

Atmospheric Mercury Observations in the Midwestern United States: Atmospheric Perspective

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- Main Collaborators
 - Prof. Britt Hall – UW-Madison
 - Dr. Helen Manolopoulos – UW-Madison
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 - Andy Rutter – UW-Madison
 - Dr. David Krabbenhoft - USGS
 - Mark Olson - USGS
- Contributors
 - Prof. Jay Turner – Washington University at St. Louis
 - Yellowstone National Park
 - Wisconsin Department of Natural Resources

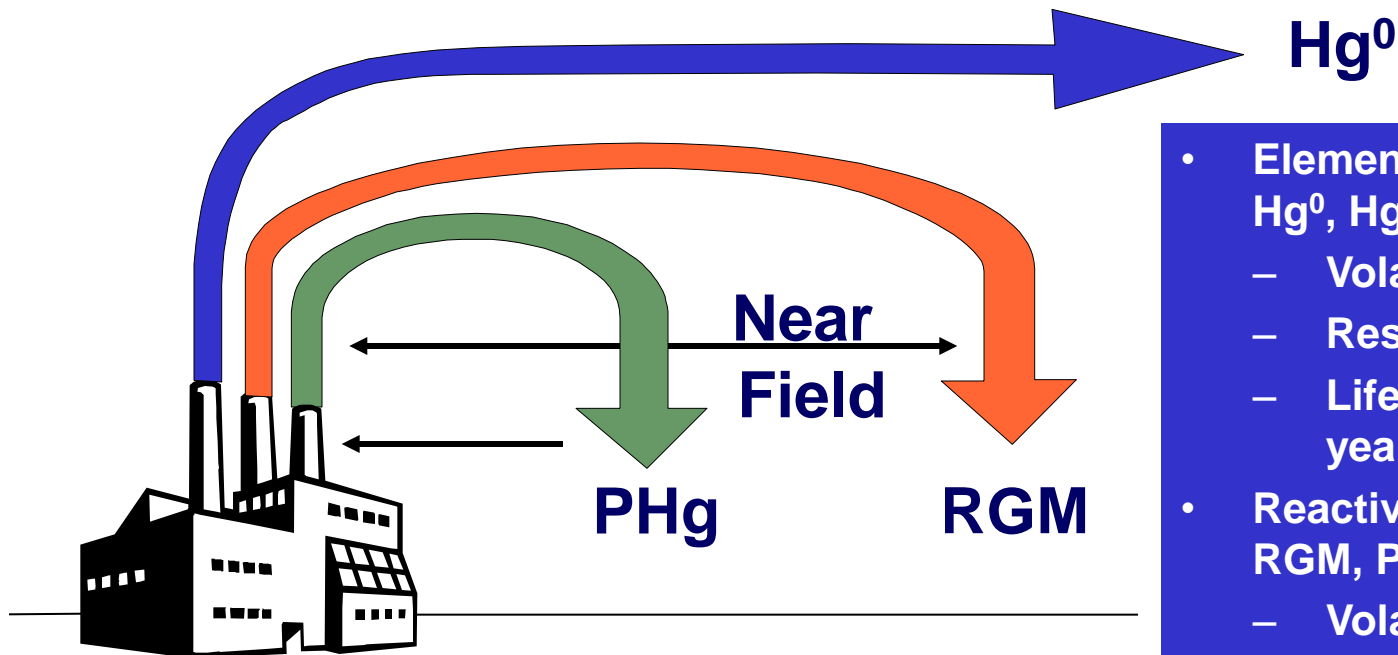


Overview

- Background
 - Atmospheric mercury
 - Atmospheric perspective
- Atmospheric Sampling
 - Wisconsin
 - Devil's Lake State Park, WI
 - Milwaukee, WI (UWM Site)
 - Mt. Horeb, WI
 - East St. Louis, Illinois
 - Yellowstone National Park



Mercury Deposition



- Dry and wet deposition of reactive Hg to local areas can be substantial
- Elemental mercury is transported globally, until oxidized

- Elemental Mercury (GEM, Hg^0 , $\text{Hg}(0)$)
 - Volatile
 - Resists oxidation
 - Life time months - years
- Reactive Mercury ($\text{Hg}(\text{II})$, RGM, PHg)
 - Volatility much lower than Hg^0
 - More water soluble
 - Life time hours - weeks



Key Questions

- How do the average concentrations of Hg in rural locations compare to urban locations
- How do the ratios of the mercury species in rural locations compare to urban locations
- Is there evidence of Hg plume
 - Elemental Mercury
 - Reactive Mercury (RGM plus particulate mercury)
- Can simultaneous measurements of other atmospheric pollutants identify sources of atmospheric mercury

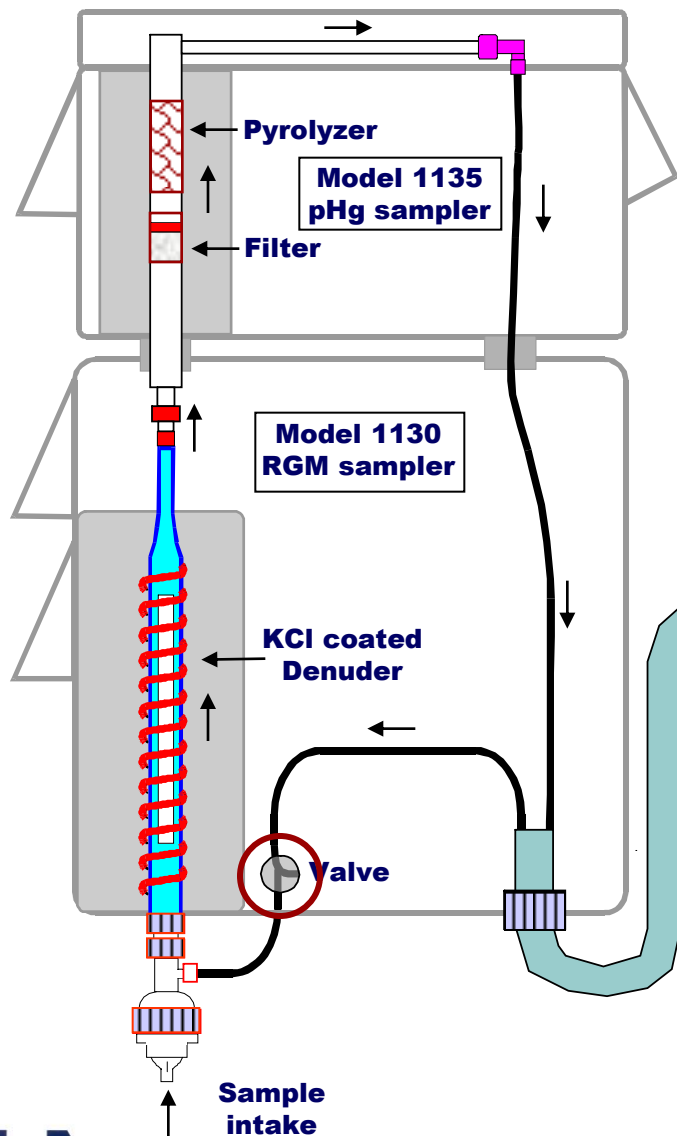


Atmospheric Sampling

- Tekran Mercury Speciation Monitor was co-located with real time air pollution measurements
 - Elemental Mercury (Hg^0)
 - Reactive Gaseous Mercury (RGM)
 - Particulate Mercury (Hg-P)
- Real Time Air Pollution Measurements
 - Meteorology
 - Criteria Gases (O_3 , SO_2 , NO_x , and CO)
 - Particulate Matter Mass
 - Particle Matter Size Distributions
 - Aerosol Radiative Properties
 - Particulate Matter Components (Ions and ECOC)
 - Aerosol Time of Flight Mass Spectrometer (ATOFMS)
 - Aerosol Mass Spectrometer (AMS)

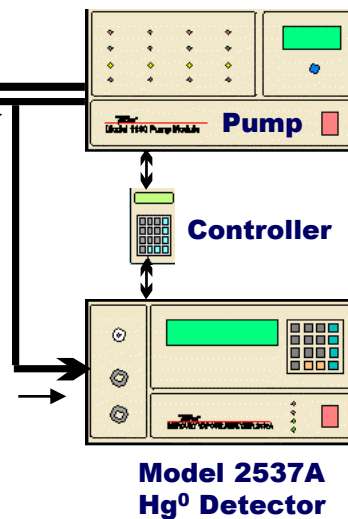


Tekran Hg analyzer



5-min composite samples are collected for Hg^0

1-hr composite samples are collected for pHg and RGM



Aerosol-Time-of-Flight Mass Spectrometer (ATOFMS)

- Source Tracking
- Aerosol Dynamics



Aerosol Time-of-flight Mass Spec (ATOFMS) provides real time size resolved chemical composition of aerosols

UW-Madison and Carleton College have a NSF ITR grant to develop data mining tools to analyze complex ATOFMS data

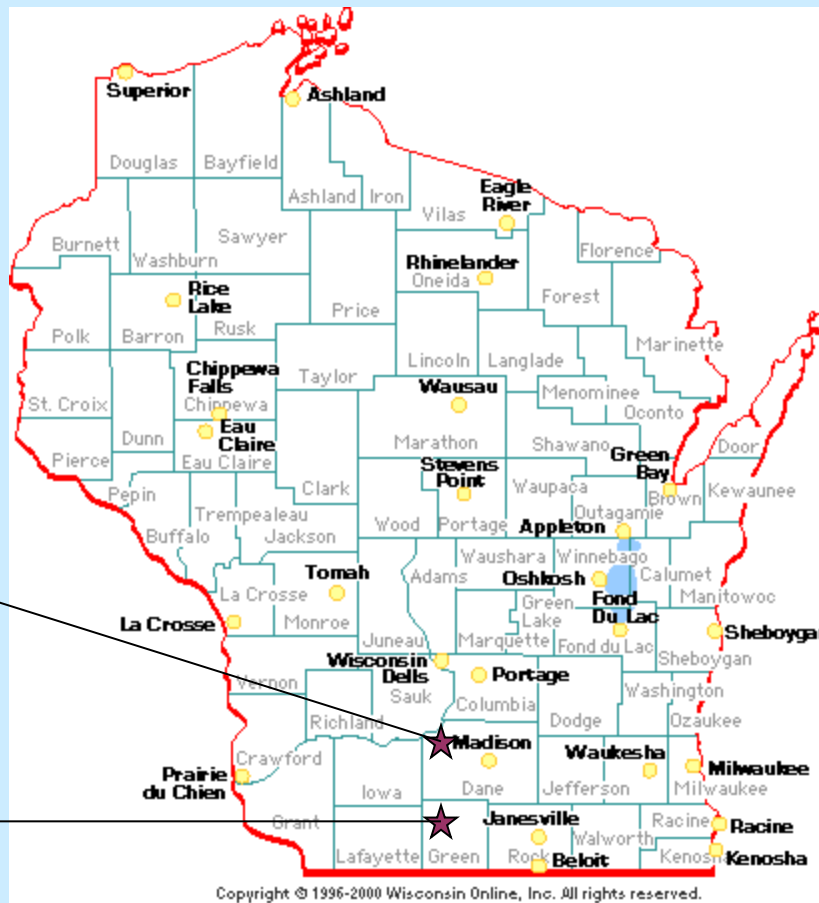


Wisconsin Sampling

- Co-located Tekrans at Devil's Lake Site
 - Two weeks
- Simultaneous Tekrans at Devil's Lake and Mt. Horeb
 - Two weeks
- A Tekran (Hg^0 , RGM and particulate mercury) was operated:
 - May 2003 to April 2004 at Devil's Lake Site
 - June 2004 to May 2005 in Milwaukee UWM Site
- Measurements co-located with
 - DNR criteria gases
 - UW 1-in-6 PM mass and composition



Wisconsin Mercury Sampling



**Devil's Lake
State Park**

Mt. Horeb



Co-located Experiment *at* Devil's Lake

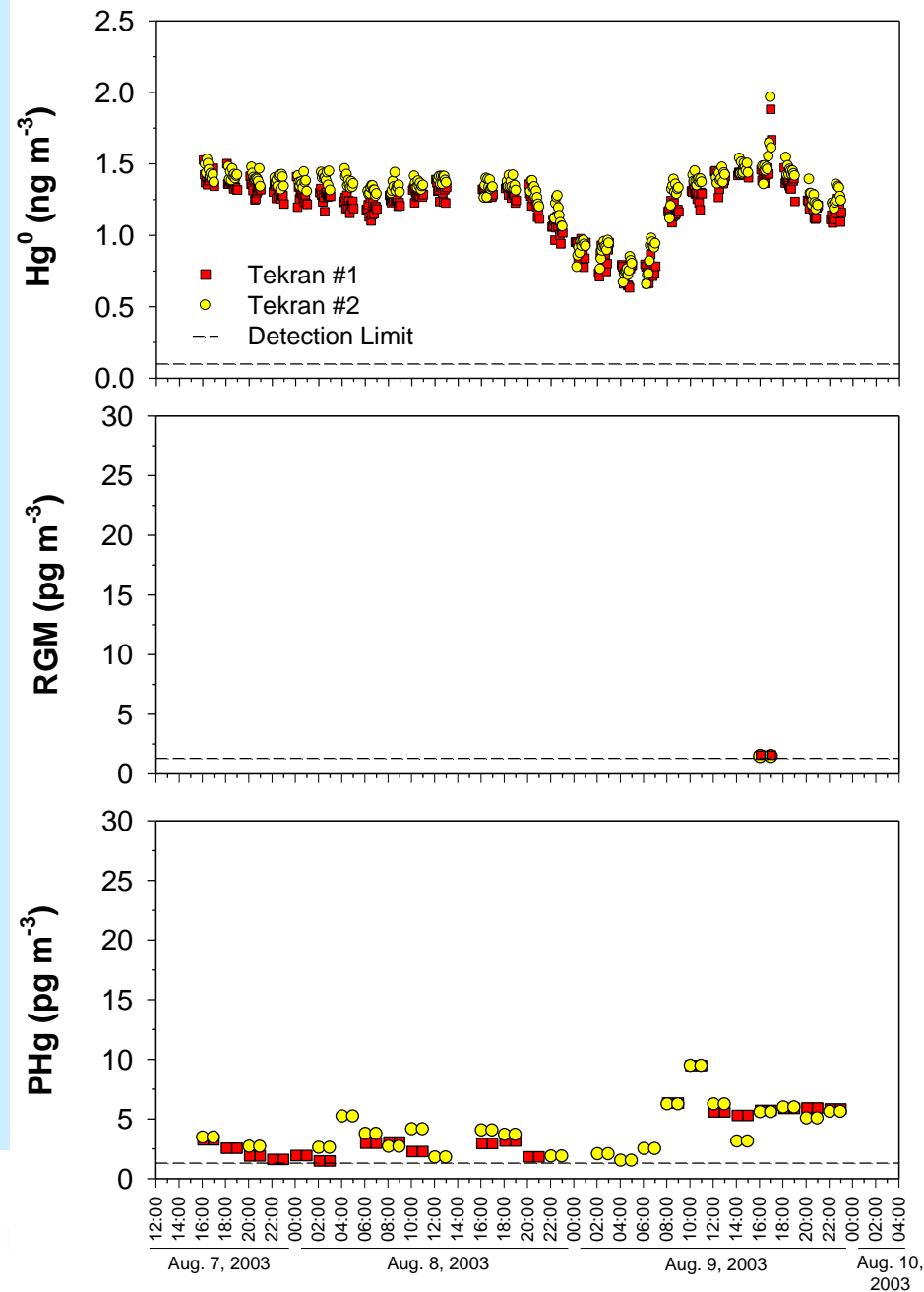


Tekran #2

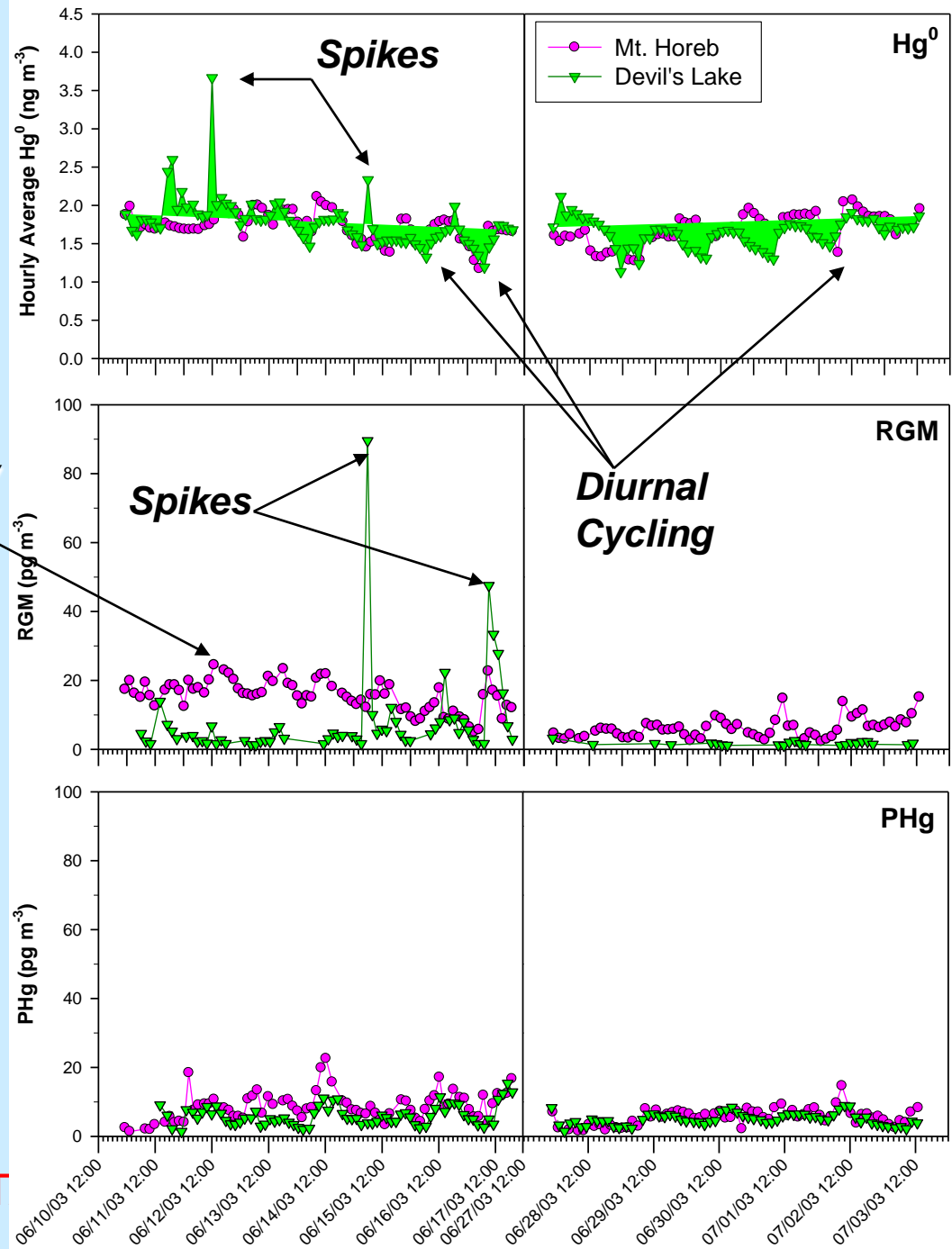


Tekran #1

17/08/2003



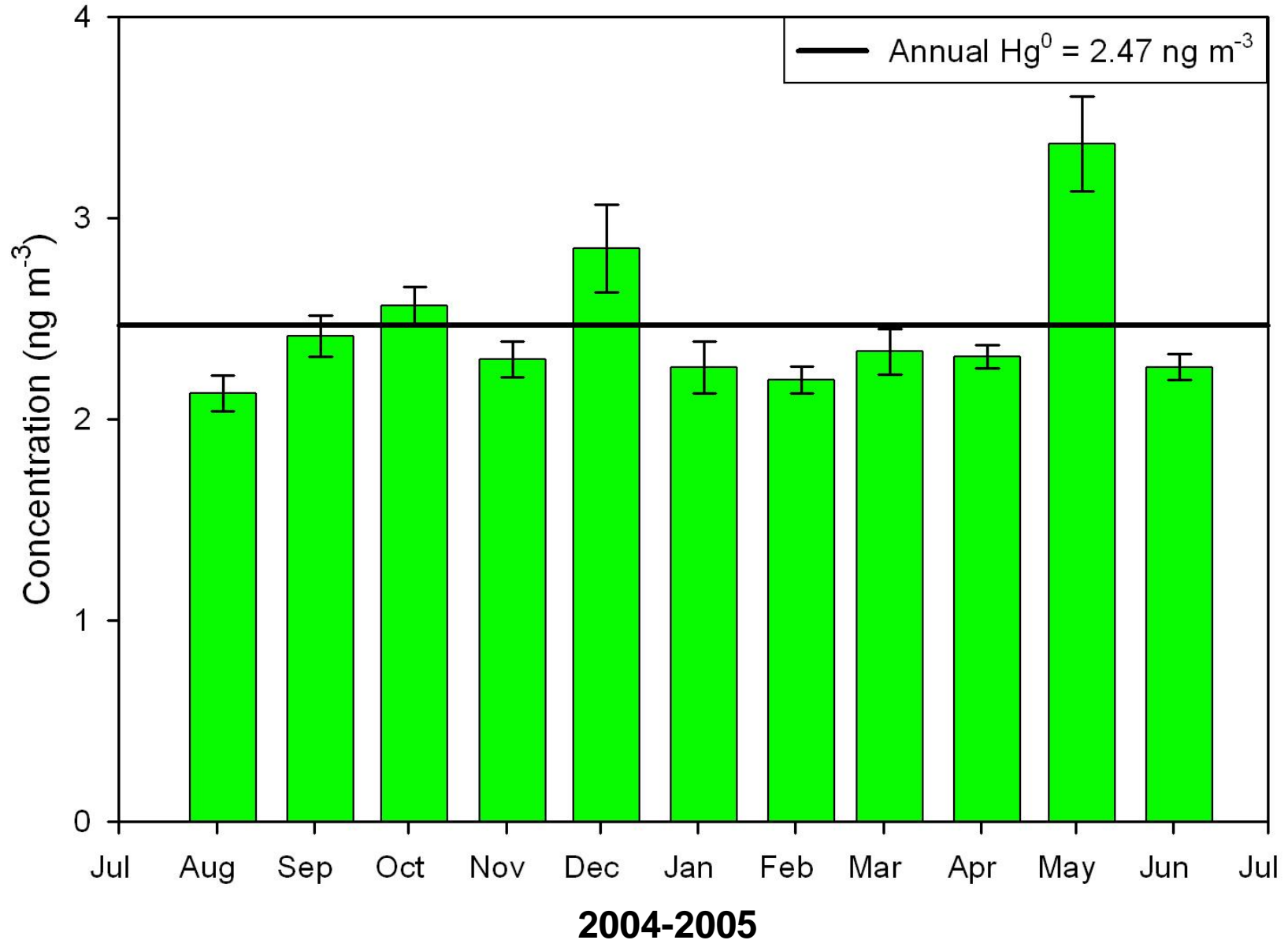
Regional Comparison of Atmospheric Hg Species



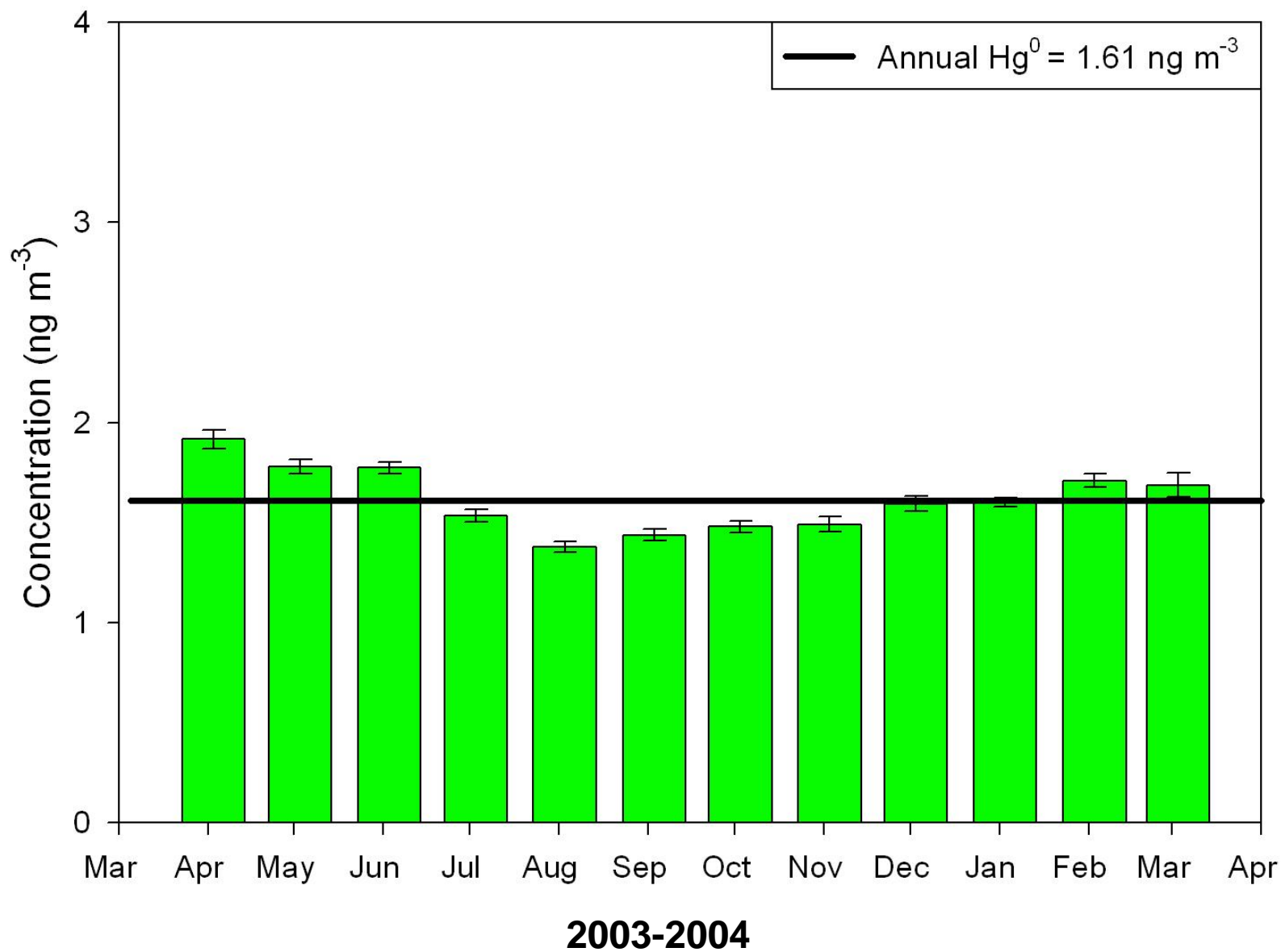
ENVIRONMENT



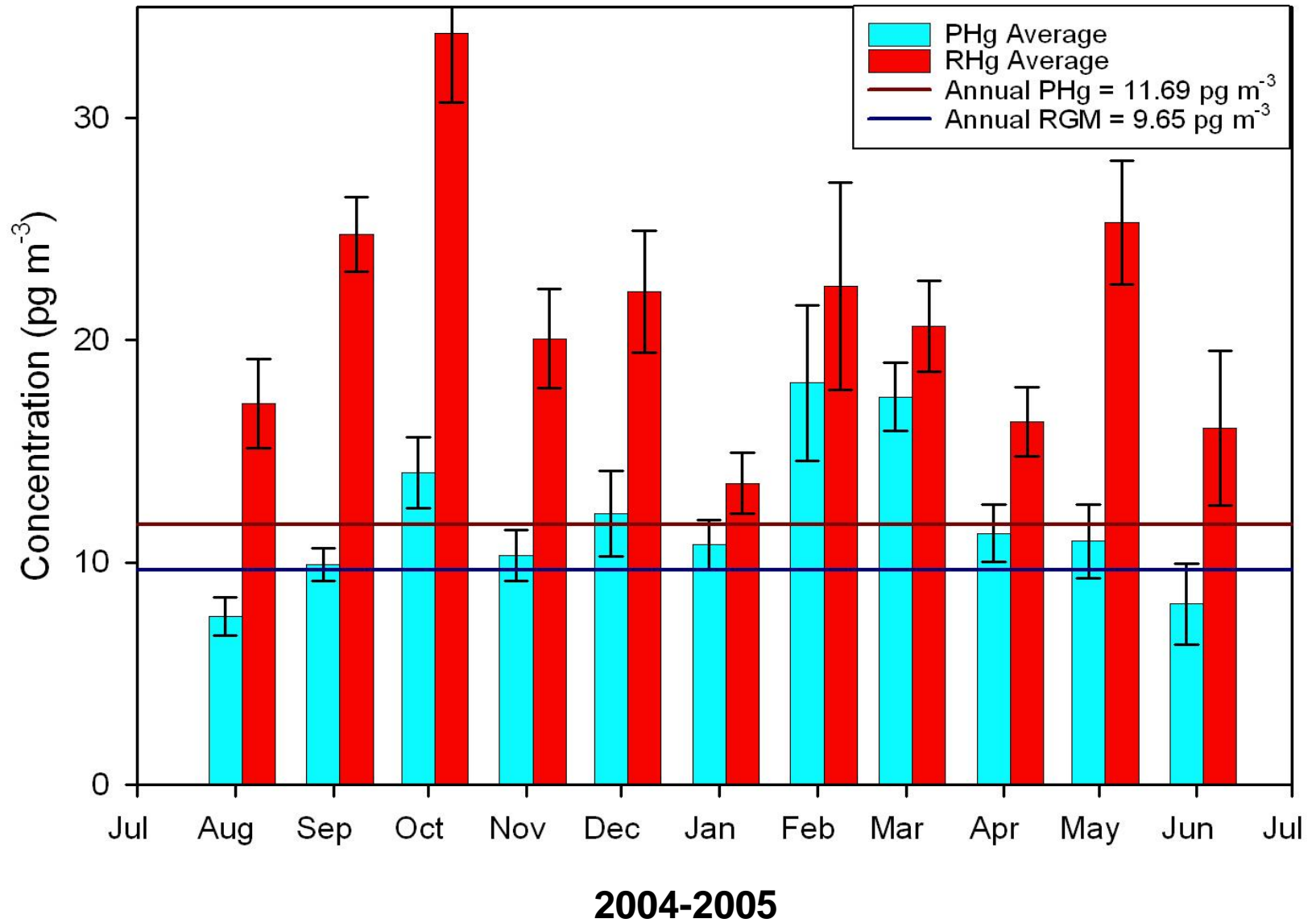
Milwaukee Elemental Mercury Monthly Averages



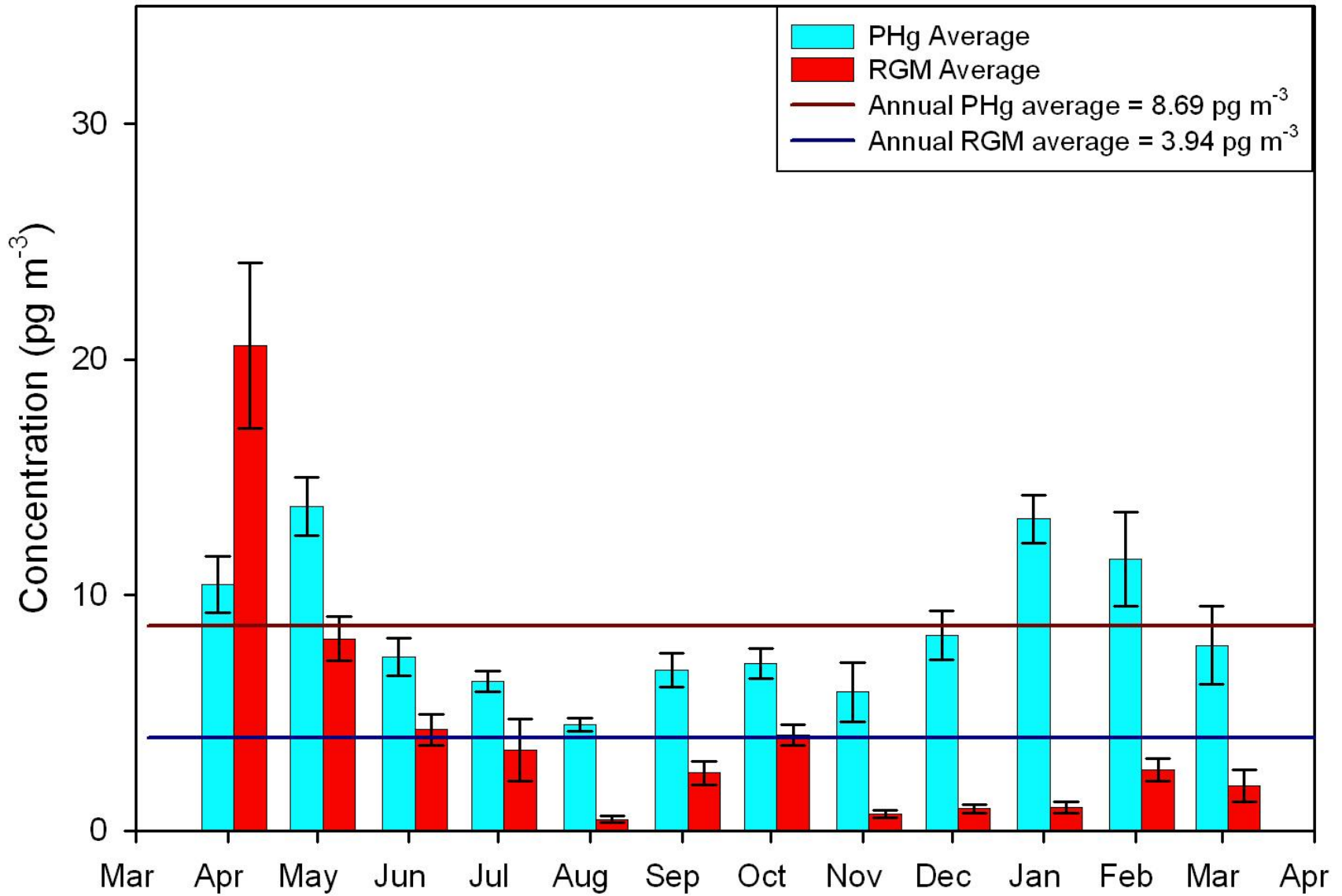
Devil's Lake Elemental Mercury Monthly Averages



Milwaukee PHg and RHg Monthly Averages



Devil's Lake PHg and RGM Monthly Averages



2003-2004

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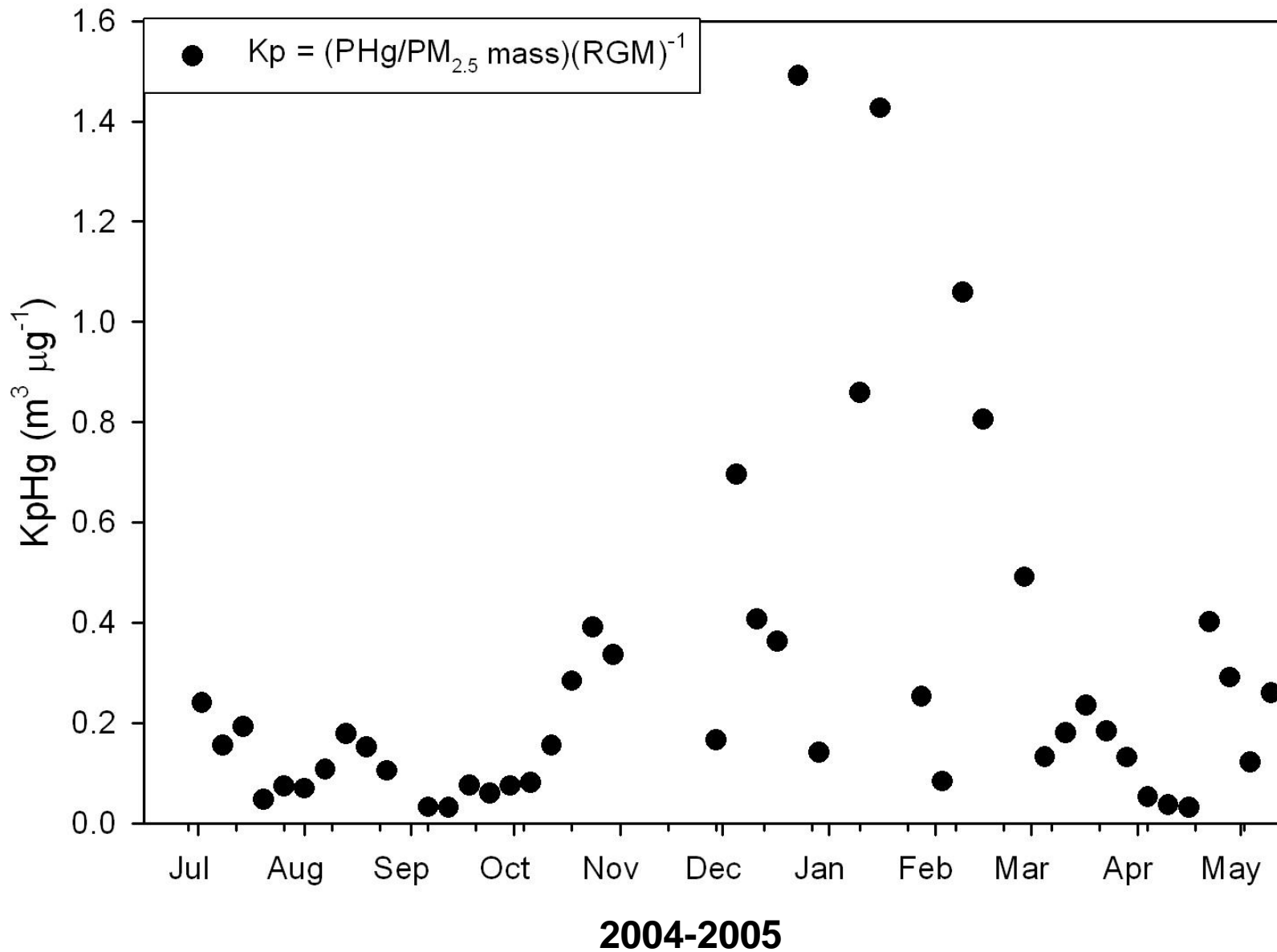


Mercury Partitioning Coefficient

$$K_p = \frac{[Hg^{2+}]_{(p)} / TPM}{[Hg^{2+}]_{(g)}} \left(\frac{m^3 \text{ air}}{\mu g \text{ part}} \right)$$



Milwaukee Mercury Partitioning



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

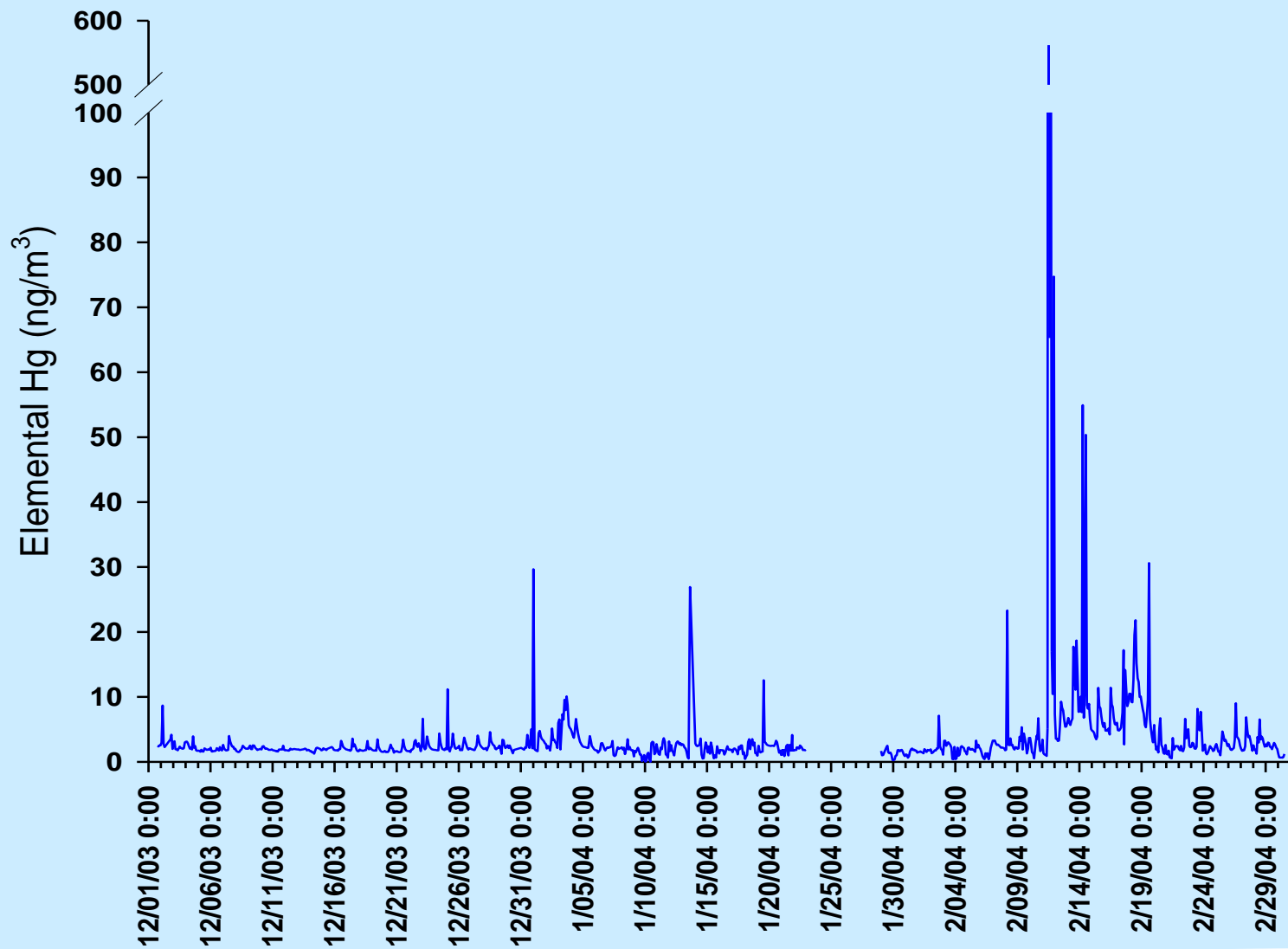
This campaign complimented analogous data collected from October to December 2002



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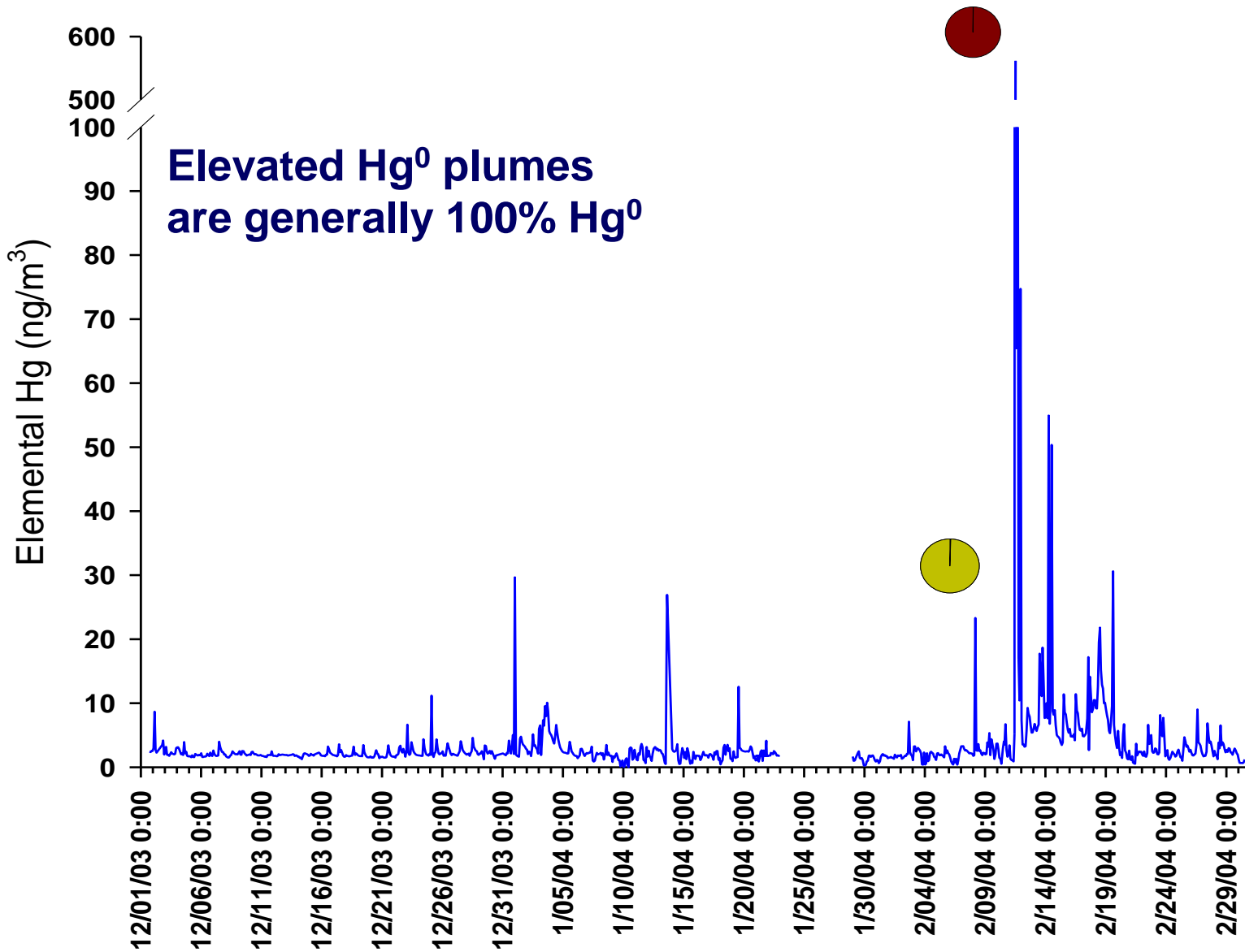


Hg⁰ in the atmosphere

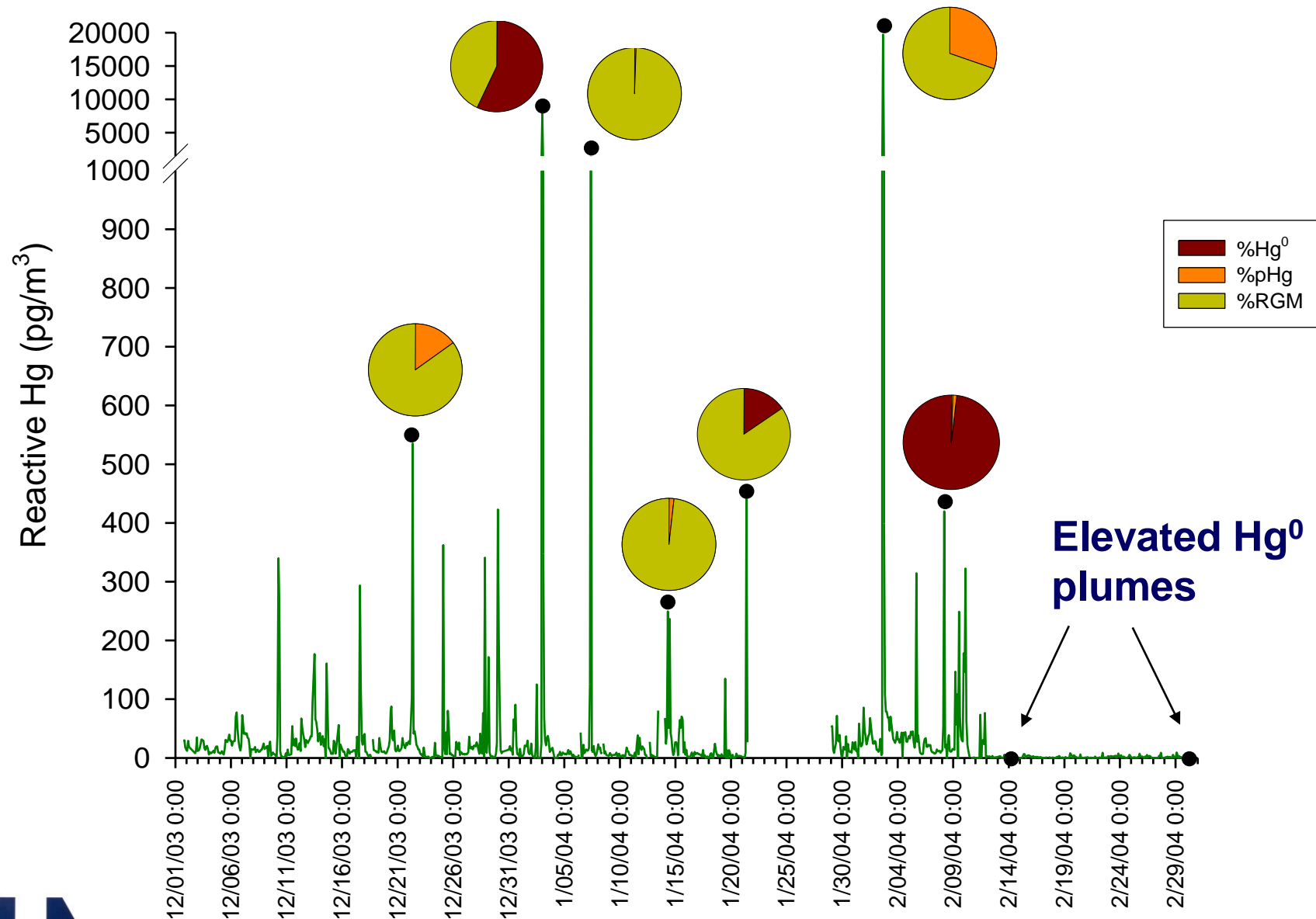


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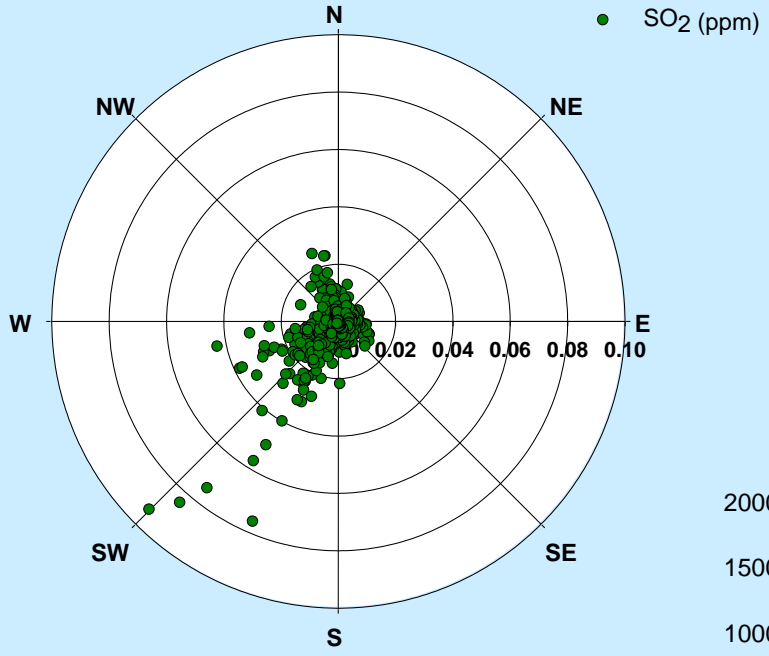
pHg and RGM in the atmosphere



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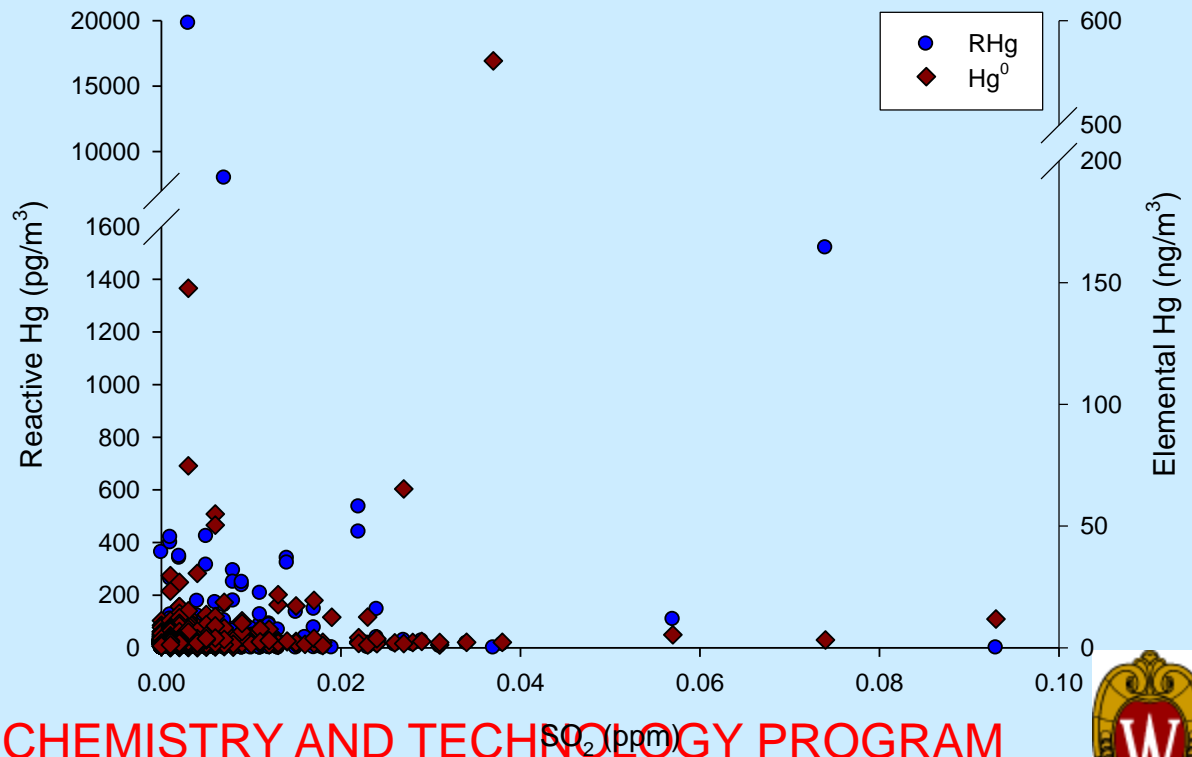


Are there pollutants co-emitted with Hg?



Elevated SO₂ concentrations track from same direction....

..but there is no correlation between Hg⁰ or RHg and SO₂

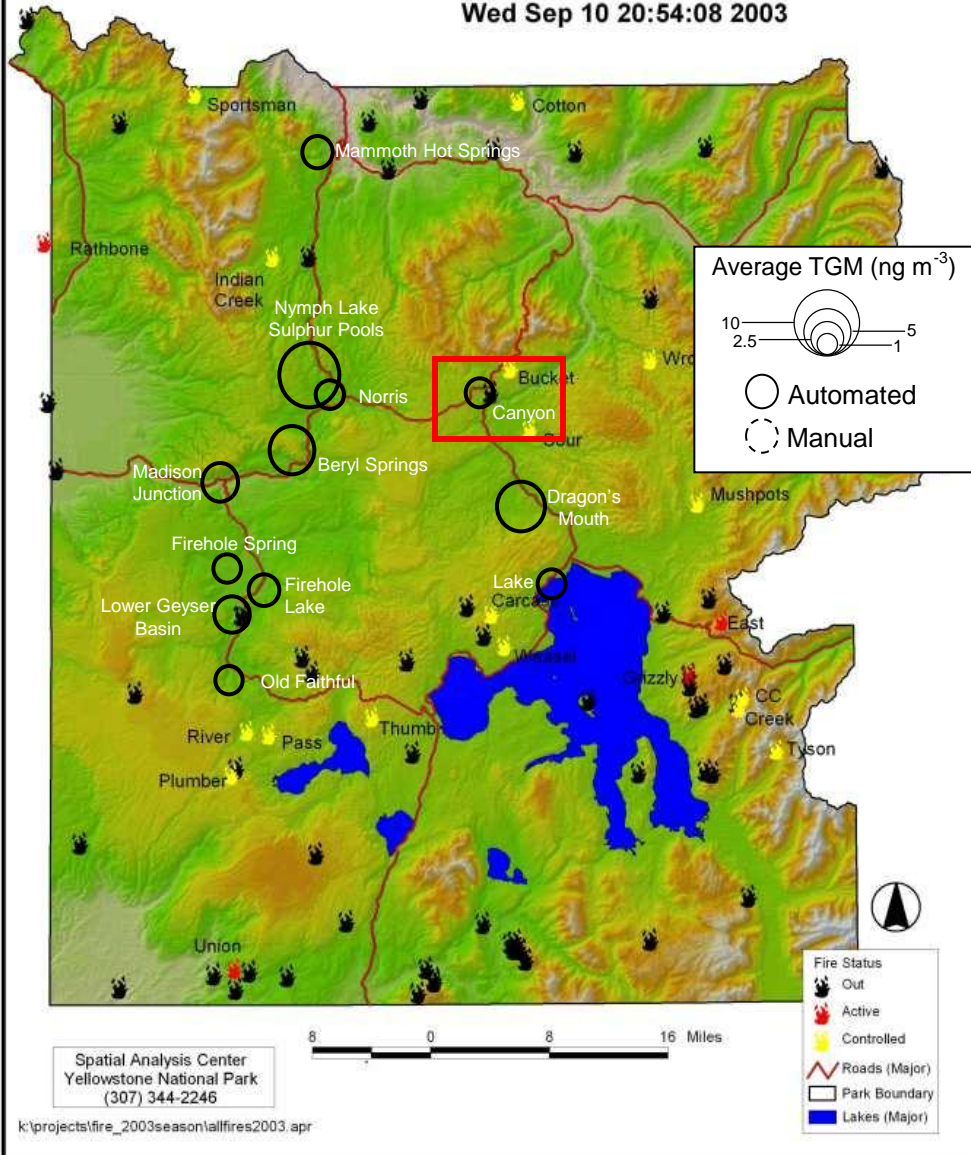


2003 Fires in Yellowstone National Park

National Park Service
U.S. Department of the Interior



Wed Sep 10 20:54:08 2003



Measured gaseous Hg (TGM) at various sites using a mobile Tekran unit

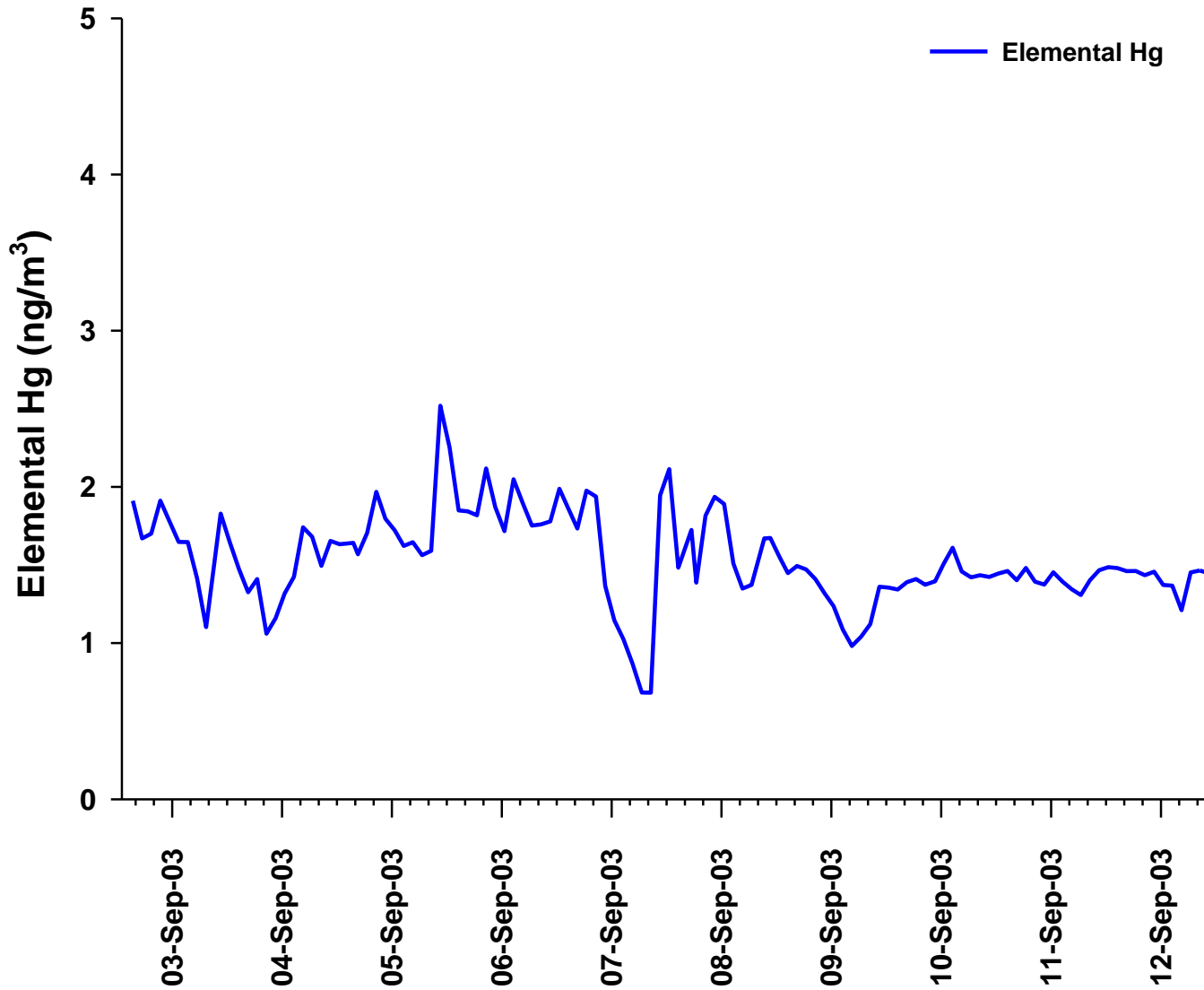
TGM at various sites differed from global background concentrations

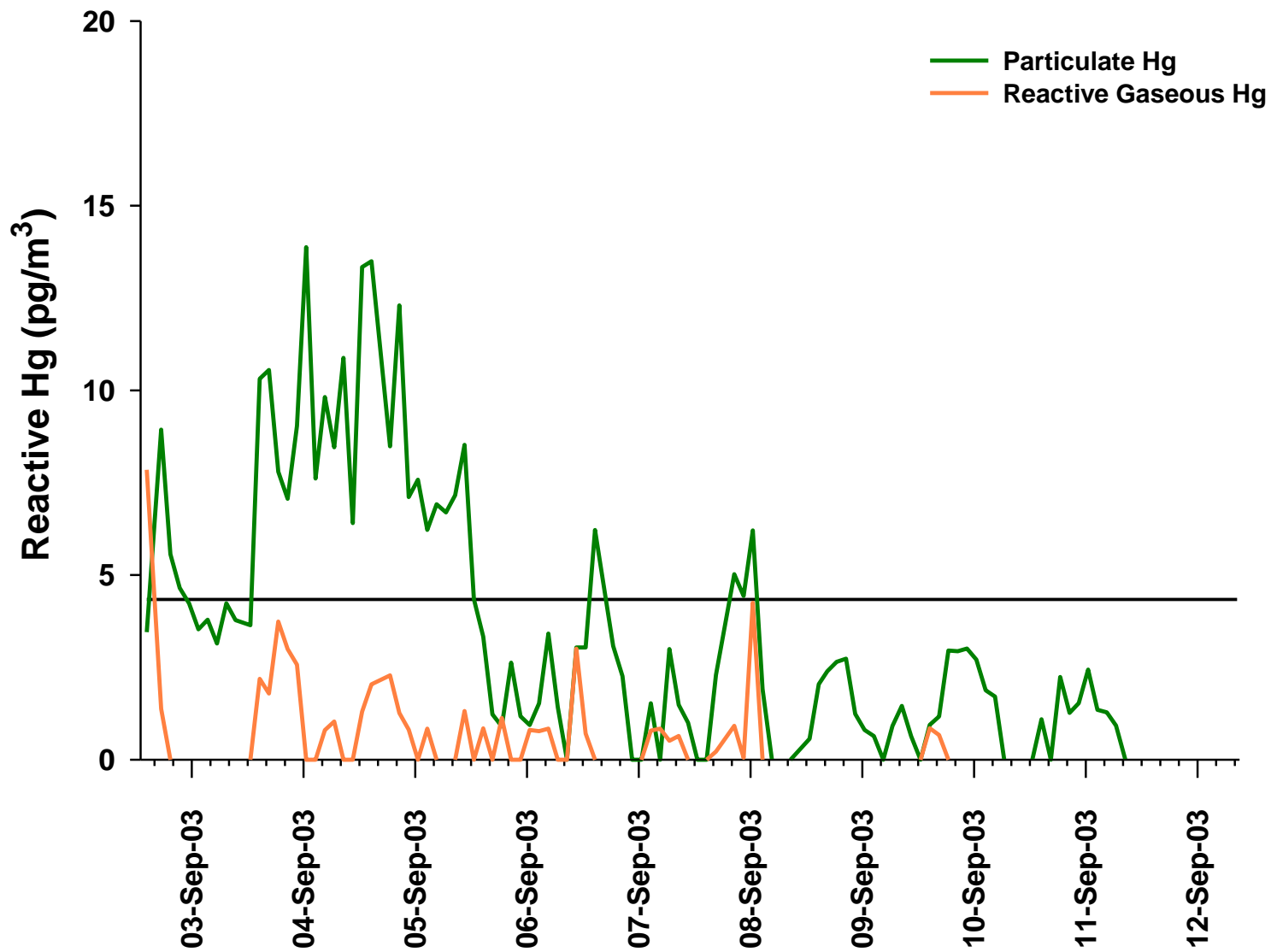
The maximum TGM concentrations was 9 ng/m³

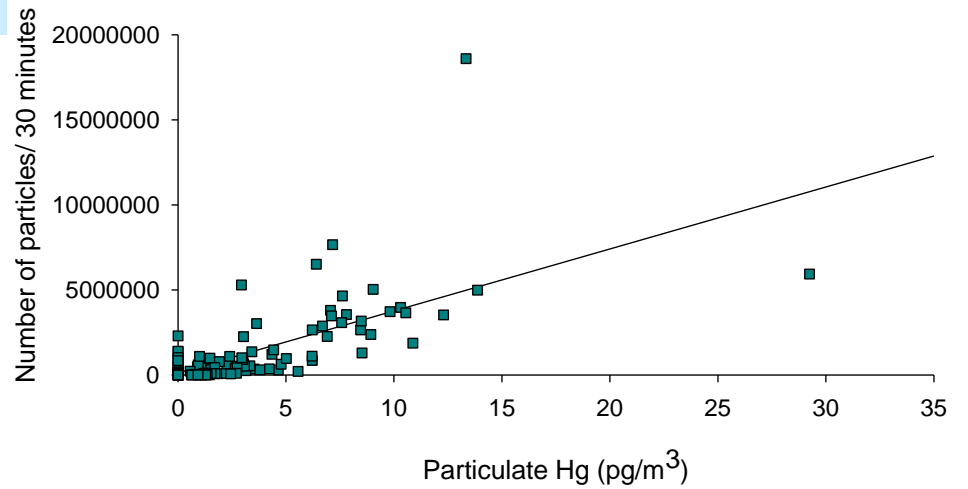
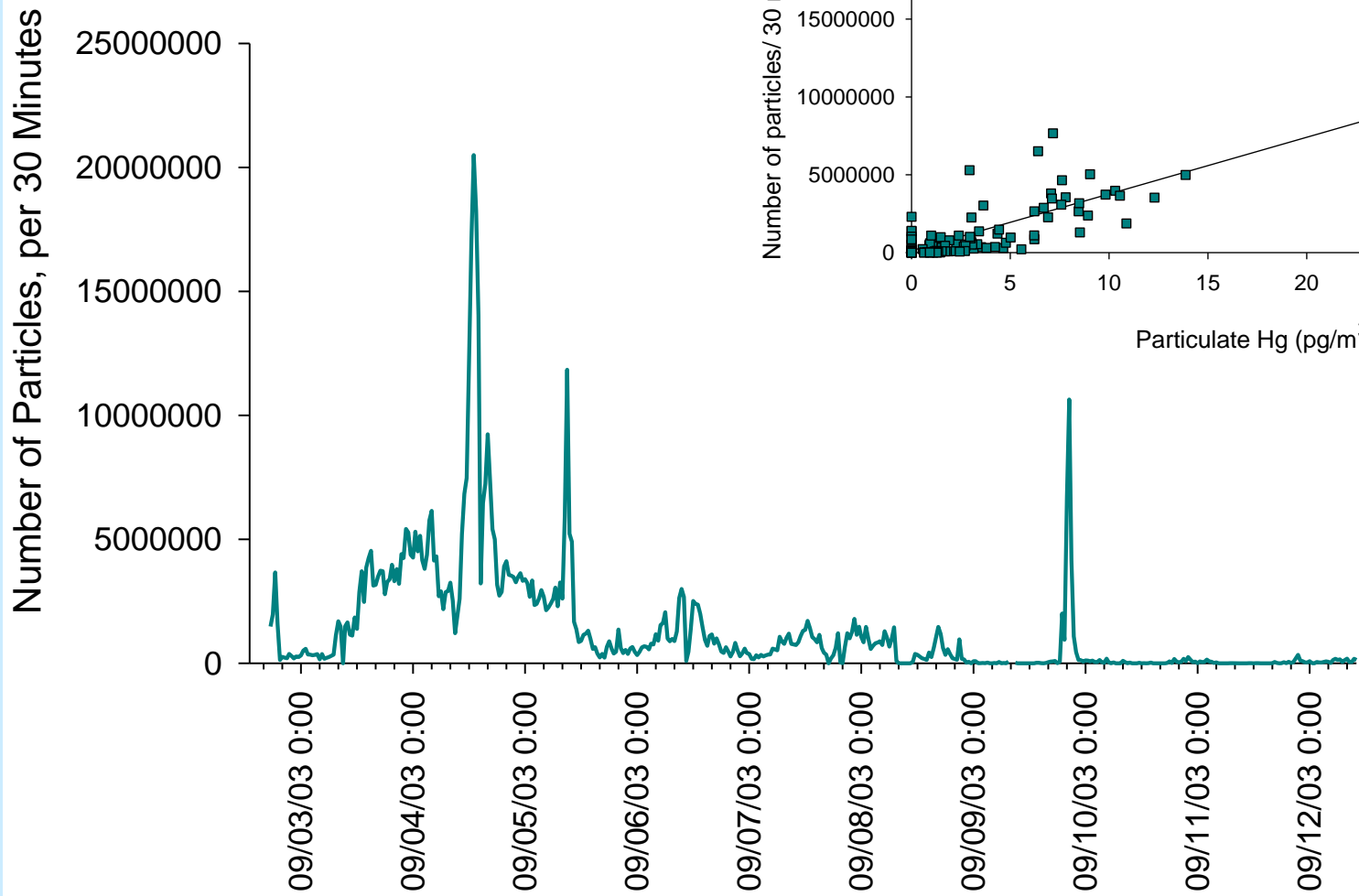
Intensive study using speciation units was performed at the Canyon site

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Conclusions

- Measurement tools exist to accurately measure atmospheric mercury species in real time
 - Co-locate with other atmospheric measurements to identify sources of specific mercury species
- Urban excess of elemental Hg, RGM and particulate mercury
 - Likely due to local sources
- Local sources appear to be important in rural locations at times
- Seasonal trends in the ratio of RGM to particulate mercury
 - Likely driven by temperature
- On-going analysis of elemental and reactive mercury plumes in St. Louis and Milwaukee

