Meteorologically Adjusted HRVOC Trends in Houston

For Jolly & Sullivan contribution to Question C

TCEQ's High Priority SIP-Relevant Science Questions

- *Description of O3 & PM formation mechanisms, as observed & inferred independent of modeling*
  - **Question C**
    - Are HRVOC / NOx emissions & resulting ambient concentrations still at the same levels in Houston as in 2000?
    - How have they changed spatially and temporally?
    - Are there specific locations where particularly large quantities of HRVOC are still being emitted?

Locations w large quantities of HRVOC still emitted?

- Yes. E.g., Sept. 15, 2006, around midnight, 6500 ppbC 1,3-Butadiene measured ~ 1 km from a source.
  - Largest 1,3-B 1-hr concentration in TCEQ database, still under investigation.
- Time series graphs show many 100+ ppbC HRVOC measurements
- E & P concentrations in Houston still 5-9 X higher than Dallas.

HRVOC&NOx same as 2000?

- Concentrations:
  - HRVOCs
    - No. Statistically significant decline in ethylene & propylene for most sites for most time periods, most wind conditions.
  - NOx
    - No. Statistically significant decline in NOx, NO2, NO, NOy at most site for most time periods.

HRVOC Trends Adjusted for Winds

- Merge auto-gc data w hourly resultant wind speed & direction.
- Categorize data by 60°-wind direction bins, 4-mph wind speed bins, 6-hour time blocks, 4 seasons of the year.
- Calculate mean HRVOC concentration by category.
- Regress mean HRVOC on year by category, using 3rd quarter of year only.

Data

- Clinton Dr., Deer Park, & Channelview data long enough to assess trends.
  - Clinton 1995 -1997 & 1999 - 2006 (11 years)
  - Deer Park 1997 – 2006 (10 years)
  - Channelview 2001 – 2006 (7 years)
- Used 3rd quarter (July, Aug., Sept.) each year.
- 6 HRVOCs: ethylene, propylene, 1-butene, c-2-butene, t-2-butene, 1,3-butadiene
  - MIRs in 3-4 range
- 6 direction bins * ~3 speed bins * 4 time-of-day bins = ~72 categories / site-species

Results

- Used categories with at least 6 years data.
- Parametrically assessed how many categories have upward / how many downward slopes.
- Next slide shows example of one regression. Next slide compiles slopes of ensemble or regressions.
- Note that statistical significance not assessed per regression – rather, based non parametrically on signs of slopes.

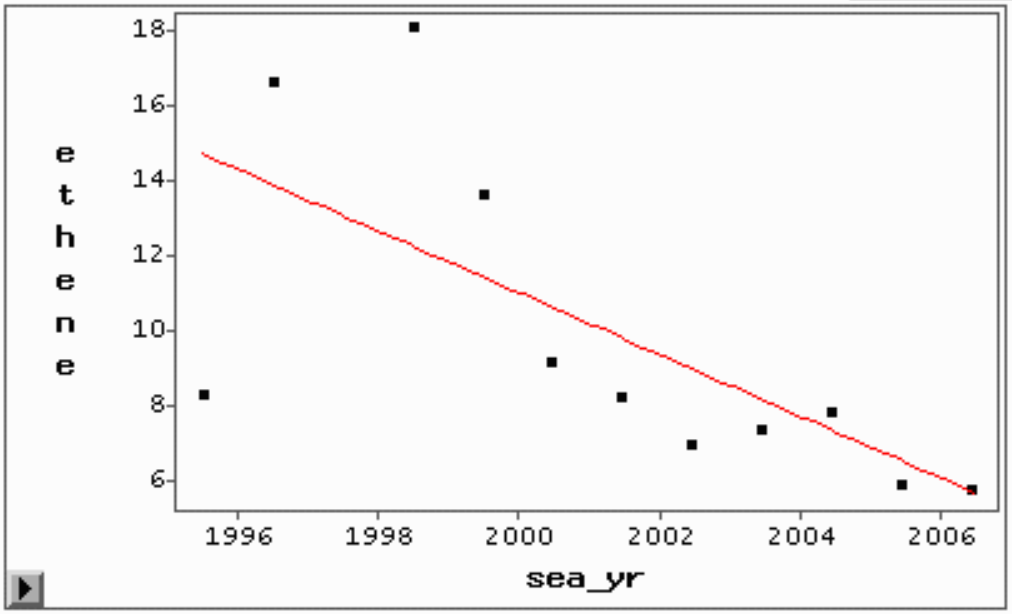
Example: Clinton, ethylene, 3rd Qtr, afternoon (12:00-17:59 CST), SE winds ≤ 4mph

Model Equation

ethene = 1662.59 - 0.8258 sea_yr

Summary of Fit

Mean of Respon	9.9242	R-Squar	0.4765
Root MSE	3.2847	Adj R-S	0.4184



speed = 2

direction = 120

day_time = 3

AIRS = 482011035

Parametric Regression Fit

		Model		Error				
Curve	Degree(Polynomi	DF	Mean Squar	DF	Mean Squar	R-Squar	F Stat	Pr > F
	1	1	88.4024	9	10.7893	0.4765	8.19	1.9E-02

Summary of slopes

	Clinton			Deer Park			Channelview		
species	# categories	# negative	%	# categories	# negative	%	# categories	# negative	%
ethylene	32	31	97%	31	29	94%	25	21	84%
propylene	33	31	94%	32	24	75%	24	23	96%
1-butene	33	26	79%	32	23	72%	25	22	88%
c2-butene	33	24	73%	32	32	100%	25	25	100%
t2-butene	33	17	52%	31	31	100%	25	25	100%
1,3-butadiene	32	28	88%	32	15	47%	25	21	84%

- HRVOCs coming down in all 17 out of 18 cells.
- 1,3-butadiene trend appears flat or rising at Deer Park, but highest values have declined.

Overall Changes at Dallas Hinton

Dallas Hinton

year	Stat	_FREQ_	ethylene	propylene	t2butene	c2butene	_1butene	_13butadiene
2000	mean	1712	2.59	1.10	0.15	0.15	0.25	0.38
2006	mean	1674	0.60	0.83	0.42	0.17	0.17	0.24
2000	median	1712	1.63	0.80	0.11	0.10	0.17	0.25
2006	median	1674	0.43	0.60	0.35	0.15	0.13	0.21
2000	p75	1712	3.07	1.37	0.17	0.16	0.29	0.44
2006	p75	1674	0.75	0.90	0.50	0.20	0.18	0.28
2000	p90	1712	5.47	1.84	0.31	0.28	0.49	0.76
2006	p90	1674	1.29	1.54	0.70	0.26	0.31	0.38
2000	p95	1712	8.03	2.34	0.46	0.44	0.70	1.07
2006	p95	1674	1.73	2.11	0.84	0.29	0.41	0.45

Overall Changes at Clinton

Houston Clinton

year	Stat	_FREQ_	ethylene	propylene	t2butene	c2butene	_1butene	_13butadiene
2000	mean	1769	5.20	6.55	2.06	1.68	2.19	2.96
2006	mean	1706	4.50	4.31	0.70	0.53	1.08	1.25
2000	median	1769	3.16	3.43	0.53	0.47	0.95	0.42
2006	median	1706	2.94	2.60	0.41	0.32	0.60	0.45
2000	p75	1769	5.88	7.18	1.85	1.55	2.68	1.37
2006	p75	1706	4.97	4.45	0.76	0.62	1.16	1.05
2000	p90	1769	11.59	14.65	5.55	4.51	5.87	5.68
2006	p90	1706	9.52	8.57	1.24	1.02	2.21	2.06
2000	p95	1769	16.76	22.06	9.00	7.17	8.13	12.16
2006	p95	1706	13.12	14.17	1.65	1.28	3.64	3.36

Overall Changes at Deer Park

Houston Deer Park

year	Stat	_FREQ_	ethylene	propylene	t2butene	c2butene	_1butene	_13butadiene
2000	mean	1199	9.33	13.46	0.27	0.24	0.94	0.48
2006	mean	1536	4.81	7.11	0.32	0.23	0.59	0.95
2000	median	1199	2.86	2.94	0.10	0.06	0.23	0.14
2006	median	1536	2.14	1.49	0.18	0.11	0.18	0.71
2000	p75	1199	7.52	6.95	0.23	0.19	0.61	0.38
2006	p75	1536	4.73	4.21	0.28	0.20	0.45	1.07
2000	p90	1199	19.85	23.06	0.58	0.50	1.86	1.07
2006	p90	1536	10.17	10.68	0.58	0.47	1.12	1.65
2000	p95	1199	40.72	71.34	1.03	1.07	4.46	1.99
2006	p95	1536	17.97	25.57	0.96	0.83	2.20	2.30

See additional exhibits

- HRVOC Time Series for Dallas & Houston 1995-2006.ppt
- HGB&BPA Aug.&Sept. NOx Diurnal Patterns, 2000, 2003, 2006.ppt

Conclusion

- Ambient concentrations are down in Houston and Dallas for NOx & VOCs, suggesting controls are effective.
- It remains to be seen how this has changed VOC/NOx ratios and affected O3 formation.