

Event Emissions and their impact on ozone formation in the Houston Galveston Area

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TERC Project H13 Scope

- Characterize the variability of emissions – both daily variability and emission events.
- Goal is to improve the emission inventory and the ability of air quality models to represent conditions in the Houston/Galveston Area
- Today's presentation will focus on event emissions, which have the most impact on improving model performance

What is an emission event?

Effective September 12, 2002, per Texas Administrative Code (TAC) Title 30 Chapter 101, reportable quantities were reduced from 5000 lbs. to 100 lbs. for most compounds in the Houston/Galveston ozone non-attainment area. Section 101.1, paragraph (83) defines a reportable emissions event as “Any emissions event which, in any 24-hour period, results in an unauthorized emission equal to or in excess of the reportable quantity...”. Alkanes remain at the 5000 lb limit provided they contain less than 0.02% of ethene (ethylene), propene (propylene), butene (butylenes), toluene, acetaldehyde, or oxides of nitrogen, and less than 2.0% of any other reportable compound. In addition, Texas House Bill (HB) 2912 requires that air emission incidents be filed electronically and be available in a publicly available database.

Key Questions

- *Are the magnitudes of emission events, singularly and collectively, significant relative to routine emissions?*
- *What variability in the emissions inventory is introduced by emission events and does the frequency of the events warrant treating their emissions as a unique type, rather than simply adding them to routine emissions (as is currently the practice)?*
- *What are the characteristics of the events in terms of time, space, and composition?*
- *How do the events influence ozone formation?*

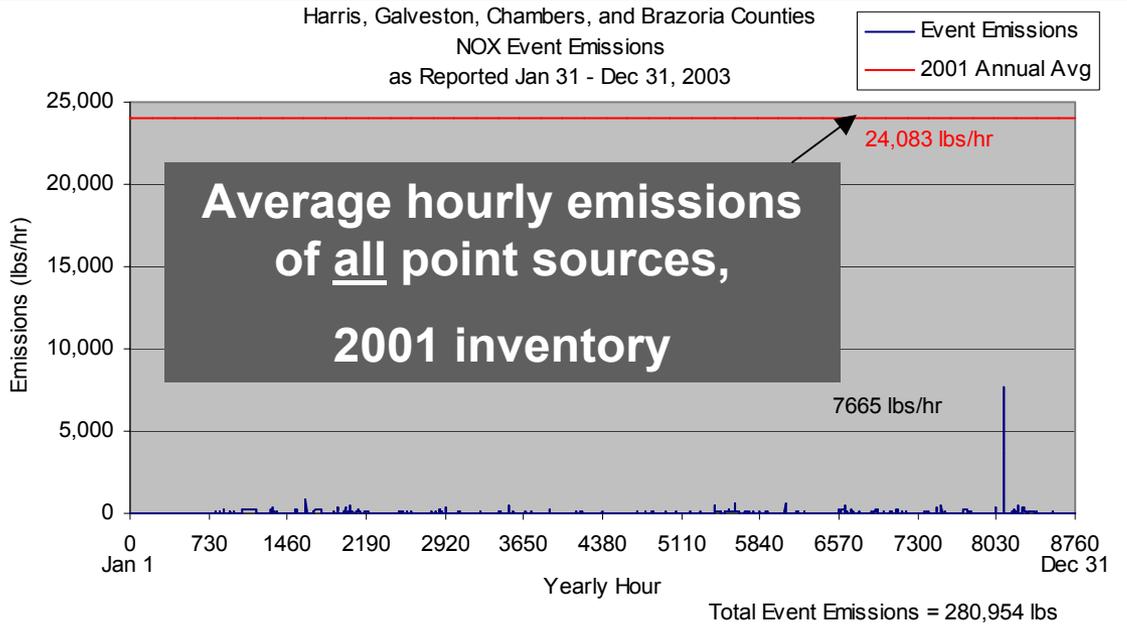
Questions 1 and 2:

Are the magnitudes of these events, singularly and collectively, significant relative to that of routine emissions?

What variability in the emissions inventory is introduced by emission events and does the frequency of the events warrant treating their emissions as a unique type, rather than simply adding them to routine emissions (as is currently the practice)?

- Focus on highly reactive volatile organic compounds (HRVOC): ethene, propene, butenes, and 1,3-butadiene
- Emissions are evaluated in terms of flow (lbs/hr)
- TCEQ Air Emission Event Report Database is used as source of data

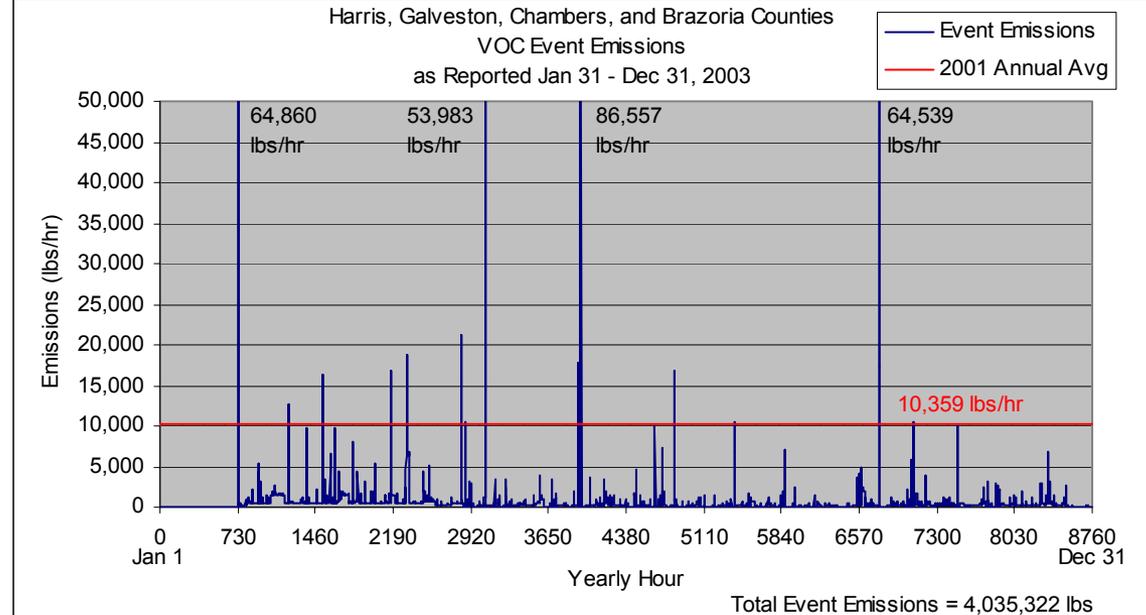
Harris, Galveston, Chambers, and Brazoria Counties
 NOx Event Emissions
 as Reported Jan 31 - Dec 31, 2003



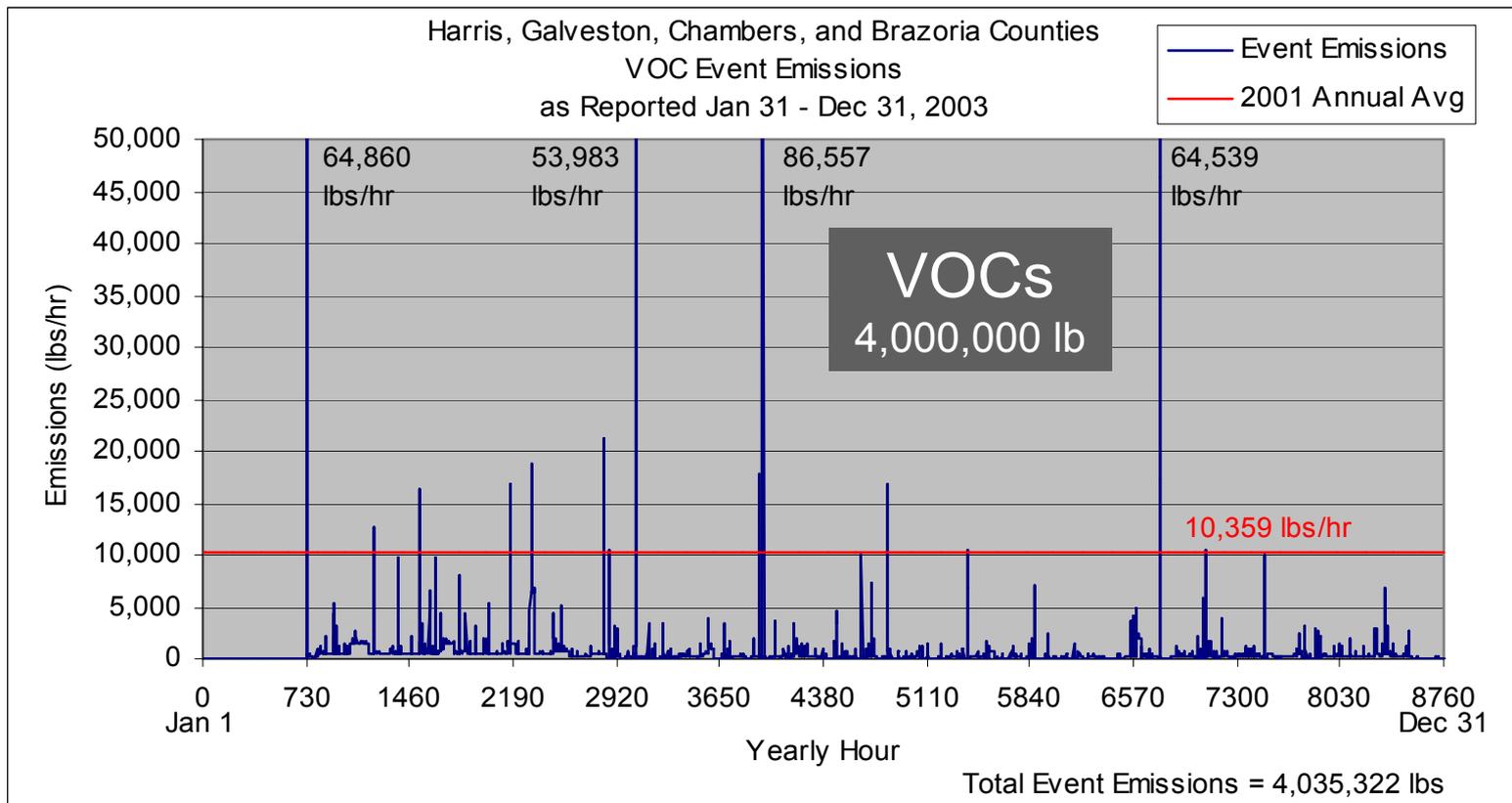
First 11 Months of reporting:

- NOx emission event emissions are small compared to annual average emissions

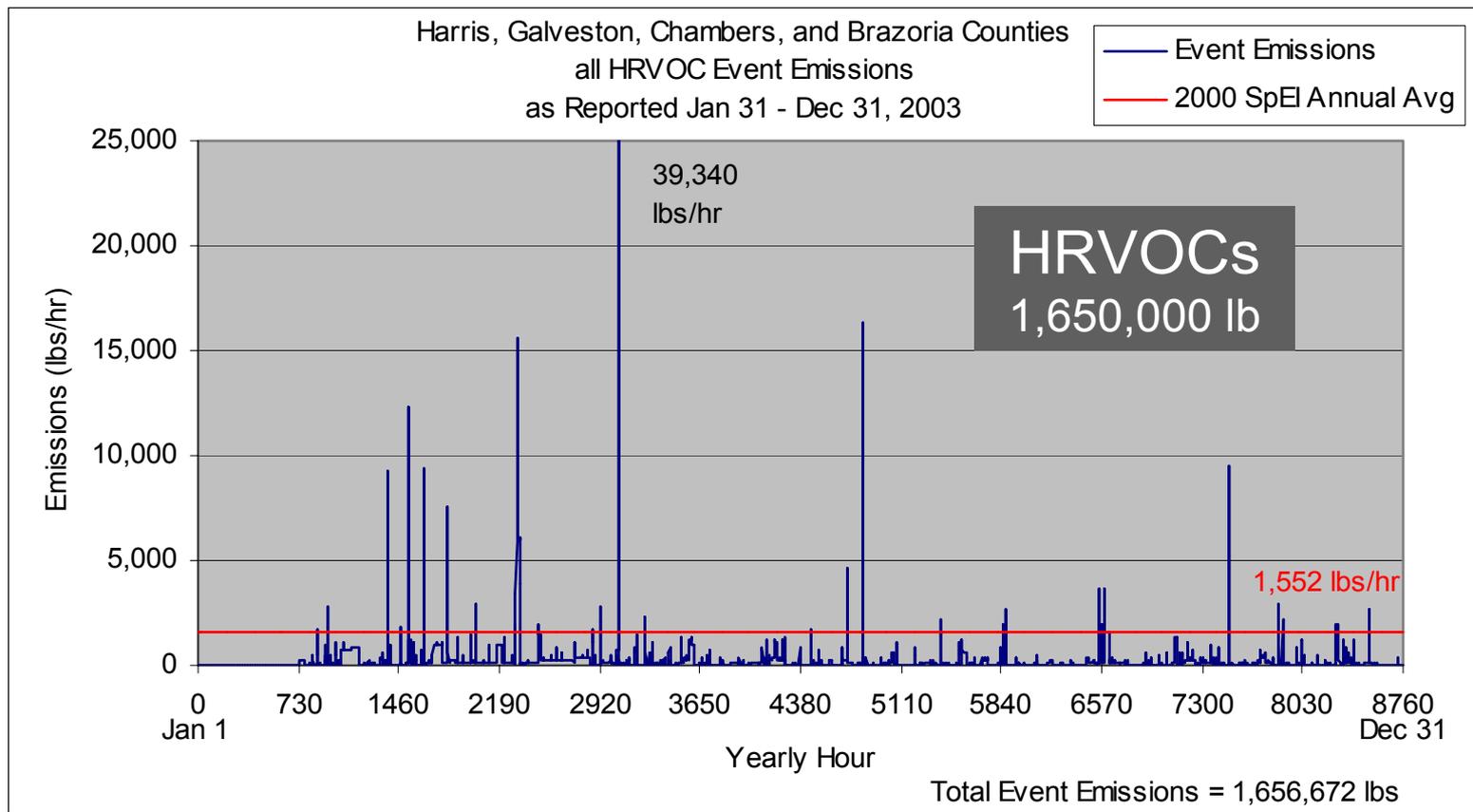
Harris, Galveston, Chambers, and Brazoria Counties
 VOC Event Emissions
 as Reported Jan 31 - Dec 31, 2003



- At specific times and locations, VOC and HRVOC emissions can be large relative to annual average emissions

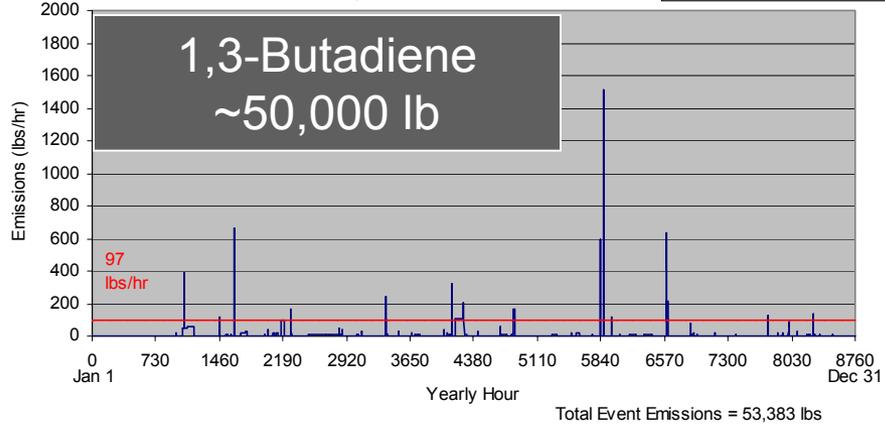


- Total mass of over 4 million pounds (2000 tons) contributes 4% to the 45,000 tons of VOC emitted over a single year from point sources in the four counties.
- 14 times (18 hours) during the eleven-month period, event emissions exceed the annual average for all facilities in the region.
- 4 times in 11 months, the flow rate of event emissions is more than five times the annual average with a maximum of 86,000 lbs/hr.

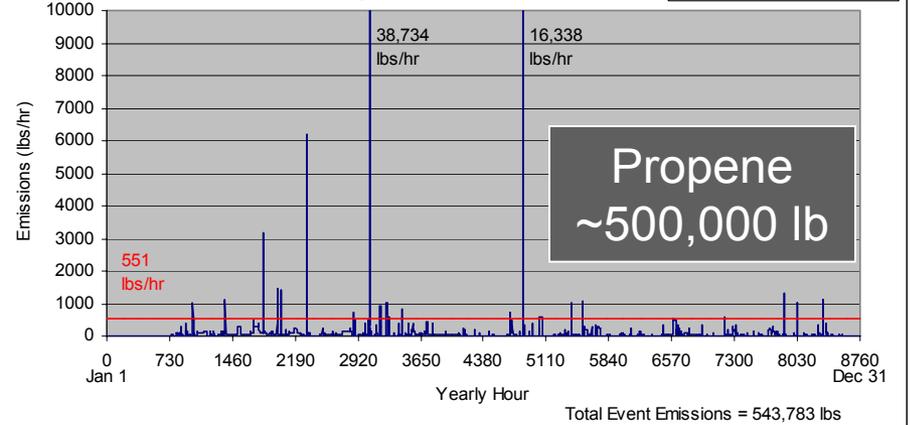


- Total mass of over 1.6 millions pounds (830 tons) is ~12% of the 6800 tons of HRVOC emitted over a single year from point sources in the four counties.
- 29 times (115 hours) during the eleven-month period, event emissions exceed the annual average.
- 7 times in 11 months, the flow rate of event emissions is more than five times the annual average with a maximum of 39,000 lbs/hr.

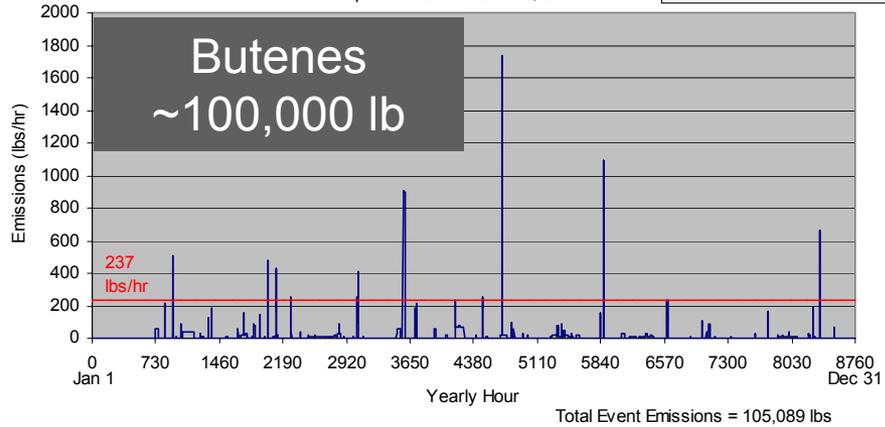
Harris, Galveston, Chambers, and Brazoria Counties
all 1,3-Butadiene Event Emissions
as Reported Jan 31 - Dec 31, 2003



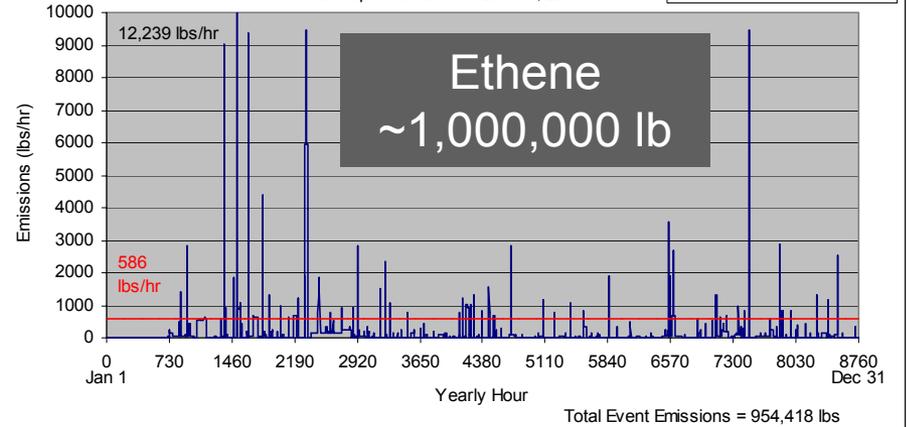
Harris, Galveston, Chambers, and Brazoria Counties
all Propene Event Emissions
as Reported Jan 31 - Dec 31, 2003



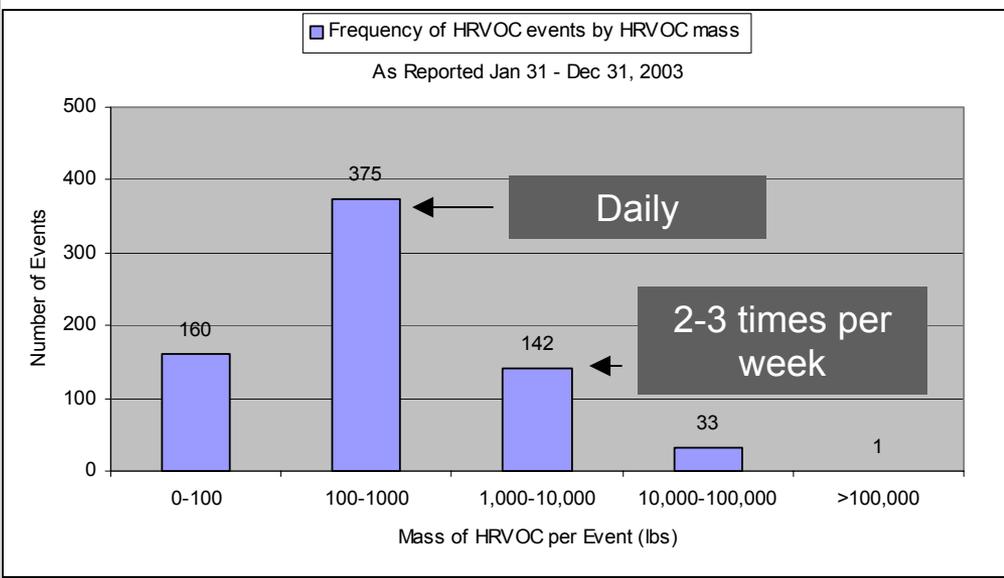
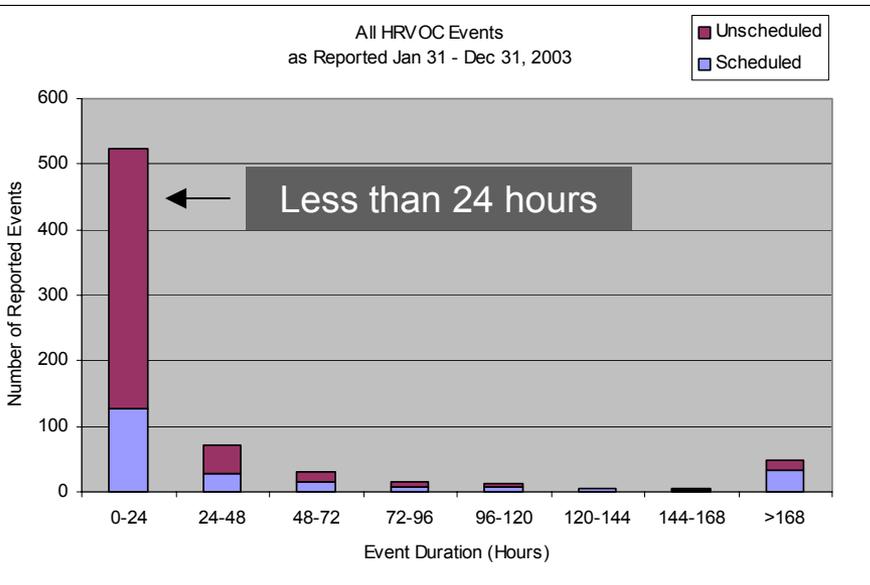
Harris, Galveston, Chambers, and Brazoria Counties
all Butene Event Emissions
as Reported Jan 31 - Dec 31, 2003



Harris, Galveston, Chambers, and Brazoria Counties
all Ethene Event Emissions
as Reported Jan 31 - Dec 31, 2003



What are the characteristics of the events in terms of time, space, and composition?



Most HRVOC events last less than a day, many last less than an hour

Largest number of events is from events of 100-1000 lb, but most of the mass is associated with events greater than 1000 lb, which occur, on average, several times per week

Conceptual model

- Events with emissions of more than 1000 pounds of HRVOCs occur several times per week, on average
- Many are relatively short (well under one hour in duration)
- Among the HRVOCs, ethene and propene dominate
- Events occur primarily in Harris and Brazoria counties at chemical manufacturing facilities

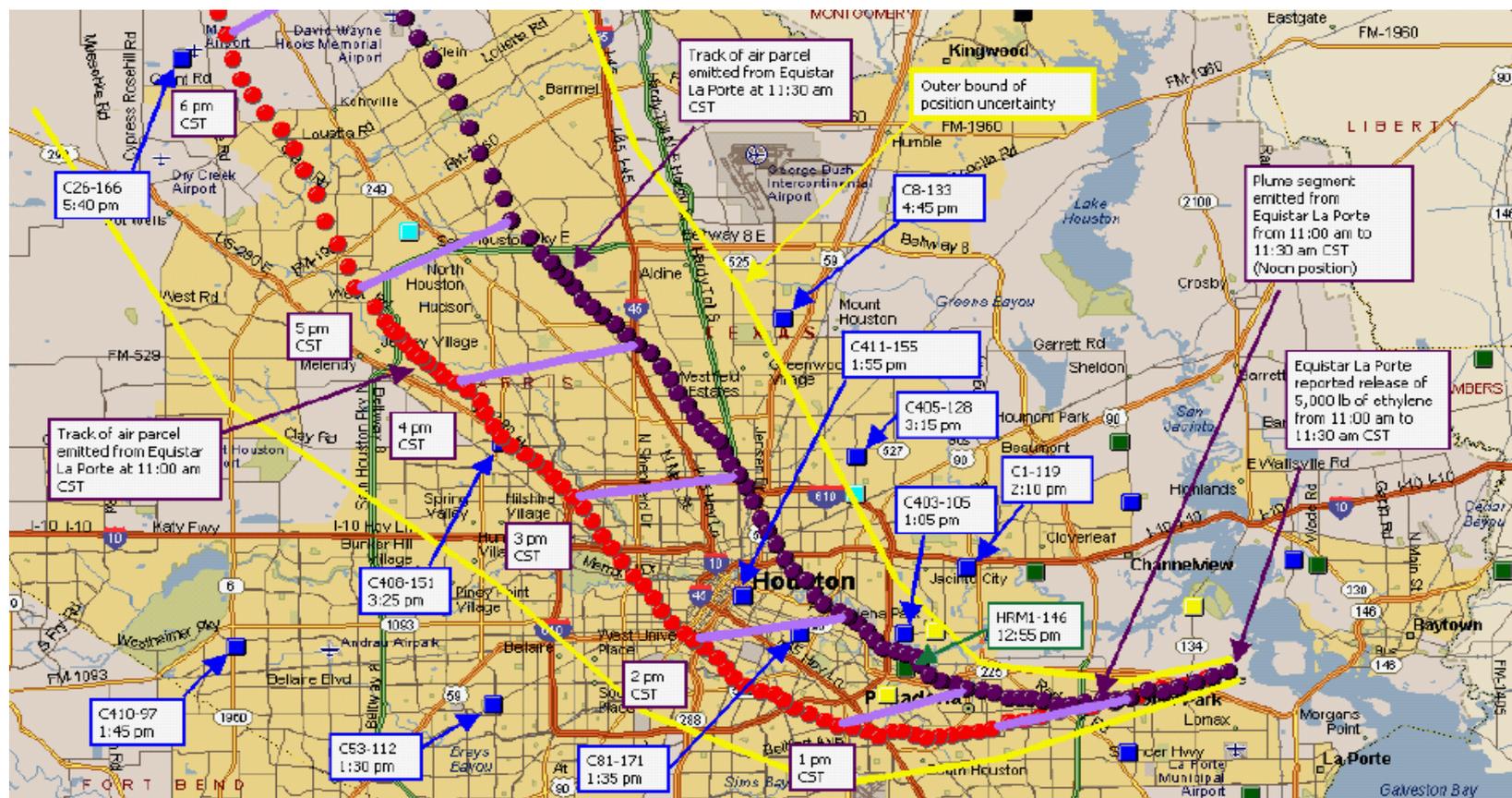
How accurate are the data and what are the consequences for ozone formation?

Compare monitoring and event data; systematic comparisons just beginning, but case study analyses by TCEQ staff are available

- Case study 1: Monitoring data from a 5000 lb, 30 minute ethylene release at LaPorte (known release – look for evidence in monitoring data)
- Case study 2: Clinton event 10/23/03 (extreme values in monitoring data – look for report of release)

10,000+ lb ethylene release at LaPorte, (6700 lb between 11 and 11:25 AM)

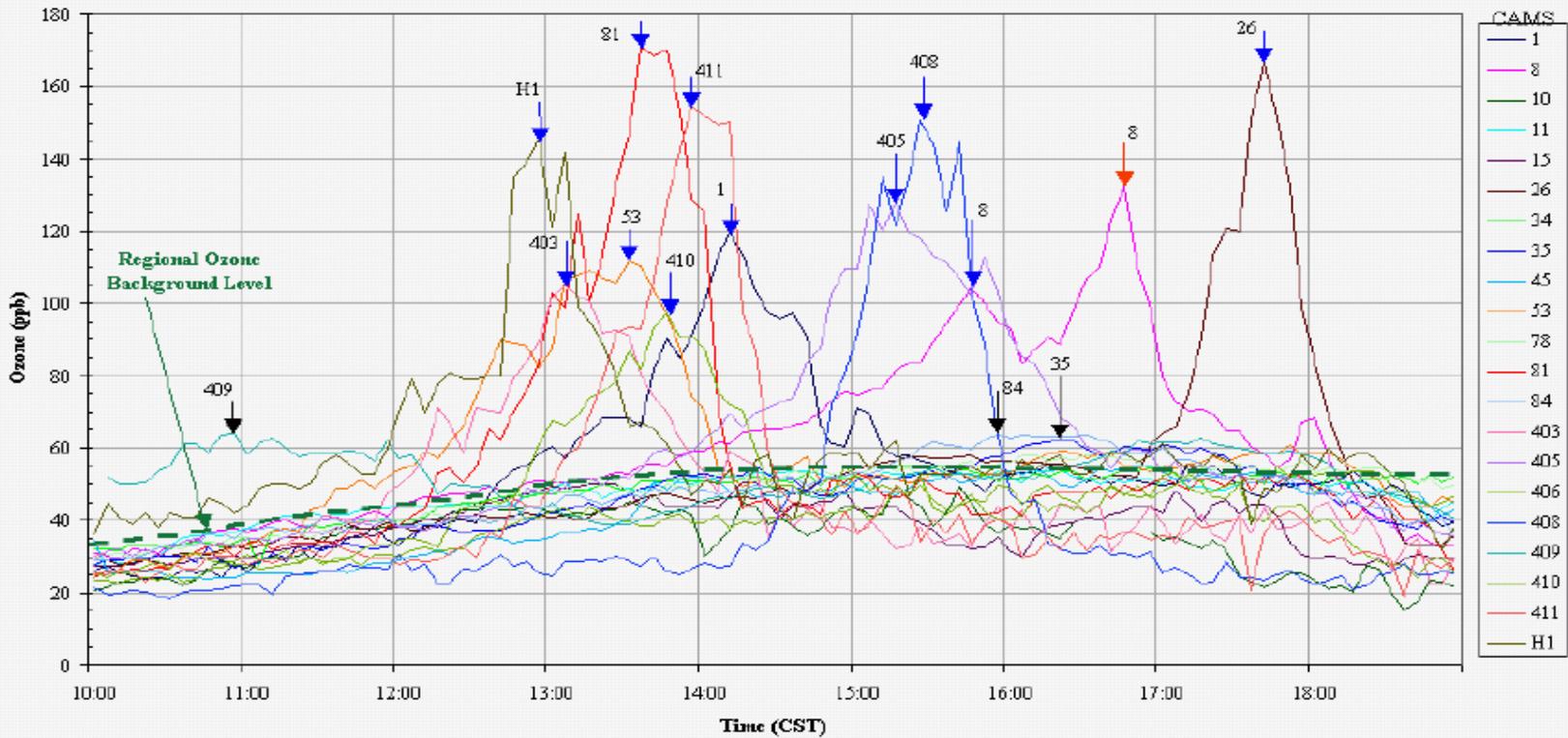
3/27/2002



Short term ozone enhancements of up to 100 ppb



Houston Ozone Peaks 3-27-2002

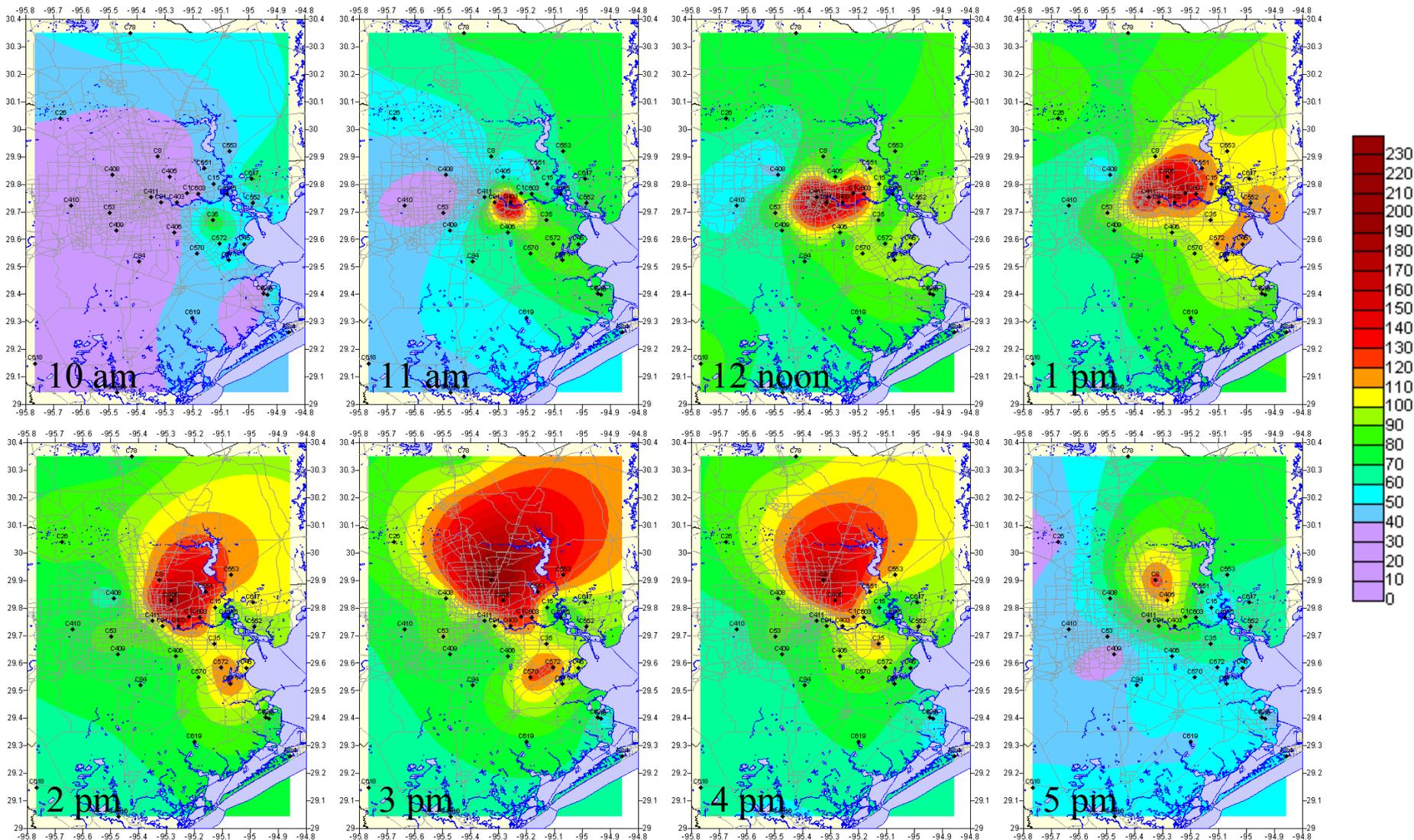


Ozone Exceedance Episode – 10-23-03

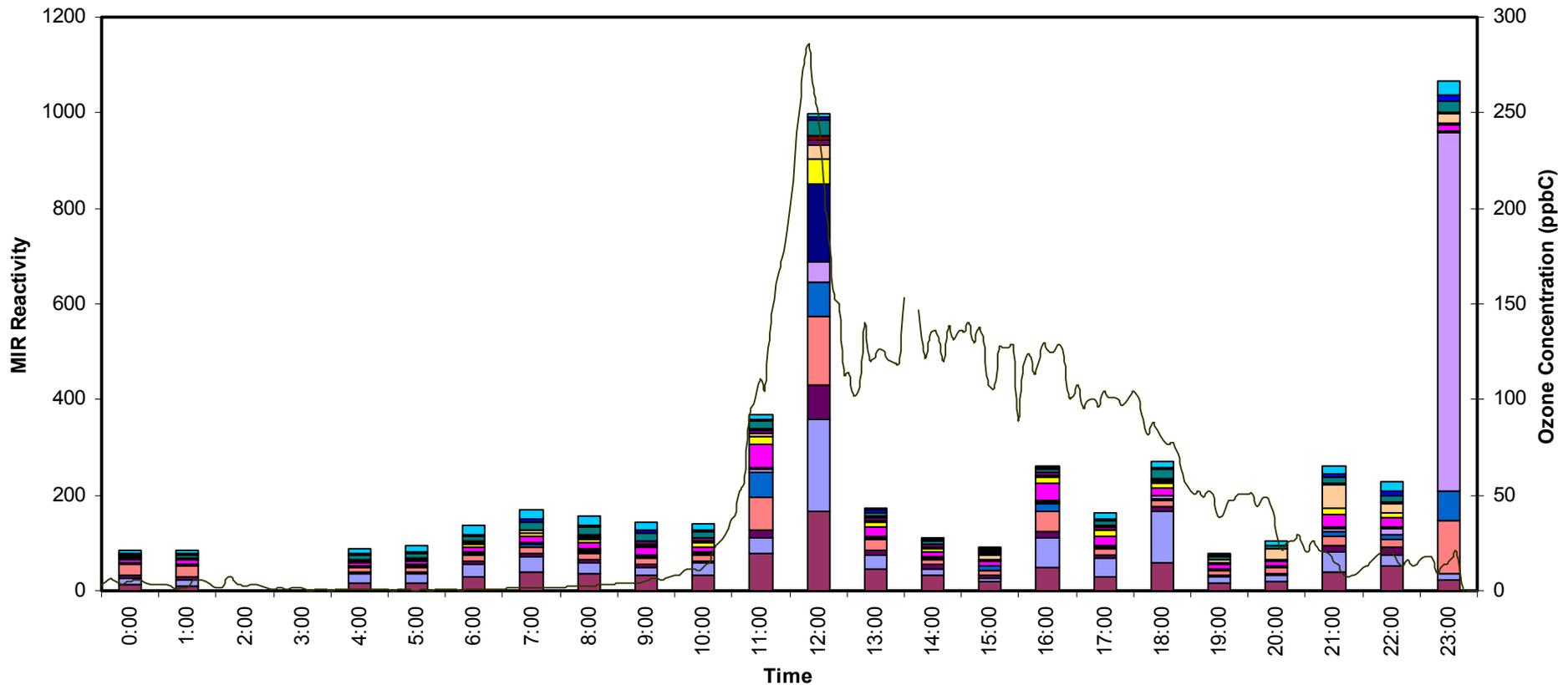
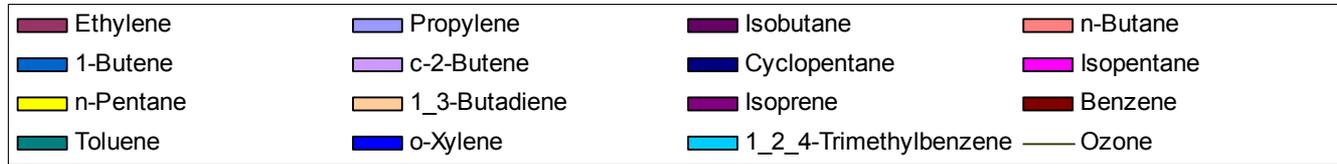
- One-hour ozone at Aldine = 229 ppb at 3pm
- Five-minute ozone at Clinton = 285 ppb at 11:50am
- One hour ozone increase at Clinton = 156
 - 40 ppb at 10am → 196 ppb at 11am
- 2 Auto-GC monitors with 1-hr ozone exceedances
 - HRM-3 = 133 ppb
 - Clinton = 196 ppb



Contour Maps Showing the Progression of High Ozone on 10-23-03



Ozone Concentration (5 Min. Data) and VOC Reactivity Vs. Time at Clinton C403 for 10-23-03



Information in emission event record?

- Search for reporting entities (entire year) within a 5-25 km radius of the Clinton monitor
- Bracket event dates
- Use information about source types and wind directions to winnow group of possible events (if necessary)
- One event report possibly related – 1,000 pound butene release – reported event length 10/22-10/23

More analysis and many more case studies needed

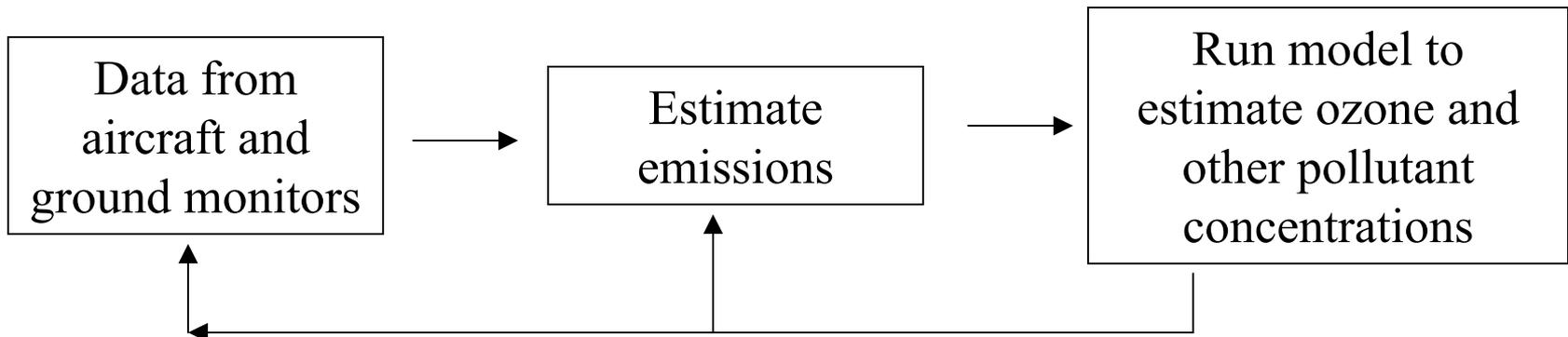
- Event database is valuable tool, but could be even more useful; to understand how the database could be modified to be more useful, we will:
 - Look in event record for explanations of extreme values of monitored concentrations
 - Look for evidence of reported events in monitoring record
 - Collect additional field data (Corpus Christi network, TexAQS II)

How do we proceed for the mid-course review?

- Account for event emissions in the August – September 2000 modeling by estimating event emissions based on a variety of ambient measurements
- For this episode, event emissions appear to contribute a PORTION of the ozone associated with peak concentrations
- Use the model to estimate ozone formation during the August-September 2000 period, with and without events. Apply control strategies to both continuous and event emissions.

Estimating event emissions during the 2000 modeling episode

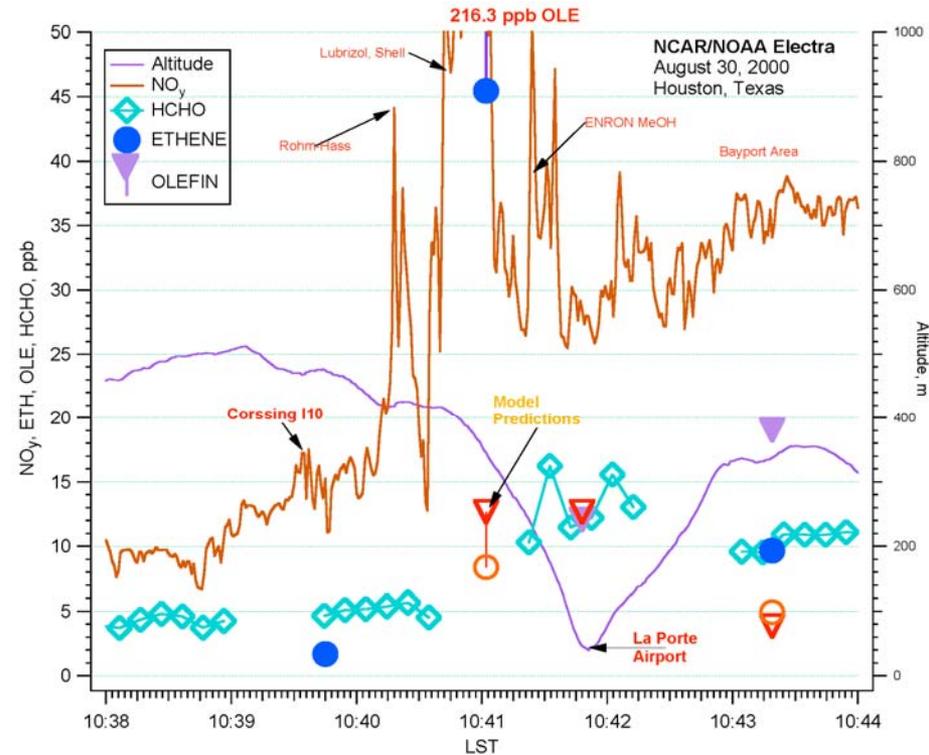
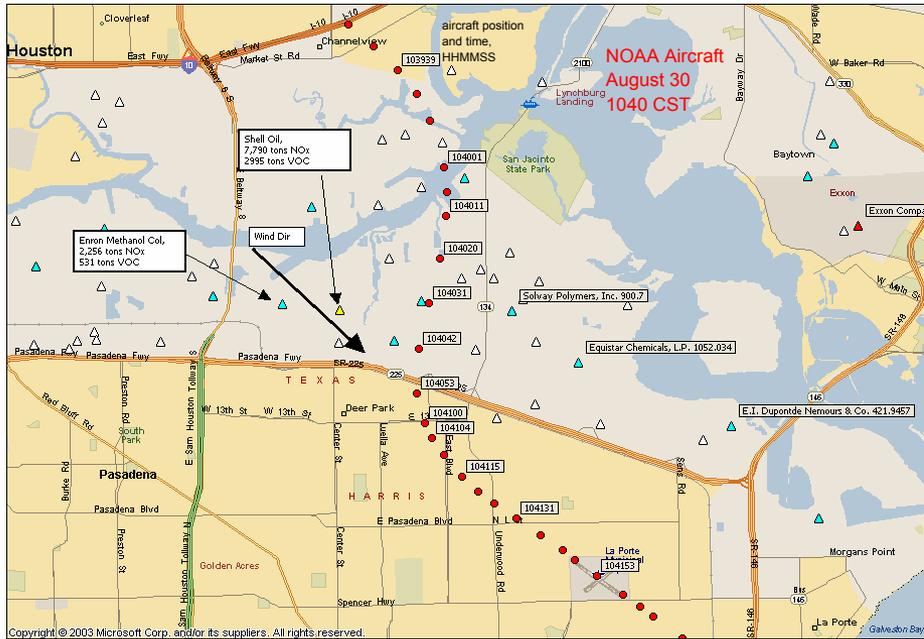
- Data from unprecedented set of monitoring data, available because of the Texas Air Quality Study
- Better model performance than any previous attempt to model Houston-Galveston area; model performs well at most areas at most times, but a portion of some of the highest ozone concentrations may be influenced by emission events



Unprecedented amount of observational data available

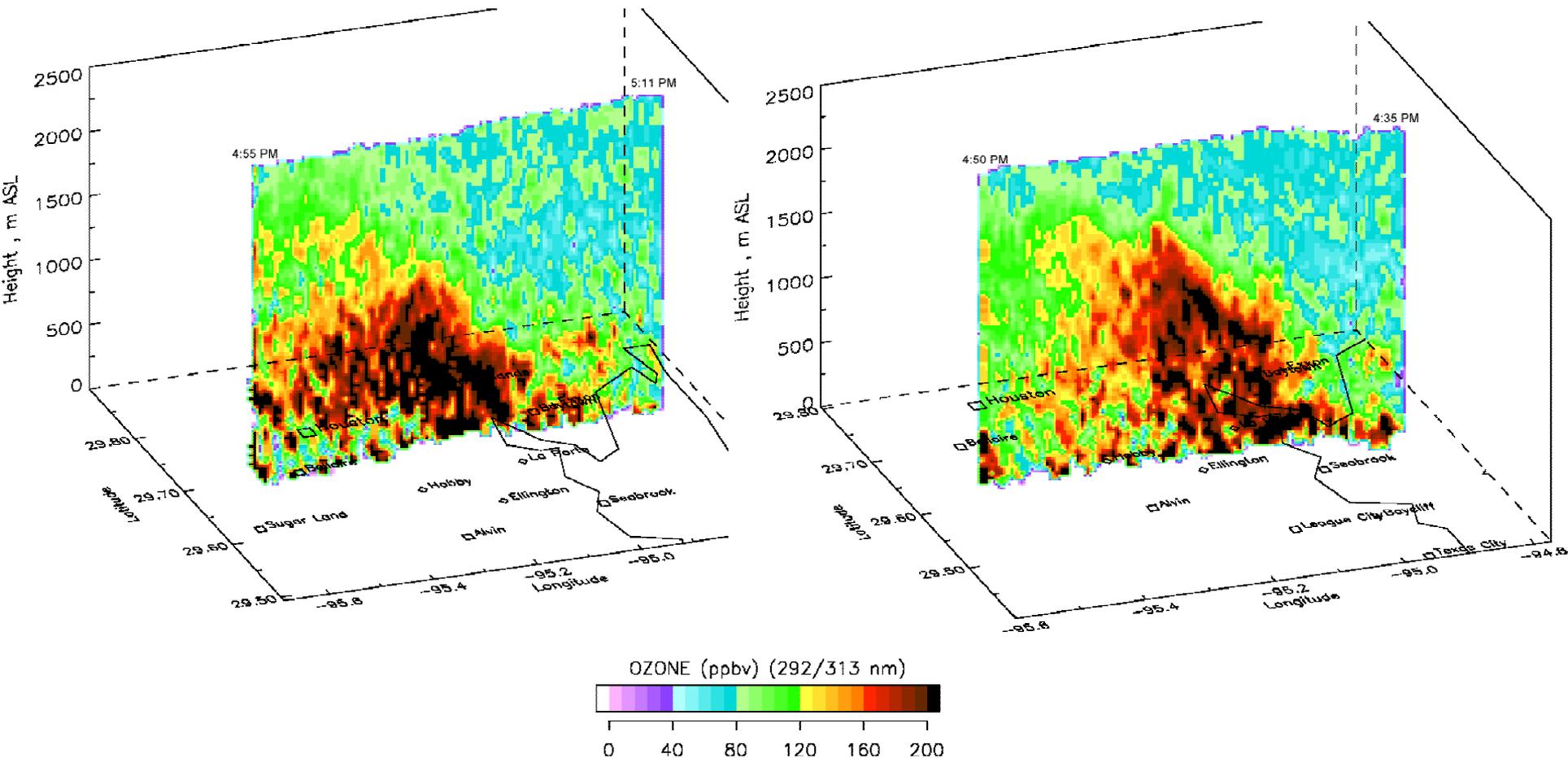
- TCEQ monitoring network
- Aircraft observations (Baylor, NOAA Electra, NOAA Lidar, DoE)
- Major ground chemistry sites (LaPorte, Williams Tower, Aldine, HRM 3 enhancements)
- Enhanced meteorological network
- others

Observational Evidence 8/30



1. NOAA aircraft, flying to the east of Deer Park at 640 m AGL, detected very high concentrations of reactive olefins (up to >100 ppb) and ethene (45 ppb) at 1042 CST. Plume is about one kilometer wide.

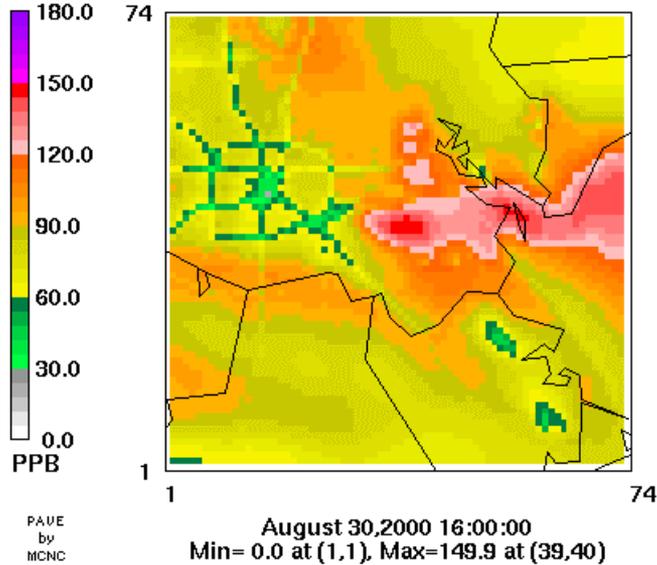
Airborne LIDAR saw O₃ plume in aloft in the afternoon



Add Event to Air Quality Model

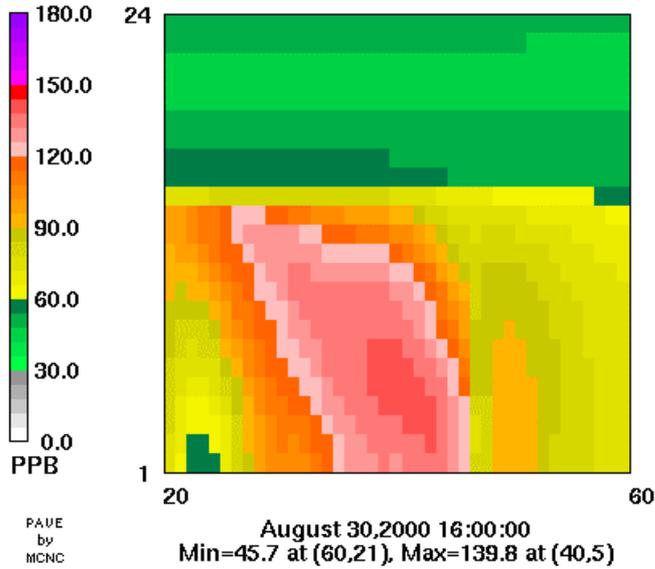
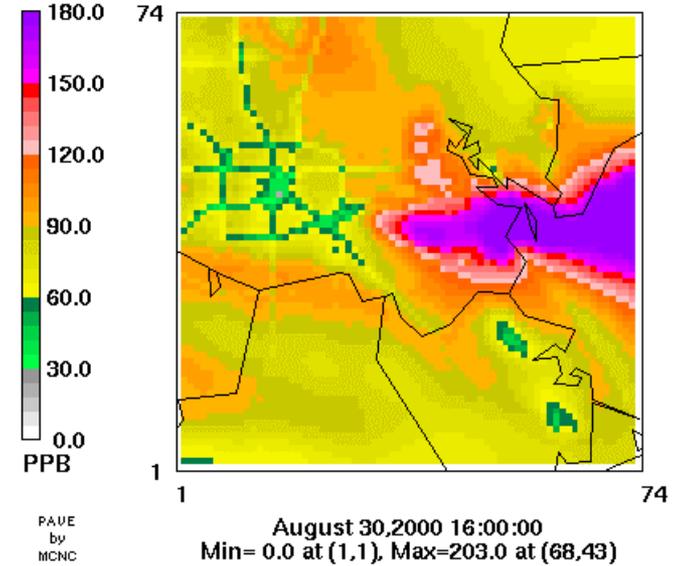
(most recent version with 1-km resolution)

Without Event

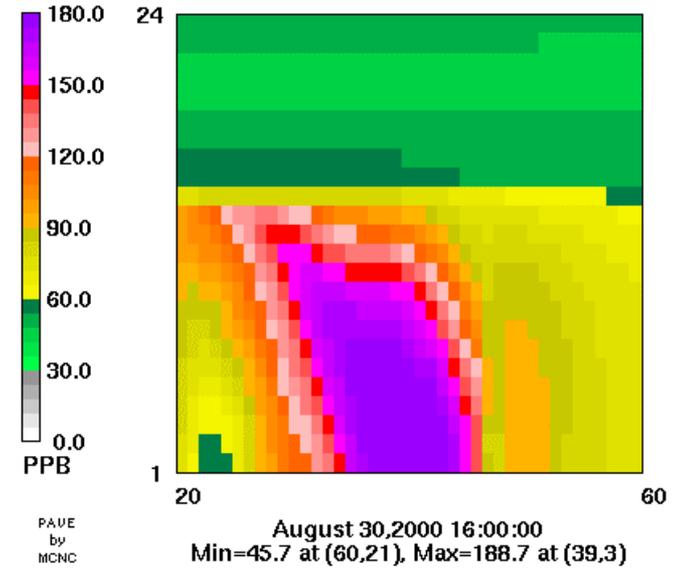


Layer One
149.9 ppb
vs
203.0 ppb

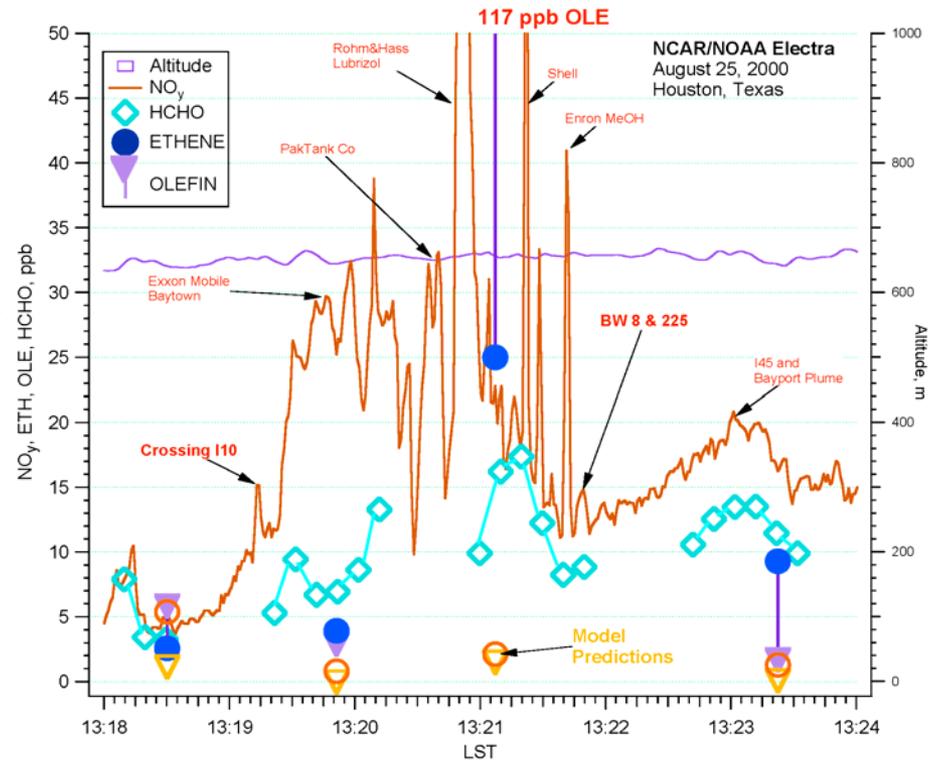
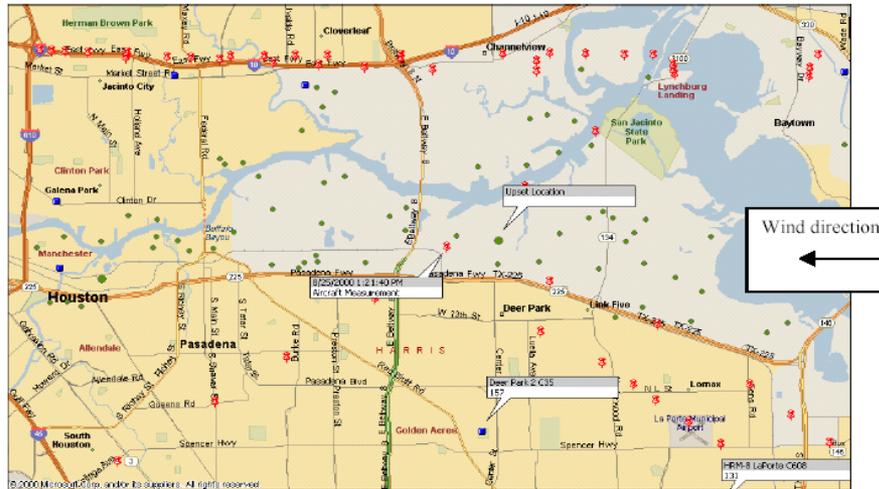
With Event



N-S Vertical
Slice, Col 52
139.8 ppb
vs
188.7 ppb

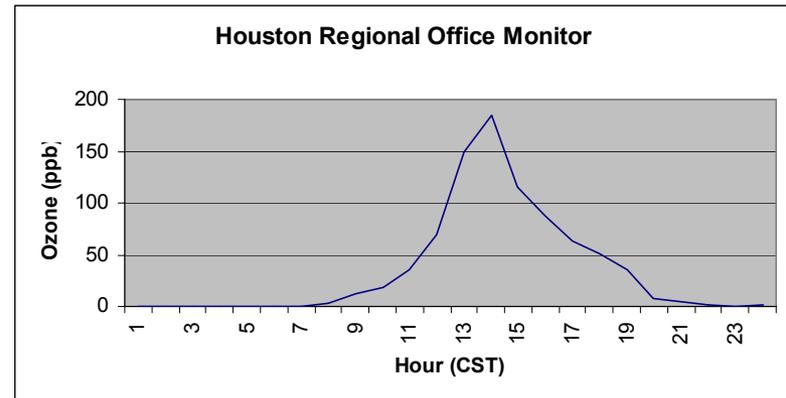
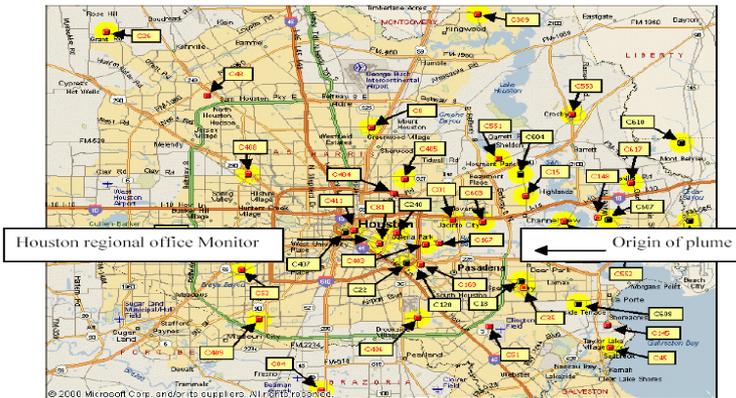


Observational Evidence 8/25



1. NOAA aircraft, flying to the west of Deer Park at 640 m AGL, detected very high concentrations of reactive olefins (up to >100 ppb) and ethene (25 ppb) at 1321 CST. Plume is only a few kilometers wide.

Add event to model, compare ozone predictions



| Time | Obs | Basecase | 723lbs/hr | 1455lbs/hr | 2910lbs/hr | 5819lbs/hr |
|------|-----|----------|-----------|------------|------------|------------|
| 10 | 36 | 36. | 36. | 36. | 36. | 36. |
| 11 | 69 | 52. | 52. | 52. | 52. | 52. |
| 12 | 150 | 89. | 89. | 89. | 89. | 89. |
| 13 | 185 | 173. | 176. | 178. | 182. | 189. |
| 14 | 116 | 132. | 133. | 134. | 137. | 141. |
| 15 | 87 | 81. | 81. | 81. | 81. | 81. |
| 16 | 63 | 53. | 53. | 53. | 53. | 53. |
| 17 | 51 | 46. | 46. | 46. | 46. | 46. |
| 18 | 36 | 36. | 36. | 36. | 36. | 36. |

Adding event emissions adds to peak ozone concentration at the ground site



Summary

- Emission events can be significant factors in ozone formation in the Houston-Galveston area
- New event databases and observational data allow these events to be characterized in much greater detail than previously possible
- For mid-course review, TERC Project H13 staff will continue extensive collaboration with TCEQ TAD staff to identify, document and model emission events in the August-September 2000 modeling episode
- Beyond the mid-course review, collection of data about emission events and modeling of emission events should continue to be refined