Multipollutant Source Apportionment: Baltimore

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Receptor models use ambient concentrations to calculate source composition and contributions.

Monitor Data

Source Compositions

CMB – chemical mass balance
Unmix – multivariate receptor model
PMF – positive matrix factorization

EPA speciate database

Introduction

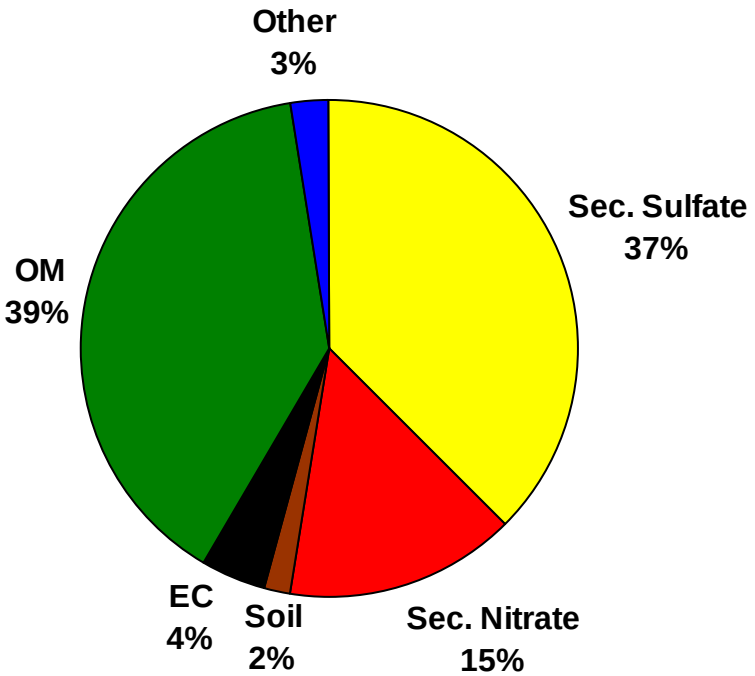
- The purpose of this analysis was to explore use of ambient source apportionment for developing more efficient integrated control strategies for “criteria” and “toxic” air pollutants.
- Positive matrix factorization (PMF) was applied to a multipollutant data set in Baltimore.
- Gaseous air toxics (10 species) were added to $PM_{2.5}$ components (19 species) data collected in 2001 - 2005.
- The original $PM_{2.5}$ - only data set had 426 samples; the combined data set had 191 samples.

Baltimore

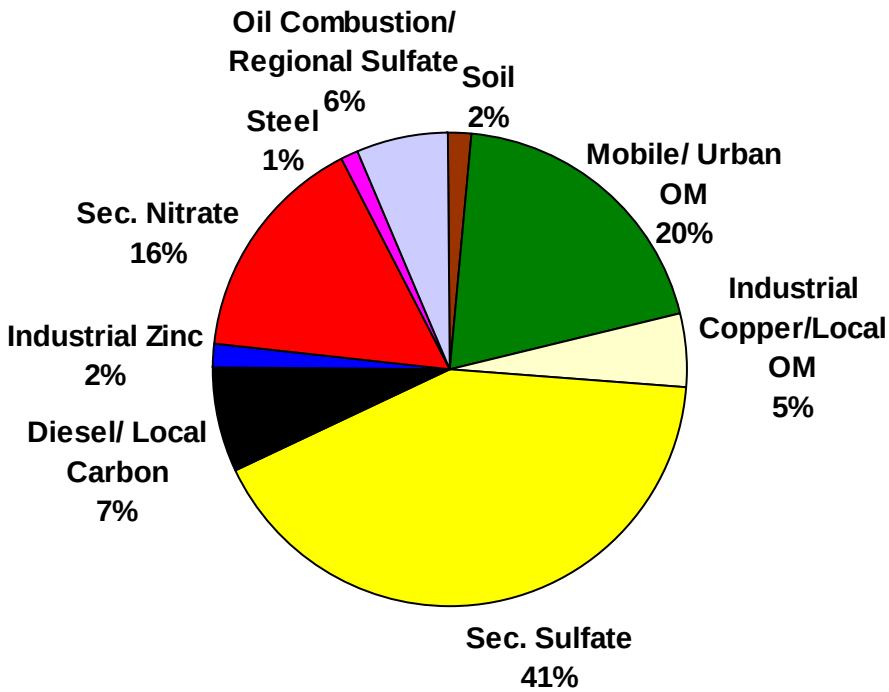
- Largest city in Maryland, over 8 million people
- Part of Baltimore/Washington MSA
- Emissions include
  - Heavy traffic and emissions of gasoline and diesel, and mobile source of air toxics
  - Sources documented in Toxic Release Inventory and National Emissions Inventory include metal processing industries (copper, zinc, and steel), oil combustion and waste incineration
- Essex site is in eastern part of Baltimore

Ambient $PM_{2.5}$ Composition and Initial Results

Ambient Composition



PMF Results

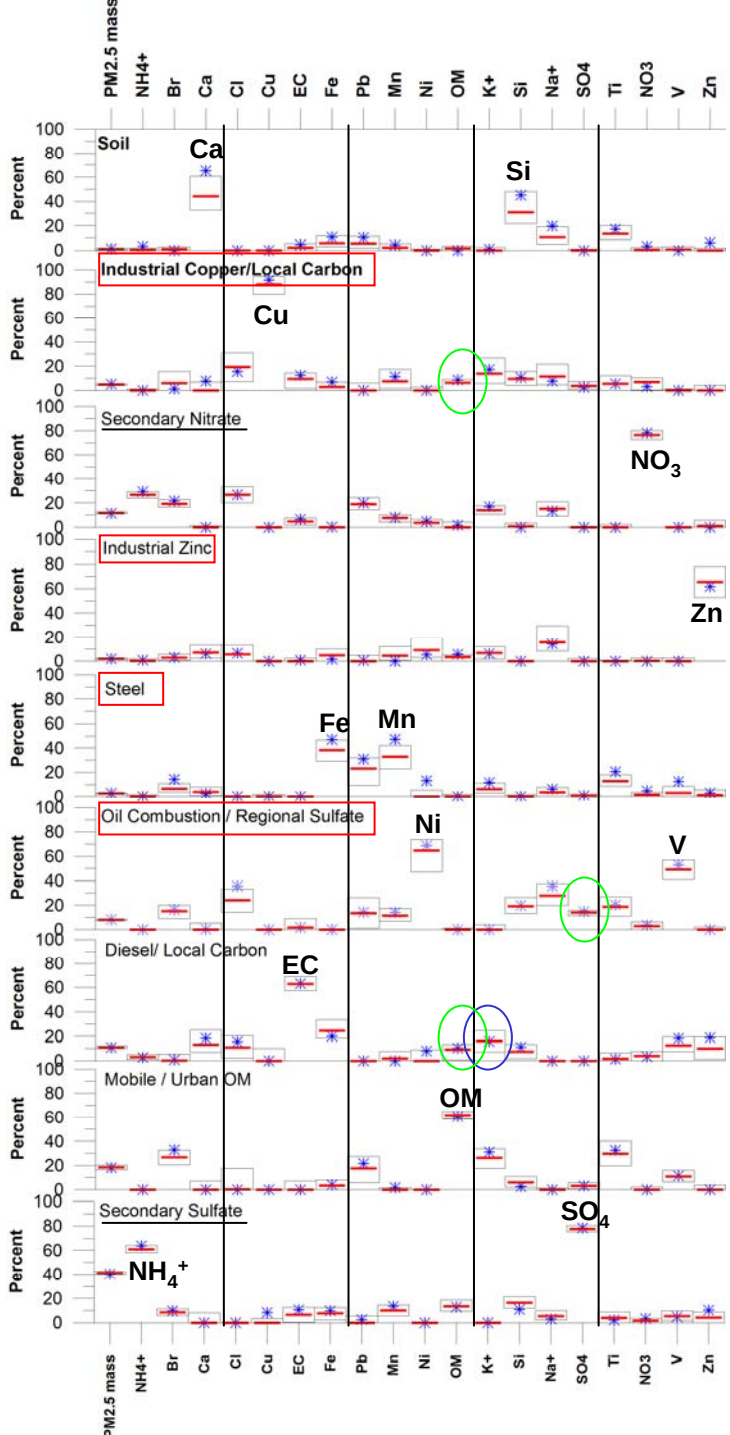


Essex site in Baltimore, Maryland (2001-2005)

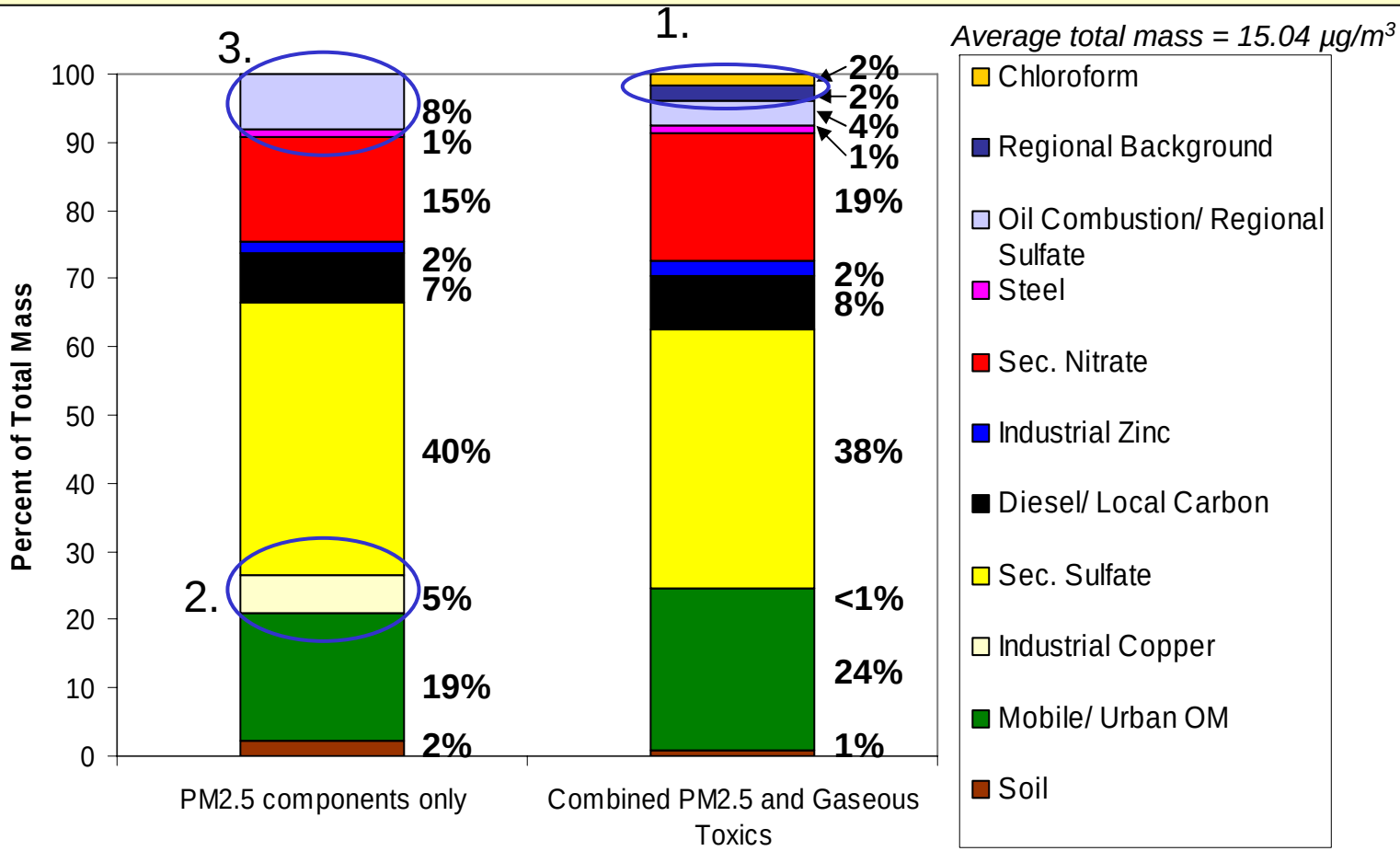
Average total mass = 15.04 µg/m³
AmmSulfate=1.29[Sulfate]*
AmmNitrate=1.35[Nitrate]*
OM=1.4[Organic Carbon- average blank value]*
Soil = 2.2[Al] + 2.49*[Si]*+1.63*[Ca]+1.94*[Ti]*
Other = sum of other species used in PMF

Factor Profiles

- As indicated by the ambient data, secondary sulfate and nitrate factors were resolved, as well as a mobile (OM) factor and a diesel (EC) factor.
- The diesel factor has a third of the K+, indicating wood burning may be influencing this factor as well.
- Several industrial factors were resolved, including copper, zinc, steel, and oil combustion.



Combined Data Set – PMF Results

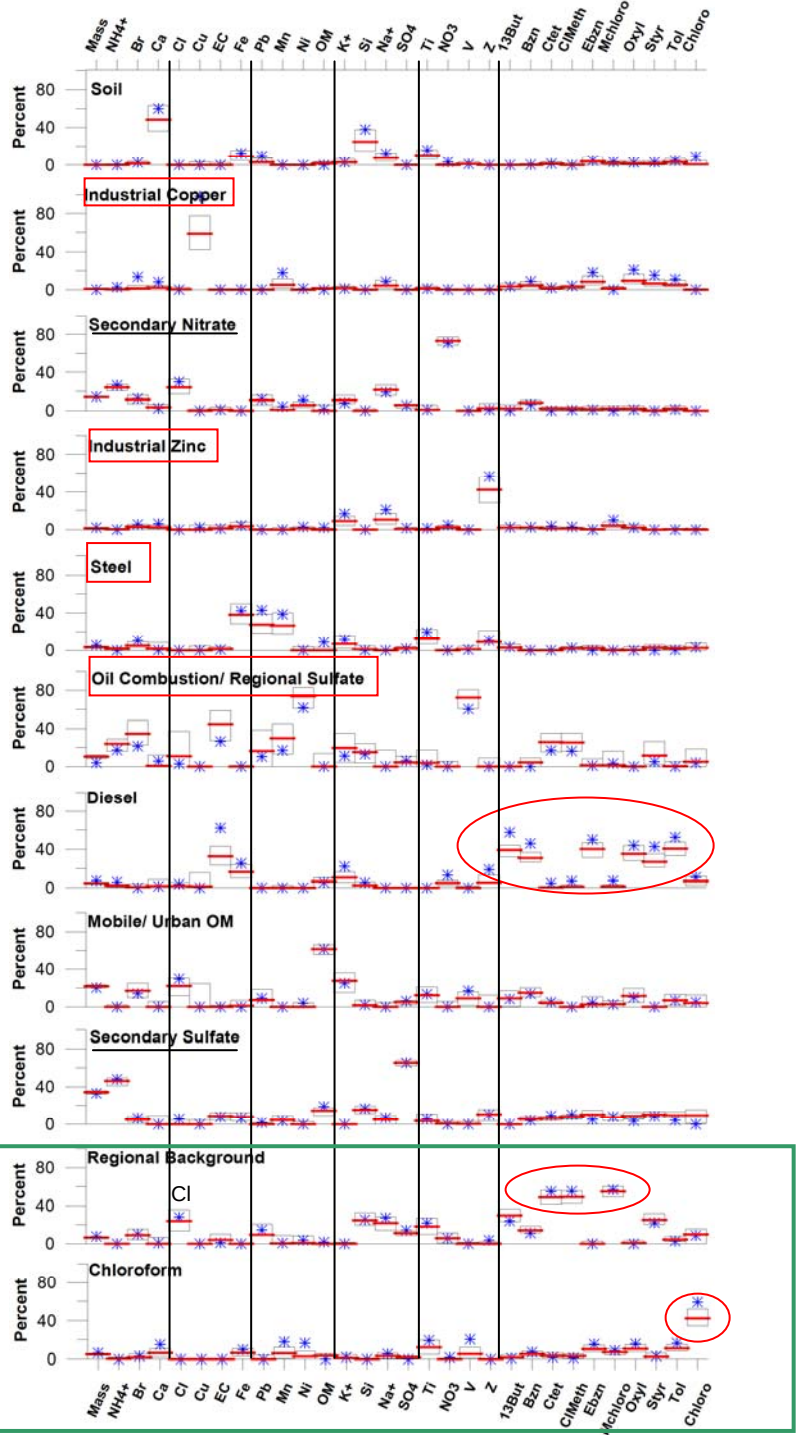


1. Two new factors were resolved, Chloroform and Regional Background.
2. The most noticeable change in mass was in the **industrial copper** factor (5% to <1%); this is mainly due to less OM being apportioned to this factor.
3. The **oil combustion** factor lost mass, mainly due to a change in the amount of sulfate apportioned to this factor.

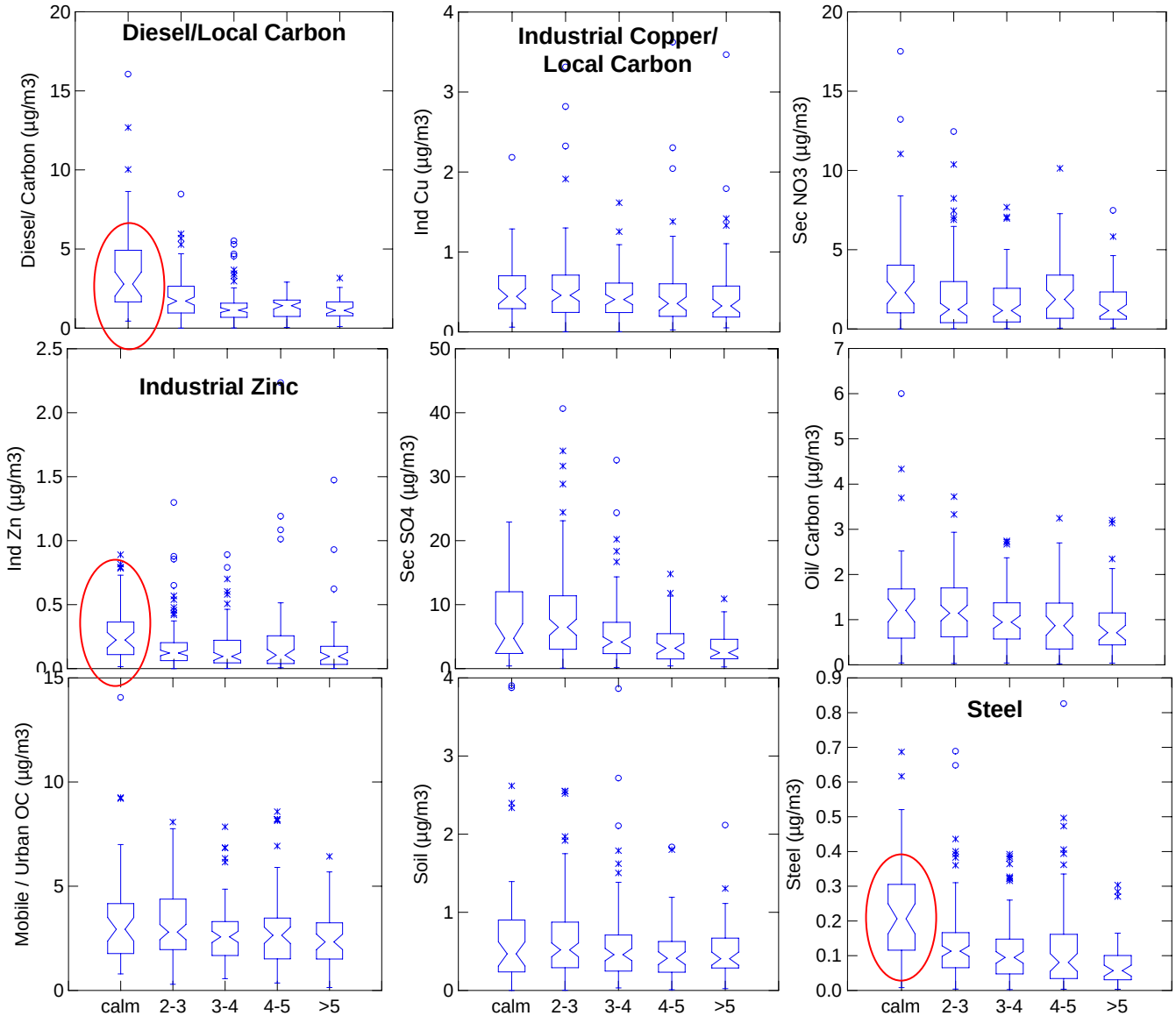
Profiles: Combined Data Set

- There was also a better division of EC and OM, with much less OM included in the **diesel** factor when the gaseous air toxics were included.
- Because OM and EC are primarily emitted from mobile sources (and therefore have the same directionality to the monitoring site) and vary together with meteorology, it is often hard to separate them using source apportionment; generally significant amounts of OM are present in the “EC” factor and vice versa.
- Traditionally, an “EC” factor is considered to represent diesel emissions. The gaseous air toxics show that, at this site, this factor actually represents “local traffic” (both diesel and gasoline emissions).

Now we can begin to see, several sources contribute to multiple air pollutants, e.g., PM2.5, air toxics, and ozone via VOC contributions.

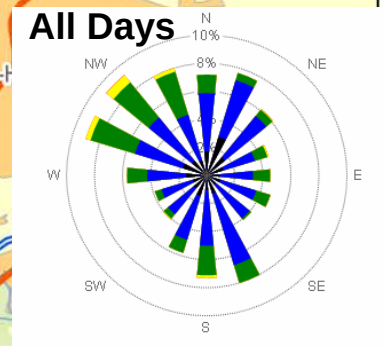


Contributions by Wind Speed (m/s)



Baltimore $PM_{2.5}$ Emissions from Steel Factories and Windrose for Highest Steel Factor Days

Wind direction on the highest steel factor days was from the south, in the direction of the large steel facility. Emissions are tons/year of $PM_{2.5}$ from the 1999 NEI.

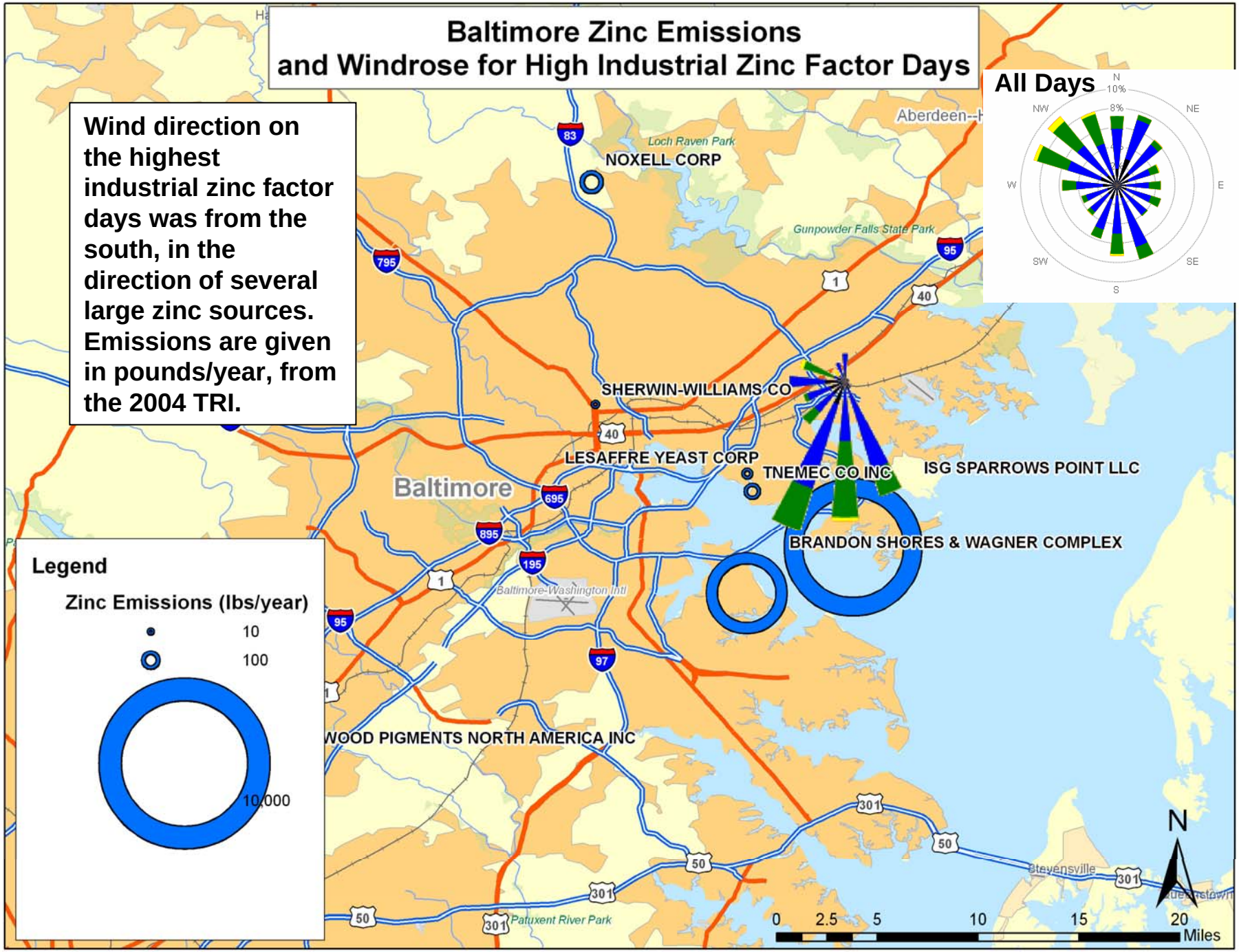


Hampstead
Aberdeen--H
Loch Raven Park
Gunpowder Falls State Park
1
40
Baltimore
Patuxent River State Park
Bethlehem Steel
Baltimore-Washington Intl
1
301
50
Stevensville
301
301
Patuxent River Park
N
0 2.5 5 10 15 20 Miles

Legend

$PM_{2.5}$ Emissions from Steel Factory (tons/year)

2,000

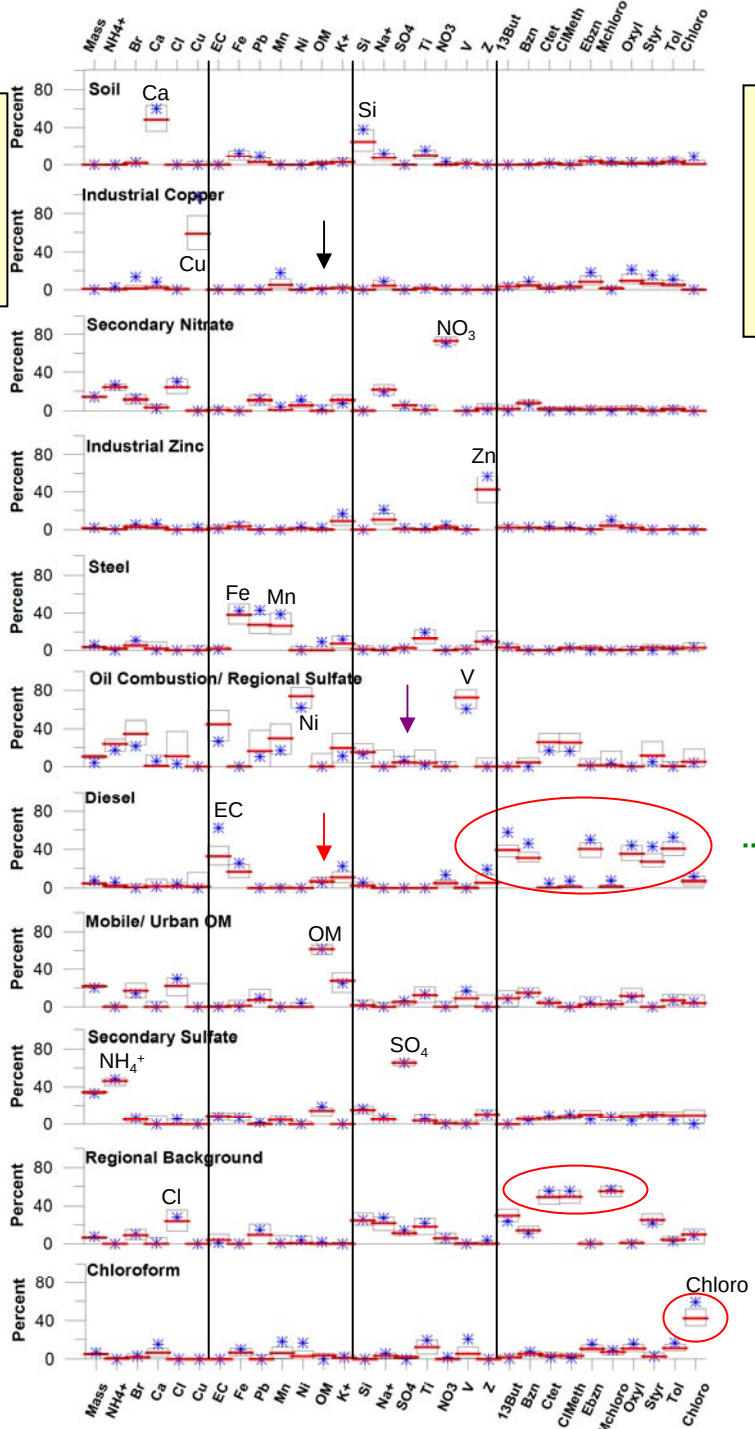

Baltimore Zinc Emissions
and Windrose for High Industrial Zinc Factor Days
Wind direction on the highest industrial zinc factor days was from the south, in the direction of several large zinc sources. Emissions are given in pounds/year, from the 2004 TRI.
All Days
N
NE
E
SE
S
SW
W
NW
10%
8%
NOXELL CORP
SHERWIN-WILLIAMS CO
LESAFFRE YEAST CORP
TNEMEC CO INC
ISG SPARROWS POINT LLC
BRANDON SHORES & WAGNER COMPLEX
WOOD PIGMENTS NORTH AMERICA INC
Baltimore
Loch Raven Park
Gunpowder Falls State Park
Baltimore-Washington Intl
Patuxent River Park
Stevensville
Legend
Zinc Emissions (lbs/year)
10
100
10,000
0 2.5 5 10 15 20
Miles

Conclusions

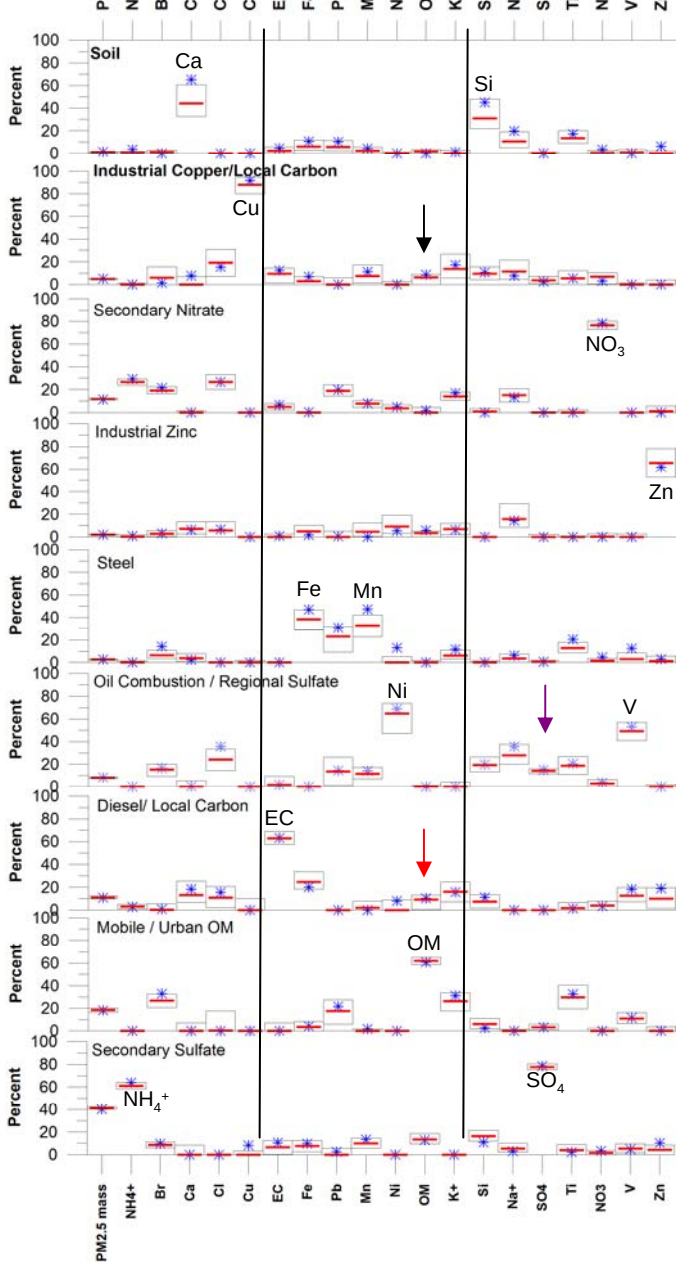
- Several industrial factors were resolved well using $PM_{2.5}$-only data set.
- Including gaseous air toxics species
  - strengthened the mobile source factor identification, mainly through better apportionment of carbon,
  - produced an additional regional background factor, and
  - provided insight into source contributions to multiple air pollutants, e.g., Diesel/Mobile sources (32% of the PM2.5 mass) contribute to $PM_{2.5}$, air toxics, and ozone via VOC contributions.
- Many sites have both $PM_{2.5}$ speciation and air toxics measurements. Similar studies at other sites would help better understand the role of gaseous air toxics in source apportionment.

Additional Information

Factor Profiles for Combined Dataset

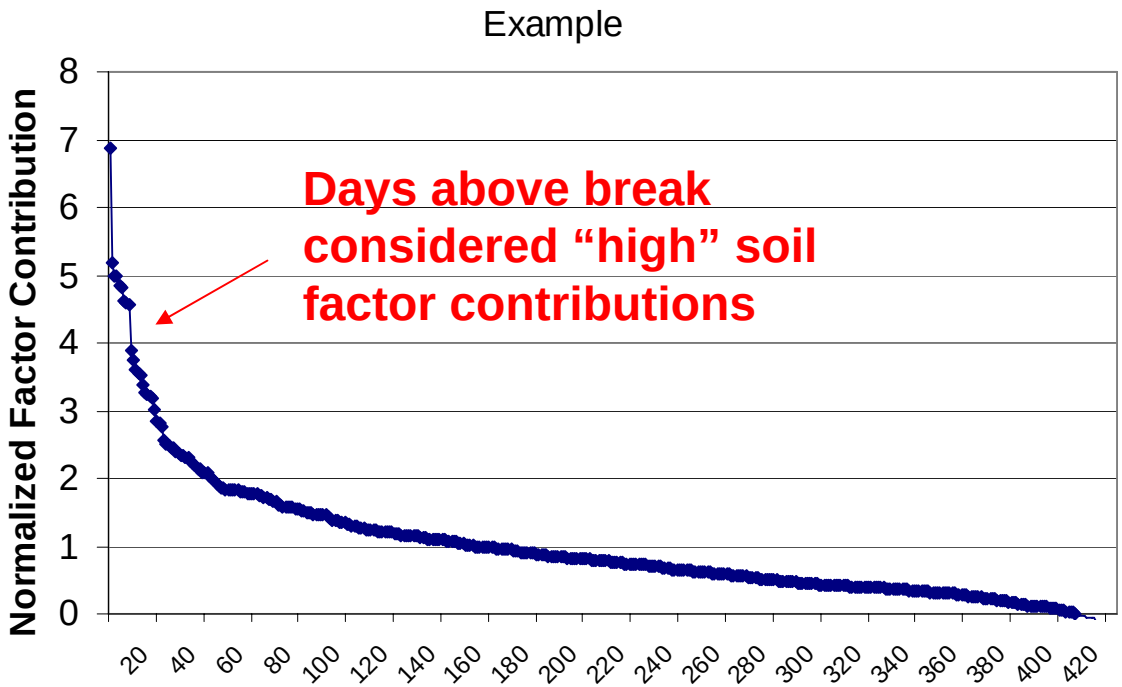


Fractor Profiles for $PM_{2.5}$ data only



Wind Roses

- Wind roses were developed and compared with maps of emissions for local/industrial sources
- The highest contribution days for each factor were determined using a graph of sorted factor contributions to find natural breaks in the data
- Calm winds (< 2 m/s) were excluded from analysis

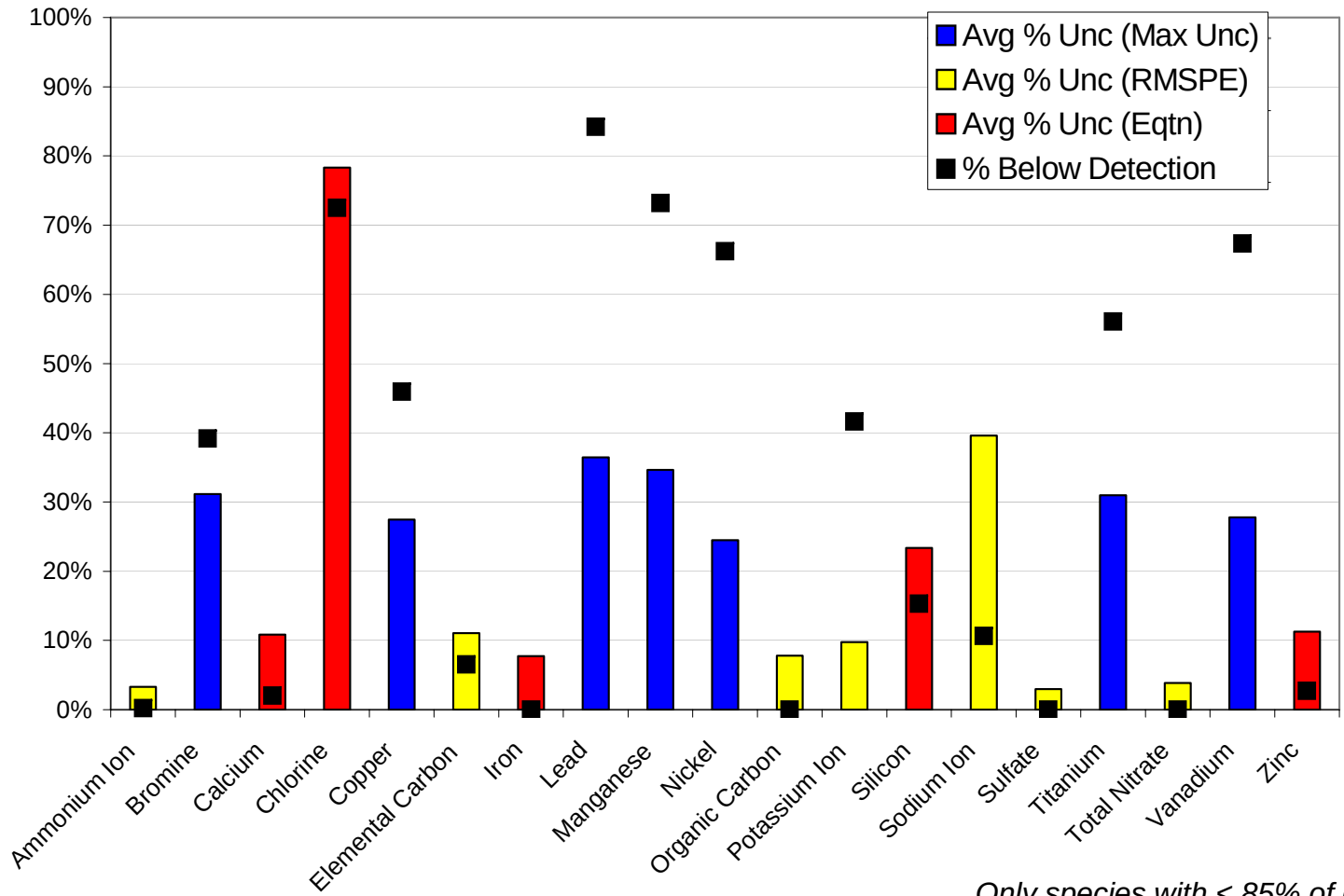


Air Toxics – Data Availability

10 species were available for inclusion in PMF

Parameter Desc	% Below Detection	Fractional Uncertainty
1,3-Butadiene	46.60%	0.21
Benzene	0%	0.16
Carbon Tetrachloride	0%	0.12
Chloroform	0%	0.15
Chloromethane	0%	0.09
Ethylbenzene	0%	0.23
Methyl Chloroform	27.75%	0.3
O-Xylene	0%	0.21
Styrene	18.90%	0.44
Toluene	0%	0.19

Below Detection/Missing Data/Uncertainties



Max Unc = max % uncertainty of reported data applied to data without reported uncertainties
RMSPE = root mean squared percent error used to calculate uncertainty as a percent of concentration
Eqtn = linear relationship between reported concentrations and uncertainties applied to data without reported uncertainties

Only species with < 85% of data below the detection limit are shown;
Average % uncertainty based on above detection limit data only

Uncertainties for PMF

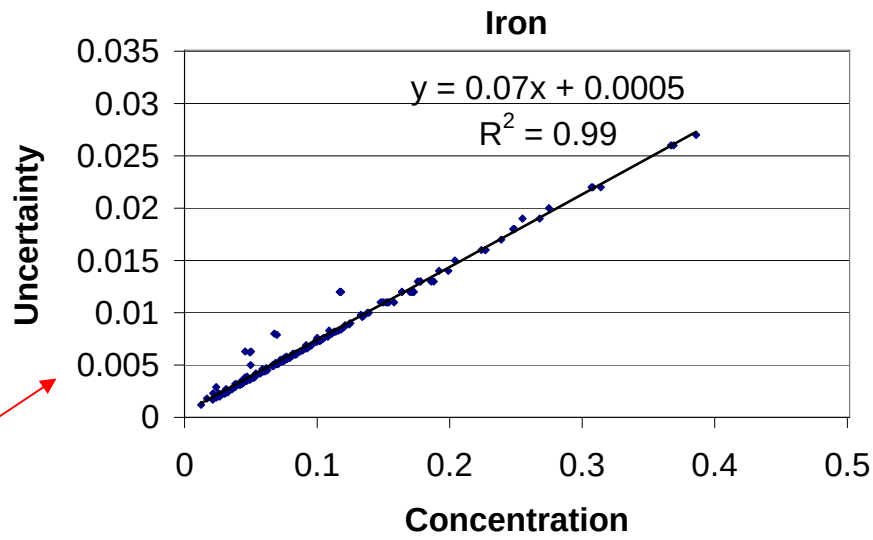
- From July 2003 forward, sample specific uncertainties were reported to AQS for $PM_{2.5}$ components and were used in PMF.
- Data prior to July 2003 do not have a similar set of uncertainties.
- Therefore, relationships between reported concentrations and uncertainties in the post-July 2003 data set were determined to predict uncertainties prior to July 2003.
- For gaseous species, fractional uncertainties developed in current EPA/STI air toxics data analysis project were used as uncertainties.

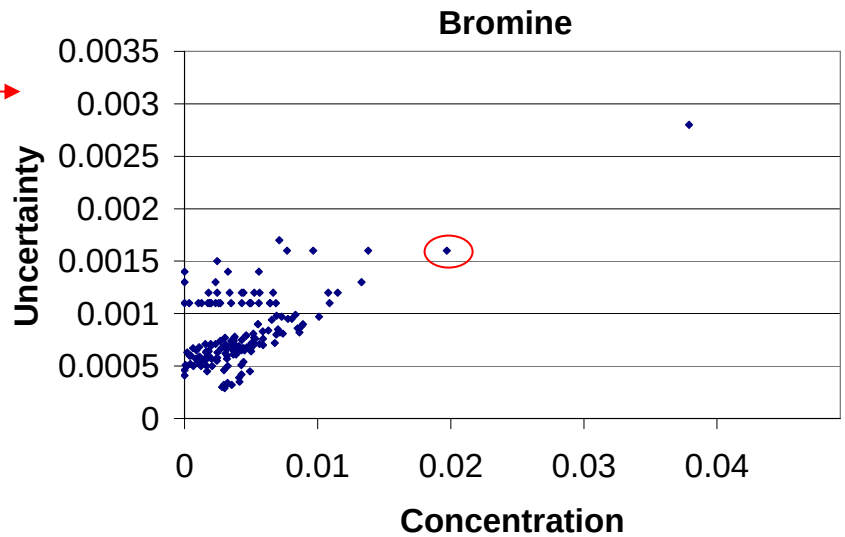
AQS = Air Quality System

Uncertainties for Data Prior to July 2003

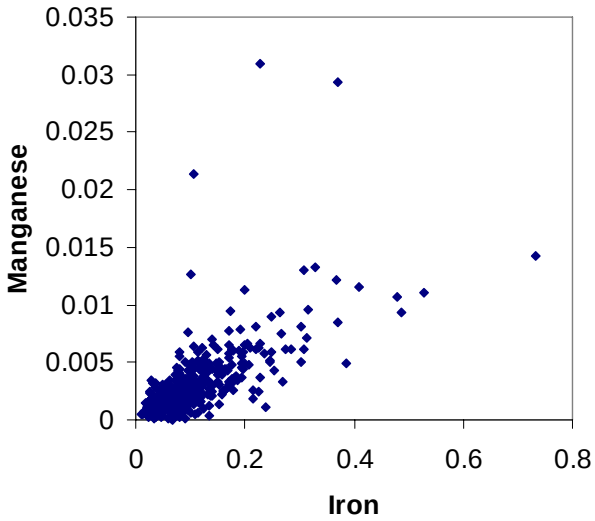
Uncertainties were calculated with methods developed for the Detroit data set:

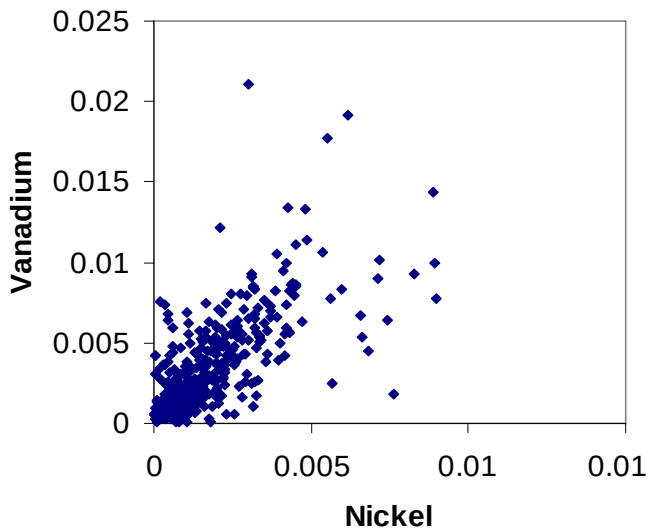
- If there was a clear relationship between concentration and uncertainty reported to AQS, a line was fit to that data and used to predict concentrations above the detection limit
- If no clear relationship existed, the maximum percent uncertainty (excluding outliers) was used
- For ions and carbon, the root median squared percent error (RMSPE) from collocated data collected at the Orange site in Cleveland was used

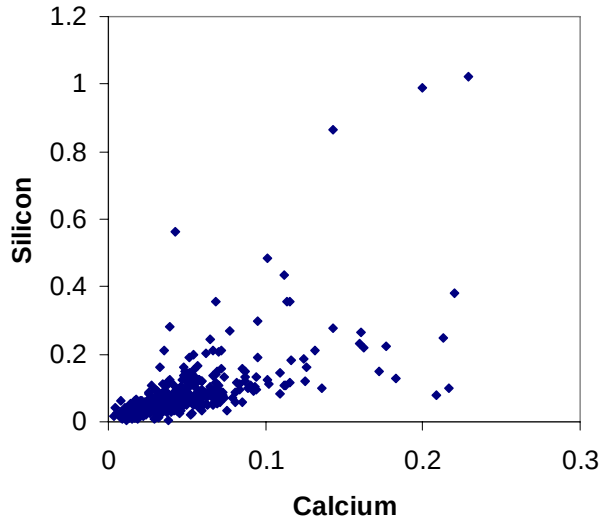




Species Correlations



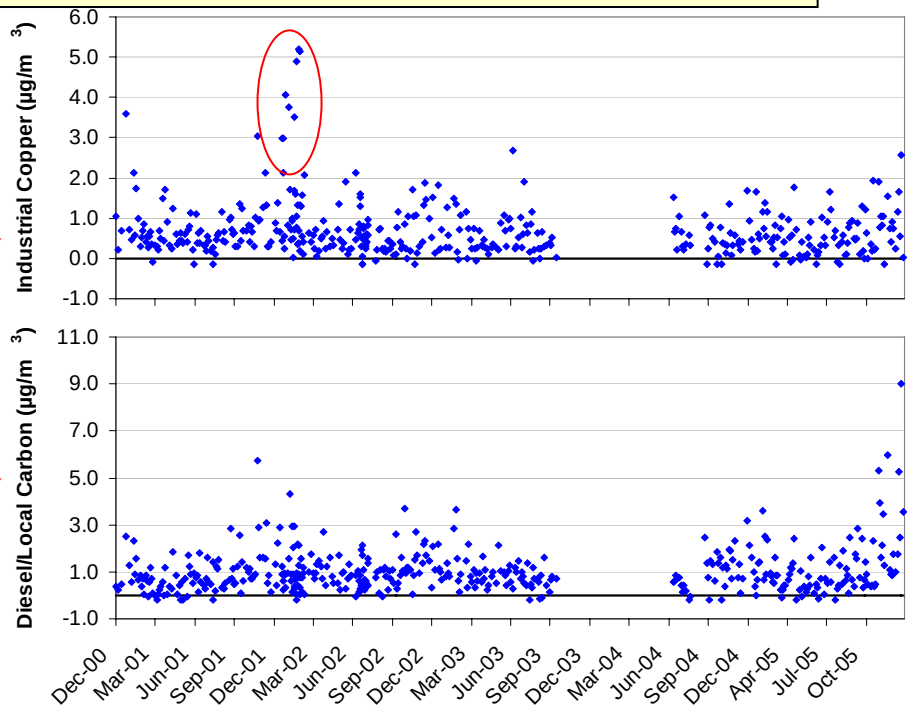


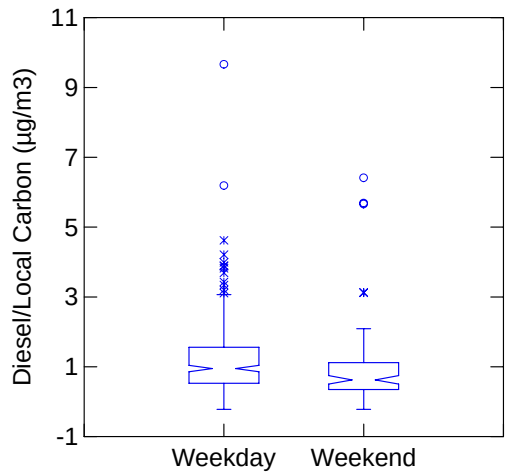


- Initial analysis showed good agreement between iron and manganese (potential steel factor); nickel and vanadium (potential oil combustion factor); silicon and calcium (soil factor); aluminum was excluded because most data were below detection.
- Some samples showed excess silicon or calcium, which will likely confound a soil factor.

Factor Contributions (seasonality, weekday/weekend)

- Secondary nitrate and sulfate factors show expected seasonality (not shown).
- Several high copper samples are seen in late 2001/early 2002.
- The diesel factor also appears to have some seasonality, most likely due to decreased mixing in the winter.
- The diesel factor showed a significant decrease in concentrations on Sunday and Monday compared with other days.





Air Toxics Time Series

- Similar seasonal patterns in factors were observed as before with $PM_{2.5}$ data only.
- Regional background factor (with chlorinated compounds) shows no seasonal pattern, as expected.
- The chloroform factor shows an increase in the summer months, as well as with wind direction from the west.