Variable Industrial VOC Emissions and their Impact On Ozone Formation in the Houston Galveston Area

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http://airchem.sph.unc.edu/Research/Projects/Texas/UT_UNC/

One Hour Ozone in Houston

- One hour ozone design values have been ~200 ppb for more than a decade.
- Previously, air quality models failed to create this much ozone and never in the right place at the right time.
- HGA's 2000 SIP required only NOx reductions and no VOC reductions.

Massive VOC Production in Houston

Houston Petrochemical Production Capacity

Compound	US%	Amount Produced			At 0.05% Loss	
		billion lbs per year	million lbs per day	million lbs per hour	tons per day	lbs per hour
Ethylene	53%	27.6	75.6	3.2	18.9	1,575
Propylene	63%	10.9	29.9	1.2	7.5	622
Butadiene	63%	2.4	6.6	0.3	1.6	137
Xylene	38%	4.9	13.4	0.6	3.4	280
Benzene	36%	0.7	1.9	0.1	0.5	40
Toluene	25%	0.4	1.1	0.0	0.3	23

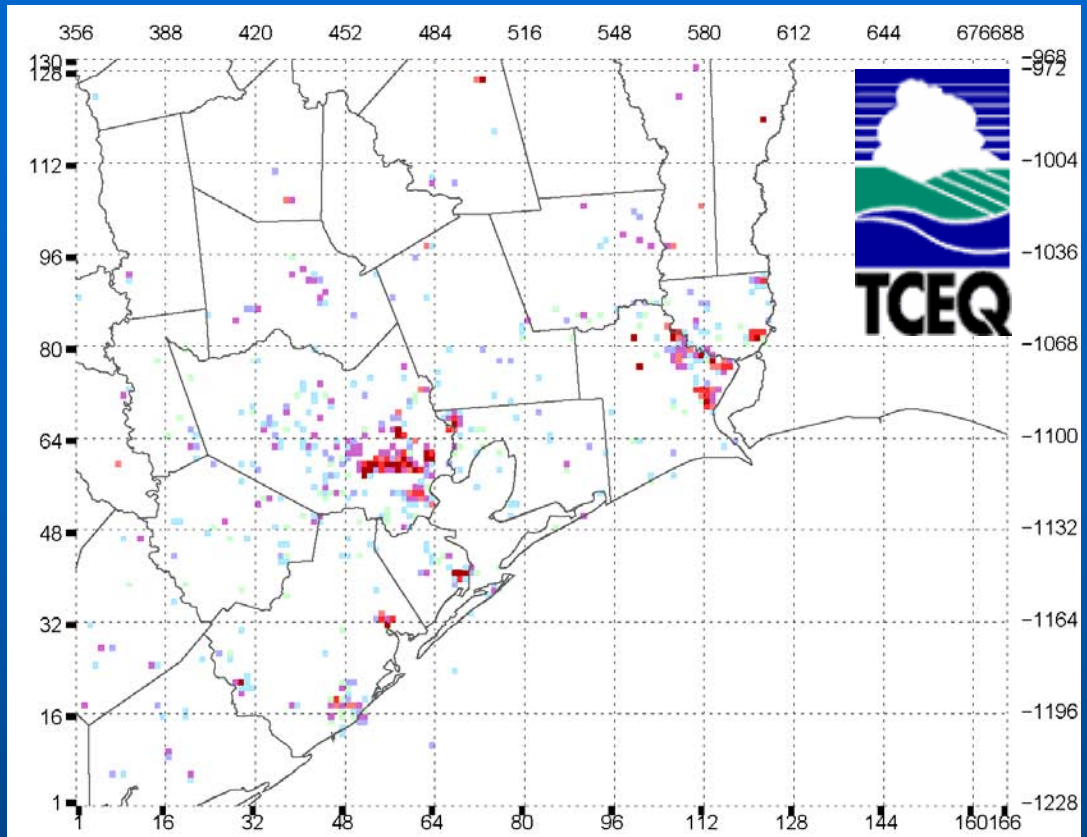
Sources: Business Houston, 2001; Houston Facts, 2000; Chemical Marketing Reporter 1996--1997; County Business Patterns, 1990; U.S. Census Bureau; after Deawon Byun

2.7 million vehicles drive 120 million miles each day

4 billion barrels of crude can be processed each day

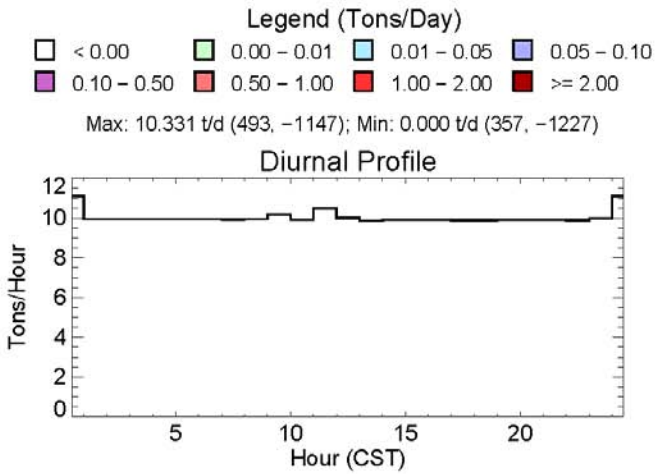
Port of Houston is 2ad largest in US in tons loaded/unloaded
More than 100 commercial docks along ship channel.

Model Pt Src VOC EI



Emissions Plotted

County	Tons/Day
Brazoria	16.59
Chambers	7.40
Fort Bend	1.34
Galveston	28.87
Harris	107.48
Liberty	1.49
Montgomery	2.00
Waller	0.41
HG SUBTOTAL:	165.57
Hardin	1.66
Jefferson	44.01
Orange	15.83
BPA SUBTOTAL:	61.50
MAP TOTAL:	240.40

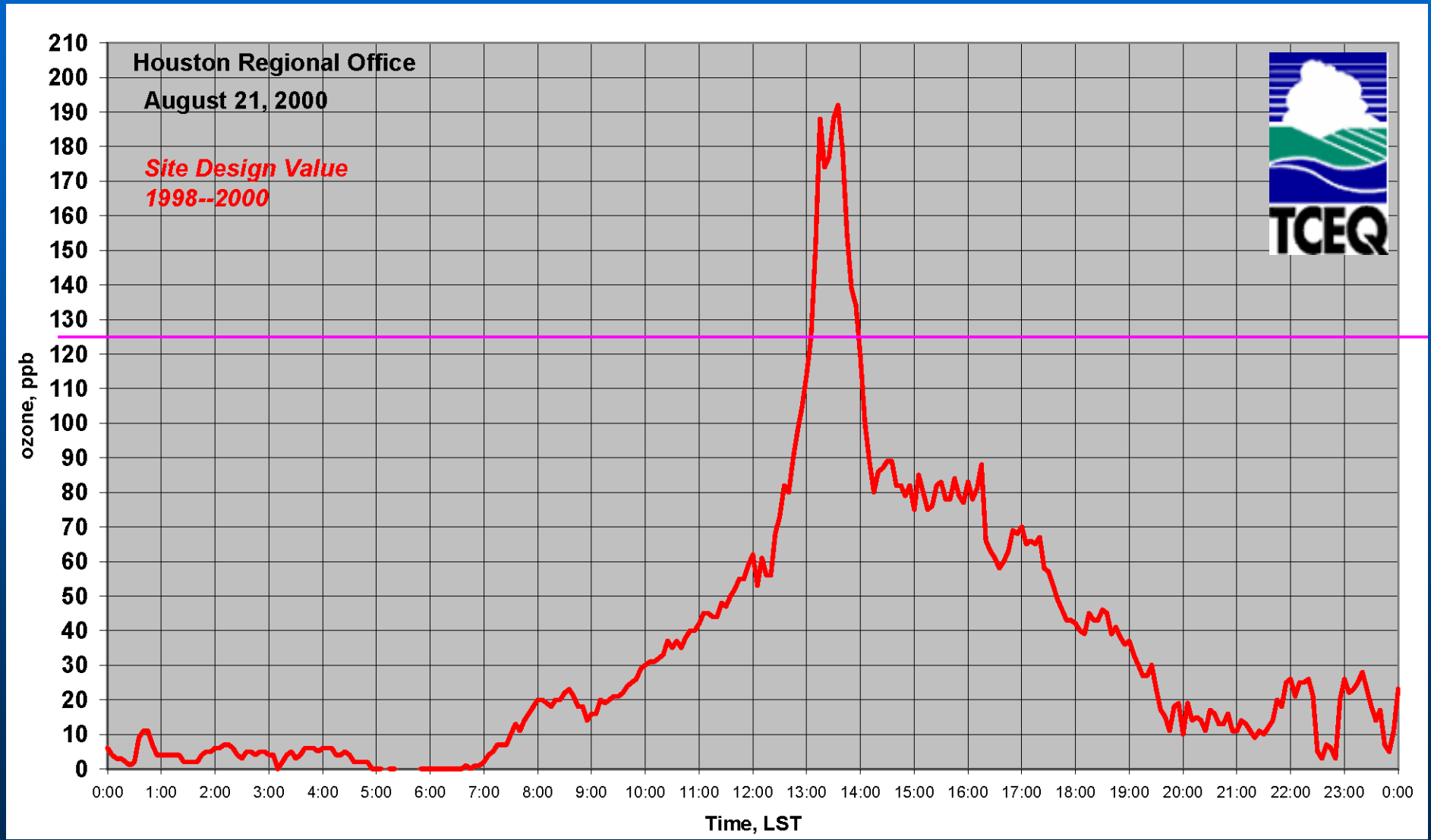


- Normal Non-EGU VOC EI with Special EI additions
- hg_02km.tx_negu_si4a Total Point Source CB–IV HC Emissions, 08/25/2000

Base inventory of 240 Tons VOC / Day of nearly constant emissions

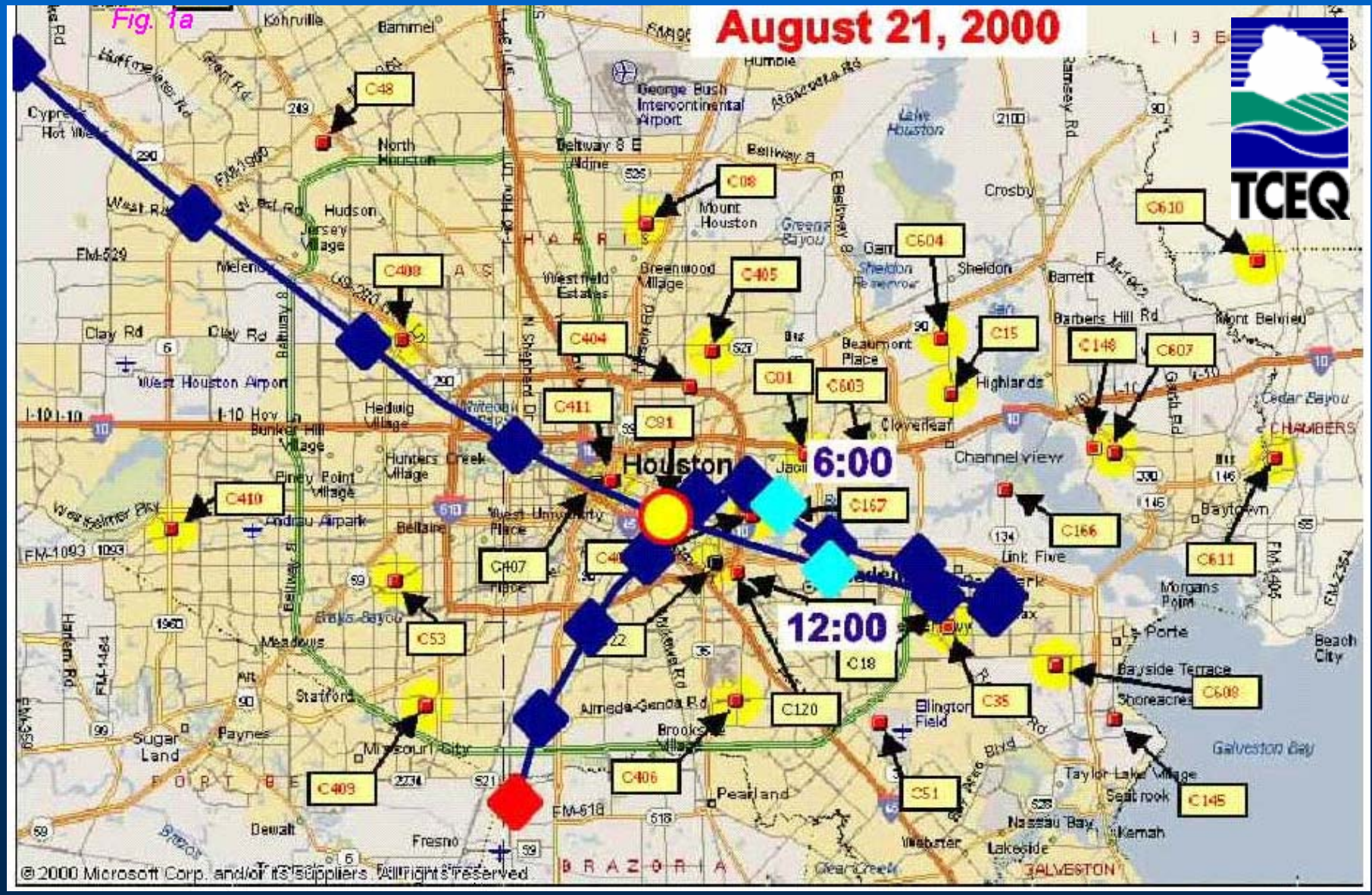
Cantu, 2002

Transient High Ozone Event, THOE

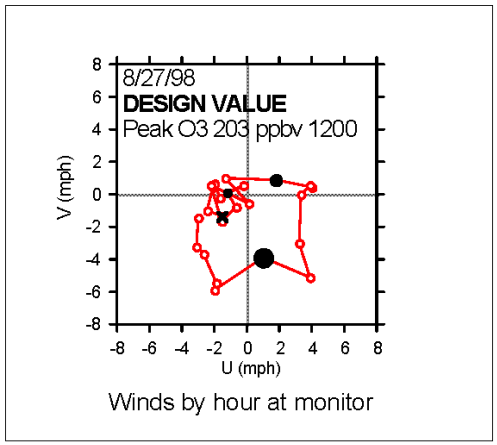


5-min ozone at TCEQ ground monitor

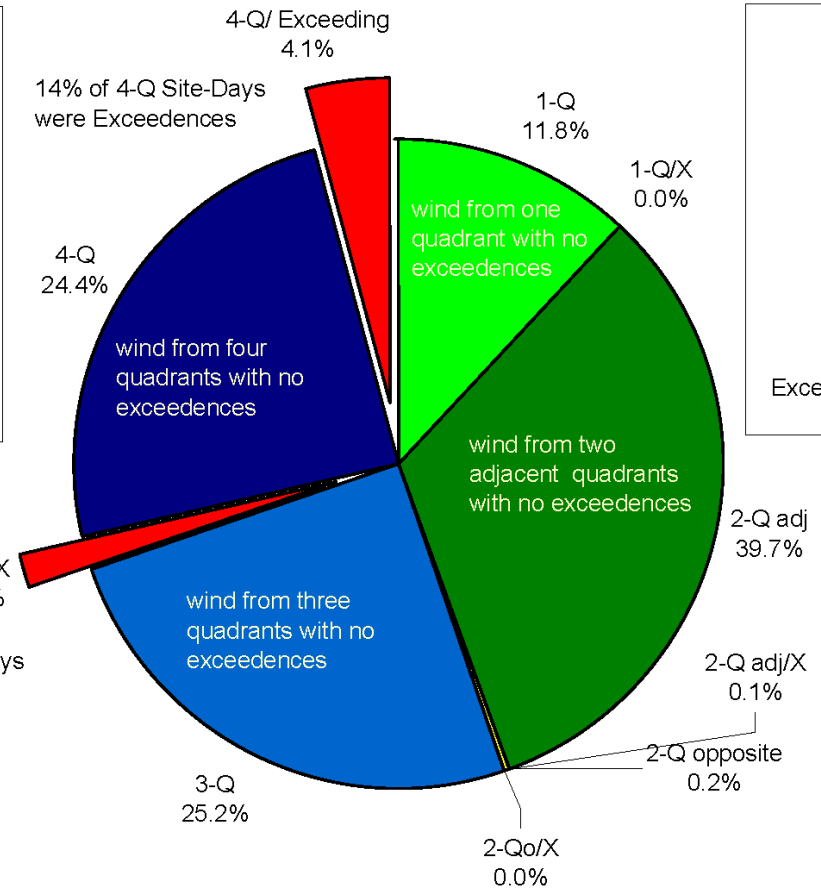
Wind Trajectory for THOE

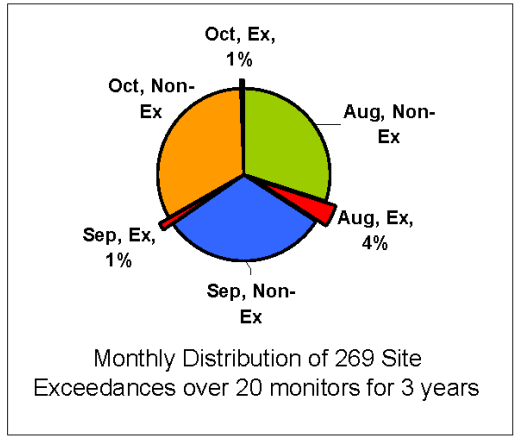


Meteorology and Ozone Exceedences



HGA Monitor Site-Days, Aug, Sept, Oct 1998-2000,
Exceeding and Not Exceeding 1-Hr O_3, Sorted by Number of Wind Quadrants During Day





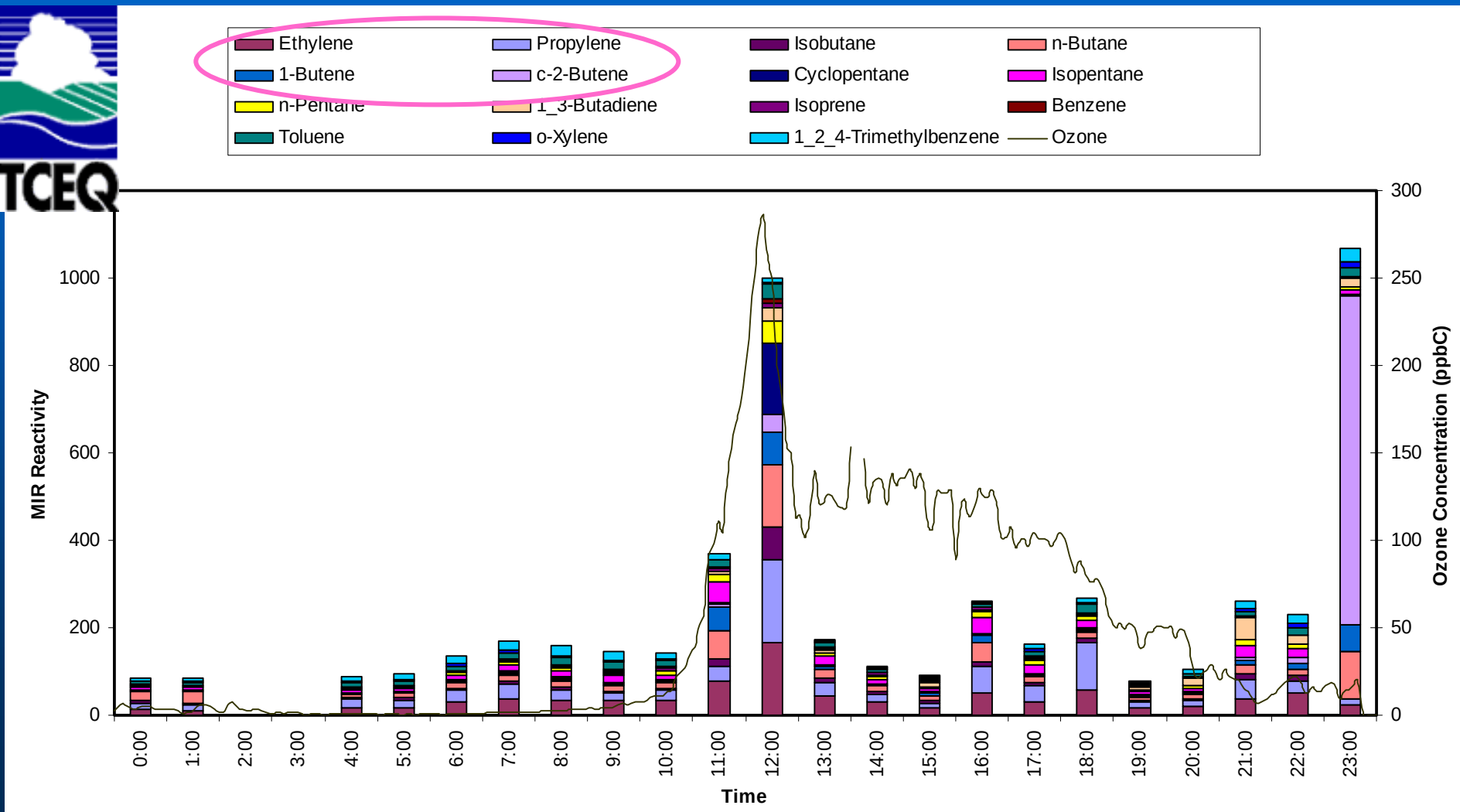
6% of 4,587 Site-Days
were Exceedences

More than half the time, winds are conducive for ozone exceedence.

Only one day in eight of these days actually has an exceedence.

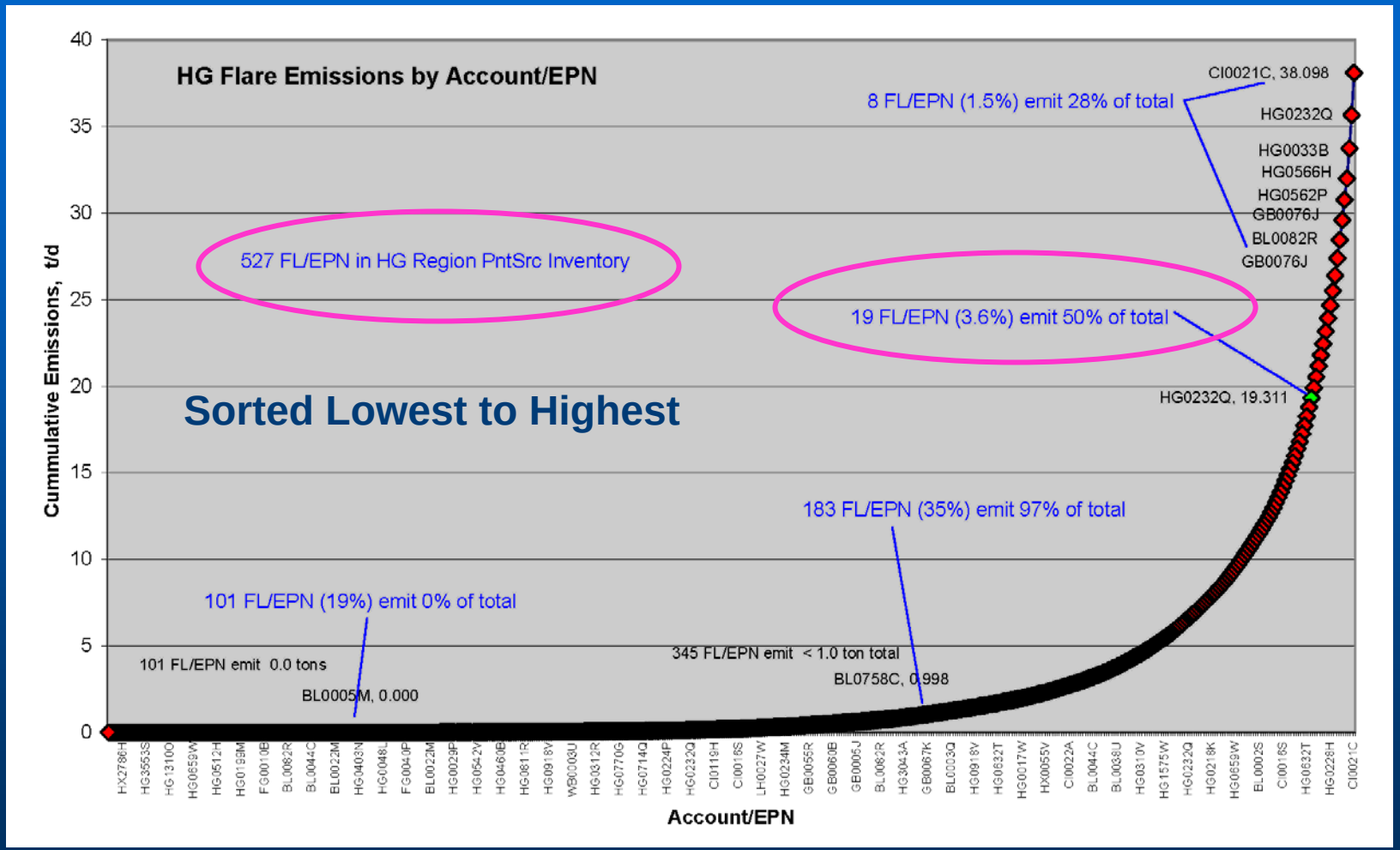
Blanchard, Jeffries, 2002

Another THOE and VOC Reactivity Clinton Site C403 for 10-23-2003



5 minute ozone and hourly auto-GC Max Inc Reactivity for VOC

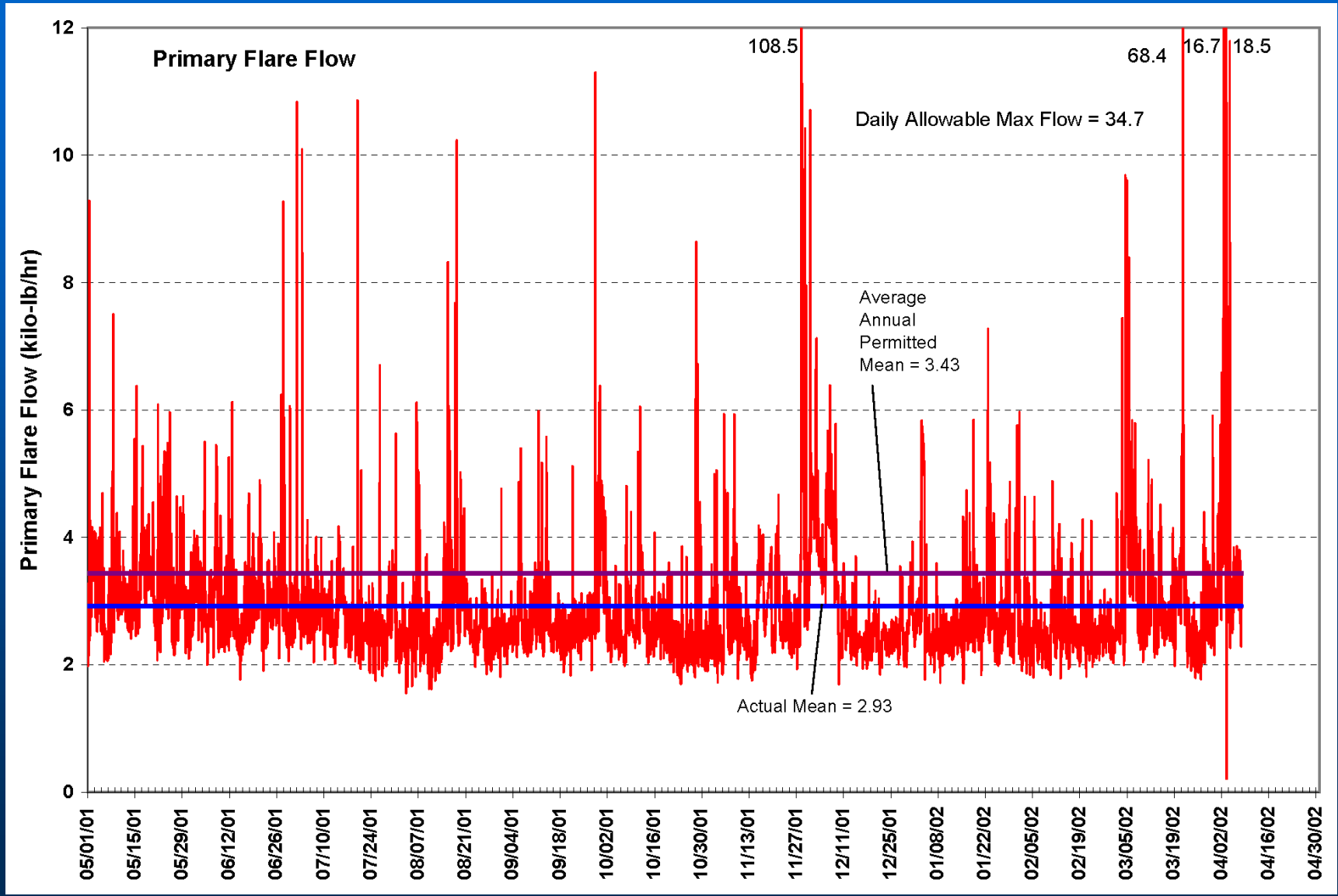
Flares as VOC Source



- 19 flares (ca. 4% of all flares) account for 50% of total VOC emissions from flares

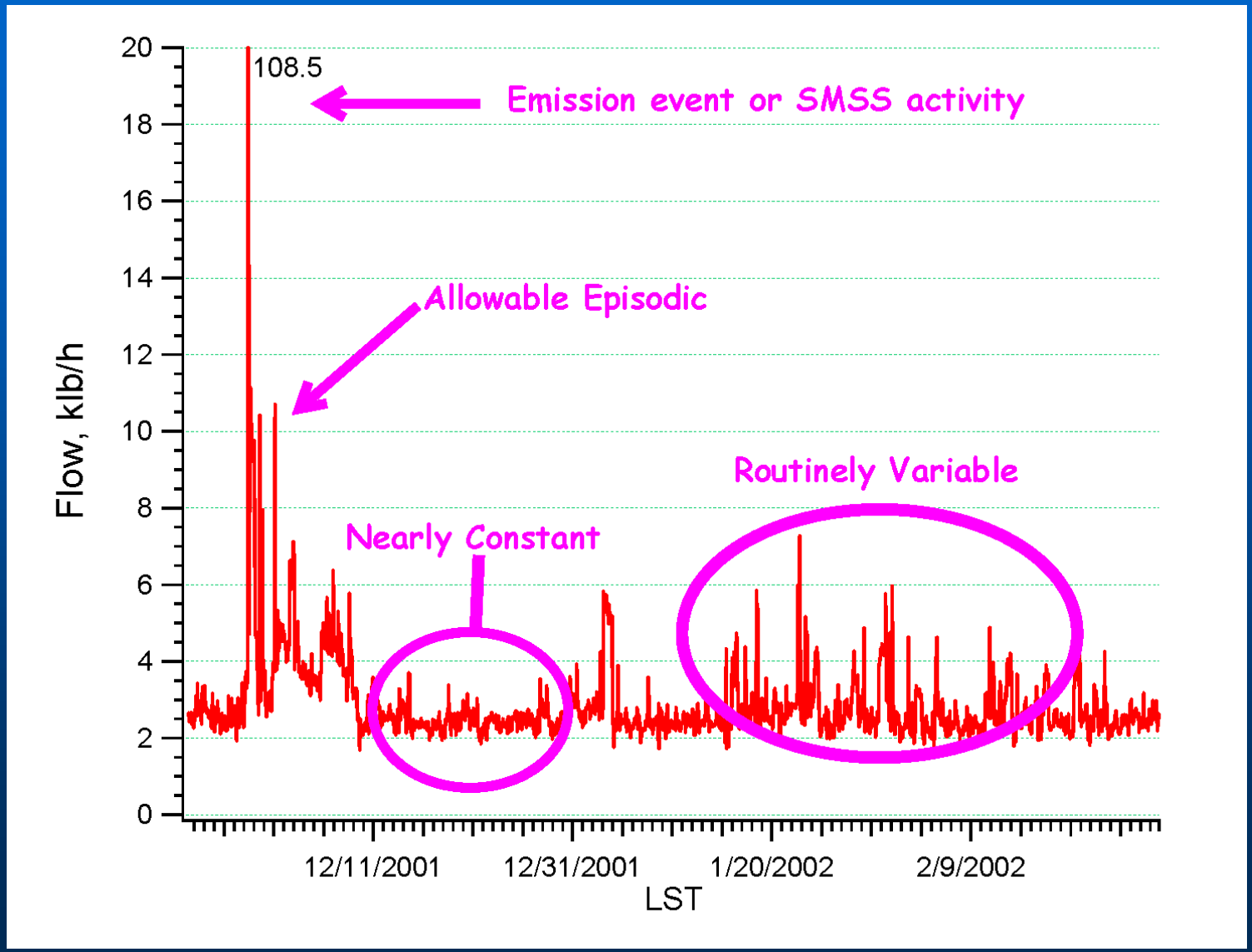
Jeffries, 2003

Hourly Timeseries for a Major Flare



MCCG, 2002

Types of Variance for a Major Flare

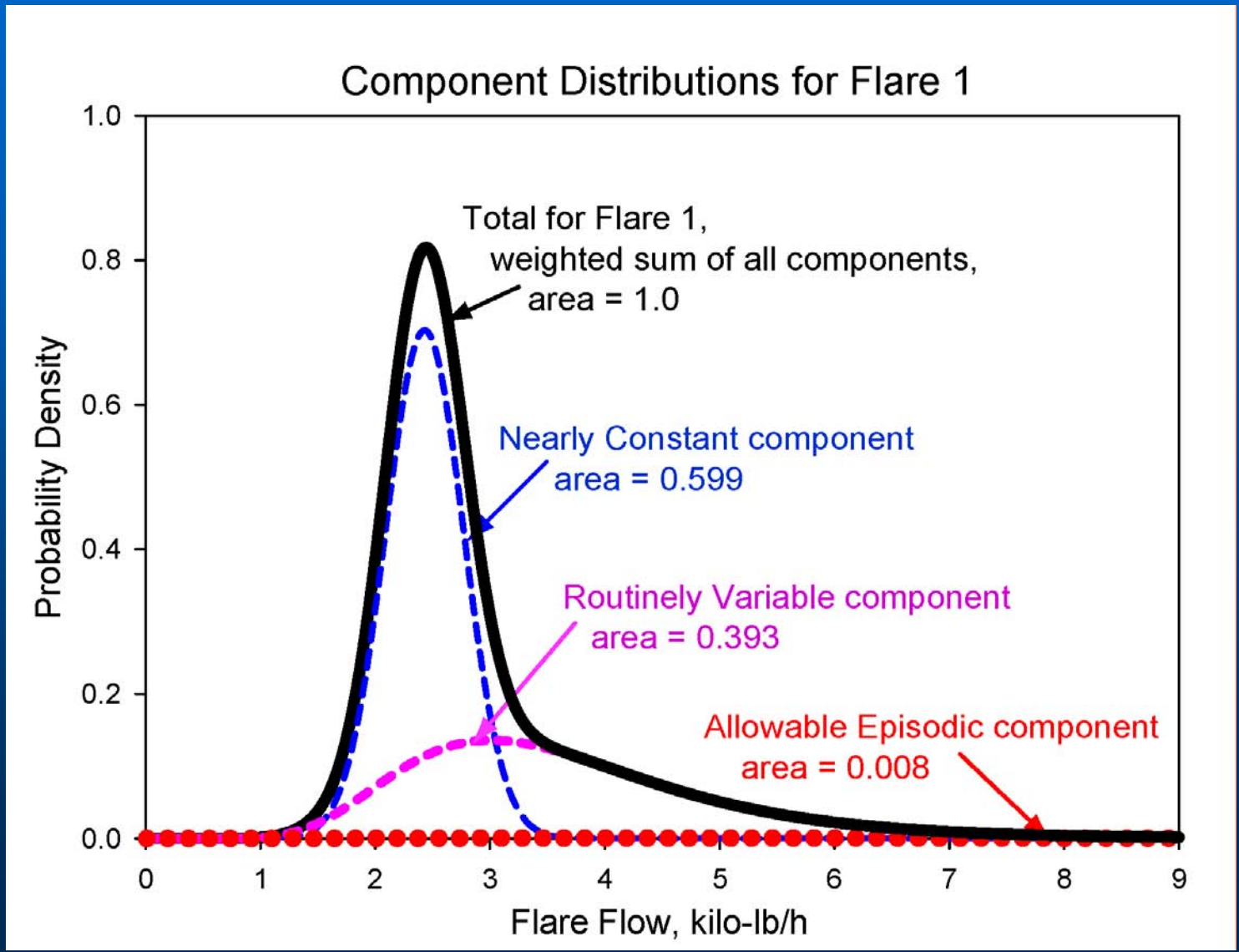


Symons, Webster, Pennington, 2003

Permitted VOC Variable Emissions

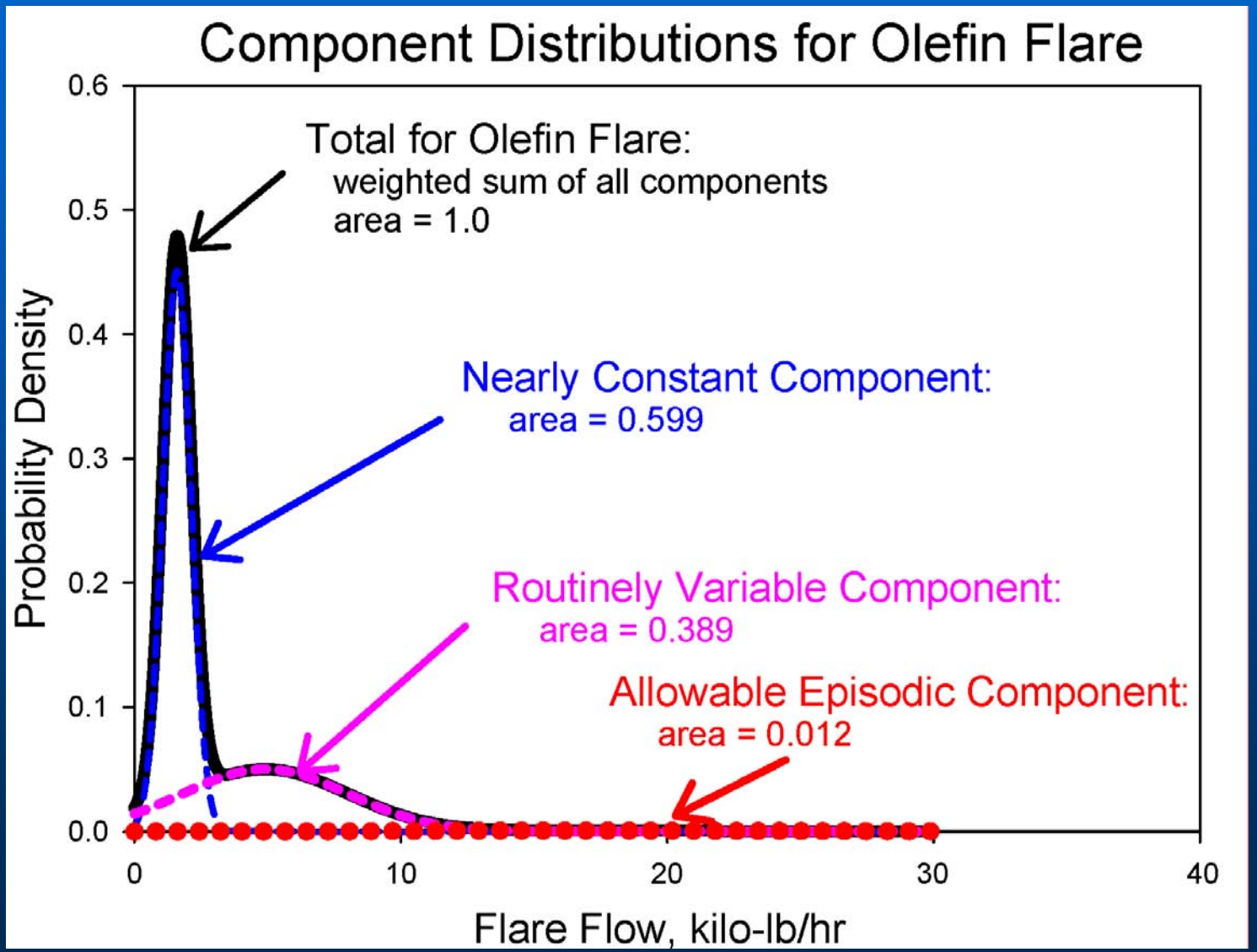
- The “nearly constant”, “routinely variable”, and “allowable episodic” emissions are included in an account’s annual and daily permitted emissions.
- Startup, shutdown, and maintenance activities are not in the permit and require TCEQ permission for “planned” emissions events.
- Unplanned emission events have to be reported if above the daily permitted value plus a “Reportable Quantity”

Combined PDF for Flare 1



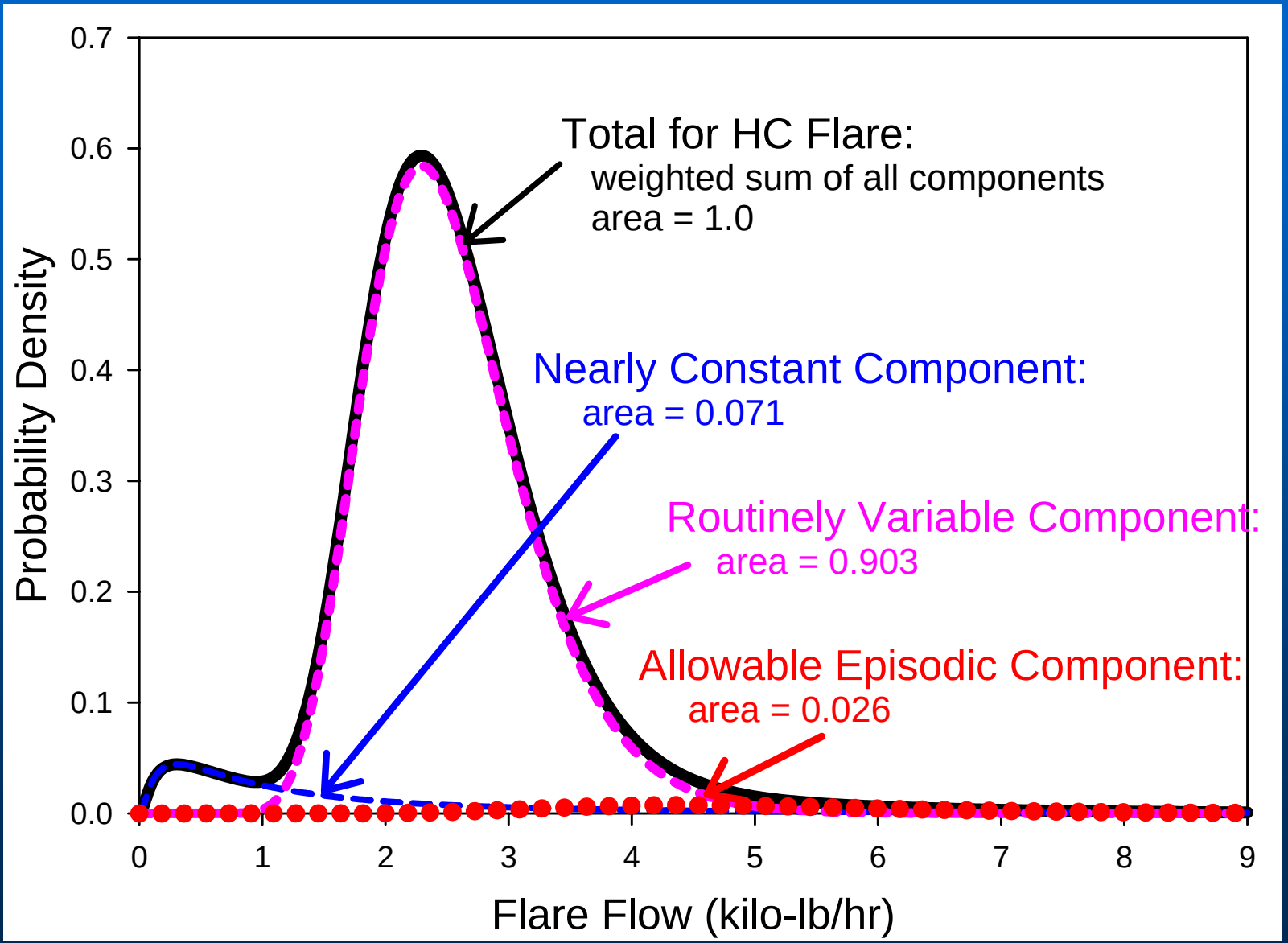
Symons, Webster, Pennington, 2003

Combined PDF for Olefin Flare

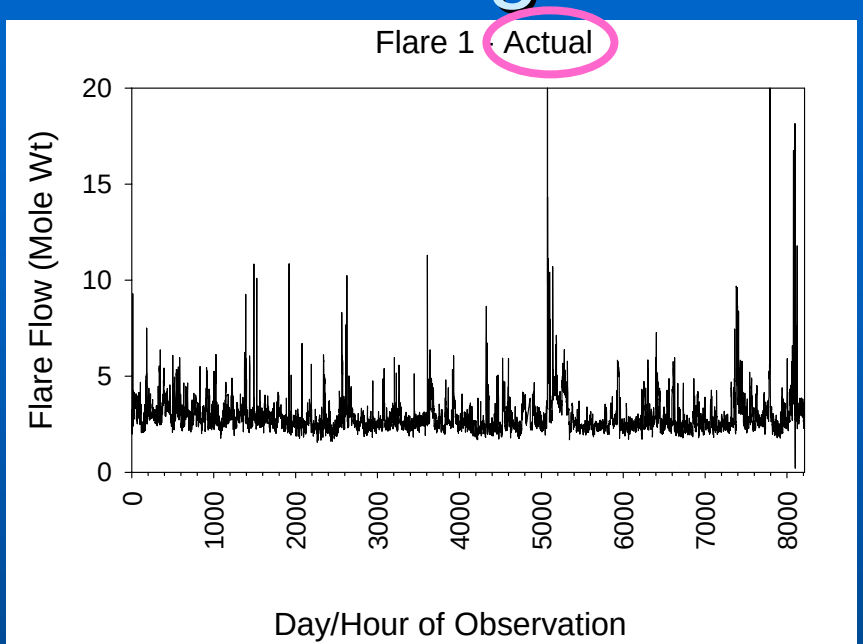


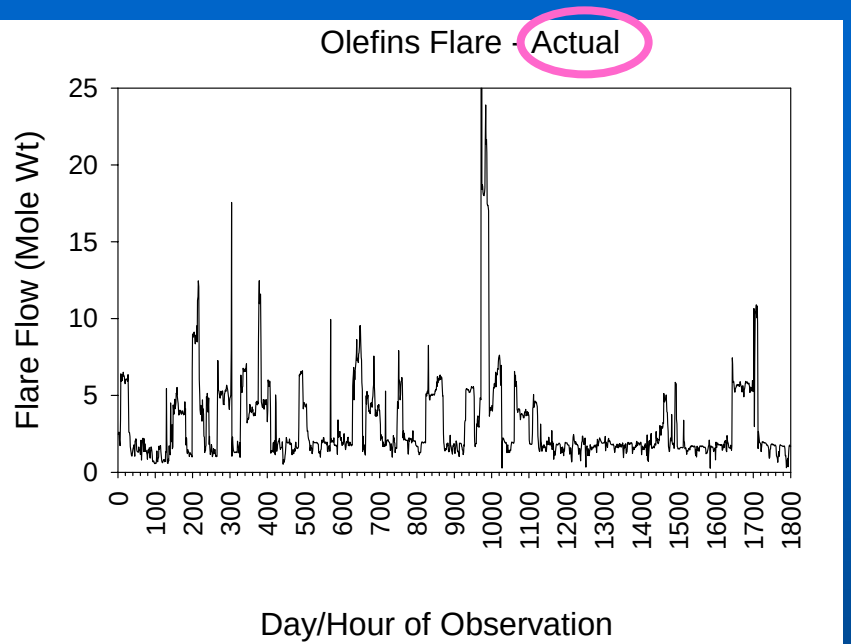
Symons, Webster, Pennington, 2003

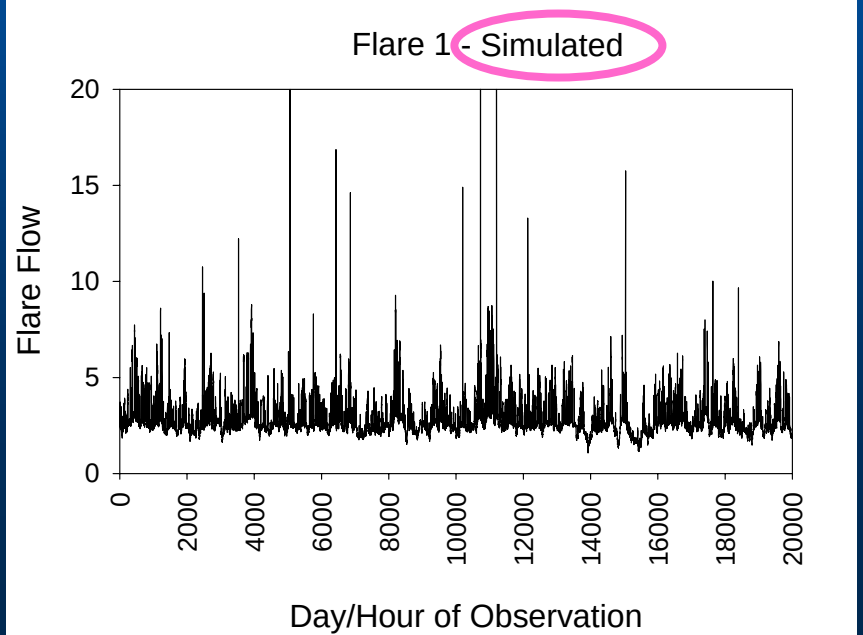
Combined PDF for HC Flare

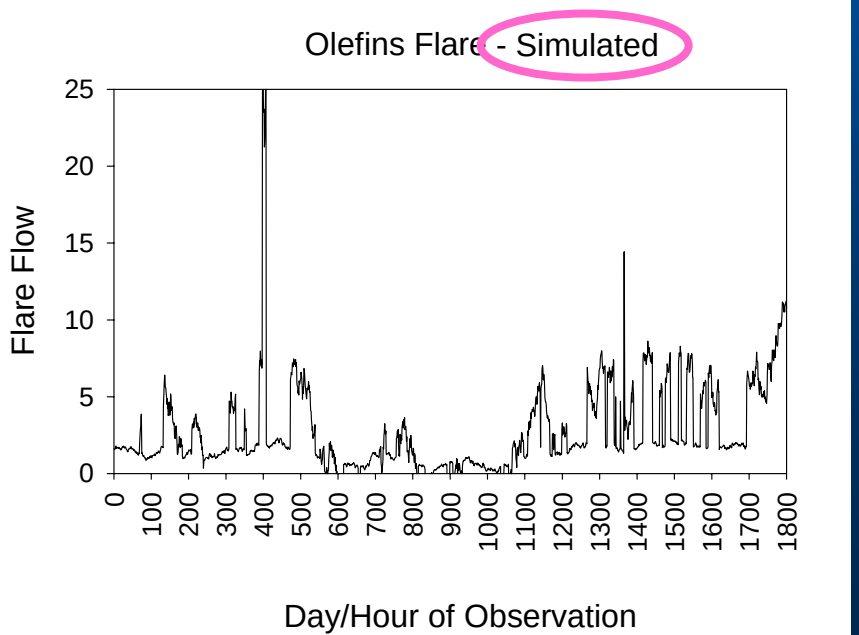


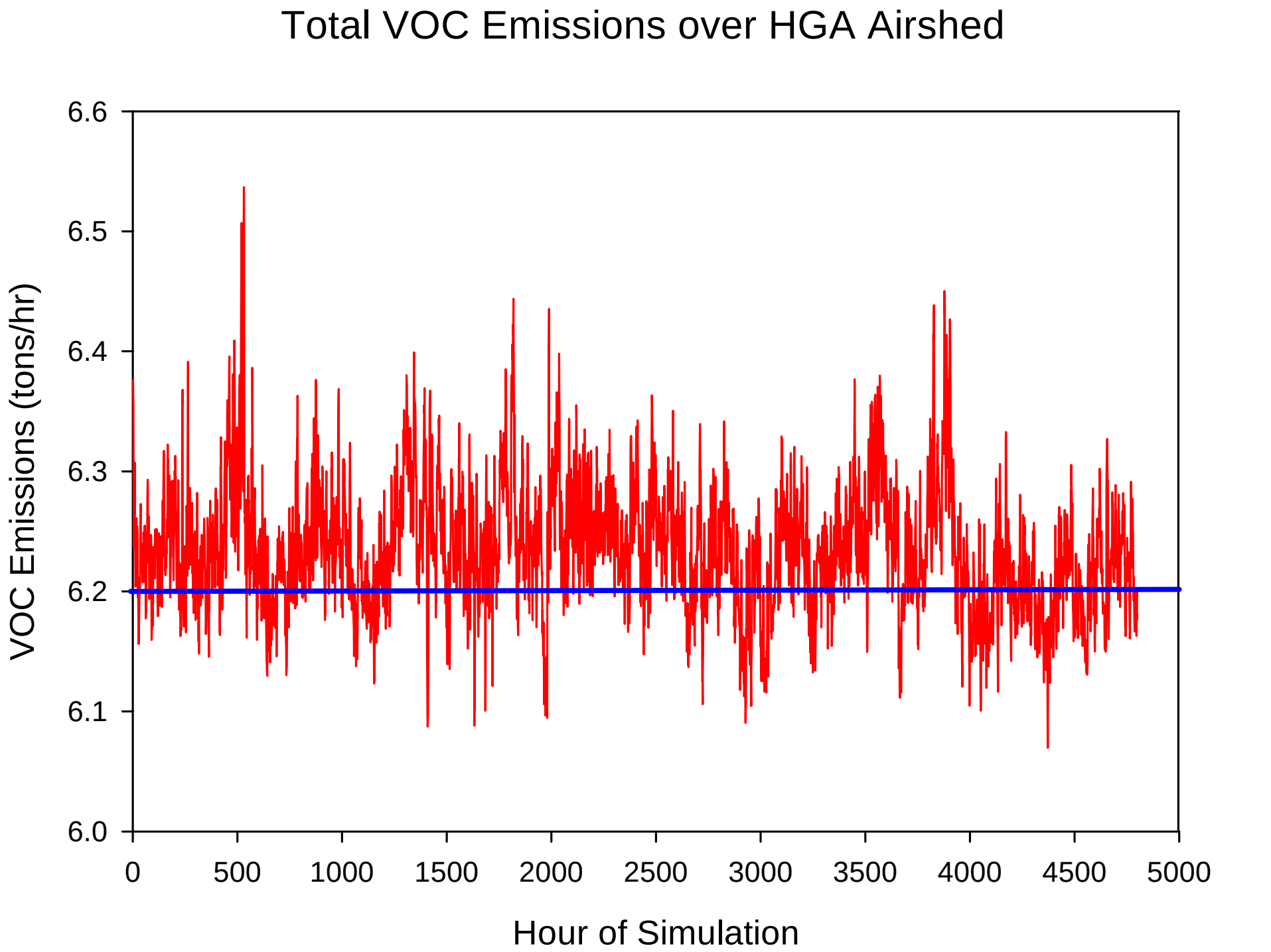
Using PDFs to Simulate Flares

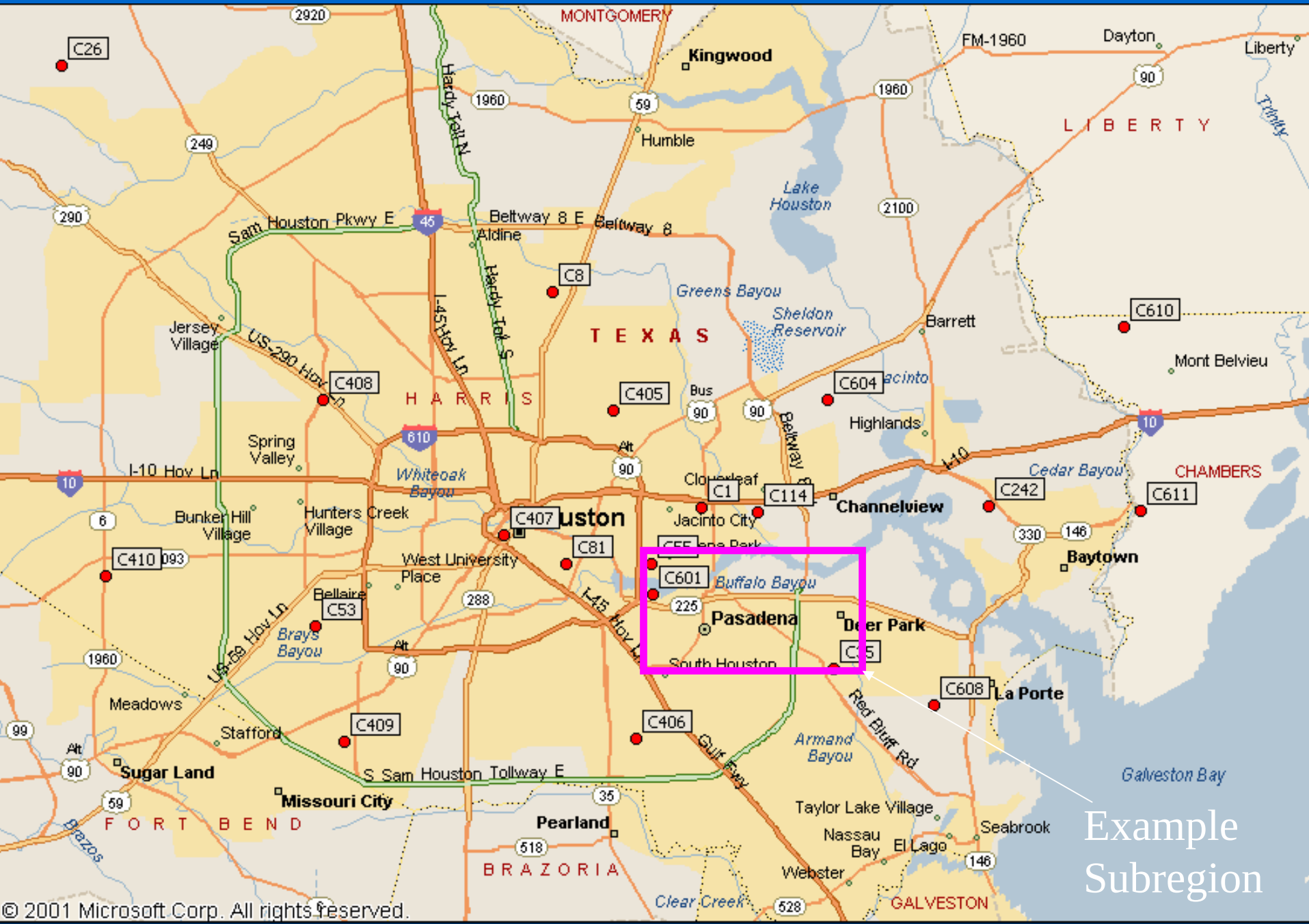









Total VOC Emissions over HGA Airshed
VOC Emissions (tons/hr)
6.6
6.5
6.4
6.3
6.2
6.1
6.0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Hour of Simulation


C26
2920
MONTGOMERY
Kingwood
FM-1960
Dayton
Liberty
90
1960
59
Humble
LIBERTY
Trinity
Hardy Toll N
249
Lake Houston
2100
290
Sam Houston Pkwy E
45
Beltway 8 E
Beltway 8
Aldine
C8
Greens Bayou
Sheldon Reservoir
TEXAS
Barrett
C610
Jersey Village
US-290 Hov Ln
I-45 Hov Ln
Hardy Toll S
C408
C405
Bus
90
C604
Mont Belvieu
HARRIS
Highlands
610
10
Spring Valley
Alt
90
Beltway 8
I-10
I-10 Hov Ln
Whiteoak Bayou
Cloverleaf
C1
C114
Channelview
Cedar Bayou
CHAMBERS
C242
C611
6
Bunker Hill Village
Hunters Creek Village
C407
uston
Jacinto City
C81
330
146
Baytown
C410
093
West University Place
C601
Buffalo Bayou
Bellaire
C53
288
225
Pasadena
Deer Park
US-59 Hov Ln
L-45 Hov Ln
Brays Bayou
Alt
90
South Houston
C608
La Porte
1960
Meadows
C409
C406
Red Bluff Rd
99
Stafford
Gulf Fwy
Armand Bayou
Galveston Bay
Alt
90
Sugar Land
S Sam Houston Tollway E
59
Missouri City
35
Taylor Lake Village
Seabrook
FORT BEND
Pearland
Nassau Bay
El Lago
146
Brazos
518
BRAZORIA
Webster
Clear Creek
528
GALVESTON
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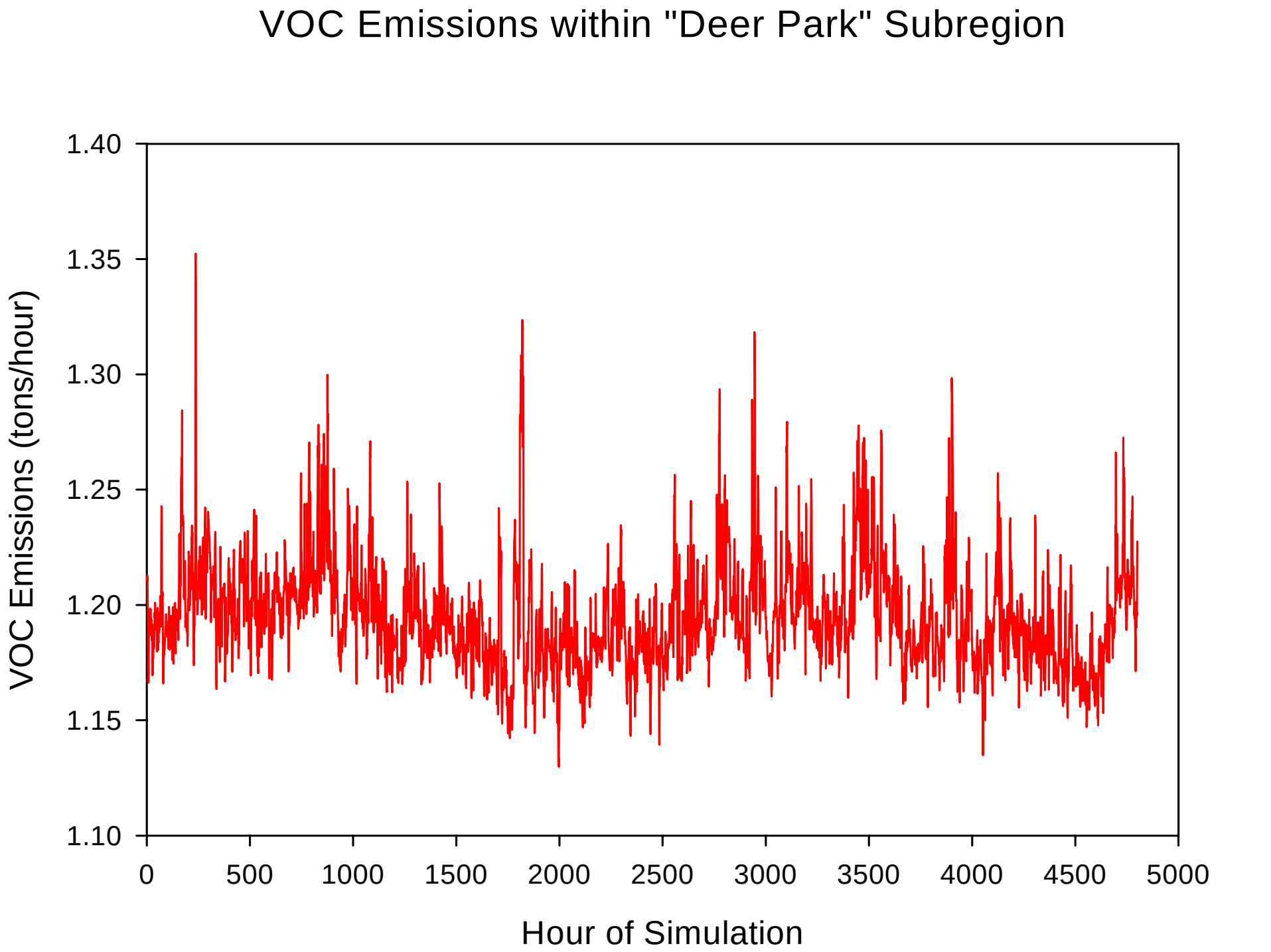
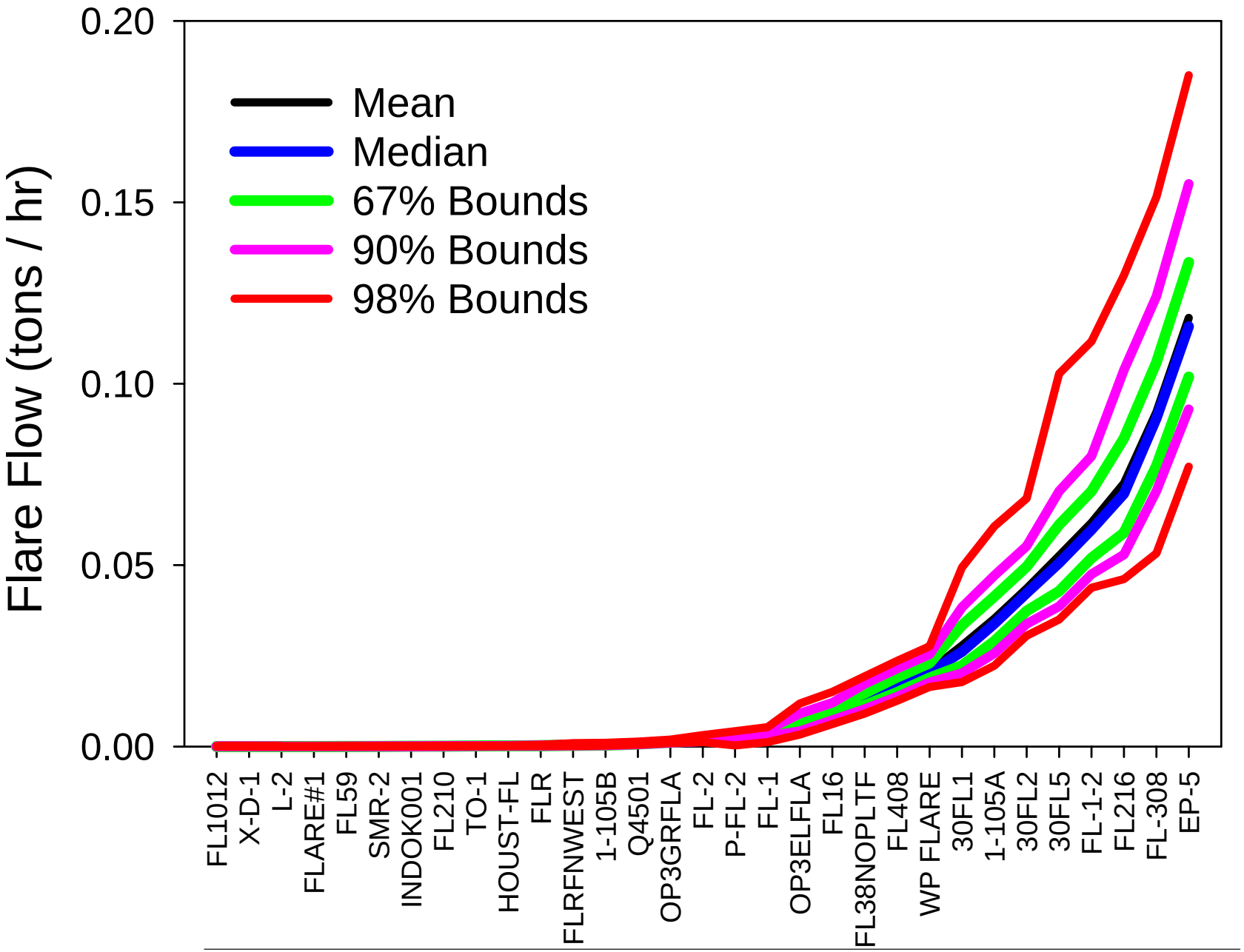
Example Subregion


VOC Emissions within "Deer Park" Subregion
VOC Emissions (tons/hour)
1.40
1.35
1.30
1.25
1.20
1.15
1.10
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Hour of Simulation

Cumulative Emissions from Flares within "Deer Park" Region



Permitted VOC Variable Emissions

- More work is needed to link physical causes to the observed FL and CT variable emissions. More measurements are needed to establish a “library” of typical behavior for these sources.
- Analysis of data from fairly representative sources suggest that multiple PDFs are needed to describe the long term source behavior. Further information is needed on duration within each component and the transition frequency among components.
- Simulations using a variety of PDFs and the annual AQ modeling Point Source EI suggest that the overall emissions variability from these permitted operations of facilities can result in a variation of about 5-10% of the entire annual EI.
- If a smaller region that contains several large sources is examined, the permitted emissions variability could cause some HRVOC concentrations to approximately double about once a month.

What is an emission event?

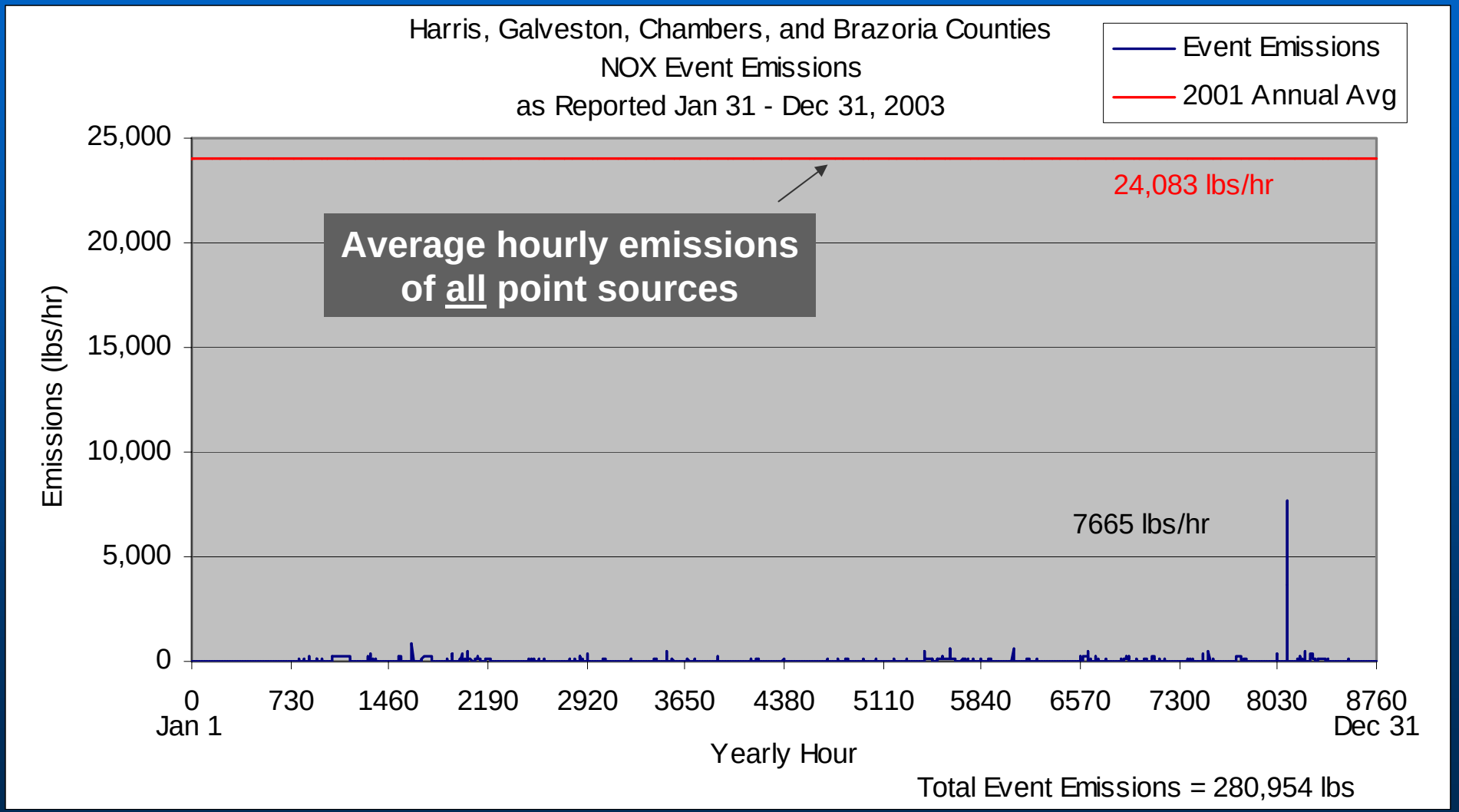
Effective September 12, 2002, per Texas Administrative Code (TAC) Title 30 Chapter 101, reportable quantities were reduced from **5000** lbs to **100** lbs for most compounds in the Houston/Galveston ozone non-attainment area. Section 101.1, paragraph (83) defines a reportable emissions event as "Any emissions event which, in any 24-hour period, results in an unauthorized emission equal to or in excess of the reportable quantity…".

In addition, Texas House Bill (HB) 2912 requires that air emission incidents be filed electronically and be available in a publicly available database.

First Year HRVOC Event Data

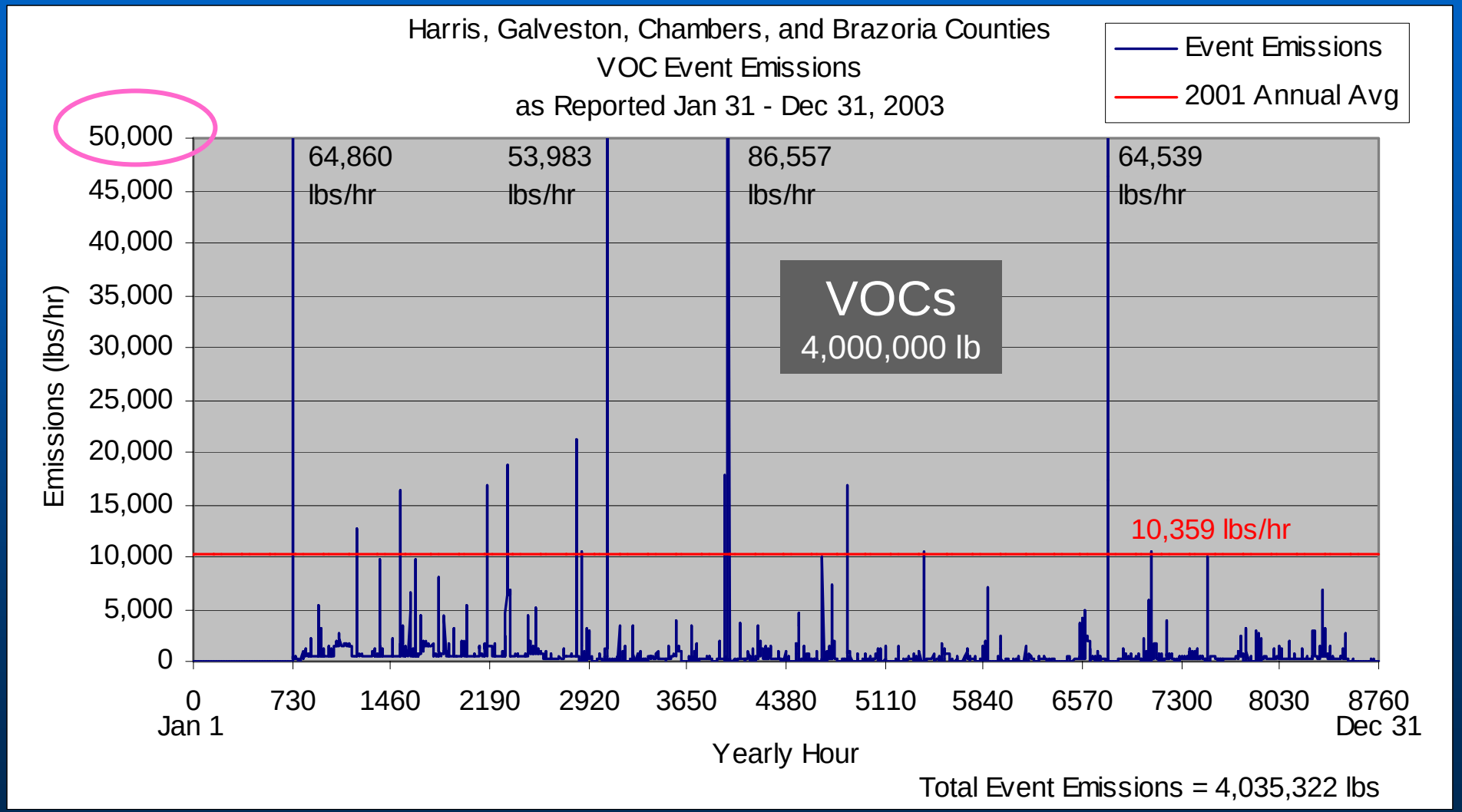
County	All Events	HRVOC Events	Event HRVOCs	
			lbs	tons
Harris	934	423	816,961	408
Brazoria	331	187	759,853	380
Galveston	329	86	69,229	35
Chambers	53	13	20,497	10
4 County Total	1,647	709	1,666,540	833
Fort Bend	40			
Montgomery	19			
Liberty	1	1	558	<1
Waller	2			
HGA Total	1,709	710	1,667,098	833
Five Others	18	1	1	<1
Region 12 Total	1,727	711	1,667,099	833

NOx event emissions are small compared to annual average emissions



First 11 Months of reporting

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

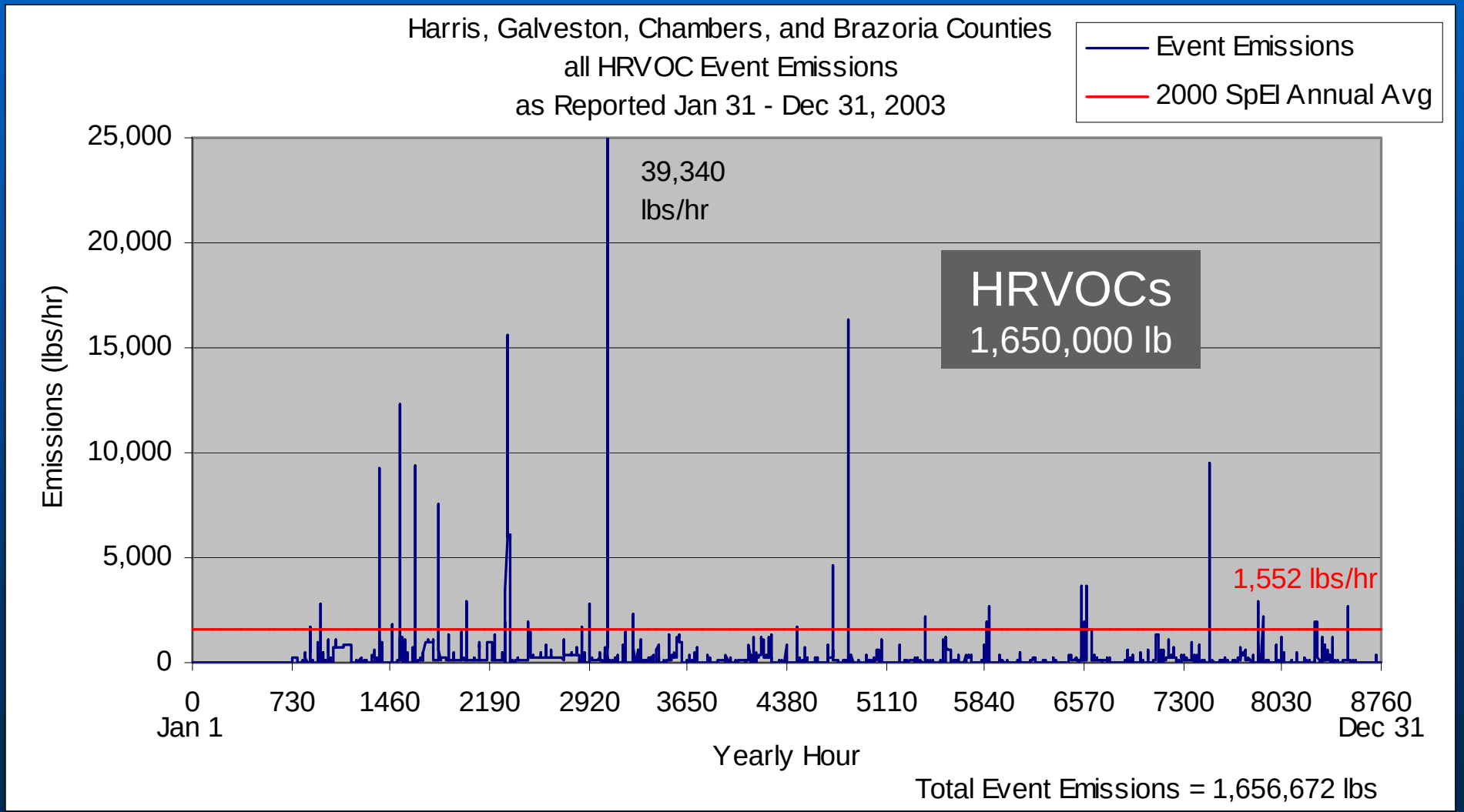


First 11 Months of reporting

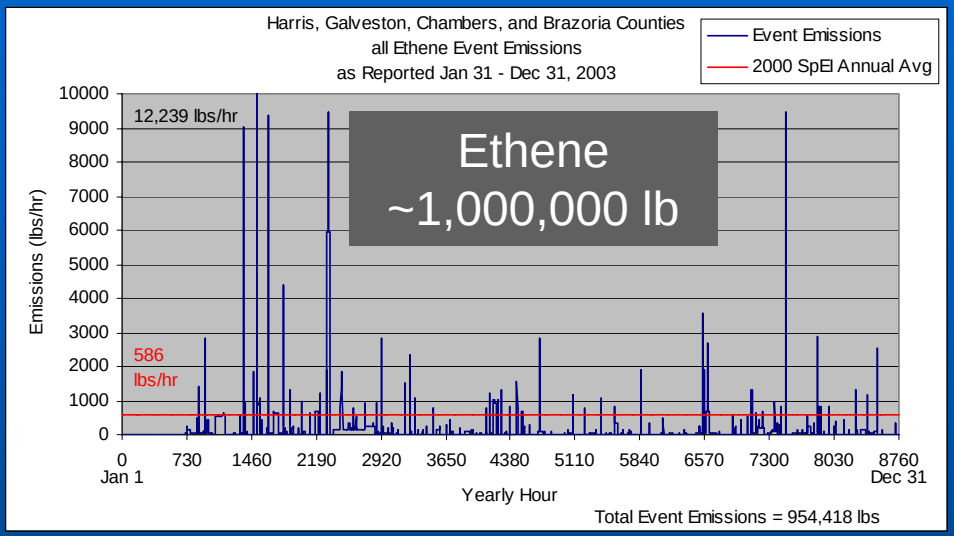
VOC Events and Averages

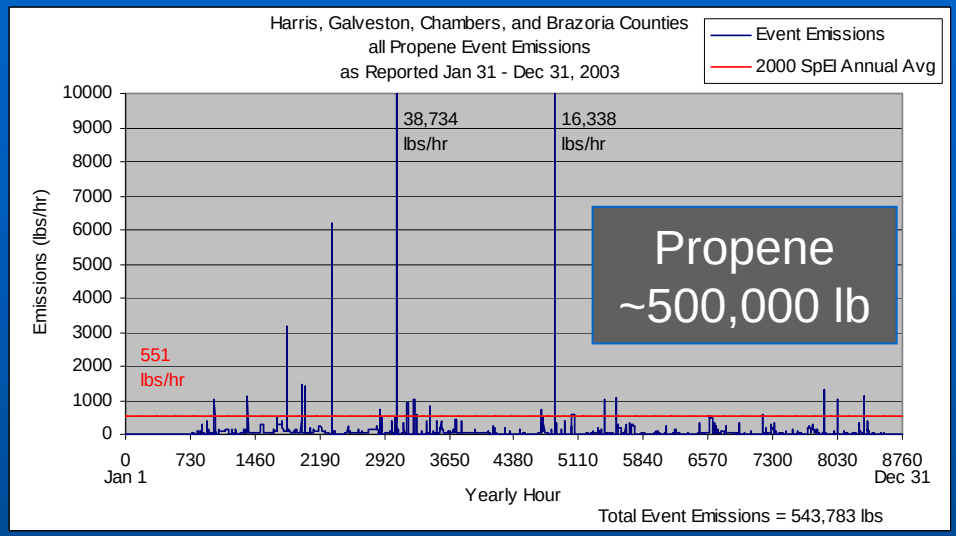
- Event total mass of over **4** million pounds (2000 tons) contributes 4% to the 45,000 tons of VOC emitted over a single year from point sources in the four counties.
- **14** times (18 hours) during the eleven-month period, an event emission exceed the annual average for all facilities in the region.
- **4** times in 11 months, the flow rate of event emissions was more than **5X** the annual average with a maximum of 86,000 lbs/hr.

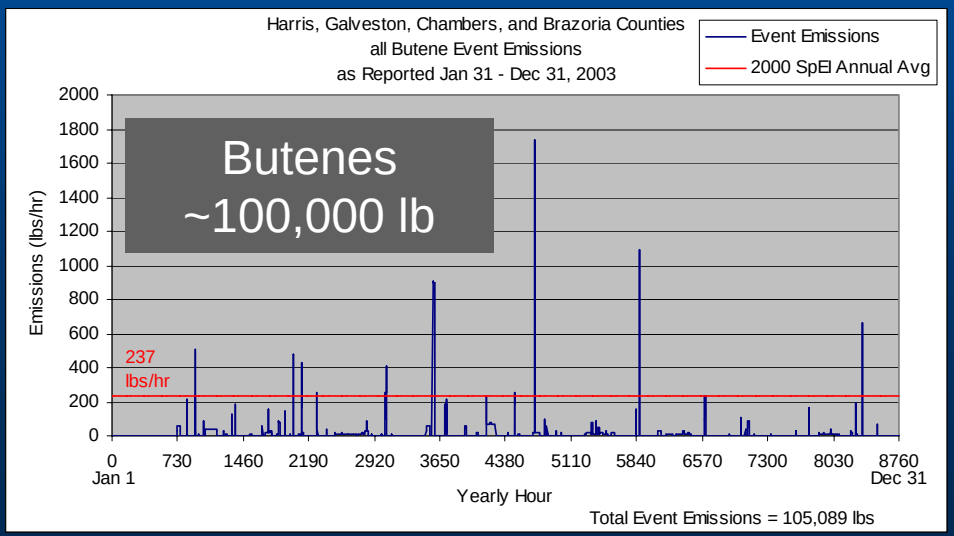
HRVOC emissions can also be large relative to annual average emissions

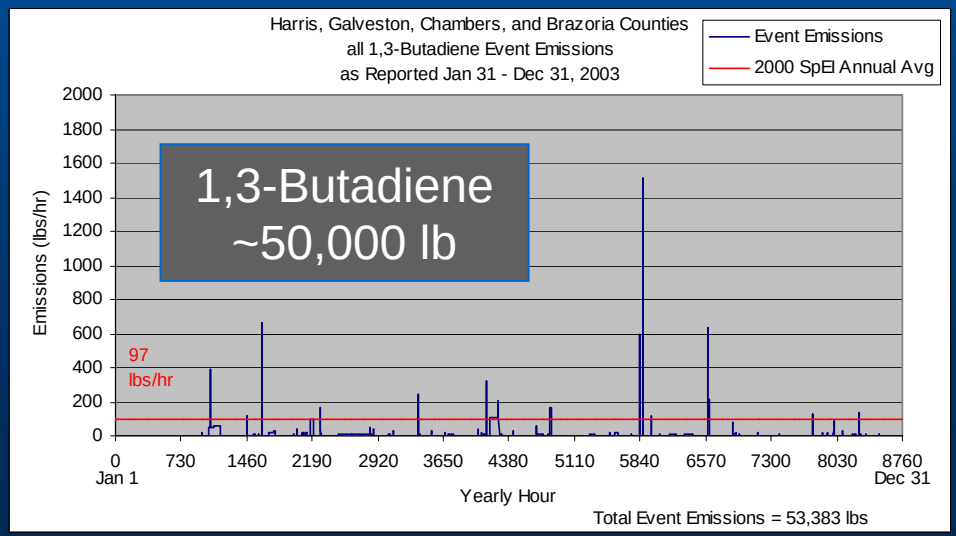


Four Major HRVOCs





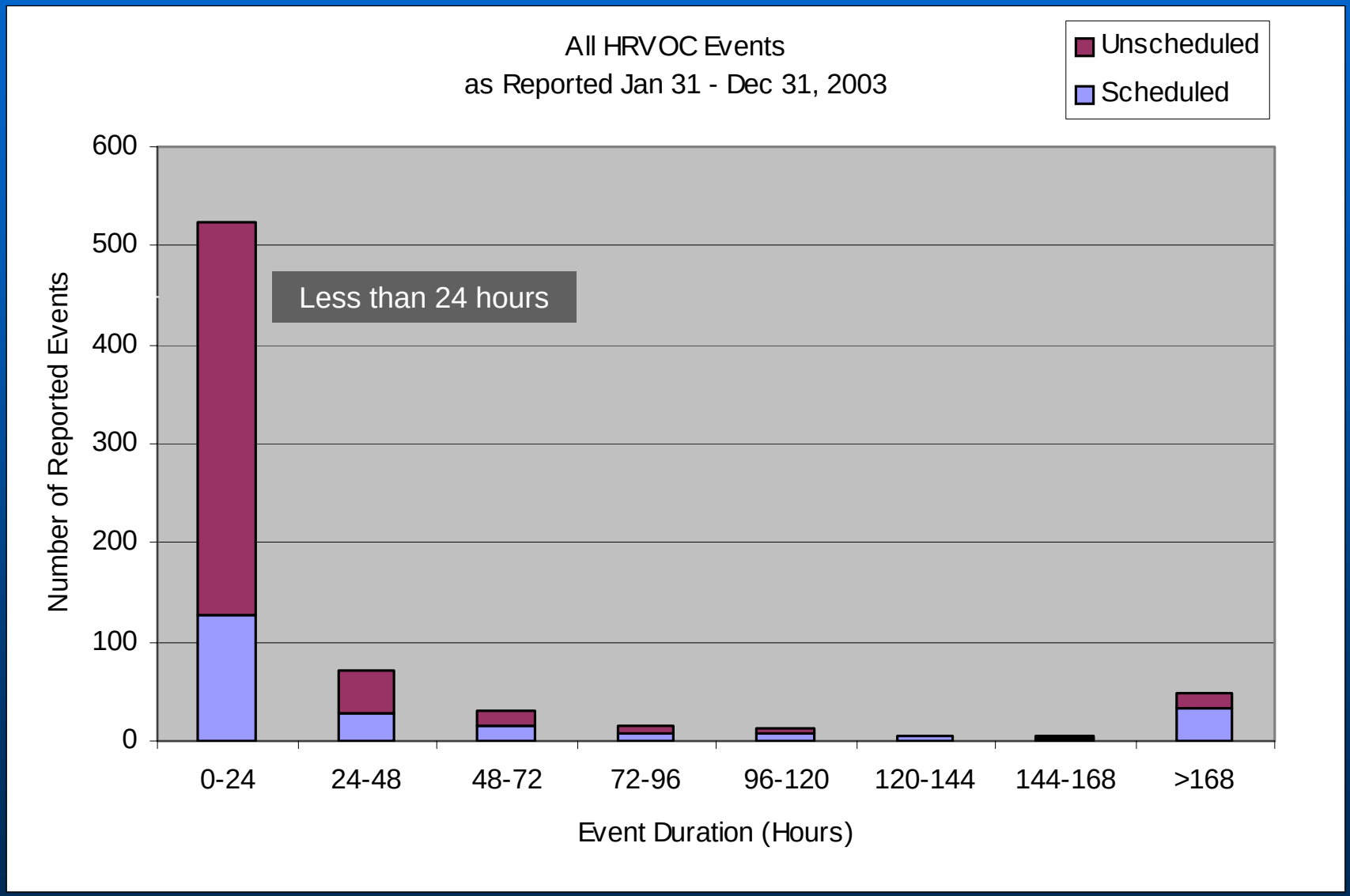




HRVOC Events and Averages

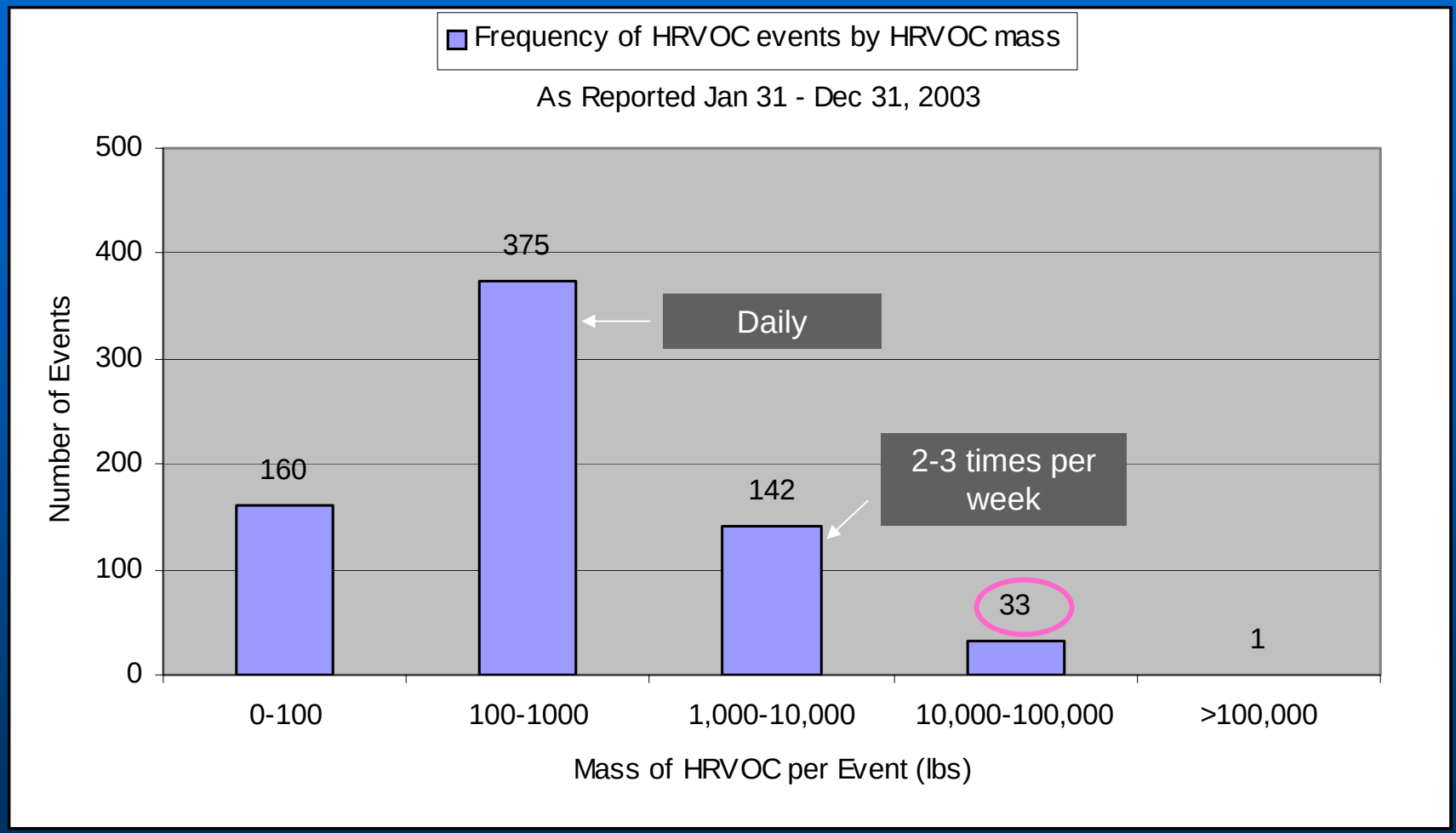
- Total mass of over **1.6** millions pounds (830 tons) is **~12%** of the 6800 tons of HRVOC emitted over a single year from point sources in the four counties.
- **29** times (115 hours) during the eleven-month period, an event emission exceed the annual average.
- **7** times in 11 months, the flow rate of an event emission was more than **5X** the annual average with a maximum of 39,000 lbs/hr.

Events: Time, Space, and Composition



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

Events: Time, Space, and Composition



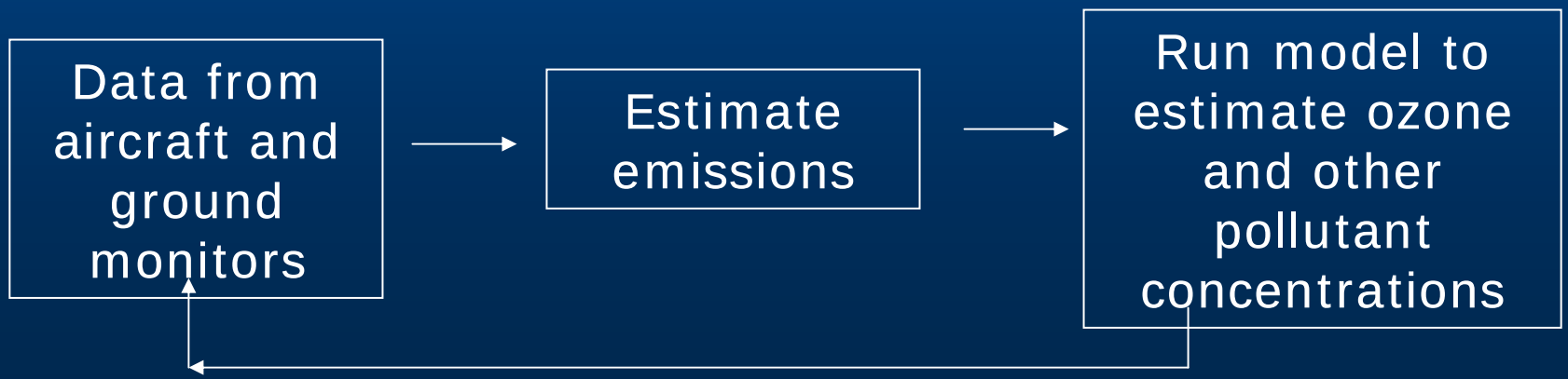
Largest number of events is from events of **100-1000 lb**, but most of the mass is associated with events **>1000 lb**, which occur, on average, several times per week

Summary of Event Magnitudes and Frequencies

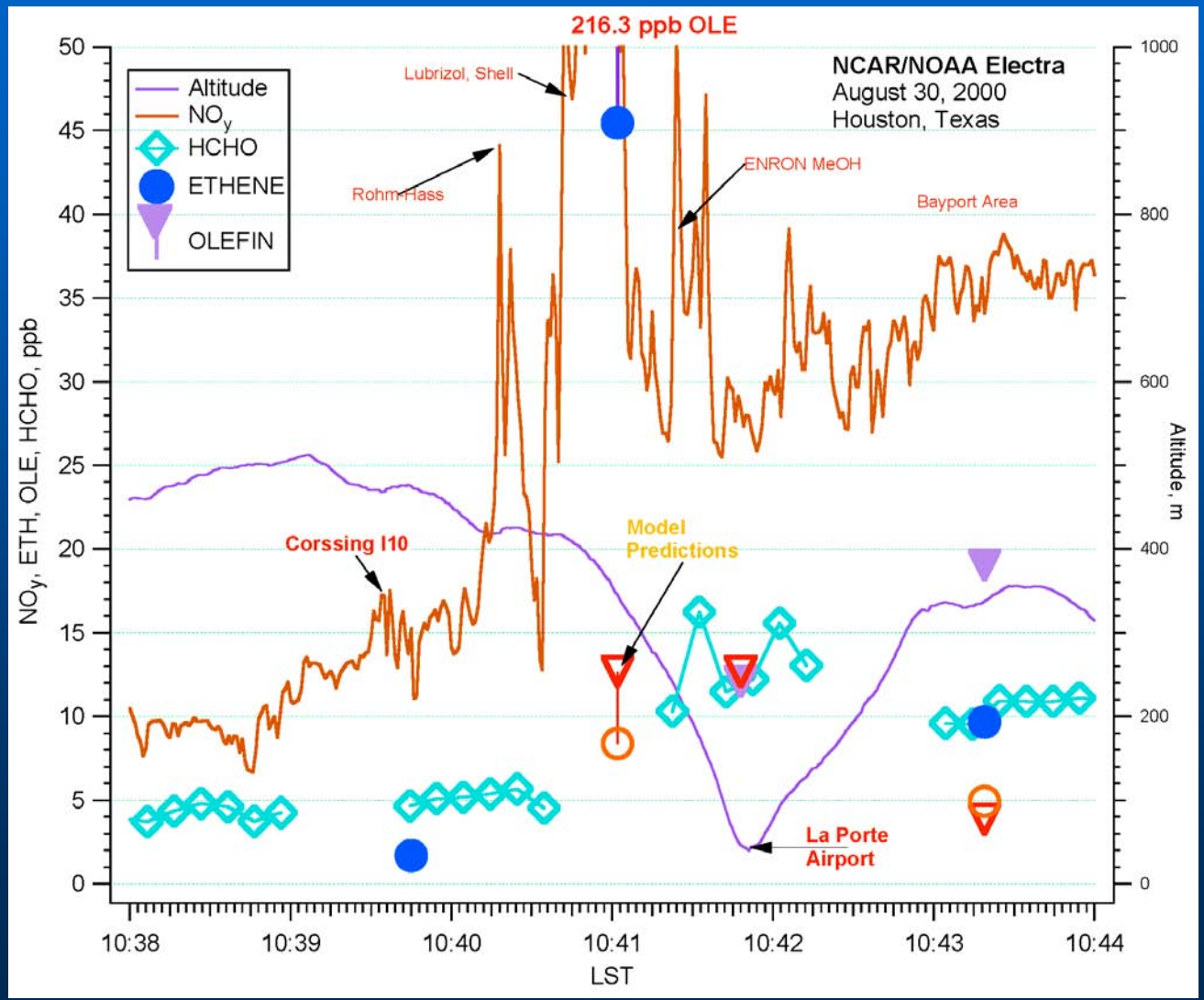
- Events with emissions of more than 1000 pounds of HRVOCs occur several times per week, on average
- Many are relatively short (well under one hour in duration)
- Among the HRVOCs, ethene and propene dominate
- Events occur primarily in Harris and Brazoria counties at chemical manufacturing facilities

Modeling Events With CAMx 4.3

- Standard TCEQ modeling did not include events in base inventory.
- Data from unprecedented set of aircraft and monitoring data was produced in the the Texas Air Quality Study
- Better model performance than any previous attempt to model Houston-Galveston area



Observational Evidence 8/30



NOAA aircraft, flying to the east of Deer Park at 640 m AGL, detected very high concentrations of propene (up to 217 ppb) and ethene (45 ppb) at 1042 CST. Plume is about one kilometer wide.

Add Event Emissions to CAMx (1-km)

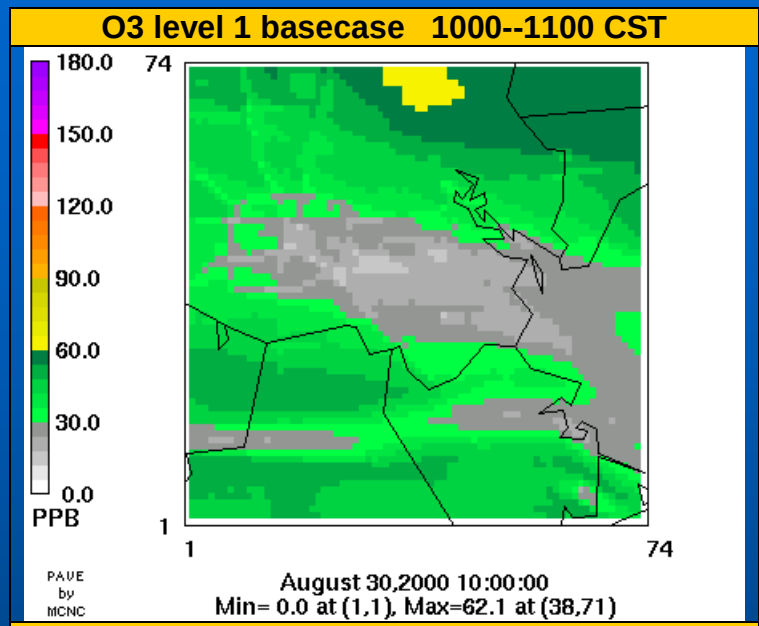
Single 1-km cell
- 1,450 lb/h ethylene
- 10,188 lb/h OLE+PAR

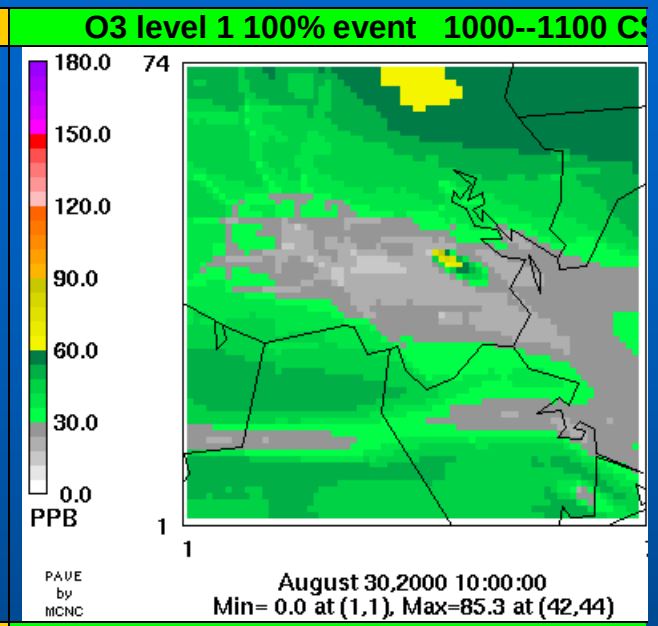
Start at 1000

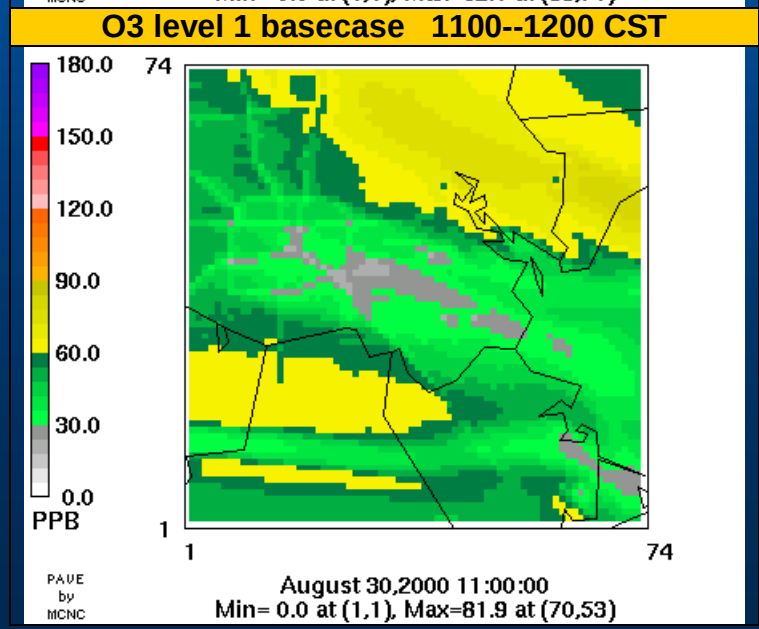
End at 1200

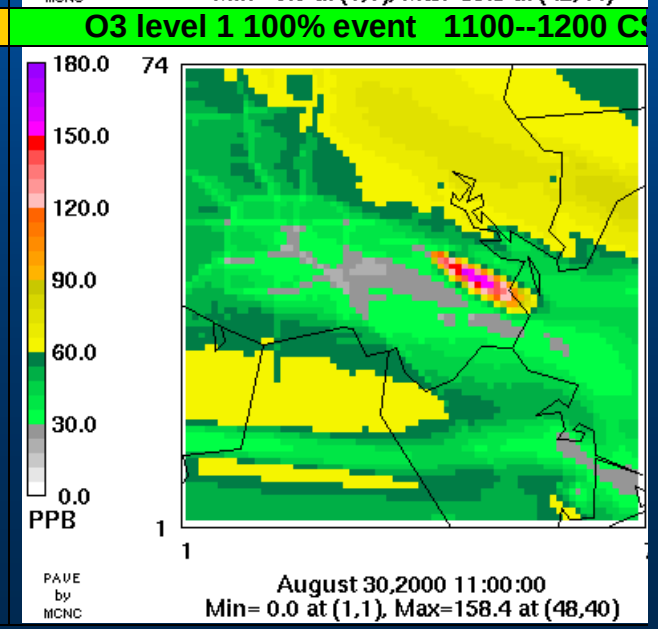
Base
- 81.9 ppb O3

Event
- 158.4 ppb O3









Add Event Emissions to CAMx, II

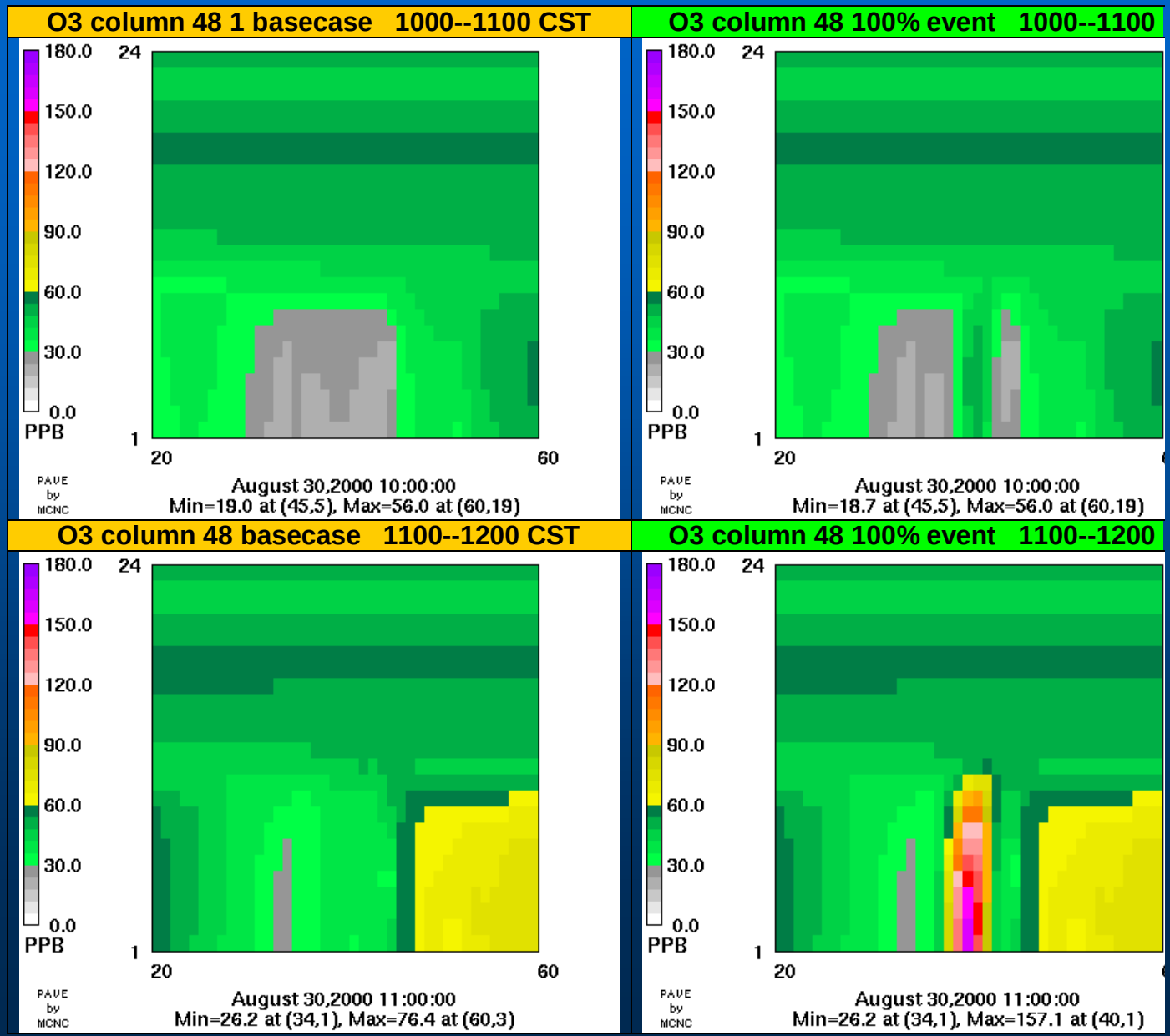
Vertical Slice

Start at 1000

End at 1200

Base
76.4 ppb O3

Event
157.1 ppb O3

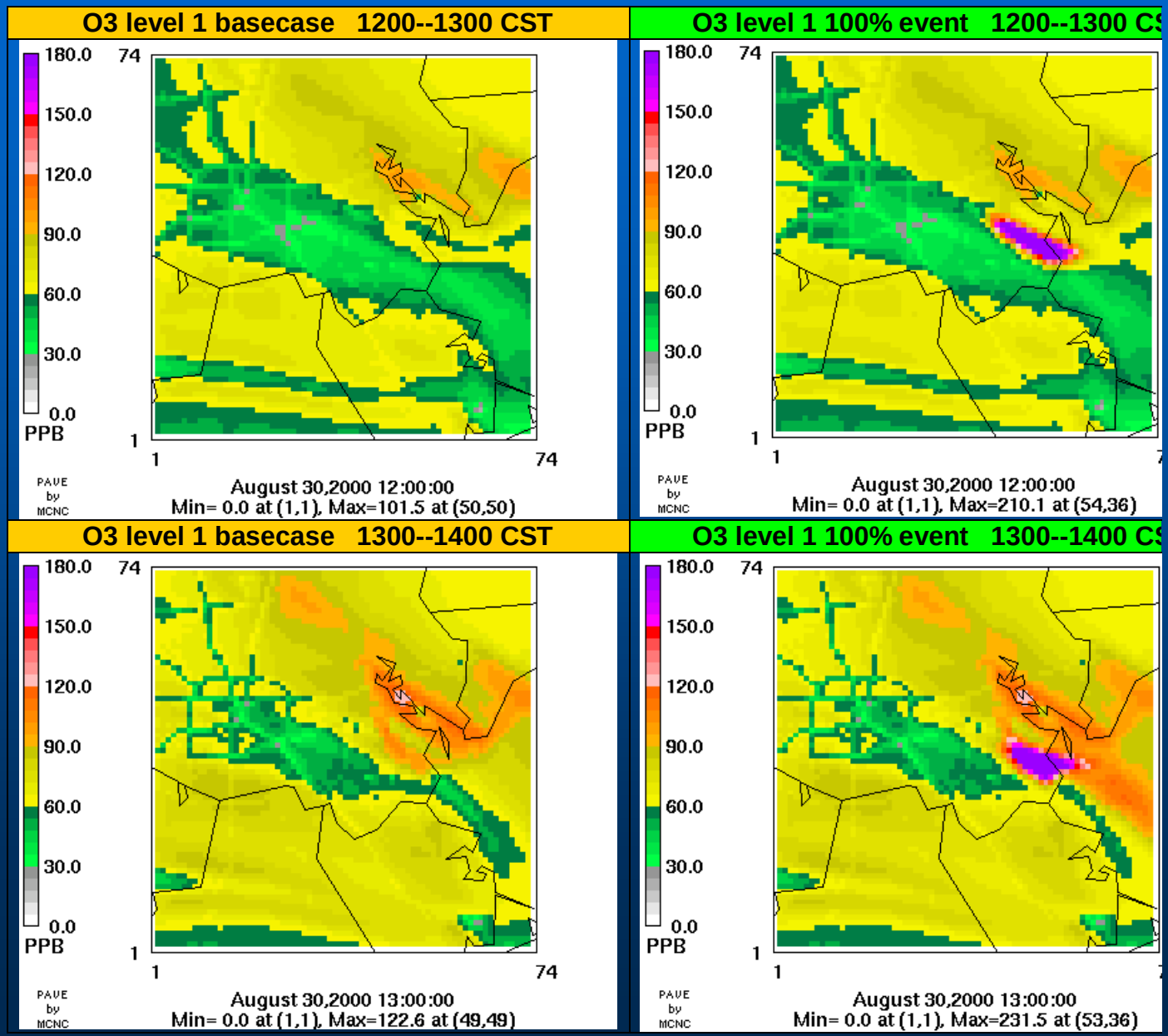


Add Event Emissions to CAMx, III

Layer One

Start at 1200

End at 1400



Base
122.6 ppb O3

Event
231.5 ppb O3

Add Event Emissions to CAMx, IV

Layer One
Layer Nine

Start at 1600

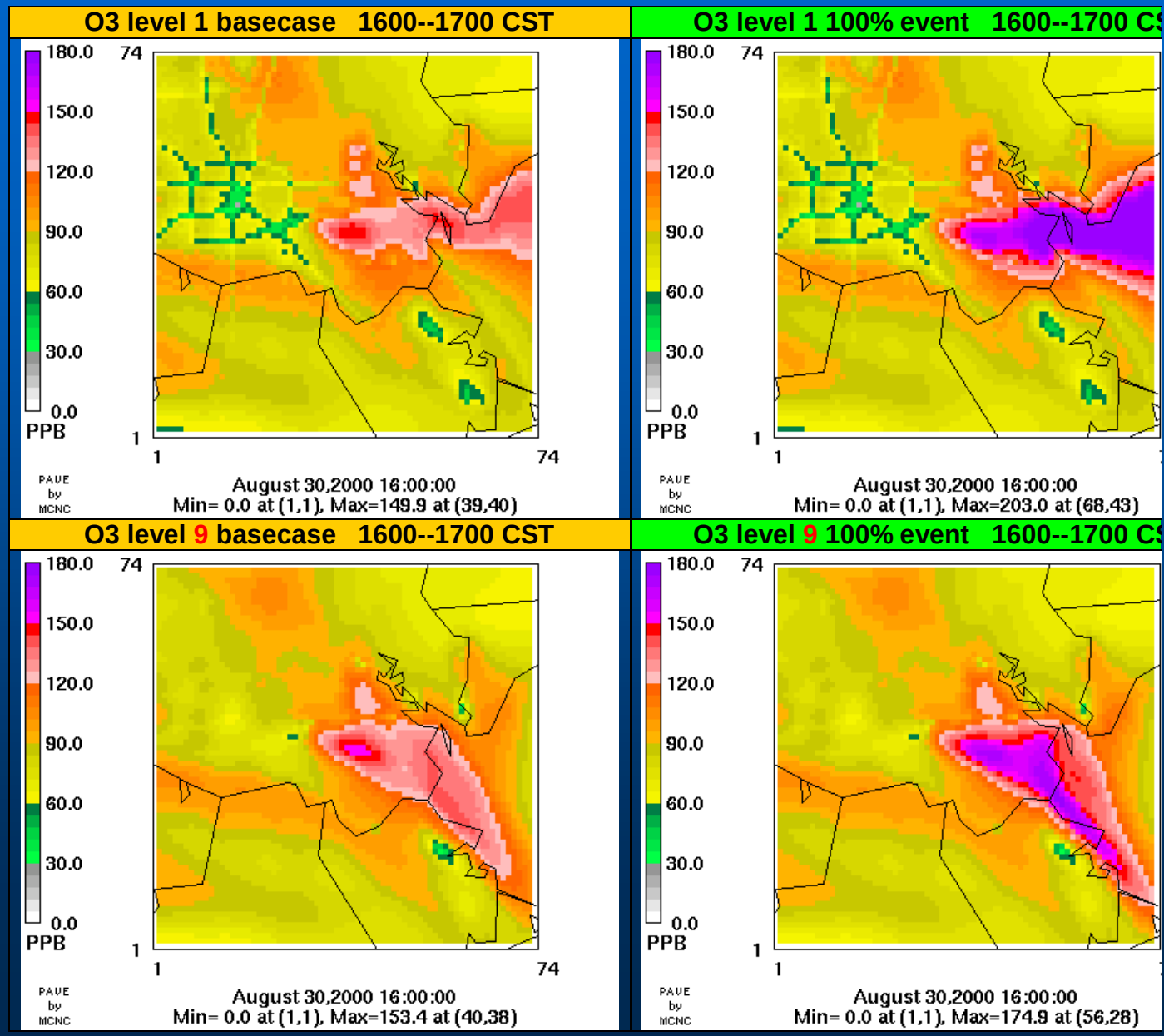
End at 1700

Base (L1)
149.9 ppb O3

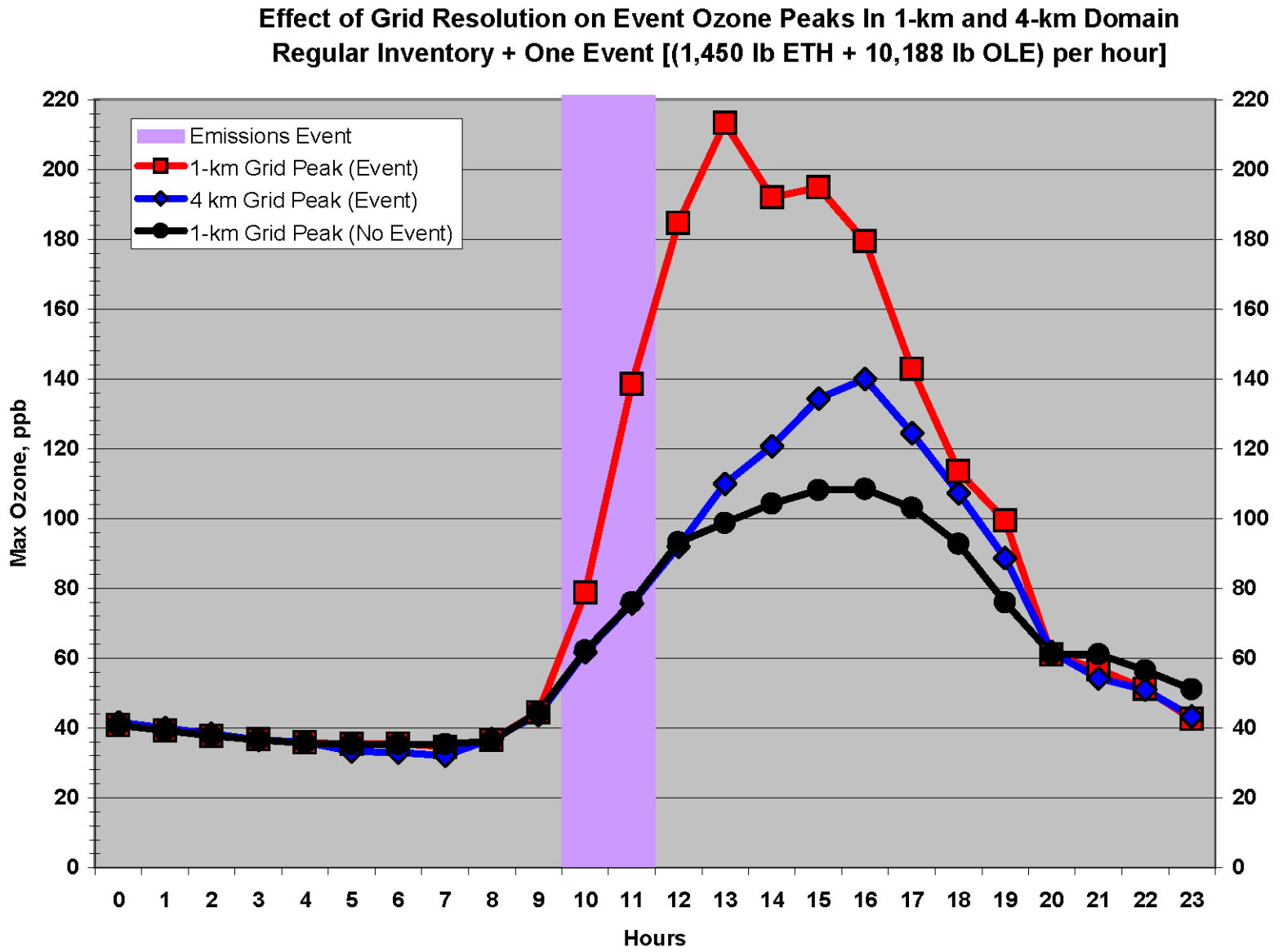
Event
203.0 ppb O3

Base (L9)
153.4 ppb O3

Event
174.9 ppb O3



Add Event Emissions to CAMx, V



Emissions Event Summary

- Emission events, sometimes impact peak ozone concentrations; when they do, a variety of air quality models suggest that the relationship of the event emission mass to the increase in peak ozone concentration is linear, up to at a mass release of at least 5000 lb
- The magnitude of the impact (increase in peak ozone per pound of event emission) depends on the location of the release, time of the release, and other emissions – values range between 1 and 4 ppb per 1000 lb of release
- Under worst case conditions, emission events are roughly additive for 2-3 hour periods (i.e., a 1000 pound total release over 2-3 hours can have up to the same impact as a 1000 pound release over 1 hour)
- The time windows during which peak ozone concentrations are most sensitive to event emissions is relatively narrow
- Statistics on the frequency of event emissions and the frequency of conditions conducive to event emissions impacting peak ozone can be used in attainment demonstrations