Inferring Industrial VOC Emissions Inventories Based Upon VOC Observations

TCEQ - Technical Analysis Division

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Why are we inferring emissions from observations?

- The TexAQS 2000 results indicate the Texas EI in the Houston-Galveston and Beaumont- Port Arthur areas underestimate VOCs.
- TCEQ photochemical modeling results for the Houston-Galveston episode indicate limited ozone production with the reported VOC emission rates.
- The current modeling adjustment is an estimate and can use improvement and/or validation.

Methodology

1. Link observations to emissions
   A. Auto-GC Hourly Data
   B. Aircraft Alkene Data
2. Compare observed VOC/NO_X ratios to reported or modeled ratios from the emissions inventory
3. Develop adjustment factors if appropriate

$$\text{Adjustment Factor} = \frac{\left(\frac{\text{Observed VOC}}{\text{Observed } NO_X}\right)}{\left(\frac{\text{Reported/Modeled VOC}}{\text{Reported/Modeled } NO_X}\right)}$$

Auto-GC Methodology

- All data through 2001 from 5 Auto-GC sites were used

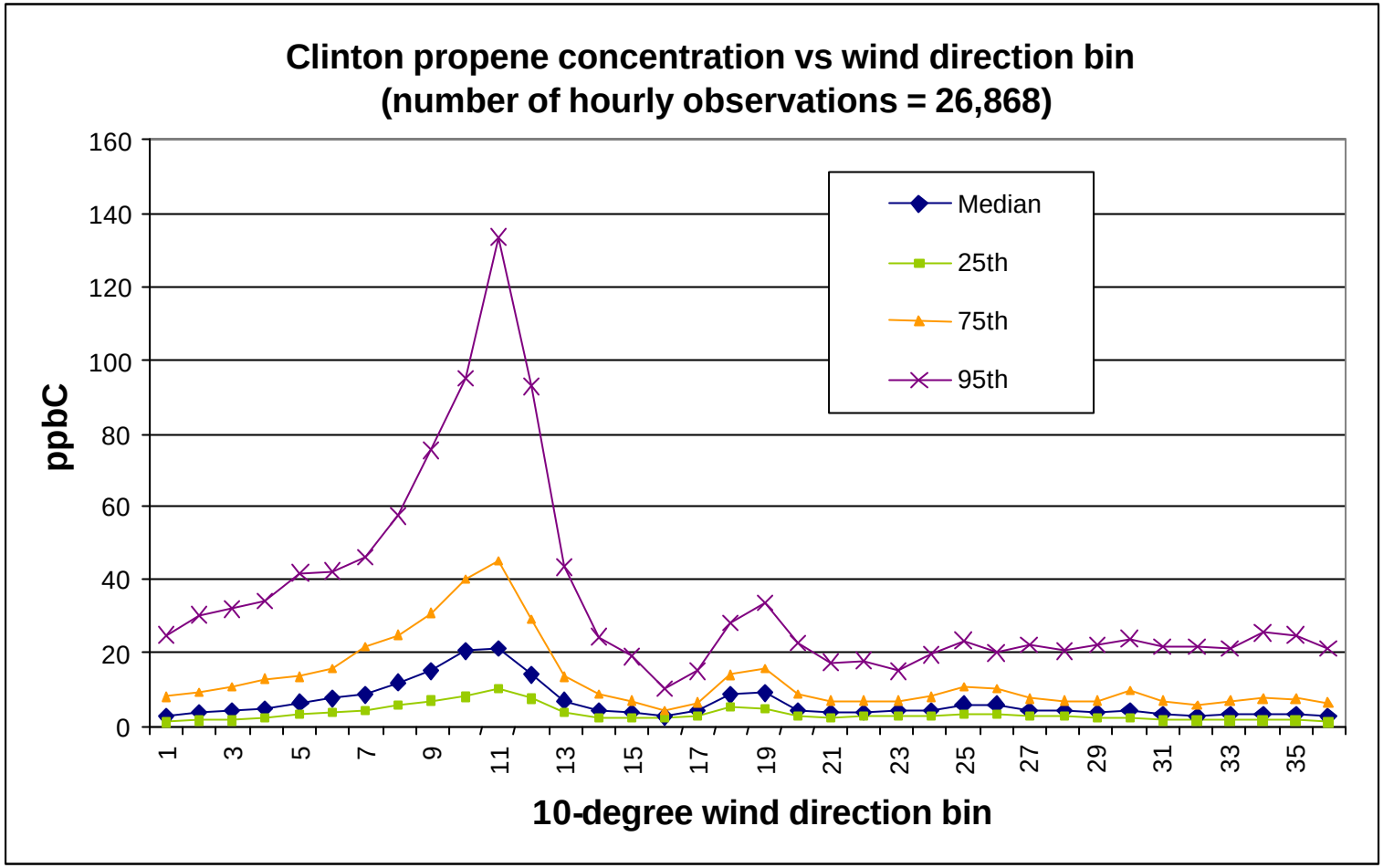
Site Name	Number of hours available
Clinton	26,868
Deer Park	17,547
HRM 7	1375
HRM 3	1505
Channelview	1195

- Source-group wedges and 10° wind bins were created at each Auto-GC site to group emission sources.

- Molar VOC/NO_X emission ratios were then compared to observed VOC/NO_X concentration ratios to see if discrepancies existed.

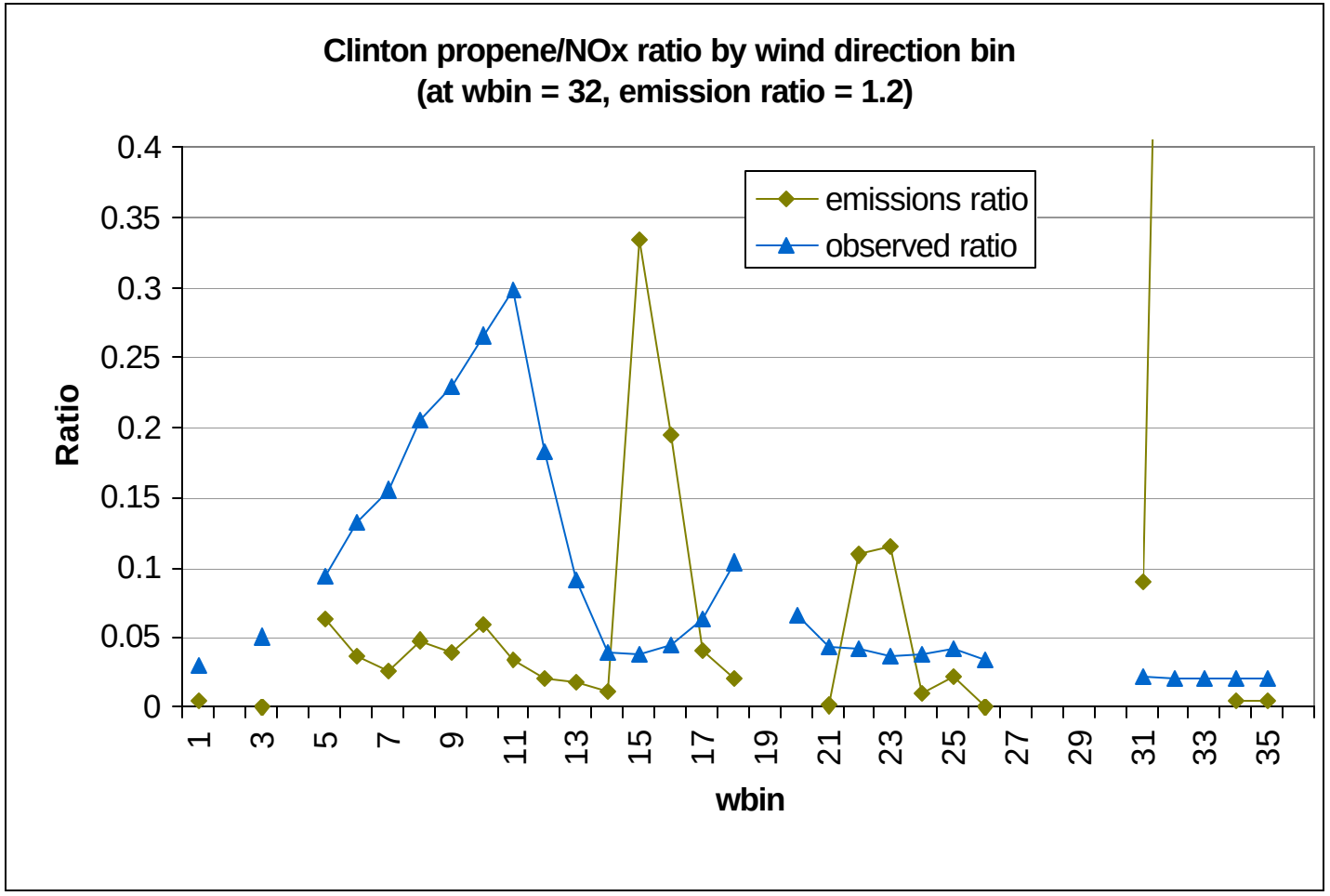
- Emission adjustment factors created using source-group wedge ratios for ethene, propene, 1,3-butadiene, and butenes.

Auto-GC: Linking Obs to Emissions

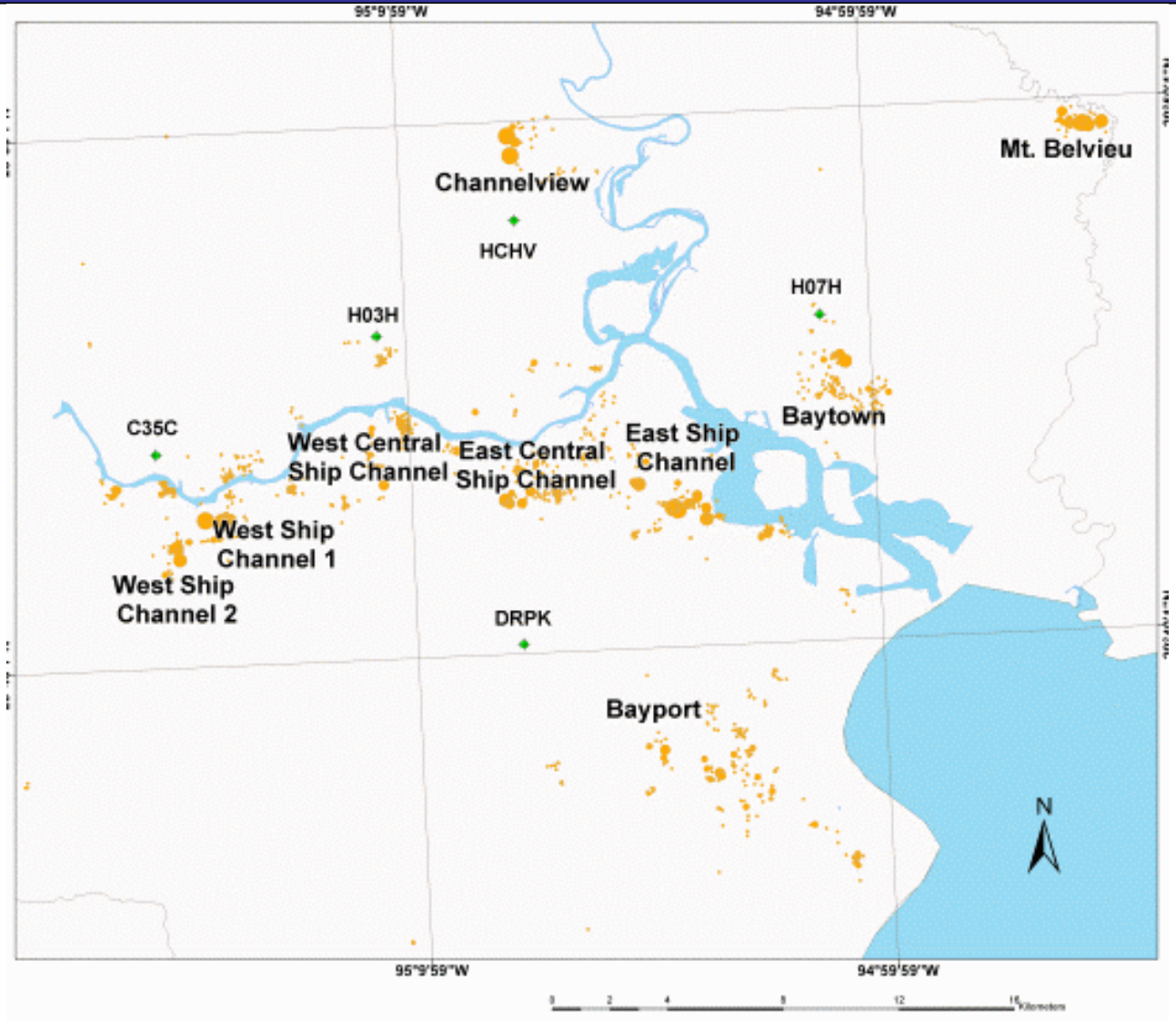


* Median concentrations used to lessen influence of “upsets”

Auto-GC: Comparing VOC/NO_X ratios



Auto-GC: Emission adjustments locations



Auto-GC: Emission adjustments by source region

Source Cluster	Reported emissions (tons/day)	Inferred emissions (tons/day)	Adj. Factor
West Ship Channel 2	1.48	3.13	**2.11**
West Ship Channel 1	1.22	1.51	**1.24**
West Central Ship Channel	1.21	2.78	**2.30**
East Central Ship Channel	0.66	5	**7.58**
East Ship Channel	8.1	47.5	**5.86**
Baytown	2.81	39.5	**14.06**
Channelview	3.16	5.95	**1.88**
Mont Belvieu	1.75	3.88	**2.22**
Bayport	0.92	11.9	**12.93**

Auto-GC: Adjustment Bias

HIGH

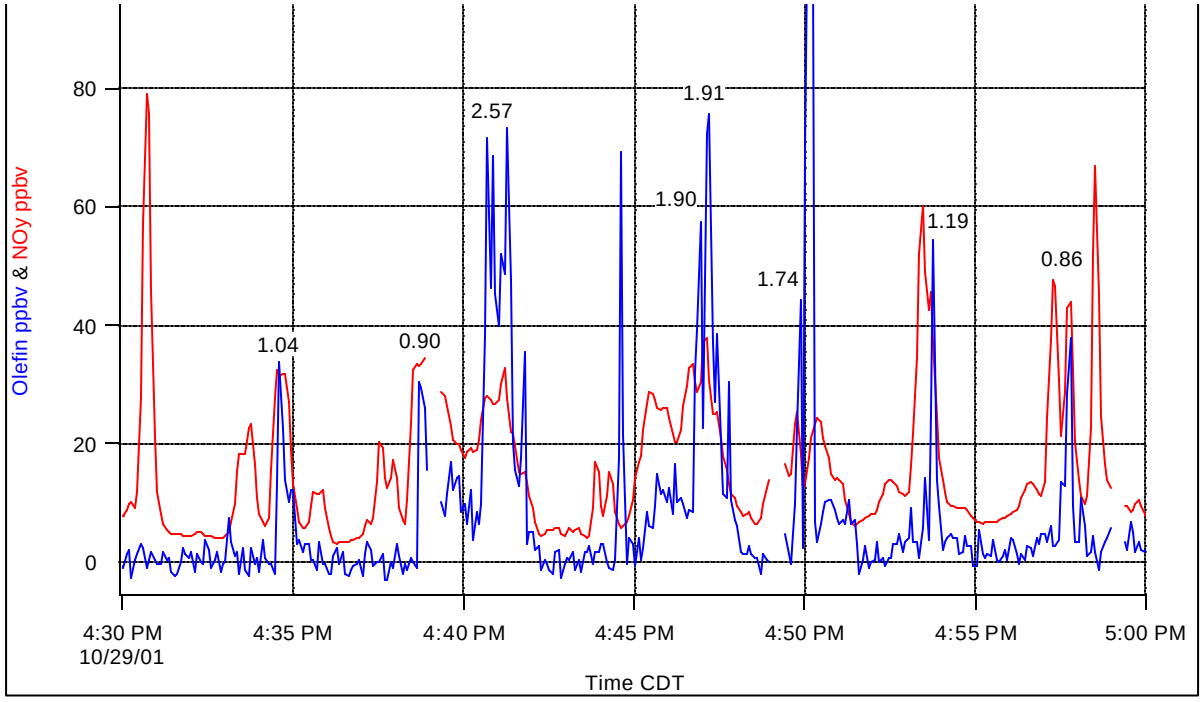
- Area and mobile VOC not included (small effect)
- No point source NO_X lost due to dispersion (large effect)
- No point source NO_X lost due to reaction to NO_Z (small effect)

LOW

- No VOC emissions lost to dispersion (large effect)
- No VOC emissions lost to reaction (large effect)
- Area and mobile NO_X emissions not included (large effect)

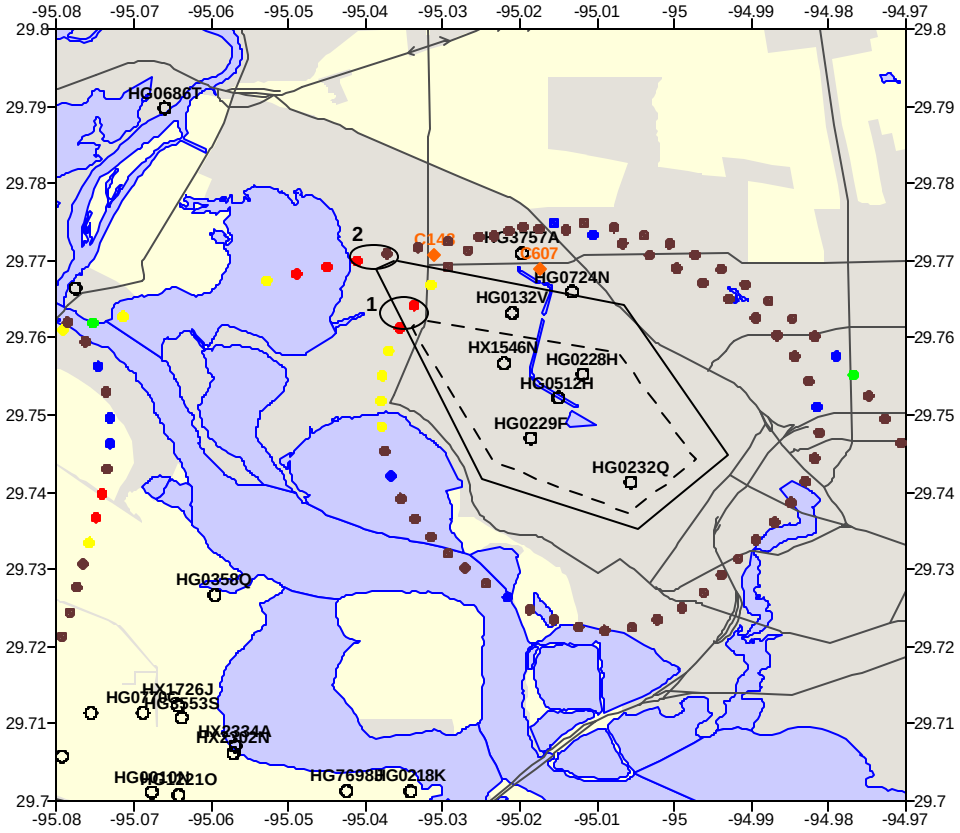
Aircraft Methodology

- Employed different techniques for 2001 and 2002/2003 data.
- 19 Flights in 2001, 17 Flights in 2002/early 2003.
- Specific points were chosen to compare to the point source emissions inventory where the aircraft encountered an olefin and NO_X plume.



Aircraft: Linking Obs to Emissions 1

For the 2001 rapid alkene data, point source emission contributions were determined visually based upon the wind direction and speed observed by the aircraft.



Plume 1:

Wind Dir = 120
Source Ole/NOx = 0.077
Observed Ole/NOy = 1.04
Adj Factor = 13.45

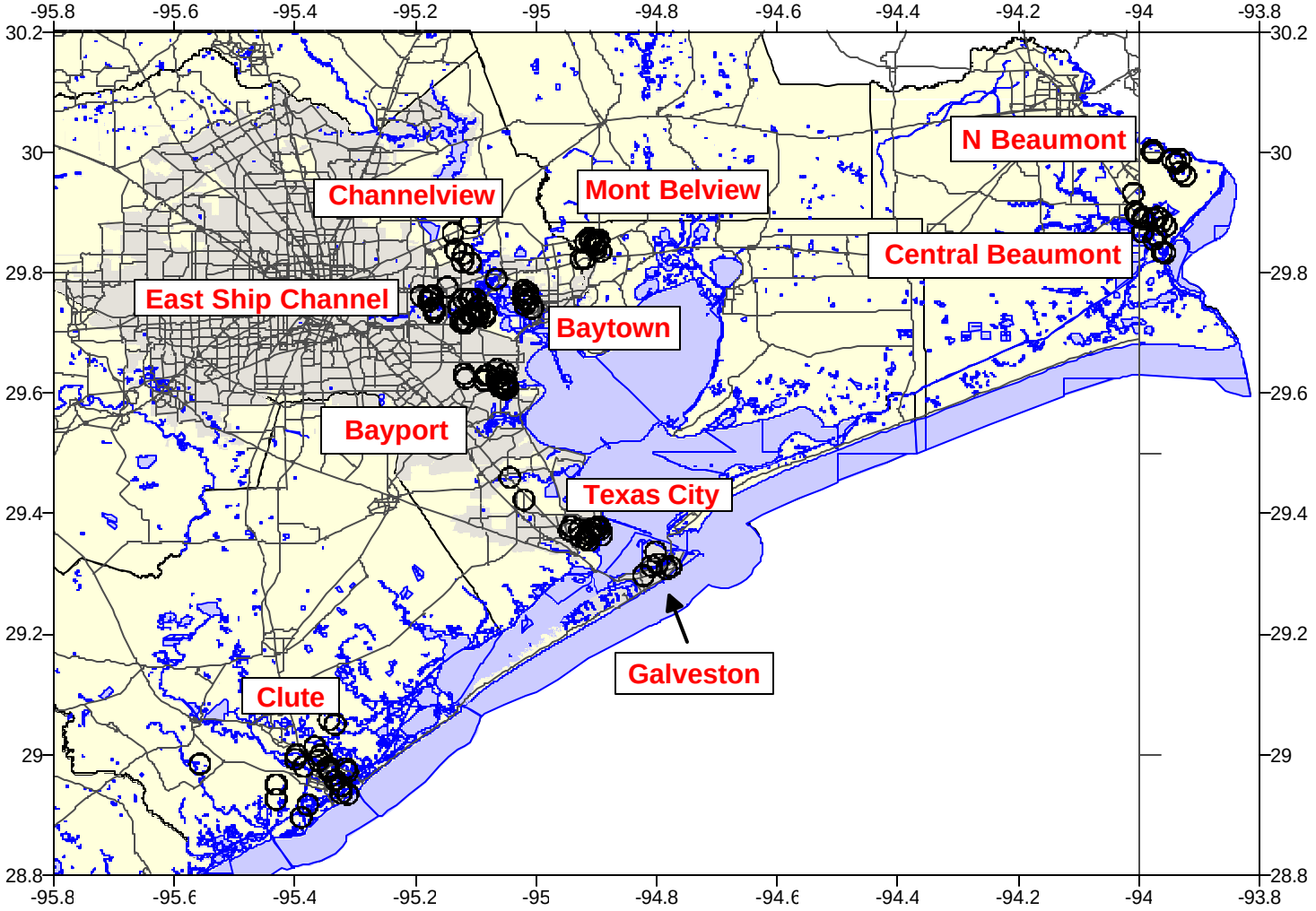
Plume 2:

Wind Dir = 130
Source Ole/NOx = 0.078
Observed Ole/NOy = 0.90
Adj Factor = 11.66

Aircraft: Linking Obs to Emissions 2

- Aircraft observed olefin/NO_Y plume ratios were compared to ISC dispersion model predicted olefin/NO_X ratios.
- Only terminal olefins (alkenes) from emission points were used in ISC runs.
- 15% of the point source ethylene emissions was also employed based on published instrument (Rapid Alkene Detector -- Hills Scientific) response to ethylene.
- Met conditions from aircraft and ground-based monitors.
  - Both observed wind direction and source-directed wind direction runs were made.

Aircraft: Emission adjustments locations

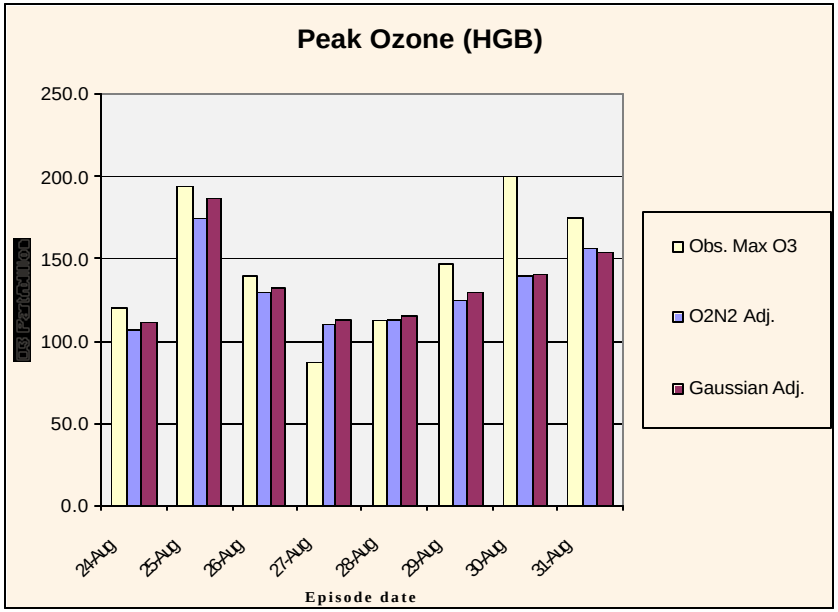


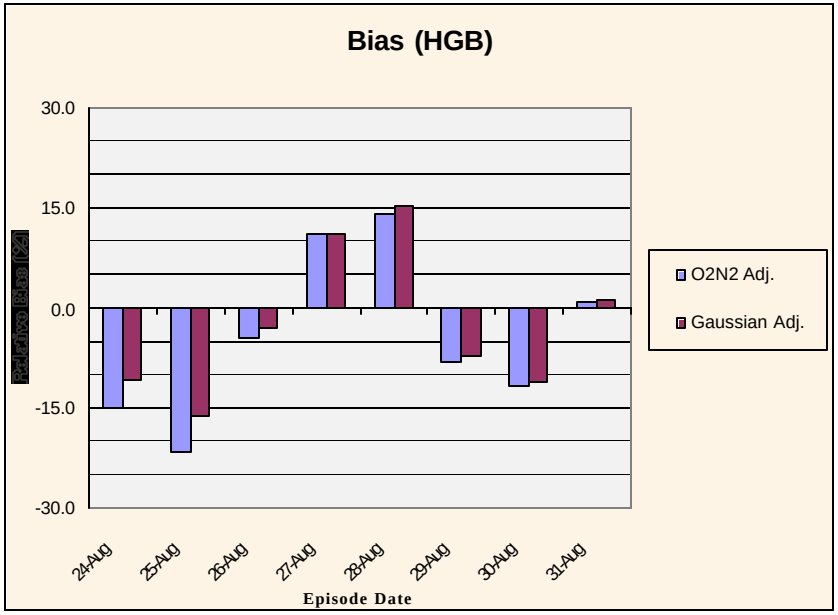
Aircraft: Emission adjustments by source region

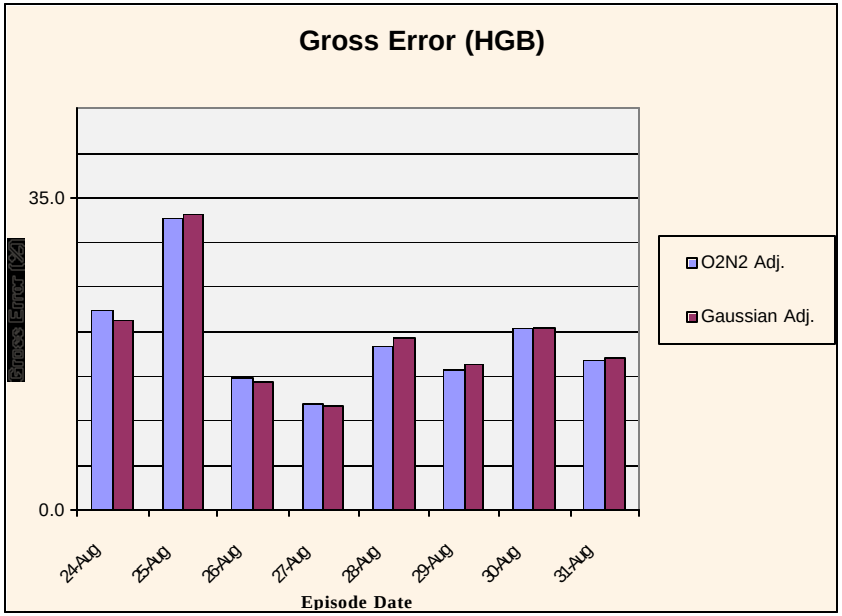
Location	2001 All Olefins	2002 ISC 15% Eth Term Ole	2002 ISC Cntrl Wdir 15% Eth Term Ole
North Beaumont	7.01	20.1	11.0
Central Beaumont	5.50	13.4	15.5
Bayport	6.68	12.1	11.4
Baytown	11.56	9.5	9.2
Mont Belvieu	4.33	7.5	5.2
Channelview	12.75	7.5	5.9
East/Central Ship Channel	3.13	7.7	6.5
West Ship Channel	NA	7.3	6.7
Galveston	9.45	17.3	11.8
Clute	5.71	6.5	12.3
Texas City	7.84	16.6	15.9
Other Areas	2.47	9.9	9.2
Avg Factor	6.95	11.3	10.1
Accounts Adjusted	147	337	332
Tons Added to Model EI	307	208	229

Model performance comparison: O2N2 vs. Gaussian modeling adjustment

4 Km grid







Aircraft: Adjustment Bias

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Conclusions

• Results suggest HG and BPA VOC median point source emission rates are significantly underestimated in certain locations of southeast Texas.

• Overall, these factors appear to agree well with the other factors that have been calculated from other aircraft or ground auto-gc work.

•More analysis and work from top-down and bottom-up methods will aid in constructing a more improved emissions inventory.

References/Acknowledgements

• Alan J. Hills and Patrick R. Zimmerman, Isoprene Measurement by Ozone-Induced Chemiluminescence, Analytical Chemistry, 1990, 62, 1055-60.

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• John Jarvie, Erik Gribbin - TCEQ

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