An Atmospheric Perspective on Toxic Metal Deposition to Water Bodies and Water Sheds

James J. Schauer, Ph.D., PE

Associate Professor

University of Wisconsin-Madison

Overview

- Background
  - Atmospheric and Aquatic Toxicity
  - Deposition of Metals and Mercury
- Historical Strategies for Atmospheric Deposition
- New Strategies for Atmospheric Deposition
- Aquatic Toxicity of Atmospheric PM
- Sources of Trace Metals from Mobile Sources
- Atmospheric Mercury Source Characterization
  - St. Louis, Missouri
  - LA Basin
- Conclusions

Atmosphere and Water Bodies

- Recycling of Metals (…except Hg)
  - Lakes and estuaries have significant recycling of pollutants
  - Recycling in the atmosphere is not a dominant source
- Deposition of Metals (…except Hg)
  - Coarse Particles have the highest deposition to the earth
  - Fine Particles have the highest deposition in the lung
- Impact of Metals (…except Hg)
  - Environmental concentrations of metals are to toxic to aquatic organisms
  - The role of atmospheric metals in particulate matter toxicity is not well understood
- Impacts of Mercury
  - Atmospheric Hg levels are generally too low to directly present a public health threat
  - The predominate concern over aquatic mercury is the bioaccumulation in the food chain and human consumption

Aquatic Toxicity (…except Hg)

- Toxicity of metals depends on the bioavailability of the metals
  - Chemical form of the metal
  - Water chemistry
- Aquatic cycling can make metals more or less toxic
- Whole Effluent Testing (WET)
  - Don't know what is toxic
  - Bioassay established allowable discharges
- Total Maximum Daily Load (TMDL)
  - Know what is toxic
  - Use a systems approach to controlling inputs
- Control and mitigation rely on understanding source/receptor relationships

Great Lakes Commission des Grands Lacs

2002 Inventory of Toxic Air Emissions Point, Area and Mobile Sources

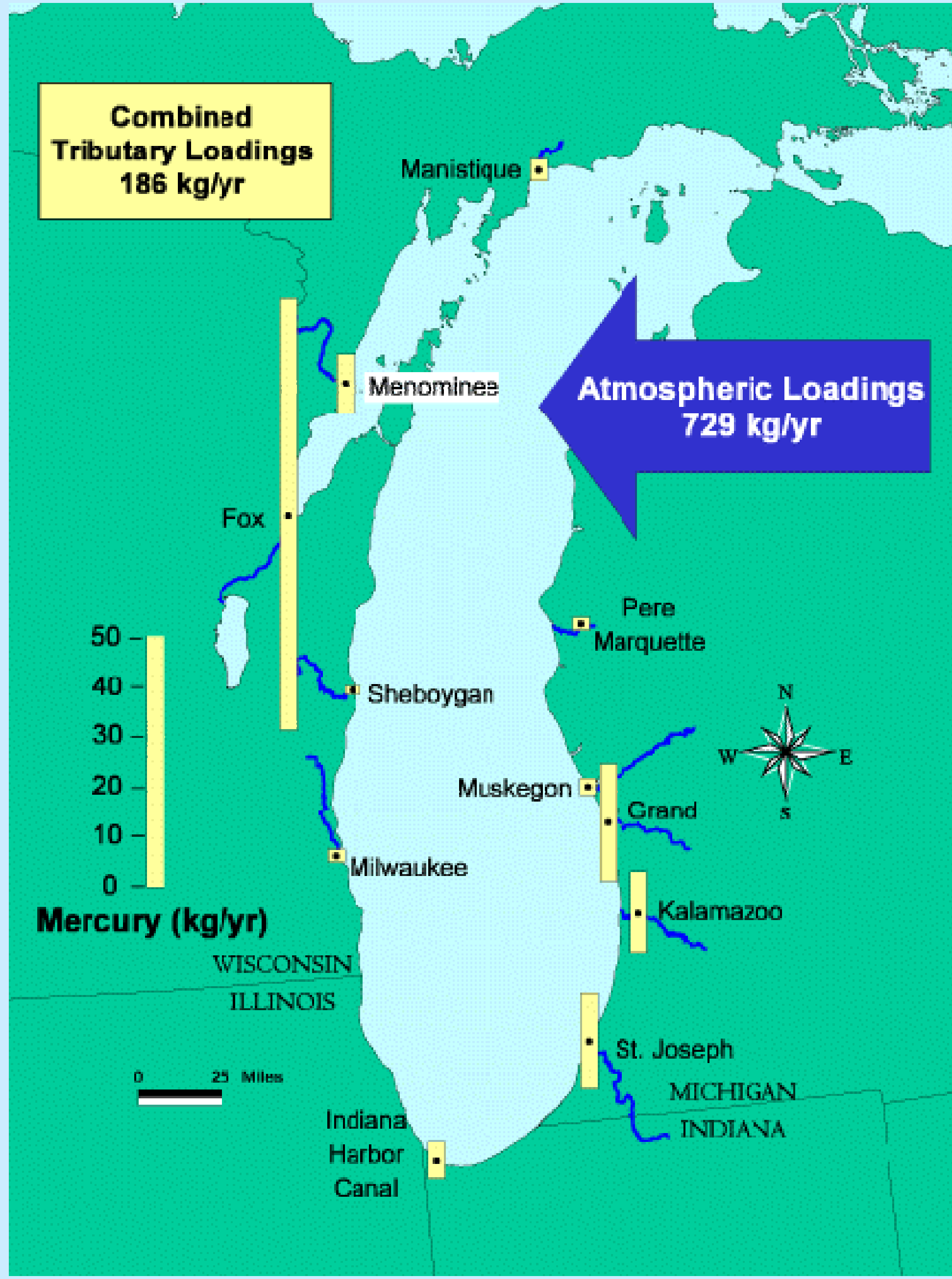
Pollutant Code (CAS Number)	Emissions (lbs.) Point	Area	Onroad	Nonroad	Total
Metal Compounds					
*Antimony (7440-36-0)	33,210	2007		24.62	35,240
*Arsenic (7440-38-2)	294,000	8151	4937	6.612	307,100
*Beryllium (7440-41-7)	13,180	1585		242	15,000
*Cadmium (7440-43-9)	78,060	5088		300.7	83,450
*Chromium (7440-47-3)	1,525,000	18,470	13,160	1360	1,558,000
*Chromium VI (18540-29-9)	19,870	362.8	3305	3368	26,910
*Cobalt (7440-48-4)	81,320	2831		28.23	84,180
*Copper (7440-50-8)	1,144,000	5230	4572	5.815	1,153,000
*Lead (7439-92-1)	1,264,000	52,300	849.4	56,530	1,373,000
*Alkylated lead	22.73	27.68			50.41
*Manganese (7439-96-5)	2,198,000	21,280	15,530	5528	2,240,000
*Mercury (7439-97-6)	64,190	3397	4952	282.4	72,820
*Nickel (7440-02-0)	858,800	44,820	11,210	18,580	933,400
*Selenium (7782-49-2)	362,300	6771	204.2	109.8	369,300
Titanium tetrachloride (7550-45-0)	561				561
Metal Total	**7,935,000**	**172,300**	**58,720**	**86,370**	**8,253,000**

http://www.glc.org/air/inventory/2002/

Lake Michigan Mass Balance

http://www.epa.gov/glnpo/lmmb/

Atrazine
PCBs
Mercury
Trans-nonachlor



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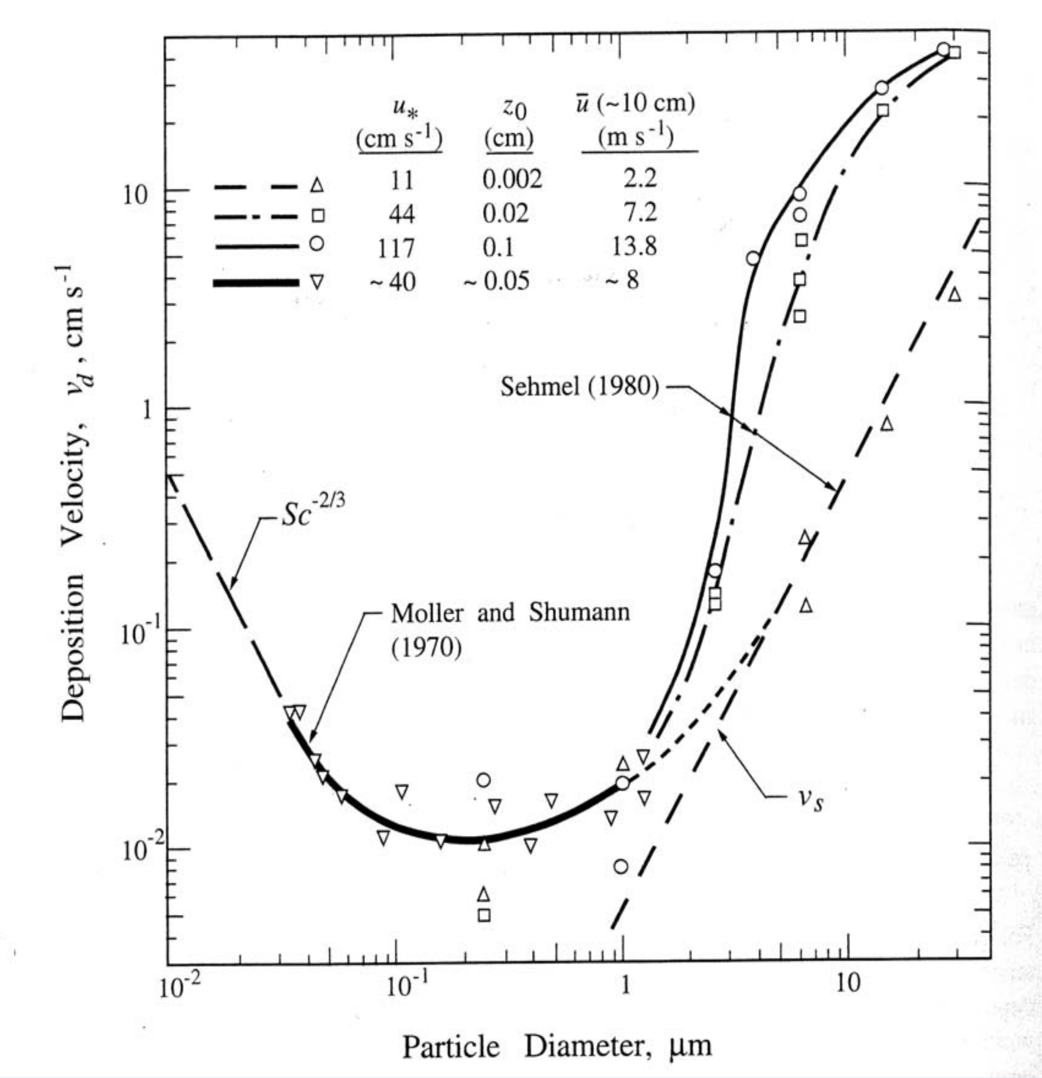
Deposition

- Wet Deposition
  - Very efficient process for soluble gases and particulate matter
  - Origin
    - In cloud scavenging
    - Scavenging of air column
- Dry Deposition
  - Deposition rate dependent on:
    - Particle size for particulate matter
    - Reactivity for gases
- Need to consider deposition to open water and watershed

Characterization of Deposition

- Deposition Velocity
  - Dry Deposition
  - Atmospheric Concentration/Deposition Flux
    - Units of Meters per second
  - Dependent on wind speed, surface, and gas and particle distribution
- Wash Out Ratio
  - Wet Deposition
    - Atmospheric Concentration/Rain Concentration
  - Dependent
    - Gases – Water solubility
    - Particles – Hydroscopic properties and size

Deposition Velocity

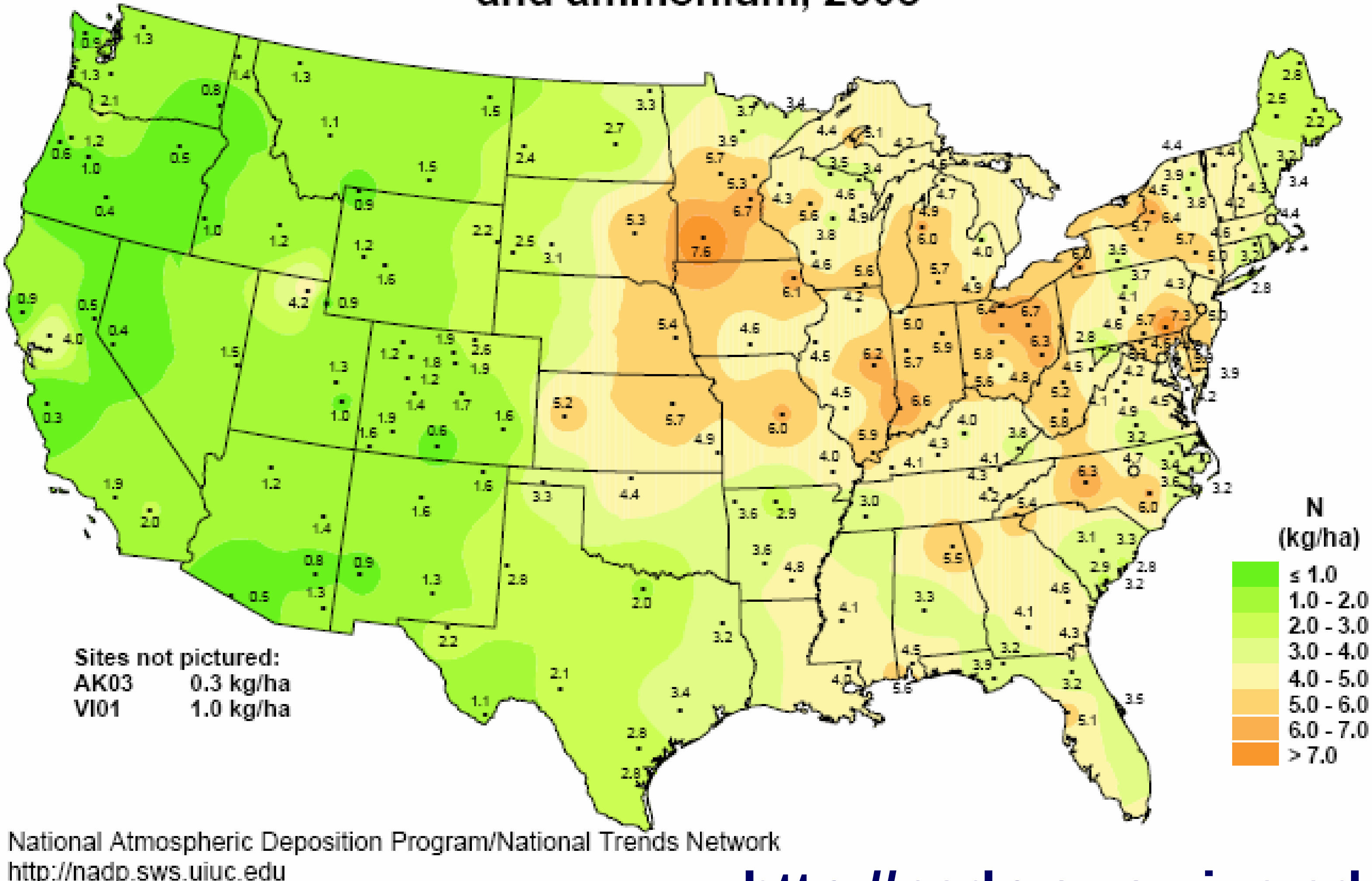


Typical Deposition Velocity, v_d (cm s^{-1}) over			
Species	Continent	Ocean	Ice/Snow
CO	0.03	0	0
NO_2	0.1	0.02	0.01
HNO_3	4	1	0.5
O_3	0.4	0.07	0.07
H_2O_2	0.5	1	0.32

From Seinfeld and Pandis
Atmospheric Chemistry and Physics

http://in.water.usgs.gov/newreports/mercury/

Inorganic nitrogen wet deposition from nitrate and ammonium, 2005



http://nadp.sws.uiuc.edu/

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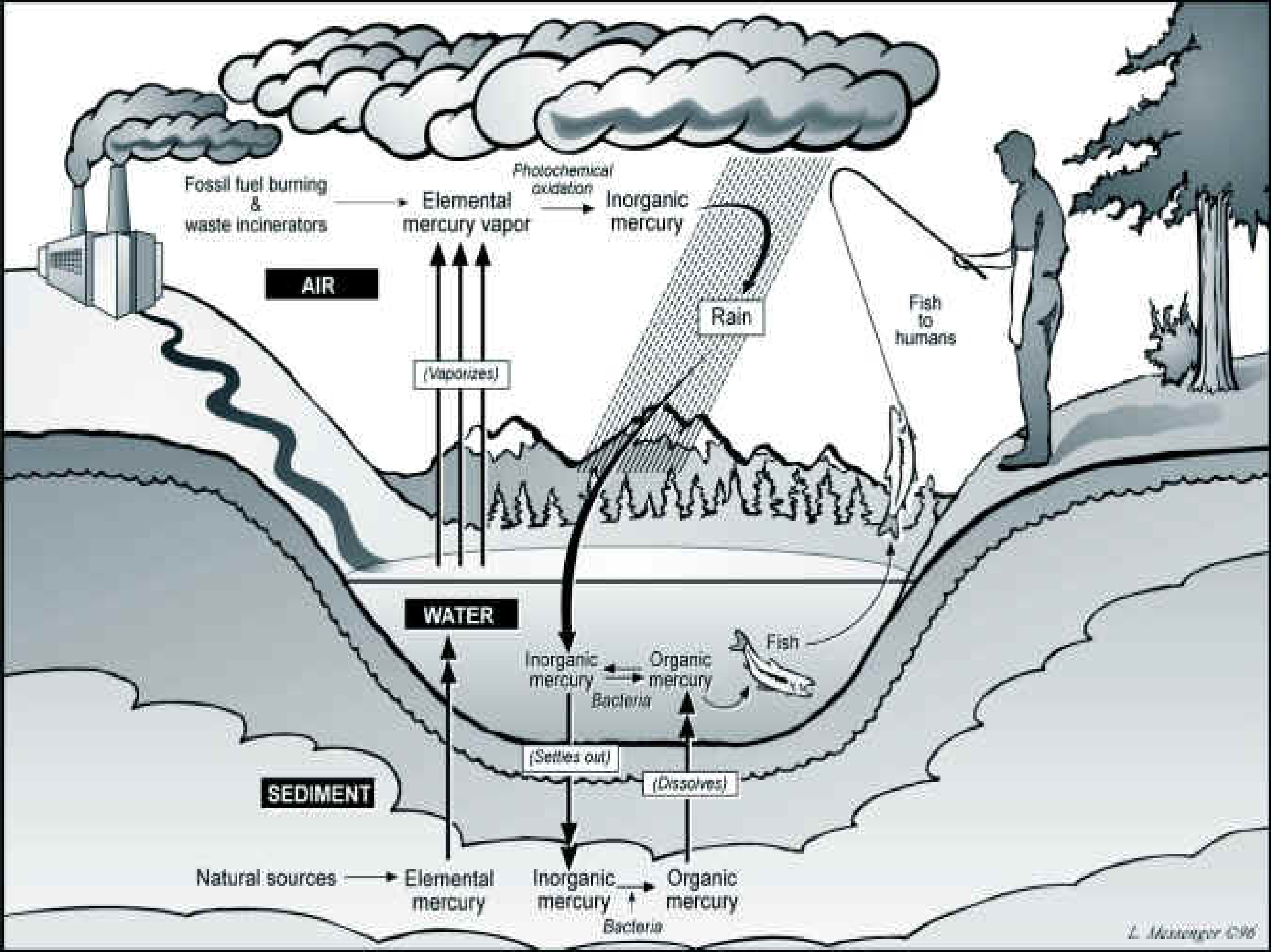
Chemical Forms of Mercury

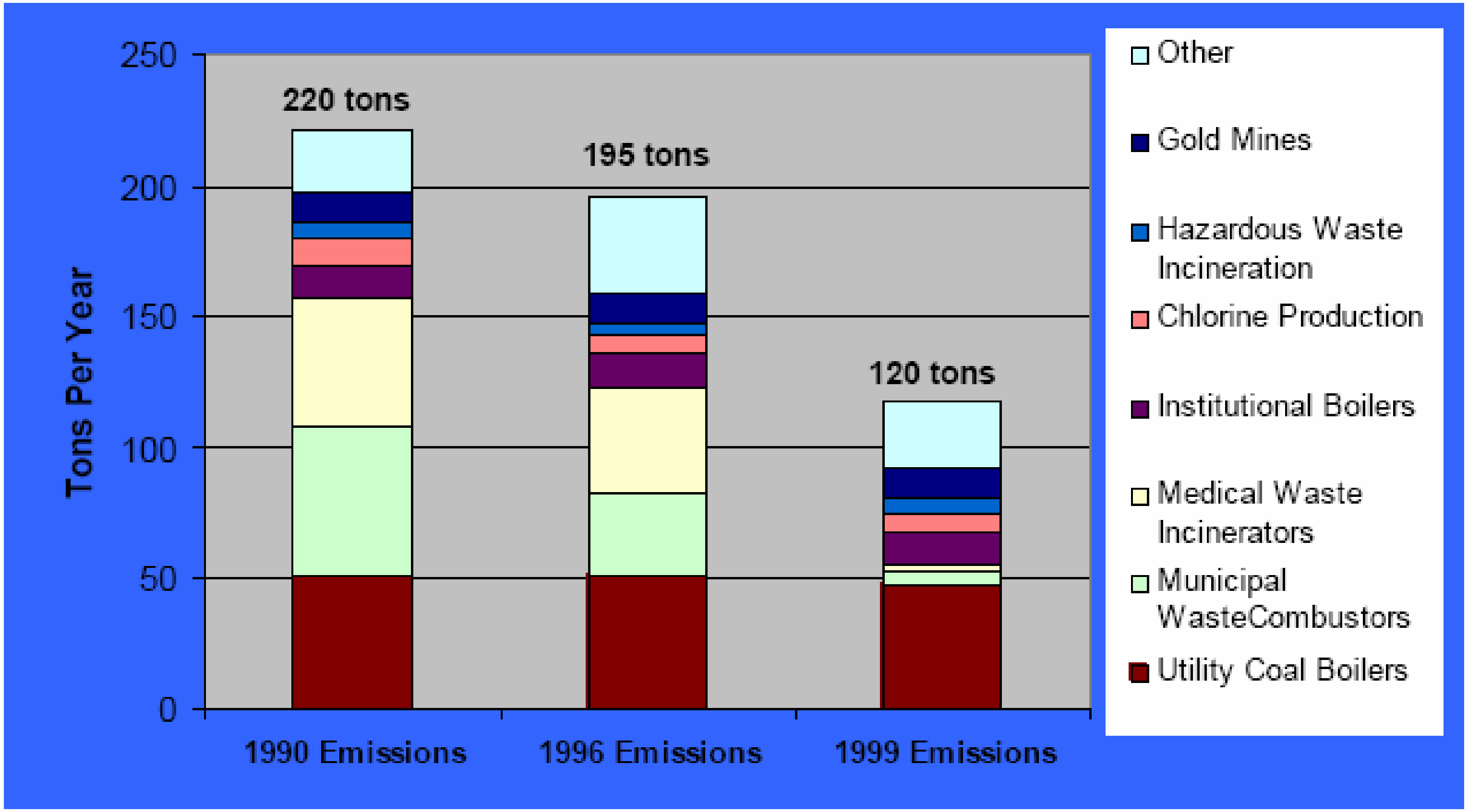
- Elemental Mercury – Hg^o
  - Very inert, low water solubility
  - Under most atmospheric condition is a gas
- Divalent Mercury - HgX_2
  - Oxidized form of mercury
  - Dominate component of atmospheric deposition
- Methyl Mercury - CH_3HgX
  - Mercury form that bioaccumulates in food web
  - Much more toxic that elemental or divalent Hg
- Dimethyl Mercury – $(CH_3)_2Hg$
  - Very toxic form of mercury
  - Role in Atmospheric cycle not well understood

Exposure Pathways

- Environmental
  - Air – Generally not a concern
  - Water – Generally not a concern
  - Soil –
    - Can be important for contaminated soils
  - Food –
    - Major driving force in protecting public health
- Occupational
  - Air
    - OSHA limits on exposure
  - Skin
    - Major concern for handling dimethyl mercury

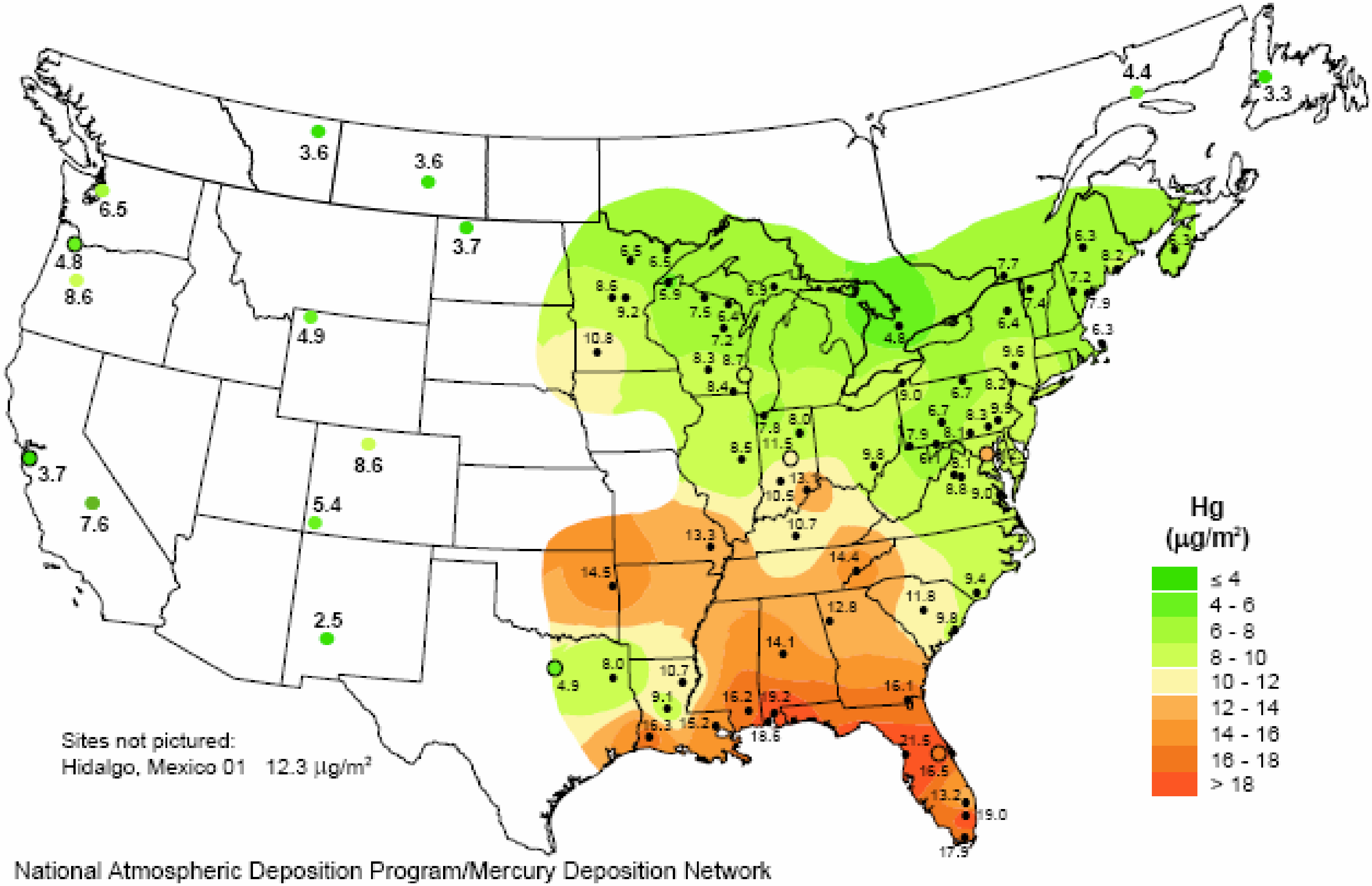

Fossil fuel burning
&
waste incinerators
Elemental
mercury vapor
Photochemical
oxidation
Inorganic
mercury
AIR
Rain
(Vaporizes)
Fish
to
humans
WATER
Inorganic
mercury
Organic
mercury
Bacteria
Fish
(Settles out)
(Dissolves)
SEDIMENT
Natural sources
Elemental
mercury
Inorganic
mercury
Organic
mercury
Bacteria

U.S. Emissions of Human-Caused Mercury Have Dropped 45% Since 1990



Source: EPA 1990, 1996 NTI and EPA 1999 NEI. Short tons per year. Adjusted for gold mines in 1990 and 1996.

Total Mercury Wet Deposition, 2005



http://nadp.sws.uiuc.edu/mdn/

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Key Questions for Atmospheric Deposition

- What is the flux of toxic metals
  - Wet and dry deposition
- What are the sources of the deposition?
  - Are the sources local or from long range transport
- Mercury Questions
  - Are local factors, including emissions of other pollutants and local meteorology, leading to enhanced oxidation of elemental mercury
  - Is direct deposition of methyl mercury an important source of methyl mercury in local lakes

Understanding Sources

- Emissions Inventory
  - Emissions inventory estimates are much more difficult than other pollutants
  - Speciation of emissions is clearly important
- Deposition Network
  - Typically measures wet deposition
  - Has been used in receptor based models
- Atmospheric Transport Models
  - Assumes good knowledge of emissions (and atmospheric chemistry of mercury)

Atmospheric Monitoring

- Long history of receptor based modeling for source apportionment
  - Compliments mechanistic air quality models
  - Receptor based models are largely based on linear combinations of sources
  - Source to deposition relationships are not linear due to “fractionation” during deposition
- Divide deposition apportionment into 2 parts
  - Sources of atmospheric concentrations
  - Deposition velocity and wash out ratios

TSP - South Shore of Lake Michigan (R. J. Sheesley et al., 2004, 2005)

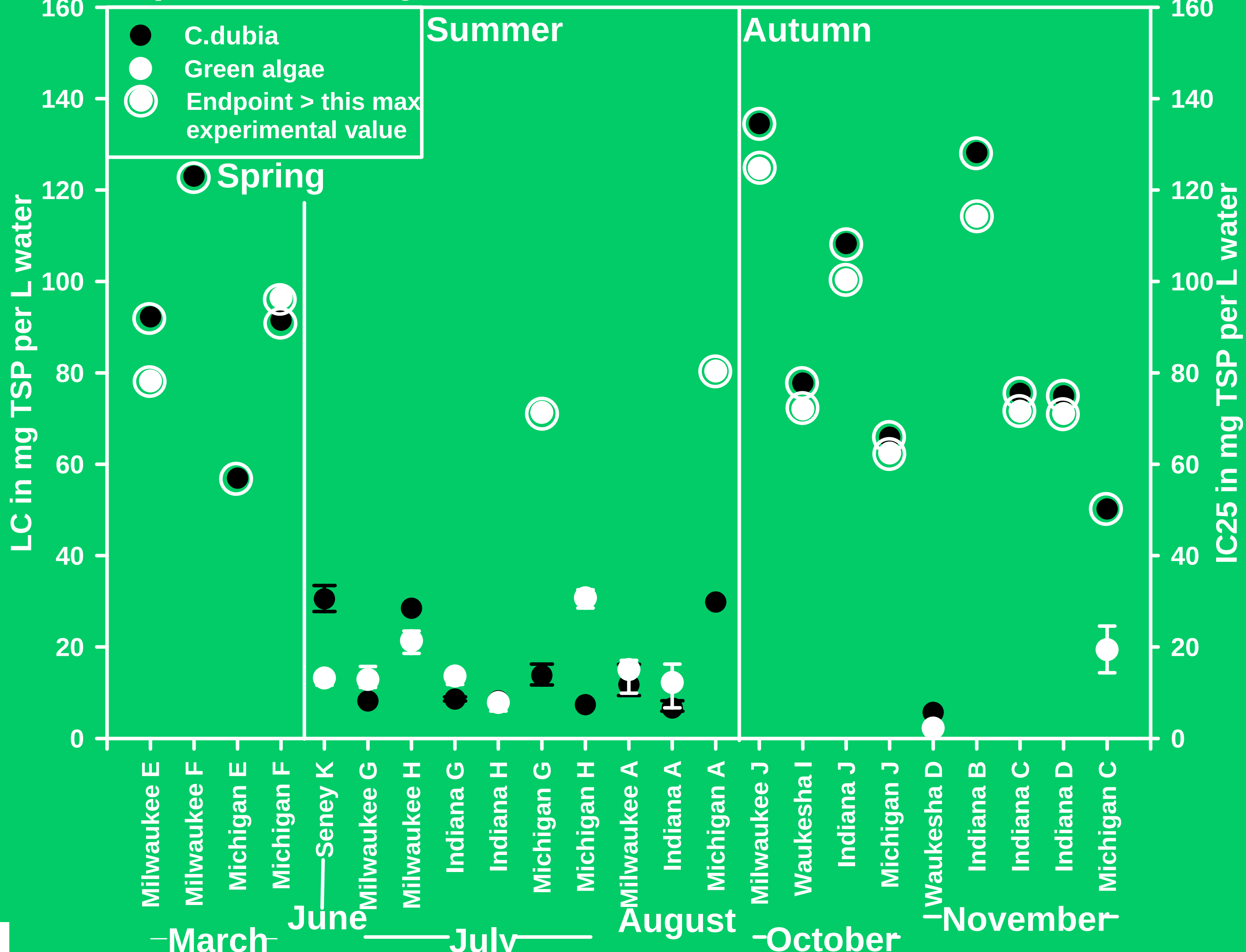
- Total suspended particulate matter (TSP) samplers operated at 4 locations around the south shore of Lake Michigan over spring, summer, and fall seasons.
  - 8 x 10 quartz filters
- One sample event collected in Michigan's upper peninsula during the summer season, equidistant from Lake Michigan and Lake Superior (Seney NWR)

1. Milwaukee, WI
   Urban location
2. Waukesha, WI
   Industrial location (suburb of Milwaukee)
3. Indiana Dunes National Lakeshore, IN
   Industrial/semi-urban impacted location
4. Warren Dunes State Park, MI
   Rural location
5. Seney National Wildlife Refuge, MI
   Remote location

Integrated Chemical and Biological Analysis

- Extract portion of filter for bioassays and chemical analysis
  - Methylene Chloride soxhlet extraction
    - Detailed organics and bioassays
    - Solvent exchange to DMSO for bioassays
  - Reconstituted lake water extraction
    - Bulk metals and bioassays
- General bioassay method
  - Soxhlet extract and water extract are diluted with additional reconstituted lake water to 150 mLs
  - Series of five 2x dilutions with four replicates at each dilution is used for all bioassays
  - Method, solvent and water blanks are run with each set of samples
  - For all endpoints (ie. LC50, IC25, EC50 or IC50) a lower value denotes a more toxic sample by causing mortality/inhibition at a lower concentration of extract in the test water

Aquatic Toxicity of Reconstituted Lake Water Extracts



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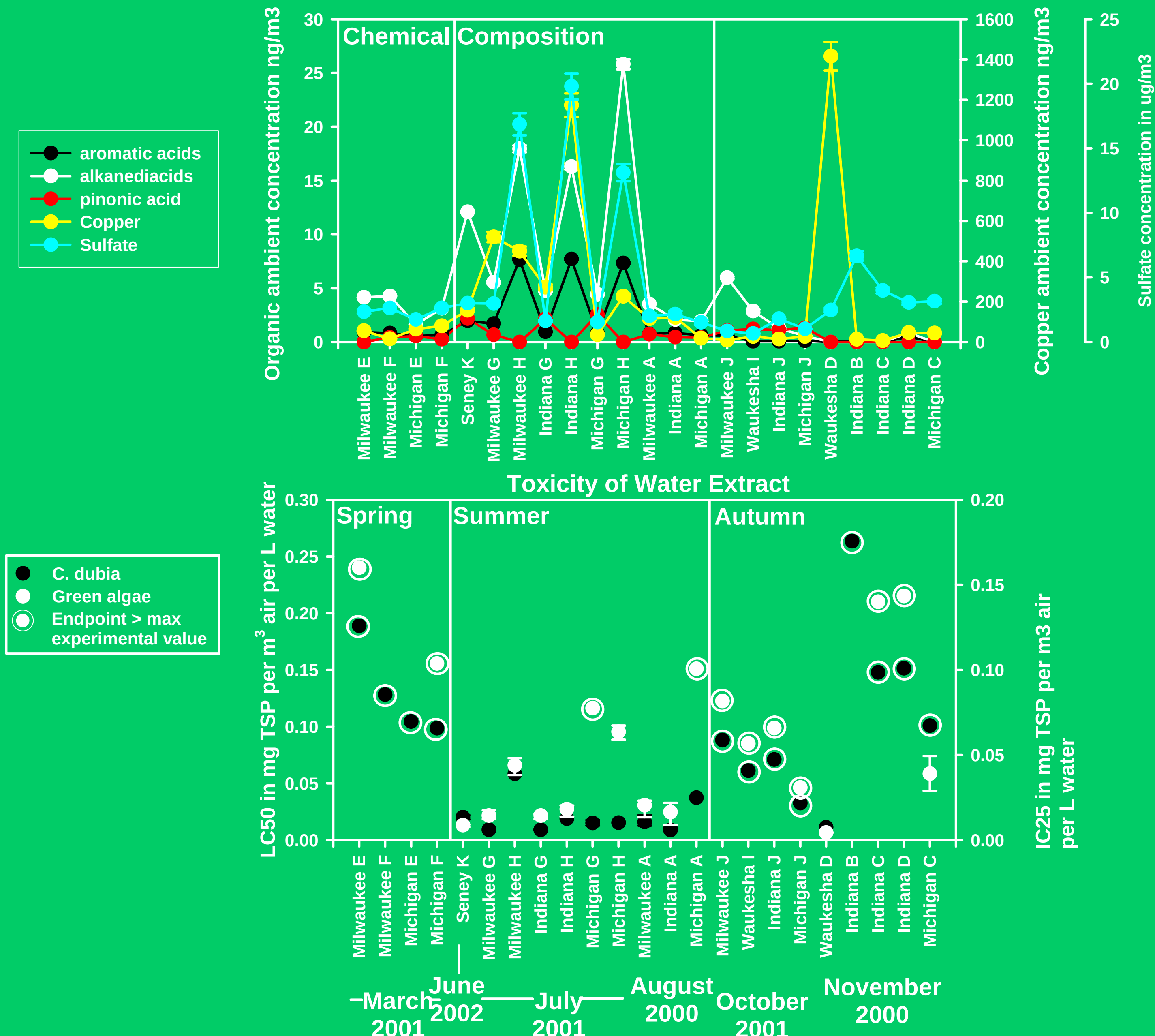

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Motor Vehicle Emission of Trace Metals

Schauer et al, 2005, Health Effects Institute Report 133

- Tunnel tests to obtain a roadway emissions profiles
- Develop source profiles for specific sources of trace metal emissions from vehicles
  - Conduct source characterization tests to develop profiles directly parallel to tunnel emission tests
    - Sample vehicles similar to tunnel fleet vehicles
    - Apply identical collection and analysis methods to all samples
- Use chemical mass balance model to apportion total roadway emissions to specific vehicle sources
- Conduct parallel ambient sampling

AIRPORT
- Howell Ave
- 3 lanes in southbound direction
- Similar to Van Nuys Tunnel (CA)
  - Completely separate opposing bores
- 770 feet long - No curvature
- Constant speeds - very limited braking
- ~8% truck traffic on weekdays
- Not cleaned - noticeable road dust

COURTHOUSE
- I-43 entrance ramp
- 2 Lanes merge into one lane
- Forced ventilation, exit at center
- 1270 feet long - ~ 45 degree curve
  - Inlet section: 715 feet - sample collection
- Moderate braking and acceleration
- ~2% truck traffic on weekdays
- Not cleaned - minimal road dust

Tunnel Tests

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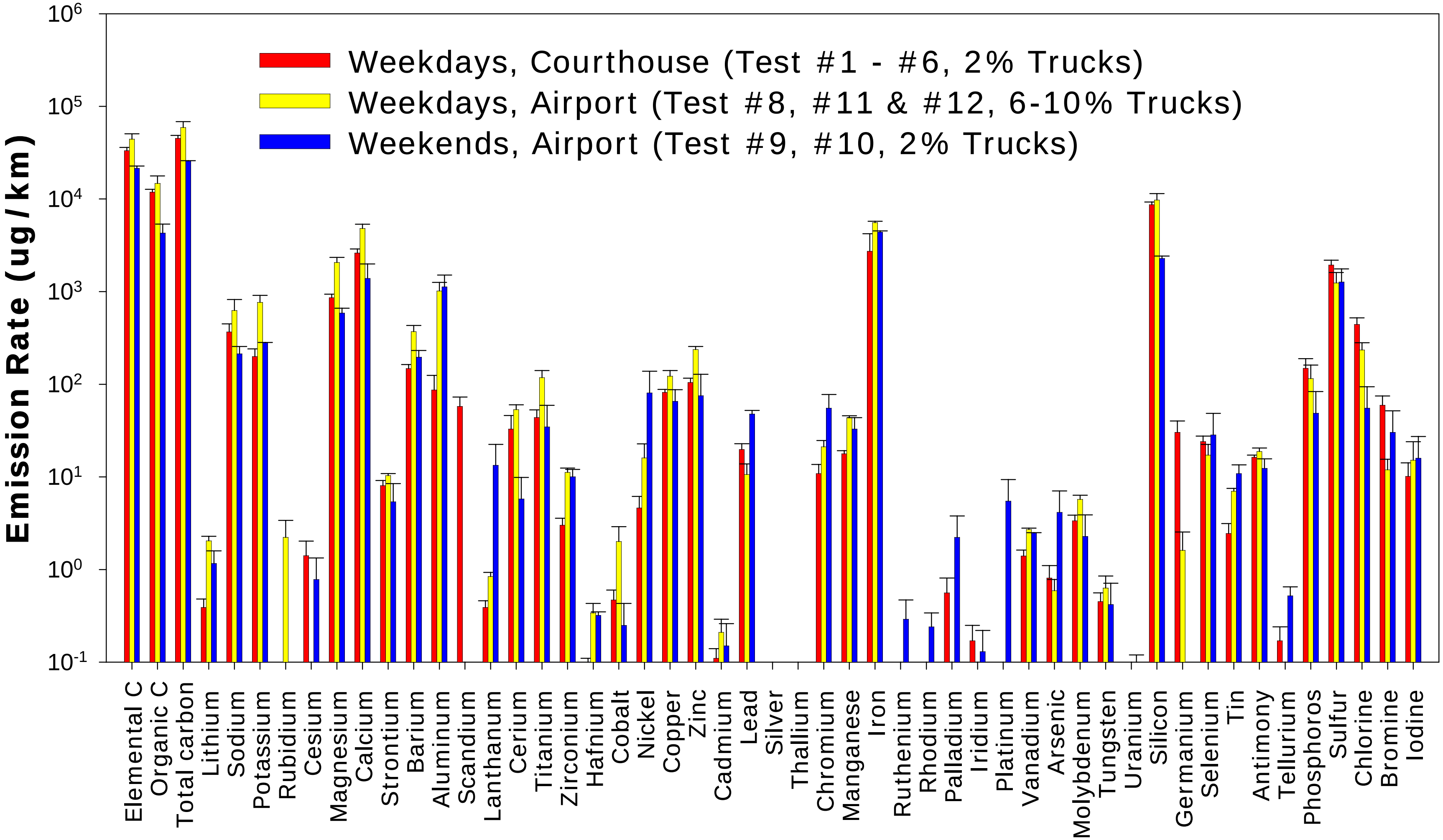
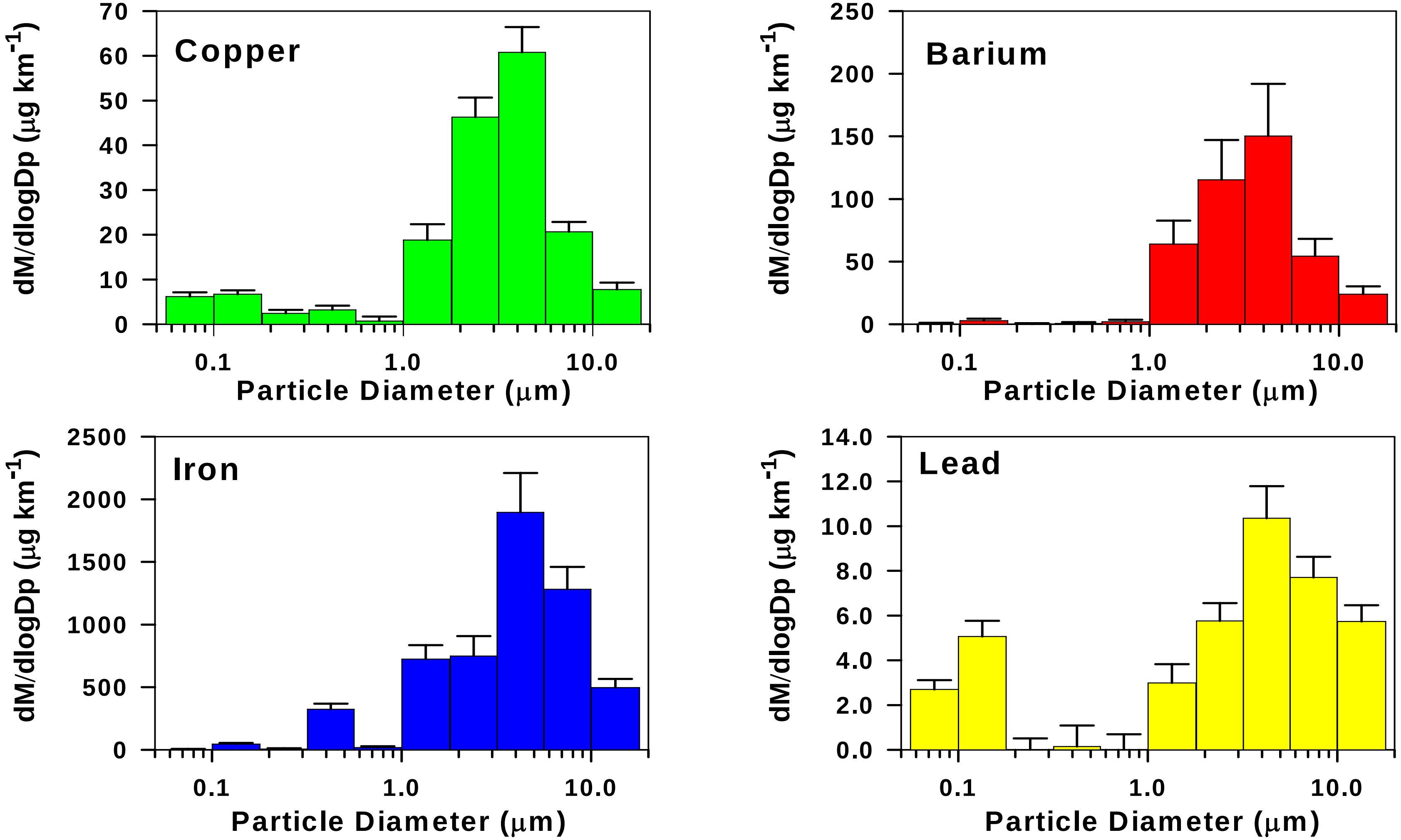


Summer tunnel test data: average emission rates from on-road vehicles at Milwaukee, Wisconsin for PM10. Error bars indicate standard errors.

Size-resolved metals emissions from motor vehicle roadway tests



Source Apportionment

- Samples were analyzed to apportion total roadway trace metals emissions to specific emission sources:
  - ROAD DUST - collected from tunnel roadway for resuspension and collection of PM10, PM2.5
  - FUEL - regular, premium, diesel from area stations
  - USED MOTOR OIL - samples from commercial garages
  - TAILPIPE EMISSIONS
    - Dynamometer tests of gasoline powered motor vehicles and diesel trucks
    - Fuel and lube oil samples from the same vehicles
  - TIRE WEAR AND BRAKE WEAR – Series of exploratory tests have been conducted

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Tire and Brake Wear Tests

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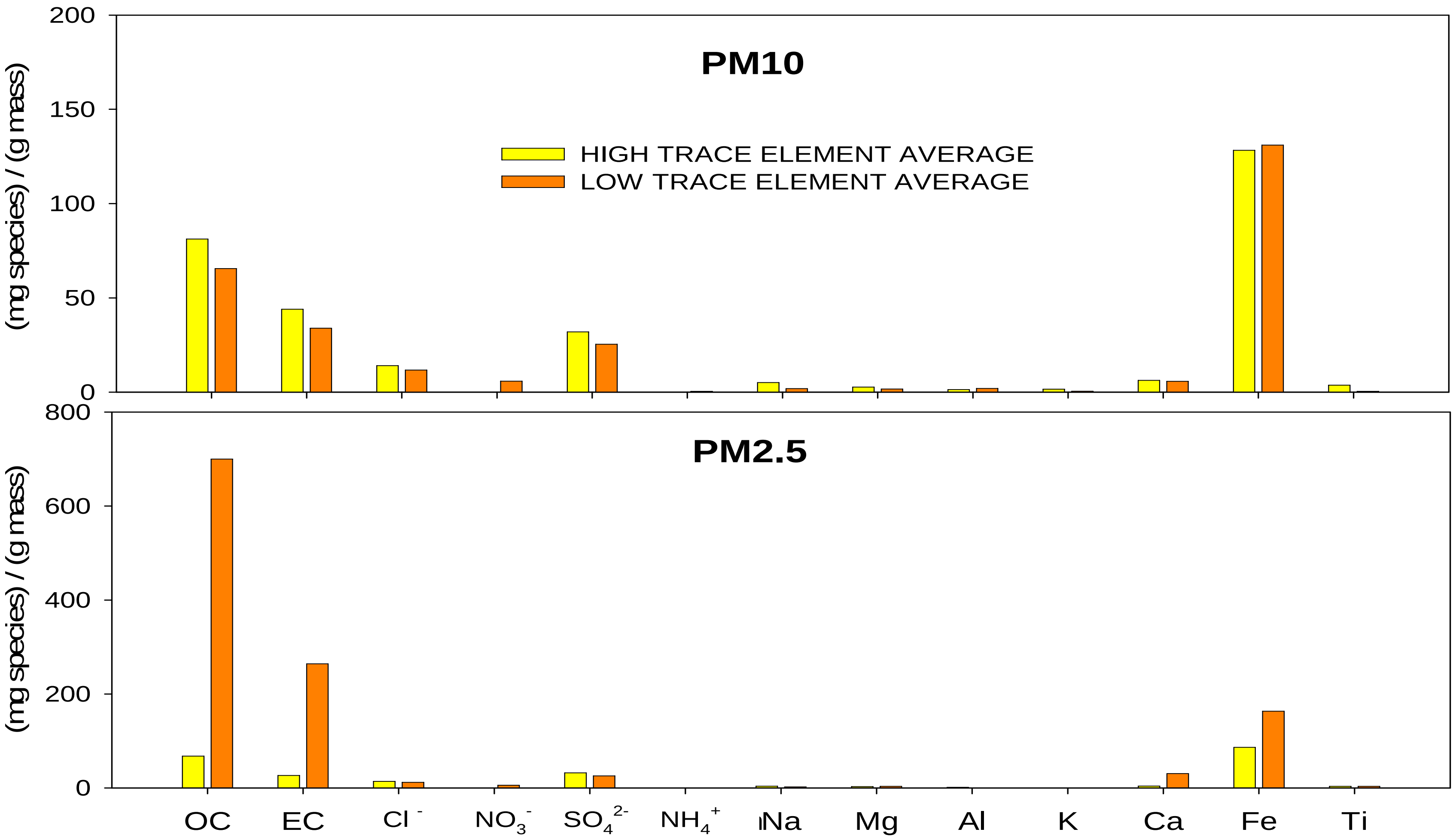
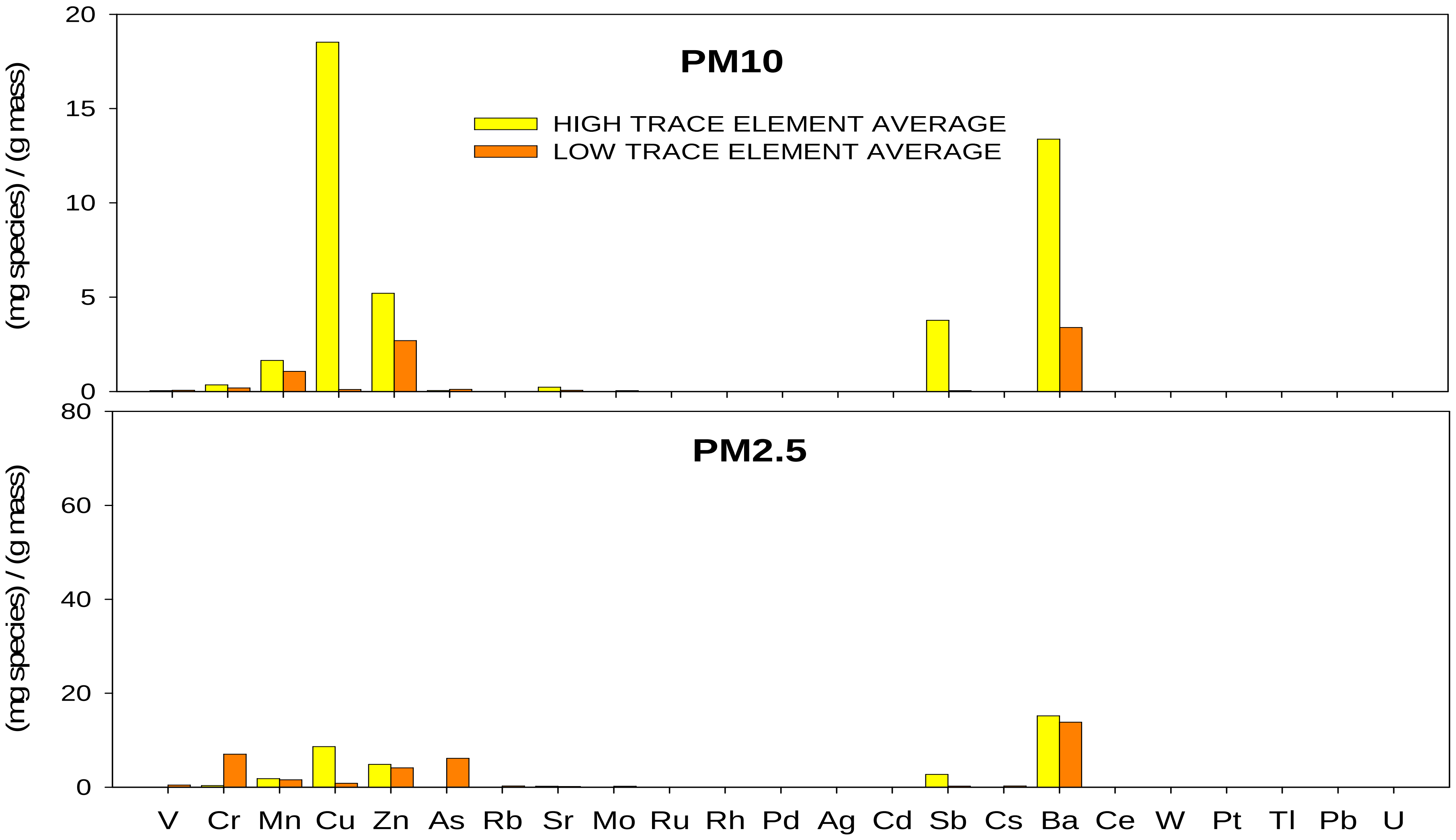
BRAKE DUST PROFILE



BRAKE DUST PROFILE



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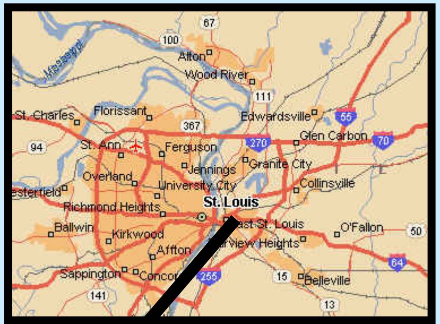
Relative source contributions to emissions of individual metals in PM10 Winter Airport Tunnel Test

St. Louis Midwest Supersite

- Located in East St. Louis, Illinois
  - 2.5 million population
  - 2.3 miles east of downtown St. Louis, MO
- Samples collection April 2001 through July, 2003
- Co-located with a broad range of integrated and semi-continuous aerosols measurements



Measuring Hg in the atmosphere at St. Louis

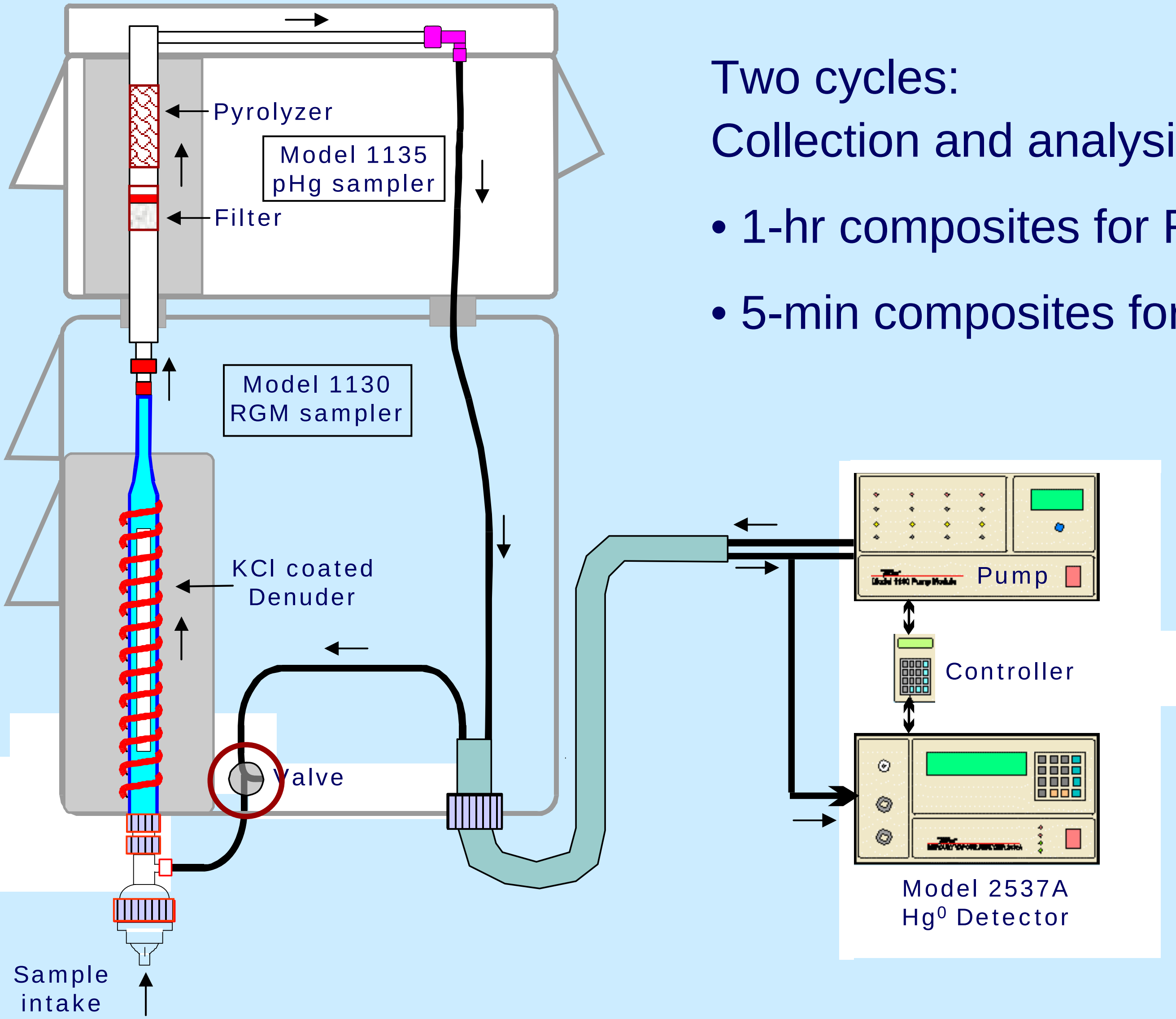
Measured atmospheric Hg at St. Louis Supersite using the mobile Tekran unit from December 1, 2003 to March 1, 2004

This campaign complimented analogous data collected from October to December 2002

TEKRAN Hg ANALYZER

Two cycles:
Collection and analysis

- 1-hr composites for RGM, pHg
- 5-min composites for Hg^0



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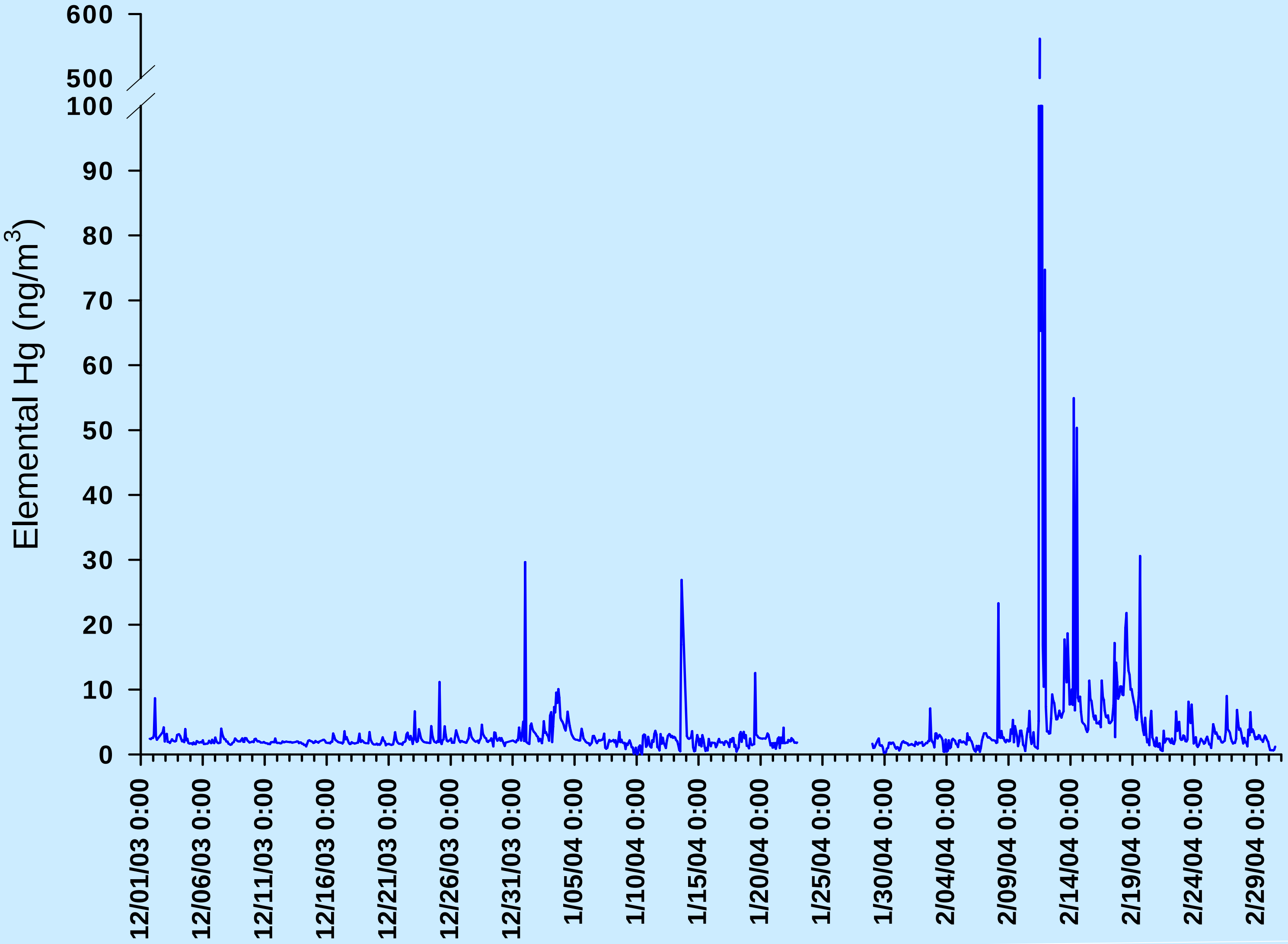
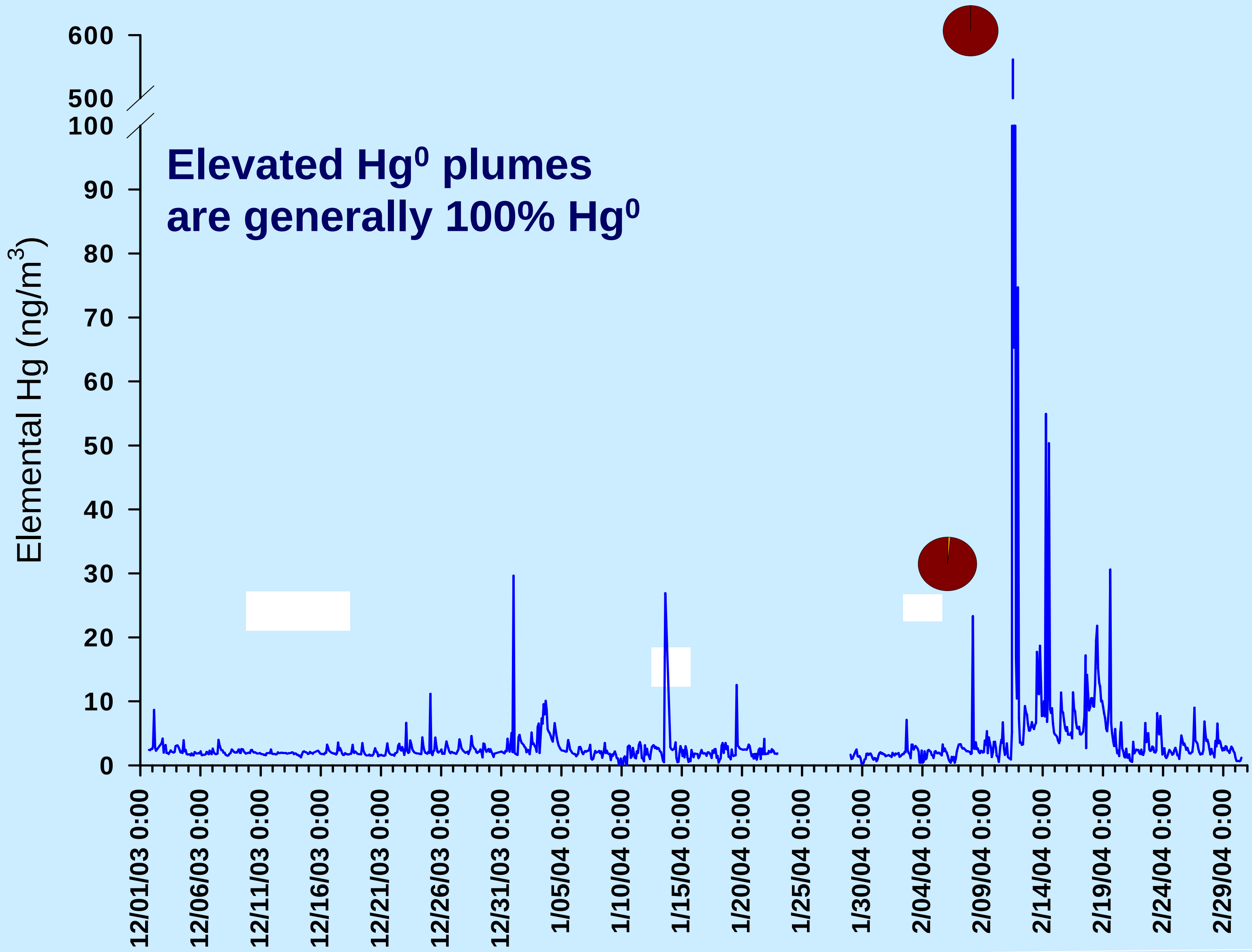
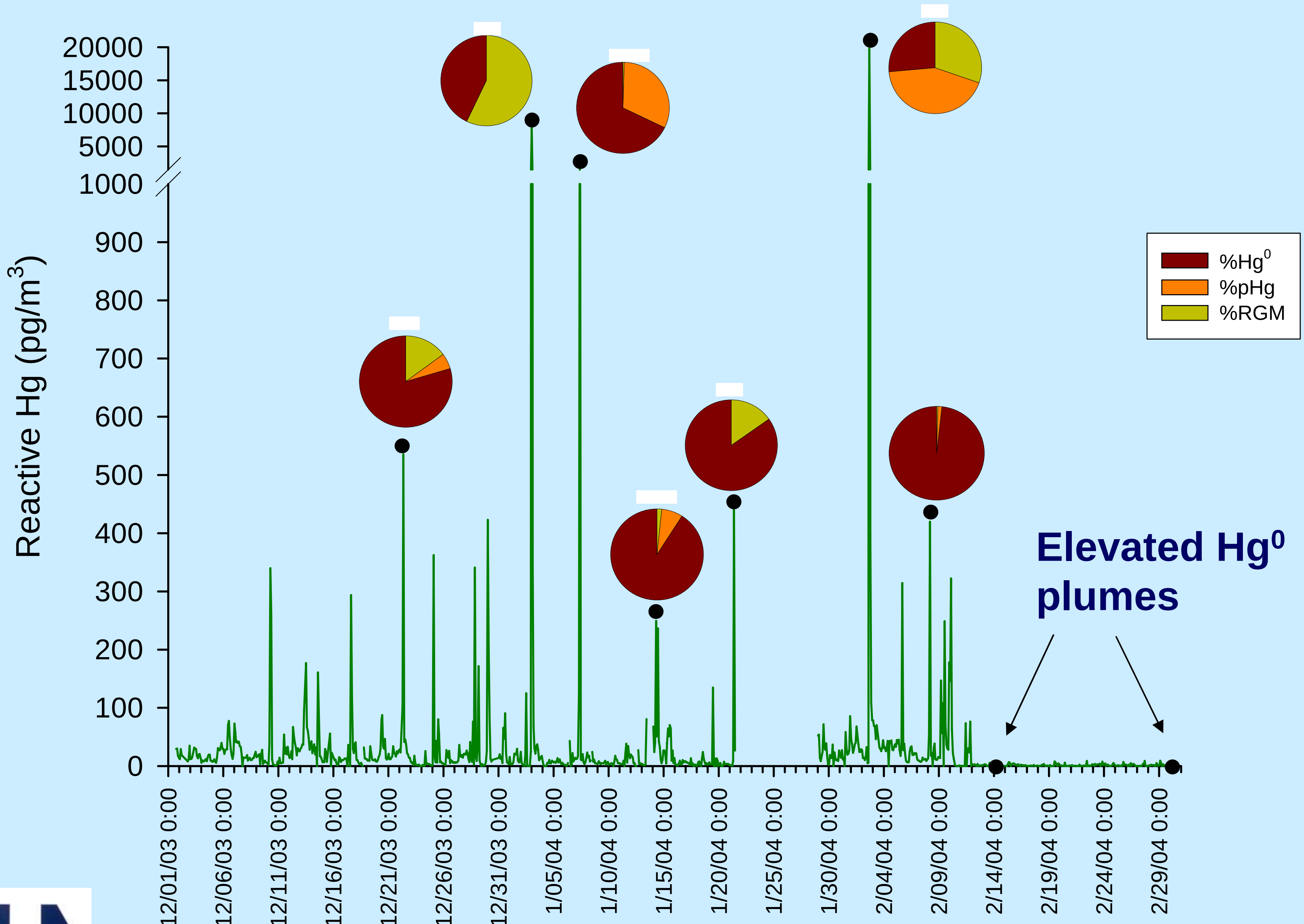
Hg^0 in the atmosphere





Elevated Hg⁰ plumes
are generally 100% Hg⁰
Elemental Hg (ng/m3)
600
500
100
90
80
70
60
50
40
30
20
10
0
12/01/03 0:00
12/06/03 0:00
12/11/03 0:00
12/16/03 0:00
12/21/03 0:00
12/26/03 0:00
12/31/03 0:00
1/05/04 0:00
1/10/04 0:00
1/15/04 0:00
1/20/04 0:00
1/25/04 0:00
1/30/04 0:00
2/04/04 0:00
2/09/04 0:00
2/14/04 0:00
2/19/04 0:00
2/24/04 0:00
2/29/04 0:00

pHg and RGM in the atmosphere



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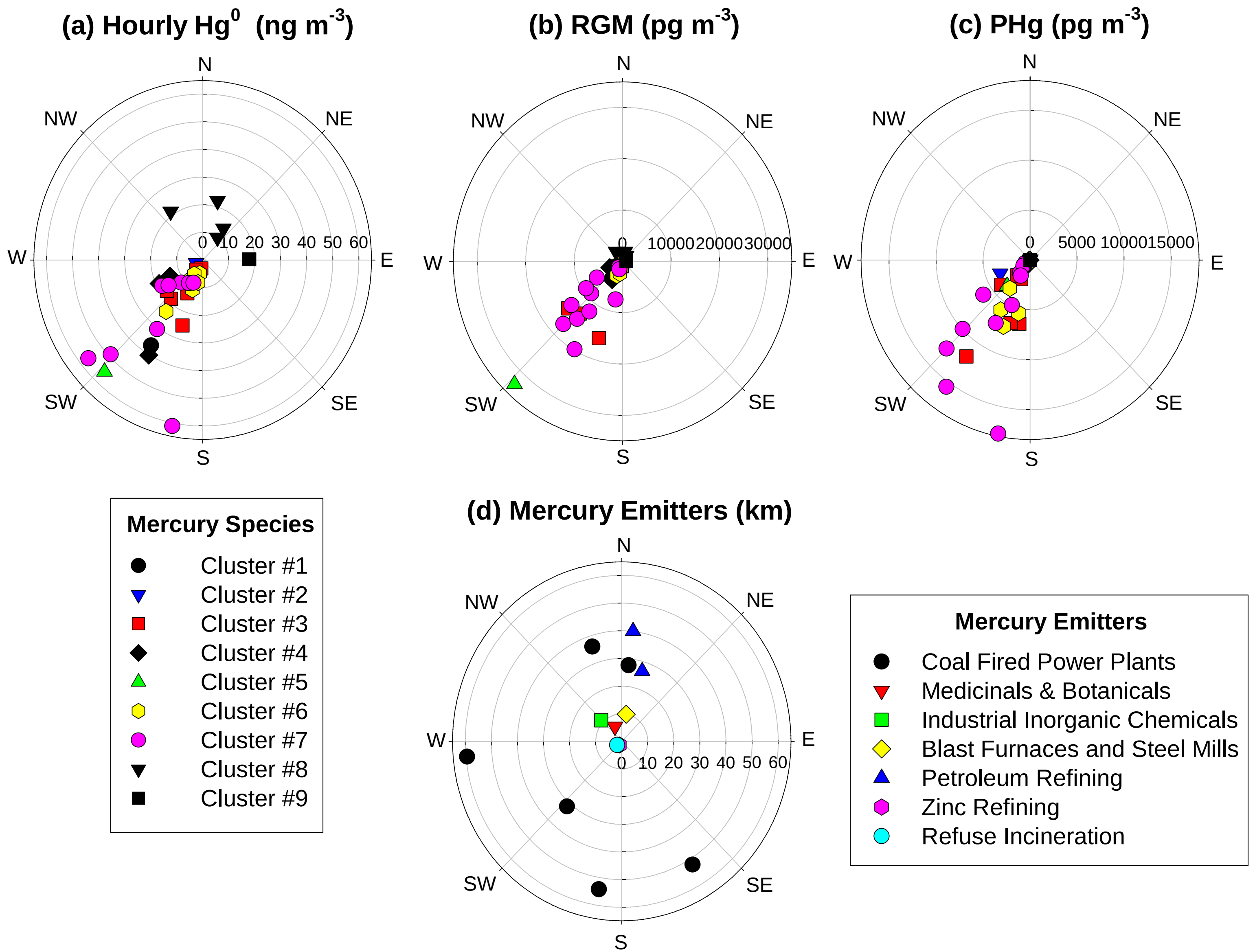
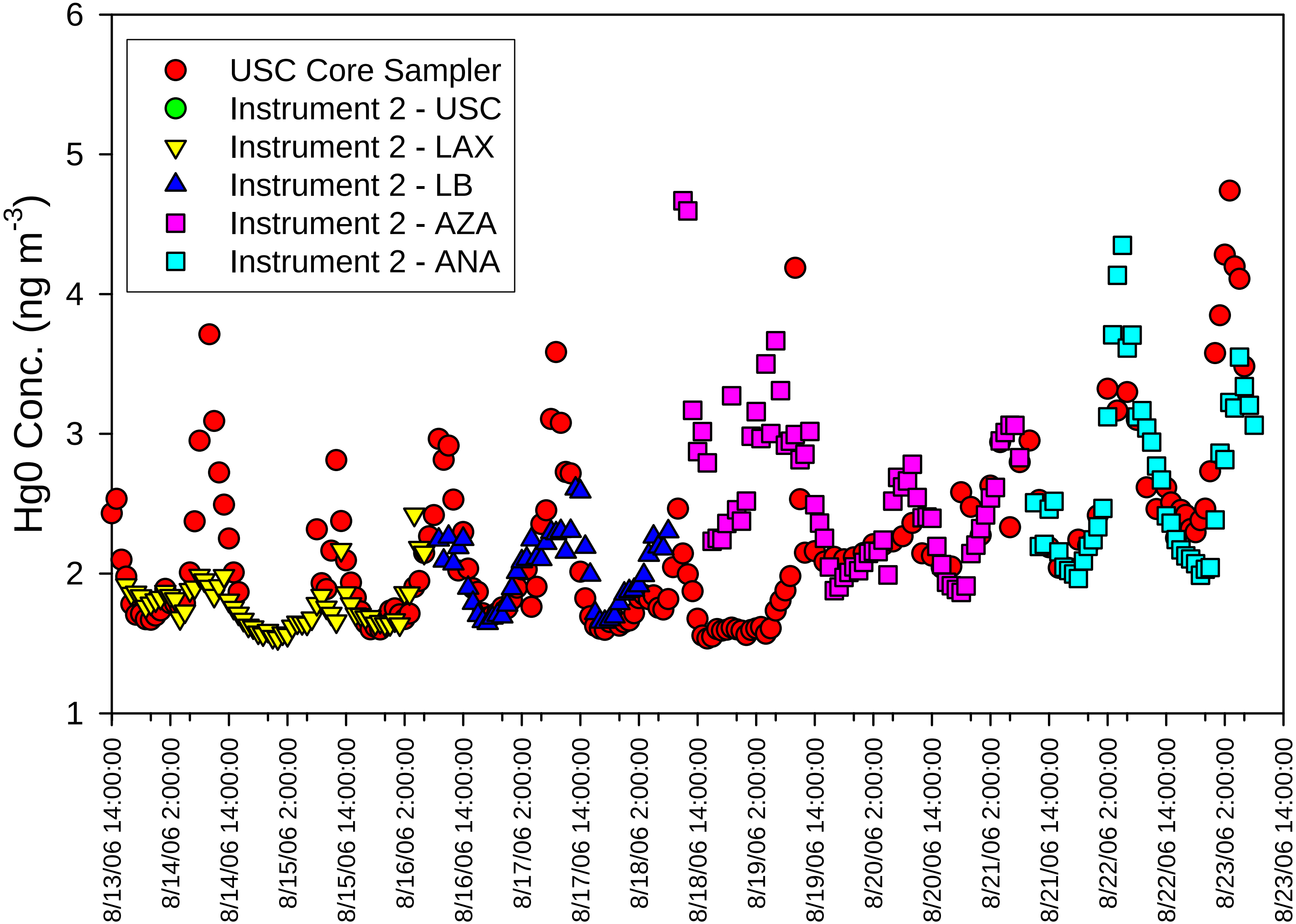
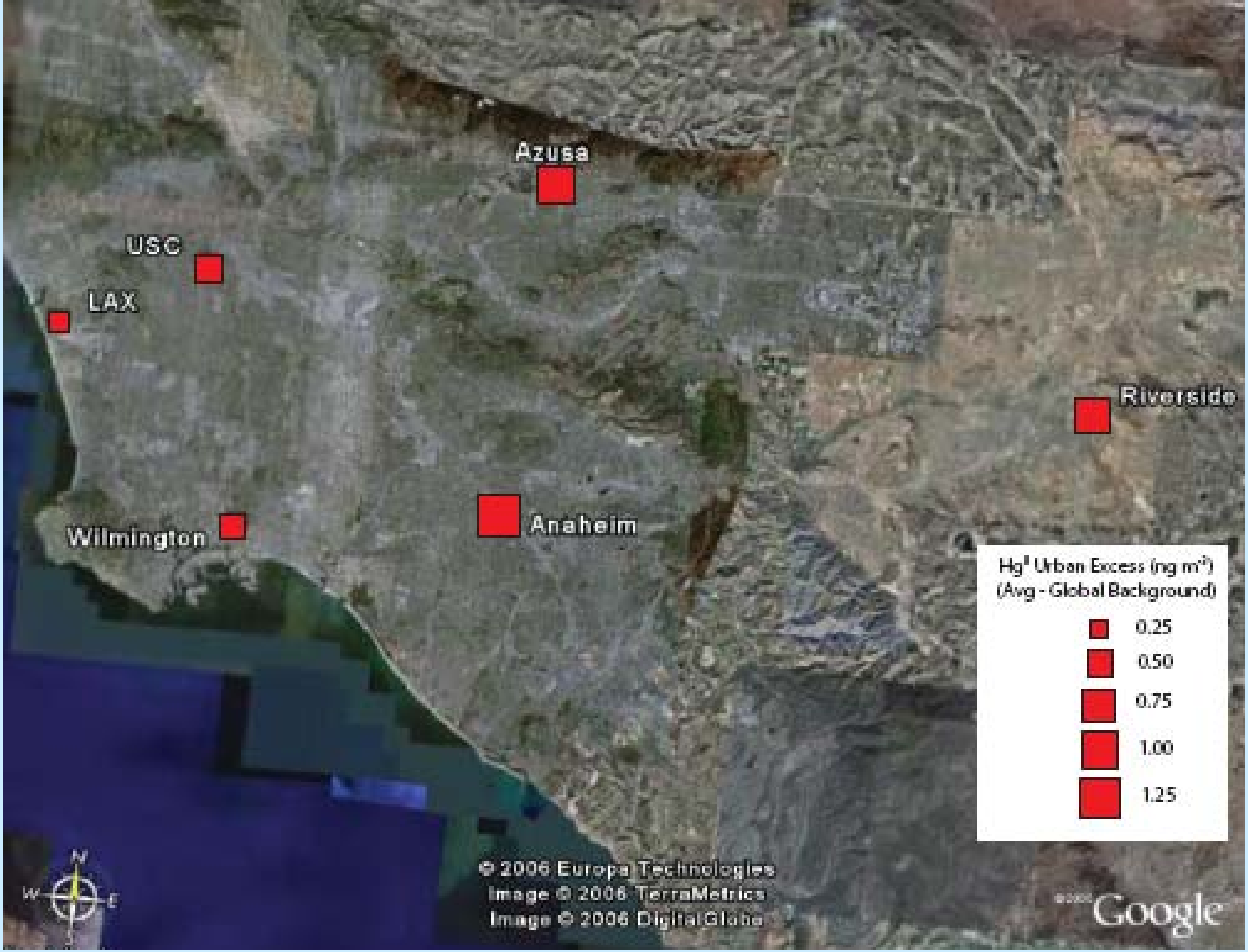

(a) Hourly Hg^0 (ng m^{-3})
(b) RGM (pg m^{-3})
(c) PHg (pg m^{-3})
N
NE
E
SE
S
SW
W
NW
0 10 20 30 40 50 60
0 10000 20000 30000
0 5000 10000 15000
Mercury Species
Cluster #1
Cluster #2
Cluster #3
Cluster #4
Cluster #5
Cluster #6
Cluster #7
Cluster #8
Cluster #9
(d) Mercury Emitters (km)
Mercury Emitters
Coal Fired Power Plants
Medicinals & Botanicals
Industrial Inorganic Chemicals
Blast Furnaces and Steel Mills
Petroleum Refining
Zinc Refining
Refuse Incineration

LA Basin Atmospheric Hg

- Summer 2005
  - Measured Elemental, RGM, and particulate Mercury in Riverside for one Month
  - Elevated Elemental and Reactive Mercury
  - Observed Mercury Plumes
- Summer 2006
  - Investigated sources of elemental mercury
  - Core sites at USC and Anaheim
  - Movable and Mobile Sites

Elemental Mercury Concentrations - LA Basin





UW-Madison Hg Measurements August 2006

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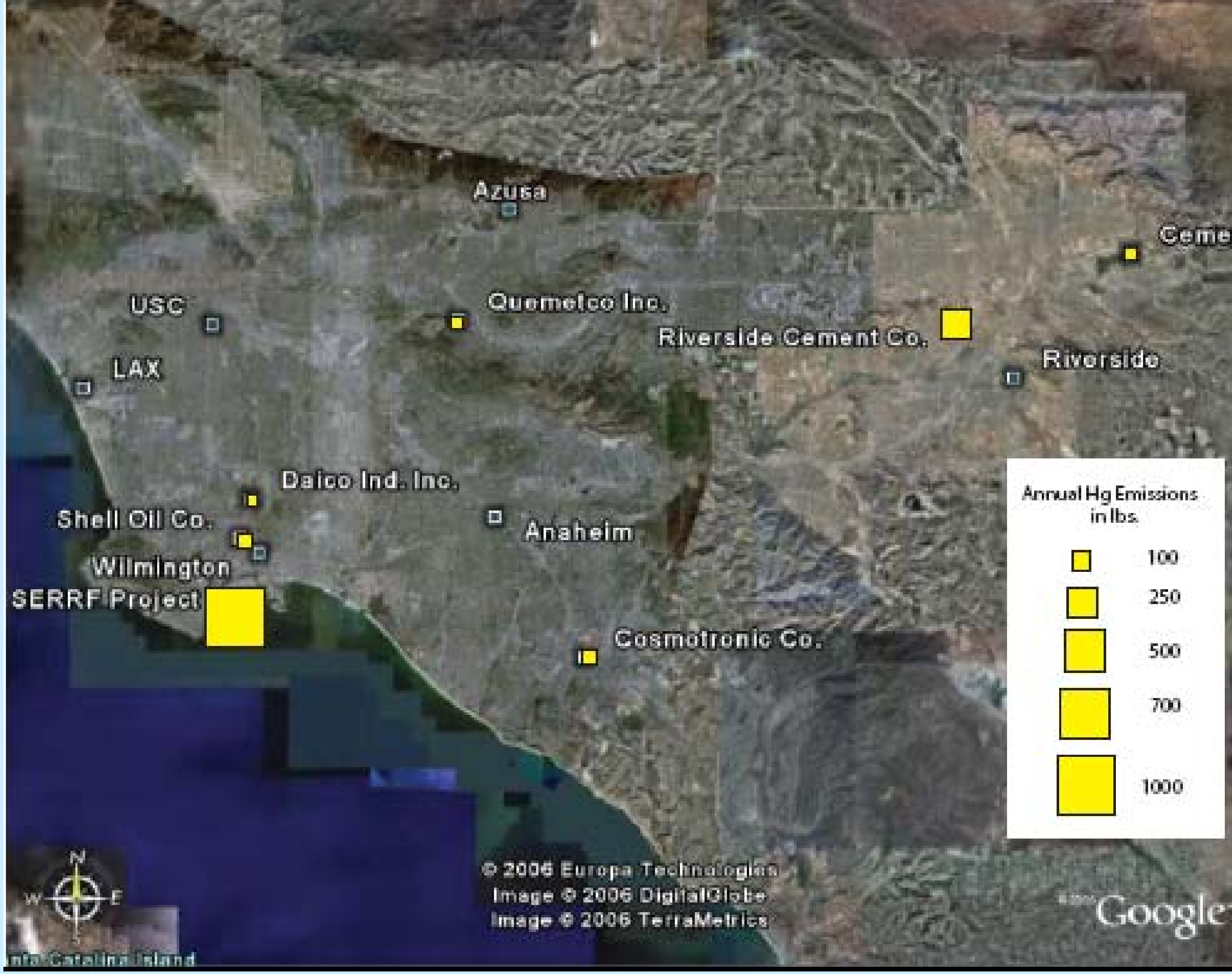

http://www.epa.gov/air/data/

Conclusions

- We need to link atmospheric monitoring efforts with water body protection strategies
- A two step process to understand the sources of toxic metal deposition can exploit existing tools in atmospheric sciences
- There are research needs on the toxicity load to water bodies
- Metals from mobile sources have been reasonable well characterized
- There is need to better understand the source of mercury species in California

Acknowledgement

- Funding:
  - US EPA STAR Program, Health Effects Institute, and UW Sea Grant Institute
- In Kind Contributions:
  - CARB, Wisconsin DNR, SCAQMD, USC, UC-Riverside
- Collaborators
  - Mercury
    - Dr. Dave Krabbenhoft, Mark Olson – USGS
    - Dr. Helen Manolopoulus, Dr. Britt Hall – UW-Madison
    - Prof. Jay Turner – Washington University
  - Aquatic Toxicity
    - Dr. Rebecca Sheesley
  - Metals
    - Dr. Glynis Lough
    - Dr. Martin Shafer