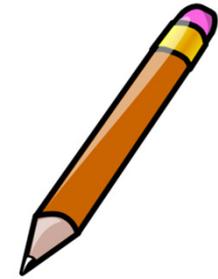


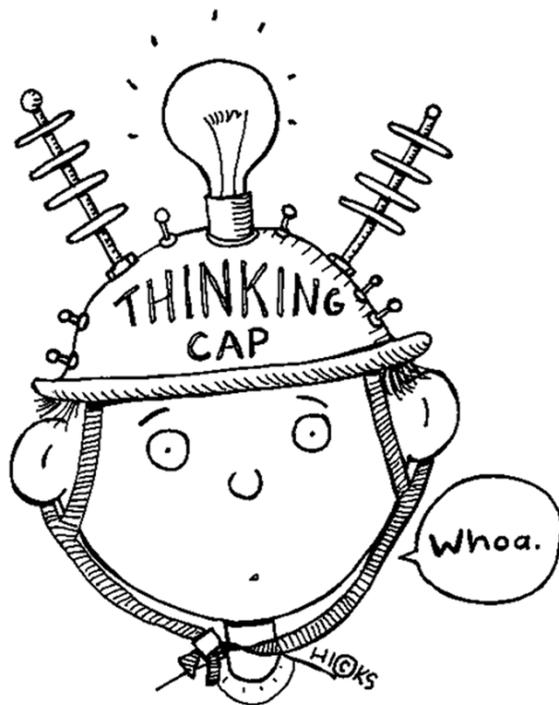
# **LONG-TERM TRENDS IN AMBIENT AIR 1,3-BUTADIENE LEVELS IN HOUSTON, TEXAS**

**Alea Bunch  
URS Corporation  
May 16, 2012**

## PROJECT OBJECTIVES:



1 – Analyze 1,3-butadiene trends in the Houston area (temporally and spatially)

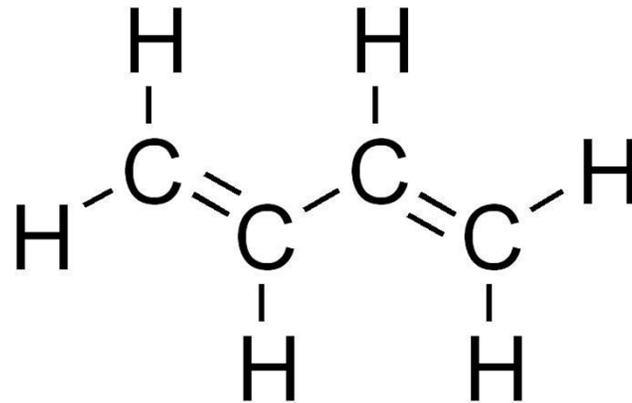


2 – Determine whether subregional differences can be detected

3 – Assess if a relationship exists between ambient concentration trends and trends in reported emissions

# 1,3-BUTADIENE

- Hazards:
  - Flammable, irritative
  - Known carcinogen
- Sources:
  - Manufacturing and processing facilities
  - Combustion (e.g. vehicle exhaust, forest fires, cigarette smoke)
- Hazardous Air Pollutant (HAP)
- Targeted by EPA's urban ATS
- Mobile Source Air Toxic (MSAT)





## GOVERNMENT REGULATION

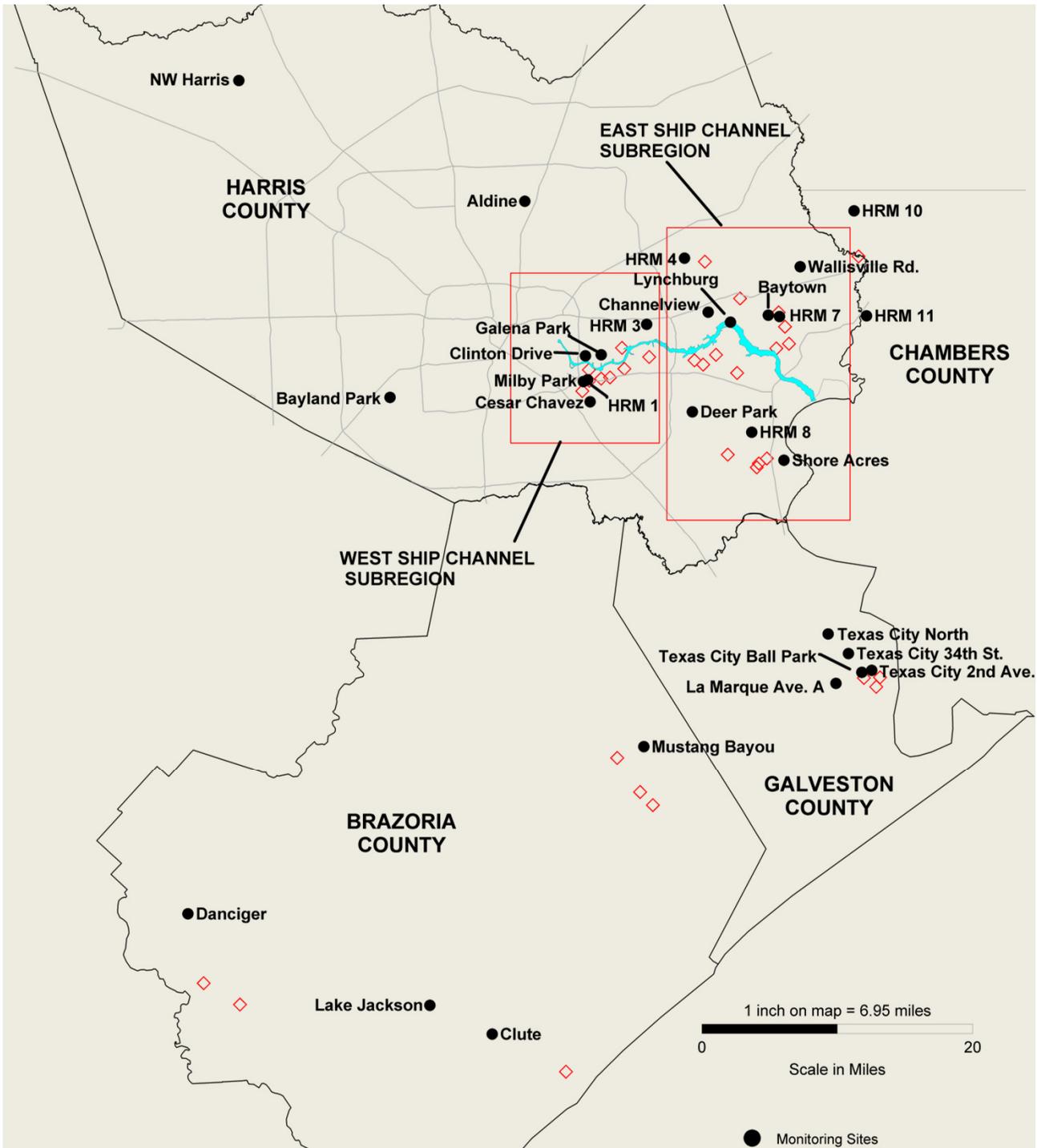
- Several EPA programs initiated in 1990 regulate the amount of manmade 1,3-butadiene emitted to the air
- National Emissions Standards established
- Tailpipe emission standards are imposed
- Texas Commission on Environmental Quality (TCEQ) regulates 1,3-butadiene as part of Houston's ozone control strategy
- Voluntary agreements between TCEQ and individual facilities in Harris County have contributed to emission reduction (VERAs)



# 1,3-BUTADIENE IN HARRIS COUNTY

- 17% of all U.S. industrial facilities that reported to the 2008 Toxics Release Inventory (TRI) are located in the Houston area
- >2.5 million passenger vehicles in Houston area





Collected archived data from 30 monitoring sites

Half of the sites are run by URS

Sites stationed in four counties

Greatest concentration of sites near the ship channel.



Typical ambient air monitoring station

VOC Canister Samplers



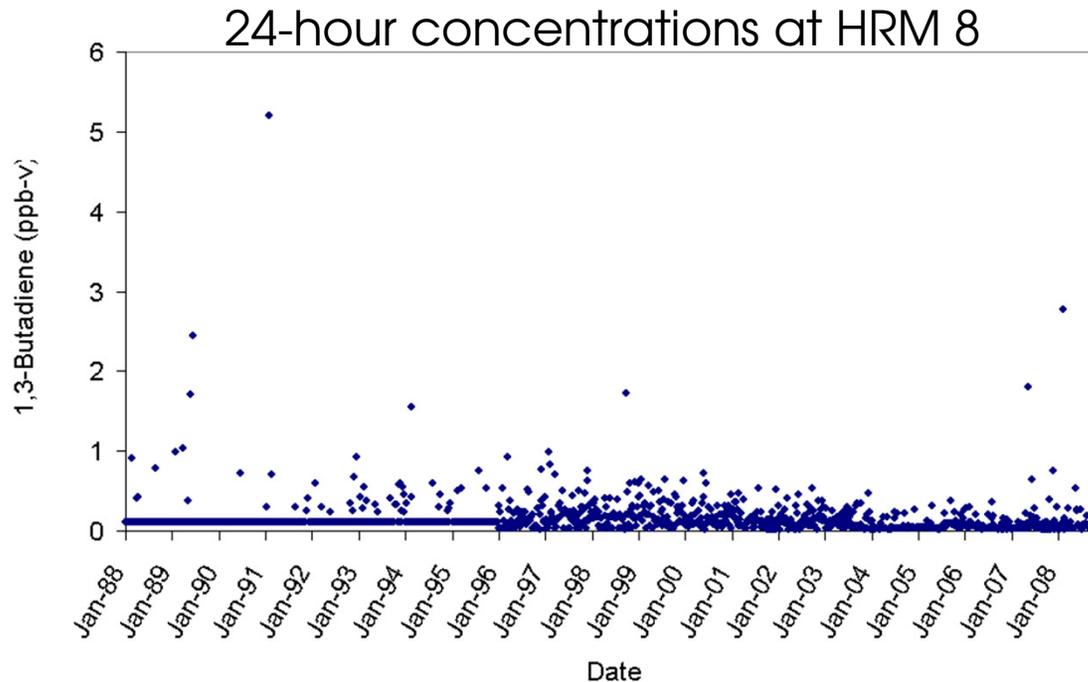
## AMBIENT 1,3-BUTADIENE DATA:



- Reviewed data from 1988 – 2008
- Required a minimum of 4 years of complete data (incl. 2008) per site
- Data completeness (minimum of 3 complete calendar quarters per year):

Sampling Method	Frequency	Min. # samples
Canister	1 every 6 days	11 per quarter
Canister	1 every 12 days	6 per quarter
Auto-GC	Hourly	68% (1489 hours)

# DATA VALIDATION



- Examined time series charts for appearance of outliers and discontinuities in the long-term records
- A change in the analytical detection technique from **flame ionization** to **mass spectrometry** at the start of 1996 caused an abrupt change in the MDL and frequency of detection. i.e. there was a baseline shift
- Excluded pre-1996 data from parts of the quantitative trend analysis

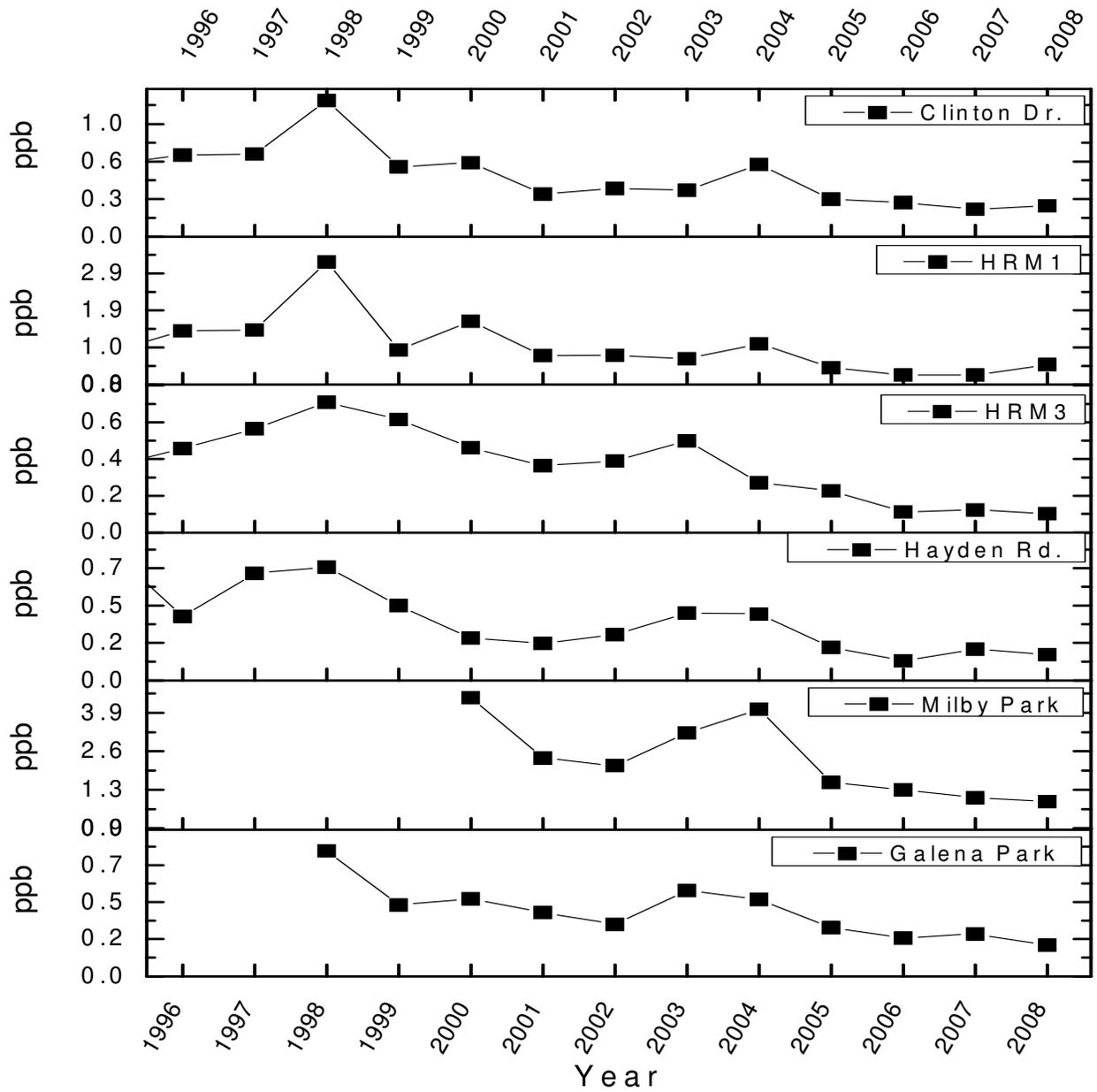
# TREATMENT OF NON-DETECTS

- Annual averages were calculated using (MDL/2) as a proxy for levels below the lower limit of detection
  - Canister: MDL = 0.01 – 0.10 ppb-v
  - Auto-GC: MDL = 0.01 ppb-v
- All valid annual averages were used in the trend analysis regardless of the percentage of samples below the MDL (EPA, June 2009)

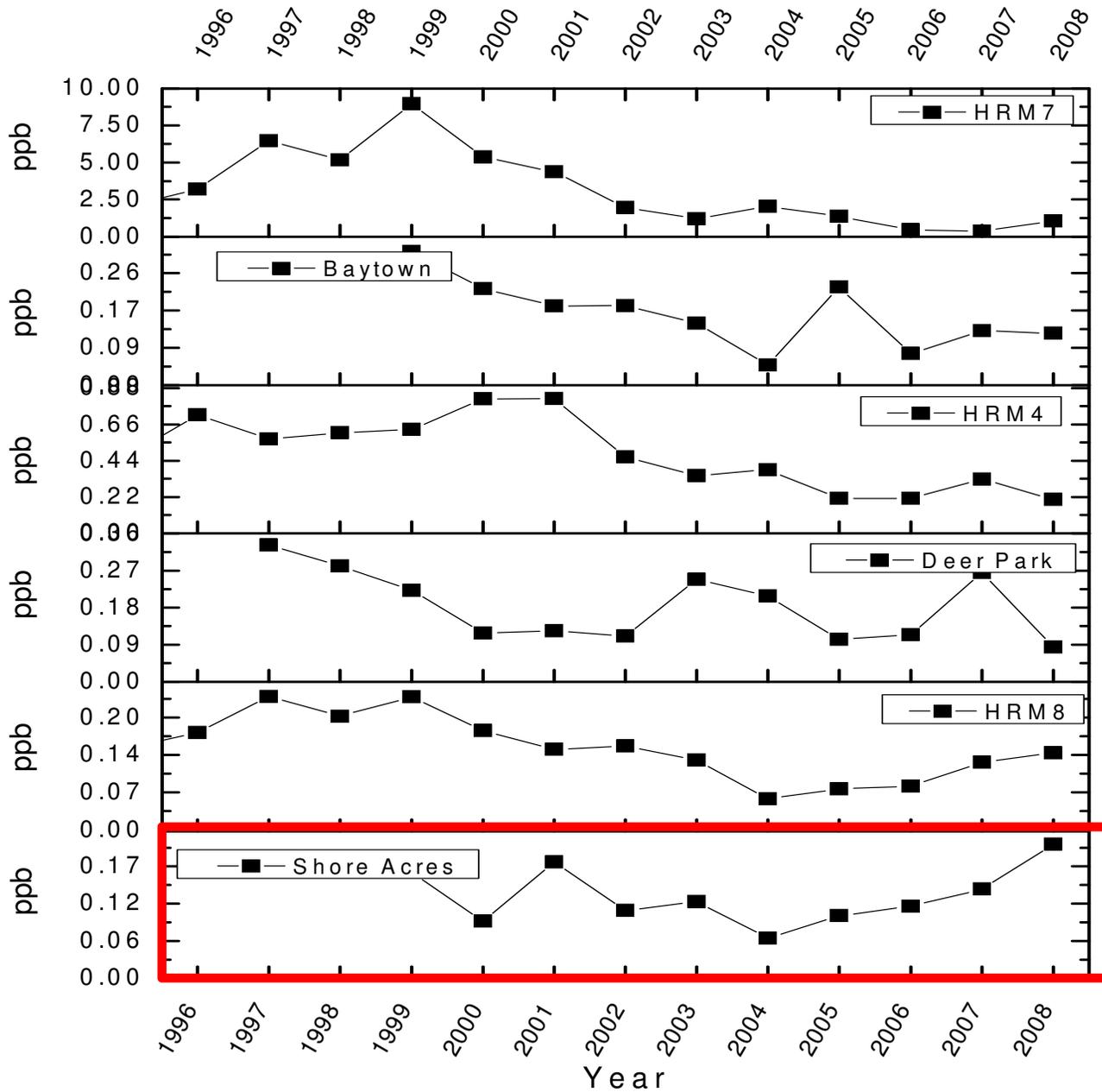
## ABSOLUTE CHANGE COMPARISON

- Compared the annual averages from the baseline year to 2008 for all 30 sites

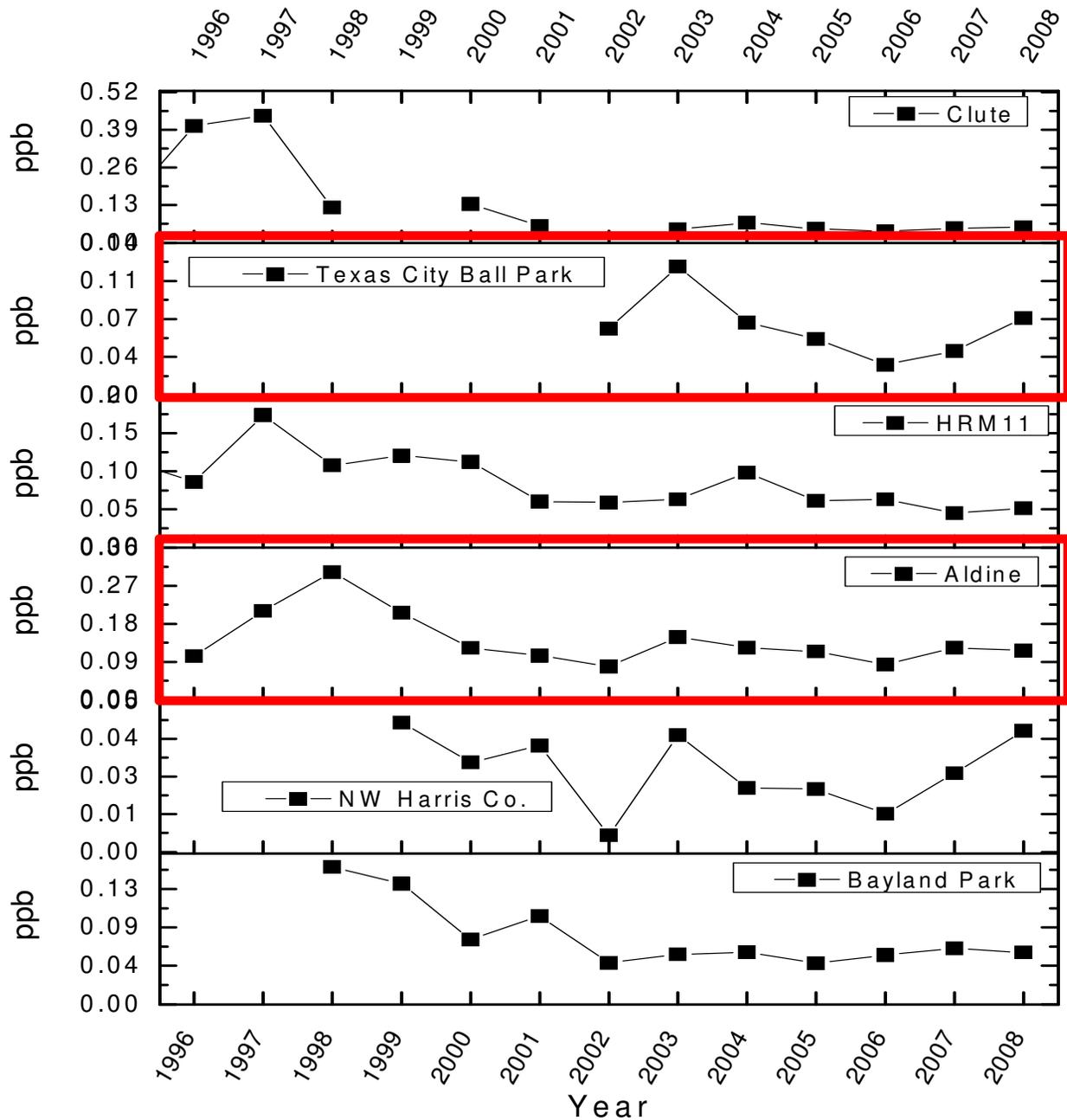
Number of Sites	Positive or Negative Change	Percent Difference
27	Negative	- 6 to -95%
3	Positive	+8 to +26%



**Time Series Charts for West Harris County Sites**



**Time Series Charts for East Ship Channel Sites**



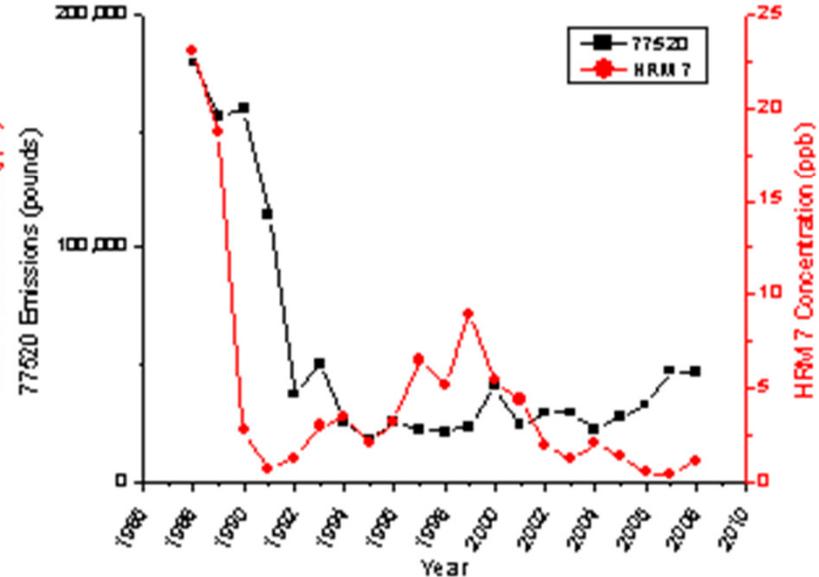
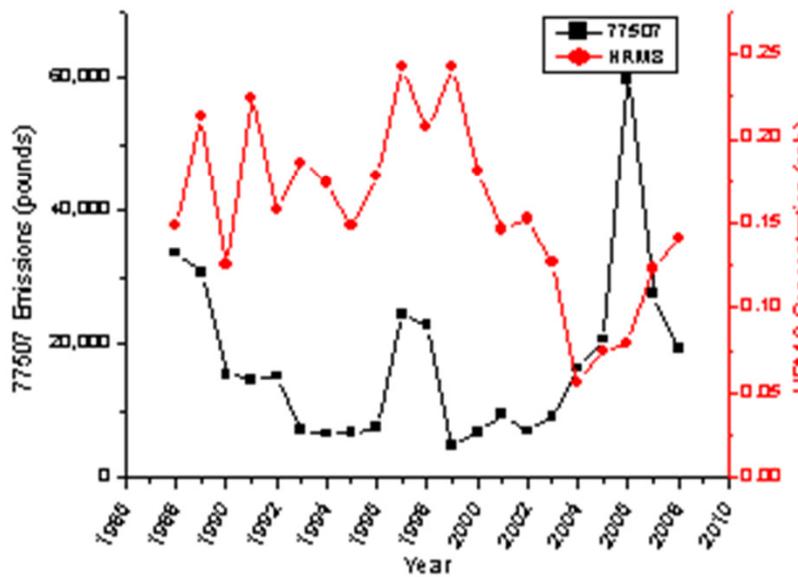
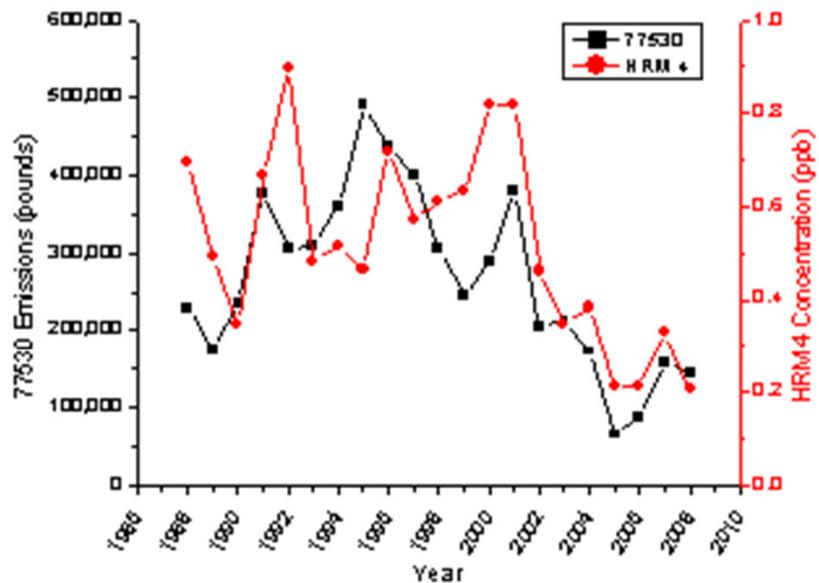
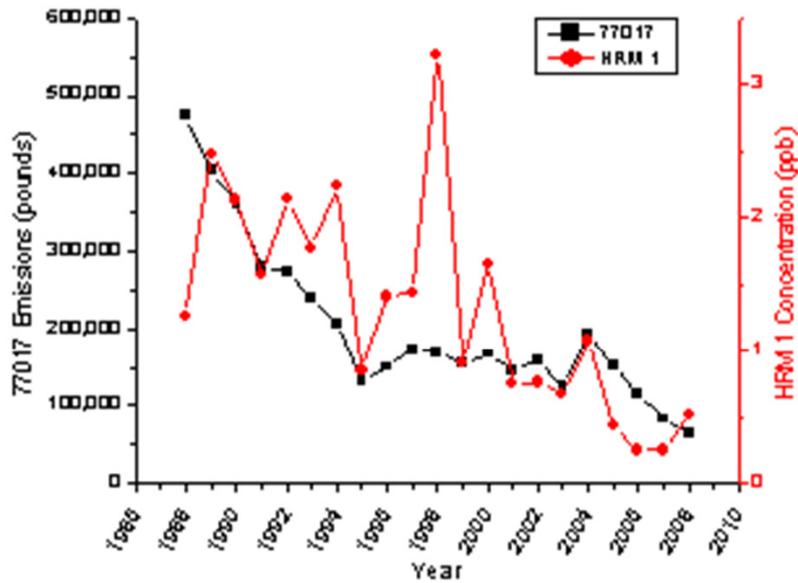
**Time Series Charts for Brazoria, Galveston, Chambers, and Suburban Harris County Sites**

## ANALYSIS RESULTS

- Performed a **least-squares regression** on all complete annual averages.
- Using  $p=0.05$ , found that **18 sites** had statistically significant negative slopes.
- The 12 sites that did not have statistically significant negative slopes were **not found to be different from zero**
  - i.e. there is no statistical difference between the baseline year and 2008.

# TOXICS RELEASE INVENTORY (TRI)

- Shows a **55%** decrease reported from Harris County stationary sources from 1988-2008
  - Compares well with the median decrease of **60%** annual average from baseline year to 2008
- Not directly comparable though since only 8 monitors were operational as early as 1988
- For a more meaningful comparison:
  - Created a time series of HRM annual average versus total annual emissions reported to TRI from all sources in the **same zip code** as the monitor.



Emission Inventory and Ambient Air Monitoring Data vs Time

# SUMMARY:

- Data from 30 air quality sampling sites in four counties were analyzed to assess trends in 1,3-butadiene levels
- Annual average concentrations were found to be lower at 27 of the 30 sites in 2008 compared with the baseline year
  - 27 sites: 40-80% lower
  - 3 sites: ≤ 26% increase
- Linear regression slopes of annual average 1,3-butadiene concentrations over time were negative, indicating **decreasing trends** at 27 of the 30 sites
  - The negative slopes were found to be **statistically different** from zero at the 95% confidence level at 18 sites

# SUMMARY (CONTINUED):

- The **greatest differences** were detected at sites in east Harris County **near the Houston Ship Channel**
- Three suburban sites had comparably lower annual average concentrations, and comparably lower or positive rates of change
- The greatest decreases in annual average 1,3-butadiene levels at most sites occurred from **1998 through 2002-2006**
  - Decreasing trends began to level off in 2007 and, at some sites, reverse
  - Any increasing trends were comparatively small

# GOING FORWARD

- Consider segmented linear trend analysis for sites where the magnitude or direction of the trend has changed significantly over time
- Strengthen weight of evidence by aggregating time series trends at nearby sites and comparing with emissions changes
- Explore hypothesis testing using nonlinear regression models
- Consider and apply nonparametric tests for trends, for example, Sen's Slope Estimator and the Mann-Kendall test
  - Both are recommended by the EPA guidance document titled, "Data Quality Assessment: Statistical Methods for Practitioners, EPA QA/G-9S"

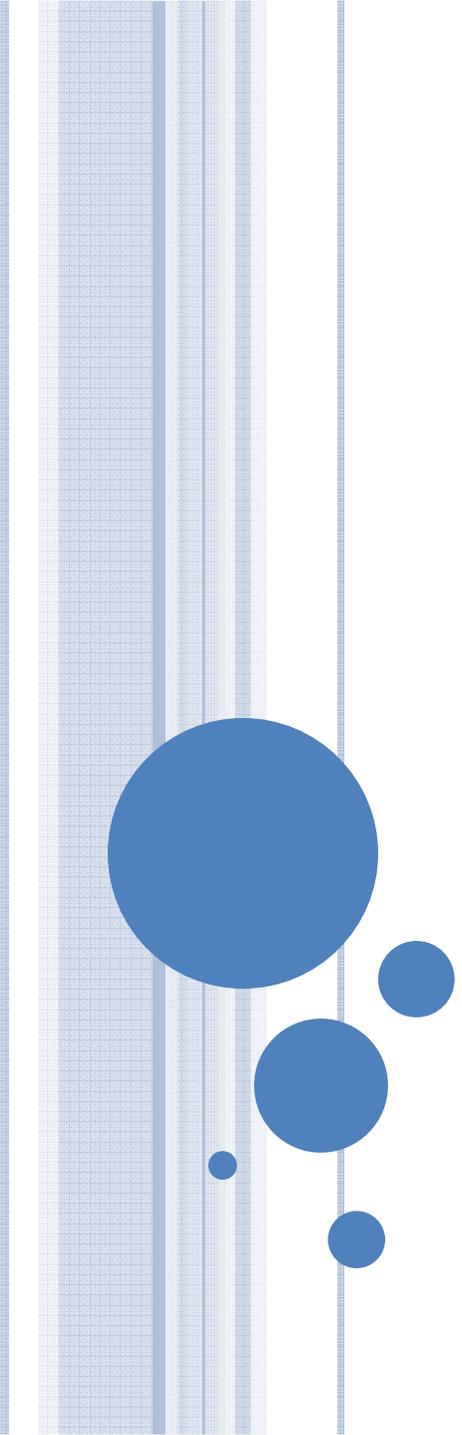


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QUESTIONS?

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