Development and Application of CMAQ-MADRID-Mercury

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Chapel Hill, NC

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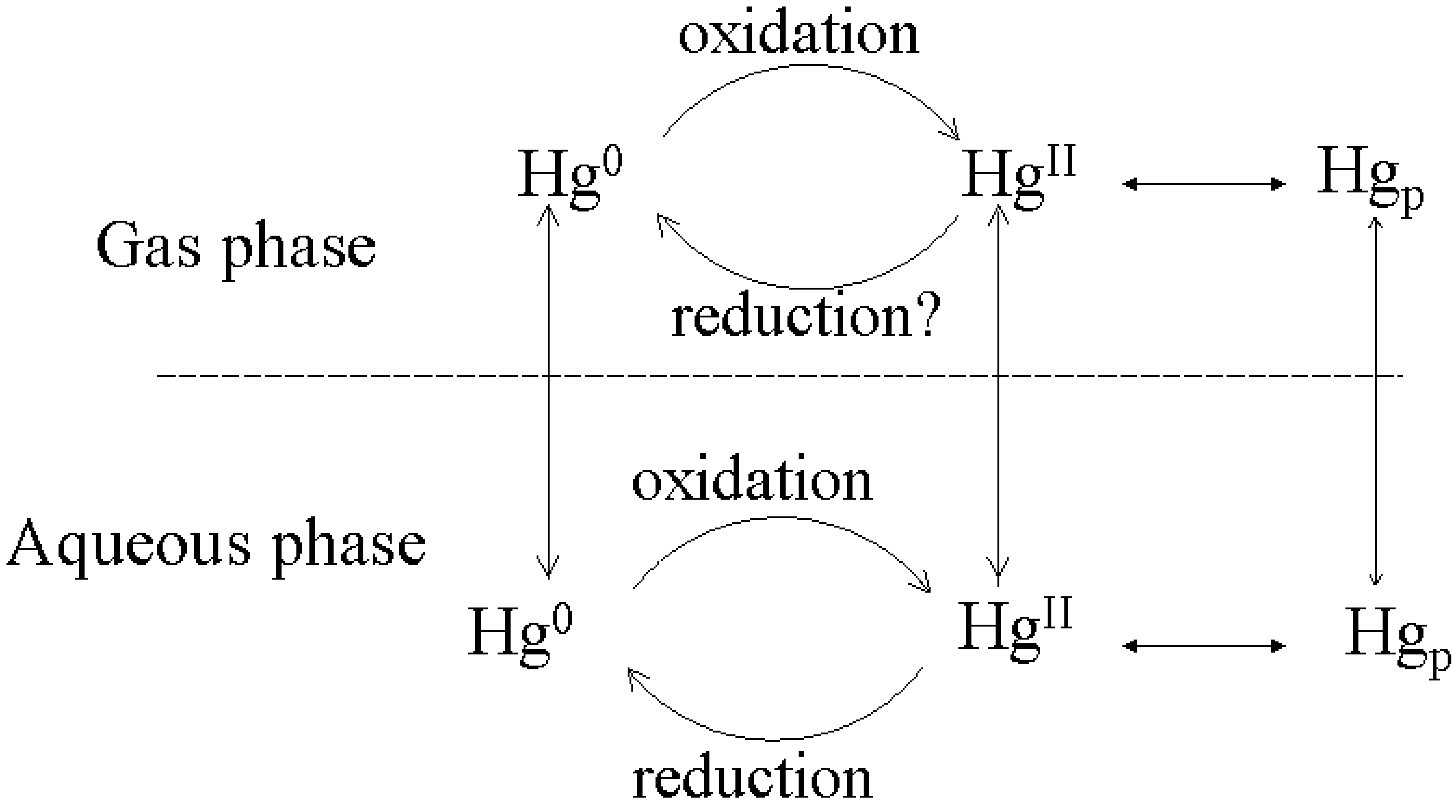
Atmospheric Mercury

- Mercury is present mostly as three “species” in the atmosphere
  - Elemental mercury
    - Hg^0
  - Divalent gaseous mercury
    - $HgCl_2$, $Hg(OH)_2$, HgO, etc.
    - referred to collectively as Hg^{II} or reactive gaseous mercury (RGM)
  - Particulate-bound mercury:
    - Hg^{II} or Hg^0 adsorbed on PM
    - mostly divalent
    - referred to collectively as Hg_p

Atmospheric Chemistry of Mercury



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Atmospheric Deposition of Mercury

- Hg^0 is not very soluble and has a low dry deposition velocity (<0.1 cm/s)
- Hg^{II} is very soluble and adsorbs readily on surfaces: it is rapidly removed by wet and dry deposition
- Hg_p is mostly in the fine particle range and will remain in the atmosphere for several days in the absence of precipitation

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Atmospheric Half-lives of Hg Species

- Hg(0)
  - Chemical oxidation: ~ 2-3 months on average*
  - Dry deposition: ~ 3 months in the boundary layer
- Hg(II) or RGM
  - Chemical reduction: fast in presence of clouds
  - Dry deposition: ~ few hours-2 days in the boundary layer
  - Wet deposition: fast
- Hg(p)
  - Dry deposition: ~ 1 week in the boundary layer
  - Wet deposition: relatively fast

* excluding Arctic and marine boundary layer chemistry

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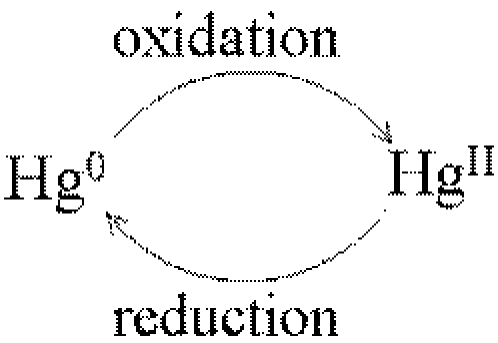
Atmospheric Half-lives of Hg Species

Hg(0) and Hg(II) may undergo several red-ox cycles before Hg(II) is removed via dry or wet deposition

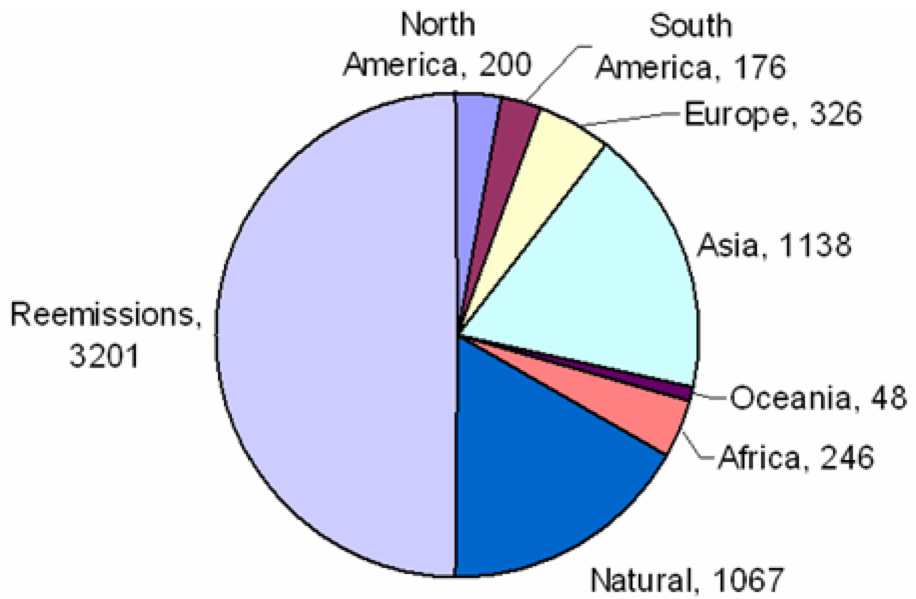


Atmospheric Hg has (currently) a half-life estimated to be ~ 10 months (lifetime of ~ 1.2 years)

=> Hg is a global pollutant

Global Mercury Emissions

- Global emissions total about 6000 Mg/y with an uncertainty of a factor of 2
- Current emissions are about 3 times pre-industrial emissions
- Re-emissions of previously deposited mercury are a significant fraction of total emissions (30 to 50%)



Annual Hg emissions (1999 estimate)

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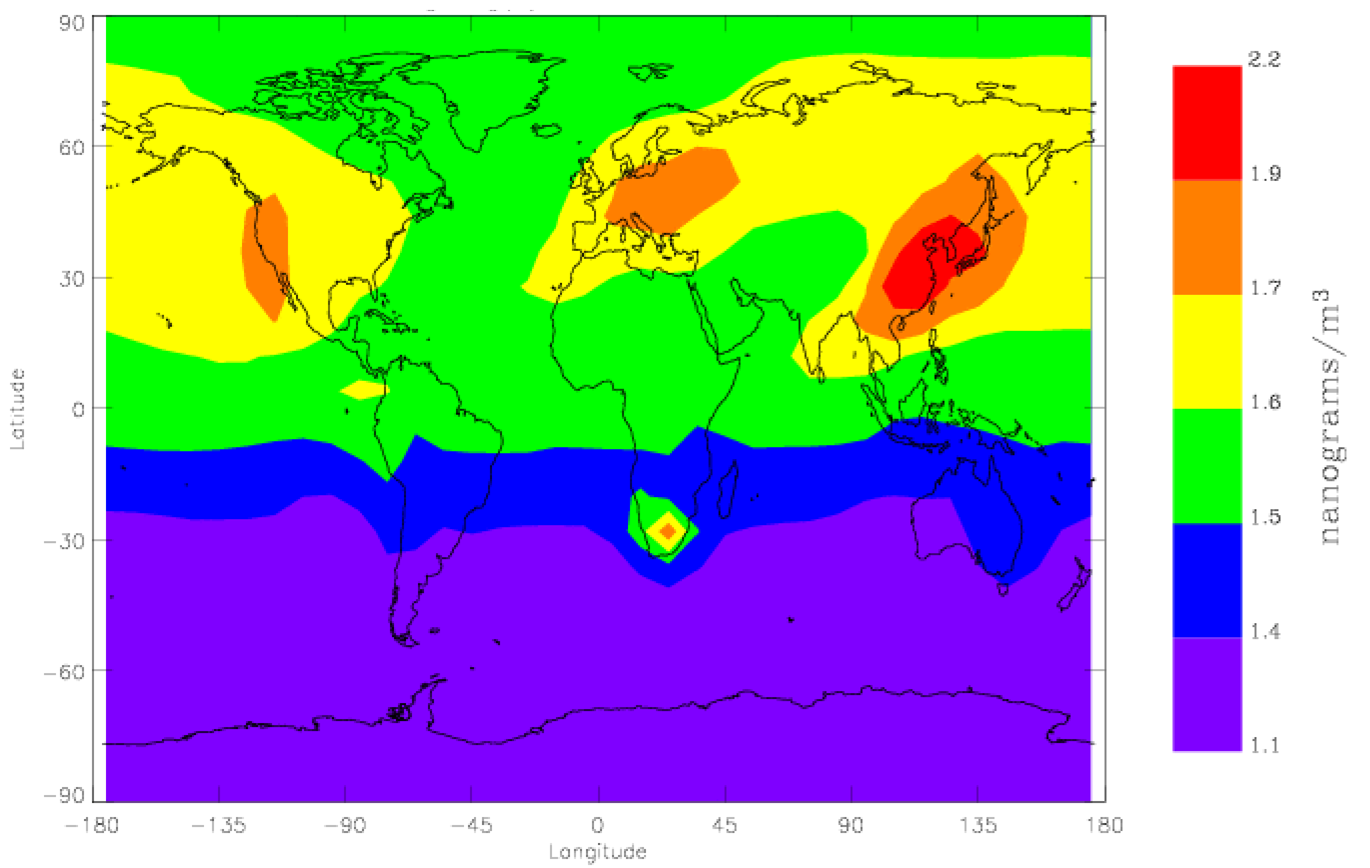
Global Simulation
Annual surface concentrations of Hg(0)



- Good agreement with data (Seigneur et al., *ES&T*, 38, 555, 2004)
- Provides boundary conditions of mercury for the continental/regional model

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"One-atmosphere" Model of Atmospheric Mercury for Continental/Regional Scales

- Single state-of-the-science model to simulate ozone, PM and mercury
- EPA CMAQ as host model (version 4.4)
- State-of-the-science treatment of PM (MADRID)
- Advanced treatment of plumes for ozone and PM (APT)
- Incorporation of mercury processes (AER chemistry and removal processes)

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"One-atmosphere" Mercury Model

- CMAQ-MADRID-Hg is currently operational
  - Initial application to the continental U.S. for 1996
  - Comparison with MDN data completed
  - Available in the Model Download section at http://www.cmascenter.org (CMAQ-MADRID 2004)

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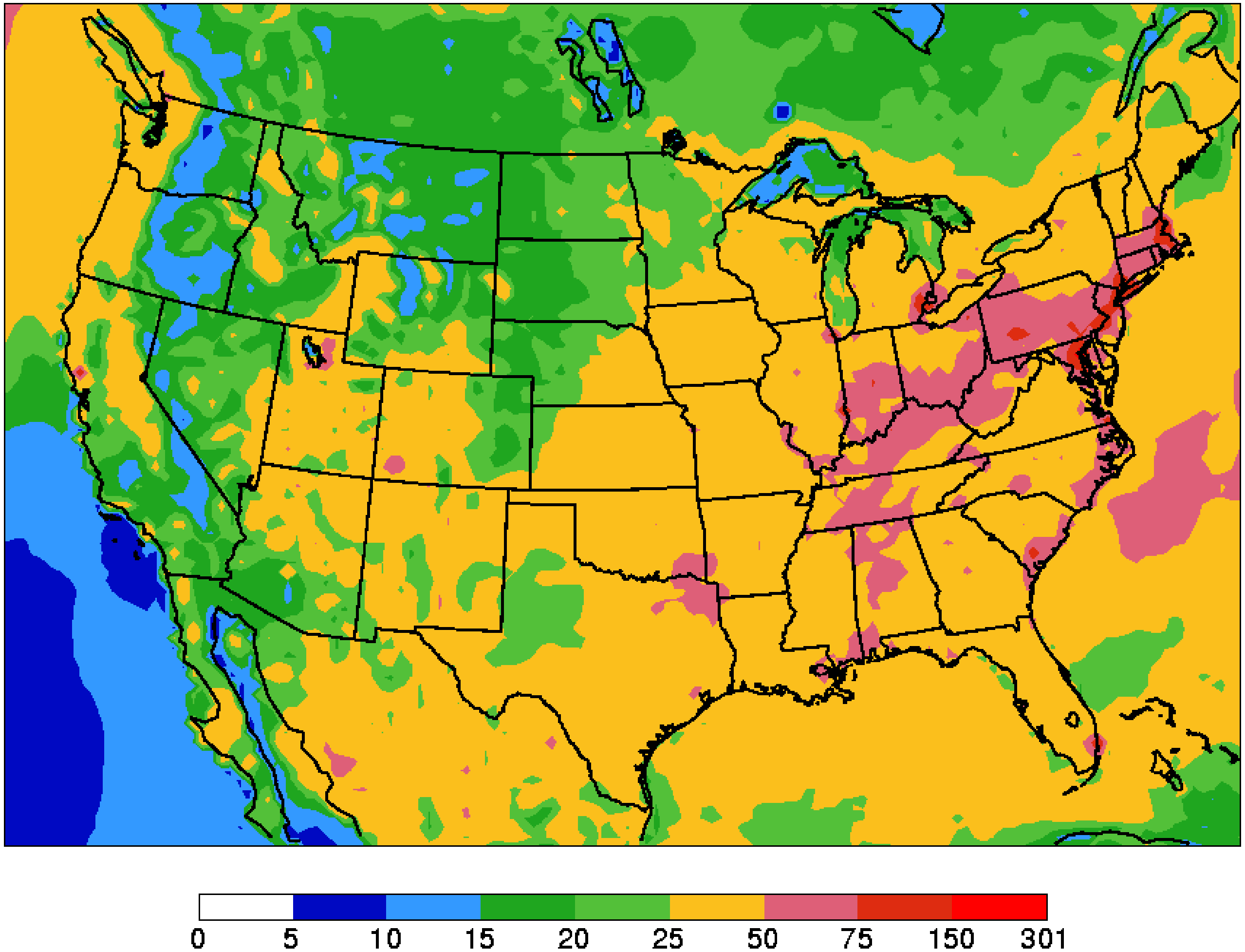
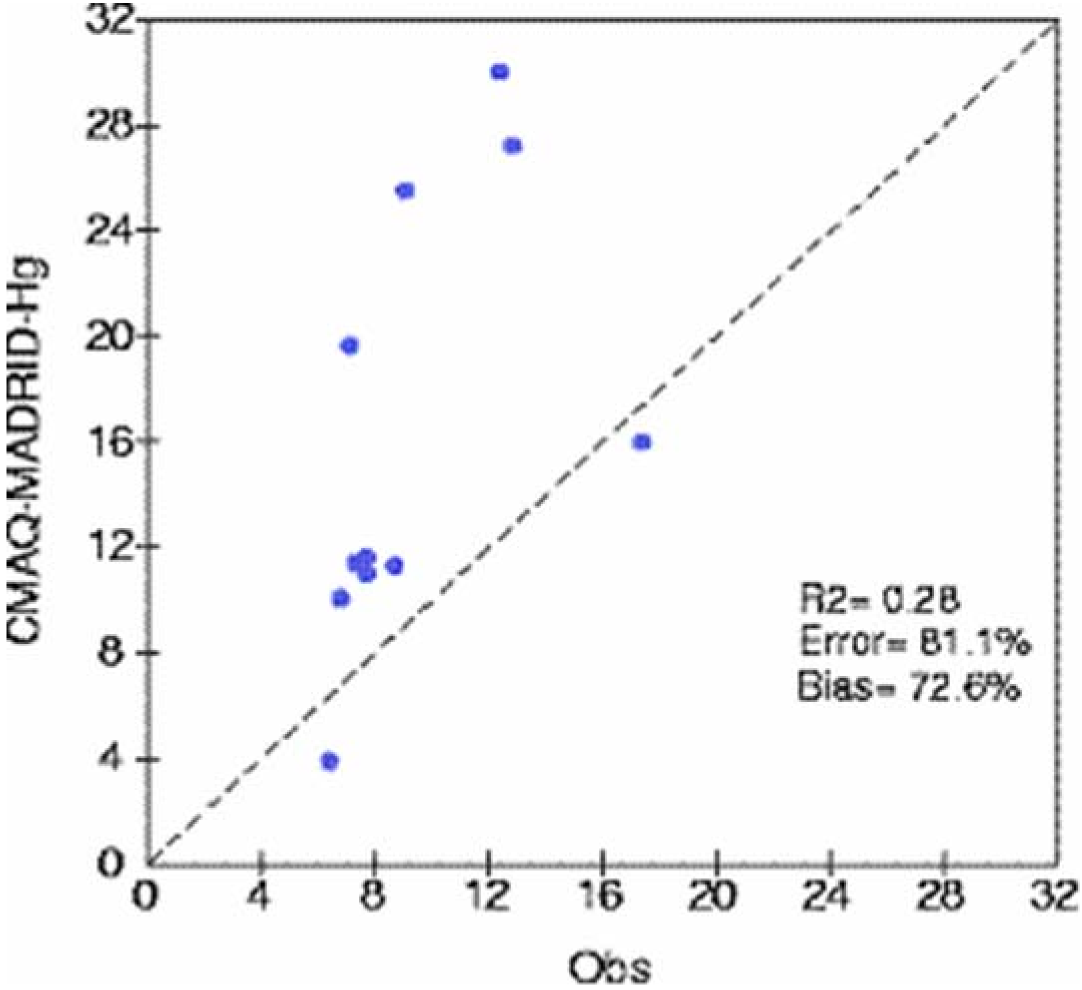
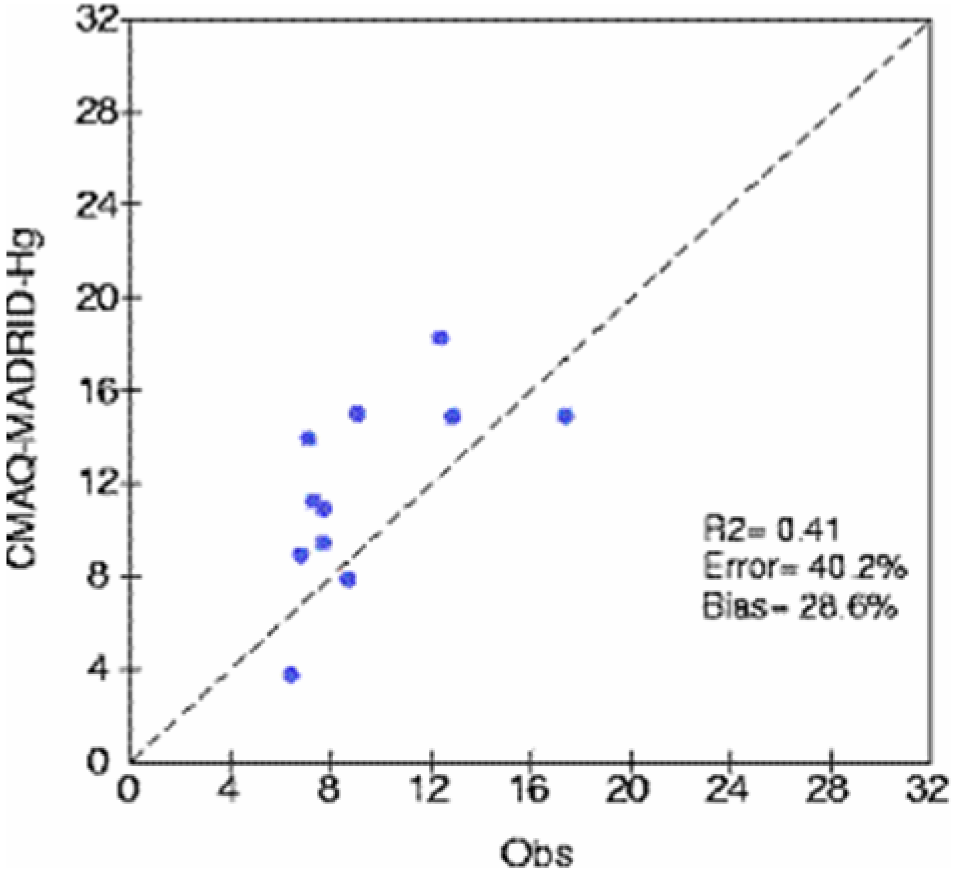
Total Hg Deposition Simulated with CMAQ-MADRID-Hg for 1996 ($\mu g/m^2$-yr)



Comparison of CMAQ-MADRID-Hg with 1996 MDN Data ($\mu g/m^2$-yr)



Comparison of CMAQ-MADRID-Hg with 1996 MDN Data ($\mu g/m^2$-yr)



Mercury deposition was adjusted based on actual precipitation amounts

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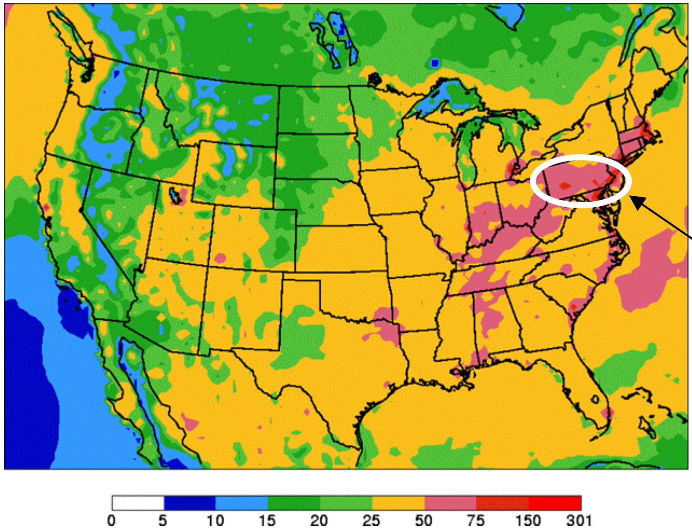
Next Steps
1. Better treatment of plumes from elevated point sources

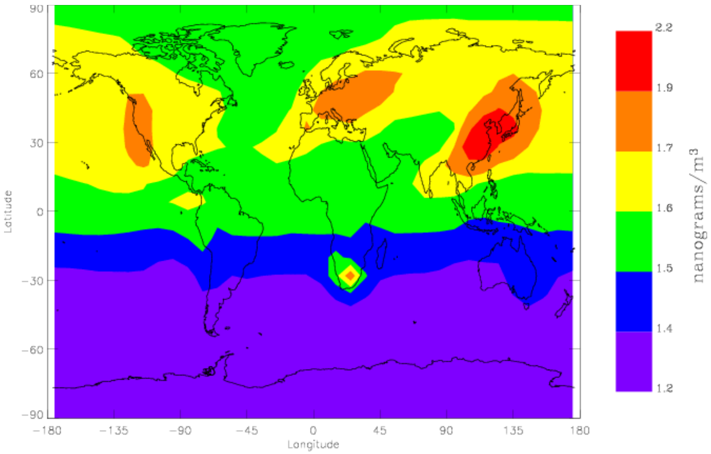
- Incorporate plume treatment within the 3-D grid model CMAQ-MADRID-Hg
  - More realistic representation of local impacts
  - Treatment of plume chemistry
  - Minimization of the “Pennsylvania anomaly”



Overestimation of Hg deposition downwind of the Ohio Valley

Power Plant Plume Mercury Chemistry

- Evidence of Hg^{II} reduction in power plant plumes
- Reduction of Hg(II) by SO_2 (possibly via heterogeneous reaction on particles) is compatible with the global Hg cycling budget
- Collaboration with Susannah Scott (UCSB) regarding laboratory experiments of plume chemistry



Plume-in-grid Treatment (APT) Effect on ozone and nitric acid

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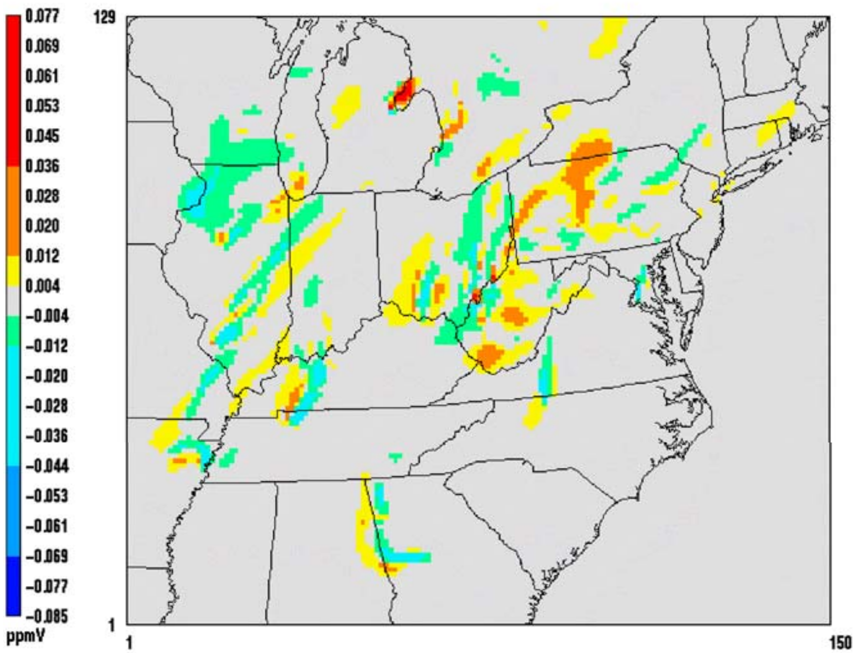
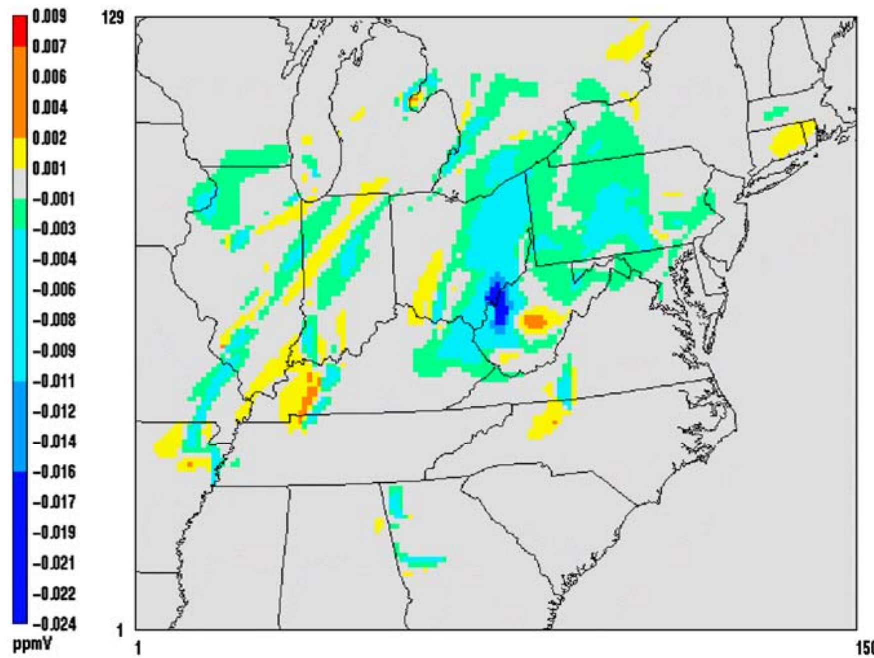
Differences between APT and the base CMAQ
(40 power plants, July 1995 simulation, eastern United States)



Differences in Ozone Concentrations



Differences in HNO_3 Concentrations

One may expect significant effects for mercury as well

Next Steps
2. Mercury Model Intercomparison

- Use of common inputs
  - Meteorology
  - Emissions
  - Boundary conditions from a global model

- EPA Models
  - CMAQ-Hg
  - REMSAD
- AER/EPRI Models
  - CMAQ-MADRID-Hg (with and without plume treatment)
  - TEAM

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Conclusions

- CMAQ-MADRID-Mercury: “One-atmosphere” mercury model developed using CMAQ as the host model
- State-of-the-science treatment of PM (MADRID) and mercury processes
- Boundary conditions from a global mercury chemistry transport model
- Initial application to continental U.S. for 1996
- Subsequent steps:
  - Plume-in-grid treatment of mercury and power plant plume mercury chemistry
  - EPA’s mercury inter-comparison study

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Acknowledgements

- EPRI

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