Temporal Trends in Air Toxics

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Big Picture Questions

- How do air toxics vary by time of day?
- How do air toxics vary by season?
- Have air toxics concentrations changed over time?

Technical Approach

Diurnal Variability

- Visual patterns
- Statistical analysis (CV, peak-to-median ratio)

Seasonal Variability

- Box whisker plots of seasonal concentrations
- Statistical quantification (CV, peak-to-median ratio)

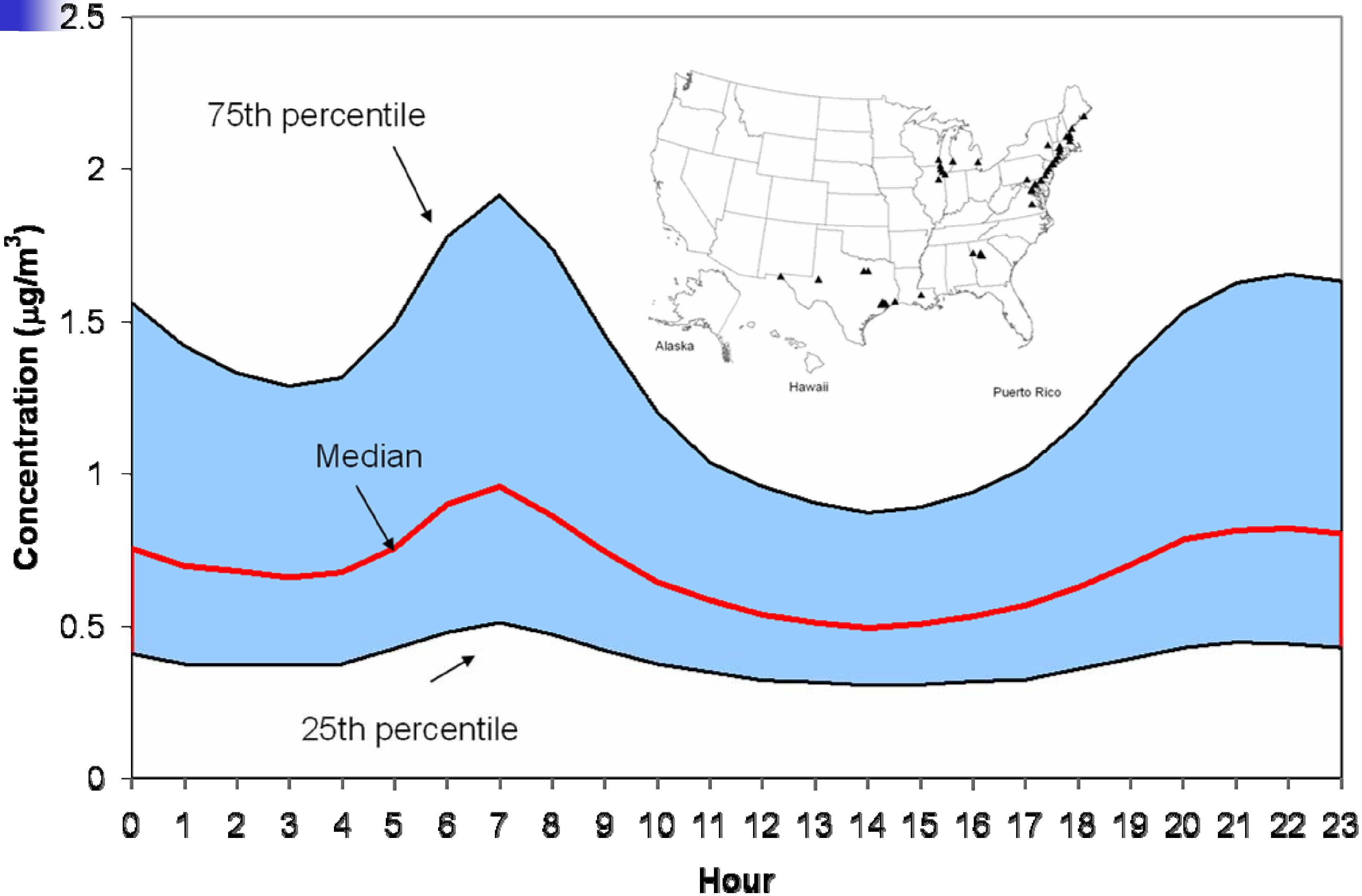
Annual Trends

- Visual analysis (national and regional)
- Linear regressions (site, regional, and national)
- Mean percentage change

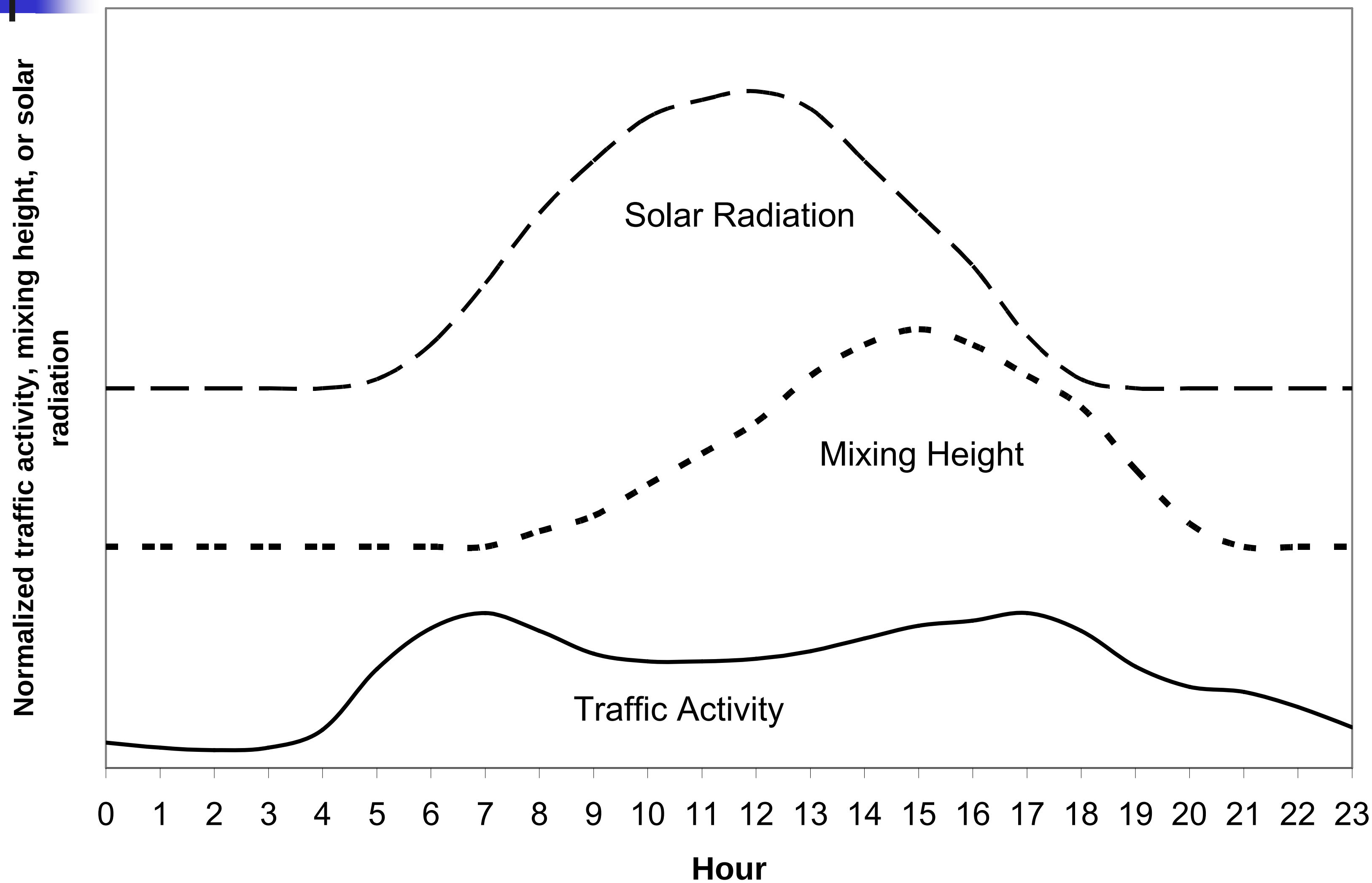
Diurnal Variability – Methods

- Available data
  - 1-hr or 3-hr sample duration
  - 14 gaseous air toxics with sufficient measurements (> 6 months of data)
  - Primarily summer data (PAMS)
- Approaches
  - Visual categorization
  - Conceptual model
  - Statistical quantification

Diurnal Pattern Identification – National Benzene



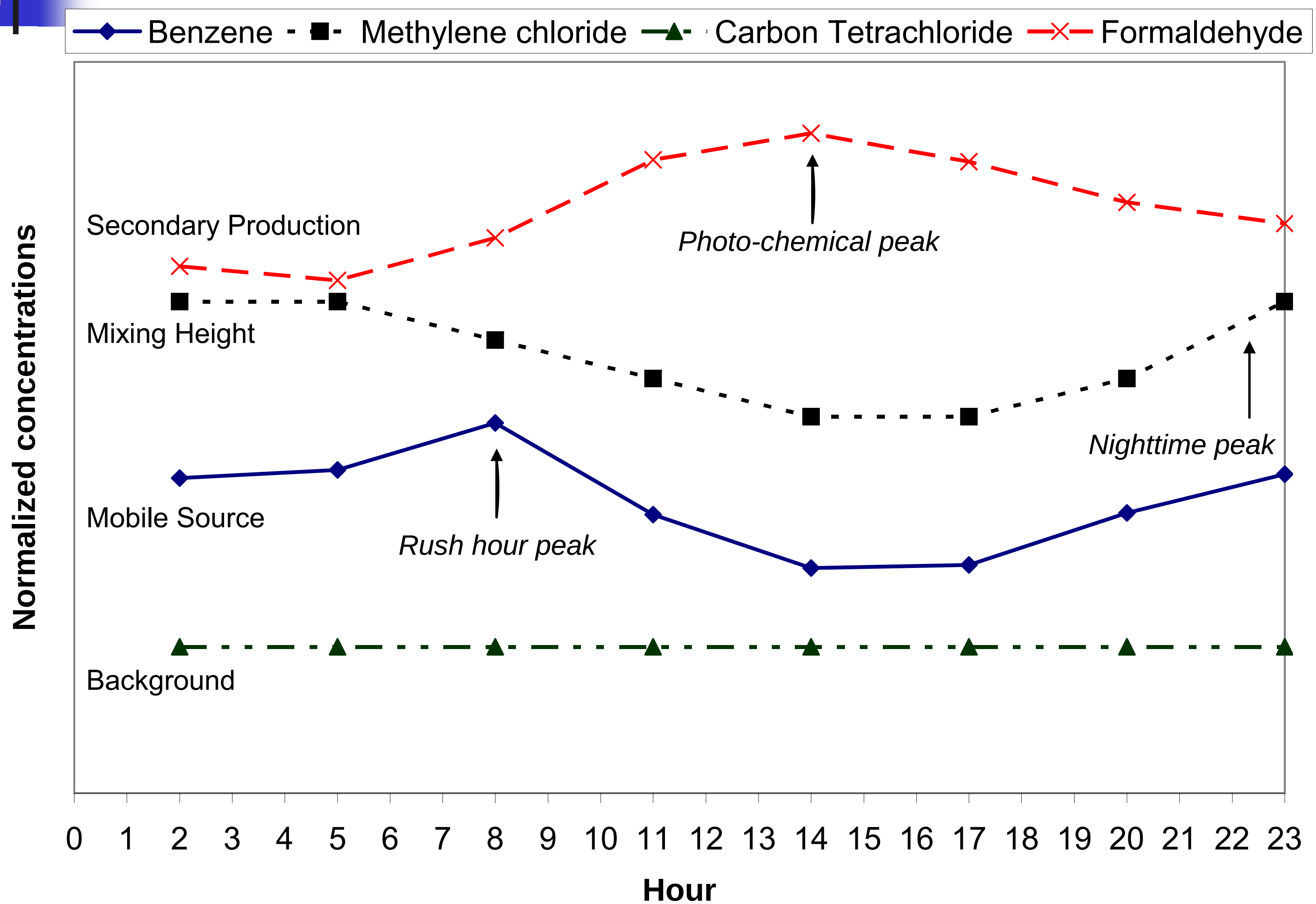
Diurnal Patterns – Key Factors



Diurnal Patterns – Conceptual Model

- Daily changes in mixing heights account for the Mixing Height pattern (i.e., higher Mixing Height, more dilution, lower concentrations)
- Emissions from mobile sources and mixing height changes account for the Mobile Source pattern
- Changes in solar radiation cause the secondary photochemistry that accounts for the Secondary Production pattern
- Background pattern concentrations are unaffected by meteorology, emissions, or transport

Diurnal Pattern Categories (1 of 2)



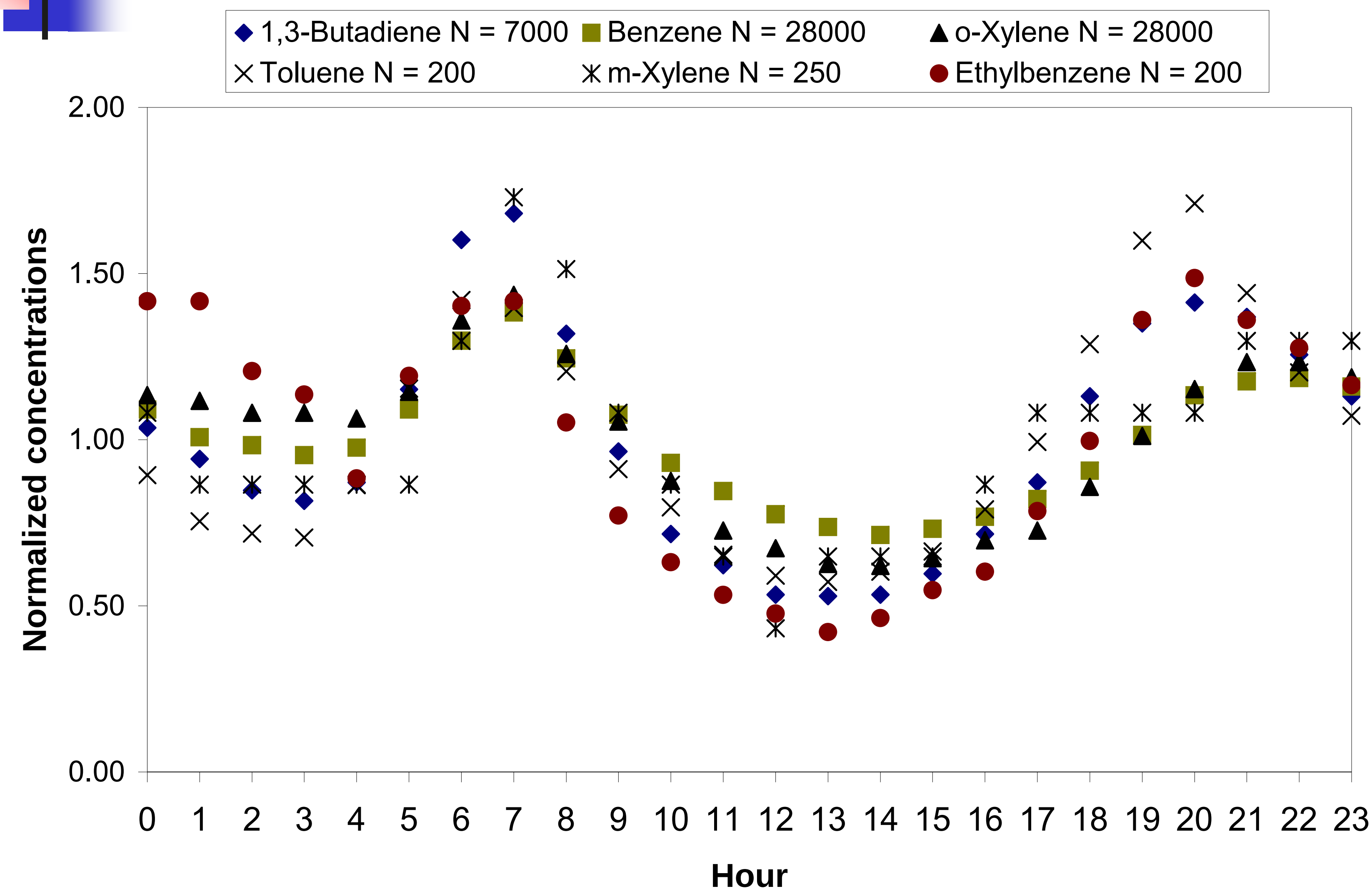
Diurnal Pattern Categories (2 of 2)

Mobile Source	Mixing Height	Secondary Production
Benzene	Methylene Chloride	Formaldehyde
o-Xylene	Chloroform	Acetaldehyde
1,3-Butadiene	Trichloroethylene	
m-Xylene		**Background**
Toluene		Carbon Tetrachloride
Ethylbenzene		

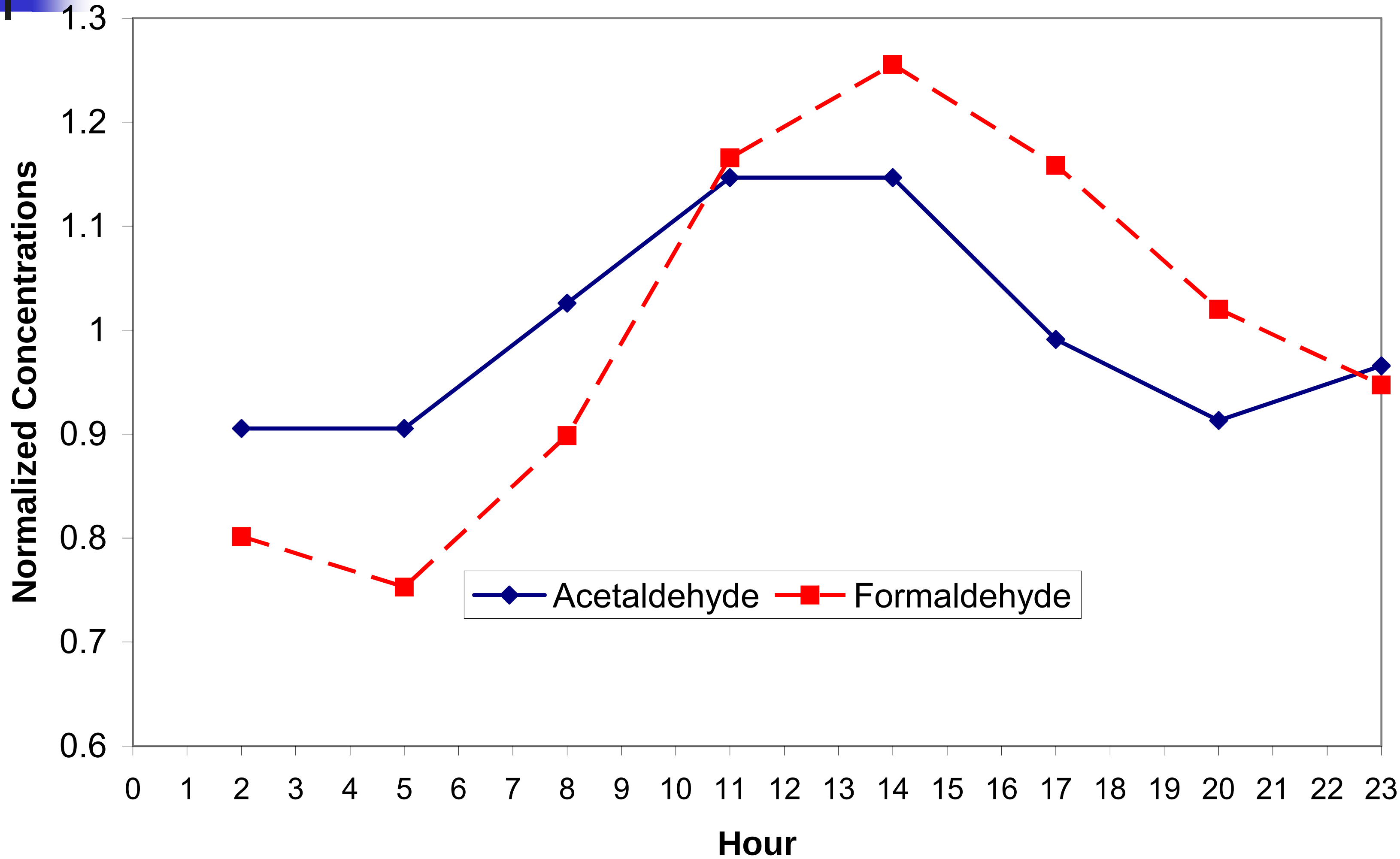
? Tetrachloroethylene ?

Mobile source-dominated
Carbonyl compounds
Chlorinated
Metals
PAHs

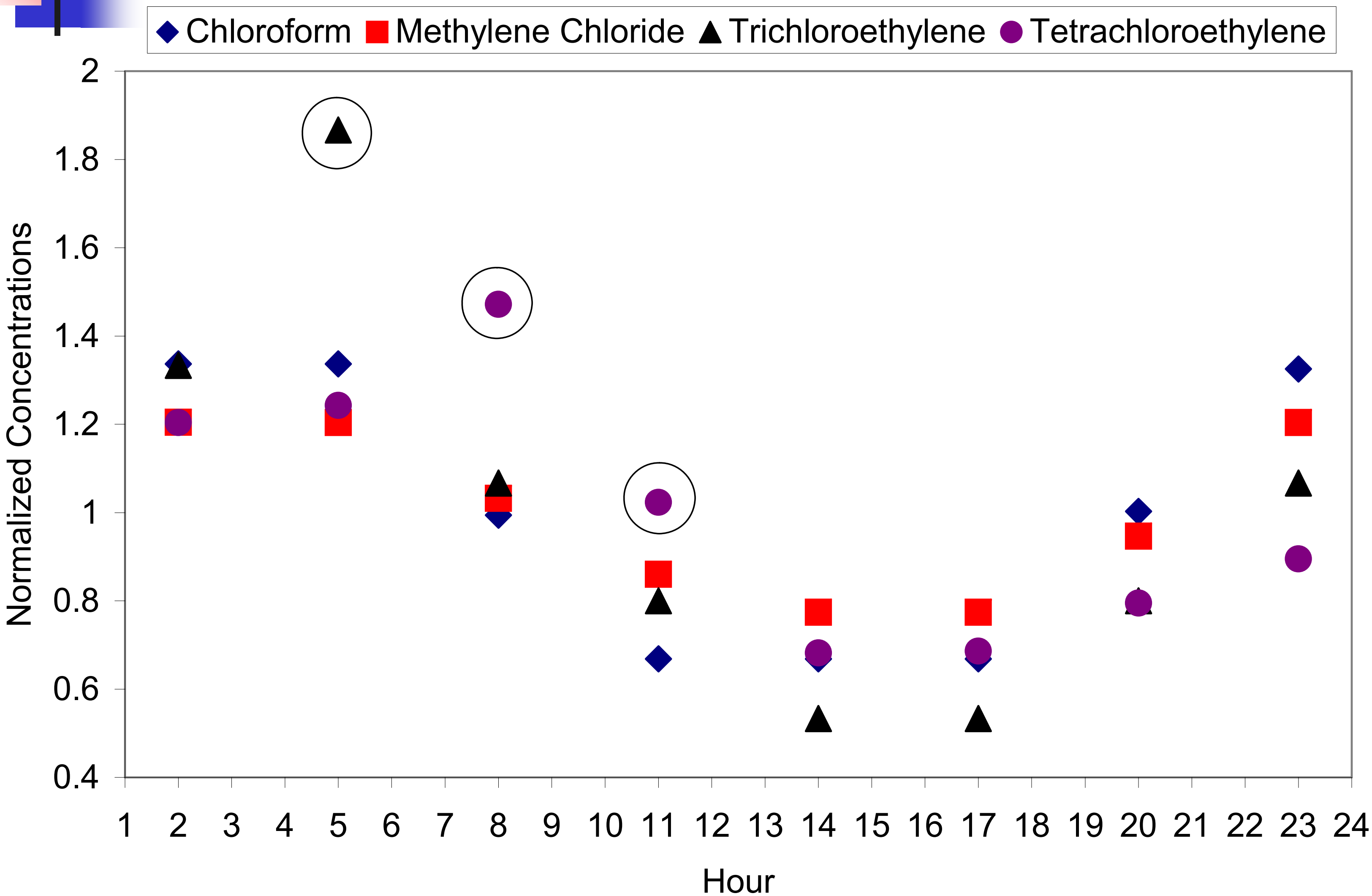
Mobile Source Pattern



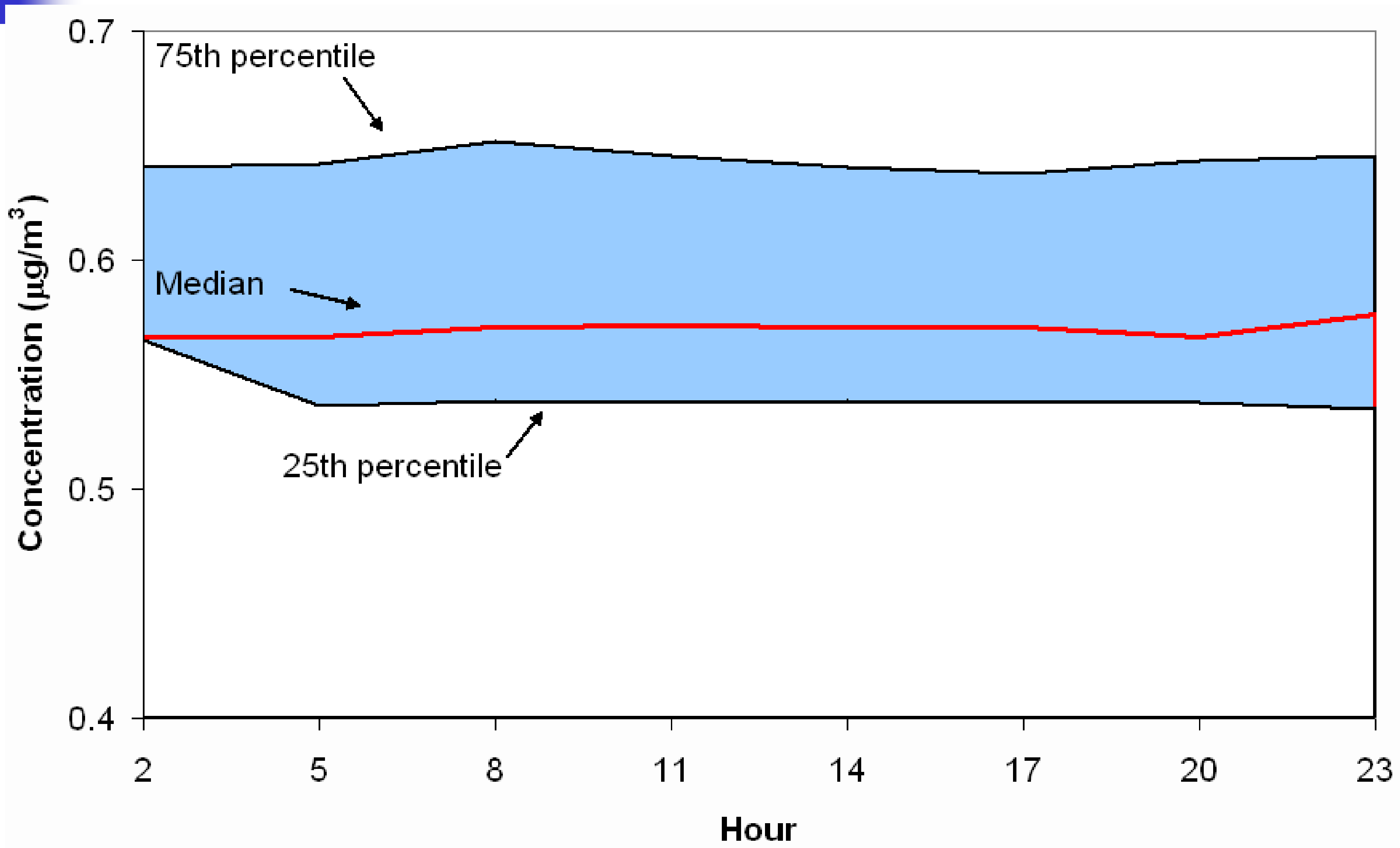
Secondary Production Pattern



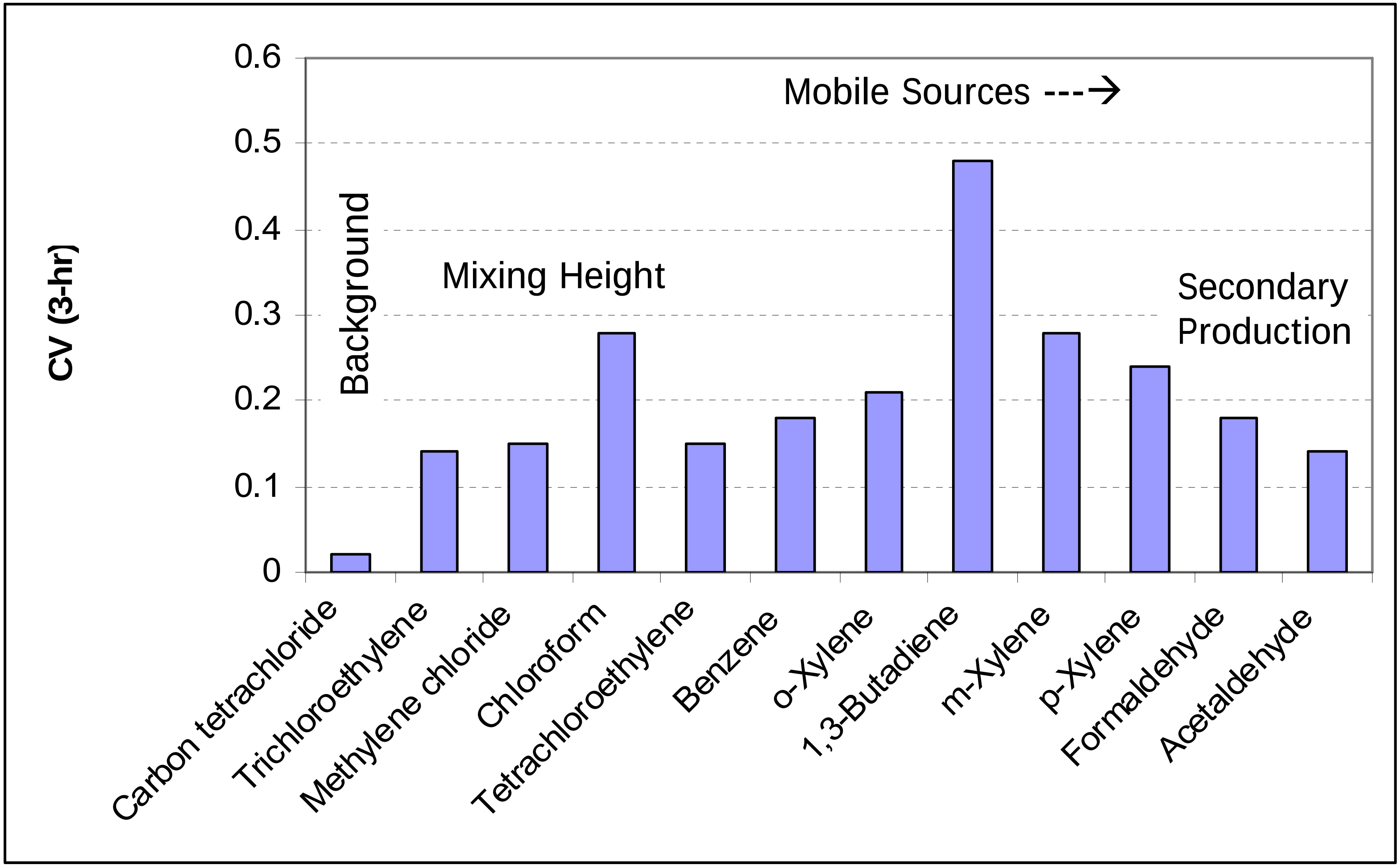
Mixing Height Pattern



Background Pattern – Carbon Tetrachloride



CVs – Diurnal Variation

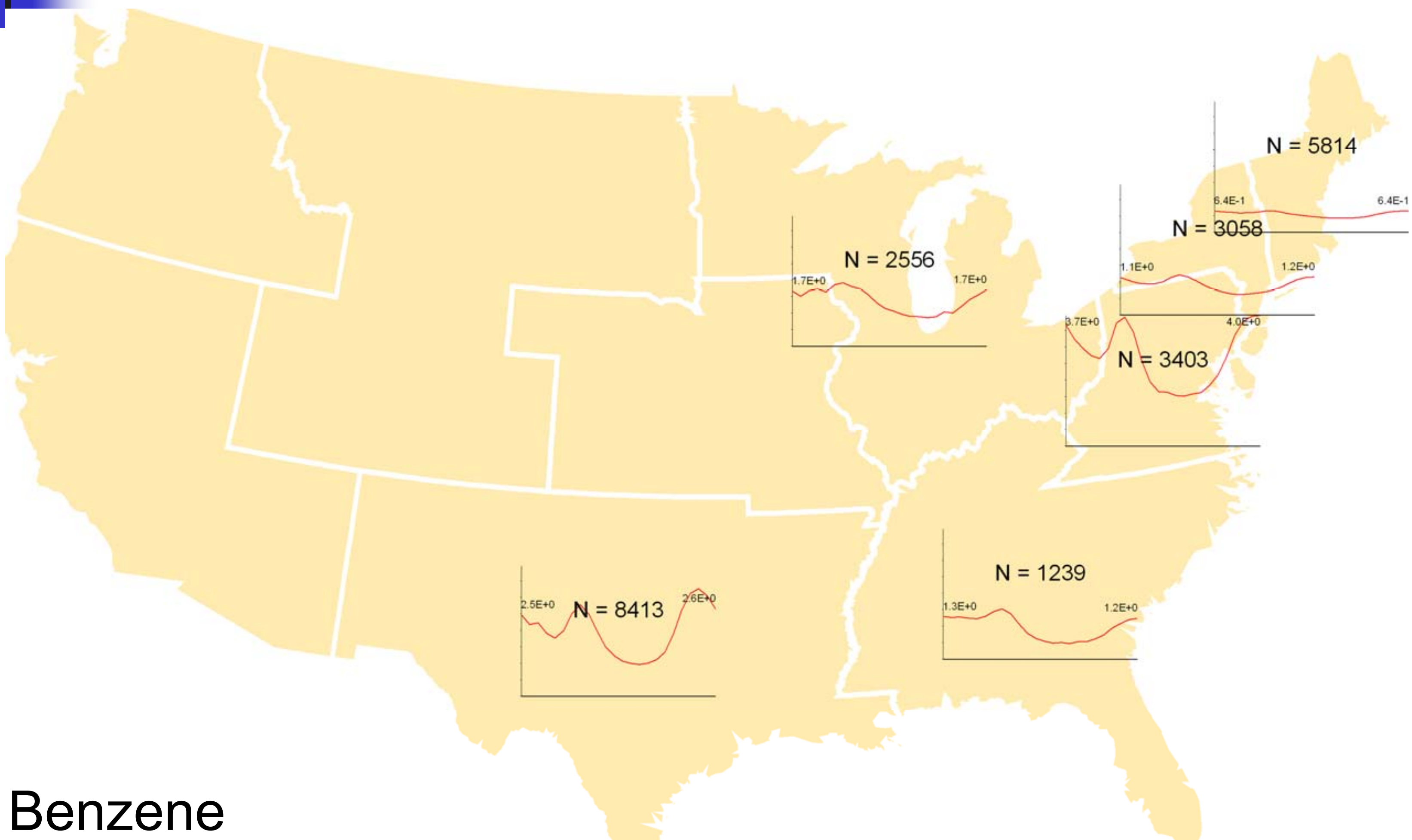


Summary Statistics – Diurnal

		1-hr		3-hr	
Species	Pattern	CV	Median (mg/m^3)	CV	Median (mg/m^3)
Carbon tetrachloride	Bkg	No Data		0.02	0.57
Trichloroethylene	MH			0.14	0.15
Methylene chloride	MH			0.15	0.27
Chloroform	MH			0.28	0.12
Tetrachloroethylene	MH or MS			0.15	0.15
Benzene	MS	0.20	0.71	0.18	0.82
o-Xylene	MS	0.27	0.32	0.21	0.50
1,3-Butadiene	MS	0.34	0.18	0.48	0.08
m-Xylene	MS	0.34	2.34	0.28	1.58
Ethylbenzene	MS	0.34	0.46	No Data	
Toluene	MS	0.34	1.79		
p-Xylene	MS	No Data		0.24	1.72
Formaldehyde	Sec	0.13	3.76	0.18	5.1
Acetaldehyde	Sec	No Data		0.14	2.98

Where:
Bkg is Background.
MH is Mixing Height.
MS is Mobile Source.
Sec is Secondary Production.

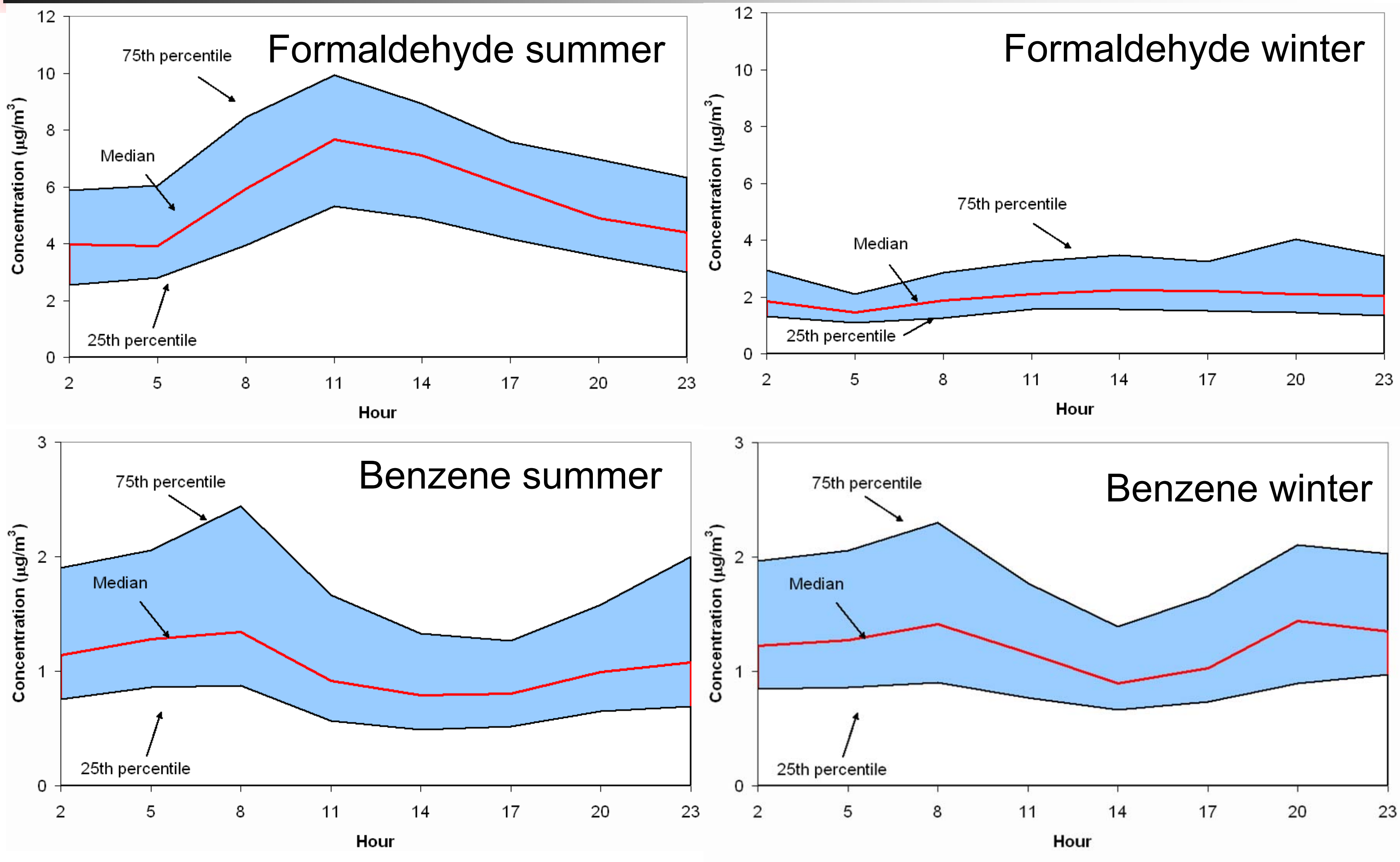
Geographical Differences?



Benzene

1-hr sample duration averages by EPA Region

Seasonal Differences?



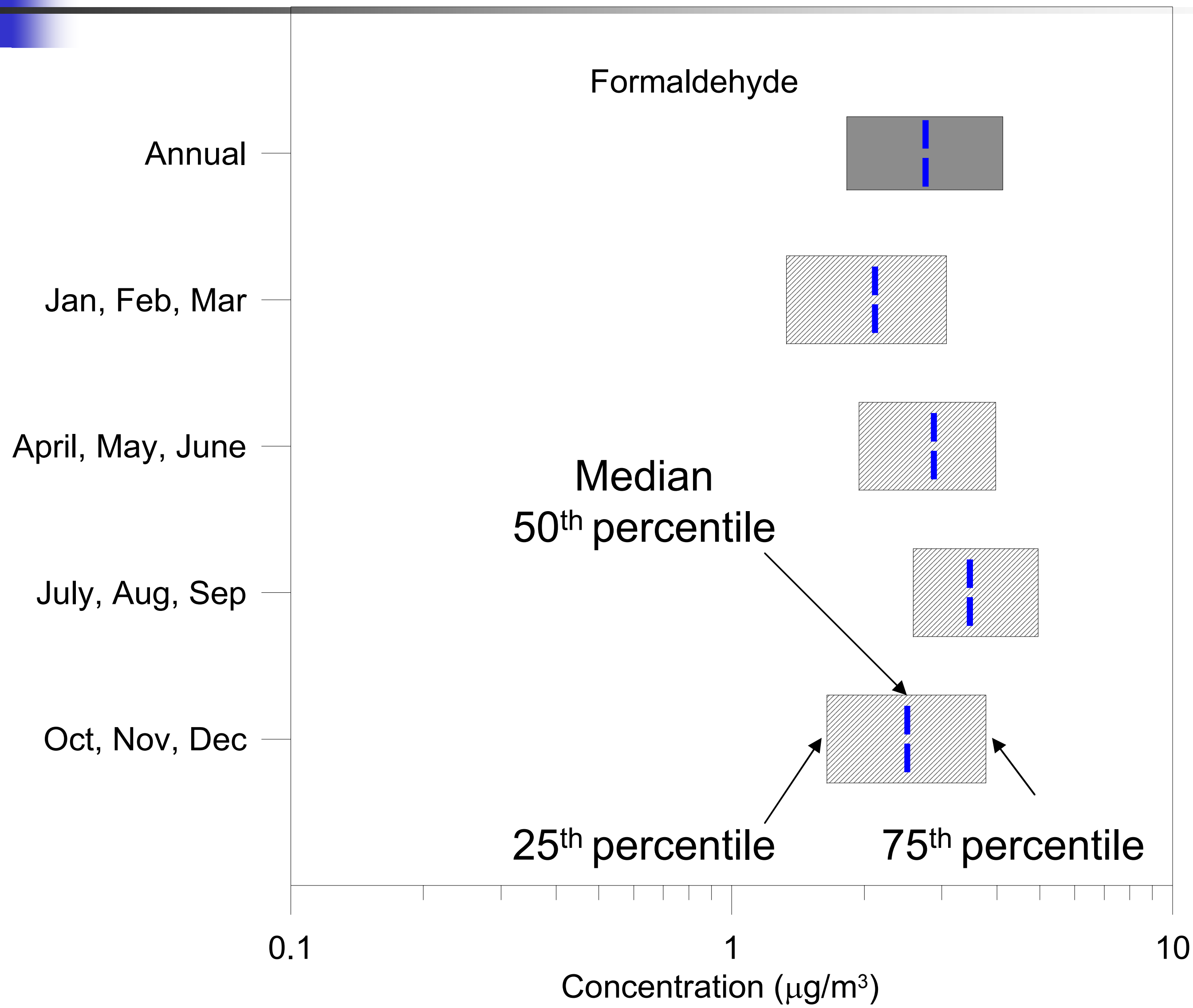
Diurnal Variability Conclusions

- Diurnal patterns have been identified and quantified.
  - Diurnal concentrations typically have a range of less than a factor of three.
  - Most HAPs diurnal patterns fit our conceptual model, which makes us confident that we can predict the diurnal patterns of other HAPs.
- Exposure models using 24-hr measurements may be able to adjust concentrations diurnally.
- Patterns may be used to adjust completeness criteria for calculating 24-hr averages from subdaily measurements.

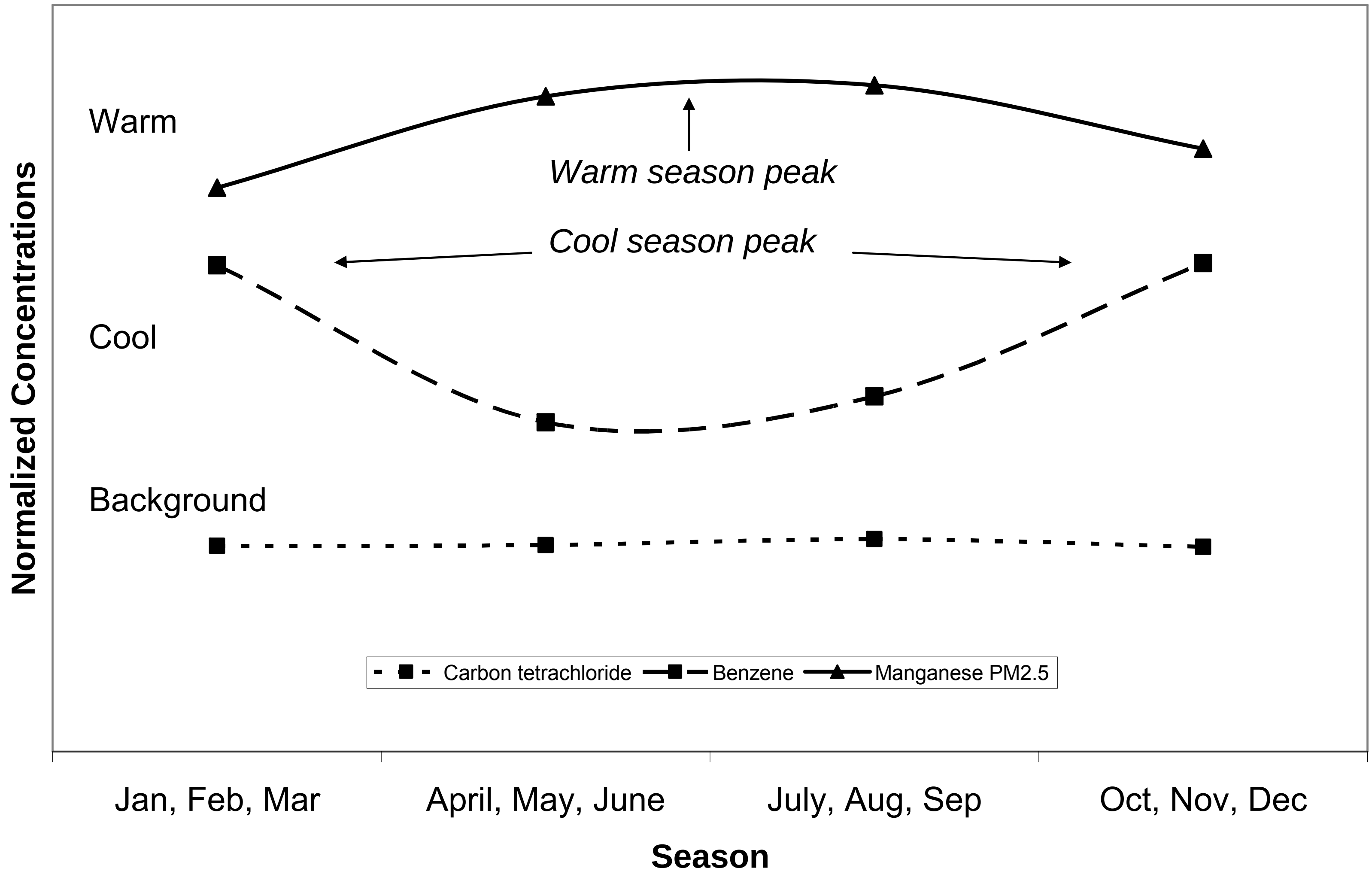
Seasonal Variations – Methods

- Available data
  - Valid seasonal average concentrations
  - Thirty-four air toxics
- Approaches
  - Visual categorization (e.g., box plots)
  - Conceptual model
  - Statistical quantification

Seasonal Pattern Identification – Formaldehyde



Seasonal Pattern Categories (1 of 2)



Seasonal Pattern Categories (2 of 2)

Warm

Formaldehyde
Acetaldehyde
Beryllium (tsp)
Nickel (tsp)
Manganese (tsp) and $PM_{2.5}$
Chromium (tsp)
Chloroform
Vinyl Chloride

Background

Carbon Tetrachloride

Cool

Indeno(1,2,3-c,d)pyrene
Benzo(b)fluoranthene
Naphthalene and *other PAHs*
Xylenes (o-, m-, and p-)
1,3-butadiene
Ethylbenzene
Benzene
Toluene
Lead $PM_{2.5}$ and (tsp)
Cadmium $PM_{2.5}$ and (tsp)
Arsenic $PM_{2.5}$
Chromium $PM_{2.5}$
Tetrachloroethylene
Methylene Chloride

Indeterminate

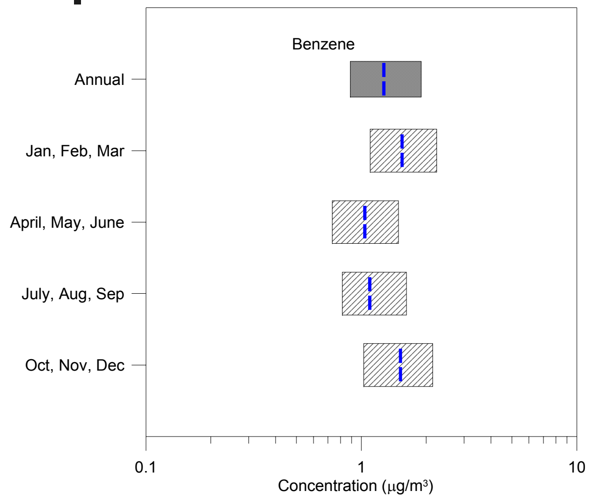
Chromium VI
Nickel $PM_{2.5}$
Arsenic (tsp)
Mercury (tsp)
Trichloroethylene

Mobile source-dominated
Carbonyl compounds
Chlorinated
Metals
PAHs

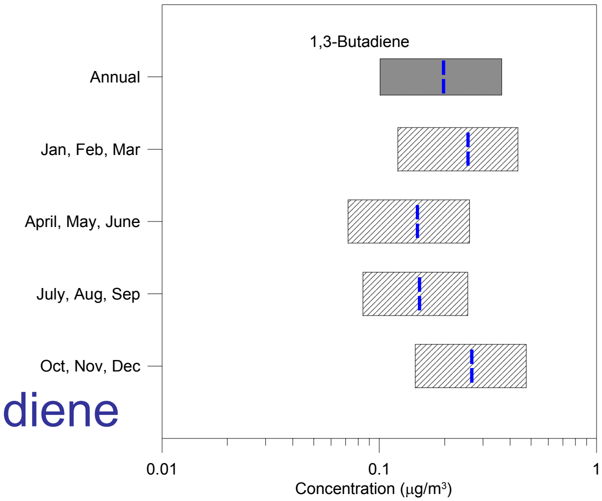
Seasonal Pattern Conceptual Model

- Cool season pattern is the default caused by meteorology
  - Mixing heights are lower in the cooler seasons; therefore, concentrations are higher
  - This pattern assumes emissions and transport are consistent throughout all seasons
- Warm season pattern = higher summer emissions, production, or transport
  - Secondary production = formaldehyde, acetaldehyde, (ozone), and $PM_{2.5}$ in the eastern half of the country
  - Emissions = higher dust due to winds and drier soil (manganese); swimming pools? = (chloroform)

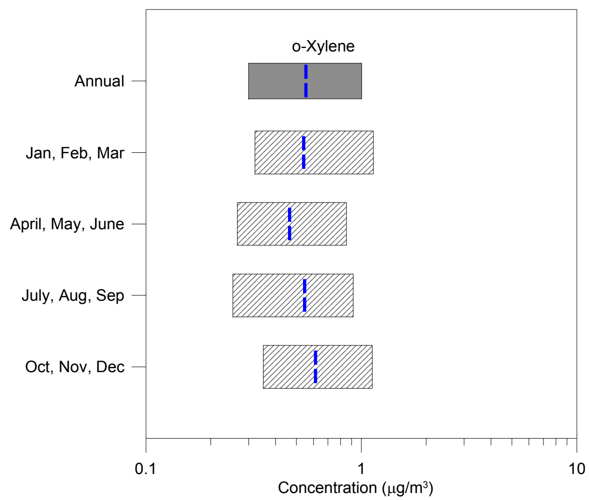
Cool Pattern Gases



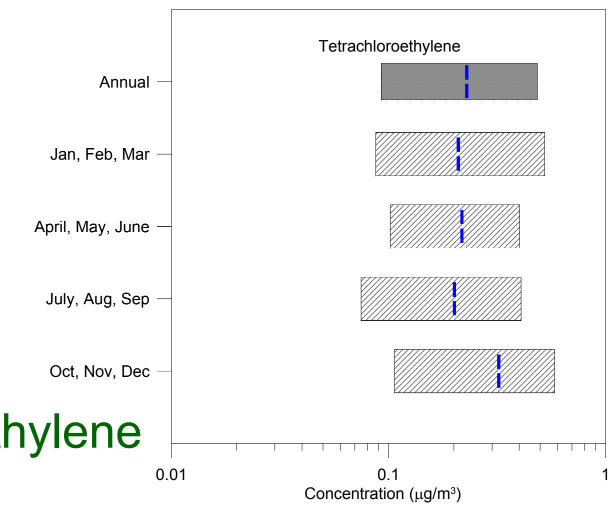
Benzene



1,3-Butadiene



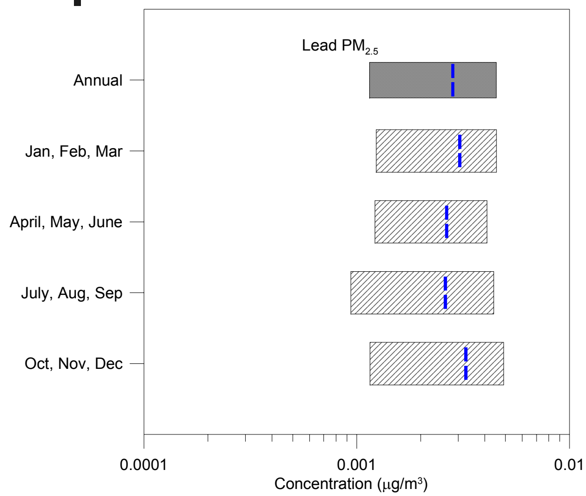
o-Xylene



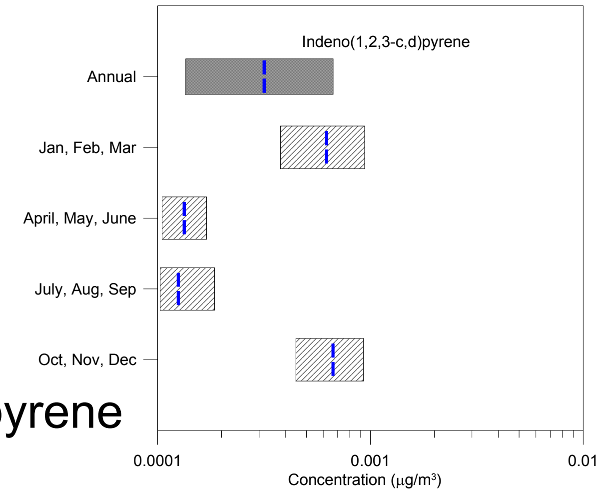
Tetrachloroethylene

Cool Pattern Metals and PAHs

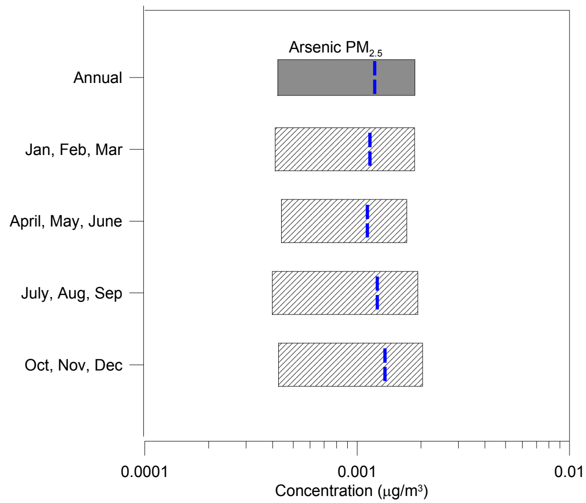
Lead $PM_{2.5}$



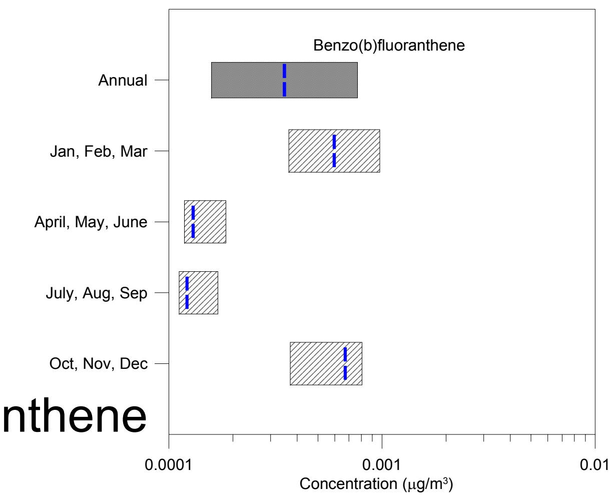
Indeno(1,2,3-c,d)pyrene



Arsenic $PM_{2.5}$

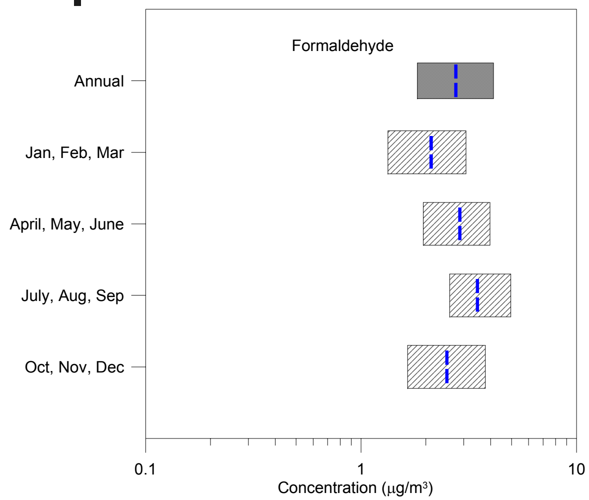


Benzo(b)fluoranthene

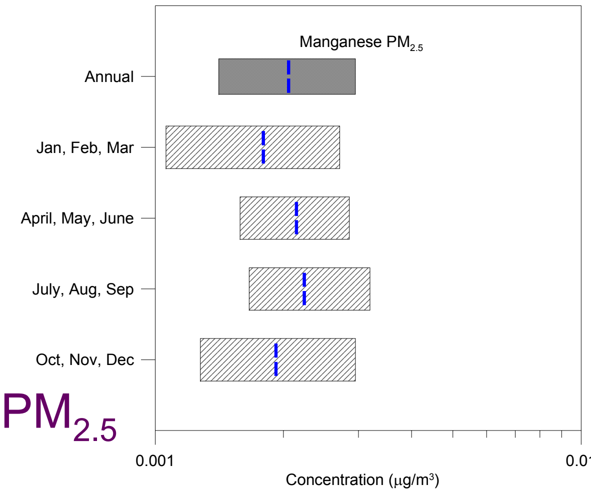


Warm Pattern and Background

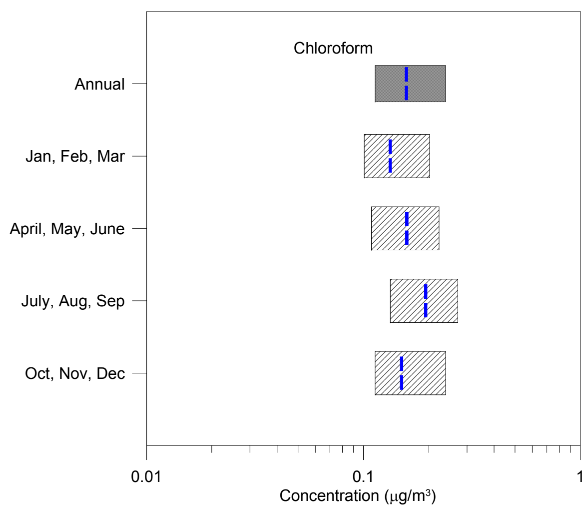
Formaldehyde



Manganese $PM_{2.5}$

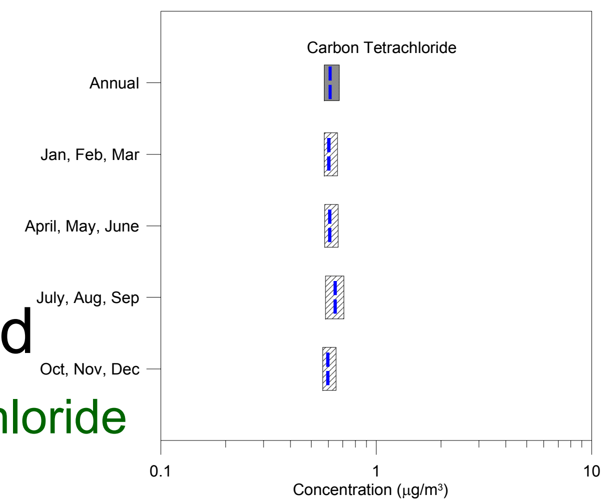


Chloroform

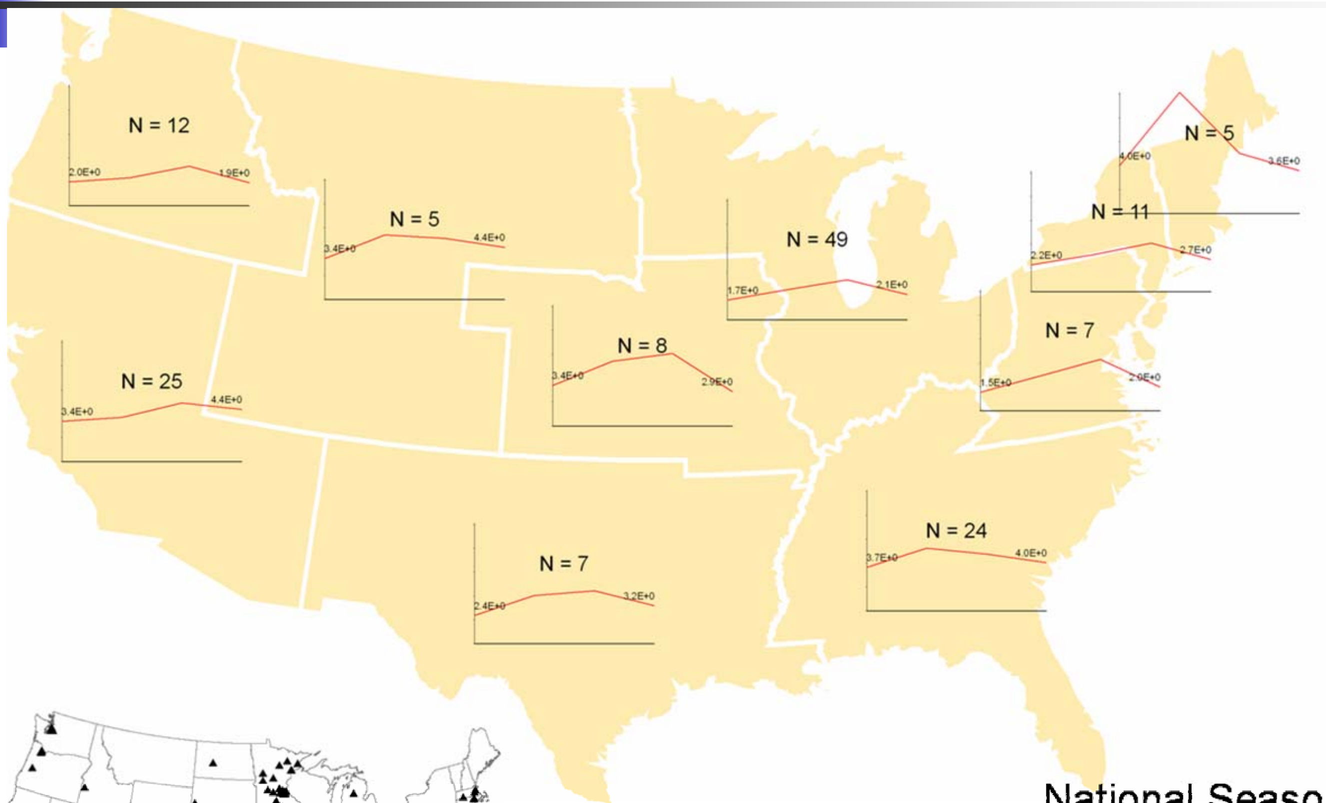


Background

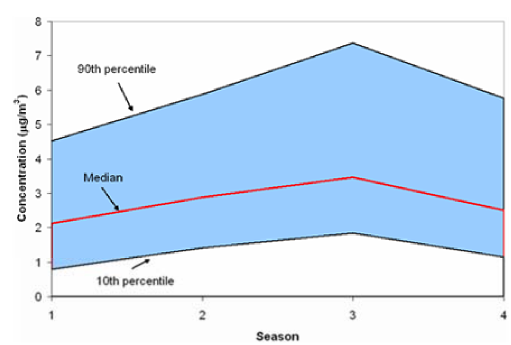
Carbon Tetrachloride



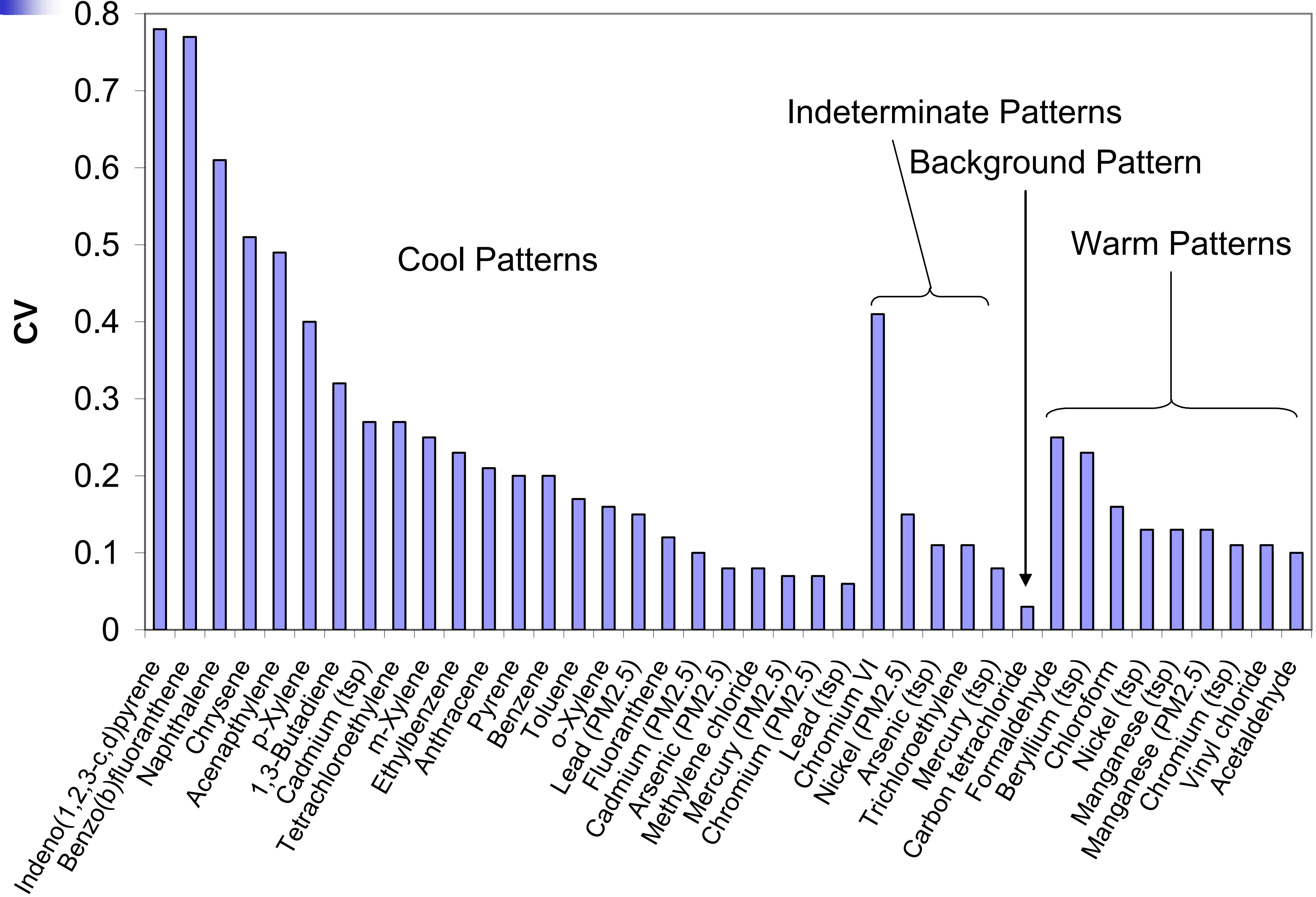
Geographic Differences – Formaldehyde



National Seasonal Pattern



CVs – Seasonal Variation



Seasonal Pattern Statistics

Species	Pattern	Variability	CV	N	Median (mg/m^3)	Max: median ratio
Indeno(1,2,3-c,d)pyrene (total PM10 and vapor)	Cool	High	0.78	133	2.0E-04	1.73
Benzo(b)fluoranthene (total PM10 and vapor)	Cool	High	0.77	69	3.6E-04	2.25
Naphthalene (total tsp and vapor)	Cool	High	0.61	28	1.7E-03	1.84
Chrysene (total tsp and vapor)	Cool	High	0.51	9	1.3E-04	2.11
Acenapthylene (total tsp and vapor)	Cool	High	0.49	6	1.1E-03	1.96
p-Xylene	Cool	High	0.40	28	2.4E+00	1.56
1,3-Butadiene	Cool	High	0.32	553	2.0E-01	1.35
Cadmium (tsp)	Cool	High	0.27	117	1.0E-03	1.45
Tetrachloroethylene	Cool	High	0.27	538	2.3E-01	1.51
m-Xylene	Cool	High	0.25	28	1.3E+00	1.10
Ethylbenzene	Cool	High	0.23	53	3.3E-01	1.22
Anthracene (total tsp and vapor)	Cool	High	0.21	9	3.8E-04	1.37
Pyrene (total tsp and vapor)	Cool	High	0.20	9	7.1E-04	1.29
Benzene	Cool	High	0.20	901	1.3E+00	1.19
Toluene	Cool	Medium	0.17	47	2.3E+00	1.17
o-Xylene	Cool	Medium	0.16	759	5.5E-01	1.21
Lead (PM2.5)	Cool	Medium	0.15	1508	2.8E-03	1.21
Fluoranthene (total PM10 and vapor)	Cool	Medium	0.12	9	9.4E-04	1.17

Table cutoff due to size. Please see McCarthy et al., 2005, Temporal Variability of Selected Air Toxics: A National Perspective. See the EPA web site for complete table.

Seasonal Variability Conclusions

- Seasonal patterns have been identified and quantified
  - Seasonal average concentrations typically have a range of less than a factor of two
  - Most HAPs seasonal patterns fit with our conceptual model, which makes us confident that we can predict the seasonal patterns of other HAPs
- Exposure models using annual averages may be able to adjust concentrations for seasonal variations
- Patterns may be used to adjust completeness criteria for calculating annual averages from seasonal averages

Annual Trends – Approach

- Available data
  - Annual averages were used from primarily urban sites
  - Fifteen air toxics had sufficient data
- Approach
  - Visual and statistical analysis of trends over three trend periods: 1990-2003, 1995-2003, and 1998-2003
  - Trend completeness: 75% of years required at a given site (e.g., 5 of 6 years between 1998 and 2005) to be included (and investigated other cut-offs)
  - National, regional, and individual site trends

Why Three Trend Periods?

Tradeoff between the length of record and the number of sites available

<u>1990 to 2003</u>

- Longest trend record
- Fewest sites
- Benzene: 8 sites

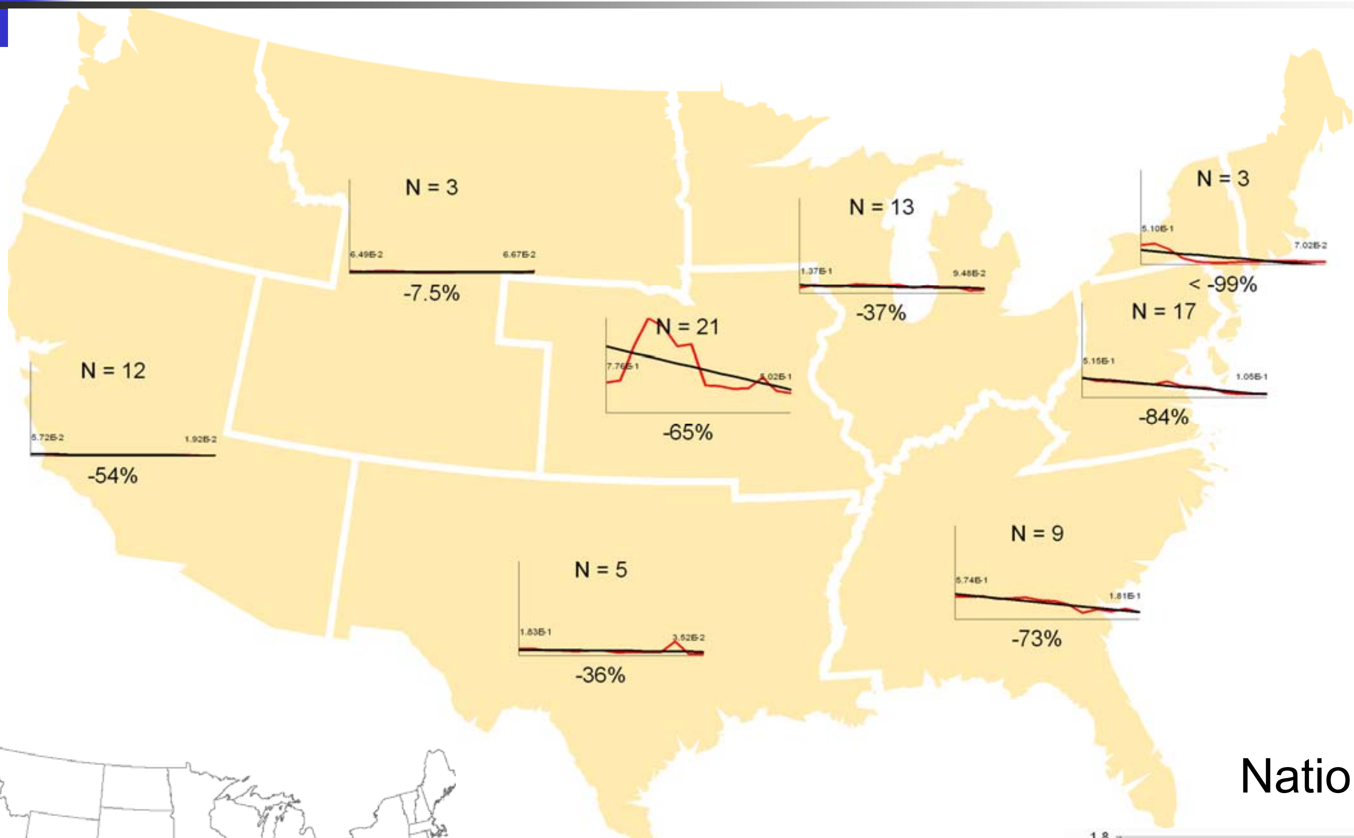
<u>1995 to 2003</u>

- Medium trend record
- Medium number of sites
- Benzene: 24 sites

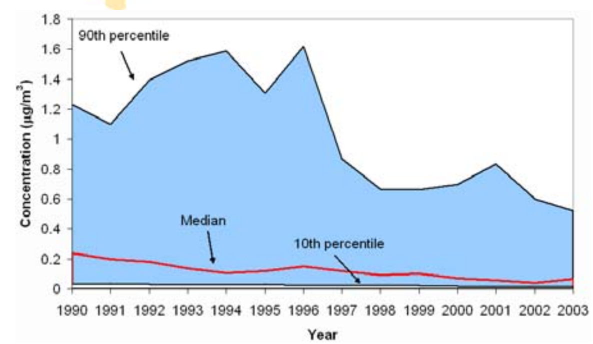
<u>1998 to 2003</u>

- Short trend record
- Largest number of sites
- Benzene: 33 sites

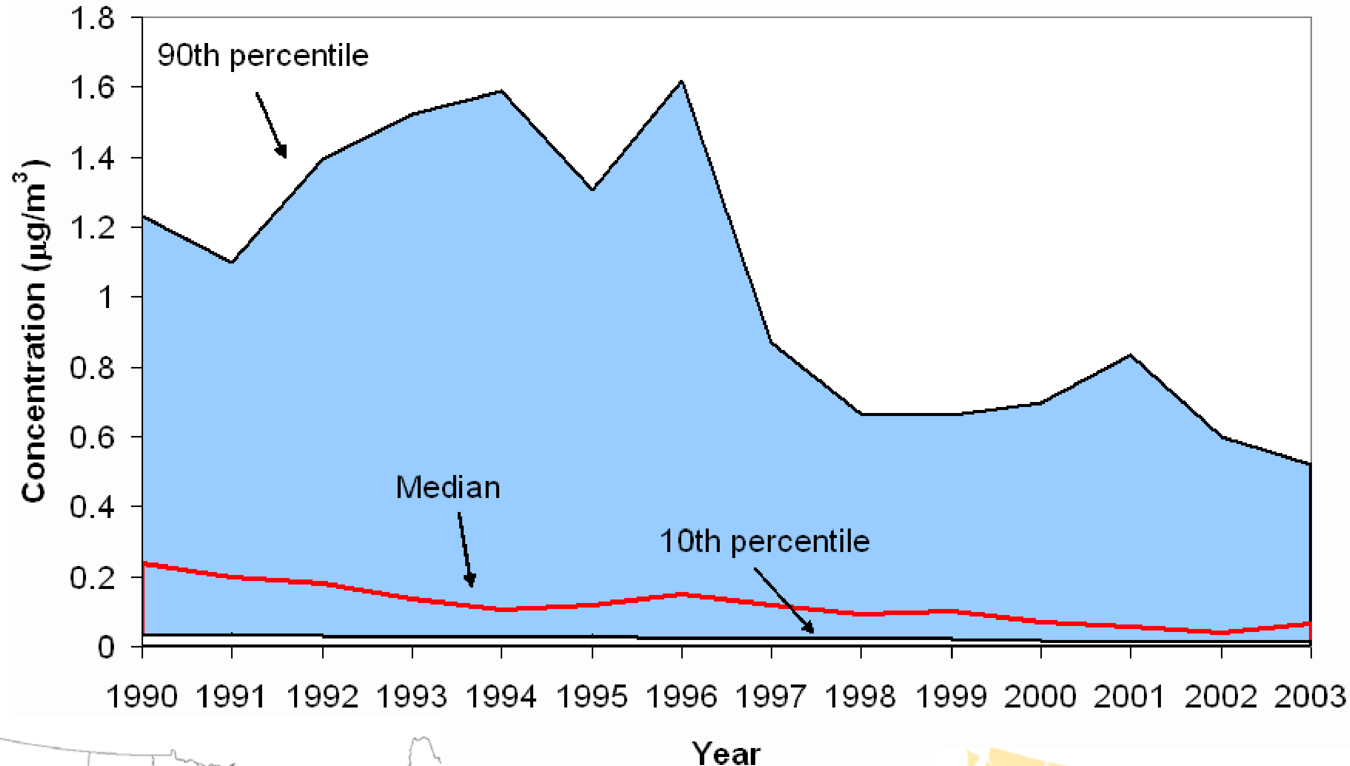
Lead (tsp) 1990 to 2003 – Regional Differences

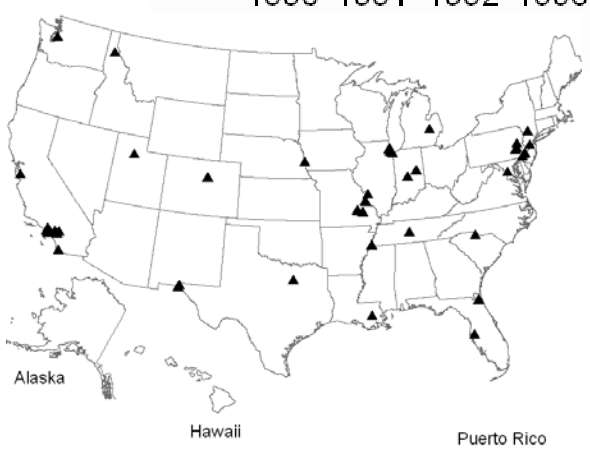


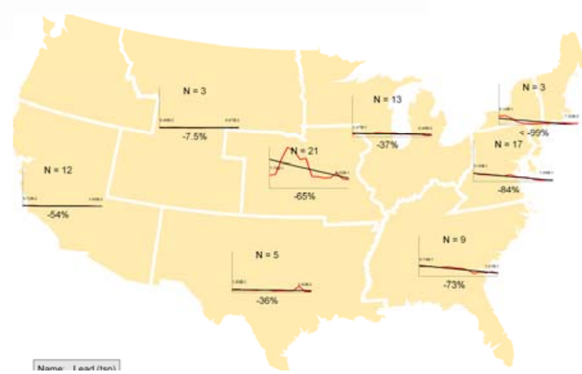
National Trend



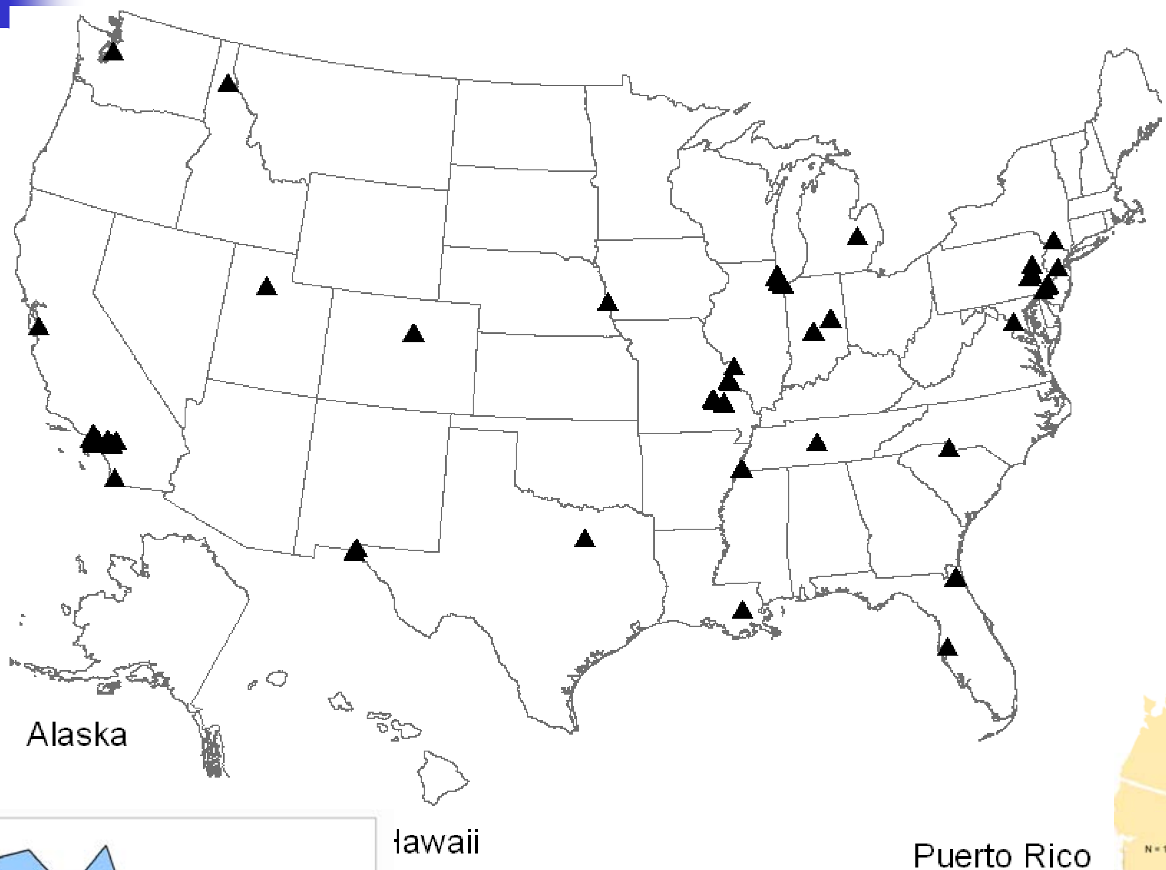
Lead (tsp) 1990 to 2003 – National Picture

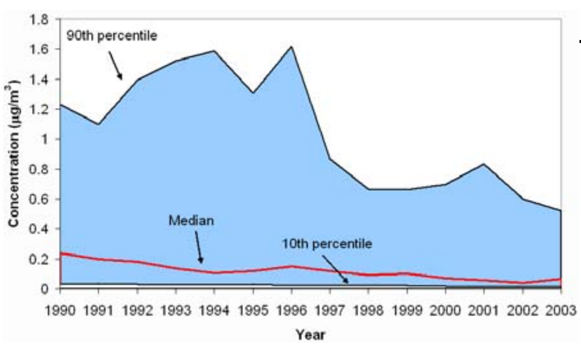


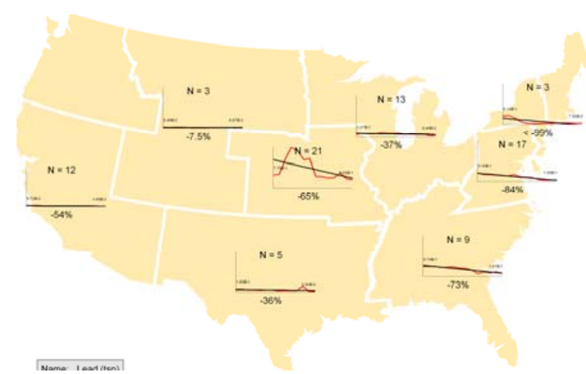




Lead (tsp) 1990 to 2003 – Site locations

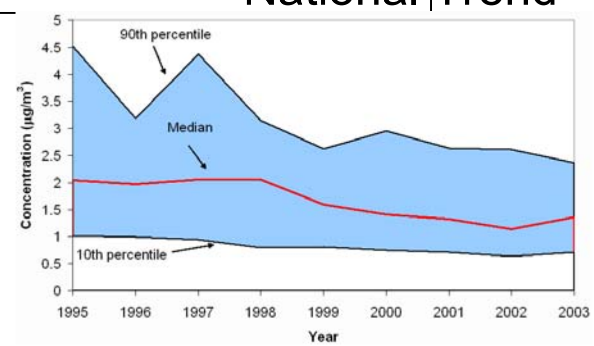




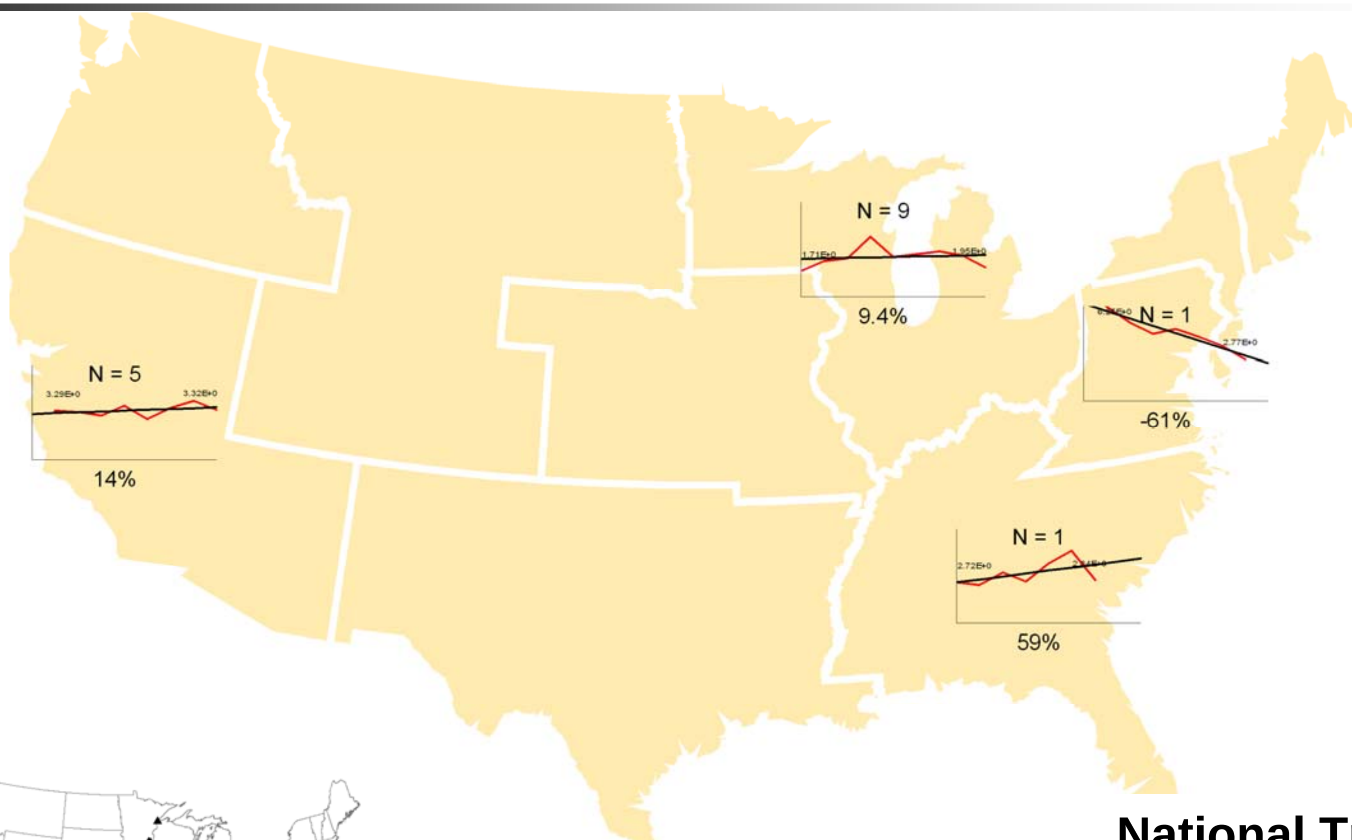


Combined Picture – Benzene 1995 to 2003

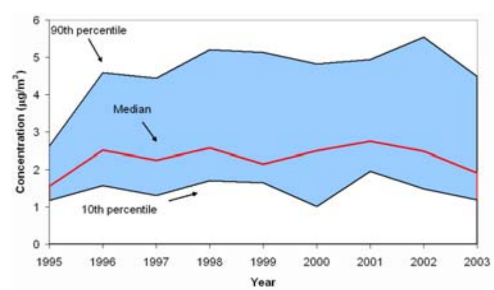
National Trend



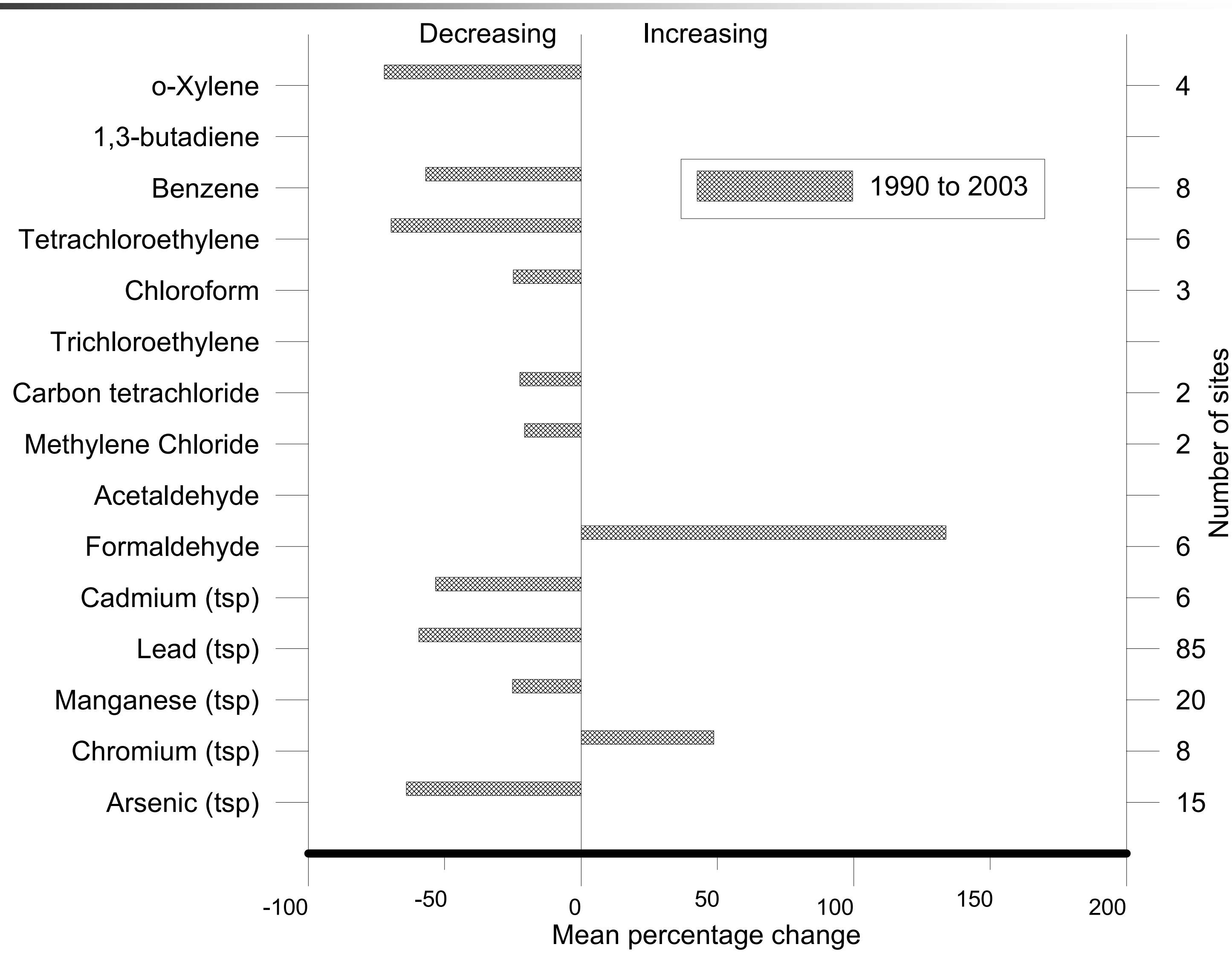
Combined Picture – Formaldehyde 1995 to 2003



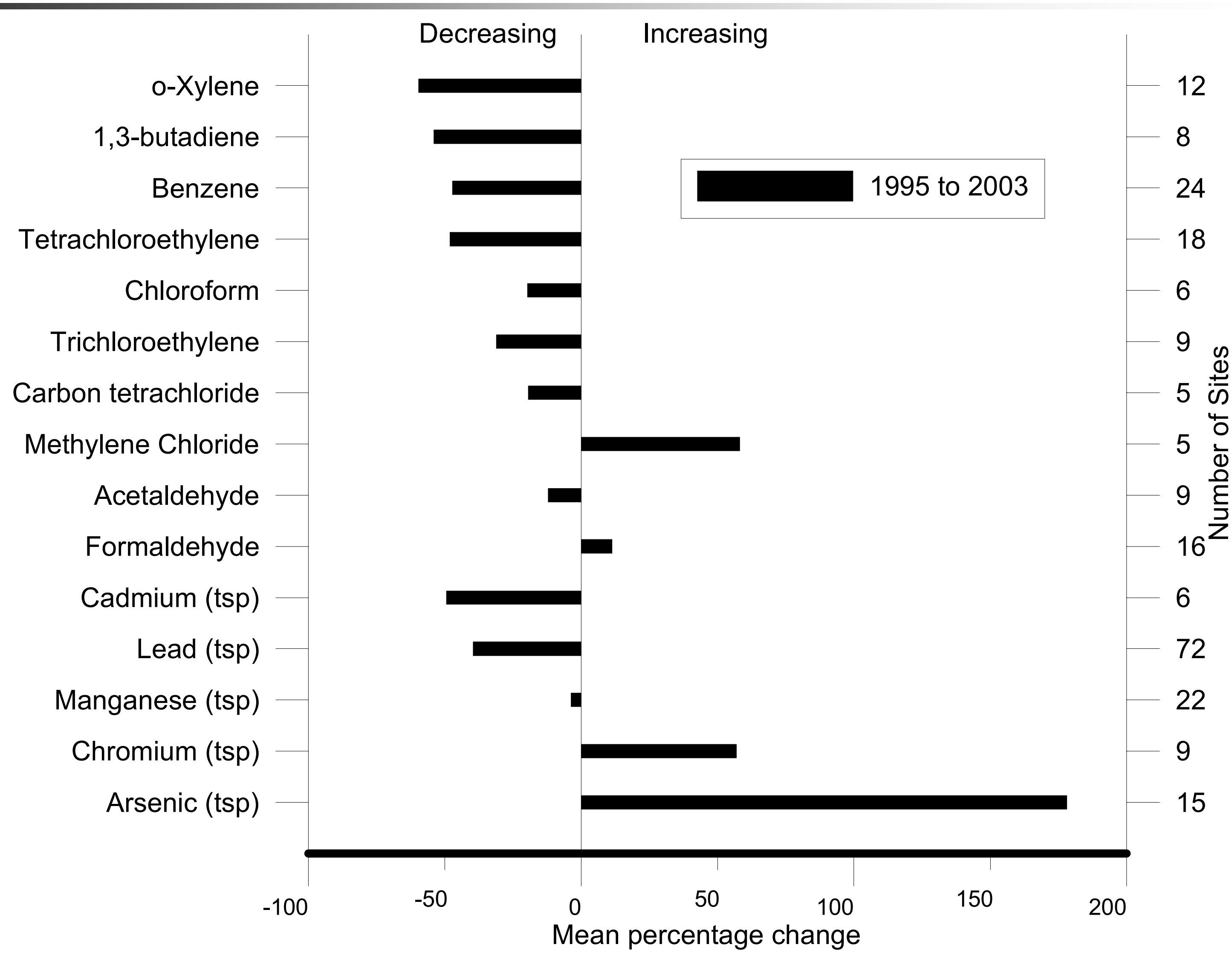
National Trend



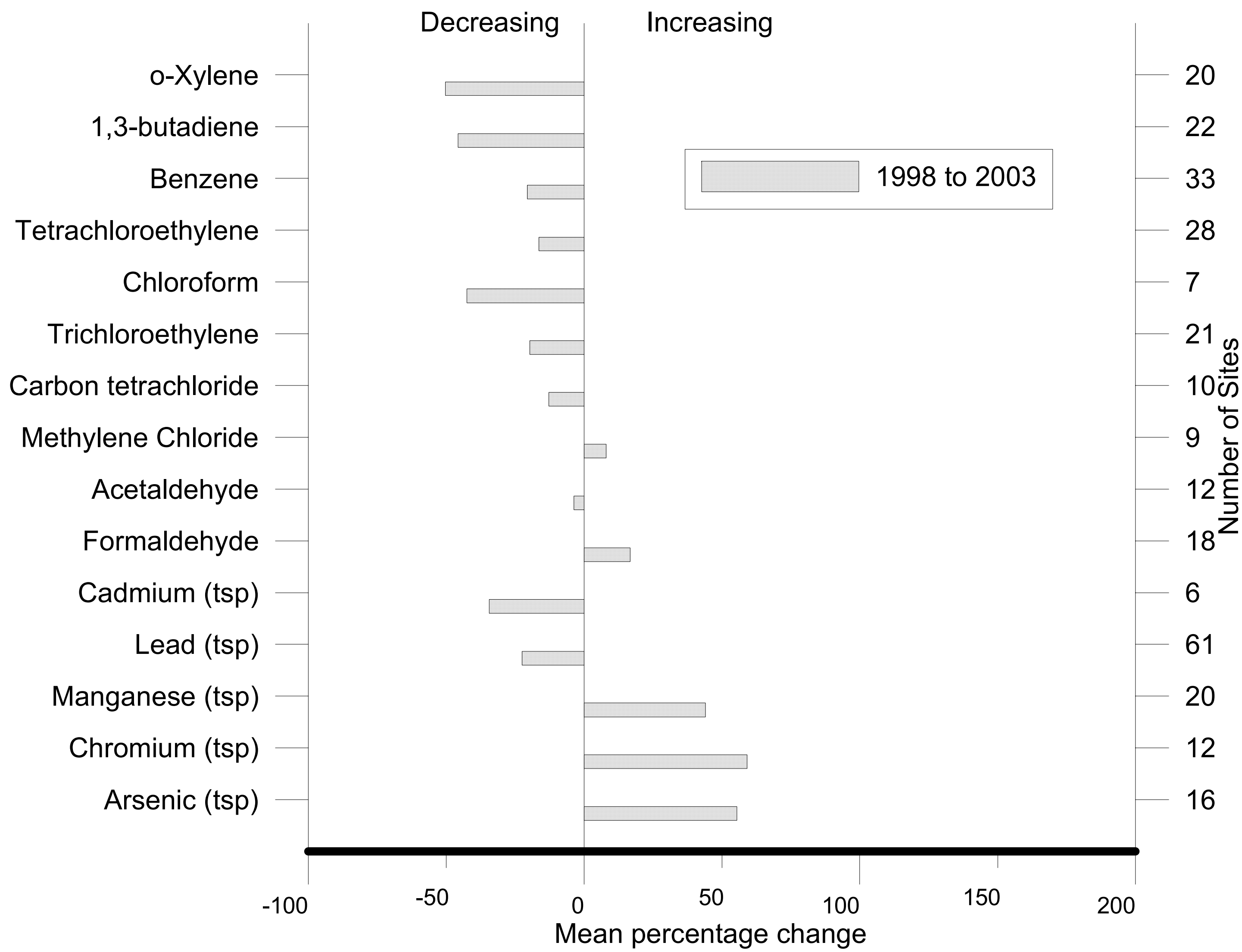
National Trends Summary – 1990 to 2003



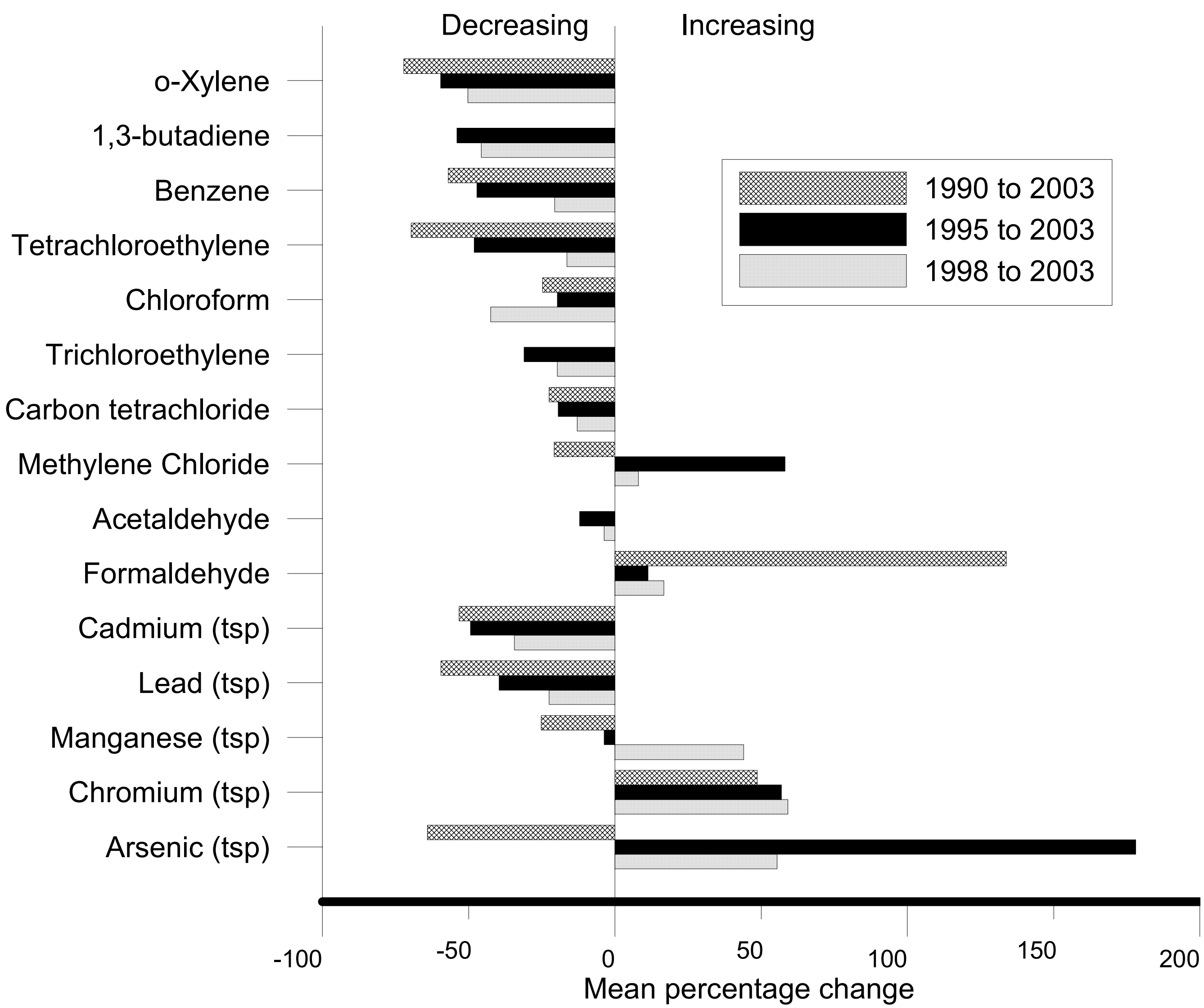
National Trends Summary – 1995 to 2003



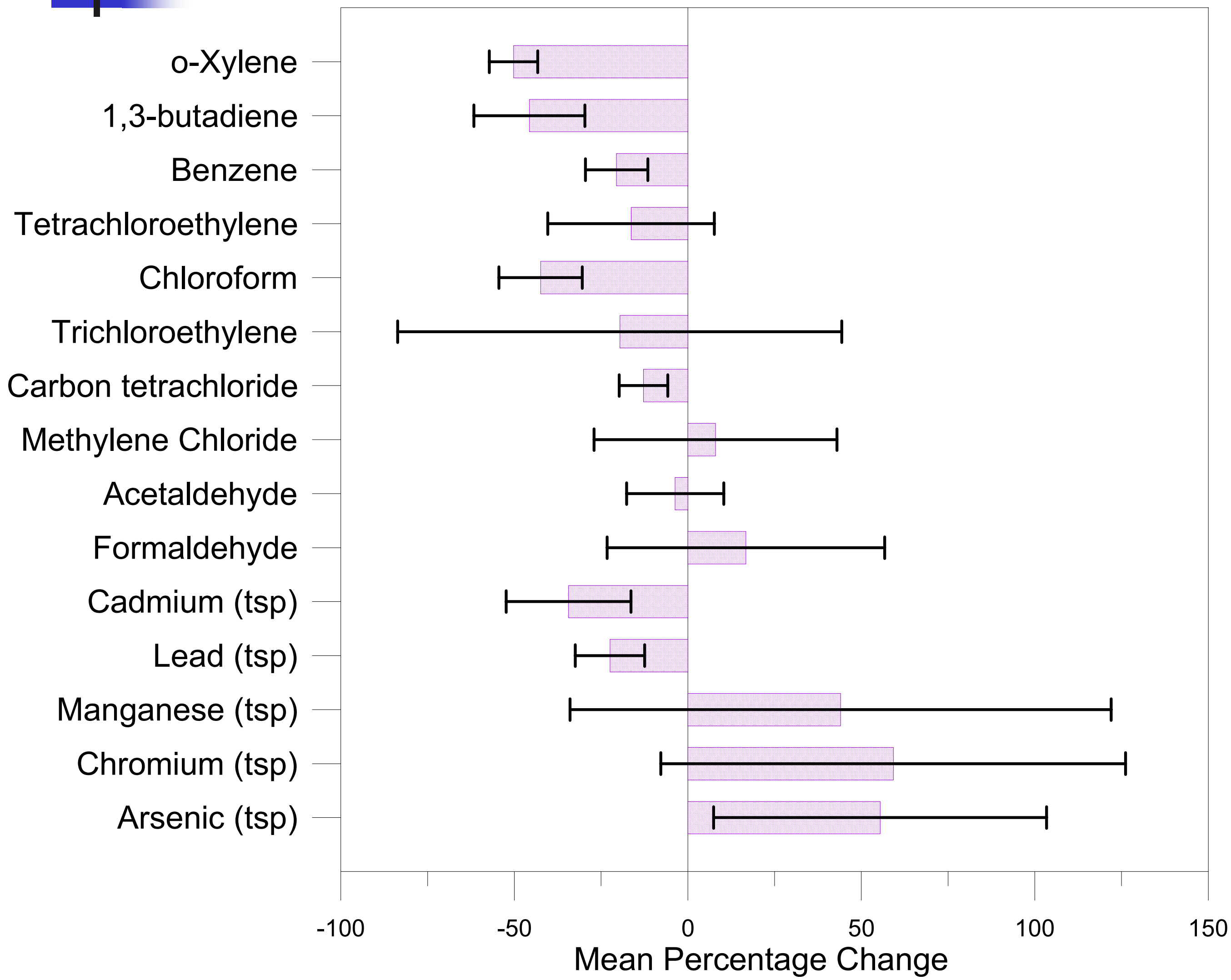
National Trends Summary – 1998 to 2003



National Trends Summary – All Trend Periods



1998 to 2003 Trends Variability



- Error bars show the variability in the mean of the population at 95% confidence interval.
- Large error bars indicate variable trends across sites, while small error bars indicate that most sites had concentrations that decreased by a similar percentage.

Trend Categories

Significant Decrease

o-Xylene
Benzene
1,3-Butadiene
Chloroform
Carbon Tetrachloride
Cadmium (tsp)
Lead (tsp)

Decreased on Average

Acetaldehyde
Tetrachloroethylene
Trichloroethylene

Increased on Average

Formaldehyde
Chromium (tsp)
Arsenic (tsp)

Mixed Trends

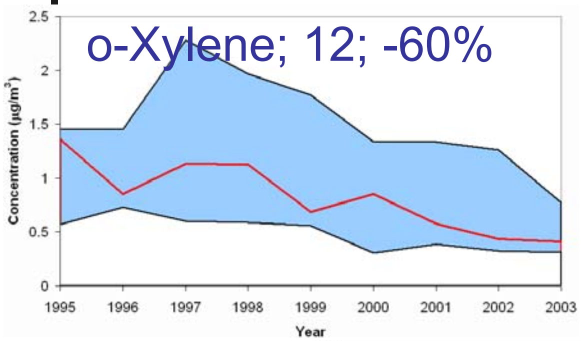
Methylene Chloride
Manganese (tsp)

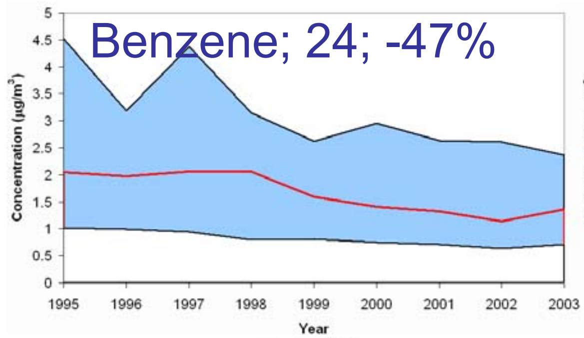
Mobile source-dominated
Carbonyl compounds
Chlorinated
Metals
PAHs

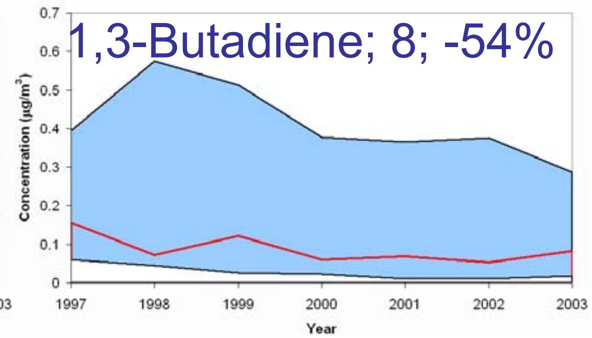
Trend Statistics

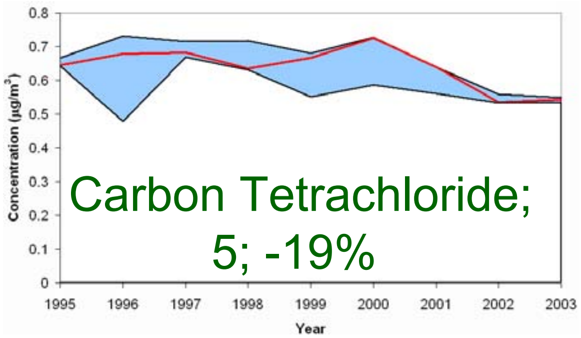
	1990 – 2003			1995 - 2003			1998 - 2003		
Pollutant	Median 1990 Concentration (mg/m³)	Mean % change and CI	# of sites (# decreasing by >10%)	Median 1995 Concentration (mg/m³)	Mean % change and CI	# of sites (# decreasing by >10%)	Median 1998 Concentration (mg/m³)	Mean % change and CI	# of sites (# decreasing by >10%)
o-Xylene	2.4	-72 ± 8	4 (4)	1.3	-60 ± 7	12 (12)	0.92	-50 ± 7	20 (18)
1,3-Butadiene	No Data			0.18	-54 ± 27	8 (7)	0.28	-46 ± 16	22 (17)
Benzene	3.7	-57 ± 13	8 (8)	2.4	-47 ± 12	24 (22)	1.9	-21 ± 9	33 (23)
Tetrachloroethylene	1.1	-70 ± 5	6 (6)	0.42	-48 ± 12	18 (16)	0.14	-16 ± 24	28 (19)
Chloroform	0.28	-25 ± 9	3 (3)	0.24	-20 ± 9	6 (5)	0.31	-42 ± 12	7 (7)
Trichloroethylene	No Data			0.11	-31 ± 86	9 (8)	0.082	-20 ± 64	21 (17)
Carbon tetrachloride	0.76	-22 ± 4	2 (2)	0.71	-19 ± 11	5 (4)	0.68	-13 ± 7	10 (7)
Methylene chloride	1.2	-21 ± 43	2 (1)	0.79	58 ± 96	5 (1)	0.69	8 ± 35	9 (3)
Acetaldehyde	No Data			1.6	-12 ± 18	9 (6)	1.7	-4 ± 14	12 (6)
Formaldehyde	1.0	134 ± 91	6 (0)	2.5	11 ± 19	16 (2)	2.4	17 ± 40	18 (5)
Cadmium (tsp)	0.0072	-53 ± 10	6 (6)	0.0030	-49 ± 8	6 (6)	0.0022	-34 ± 18	6 (5)
Lead (tsp)	0.20	-60 ± 9	85 (73)	0.096	-40 ± 13	72 (58)	0.073	-22 ± 10	61 (40)
Manganese (tsp)	0.033	-25 ± 7	20 (17)	0.029	-4 ± 14	22 (12)	0.027	44 ± 78	20 (6)
Chromium (tsp)	0.0066	49 ± 66	8 (4)	0.0043	57 ± 42	9 (0)	0.0051	59 ± 67	12 (3)
Arsenic (tsp)	0.0016	26 ± 61	15 (8)	0.0014	178 ± 203	15 (5)	0.0018	55 ± 48	16 (4)

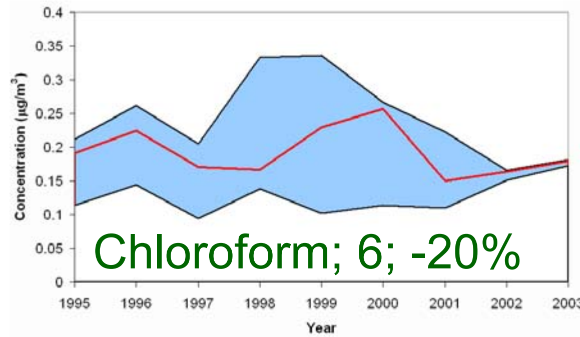
Decreasing Trends – 1995 to 2003

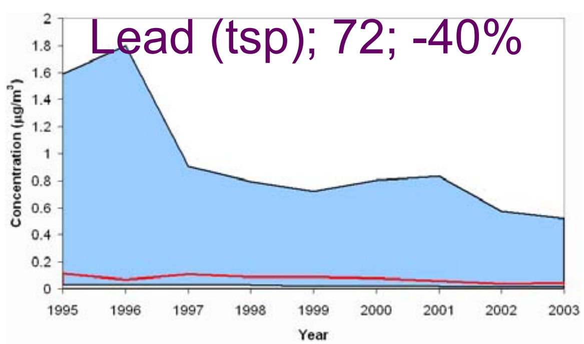


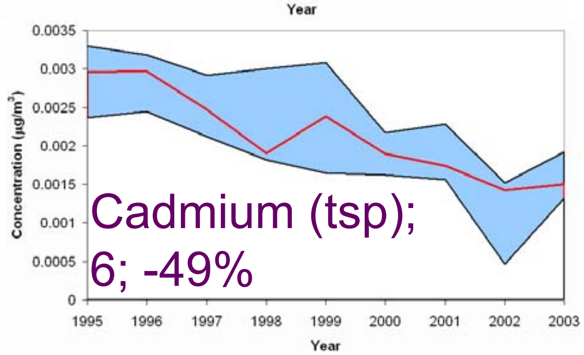




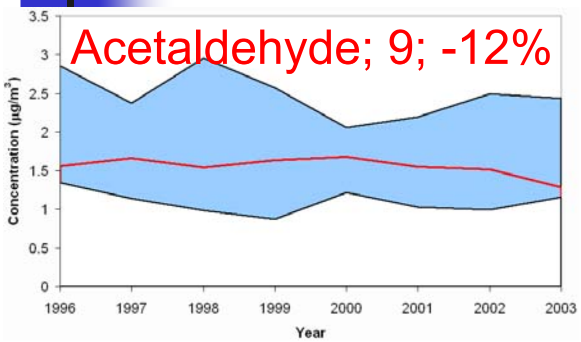


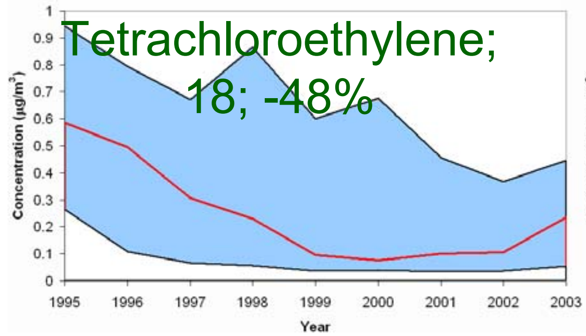


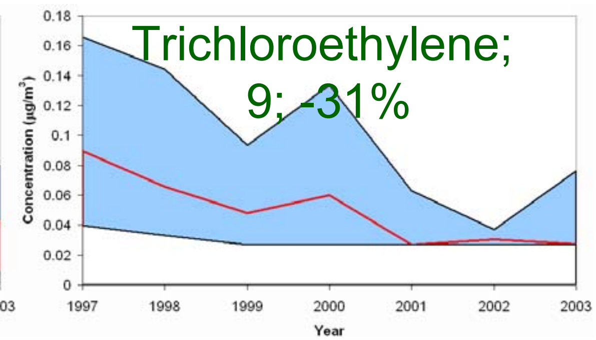


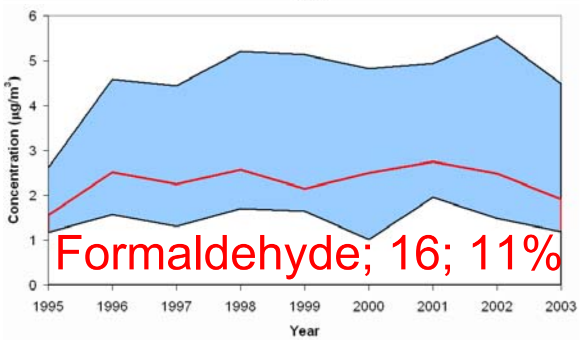


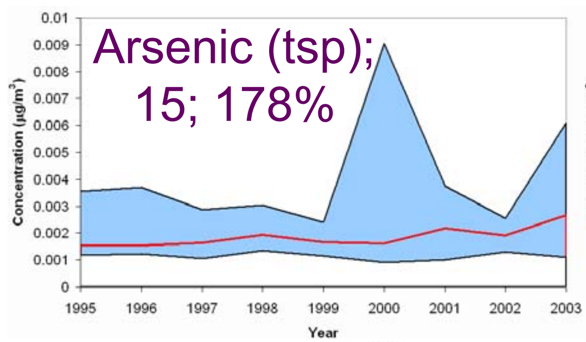
Other Trends – 1995 to 2003

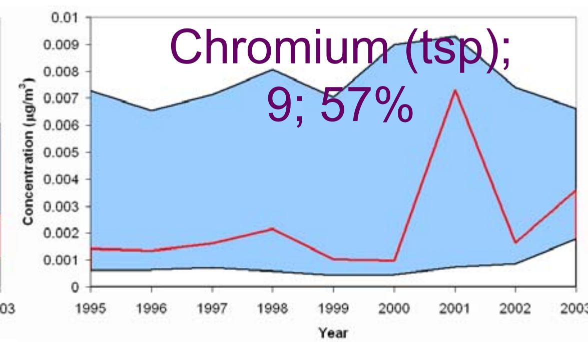


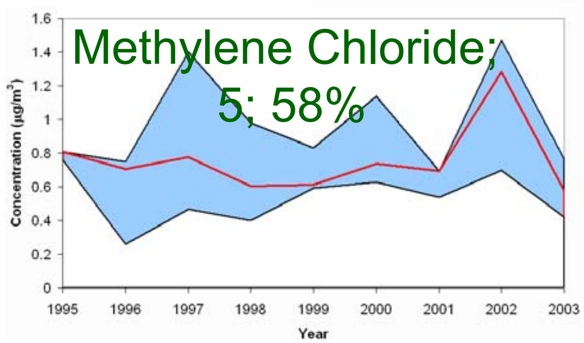


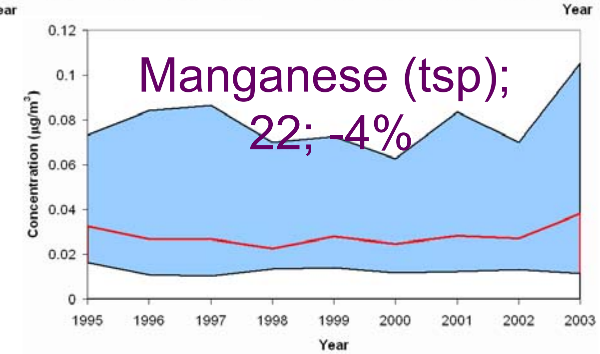












Trends Conclusions

- Concentrations of about half the air toxics have significantly decreased
- Other air toxics had changes that were increasing, decreasing, or both, but were not statistically significant
- A single, consistent "air toxics" trend does not exist

References

McCarthy M.C., Hafner H.R., Chinkin L.R., Touma J.S., and Cox W.M. (2005) Temporal variability of selected air toxics: a national perspective. Prepared for the United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, and Sonoma Technology, Inc., Petaluma, CA. Available on the Internet at <http://www.epa.gov/ttn/amtic/toxdat.html> last accessed September 2, 2005.

Acronyms

CV: Coefficient of Variation; Standard deviation divided by the mean

HAP: Hazardous Air Pollutant

MACT: Maximum Achievable Control Technology

PAMS: Photochemical Assessment Monitoring Stations

PM: Particulate Matter

tsp: total suspended particulate