Sensitivity of Heterogeneous Atmospheric Mercury Processes to Climate Change

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Start Date: Feb 15, 2007

Overall Project Goal

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  - Quantify the impact of climate change on key atmospheric processes that control the fate of mercury in transport from emissions to deposition
  - Examine the **incremental** impact of climate change variables on heterogeneous atmospheric mercury oxidation and depositional processes.
    - Deposition
    - Heterogeneous Atmospheric Oxidation
  - Modeling **sensitivity** using existing speciated atmospheric mercury measurements
    - Remote location
    - Urban location

Project Objectives

- Quantify the sensitivity of dry deposition of elemental mercury, reactive gaseous mercury (RGM) and particulate mercury to:
  - T, RH, ozone, nitrogen oxides, and sunlight intensity
- Quantification of sensitivity of atmospheric mercury oxidation and reduction reaction in fog and cloud water to:
  - T, sunlight intensity, and the aqueous composition
- Investigate the oxidation of elemental mercury in the presence of the complex atmospheric reactions that produce photochemical smog and secondary organic aerosols
- Investigate the sensitivity of mercury deposition to climate change variables using a regional chemical transport model
  - Analyze base case of a year long data sets of hourly speciated atmospheric mercury and event based wet deposition data

Experimental Approach

- An integrated laboratory and modeling approach that builds upon expertise in laboratory based low-level atmospheric mercury experiments developed under a prior STAR project.
  - Studies of mercury cycling to plant and soil surfaces at the UW-Madison Biotron controlled environment using on-line mercury instruments and mercury isotope spiking studies
  - Laboratory studies of the chemical transformations of mercury with cloud and fog water collected using ultra-clean sampling methods along with parallel studies using artificial cloud and fog waters
  - Smog chamber studies of mercury oxidation during controlled ozone and SOA formation studies using expertise at the University of New Hampshire
  - Regional chemical transport modeling to study atmospheric mercury deposition sensitivity to temperature, precipitation, and atmospheric circulation patterns associated with climate change

Outline

- Background
- Dry Deposition Experiments
- Cloud and Fog Water Experiments
- Smog Chamber Experiments
- Modeling
- Expected Outcomes


GEOCHEMICAL MERCURY CYCLE
SOLAR
LONG-TERM
TRANSPORT
T, RH
Hg^0
$Hg^{2+}X$
$h\nu$
HO_2
S(IV)
$OH^\cdot$
O_3
HOCl, OCl$^-$
HOBr, OBr$^-$, Br_2
SO_4^{2-}
$NO_x, O_2, OH^\cdot$
$X_x, XO_x, NO_3^?, ?, HO_2^?$
WET
DRY
FLUXES
△ FUEL USE
△ LAND COVER
△ TERRESTRIAL & AQUATIC ECOSYSTEMS

Heterogeneous Processes: Key Uncertainties

- Gas/Particle Partitioning of Reactive Hg
  - *Addressed in prior STAR Project*
- Dry deposition of different forms of Hg
  - Elemental, RGM, Particulate Mercury
  - Interaction with different surfaces
  - Impact of other atmospheric oxidants
- Heterogeneous conversions of Hg
  - Clouds and fogs
  - Complex Photochemical Smog
    - Aerosols
    - Reactive intermediates

Assessing the Impact of Climate Change

- Need an incremental impact approach
  - Most prior Hg research has looked at best estimate of current and pre-industrial fluxes
- Key parameters of interest
  - Temperature, Humidity and Rainfall
  - Atmospheric Circulation Patterns
  - Co-Pollutants and Atmospheric Oxidation
  - Aerosol Composition
  - Cloud and Fog Composition
  - Mercury Emissions and Emission Speciation
  - Land Use

Dry Deposition Experiments

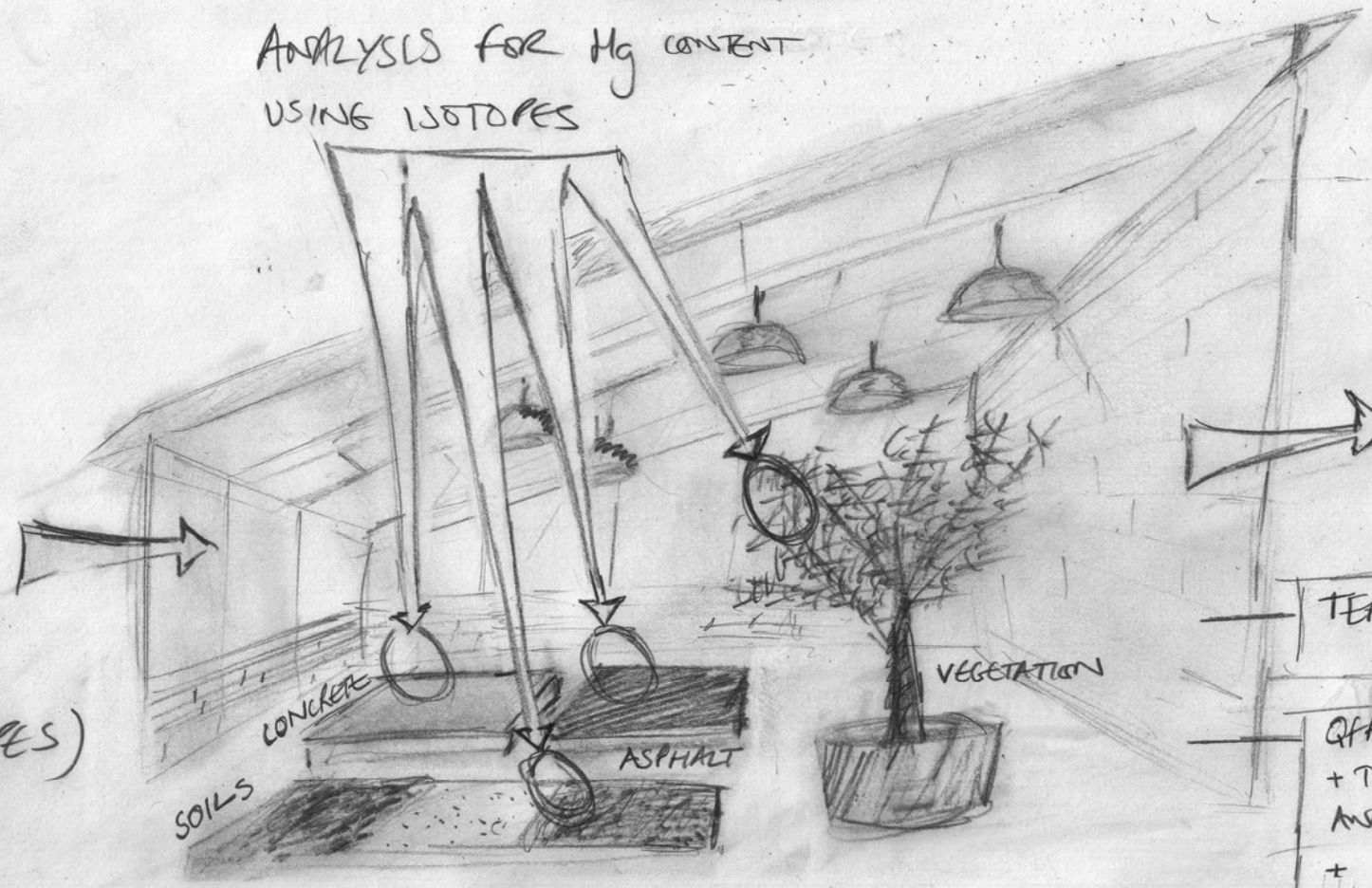
- Quantify the sensitivity of the net flux of gaseous elemental mercury (GEM) and reactive mercury to plant, soil and engineered surfaces
  - Light intensity – 600-900 W m^{-2}
  - Temperature – 15-25 C
  - Ozone – 0-200 ppm
  - Soil moisture – 15-50 %
  - Relative Humidity – 20-80 %
- Utilize isotopically enriched Hg (199, 200, 202) to simultaneous study fluxes
- Utilize real time monitoring of Hg and other experimental parameters

DRY DEPOSITION

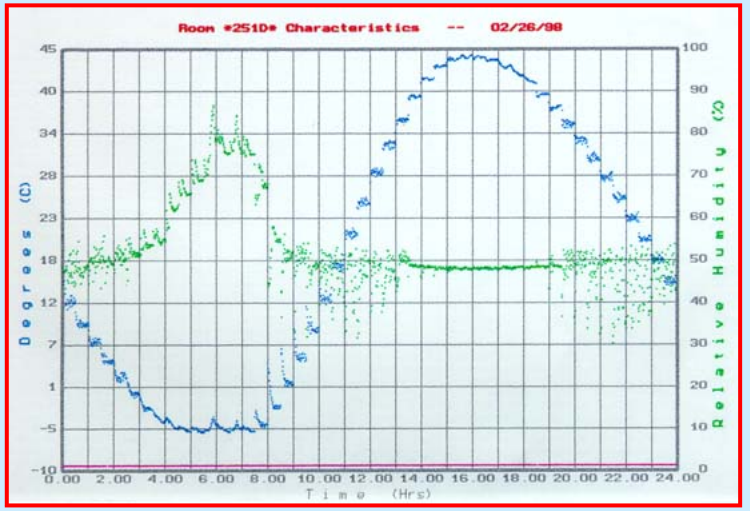
BIOTRON – CONTROLLED : T, $I_{h\nu}$, RH

– MONITOR : T_{AIR}, RH, O_3, CO_2, $I_{h\nu}$
T_{SOIL}, SOIL MOISTURE

ANALYSIS FOR Hg CONTENT
USING ISOTOPES



UW-Madison BIOTRON



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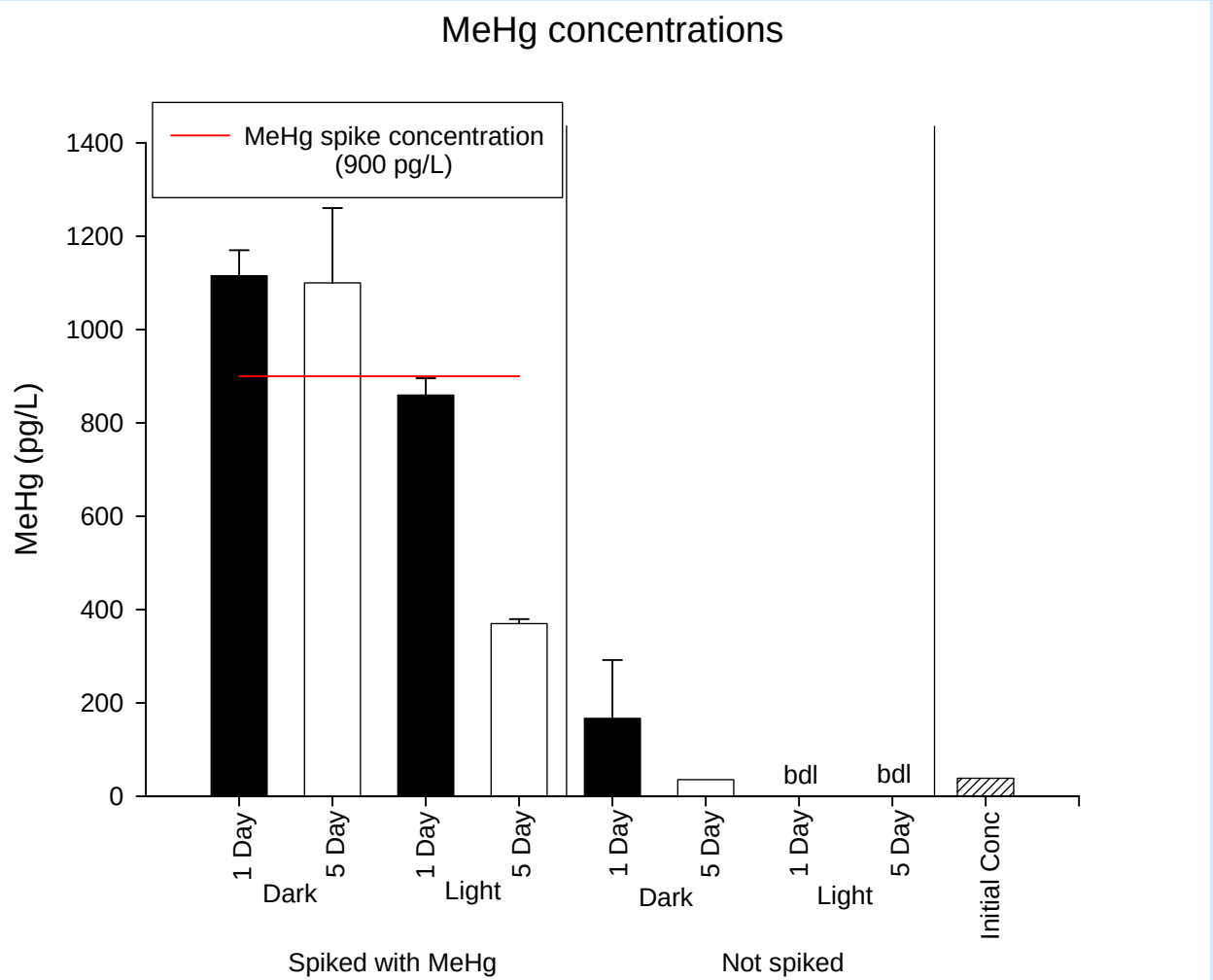
Cloud and Fog Water Experiments

- Explore the sensitivity of the net oxidation of dissolved elemental mercury to:
  - Light intensity
  - Temperature
  - Water composition and pH
    - Bulk composition
    - Trace metals
  - Oxidants
- Atmospheric & synthetic cloud and fog water
- Exploit isotopically labeled Hg

Demethylation in Rain Water



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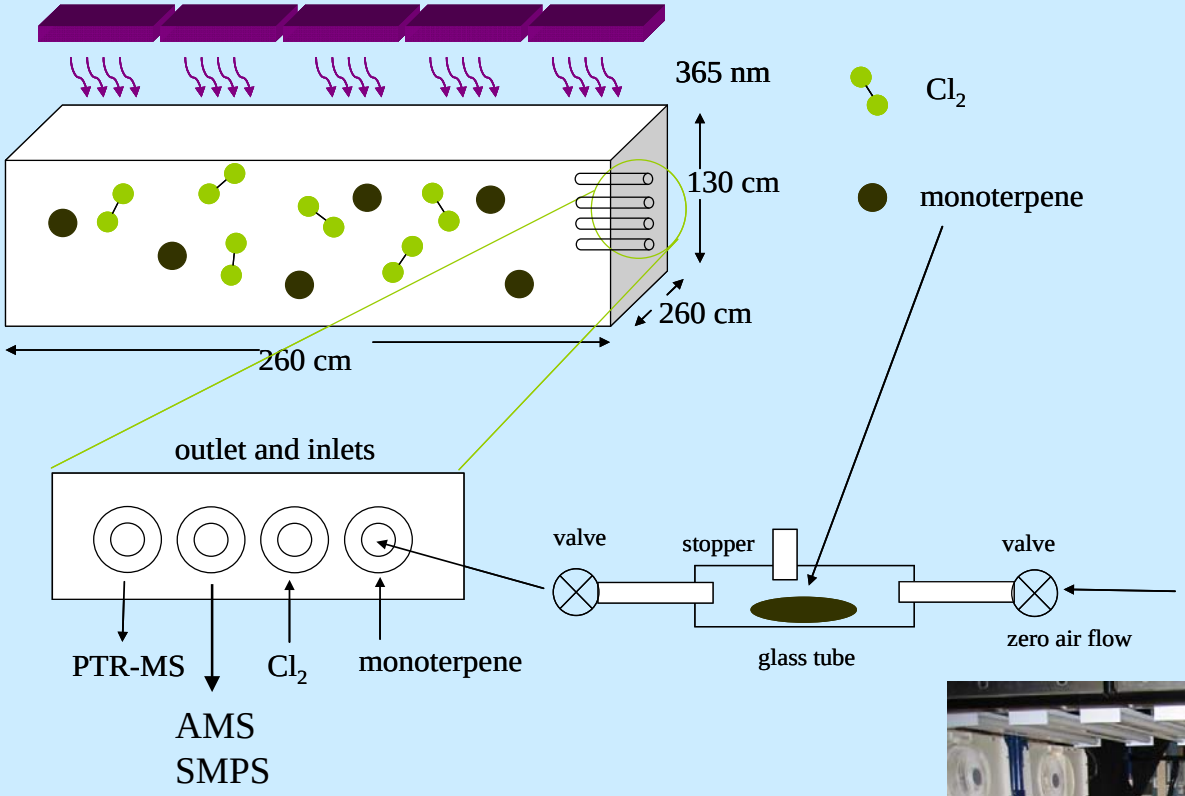
Smog Chamber Experiments

- Explore the oxidation of mercury and potential production of methyl mercury in photochemical smog
  - Reference to ozone, chlorine, and other known gas-phase Hg oxidants
- Quantify the gas to particle partitioning of reactive mercury to SOA



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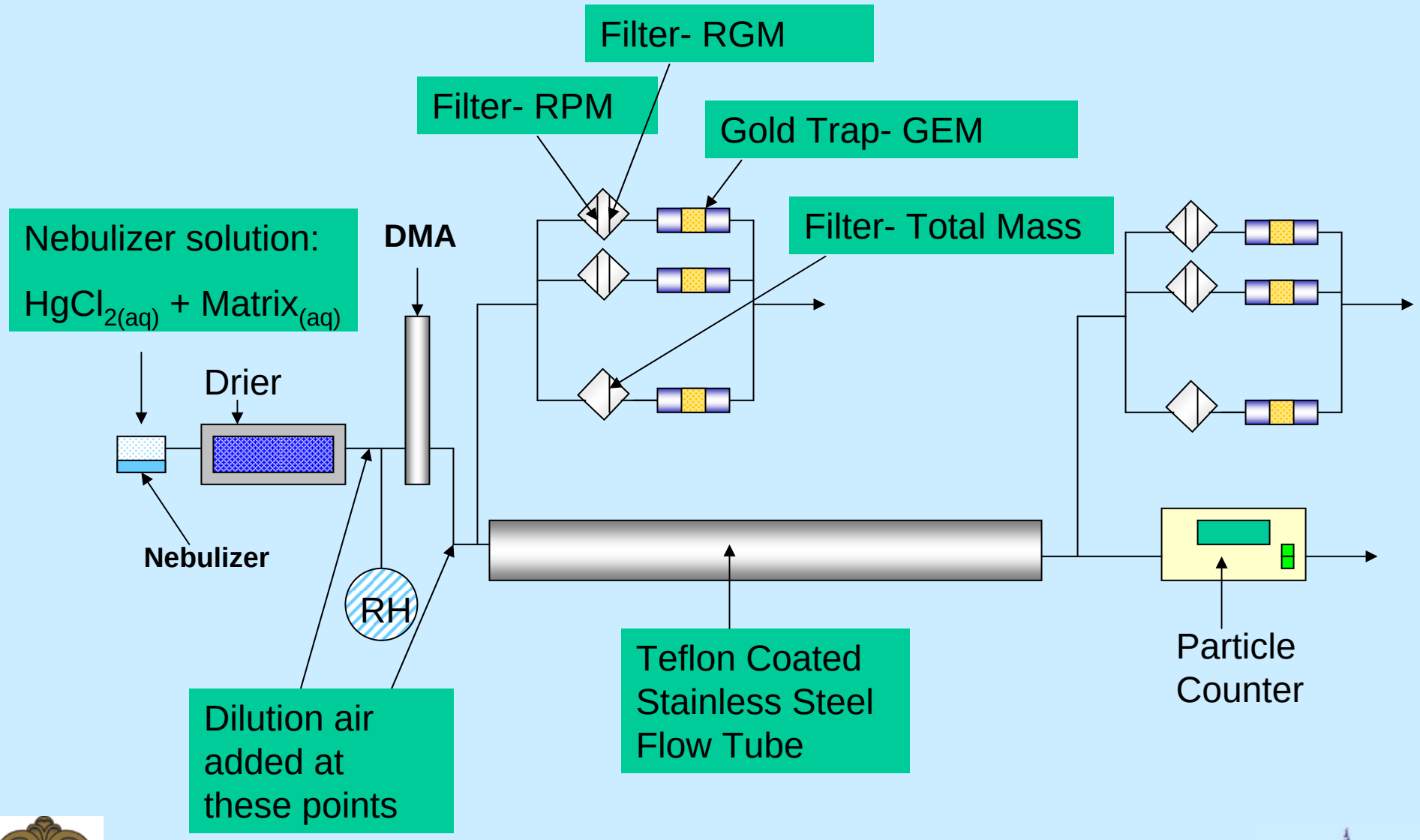
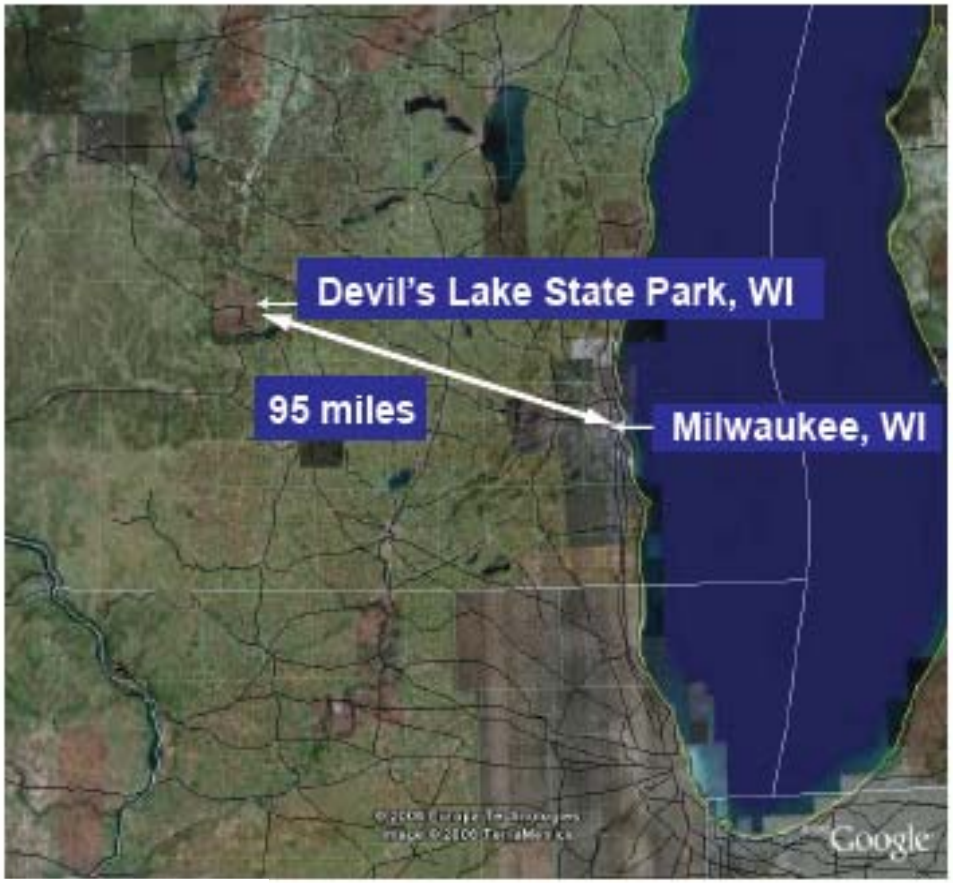

Filter- RGM
Filter- RPM
Gold Trap- GEM
Filter- Total Mass
Nebulizer solution:
$HgCl_{2(aq)}$ + $Matrix_{(aq)}$
DMA
Drier
Nebulizer
RH
Dilution air added at these points
Teflon Coated Stainless Steel Flow Tube
Particle Counter

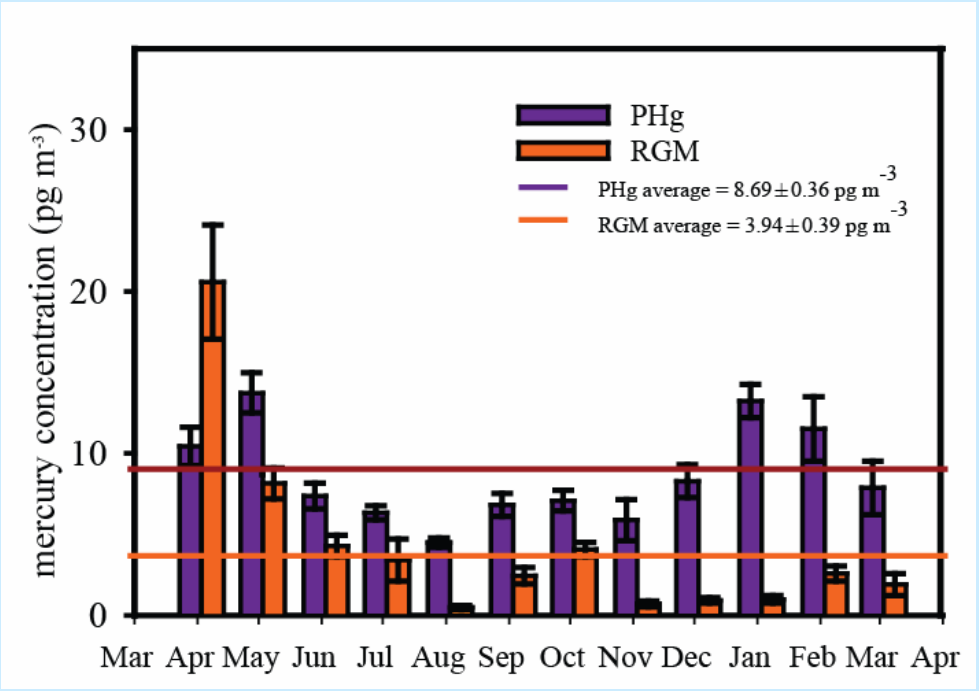
Sensitivity Modeling

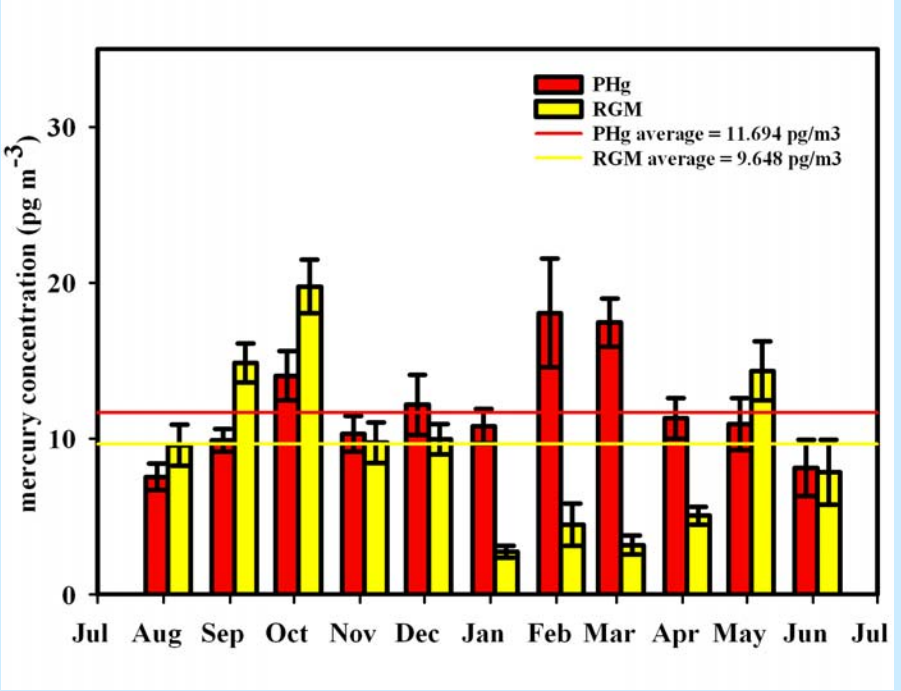
- Mercury Modeling
  - Update cloud and fog Hg chemical processes
  - Update modules
    - Gas to particle partitioning – Prior work
    - Emissions from soils – Literature
    - Photochemical smog processing
  - National Emissions Inventory
    - Consistency checks with analysis of real time data
- Use existing atmospheric measurements and wet deposition data for model validation
- Model climate scenarios
  - Temp, humidity, cloud cover, cloud chemistry
  - Emissions scenarios

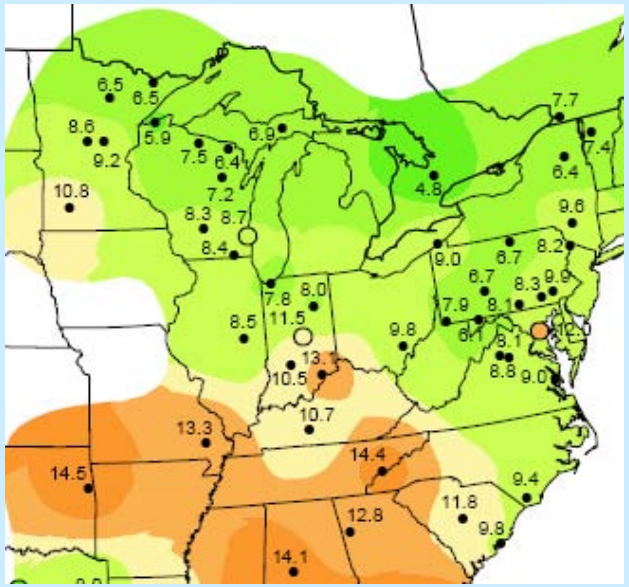
Existing Mercury Monitoring Data

- Tekran Speciation Unit
  - GEM, RGM, and Hg-P
  - Hourly data
  - Devil's Lake
    - April 2003- March 2004
  - Milwaukee
    - May 2004- June 2005
- Hg Wet deposition
  - Event based monitoring









Atmospheric Measurements
-Devil's Lake – MDN and TMDL Site
-Milwaukee
-Full year of hourly speciated Hg
Event Based Wet Deposition
- Devil's Lake – MDN and TMDL Site

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Expected Outcomes

- Improved understanding of mercury cycling and sensitivity to climate variables
  - Dry deposition to plant, soil and engineered surfaces
  - Cloud and fog processing
  - Processing in photochemical smog
- CMAQ model developments
  - Model performance evaluation with atmospheric measurements
  - Heterogeneous processes including partitioning, smog processing, and cloud and fog processing
  - Improvements in dry deposition representation
  - Descriptions of perturbations of mercury chemistry caused by effects of climate change