

US EPA ARCHIVE DOCUMENT

Sensitivity of Heterogeneous Atmospheric Mercury Processes to Climate Change

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to Climate Change - EPA-G2006-STAR-J1



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



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Outline

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



GEOCHEMICAL MERCURY CYCLE

 SOLAR

T, RH

LONG-TERM
TRANSPORT

SO_4^{2-}

Hg^0
 Hg^{2+}
 $h\nu$
 HO_2
 $S(IV)$

OH^+
 O_3
 $HOCl/Cl_2$
 $HOBr/Br_2$

NO_x , O_2 , OH
 X , XO_x , NO_3 , HO_2

WET

DRY

FLUXES

Hg^0
 Hg^{2+}

Δ FUEL USE

Δ LAND COVER

Δ 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

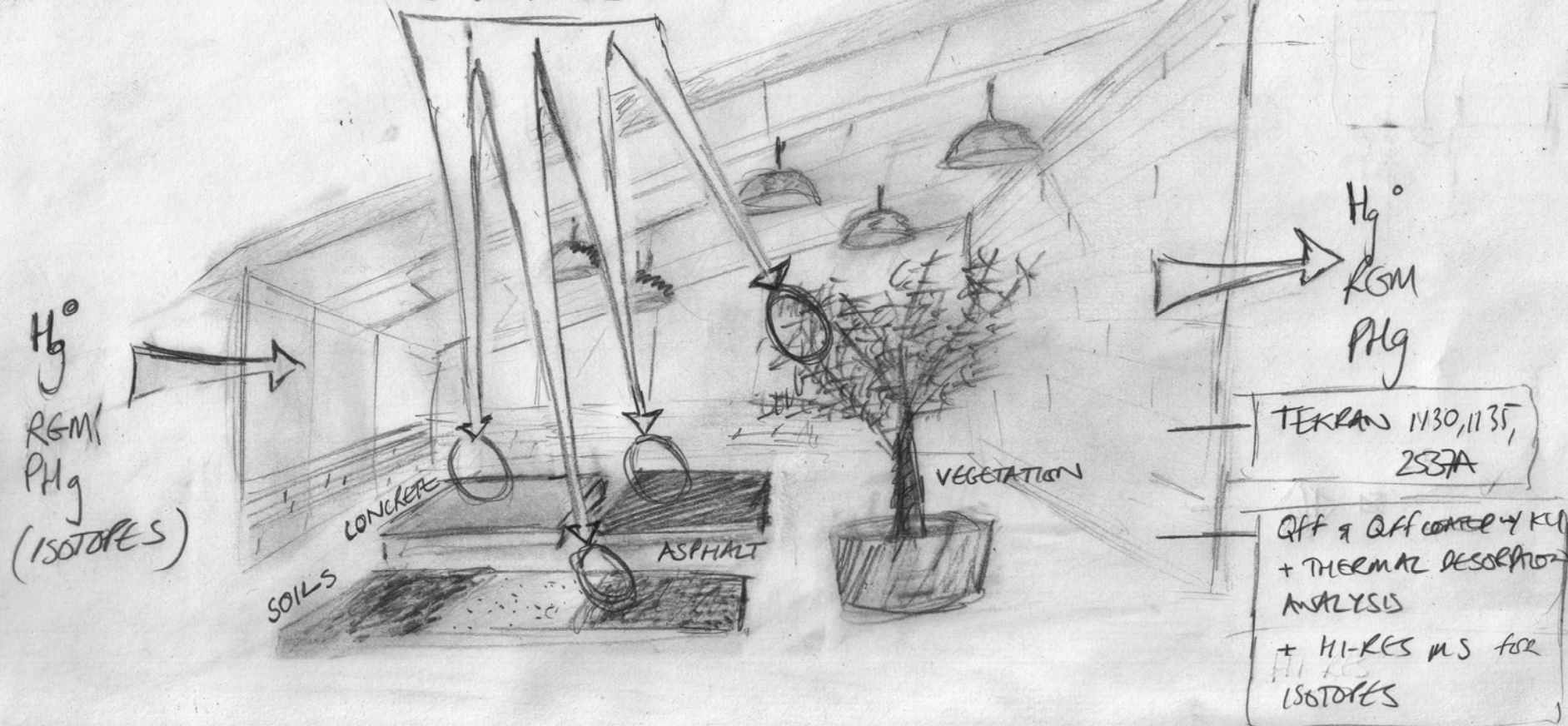


DRY DEPOSITION

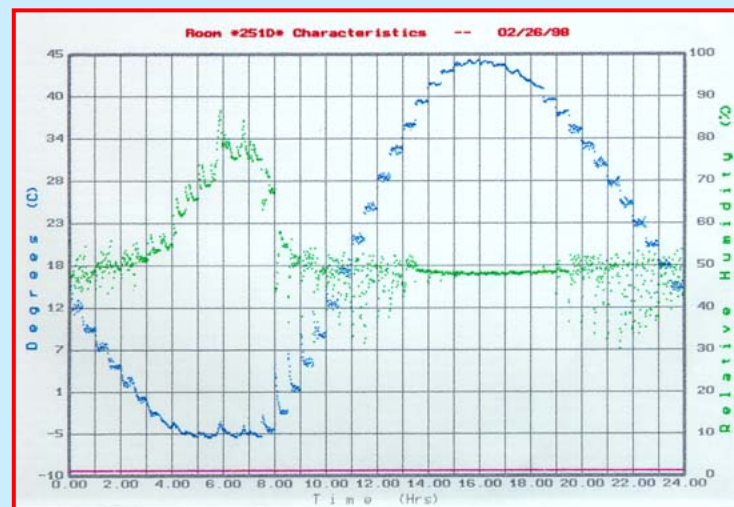
BIOTRON - CONTROLLED: T , I_{hv} , RH

- MONITOR: T_{AIR} , RH , O_3 , CO_2 , I_{hv}
 T_{SOIL} , SOIL MOISTURE

ANALYSIS FOR Hg CONTENT
USING ISOTOPES



UW-Madison BIOTRON



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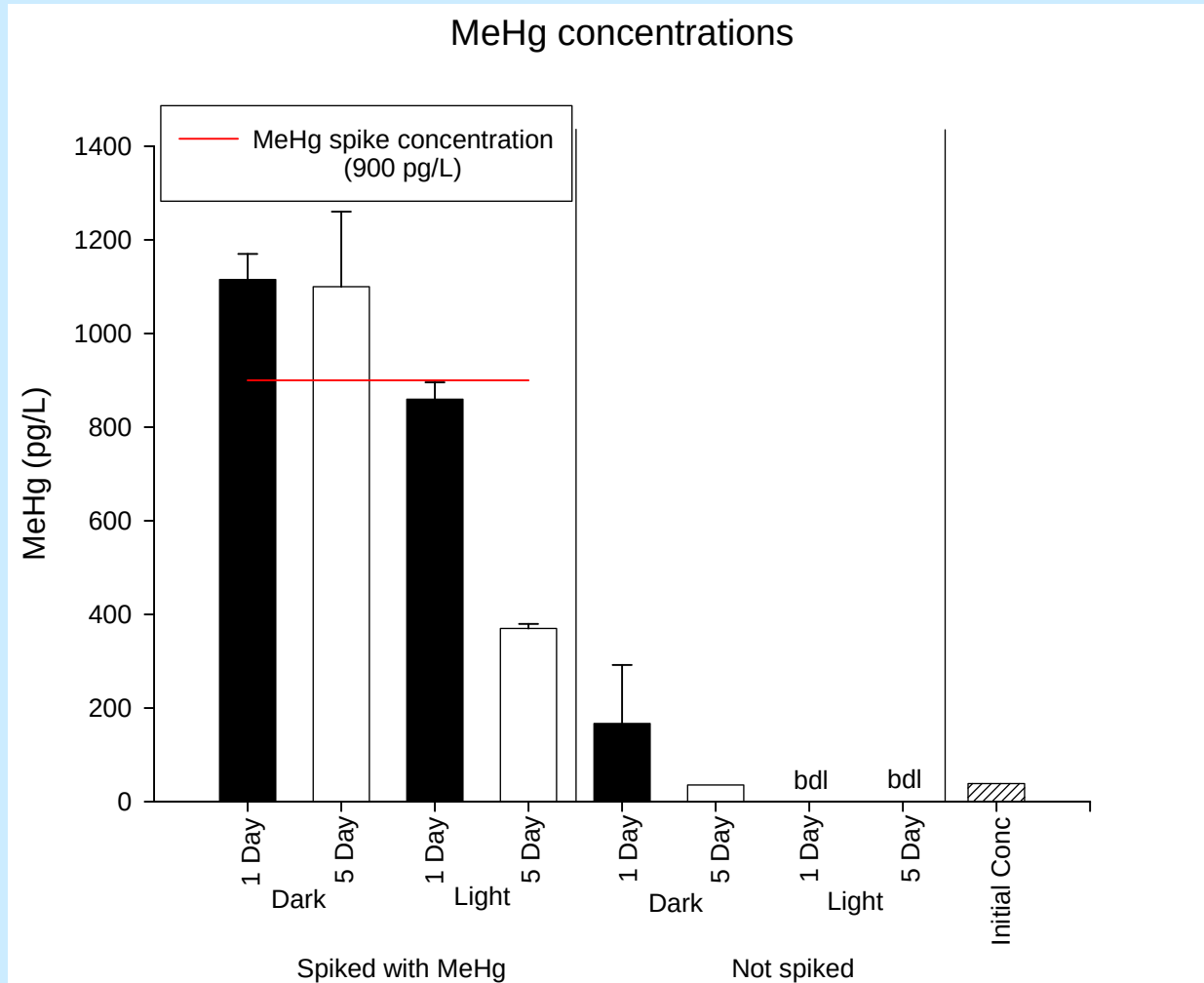


Cloud and Fog Water Experiments

- 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



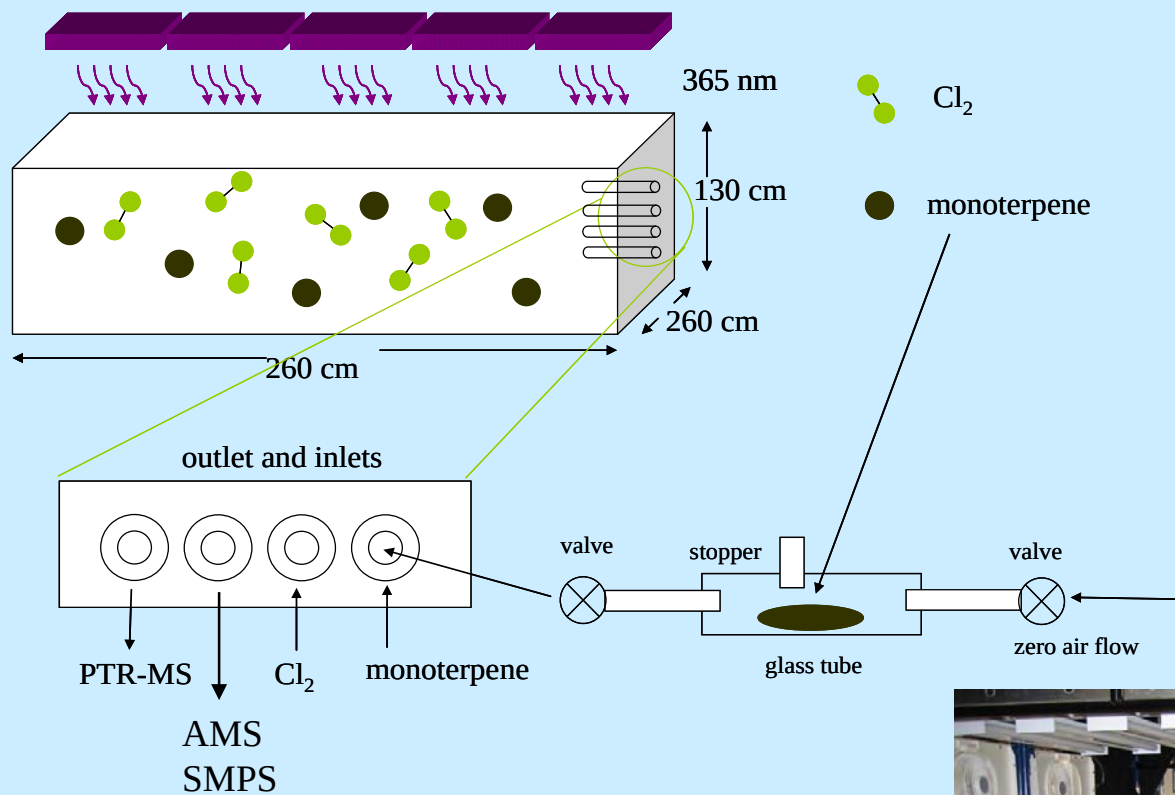
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Smog Chamber Experiments

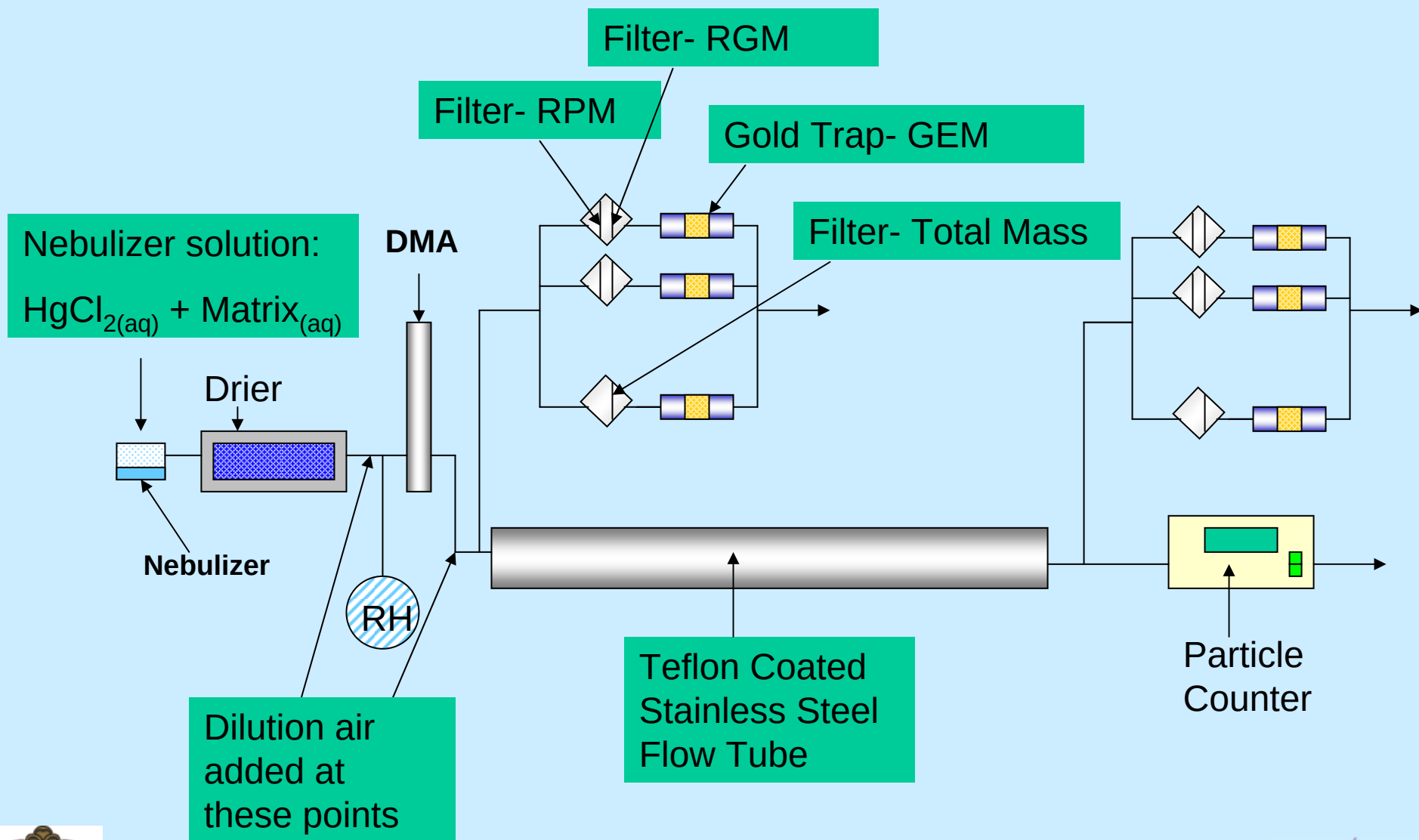
- Explore the oxidation of mercury and potential production of methyl mercury in photochemical smog
 - Reference to ozone, chlorine, and other known gas-phase Hg oxidants
- Quantify the gas to particle partitioning of reactive mercury to SOA





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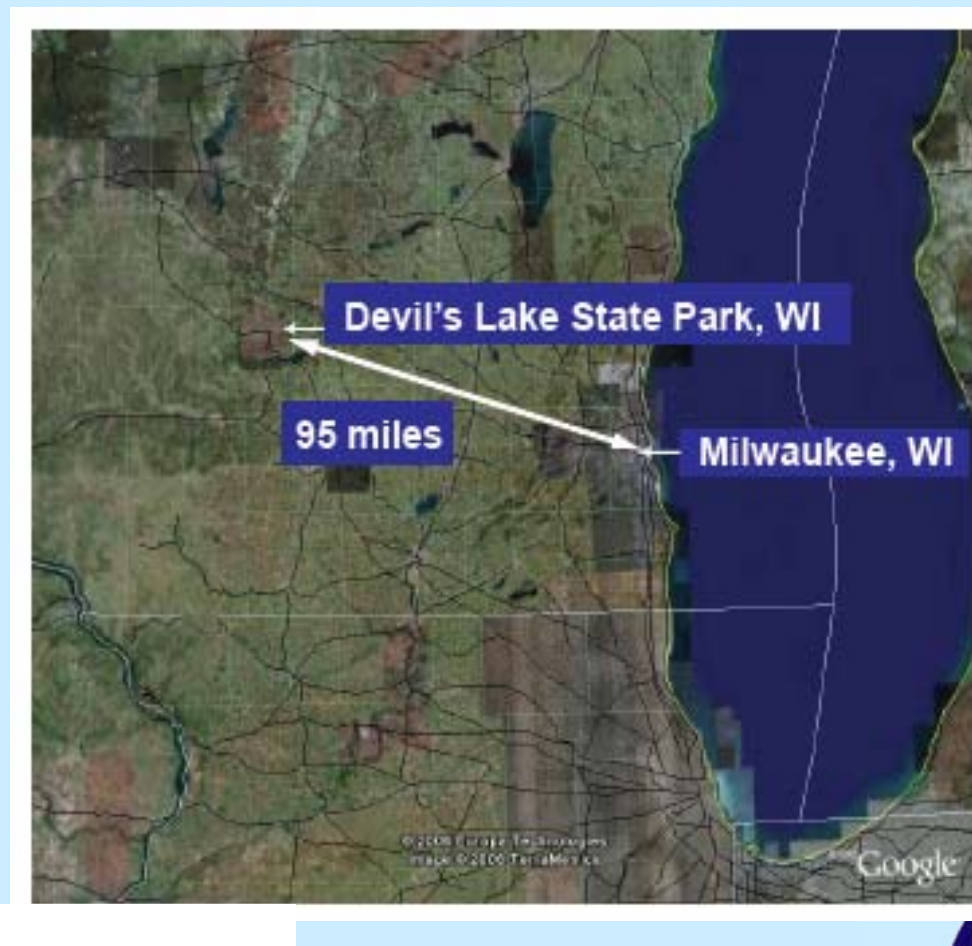
Sensitivity Modeling

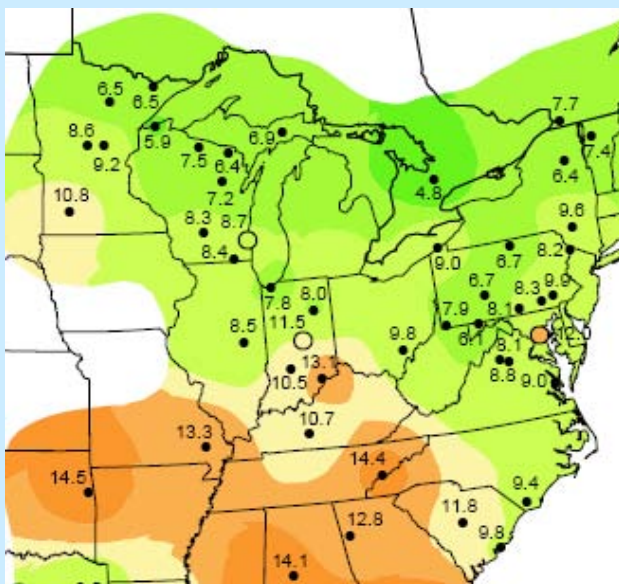
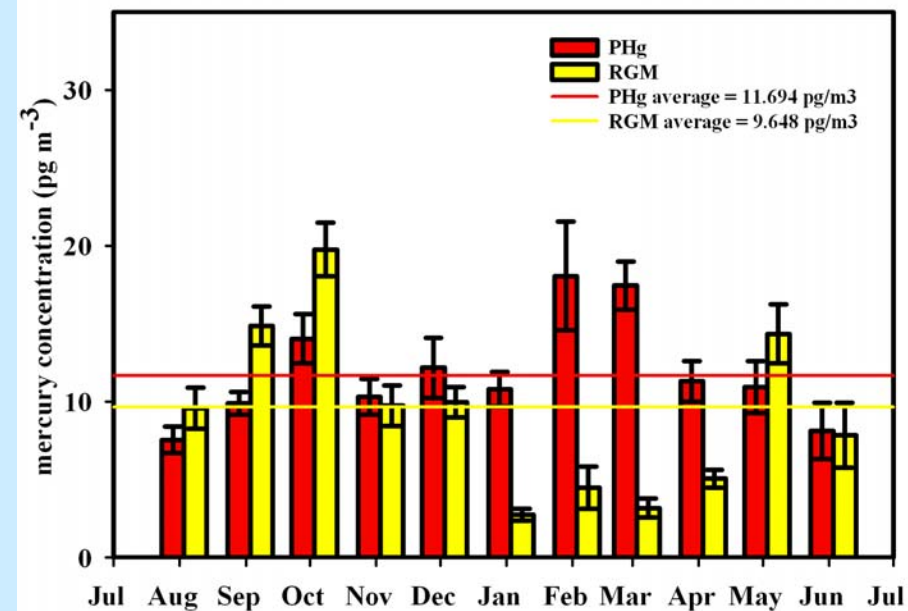
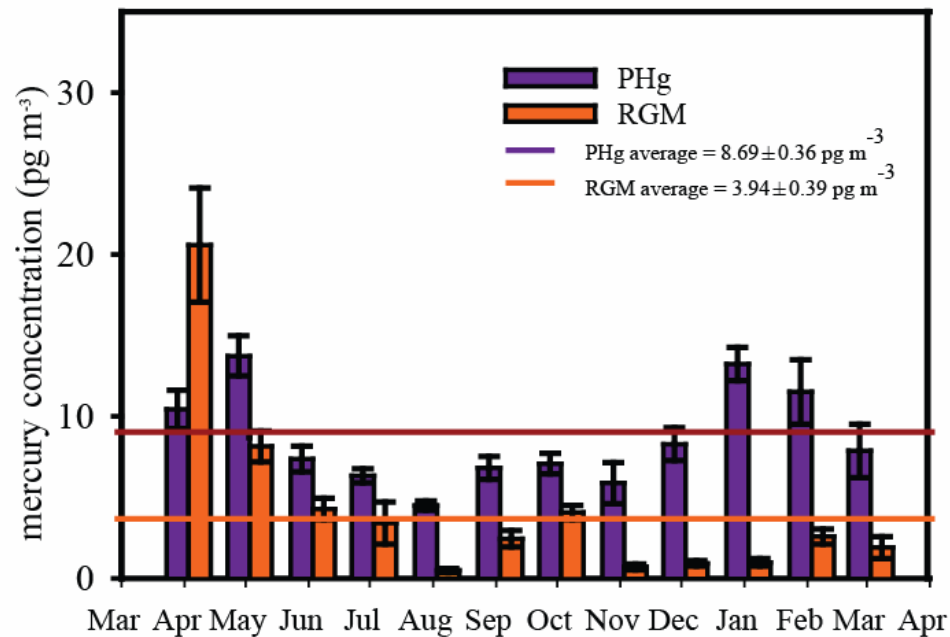
- Mercury Modeling
 - Update cloud and fog Hg chemical processes
 - Update modules
 - Gas to particle partitioning – Prior work
 - Emissions from soils – Literature
 - Photochemical smog processing
 - National Emissions Inventory
 - Consistency checks with analysis of real time data
- Use existing atmospheric 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

