An Analysis of Speciated $PM_{2.5}$ Data in the MARAMA Region

Bill Gillespie

National Air Monitoring Conference

November 7, 2006

MARAMA

Presentation Outline

- Content of MARAMA's final report
- Processing speciated $PM_{2.5}$ data
- Results
  - Analysis of Philadelphia speciation data
  - A quick look at Elizabeth, NJ
  - Regional results
  - A quick look at trajectory analyses
- Selected findings from MARAMA's analysis
- Some concluding thoughts

MARAMA

EPA Region 3's $PM_{2.5}$ Speciation Grant

- In 2004, EPA awarded MARAMA a grant to:
  - Complete the development of $PM_{2.5}$ air quality forecasting tools
  - Analyze speciated $PM_{2.5}$ data in the Region
- EPA asked MARAMA to:
  - Develop a guide to help analysts access, process & analyze speciation data
  - Analyze some data

MARAMA

The Final Report Table of Contents

- Executive Summary
- Introduction
  - The $PM_{2.5}$ Air Quality Monitoring Network
  - The $PM_{2.5}$ Speciation Monitoring Program
- Methodology and Data Handling Techniques
- Regional Comparisons of $PM_{2.5}$ Species
- Site Information and Analyses (12 sites)
- Key Findings and Future Directions
- References

MARAMA

The Final Report; Appendices

- Analytes in the Speciation Program
- FRM Time Series (2001-2003)
- Null and Flagged Data Analysis
- Organic Carbon Blank Analysis
- Minimum Detection Limit (MDL) Analysis

MARAMA's report is available on the web at:
http://www.marama.org/reports/

MARAMA

Accessing & Processing Speciation Data

- Before you can analyze speciation data, you have to obtain and process it…
- Data is available from:
  - AQS (user id and password required)
  - EPA's TTN web site at: http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm
  - AIR Explorer at:
  - http://www.epa.gov/airexplorer/

MARAMA

Accessing & Processing Speciation Data

- Processing AQS or TTN data
  - Filter for:
    - monitoring site,
    - Parameter Occurrence Code (POC),
    - 61 parameter (specie) codes
  - Examine null & flagged data
  - Treat exceptional events

MARAMA

Accessing & Processing Speciation Data

- Processing AQS or TTN data (continued):
  - Obtain organic carbon (OC) blank data, convert units, plot blank time series, and calculate site averages
  - "Blank correct" organic carbon data (subtract the average OC blank from each OC measurement)
  - Apply an OM/OC ratio to blank-corrected OC data to convert OC measurements to organic carbon mass (OM) estimates. Assumes you know the OM/OC ratio!
  - Calculate a "reconstructed mass" (RCM), a sum of the constituent species
  - Examine resulting data set; perform more QA

MARAMA

Precision & Stated Accuracy of Major $PM_{2.5}$ Species

Constituent	Average Percent of Total $PM_{2.5}$ Mass	Precision (R^2)	Uncertainty (from AQS)	Comment on Measurement
Sulfate	34	0.98	9	Very precise; reasonably accurate.
Organic Carbon Mass/Organic Carbon	32	0.83	OC 13, OM ?	OC measurements reasonably precise; OCM poorly known
Ammonium	13	0.96	7	Very precise; some NH_3 loss issues; less loss than FRM
Nitrate	11	0.98	12	Very precise; some NO_3 loss issues; less loss than FRM
Elemental Carbon	5	0.75	51	Fairly precise; less accurate.
Geological	4	NC	Various	
Trace Elements	2	NC	Various	Some measurements < MDL
Salt	<1	NC	NC	

Calculations in Speciated Mass Analyses

1. Sulfate Mass = Sulfate Measurement
2. OM = (OM/OC) x OC Measurement
3. Ammonium Mass = Ammonium Measurement
4. Nitrate Mass = Nitrate Measurement
5. Elemental Carbon Mass = Elemental Carbon Measurement
6. Geological Mass = 3.73*Si + 1.63*Ca + 2.42*Fe+1.94*Ti
7. Salt Mass = 1.65*Cl
8. Trace Element Mass = (Sum of trace element masses) - (Si+Ca+Fe+Ti+S+Cl masses)

Reconstructed Mass (RCM) = Sum of items 1-8 above

Unidentified Mass = Gravimetric Total Mass - RCM

OM/OC ratio usually not known; MARAMA applied 1.6 and got reasonably good mass closure at urban sites

Neil Frank's Alternative crustal equation

MARAMA

Primer on the OM/OC Ratio

- The OM/OC ratio is a ratio of:

$$\frac{\text{Molecular weight of the organic species on the sample filter}}{\text{Carbon weight given off by those species during lab analysis}}$$

- Ratio varies hour-to-hour, day-to-day, season-to-season, site-to-site…
- Ratio is poorly known at most sites
- Ratios are higher at rural sites than urban sites because of the presence “aged” (larger molecular weight) organic aerosol

MARAMA

Changes to the STN Trace Element Program

- Many trace element measurements were:
  - Below the Method Detection Limit (MDL)
  - Much less precise than SO_4, OC, NH_4, NO_3, EC
- EPA and Research Triangle Institute have examined the problem
- EPA proposes to:
  - Reduce number of trace element measurements in STN to the 24 made in IMPROVE plus 7 more
  - Drop 17 trace element measurements in STN

MARAMA

Retained Trace Element Measurements

IMPROVE XRF Measurements

Al	Aluminum
As	Arsenic
Br	Bromine
Ca	Calcium
Cl	Chlorine
Cr	Chromium
Cu	Copper
Fe	Iron
Pb	Lead
Mg	Magnesium
Mn	Manganese
Ni	Nickel
P	Phosphorus
K	Potassium
Rb	Rubidium
Se	Selenium
Si	Silicon
Na	Sodium
Sr	Strontium
S	Sulfur
Ti	Titanium
V	Vanadium
Zn	Zinc
Zr	Zirconium

Additional 7 STN Measurements

Ba	Barium
Ce	Cerium
Eu	Europium
La	Lanthanum
Hg	Mercury
Sm	Samarium
Tb	Terbium

MARAMA

Dropped Trace Element Measurements

STN Measurements to be Dropped (17)	
Sc	Scandium
Co	Cobalt
Ga	Gallium
Y	Yttrium
Nb	Niobium
Mo	Molybdenum
Ag	Silver
Cd	Cadmium
In	Indium
Sn	Tin
Sb	Antimony
Cs	Cesium
Hf	Hafnium
Ta	Tantalum
W	Tungsten
Ir	Iridium
Au	Gold

Source apportionment studies should evaluate all trace element data to determine if it is of sufficient quality to use in these analyses.

Source apportionment modelers should:

- determine how often the species is above its MDL, and
- look at the species signal-to-noise ratio

MARAMA

The "Bottom Line" on STN Speciation Data

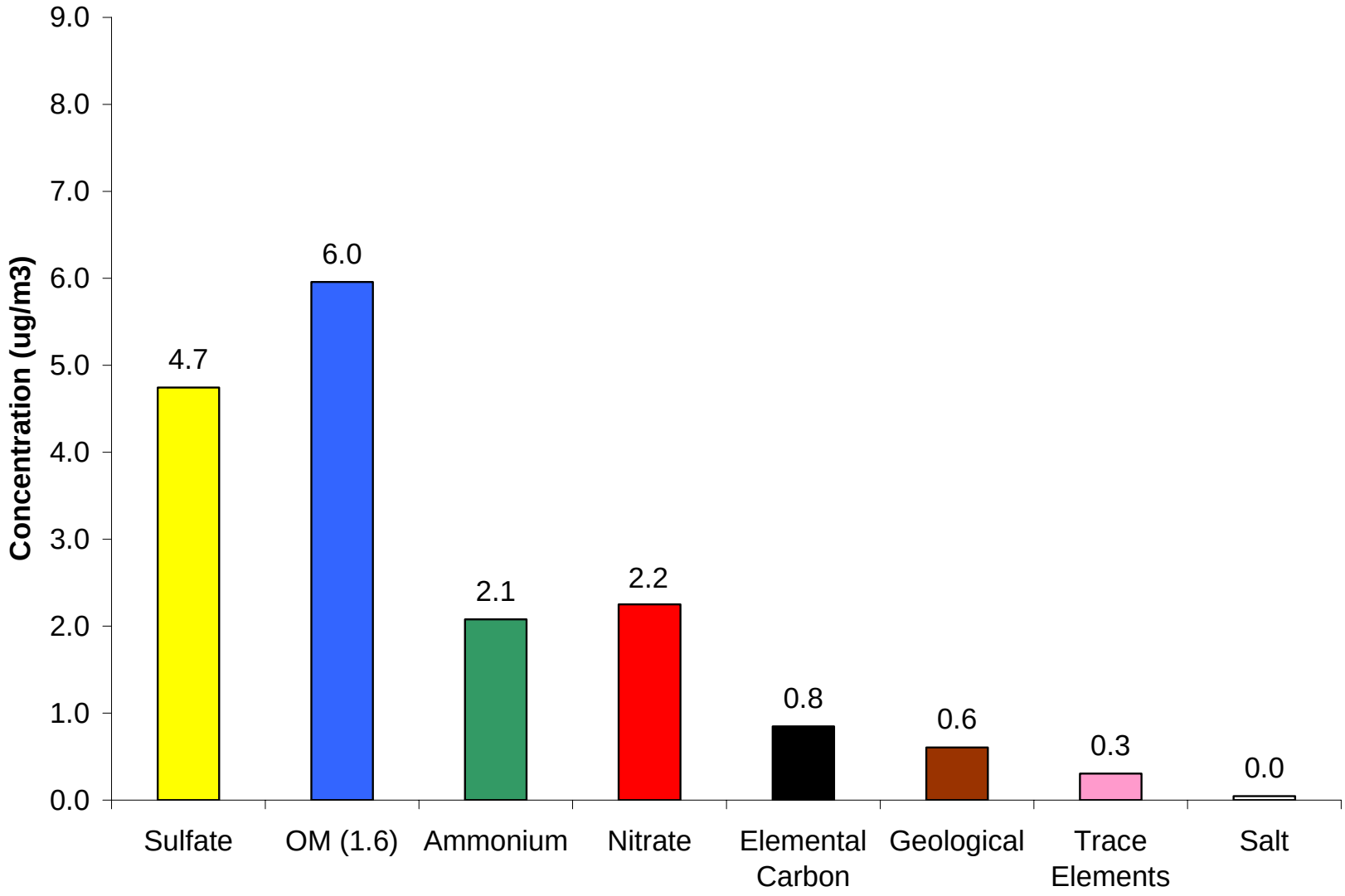
- Sulfate measurements are precise and quite accurate
- Ammonium and nitrate measurements are precise, may exhibit some loss of specie, FRM measurements lose even more NH_4 and NO_3 than STN measurements
- Elemental carbon measurements are reasonably precise, some accuracy issues, will soon change to IMPROVE TOR method
- OM poorly known. Estimate OM/OC ratio or use the "SANDWICH" method to calculate organic carbon mass
- Some trace element measurements were imprecise and < MDL. Use these data with care.

MARAMA

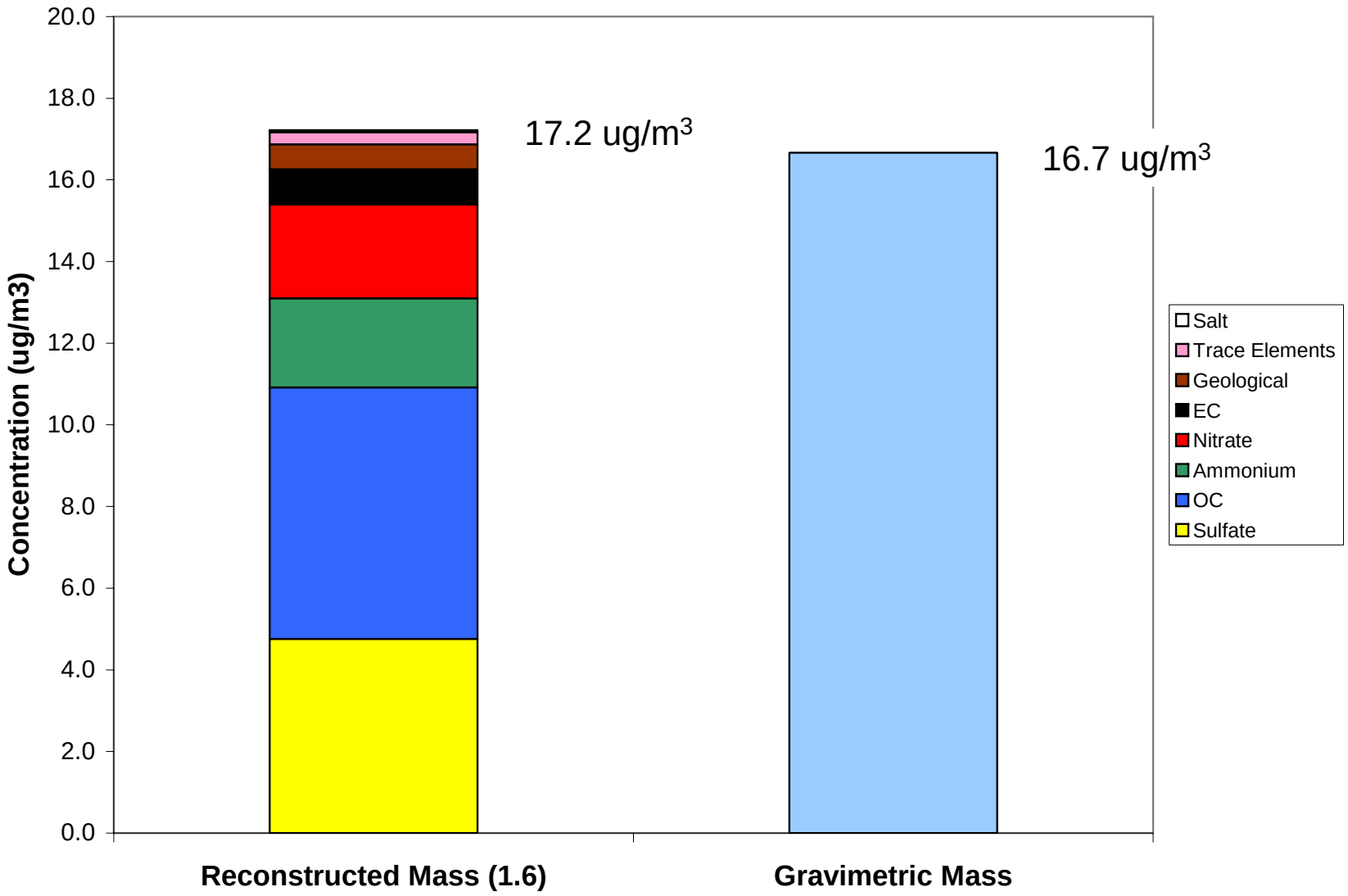
Philadelphia Analysis
2001-2003 Data

MARAMA

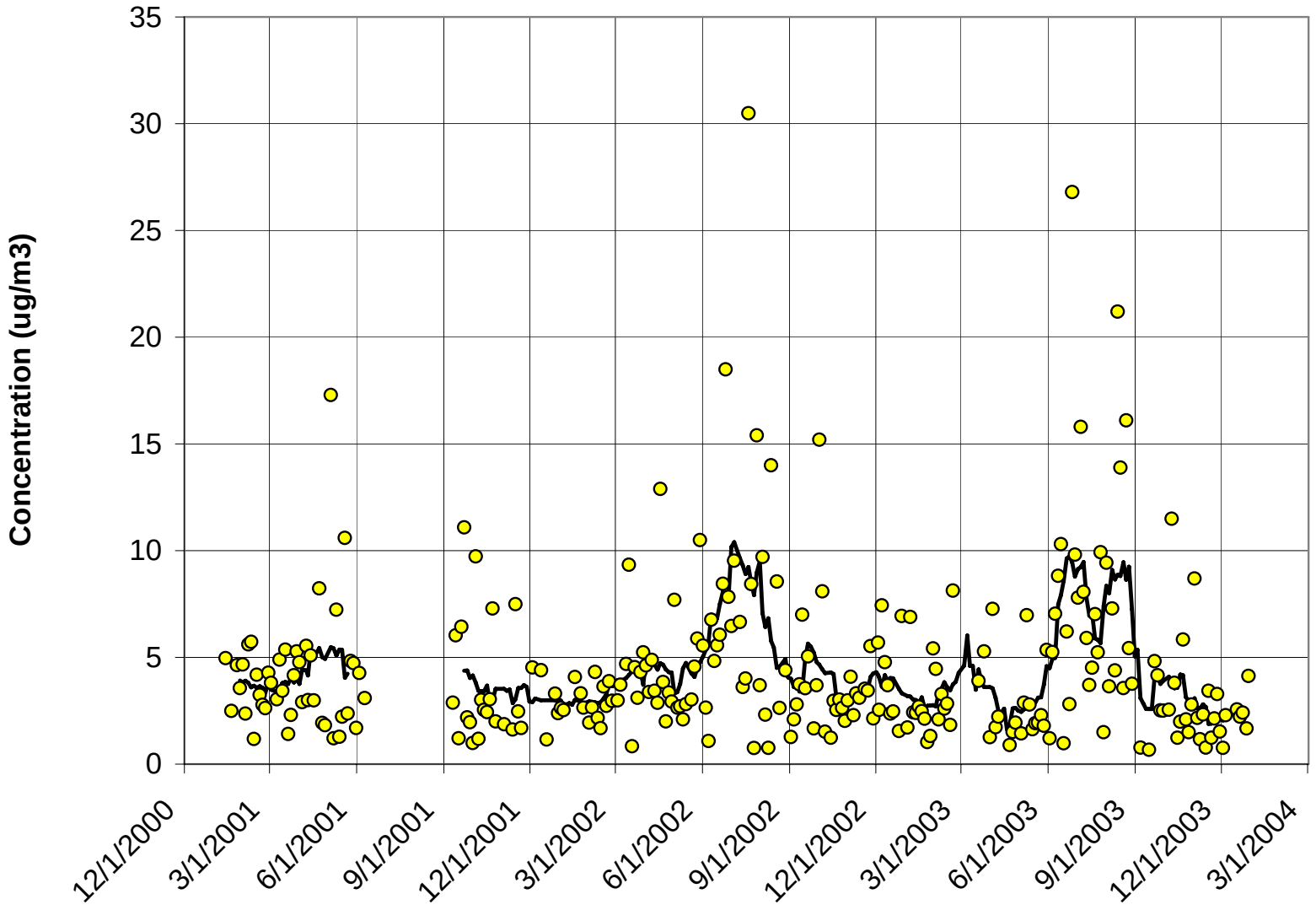
Philadelphia: Major Constituents of $PM_{2.5}$ Mass



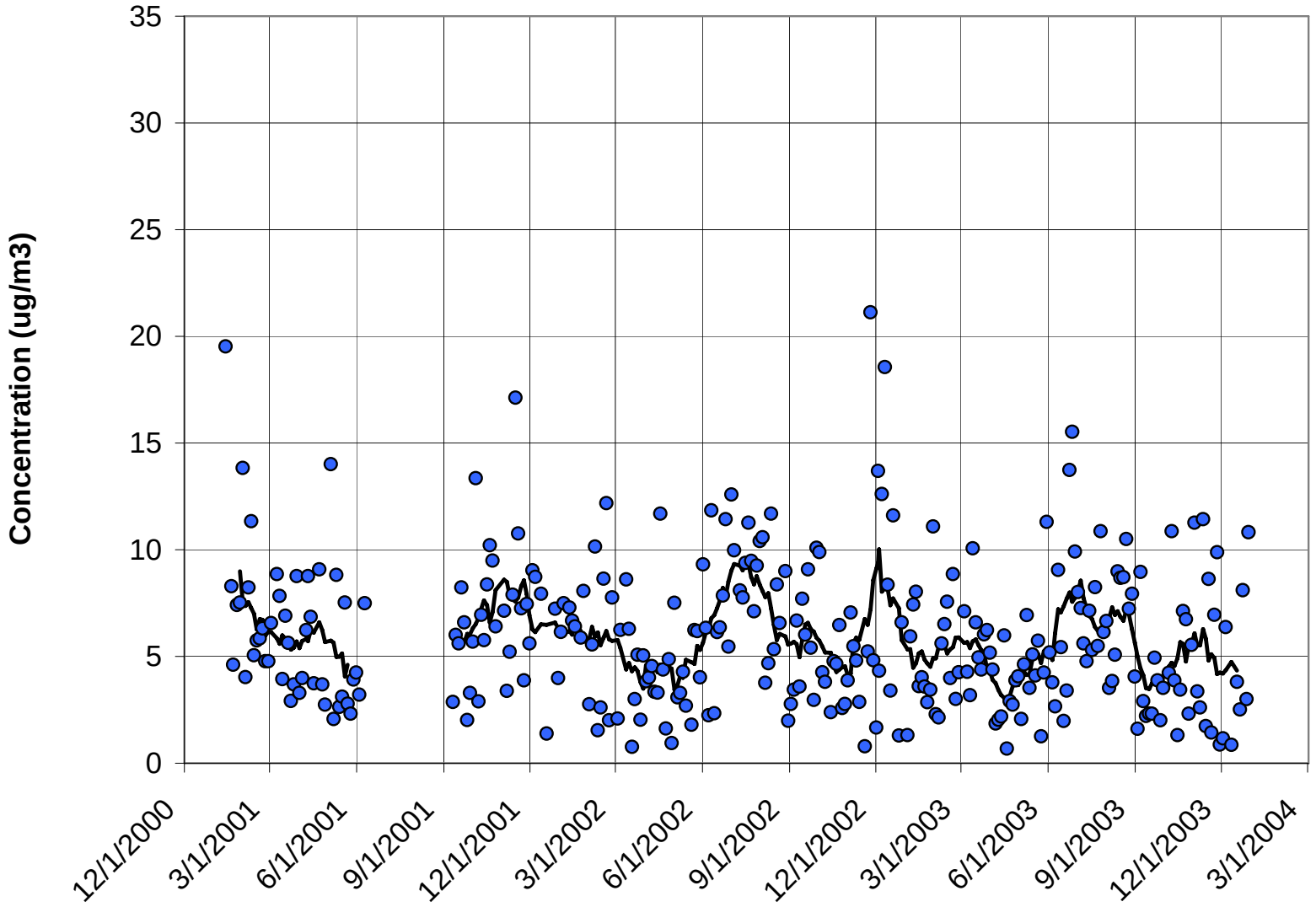
Comparison of RCM & Gravimetric Mass



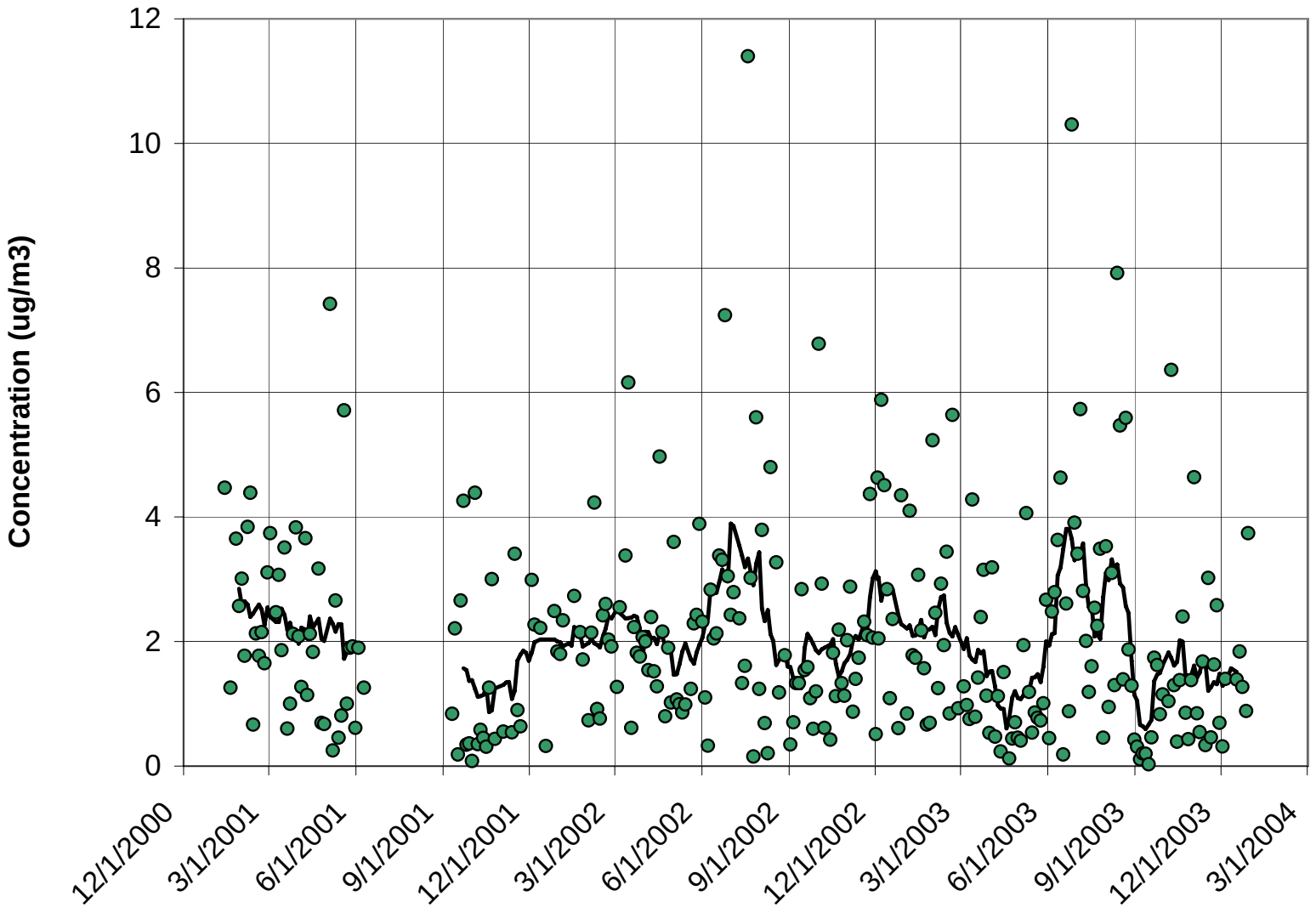
Sulfate Time Series



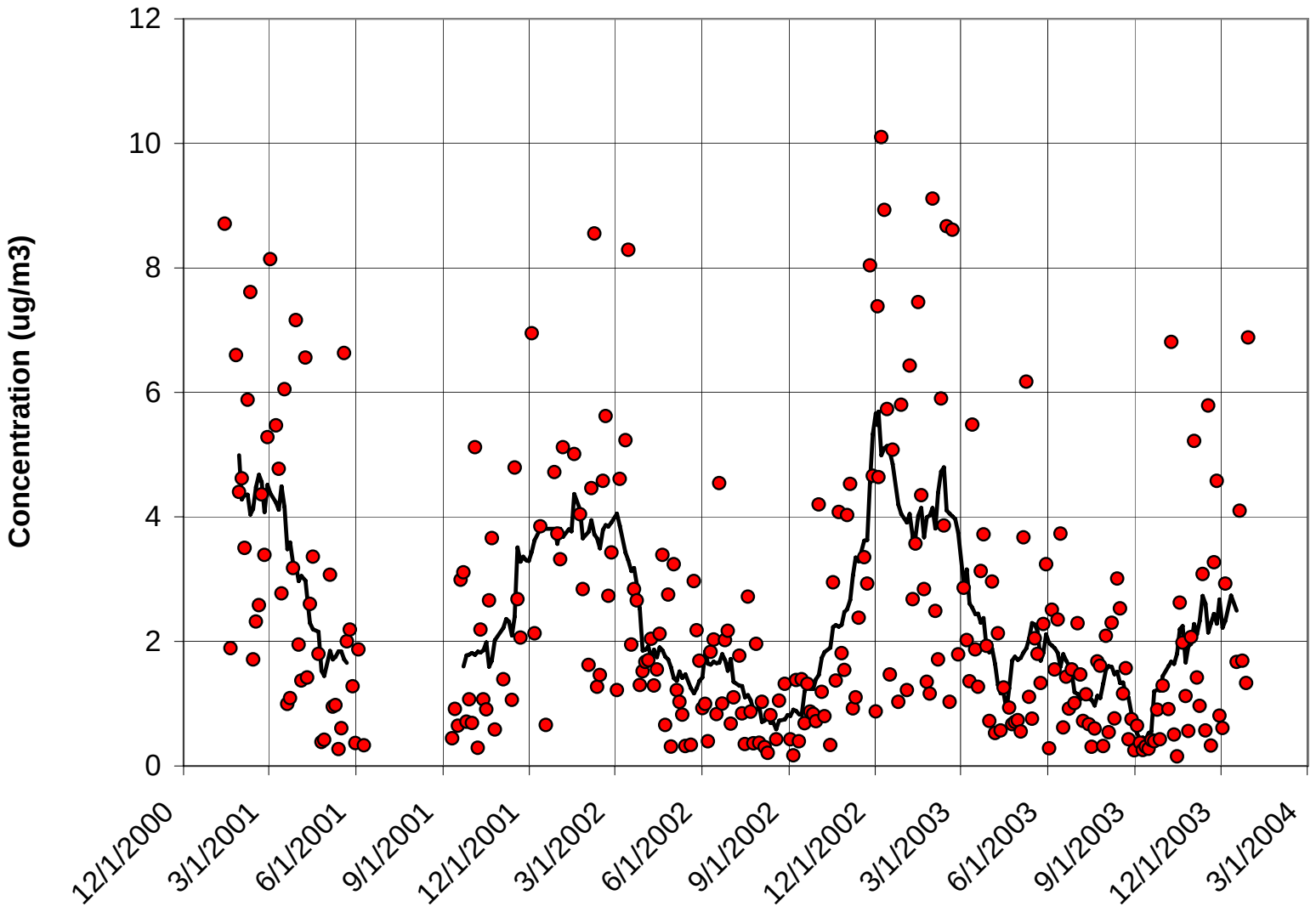
Organic Carbon Time Series



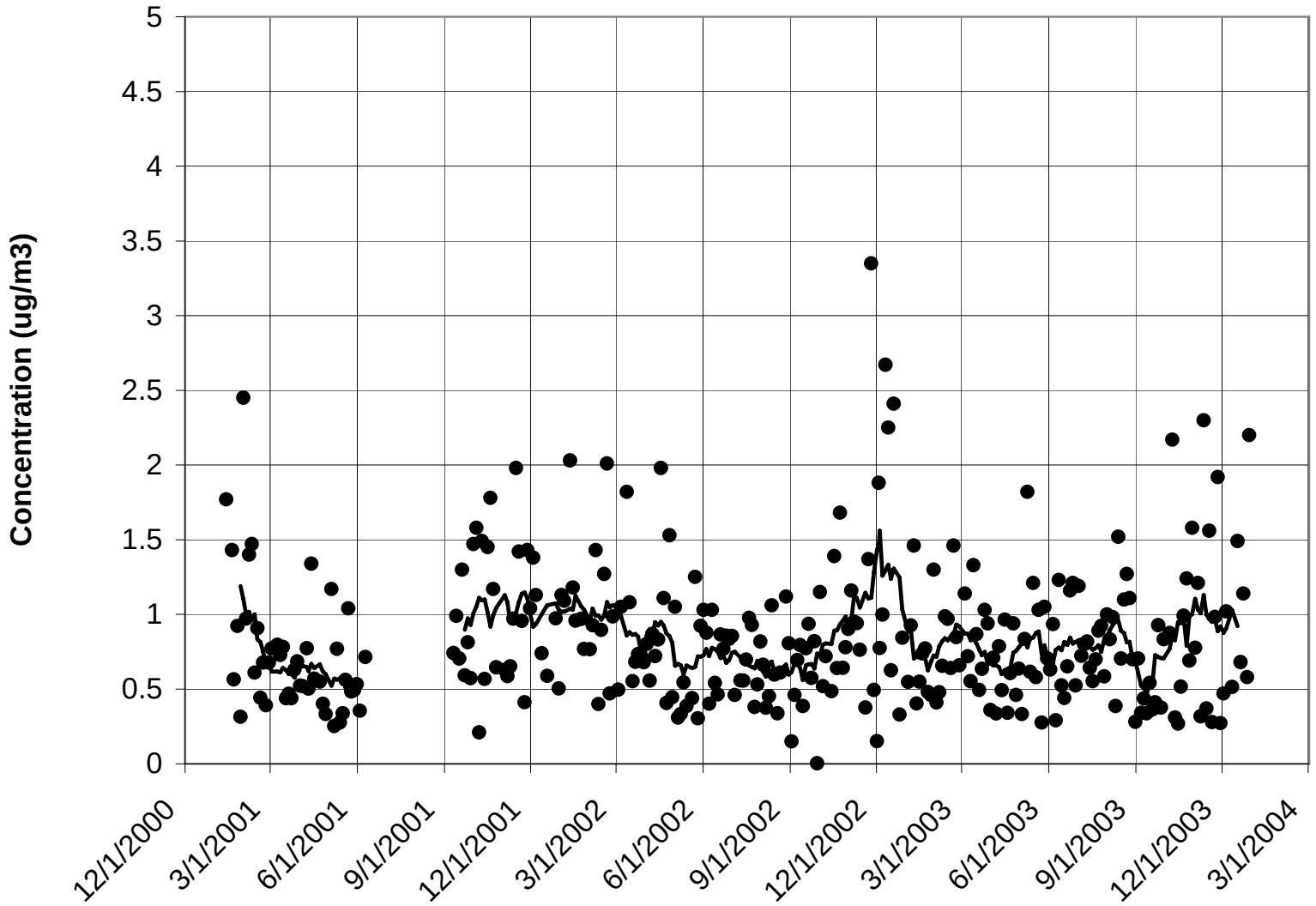
Ammonium Time Series



Nitrate Time Series



Elemental Carbon Time Series



Seasonal Summary

Seasonal analyses help analysts understand the nature of the $PM_{2.5}$ problem

Season	Sulfate	OM (1.6)	Ammonium	Nitrate	EC	STN Gravimetric Mass
Winter	**3.29**	6.22	2.31	**4.19**	**0.99**	15.97
Spring	3.83	**4.46**	1.72	2.08	0.78	14.25
Summer	**7.65**	**7.36**	**2.85**	**1.29**	**0.76**	**21.27**
Fall	3.74	5.80	**1.51**	1.79	0.88	**12.88**
Average	4.74	5.96	2.08	2.25	0.85	16.10

Red text indicates high seasonal average; green text low seasonal averages

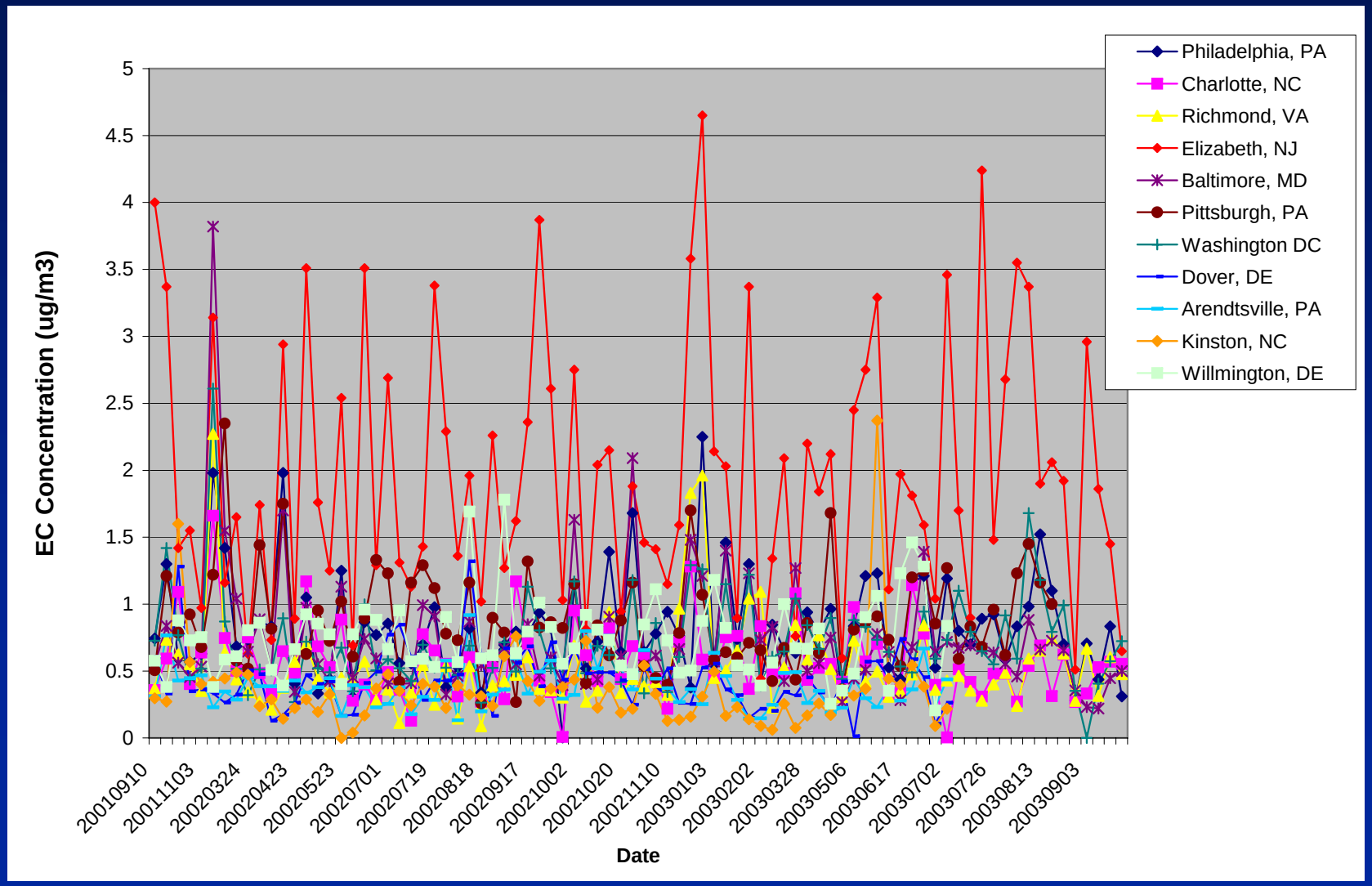
MARAMA

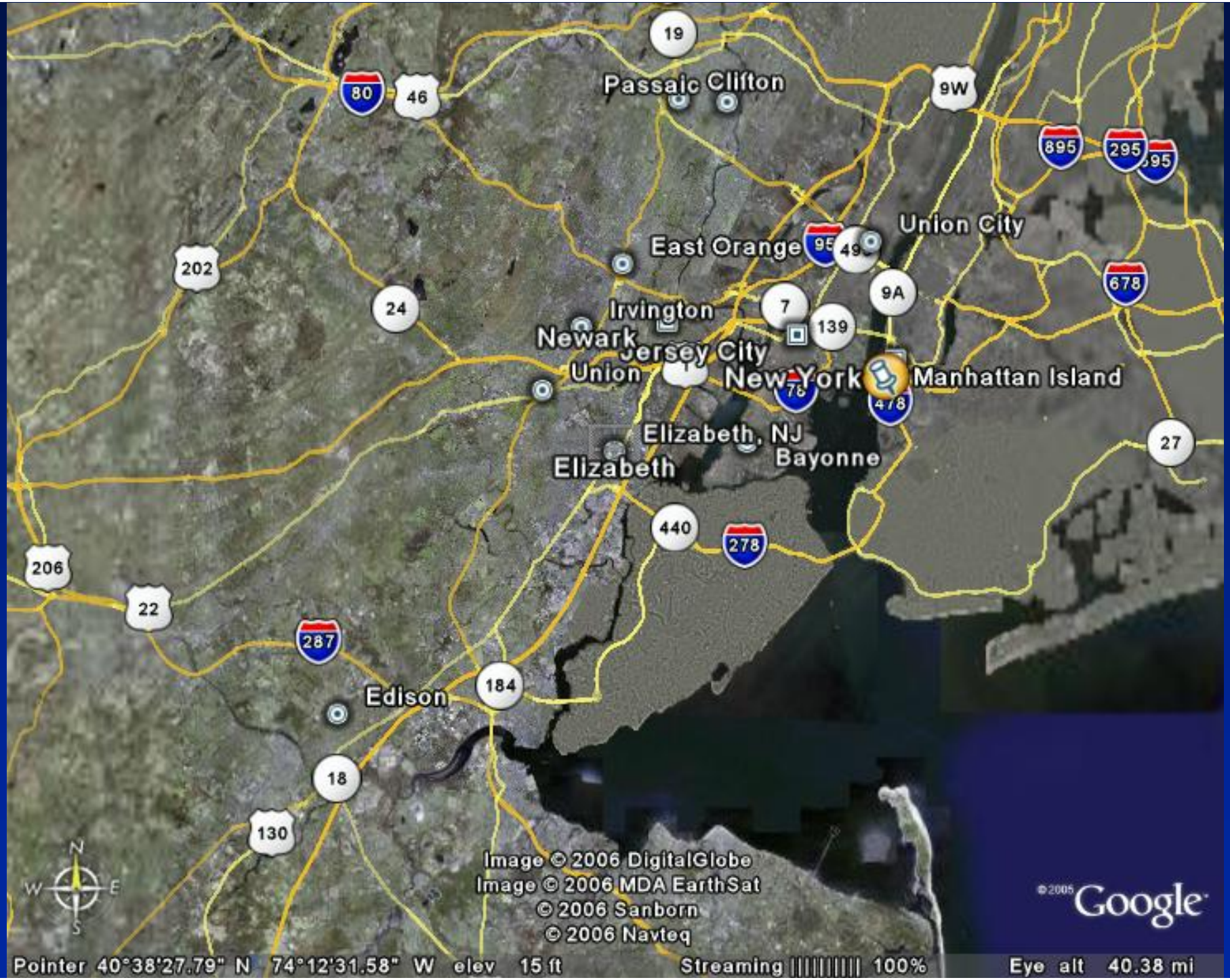
Understanding the Character of a Site is Important…

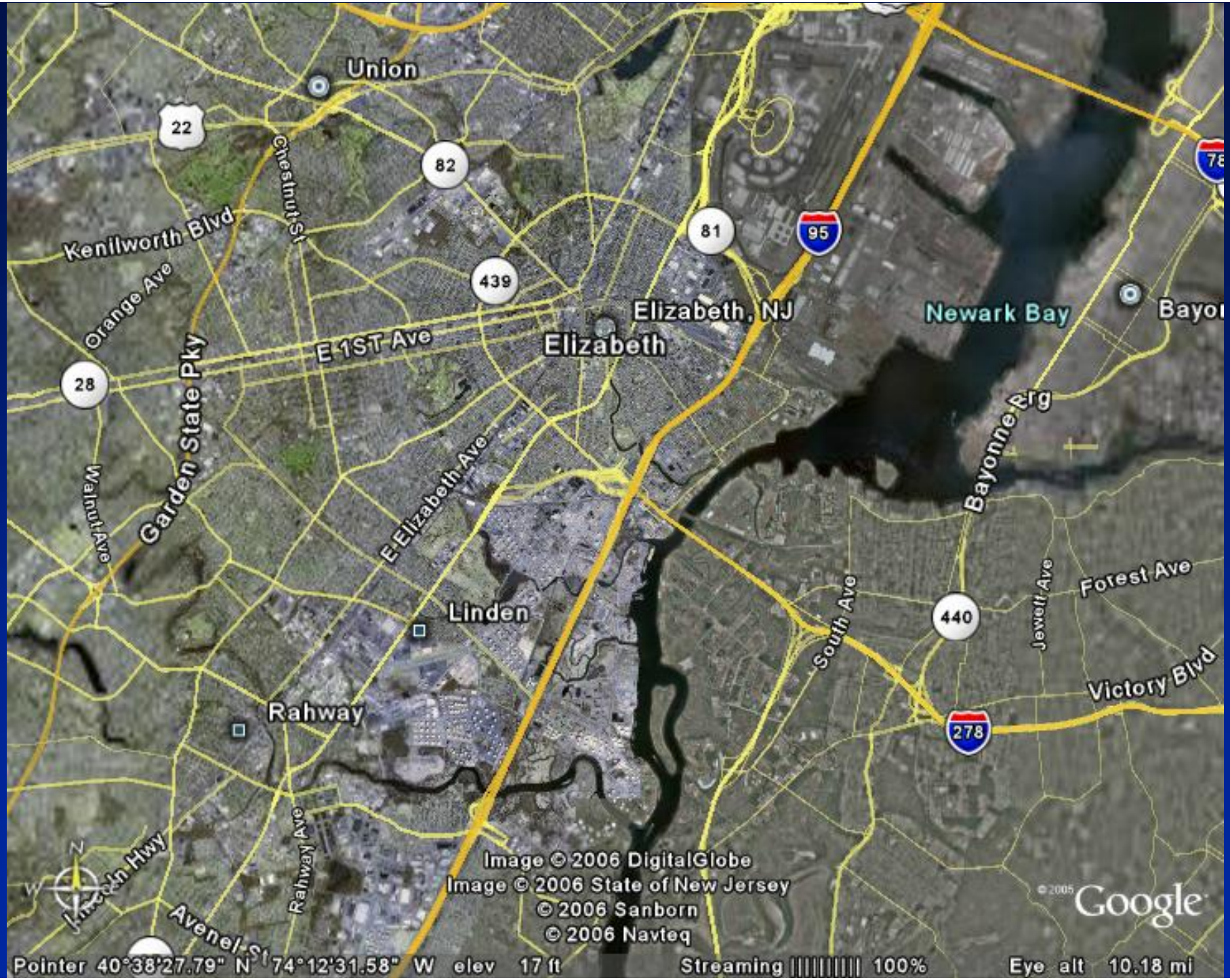
MARAMA

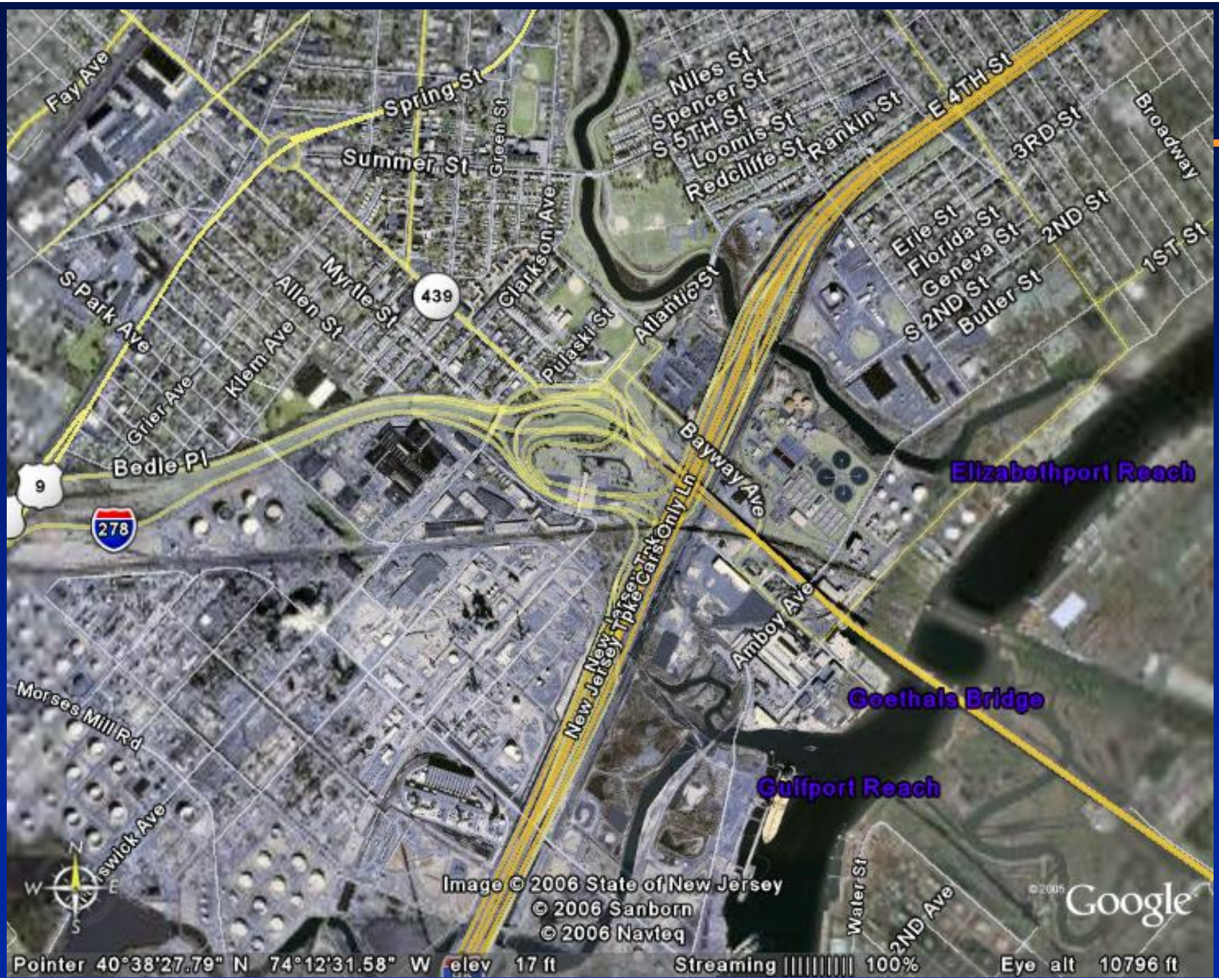
Elizabeth, NJ

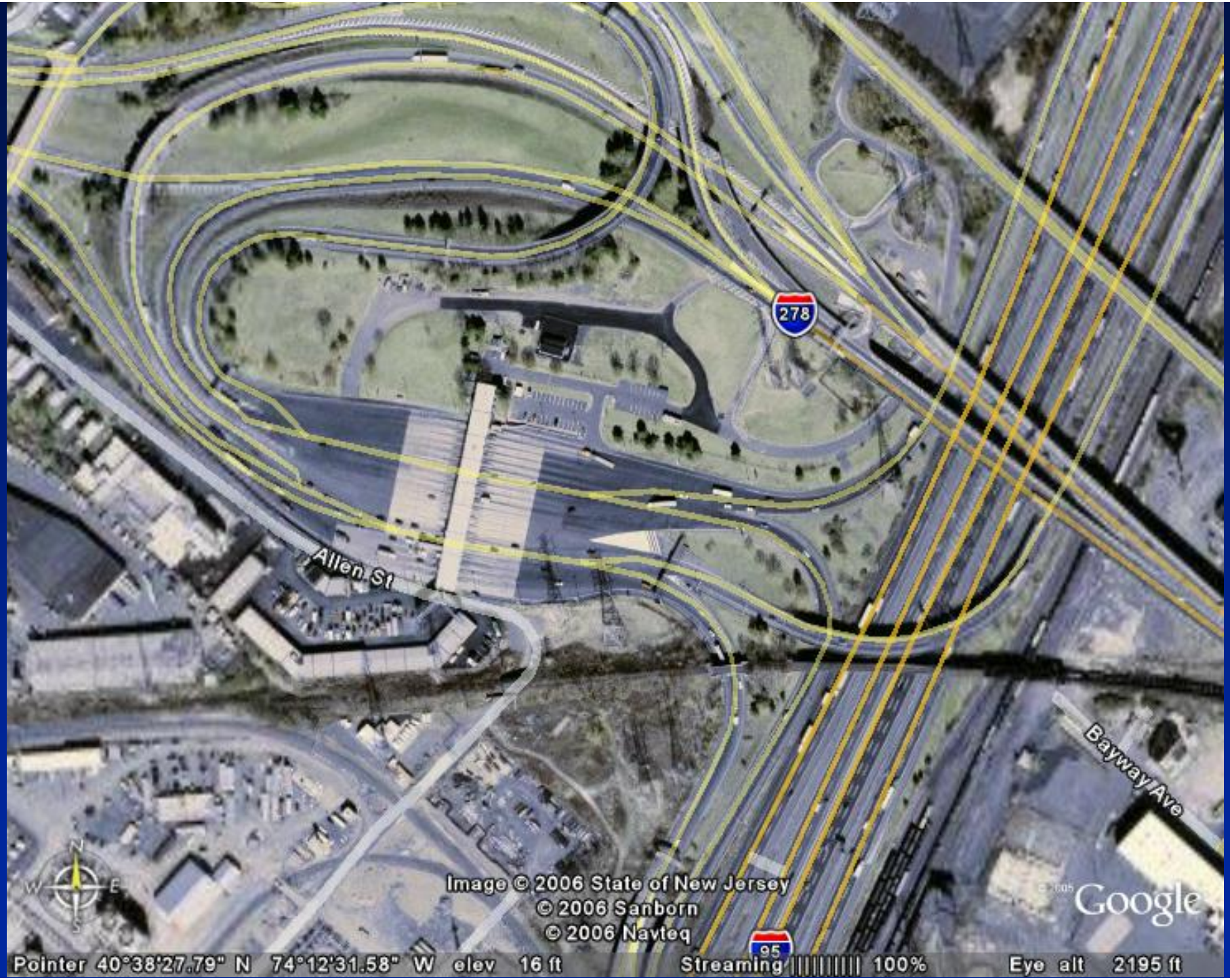
Elemental carbon time series for eleven monitors. Elizabeth, NJ in red.

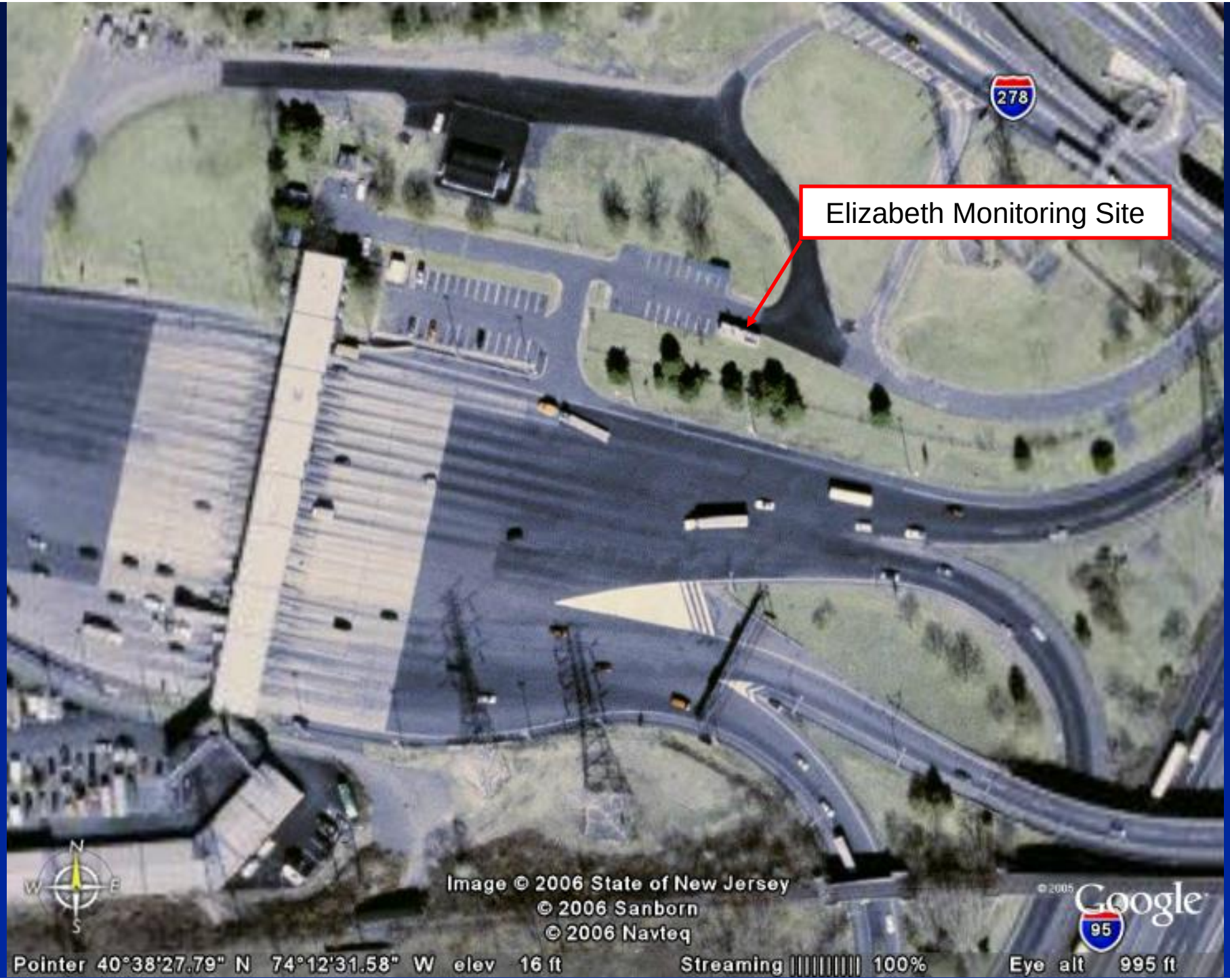



19
Passaic Clifton
80
46
9W
895
295
Union City
East Orange
95
202
24
678
9A
Irvington
7
139
Newark
Jersey City
Union
New York
Manhattan Island
78
478
Elizabeth, NJ
Bayonne
Elizabeth
27
440
278
206
22
287
184
Edison
18
130
Image © 2006 DigitalGlobe
Image © 2006 MDA EarthSat
© 2006 Sanborn
© 2006 Navteq
©2005 Google
Pointer 40°38'27.79" N 74°12'31.58" W elev 15 ft
Streaming 100%
Eye alt 40.38 mi


Union
22
82
Chestnut St
Kenilworth Blvd
Orange Ave
439
81
95
Elizabeth, NJ
Newark Bay
Bayou
E 1ST Ave
Elizabeth
28
Garden State Pky
Bayonne Brg
Walnut Ave
E Elizabeth Ave
Linden
South Ave
440
Jewett Ave
Forest Ave
Victory Blvd
Rahway
278
Rahway Ave
Lincoln Hwy
Avenel St
Image © 2006 DigitalGlobe
Image © 2006 State of New Jersey
© 2006 Sanborn
© 2006 Navteq
© 2005 Google
Pointer 40°38'27.79" N 74°12'31.58" W elev 17 ft
Streaming |||||||||| 100%
Eye alt 10.18 mi


Fay Ave
Spring St
Summer St
Green St
Niles St
Spencer St
S 5TH St
Loomis St
Redcliffe St
Rankin St
E 4TH St
3RD St
Broadway
Clarkson Ave
Erie St
Florida St
Geneva St
S 2ND St
Butler St
2ND St
1ST St
S Park Ave
Allen St
Myrtle St
439
Pulaski St
Atlantic St
Klem Ave
Grier Ave
Bedle Pl
9
278
Bayway Ave
New Jersey Tpke Cars Only Ln
New Jersey Tpke Trucks Only Ln
Amboy Ave
Elizabethport Reach
Goethals Bridge
Gulfport Reach
Morses Mill Rd
Water St
2ND Ave
Image © 2006 State of New Jersey
© 2006 Sanborn
© 2006 Navteq
Google
Pointer 40°38'27.79" N 74°12'31.58" W elev 17 ft
Streaming 100%
Eye alt 10796 ft


278
Allen St
Bayway Ave
95
Image © 2006 State of New Jersey
© 2006 Sanborn
© 2006 Navteq
Google
Pointer 40°38'27.79" N 74°12'31.58" W elev 16 ft
Streaming 100%
Eye alt 2195 ft


Elizabeth Monitoring Site
278
95
Image © 2006 State of New Jersey
© 2006 Sanborn
© 2006 Navteq
Google
Pointer 40°38'27.79" N 74°12'31.58" W elev 16 ft
Streaming 100%
Eye alt 995 ft

Elizabeth, NJ

Average elemental carbon concentration at Elizabeth is more than twice the concentration of other major urban areas and about 4 to 5 times the concentration of rural locations.

Site and State	Carbon Mass (µg/m3)1 (OM/OC =1.6)	Sulfate (µg/m^3)	Ammonium (µg/m^3)	Nitrate (µg/m^3)	Elemental Carbon (µg/m^3)
Arendtsville, PA*	3.90	**6.12**	**2.36**	1.95	0.39
Baltimore, MD	5.82	5.13	1.94	1.84	0.77
Charlotte, NC	5.86	4.96	1.60	**0.94**	0.62
Dover, DE*	**3.62**	4.65	1.89	1.87	0.47
Elizabeth, NJ	**6.93**	4.81	2.19	2.27	**1.82**
Kinston, NC*	4.47	**4.11**	**1.51**	1.10	**0.36**
Philadelphia, PA	5.96	4.74	2.08	2.25	0.85
Pittsburgh, PA	5.47	6.00	2.28	1.77	0.85
Richmond, VA	6.81	4.97	1.89	1.20	0.56
Washington DC	5.70	5.44	2.02	1.68	0.73
Wilmington, DE*	5.02	5.24	2.33	**2.48**	0.78

Regional Results

9/10/01 to 10/12/03 Data

MARAMA

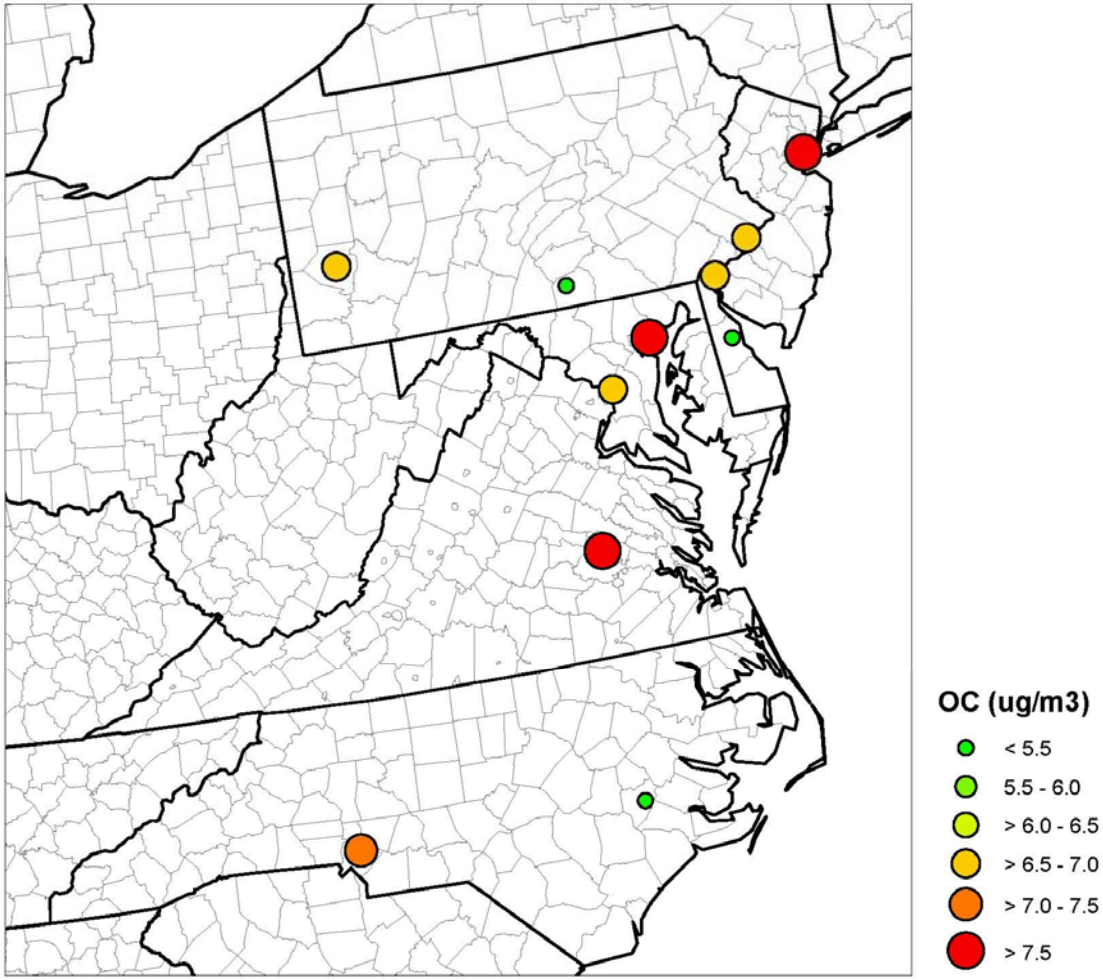
Sites Studied

- 12 Monitoring Sites
  - Arendtsville, PA (1-in-6)
  - Baltimore, MD; Essex
  - Charlotte, NC; Garinger H.S.
  - Dover, DE (1-in-6)
  - Elizabeth, NJ; Elizabeth Lab
  - Kinston, NC (1-in-6)
  - Philadelphia, PA; AMS Lab
  - Pittsburgh, PA; Lawrenceville
  - Richmond, VA; DEQ Monitoring Office
  - South Charleston; WV (2004 data only)
  - Washington, DC; McMillan Reservoir
  - Wilmington, DE; Martin Luther King Ave. (1-in-6)

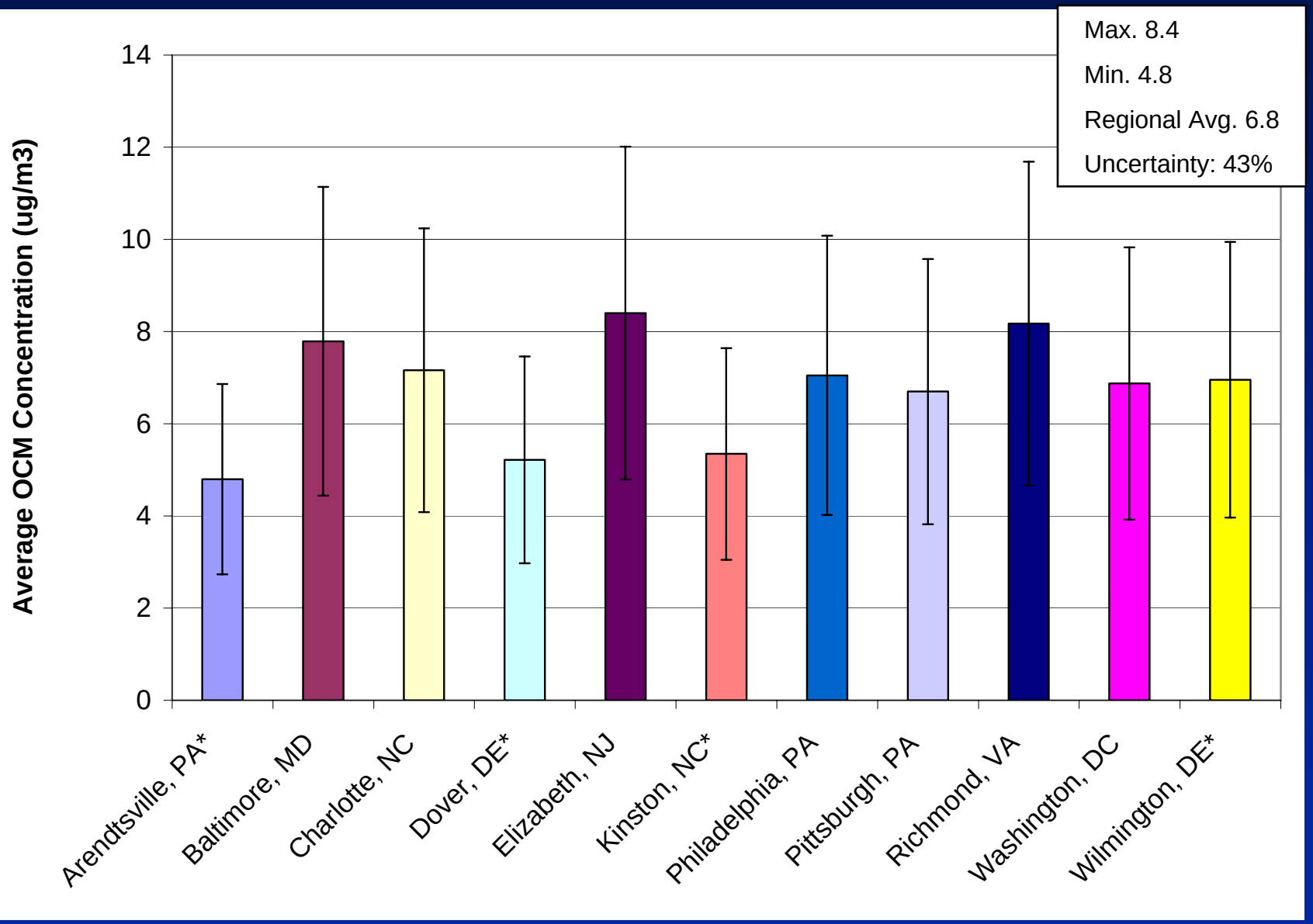
MARAMA

The Regional Analysis: Organic Carbon Mass

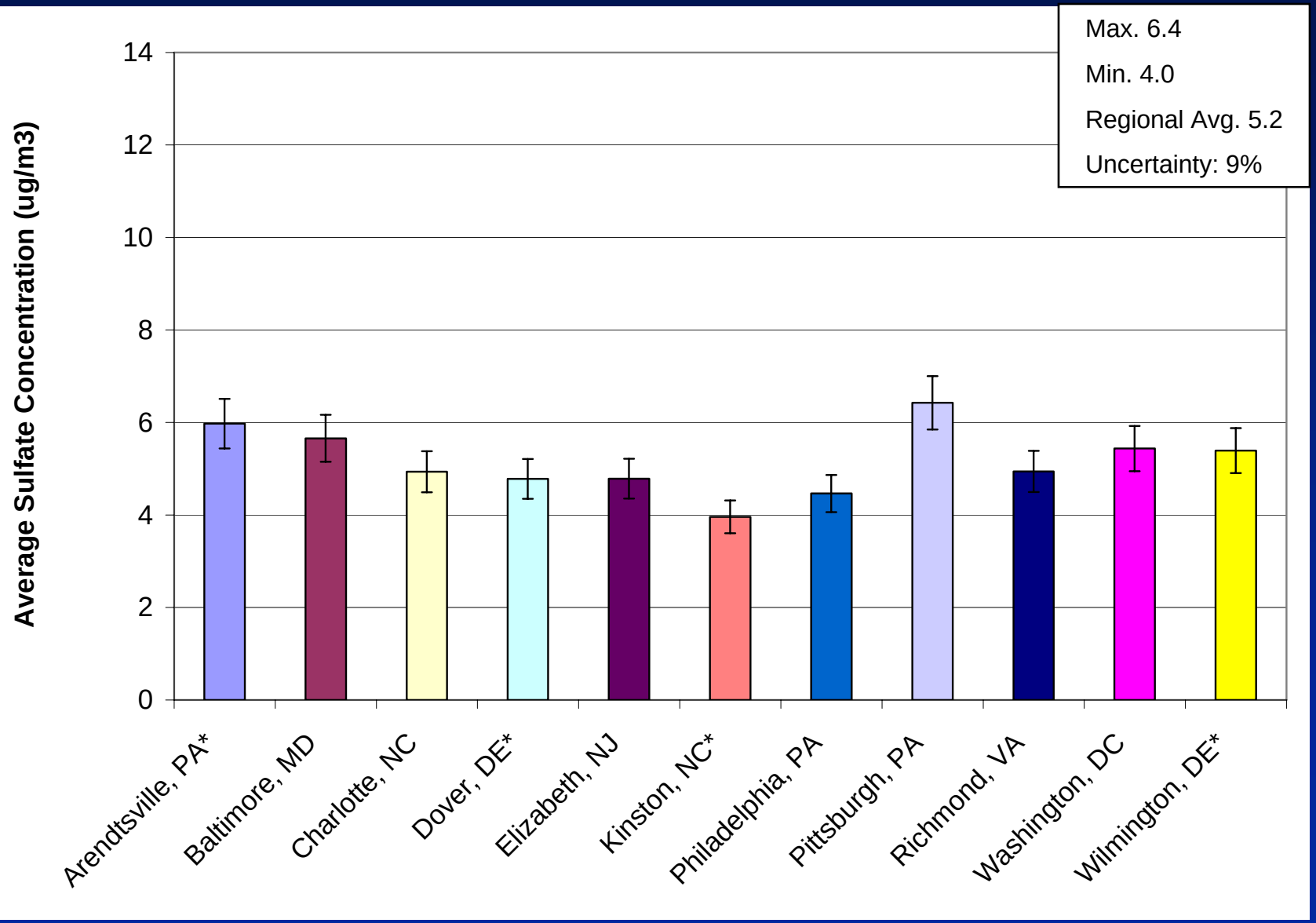
Site Name & State	Average Organic Carbon Mass (ug/m3)
Arendtsville, PA*	**4.8**
Baltimore, MD	7.8
Charlotte, NC	7.2
Dover, DE*	5.2
Elizabeth, NJ	**8.4**
Kinston, NC*	5.3
Philadelphia, PA	7.0
Pittsburgh, PA	6.7
Richmond, VA	8.2
Washington, DC	6.9
Wilmington, DE*	7.0
Average	**6.8**
* = 1-in-6 monitor	



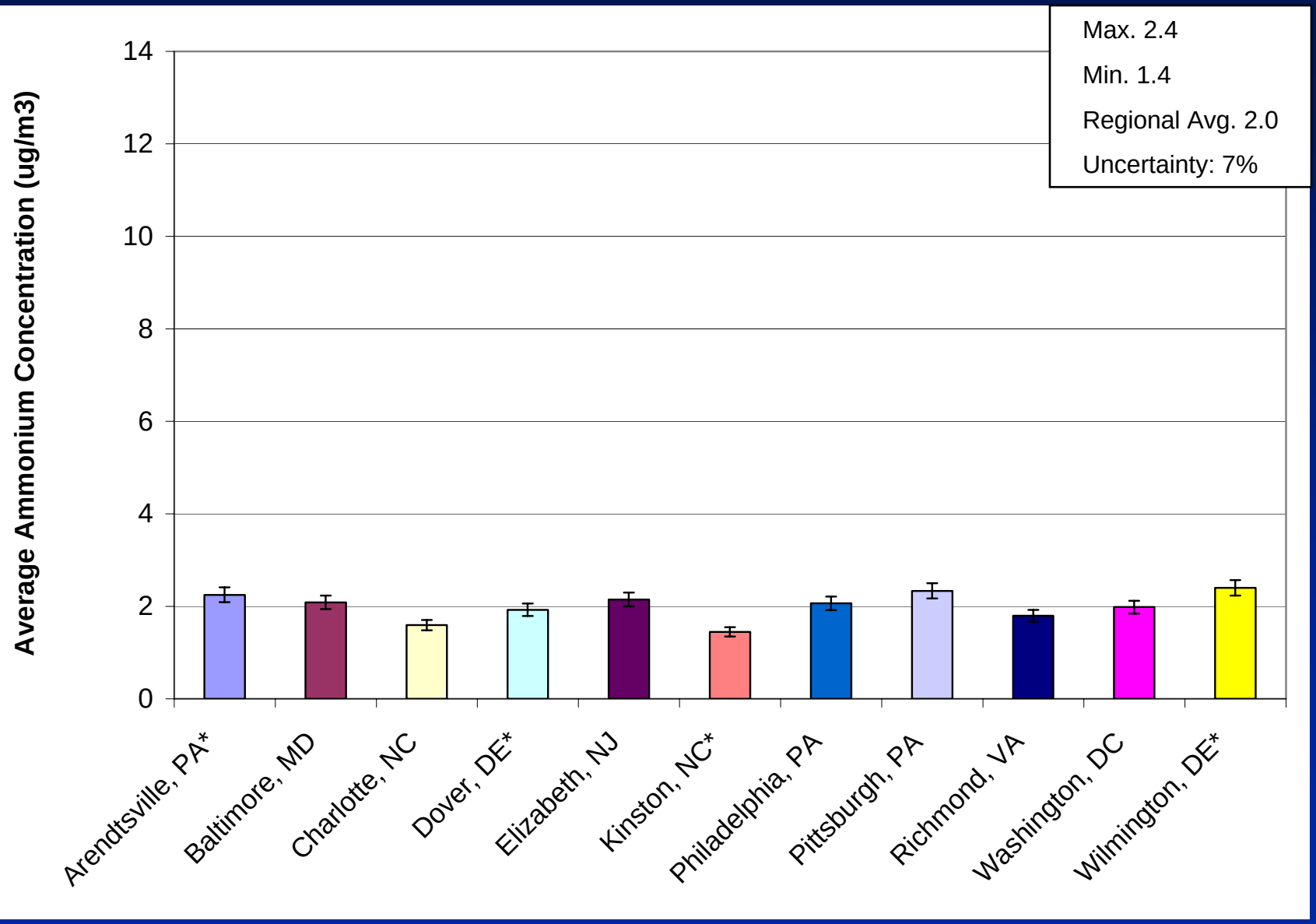
The Regional Analysis: Organic Carbon Mass



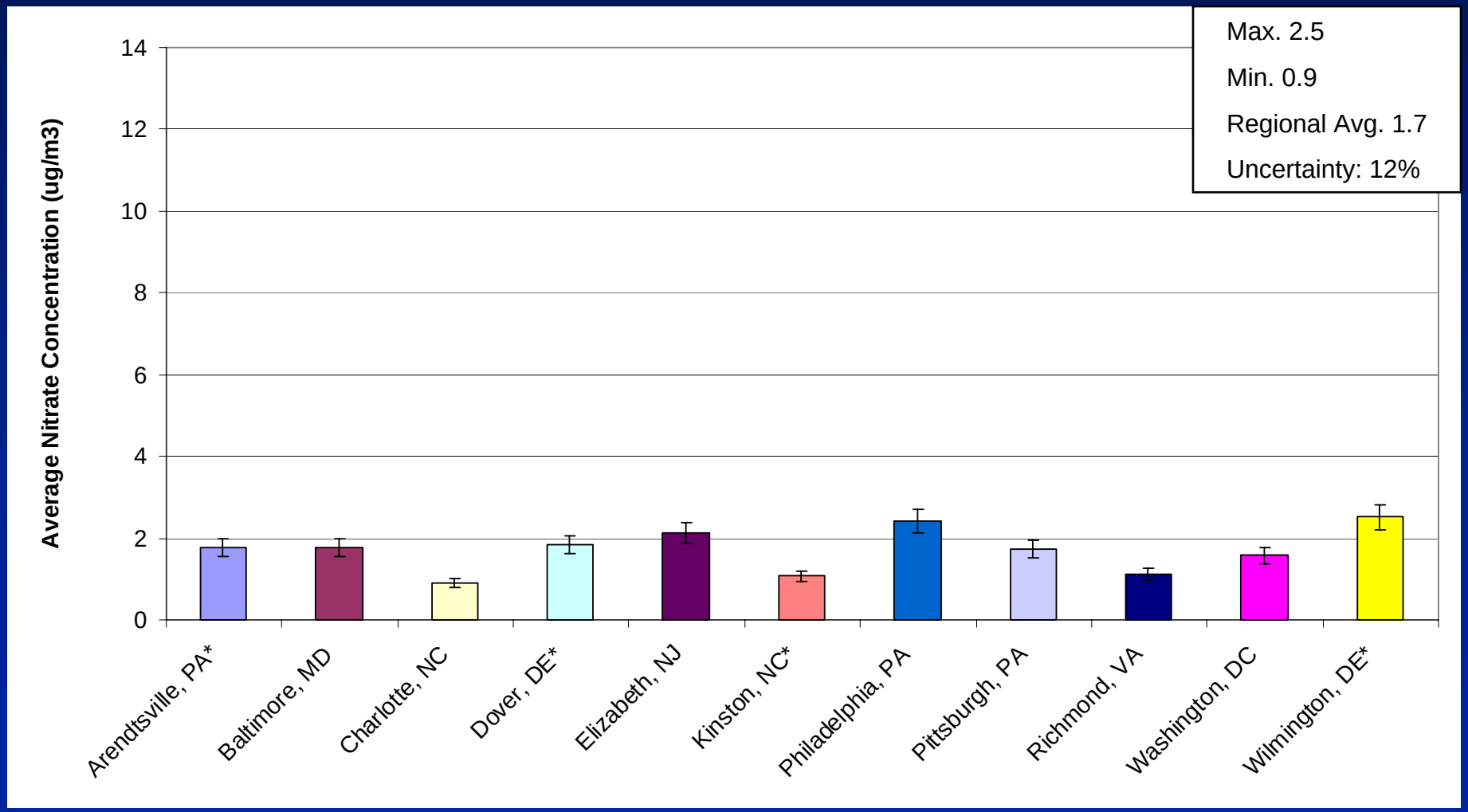
The Regional Analysis: Sulfate, 2001-2003



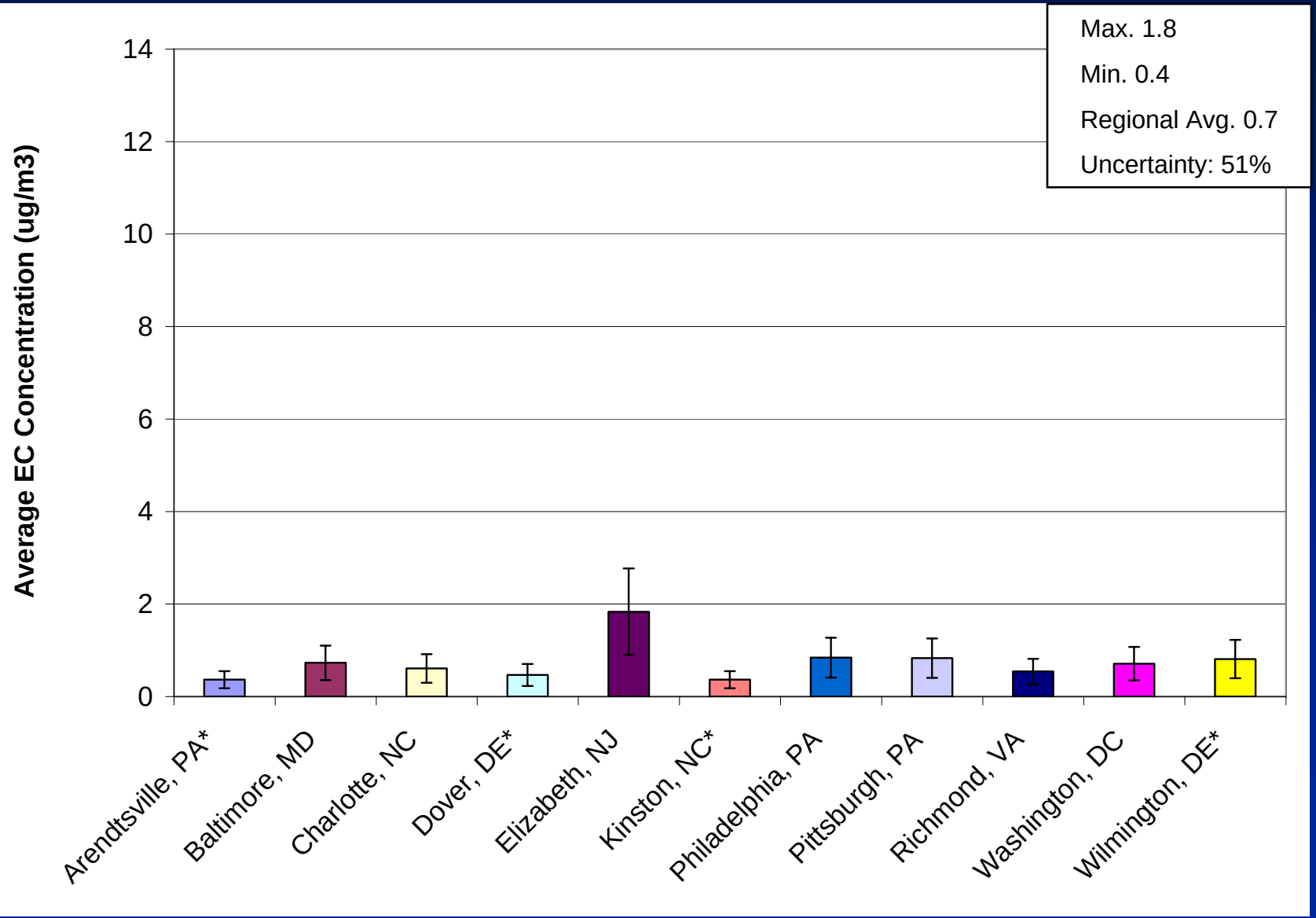
The Regional Analysis: Ammonium



The Regional Analysis: Nitrate



The Regional Analysis: Elemental Carbon



Trajectory Analysis of the 5% "Cleanest and "Dirtiest" Days

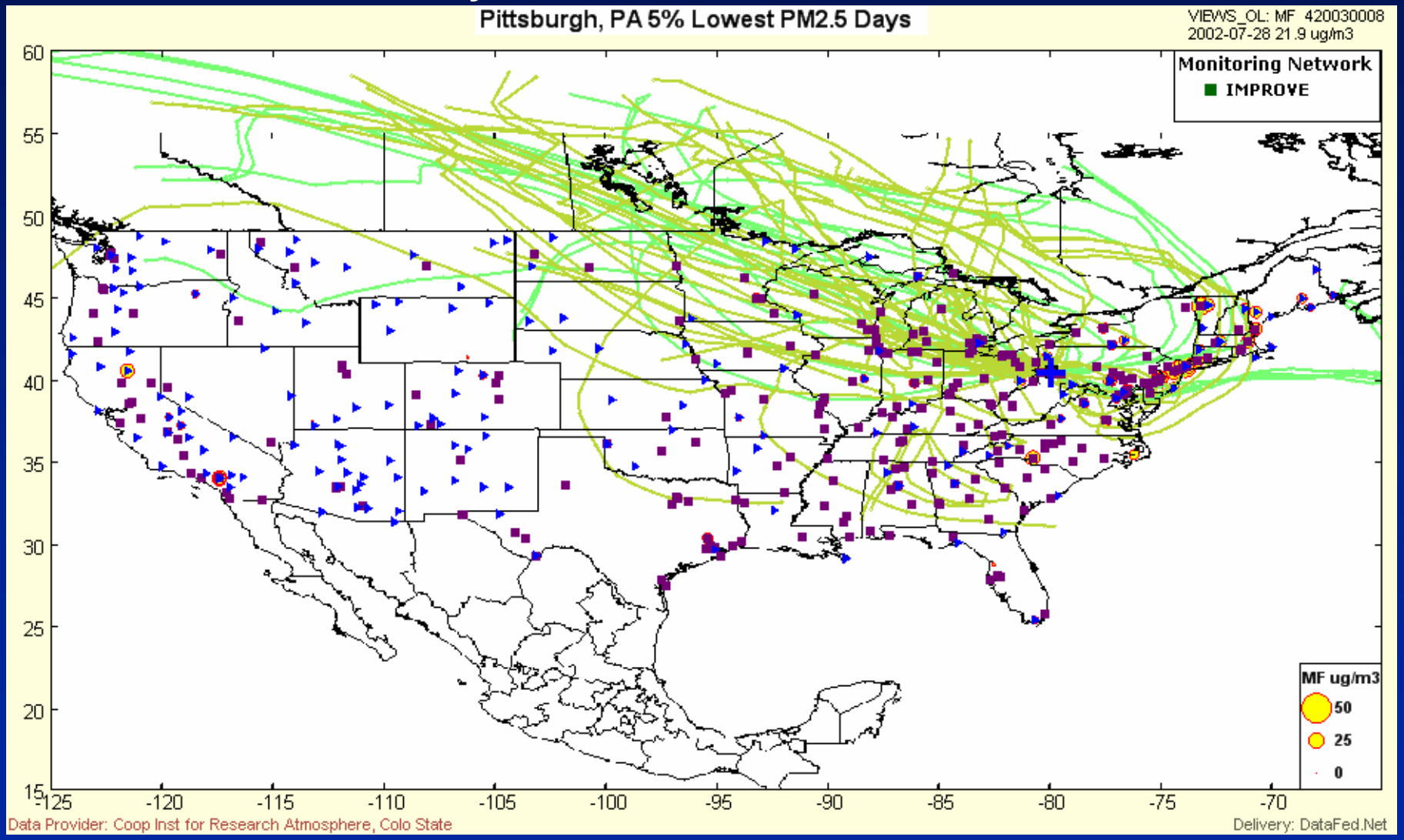
The Combined Aerosol Trajectory Tool (CATT)

http://datafedwiki.wustl.edu/index.php/CATT

MARAMA

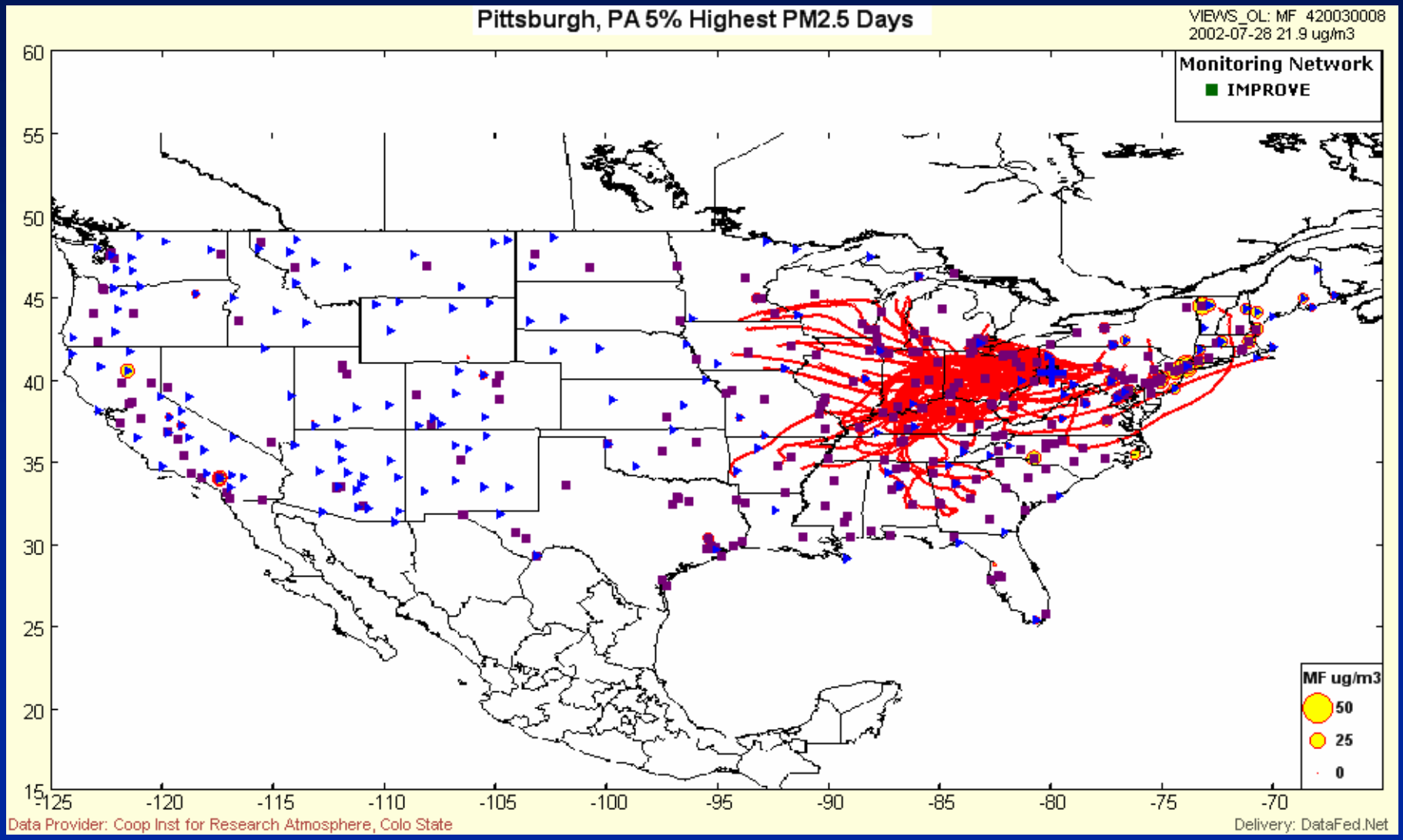
Back Trajectory Analysis; Pittsburgh, PA

5% “Cleanest” Days, 2001-2003



Back Trajectory Analysis; Pittsburgh, PA

5% “Dirtiest” Days, 2001-2003



Selected Findings from the MARAMA Analysis

- Organic Carbon Mass
  - Researchers have measured higher OM/OC ratios than previously. Higher OM/OC ratios mean a larger fraction of total mass is OM
  - OM and sulfate were the largest contributors to $PM_{2.5}$ mass at all sites studied
  - At an OM/OC ratio of 1.6, OM was the largest contributor to $PM_{2.5}$ mass at 7 of the 11 sites studied
  - At most sites, OM was highest in summer; lowest in spring

MARAMA

Selected Findings from the MARAMA Analysis

- Sulfate
  - Sulfate was the largest contributor to $PM_{2.5}$ mass at 4 of the 11 sites studied
  - Sulfate was highest in summer, often episodic in nature, and well correlated with ammonium
  - If sulfate and ammonium concentrations are added together, combined concentrations were the largest contributor to $PM_{2.5}$ mass at all sites.

MARAMA

Selected Findings from the MARAMA Analysis

- Ammonium
  - Ammonium concentrations were fairly uniform across the MARAMA Region
  - In many cases, urban sites produced somewhat higher ammonium concentrations than rural sites

MARAMA

Selected Findings from the MARAMA Analysis

- Nitrate
  - Nitrate made a much smaller contribution to $PM_{2.5}$ mass than OM and sulfate species
  - Nitrate concentrations peak in winter and are low in summer
  - High nitrate concentrations are associated with cold temperatures and low UV radiation (winter and more northern climates)
  - Lower average nitrate concentrations occurred in the southern part of the MARAMA Region, & conversely

MARAMA

Selected Findings from the MARAMA Analysis

- Elemental Carbon
  - EC concentrations were small relative to other $PM_{2.5}$ mass constituents
  - EC concentration correlates well with population
  - Higher EC concentrations were observed in urban areas than in rural areas
  - One urban site (Elizabeth, NJ) exhibited “hot spot” effects

MARAMA

Some Concluding Thoughts…

- Is speciated data valuable/worth analyzing? Yes!
- Speciation program provides excellent information on the constituents of $PM_{2.5}$ mass & will allow the analysis of long-term trends
- Is working with the data challenging? Yes! But it can be done.
- A web site is needed to provide data analysts with the information they need to properly adjust and use speciation data
- Are better methods needed for OM. Absolutely! A SANDWICH may be the answer…

MARAMA