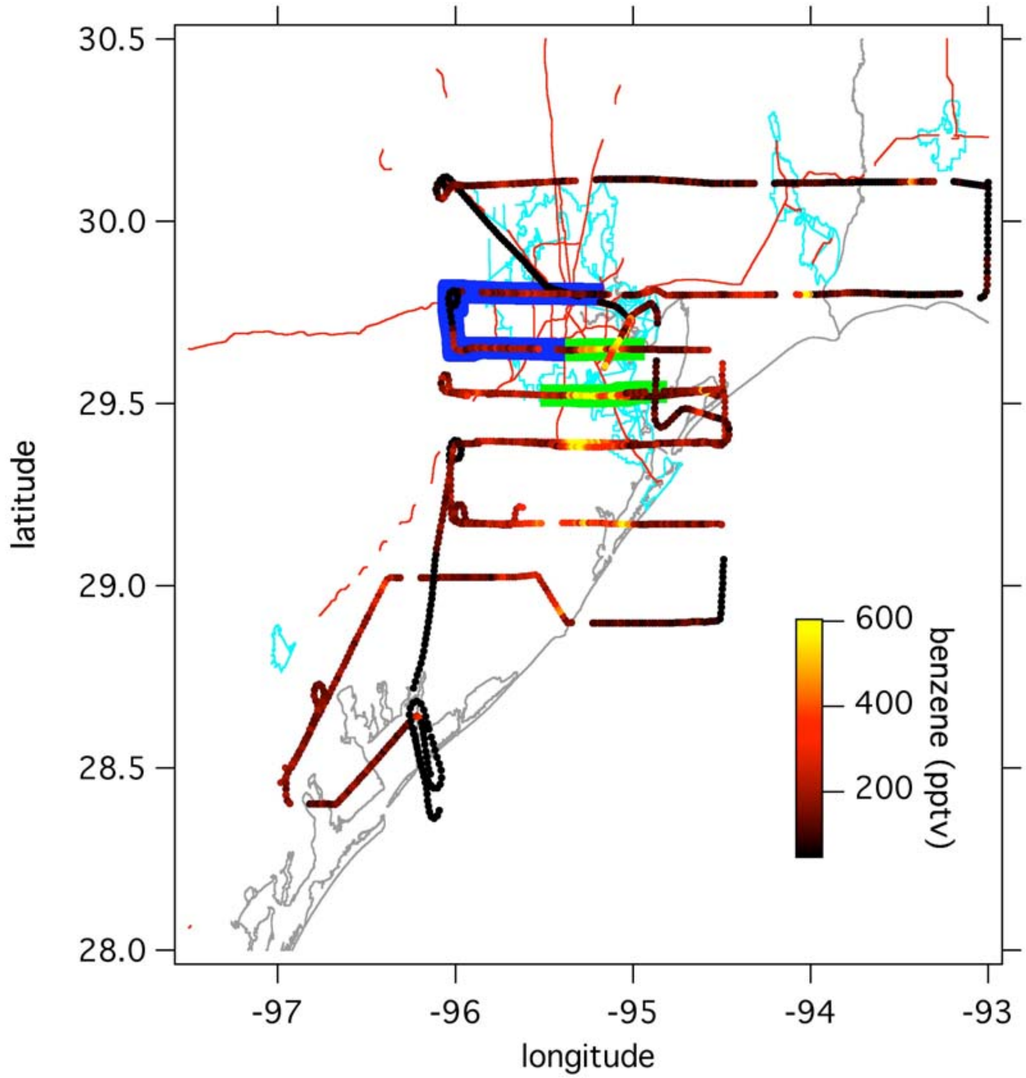


➢ Emissions from downtown Houston similar to Dallas and other U.S. cities

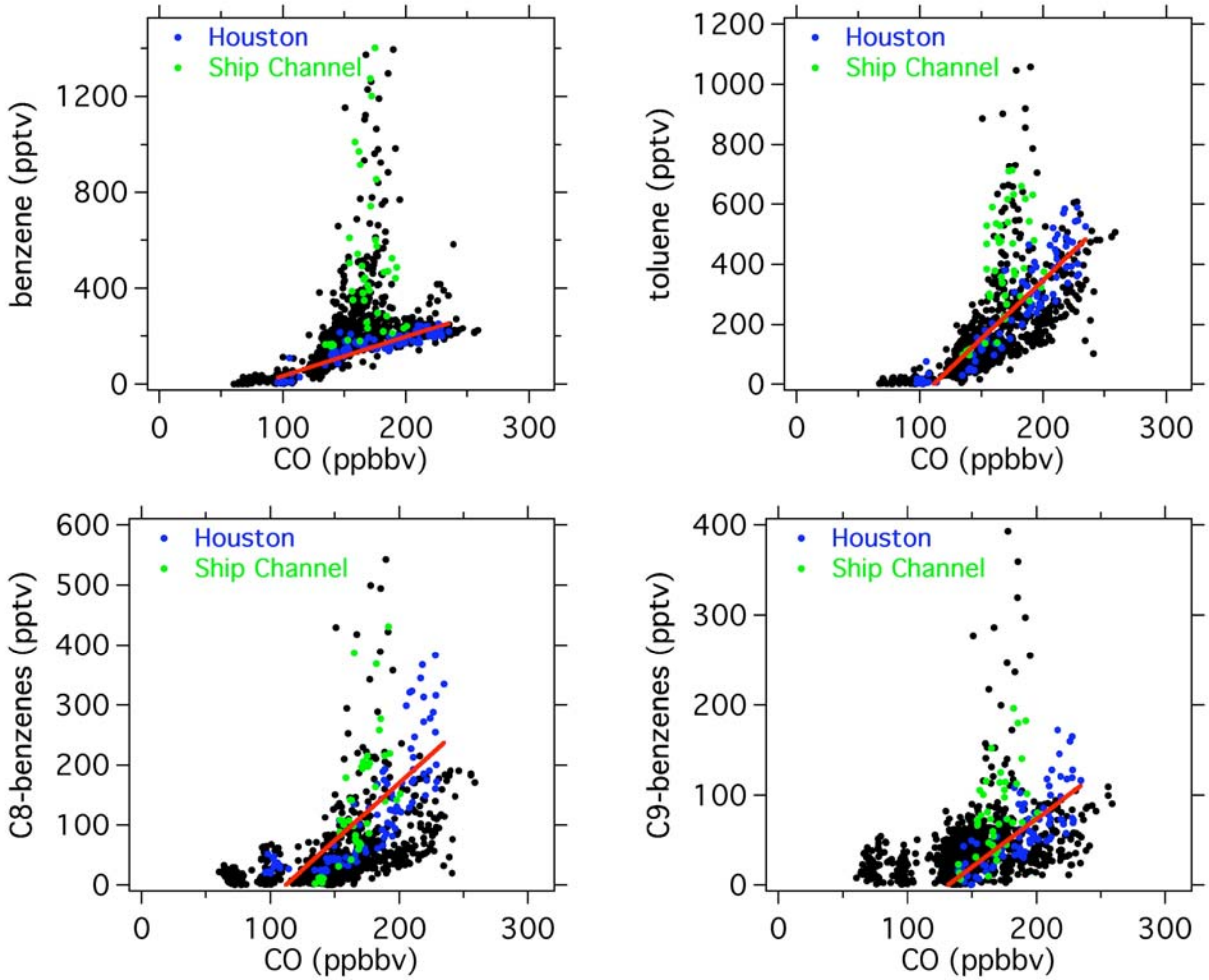
Urban vs. Petrochemical Emissions of Aromatics

HOUSTON

SHIP CHANNEL



Urban vs. Petrochemical Emissions of Aromatics



- ➢ Additional enhancements of aromatics over the HSC

Questions F, K – VOC- vs NOx-sensitive photochemistry

- **1-hr vs 8-hr SIP modeling and process analyses**
  (Will Vizuete)

Rapid Science Synthesis Workshop Meeting

September 29, 2006

UNC CAMx Model Analysis of August 2000 Simulations

William Vizuete

Harvey Jeffries

UNC
SCHOOL OF PUBLIC HEALTH
DEPARTMENT OF ENVIRONMENTAL SCIENCES AND ENGINEERING

Outline

- SIP Modeling changes from 1-hour to 8-hour
  - Meteorology Changes
  - Emission Input Changes
  - Surface and Aloft Changes
- Process Analysis results
  - Current Model
  - Formaldehyde Sensitivity

Work Supported By

- Eight Hour Ozone Coalition

- HARC H60 "Regional Transport Modeling for East Texas"
  - Jay Olaguer, Project Officer.

Also thank Jim Smith, TCEQ for supplying CAMx ready outputs for base1b 8-H SIP Case

Also thank Dennis McNally and Tom Tesche Alpine Geophysics for sharing simulation results.

UNC MAQ group

SIP Modeling Changes: 1H case to 8H case

- Changes in inputs to model HGA September/August 2000 episode along with remaining performance problems highlight areas for fruitful research.
- Issues or questions remain in:
  - Meteorology, esp. pbl and vertical mixing
  - Emissions, esp. in NO, CO, and HRVOCs
  - Chemistry, esp. in radical source strength

Summary Meteorology Changes

- Improved daytime wind speeds
- Night wind speeds still greater than a factor of 2
- Vertical mixing increases (Kv) greater than a factor of 7

Summary Emissions

- Important differences between MCR 1-h (base5b) and 8-h (base1b) emissions for NOx, CO, HRVOCs.
- NOx and CO decreased in Harris Co. Likely change in mobile sources. Reason?
- ETH showed both decreases and increases.
- OLE showed mostly decreases.
- ALD2 showed decreases in mobile source region and 1.0 ppb increases in Ship Channel.
- Decreases in NOx and CO should help model fit to observations.

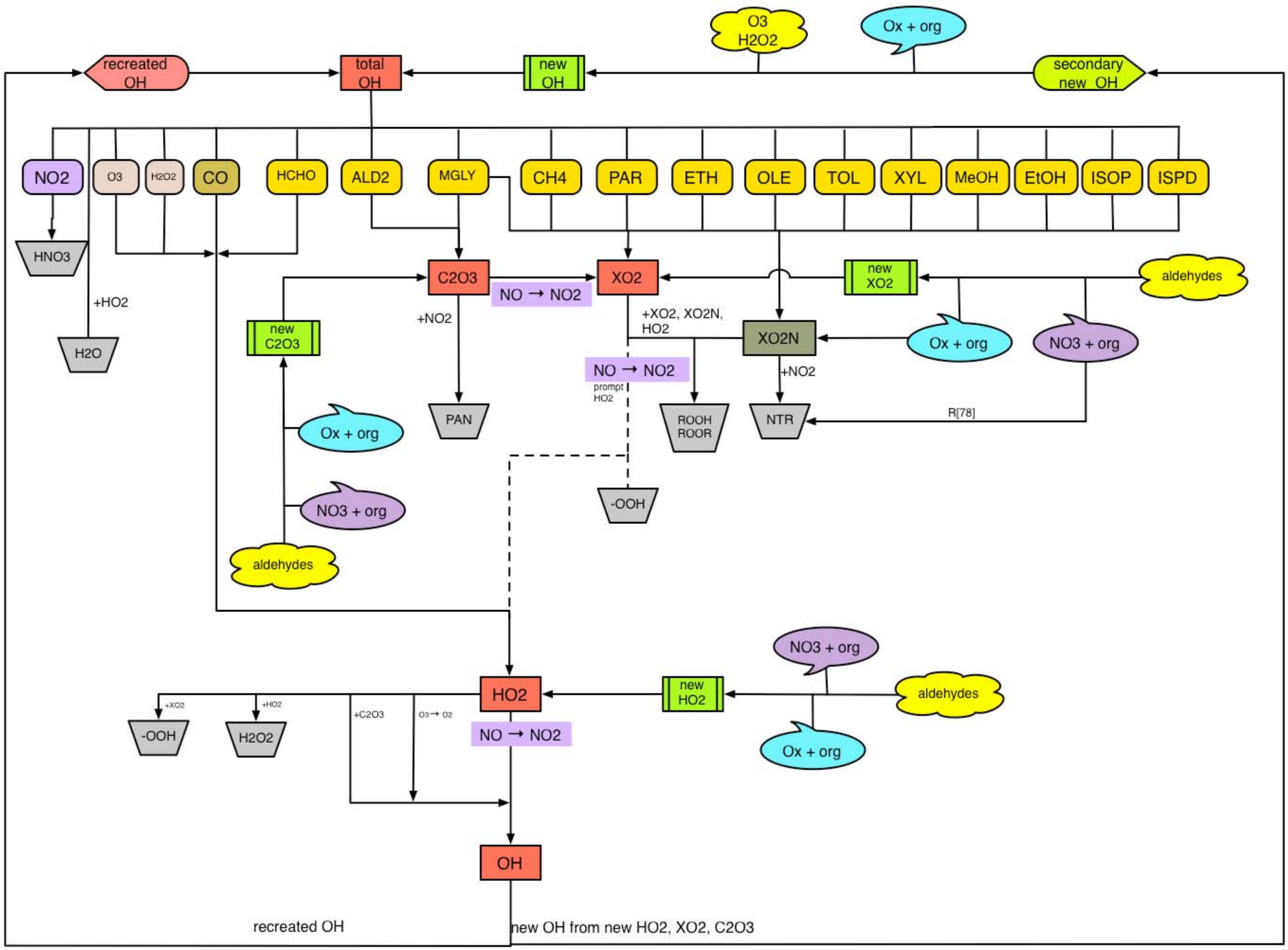
Summary Surface and Aloft Concentrations

- 8H model is still rich in NOx (esp NO_2), CO, HRVOCs at surface.
- 8H model is still very low in CO at layer 4 at night.
- 8H model became worse in layer 9 for CO, NO, O_3 in east.
- 8H model remains biased very high in HRVOC in east.
- 8H model is now very good for ISOP at surface.
- 8H model peak ozone are affected, but not dramatically.

pyPA hydroxyl radical and NO chemical cycles

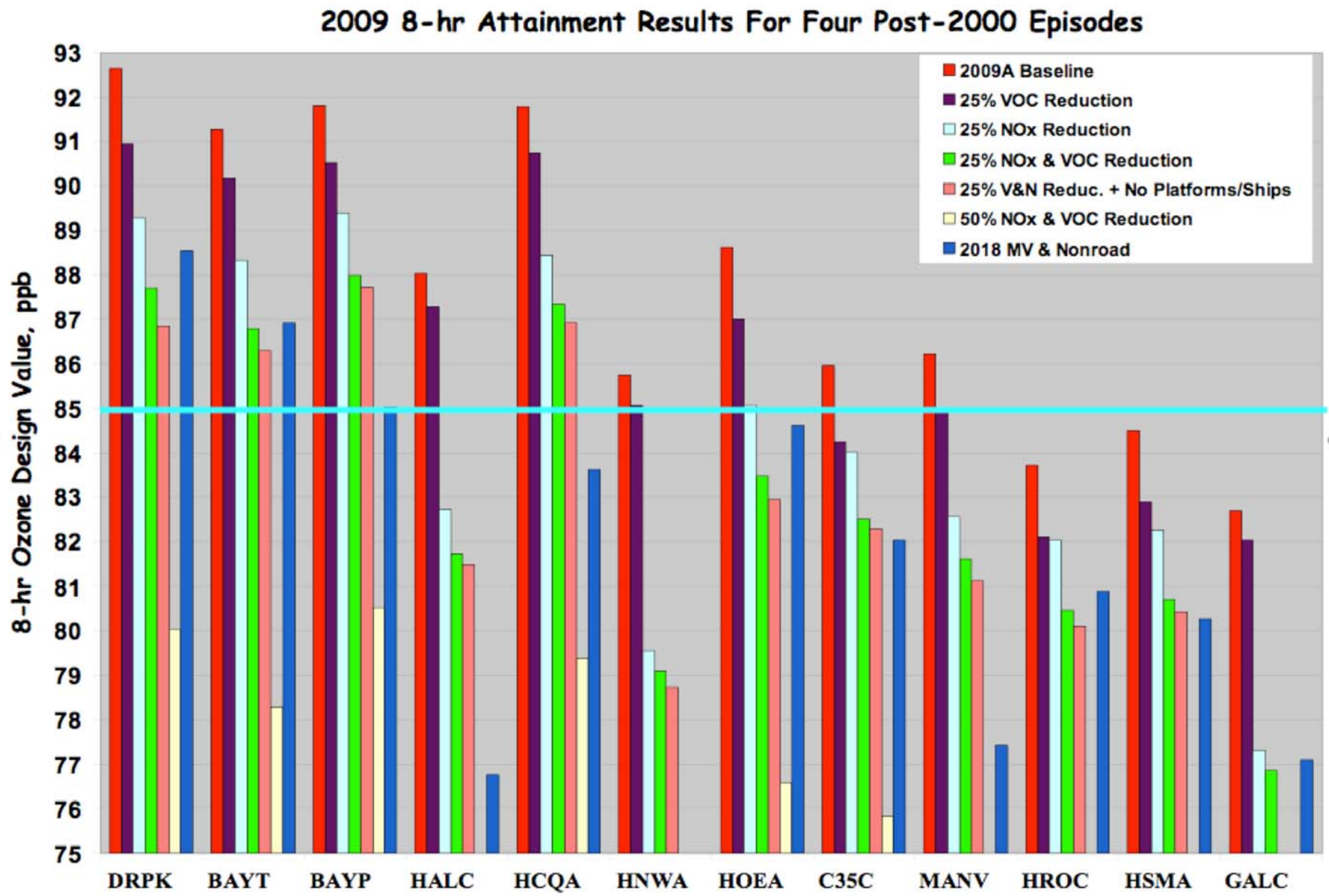
- 8-hour Model
- FORM increases sensitivity run

Organic Radical Cycle

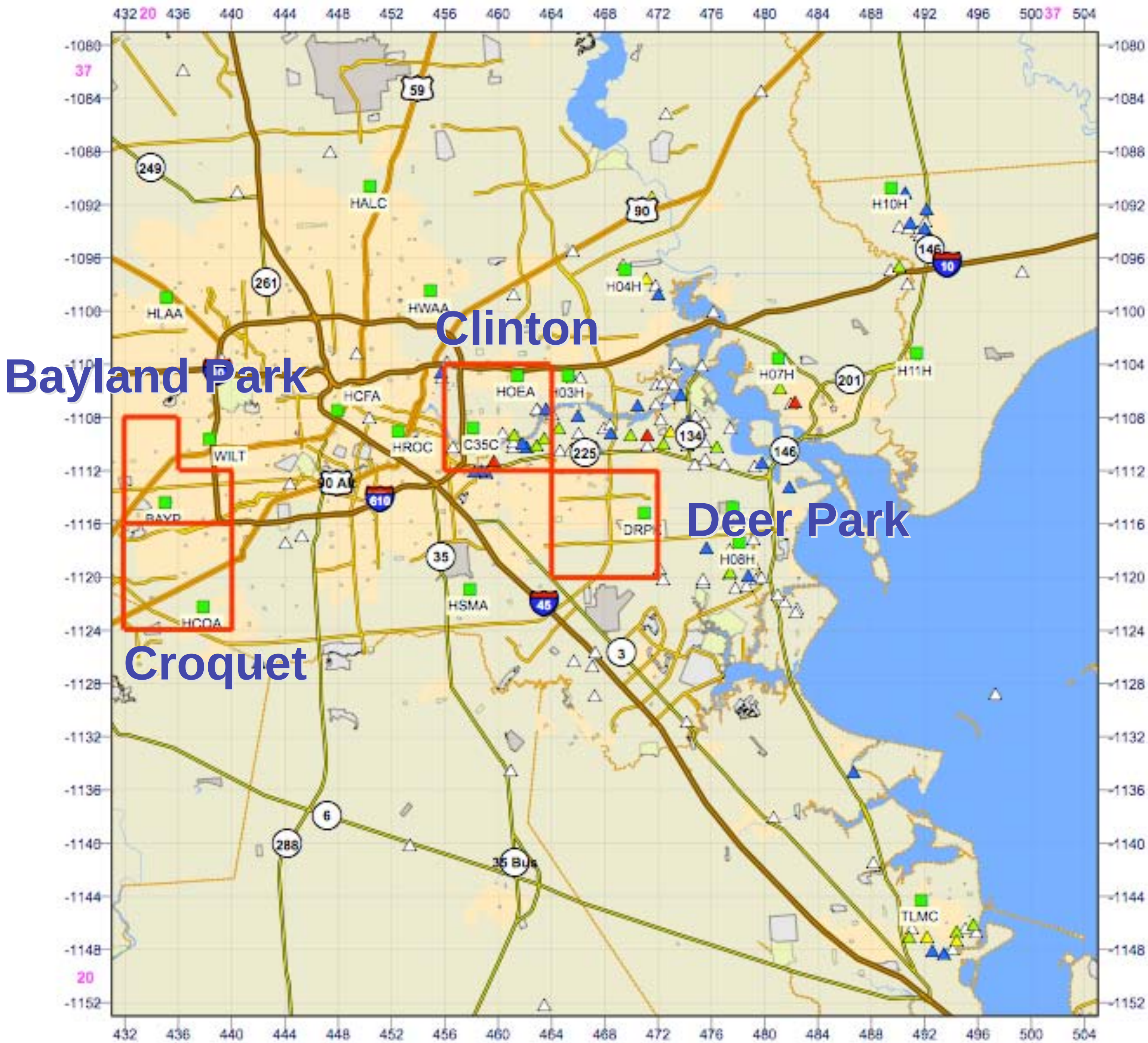


pyPA - 8 Hour Model

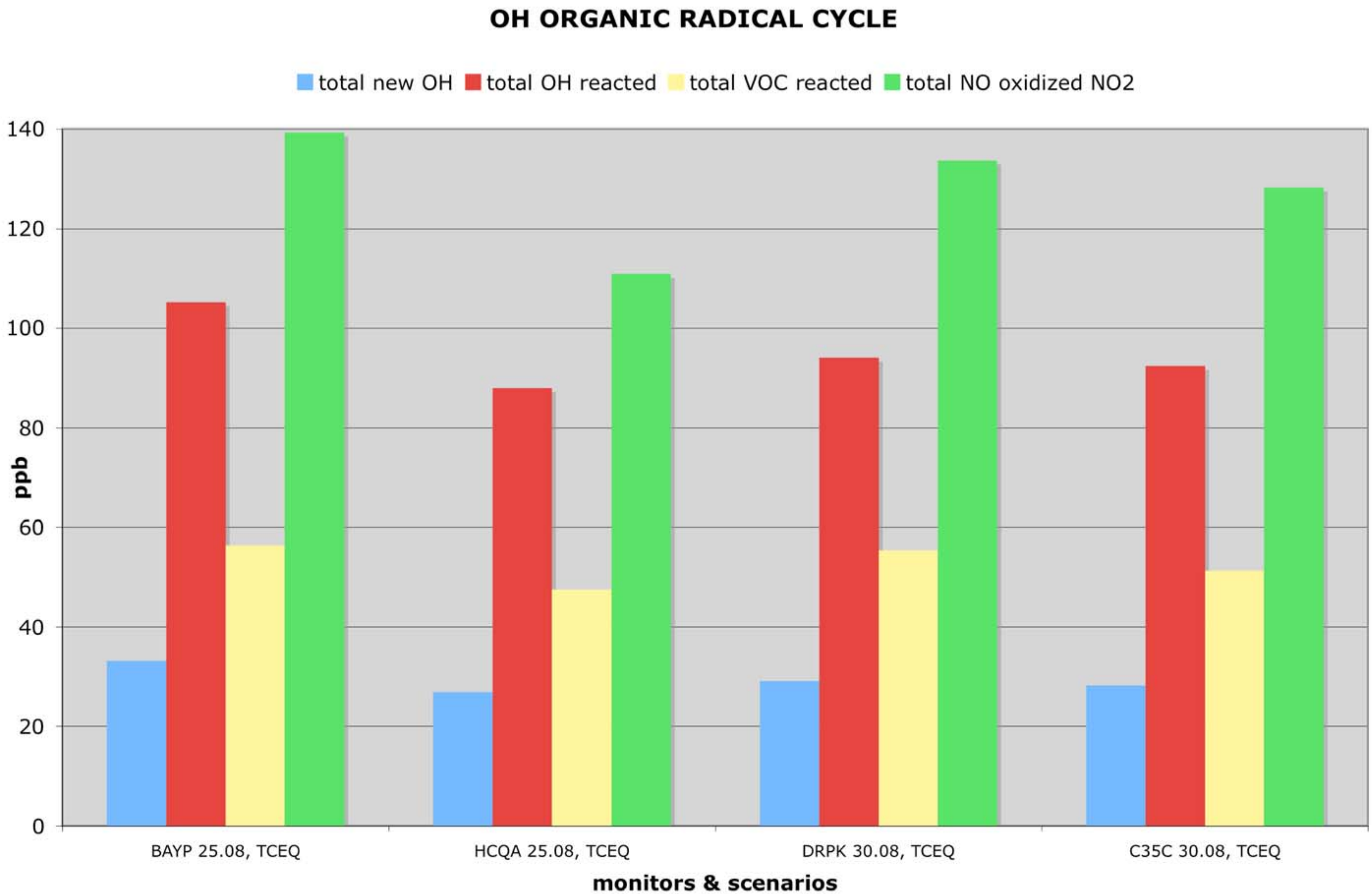
- PA Focus Areas: Bayland Park (8/25), Clinton (8/30), Deer Park (8/30), Croquet (8/25)
- Detailed inspection of NO, NO2 and O3 time series for MCR(1-h) and b1b (8-h) model
- OH reactions with NOx, Organics, OH chain length
- NO cycle length



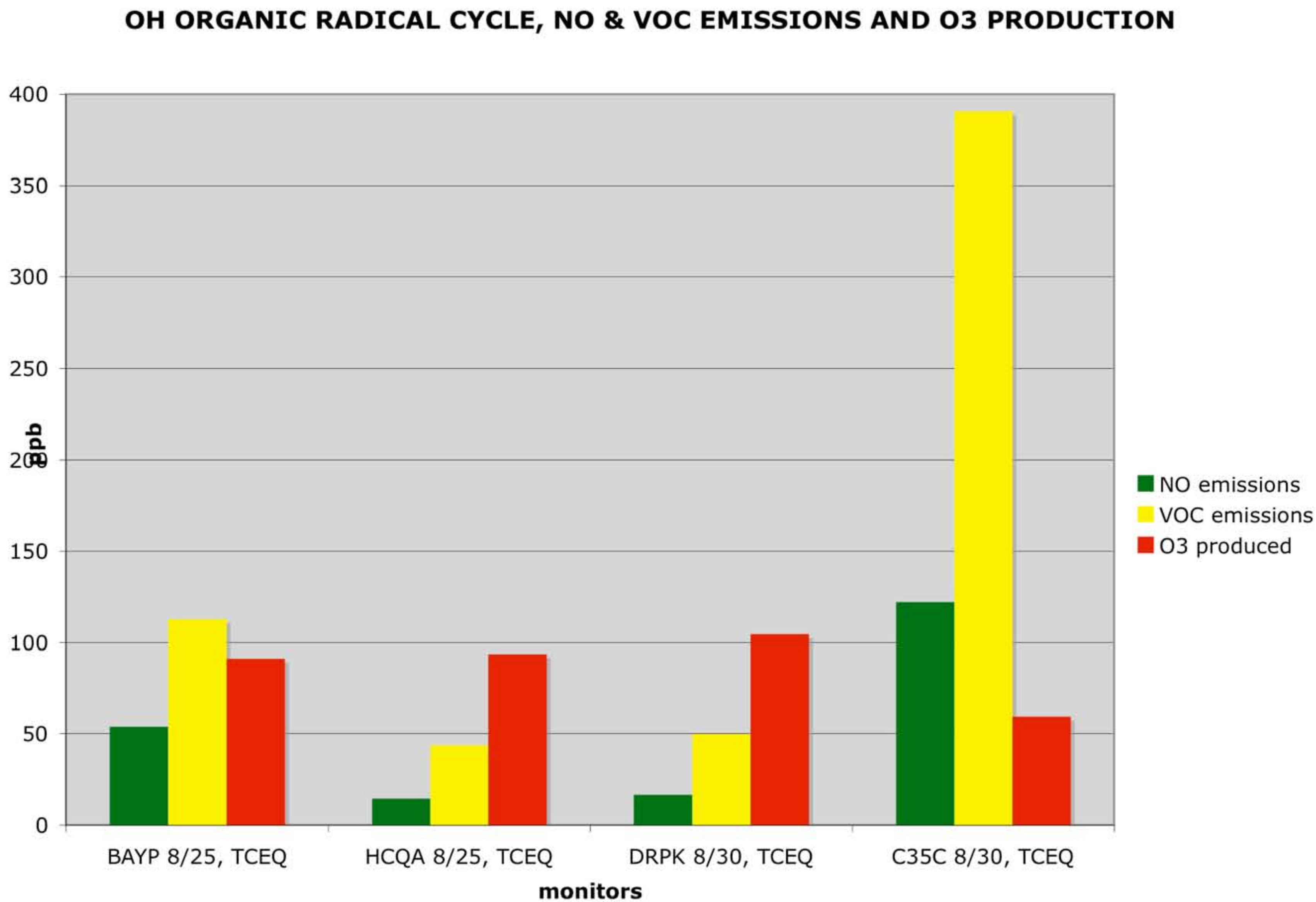
2009 8-hr Attainment Results For Four Post-2000 Episodes
8-hr Ozone Design Value, ppb
93
92
91
90
89
88
87
86
85
84
83
82
81
80
79
78
77
76
75
2009A Baseline
25% VOC Reduction
25% NOx Reduction
25% NOx & VOC Reduction
25% V&N Reduc. + No Platforms/Ships
50% NOx & VOC Reduction
2018 MV & Nonroad
DRPK
BAYT
BAYP
HALC
HCQA
HNWA
HOEA
C35C
MANV
HROC
HSMA
GALC

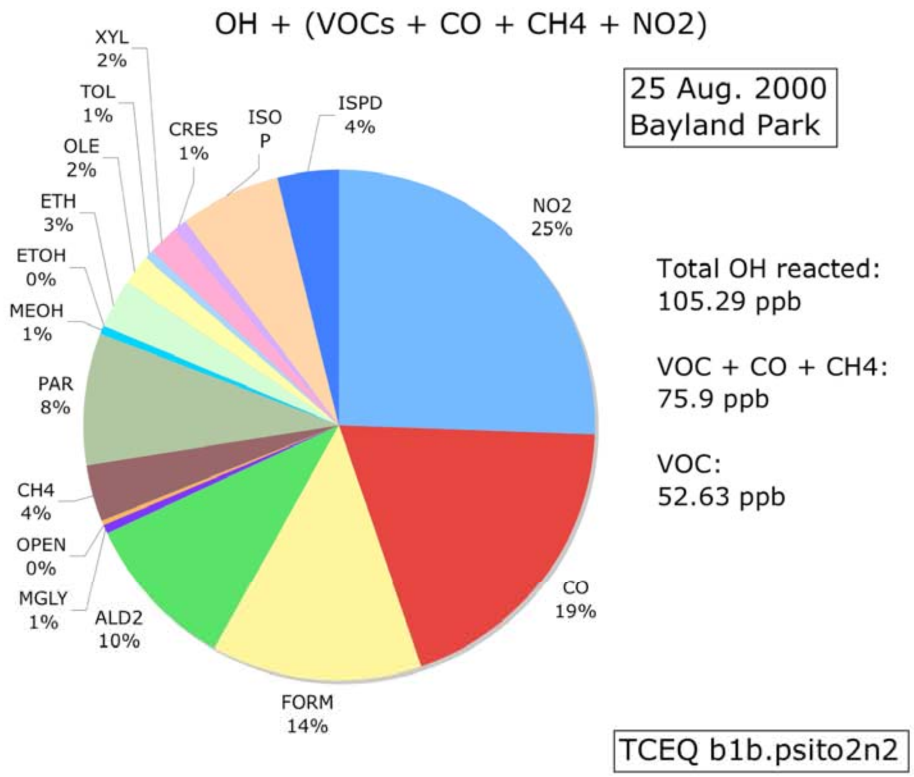

Clinton
Bayland Park
Deer Park
Croquet
HALC
HWAA
HLAA
HCFA
HROC
HOEA
H03H
C35C
WILT
BAYP
HCDA
HSMA
DRPK
H04H
H07H
H08H
H10H
H11H
TLMC

Daily Total Reaction Masses



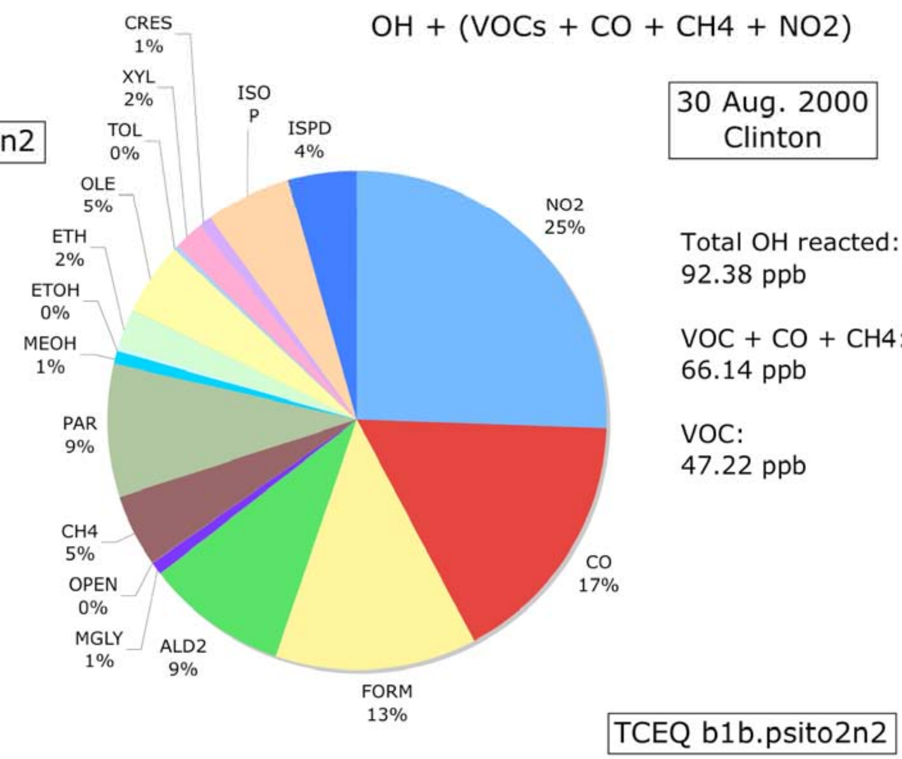
Daily Total Emissions and Ozone Production





8/25
b1b

8/30
b1b



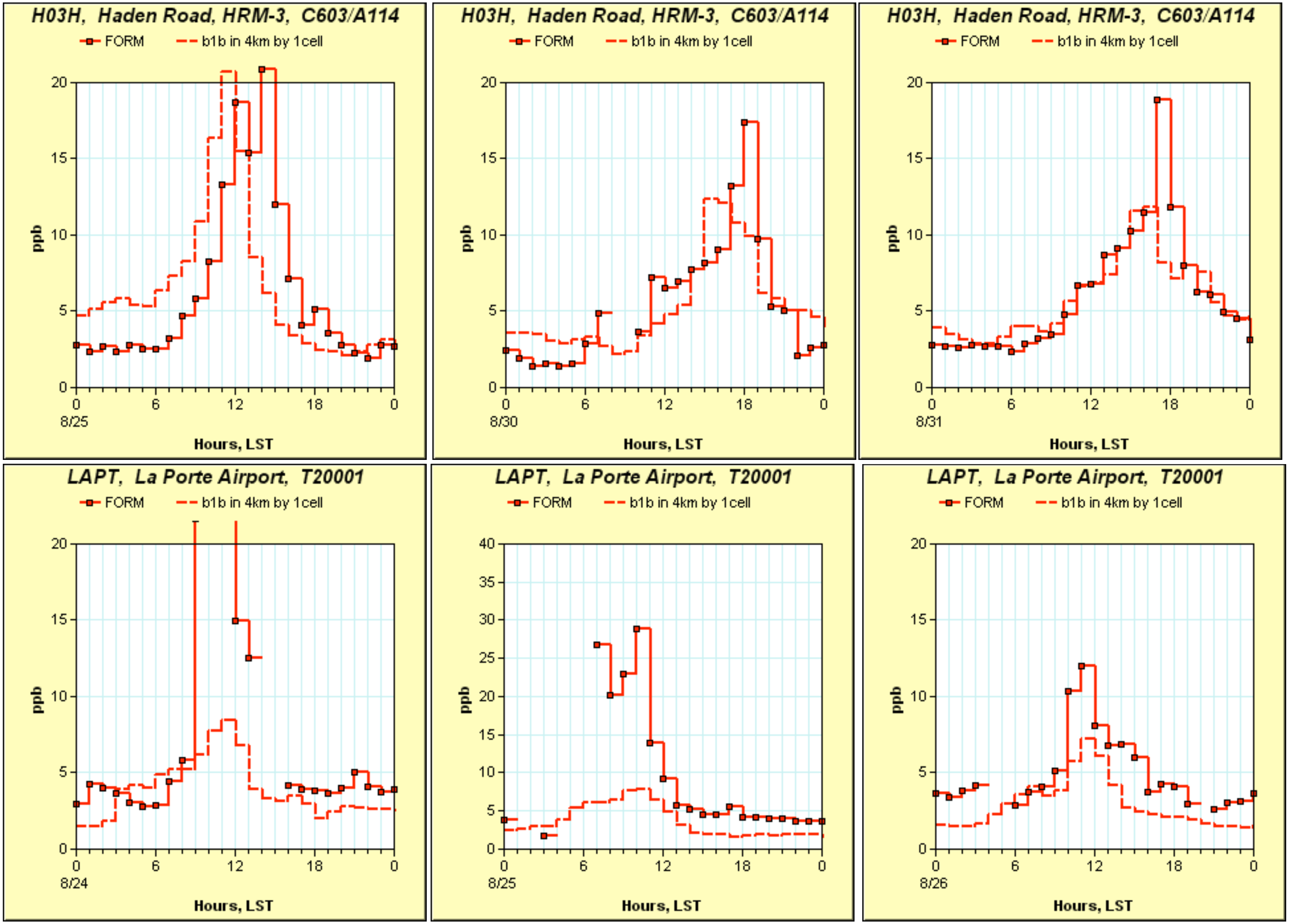
Summary Process Analysis of Chemistry

- All four focus areas show very similar new OH radical source strength (that are somewhat low compared to other PA results in other areas).
- A significant portion of the total OH reaction (=new OH x chain length) is with NO_2, CO, CH_4, and other non-NO oxidizing paths. (From 38% of all reacted OH at Aldine to 47% at Bayland)
- The absolutely maximum amount of O_3 that can be formed at the four sites ranged from 127 ppb to 150 ppb *minus* the emitted NO which ranged from 22 to 123 ppb, thus limiting chemical ozone to values between 36 and 103 ppb of ozone.
- Thus the chemical production of O_3 is inversely proportional to the NO_x at these four sites.
- PAN is predicted to be very low at these sites, so is RNO_3.

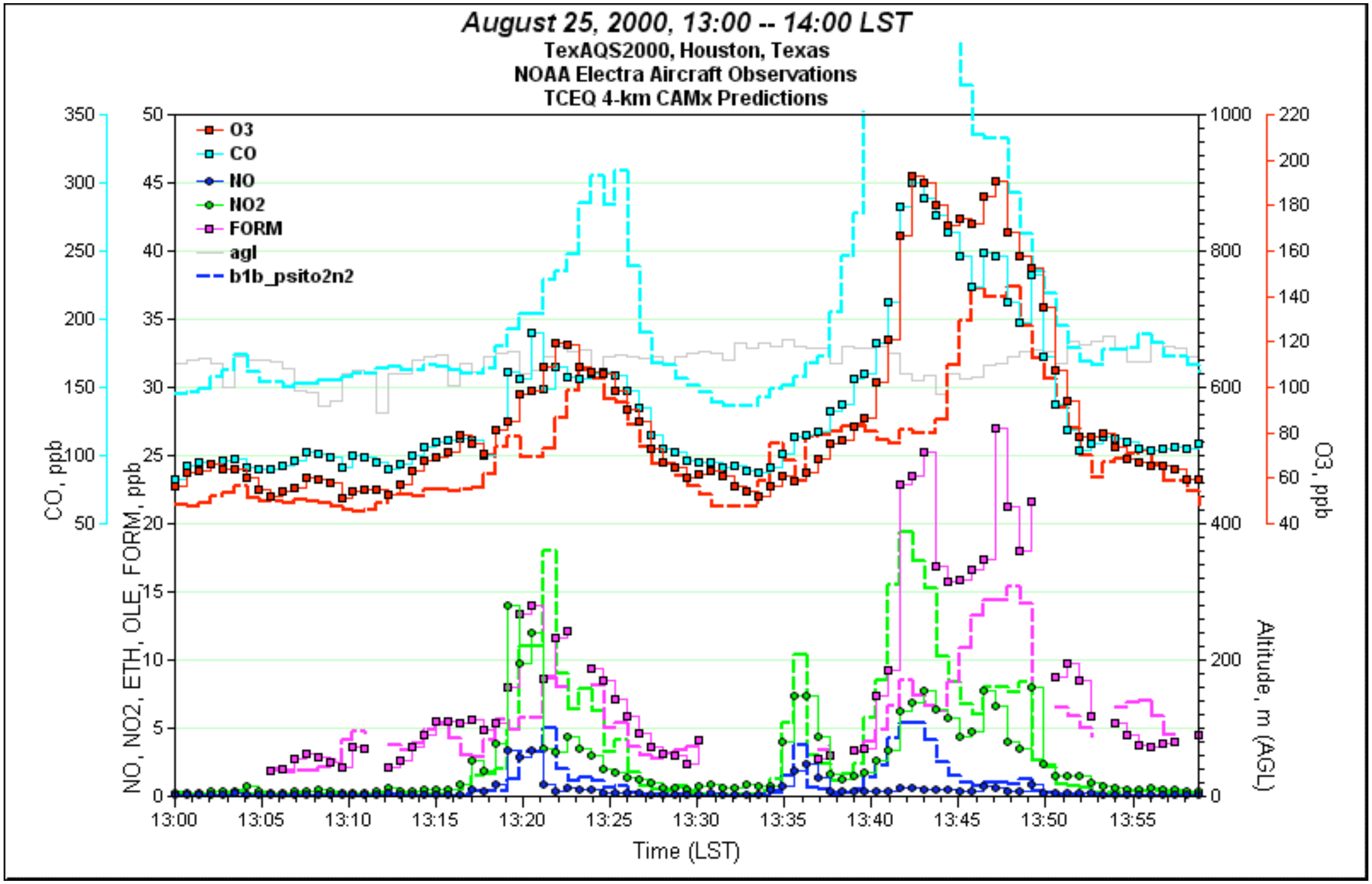
CAMx FORM Sensitivity

- Could FORM be a missing source of radicals?
- Observational Evidence
  - Monitor
  - Aircraft

FORM OBS Monitor



Aloft (NOAA) obs, b1b (8H)



CAMx Sensitivity Runs FORM Assumptions

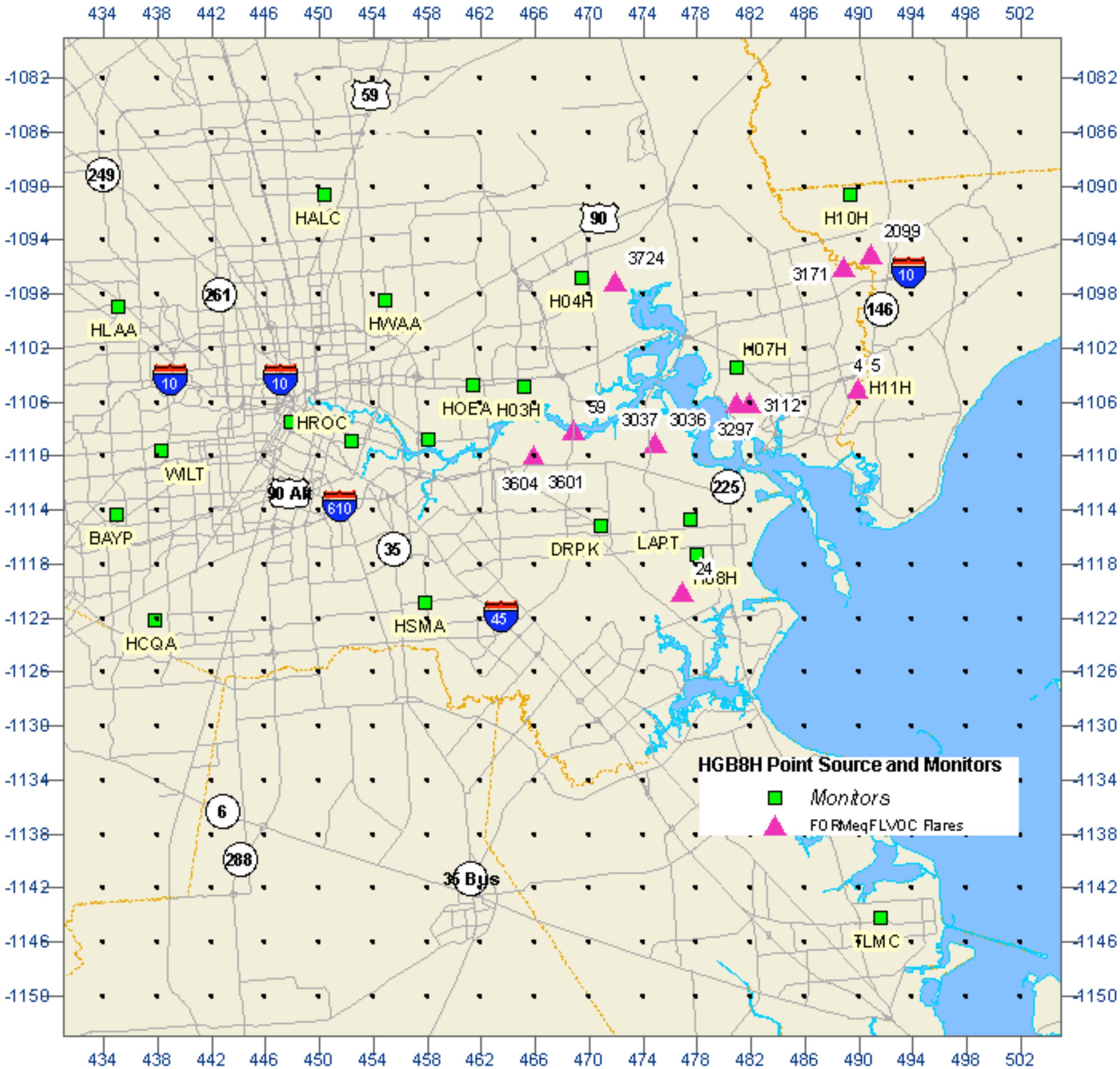
- Two potential sources of HCHO are:
  - Flares
    - 98-99% combustion assumed, 1% to 2% emitted VOC composition is assumed same as that fed to flare; rest assumed to be CO2. We assumed that HCHO emitted was equal to VOC emitted.
  - Mobile sources
    - New data (SWRI, 2005) on Heavy Duty Diesel show that HCHO is 23% of VOC and ethene is 18% of THC. HCHO was 5% of CO. We added HCHO at 4% of low level CO.

*Reference: Diesel Exhaust Standard-Phase II: CRC Project No. AVFL-10b
SwRI Poject No. 03.10410 Fanick, Robert. 2005

CAMx EI FORM Increases

- Sensitivity UNC1 - Assumed that VOCs fed to flares were partially converted to HCHO and that an amount equal to another 1% was emitted as HCHO. This added a total of 55, 58, and 59 tons on 25th, 30th and 31st. to 13 flares located mainly in the eastern part of Houston
- Sensitivity UNC2 - Based on AC obs, assumed that MV emissions did not have enough HCHO. An appropriate factor appeared to be 4% of CO. This added 167, 156, and 145 tons on 25, 30, and 31.

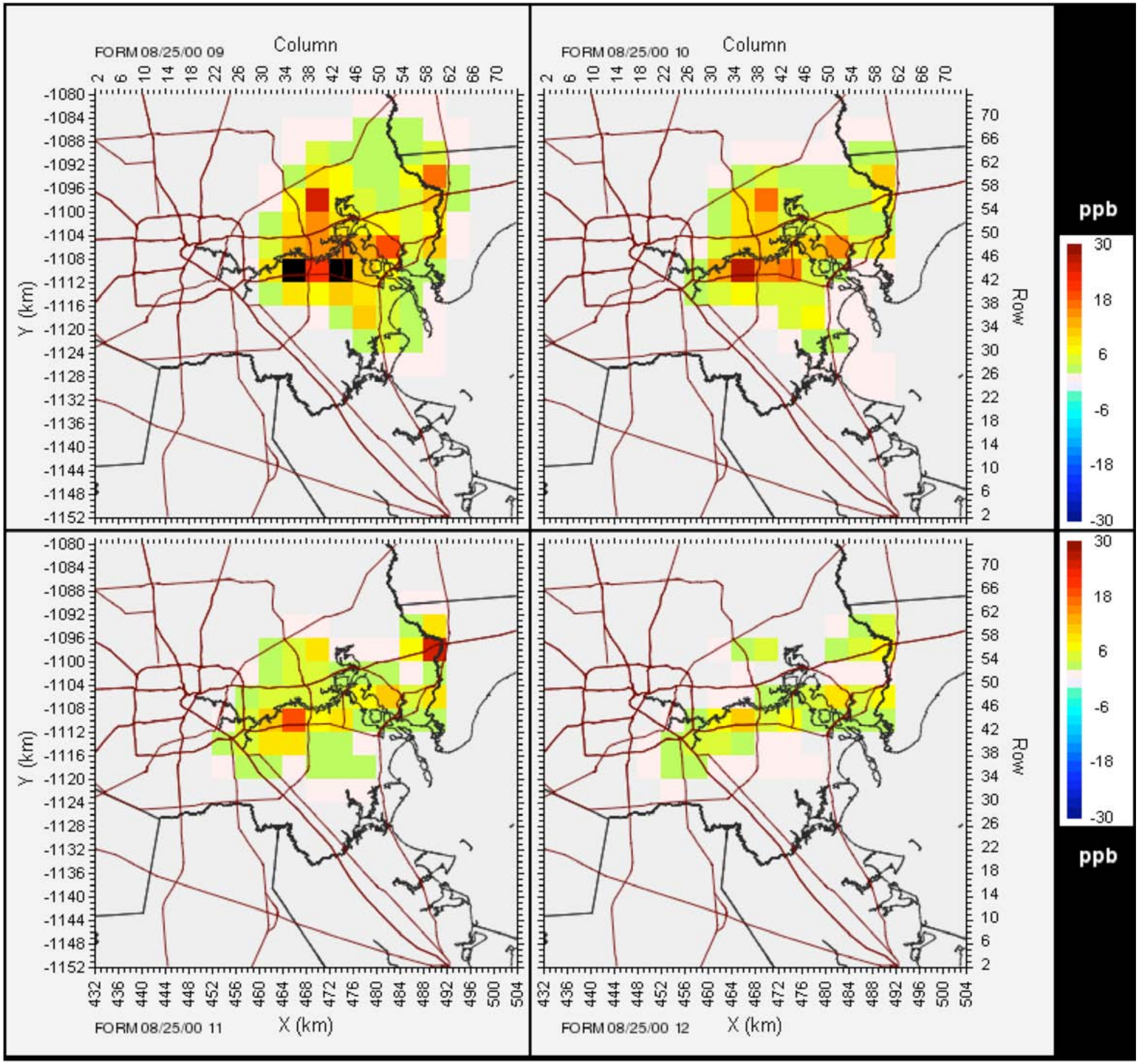
FORMeqFLVOC
Modified Point Sources



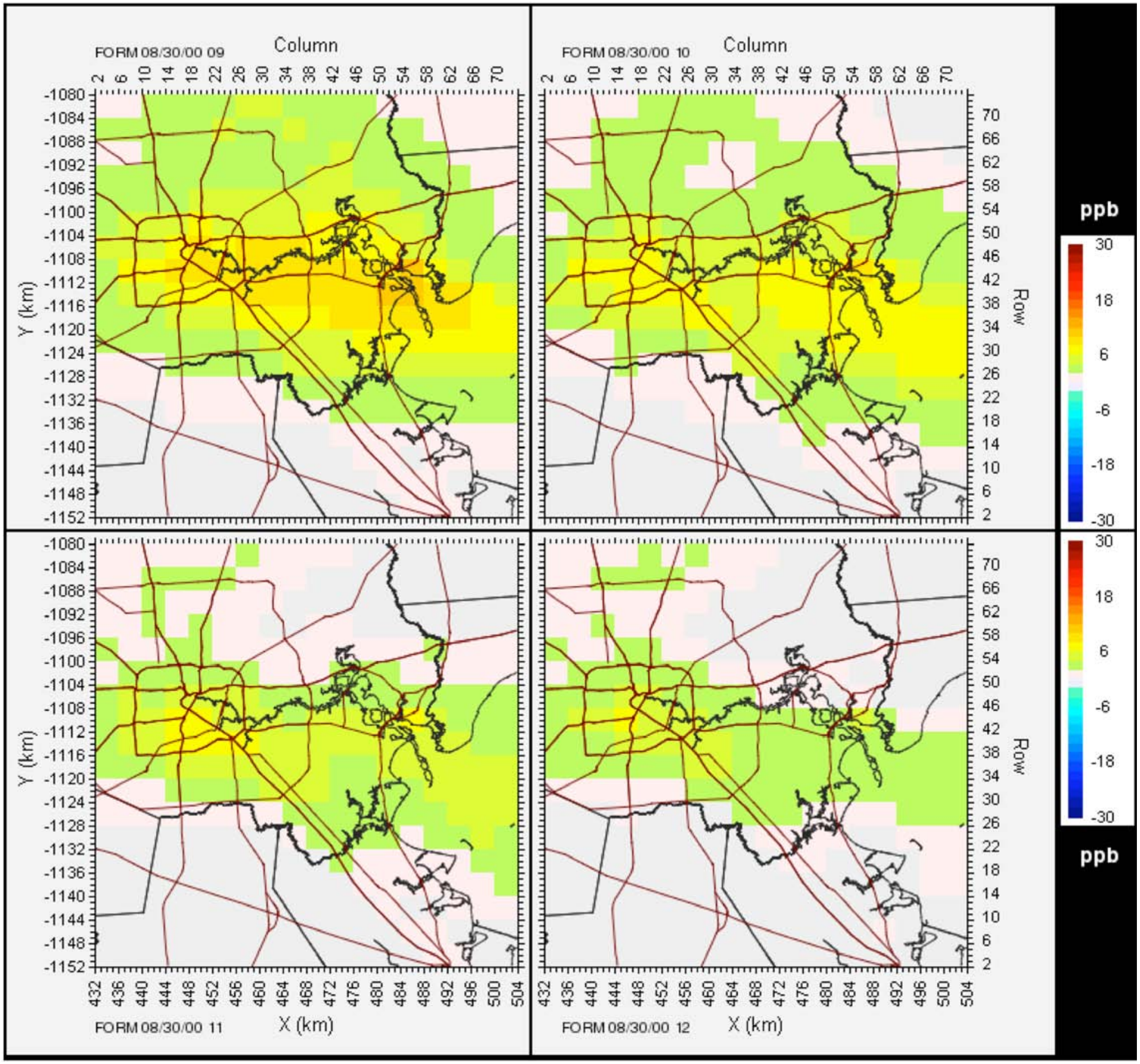
Delta FORM, ppb O8/25 09-12h

(UNC1-b1b)

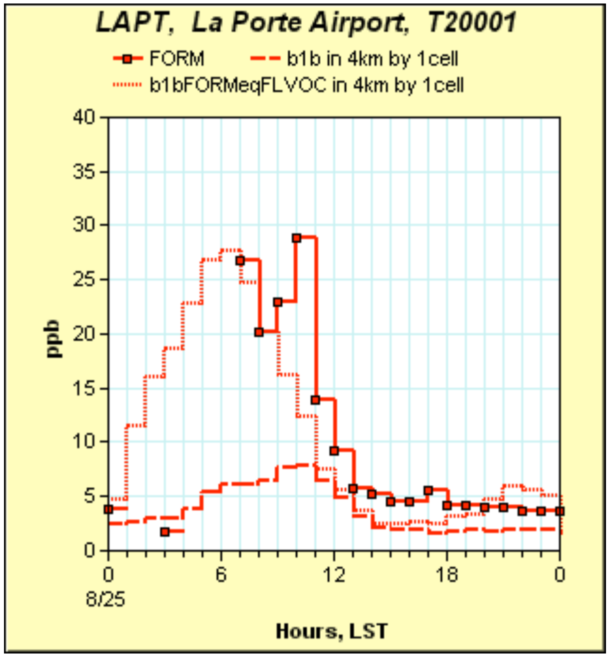
Flare case.

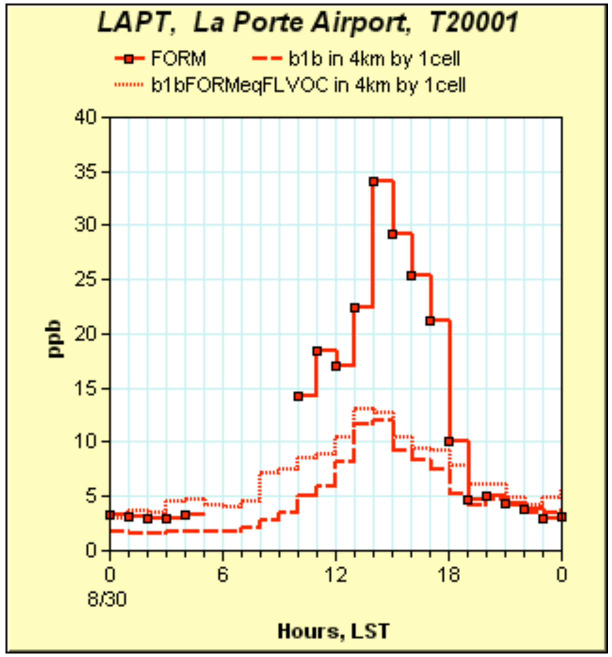


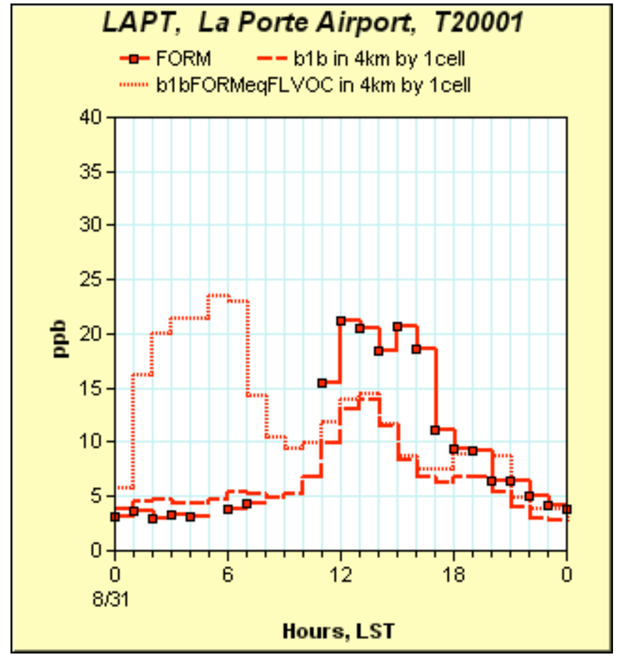
Delta FORM, ppb O8/30 09-12h
(UNC2-b1b) CO case.



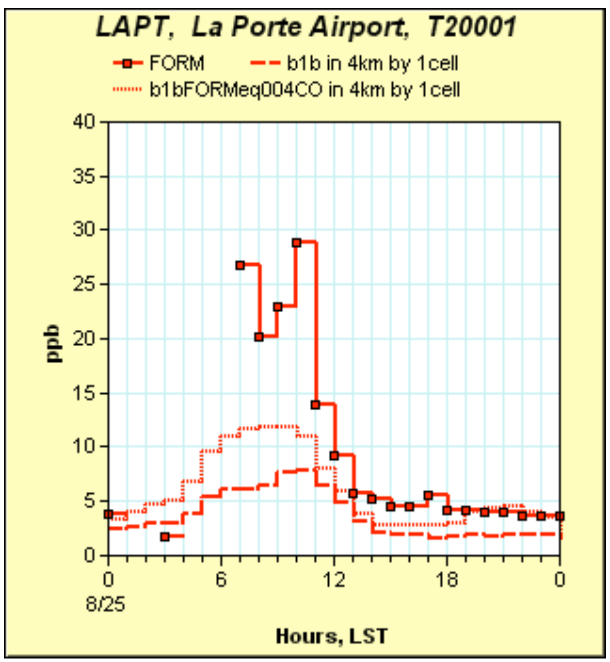
Obs b1b UNC1

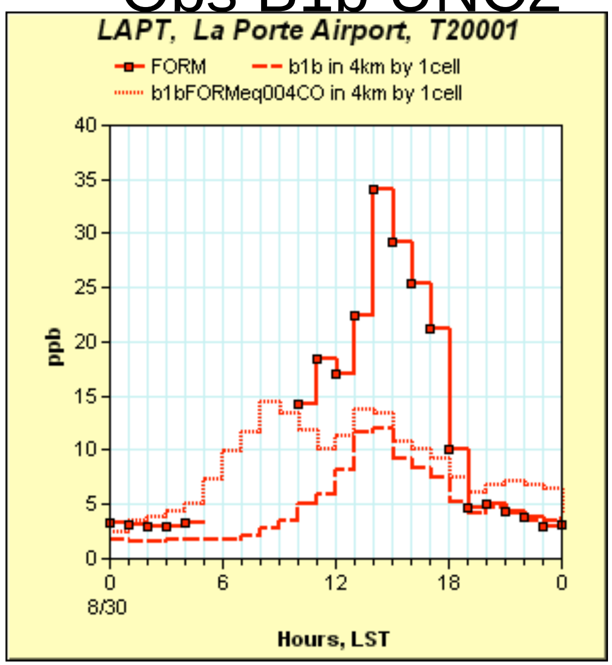


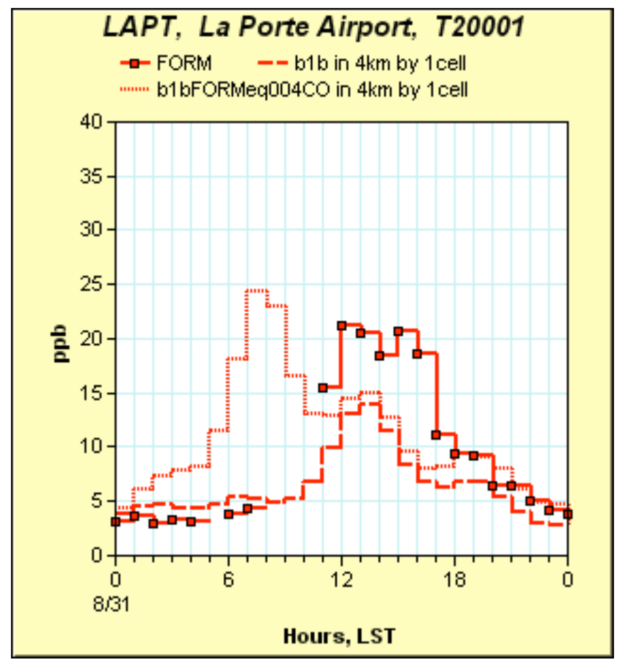




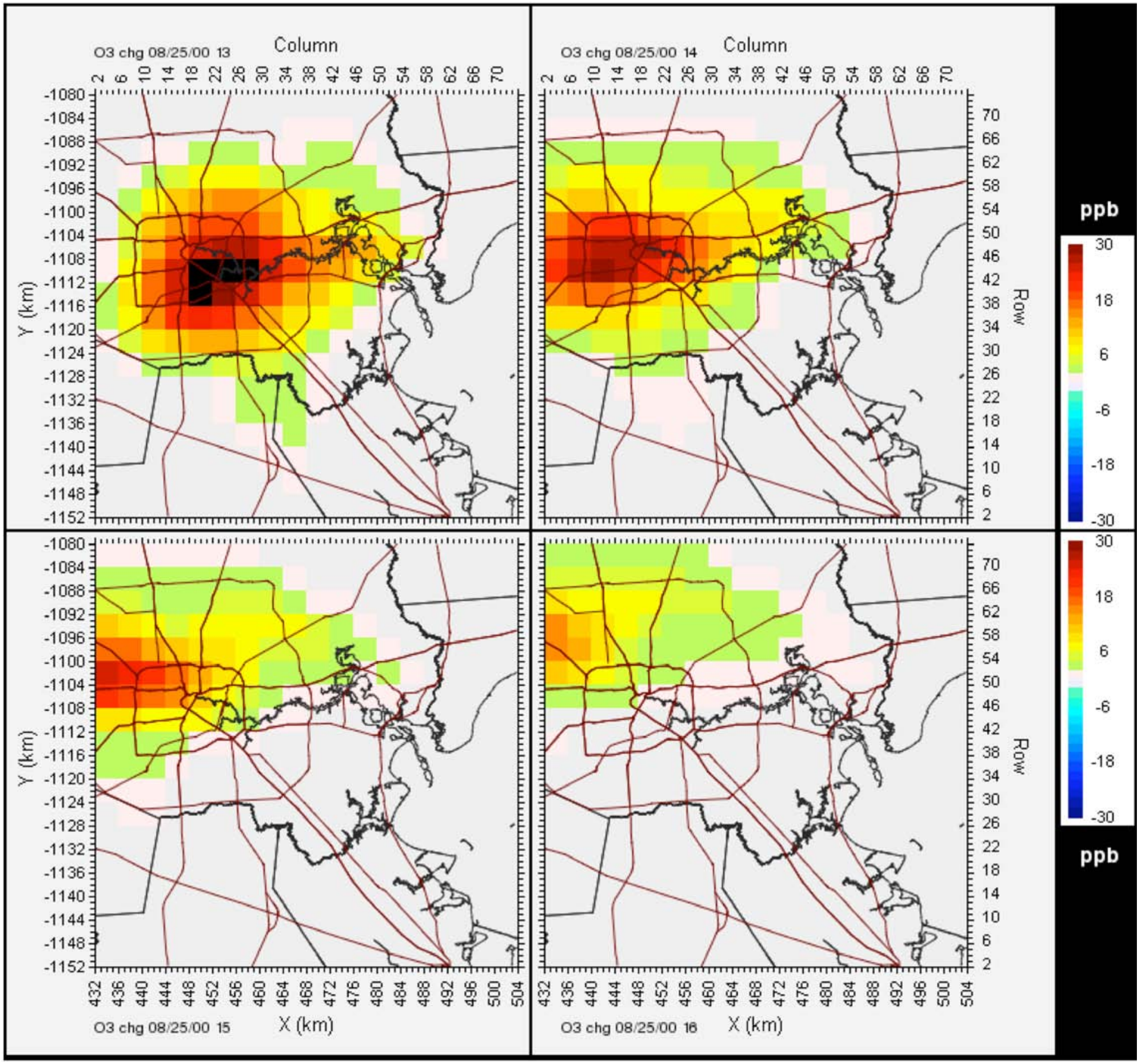
Obs B1b UNC2





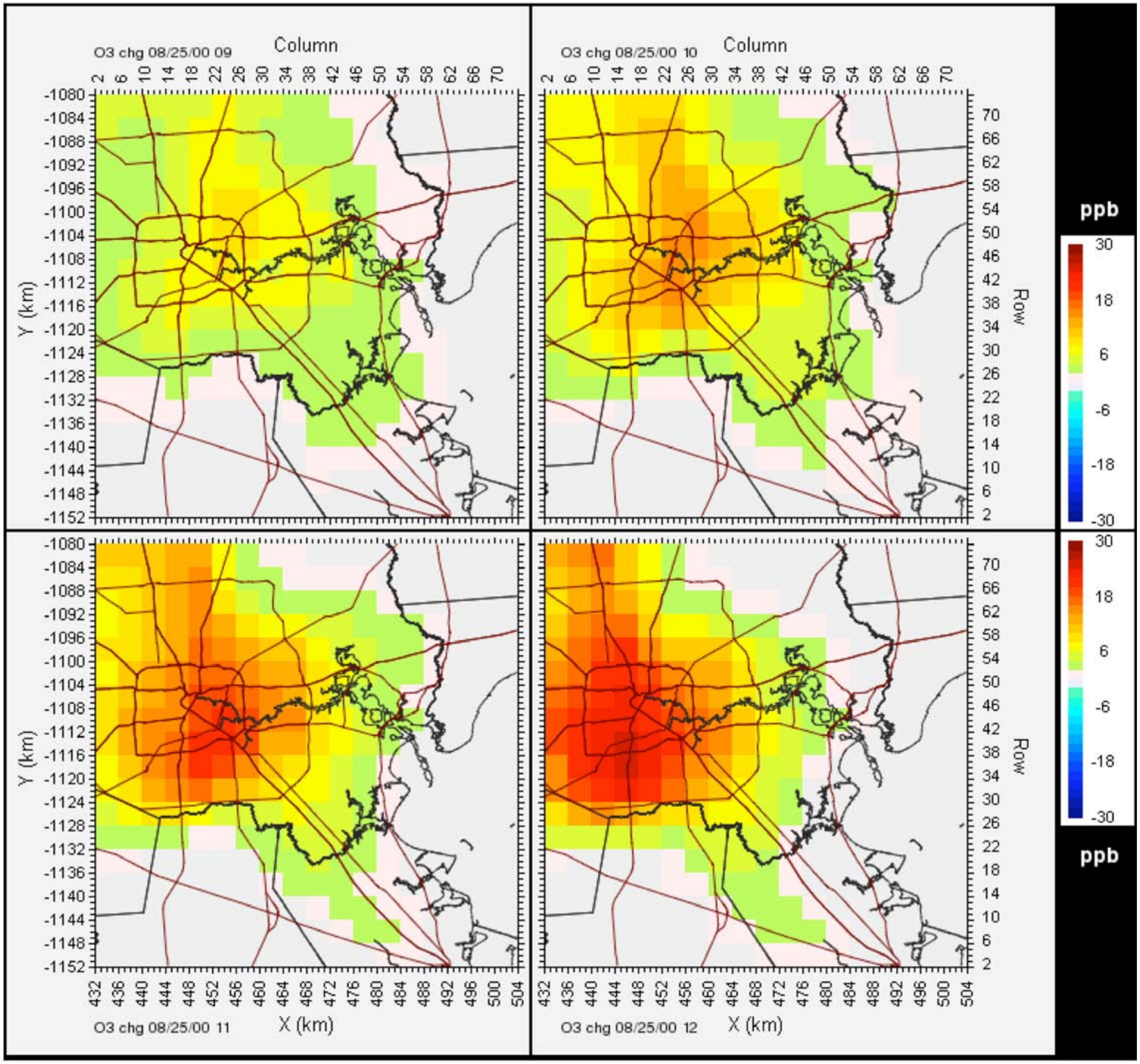


Delta Ozone, ppb O8/25 13-16h
(UNC1-b1b)
Flare case.

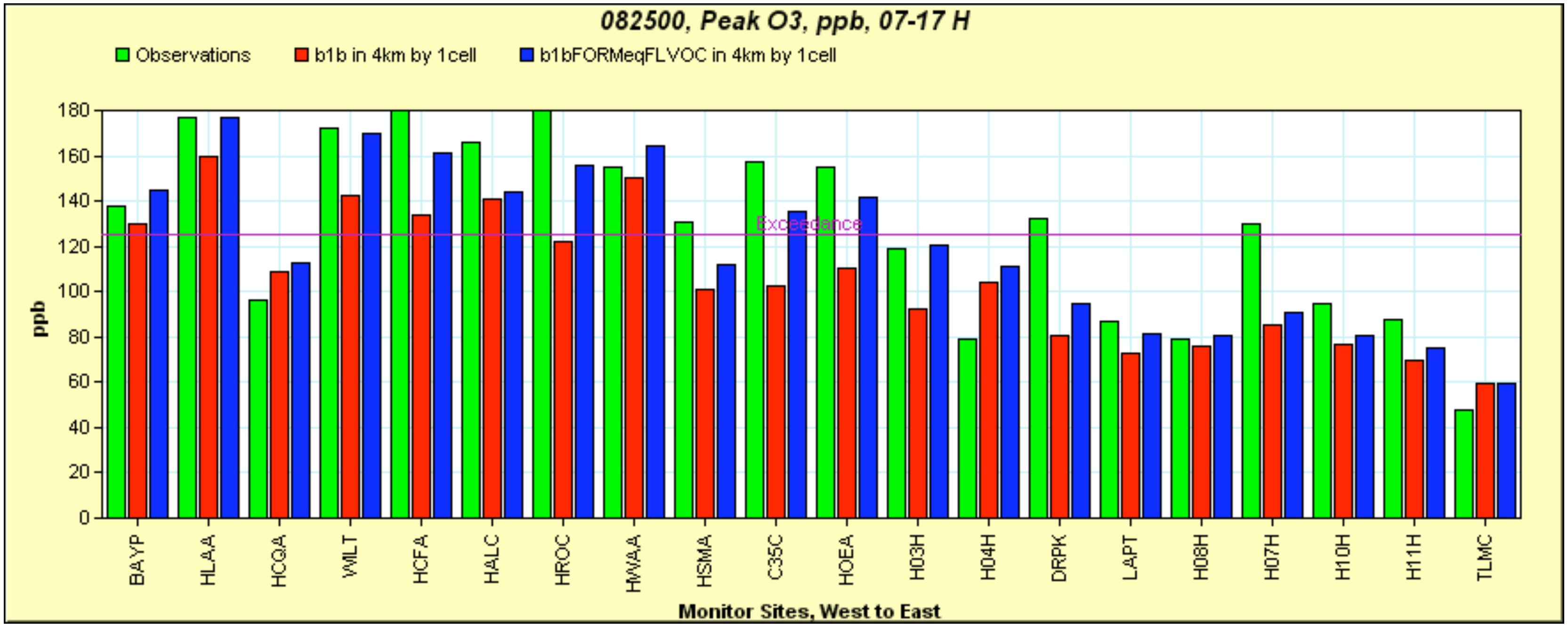


Delta Ozone, ppb O8/25 09-12h

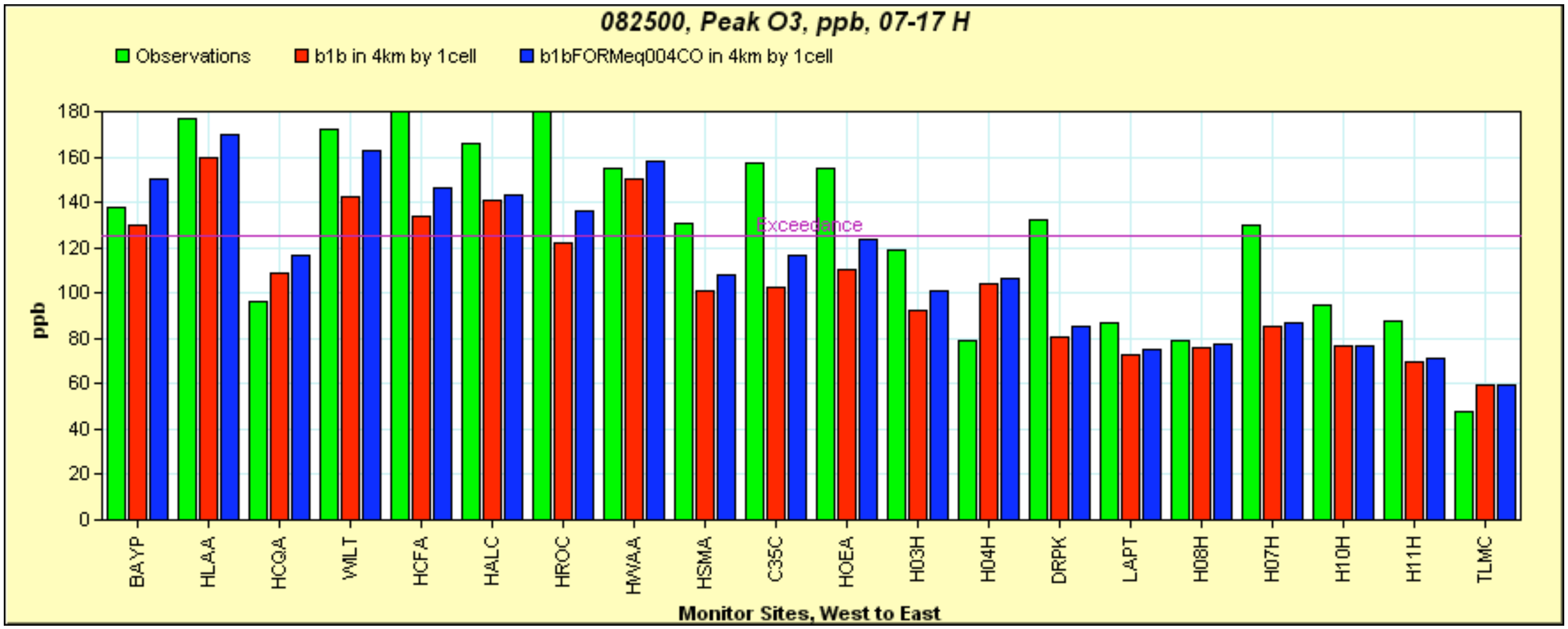
(UNC1-b1b) CO case.

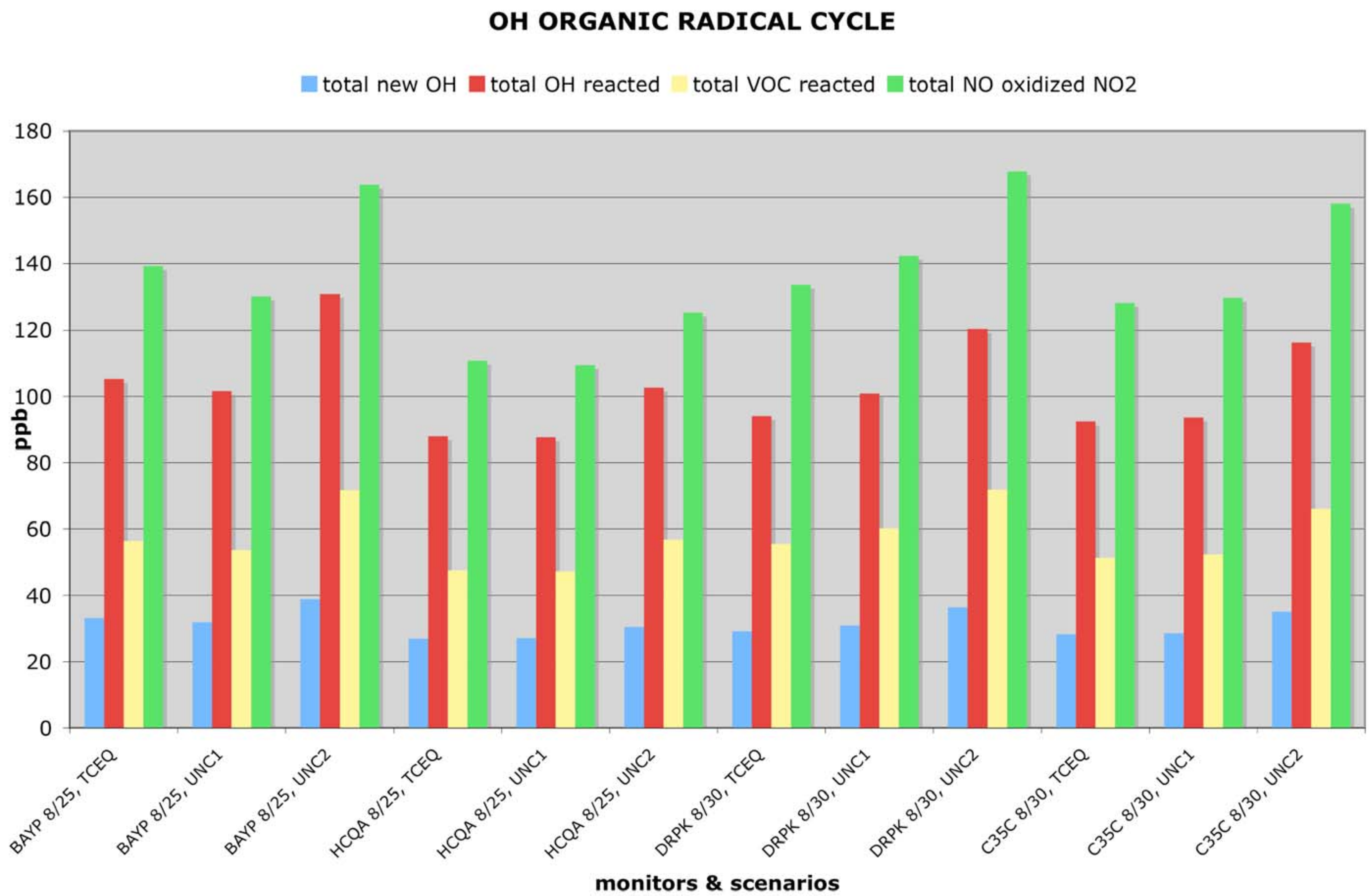


Obs
b1b
UNC1

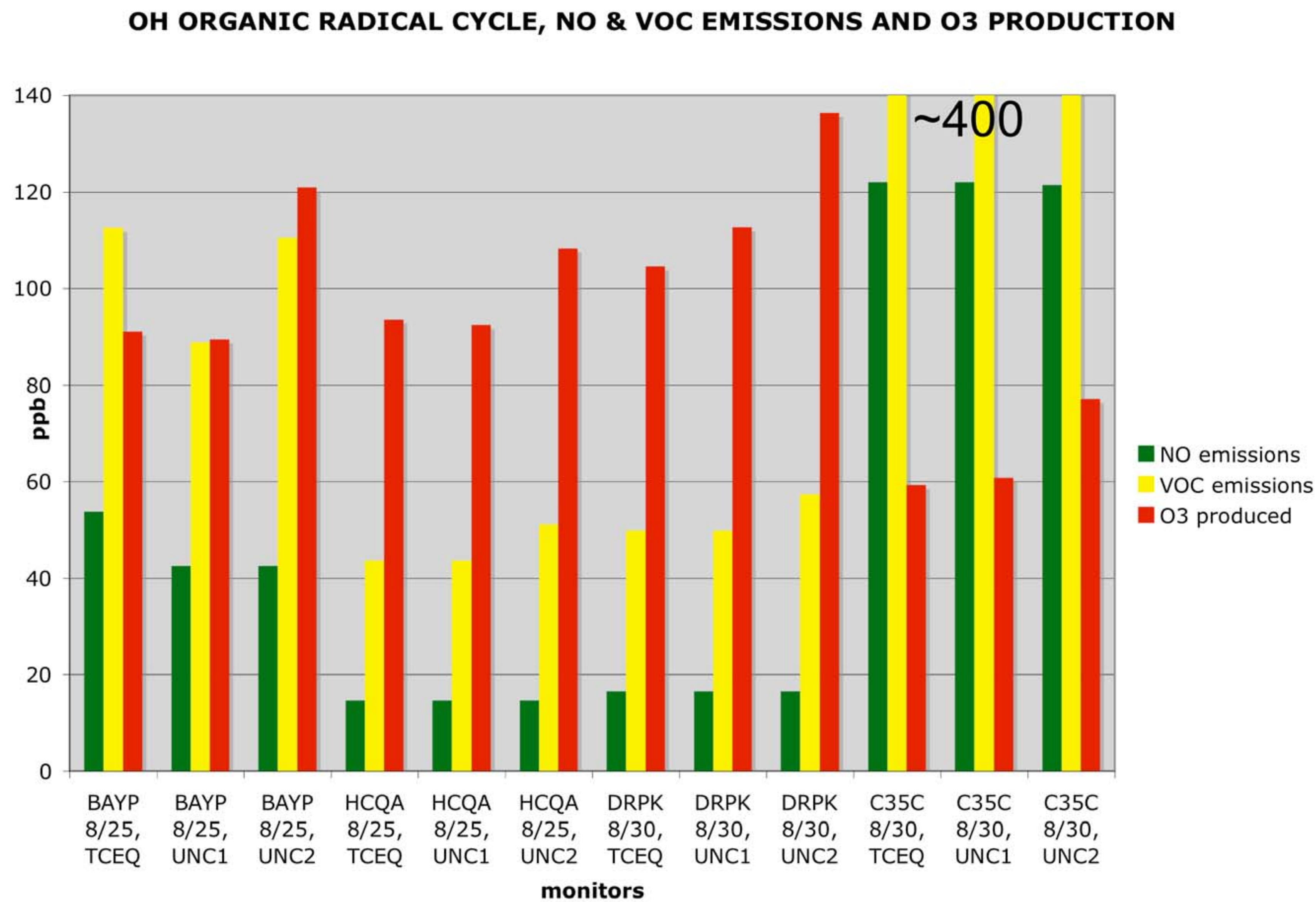


Obs
B1b
UNC2

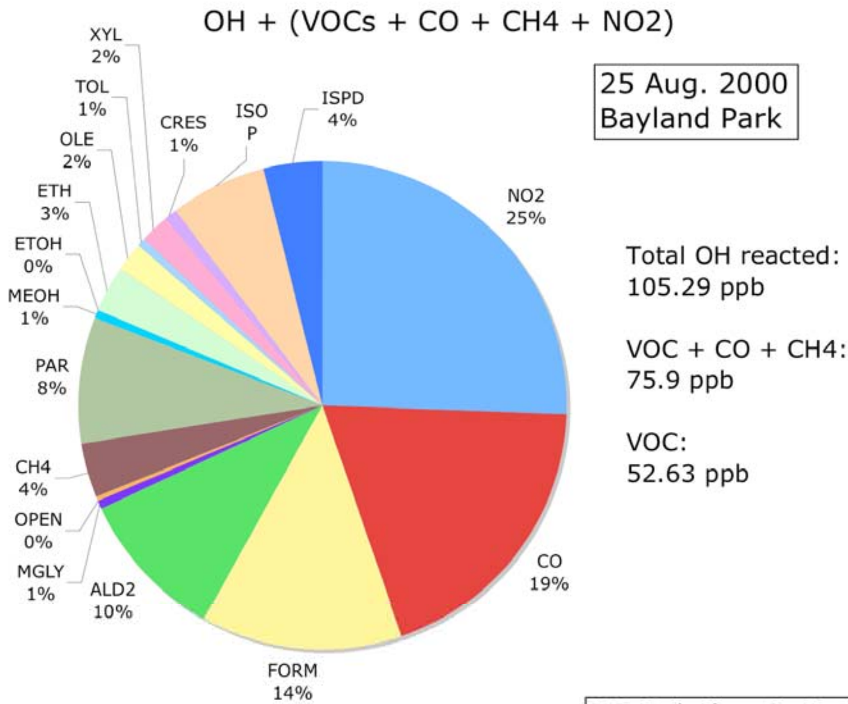




OH ORGANIC RADICAL CYCLE
total new OH
total OH reacted
total VOC reacted
total NO oxidized NO2
ppb
180
160
140
120
100
80
60
40
20
0
BAYP 8/25, TCEQ
BAYP 8/25, UNC1
BAYP 8/25, UNC2
HCQA 8/25, TCEQ
HCQA 8/25, UNC1
HCQA 8/25, UNC2
DRPK 8/30, TCEQ
DRPK 8/30, UNC1
DRPK 8/30, UNC2
C35C 8/30, TCEQ
C35C 8/30, UNC1
C35C 8/30, UNC2
monitors & scenarios

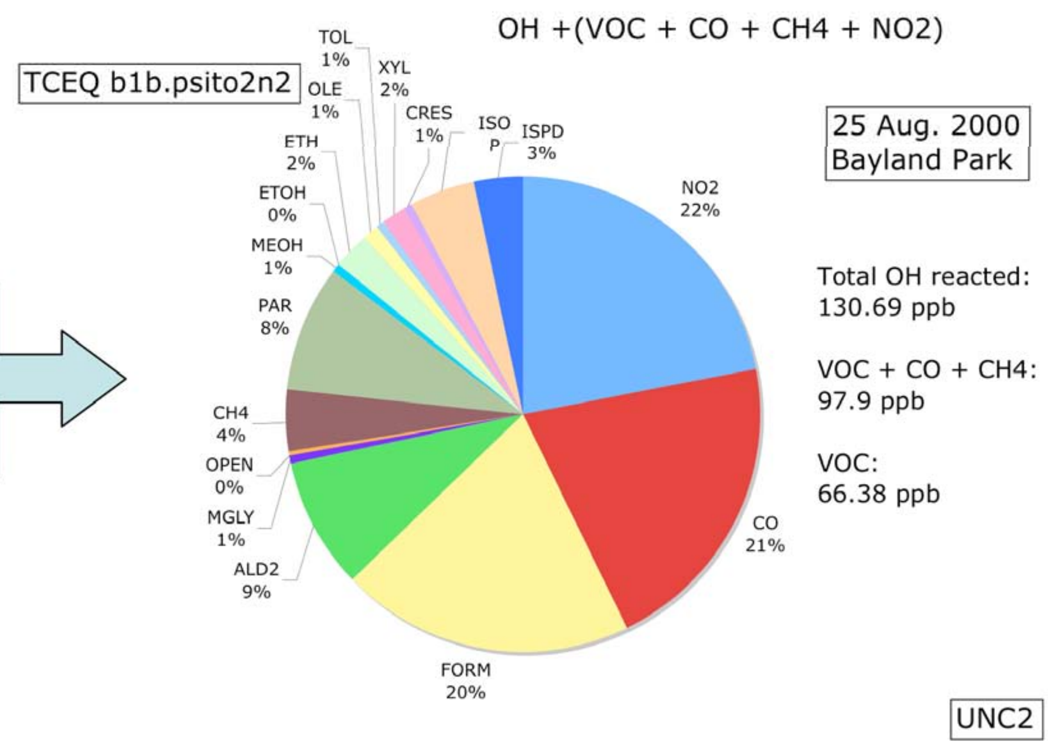


OH ORGANIC RADICAL CYCLE, NO & VOC EMISSIONS AND O3 PRODUCTION
140
120
100
80
60
40
20
0
ppb
~400
NO emissions
VOC emissions
O3 produced
BAYP 8/25, TCEQ
BAYP 8/25, UNC1
BAYP 8/25, UNC2
HCQA 8/25, TCEQ
HCQA 8/25, UNC1
HCQA 8/25, UNC2
DRPK 8/30, TCEQ
DRPK 8/30, UNC1
DRPK 8/30, UNC2
C35C 8/30, TCEQ
C35C 8/30, UNC1
C35C 8/30, UNC2
monitors


OH + (VOCs + CO + CH4 + NO2)
25 Aug. 2000
Bayland Park
XYL 2%
TOL 1%
OLE 2%
ETH 3%
ETOH 0%
MEOH 1%
PAR 8%
CH4 4%
OPEN 0%
MGLY 1%
ALD2 10%
FORM 14%
CO 19%
NO2 25%
CRES 1%
ISO P
ISPD 4%
Total OH reacted:
105.29 ppb
VOC + CO + CH4:
75.9 ppb
VOC:
52.63 ppb

b1b

UNC2


OH +(VOC + CO + CH4 + NO2)
TCEQ b1b.psito2n2
25 Aug. 2000
Bayland Park
TOL 1%
XYL 2%
OLE 1%
CRES 1%
ISO P
ISPD 3%
ETH 2%
ETOH 0%
MEOH 1%
PAR 8%
CH4 4%
OPEN 0%
MGLY 1%
ALD2 9%
FORM 20%
CO 21%
NO2 22%
Total OH reacted:
130.69 ppb
VOC + CO + CH4:
97.9 ppb
VOC:
66.38 ppb
UNC2

Summary Process Analysis of Chemistry

- Flare imputation caused >30 ppb increase in ozone concentrations
- CO ratio caused >18 ppb increase ozone concentrations, more distributed
- Increased peak ozone at almost every monitor causing 4 monitors to match observations
- ~20% increase in new OH and ~30% in ozone production
- Still did not match observed HCHO.

SIP-related research questions

- What are the appropriate nighttime values of pbl and mixing to balance the surface EI with observed concentrations?
- What can be measured to help constrain the representation of vertical mixing during daytime?
- What are the “correct” values of NO emissions?.
- What measurements can be used to corroborate the NOx emissions?
  - PAN, RNO3 and HNO3 hourly concentrations at multiple stations W-E and N-S
  - NOy monitors at many more surface sites
- What is the origin of the CO prediction problems? Mobile sources? Dispersion?
  - Add high resolution CO monitors to the NOy monitors at more stations and at Williams Tower
  - Compare CO/NOy emission ratios predicted by mobile model with obs. Are there problems in Dallas too?
  - Are winds too fast at layer 4 of model at night? Does the residual layer get blown away?

How can observation and modeling approaches be used for determining (i) the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and NOx emissions, and (ii) the spatial/temporal variation of these sensitivities?

- Sensitivities to precursor emissions difficult to infer in current model
- Overprediction in precursor emissions
- Lack of Ozone production
- Radical Sources
- What are the implications from insufficient radical source?
  - The deficient radical sources result in insensitivity to VOC precursors and inhibition due to elevated levels of NOx.
  - With current model configuration VOC control strategies would have little effect in future ozone values.
- How can we assess the correct radical source strength at surface sites?
  - Should we be making Kleinman-like measurements at several monitor sites and apply his steady state model to estimate P(O3) and infer radical source strengths from measurements that can be compared with model?
  - Other Radical sources HONO?