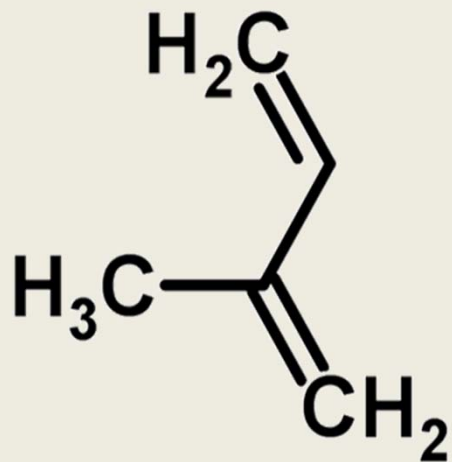




Emissions and monitoring trends of lower olefins across Texas from 2002 to 2012

International Symposium: Evaluation
of the Health Risks of Lower Olefins

November 5th – 6th



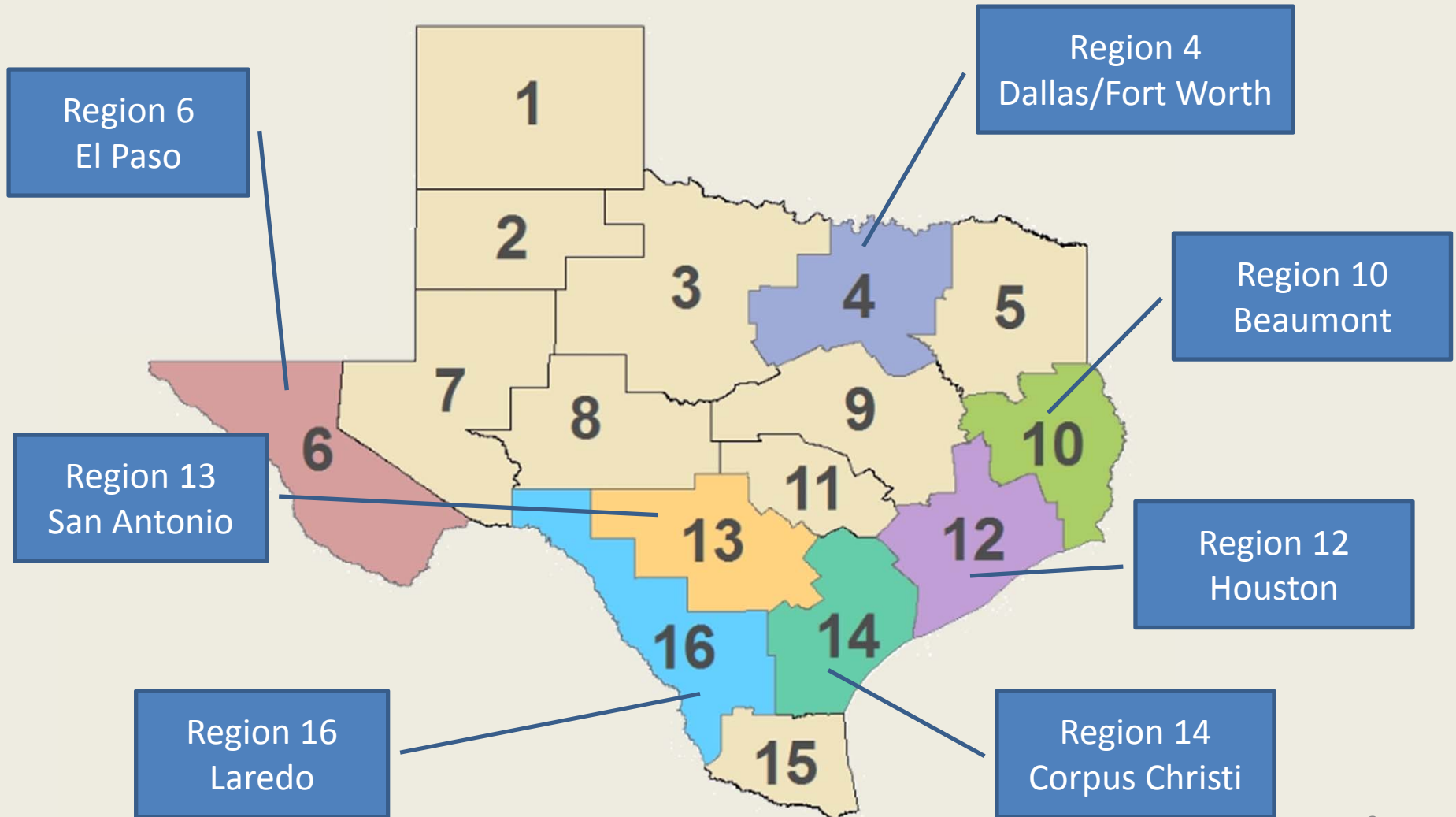
Slides Prepared for the 2014 Symposium on Understanding the Health Risks of Lower Olefins

Air Monitoring in Texas

- Largest ambient air toxics monitoring network in the country
 - 101 sites across the state
 - 83 specifically for VOCs
 - Doesn't include all on-site/industry monitors
- 1990 Clean Air Act identifies 187 toxics
 - TCEQ analyzes ~120 of those

Total # Sites for Air Toxics	101
Total # Sites by type	
VOCs	83
SVOCs (PAHs)	4
Carbonyls	6
Metals (PM2.5 and PM10)	9
Metals (lead)	14
H2S	13

Major TCEQ Monitoring Regions



Study purpose

- Evaluate the spatial and temporal trends of the identified lower olefins in Texas
 - Chloroprene was not included since there are no available monitoring data and very low reported emissions
 - Monitoring trends for each olefin
 - Top five monitoring sites for 2012 identified
 - Trend data for those sites from 2002 to 2012
 - Emissions data for each olefin
 - Top five industrial sources for 2012 identified
 - Total emissions by region calculated
 - Monitoring sites within two miles also identified

Methods for Data Collection

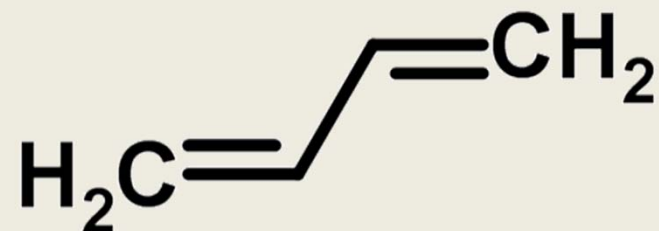
- Monitoring data
 - Sources
 - TCEQ air monitoring databases (e.g., the Texas Air Monitoring Information System (TAMIS))
 - Industry-sponsored monitoring network
 - Monitors
 - 24 hour canister samples
 - 1 sample taken every 6 days
 - Samples sent to TCEQ AL for analysis
 - 1 hour AutoGC
 - 24 samples taken every day
 - Samples analyzed automatically on site
- Emissions data
 - Emissions Inventory (EI) reported to TCEQ
 - Toxics Release Inventory (TRI) reported to EPA

Air Monitoring Comparison Values (AMCVs)

- Chemical-specific air concentrations derived to protect human health and welfare, including odor, animals, and vegetation
- Values derived by the TCEQ Toxicology Division for use in Air Monitoring
 - Different than the Effects Screening Levels (ESLs) used in Air Permitting
- Each data set was compared to its lowest respective AMCV

1,3-Butadiene

- Uses:
 - Manufacturing of styrene-butadiene rubber (SBR) (synthetic rubber) and thermoplastic resins.
 - Intermediate to produce a variety of industrial chemicals (e.g., polymers, elastomers)
- Sources:
 - Mostly from emissions from gasoline- and diesel-powered vehicles and equipment



Top 5 Monitored Sites in 2012 - 1,3-Butadiene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

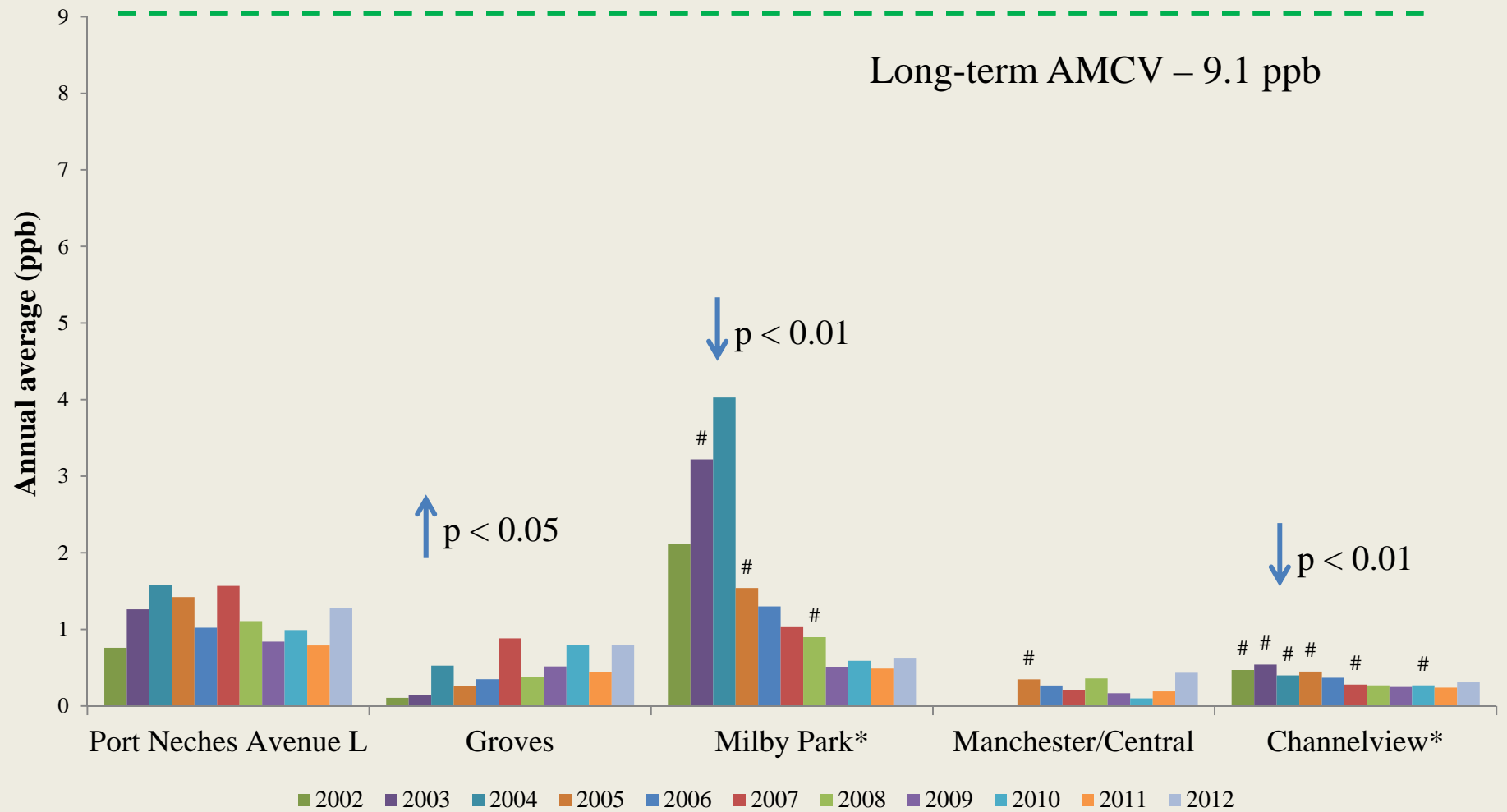
Site	Region	Mean \pm SD (ppb)	Median (ppb)	High 24h (ppb)	% > MDL	Sample completeness
Port Neches	10 Beaumont	1.28 \pm 1.62	0.62	9.08	72%	100%
Groves	10 Beaumont	0.80 \pm 1.51	0.12	7.16	41%	97%
Milby Park *	12 Houston	0.62 \pm 1.9	--	9.37	--	87%
Manchester/ Central	12 Houston	0.43 \pm 1.70	0.09	12.06	16%	84%
Channelview *	12 Houston	0.31 \pm 0.9	--	3.97	--	77%

Long-term AMCV – 9.1 ppb

75% is considered complete

Monitoring Trends From 2002 to 2012 at the Top 5 EI Sites - 1,3-Butadiene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

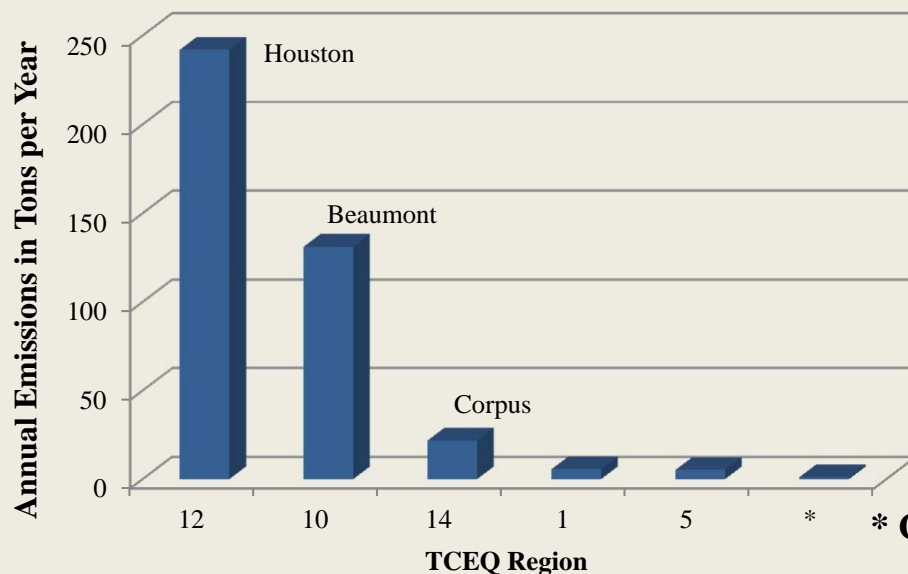


Arrows show significant trends using Spearman's rank correlation

- data less than 75% complete

Emissions Inventory Data – 1,3-Butadiene

Company	Site Usage	Region	Annual Emissions (TPY)		
			2002	2012	Difference
Equistar Chemicals LP, Channelview	Industrial Chemicals	12	148	72	-51 %
INEOS USA LLC, Chocolate Bayou	Industrial Chemicals	12	98	44	-55 %
BASF Total Petrochemicals LLC	Industrial Chemicals	10	9	38	+318 %
Lanxess Corp, Orange Plant	Synthetic Rubber	10	30	24	-18 %
Shell Chemical LP, Deer Park	Petroleum Refining	12	80	24	-70 %
	Total Emissions	Texas	675	407	-40 %



According to EPA's TRI, Texas generates 80% of the total air emissions of 1,3-butadiene compared to the rest of the US

* Combined emissions from Regions 3, 4, 6, 7, 8, 9, 11, 13

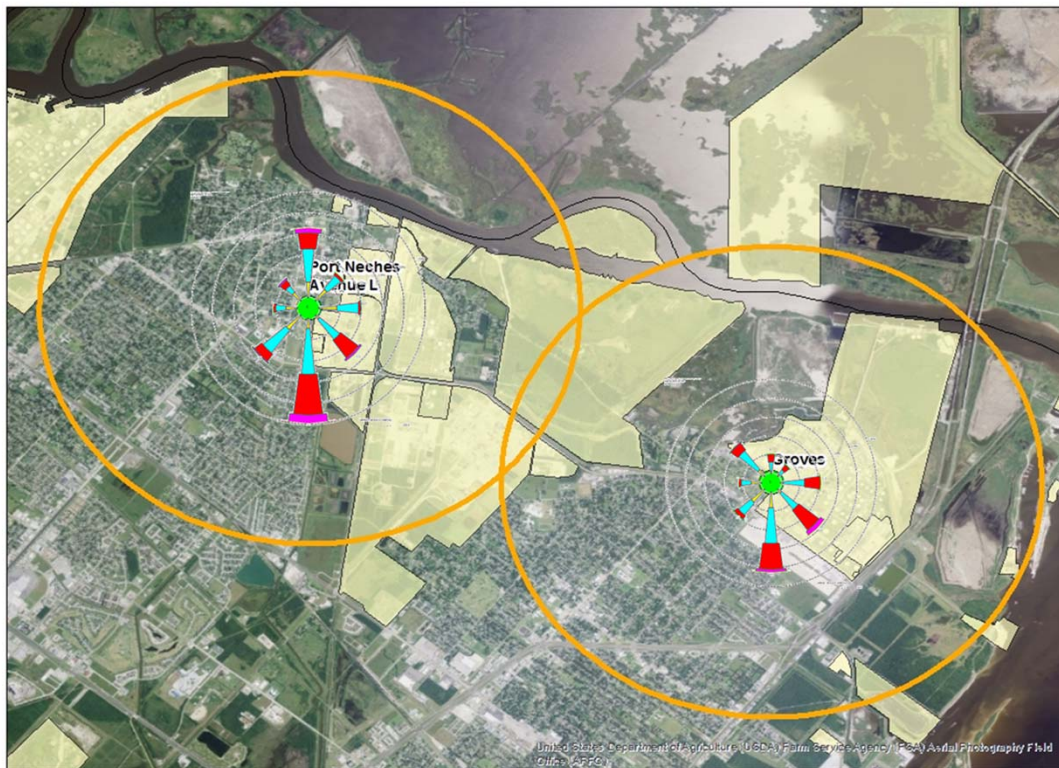
Emissions Inventory Data – 1,3-Butadiene

Facility	% Emissions in Texas	Other olefins emitted (% in Texas)			Monitors within 2 miles
		Ethylene (ranked)	Isoprene (ranked)	Propylene (ranked)	
Equistar Chemicals LP, Channelview	17.6	1.7	4.9 (5th)	4.7	Channelview* (upwind)
INEOS USA LLC, Chocolate Bayou	10.9	2.9	--	6.8 (3rd)	--
BASF Total Petrochemicals LLC	9.3	3.3	--	8.8 (2nd)	Groves*
Lanxess Corp, Orange Plant	6.0	0.09	--	0.7	--
Shell Chemical LP, Deer Park	6.0	1.2	5.3 (4th)	2.9	--

Bolded facilities (and emissions) are in the top five emitters for more than one olefin

*Monitors in top five for 1,3-butadiene: #2 Groves, #5 Channelview

Monitor Locations and Emission sites for 1,3-Butadiene – Port Neches and Groves, Region 10, Beaumont

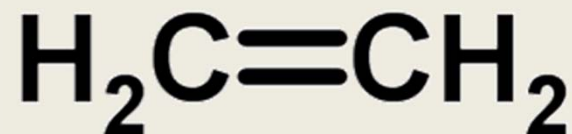


Rank	Monitor	Region	Mean (ppb)
1	Port Neches	10 Beaumont	1.28
2	Groves	10 Beaumont	0.80

Monitor	Reported emissions with in 2 miles (TPY)	Emissions nearby/ total state
Port Neches	19.7	4.8 %
Groves	53.5	13.1 %

Ethylene

- Uses:
 - High-production-volume chemical, primarily used as an intermediate in the production of other chemicals
 - Natural plant hormone, enhances the ripening process of fruits, vegetables, and flowers
- Sources:
 - Produced during incomplete combustion of biomass and fossil fuels, forest fires, and active volcanic events.
 - Large proportion in urban air due to vehicular traffic emissions



Top 5 Monitored Sites in 2012 - Ethylene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

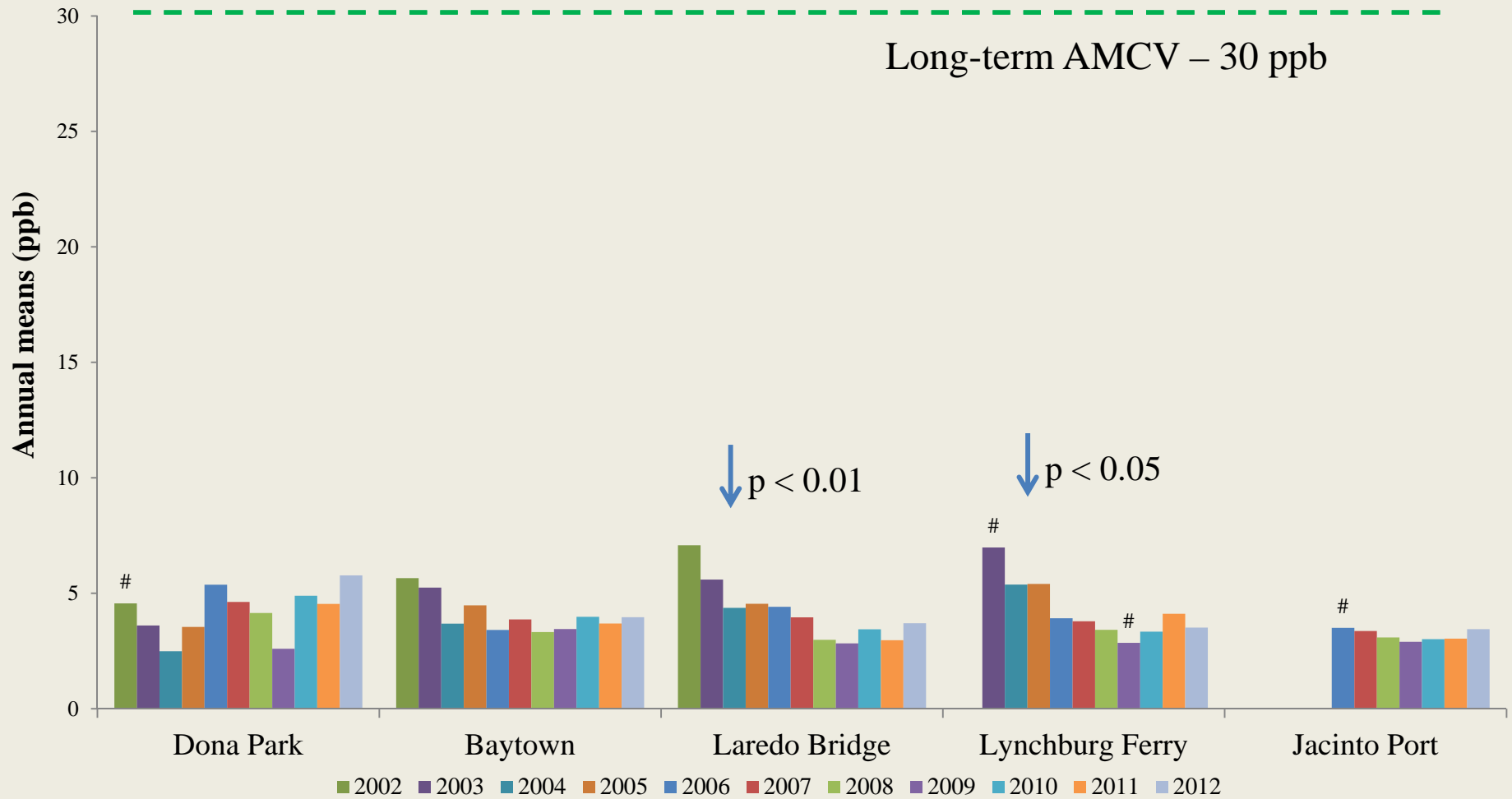
Site	Region	Mean \pm SD (ppb)	Median (ppb)	High 24h (ppb)	% > MDL	Sample completeness
Dona Park	14 Corpus Christi	5.77 \pm 8.81	2.82	51.79	89	90%
Baytown	12 Houston	3.96 \pm 2.18	3.77	9.24	100	79%
Laredo Bridge	16 Laredo	3.70 \pm 1.31	3.62	6.19	100	79%
Lynchburg Ferry	12 Houston	3.51 \pm 2.01	3.61	8.1	100	90%
Jacinto Port	12 Houston	3.44 \pm 2.52	2.725	12.74	100	89%

Long-term AMCV – 30 ppb

75% is considered complete

Monitoring Trends From 2002 to 2012 at the Top 5 EI Sites - Ethylene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

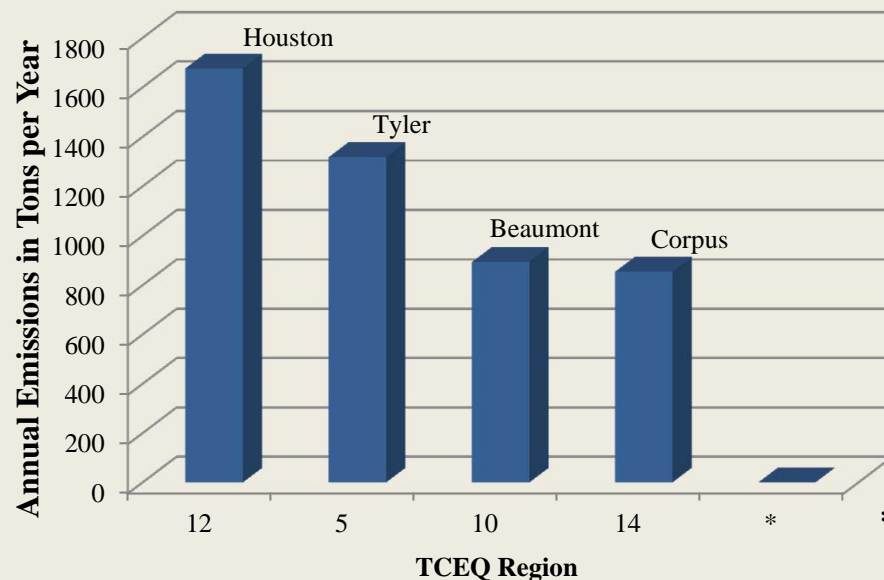


Lines show significant trends using Spearman's rank correlation

- data less than 75% complete

Emissions Inventory Data – Ethylene

Company	Site Usage	Region	Annual Emissions (TPY)		
			2002	2012	Difference
Westlake Longview Corp	Plastic Materials/Resins	5	--	728	--
Eastman Chemical Company	Industrial Chemicals	5	1687	565	-67 %
Union Carbide Corp, Seadrift Plant	Industrial Chemicals	14	1095	473	-57 %
Ei Dupont De Nemours & Company	Industrial Chemicals	10	380	366	-4 %
Formosa Plastics Corp Texas	Plastic Materials/Resins	14	195	243	+25 %
Total Emissions		Texas	7000	4766	-32 %



According to EPA's TRI, Texas generates 62% of the total air emissions of ethylene compared to the rest of the US

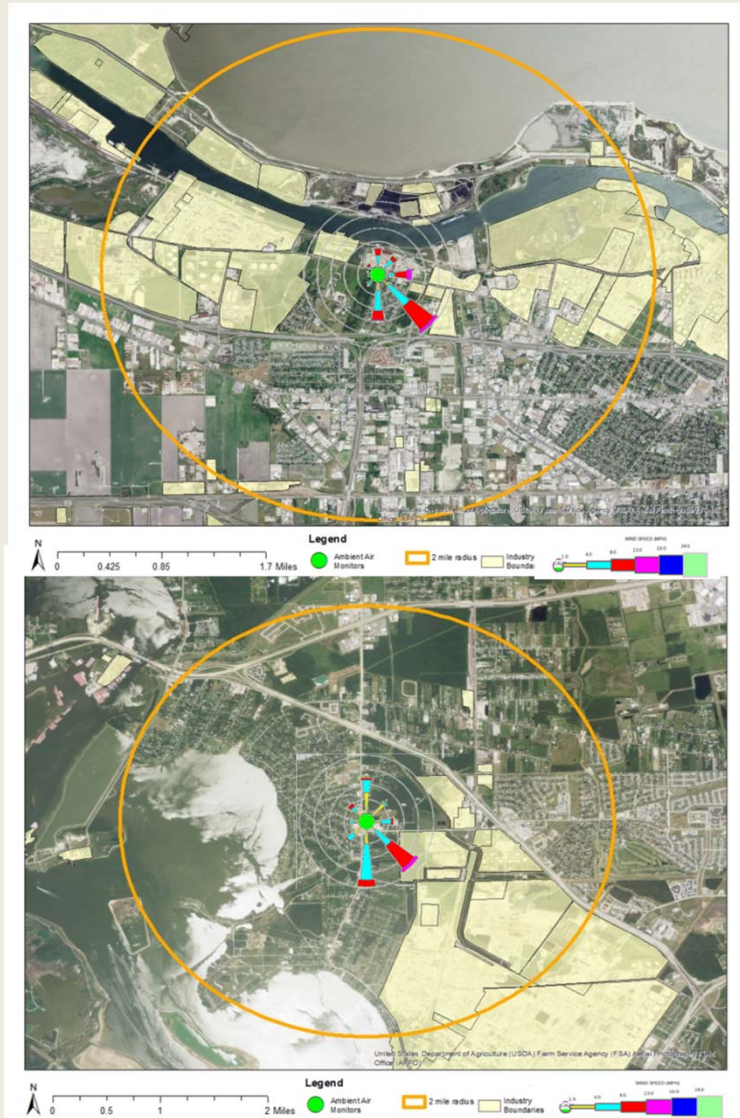
* Combined emissions from Regions 1, 3, 6, 7, 9, 11, 13

Emissions Inventory Data – Ethylene

Facility	% Emissions in Texas	Other olefins emitted (% in Texas)			Monitors within 2 miles
		Butadiene (ranked)	Isoprene (ranked)	Propylene (ranked)	
Westlake Longview Corp	15.3	--	--	--	--
Eastman Chemical Company	11.9	1.2	--	9.8 (1st)	--
Union Carbide Corp, Seadrift Plant	9.9	--	--	--	--
El Dupont De Nemours & Company	7.7	0.5	0.2	1.2	
Formosa Plastics Corp Texas	5.1	0.3	0.2	2.2	Point Comfort Monitors: North Site; City Hall; Plant Site; Park Site; School

Bolded facilities (and emissions) are in the top five emitters for more than one olefin

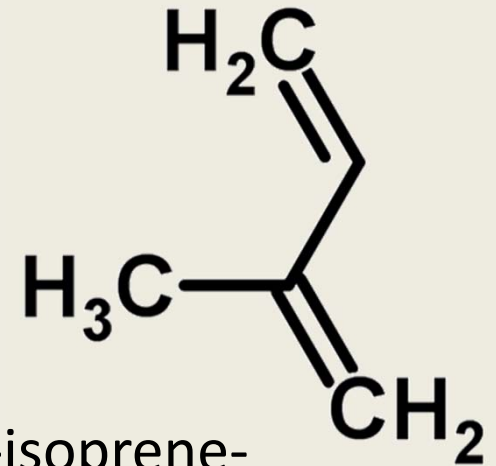
Monitor Locations and Emission sites for Ethylene – Dona Park, Region 14, Corpus Christi and Baytown, Region 12, Houston



Rank	Monitor	Region	Mean (ppb)
1	Dona Park	14 Corpus Christi	5.77
2	Baytown	12 Houston	3.96

Monitor	Reported emissions with in 2 miles (TPY)	Emissions nearby/ total state
Dona Park	9.8	0.2 %
Baytown	114.3	2.4 %

Isoprene



- Uses:
 - Manufacturing of synthetic rubber, styrene-isoprene-styrene block co-polymers and butyl rubber
 - Production of hydrocarbon resins and synthesis of terpenes
- Sources:
 - Released in oil fires, tobacco smoke, and automobile exhaust
 - Produced naturally by plants, animals, and bacteria, amount produced naturally far exceeds that which is produced synthetically

Top 5 Monitored Sites in 2012 - Isoprene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

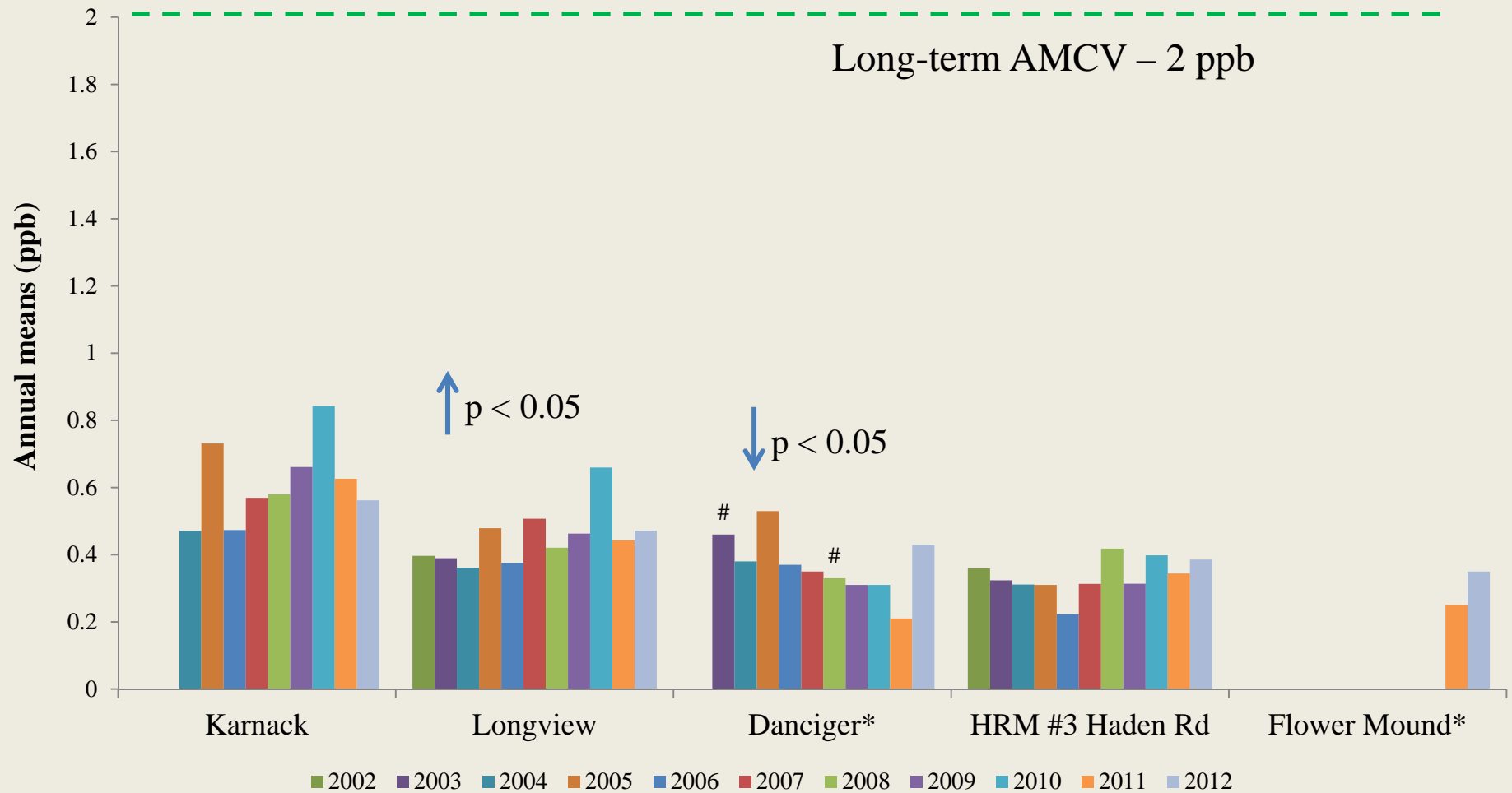
Site	Region	Mean \pm SD (ppb)	Median (ppb)	High 24h (ppb)	% > MDL	Sample Completeness
Karnack	5 Tyler	0.56 \pm 0.76	0.19	3.42	47	98%
Longview	5 Tyler	0.47 \pm 0.59	0.13	2.43	45	95%
Danciger *	12 Houston	0.43 \pm 0.80	--	3.74	--	83%
HRM #3 Haden Rd	12 Houston	0.38 \pm 0.45	0.17	1.76	38	98%
Flower Mound *	4 Dallas	0.35 \pm 0.90	--	2.68	--	83%

Long-term AMCV – 2 ppb

75% is considered complete

Monitoring Trends From 2002 to 2012 at the Top 5 EI Sites - Isoprene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

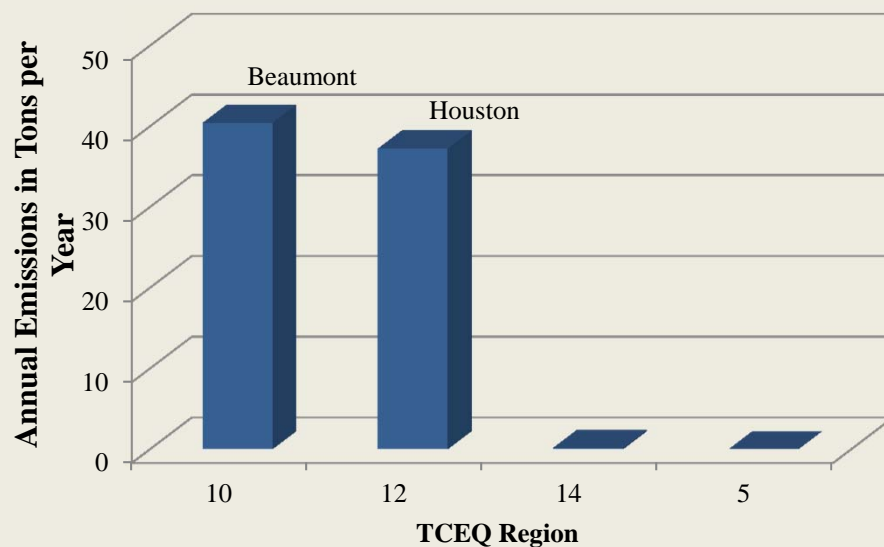


Lines show significant trends using Spearman's rank correlation

- data less than 75% complete

Emissions Inventory Data – Isoprene

Company	Site Usage	Region	Annual Emissions (TPY)		
			2002	2012	Difference
Goodyear Tire & Rubber Co	Synthetic Rubber	10	104	40	-61 %
Vopak Terminal Deer Park Inc	Special Warehouse/Storage	12	22	11	-49 %
Exxonmobil Chemical Company	Industrial Chemicals	12	5	4	-14 %
Shell Chemical LP, Deer Park	Petroleum Refining	12	26	4	-84 %
Equistar Chemicals LP, Channelview	Industrial Chemicals	12	11	4	-66 %
Total Emissions		Texas	212	78	-63 %



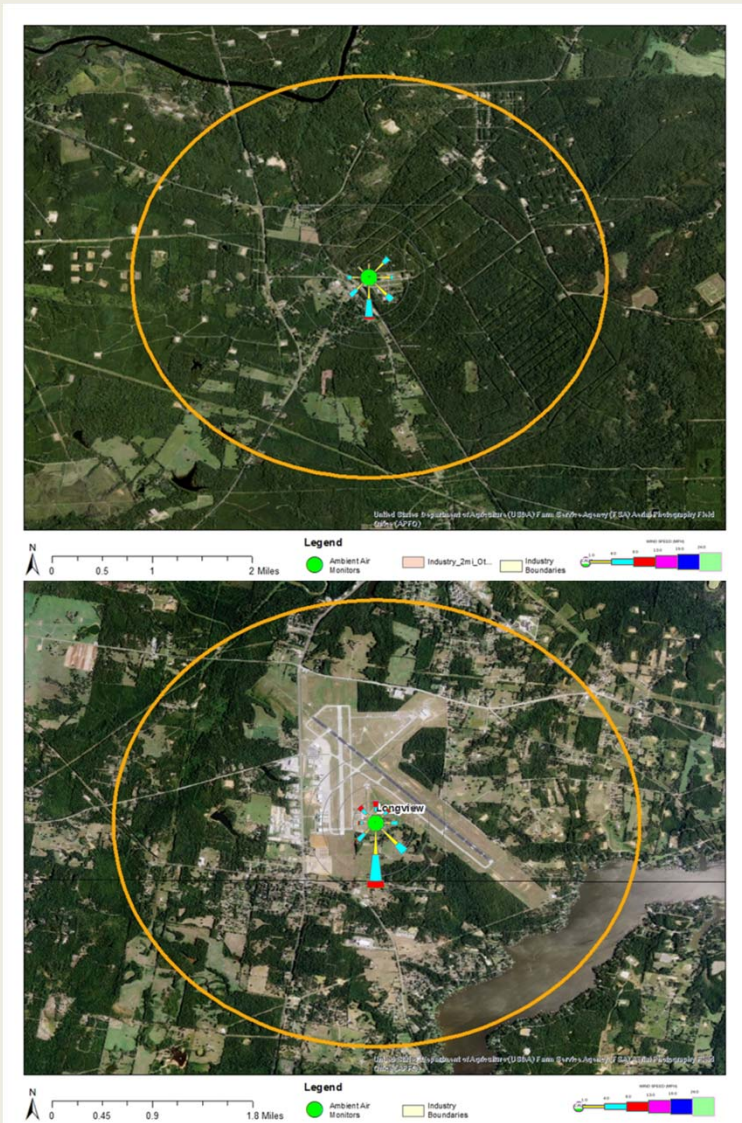
According to EPA's TRI, Texas generates 76% of the total air emissions of isoprene compared to the rest of the US

Emissions Inventory Data – Isoprene

Facility	% Emissions in Texas	Other olefins emitted (% in Texas)			Monitors within 2 miles
		Butadiene (ranked)	Ethylene (ranked)	Propylene (ranked)	
Goodyear Tire & Rubber Co (Beaumont)	51.7	3.4	--	0.03	--
Vopak Terminal Deer Park Inc	14.5	--	--	--	Lynchburg Ferry
ExxonMobil Chem Co (Baytown Olefins)	5.5	4.7	1.3	3.1	HRM 7; Baytown
Shell Chemical LP, Deer Park	5.3	6.0 (5 th)	1.2	2.9	--
Equistar Chemicals LP, Channelview	4.9	17.6 (1 st)	1.7	4.7	Channelview (upwind)

Bolded facilities (and emissions) are in the top five emitters for more than one olefin

Monitor Locations and Emission sites for Isoprene – Karnack and Longview, Region 5, Tyler



Rank	Monitor	Region	Mean (ppb)
1	Karnack	5 Tyler	5.77
2	Longview	5 Tyler	3.96

Monitor	Reported emissions with in 2 miles (TPY)	Emissions nearby/ total state
Karnack	0	0
Longview	0	0

Propylene



- Uses:
 - Produced and consumed in refinery operations for the production of gasoline components
 - Chemical intermediate in the manufacturing of other chemicals
 - Used in polymerized form for plastics and carpet fibers
- Sources:
 - Emitted by certain tree species and other types of vegetation
 - Combustion product present in cigarette smoke, aircraft exhaust, and motor vehicle exhaust.

Top 5 Monitored Sites in 2012 - Propylene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

Site	Region	Mean \pm SD (ppb)	Median (ppb)	High 24h (ppb)	% > MDL	Sample completeness
HRM 7	12 Houston	7.9	--	113	--	--
Baytown	12 Houston	5.78 \pm 7.17	4.515	47.56	94	79%
HRM 8	12 Houston	3.33	--	14.3	--	--
HRM #3 Haden Rd	12 Houston	3.17 \pm 6.53	1.24	32.85	83	98%
Groves	10 Beaumont	3.01 \pm 3.04	2.10	17.32	97	97%

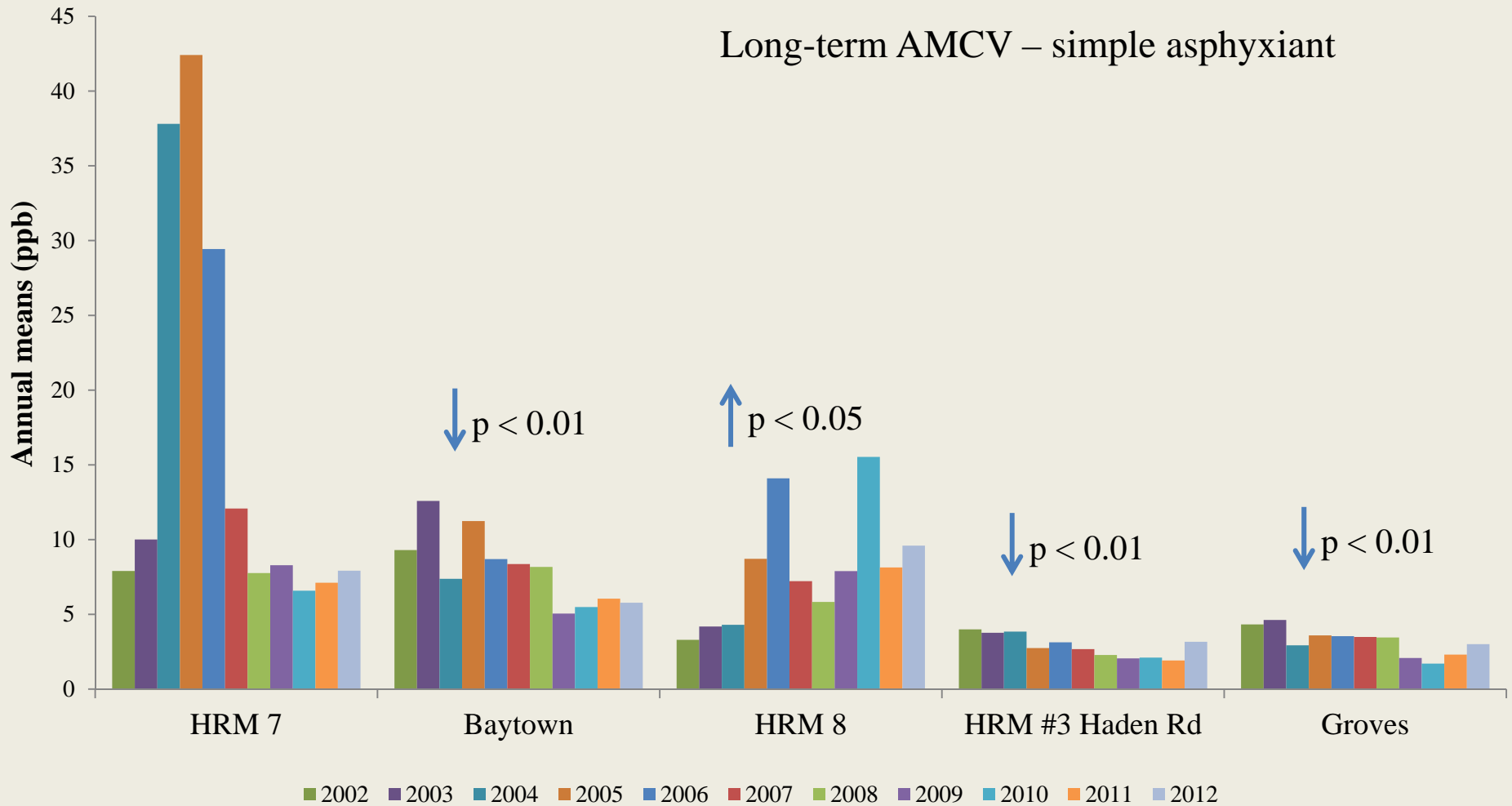
Long-term AMCV – asphyxiant

75% is considered complete

Monitoring Trends From 2002 to 2012 at the Top 5 EI Sites - Propylene

(based on hourly autoGC data* or every sixth-day 24-hr canister data)

Long-term AMCV – simple asphyxiant

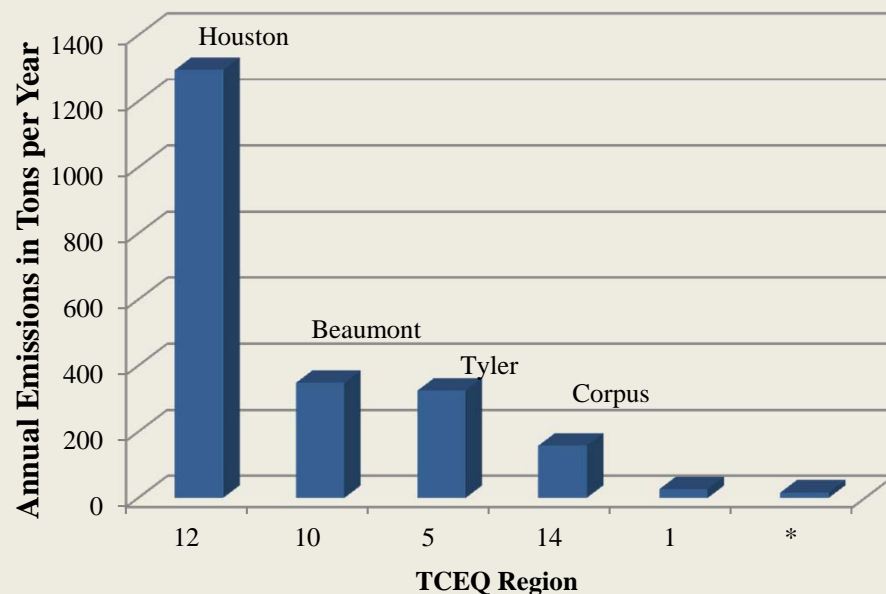


Arrows show significant trends using Spearman's rank correlation

- data less than 75% complete

Emissions Inventory Data – Propylene

Company	Site Usage	Region	Annual Emissions (TPY)		
			2002	2012	Difference
Eastman Chemical Company	Industrial Chemicals	5	341	212	-38 %
BASF Total Petrochemicals LLC	Industrial Chemicals	10	9	191	+1999 %
INEOS USA LLC, Chocolate Bayou	Industrial Chemicals	12	98	147	+50 %
ExxonMobil Chemical Company	Industrial Chemicals	12	174	107	-38 %
Equistar Chemicals LP, Bayport	Plastic Materials/Resins	12	39	105	+172 %
	Total Emissions	Texas	3251	2168	-33 %



According to EPA's TRI, Texas generates 54% of the total air emissions of propylene compared to the rest of the US

* Combined emissions from Regions 4, 6, 7, 9, 11, 13

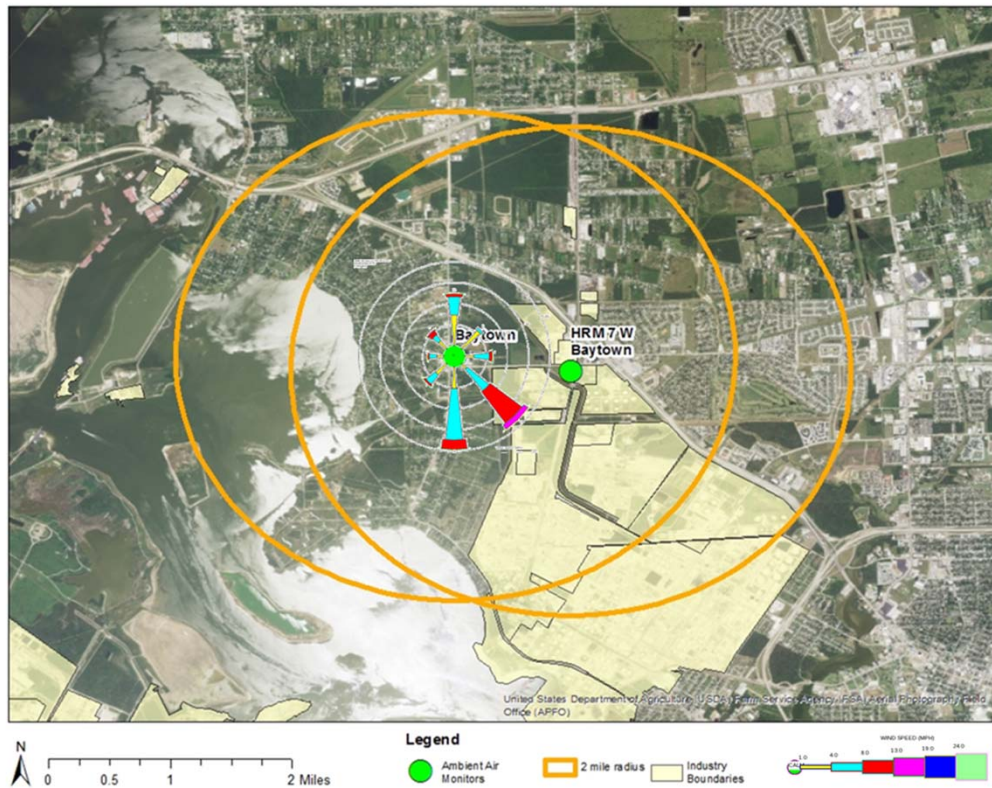
Emissions Inventory Data – Propylene

Facility	% Emissions in Texas	Other olefins emitted (% in Texas)			Monitors within 2 miles
		Butadiene	Ethylene	Isoprene	
Eastman Chemical Company	9.8	1.2	11.9 (1 st)	--	--
BASF Total Petrochemicals LLC	8.8	9.3 (3 rd)	3.3	--	Groves*
INEOS USA LLC, Chocolate Bayou	6.8	10.9 (2 nd)	2.9	--	--
ExxonMobil Chem Co (Baytown Chemical)	4.9	0.1	0.9	1.8	HRM 7*; Baytown*
Equistar Chemicals LP, Bayport	4.8	--	--	--	HRM 8*; Shore Acres (upwind)

Bolded facilities (and emissions) are in the top five emitters for more than one olefin

*Monitors in top five for propylene:
#1 HRM 7, #2 Baytown,
#3 HRM 8, #5 Groves

Monitor Locations and Emission sites for Propylene – HRM 7 and Baytown, Region 12, Houston



Rank	Monitor	Region	Mean (ppb)
1	HRM 7	12 Houston	7.90
2	Baytown	12 Houston	5.78

Monitor	Reported emissions with in 2 miles (TPY)	Emissions nearby/ total state
HRM 7	189	8.7 %
Baytown	189	8.7 %

Conclusions on Lower Olefins in Texas

- Monitoring
 - Measured ambient air concentrations low and well below AMCVs
- Emissions
 - Texas industries are major emitters of the lower olefins
 - General decreasing trends of reported olefin emissions
- Monitored values do not always correlate well with reported emissions

Acknowledgements

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