Exploratory Analyses:

Meteorologically Adjusted Trends
Links Between Ozone, PM, and Air Toxics
Comparison of Annual Trends With MACT

Prepared by:
Michael C. McCarthy
Elizabeth M. Cozzo
Sean M. Raffuse
Hilary R. Hafner

Sonoma Technology, Inc.
Petaluma, CA

Presented to:
Air Toxics Monitoring Data Analysis Workshop
Raleigh, NC
September 28, 2005

Exploratory Analysis Overview

- Proof-of-concept tasks
  - Key question—are these avenues of exploration worth further effort?
- Three separate mini-talks
  - Meteorological trends adjustment
  - Links between ozone, $PM_{2.5}$, and air toxics ("Nexus")
  - Comparison of annual trends with Maximum Achievable Control Technology (MACT)

Met-Adjusted Trends – Background and Objectives

- Background
  - Differences in meteorology between years can affect pollutant concentrations and obscure (or falsely indicate) actual trends because of emissions changes
  - Adjustment for annual trends for the influence of meteorology has been performed for ozone, for example, but not for air toxics
- Objectives
  - Apply meteorological trend adjustment to one or two air toxics at a few sites to determine if
    - meteorology affects air toxics concentrations
    - meteorologically adjusted trends are different than unadjusted trends
    - this topic is worthy of a more detailed and thorough investigation

Met-Adjusted Trends – Approach

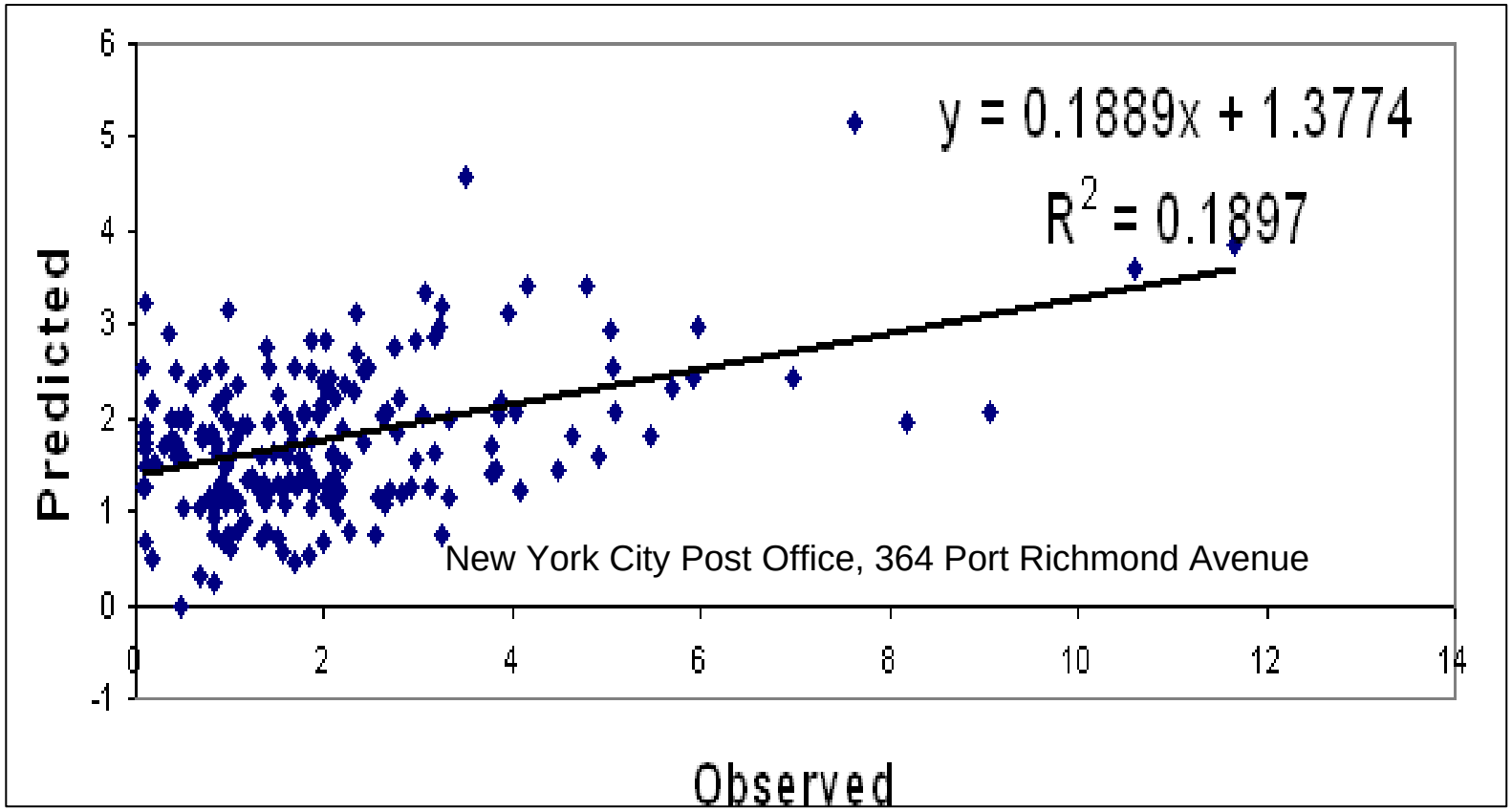
- Selected likely cities based on length of trend records and use in other exploratory analyses
- Constructed database of meteorology from National Weather Service data
- Determined which meteorological parameters had the highest correlations with observed 24-hr average concentrations collected every sixth day for benzene and lead (tsp) in New York
- Used three to five meteorological parameters in a multi-linear regression model to predict concentrations
- Adjusted model-predicted concentrations based on a linear trend fit to residuals as a function of time

Meteorological Parameters

- Maximum daily surface temperature
- Minimum daily surface temperature
- Average daily surface temperature
- Average daily wind speed
- Daily wind vector components (u and v) and magnitude
- Average aloft minus surface temperature (700, 850, and 925 mb)
- Daily average 500-mb height
- Total daily precipitation
- Average sea level pressure

Parameters used in linear model:
Blue = benzene parameters
Red = lead (tsp) parameters

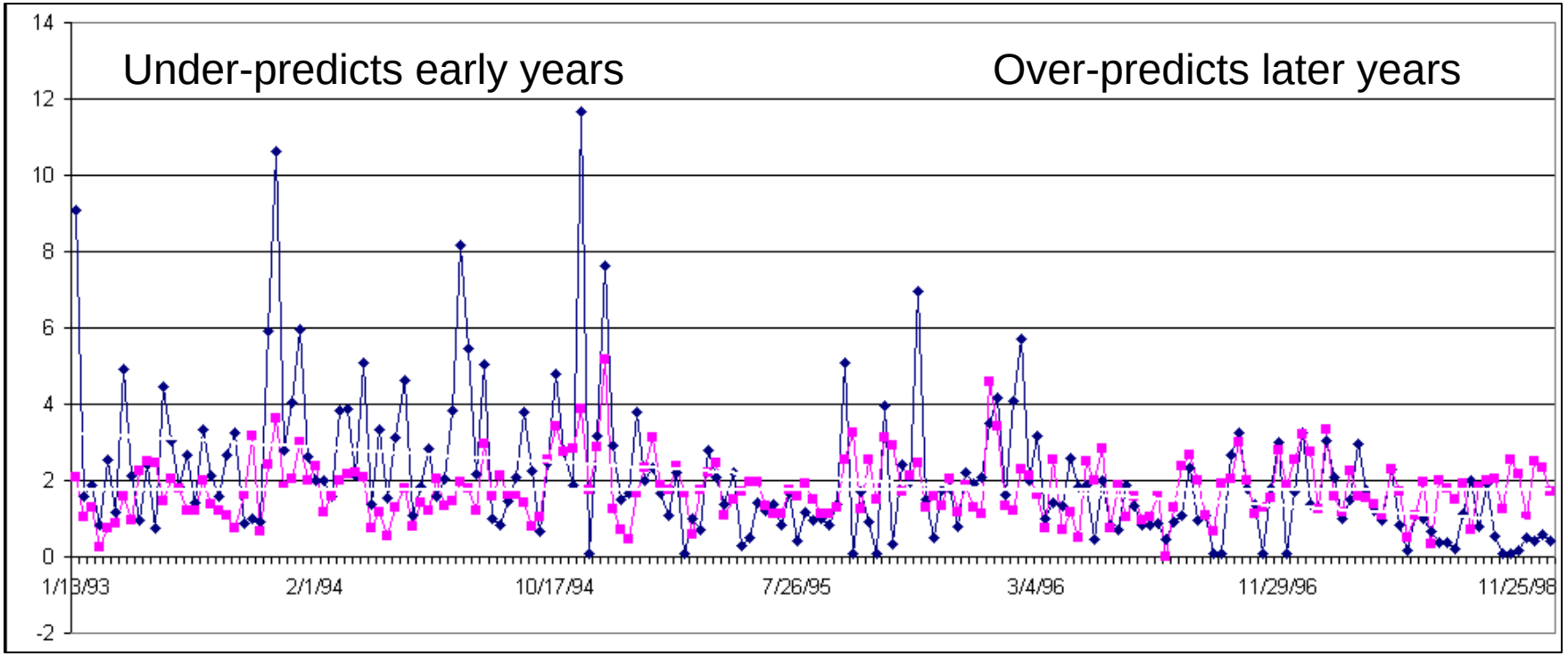
Met-Adjusted Trends – Results for Benzene in New York (1 of 5)



Observed and predicted daily average benzene concentrations. Predicted daily average benzene concentrations originated from linear regression model analysis using meteorological parameters.

Met-Adjusted Trends – Results for Benzene in New York (2 of 5)

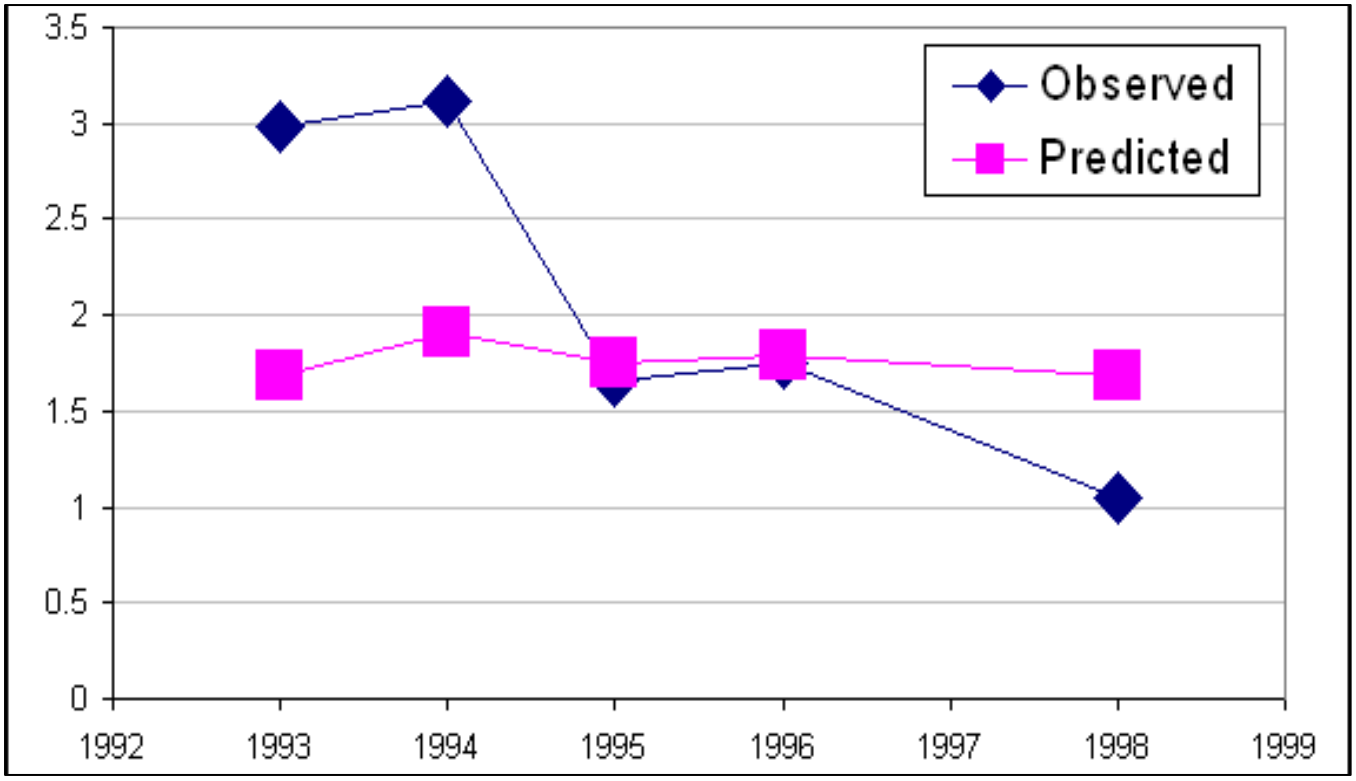
Time series of observed and predicted daily average benzene concentrations



Observed

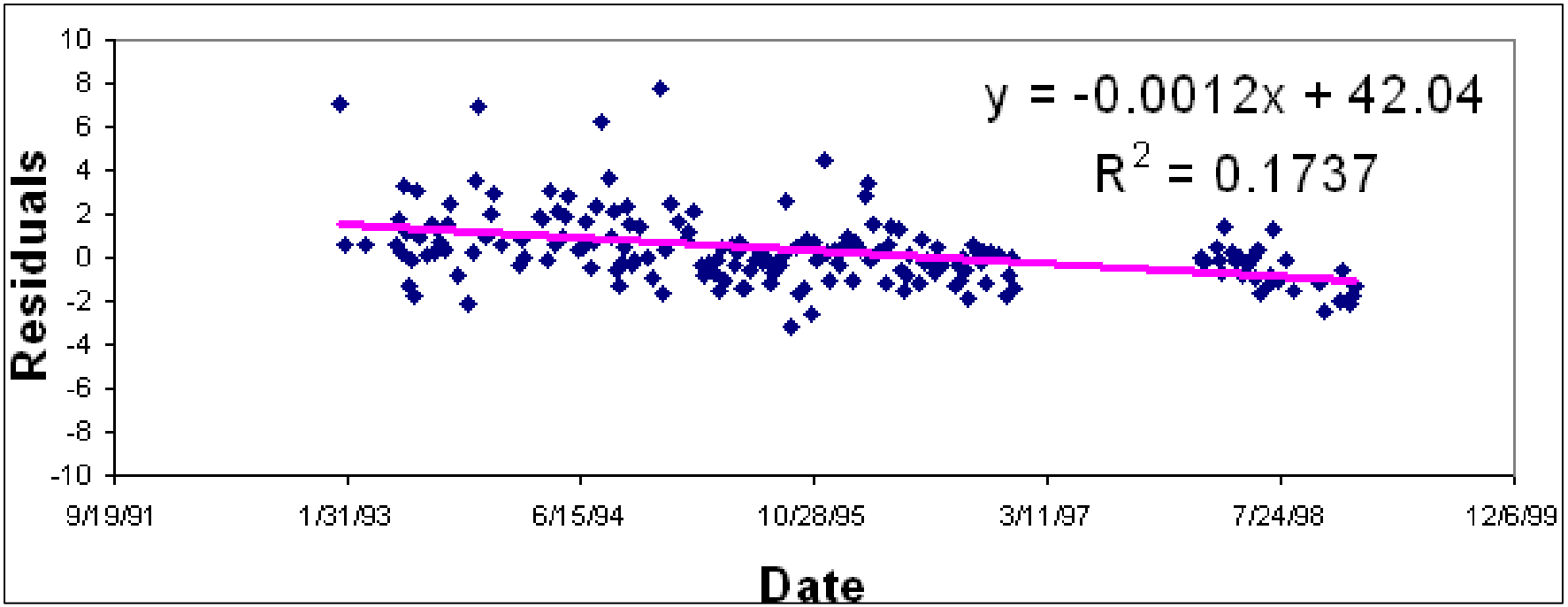
Predicted

Met-Adjusted Trends – Results for Benzene in New York (3 of 5)



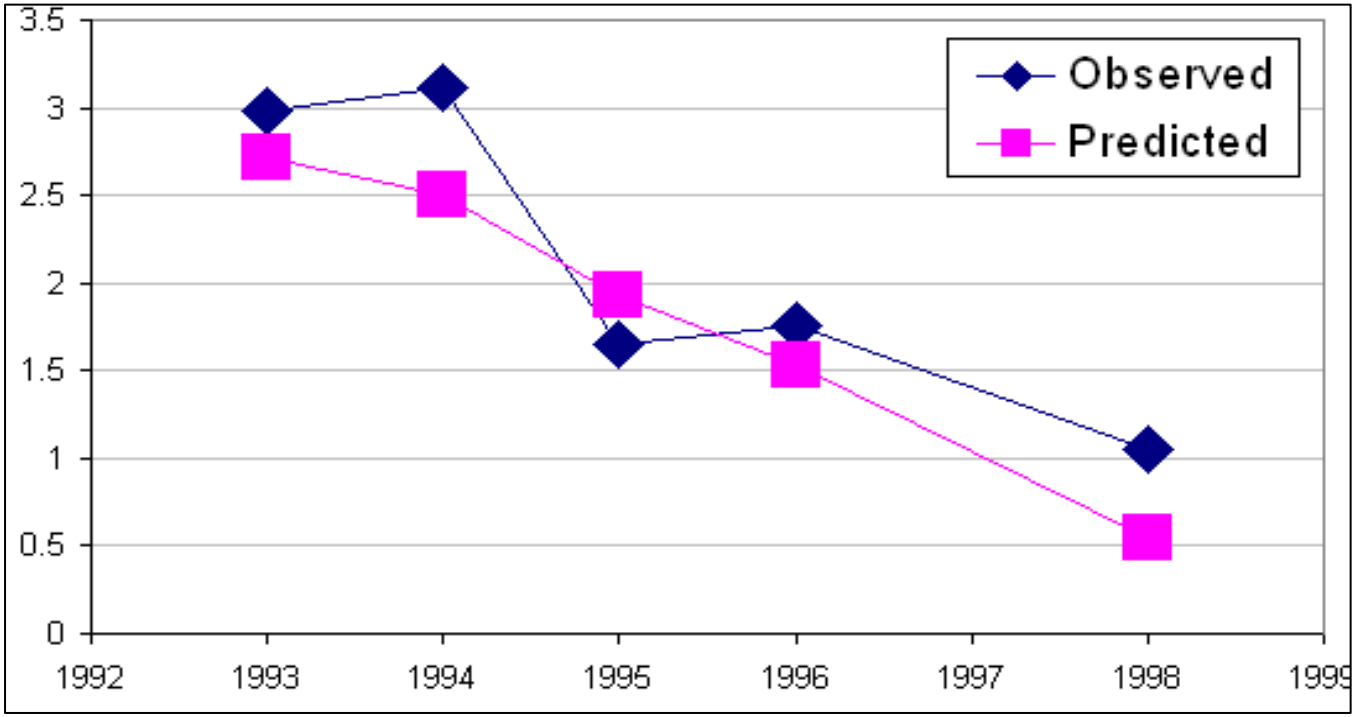
Meteorology alone does not account for the observed benzene trend.

Met-Adjusted Trends – Results for Benzene in New York (4 of 5)



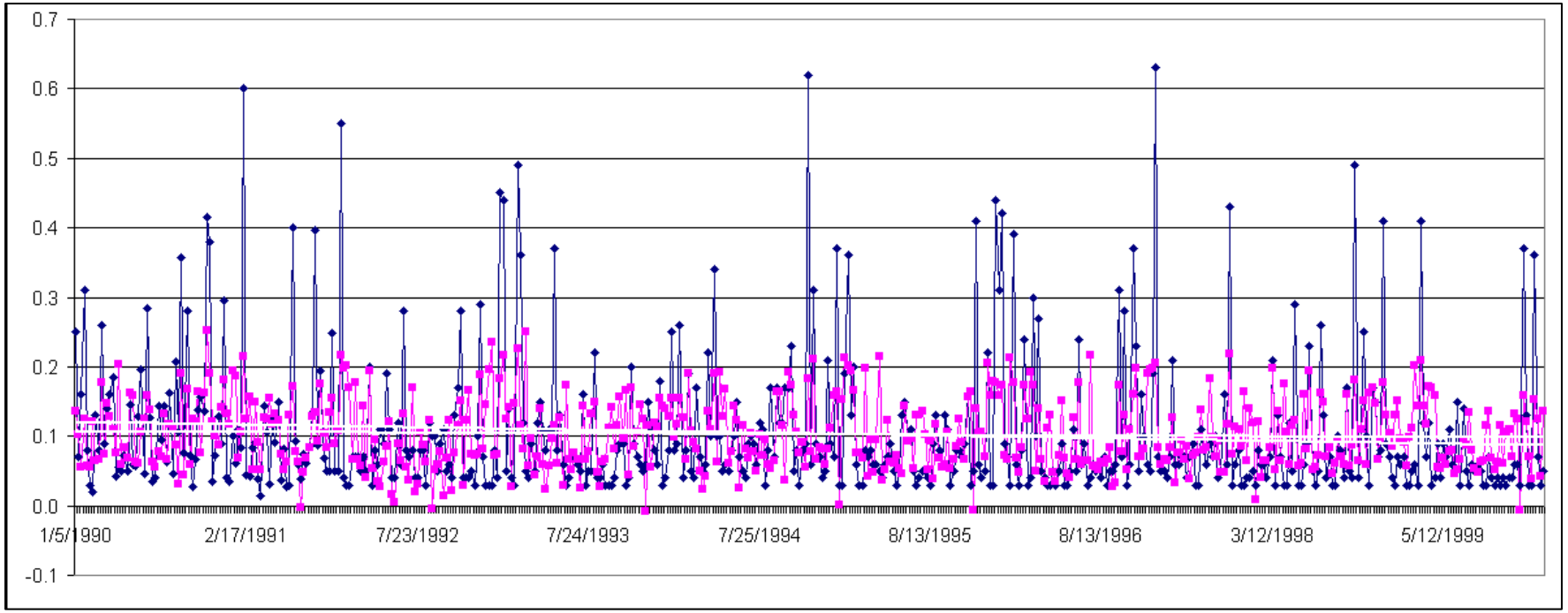
Residuals of predicted versus observed daily average benzene concentrations as a function of date and a trend line. Residuals decrease as a function of time, which may be a result of decreasing emissions or transport.

Met-Adjusted Trends – Results for Benzene in New York (5 of 5)



Decreasing emissions or transport accounted for the bulk of the observed trend. Meteorological adjustments smoothed bumps in the trend.

Met-Adjusted Trends – Results for Lead (tsp) in New York (1 of 3)

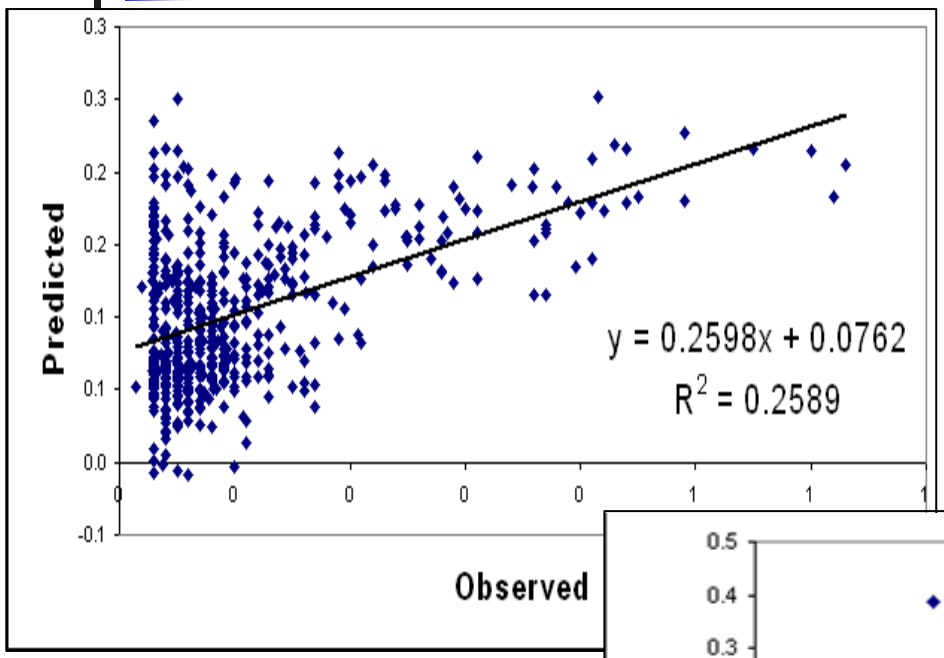


Observed

Predicted

What about other air toxics?
New species and site:
Lead (tsp) at 301 Greenpoint Avenue, New York City

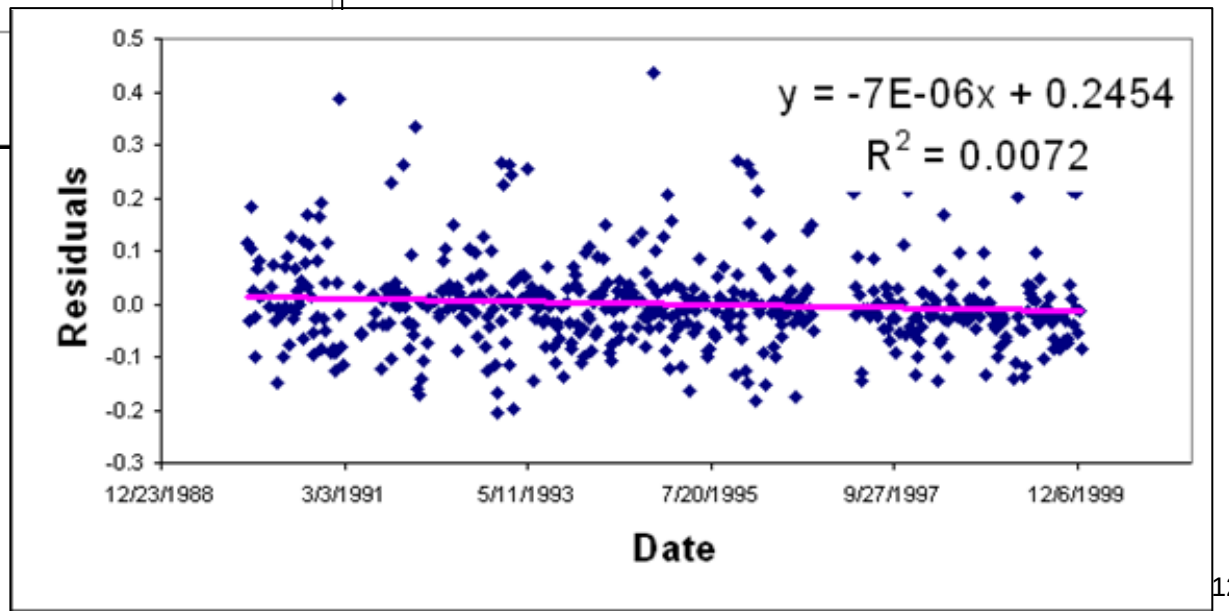
Met-Adjusted Trends – Results for Lead (tsp) in New York (2 of 3)



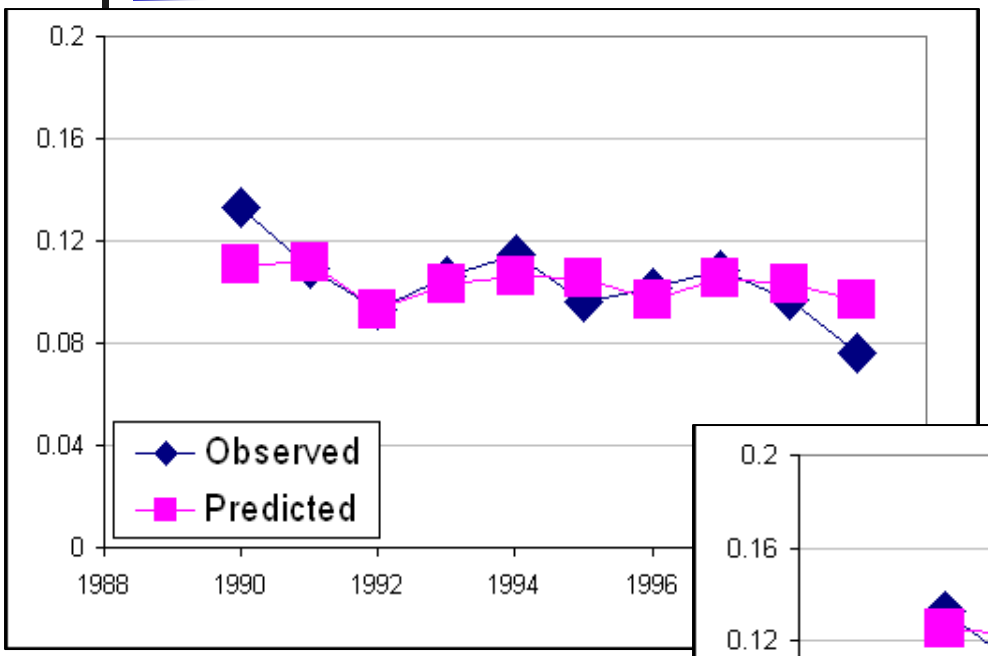
Observed versus Predicted concentrations

The same process was performed and similar results were found

Residuals as a function of time

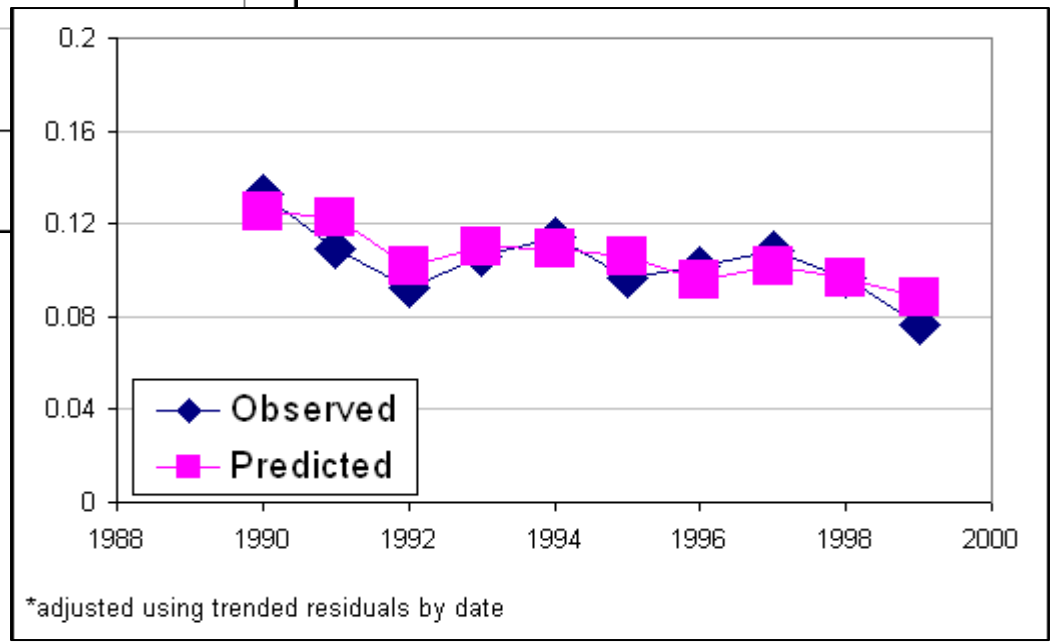


Met-Adjusted Trends – Results for Lead (tsp) in New York (3 of 3)



Met-adjusted trends alone do not account for observed trends.

Accounting for trends in emissions and transport is necessary to match observed data. Met-adjustment smoothed the underlying trend.



Met-Adjusted Trends – Summary and Conclusion

- Meteorology accounted for 15-25% of total variance for benzene and lead (tsp).
- Meteorological adjustments smoothed trends.
- Meteorological trends adjustment appeared to be important for trend detection in benzene and lead (tsp), and may be important for other air toxics as well.

Further investigation is warranted.

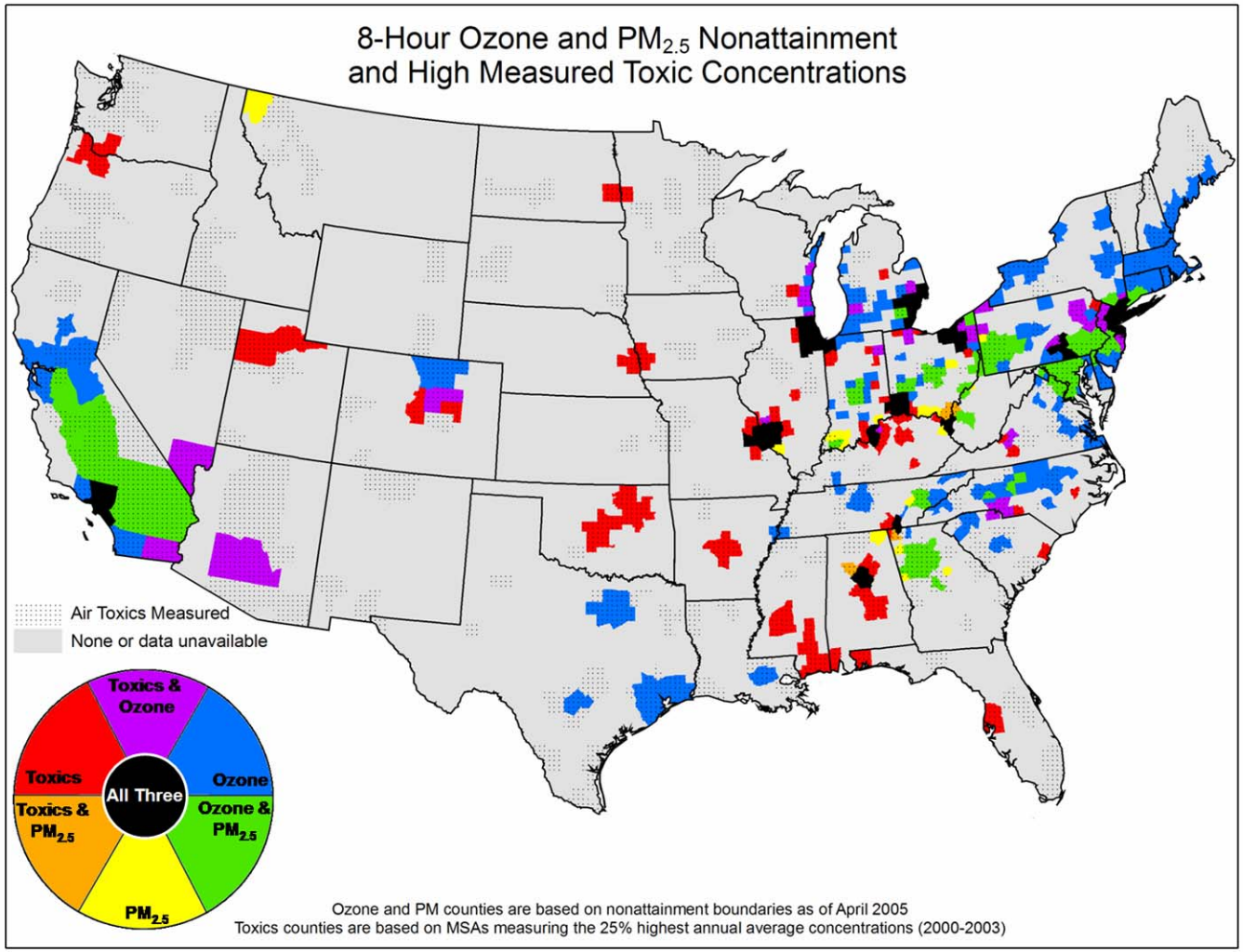
Nexus – Background and Objectives

- Background
  - Major efforts are underway to regulate urban sources of ozone, PM, and air toxics
  - National Academy of Sciences suggests that urban air quality should be investigated as “one atmosphere” rather than compartmentalizing air quality issues
- Objectives
  - Examine where high concentrations of ozone, PM, and air toxics occur
  - Explore potential correlations between ozone, PM, and air toxics
  - Is this topic worthy of a more detailed and thorough investigation?

Nexus – Approach

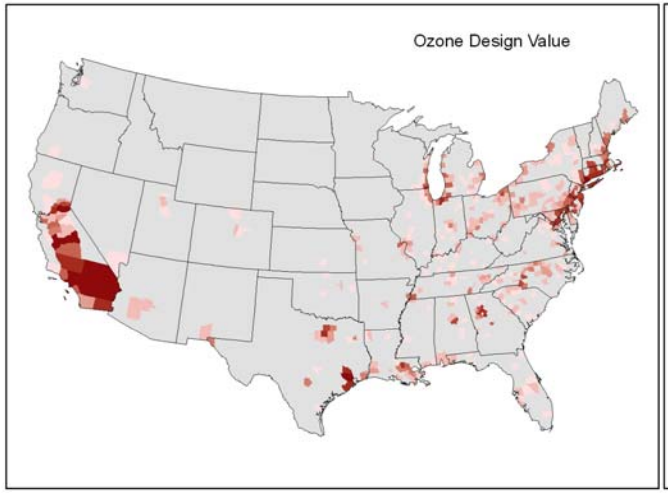
- Created a nationwide map of areas where high concentrations of air toxics, ozone, and PM occur
- Created a database with ozone, $PM_{2.5}$, and air toxics concentrations for Los Angeles, New York, Chicago, and Philadelphia from 2000 to 2003 (summer only)
- Examined correlations among citywide average concentrations
- Examined correlations among collocated pollutants (a relatively rare occurrence)

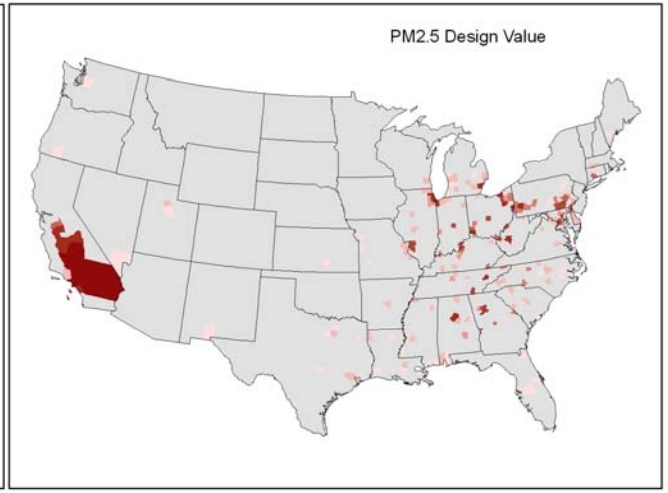
Where are Concentrations of Ozone, $PM_{2.5}$, and Air Toxics High? (1 of 4)



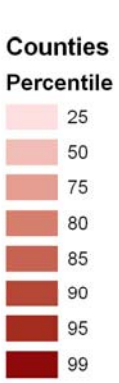
- Map of ozone and $PM_{2.5}$ nonattainment areas and counties with highest 25% of air toxics concentrations
- Since the same set of air toxics are not measured in each county, a ranking system was used

Where are Concentrations of Ozone, $PM_{2.5}$, and Air Toxics Risk High? (2 of 4)



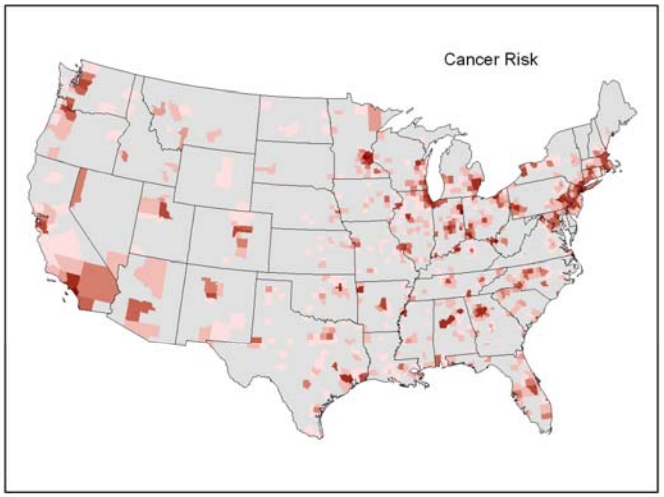


Ozone, PM2.5, and Cancer Risk Percentiles



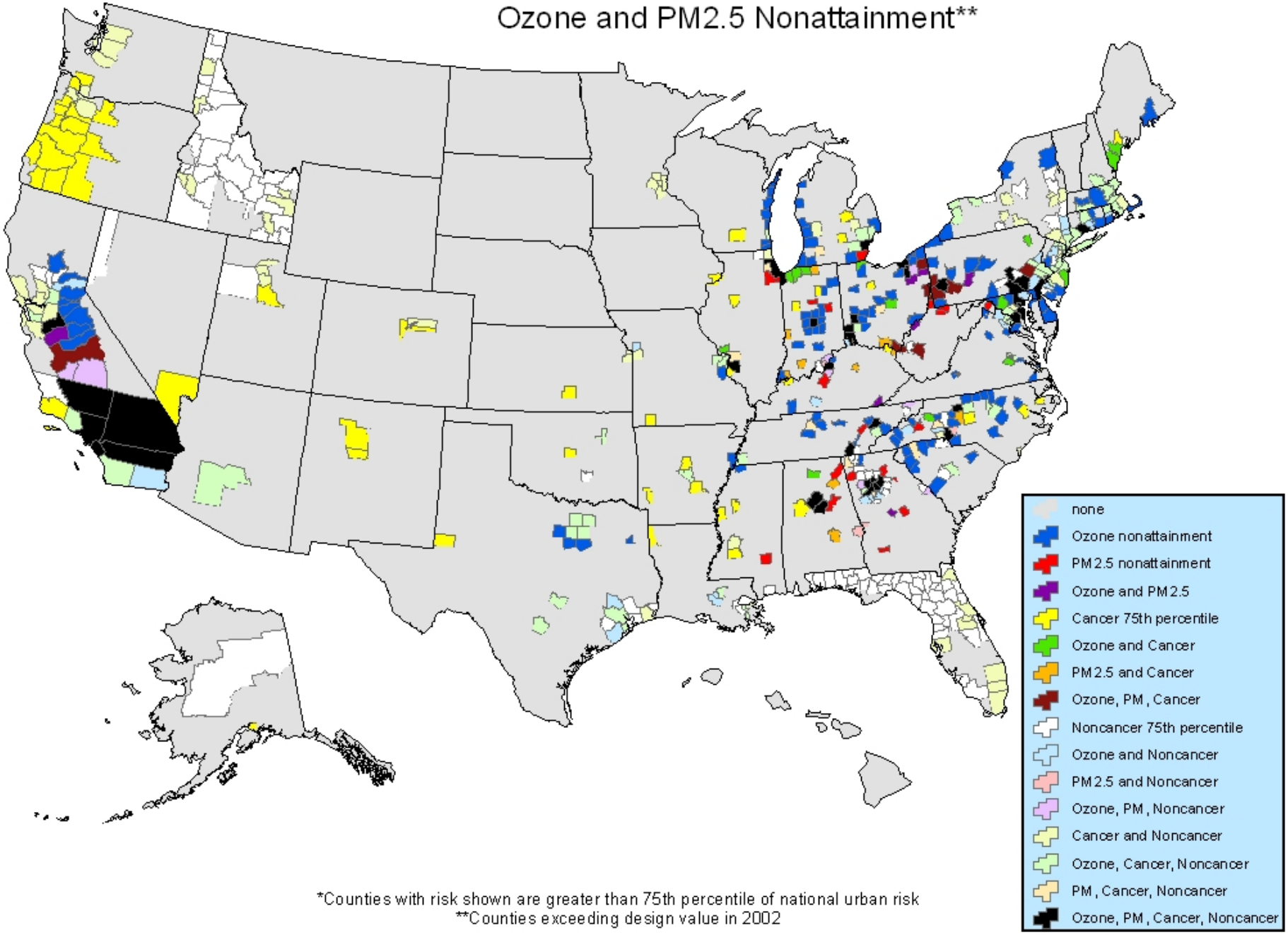
Percentile	Ozone (ppm)	$PM_{2.5}$ (µg/m³)	Cancer Risk*
25	0.095	10.8	27
50	0.106	13.1	33.1
75	0.116	15.1	43.1
80	0.119	15.6	46.7
85	0.123	16.2	50.7
90	0.127	16.8	56.5
95	0.133	17.6	69.8
99	0.148	22.2	95.2

* Per million cancer risk, percentile based on urban counties only
Ozone 1-hr design value 2002, PM2.5 annual design value 2002



- Maps of low to high ozone and $PM_{2.5}$ design values and cancer risk from the 1996 National Air Toxics Assessment Model (NATA).
- Because of differences in cancer risks, high concentrations of air toxics do not necessarily equal high risk.

Cancer and Noncancer Risk*, Ozone and PM2.5 Nonattainment**



*Counties with risk shown are greater than 75th percentile of national urban risk
**Counties exceeding design value in 2002

Where are Concentrations of Ozone, $PM_{2.5}$, and Air Toxics High? (4 of 4)

- Areas of high air toxics concentrations are often associated with high $PM_{2.5}$ and ozone concentrations.
- Areas predicted to have high cancer risk are often associated with high $PM_{2.5}$ and ozone concentrations—air toxics, ozone, and $PM_{2.5}$ air quality issues are spatially correlated.
- But, do concentrations correlate temporally?

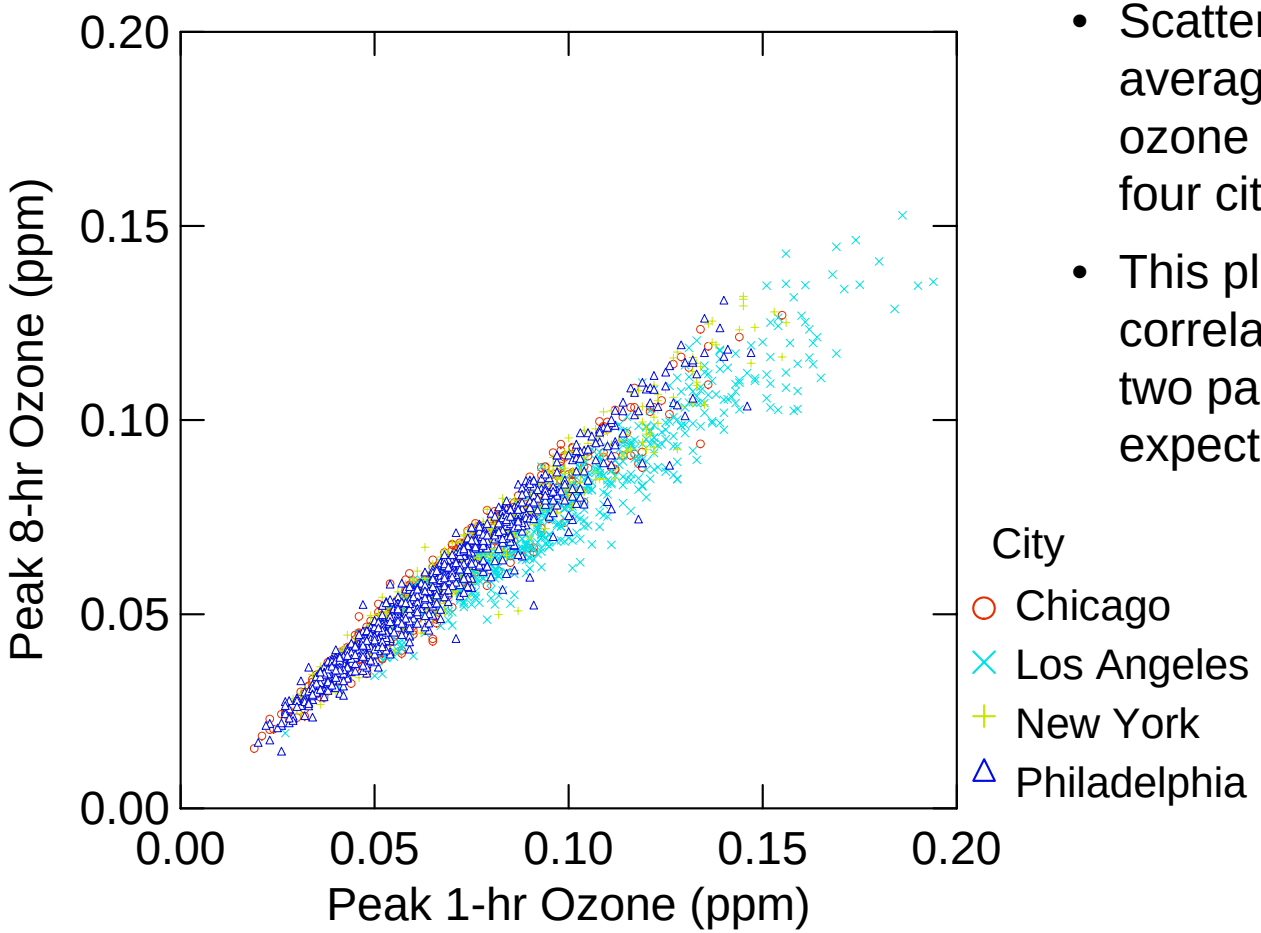
Exploring Links between Ozone, $PM_{2.5}$, and Air Toxics

- Correlations were created for multiple air toxics, ozone, and $PM_{2.5}$ parameters for New York, Los Angeles, Chicago, and Philadelphia
  - Peak 1-hr and 8-hr ozone
  - Peak 1-hr and 24-hr average $PM_{2.5}$
  - 0600 to 0900 benzene, toluene, o-xylene, etc. (from PAMS sites)
  - 1200 to 1500 formaldehyde and acetaldehyde (from PAMS sites)
  - 24-hr air toxics (VOCs, $PM_{2.5}$ metals, and tsp metals)

Nexus – Discussion

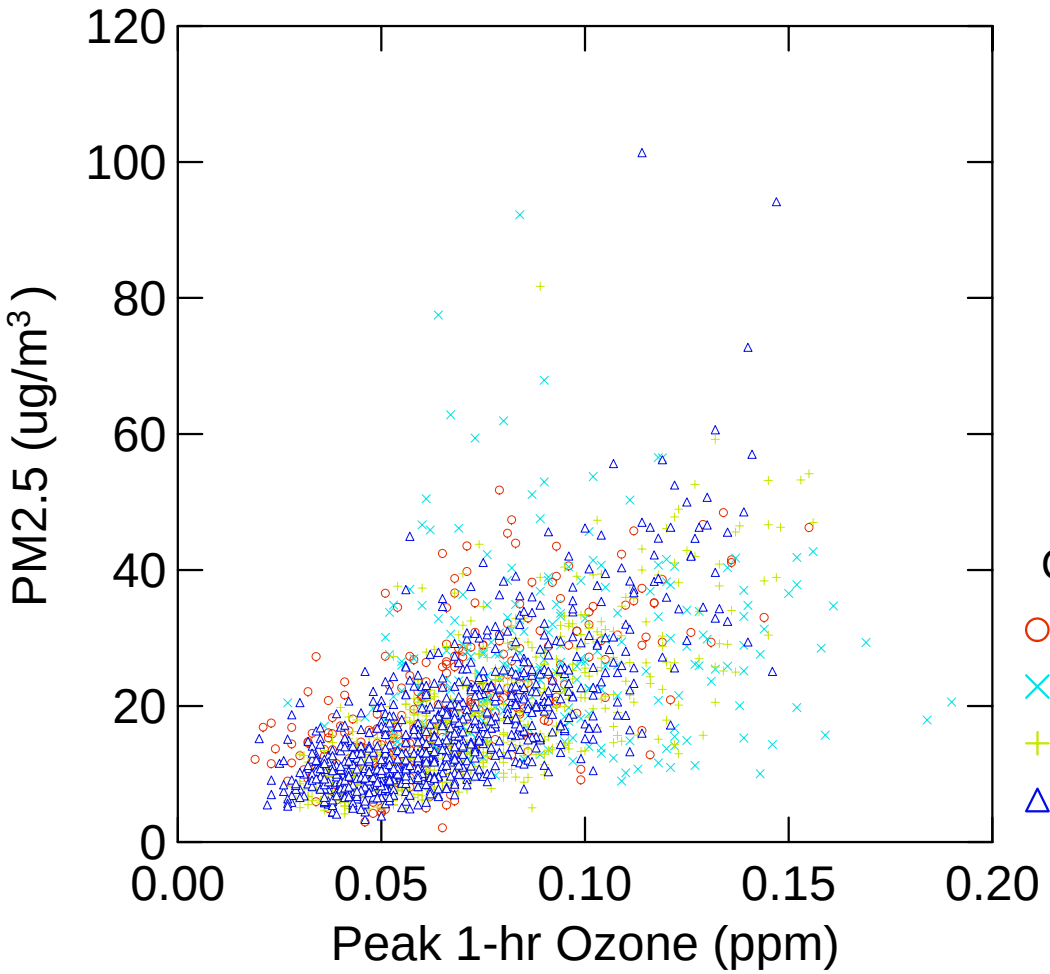
- Temporal correlations are not expected to exist for many of the nexus pollutants
  - Diurnal and seasonal patterns of the pollutants are based on meteorology, emissions, and photochemistry.
  - Time lags are not captured well by 24-hr samples. (Conditions leading to high ozone are conducive to sulfate formation. Higher sulfate leads to higher $PM_{2.5}$. Thus, $PM_{2.5}$ may lag peak ozone by a day or two.)
  - Primary emission pollutants will not correlate well with secondarily produced pollutants (e.g., benzene and ozone).

Correlation Analyses (1 of 4)



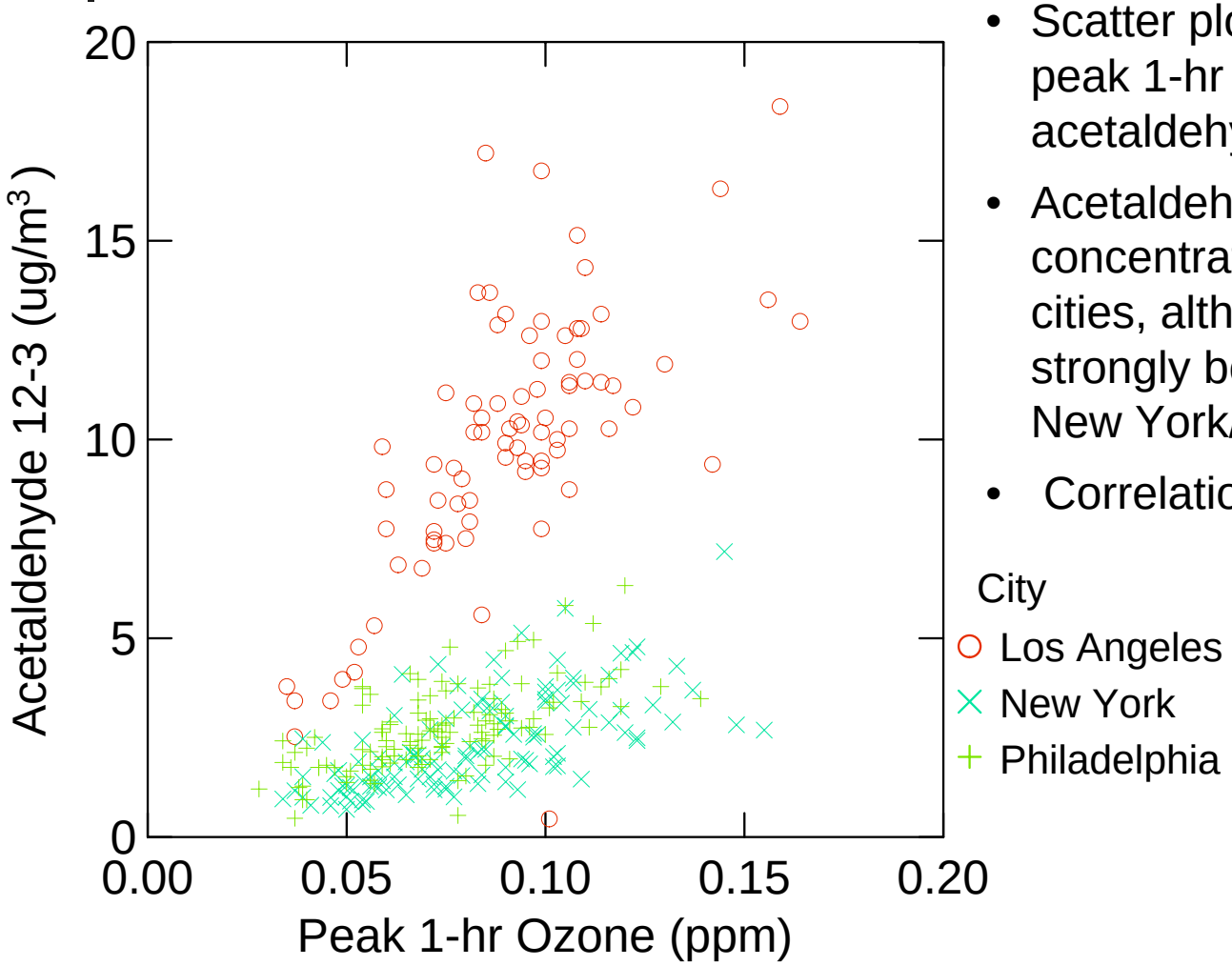
- Scatter plot of citywide average 1-hr and 8-hr peak ozone concentrations in the four cities
- This plot shows a tight correlation between these two parameters, as expected

Correlation Analyses (2 of 4)



- Scatter plot of citywide average peak 1-hr ozone and 24-hr $PM_{2.5}$ concentrations in the four cities
- This plot shows a more scattered relationship, but a correlation does still exist for eastern cities
- The correlation may be better if a time lag was incorporated

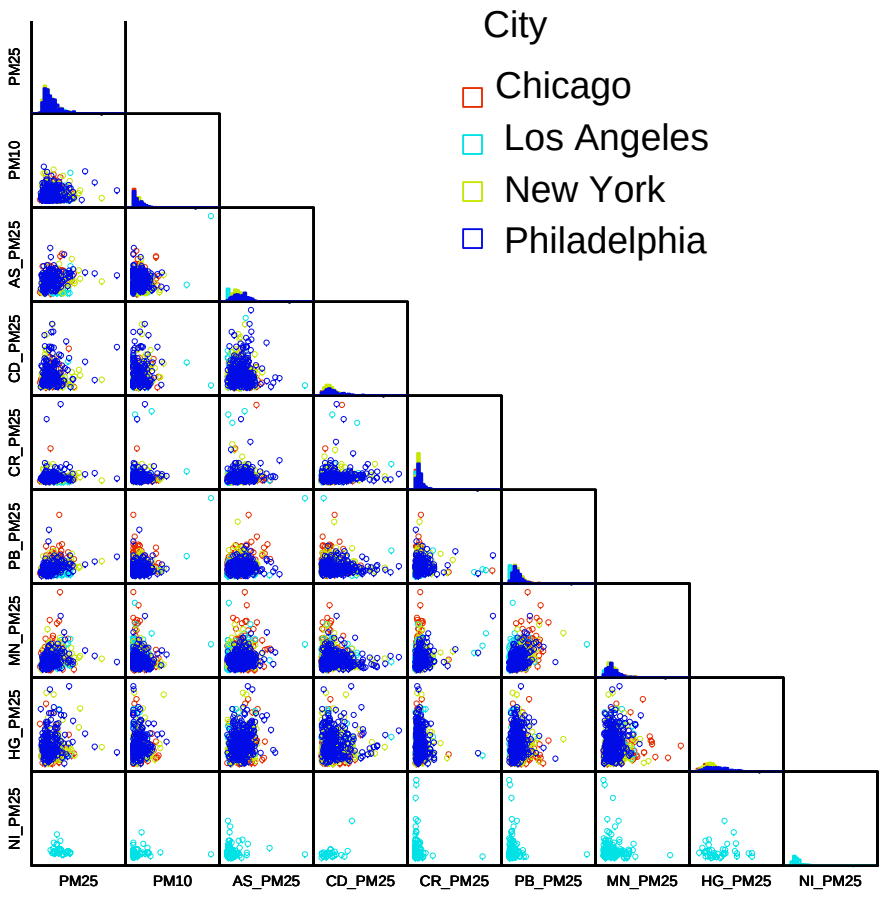
Correlation Analyses (3 of 4)



- Scatter plot of citywide average peak 1-hr ozone and afternoon acetaldehyde concentrations
- Acetaldehyde and ozone concentrations correlate in all three cities, although the slopes differ strongly between Los Angeles and New York/Philadelphia
- Correlation is not causation.

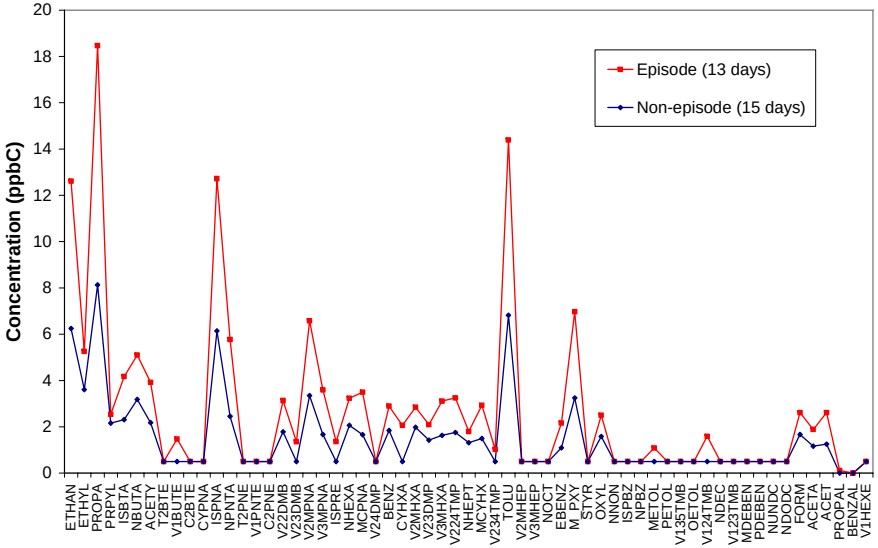
Correlation Analyses (4 of 4)

- Scatter plots of citywide average 1-hr and 8-hr ozone and 24-hr average chlorinated volatile organic compound (VOC) concentrations showed no correlations
- Scatter plots of citywide average $PM_{2.5}$ mass and $PM_{2.5}$ metal concentrations showed weak or no correlations



Other Links

- In the Northeast and California, on the morning of high ozone concentration days (episodes), nearly all the measured VOCs, including air toxics, typically had higher concentrations because of lower mixing heights on these days compared to average days.
- In Houston, concentrations were similar on episode/non-episode days; i.e., on any given day with the correct meteorology, an ozone episode can occur.



Fingerprint plot of hydrocarbons on ozone episode and non-episode days in Fresno, California.

Nexus – Principal Component Analysis (PCA)

Factor New York MSA	Percent of variance explained	Key pollutants	Comment
Photochemical-Secondary	25	Ozone formaldehyde acetaldehyde	*Share similar formation mechanism*
Mobile sources and/or industrial	14	1,3-butadiene benzene	*Also contained several metals and 1,2-dichloropropane*
Unresolved	60		*No clear source types*

PCA usually shows separation among air toxics; more species, especially non-toxics species, are needed to better resolve sources.

Nexus – Summary and Conclusions

- Ozone and $PM_{2.5}$ correlated at eastern cities, but not for Los Angeles (consistent with different composition of PM among the sites investigated).
- Acetaldehyde and formaldehyde correlated with ozone, but this was likely because of similar photochemical production mechanisms, rather than source similarities (i.e., not a causal association).
- Most air toxics did not correlate well with ozone, $PM_{2.5}$, or other air toxics.

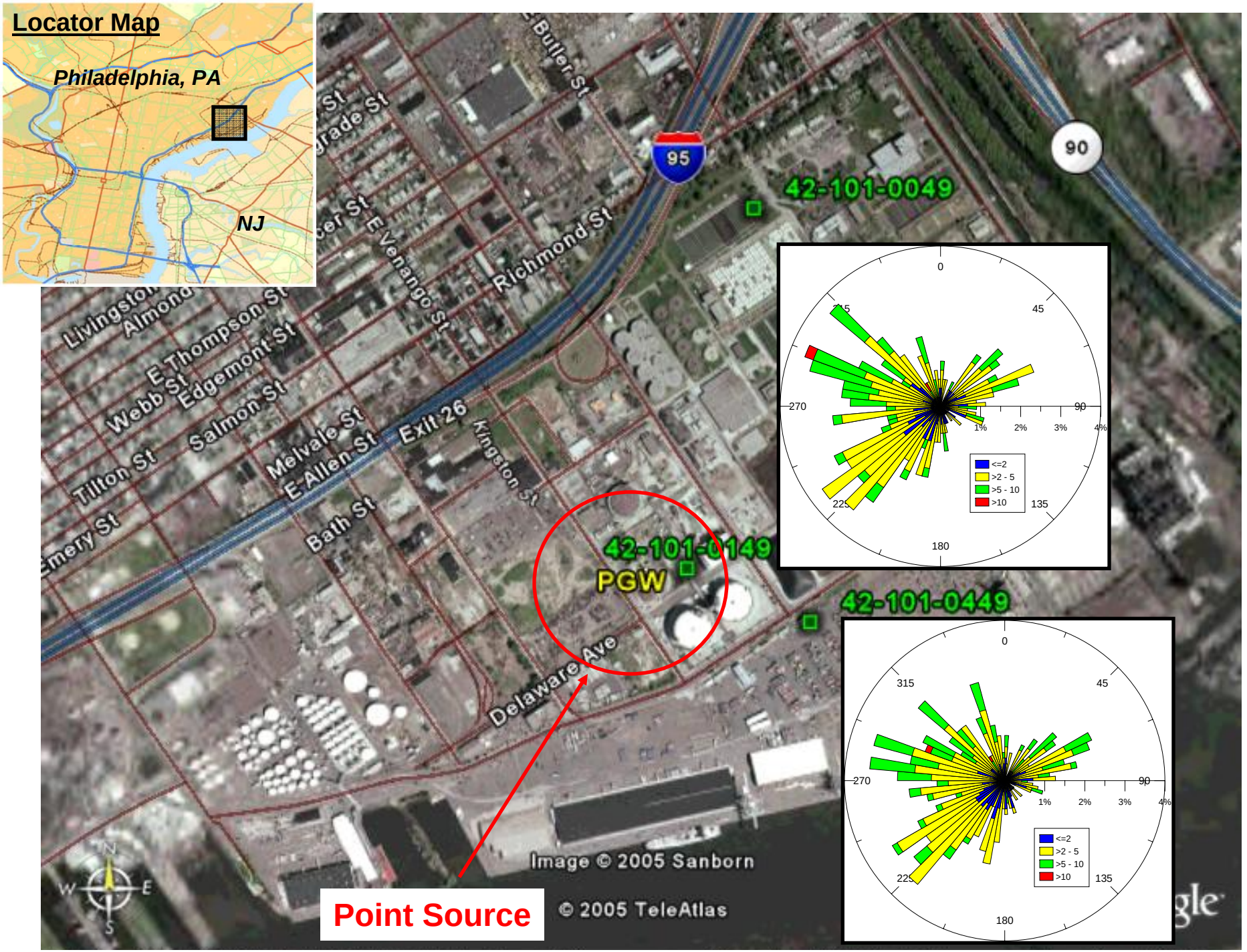
A simple approach is inadequate. Further investigation using correlations of ambient concentrations is not recommended.

MACT – Background and Objectives

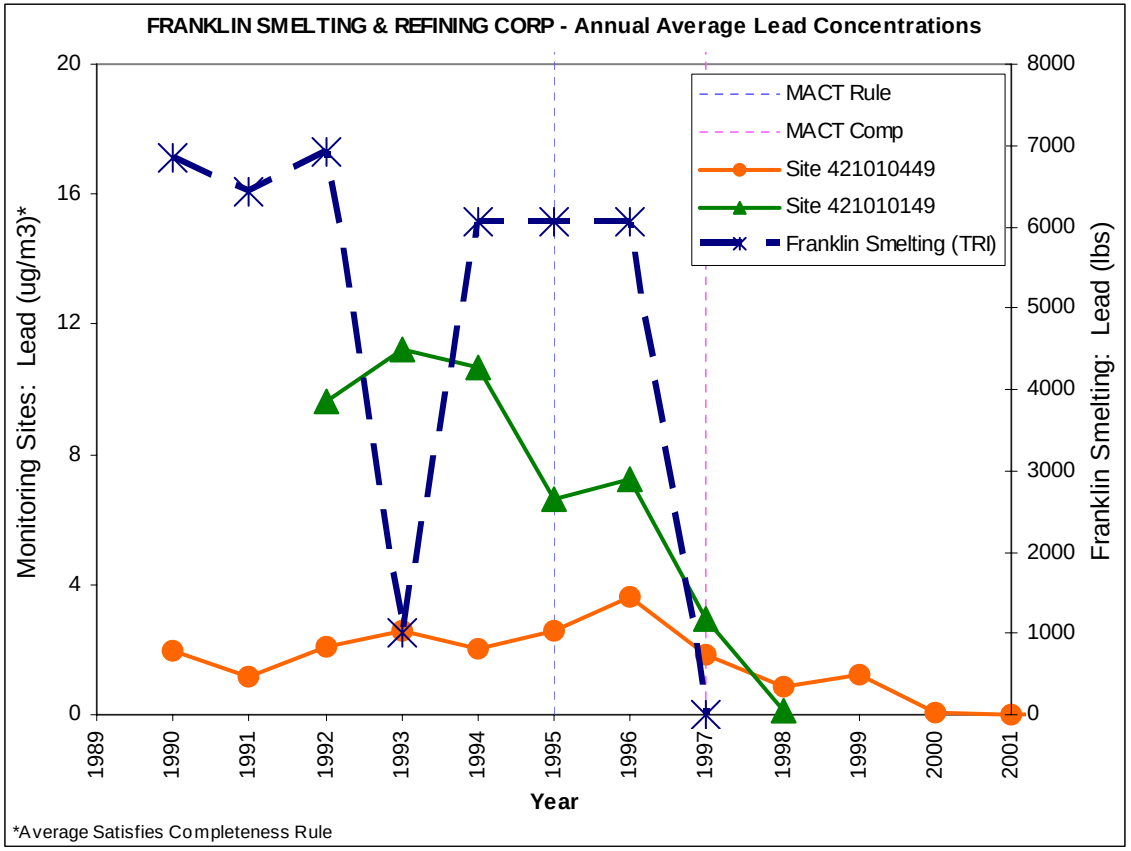
- Background
  - Policy makers want to know if trends in air toxics concentrations are attributable to specific control measures.
  - Many air toxics have MACT regulations in place during the study period.
- Objectives
  - Use a few case studies to examine if changes in ambient concentrations can be tied to MACT control measures.
  - Use metadata such as wind direction, satellite photography, emissions information, MACT implementation dates, and local knowledge to attempt to tie MACT implementation to changes in concentrations.
  - Is this topic worthy of a more detailed and thorough investigation?

MACT – Approach

- Choose pollutants and sites with data before and after MACT regulations were in place
- Assess site metadata (maps, winds, etc.)
- Assess trends in concentrations
- Assess trends in emissions
- Contact local experts


Locator Map
Philadelphia, PA
NJ
95
90
42-101-0049
42-101-0149
PGW
42-101-0449
Richmond St
Venango St
Butler St
E Thompson St
Webb St
Edgemont St
Salmon St
Melvale St
E Allen St
Exit 26
Kingston St
Bath St
Tilton St
Delaware Ave
0
45
90
135
180
225
270
315
1%
2%
3%
4%
<=2
>2 - 5
>5 - 10
>10
Image © 2005 Sanborn
© 2005 TeleAtlas
Point Source

Lead (tsp) in Philadelphia (1 of 2)



- Lead (tsp) sites next to a smelter in Philadelphia are shown as the orange and green lines.
- Toxics release inventory countywide emissions for Franklin Smelting are shown as the blue line.
- Years of a MACT rule regulating primary and secondary lead smelters are shown as the blue (rule phase-in) and pink (compliance) dotted lines.

Lead (tsp) in Philadelphia (2 of 2)

- Concentrations at two sites near a lead smelter decreased substantially during the MACT implementation and compliance period.
- Emissions from the facility decreased when compliance was required.
- Was MACT responsible for declining concentrations?

Reductions Were Not Because of MACT

- The Franklin Smelter installed PM_{10} controls in 1996 because the sites located near the smelter plume were in PM_{10} nonattainment.
- Reductions in lead were a byproduct of these PM_{10} controls, not MACT.
- Local knowledge[1] was necessary to identify the type of controls responsible for the decrease in concentrations.

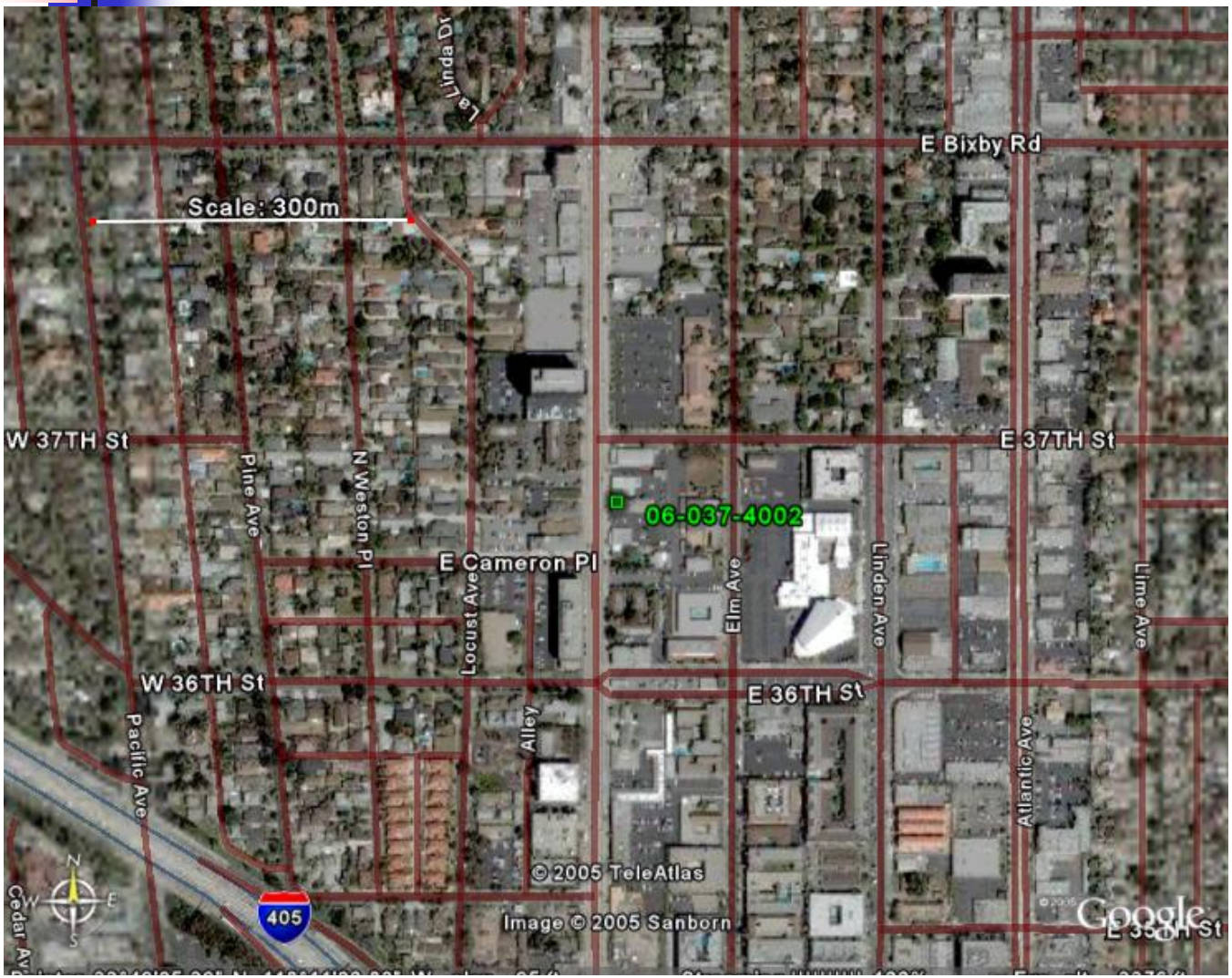
[1] (Catherine Brown, currently at EPA Region 9)

MACT – Tetrachloroethylene in Los Angeles (1 of 7)

Burbank

- Area sources of tetrachloroethylene (e.g., dry cleaners) are not visible on area maps.
- Area source emissions are not available in the Toxics Release Inventory.

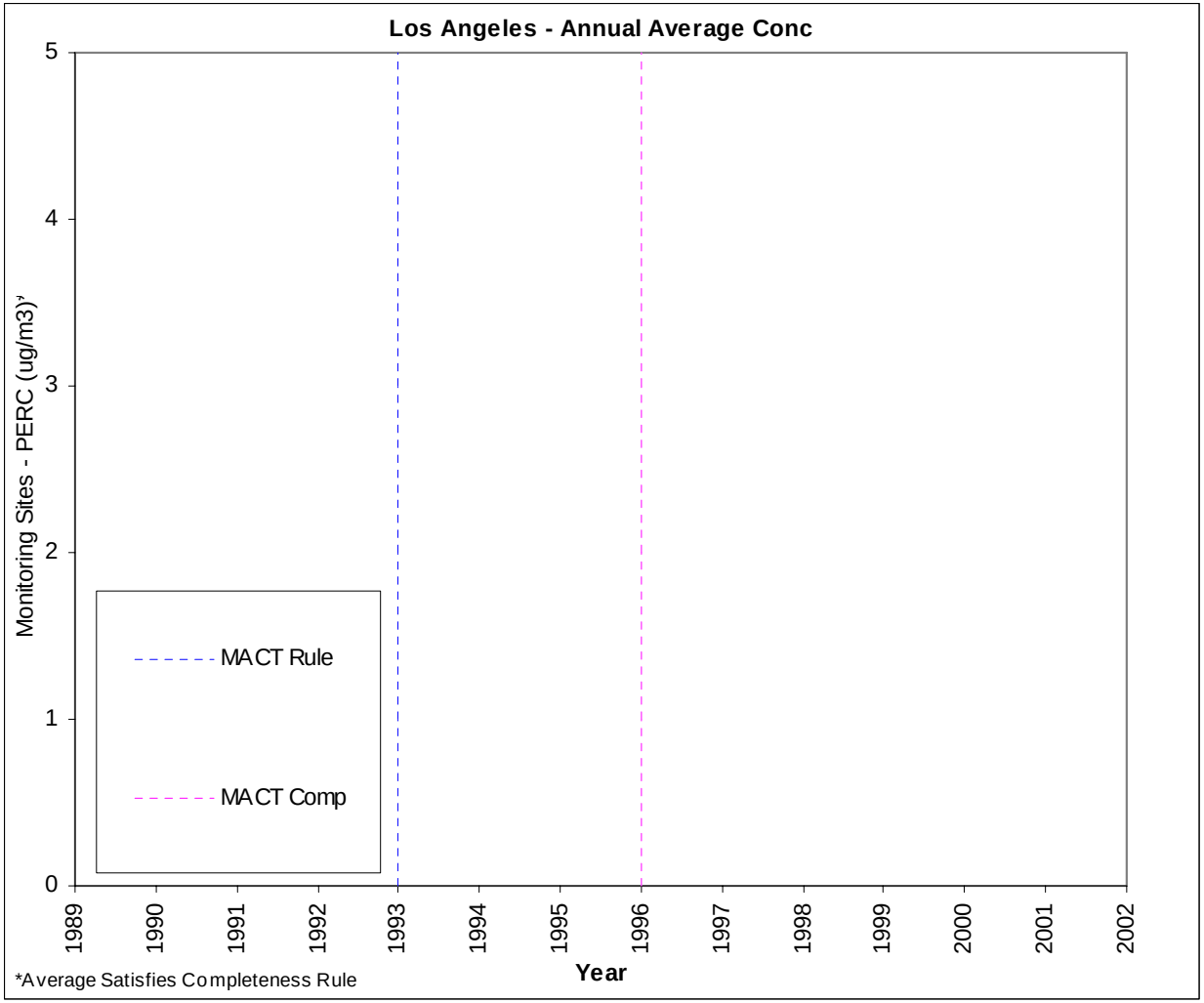
MACT – Tetrachloroethylene in Los Angeles (2 of 7)



Long Beach

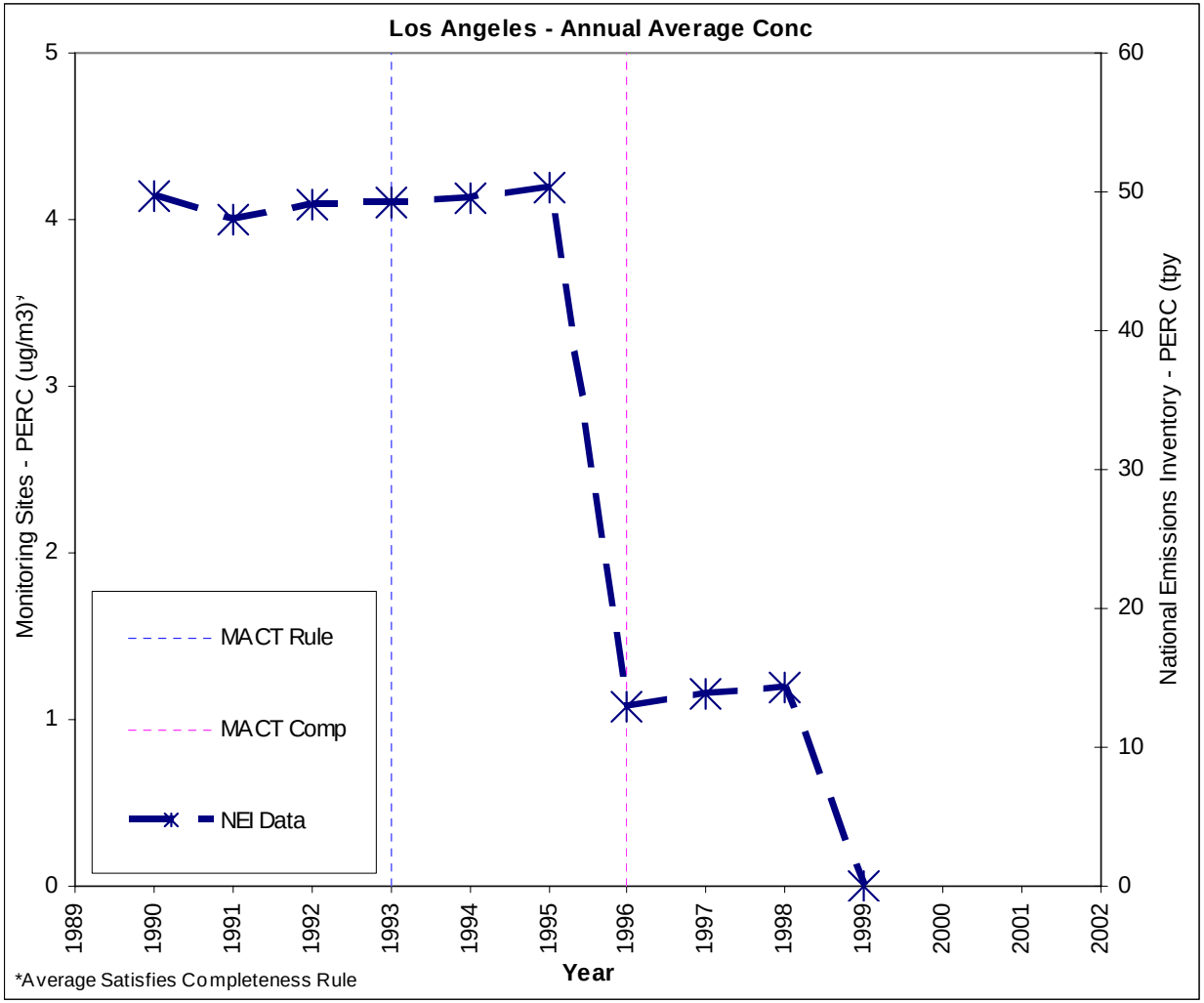
Same story.

MACT – Tetrachloroethylene in Los Angeles (3 of 7)



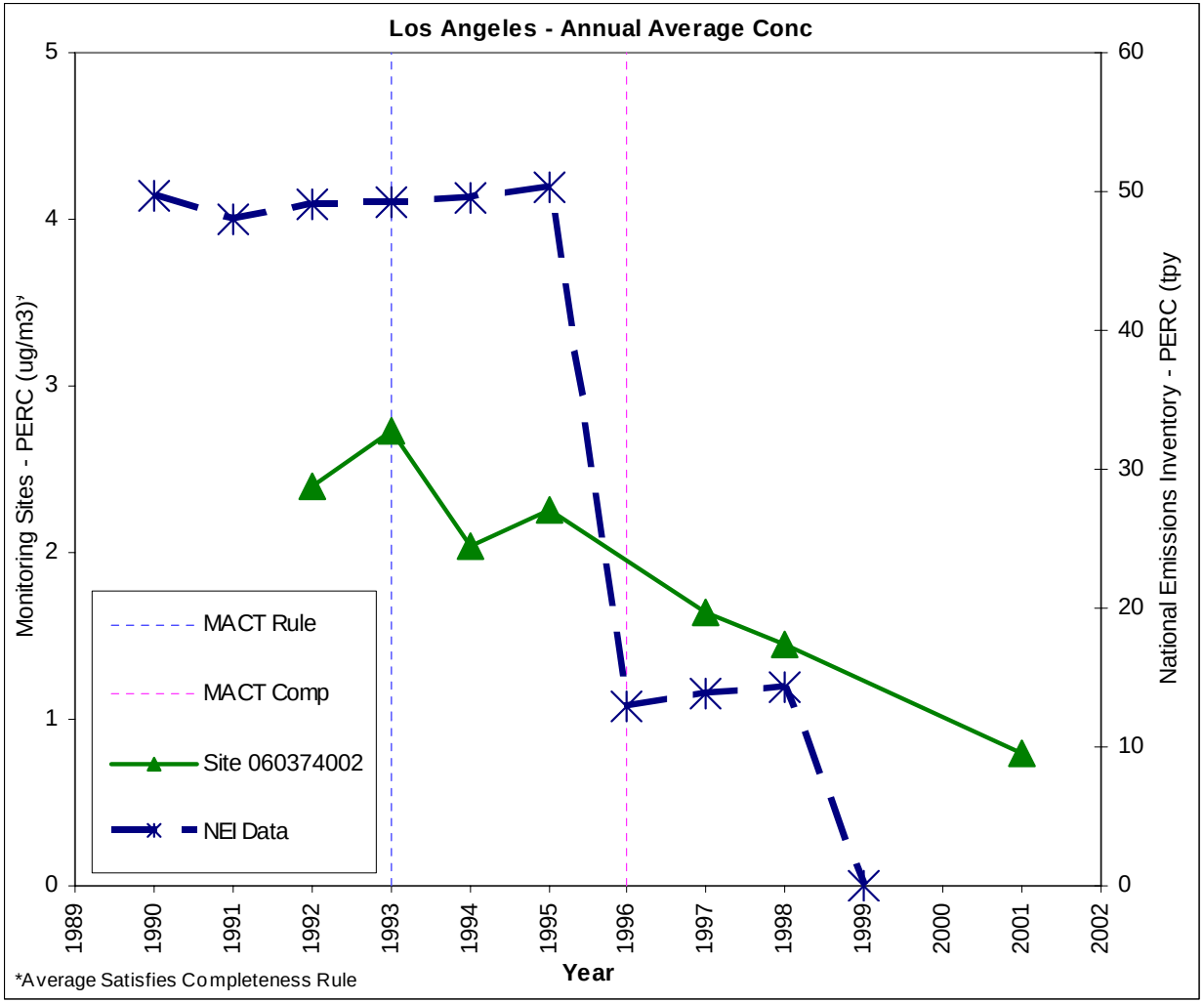
MACT regulation implementation (shown as the blue dotted line) and compliance dates (shown as the pink dotted line).

MACT – Tetrachloroethylene in Los Angeles (4 of 7)



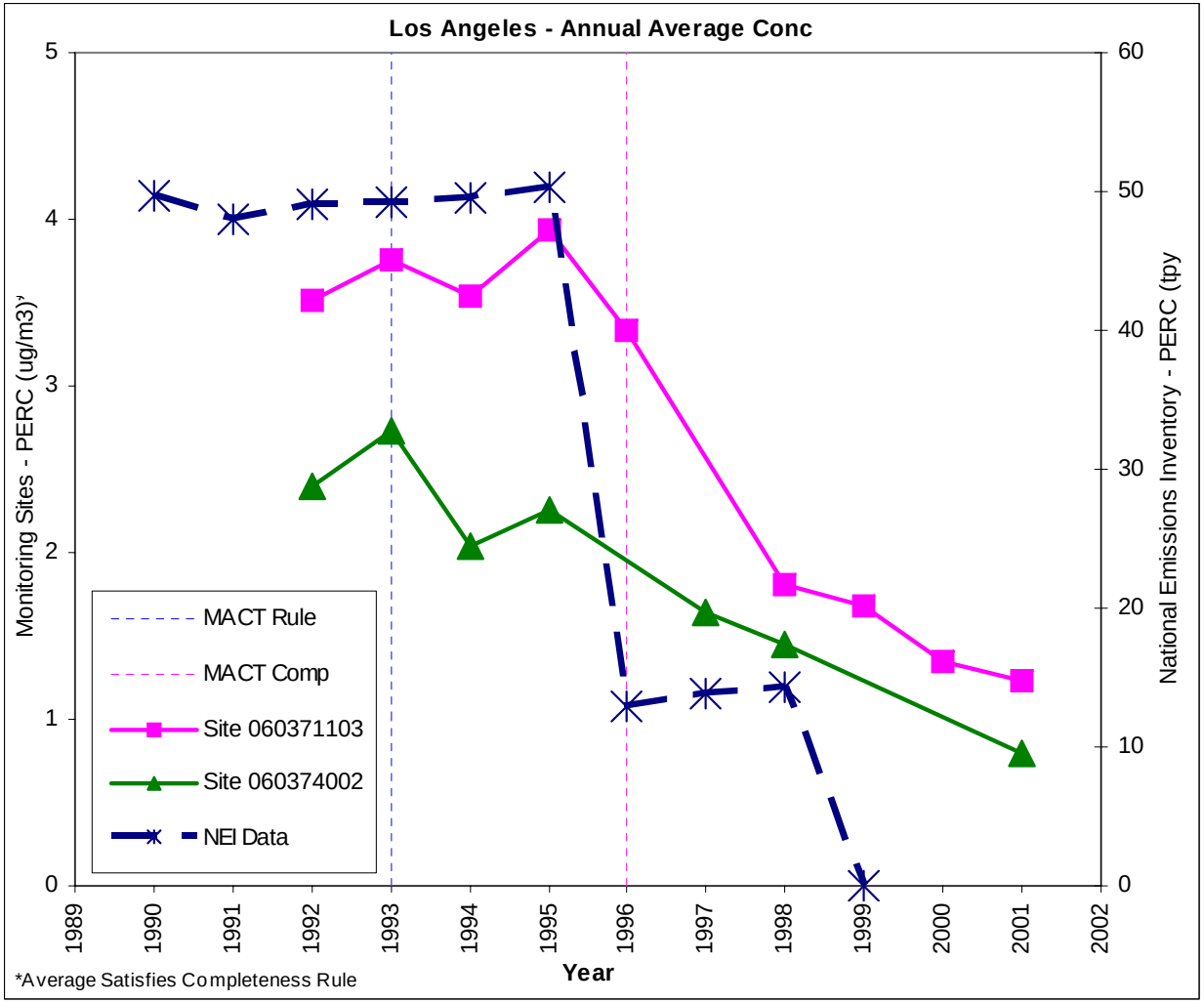
National Emission Inventory tetrachloroethylene emissions data for dry cleaners in Los Angeles county are shown as the dashed blue line.

MACT – Tetrachloroethylene in Los Angeles (5 of 7)



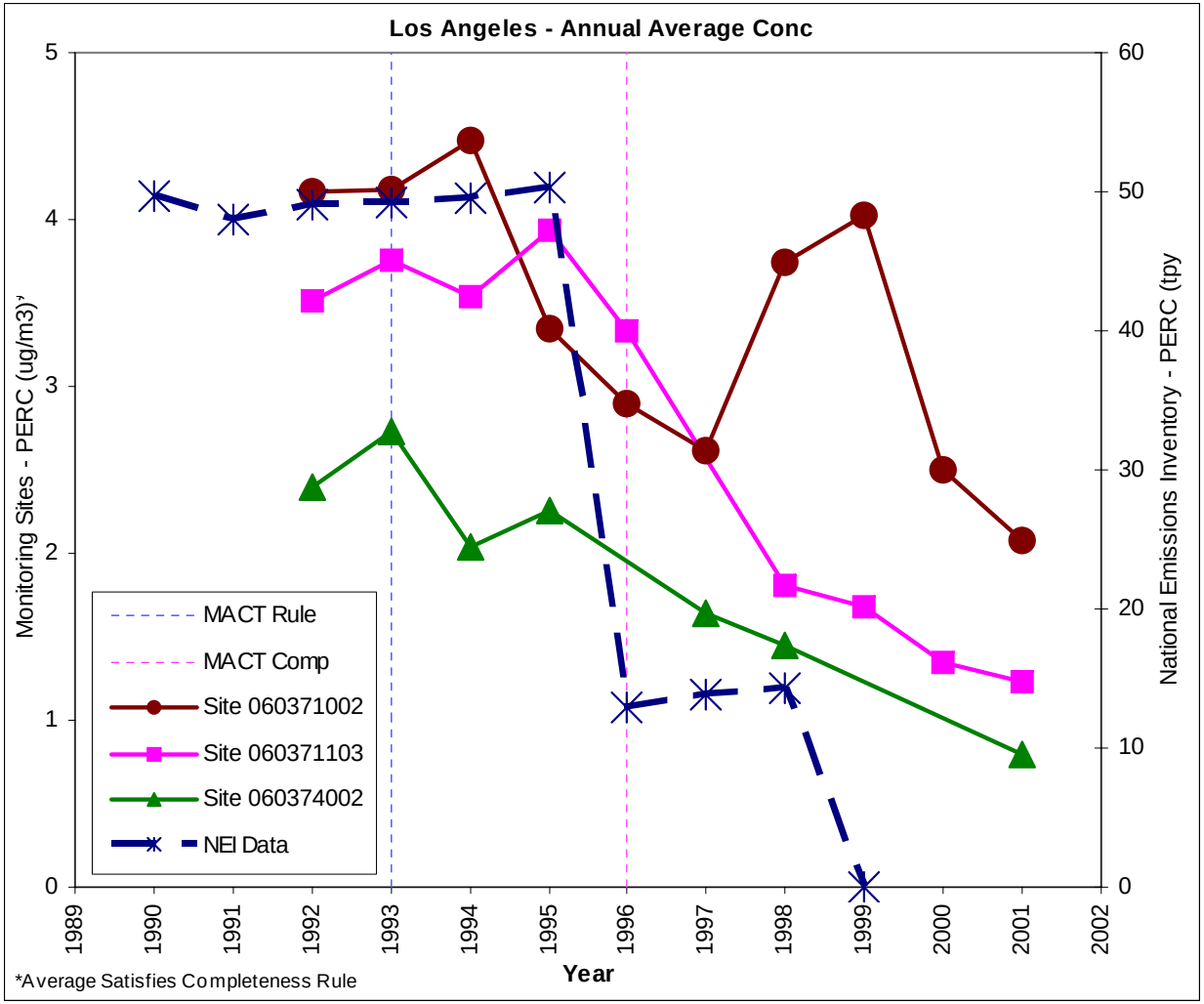
- Tetrachloroethylene concentrations at Long Beach are shown as the green line.
- Concentrations decreased over the entire time period. It is not clear that the decrease from 1993 to 1997 resulted from MACT.

MACT – Tetrachloroethylene in Los Angeles (6 of 7)



- Tetrachloroethylene concentrations at Los Angeles, North Main are shown as the pink line.
- Concentrations decreased rapidly from 1995 to 1998, which coincides with the MACT compliance dates.

MACT – Tetrachloroethylene in Los Angeles (7 of 7)



- Tetrachloroethylene concentrations at Burbank are shown as the brown line.
- Concentrations decreased rapidly from 1994 to 1997, which coincides with the MACT implementation and compliance dates.
- It is not known why concentrations increased in 1998 and 1999 before decreasing again in 2000 and 2001.

MACT – Summary and Conclusions

- Ambient concentration data are a useful tool for investigating control measures
- Trends in concentrations can be correlated with trends in emissions and MACT regulations, but cannot be verified without speciated inventories of major nearby emissions sources and local knowledge of why these changes occurred
- Necessary metadata is difficult to obtain (e.g., collocated meteorology, emissions, MACT regulations, and local knowledge)

Further investigation of MACT case studies should be performed in coordination with or by the local or state Air Quality (AQ) agencies

Acronyms

AQ	= Air Quality
MACT	= Maximum Achievable Control Technology
NATA	= National Air Toxics Assessment
PCA	= Principal component analysis
$PM_{2.5}$	= Particulate matter less than 2.5 microns
PM	= Particulate matter
tsp	= total suspended particulate
VOC	= Volatile organic compound