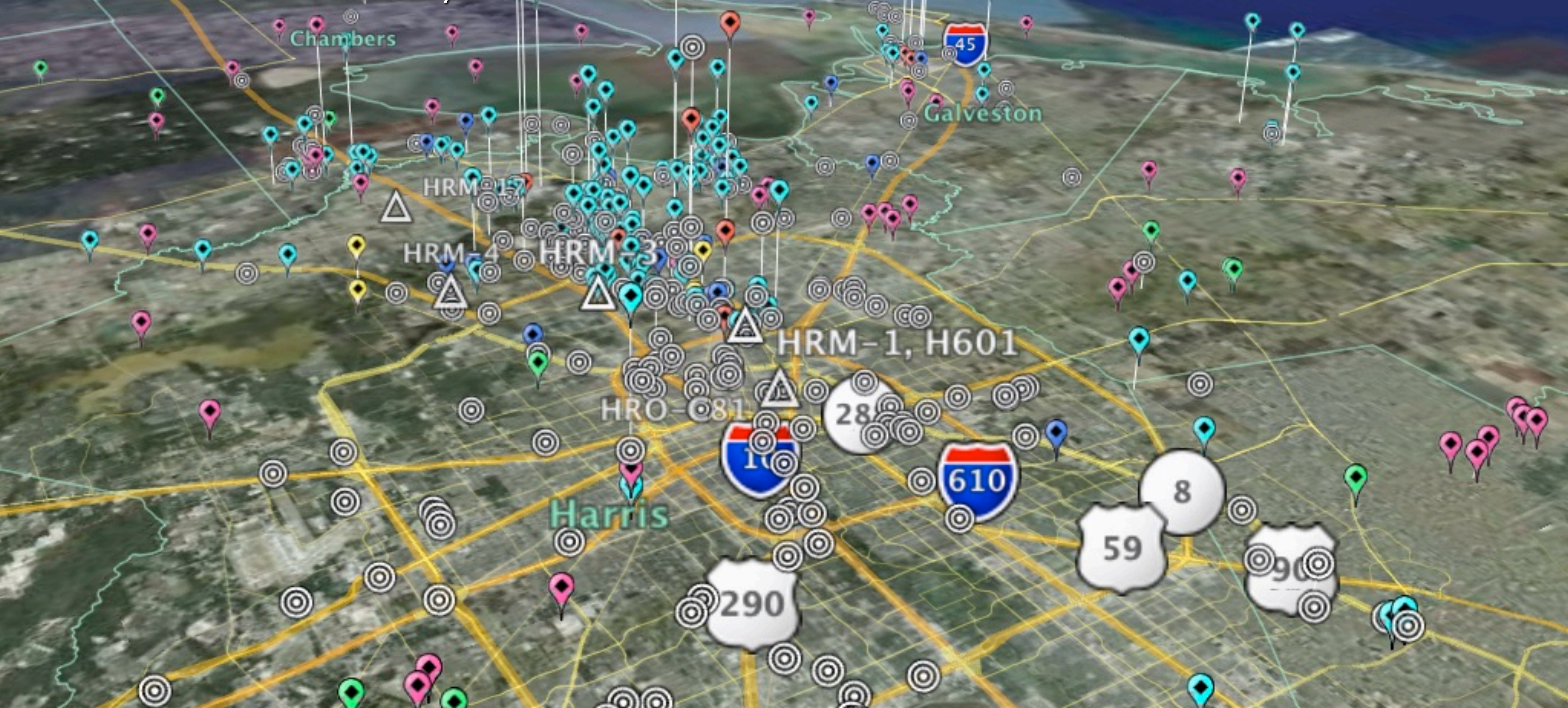
Influence of Highly Variable Spatial and Temporal VOC Emissions in Houston Texas on 1-h and 8-h Ozone SIP Modeling. Is this relevant to California?

Harvey Jeffries
Dept. Environmental Science and Engineering
Gillings School of Global Public Health
University of North Carolina

Chair's Air Pollution Seminar
March 24, 2009

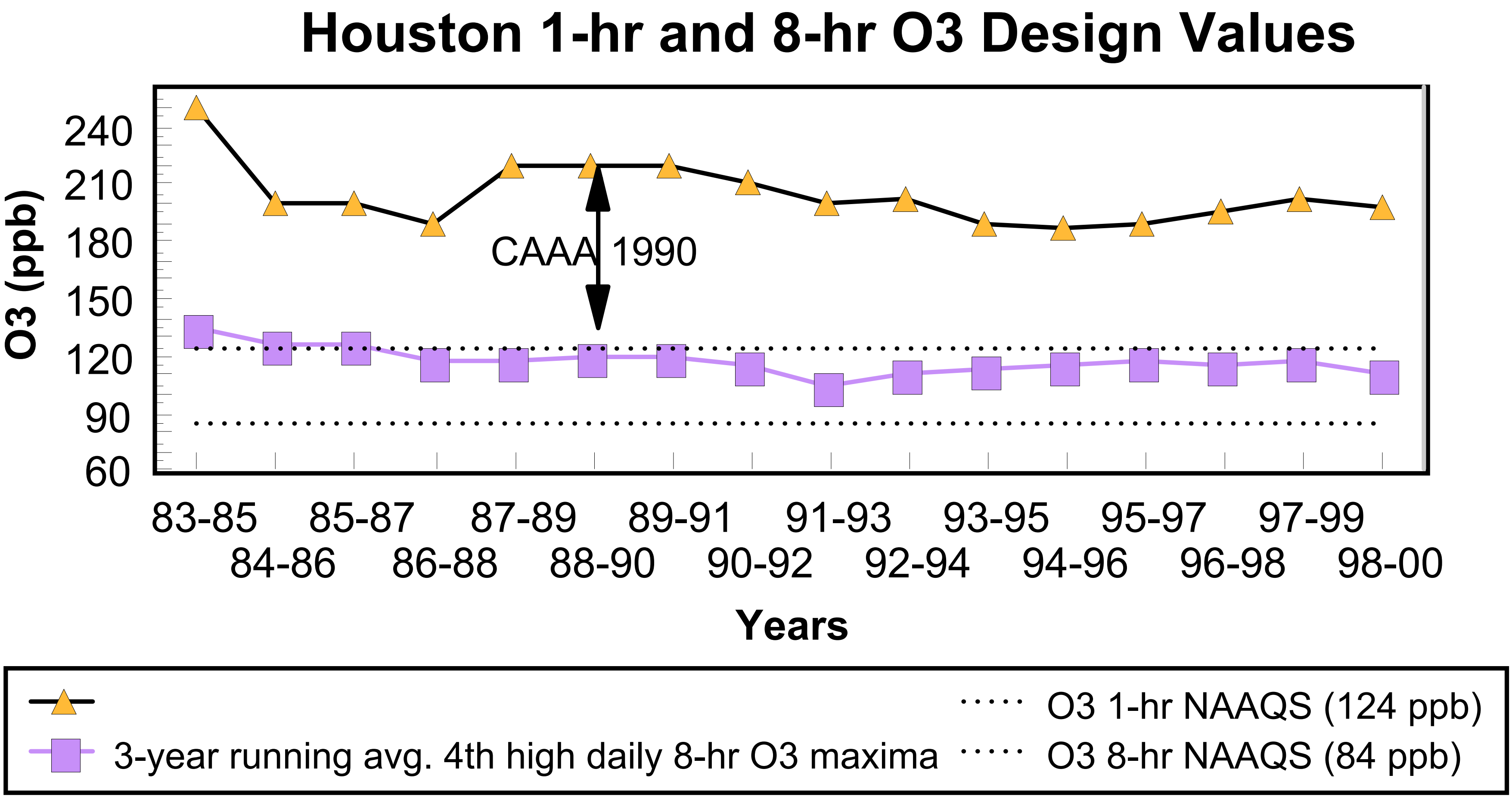


Acknowledgements

- David Allen, University of Texas, Austin
  - Yosuke Kimura, UT students
- William Vizuete, UNC
  - Barron Henderson, Lerian Biton, UNC students
- Mort Webster, Mike Symons, UNC
- Al Hendler, URS Corp, Austin TX
- Byeong-Uk Kim, Ga Dept of Envr.
- Texas Environmental Research Consortium / Houston Advanced Research Center
- Business Coalition for Clean Air
- Midcourse Correction Group
- ExxonMobil Foundation

Topics

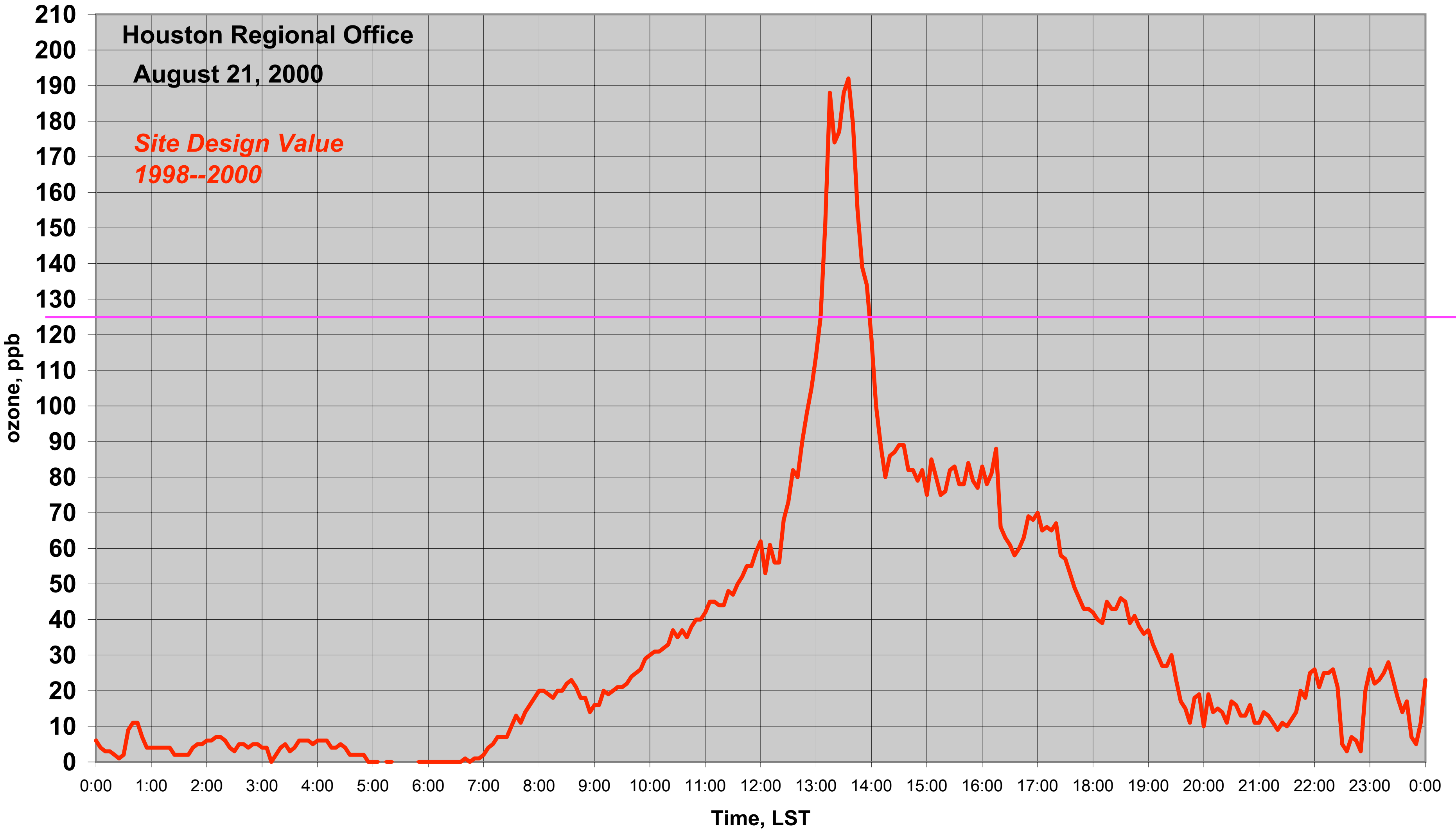
- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events



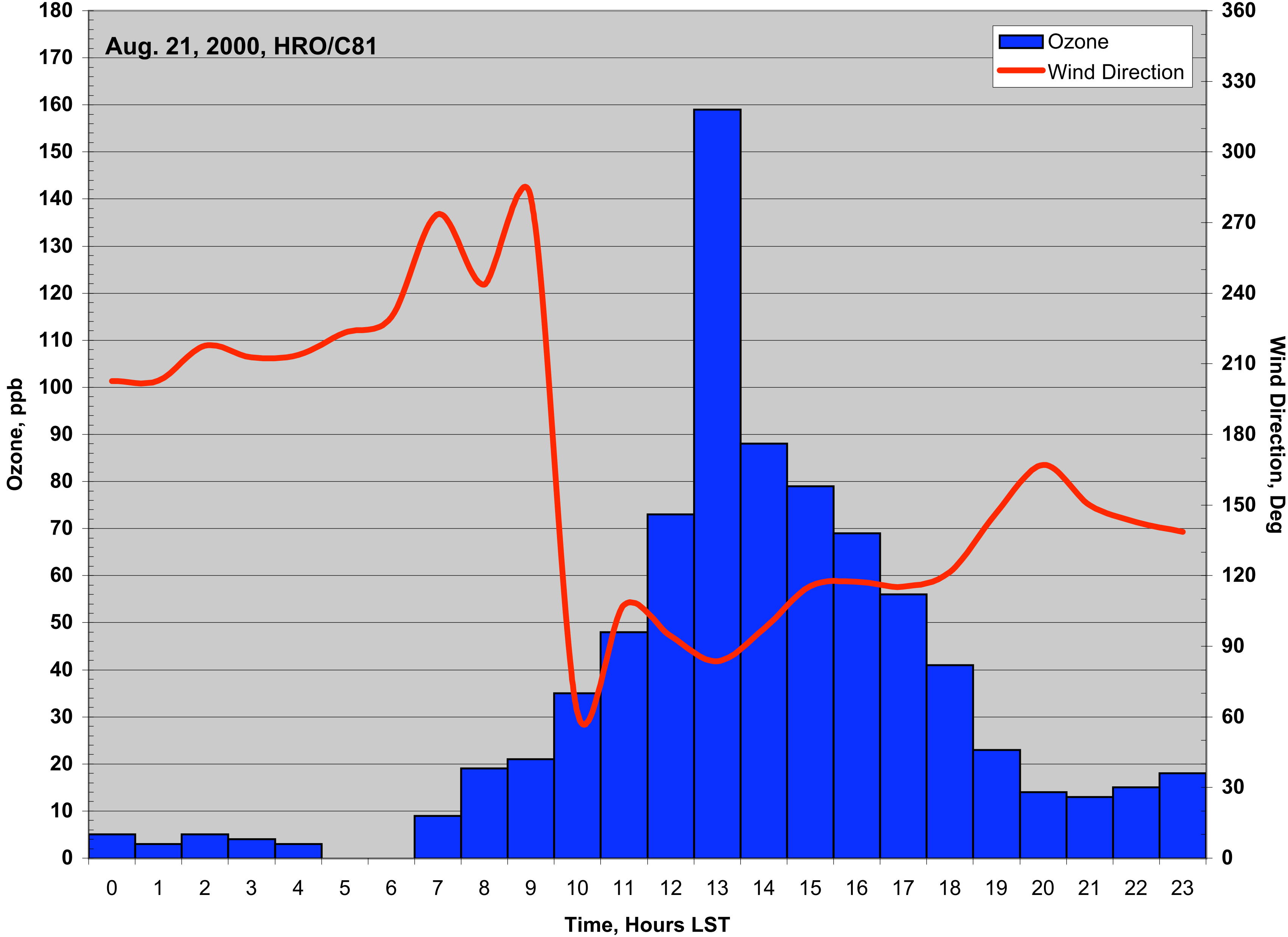
Houston 1-hr and 8-hr O3 Design Values
O3 (ppb)
240
210
180
150
120
90
60
CAAA 1990
83-85
84-86
85-87
86-88
87-89
88-90
89-91
90-92
91-93
92-94
93-95
94-96
95-97
96-98
97-99
98-00
Years
3-year running avg. 4th high daily 8-hr O3 maxima
O3 1-hr NAAQS (124 ppb)
O3 8-hr NAAQS (84 ppb)

Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events



Houston Regional Office
August 21, 2000
Site Design Value
1998--2000
ozone, ppb
Time, LST
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
21:00
22:00
23:00
0:00



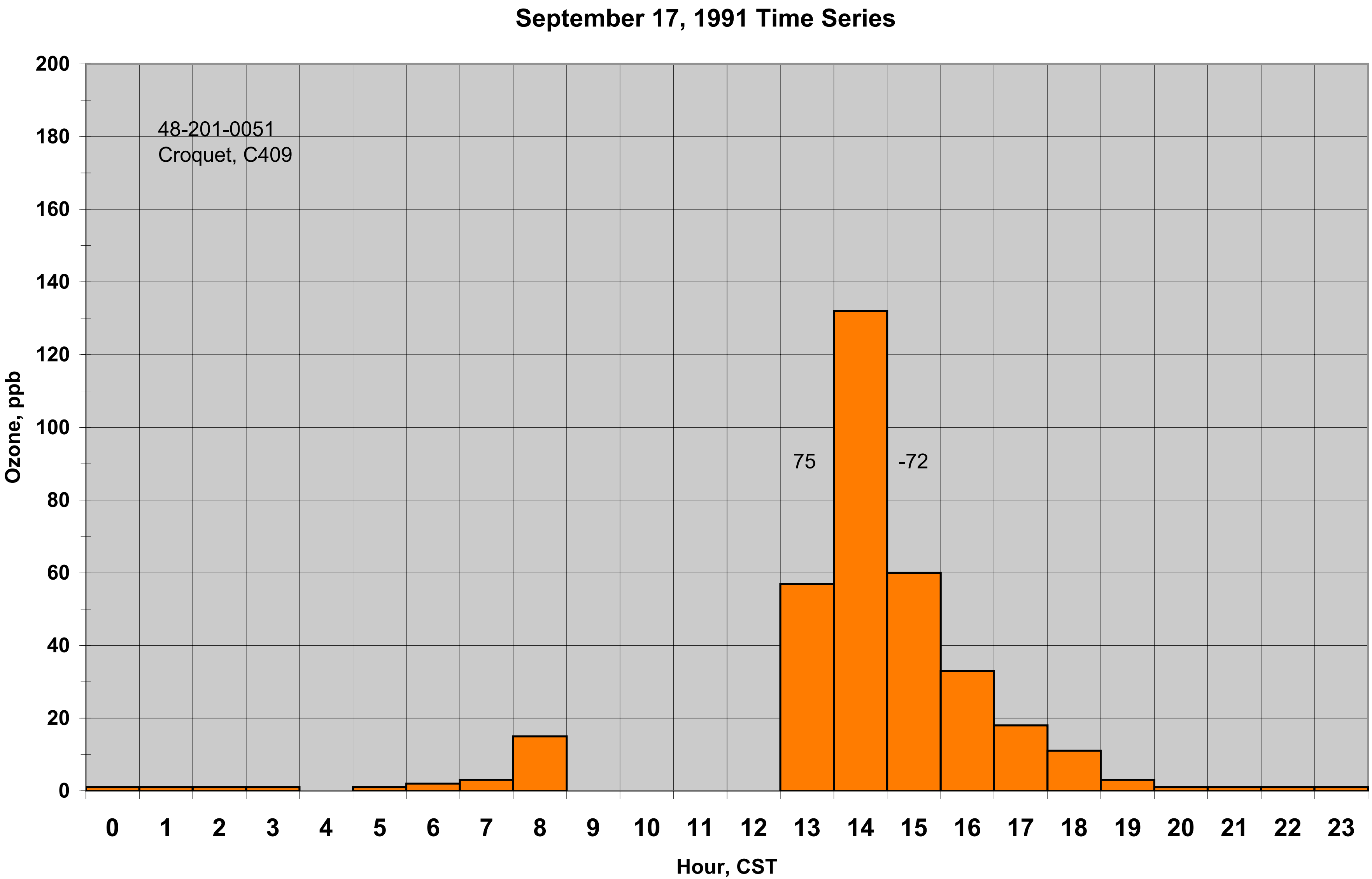
Aug. 21, 2000, HRO/C81
Ozone
Wind Direction
Ozone, ppb
Wind Direction, Deg
Time, Hours LST
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
0 30 60 90 120 150 180 210 240 270 300 330 360
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

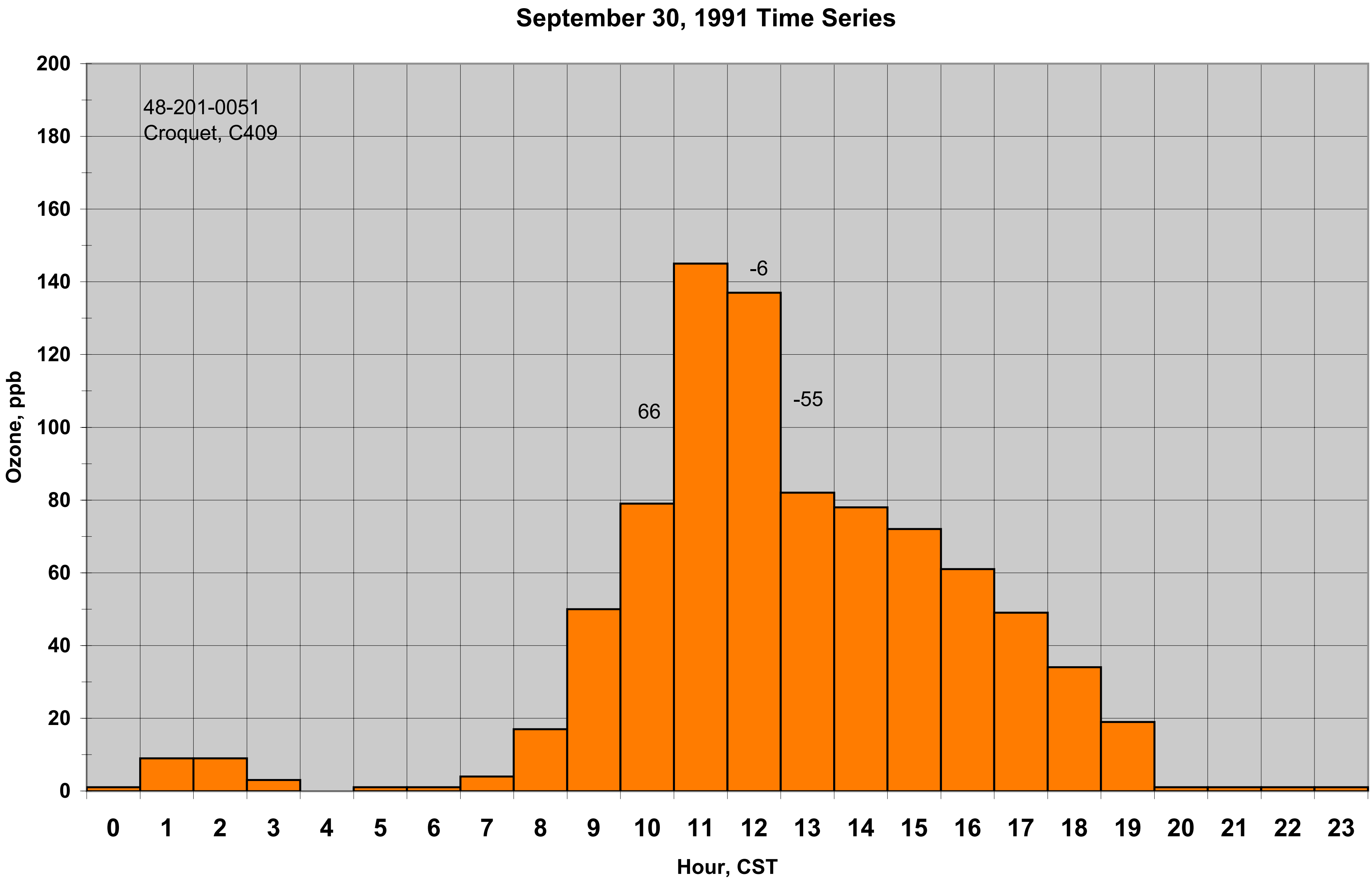

August 21, 2000
6:00
12:00
C26
C309
C48
C08
C610
C604
C408
C405
C404
C15
C148
C607
C01
C603
C411
C81
C410
C167
C166
C611
C407
C53
C22
C18
C35
C608
C120
C409
C406
C51
C145
Houston
MONTGOMERY
HARRIS
LIBERTY
CHAMBERS
FORT BEND
BRAZORIA
GALVESTON
George Bush Intercontinental Airport
West Houston Airport
Andrau Airpark
Galveston Bay
Lake Houston
Sugar Land
Missouri City
Pearland
Baytown
La Porte
Channelview
Highlands
Crosby
Humble
Kingwood
Tomball
Katy
Stafford

What are THOEs and ROFs?

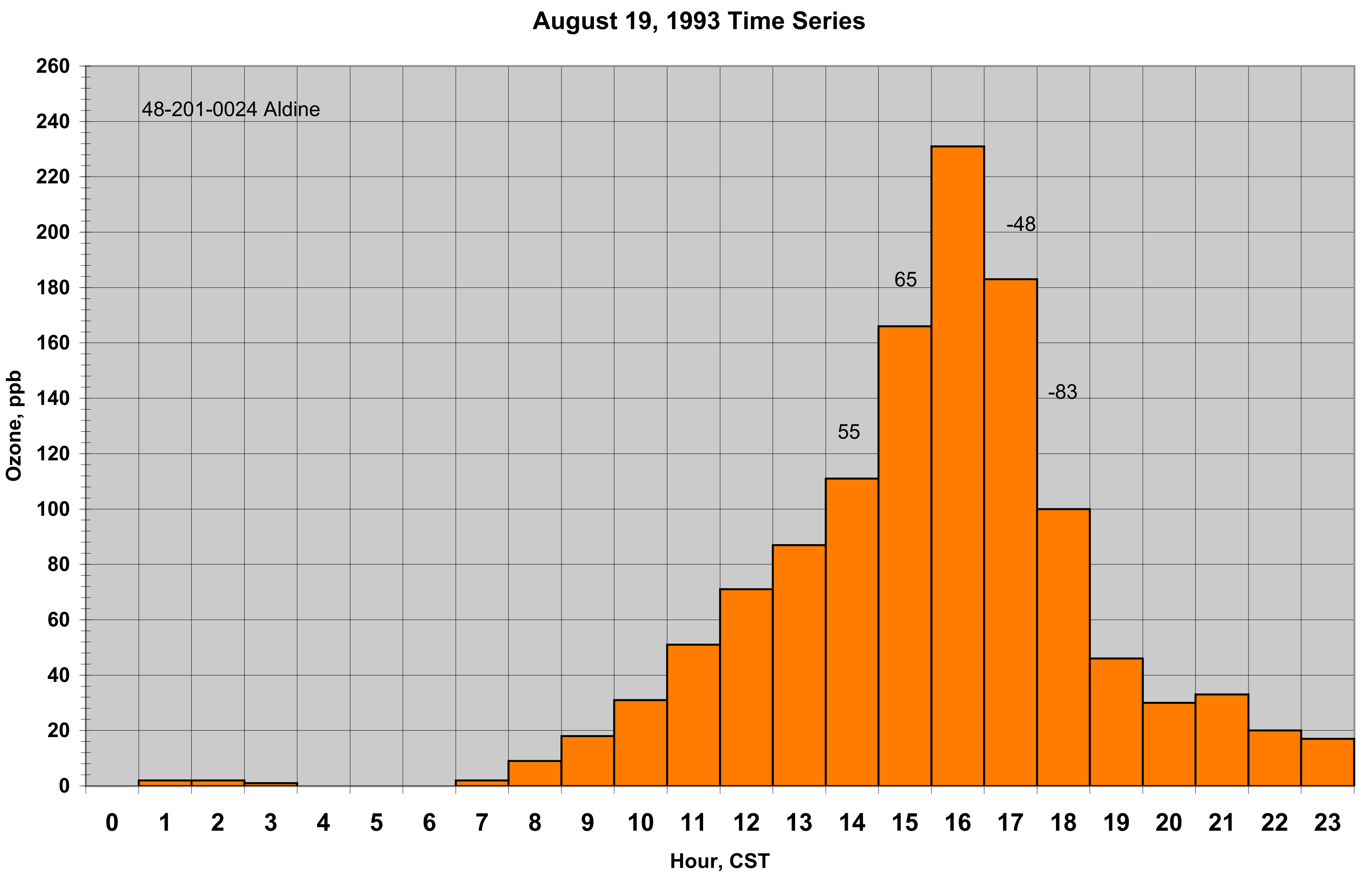
Concepts are related but different.

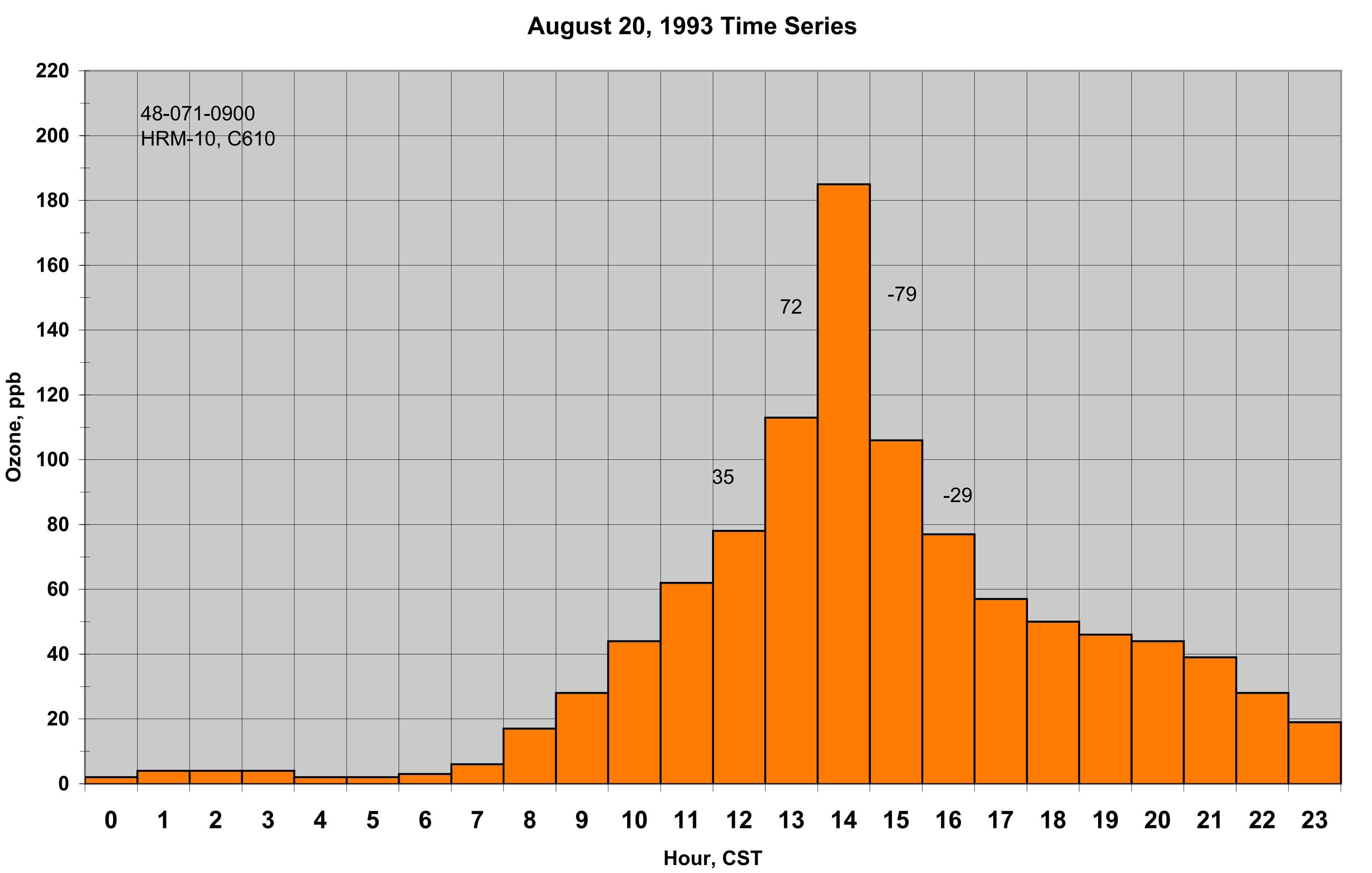
A THOE is part of an observed ozone timeseries at a regulatory monitor that meets certain criteria based in part on model performance. It is a rapid change in ozone concentration, usually followed by a rapid decline.


September 17, 1991 Time Series
Ozone, ppb
200
180
160
140
120
100
80
60
40
20
0
48-201-0051
Croquet, C409
75
-72
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
Hour, CST



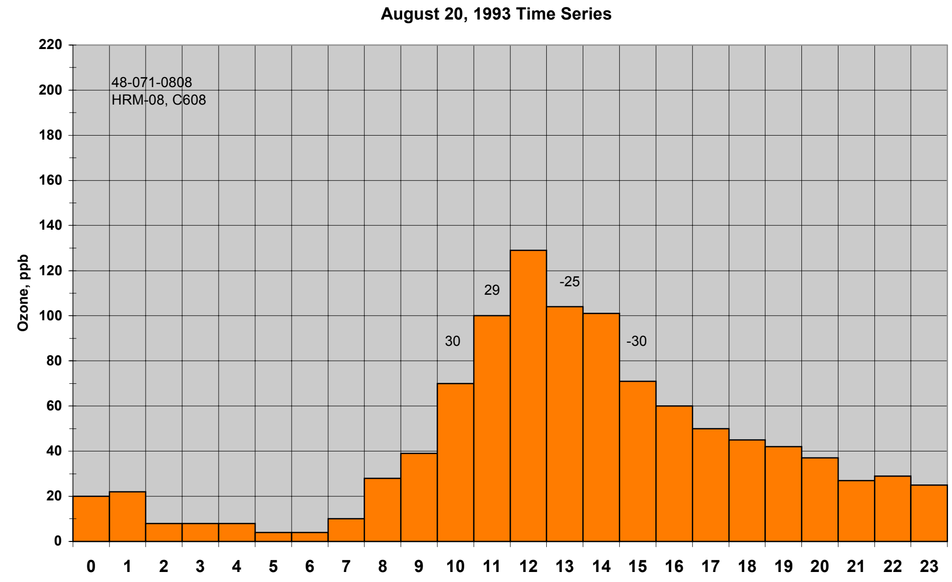
September 30, 1991 Time Series
48-201-0051
Croquet, C409
Ozone, ppb
Hour, CST
200
180
160
140
120
100
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
66
-6
-55


August 19, 1993 Time Series
48-201-0024 Aldine
Ozone, ppb
Hour, CST
55
65
-48
-83
0
20
40
60
80
100
120
140
160
180
200
220
240
260
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

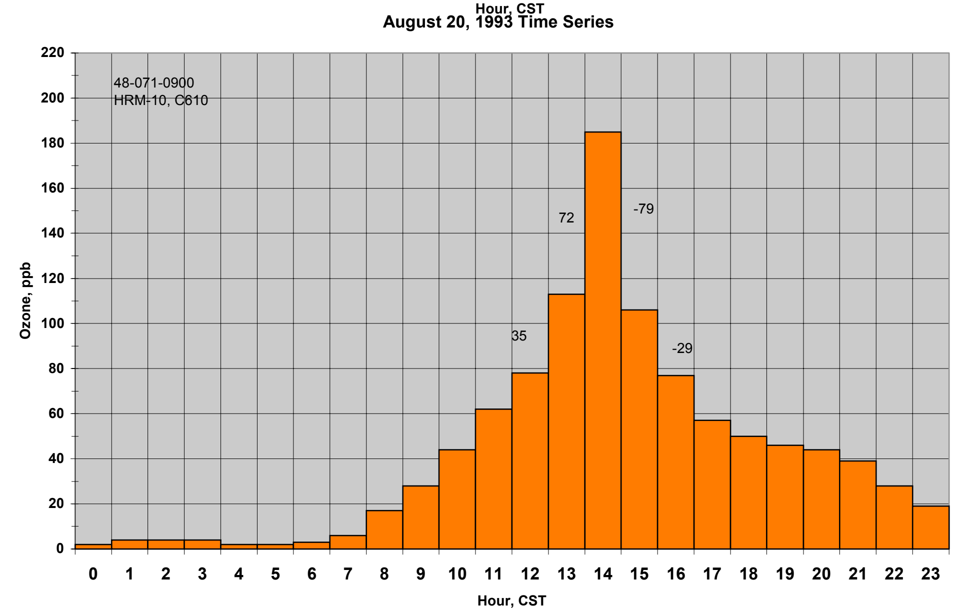

August 20, 1993 Time Series
48-071-0900
HRM-10, C610
Ozone, ppb
Hour, CST
0
20
40
60
80
100
120
140
160
180
200
220
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
35
72
-79
-29

Two observed ozone patterns in Houston

- *Typical ozone:* daily smooth small increases and decreases in observed values (same as other cities). Hourly change is less than 40 ppb.

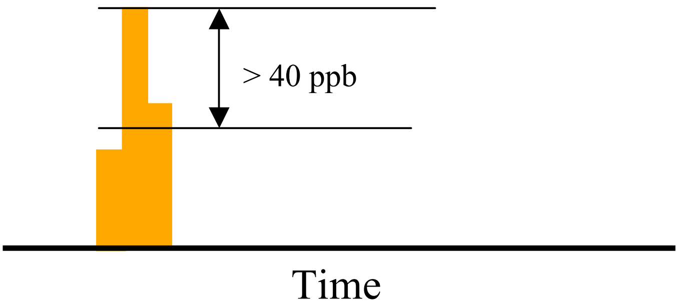


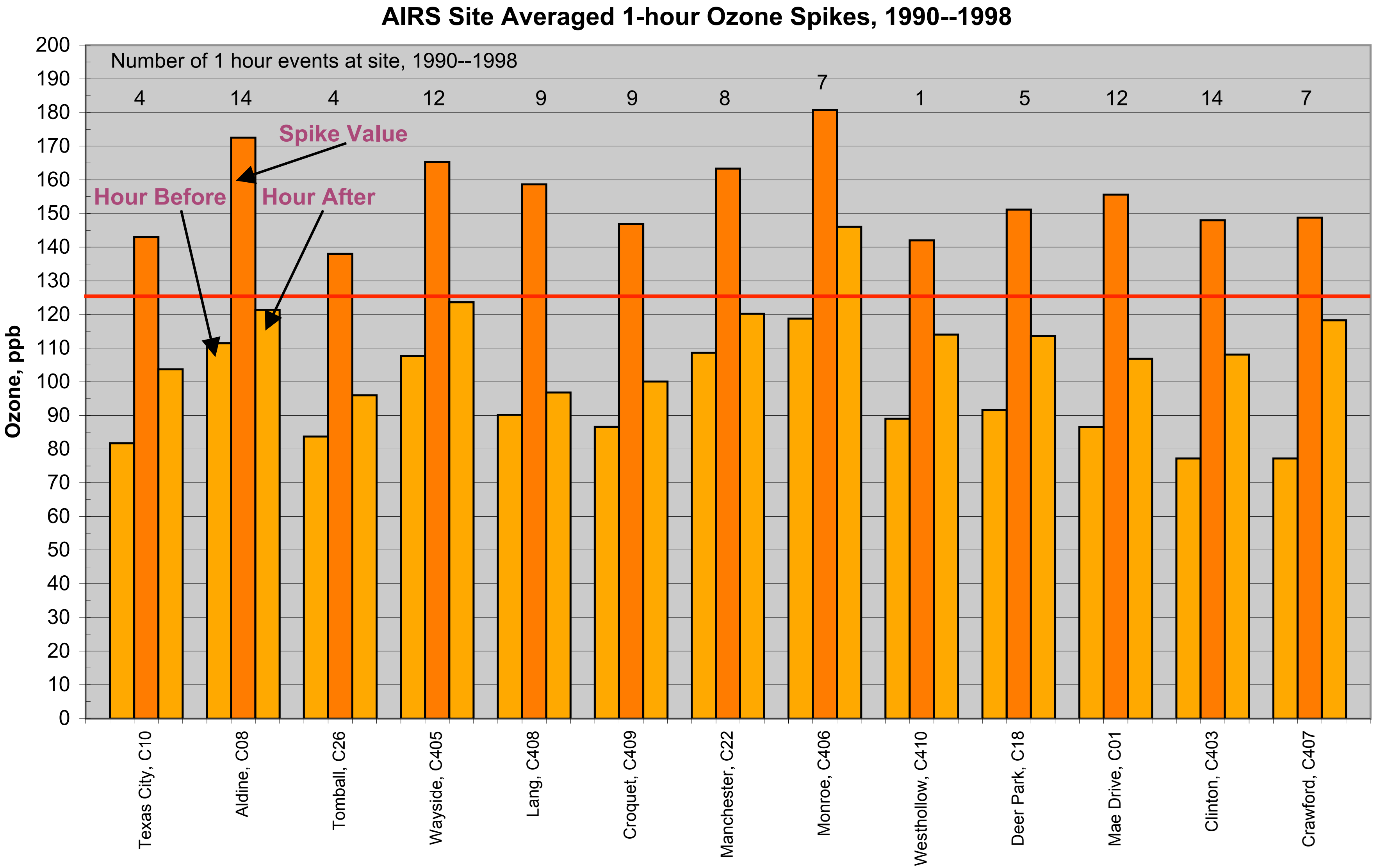
- *Atypical ozone:* one-hour “spikes” that are more than 40 ppb higher than the previous hour and that are followed by ozone values similar to those before the spike.



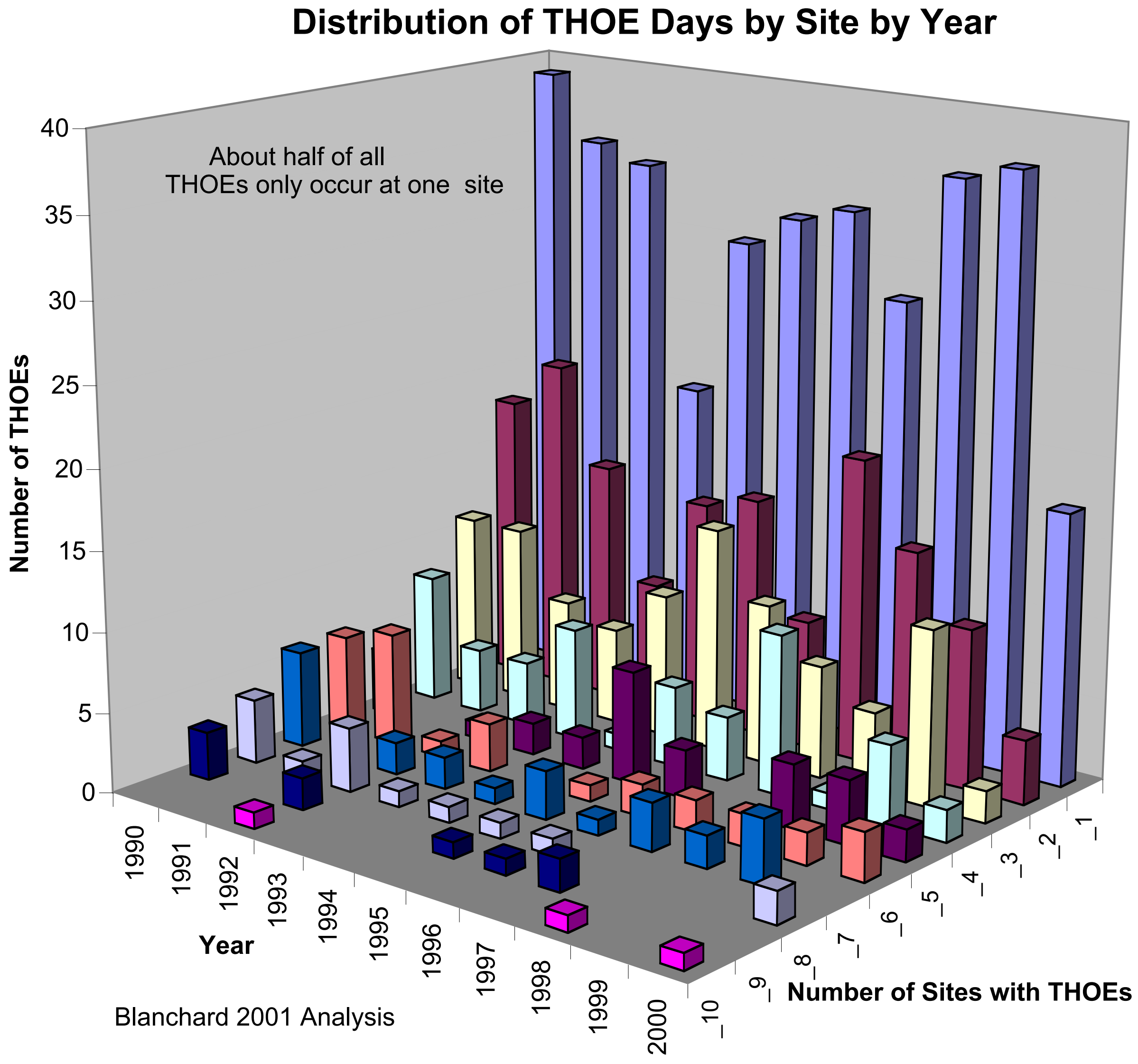
AIRS Dataset Analysis

Our first scan through the AIRS dataset was an automatic scan using a definition of a “spike” as a 1-h ozone value that was 40 ppb higher than the hour before averaged with the hour after.





AIRS Site Averaged 1-hour Ozone Spikes, 1990--1998
Number of 1 hour events at site, 1990--1998
4
14
4
12
9
9
8
7
1
5
12
14
7
Spike Value
Hour Before
Hour After
Ozone, ppb
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Texas City, C10
Aldine, C08
Tomball, C26
Wayside, C405
Lang, C408
Croquet, C409
Manchester, C22
Monroe, C406
Westhollow, C410
Deer Park, C18
Mae Drive, C01
Clinton, C403
Crawford, C407


Distribution of THOE Days by Site by Year
About half of all
THOEs only occur at one site
Number of THOEs
0
5
10
15
20
25
30
35
40
Year
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
Number of Sites with THOEs
_1
_2
_3
_4
_5
_6
_7
_8
9_
_10
Blanchard 2001 Analysis

With THOEs:

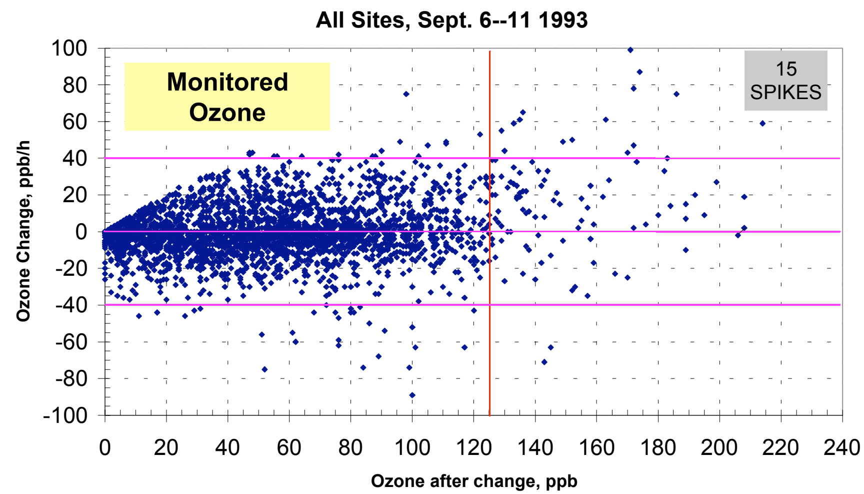
- Can not tell which VOCs actually created the ozone
  - Photochemistry happened away from the monitor.
  - Rotating wind field advects a narrow (few kms wide) ozone plume across monitor.
  - THOEs result in the highest ozone observed at monitors and dominate the "ozone design value" for EPA's control calculations for SIPs. Half of all THOEs only occur at one monitor.
  - Models have a difficult time reproducing the observed THOEs.
- THOEs are a result, not a cause.
  - Chemistry in area of monitor is not likely fast enough to cause the observed ozone values.
  - Many THOEs may be "old" photochemical systems, that is, much of the NOx needed to make ozone may have already been oxidized to HNO3, RNO3, PAN, and not available to keep making ozone.
- Ambient VOC monitors (auto_GCs) are used for VOC.

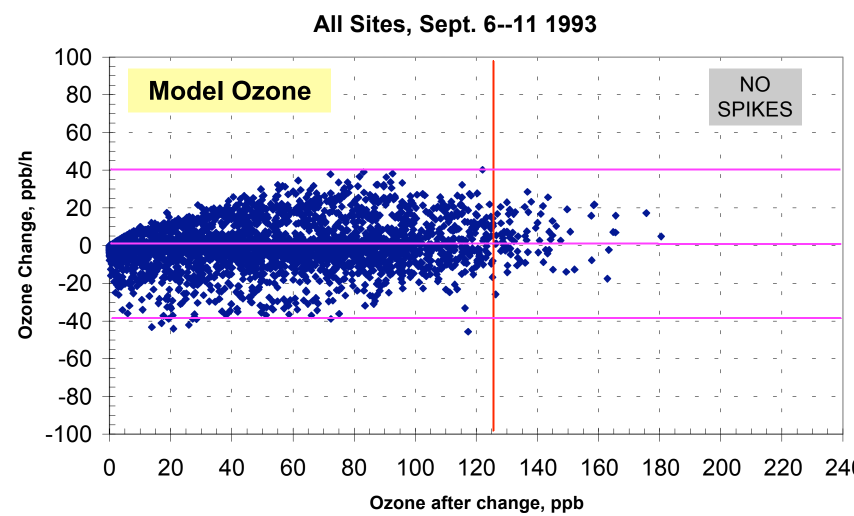
TCEQ 2000 SIP
Based on Sept 6-11, 1993

- TCEQ had tried to model seven episodes from the 1993 COAST Study in Houston. All failed but Sept 6-11.
- This case seemed to pass the EPA "tests".
- Closer examination by HEJ in Aug 2000 showed major problems.
- HEJ and Stakeholders meet with TCEQ staff and Commissioners - Sep-2000 to Apr-2001
- A $28 Million TexAQS field program (Aug,Sep-2000) was underway as TCEQ was trying to get a SIP out the door.

Model reproduces only typical pattern

- The Sept. 6—11, 1993 episode had *15* one hour ozone observations that were greater than 40 ppb (one was 100 ppb) higher than the previous hour.
- For all hours at all monitors, the Sept 1993 model *never* predicted an hourly ozone increase greater than 40 ppb
- The model predicted the typical 20-30 ppb per hour increases that were observed most of the time.
- Because it does not have the proper emissions inventory inputs, the model failed to predict even one observed ozone highest peak value during the episode





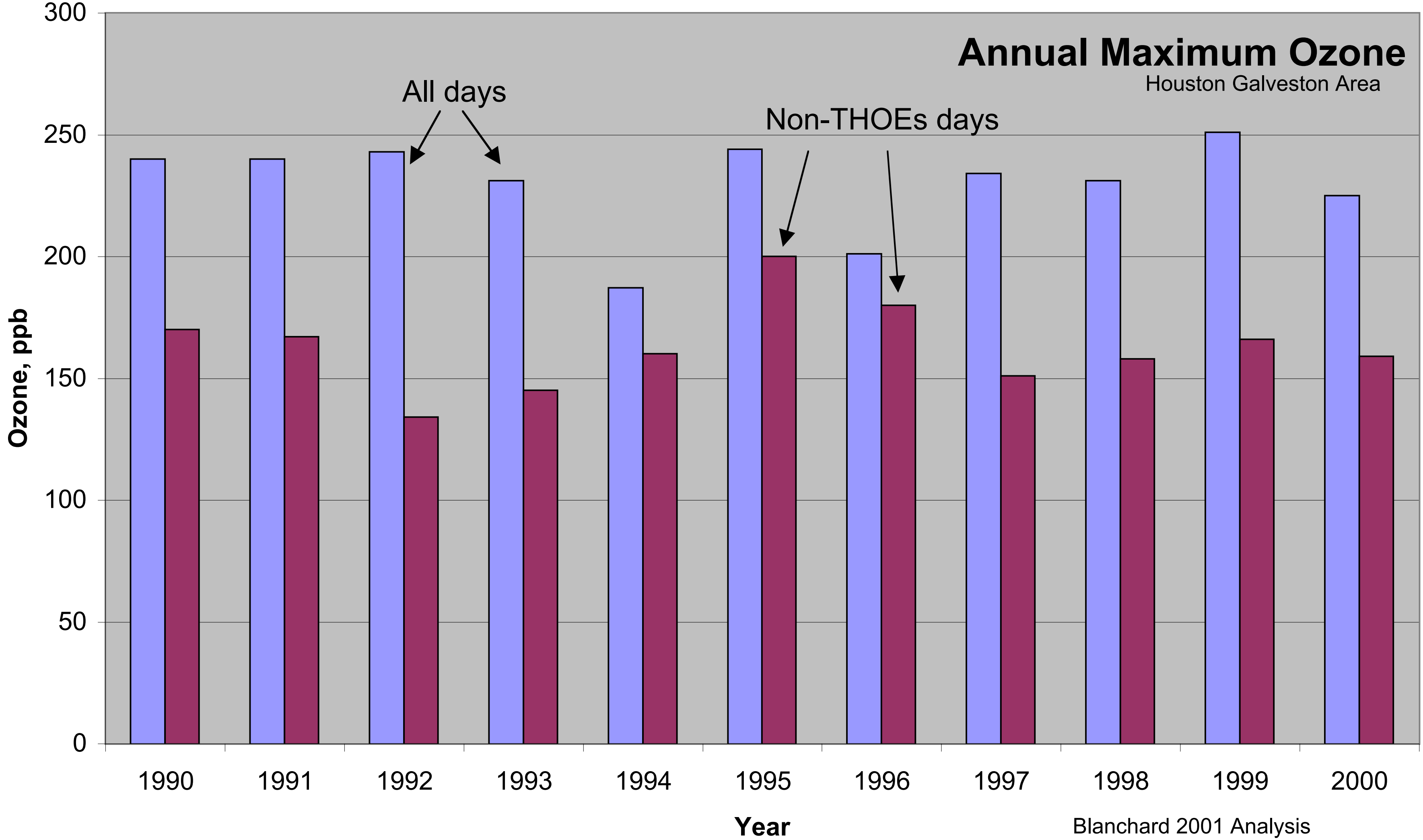
TCEQ 2000 SIP
Based on Sept 6-11, 1993

- Model not responsive to VOC
- Model only mildly responsive to NOx reductions
- SIP required 90% NEGU and EGU NOx reductions
  - Initial Costs: $4.5 billion. Yearly Costs: $3-4 b

- Worse, model could not demonstrate attainment even with this level of reductions. There was a "NOx gap" requiring: speed limit changes, lawn and garden equipment be electric, etc etc...
- Observations suggested it was VOC, more than NOx.

Spikes will not be controlled by 2000 SIP NOx reductions

- Spike production requires a minimal amount of NOx and episodic very reactive compound releases
- Even with the 2000 SIP NOx control strategy there will still be sufficient morning NOx to react with episodic reactive VOC to create spikes
- The ambient NOx concentrations resulting from either 80% or 90% point source NOx controls will not prevent spike ozone exceedances
- The current strategy will not attain the NAAQS


Annual Maximum Ozone
Houston Galveston Area
All days
Non-THOEs days
Ozone, ppb
300
250
200
150
100
50
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
Year
Blanchard 2001 Analysis

The Solution: Two-Part Attainment Demonstration

- Two causes of ozone exceedances require two solutions
- Use the current model to design control strategies for *typical* ozone exceedances
- Address ozone *spikes* separately, through other means

The Solution, Part 2: Spike Ozone

- Enforceable commitment will address ozone spikes
  - A stakeholder process to contain defined milestones for the following actions:
    - Complete short-term study of causes of ozone spikes in HGA
    - Identify suite of mitigation measures (e.g., best management practices)
    - Codify mitigation measures in rules by 2005
  - The process will include participation of emitters of episodic highly reactive compounds and utilize Texas 2000 field study data
- Our process is similar to enforceable commitments in other states.

TCEQ 2000 SIP
Based on Sept 6-11, 1993

- TCEQ held firm to their SIP
- Stakeholders sued in State Court, May 12, 2001
- Judge agreed with Stakeholders; enters "stay"
- TCEQ agrees to revise SIP (already submitted to EPA) and to undertake analysis of the science over 18 months and make mid-course corrections as needed.
- Additional $12 M were allocated by Tx legislature for Accelerated Science
- Additional $4.5 M and $2 M were raised by Stakeholders.

Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events

Rapid Ozone Formation

is a special point-model computed value based on a whole set of observed species including VOCs (NOx, HCHO, hv, etc) measured at a single point.

It is expressed as an instantaneous rate at a point in space and time, i.e., it is a rate of increase in ozone that is consistent with the measurements at that point.

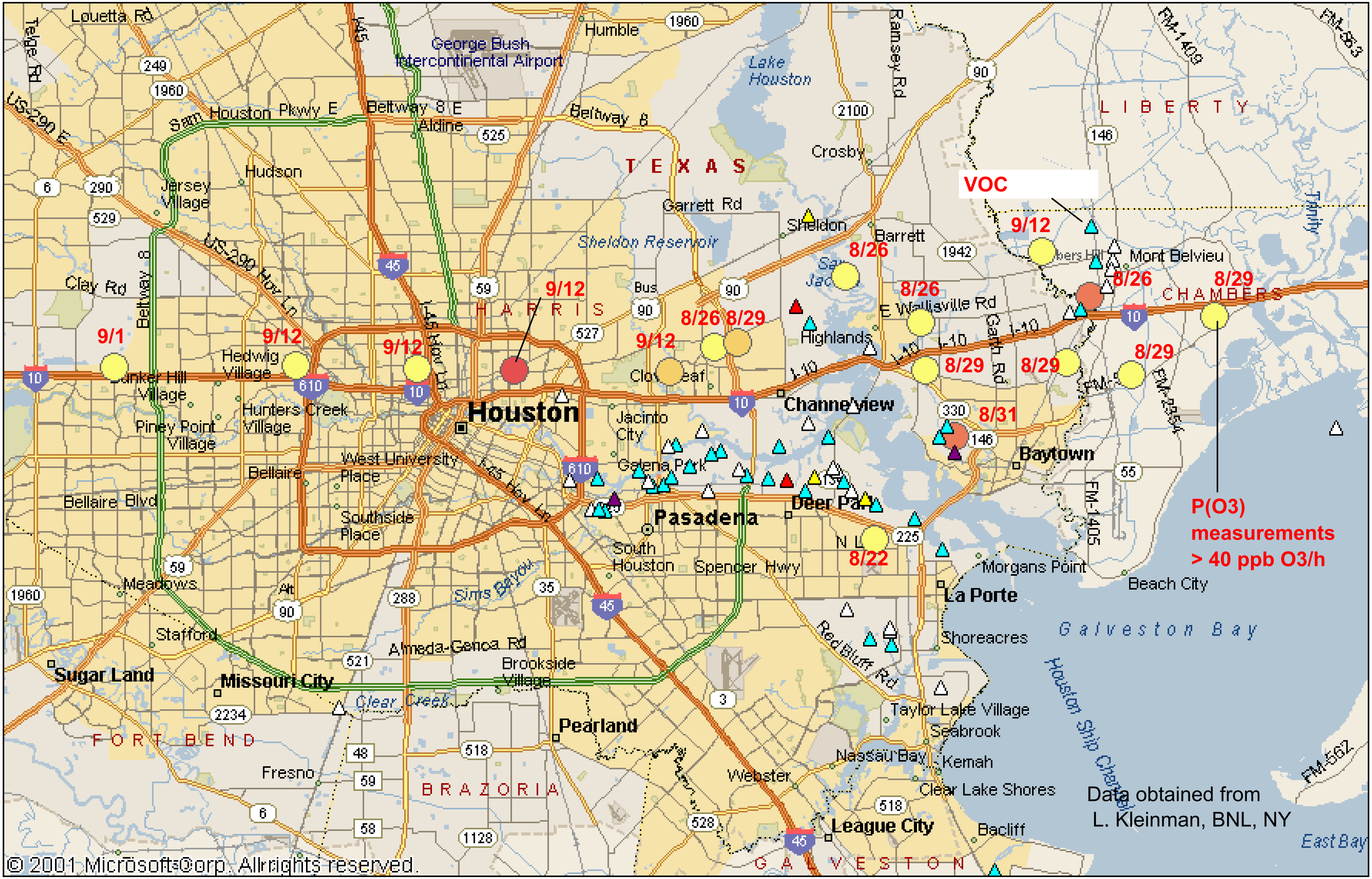
With ROF events:

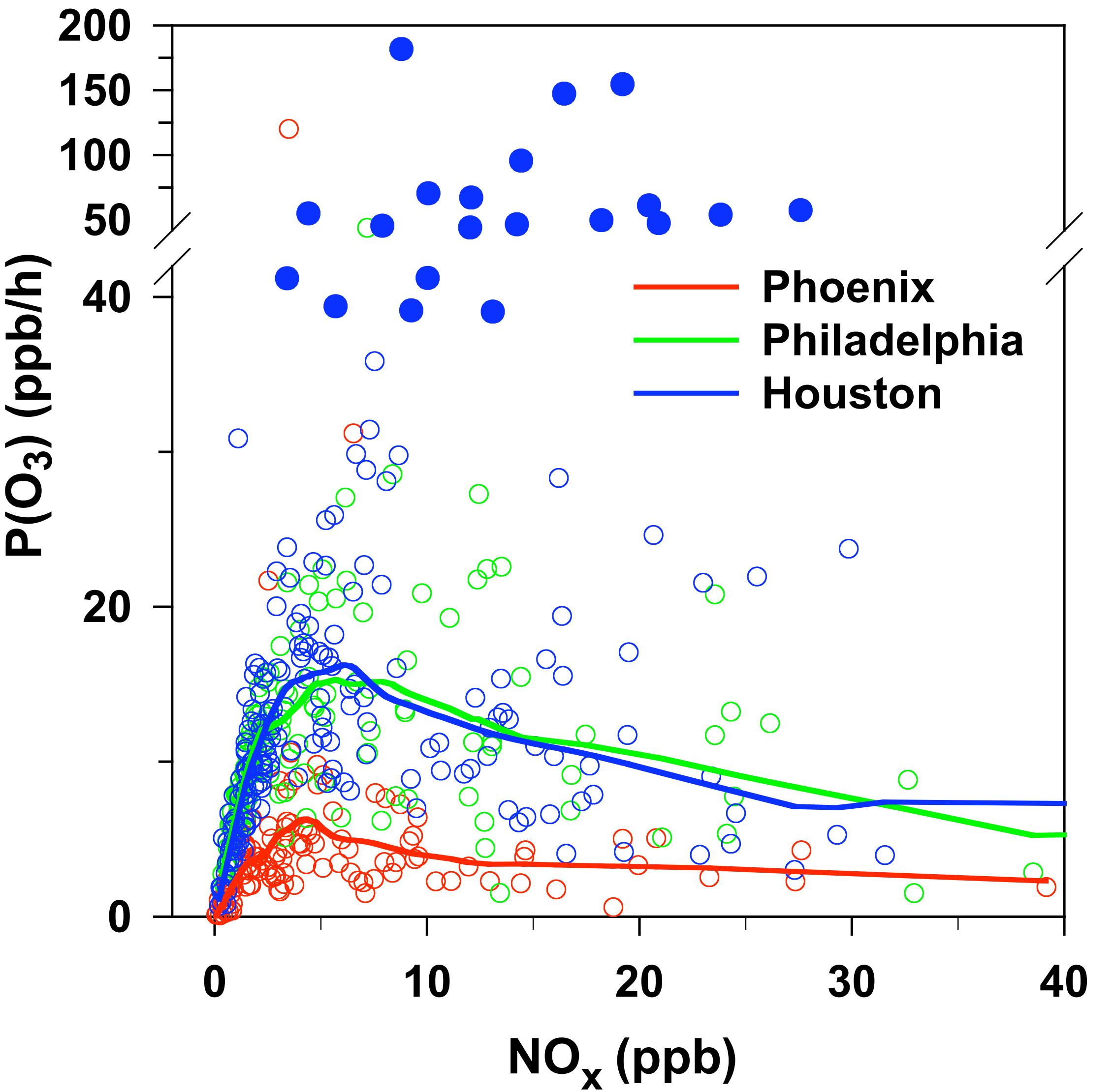
Know which VOCs actually are creating ozone

- Rate of photochemistry happening at measurement point.
- In high ROF events, there may not be much ozone.

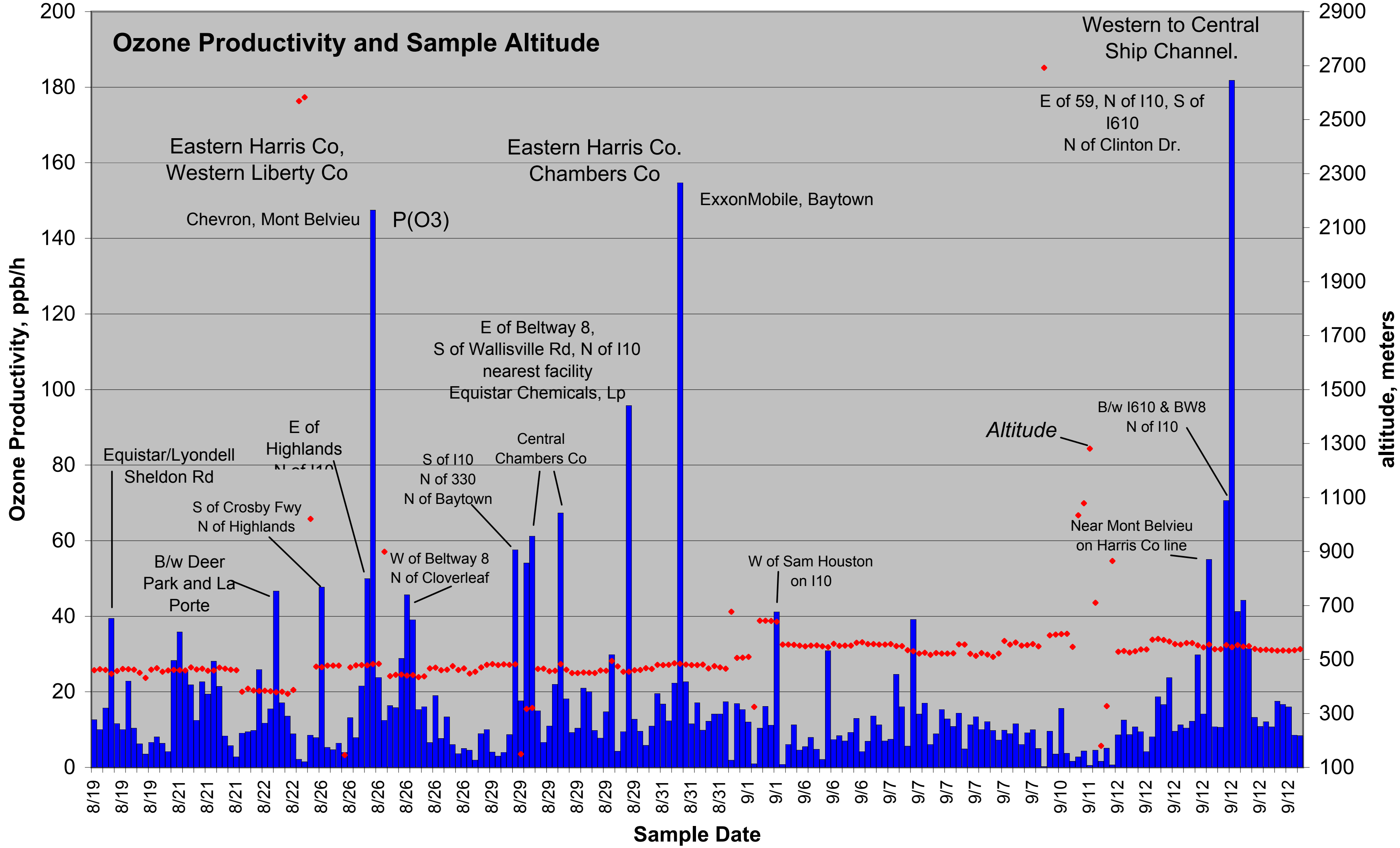
Also know the NOx environment.

- Peter Daum and Larry Kleinman have published "ozone productivity" as function of NOx.
- Many samples like other cities where ozone productivities have been measured.
- About 10% of samples are greater than ever measured in any city, up to 180 ppb O3/hour.

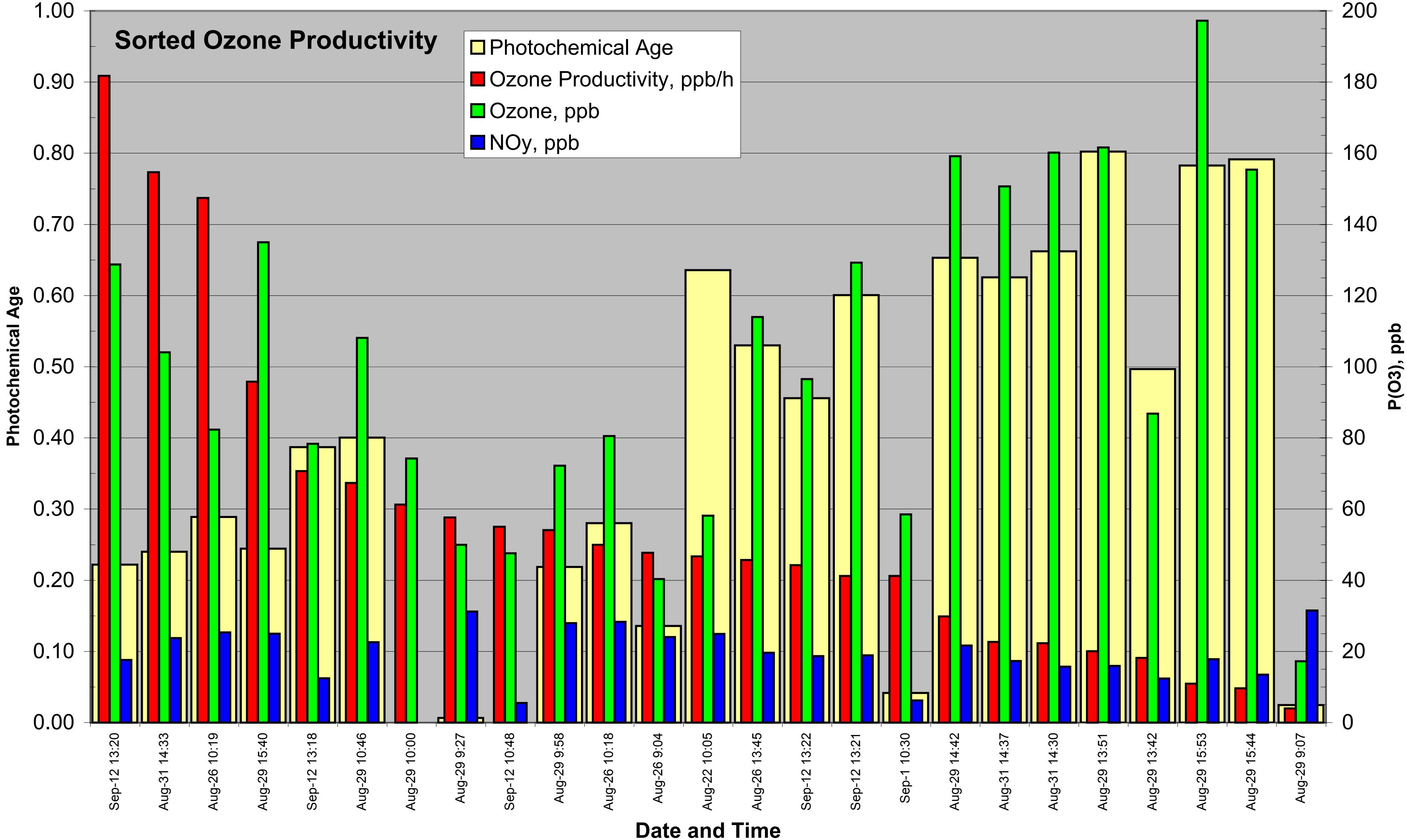

VOC
9/12
8/26
8/29
9/1
9/12
9/12
9/12
9/12
8/26 8/29
8/26
8/26
8/29
8/29
8/29
8/31
8/22
P(O3) measurements > 40 ppb O3/h
Data obtained from L. Kleinman, BNL, NY
T E X A S
H A R R I S
L I B E R T Y
C H A M B E R S
F O R T B E N D
B R A Z O R I A
G A L V E S T O N
Houston
Pasadena
Baytown
Channelview
Deer Park
La Porte
Sugar Land
Missouri City
Pearland
League City
Humble
George Bush Intercontinental Airport
Lake Houston
Crosby
Sheldon
Barrett
Highlands
Mont Belvieu
Sheldon Reservoir
Hudson
Jersey Village
Hedwig Village
Hunters Creek Village
Piney Point Village
Bellaire
West University Place
Southside Place
Jacinto City
Galena Park
South Houston
Spencer Hwy
Morgans Point
Beach City
Shoreacres
Galveston Bay
Houston Ship Channel
Taylor Lake Village
Seabrook
Nassau Bay
Kemah
Clear Lake Shores
Bacliff
Webster
Brookside Village
Almeda-Genoa Rd
Sims Bayou
Clear Creek
Stafford
Meadows
Fresno
Red Bluff Rd
Louetta Rd
Sam Houston Pkwy E
Beltway 8 E
Aldine
Garrett Rd
E Wallisville Rd
Bellaire Blvd
Clay Rd
East Bay
© 2001 Microsoft Corp. All rights reserved.



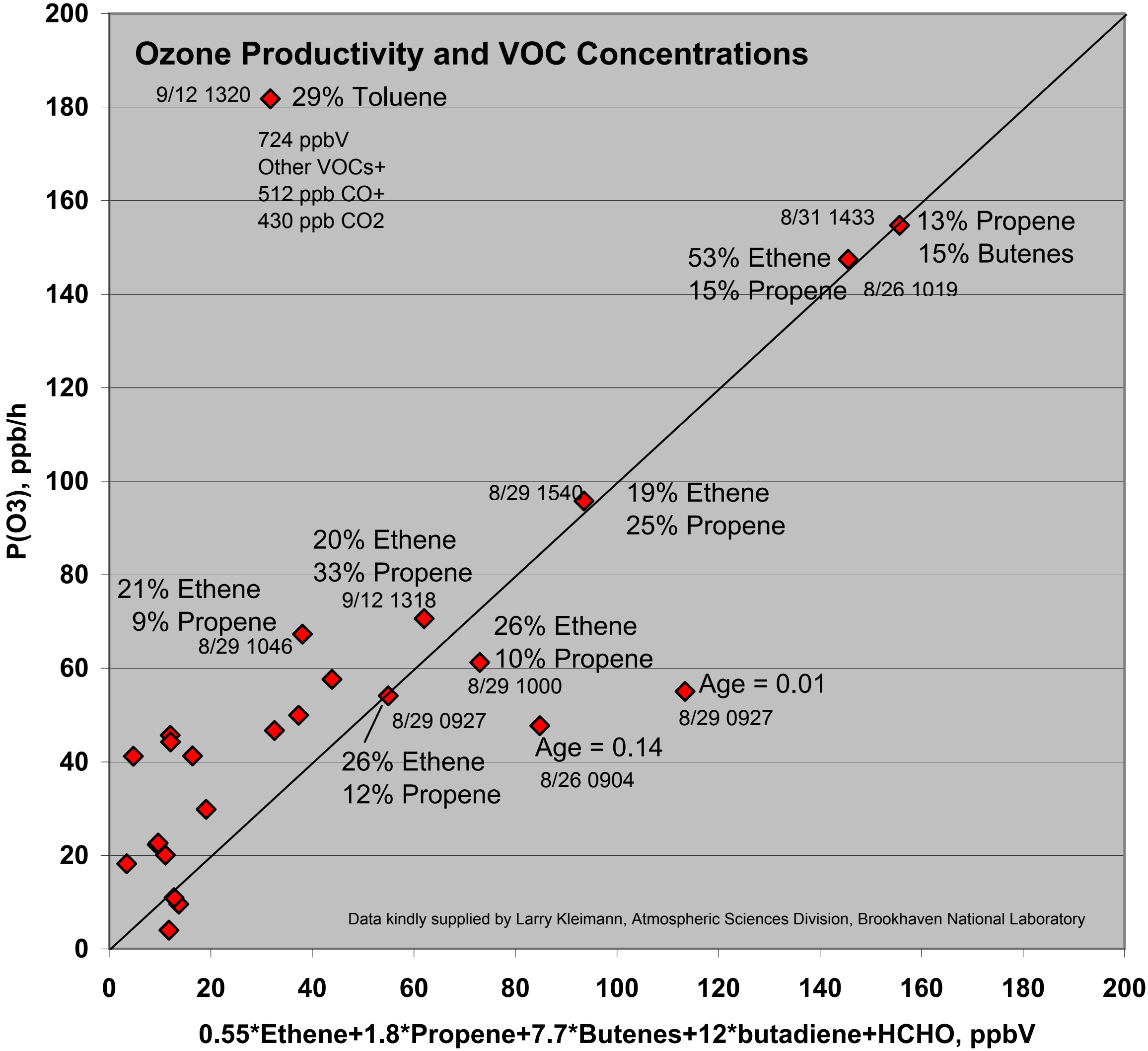
200
150
100
50
40
20
0
P(O3) (ppb/h)
Phoenix
Philadelphia
Houston
0
10
20
30
40
NOx (ppb)



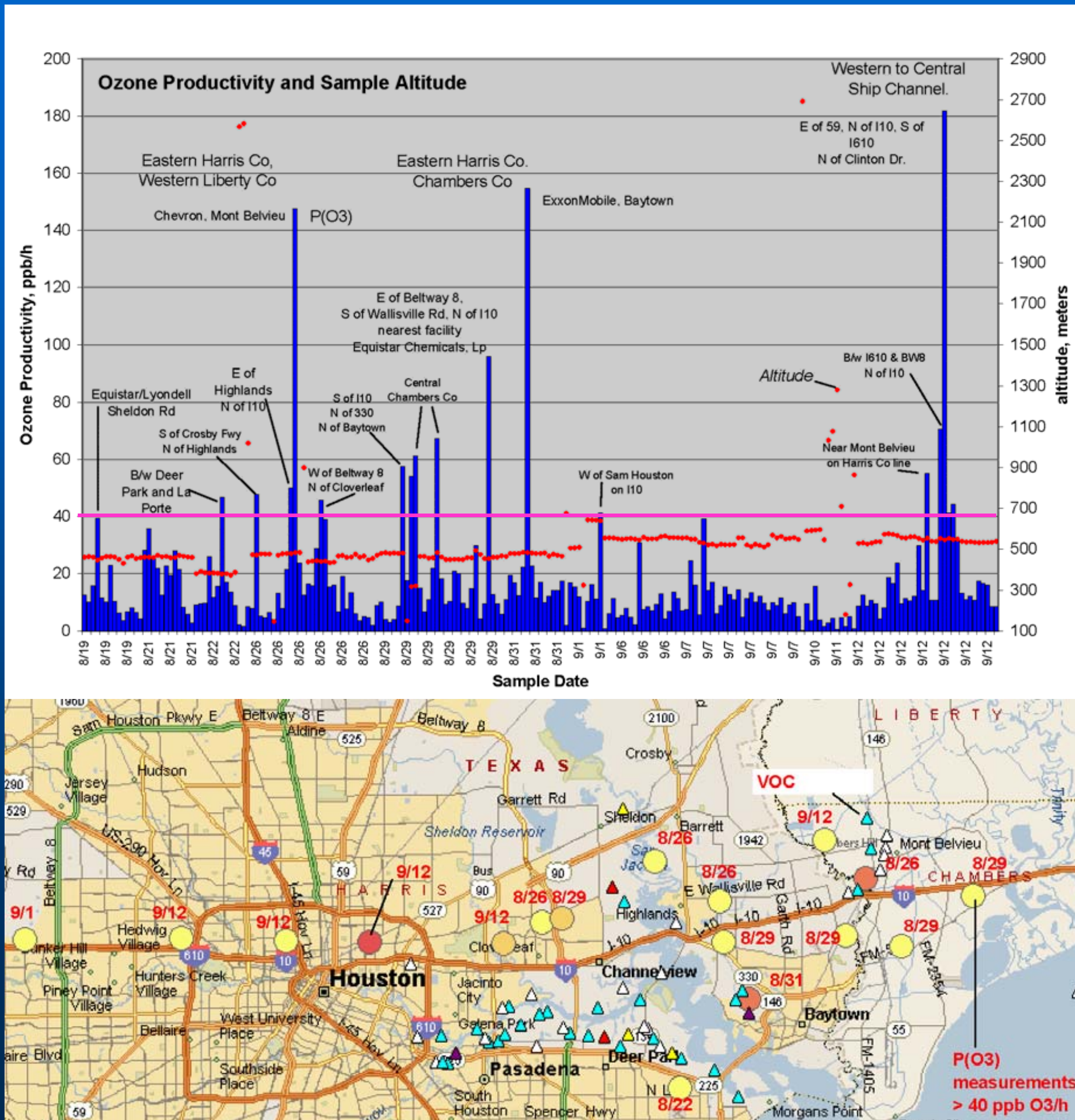
Ozone Productivity and Sample Altitude
Ozone Productivity, ppb/h
altitude, meters
Sample Date
Western to Central Ship Channel.
E of 59, N of I10, S of I610
N of Clinton Dr.
Eastern Harris Co, Western Liberty Co
Eastern Harris Co. Chambers Co
Chevron, Mont Belvieu
P(O3)
ExxonMobile, Baytown
E of Beltway 8,
S of Wallisville Rd, N of I10
nearest facility
Equistar Chemicals, Lp
Altitude
B/w I610 & BW8
N of I10
Central Chambers Co
S of I10
N of 330
N of Baytown
E of Highlands
Equistar/Lyondell
Sheldon Rd
S of Crosby Fwy
N of Highlands
B/w Deer Park and La Porte
W of Beltway 8
N of Cloverleaf
W of Sam Houston on I10
Near Mont Belvieu on Harris Co line



Sorted Ozone Productivity
Photochemical Age
Ozone Productivity, ppb/h
Ozone, ppb
NOy, ppb
Photochemical Age
P(O3), ppb
Date and Time
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
200
180
160
140
120
100
80
60
40
20
0
Sep-12 13:20
Aug-31 14:33
Aug-26 10:19
Aug-29 15:40
Sep-12 13:18
Aug-29 10:46
Aug-29 10:00
Aug-29 9:27
Sep-12 10:48
Aug-29 9:58
Aug-26 10:18
Aug-26 9:04
Aug-22 10:05
Aug-26 13:45
Sep-12 13:22
Sep-12 13:21
Sep-1 10:30
Aug-29 14:42
Aug-31 14:37
Aug-31 14:30
Aug-29 13:51
Aug-29 13:42
Aug-29 15:53
Aug-29 15:44
Aug-29 9:07


Ozone Productivity and VOC Concentrations
9/12 1320
29% Toluene
724 ppbV
Other VOCs+
512 ppb CO+
430 ppb CO2
8/31 1433
13% Propene
15% Butenes
53% Ethene
15% Propene
8/26 1019
8/29 1540
19% Ethene
25% Propene
20% Ethene
33% Propene
9/12 1318
21% Ethene
9% Propene
8/29 1046
26% Ethene
10% Propene
8/29 1000
Age = 0.01
8/29 0927
8/29 0927
Age = 0.14
8/26 0904
26% Ethene
12% Propene
Data kindly supplied by Larry Kleimann, Atmospheric Sciences Division, Brookhaven National Laboratory
P(O3), ppb/h
0.55*Ethene+1.8*Propene+7.7*Butenes+12*butadiene+HCHO, ppbV
0
20
40
60
80
100
120
140
160
180
200

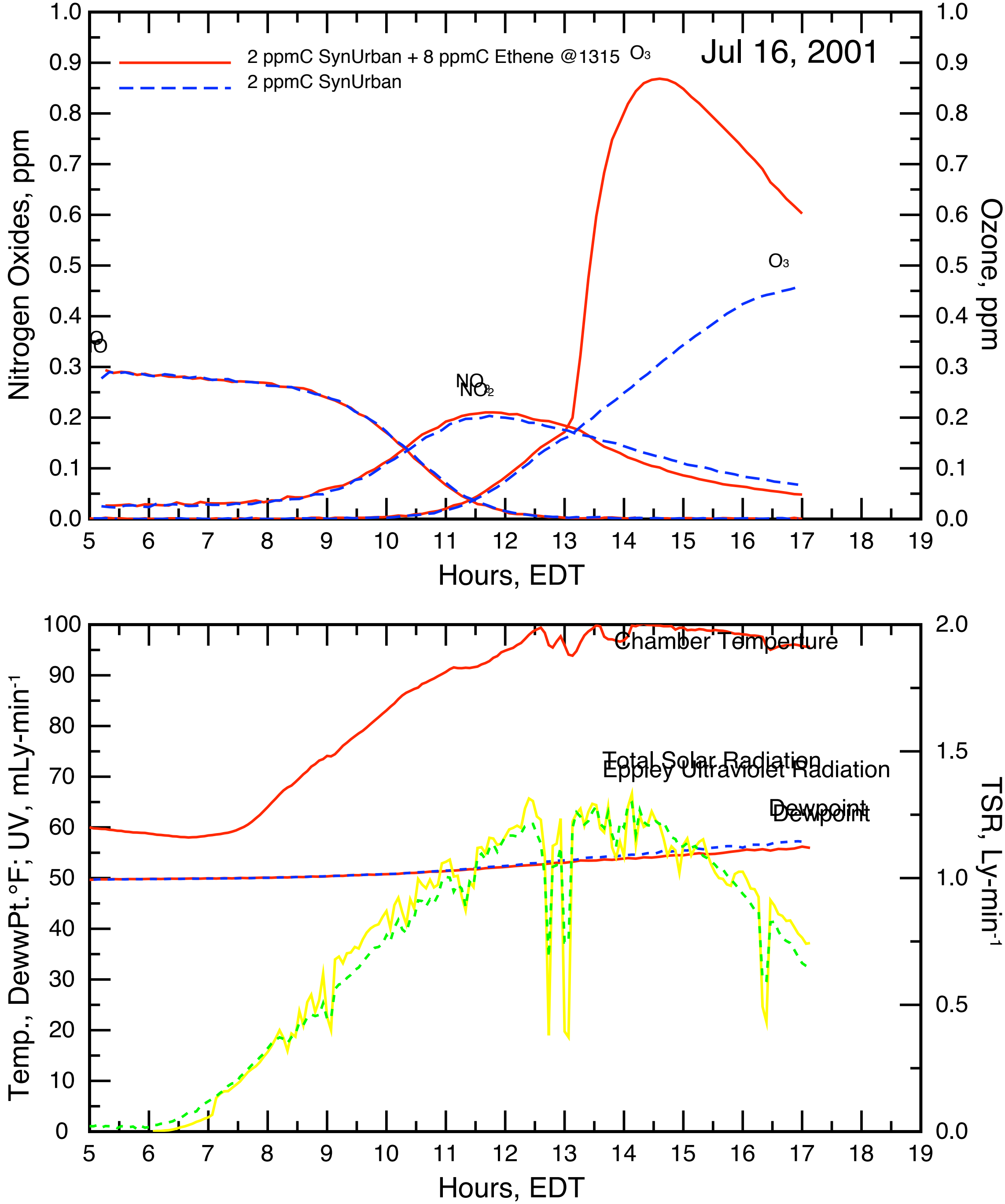
Observations: aircraft VOCs



- Only 17 of 211 Rapid Ozone Formation aircraft measurements > 40 ppb/h
- All high ROF events associated with high concentrations of 2-5 HRVOCs
- All high ROF events are near large industrial point sources of VOCs
- High ROF and HRVOCs are observed at different sites on different days and not at same site each day

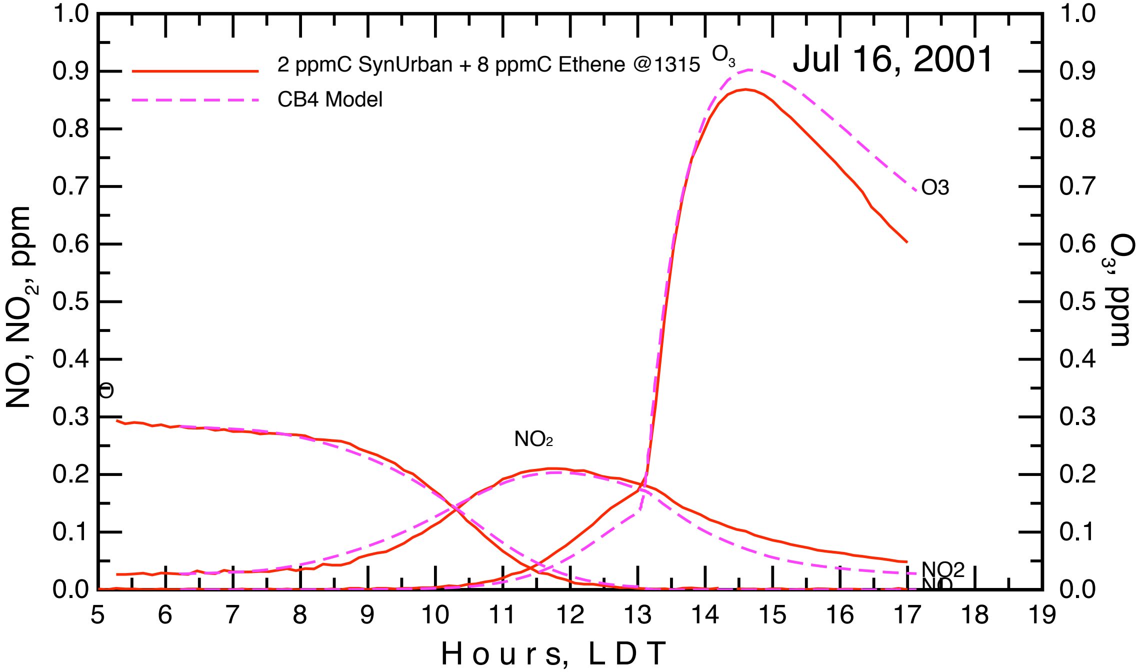
Data of Klineman and Daum, 2002

Jeffries, Blanchard 2002

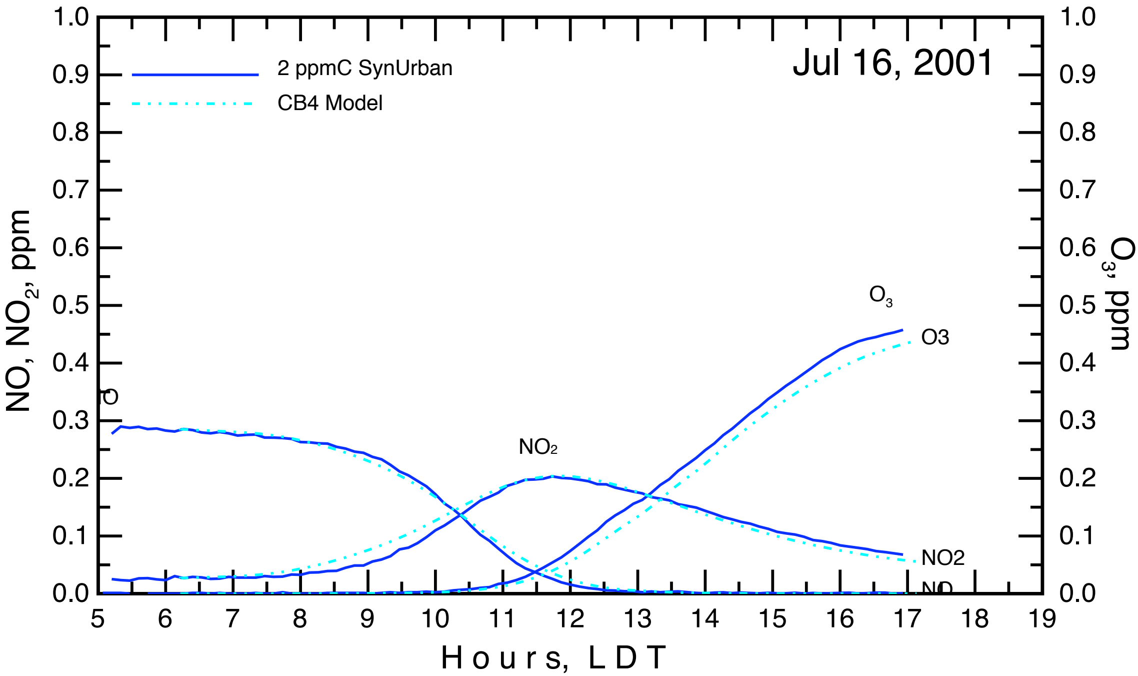


Jul 16, 2001
2 ppmC SynUrban + 8 ppmC Ethene @1315
2 ppmC SynUrban
O3
NO
NO2
Nitrogen Oxides, ppm
Ozone, ppm
Hours, EDT
Chamber Temperture
Total Solar Radiation
Eppley Ultraviolet Radiation
Dewpoint
Temp., DewwPt. °F; UV, mLy-min-1
TSR, Ly-min-1
Hours, EDT

Title:



2 ppmC SynUrban + 8 ppmC Ethene @1315
CB4 Model
Jul 16, 2001
O3
NO2
NO
NO, NO2, ppm
O3, ppm
Hours, LDT



2 ppmC SynUrban
CB4 Model
Jul 16, 2001
O3
NO2
NO
NO, NO2, ppm
O3, ppm
Hours, LDT

Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events

Houston Petrochemical Production Capacity

Compound	US%	Amount Produced: billion lbs per year	Amount Produced: million lbs per day	Amount Produced: million lbs per hour	At 0.05% Loss: tons per day	At 0.05% Loss: 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

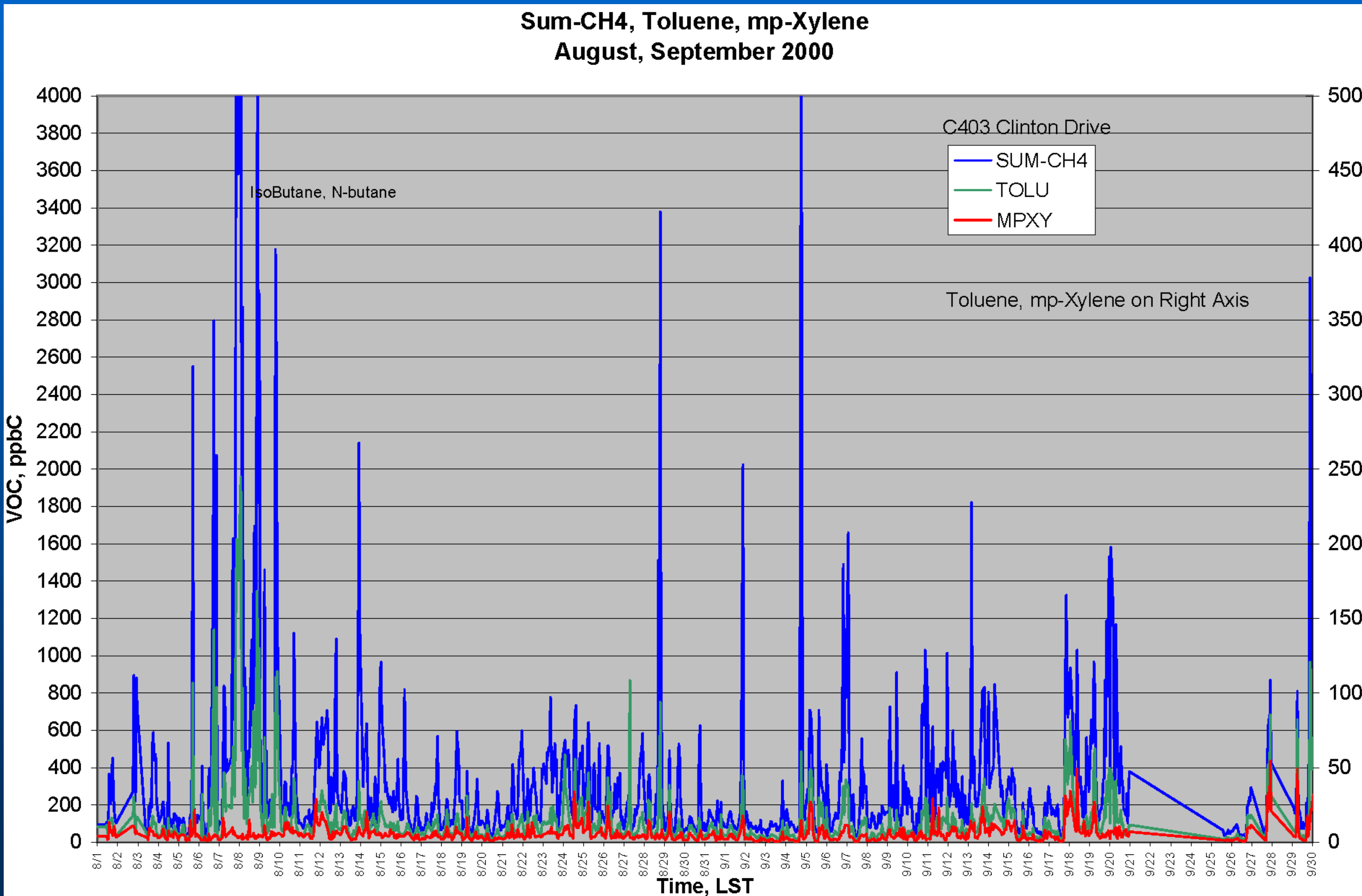
Sources: Business Houston, 2001; Houston Facts, 2000; Chemical Marketing Reporter 1996--1997; County Business Patterns, 1990; U.S. Census Bureau; after Deawon Byun

2.7 million vehicles drive 120 million miles each day

4 billion barrels of crude can be processed each day

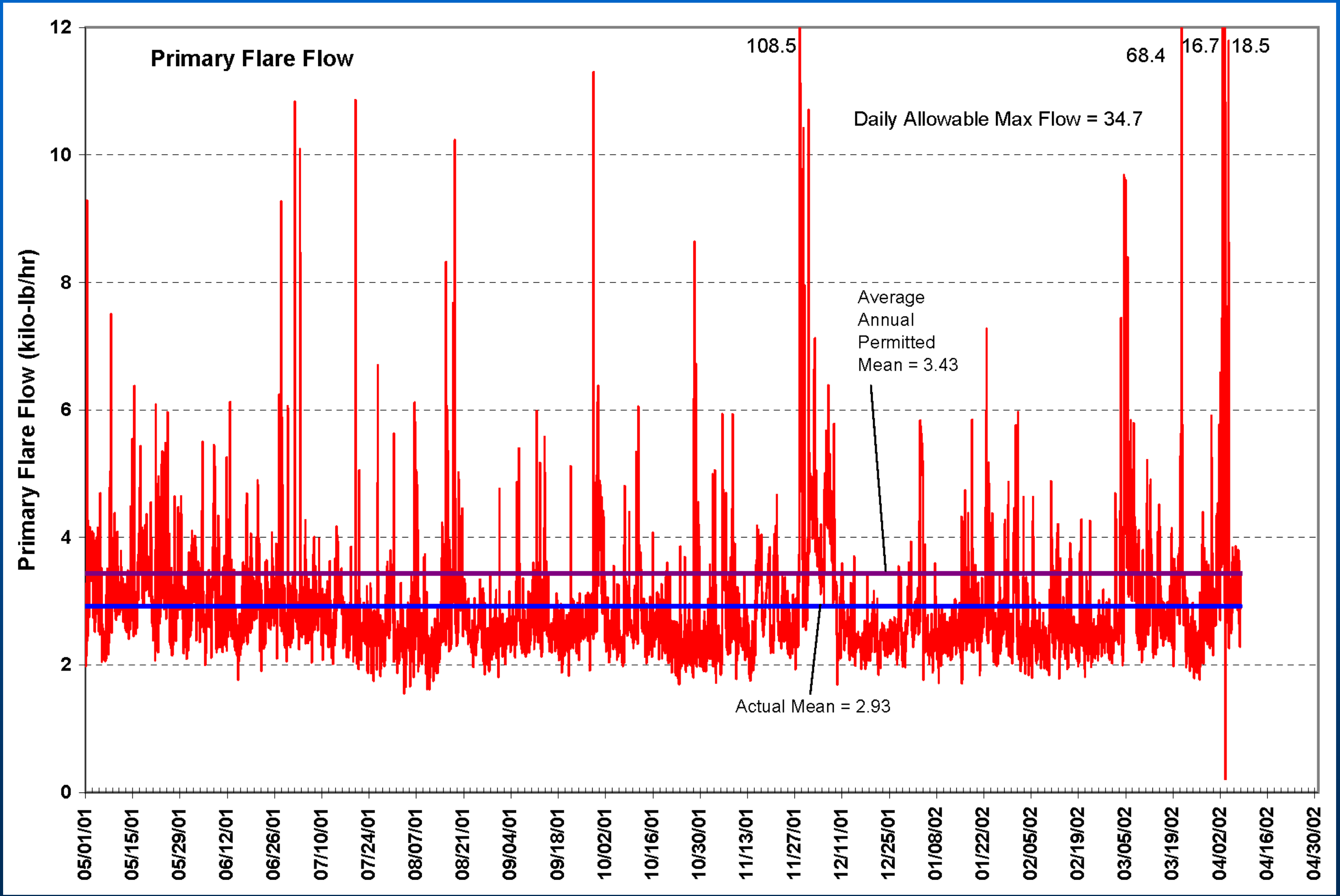
Port of Houston is 2ad largest in US in tons loaded/unloaded
More than 100 commercial docks along ship channel.

Observations: auto_GC



Sexton, Jeffries, 2001

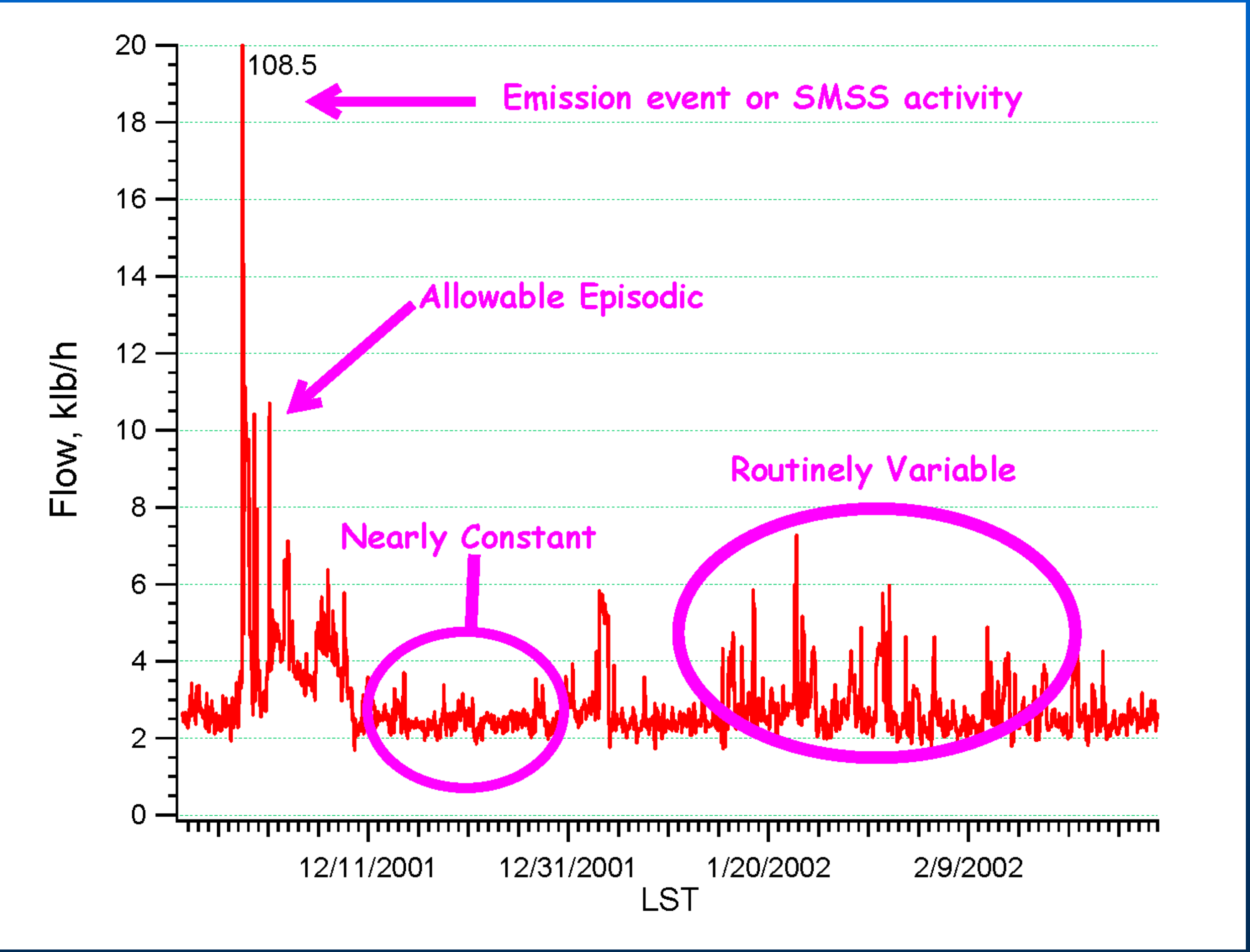
Hourly Timeseries for a Major Flare



One Year

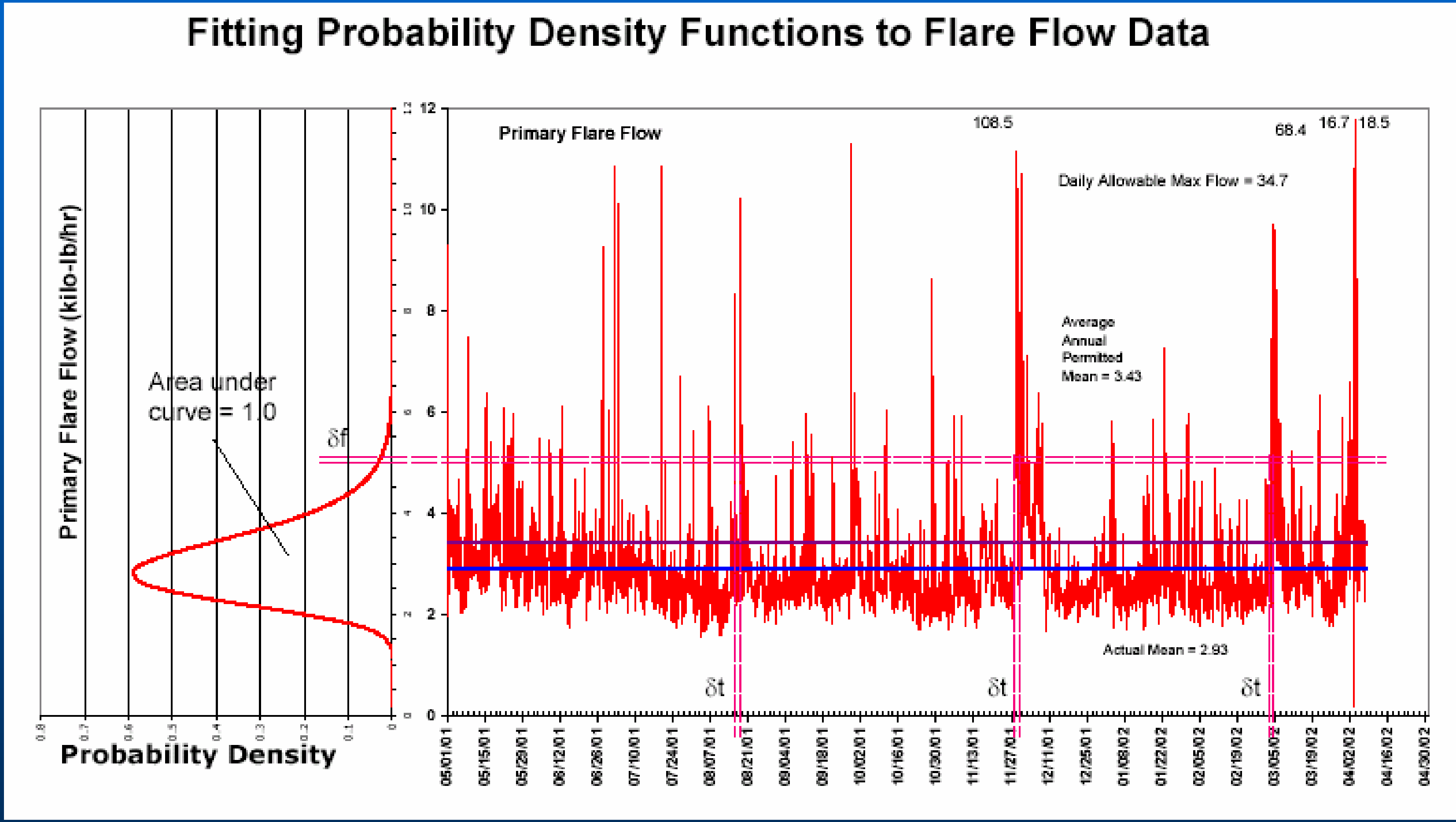
MCCG, 2002

Types of Variance for a Major Flare



Symons, Webster, Pennington, 2003

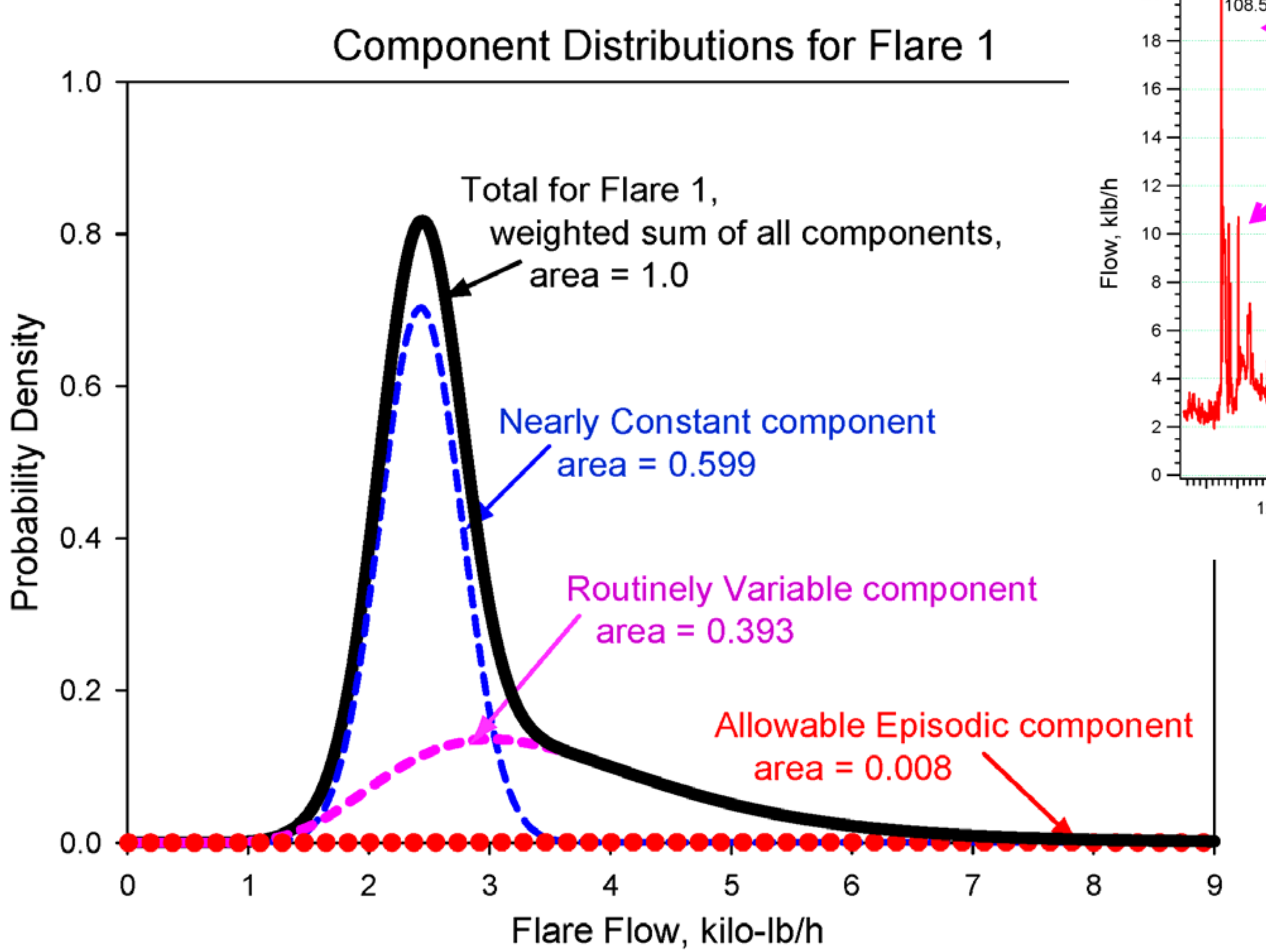
Modeling variability in point source VOC emissions

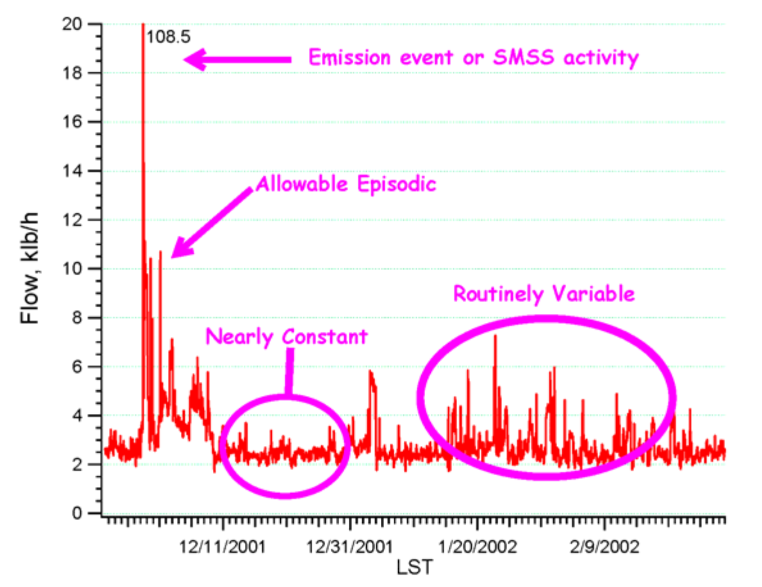


Use a probability distribution function (PDF) to describe the variability in the emissions

Jeffries, 2002

Application of Statistical Mixture Theory Leads to Multiple Overlapping PDFs

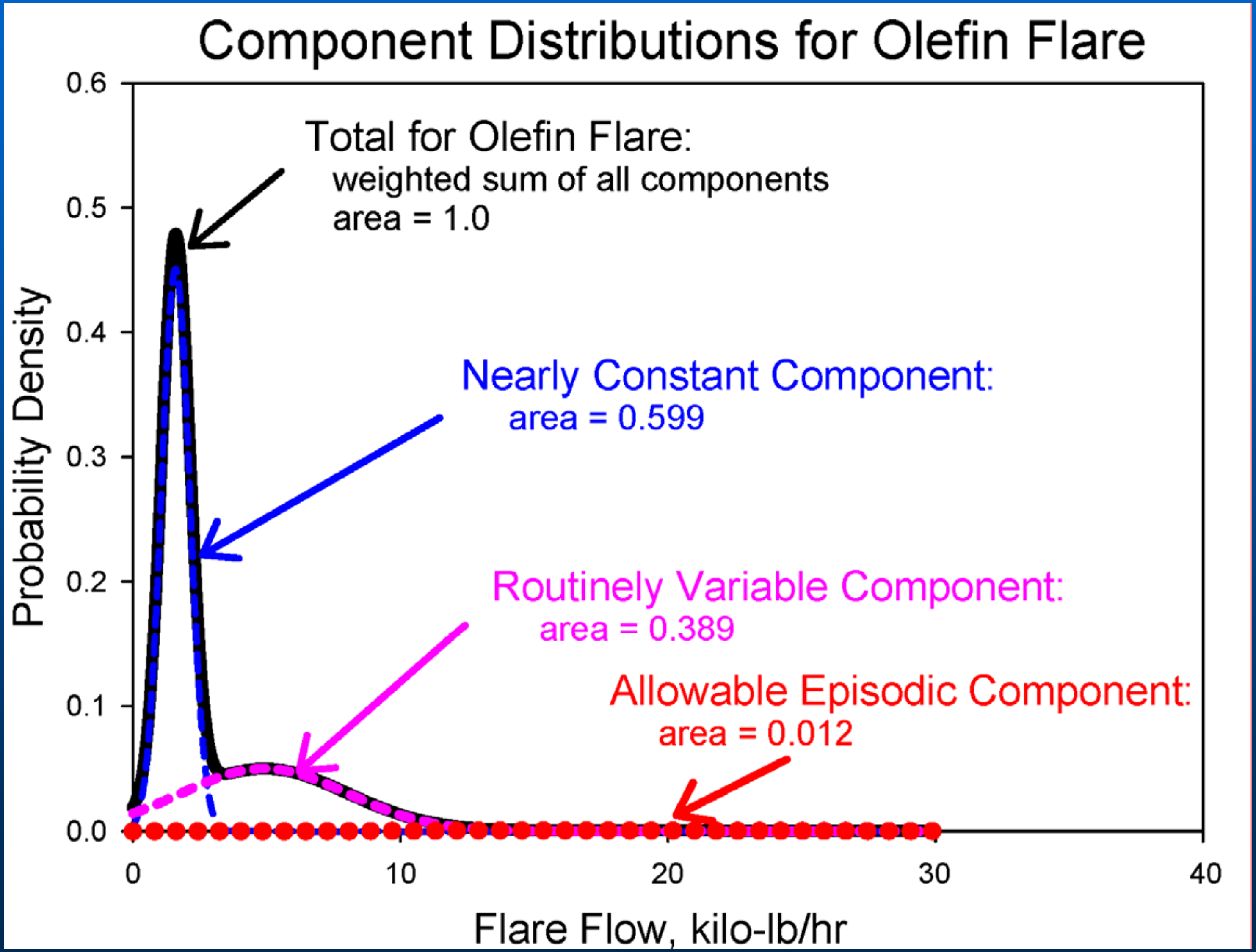




Use this in simulations.

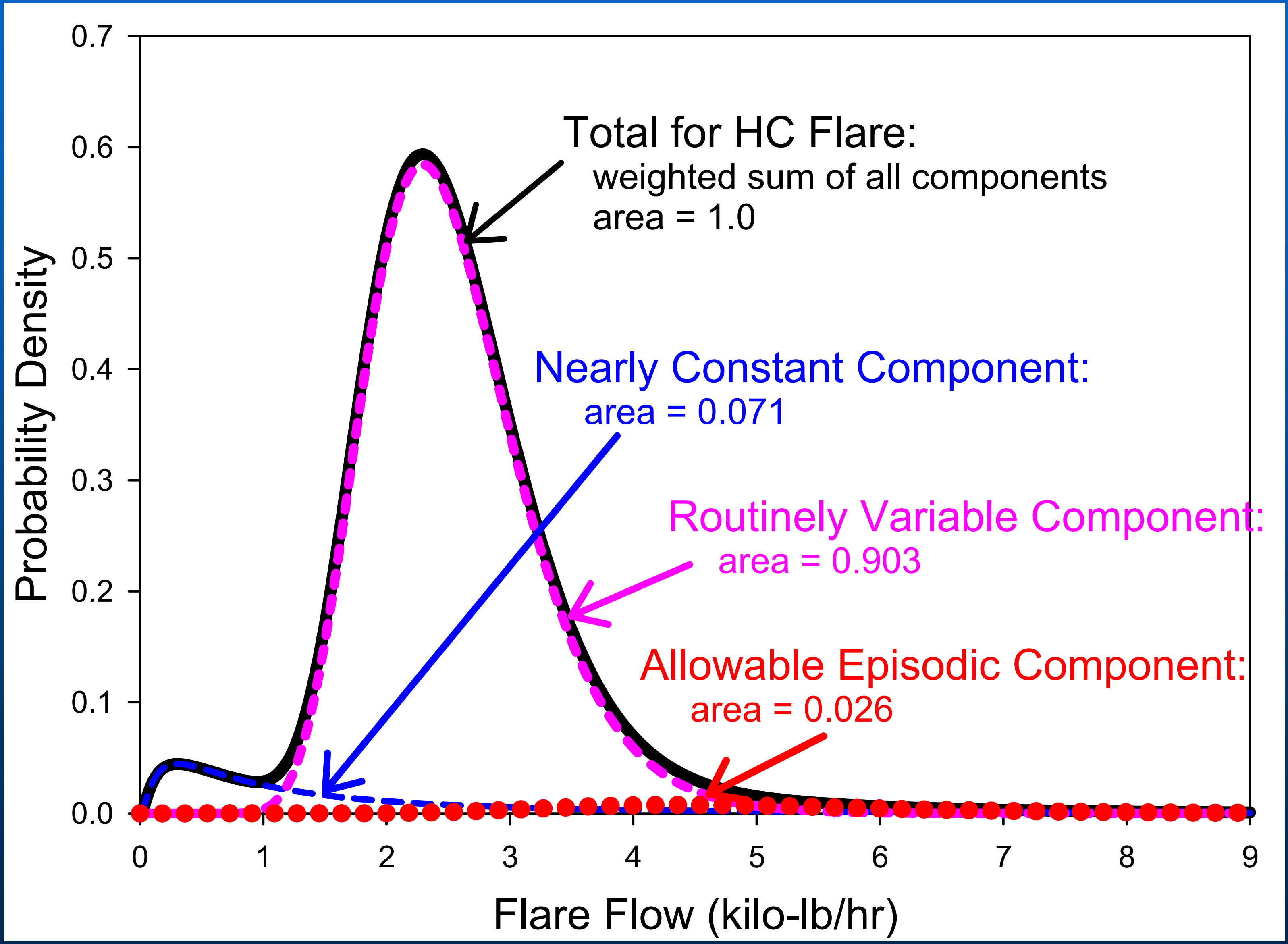
Symons, Webster, Pennington, 2003

Combined PDF for Olefin Flare



Symons, Webster, Pennington, 2003

Combined PDF for HC Flare



Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Atmospheric Environment 41 (2007) 9580–9593

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

The effect of variability in industrial emissions on ozone formation in Houston, Texas

Mort Webster[a,*], Junsang Nam[b], Yosuke Kimura[b], Harvey Jeffries[c], William Vizuete[c], David T. Allen[b]

[a]*Department of Earth, Atmosphere, and Planetary Sciences, Massachusetts Institute of Technology, E40-408, 77 Massachusetts Avenue, Cambridge, MA 02139, USA*

[b]*University of Texas, Center for Energy and Environmental Resources, 10100 Burnet Road, M/S R7100, Austin, TX 78758, USA*

[c]*Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, NC 27599, USA*

Received 22 December 2006; received in revised form 17 August 2007; accepted 17 August 2007

Abstract

Ambient observations have indicated that high concentrations of ozone observed in the Houston/Galveston area are associated with plumes of highly reactive hydrocarbons, mixed with NO_x, from industrial facilities. Ambient observations and industrial process data, such as mass flow rates for industrial flares, indicate that the VOCs associated with these industrial emissions can have significant temporal variability. To characterize the effect of this variability in emissions on ozone formation in Houston, data were collected on the temporal variability of industrial emissions or emission surrogates (e.g., mass flow rates to flares). The observed emissions variability was then used to construct regionwide emission inventories with variable industrial emissions, and the impacts of the variability on ozone formation were examined for two types of meteorological conditions, both of which lead to high ozone concentrations in Houston. The air quality simulations indicate that variability in industrial emissions has the potential to cause increases and decreases of 10–52 ppb (13–316%), or more, in ozone concentration. The largest of these differences are restricted to regions of 10–20 km^2, but the variability also has the potential to increase regionwide maxima in ozone concentrations by up to 12 ppb.

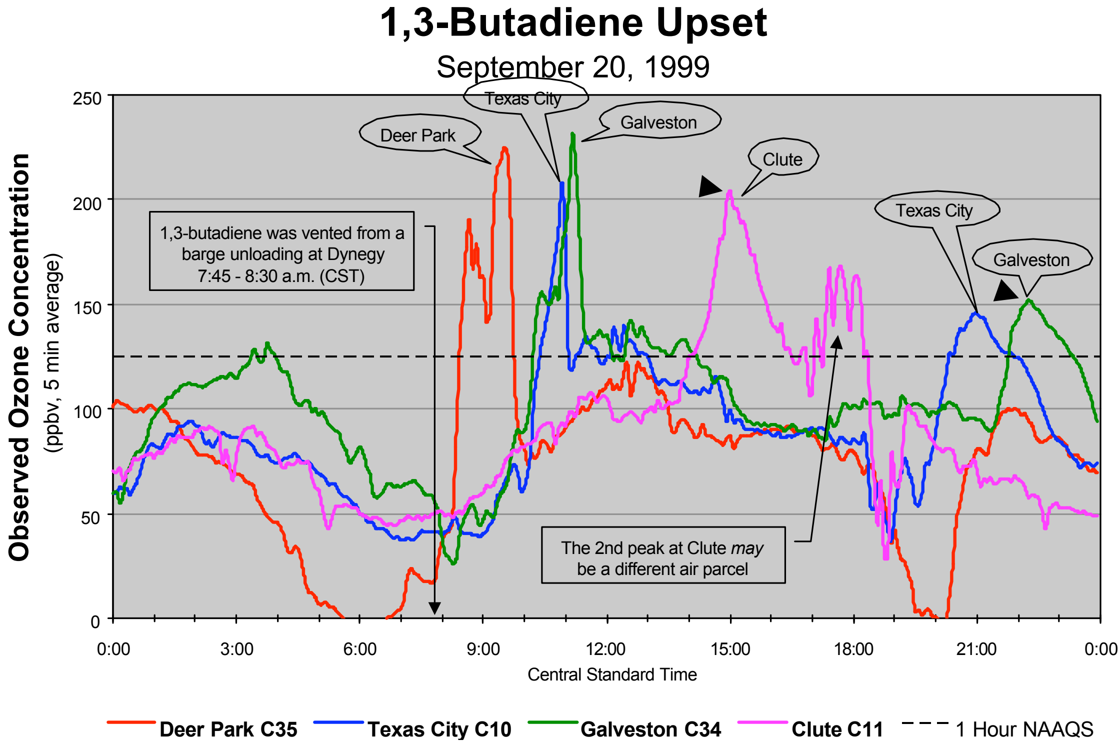
Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events

What is an emission event?

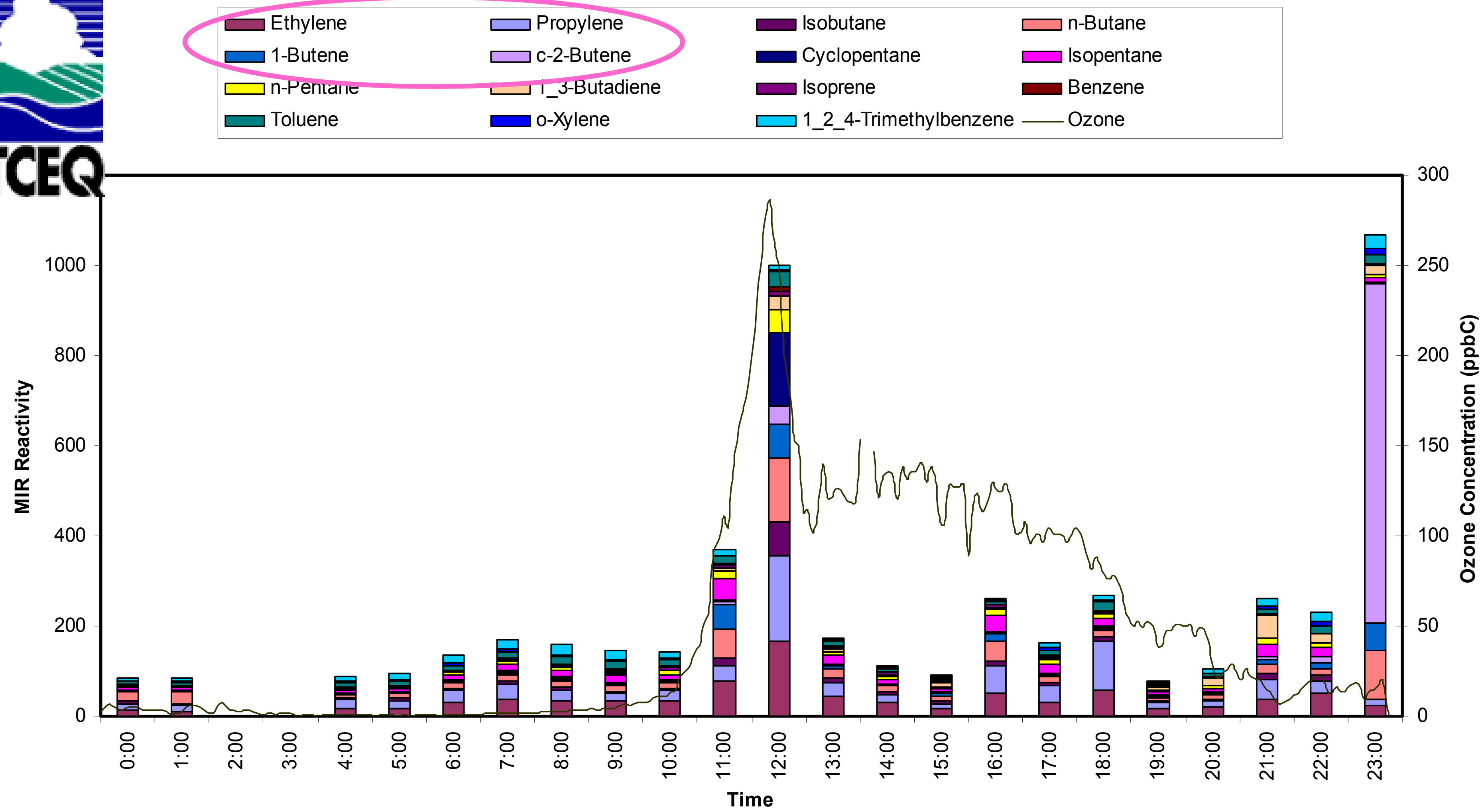
Effective September 12, 2002, per Texas Administrative Code (TAC) Title 30 Chapter 101, reportable quantities were reduced from **5000** lbs to **100** lbs for most compounds in the Houston/Galveston ozone non-attainment area. Section 101.1, paragraph (83) defines a reportable emissions event as "Any 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.



1,3-Butadiene Upset
September 20, 1999
Observed Ozone Concentration
(ppbv, 5 min average)
250
200
150
100
50
0
0:00
3:00
6:00
9:00
12:00
15:00
18:00
21:00
0:00
Central Standard Time
Deer Park
Texas City
Galveston
Clute
Texas City
Galveston
1,3-butadiene was vented from a barge unloading at Dynegy 7:45 - 8:30 a.m. (CST)
The 2nd peak at Clute may be a different air parcel
Deer Park C35
Texas City C10
Galveston C34
Clute C11
1 Hour NAAQS

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

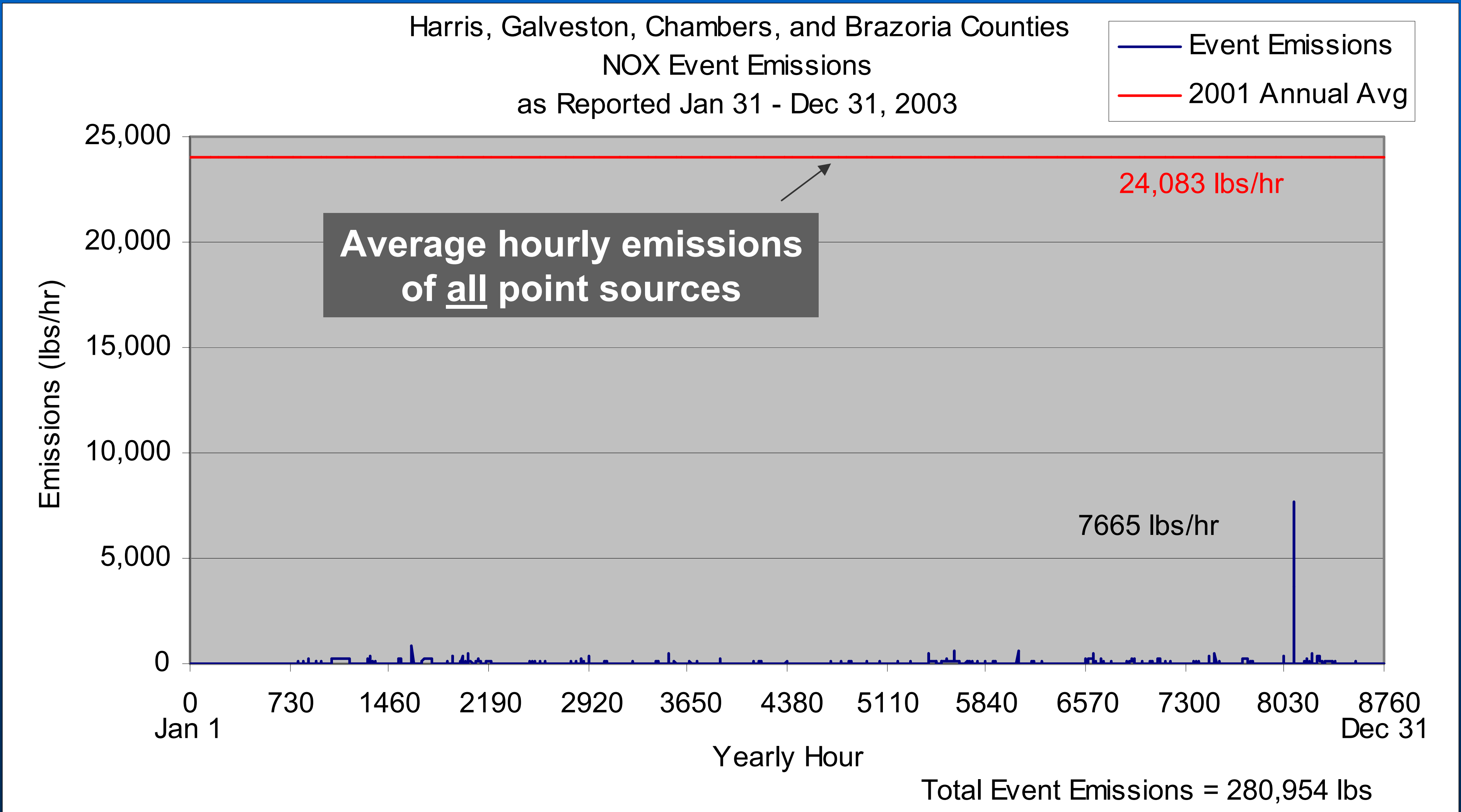


5 minute ozone and hourly auto-GC Max Inc Reactivity for VOC

First Year HRVOC Event Data

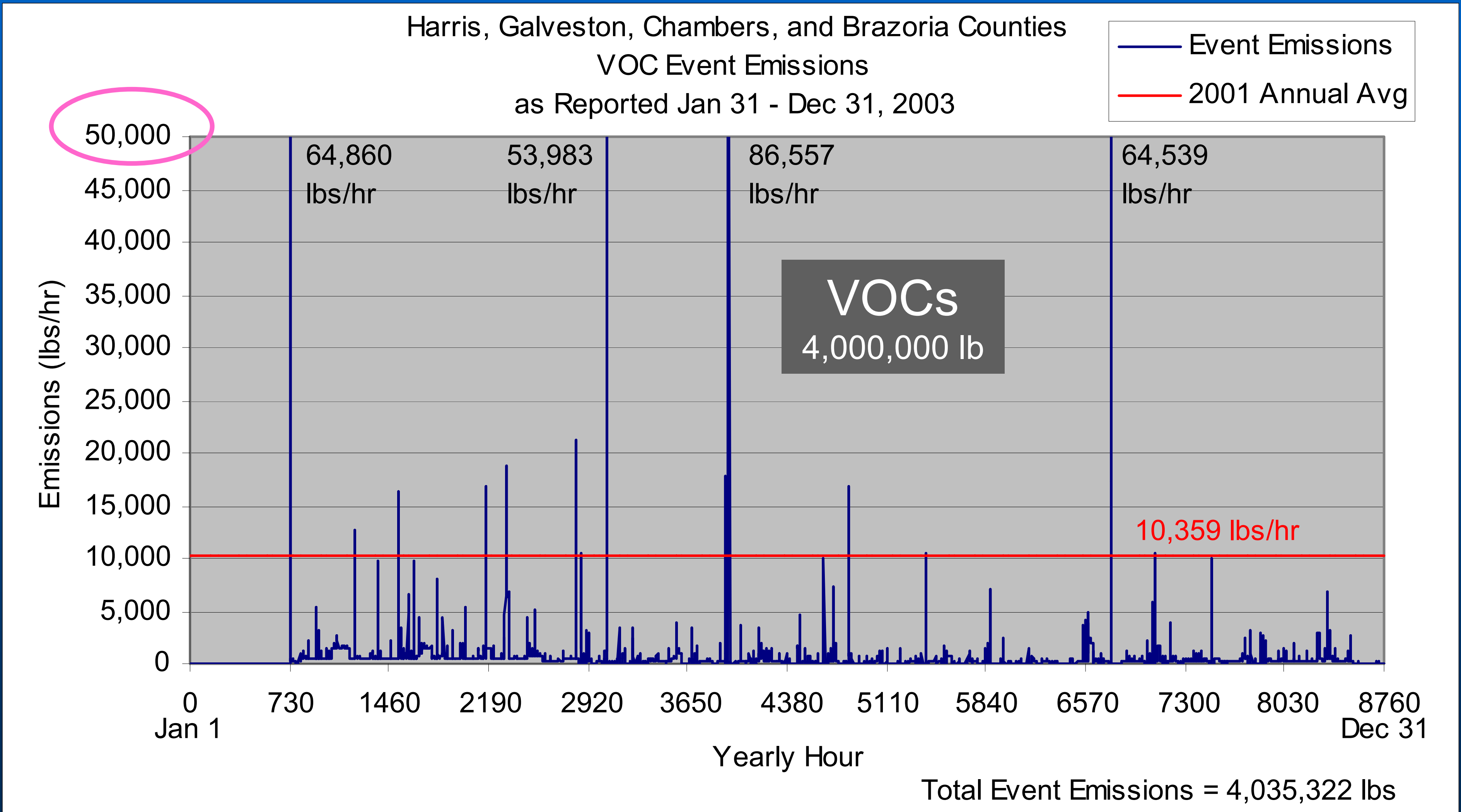
County	All Events	HRVOC Events	Event HRVOCs	
			lbs	tons
Harris	934	423	816,961	408
Brazoria	331	187	759,853	380
Galveston	329	86	69,229	35
Chambers	53	13	20,497	10
4 County Total	1,647	709	1,666,540	833
Fort Bend	40			
Montgomery	19			
Liberty	1	1	558	<1
Waller	2			
HGA Total	1,709	710	1,667,098	833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

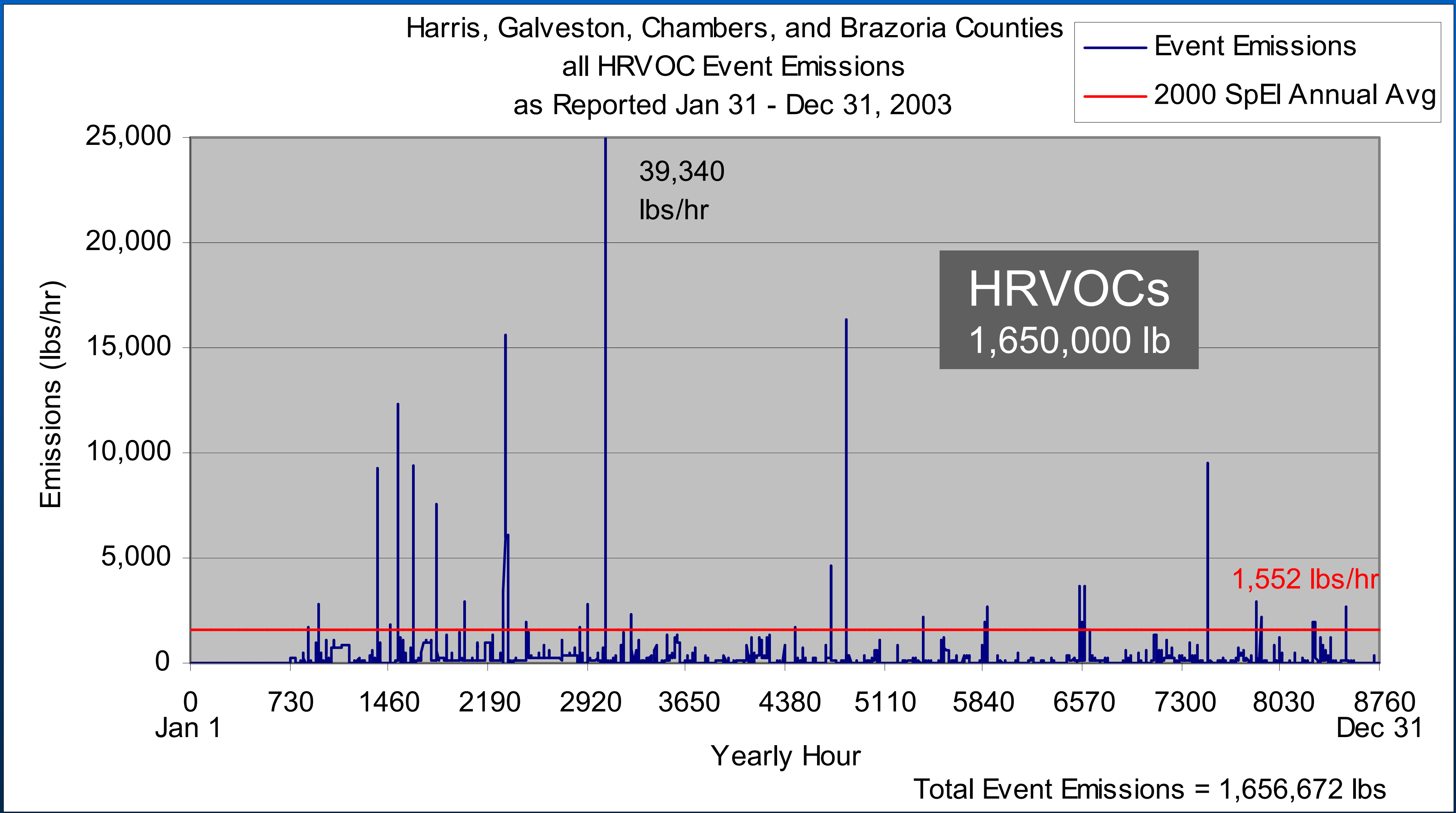


First 11 Months of reporting

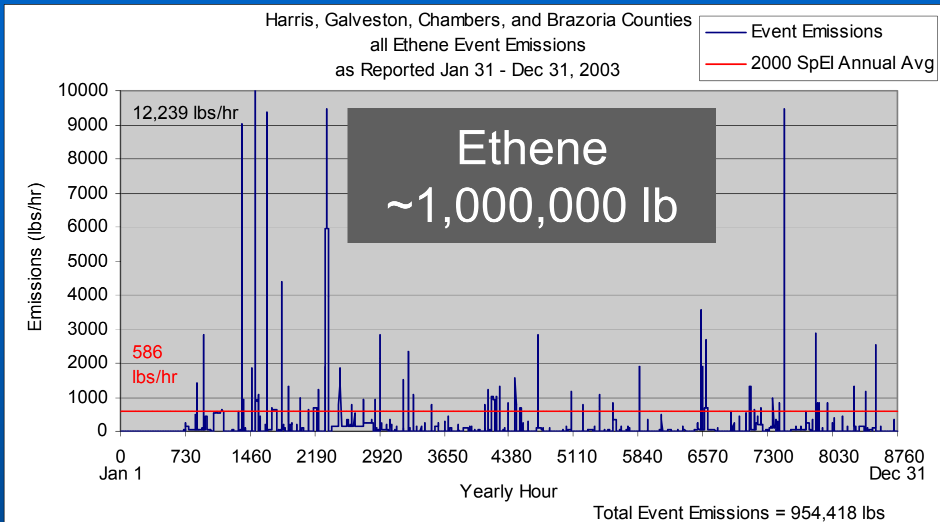
VOC Events and Averages

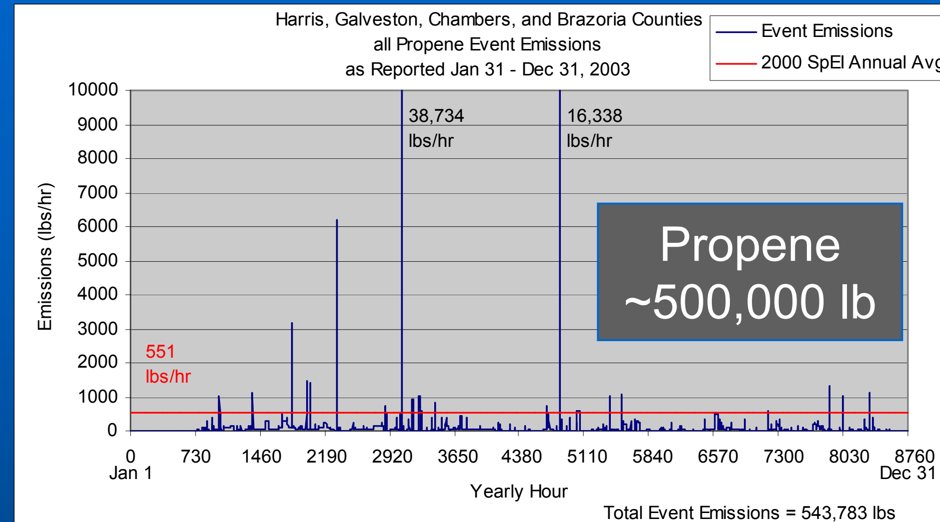
- Event total mass of over **4** million pounds (2000 tons) contributes 4% to the 45,000 tons of VOC emitted over a single year from point sources in the four counties.
- **14** times (18 hours) during the eleven-month period, an event emission exceed the annual average for all facilities in the region.
- **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.

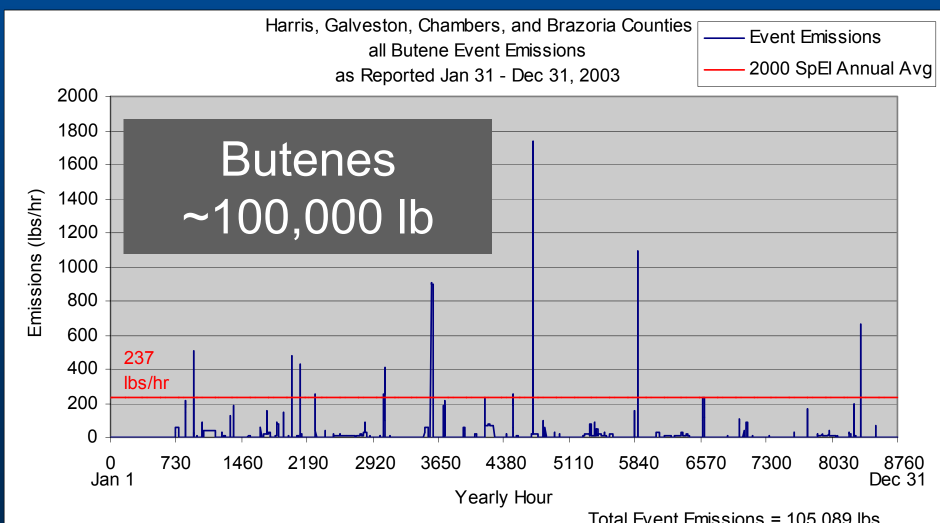
HRVOC emissions can also be large relative to annual average emissions

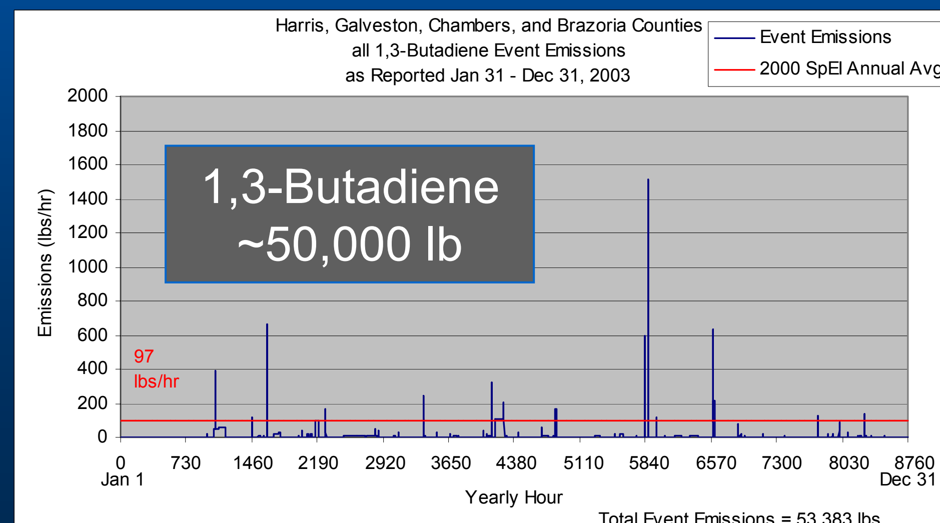


Four Major HRVOCs





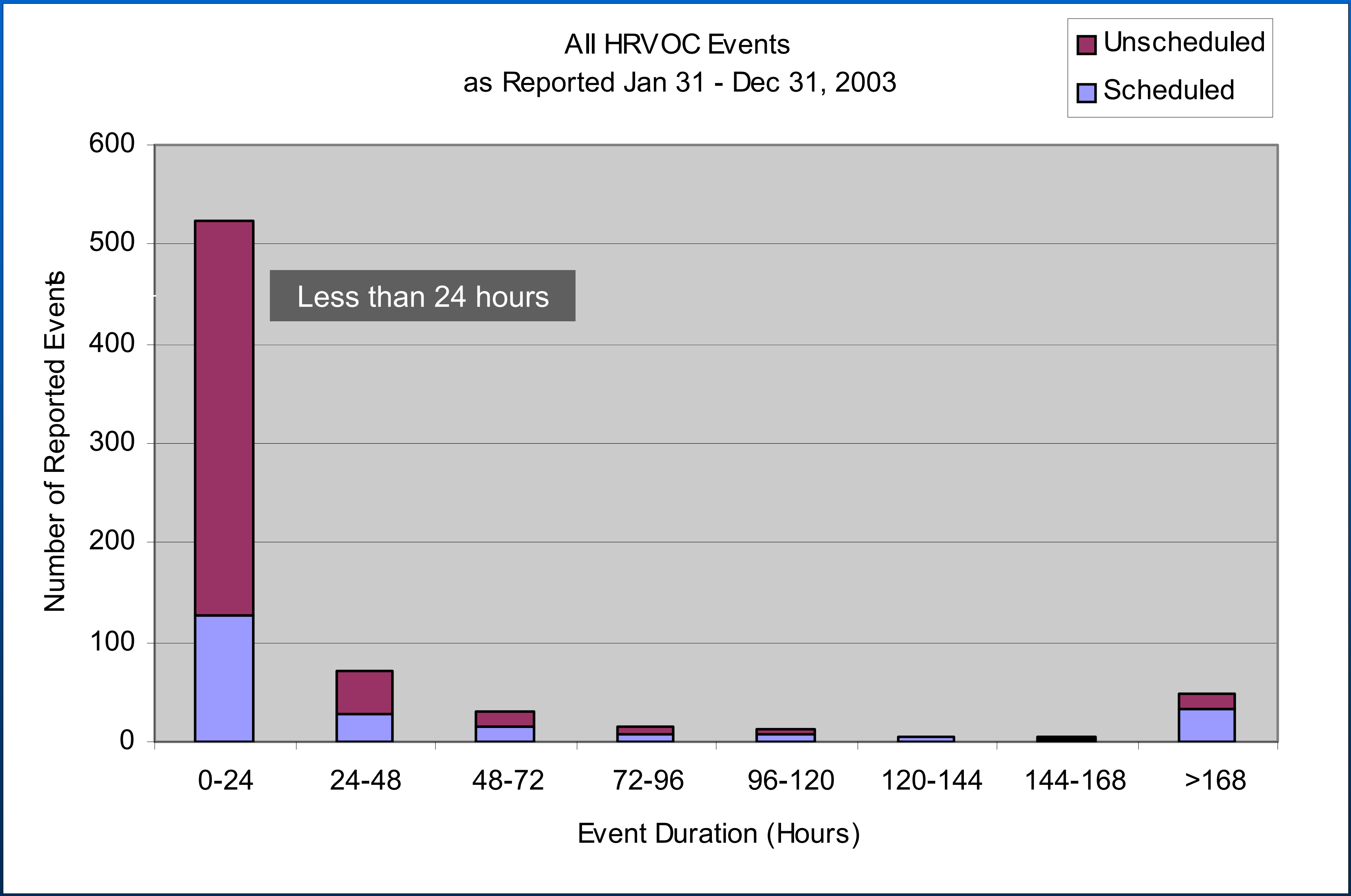




HRVOC Events and Averages

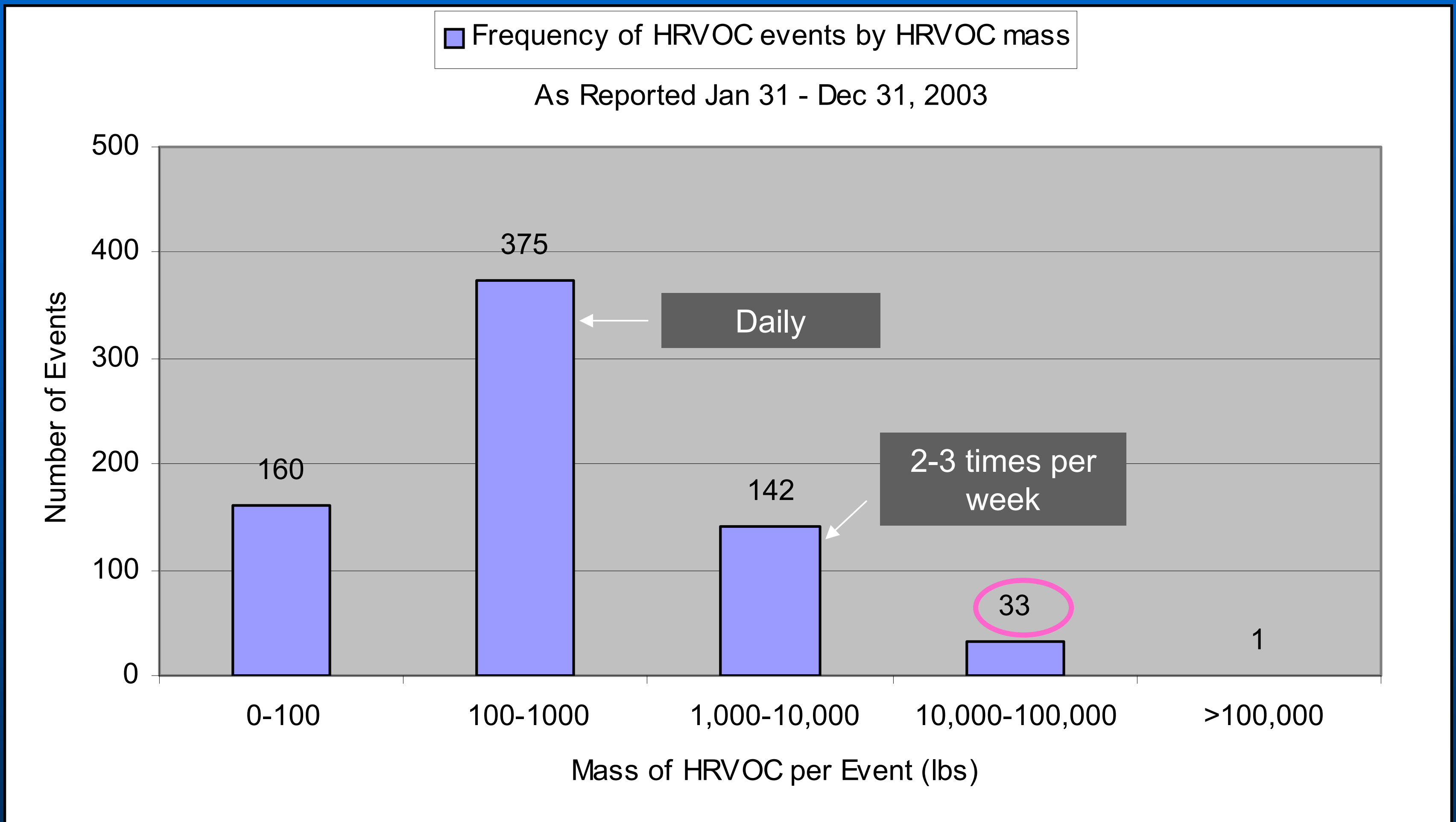
- Total mass of over **1.6** millions pounds (830 tons) is **~12%** of the 6800 tons of HRVOC emitted over a single year from point sources in the four counties.
- **29** times (115 hours) during the eleven-month period, an event emission exceed the annual average.
- **7** times in 11 months, the flow 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

Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Atmospheric Environment 39 (2005) 3785–3798

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Hydrocarbon emissions from industrial release events in the Houston-Galveston area and their impact on ozone formation

Cynthia Folsom Murphy, David T. Allen*

Center for Energy and Environmental Resources, University of Texas at Austin, 10100 Burnet Road, Mail Code R7100, Austin, TX 78758, USA

Received 16 November 2004; received in revised form 17 February 2005; accepted 17 February 2005

Abstract

Ambient measurements have shown that ozone formation in the Houston-Galveston area of Texas is frequently much more rapid than in other urban areas. One of the contributing factors is believed to be short-term episodic or "event" emissions from industrial facilities, particularly releases that contain significant mass fractions of highly reactive volatile organic compounds (HRVOCs). In this work, time series analyses are used to compare average annual flow rates for air pollutant emissions with those released during reported emission events. The results indicate that the magnitude and frequency of HRVOC event emissions are an important element in accurately reflecting ozone precursor emission patterns in the Houston-Galveston area, particularly in Harris, Brazoria, Galveston, and Chambers counties. More than 50% of the reported episodic (event) emissions of HRVOCs are ethene and approximately a third are propene; the remainders are isomers of butene and 1,3-butadiene. Most events last less than 24 h. The mass released in an event can vary from a few hundred to more than 100,000 lb, and the dominant type of industrial source is chemical manufacturers (SIC 2869). Daily emissions from a single facility can vary from annual average emissions by multiple orders of magnitude at a frequency of several times a year. Because there are so many facilities in the Houston-Galveston area, HRVOC emission variability of this magnitude can be expected daily, at some time and some location in the Houston-Galveston area. If the emission variability occurs at times and locations where atmospheric conditions are conducive to ozone formation, both ambient data and photochemical modeling indicate that industrial emission events can lead to elevated concentrations of ozone. Specifically, peak, area-wide ozone concentration can be increased by as much as 100 ppb for large HRVOC emission events.

FLIR GasFind IR Camera

AGENCY / COMMERCIAL USE

- 2004 & 2005: Some Petrochemical Companies Have Voluntarily Used LSI (Land & Air)
- August 2005: FLIR Begins Delivery of Cameras to companies
- 2006: TCEQ purchases cameras
  - Pollution Prevention Division
  - Field Monitoring Division
  - Region 12 Houston
- 2006: EPA NEIC; LADEQ purchases cameras

TexAQS II Remote Sensing VOC Project

Select Raw Footage: Houston Ship Channel

July 11 - 13, 2005


67min
SP
0:09:55:22
JUL 12 2005
11:43:11AM


66min
SP
0:10:49:24
JUL 12 2005
11:53:57AM


59min
SP
0:16:36:06
JUL 12 2005
3:05:59PM

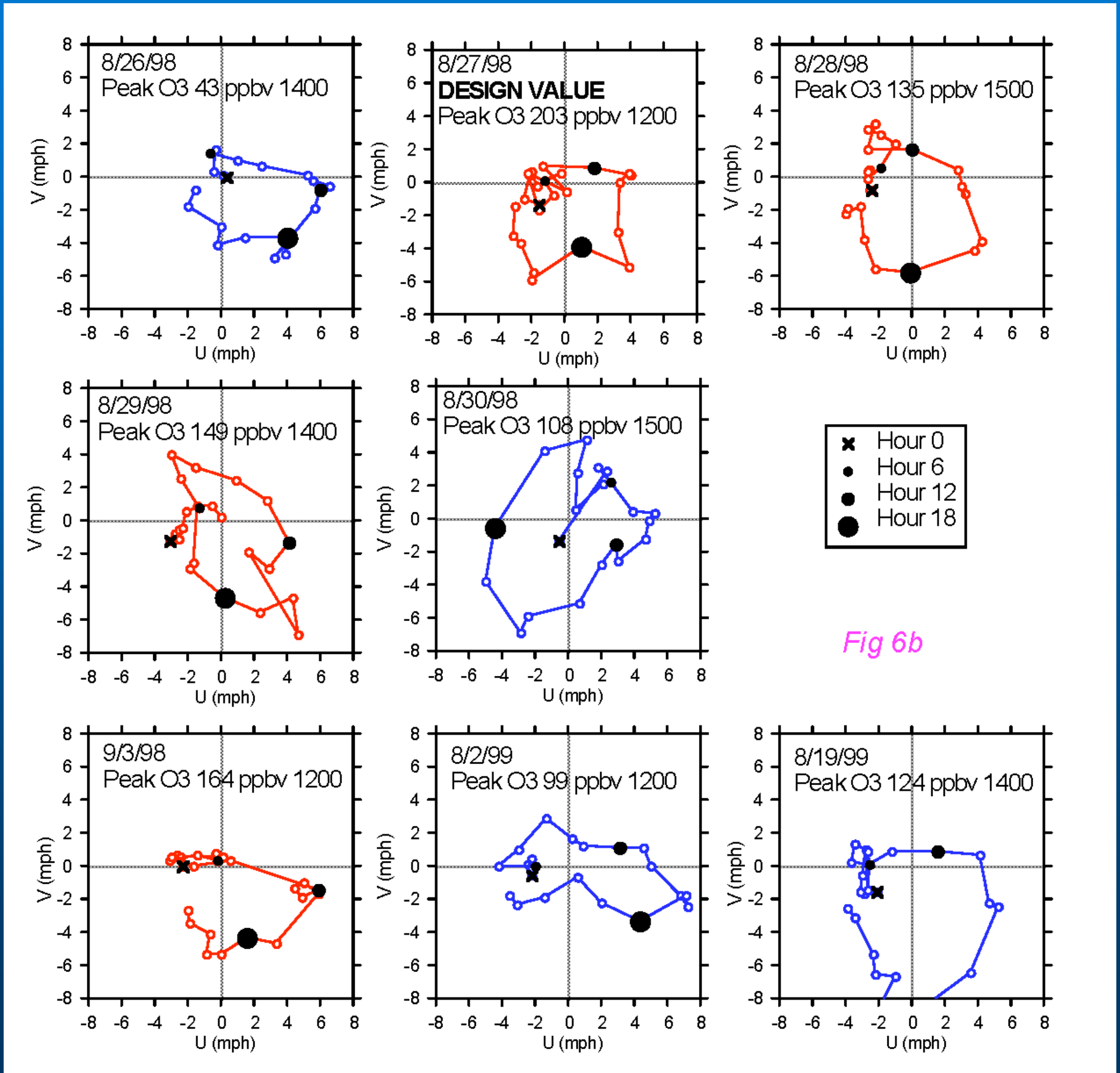

65min
SP
0:11:37:27
JUL 12 2005
12:03:12PM

Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events


August 21, 2000
6:00
12:00
C26
C309
C48
C08
C610
C604
C408
C405
C404
C15
C148
C607
C01
C603
C411
C81
C167
C166
C410
C407
C611
C53
C18
C120
C35
C608
C406
C409
C51
C145
Houston
HARRIS
MONTGOMERY
LIBERTY
CHAMBERS
FORT BEND
BRAZORIA
GALVESTON
George Bush Intercontinental Airport
Galveston Bay
Lake Houston
© 2000 Microsoft Corp. and/or its suppliers. All rights reserved.

Wind Field Has Strong Effect on Ozone Exceedences



Ozone exceedences in Houston are associated with wind that blows from 3 or 4 quadrants during the day.

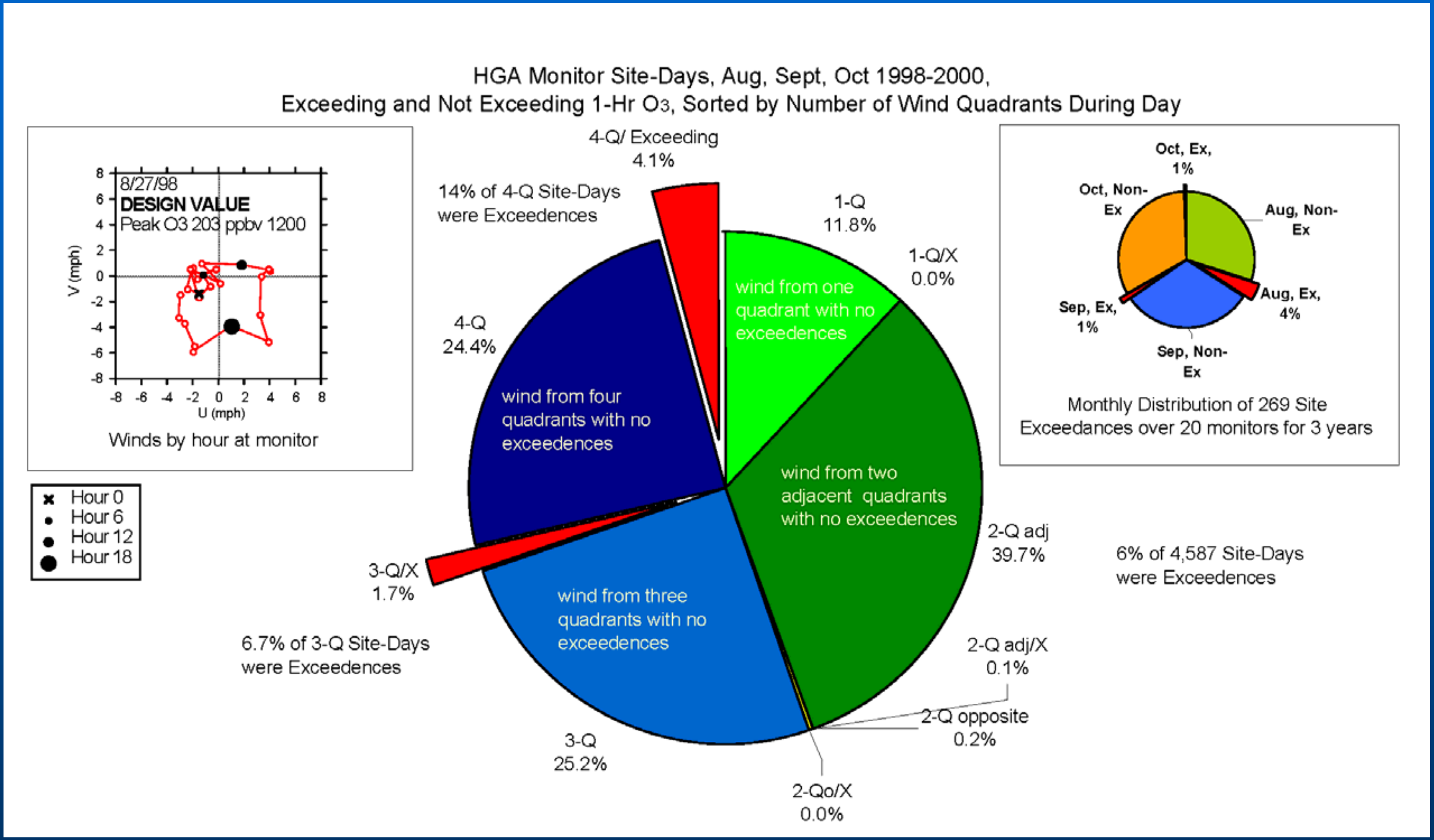
Compare
6 h winds with
18 h winds

Red Hodograms
are exceedence days

Exceedence days have slow 6-12 h winds and faster 18 h winds

Blanchard, Jeffries, 2002

Meteorology and Ozone Exceedences



More than half the time, winds are conducive for ozone exceedence.
Only one day in eight of these days actually has an exceedence.

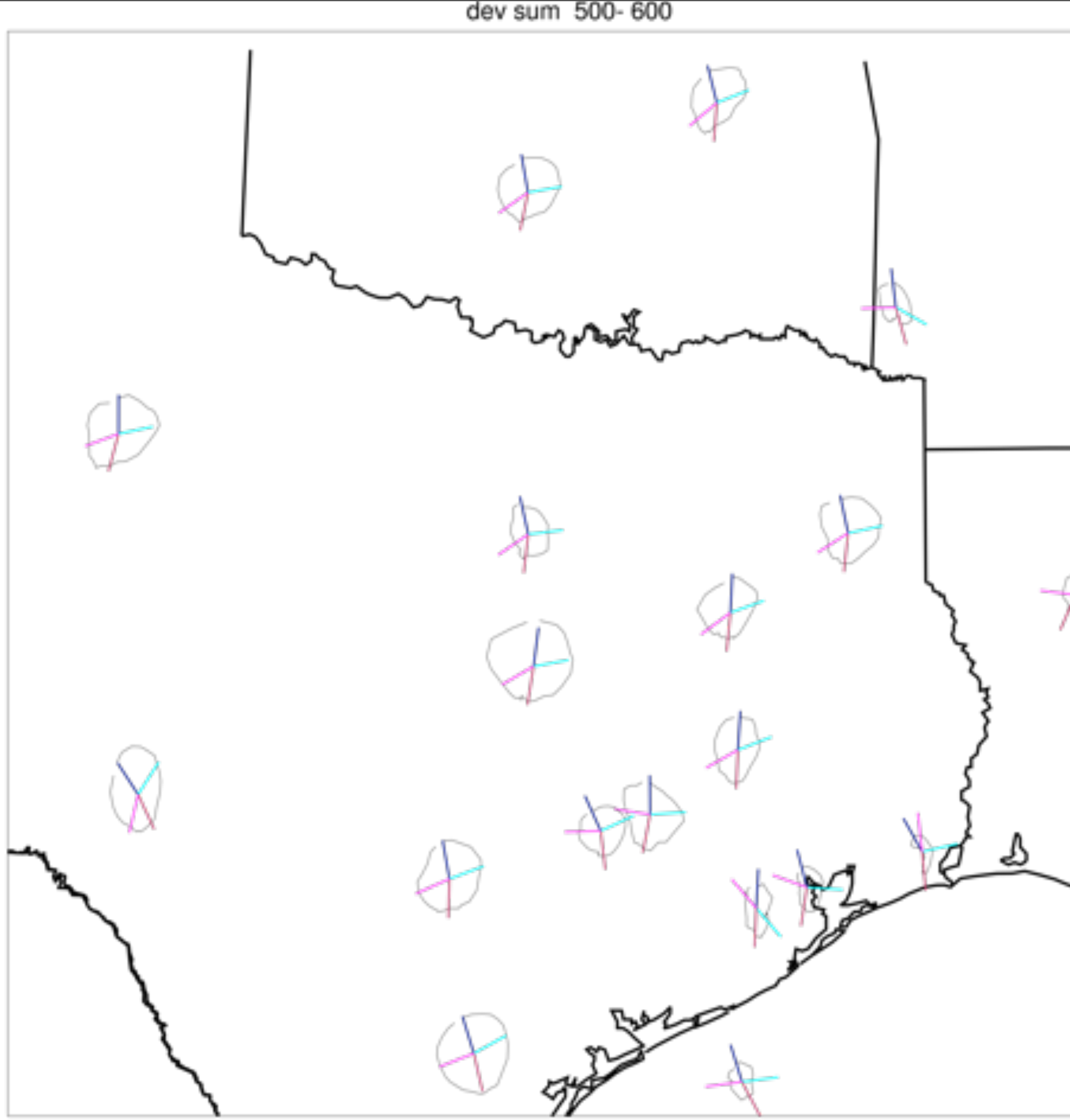
Blanchard, Jeffries, 2002

John W. Nielsen-Gammon and Andrew P. McNeel, TAMU, AMS 2009

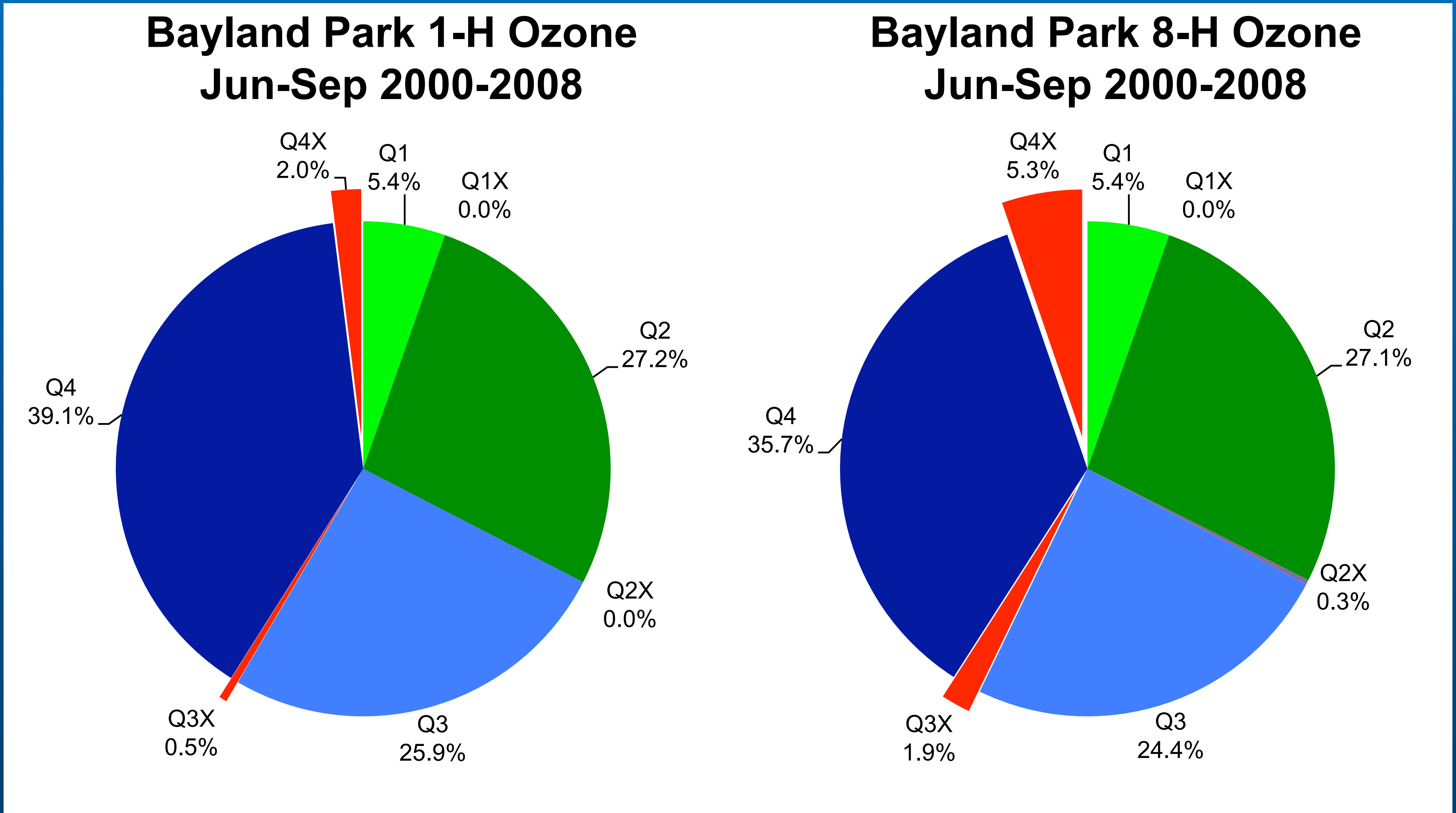
SUMMERTIME COMPOSITE, 100-200 METERS AGL

- Each station: hodograph
- Length of tick marks: 3 m/s
- Black: midnight
- Teal: 6 AM
- Brown: noon
- Pink: 6 PM

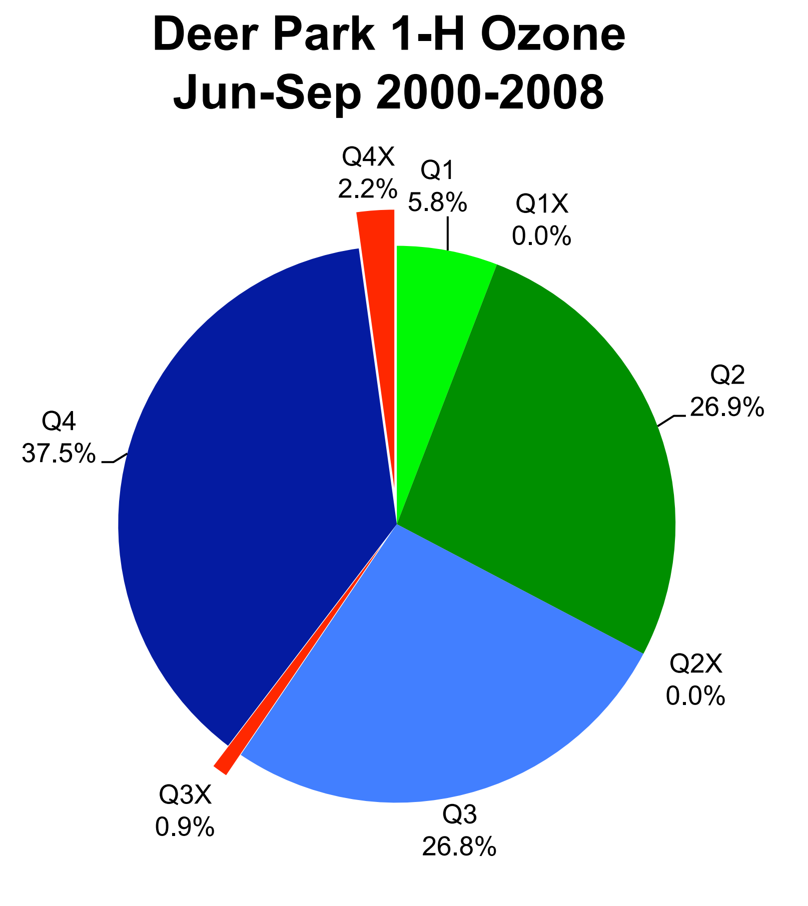
500-600 m AGL

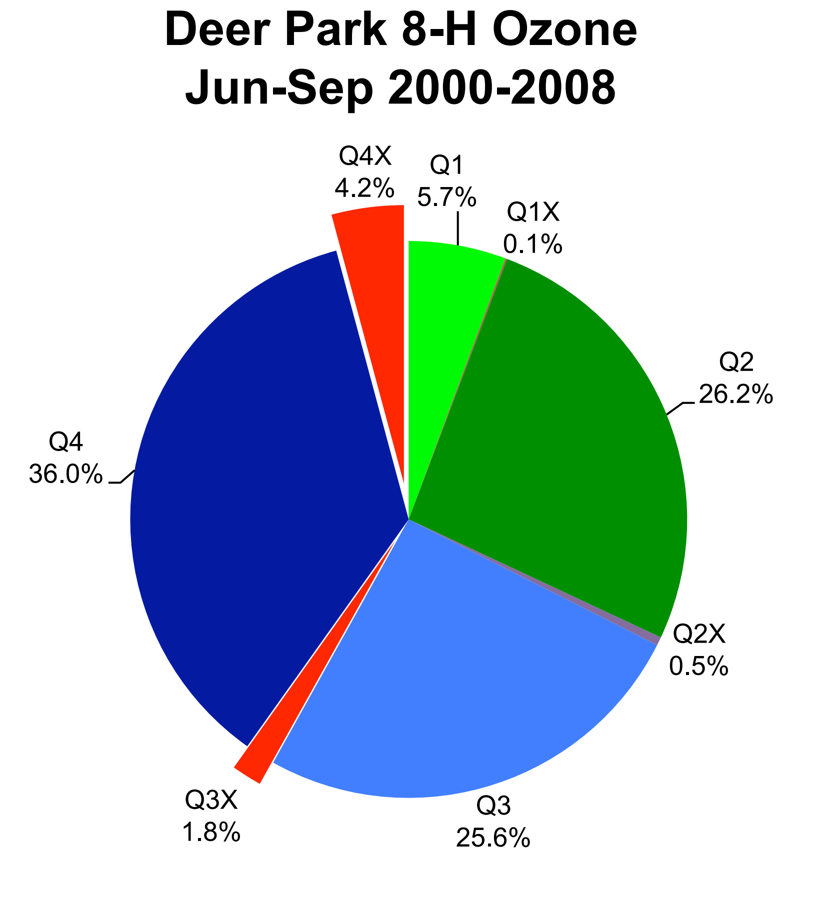


Meteorology and Ozone Exceedences, Updated

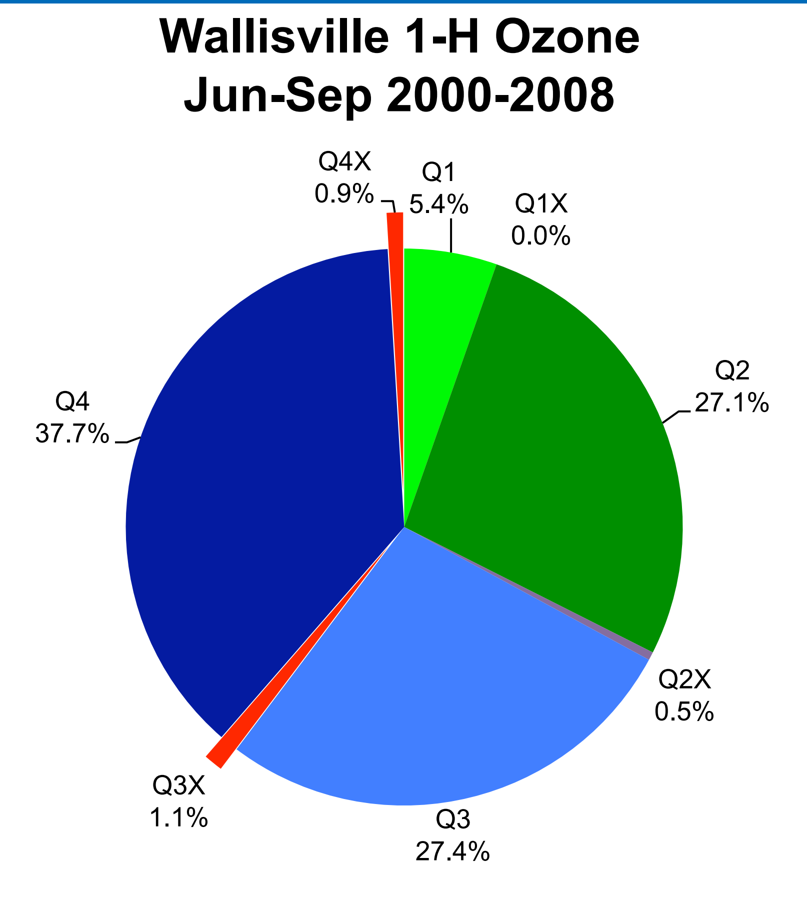


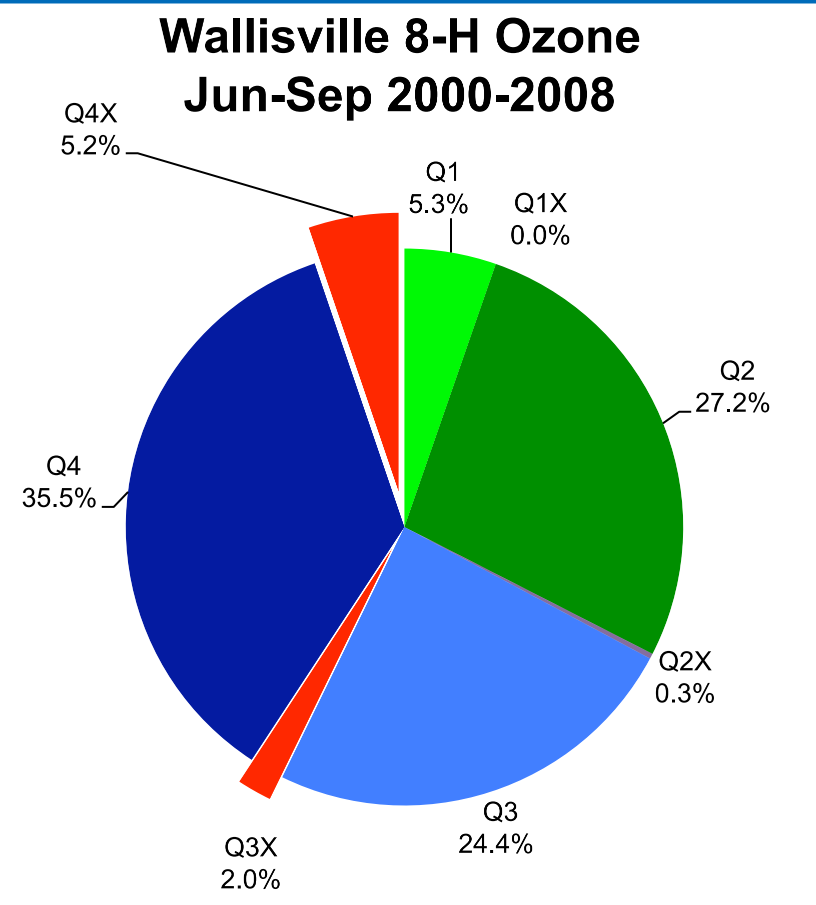
Meteorology and Ozone Exceedences, Updated



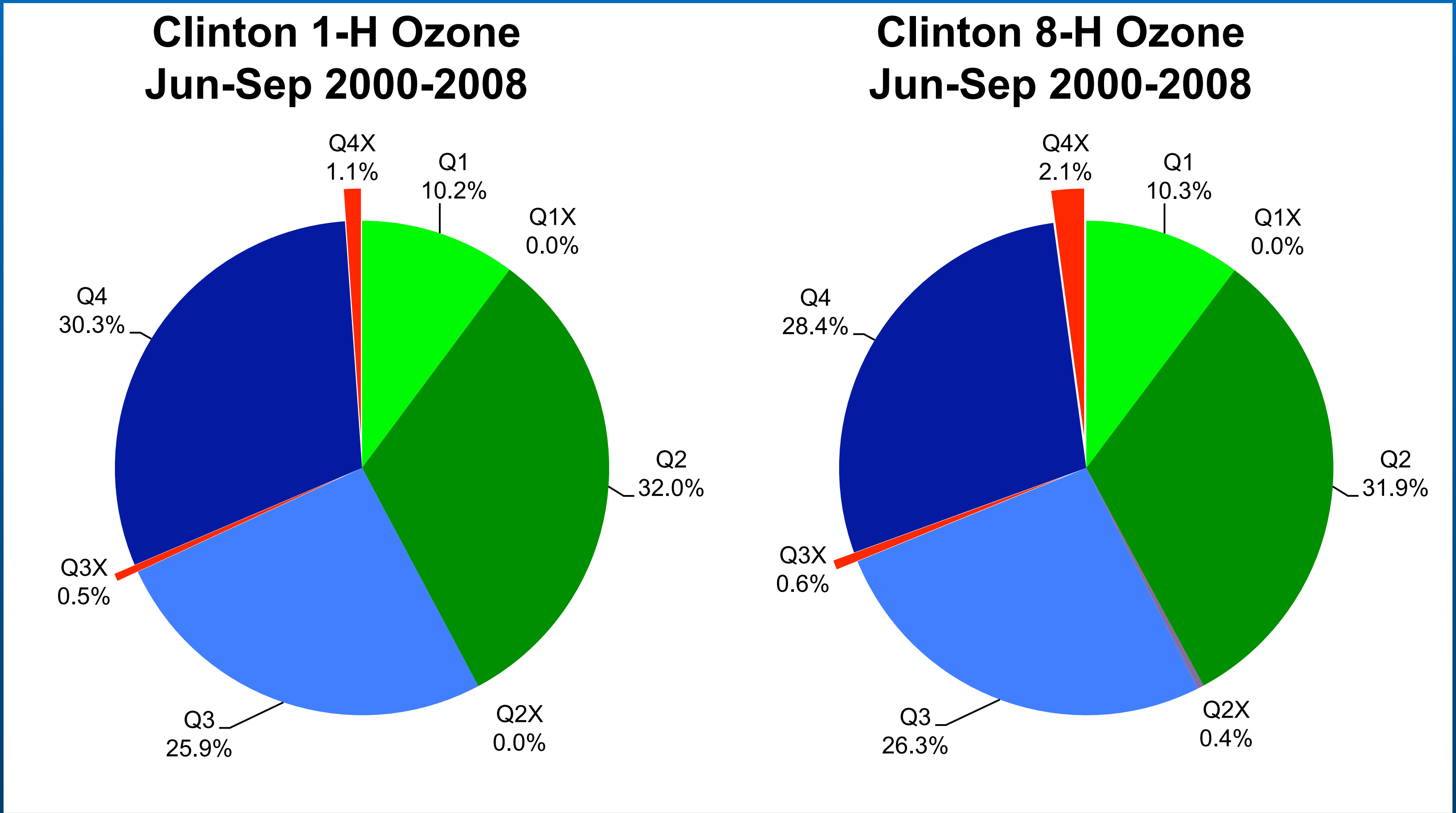


Meteorology and Ozone Exceedences, Updated

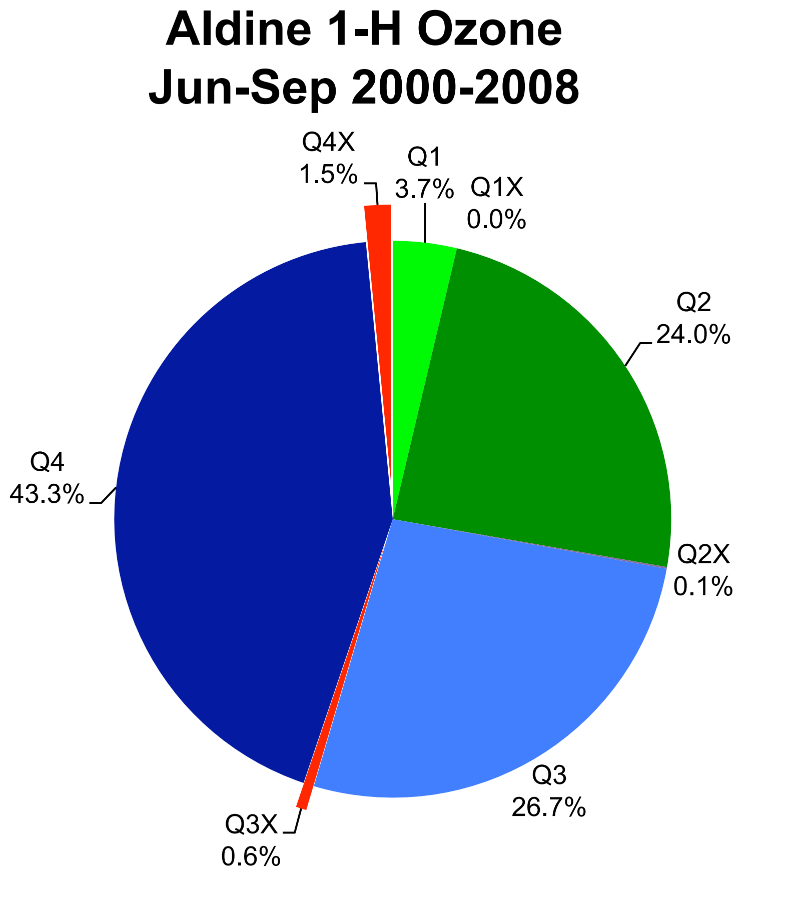


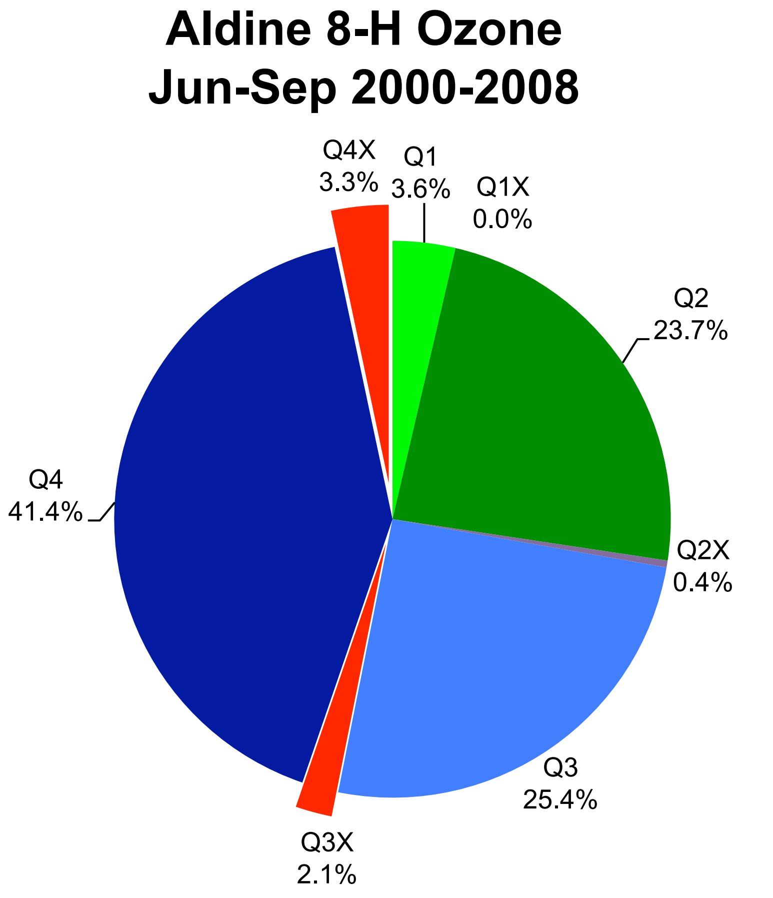


Meteorology and Ozone Exceedences, Updated

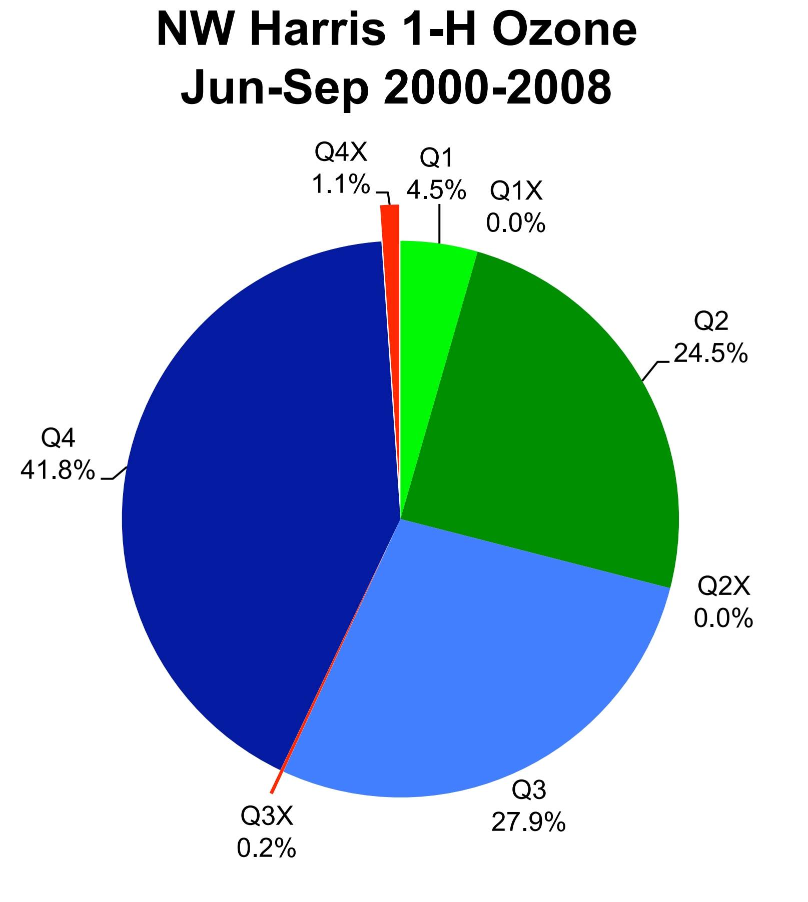


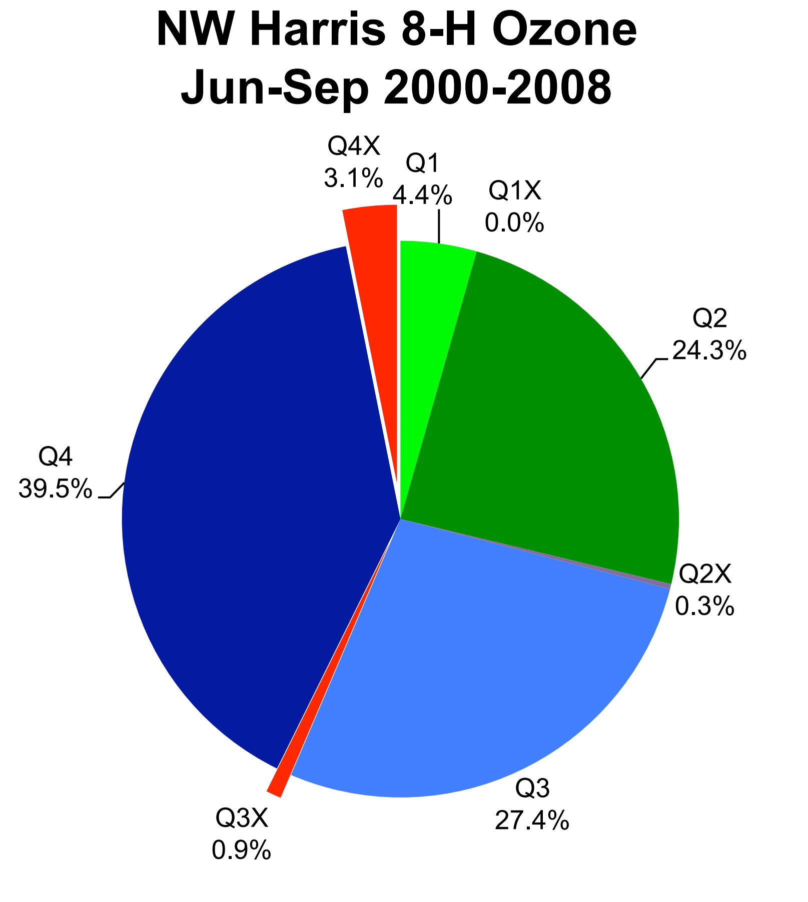
Meteorology and Ozone Exceedences, Updated



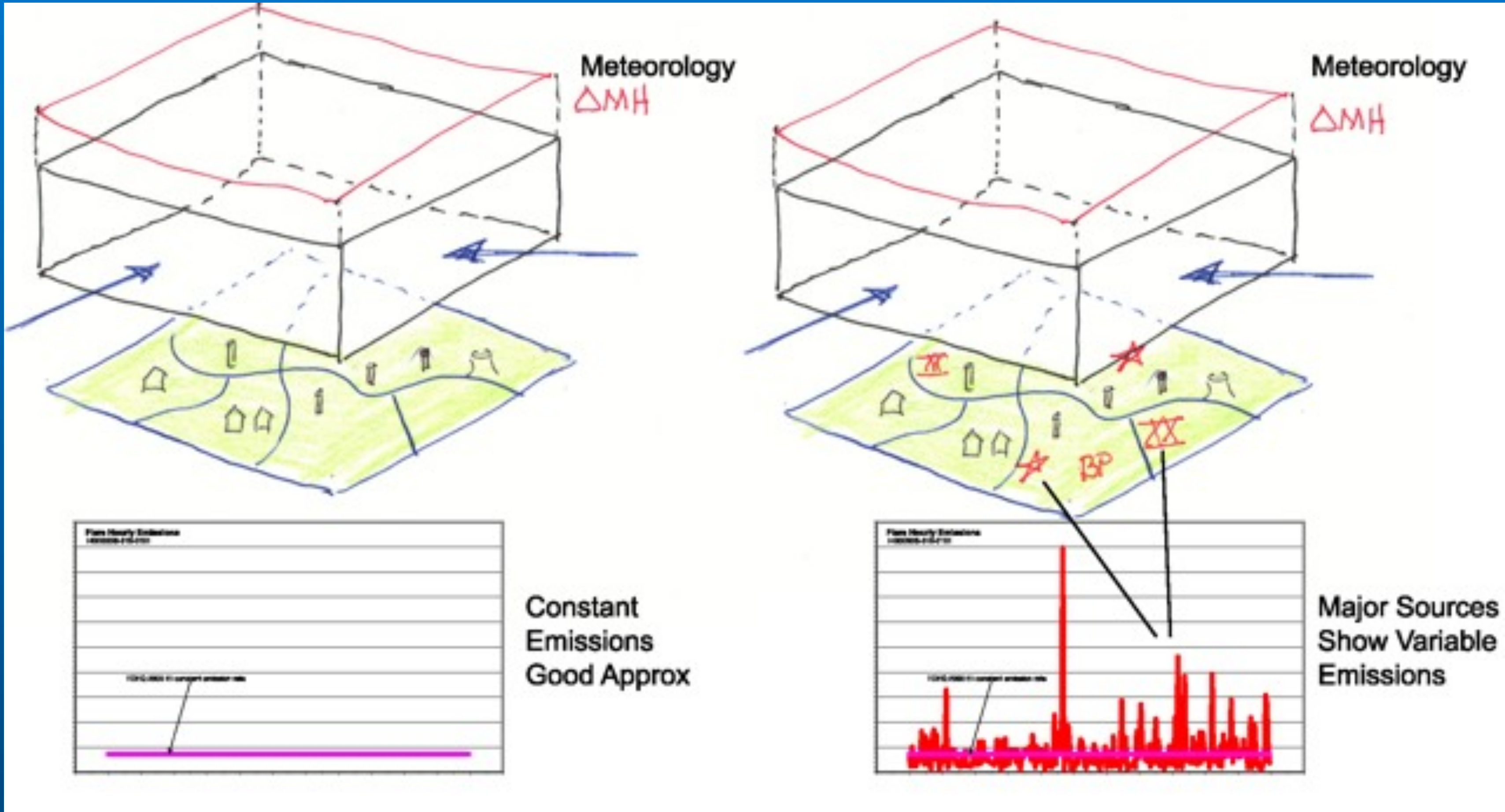


Meteorology and Ozone Exceedences, Updated





Conceptual issue



In most of US, industrial emissions are relatively constant or are small enough that meteorology is cause of "worst conditions"

In HGA, both meteorology and ***emissions*** are cause of "worst conditions"

Jeffries, 2002

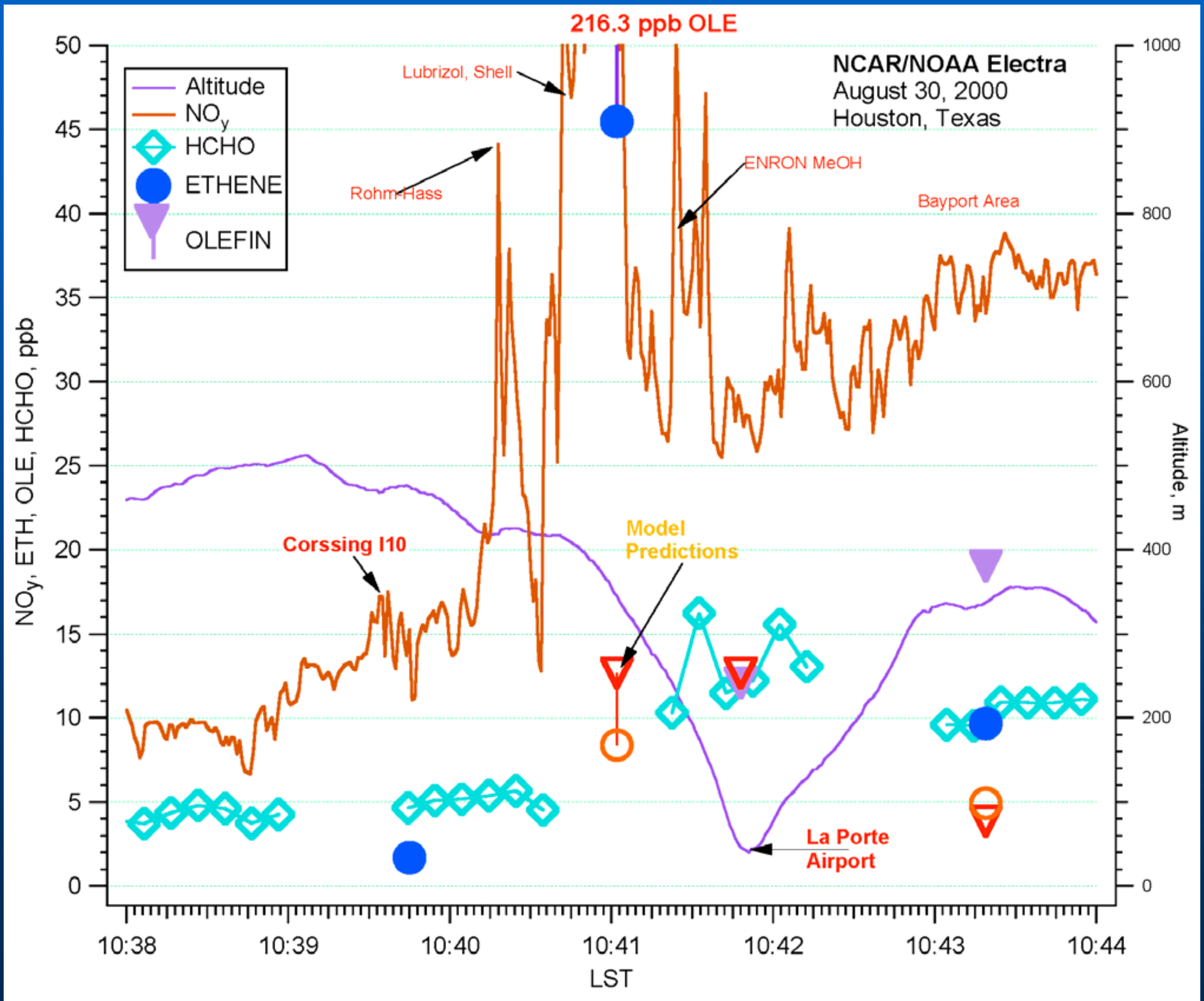
Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events

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

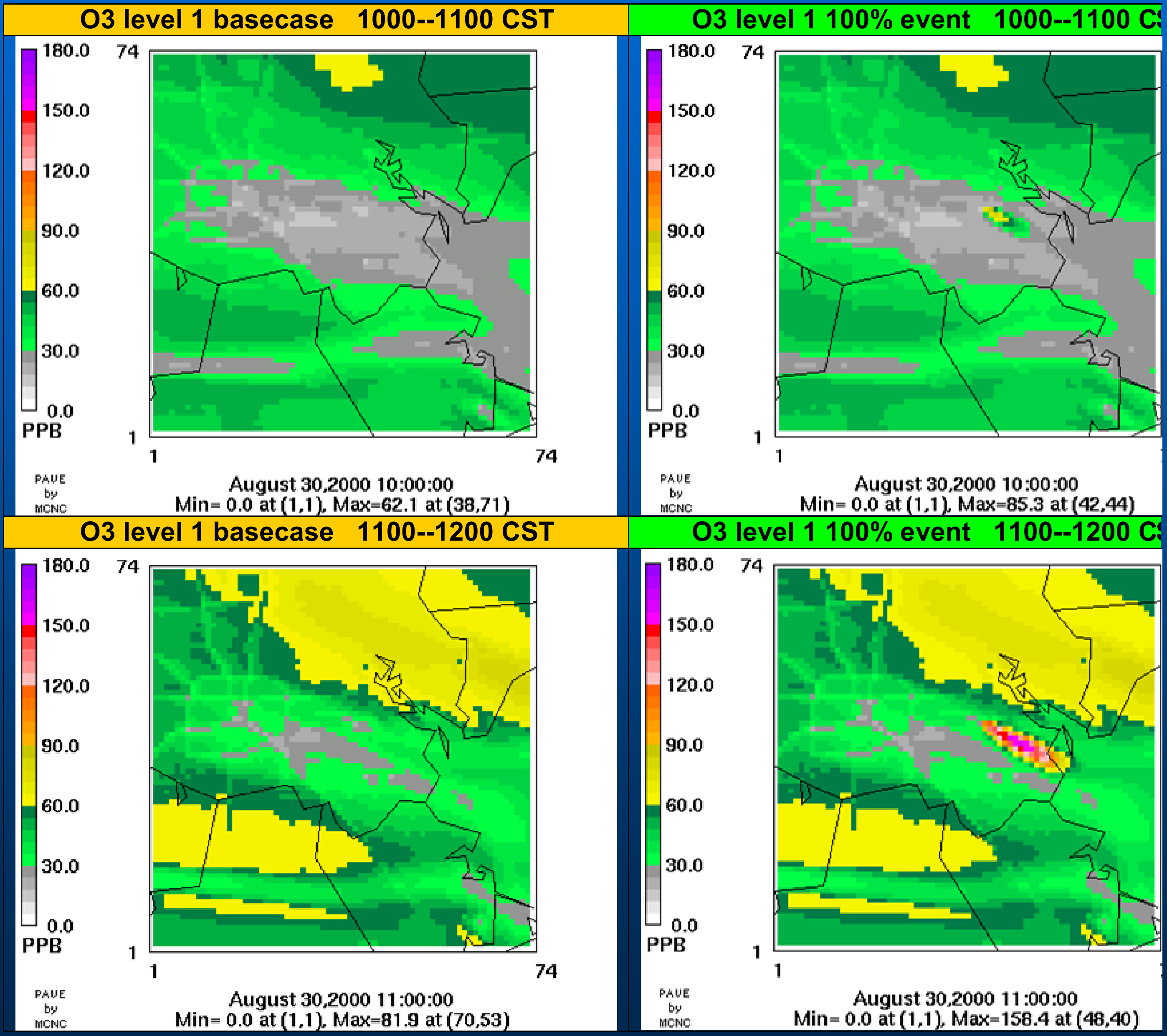
10,188 lb/h OLE+PAR

Start at 1000

End at 1200

Base 81.9 ppb O3

Event 158.4 ppb O3

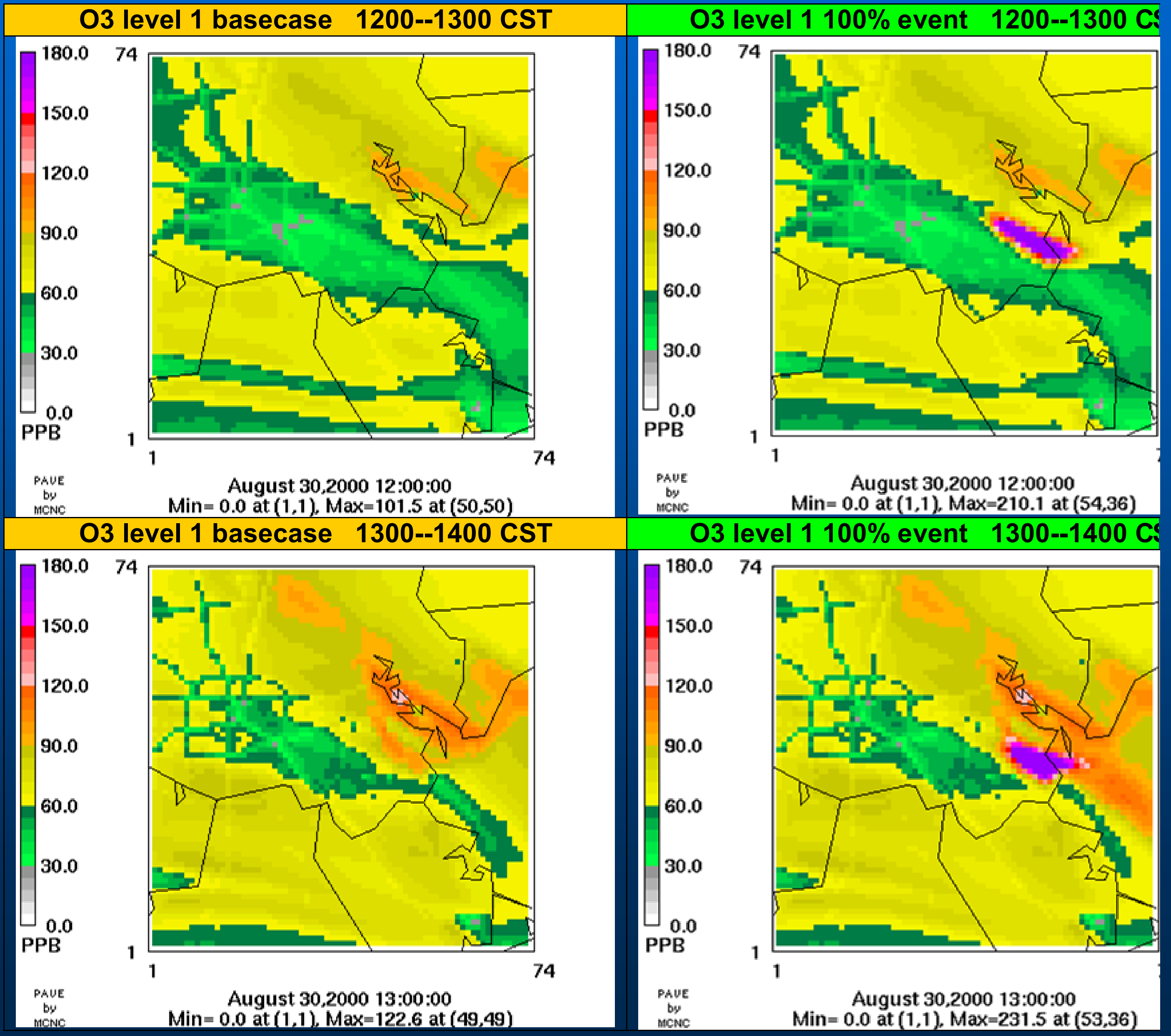


Add Event Emissions to CAMx, III

Layer One

Start at 1200

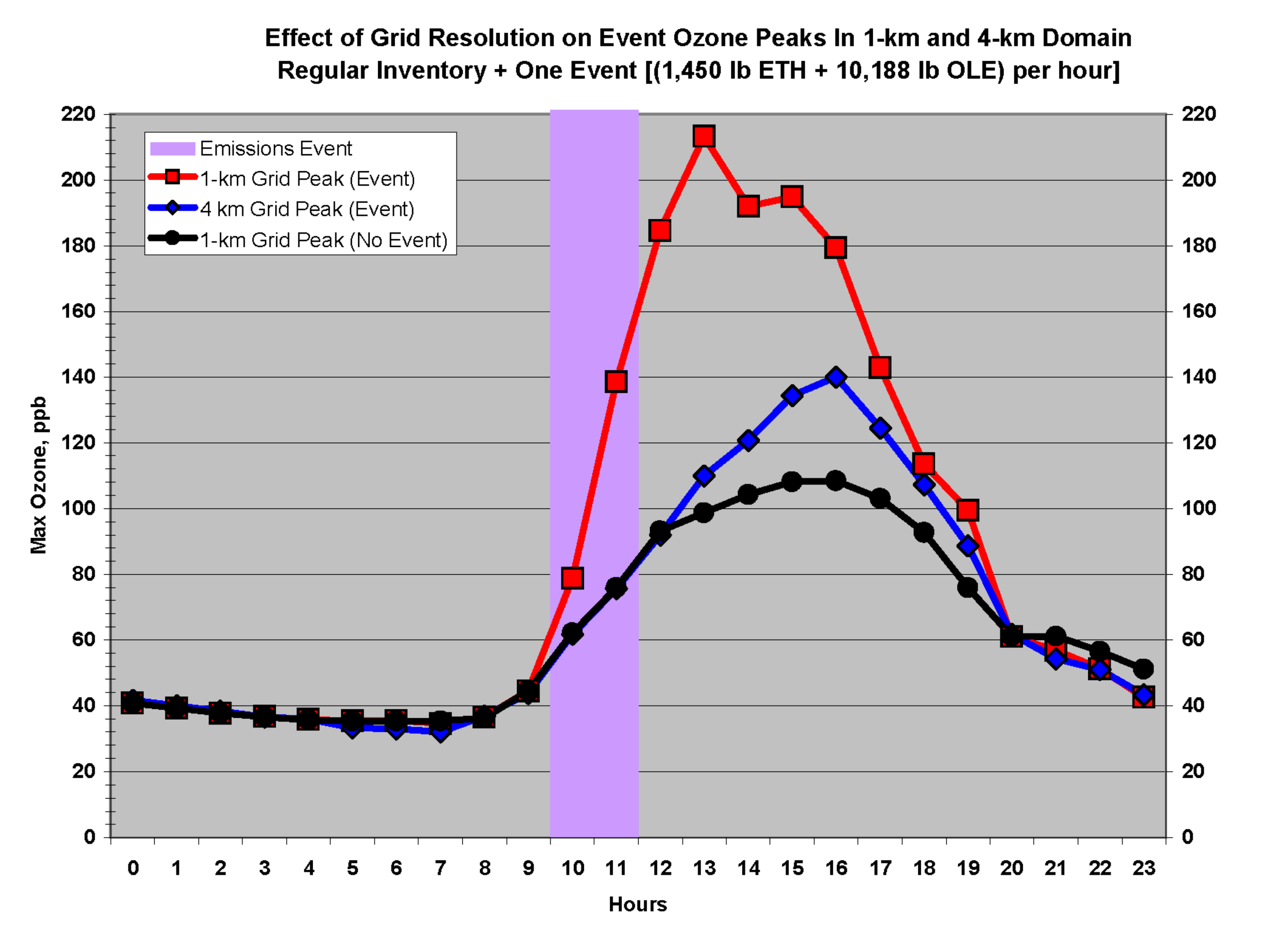
End at 1400



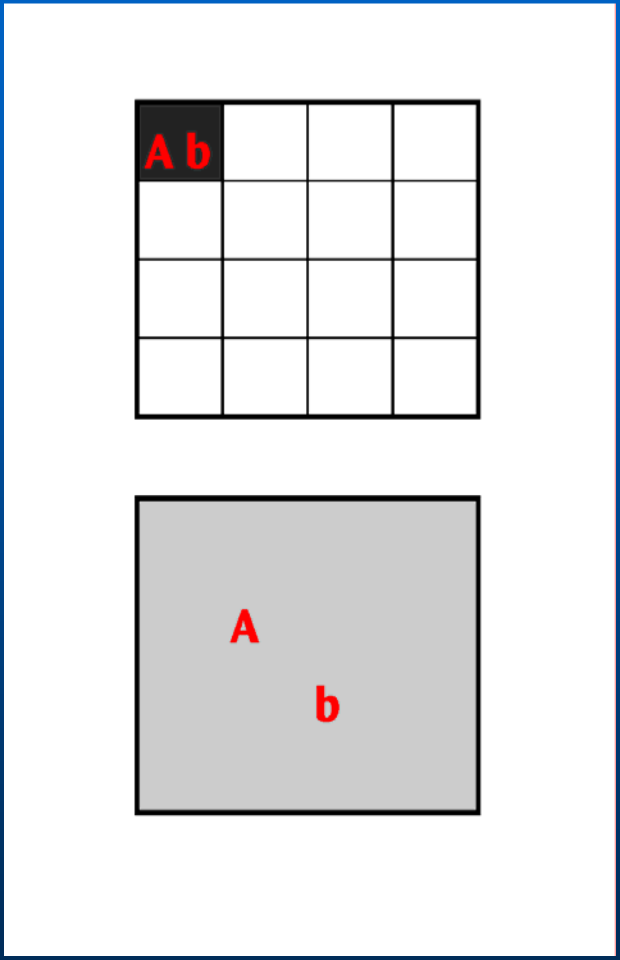
Base
122.6 ppb O3

Event
231.5 ppb O3

Add Event Emissions to CAMx, V

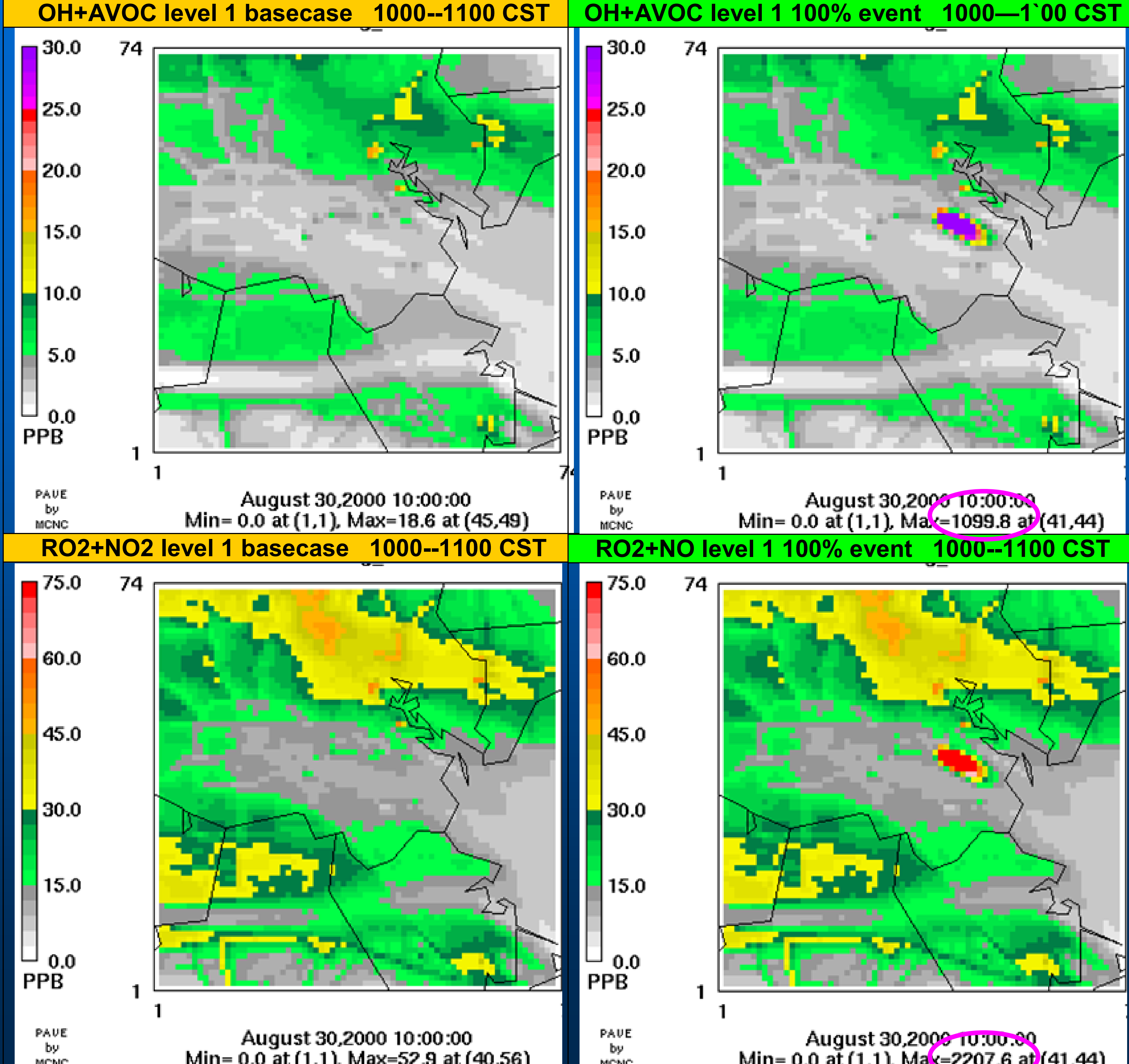


PA Explains Why This Happens



- Transport is related to
  [A] * u
  [b] * u
- Chemistry is related to
  [A] * [b]
- [A] and [b] both increase by 16 at 1km
- u is constant
- trans inc linearly
  chem inc by square

PA Processes for VOC Event are ca. 50x higher



The Influence of Model Resolution on Ozone in Industrial VOC Plumes

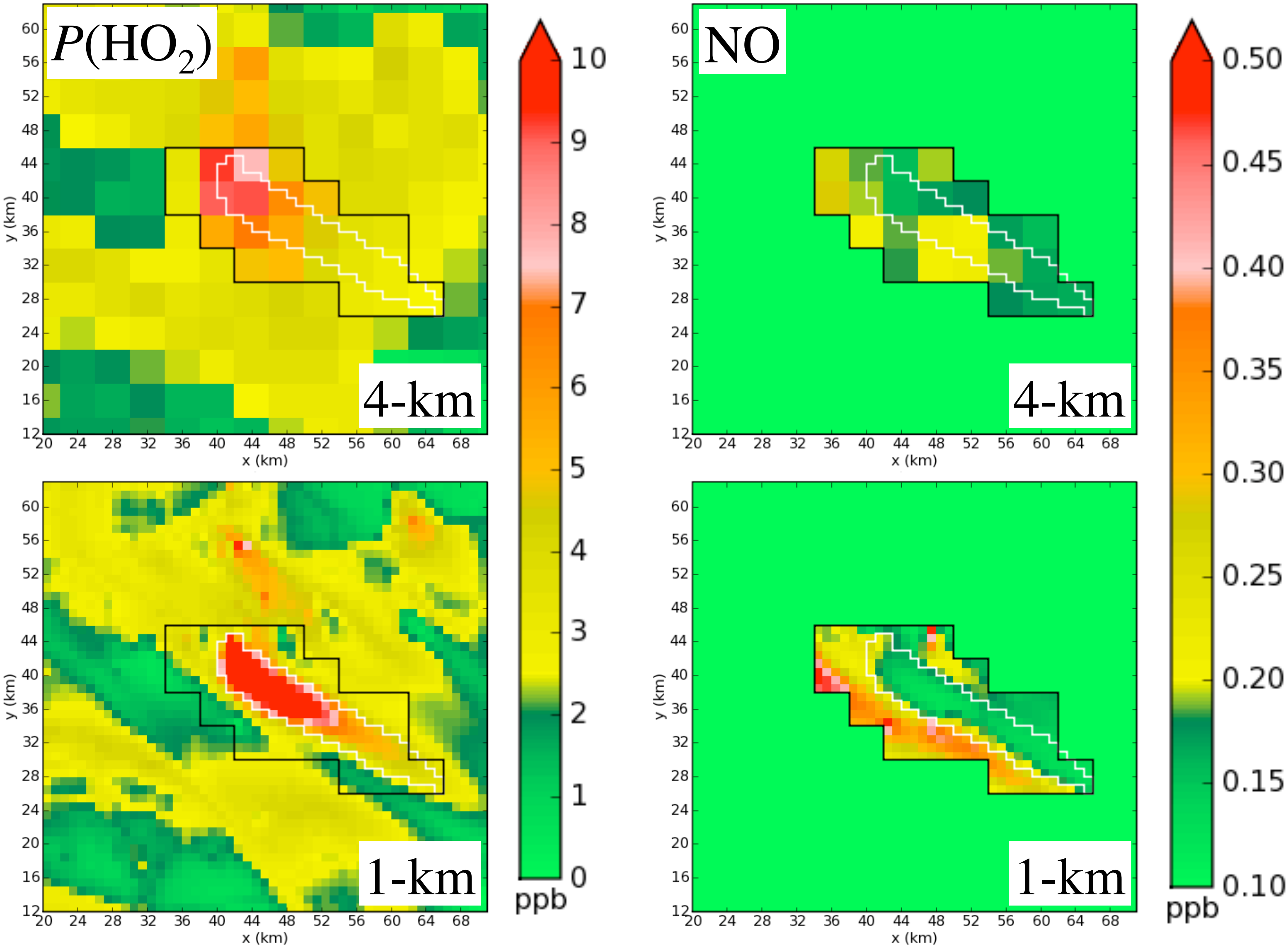
Barron H. Henderson [a], William G. Vizuete [a,*]
Harvey E. Jeffries [a] Byeong-Uk Kim [b]

[a] *University of North Carolina Chapel Hill, Department of Environmental Science and Engineering, 113 Rosenau Hall CB#7431, Chapel Hill, NC 27599*

[b] *Georgia Environmental Protection Division, 4244 International Parkway, Suite 120, Atlanta, GA 30354*

Abstract

The Houston ozone (O_3) nonattainment area frequently experiences large industrial releases of volatile organic compounds (VOCs). Released VOCs have been shown to create plumes with O_3 production rates 2 to 5 times higher than typical urban conditions. The O_3 production in simulated industrial releases shows sensitivity to horizontal grid resolutions, but has not been fully explored. This study uses Process Analysis to compare O_3 production and precursors in two simulated industrial VOC releases, each with a different horizontal grid size. Finer grid size produces the same spatially aggregated "Odd Oxygen" (O_x) mass, but produces less spatially aggregated O_3 mass (3%) while increasing the peak O_3 concentration (46%). Finer grid size alters the processes producing O_x and alters the O_3 response to potential changes in NO_x and VOC emissions. The latter is an important factor in assessing efficacy of control policies and, potentially, which control path to pursue. Future studies will apply process analysis to quantify the influences of grid size on specific emission reduction strategies.



P(HO2)
NO
4-km
4-km
1-km
1-km
y (km)
x (km)
ppb
ppb

TCEQ Midcourse SIP, 2004

- SIP based on Aug/Sep 2000 episode
  - "Imputes" HRVOC EI ~ 6 x NOx at 81 src
- SIP adopts 2-cause approach
  - Cites Jeffries and Allen and HARC event modeling work
- Adopts a 1200 lb/h "not to exceed" emission limit on HRVOCs and an annual VOC cap.
- Quickly moves from 1-h to 8-h ozone and tries to follow EPA emerging path

Topics

- Why is ozone so high in Houston?
- Measurements:
  - THOEs – Transient High Ozone Events
  - ROF - Rapid Ozone Formation
- Where does all that VOC come from?
  - Stochastic Emissions
  - Event Emissions
- What is role of meteorology?
- Can these be modeled?
- New 8-h methods and THOEs and Events

TCEQ SIP, 2007

- SIP based on 2005 episodes
- TCEQ and Governor request and receive a "double bump-up", with "early attainment"
- EPA wants new SIP 2010, showing attainment of 8-h std by 2018
- TCEQ models 3 episodes in 2005 and 3 episodes in 2006 including June and July episodes.

EPA 8-H Ozone Attainment Test

- Based on a mixture of observations and modeling.
- Observations are “averaged” over 3 to 5 years with different weighting schemes
- Models are used in a “relative” or “RRF” sense
  - Basecase -- ‘evaluate’ model performance
  - Baseline -- ‘average’ inventory for DV year
  - Future -- ‘controlled’ inventory
- Monitor by monitor test
  - “Near” monitor in models
  - Want 10+ days for RRF calc each monitor.

Attainment Test

Step 3: Compute the future design value (DV_F) at each monitor

Example at HGB monitor "β":

'03, '04, '05 Meteorology

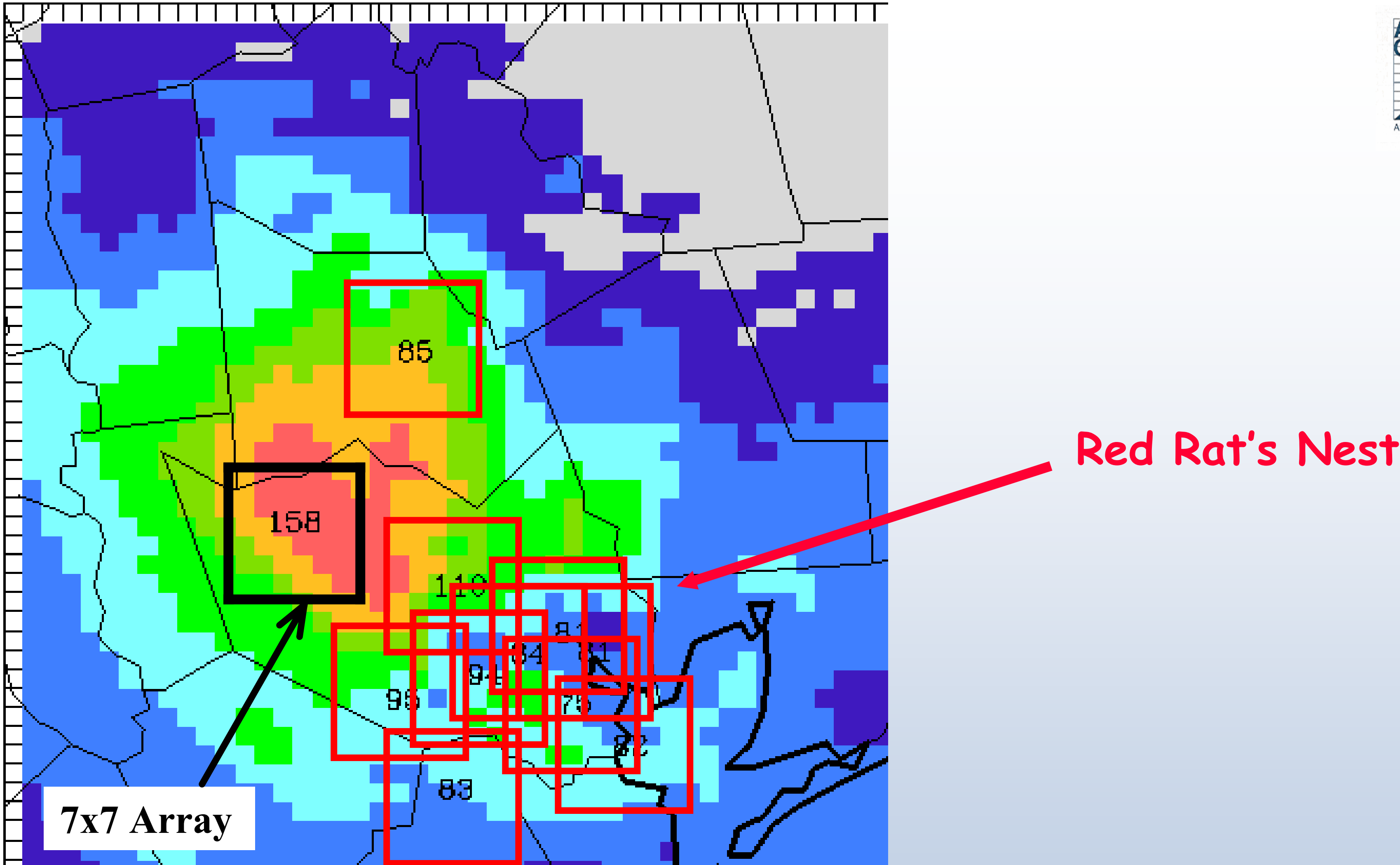
2009 Emissions, processed with '03, '04, '05 Meteorology

$$DVF_{\beta} = \frac{\text{Mean projected peak 8-hr daily max "near" monitor "}\beta\text{"}}{\text{Mean projected peak 8-hr daily max "near" monitor "}\beta\text{"}} * DVC_{\beta}$$

'Weighted' DV based on observed 2000-2004 O_3 data

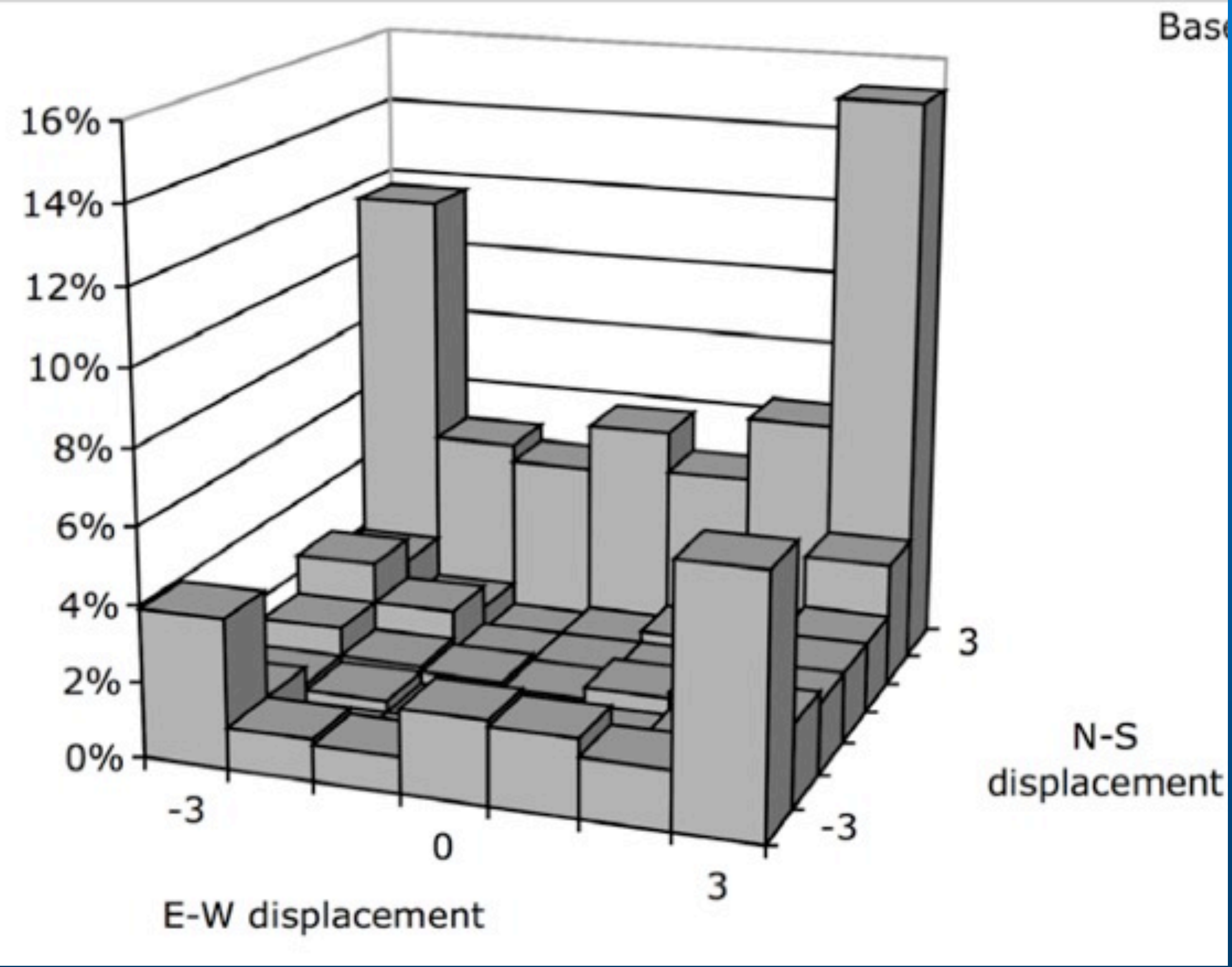
'03, '04, '05 meteorology

2002 'Typical' emissions, processed with '03, '04, '05 meteorology



We need an objective scheme for blending array sizes (e.g., 2x2, 3x3, 5x5, 7x7) across the full HGB domain!

Probability of cell selections within the RRF array around all monitor locations for the b1bpsito2n2 scenario

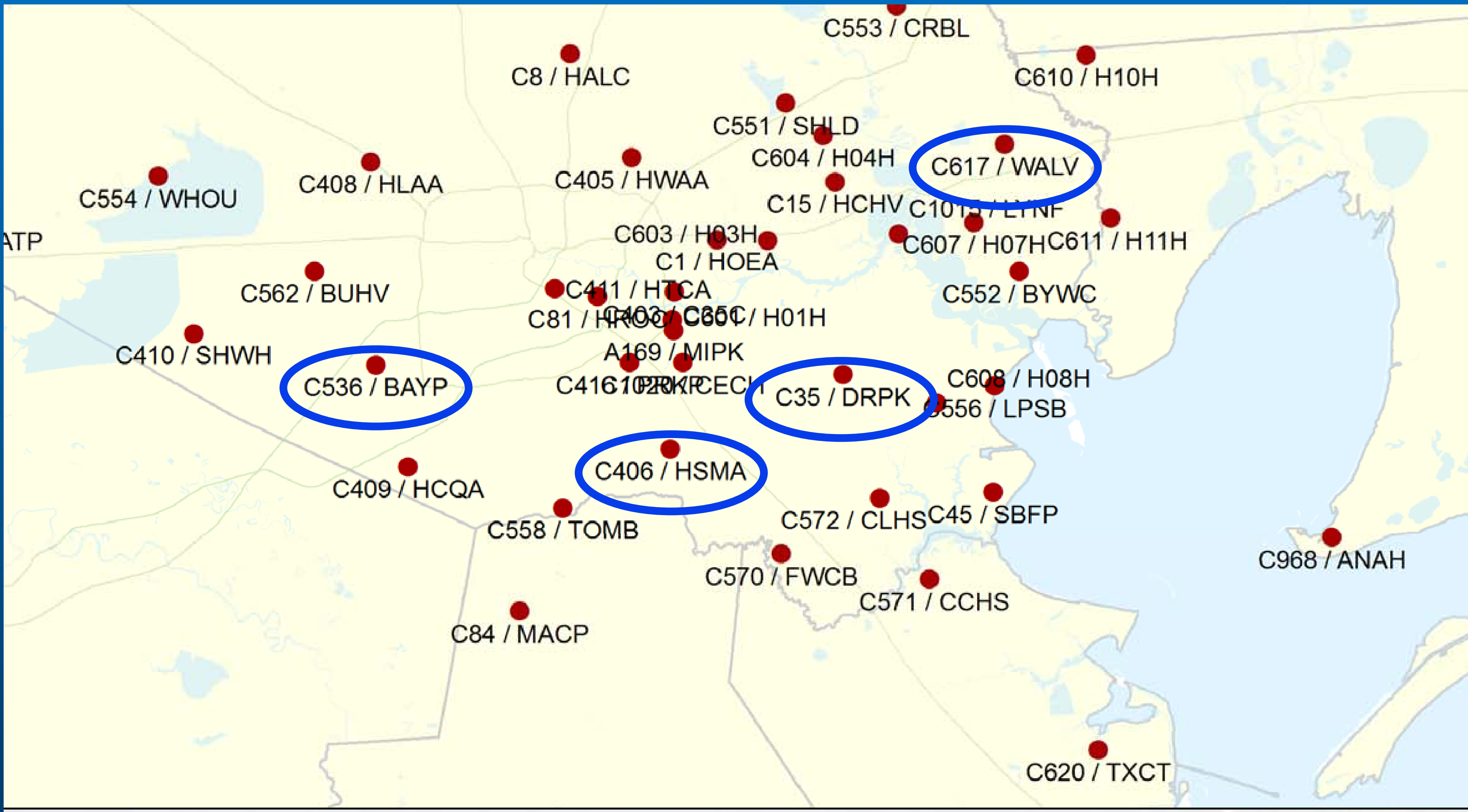


7 X 7 Grid Cells

TCEQ SIP, 2010

- SIP based on 6 2005-2006 episodes
  - DV base year 2005
- Performance issues, but eval at 8-h
- No ‘imputed’ VOC, but 2006 SI is small
- 2-km grid modeling for several episodes
- Complex met for 2006 episodes - predicted rain, clouds, flows.
- PA says “short of radicals” like 2000

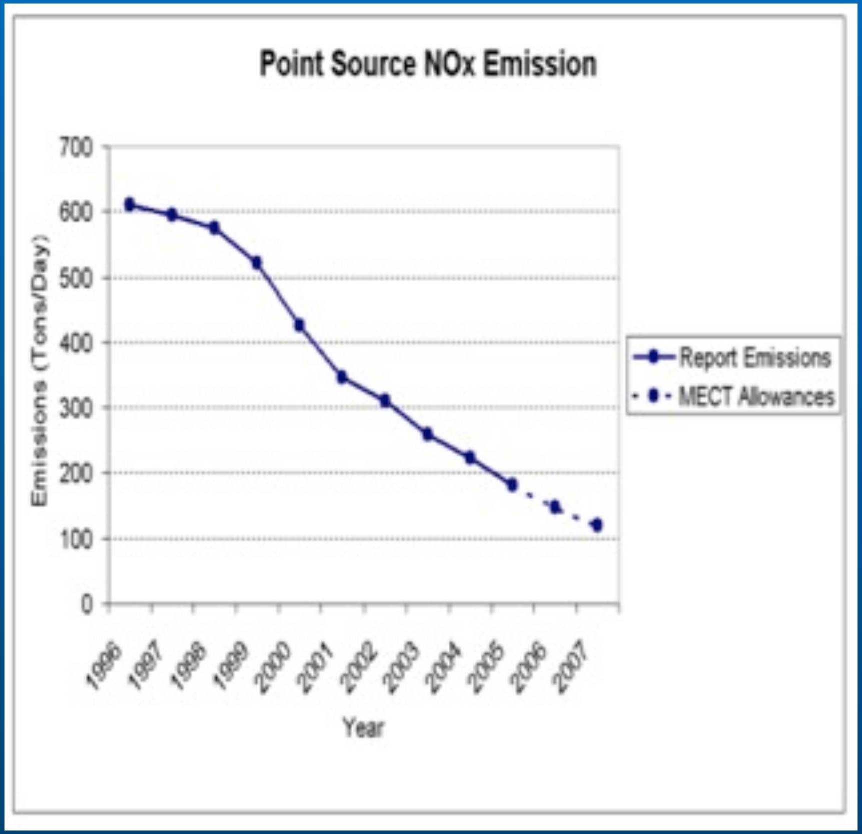
TCEQ Future Case (2018) Predictions: Four Monitors > 85



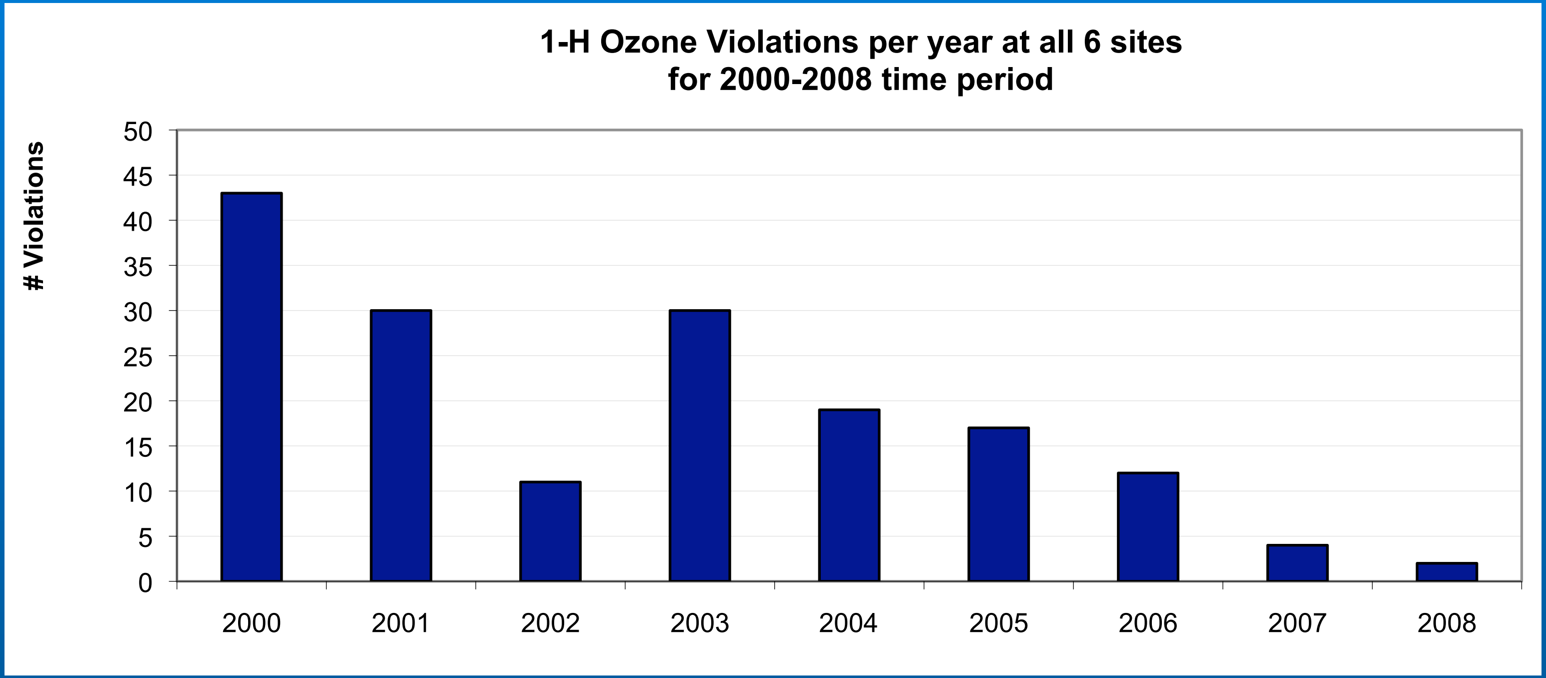
TCEQ Future Case (2018) Estimated Further Controls

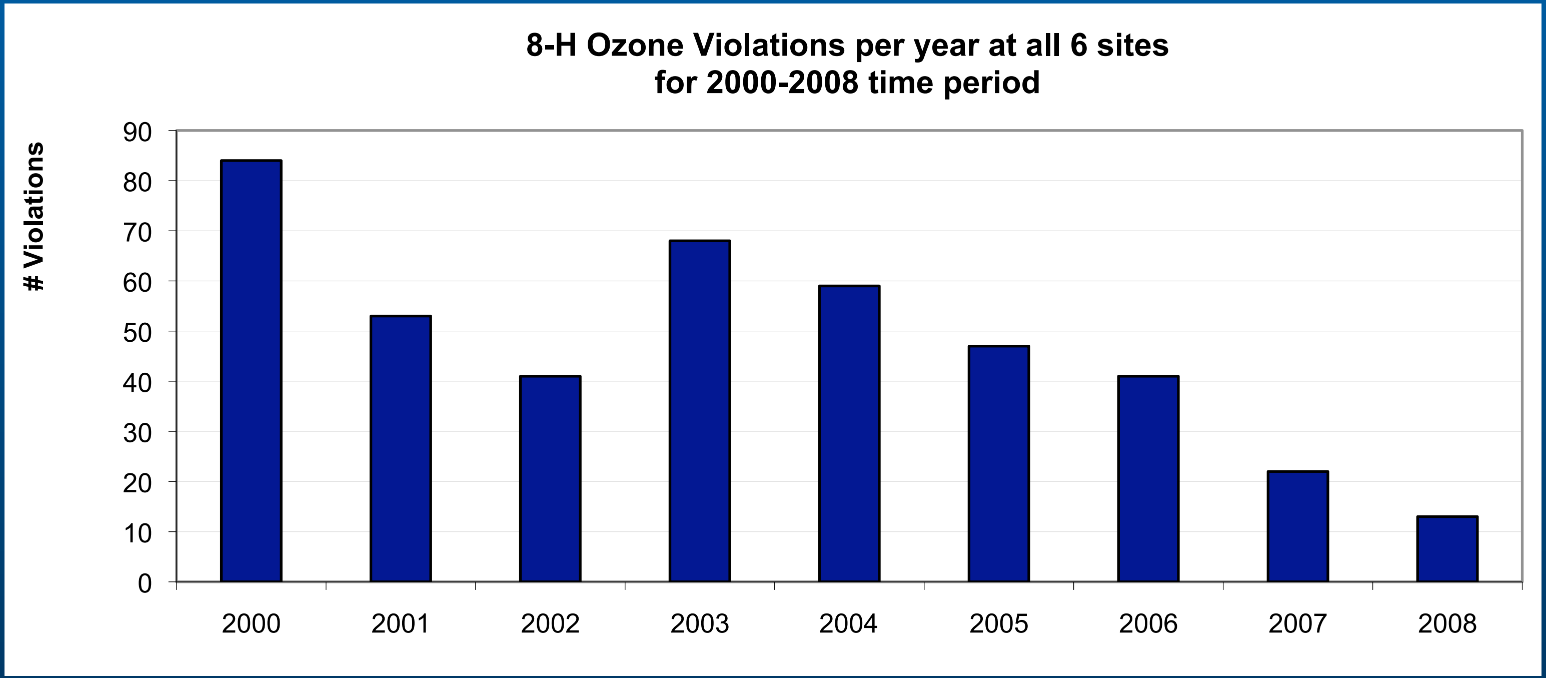
Tested Only Across The Board Reductions

- Estimated Further Reductions Needed
- 90 t/d NOx more reduction for BAYP, HSMA, and WALV monitors
- 100 t/d NOx more reduction for DRPK



Actual Emissions Trends


1-H Ozone Violations per year at all 6 sites
for 2000-2008 time period
Violations
50
45
40
35
30
25
20
15
10
5
0
2000
2001
2002
2003
2004
2005
2006
2007
2008


8-H Ozone Violations per year at all 6 sites
for 2000-2008 time period
Violations
90
80
70
60
50
40
30
20
10
0
2000
2001
2002
2003
2004
2005
2006
2007
2008

Houston Critical Sites Daily 8-h ozone max (ppb) and dates (mm/dd)

1st highes	2003		2004		2005		2006		2007		2008	
BAYP	129	8/22	114	9/29	106	9/5	124	8/31	92	7/24	92	8/4
HSMA	102	5/18	107	7/27	107	10/9	106	6/29	93	10/3	74	10/25
WALV	106	9/13	104	9/30	117	6/2	100	6/5	108	5/15	97	10/25
DRPK	126	5/29	108	7/13	104	7/8	121	9/1	98	10/3	91	10/25

2nd highes	2003		2004		2005		2006		2007		2008	
BAYP	124	4/26	110	7/20	103	8/2	119	6/29	91	10/3	89	10/9
HSMA	101	5/29	101	6/19	104	9/4	106	6/14	87	9/21	74	9/27
WALV	105	8/8	98	8/4	105	8/21	98	6/4	102	6/4	91	9/30
DRPK	117	8/23	114	9/29	99	8/21	111	6/8	88	9/23	86	9/30

3rd highes	2003		2004		2005		2006		2007		2008	
BAYP	114	5/29	107	9/30	101	6/21	110	9/7	89	9/16	85	10/19
HSMA	94	6/7	98	9/29	102	9/20	104	8/17	77	7/24	72	9/30
WALV	102	7/18	94	11/6	104	10/18	97	6/8	96	11/4	86	5/8
DRPK	115	5/18	99	9/30	92	10/17	104	8/17	88	7/24	79	8/26

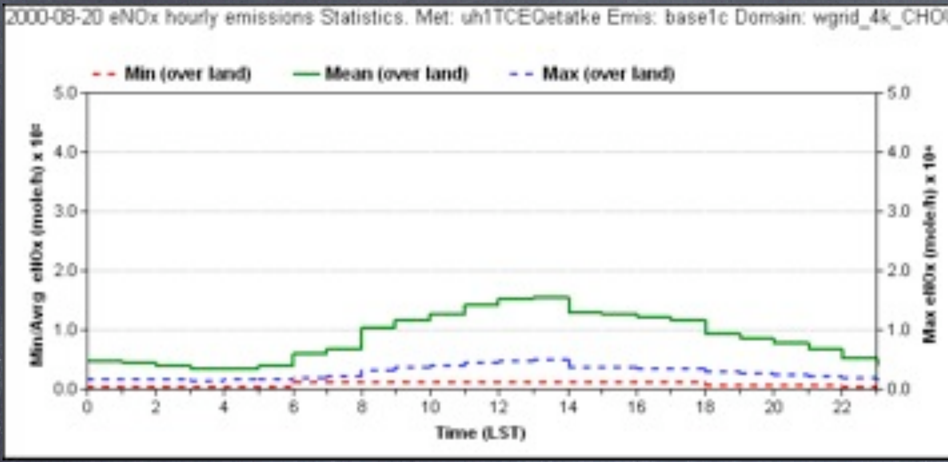
4th highes	2003		2004		2005		2006		2007		2008	
BAYP	107	9/8	104	8/17	100	6/22	106	6/28	84	9/21	83	9/30
HSMA	94	4/26	97	9/11	100	10/17	99	8/31	72	8/13	72	8/4
WALV	101	10/21	94	6/4	94	7/11	93	6/10	92	6/5	85	6/18
DRPK	113	9/8	97	8/5	92	6/22	101	6/12	86	6/4	76	10/2

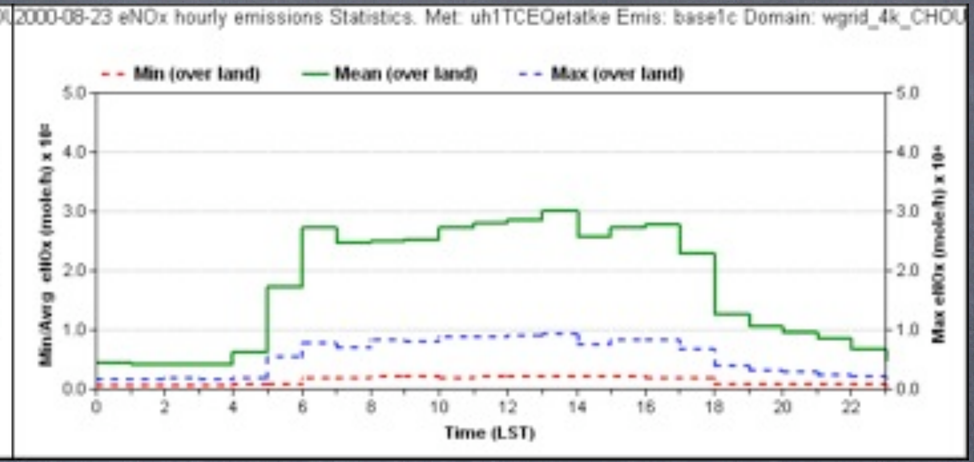
design val	2003	2004	2005	2006	2007	2008
BAYP	-	-	104	103	97	91
HSMA	-	-	97	99	90	81
WALV	-	-	96	94	93	90
DRPK	-	-	101	97	93	88

*DVBs**	2003	2004	2005	2006	2007	2008
BAYP	-	-	101	97	-	-
HSMA	-	-	95	90	-	-
WALV	-	-	94	92	-	-
DRPK	-	-	97	92	-	-

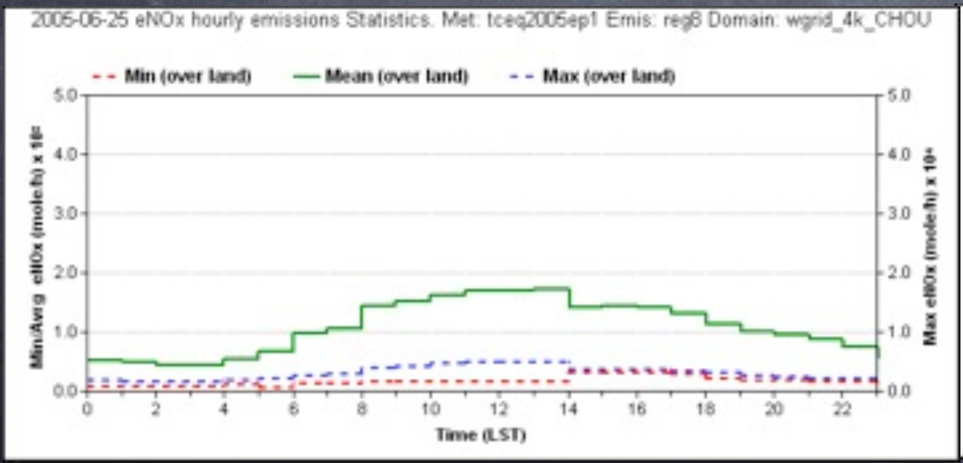
*THOE	*weekend
BAYP	17% days have THOE; 17% are weekend
HSMA	38% days have THOE; 38% are weekend
WALV	46% days have THOE; 29% are weekend
DRPK	38% days have THOE; 21% are weekend

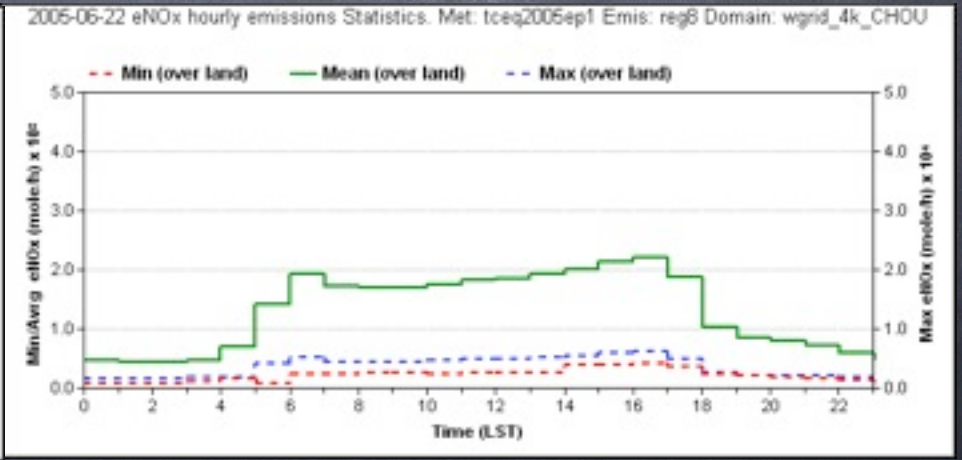
NOx Emissions: Weekday vs Weekend (CHOU Domain)





Sunday, 8/20/2000 2000_08_hg_TCEQ Wednesday, 8/23/2000

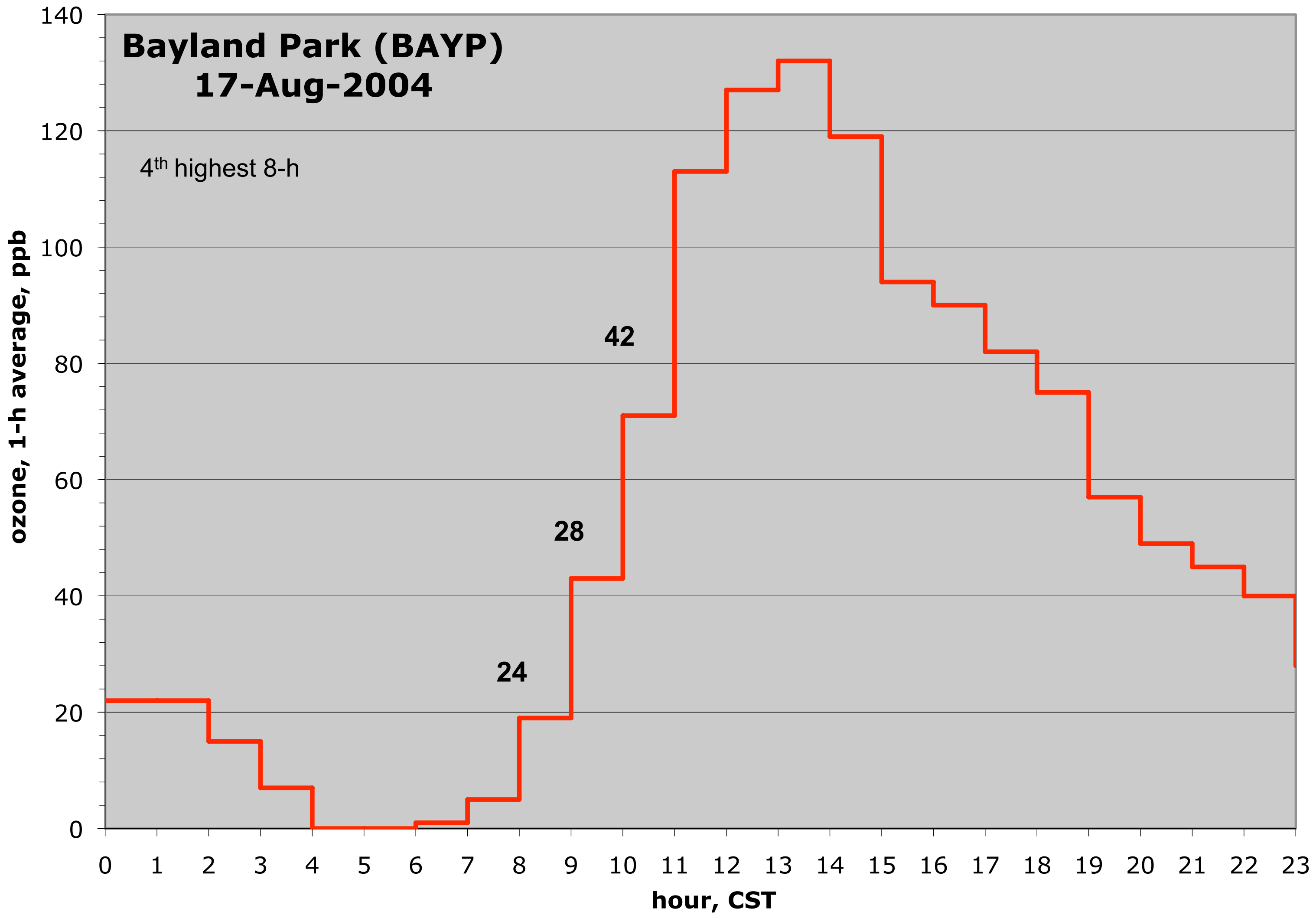




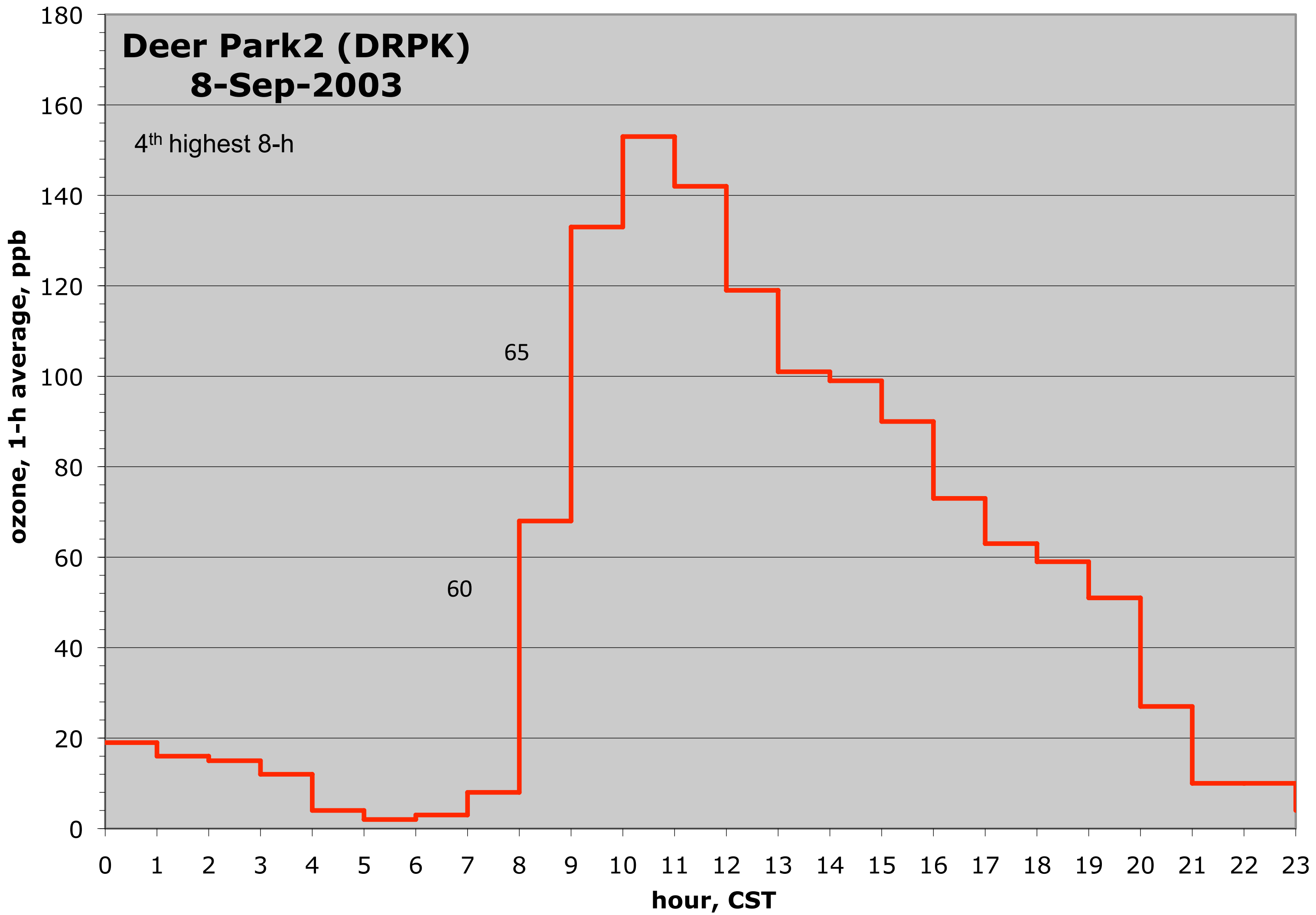
Saturday, 6/25/2005 2005_06_hg_TCEQ Thursday, 6/22/2005

Air Quality Modeling for SIP Development

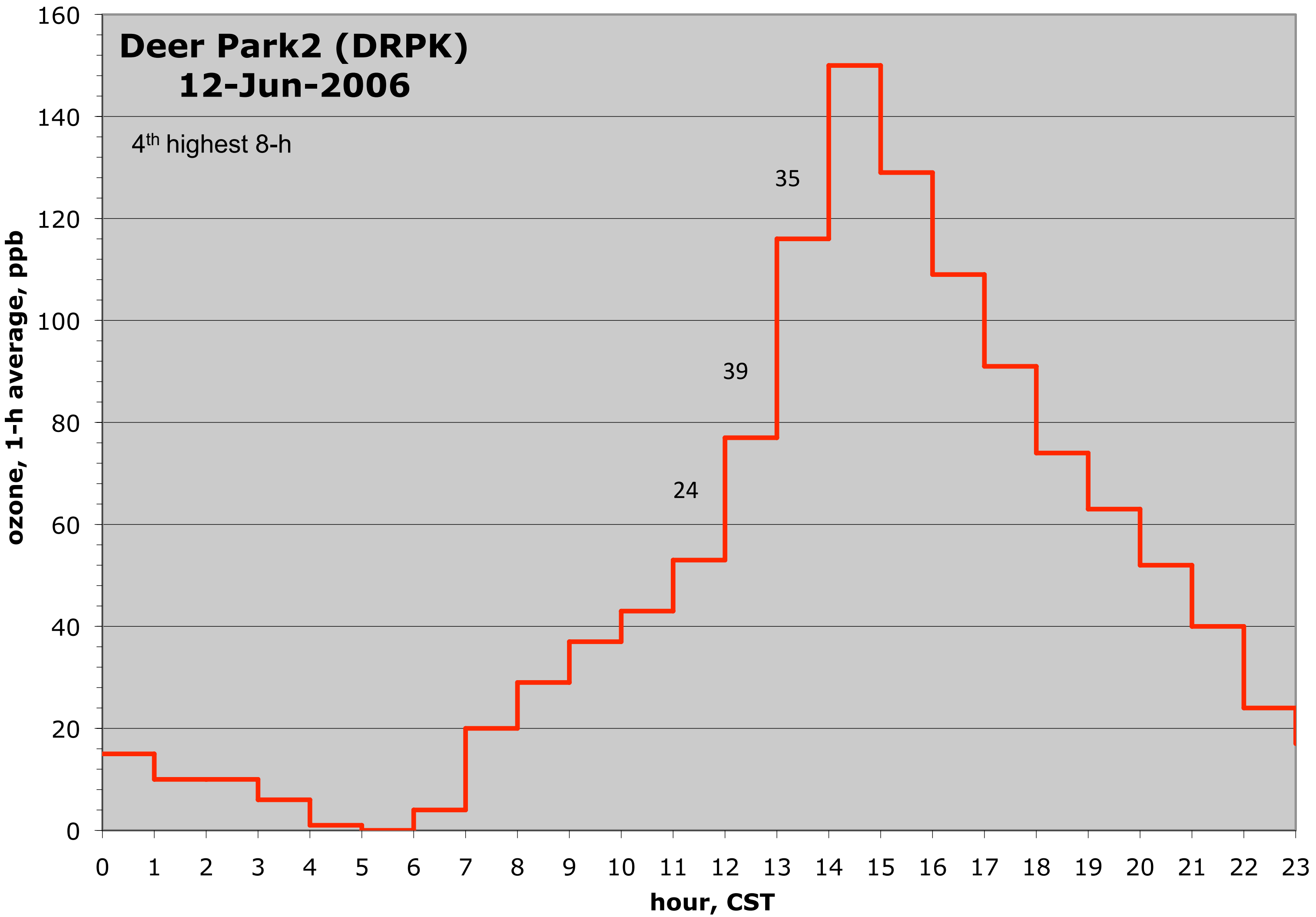
- In HGA, historical episodes are merely emission snapshots and are not likely to be representative of future conditions.
- In doing AQ Modeling we need to separate emissions that change from episode to episode from those that remain nearly constant
- In evaluating SIP effectiveness, need to consider an album of many industrial emission snapshots

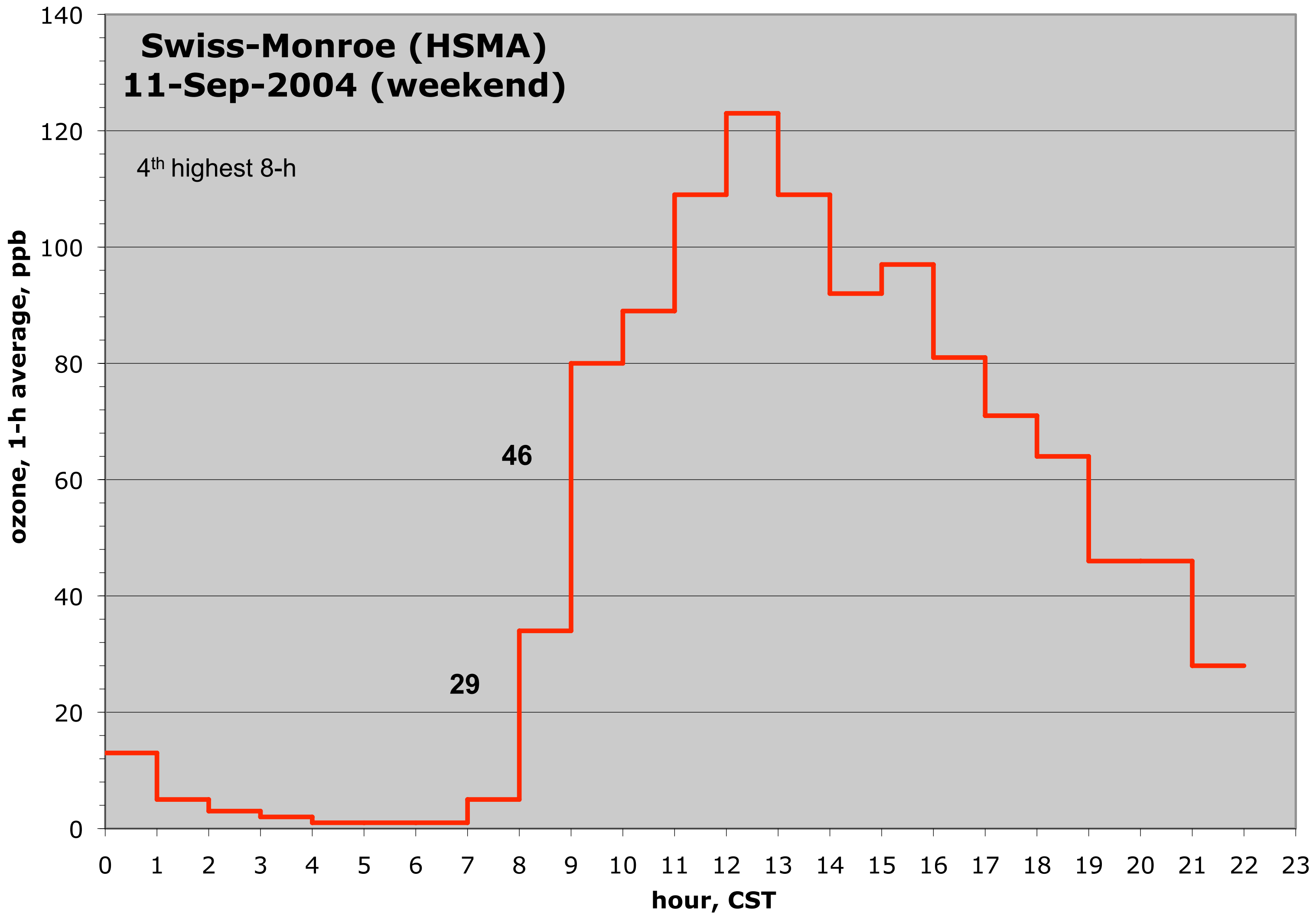


Bayland Park (BAYP)
17-Aug-2004
4th highest 8-h
42
28
24
ozone, 1-h average, ppb
0
20
40
60
80
100
120
140
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
hour, CST

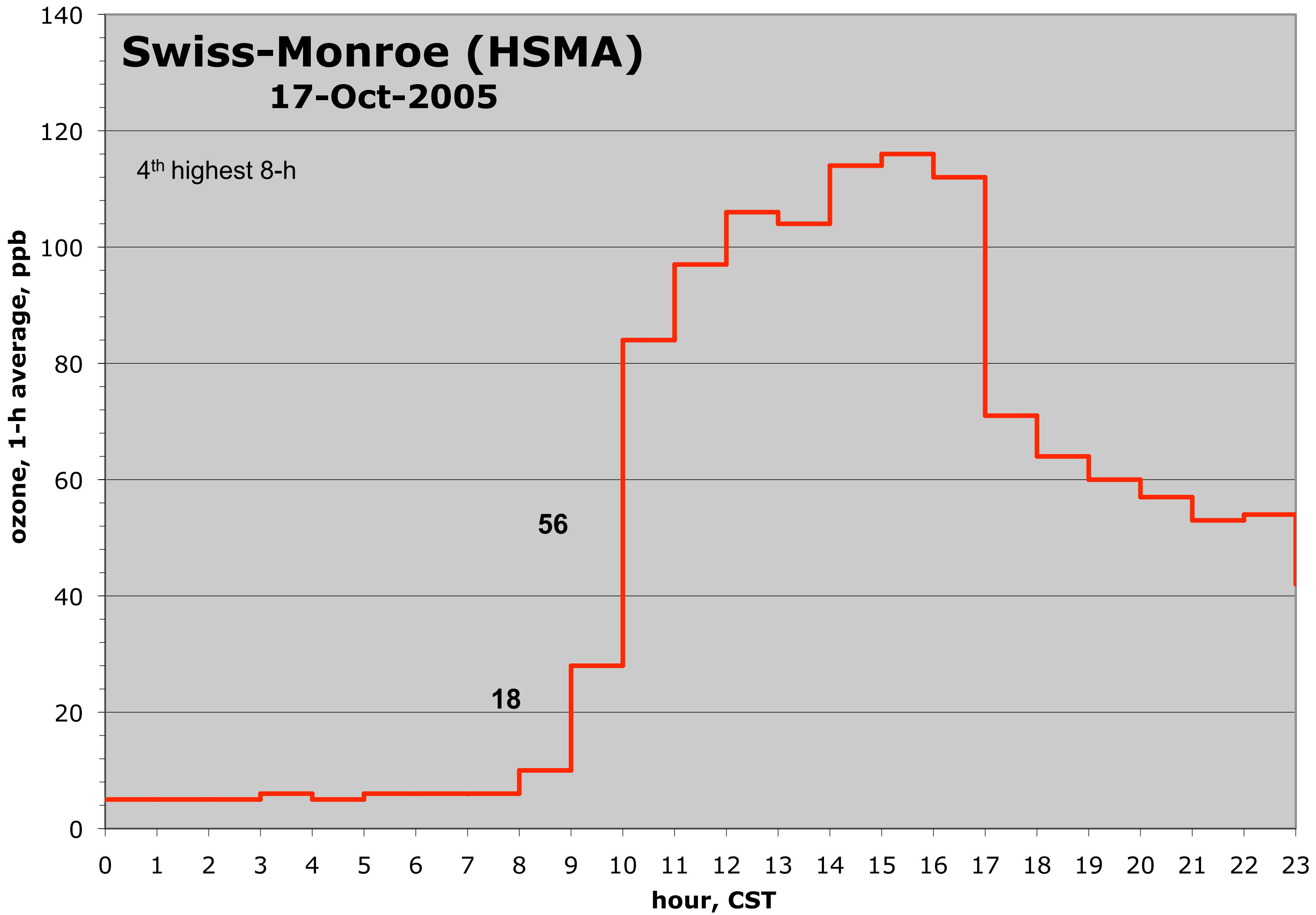


Deer Park2 (DRPK)
8-Sep-2003
4th highest 8-h
65
60
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
160
180
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

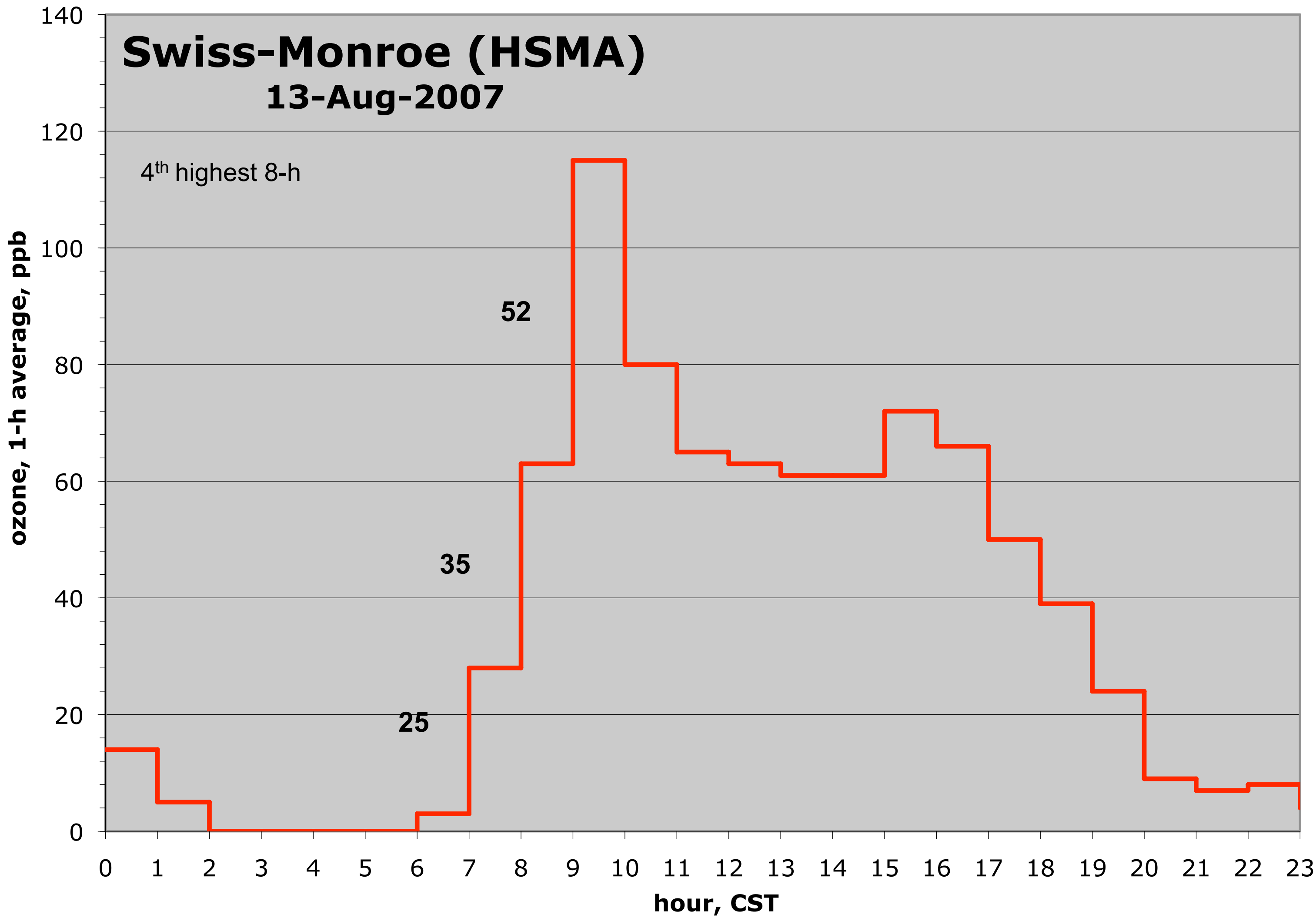

Deer Park2 (DRPK)
12-Jun-2006
4th highest 8-h
35
39
24
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
160
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



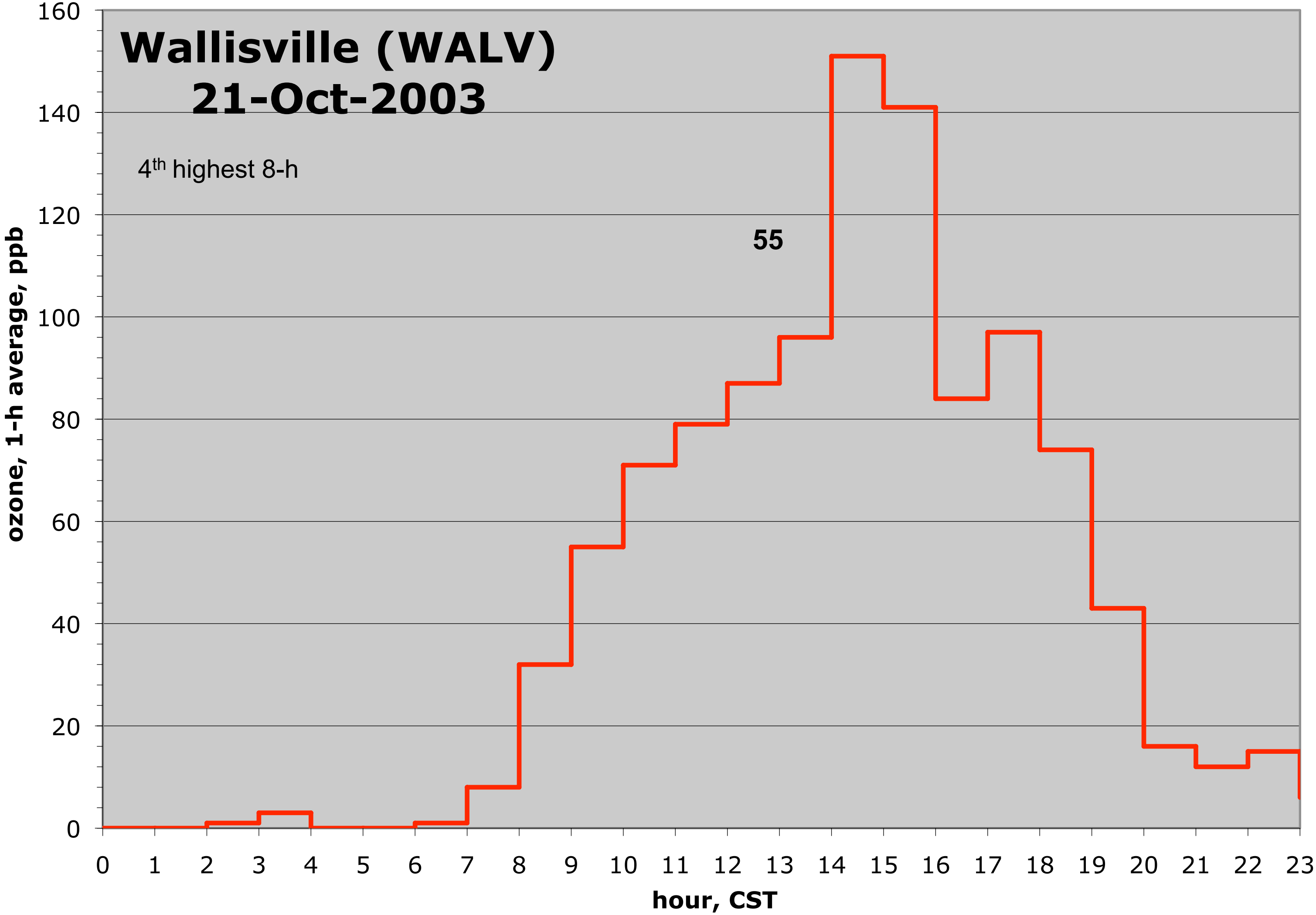
Swiss-Monroe (HSMA)
11-Sep-2004 (weekend)
4th highest 8-h
46
29
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



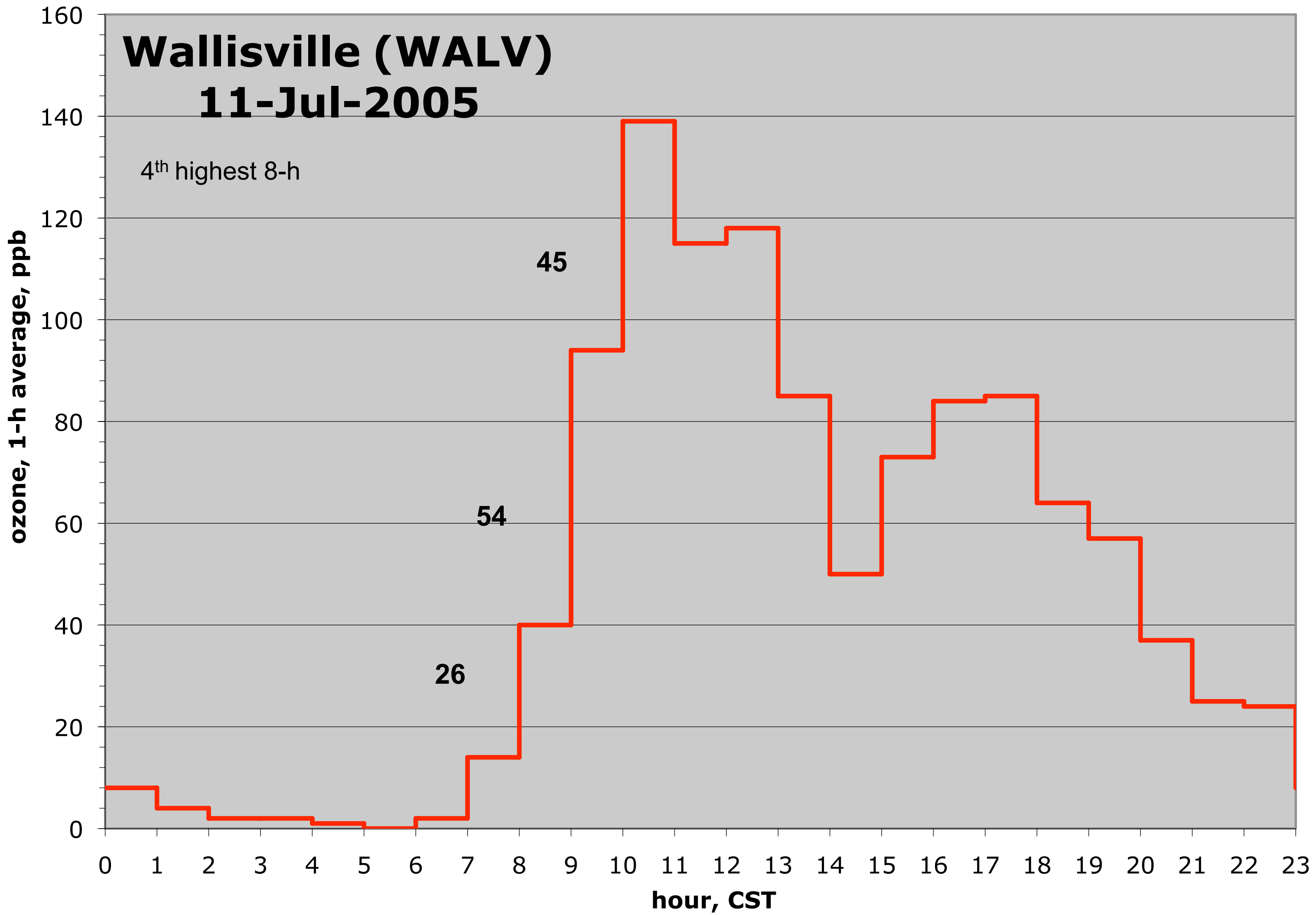
Swiss-Monroe (HSMA)
17-Oct-2005
4th highest 8-h
56
18
ozone, 1-h average, ppb
hour, CST
140
120
100
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



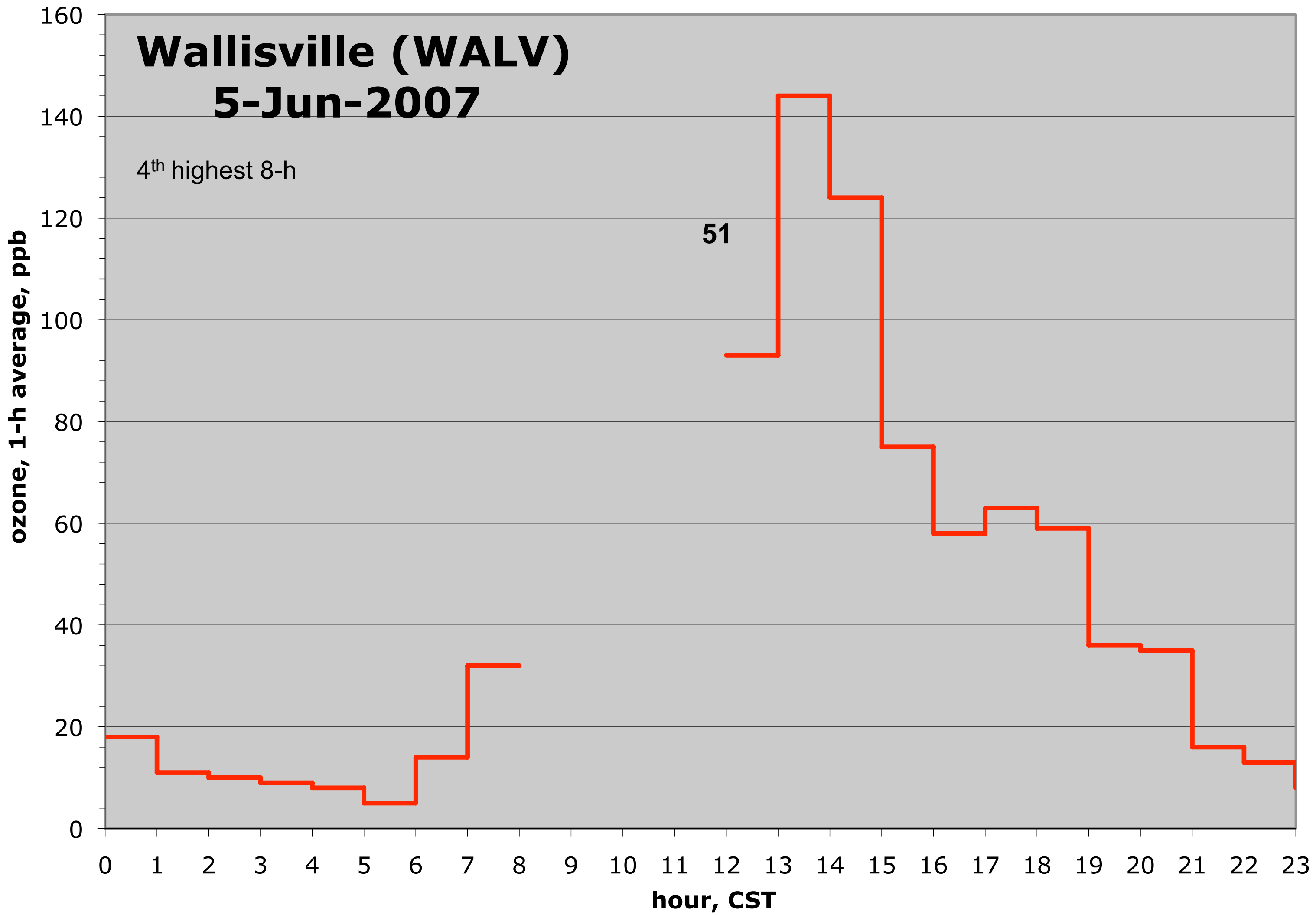
Swiss-Monroe (HSMA)
13-Aug-2007
4th highest 8-h
52
35
25
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23



Wallisville (WALV)
21-Oct-2003
4th highest 8-h
55
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
160
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



Wallisville (WALV)
11-Jul-2005
4th highest 8-h
45
54
26
ozone, 1-h average, ppb
hour, CST
0
20
40
60
80
100
120
140
160
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



Wallisville (WALV)
5-Jun-2007
4th highest 8-h
51
ozone, 1-h average, ppb
0
20
40
60
80
100
120
140
160
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
hour, CST

EPA 8-H Ozone Attainment Test

- Method appears to ignore "cause-and-effect" process and substitutes "stability of reduction factor" as measure of adequacy
  - Not required for the model to actually reproduce the 'cause' of any DVb violation.
- Observations are "averaged" over different source to receptor relationships, over weekday and weekend emissions, over time with changing controls
- Model values are selected "for the max" even if counter to cause and effect
- One set of "baseline" emissions assumes that all causal variability is due to met

Where does this leave citizens of Houston?

- EPA 8-h attainment paradigm is basically incapable of effectively dealing with the ozone formation phenomena in Houston.
- Industry has met the 80% NOx reduction and many have on their own made large progress in reducing HRVOCs and 'events'
- Reductions in ozone and precursors are occurring faster than TCEQ's modeling based in 2005 and 2006
- The TCEQ's "short-term" VOC emission limit appears not to be enforced (event reports are still showing extreme 'event' emissions; some sources are reporting large events *every day)*
- History appears to repeat itself in Houston AQ

Questions & Comments