Contrasting effects of different anthropogenic source types on ozone formation in Houston

T.B. Ryerson, M. Trainer, D.K. Nicks Jr., A.J. Neuman, R.W. Dissly, J.S. Holloway, R.O. Jakoubek, D.D. Parrish, G.J. Frost, C. Wiedinmyer, D.T. Sueper, W.C. Kuster, P.D. Goldan, G. Huebler, W.M. Angevine, and F.C. Fehsenfeld

Aeronomy Laboratory, NOAA, Boulder, CO

S.G. Donnelly, S. Schauffler, E. Atlas, A.J. Weinheimer, F. Flocke, B.P. Wert, W.T. Potter, and A. Fried

Atmospheric Chemistry Division, NCAR, Boulder, CO

C.J. Senff, L.S. Darby, R.M. Banta, R.J. Alvarez

Environmental Technology Laboratory, NOAA, Boulder, CO

Additional thanks for:

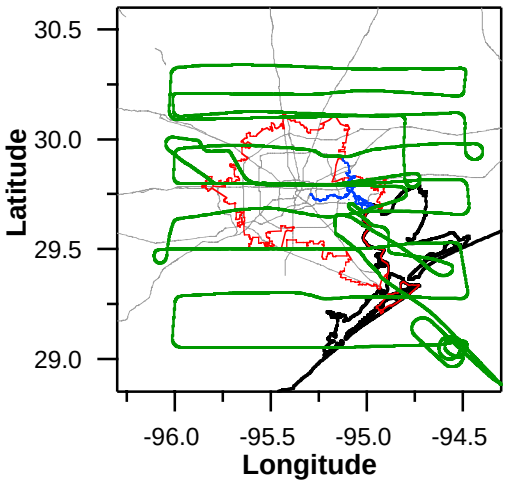
Surface ozone and wind observations (TNRCC)
Twin Otter ozone data (Baylor University)

TexAQS 2000: Electra flight data used to:

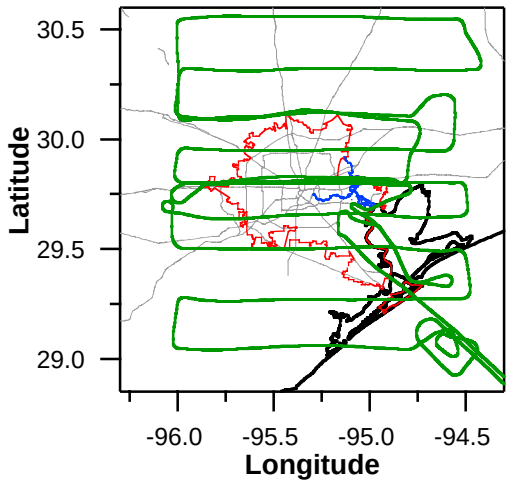
- **differentiate between source types**
  petrochemical, urban, and power plant

- **assess observed differences in**
  ozone production rate
  ozone production yield

Sunday, August 27
(87 ppbv at Conroe)

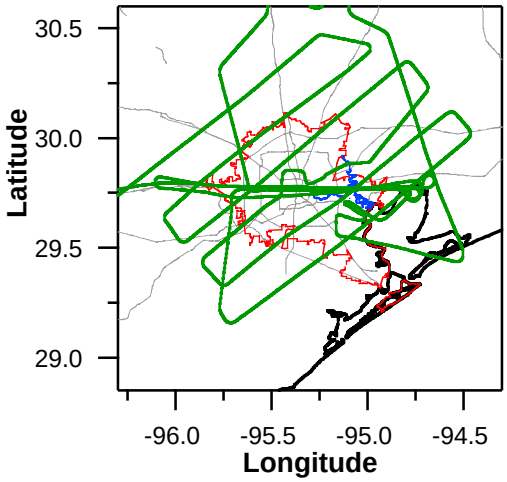


Monday, August 28
(112 ppbv at Conroe)



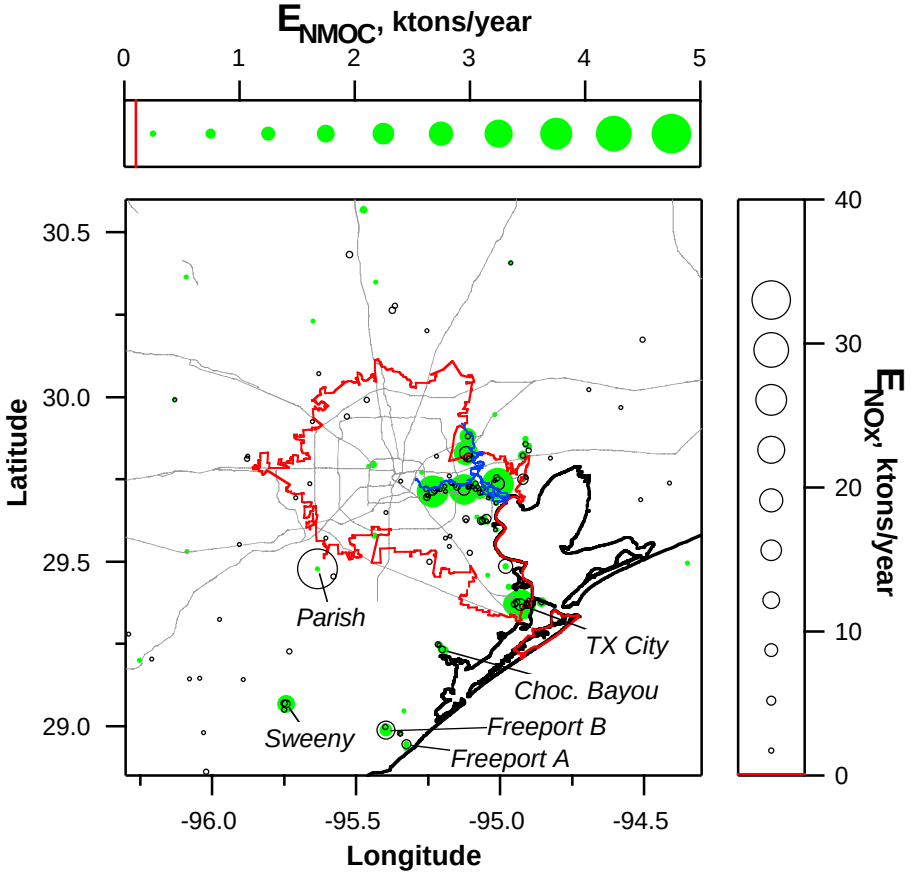
- **contrast non-exceedance with exceedance days**

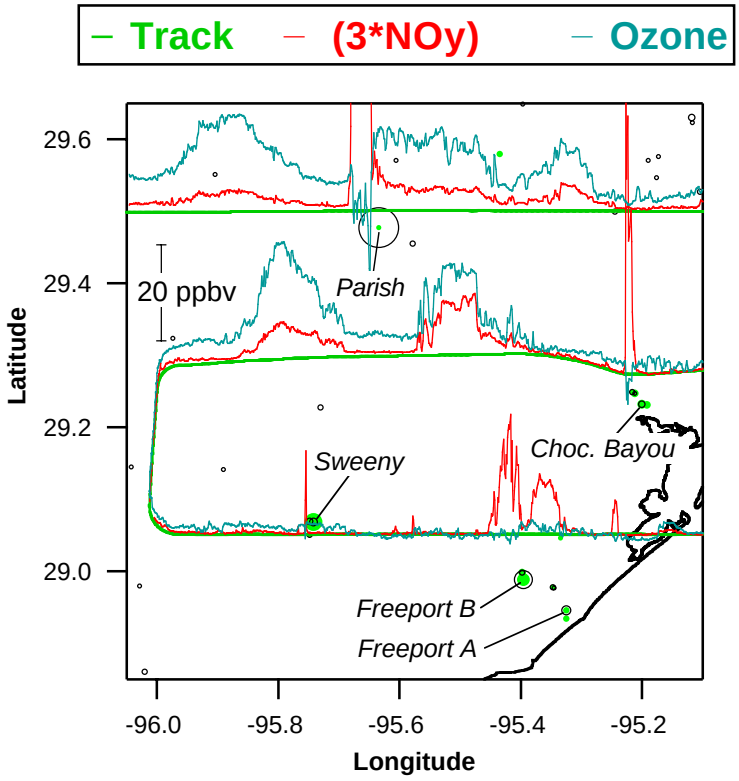
Friday, August 25
(194 ppbv at Crawford)



Use Aug. 27 & 28 to study:

- isolated petrochemical plumes S. of Houston
- coalesced Ship Channel and TX City plume
- contrast source types:
  - *power plant*
  - *urban*
  - *petrochemical*



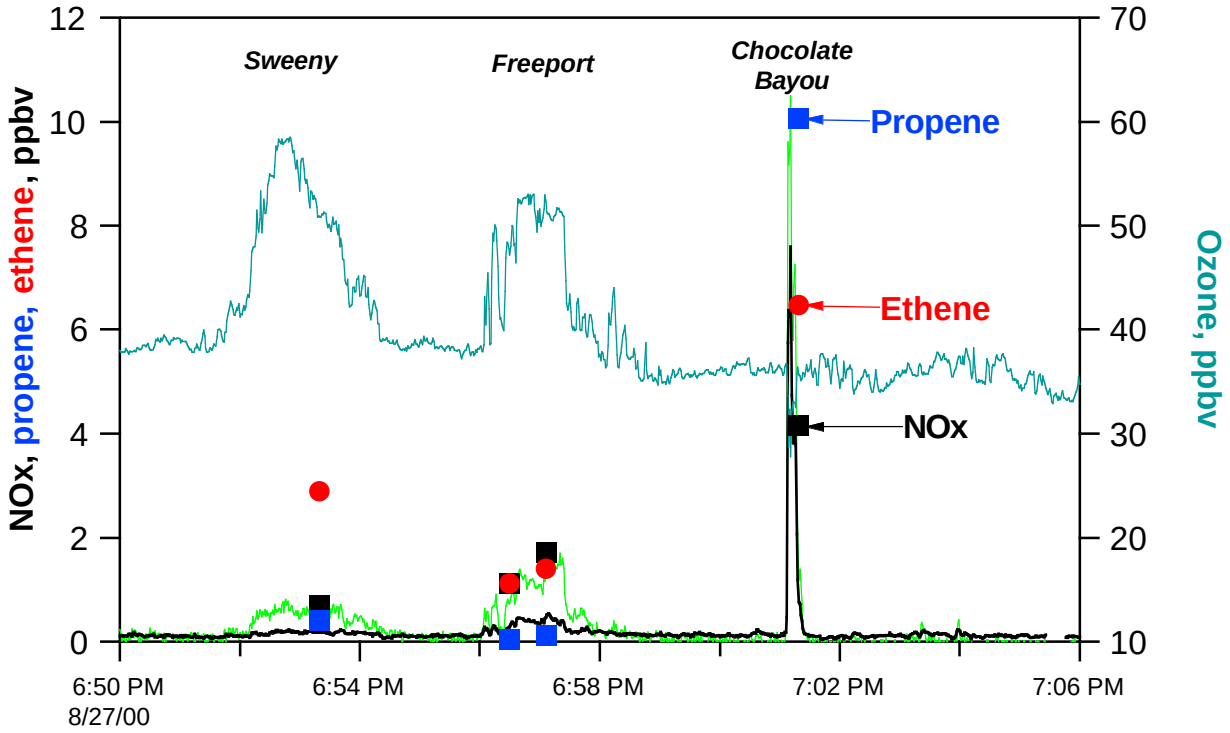


Prompt ozone formation observed downwind of isolated complexes

- use (speciated VOC)/NOx:
  - compare to inventories
  - contrast effects on HOx
- estimate plume ozone formation rates & yields

Evaluation of alkene emissions inventories

- use measured (ethene/NOx) and (propene/NOx)



Order of magnitude estimates:

measured (propene/NOx) ~ 1
measured (ethene/NOx) ~ 1

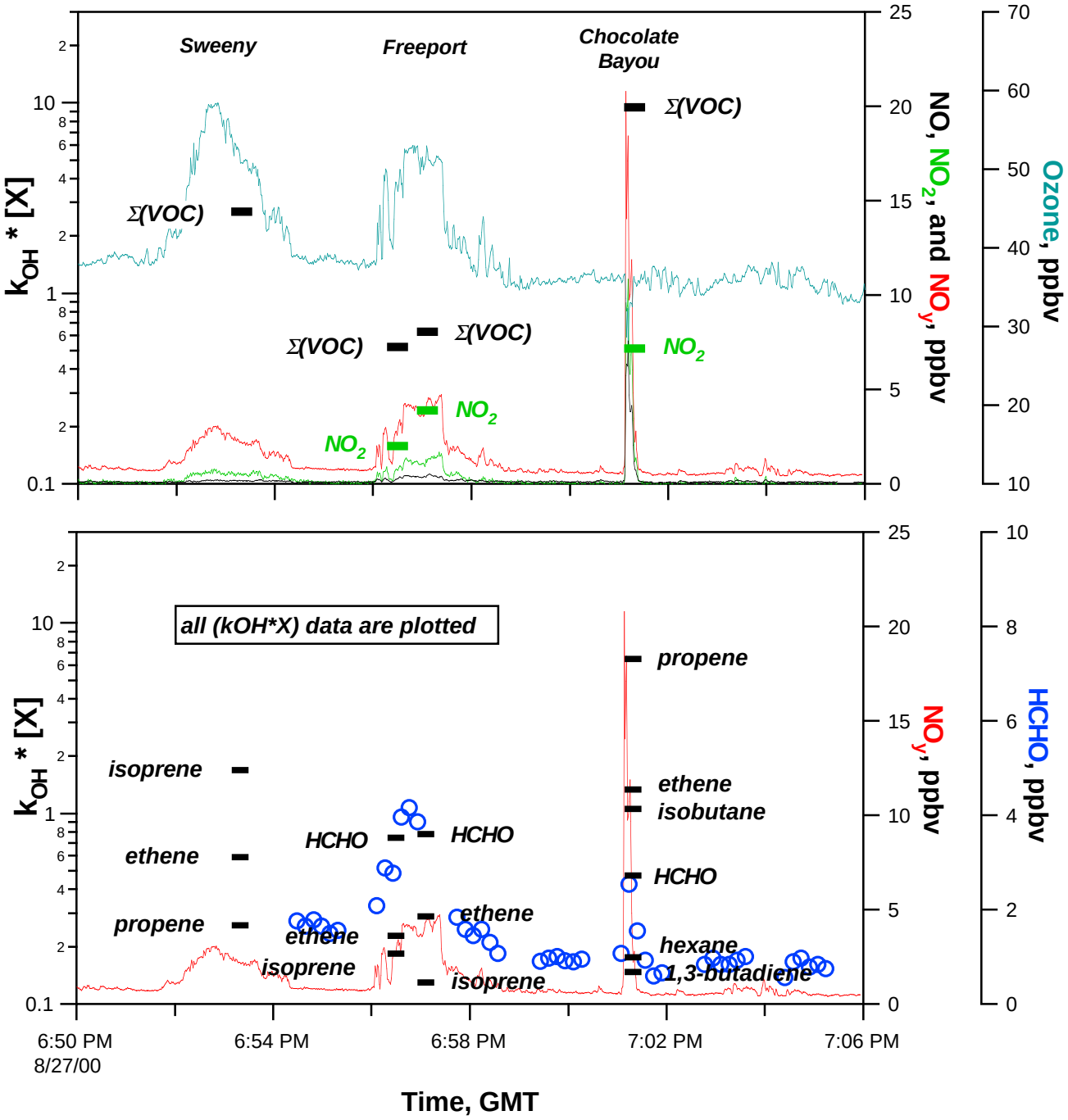
- **TNRCC PSDB predicts much, much lower (alkene/NOx) ratios from these sources:**

	(Total NMOC)/NOx, mol/mol:
Choc. Bayou:	0.3
Freeport:	0.1
Sweeny:	0.2

using average NMOC mass of 58 g/mol (C_4H_{10})

Relative OH reactivities:

isolated petrochemical plumes
August 27, 2000

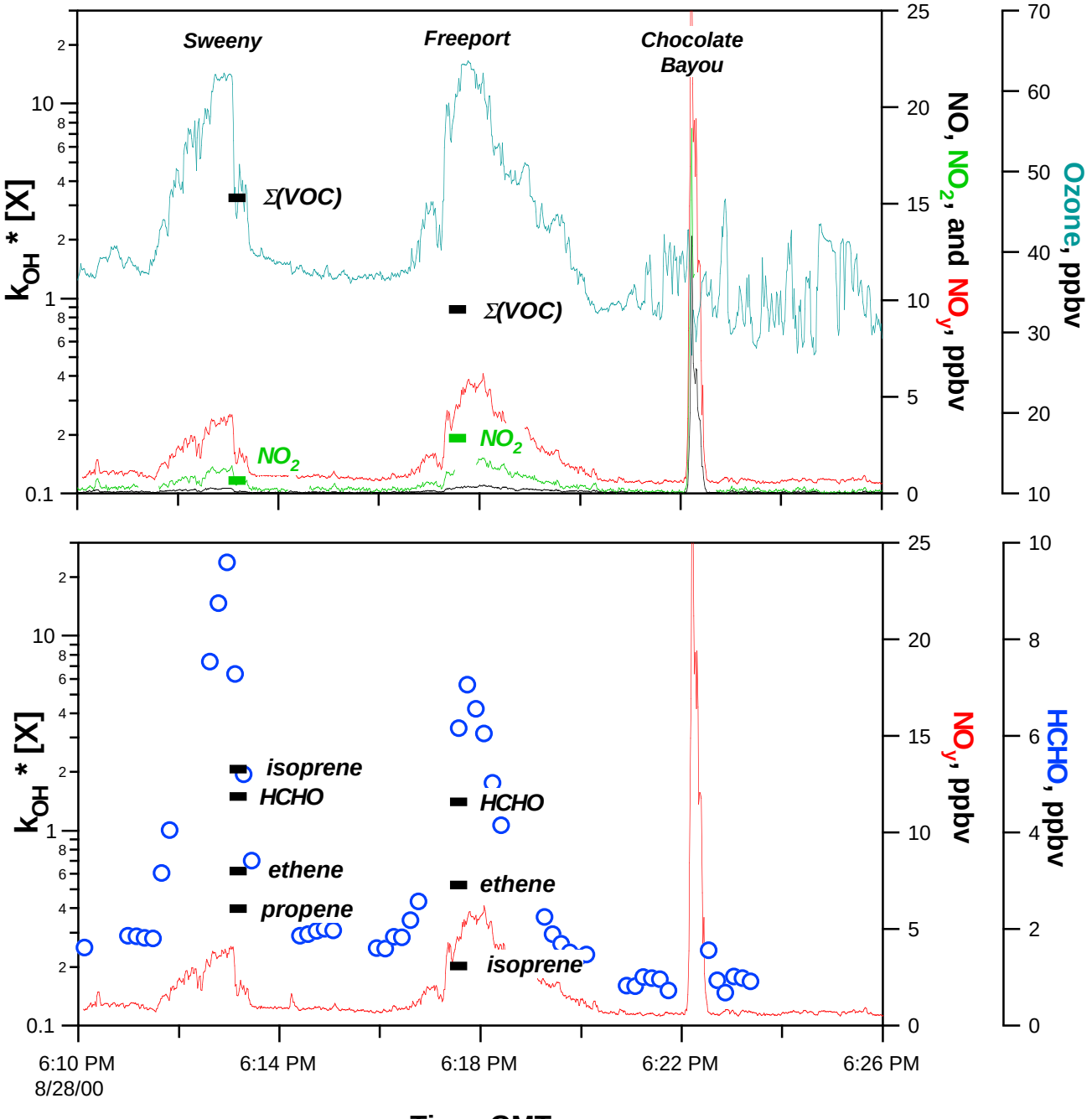


- **alkenes dominate plume VOC reactivity**

- **all other compounds (alkanes, aromatics) do not contribute substantially to observed rapid ozone formation**

Similar picture on the following day

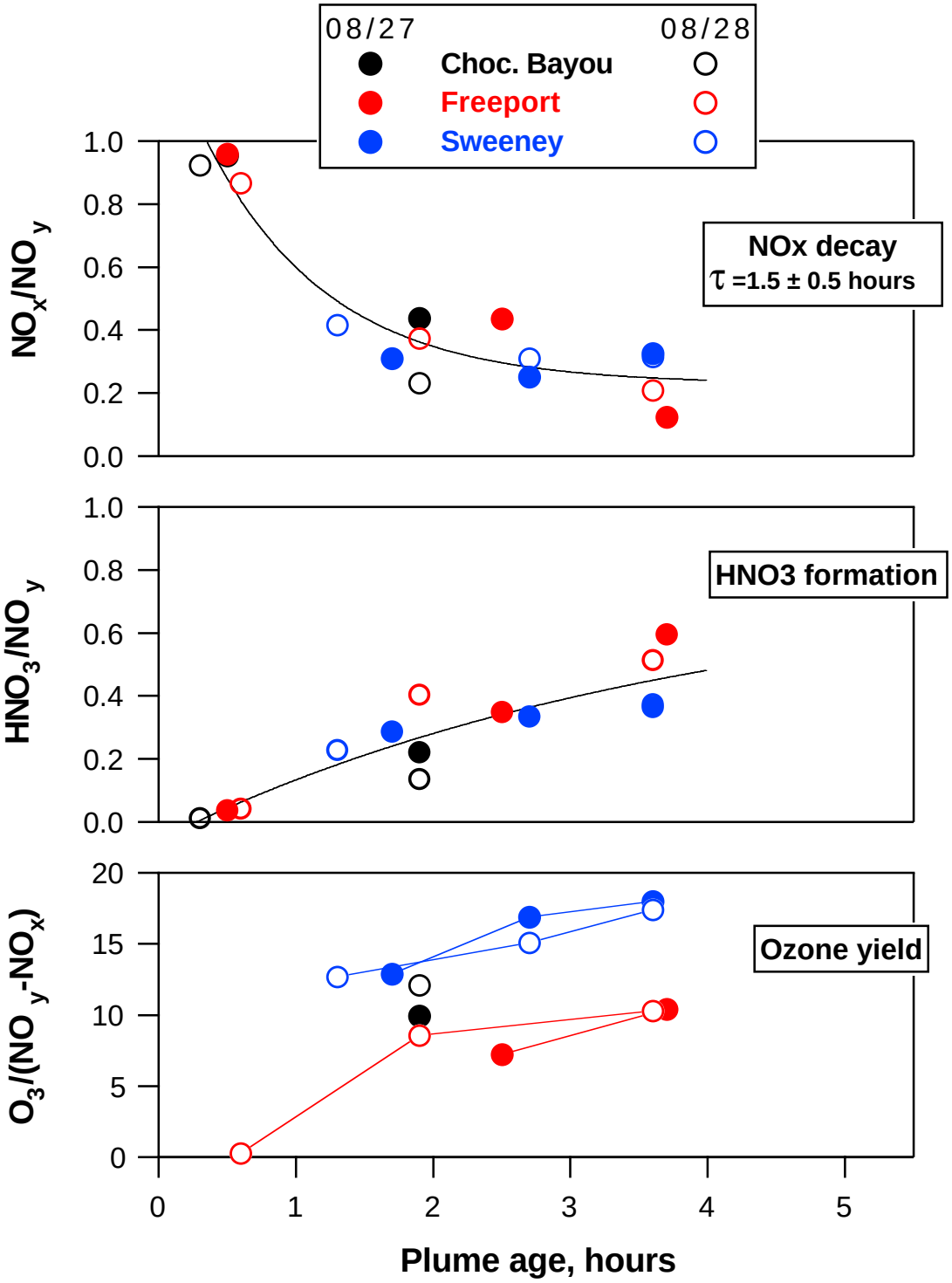
August 28, 2000



- **No reported emissions upsets on either day**
- **Emissions representative of business-as-usual**

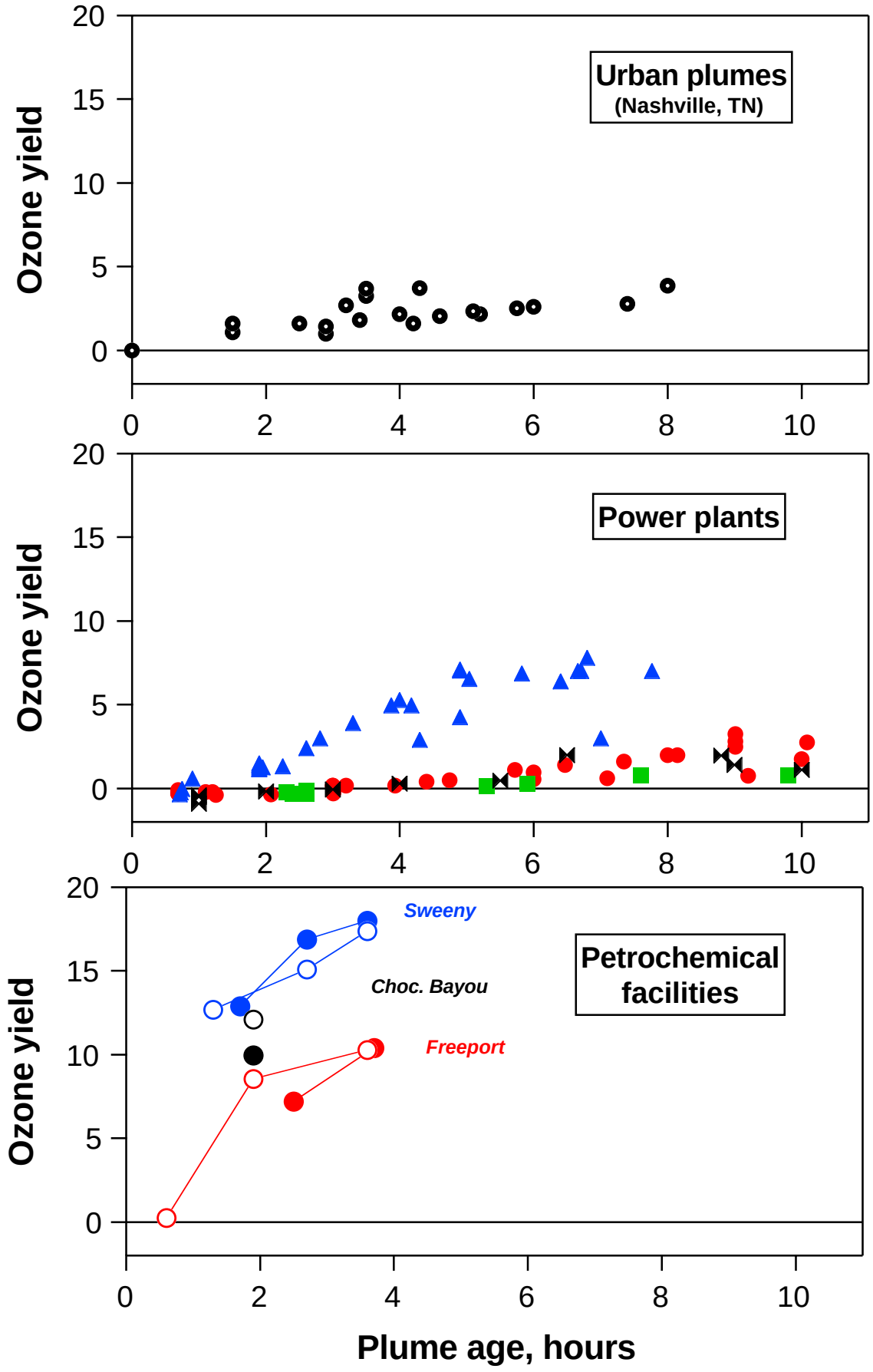
Isolated petrochemical plumes
August 27 and 28, 2000

Rapid photooxidation observed; ozone formed in very high yield



Source comparison

Data from 1995, 1999, and 2000



Lagrangian plume model results

(M. Trainer, NOAA)

- **Model dispersion and emissions ratios constrained by Aug. 28 Electra data**

Sweeny

$E_{ethene} = 5 \times E_{NOx}$

$E_{propene} = 2 \times E_{NOx}$

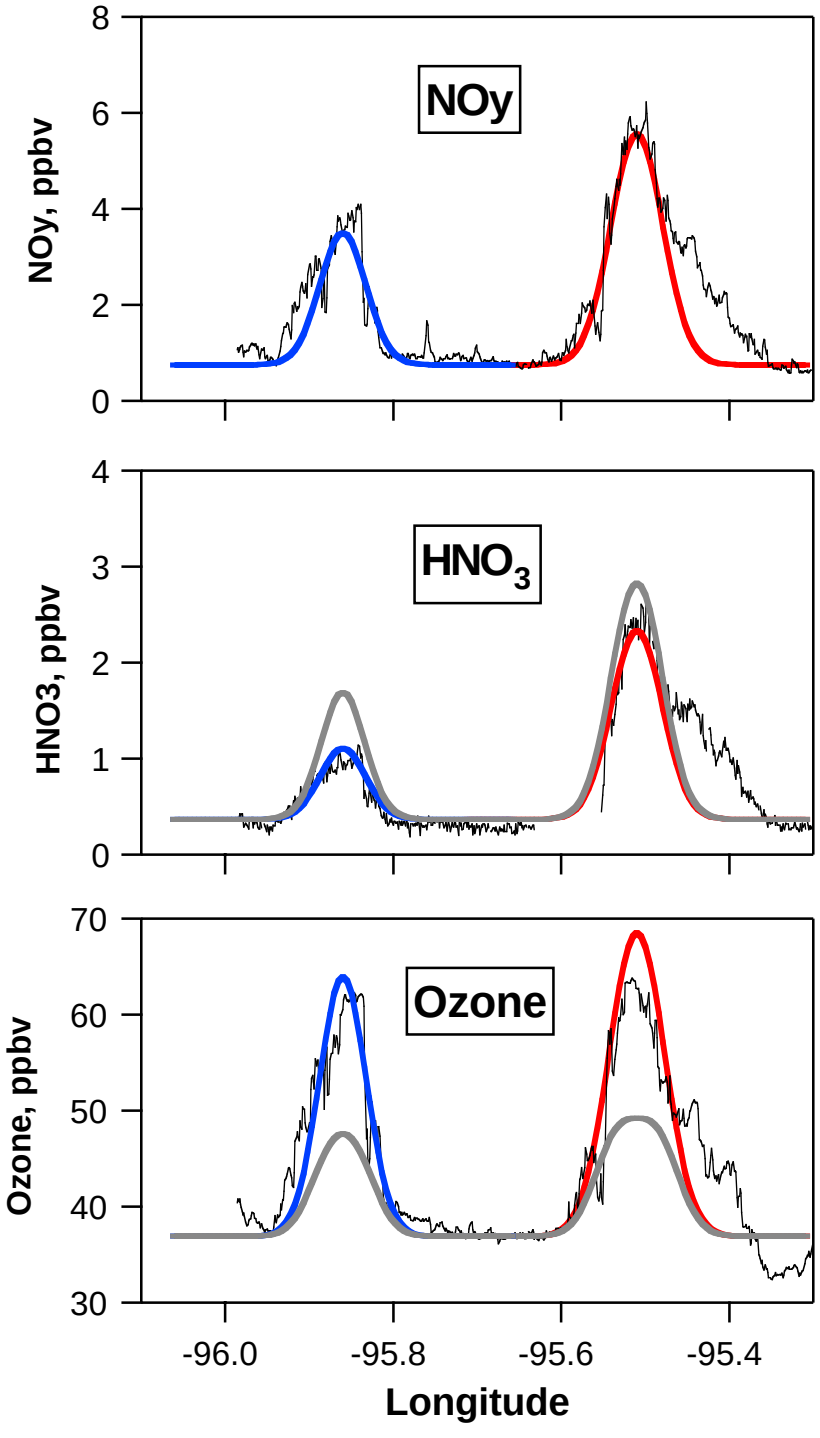
(no alkenes)

Freeport

$E_{ethene} = E_{NOx}$

$E_{propene} = E_{NOx}$

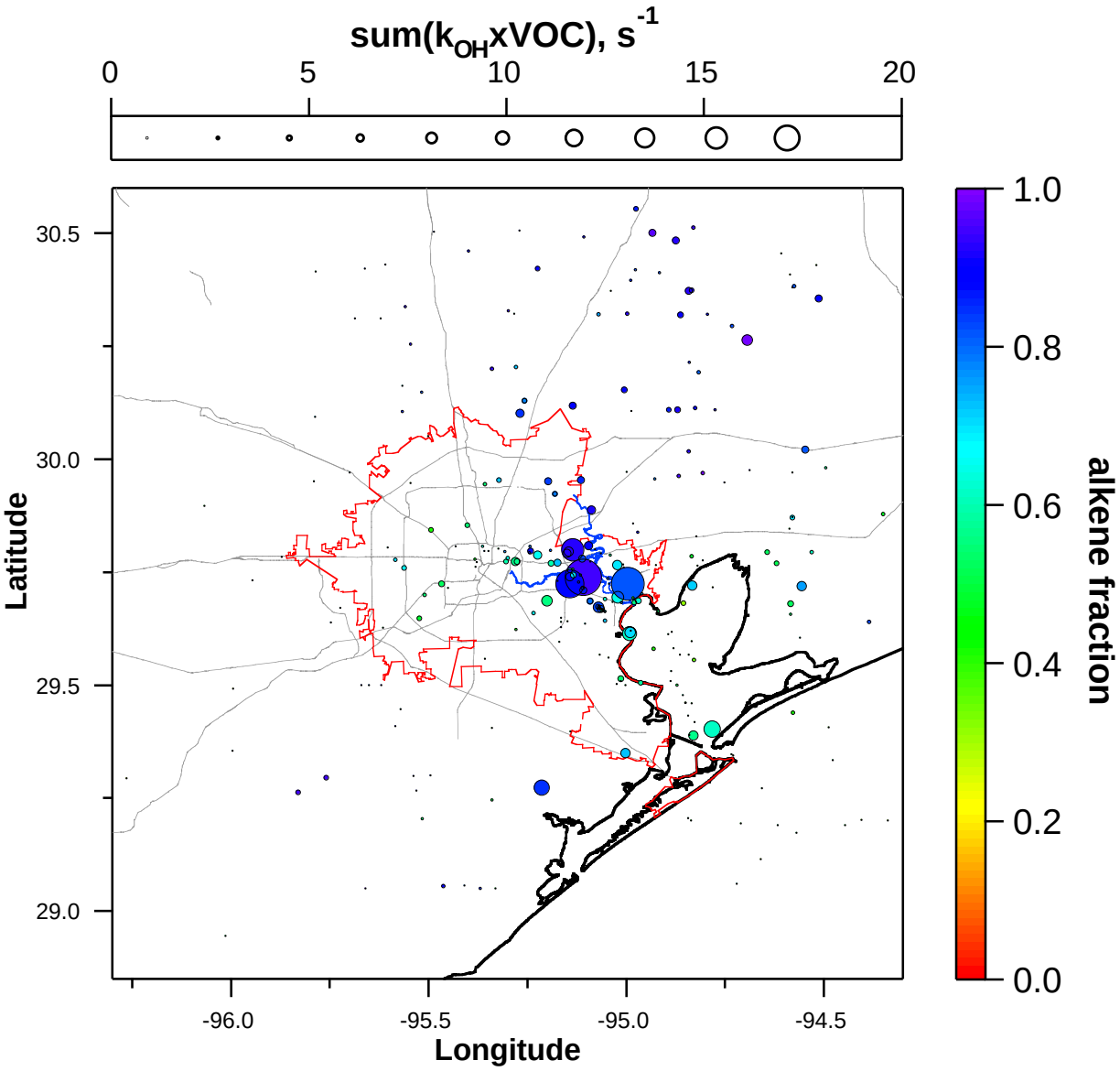
(no alkenes)



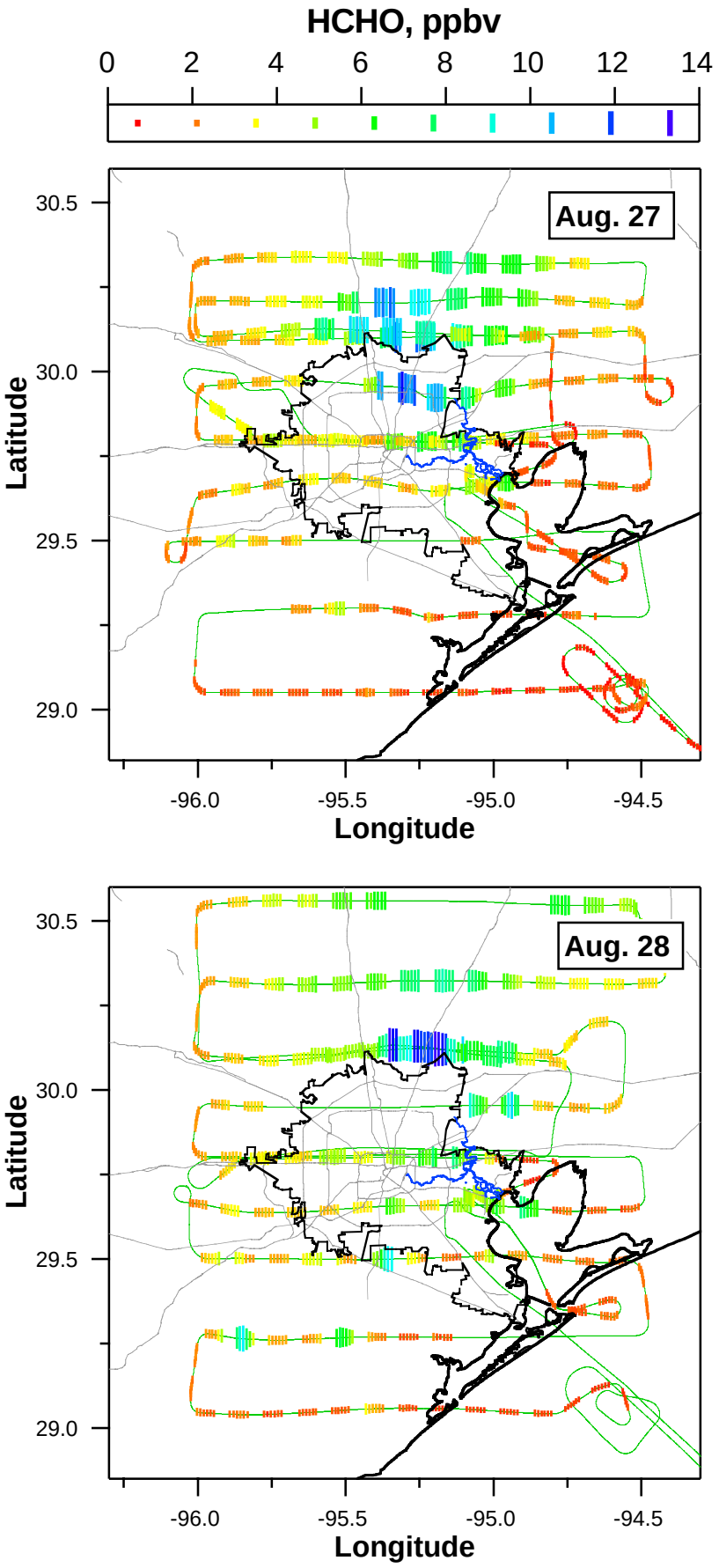
- **OH chemistry only; model simulates the observed HNO_3, PANs, HCHO, and ozone**
- **Rapid ozone formation is consistent with observed ratios of (alkene/NOx) in these plumes**

Coalesced Ship Channel and TX City plumes: relative OH loss rates

WAS and in-situ GC samples below 1500m entire TexAQS mission, August-September



- **Reactivity over petrochemical source regions is extremely high**
- **Dominated by propene, ethene, 1,3-butadiene**
- **Enhancements consistent with LaPorte data throughout the TexAQS study period**



Formaldehyde data

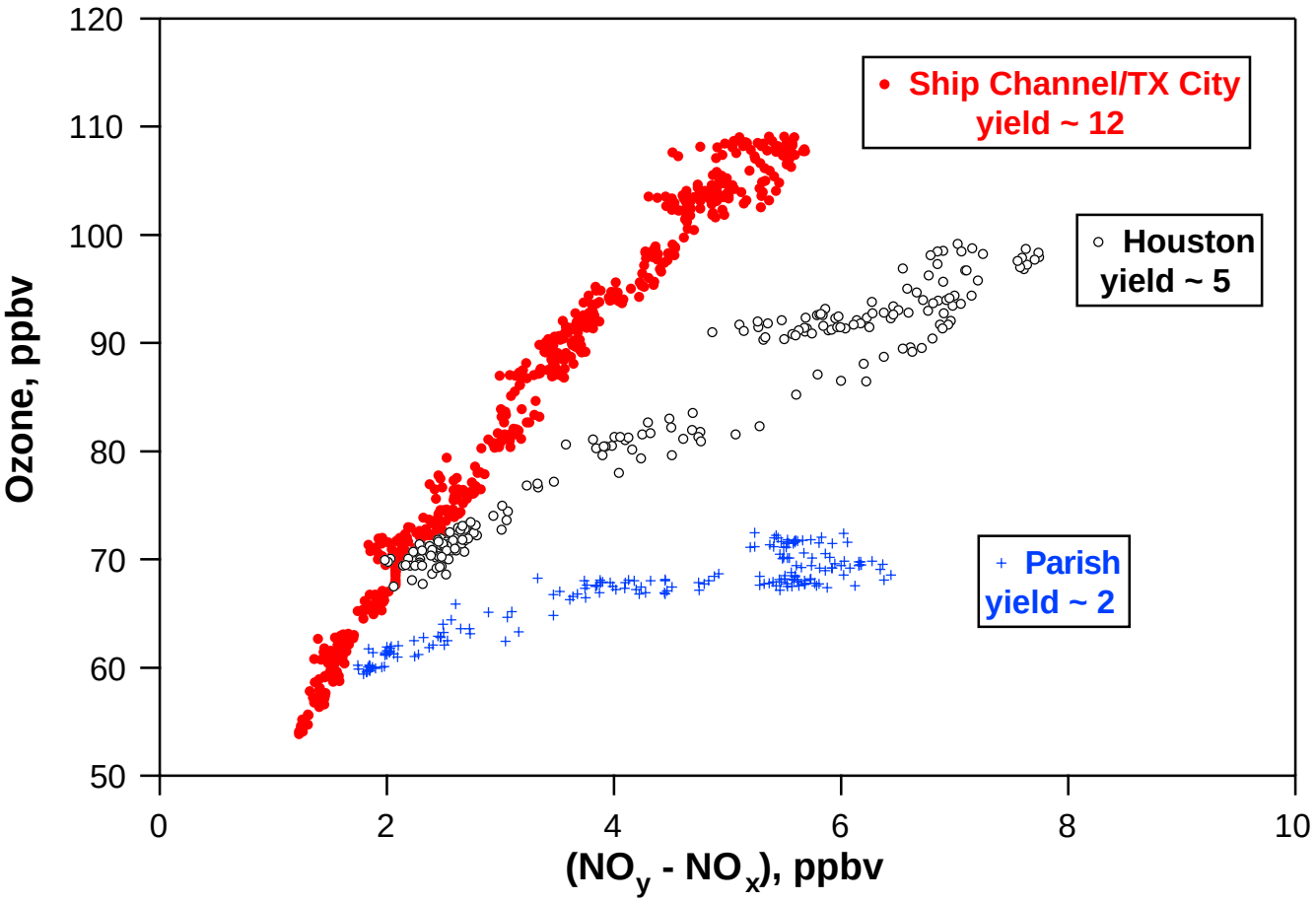
August 27 and 28, 2000

- **HCHO not emitted in substantial amounts;**
- **Produced as a result of (alkene+OH) reactions**
- **Distributions of alkenes, aldehydes, and ozone consistent with different formation & decay rates**

Ozone yield comparison

Electra data, August 28, 2000

- **plumes characterized by (NO_x/NO_y) = 0.20**



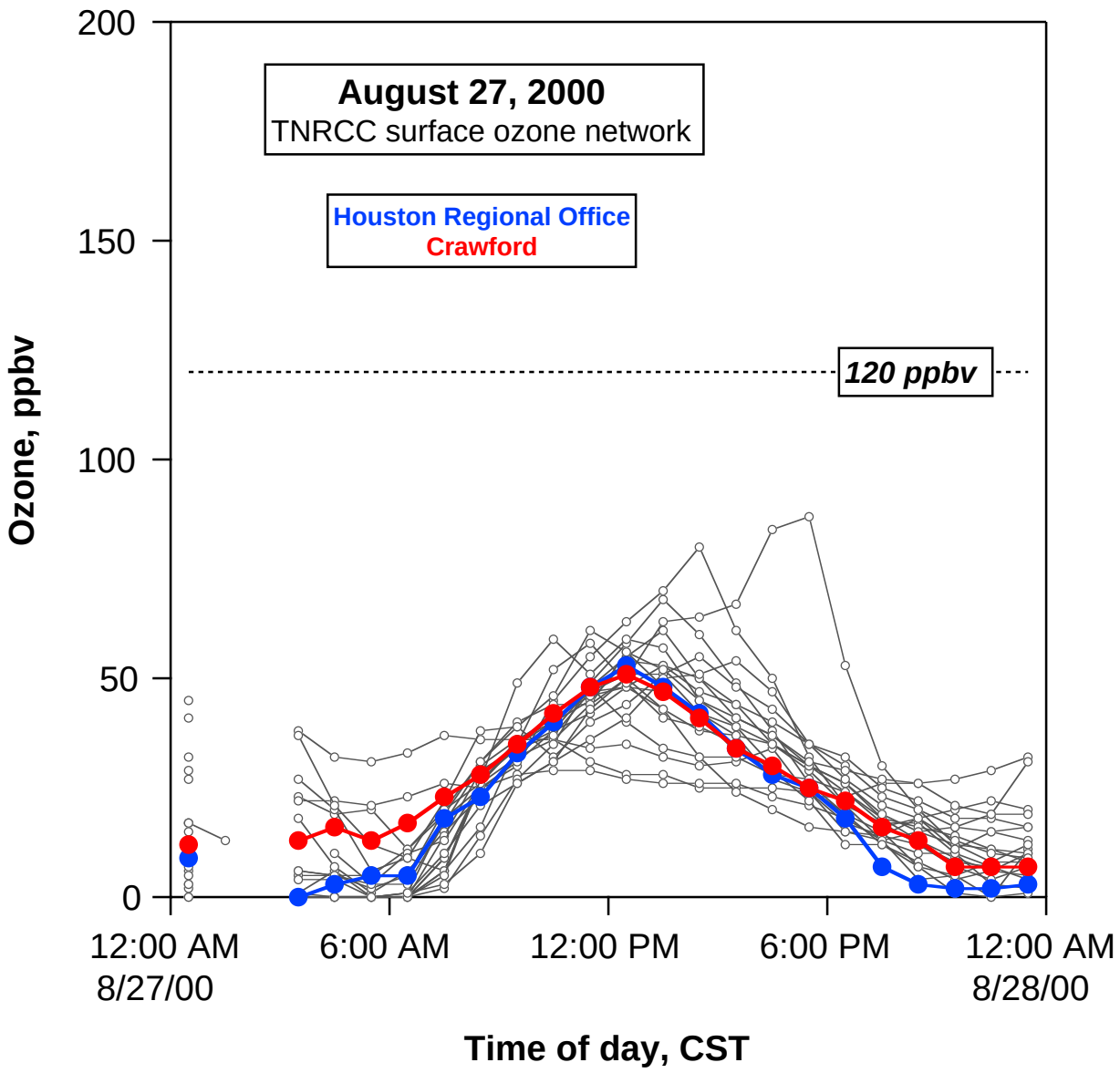
- **Coalesced Ship Channel/TX City ozone yield similar to those derived in isolated petrochemical plumes on the same day**

- **No reported upsets at these times; interpreted as "business as usual" for both days**

- **Large co-located emissions of reactive alkenes and NOx consistently result in *rapid* and *efficient* ozone formation downwind**

August 27 and 28, 2000:

- **ozone concentrations nothing to write home about**



- **What's so different about an exceedance day?**

Preliminary conclusions

- **Measurements strongly suggest alkene emissions are not accurately included in inventories**

  - *models will not accurately simulate observations until the alkene inventories are realistic*

- **Measurements and models further suggest that, in general, routine emission of alkenes, appropriate meteorology, and OH chemistry alone are sufficient to explain the observed ozone**

  - *upsets may play a part, but business-as-usual emissions appear to be sufficient*

  - *exceedances are possible on a daily basis; actual occurrence is dependent upon meteorology*

- **Anthropogenic emission of large amounts of very reactive alkenes (ethene, propene, 1,3-butadiene) co-located with NOx emission is the primary cause of ozone exceedances above 200 ppbv in the Houston area**