

# **Atmospheric Model Evaluation that leads to a better understanding of the factors that control ozone concentrations in the lower troposphere**

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## **Approach:**

Field experiments that emphasize processes in order to evaluate components of the Modeling System:

Emissions of Precursors

Chemical Production and Loss

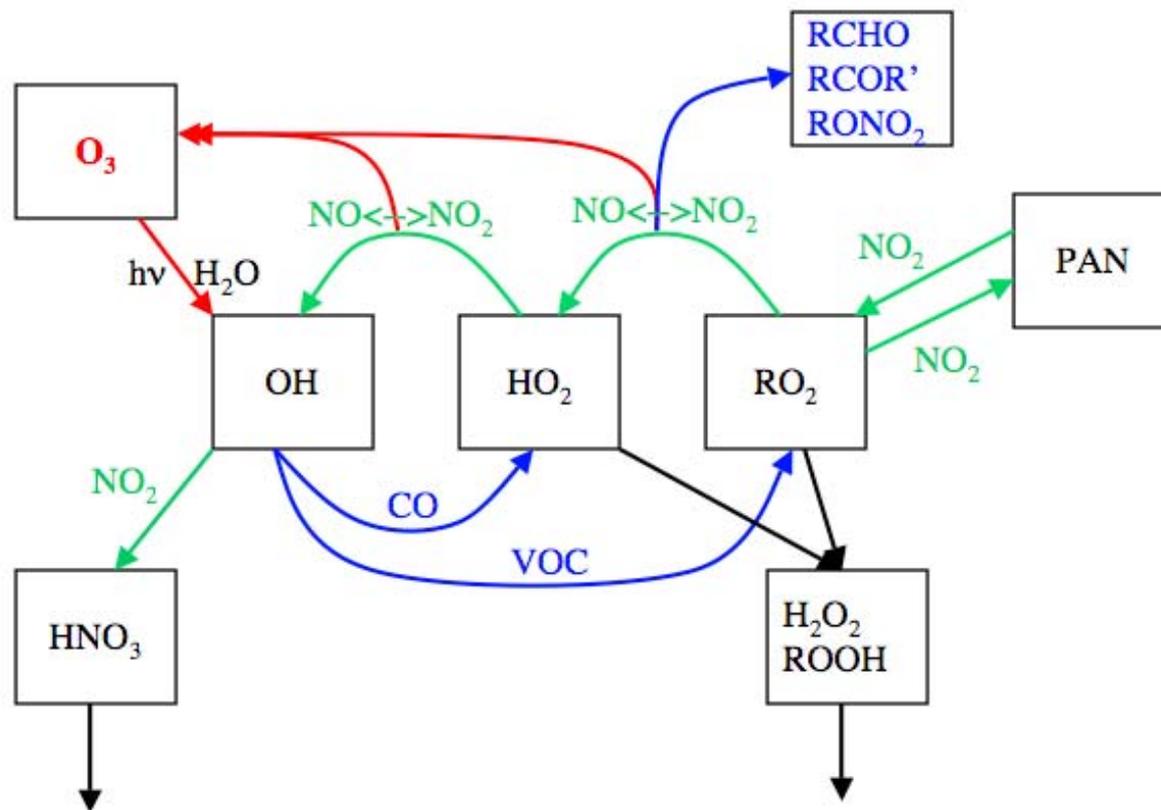
Transport and Dispersion of Precursors and Ozone

Loss by Surface Deposition

## **Example:**

Rapid ozone formation in Houston

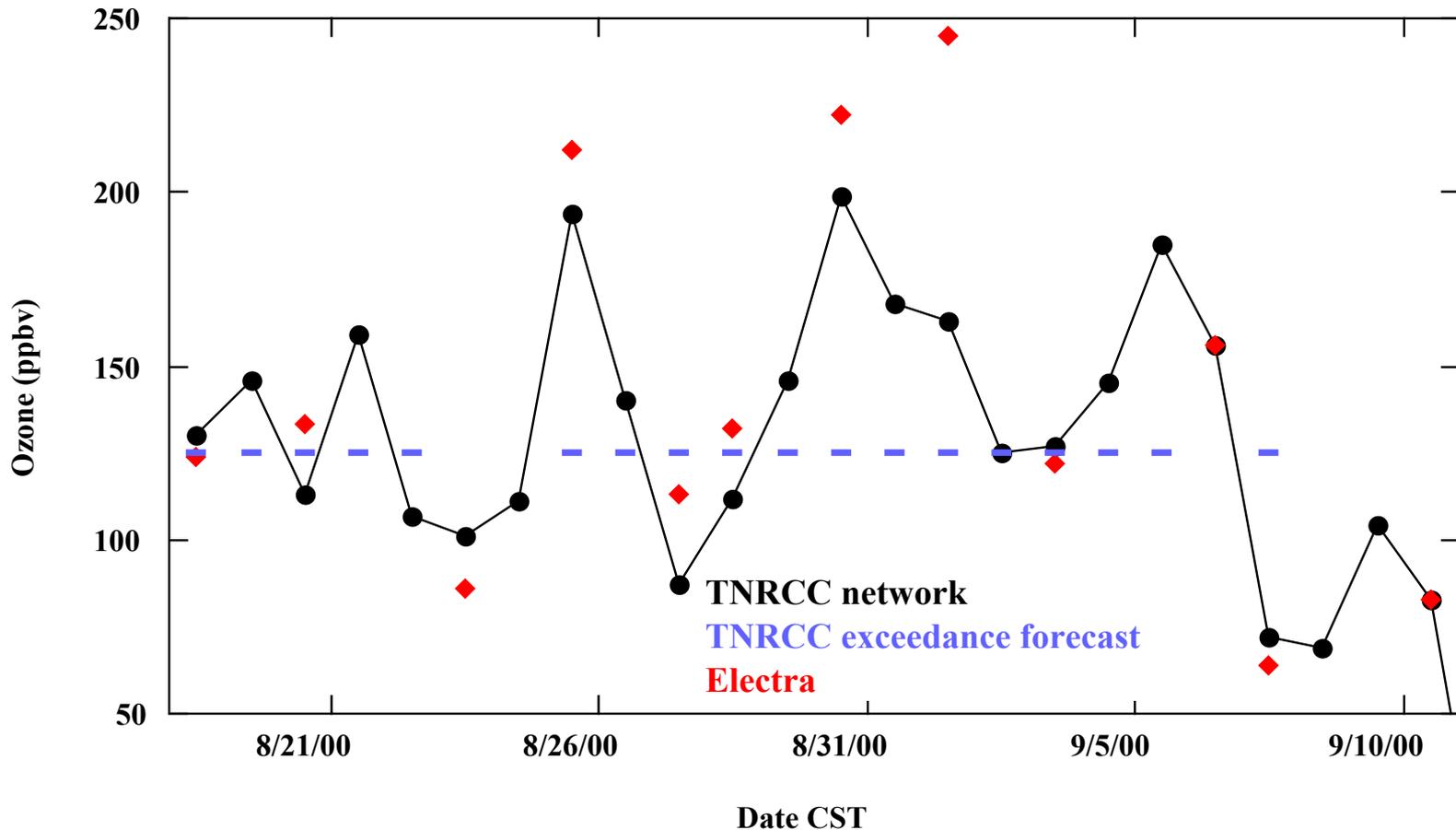
# Ozone Formation in the Oxidation of Hydrocarbons in the Presence of Nitrogen Oxides



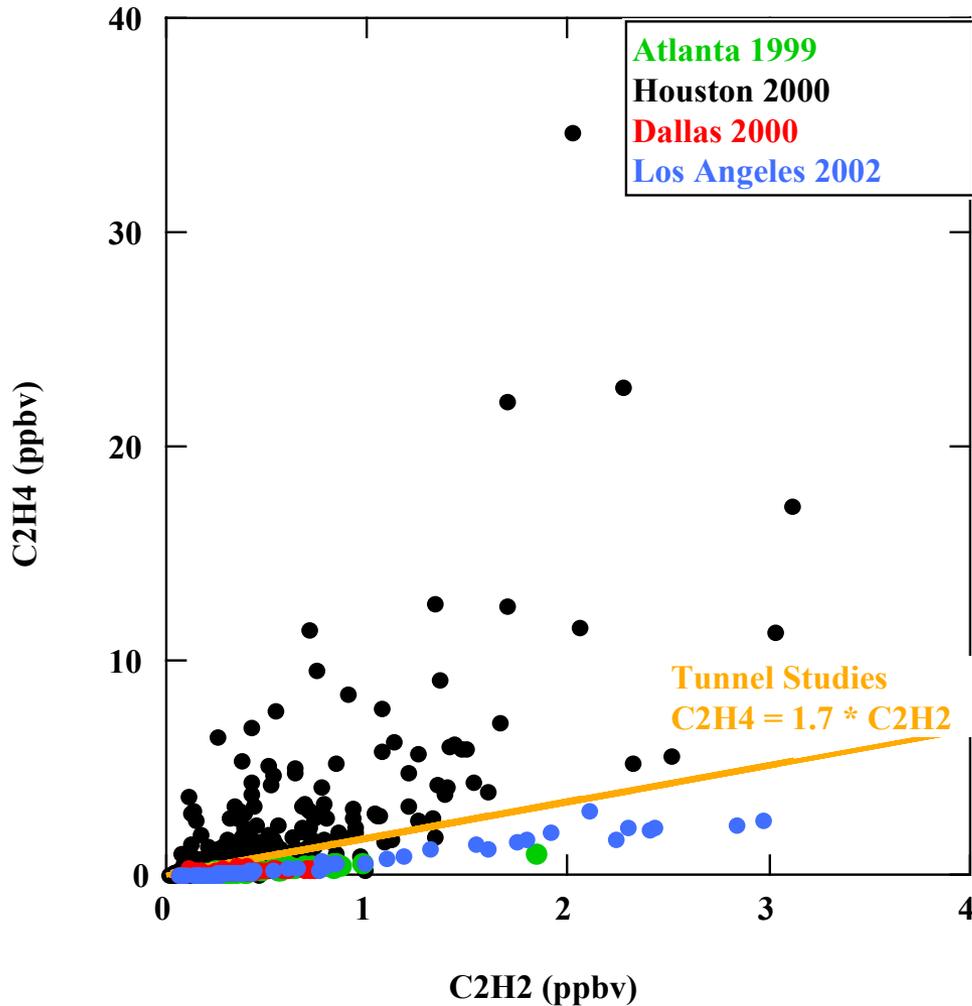
**Ozone Production Efficiency:** OH reacts with CO, VOCs <--> OH reacts with NO<sub>2</sub>

**Secondary Products** like CH<sub>2</sub>O and PAN reflect on hydrocarbon chemistry

Houston regularly violates the 120 ppbv 1hour ambient ozone standard.  
Peak concentrations are over 200 ppbv.  
Regulatory photochemical transport models can not reproduce the peak concentrations.  
=> Development of a reliable emission control strategy is difficult.



Maximum 1hr O<sub>3</sub> of TNRCC network and O<sub>3</sub> maxima during Electra flights  
During Texas Air Quality Study 2000.



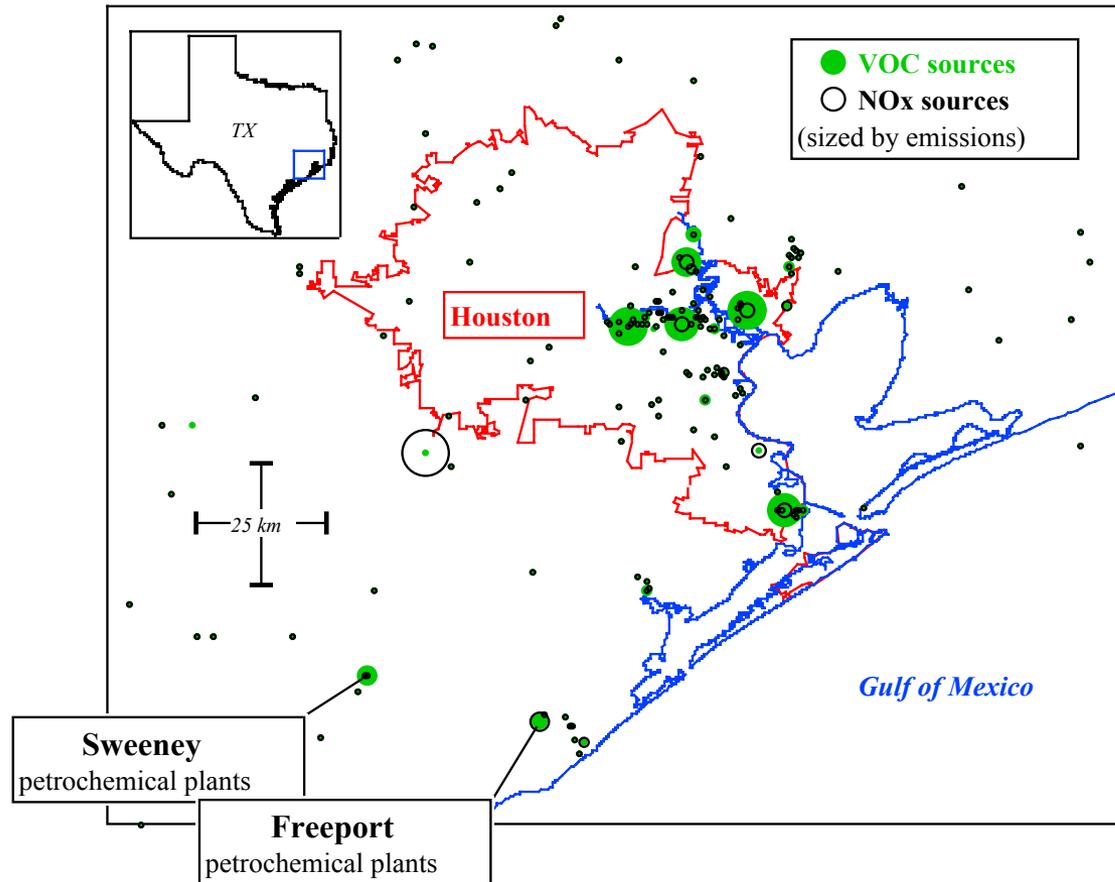
**What does set Houston apart from other urban areas?**

Ambient reactive hydrocarbon concentrations over Houston are much larger than expected for typical automotive urban emissions.

Airborne hydrocarbon measurements over Houston and other urban air sheds.

# Rapid and efficient formation of ozone in plumes from petrochemical industries

Co-located anthropogenic  $\text{NO}_x$  and alkene emissions

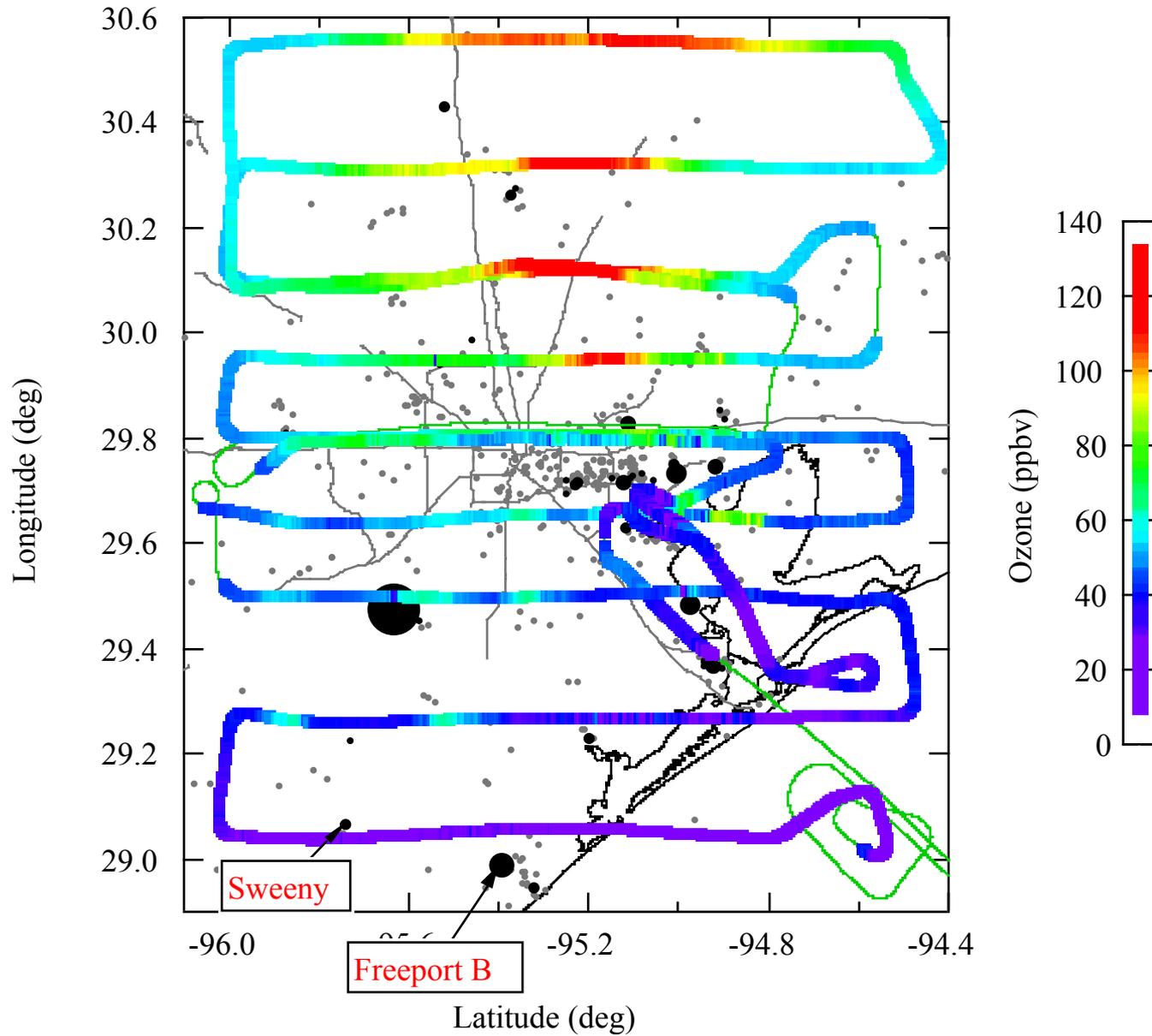


Aircraft data from the 2000 Texas Air Quality Study, TexAQS

28 August 2000

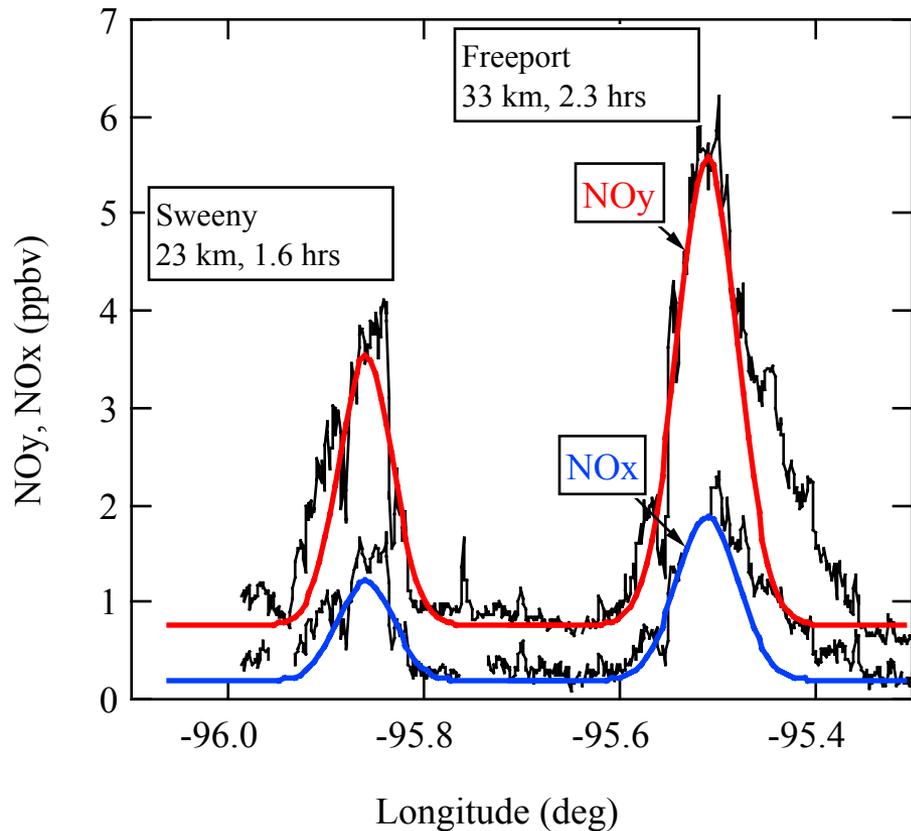
NCAR Electra TEXAQS 2000 Flight

color coded according to Ozone for altitude below 1000 m



# Measurement and Modeling of Ozone Formation in Plumes of isolated Petrochemical Facilities

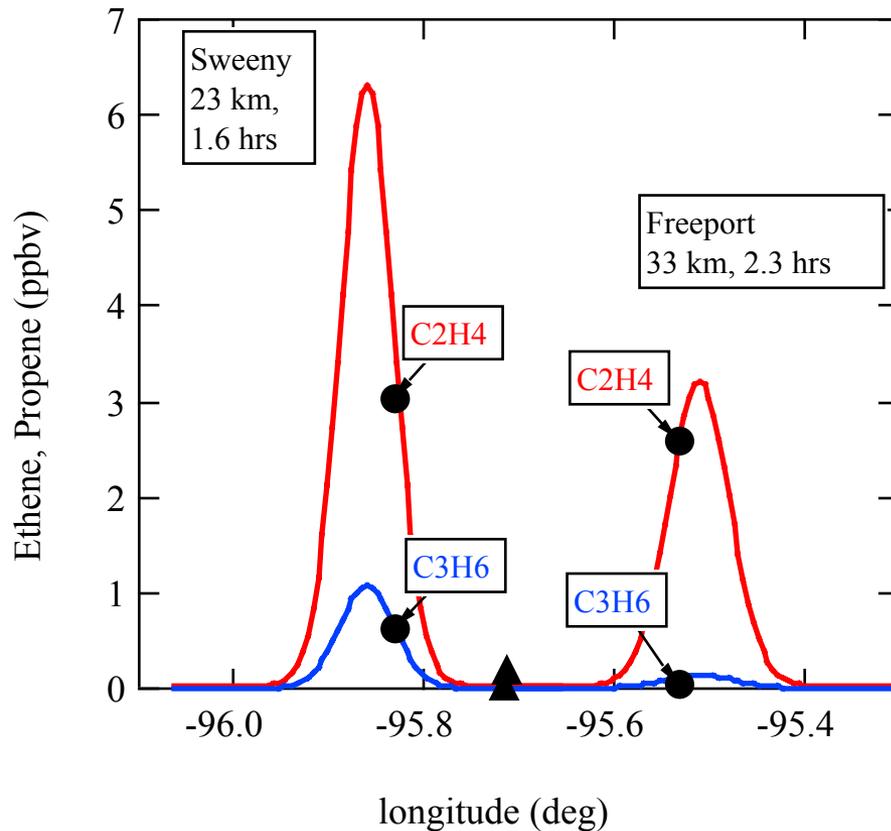
Model  $\text{NO}_x$  emissions agree with 1999 TNRCC inventory



Sweeny:  $\text{ENO}_x = 15 \text{ kmole/h}$   
 Freeport:  $\text{ENO}_x = 30 \text{ kmole/h}$

Area source of isoprene

TNRCC inventory underpredicts Alkene/ $\text{NO}_x$  molar ratios by factors of 50 to 200

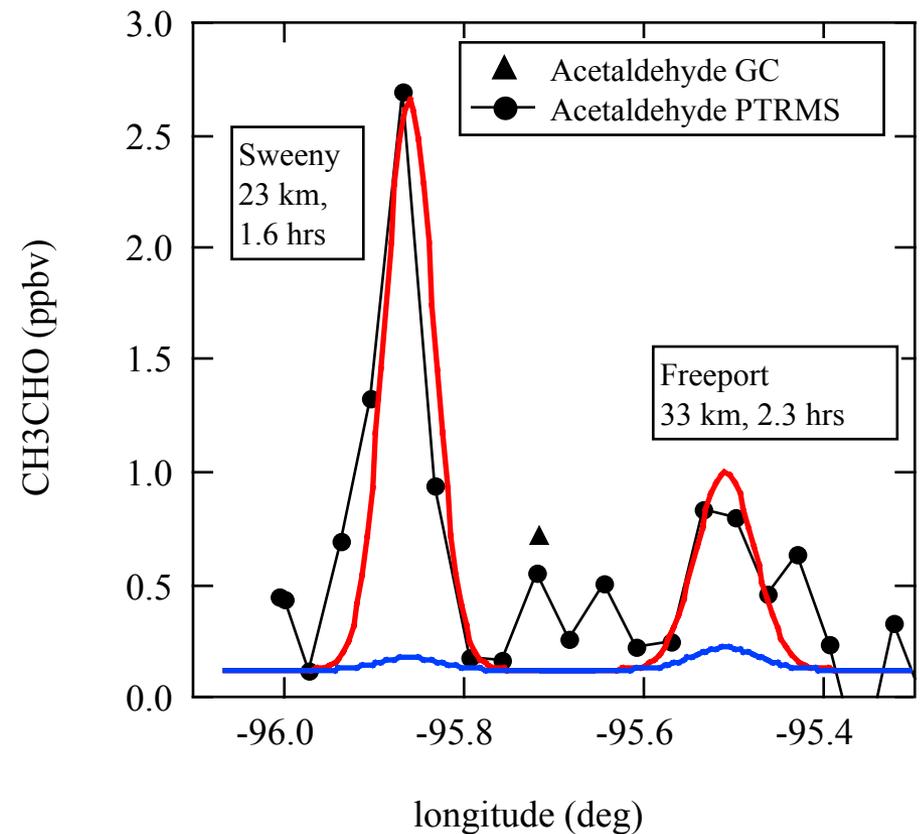
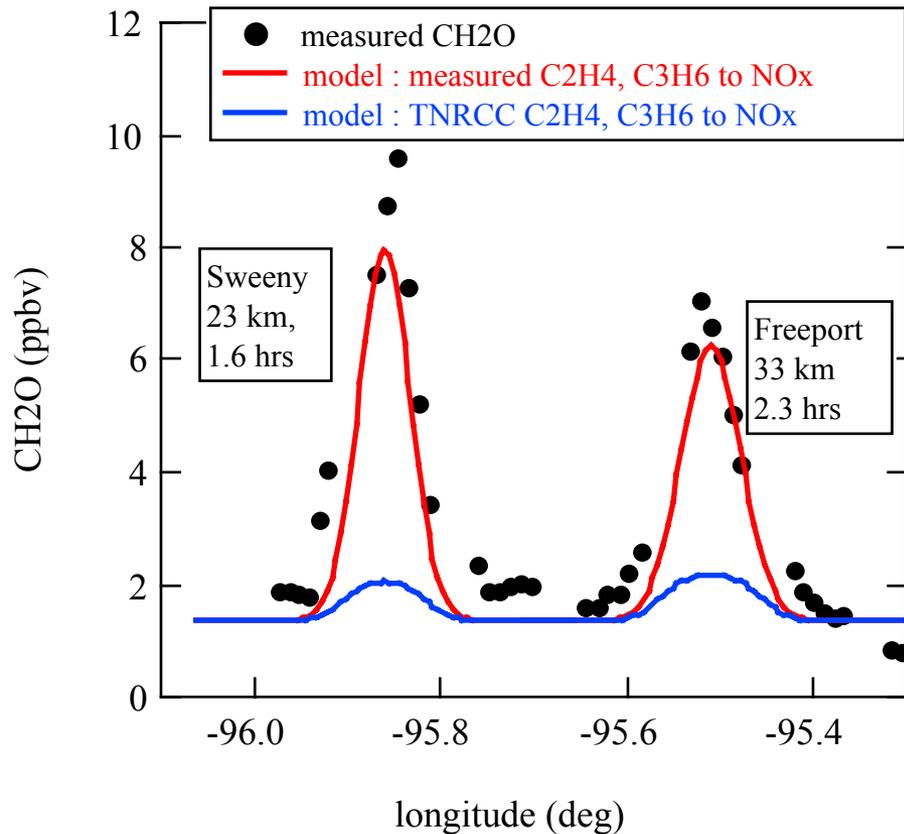


Sweeny:  $\text{C}_2\text{H}_4/\text{NO}_x = 3.6$ ,  $\text{C}_3\text{H}_6/\text{NO}_x = 2.0$

Freeport:  $\text{C}_2\text{H}_4/\text{NO}_x = 1.5$ ,  $\text{C}_3\text{H}_6/\text{NO}_x = 0.5$

Model with measured ethene, propene to  $\text{NO}_x$  emission ratios reproduces measured  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{CHO}$ .

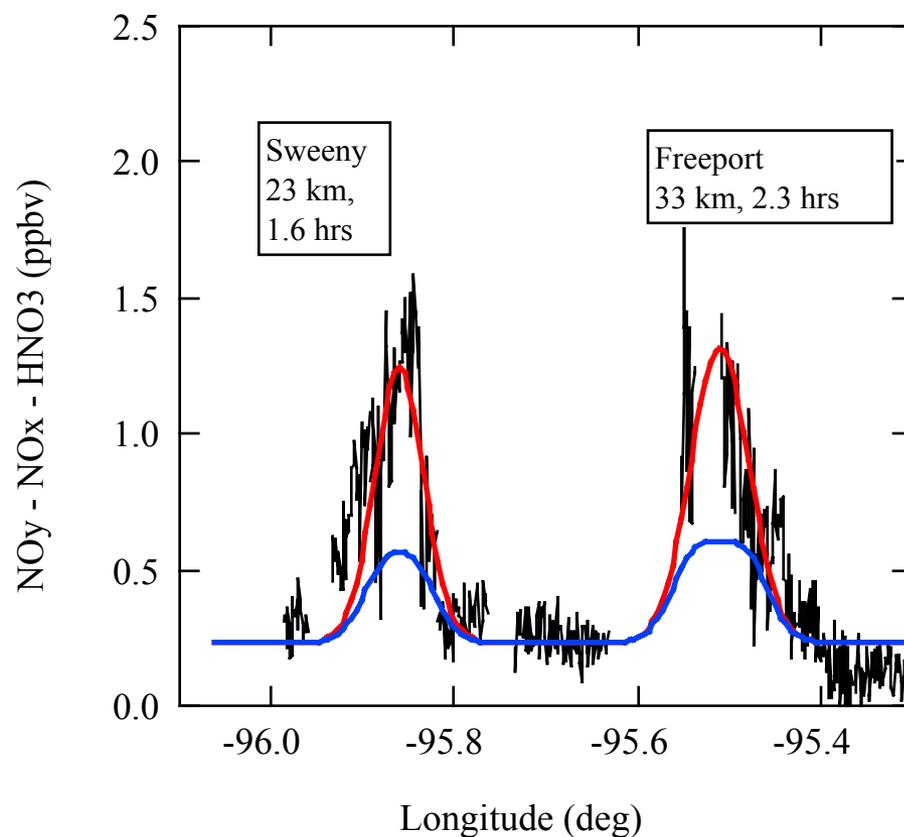
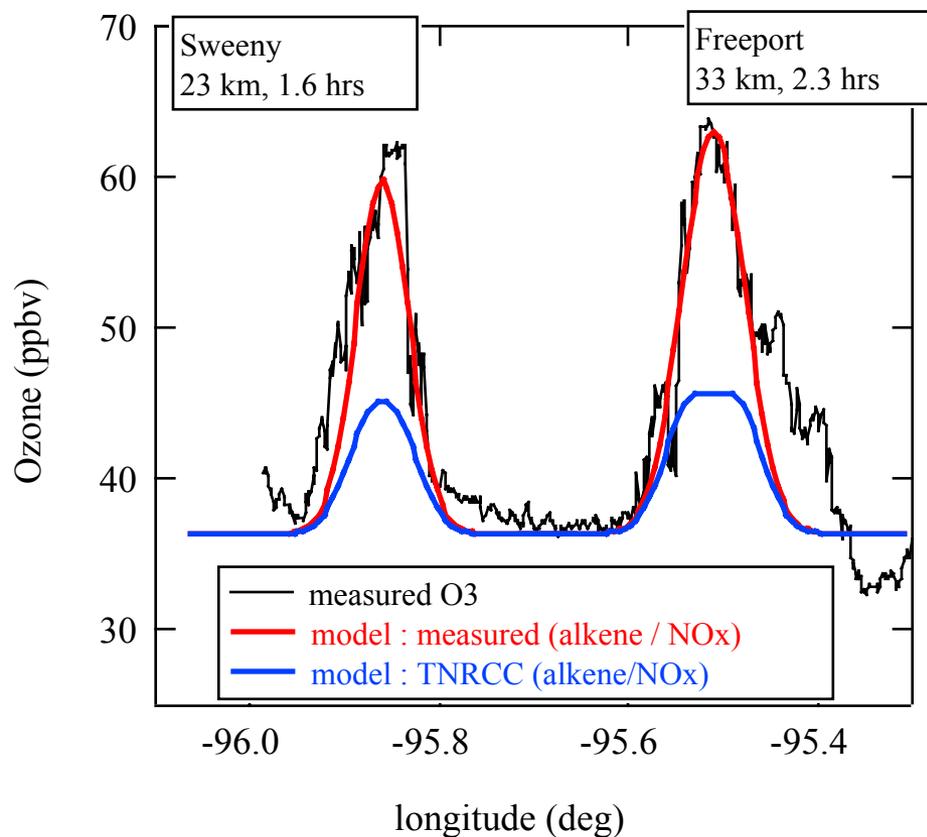
$\text{CH}_2\text{O}$  is formed in the oxidation of ethene and propene  
 $\text{CH}_3\text{CHO}$  is formed in the oxidation of propene.



Acetaldehyde PTRMS measurement  
by Hansel & Wiesthaler

Model with measured ethene, propene to  $\text{NO}_x$  emission ratio reproduces rapid formation of Ozone and PAN.

Oxidation of propene in presence of  $\text{NO}_x$  leads to formation of PAN



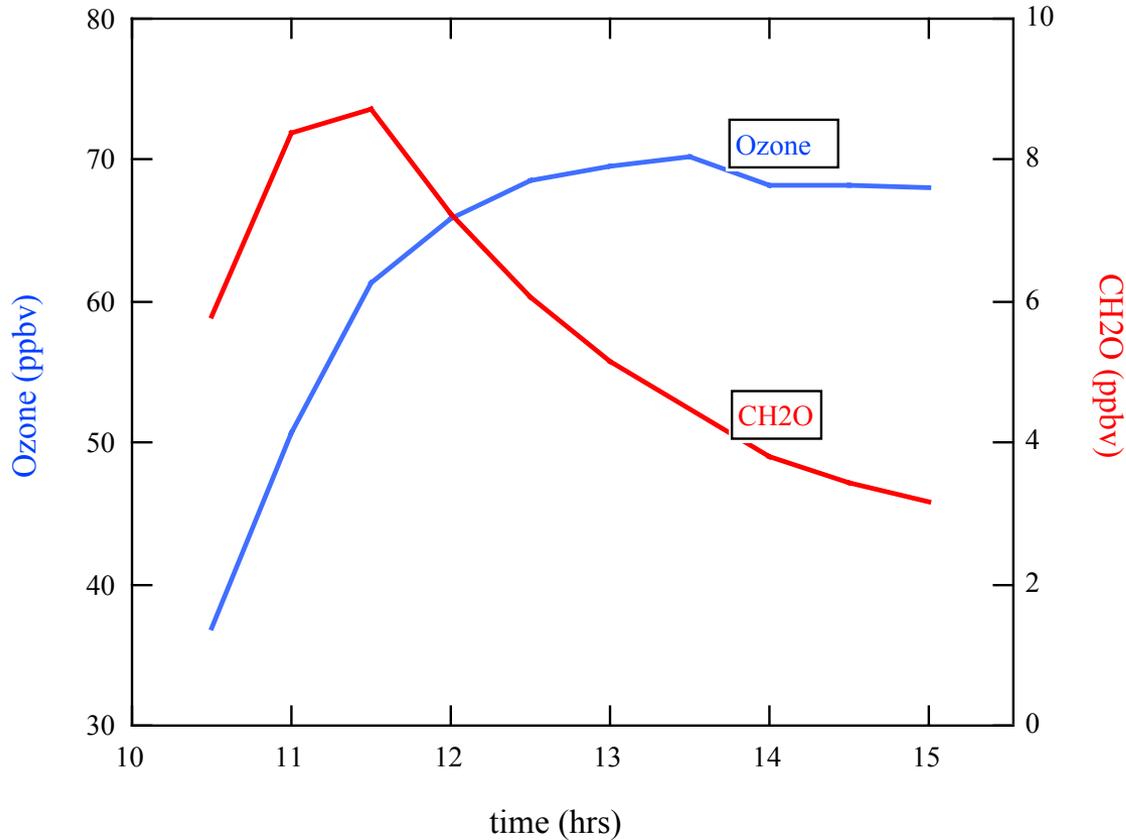
Approximation:  $\text{PAN} = (\text{NO}_y - \text{NO}_x - \text{HNO}_3)$

TexAQS 2000 measurements indicate that  $\text{NO}_x$ ,  $\text{HNO}_3$ , and PAN are the major components of  $\text{NO}_y$ .

Measurements of PAN by GC every 3 min.

CH<sub>2</sub>O is formed more rapidly than Ozone

CH<sub>2</sub>O has a shorter lifetime than Ozone



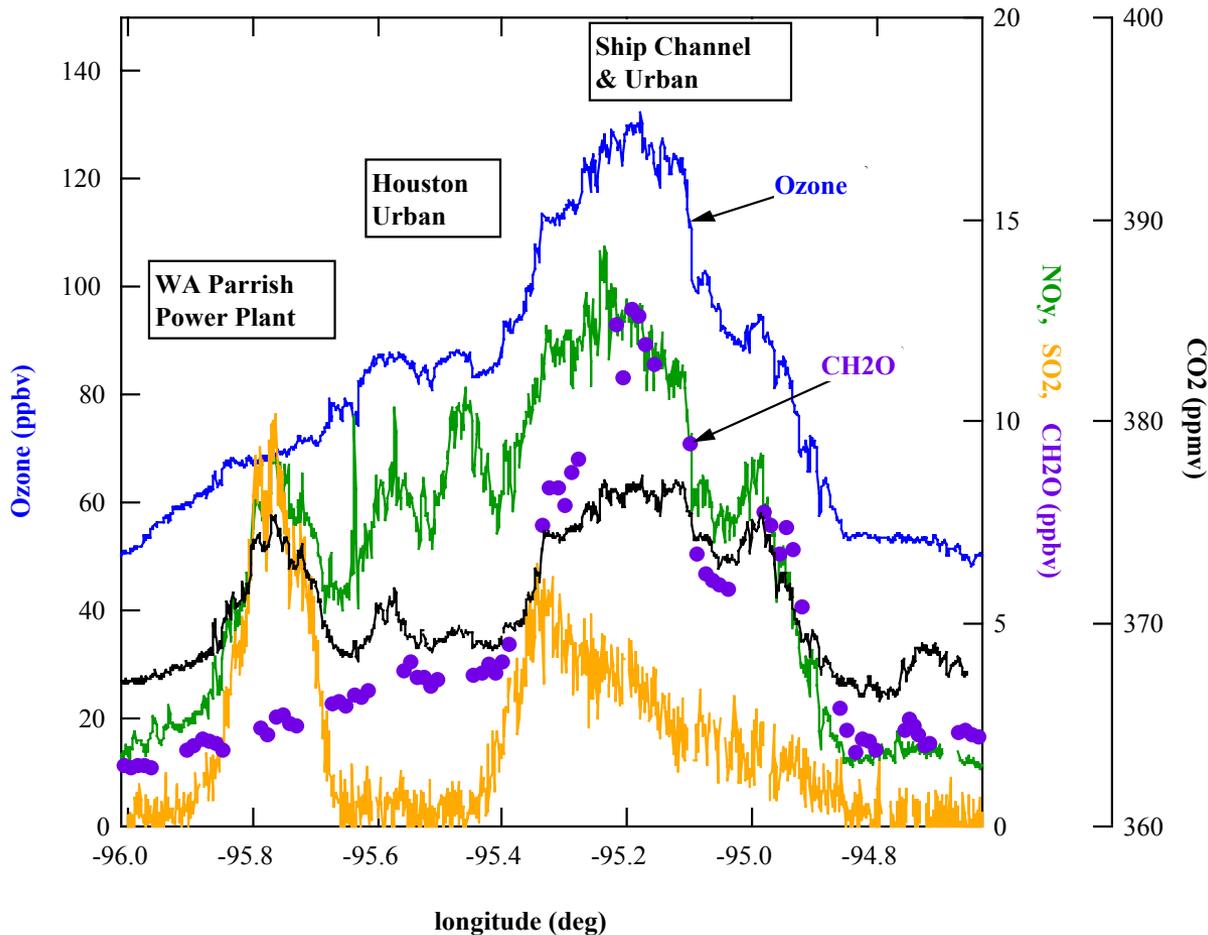
No significant direct emissions of CH<sub>2</sub>O or CH<sub>3</sub>CHO seen in the measurements

ENO<sub>x</sub> = 30 kmole/h, EC<sub>2</sub>H<sub>4</sub> = EC<sub>3</sub>H<sub>6</sub> = ENO<sub>x</sub>

wsp = 4m/s, emit at 10 am

F(isoprene) = 5.2E15 molec m<sup>-2</sup> s<sup>-1</sup> at 30 C, noon

## Electra Flight 28 August 2000, 40 km North of Houston



Chemical Transformation:

Highest Ozone and CH2O values are always associated with petrochemical plumes

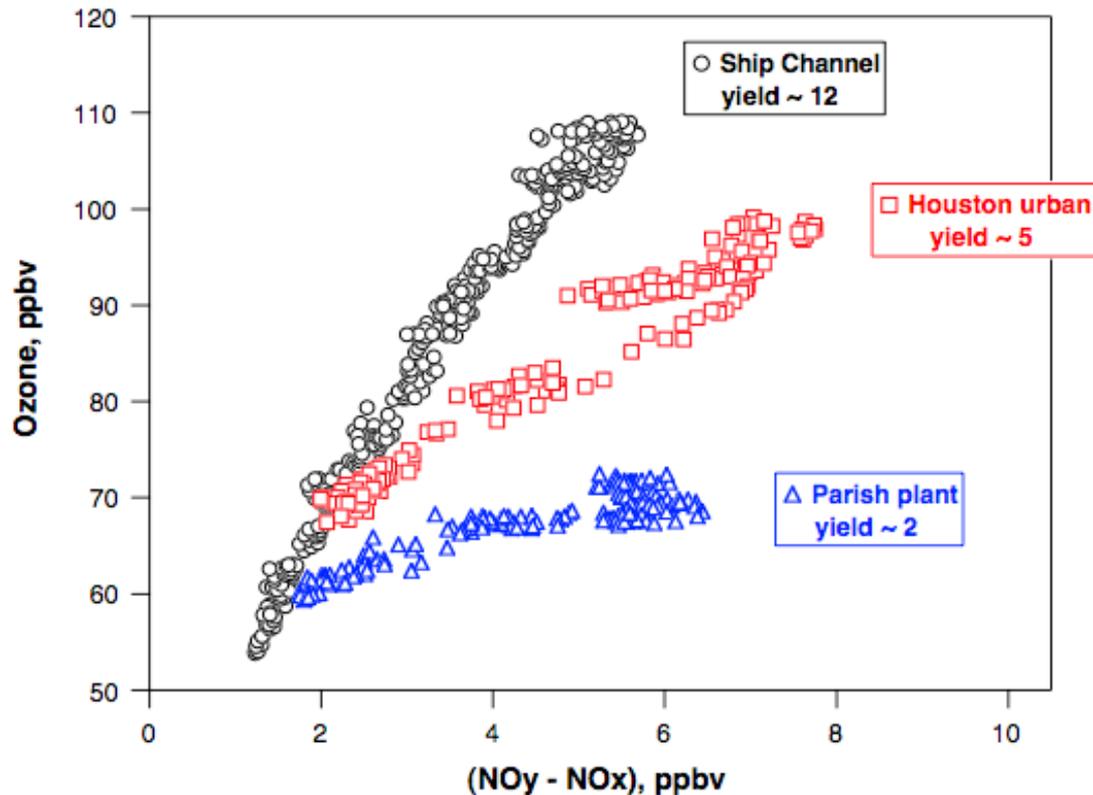
Reactivity is due to petrochemical emissions of light alkenes

**Questions in 2006:**

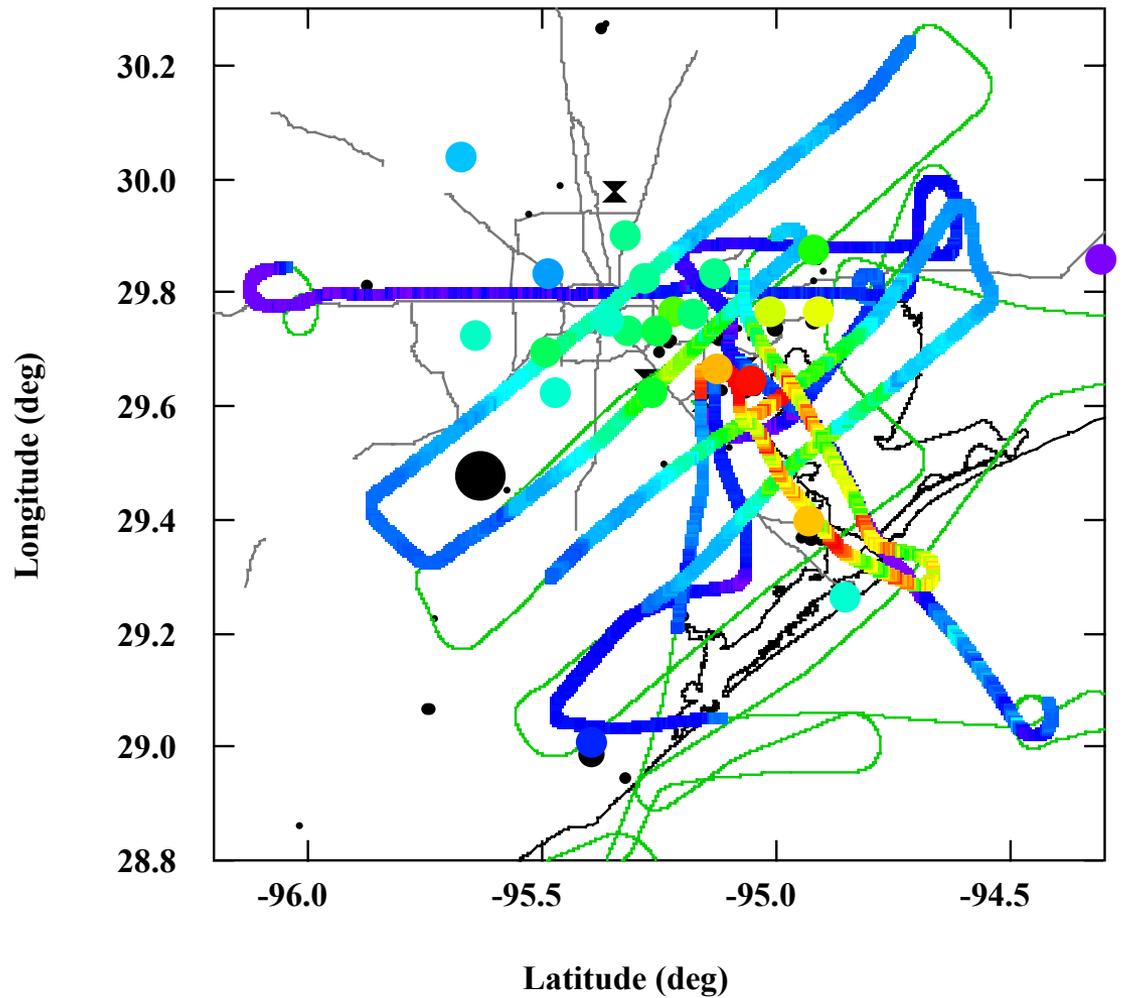
What are the consequences of the change in the emissions from point sources since 2000?

## Large differences in ozone yield observed

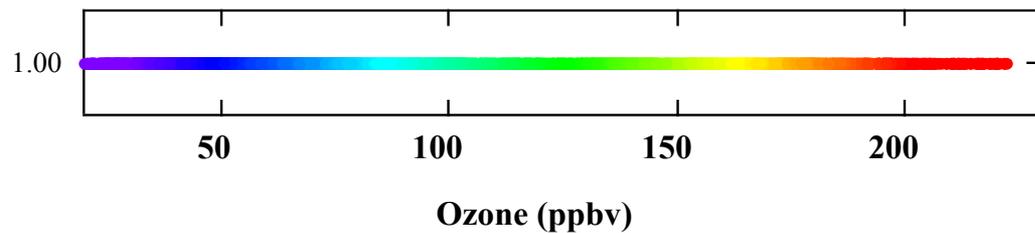
Transects equally oxidized -  
(NO<sub>x</sub>/NO<sub>y</sub>) ~ 0.20  
Electra 08/28/00 flight data



- Houston urban yield similar to other cities studied
- Power plant yield similar to other low-VOC plumes
- Coalesced plume from Ship Channel petrochemical industry emissions similar to isolated refineries

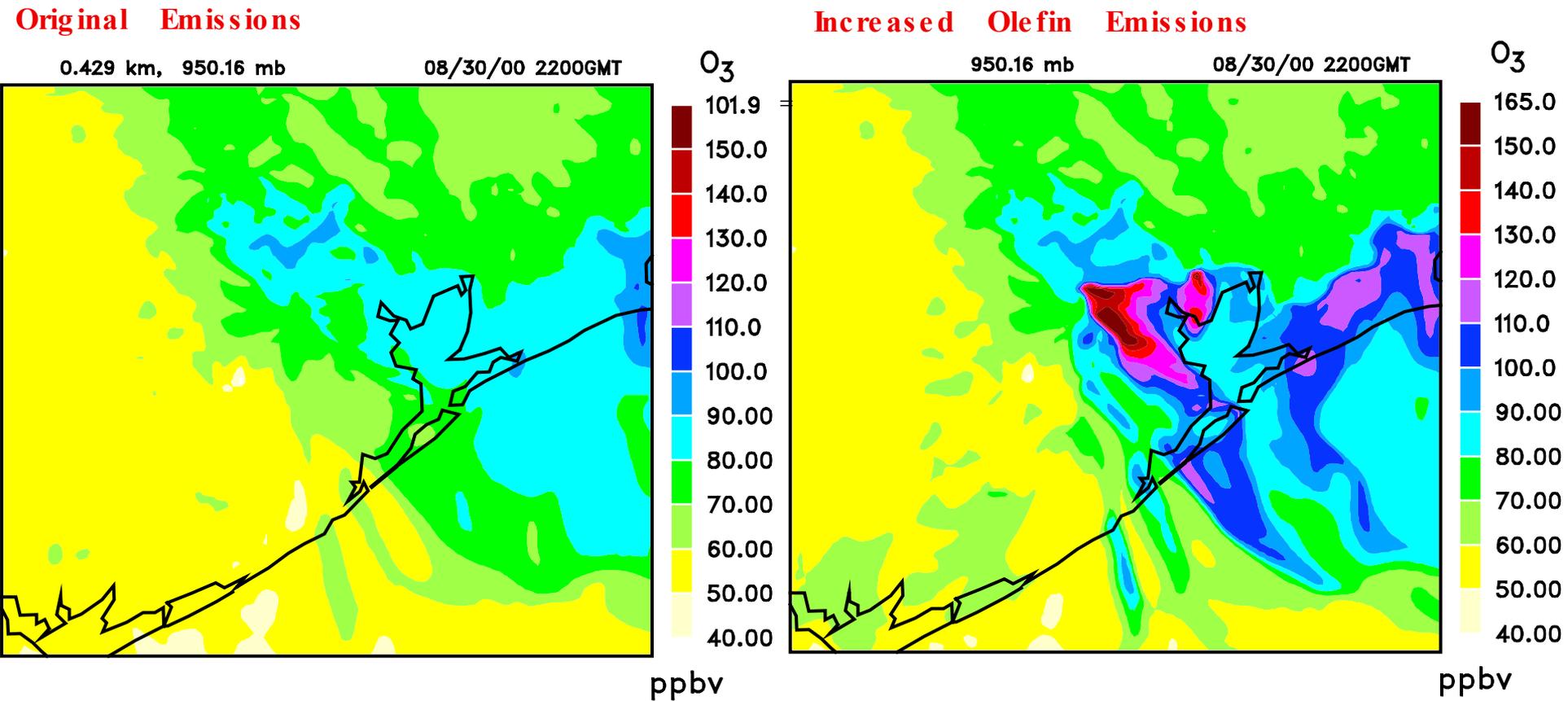


Aircraft and ground monitors measured high Ozone (>200 ppbv) on 30 August, 2000.



Update of emission factors of olefin processing facilities according to measurements / model of isolated facilities.

**==> Photochemical transport model captures high, localized ozone concentrations in the plume from industrial complexes.**



Photochemical transport model: Georg Grell and Stuart McKeen

**Measurements of secondary species can provide critical tests for photochemical model systems:**

**Results of Texas Air Quality Study 2000:**

Measurements of photochemical products such as **CH<sub>2</sub>O** and **CH<sub>3</sub>CHO** were critical in establishing the important role that light alkenes, i.e. **Ethene** and **Propene**, play in the rapid and efficient formation of ozone in the Houston air shed.

**Other examples:**

Ambient measurements of **Methylviyl ketone** and **Methacrolein**, **MPAN** and **PPN to PAN** ratios reflect the role of biogenic isoprene emissions.

**Alkylnitrate** measurements can provide a photochemical signature of **alkane** chemistry

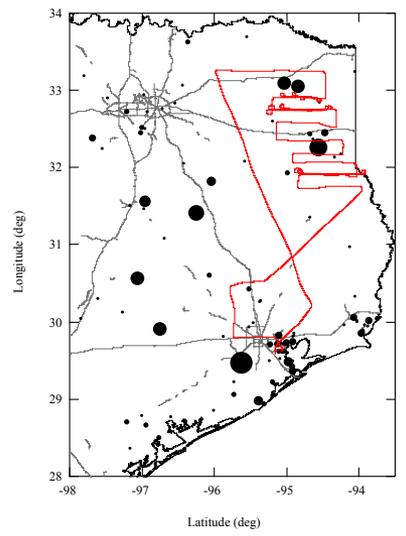
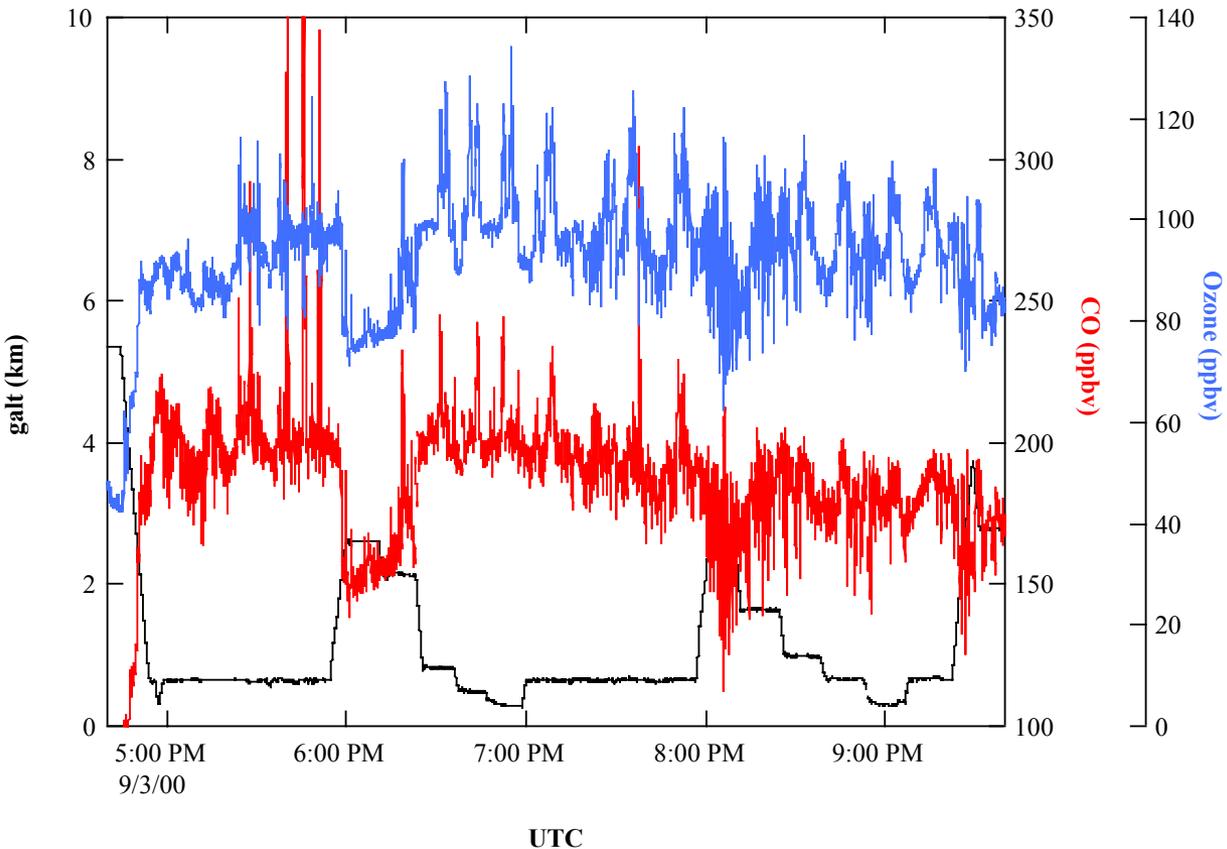
## **Questions and Goals of 2006 Texas Air Quality Study II:**

What are the consequences of reductions of NO<sub>x</sub> emissions from point sources since 2000?

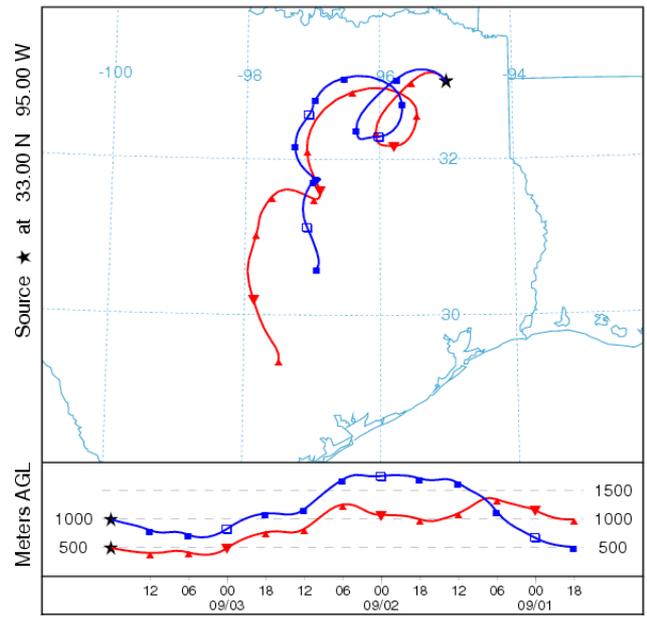
What are the sources of the VOC emissions from petrochemical facilities?  
Are they intermittent or continuous?

Have the VOC emissions changed since 2000?

What are the requirements to meet the 8 hr ozone standard in  
near non-attainment areas of eastern Texas?



NOAA HYSPLIT MODEL  
Backward trajectories ending at 18 UTC 03 Sep 00  
EDAS Meteorological Data



## Regional Transport to NE Texas

### What are the implications for the 8hr O3 standard

Example: 3 September, 2000  
High regional CO and  
Ozone concentrations higher than 80 ppbv.

Accumulation of CO emissions during transport  
in the PBL leads to high CO over NE Texas.