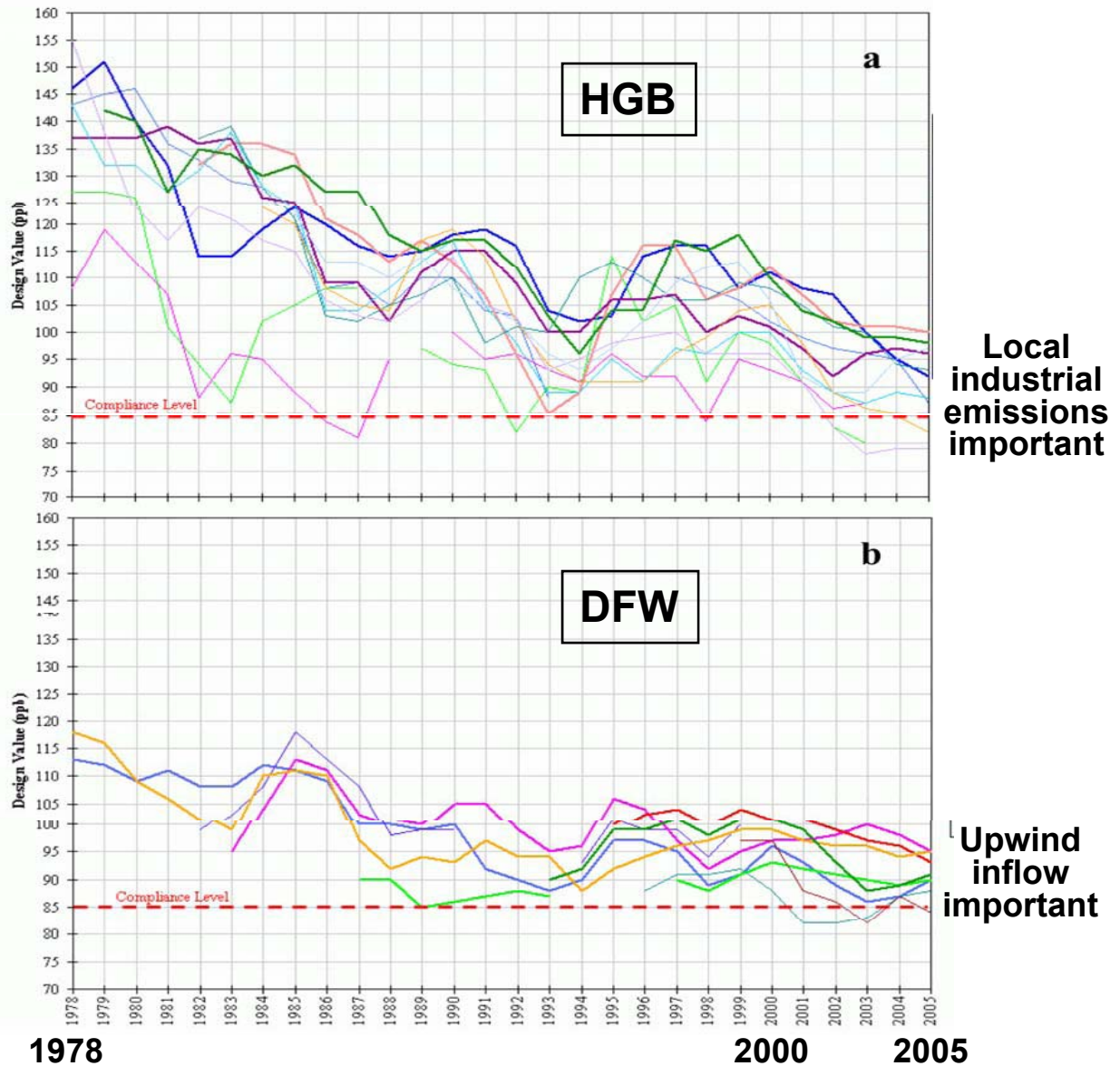




## Trend of the 8-h Ozone Design Values (1978 – 2005) in HGB and DFW



- Decrease of ODV in both HGB and DFW from 1978 to 2005, more in HGB  
ODV similar in HGB and DFW in 2005, and still above compliance level
- Role of upwind inflow substantial in DFW  
Role of photochemical production from local comparable co-emissions of HRVOC and NO<sub>x</sub> from industrial sources substantial in HGB
  - Importance of accurate EI of industrial emissions in HGB
  - Substantially more 1-h exceedances in HGB
  - 60% of 8-h exceedances associated with the 1-h exceedances

Taken from: RSS-Intro.

## **Electrical Generating Units**

(Ryerson et al. NOAA; RSS-D1)

- \* **Several large EGUs in E. Texas have substantially decreased their NO<sub>x</sub> emissions per unit power generated since 2000 (down to ~ 1/4)**

**SO<sub>2</sub> emissions have generally not changed much, with a few exceptions , where they have even increased by ~ x 2**

**Large CO emission discrepancies noted in 2000 have been reconciled by substantial increases in the inventory CO**

**Above based on verification using NOAA aircraft data of  
NO<sub>x</sub>/CO<sub>2</sub> ,                      SO<sub>2</sub>/CO<sub>2</sub>,    and        CO/CO<sub>2</sub>  
in the near-field (< 10 km from the source)**

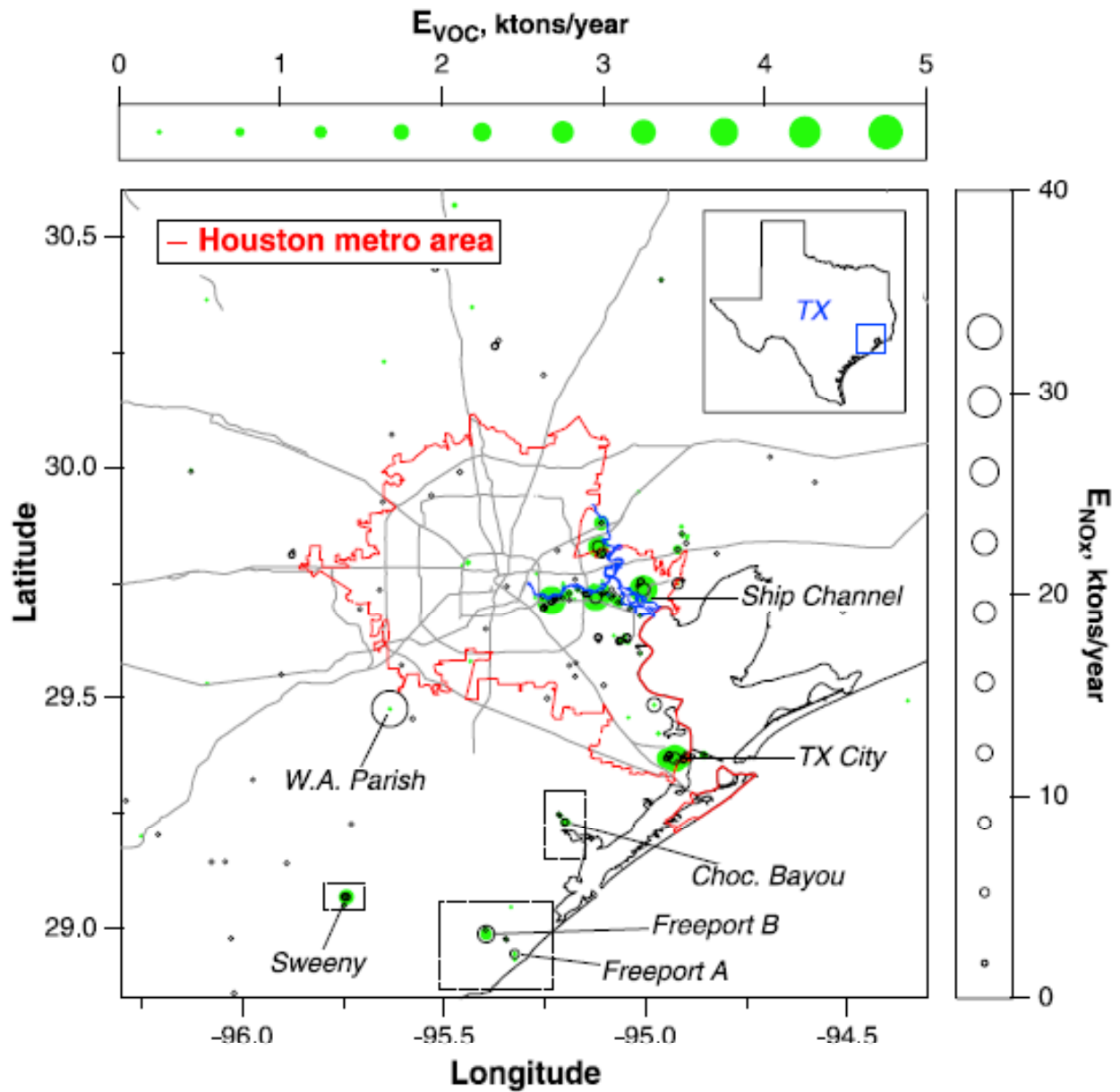
- \* **Quantitative agreement between CEM values and aircraft data (where both available)**

**→ emissions from sources equipped with CEMs are accurate and well known**

# INDUSTRIAL POINT SOURCES

(with co-emissions of HRVOC and NOx)

## Background



### Main HGB Industrial source complexes

1. Houston Ship Channel (HSC)
2. Texas City
3. Chocolate bayou
4. Freeport
5. Sweeny

# INDUSTRIAL POINT SOURCES

## Background

... continued

**TexAQS 2000** --- **Top-down Emissions Verification (TDEV)** NOT a significant planned measurement activity.

Yet, a major finding of TexAQS I was that the EIs of these sources grossly underestimated (by 1- 2 orders of magnitude) the emissions of HRVOCs (e.g., ethene and propene) from industrial sources. Instead of ambient HRVOC/NO<sub>x</sub> being 0.01 – 0.1 (as suggested by EI), They were more like >1.

Thus, with comparable high co-emissions of HRVOC and NO<sub>x</sub>, ozone production was fast close to the sources in narrow plumes. This led to violations of the 1-h ozone NAAQS, in the form of THOEs.

The above **TDEV** was based on:

1. Observed, **very sparse** HRVOC/NO<sub>x</sub> concentration ratios based on **canister data of speciated VOC in aircraft**, typically >10km downwind, where these precursors were significantly, and unequally, depleted chemically, implying that the finding had substantial uncertainty;  
*(Ryerson et al., 2003)*
2. More rigorous TDEV studies involving reconciliation of the emissions with ambient species concentrations (aircraft) based on diagnostic Lagrangian Reactive Plume Modeling (LRPM) suggested that :
  - NO<sub>x</sub>-EIs were generally within x2 of the inferred emissions, based on direct comparison of model and data close to the sources;
  - ethene and propene EIs were under-estimates by 1 – 2 orders of magnitude, based on **LRPM-reconciliation of iteratively adjusted emissions of ozone precursors with observed data of secondary products like O<sub>3</sub> and especially HCHO**  
*(Gillani & Wu, 2003 a,b)*

**Similar LRPM diagnostic analyses based on 2006 data is currently in progress**

# INDUSTRIAL POINT SOURCES --- **TexAQS2006**

## **Main Chemical Measurements**

This time, TDEV was explicitly part of the planned measurement and analysis program. Measurement platforms included :

### **Aircraft**

#### NOAA P-3

Continuous data of ethene (LPAS)  
(Laser PhotoAcoustic Spectrometer)

Continuous data of higher-C VOCs  
(PTR-MS = Proton Transfer Reaction Mass-Spec)  
**No ethene and propene**

Canister data of speciated VOC (WAS)

#### Baylor Aztec

5 dedicated TDEV missions

**RAD**  
(Reactive Alkene Detector)

**No continuous speciated VOC**

Canister data of speciated VOC

+ continuous NO/NO<sub>x</sub>/NO<sub>y</sub>, O<sub>3</sub>, HCHO etc.

Limited close-in flying

More extensive close-in flying at discrete heights

### Chalmers U. SOF (Solar Occultation Flux)

Solar-tracking device to continuously measure overhead burden ( $B_i = \int C_i dz$ ) of IR-absorbing species (e.g., ethene, propene, total alkanes), with on-line FTIR analysis, in a mobile ground vehicle

→ Total species flux ~ 2D integral of  $\int (B_i \times WS) dy$

Main sources of uncertainty of the method

- 1) No vertical resolution, hence
- 2) uncertainty about weighting with WS
- 3) No accounting for chemical depletion between emission and sampling

Modeling to address these issues is in progress (at UAH)

### TCEQ Surface Measurements (e.g., AutoGCs)

## Results of Industrial Point-source TDEV

1) Diagnostic analysis of SOF and aircraft data still on-going for 5 days (UAH)

2) Results of NOAA-P3 and TCEQ Data Analyses

Comparison of ethene/NO<sub>x</sub> ratios measured during TexAQS 2000 and TexAQS 2006 indicate that ethene emissions from industrial sources in HGB have decreased by ~ 40% (+ 20%).

*(de Gouw et al.-NOAA; Atlas et al.-U. Miami --- RSS-C1)*

*Auto-GC data from surface monitors indicate similar results*

*(Estes et al.,-TCEQ --- RSS-C1)*

Decrease in ethene/NO<sub>x</sub> due to change in emissions or met/chem?

Data of other species are qualitatively consistent with such emission trends, e.g.,

- HCHO data (secondary product of HRVOC)
- Ozone production downwind of industrial sources, based on data of four flights in 2000 and three flights in 2006, also qualitatively confirm this ...

The maximum observed ozone in 2006 was commensurately lower in 2006 than in 2000.

Other general characteristics of the chemistry did not change significantly: e.g., VOC composition and contribution to OH-reactivity

VOC composition --- propene : ethene : 1-butene ~ 50 : 20-25 : 5-10%;  
Ozone production efficiency --- similar

*(Ryerson et al., 2006 – NOAA)*

Surface monitoring data also support similar conclusions:

--- 8- h ODV at Aldine dropped from ~108 ppb in 2000 to ~ 90 ppb in 2006)

*(Sullivan et al, UT --- RSS-A3)*

Despite the 40% or so decrease in HRVOC emissions since 2000, these EIs continue to remain under-estimates by about one order of magnitude.

Efforts are under way, however, to improve the EIs.

(Jolly et al, TCEQ --- RSS-C4)



TCEQ collected a Special Hourly EI during 15 Aug – 15 Sep 2006, for VOC, NOx, SO2 and CO from 141 predetermined industrial sources in E. Texas (HGB, DFW, BPA etc), selected based on the following criteria:

- Sources subject to HRVOC rules;
- NOx, SO2 sources equipped with CEMs;
- sources located near ambient air monitoring sites.

For HRVOC, reported emissions were based on process flow monitoring (flares, cooling towers), required since Jan 2006.

The Special Inventory showed a 2.4 fold increase in emissions from flares Compared to those in regular inventory. Overall, the total reported ethene and propene emissions in HGB approximately doubled in the Special Inventory.

Inventories for NOx point sources at petrochemical facilities equipped with CEMS appear to be relatively accurate.

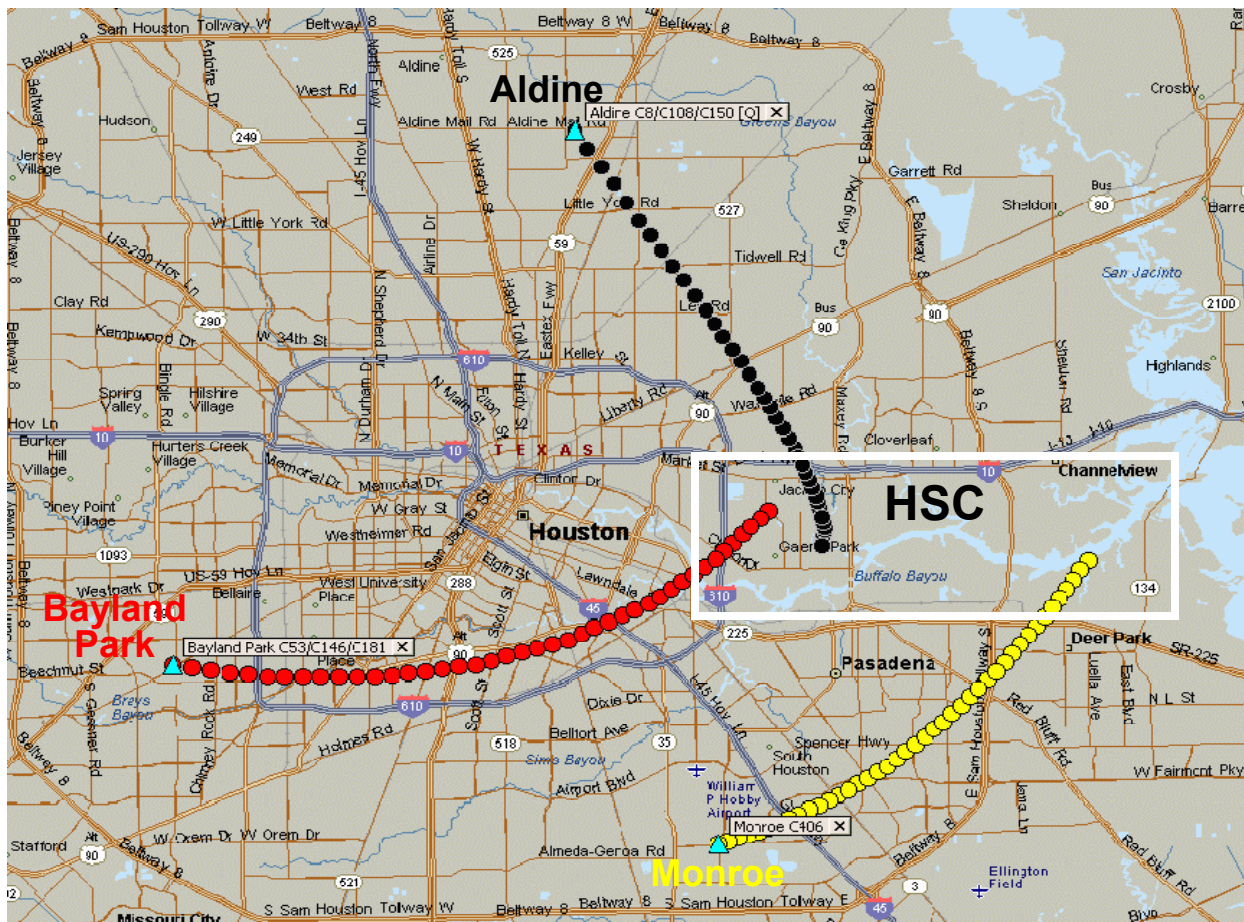
(Trainer et al., Ryerson et al., NOAA – RSS-A1, C1)

This is based on aircraft and CEMS data of NOx/CO2. The two data sets show consistency, even in cases where there are significant changes in NOx emissions between 2000 and 2006.

**Emissions from the HSC play a major role in not only the 1-h exceedances, but also the 8-h exceedances in the HGB area**

**8-h back-trajectory ensemble analysis for  
Aldine, Bayland Park and Monroe  
(locations of the highest 8-h ODVs in 2006) for 2000-2006  
lead back to HSC, indicating that the HSC emissions cause not only  
1-h ozone exceedances, but also the 8-h exceedances.**

*(Sullivan et al, UT --- RSS-A3)*



### 3. SOF (and DOAS) Results

Mellqvist et al.  
2007

IR-absorption  
(FTIR analysis)

Speciated VOC: ethene,  $\epsilon \sim 3\%$   
propene,  $\epsilon \sim 25\%$   
 $\Sigma(\text{alkanes}), \epsilon \sim 7\%$   
+

Other errors (mainly wind weighting)

Total estimated error  $\sim \pm 35\%$   
in calculated flux

Scattering of UV/vis  
SO<sub>2</sub>, NO<sub>2</sub>

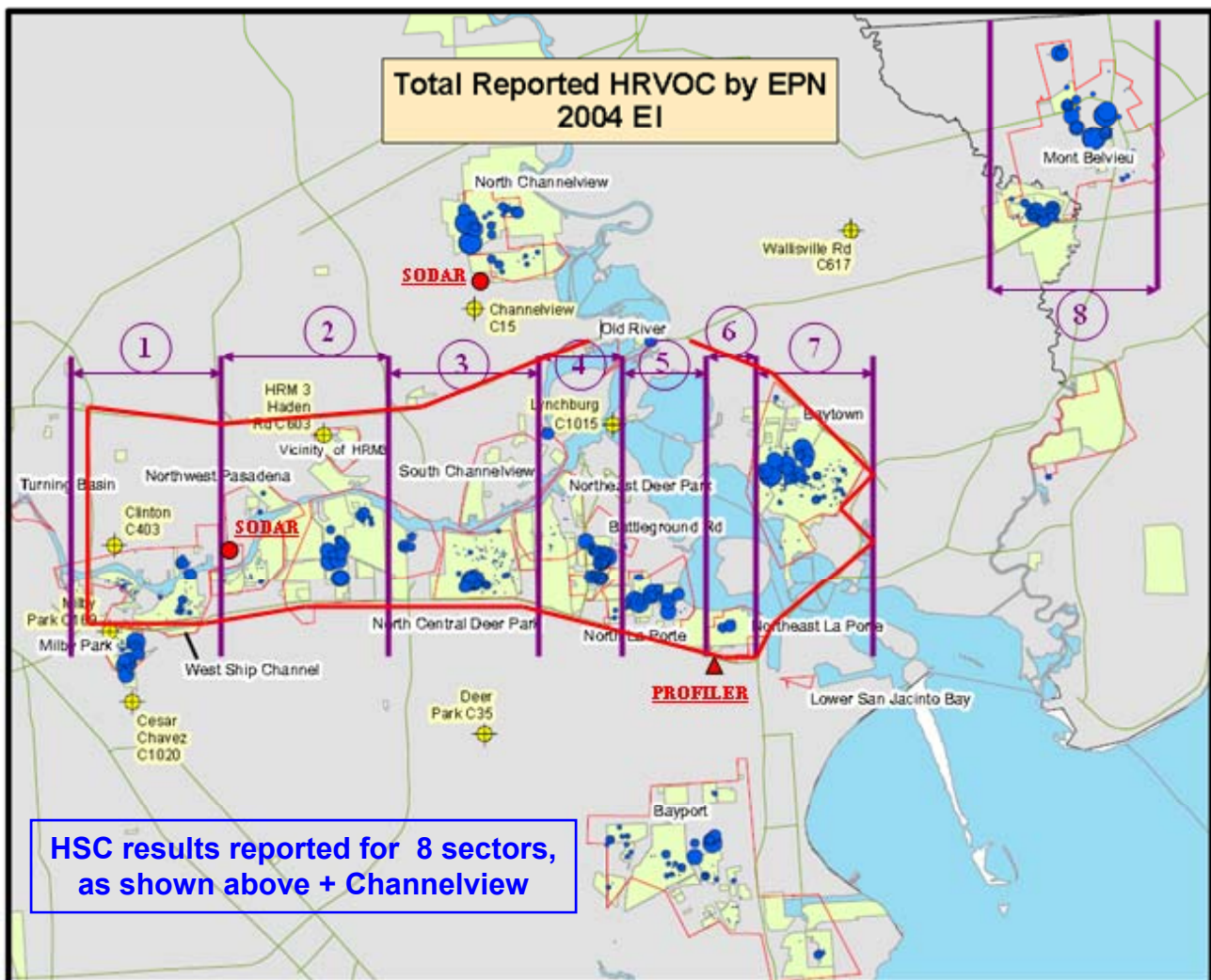
Winds info for HSC based on  
LaPorte profiler, 2 SODARs  
& an on-board minisonde

$\epsilon(\text{WS}) \sim \pm 30\%$

$\epsilon(\text{WD}) \sim \pm 15\%$

Measurements: HSC = 10 days  
(Aug 30 – Sep 30) TC = 2 days  
CB & FR = 1 day  
Sw = 2 days

SOF-Box around target source;  
Repeated traverses  
Typically  $\sim 0.5 - 3$  km downwind



## Summary of SOF/DOAS Results

	SOF			DOAS
<b>HSC</b>	<u>Ethene</u>	<u>Propene</u>	<u>Alkane</u>	<u>NO2</u>
Sectors 1-7	~ 860 ± 180 kg/h	~ 1510 ± 530	11530 ± 4200	4540 ± 1860
Mt. Belvieu	~ 400 ± 50 kg/h	~ 420 ± 280	863	270 ± 110
Channelview	~ 64 ± 32 kg/h			240 ± 120
<b>Other</b>	<div style="display: flex; align-items: center; justify-content: center;"> <span style="font-size: 2em; margin-right: 10px;">↑</span>           Variability of results         </div>			
Texas City	~ 83 + 12		2890 ± 400	642 ± 241
Choc. Bayou	~ 136	~ 273		268 ± 56
Freeport	~ 250			752 ± 127
Sweeny	~ 160	~ 122	3633	398 ± 53

	<u>Ethene</u>	<u>Propene</u>	<u>NO2</u>
$Q_{MEAS}$	~ 6 – 18 (HSC)	~ 15 – 87	< 2
$Q_{EI}$	~ 12 – 41 (other)	~ 11 - 32	

*Results showed quite a bit of variability of SOF results from traverse to traverse for both ethene and propene, more so for propene, with a significant variability particularly for flares.*

**NOAA-P3 results for the same sources on the same day generally give values within x2**

*(deGouw et al., NOAA)*

**Diagnostic TDEV analyses based on LRPM and 5 days of SOF/Aztec/P-3 data for various industrial sources is still on-going at UAH**

## **Emissions from Ships and Offshore Platforms** **(e.g., in HSC)**

**During TexAQS 2006, emissions in exhaust plumes from over 200 marine vessels in Galveston Bay and the HSC were measured on the Ron Brown ship of NOAA.**

**$C_i/CO_2$  used to generate emission factors (g/kg-fuel) for  
 $i = NO_x, SO_2, CO, HCHO, LAC, \dots$  LAC = light absorbing C (black C)**

**Many Els use constant EFs.**

**This study →**

- 1. EF( $NO_x$ ) varies with vessel speed (emissions also when vessel is docked)**
- 2. Emissions of  $NO_x, SO_2, CO$  from commercial marine vessels cannot be neglected for port regions and possibly for offshore areas**
- 3. Vessel traffic, especially in the HSC, usually was significant even on weekends and holidays**
- 4. EF measurements are consistent with literature data, but for  $NO_x$ , there is strong dependence on vessel speed**
- 5. Emissions of  $NO_x, SO_2, CO$  from offshore platforms may not be significant, but thorough exploration is required**

***(Williams et al., NOAA - RSS-A1, C1)***

## Emissions from Mobile Sources

Verification of Els (based on EPA-MOBILE6 model) using NOAA aircraft data (Electra/2000 and P-3/2006) and Washburn Tunnel data

(Houston)  
1200 – 1400  
1600 - 1800

### Findings

1. Significant shortcomings in EI
2. EI-CO = overestimated by factor of 2 – 4
3. EI-NO<sub>x</sub> accurate for 2000, but an under- estimate in 2006
4. EI-VOC = under- estimate in 2006

*(Frost et al., NOAA – RSS-D2)*

1. Results of aircraft and tunnel data fairly consistent in 2000
2. Increase in CO/CO<sub>2</sub> and CO/NO<sub>x</sub> from midday to afternoon rush period  
(Explanation: At midday, higher fraction of heavy-duty diesel vehicles (emit more NO<sub>x</sub>), while during rush period, higher fraction of gasoline vehicles (emit more CO)

*(McCaughy et a., 2004)*

Verification of Els and ambient surface concentrations (EPA-AIRS and TCEQ)

### Findings

1. (CO/NO<sub>x</sub>)-EI fairly constant for 2000 and 2006, but ambient data imply the ratio to be substantial over- estimates, more in 2006 than in 2000
2. Decrease in CO/NO<sub>x</sub> emissions due to a combination of decrease in E(CO) and increase in E(NO<sub>x</sub>)
3. VOC emissions have decreased at a similar rate as CO emissions (as expected, due to catalytic convertors)
4. MOBILE6 did a good job with EI-(VOC/NO<sub>x</sub>) in 2000 but did not accurately capture its decrease in 2006

*Parrish et al., NOAA- RSS-D2 and Parrish (2006)*

## **Emissions from Mobile Sources ... contd.**

1. Mobile source VOC speciation in HGB and DFW agree well with measurements in NE USA (NYC, Boston)
2. Speciation in Els is, by comparison, poor.

*deGouw et al., NOAA – RSS-D5; Warneke et al., 2007*

## Results of Texas Roadway Study, Summer 2007 (UT, Rice and TAMU)

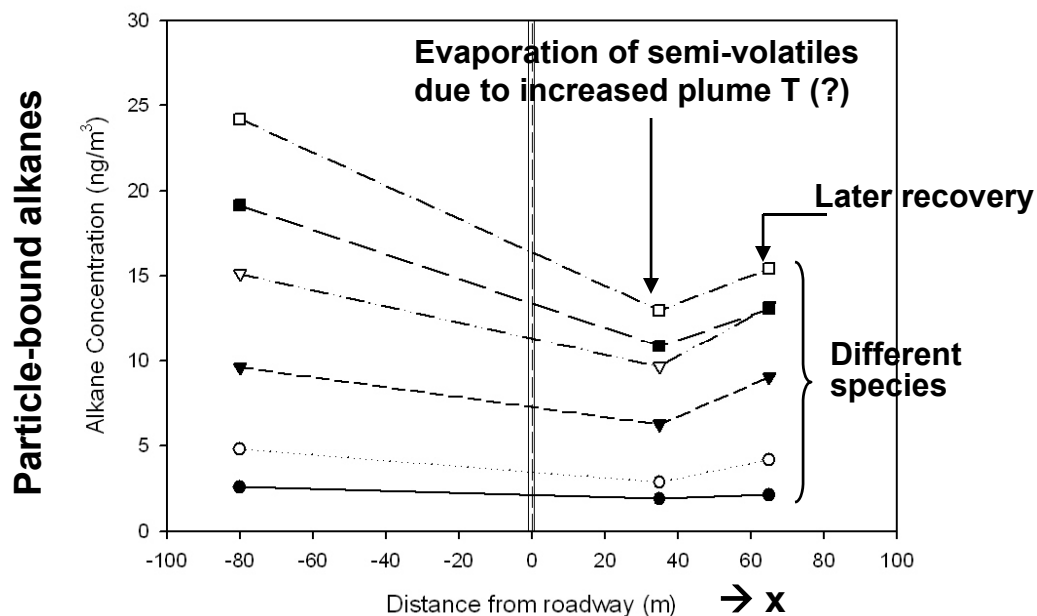
Measurements upwind and downwind of three types of roadways.

### Measured species:

- NO<sub>x</sub>, CO, VOC (including several carbonyls)
- several particle-bound organics (PAHs, alkanes, hopanes)
- PM<sub>2.5</sub> mass and carbon content
- UFP (ultrafine particles < 100 nm)

### Results

- CO, NO, NO<sub>x</sub> decayed exponentially with  $x$  within 150 m to background levels
- Primary aldehydes (incl. HCHO) decayed similarly over 65m, but acetaldehyde increased with  $x$ , suggesting chemical production
- EC decayed like other primary emissions; OC increased (secondary)
- 10 PAH compounds showed similar decay (65 m), but particle-bound alkanes showed the following distinct behavior with  $x$ :



*(McDonald-Buller, private communication)*

**Results of Texas Roadway Study, Summer 2007 ... cont'd.**  
**--- Evaluation of MOBILE6 ---**

**Downwind of a highway with dominant truck traffic**

**Comparison of CO/NO<sub>x</sub>**  
**(MOBILE6 emissions processed by CALINE4 model)**

**Model generally over-predicted by up to x3**  
**consistent with other studies**

***(DenBleyker et al., 2008)***

# Biogenic Emissions

*Large variability (inhomogeneous emissions?)*

## Measurements

NOAA P-3: WAS (canister) and PTR-MS (continuous)

## Comparison of “observed” and BEIS3-EI

“Observed” E based on  
- Measured C assumed constant over mixing height  
- Parameterized OH

BEIS-3 emission input to FLEXPART (Lagr. particle model)  
Model C compared to measured C for several days of data

Model and “observed” emissions compared for one day’s data

Both comparisons generally within x2 in E. Texas

FLEXPART overpredicted by more for regions to the SW of Houston and S of Dallas (possibly due to difference between actual landuse and that assumed in BEIS-3)