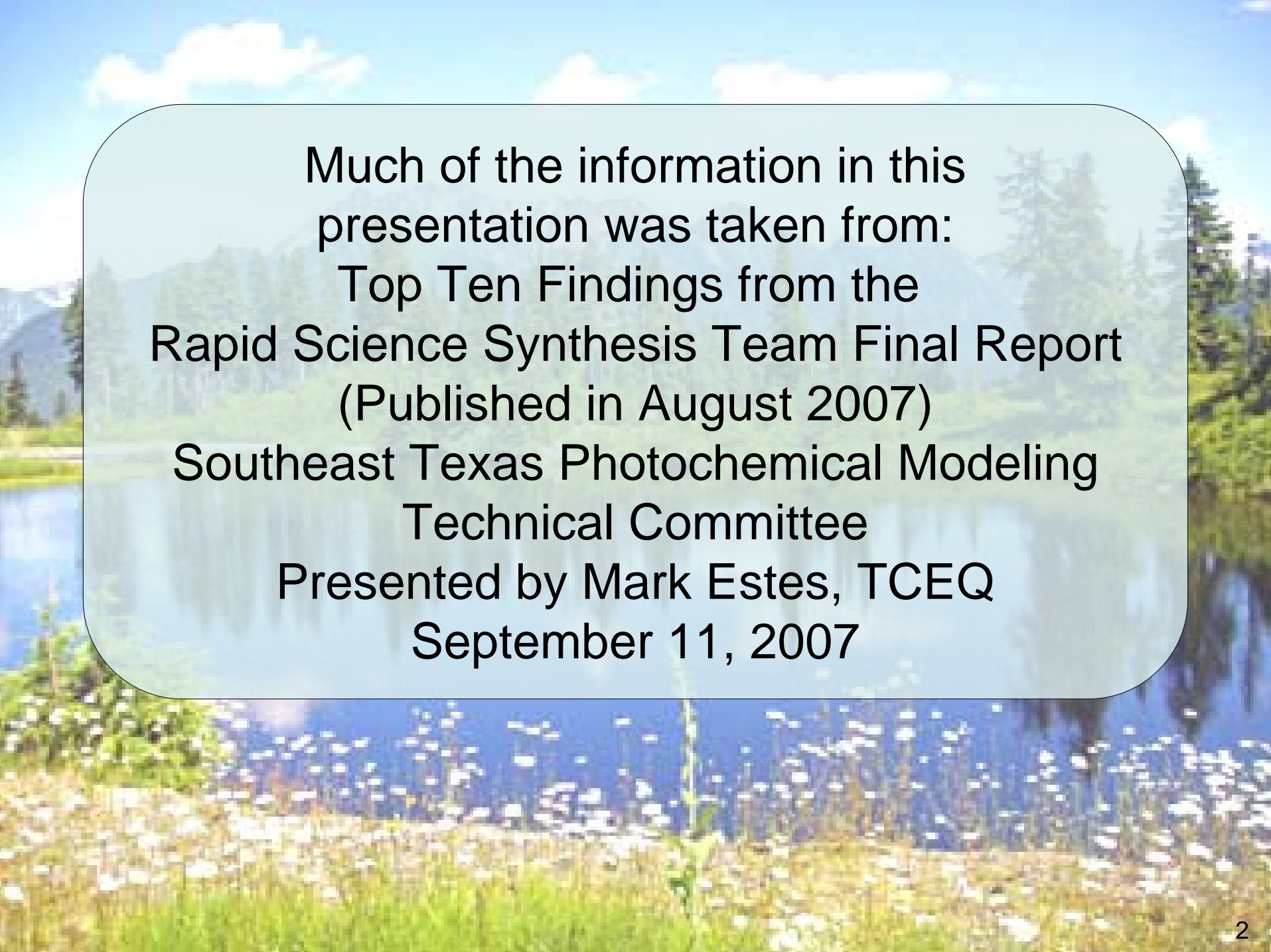


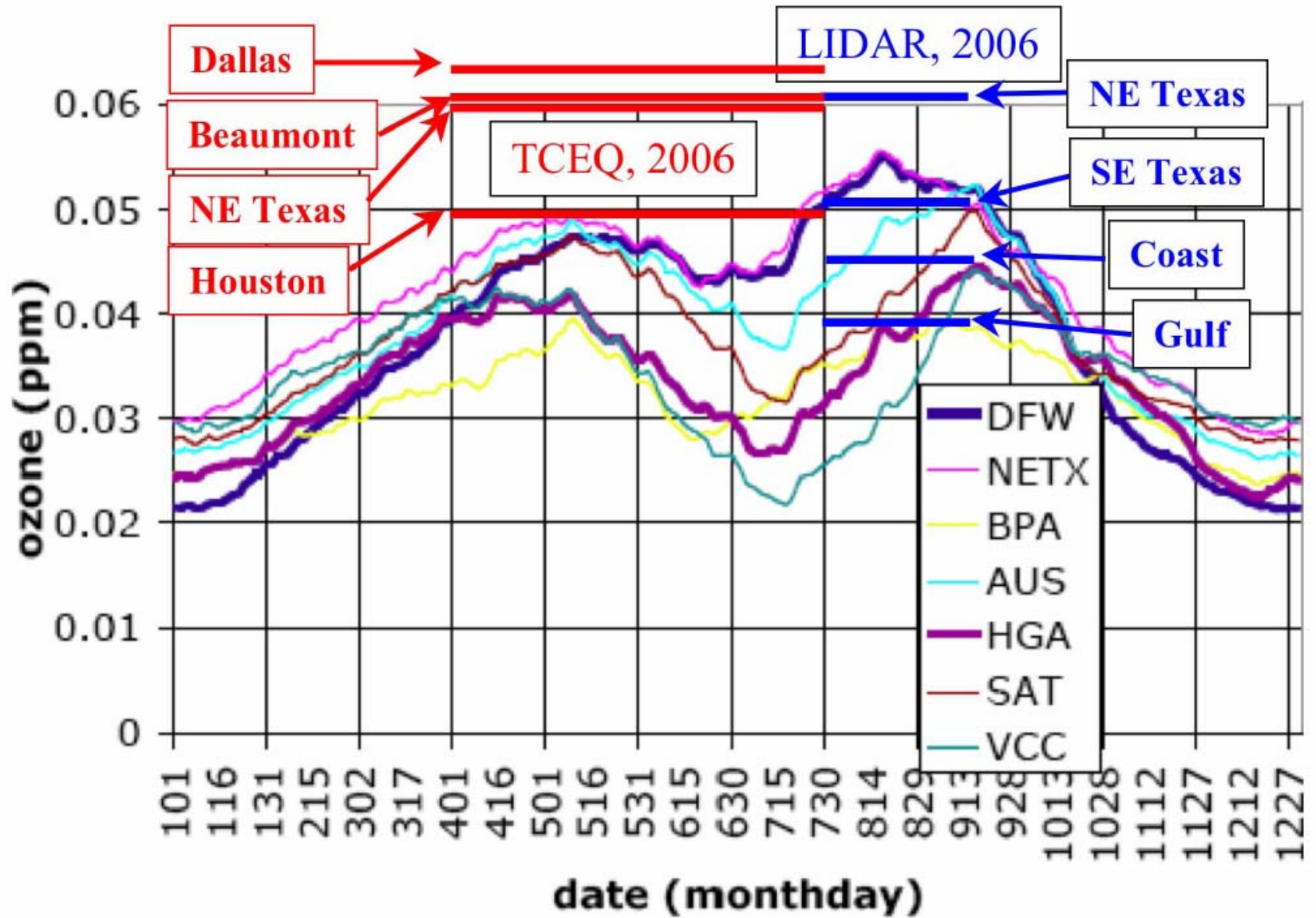
TexAQS II and Emissions Inventories


Alex Cuclis
Houston Advanced Research Center
RAQPC
October 25, 2007



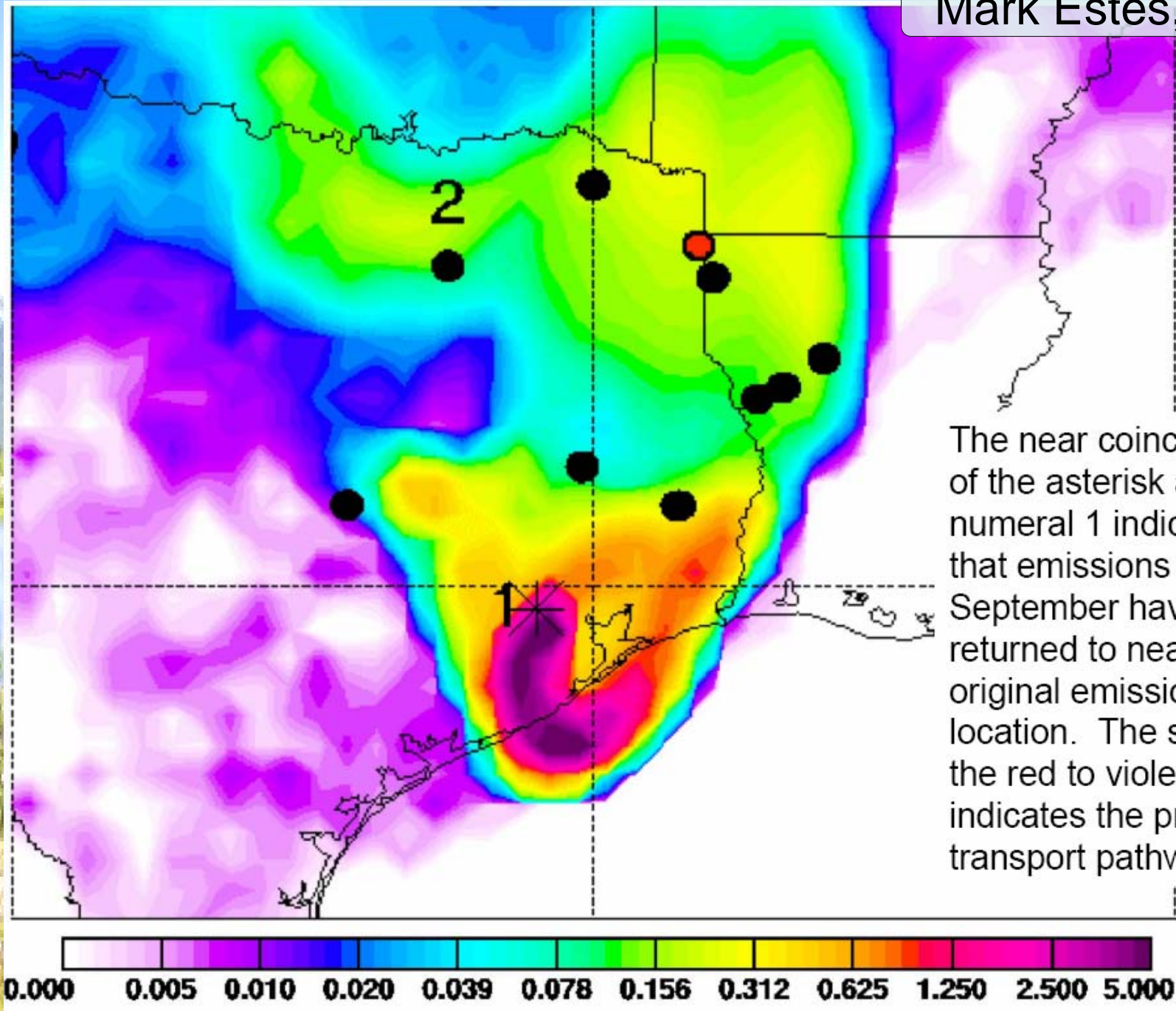
Much of the information in this presentation was taken from:
Top Ten Findings from the
Rapid Science Synthesis Team Final Report
(Published in August 2007)
Southeast Texas Photochemical Modeling
Technical Committee
Presented by Mark Estes, TCEQ
September 11, 2007

1. Background ozone can be Higher than 85 ppbv, but it's usually about 50 ppbv.





2. “Background ozone” may include recirculated pollution



The near coincidence of the asterisk and the numeral 1 indicates that emissions from 26 September have been returned to near the original emission location. The shape of the red to violet colors indicates the primary transport pathways.

3. Use latest versions of both the Carbon Bond and SAPRC chemical mechanisms when testing control strategies. Stay tuned for more information about this topic.

4. Industrial emissions >> high
HRVOCs+NOx plume(s) >>
rapid & efficient ozone formation
>> plume(s) of high ozone +
wind shift (bay breeze/coastal
oscillation) >> “transient” high
Ozone.

5. Power plant NO_x emissions have decreased substantially since 2000. CEMS-based emission estimates are accurate.

Table D1. Measured emissions relative to CO₂ for EGUs in East Texas.

EGU name	NCAR Electra aircraft data 2000			NOAA WP-3D aircraft data 2006			NOx emissions decreased by factor of:
	SO ₂	CO	NOx	SO ₂	CO	NOx	
Monticello	3.5	6.4	1.0	2.8	5.4	0.80	1.25
Welsh	1.5	1.7	0.80	1.7	1.7	1.20	1.5 (increase)
Martin Lake	1.4	4.0	1.3	3.0	6.1	0.80	1.6
Big Brown	4.8	2.9	1.5	7.8	6.8	0.66	2.3
W.A. Parish	2.1	(variable)	0.88	2.1	(variable)	0.25	3.5

Emissions values presented as molecules per 1000 molecules of CO₂ emitted.

6. There are discrepancies between observed mobile CO/NO_x and estimated mobile emissions. [But most recent EI (ca. Sept 2007) has not been compared to the observations yet.]

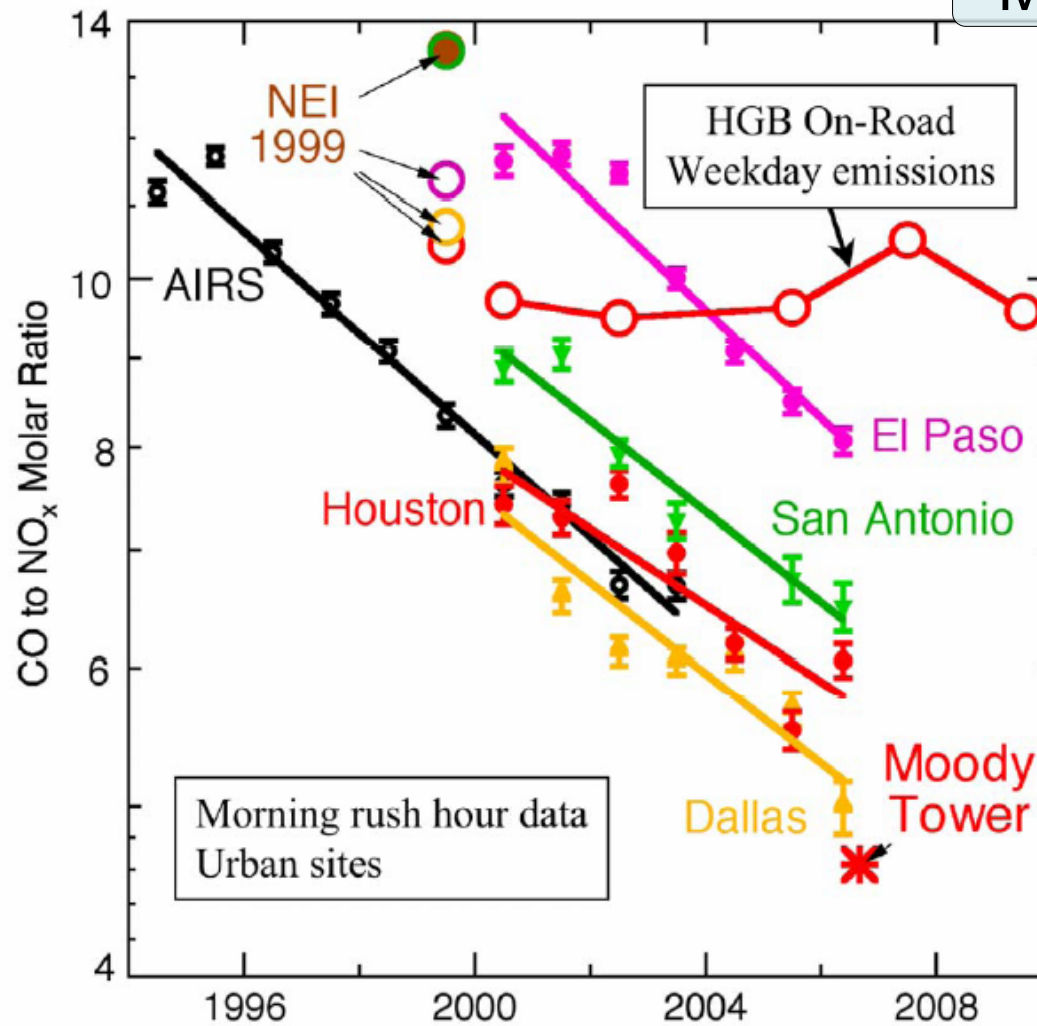
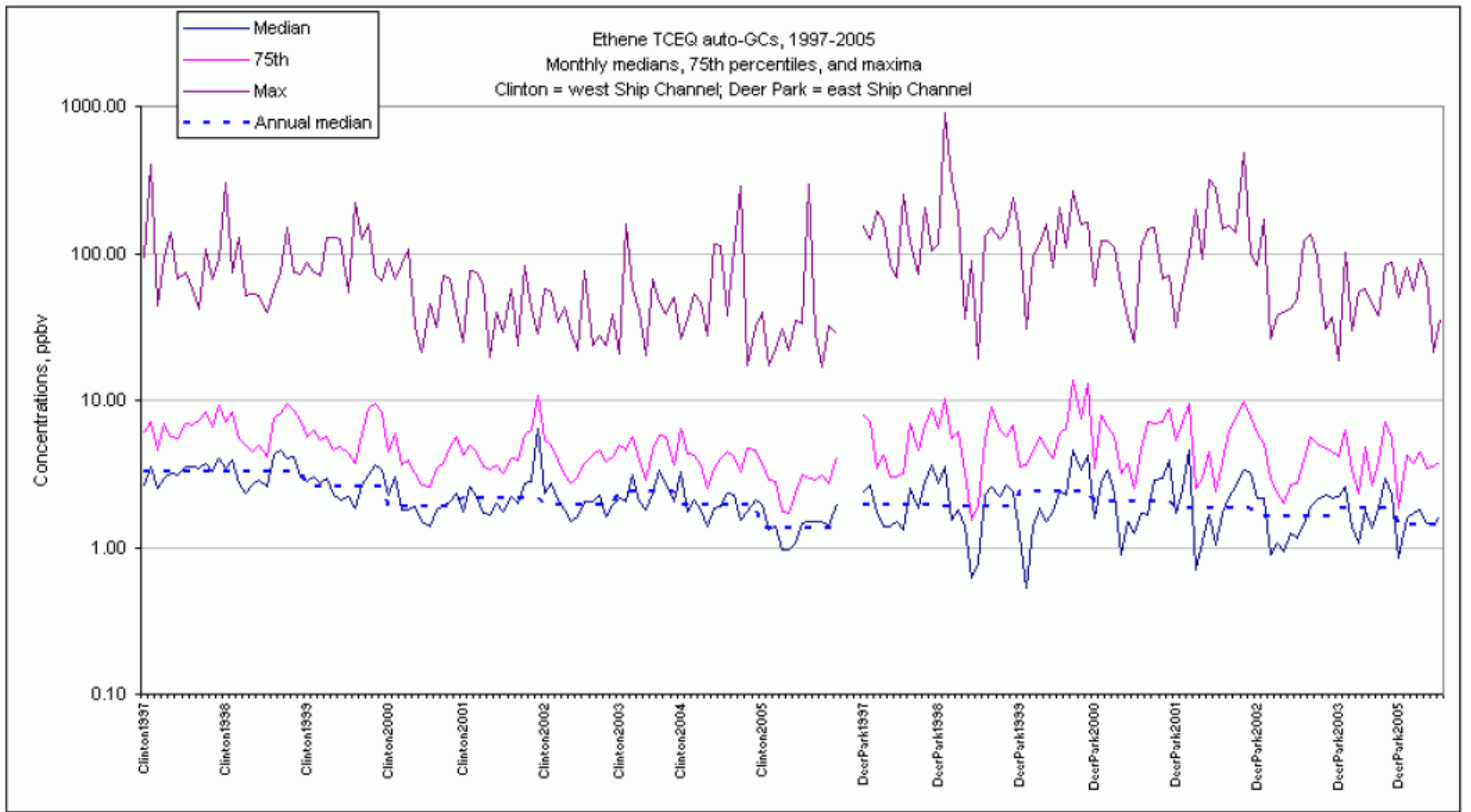


Figure D3. Determination of CO to NO_x ratio in Texan on-road mobile emissions from monitoring data (solid symbols) compared to the HGB emission inventory (open symbols) color coded according to urban area. The black symbols are for all stations in the EPA AIRS network.

7. Secondary HCHO >> Primary HCHO. There's no unambiguous evidence so far that there are huge sources of primary HCHO that aren't already in the EI.

8. For both Houston and Dallas:
local contributions to 8-hr ozone
exceedances = regional
contributions to 8-hr ozone
exceedances.

9. Ethene concentrations have decreased by about 40% since 2000.



11 September 2007

Air Quality Division: MJE

11

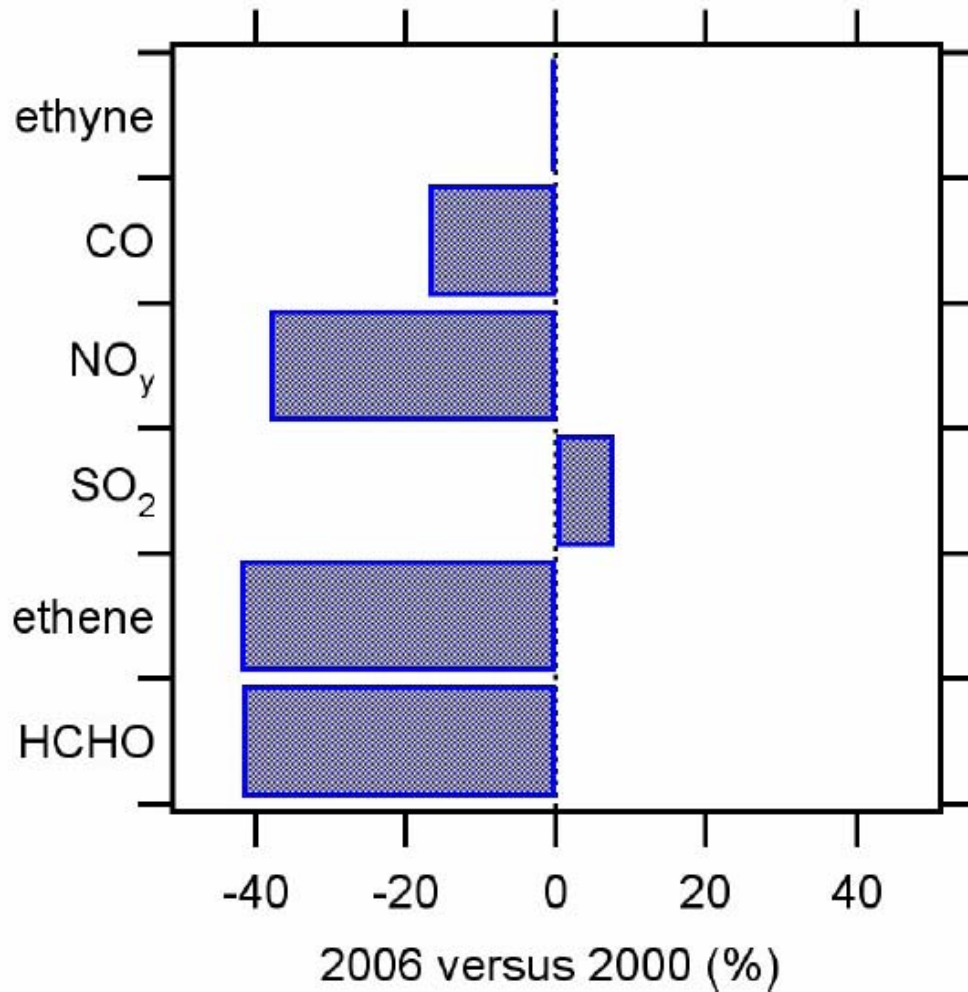


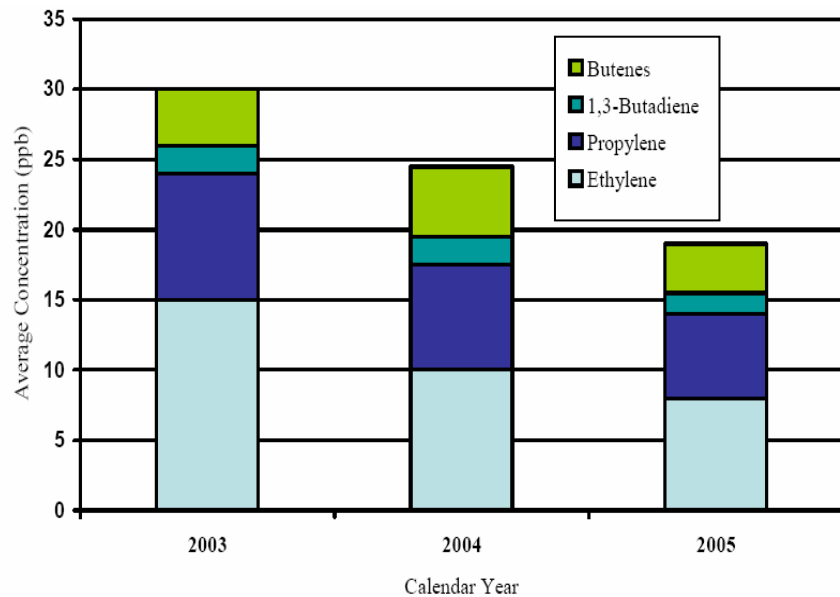
Figure C3: Difference in median mixing ratio for several trace gases measured from the NOAA WP-3D inside a box around Houston and below 1000 m altitude.

10. Measurements of ethene emission fluxes from petrochemical facilities during TexAQS 2006 indicate that the 2004 TCEQ point source database underestimates these 2006 emissions by one to two orders of magnitude.

Emissions Data

In HGB the relationship between measured and reported emissions is not clear.

Measured (auto-GC)



Reported (AP-42, etc.)

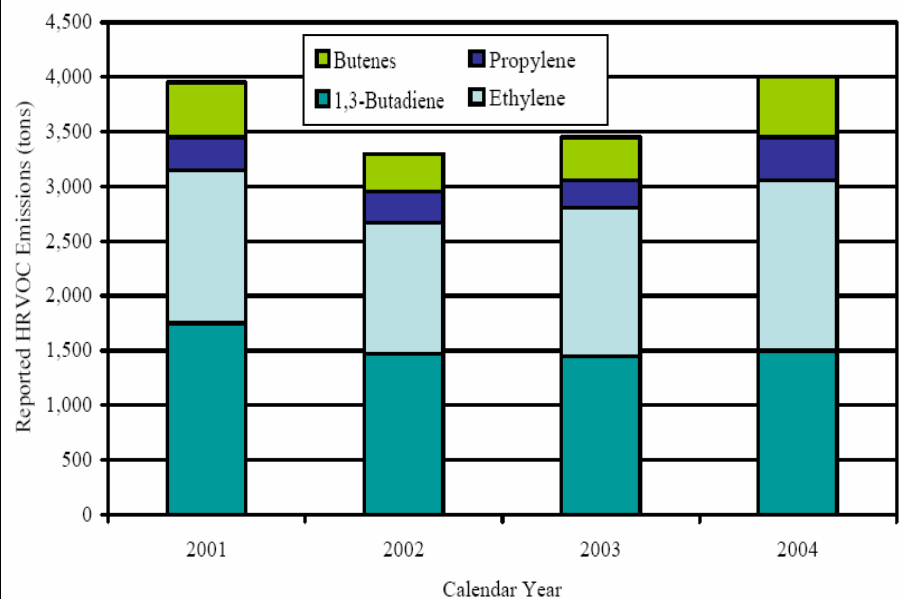


Table I. Measured emission rates obtained by SOF in this study, and the inventory numbers for non methane hydrocarbons

Species	Ethene kg/h		Propene kg/h		Alkanes kg/h		Tot. VOCs kg/h
	Meas.	Invent.	Meas.	Invent.	Meas.	Invent.	Invent.
HSC	860	47	1500	61	12400	1500	3090
Mt Belvieu	404	44	400	9	860	260	265
Baytown	72	6	260	3	980	202	437
Texas City	83	8	-	-	2890	348	686
Channelview	64	11	-	-	-	42	170
Sweeny	163	4	126	4	3630	113	137
Freeport	250	21	-	-	-	44	148
Bayport	170**	4	-	-	-	94	151
Chocolate Bayou	136**	10	273	24	-	107	150

* Nonmethane hydrocarbons corresponding to alkanes and unspeciatiated VOC as in the 2004 inventory database, ** Uncertain due to few measurements.

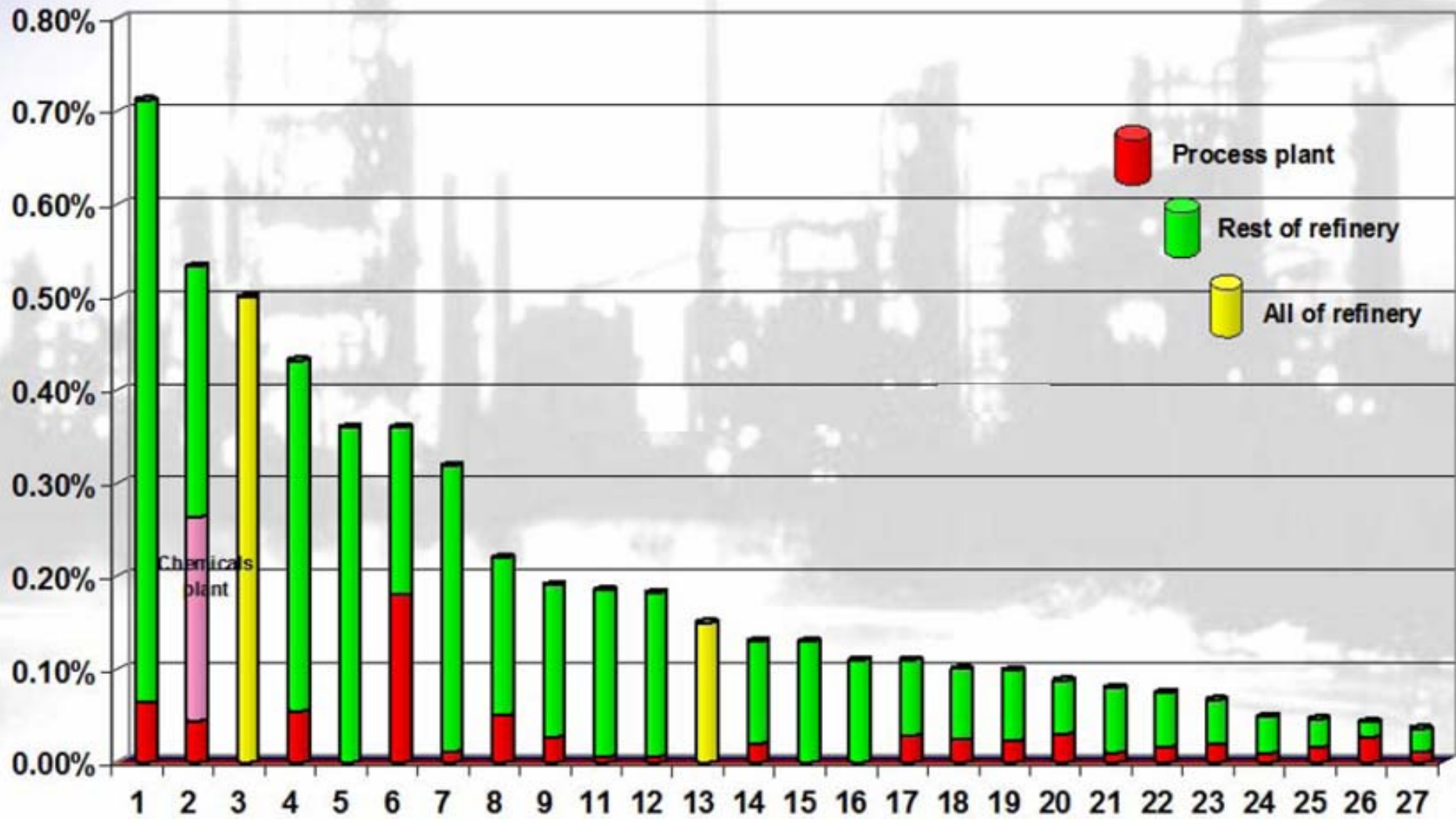
Flux estimates from the SOF and WP-3D measurements were compared for different sources (Sweeny, Freeport, Texas City) and generally agreed within a factor of 2, with no systematic difference as to which technique was higher or lower. (RSST)

DIAL Catch-22

To Measure or Not to Measure?

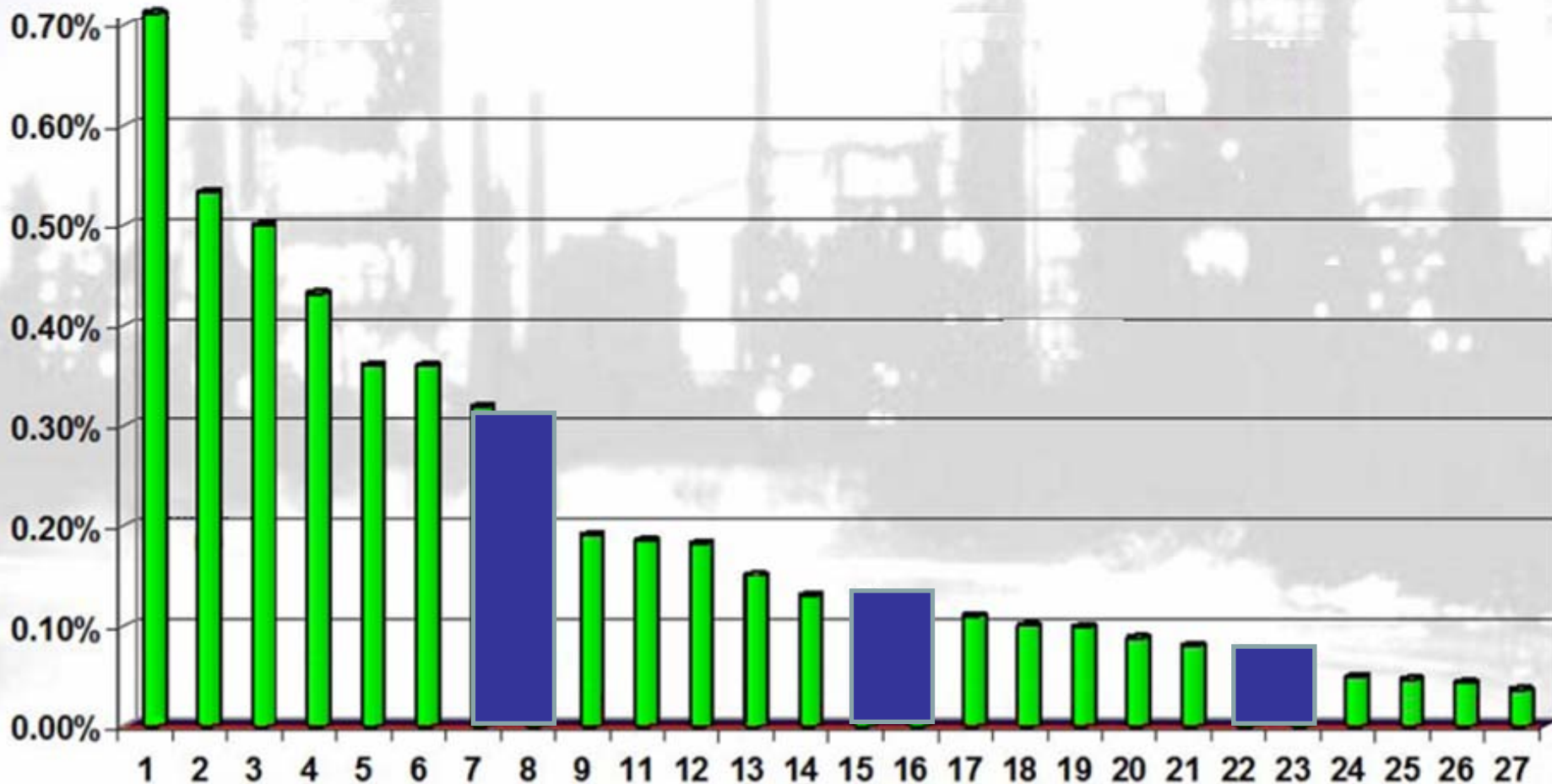
That is the Question...

Spectrasyne DIAL Refinery VOC Emission Comparisons



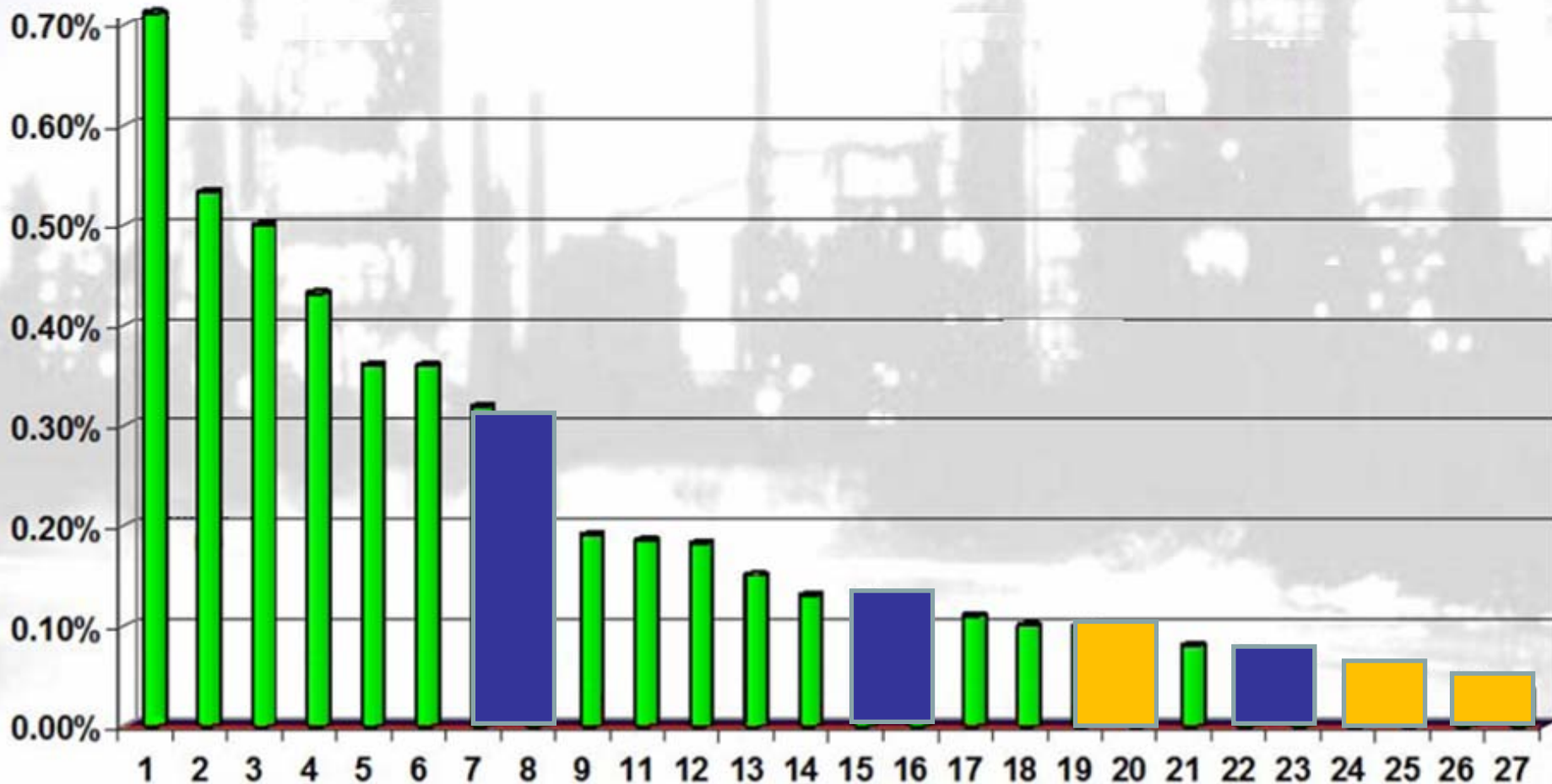
.15 Spectrasyne DIAL Refinery VOC Emission Comparisons

.12 NPL



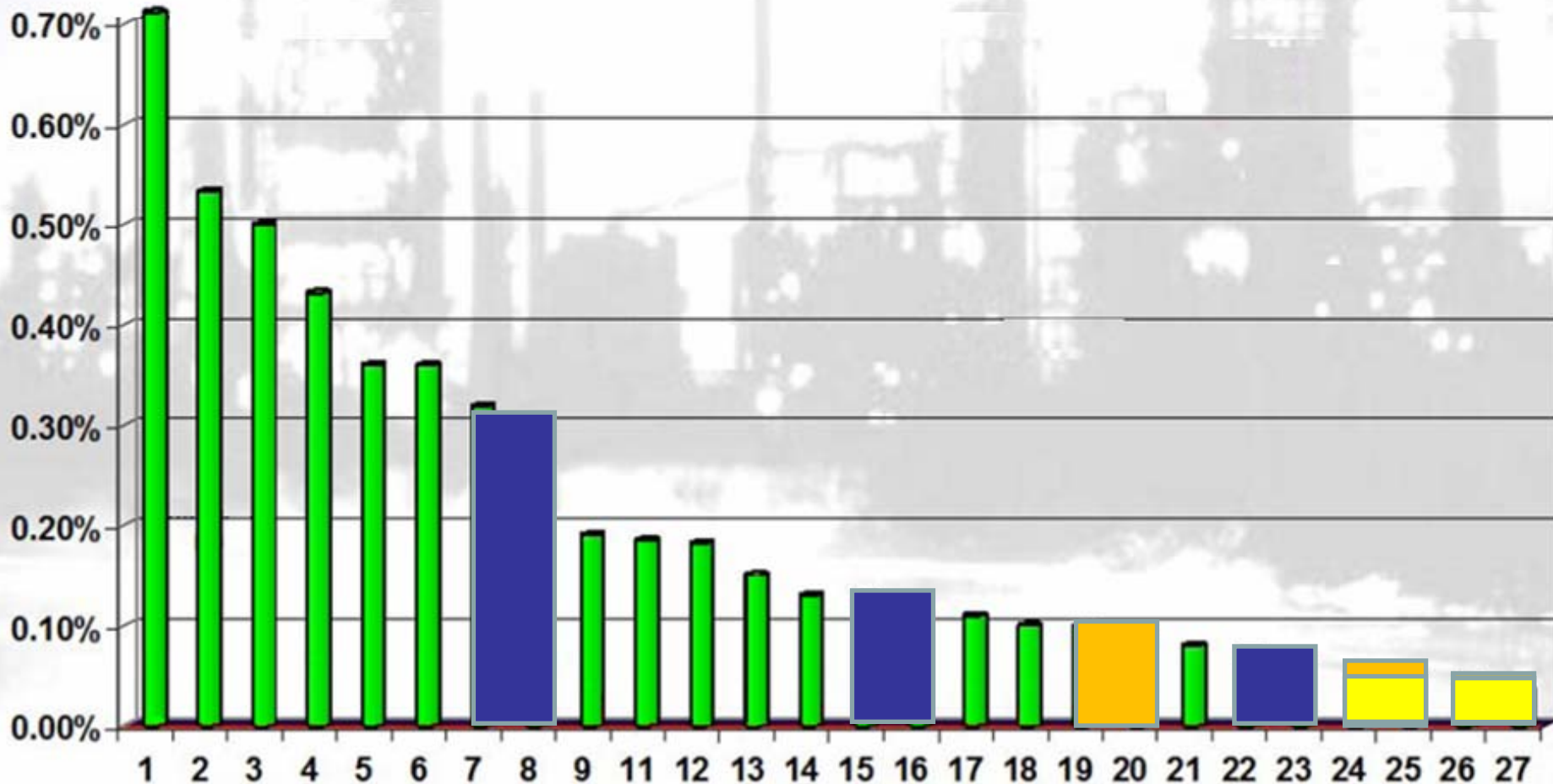
.15 Spectrasyne DIAL Refinery VOC Emission Comparisons

.12 NPL **.05 SOF**



.15 Spectrasyne DIAL Refinery VOC Emission Comparisons

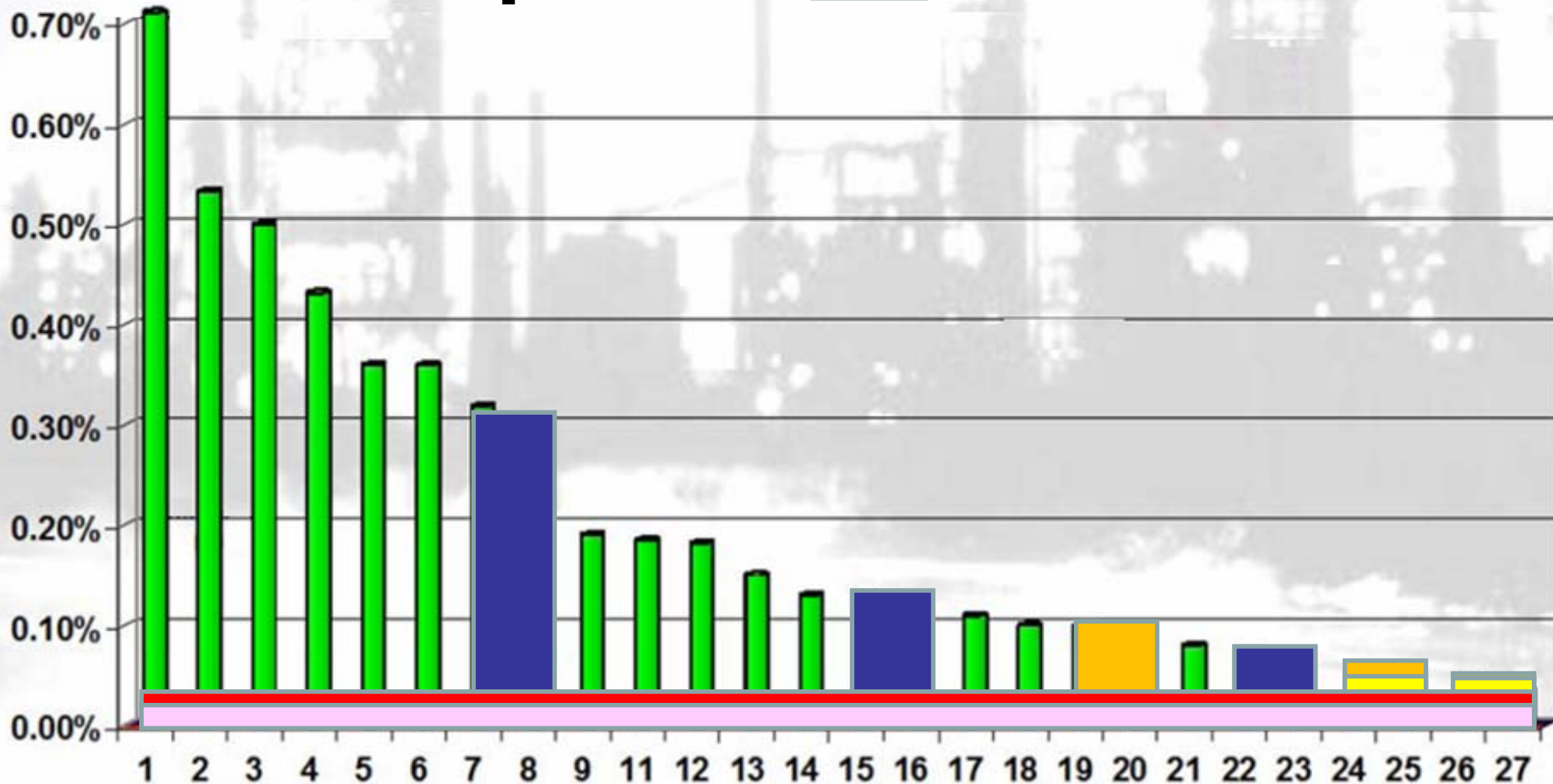
.12 NPL **.05 SOF** **.04 Shell**



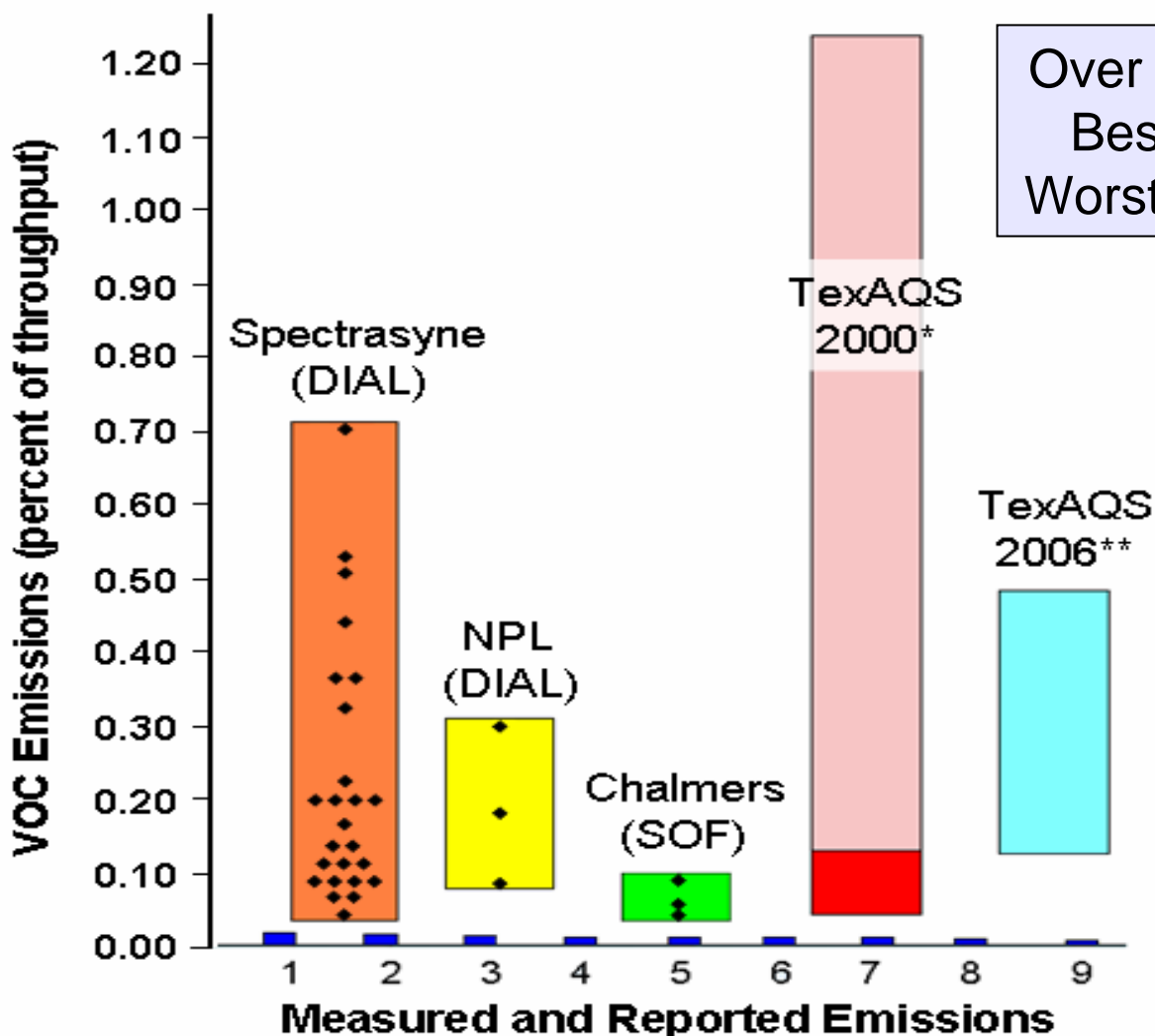
.15 Spectrasyne DIAL Refinery VOC Emission Comparisons

.12 NPL **.05 SOF** **.04 Shell**

HGB Reported **.012 2004** **.018 1999**



Refinery VOC Emissions



Over 30 DIAL & SOF Surveys
 Best Case = 3 X Reported
 Worst Case = 20+ X Reported

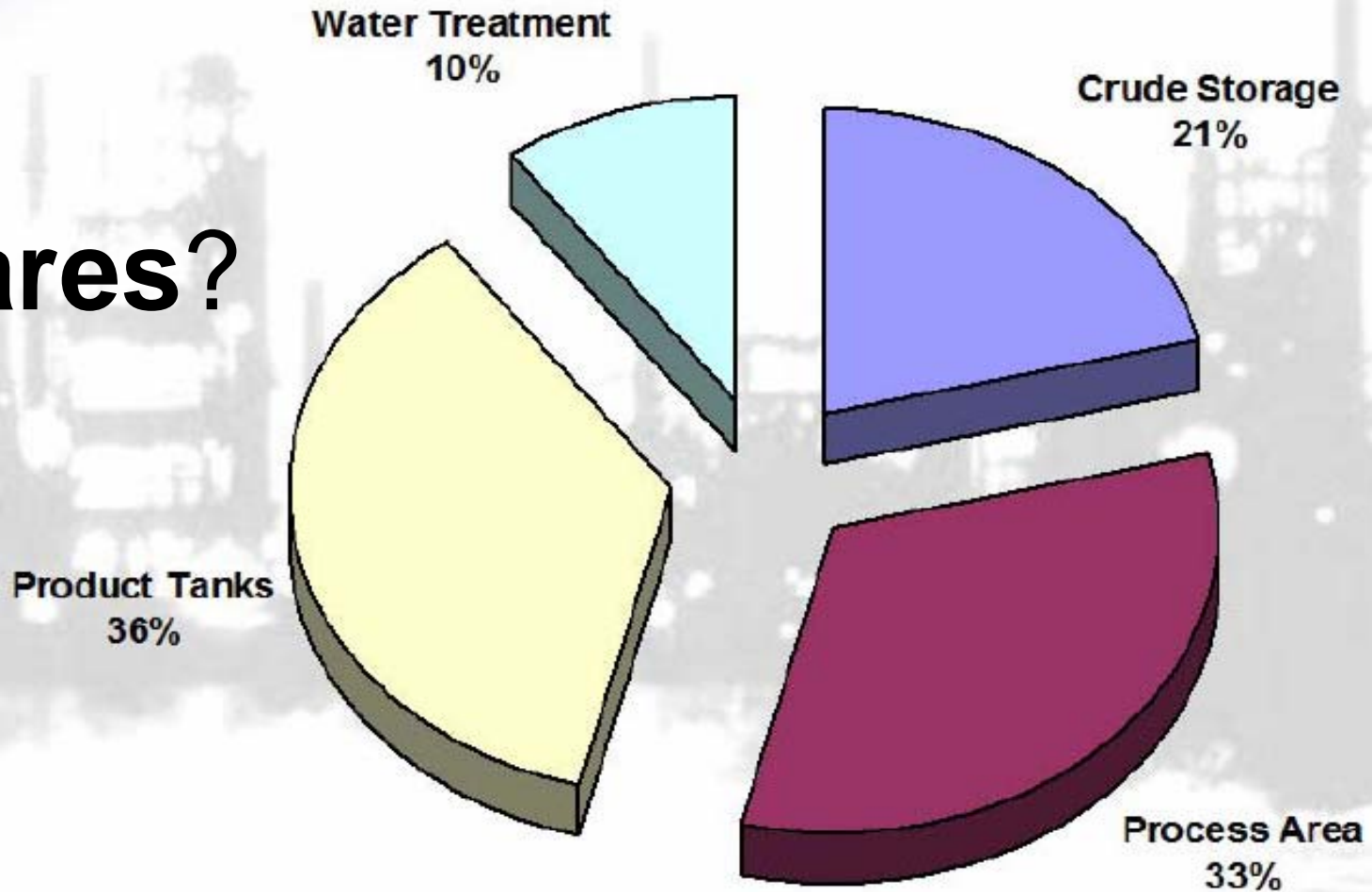
1-9 Houston Area Refineries 2004 Reported Emissions (dark blue)

*In TexAQS 2000 David Allen noted that VOC/NOx ratios were *consistently* 3-10 times higher (red) than reported emissions, and in some cases were 100 times higher (pink).

**In TexAQS 2006 Solar Occultation Flux (SOF) measurements indicated that VOC emissions were 10 - 40 times higher (light blue) than reported values.

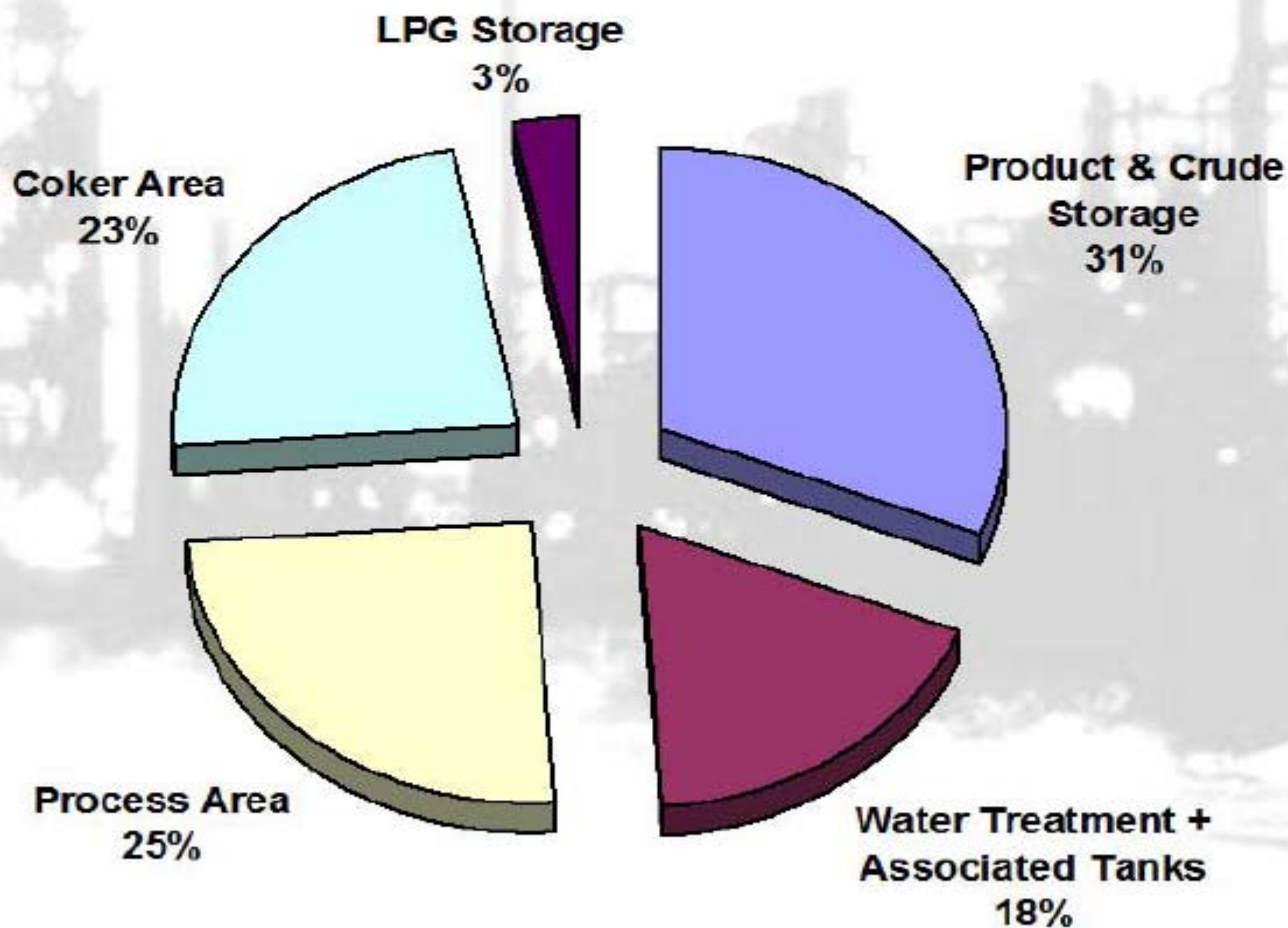
Simple Refinery Emissions by Area

Flares?



Spectrasyne

Large Complex Refinery With Coker VOCs by Area



Emission Sources

Tanks

-Seals, Landings, “Splatterings”, Fittings

Flares

-Minimization, Steam/Air Assist, Flow, Wind

Delayed Cokers

**-De-heading, Drilling, Fugitives
(Alberta and the 2 ½ times factor)**

Water Treatment

-Recovery, Aeration, Mixing

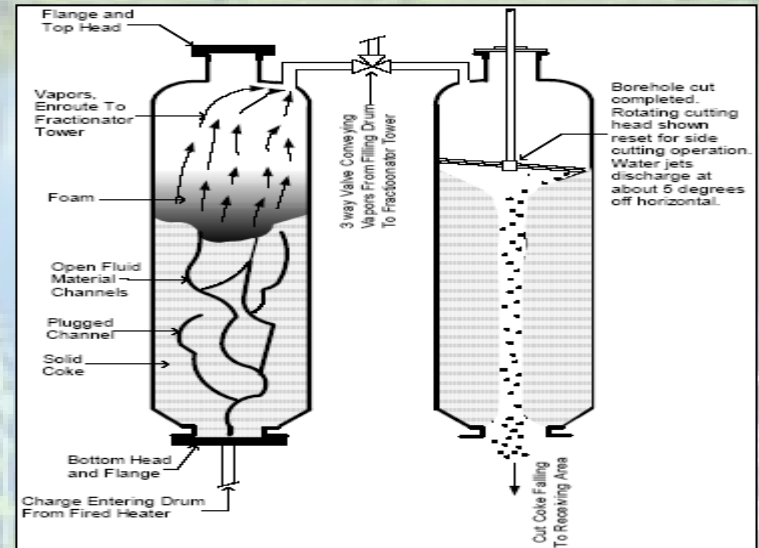
Type of Survey	NPL	Spectrasyne
Petrochemical Plants	>14	30
Delayed Cokers	1	3 or 4
Natural Gas Plants	4	21
Flares	5	20
Chemical Plants	2	10
Tank Studies	2	7
Coke Works	1	0
Shipping Terminals	1	17
Oil Product Terminal	1	6
Power Stations	4	0
Plume Dispersion Studies*	2	5
Rail Loading Terminals	3	2
Crude Oil Terminal	0	11
Airport	0	1
Other	5	12
Total	>78	142

Refinery Cokers



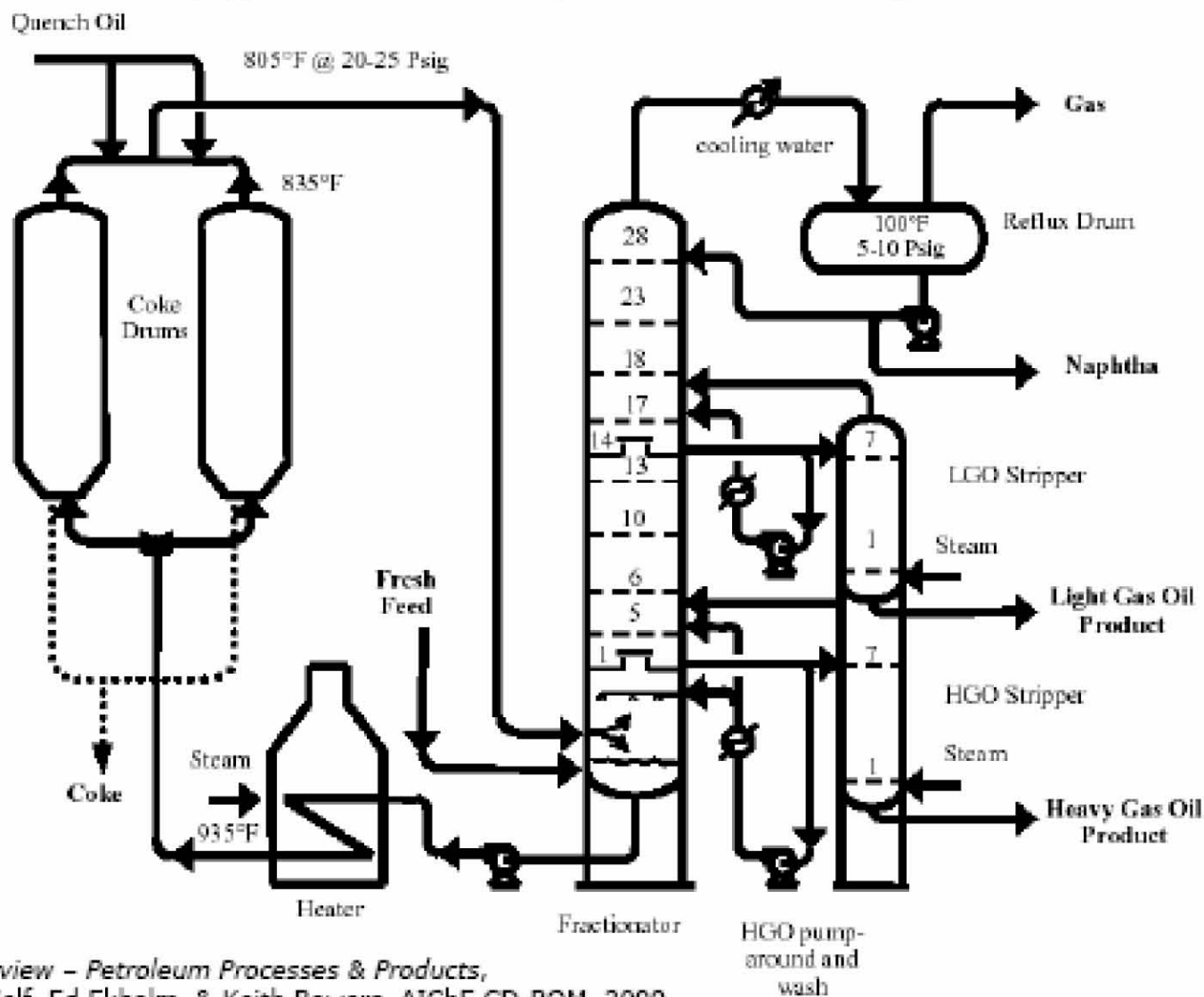
Coke drums can be 80 - 100 ft tall and up to 27 ft in diameter.

Drilling derricks on top of the coke drums contain water jets that are used to cut the solid coke out of the drum.



<http://primis.phmsa.dot.gov/comm/images/RefineryProcess.jpg>

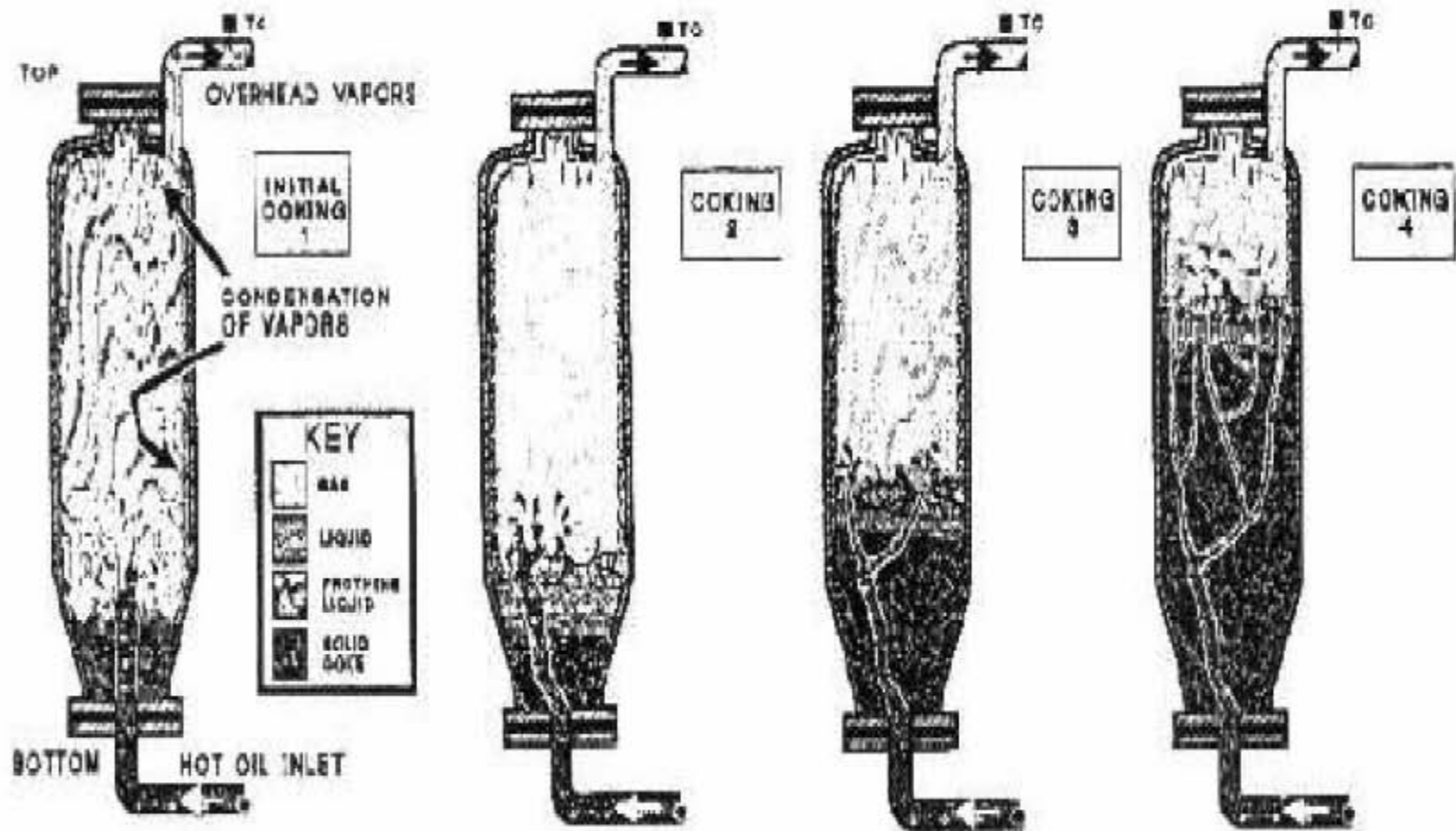
Typical Delayed Coking Unit



Source:
Refining Overview - Petroleum Processes & Products,
 by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

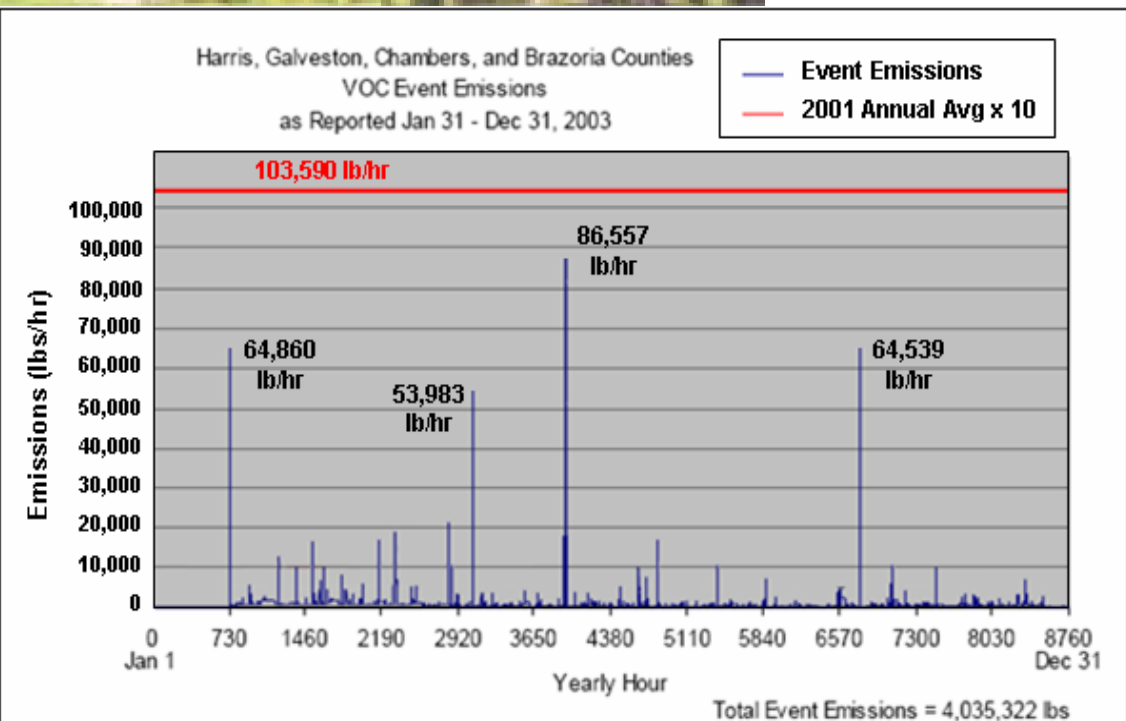
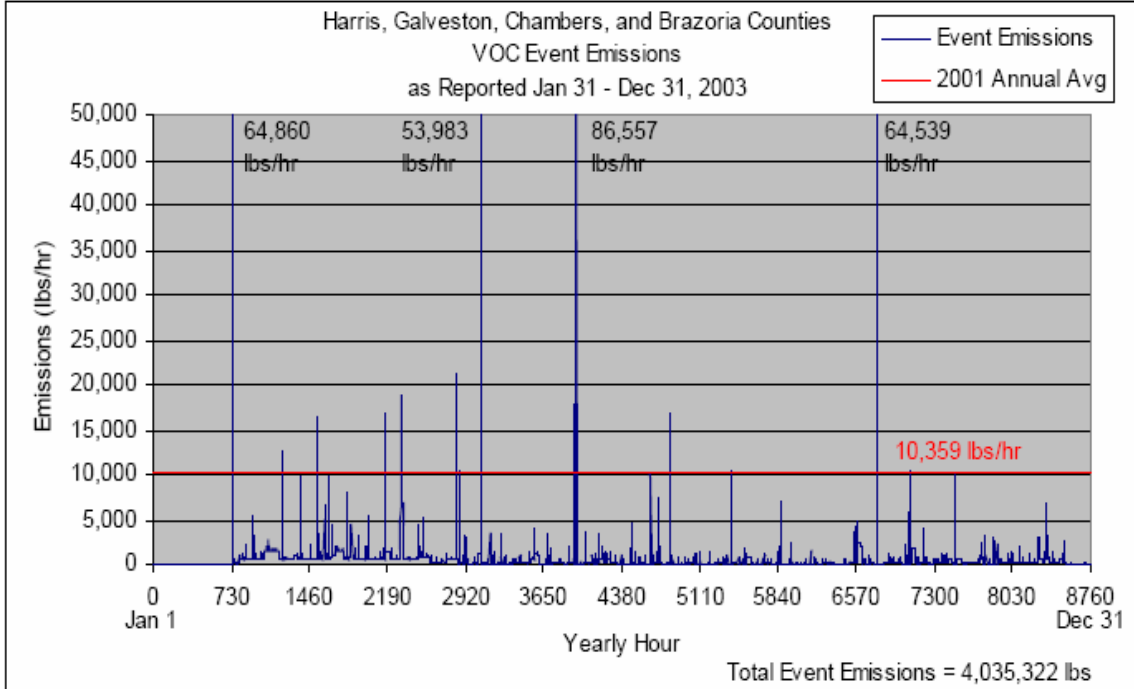
Figure 3. Great Lakes Carbon Coke Formation Model: How Coke Forms in the Drum

According to Spectrasyne most VOCs are measured during the drilling process.



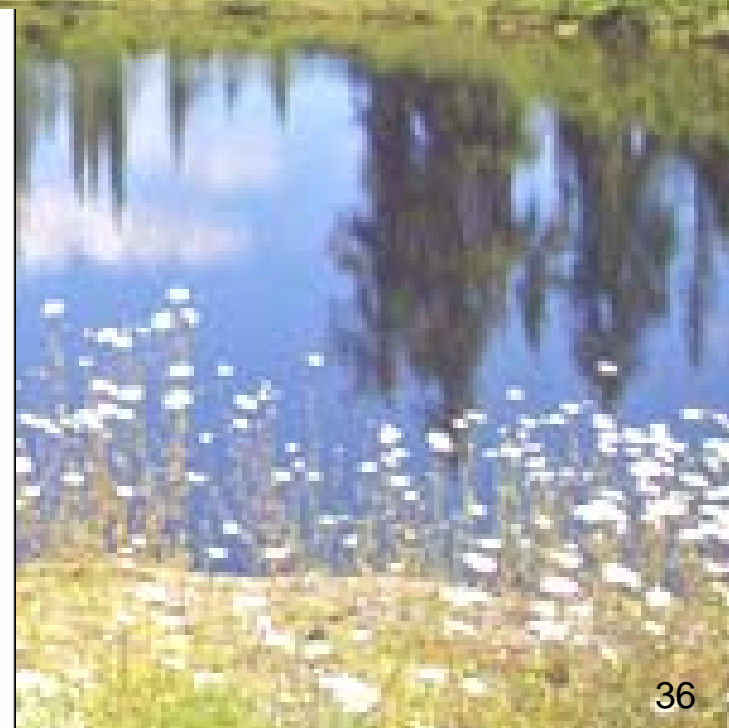
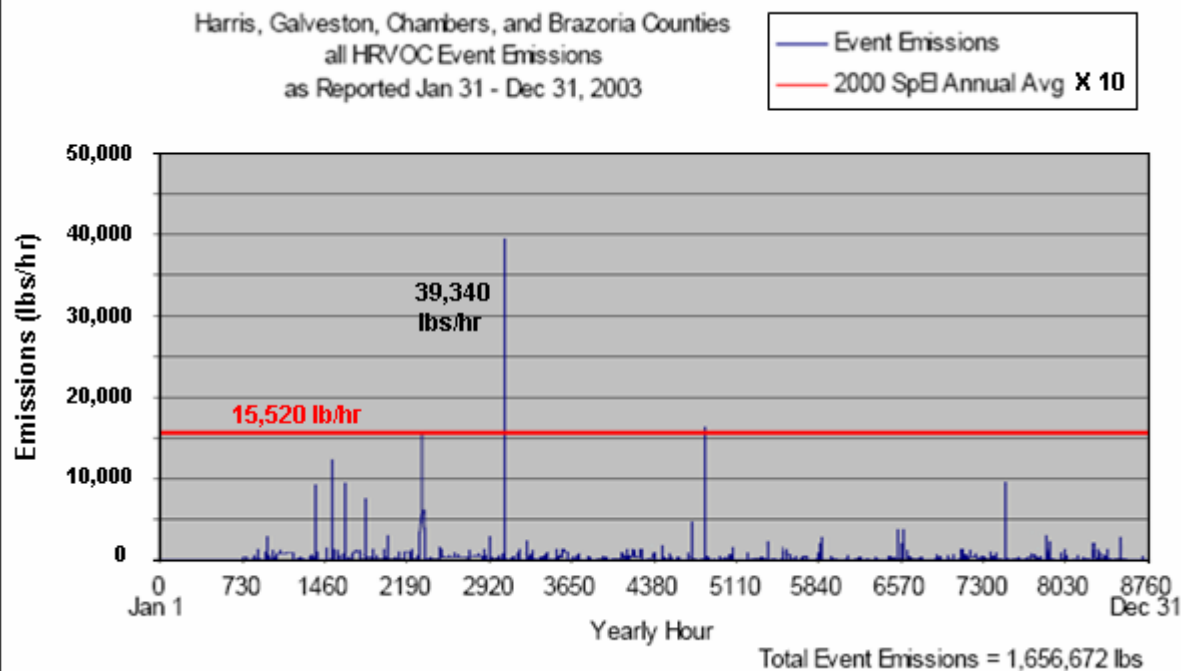
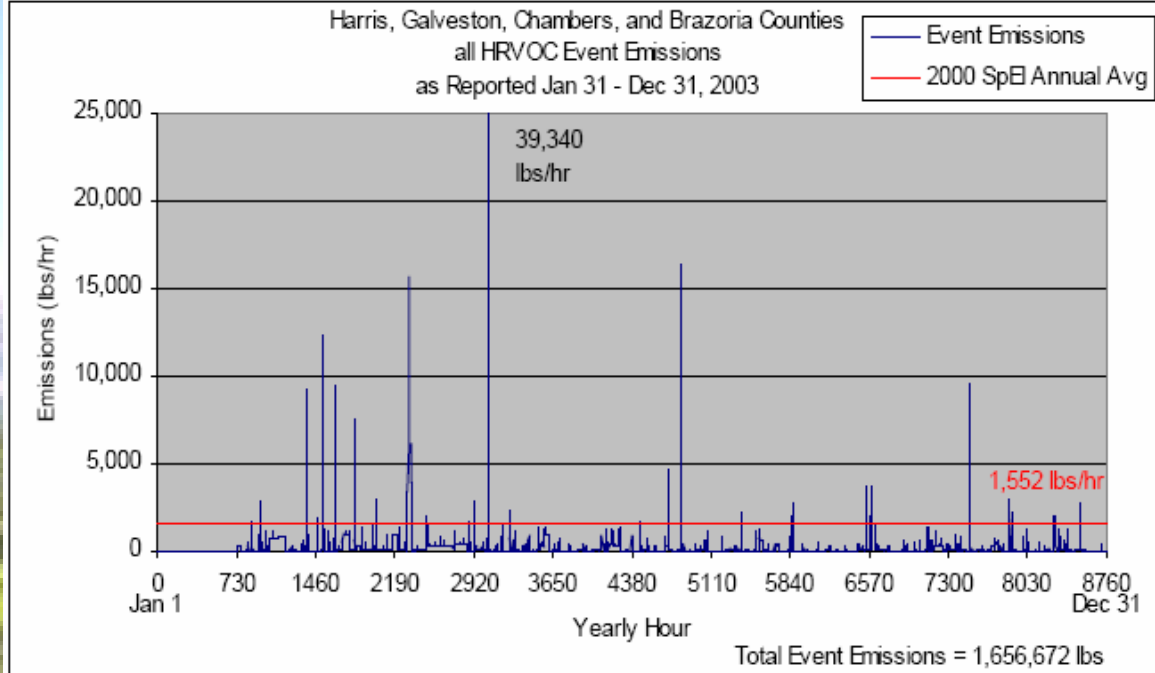
Great Lakes Carbon Corporation
<http://www.gllcarbon.com/ref/delayed.PDF>

HARC Project H-13 by Jeffries and Allen shows that emission events can have a significant impact on ozone in HGB.



However, if the routine emissions are off by a factor of ~ 10, then the relative impact of emission events May be diminished.

A similar result can be seen for HRVOC emission events.



“I quite agree with your take on the inventory issue, and the first-order nature of the emissions problems that you lay out. I think you can use the RSST (Rapid Science Synthesis Team) report to bolster your case as well, if that would help - finding C2 especially. The 2006 and 2000 studies both point to the inventory discrepancies of factors of 10 to over 100, compared to routine emissions, being more important than almost any upset.”

- Tom Ryerson, NOAA

Improving Emissions Estimates

- Chemical Engineers – Apply Process Knowledge and Good Engineering Judgment.
- Identify Typical, Extreme Upset and Ideal Conditions and Do the Math.
- Chemists – Use Best Analytical Techniques – Know When Quantification is Required.
- Operators (and others) – Develop an Environmental Culture = Personal Safety.
- Understand the Economics – If the Greenest Refineries Become Least Competitive, No One Wins.