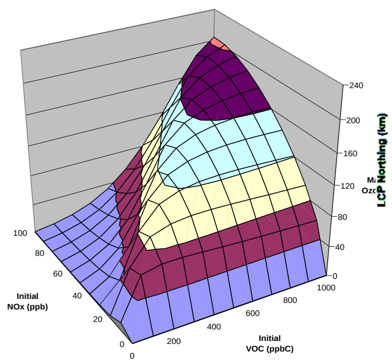
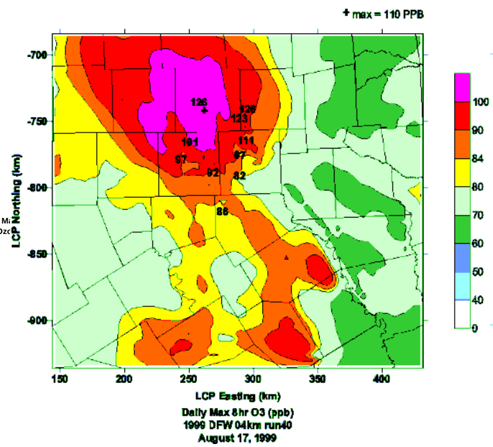
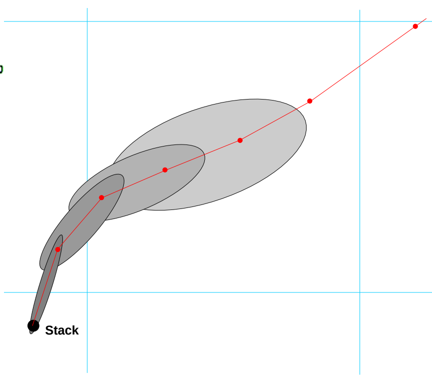
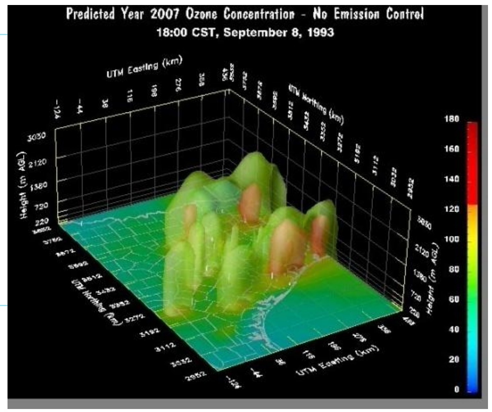
Mercury Modeling
Current State of the Science









Krish Vijayaraghavan
ENVIRON International Corp

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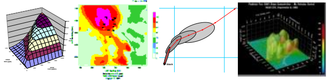

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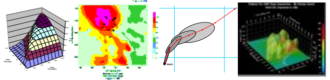
Hg Deposition Characteristics and Residence Times

- Elemental mercury (Hg0)
  - Not very soluble in water
  - Low dry deposition velocity (<0.1 cm/s)
  - Residence time of several weeks to months
- Divalent mercury (HgII a.k.a. RGM)
  - Highly soluble in water and adsorbs on surfaces easily
  - Rapidly removed by wet and dry deposition
  - Residence time of minutes to days
- Particulate mercury (Hgp)
  - Properties are between those of Hg0 and HgII
  - Residence time of several days in the absence of precipitation

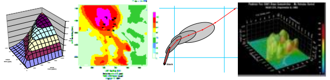


Types of Atmospheric Mercury Models

- Puff/Plume Models (SCICHEM)
- 3-D Deterministic Chemistry Transport Models
  - Gridded and Plume-in-grid models
  - Global (CTM-Hg, GEOS-Chem, GRAHM, ECHMERIT etc.)
  - Regional (CMAQ, CAMx, AMSTERDAM, TEAM etc.)
- Source-receptor models (PMF etc.)
- Back-trajectory models (HYSPLIT)

Challenges for Hg Atmospheric Modeling

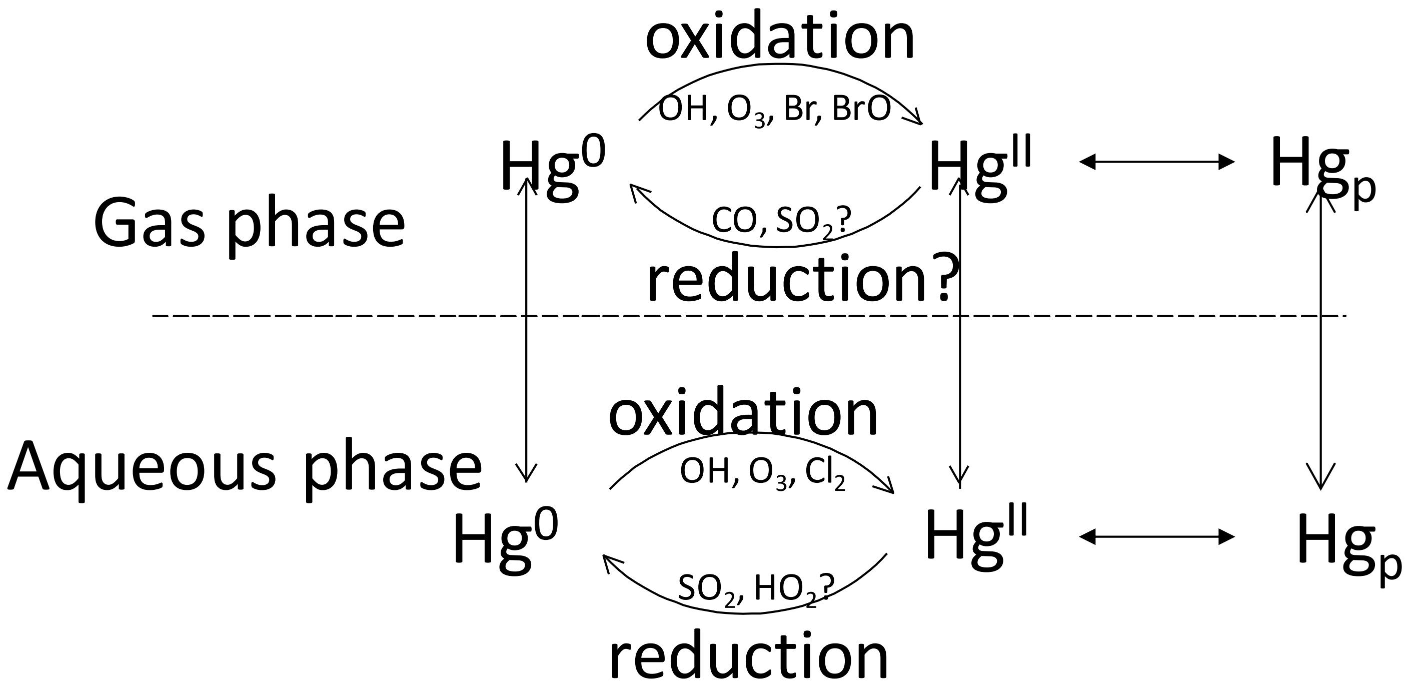
- Uncertainties in Chemistry
- Gaps in Emissions inventories
- Importance of plume-in-grid modeling
- Role of inter-continental transport
- Need for sound meteorological inputs
- Paucity of Hg measurements
- Meeting needs of aquatic modelers



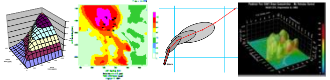
Uncertainties in Hg Chemistry

- Limited experimental data
- Uncertainties in the following:
  - Oxidation by ozone and halogens
  - Aqueous-phase reduction by HO_2
  - Gas-phase or heterogeneous reduction by SO_2, CO
  - Gas-phase adsorption on PM
  - Others

Uncertainties in Hg Chemistry

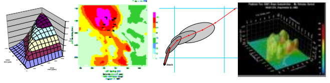


(adapted from Vijayaraghavan et al., 2005 and Lindberg et al., 2007)



Gaps in Emissions Inventories

- US EGU emissions are best characterized
  - Gaps in many other categories
- Sources outside the U.S are highly uncertain or unknown
  - In particular: China and India
- Natural sources (soils, vegetation, oceans, volcanoes)
- Emissions of previously deposited Hg
  - Re-emissions (e.g., wildfires)



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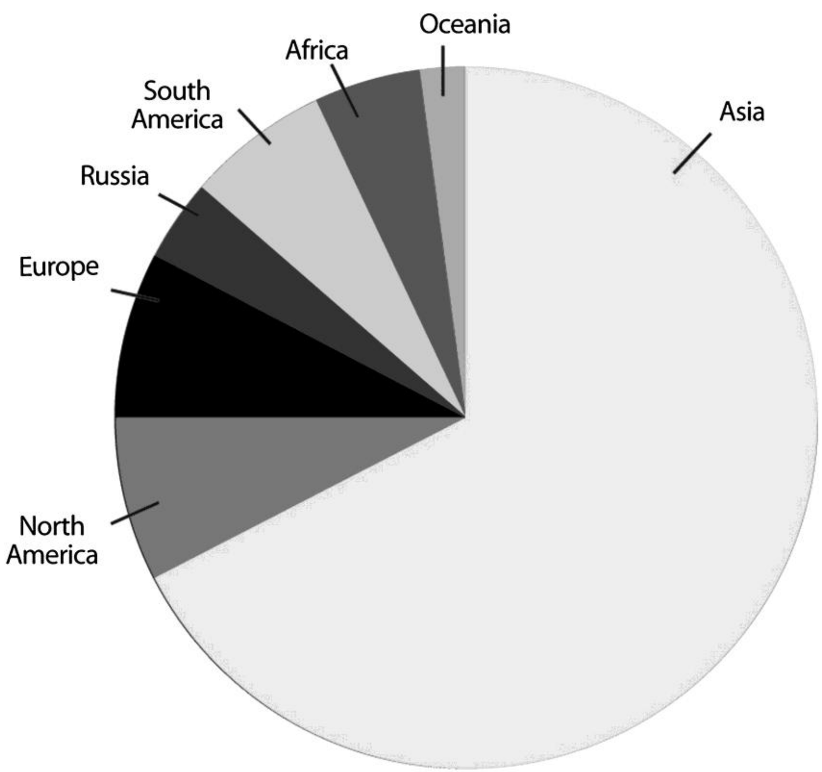
Gaps in Emission Inventories

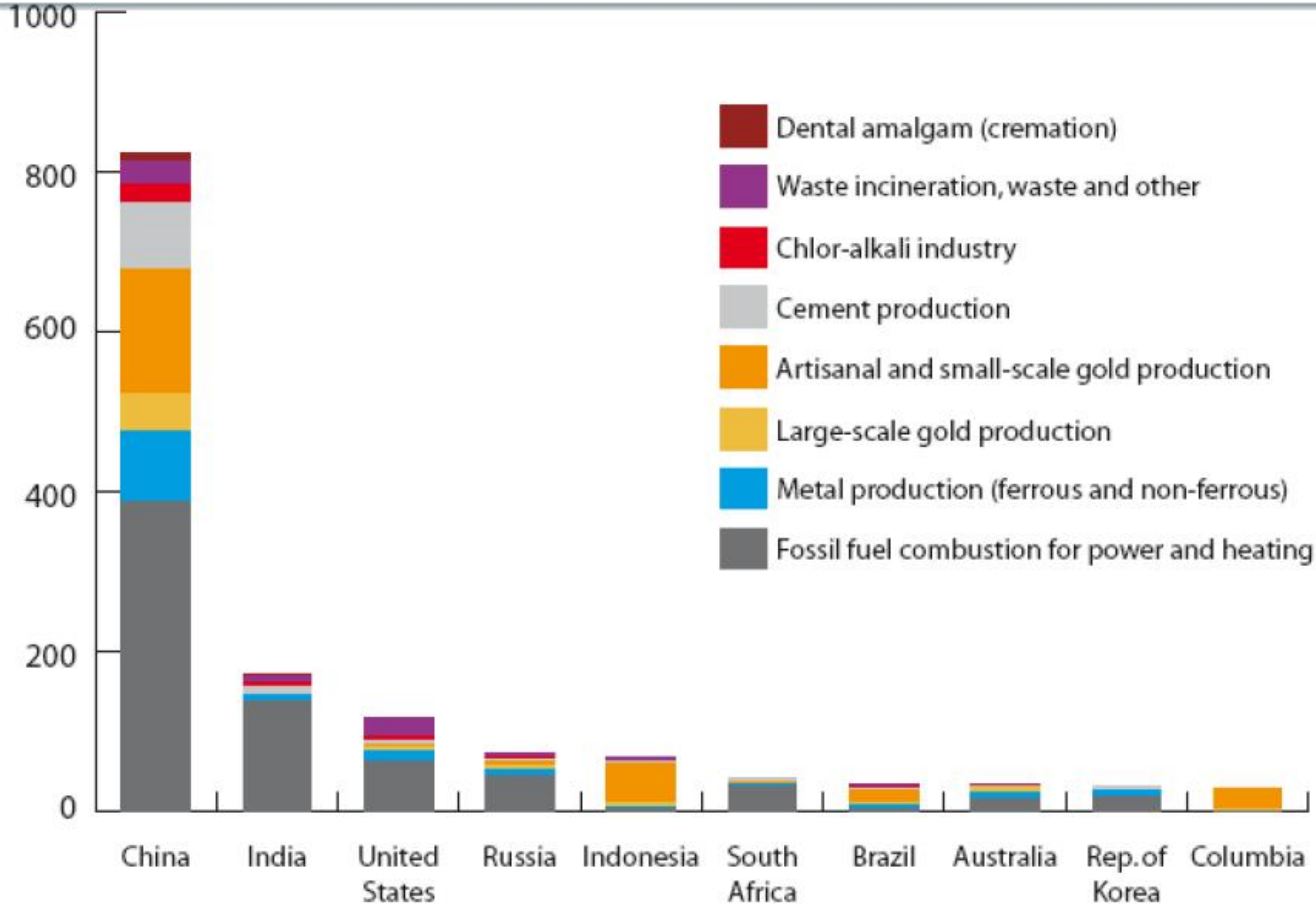
Emission type	CTM-Hg	GEOS-Chem	GRAHM
Anthropogenic	34%	37%	29%
Natural and re-emission	66%	63%	61%
Total (t/yr)	**6540**	**9230**	**5700**

Emissions inventories in some global mercury models (Source: AMAP/UNEP, 2008)

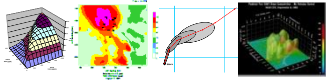


2005 Global anthropogenic Emissions (Source: Pacyna and Pacyna, 2010)

Hg Emissions
Ten largest emitting countries (tons per year)



AMAP/NILU/IVL, 2008



Importance of Plume-in-Grid modeling of Hg

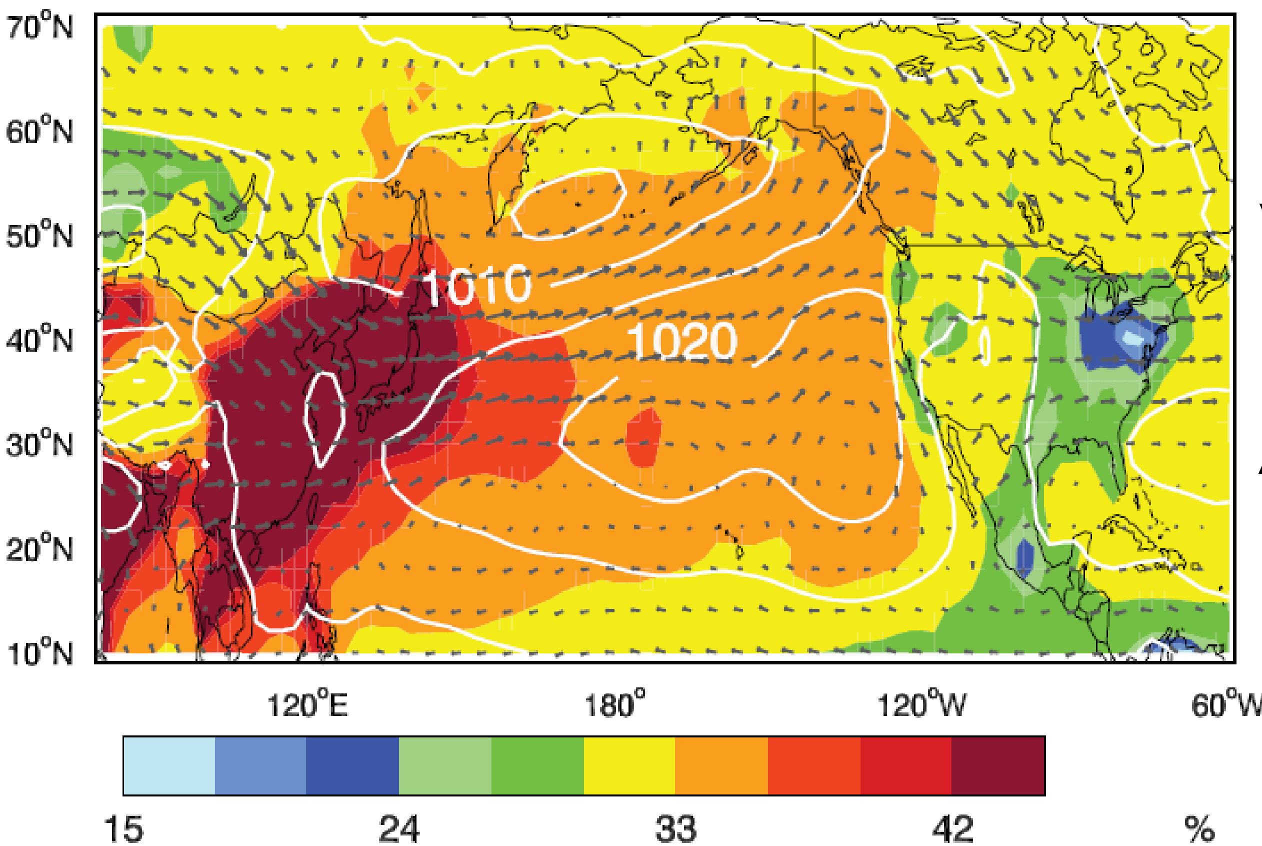
- Many large sources are elevated point sources
- Plume chemistry and transport are different from those in the background
- Proper treatment is required for accurate source attribution
- Plume-in-grid modeling offers the best of both worlds:
  - single source puff modeling
  - 3-D gridded modeling

Role of Inter-Continental Transport

- Long residence time of Hg(0)
  - Long range transport is important
- Observational evidence of LRT
  - e.g., Mt. Bachelor observatory in Washington
- Incorporated in regional models through BCs from global models
- Disparity in global model background results, esp. at higher altitudes

Role of Inter-Continental Transport

Percent contribution from Asian tracers in GEOS-Chem to total (wet + dry) deposition (Source: Strode et al., 2008)



White - Sea level pressure

Arrows - wind direction

Need for Sound Meteorological Inputs

- Clouds and aqueous-phase chemistry:
  - Location, height/depth, type, water content, entrainment/detrainment/mixing rates, precursor distributions
- Hg wet deposition strongly influenced by precipitation (and clouds/cloud mixing)
- Hg dry deposition is dependent on meteorology
- Regional models currently use met driven by MM5, WRF, NCEP etc.
  - Each has its limitations

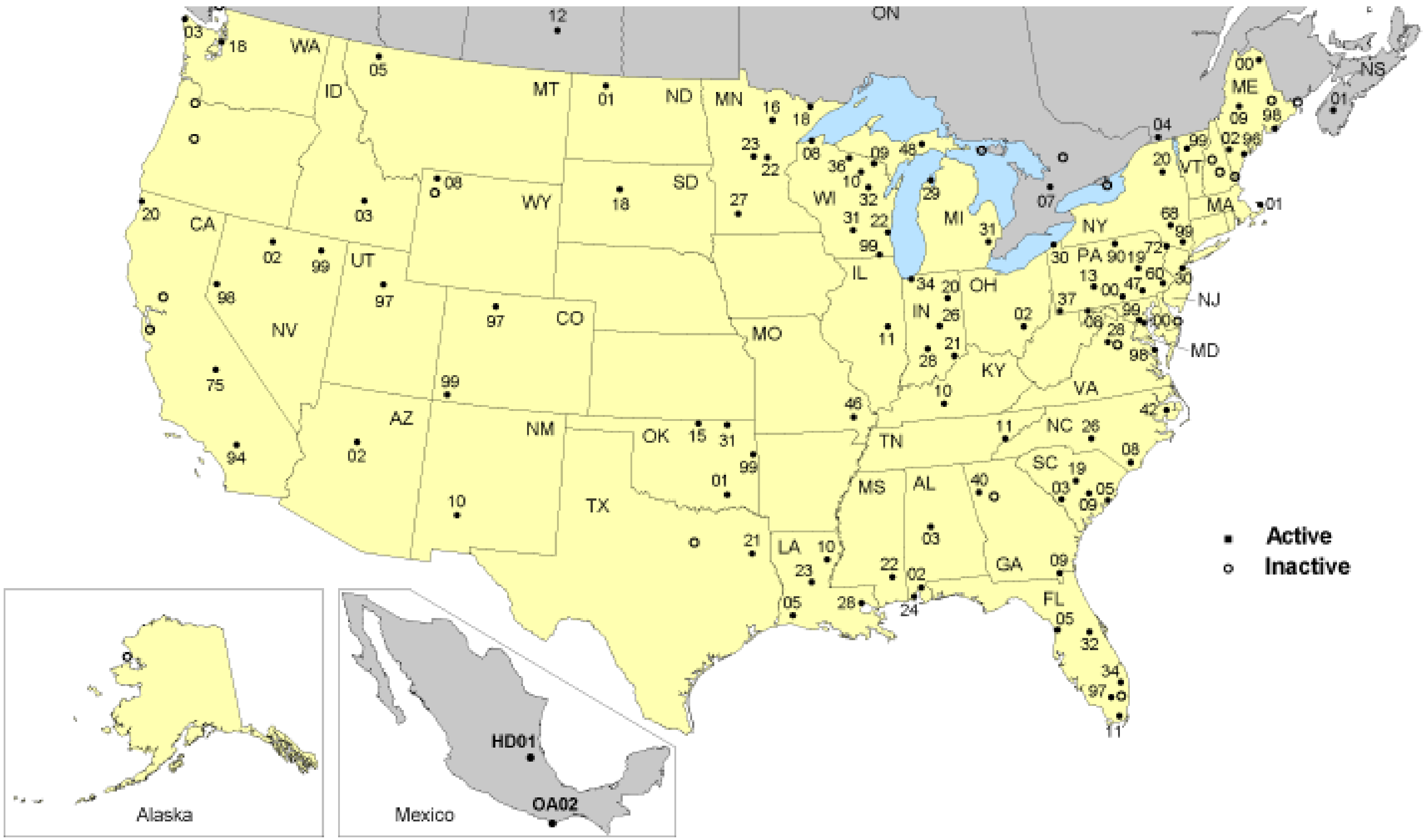
Paucity of Hg Measurements

- Data needed to evaluate and constrain models
- Wet deposition measurements for over 25 years through NADP/MDN
- However, ambient air concentrations and dry deposition measurements are:
  - Fairly recent
  - e.g., AMNet provides air concentrations
- Historical state-specific studies

Hg Measurements in U.S.

Mercury Deposition Network – MDN (Wet Deposition)

(Source: http://nadp.sws.uiuc.edu/mdn)



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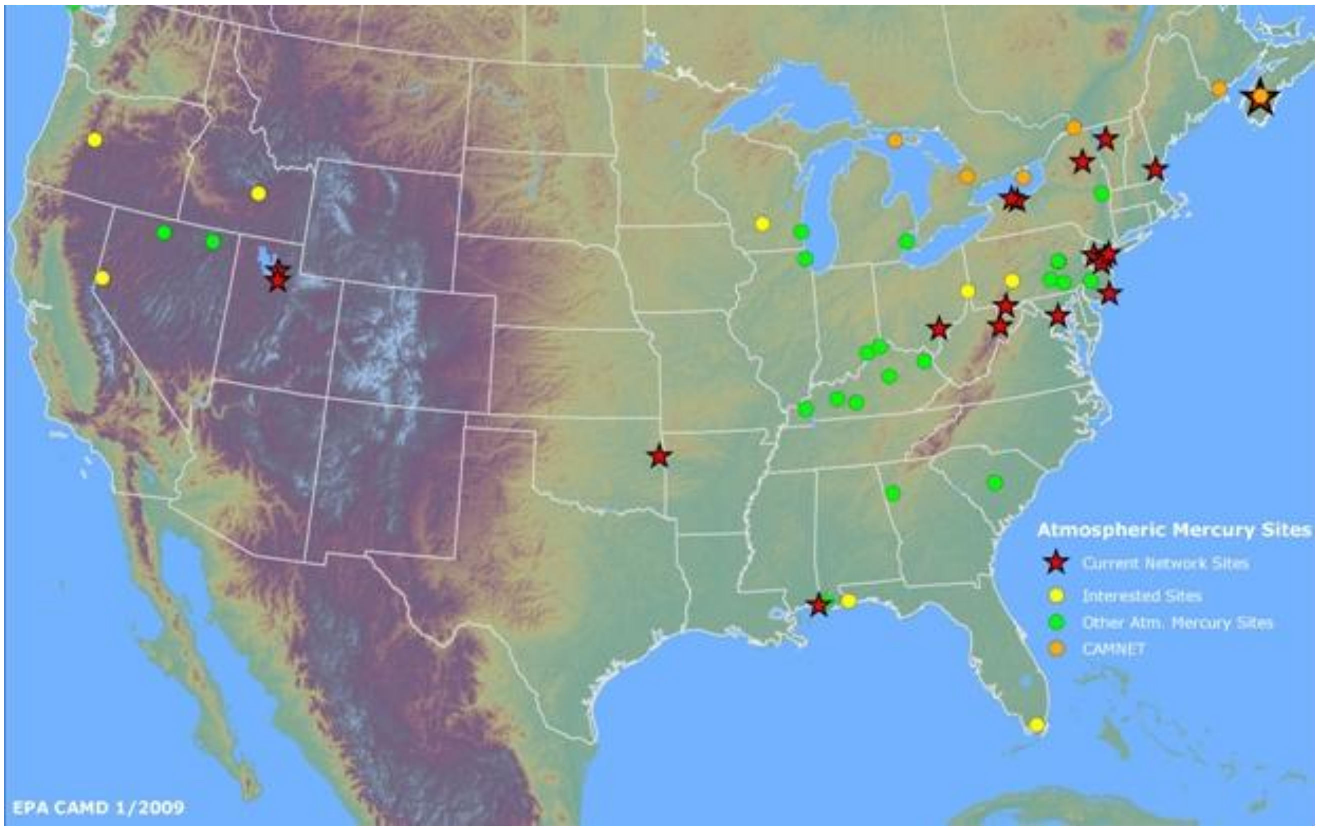
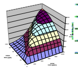
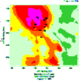
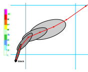
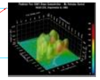
Hg Measurements in U.S.

Atmospheric Mercury Network (AMNet) (Air Concentrations)
(Source: http://nadp.sws.uiuc.edu/amn)



Hg(0), RGM and Hg(p)

Also used in dry deposition calculations



Meeting Needs of Aquatic Modelers

- Hg TMDLs require source attribution of all sources
  - Not just local sources as done for other TMDLs
- Watershed models traditionally acquire inputs from observations but:
  - These are limited in space and time
- Atmospheric models can provide inputs to study Hg from source to sink
- Need to reconcile:
  - Differences in temporal and spatial resolutions
  - Treatment of species between air and watershed models

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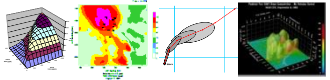
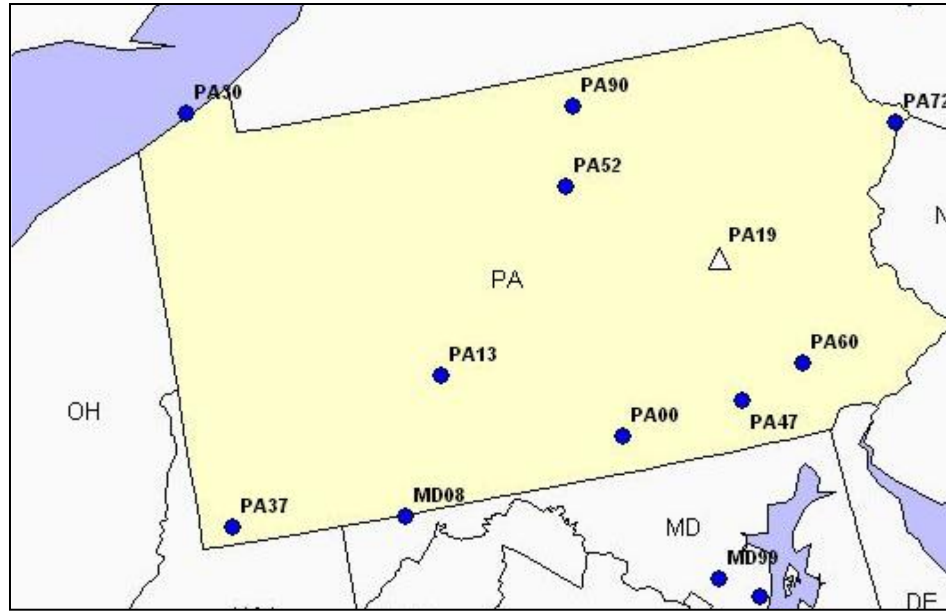
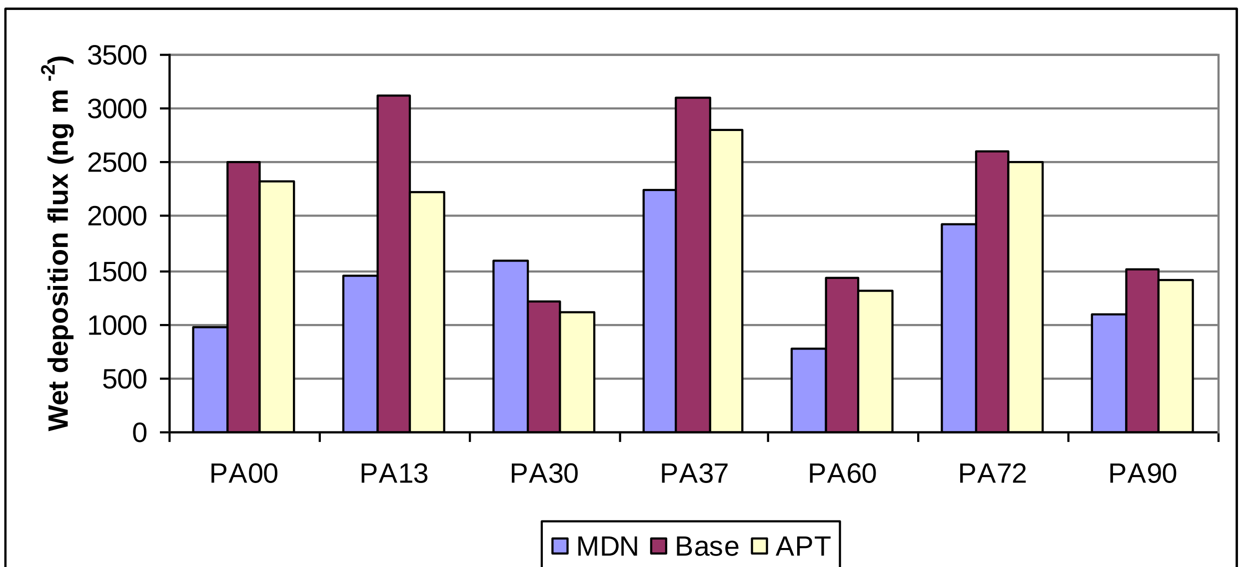


Example Application





Observed and simulated wet deposition flux in Aug-Sep 2001 MDN, No PinG, With PinG (source: Vijayaraghavan et al., 2008)