“Mercury Modeling”

or

“How to Confuse Policymakers Without Really Trying”

O. Russell Bullock, Jr.

NOAA Atmospheric Sciences Modeling Division

in partnership with the U.S. EPA at its National Exposure Research Laboratory

Environmental Monitoring, Evaluation and Protection in New York:
Linking Science and Policy

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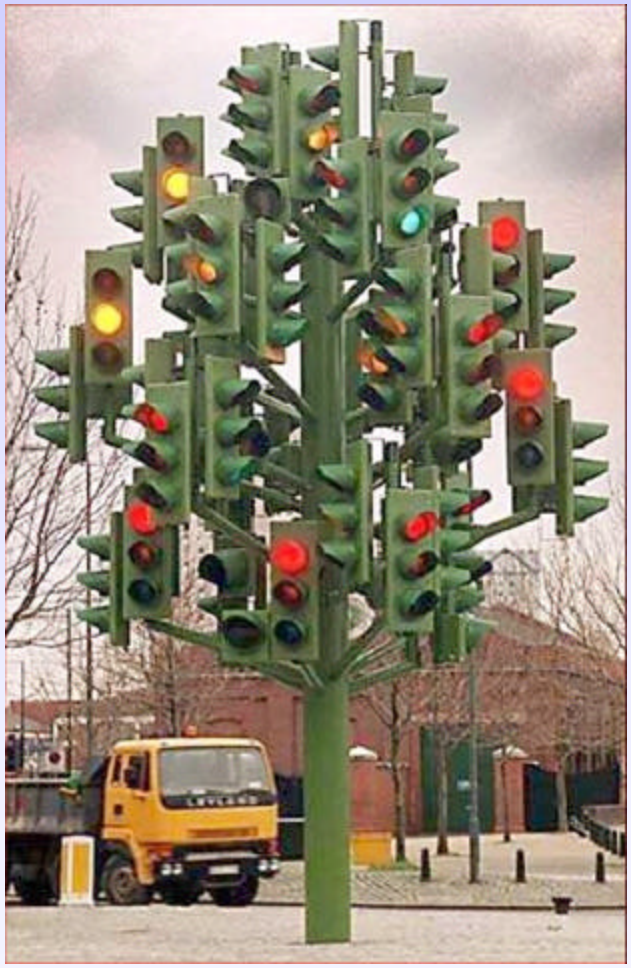
Environmental Mercury Modeling

State of the Science

- We know that atmospheric deposition supplies almost all of the Hg that eventually ends up in fresh-water fish.
- We know that atmospheric Hg exists in various forms that behave differently in regard to atmospheric transport and deposition.
- Current atmospheric Hg research is focusing on:
  - How much of each form of Hg is emitted by various sources?
  - How transformations among various forms of Hg occur?
  - How each of these forms of Hg are deposited?
  - How much of deposited Hg is re-emitted? How fast?
- Simulation models are being used to see how well our understandings of these various processes and their interactions agree with observations in the real world.

- Various simulation models are also being used by governments and industry to estimate source-receptor relationships……..

Let’s just say they’re giving mixed signals.



Currently Measurable Forms (Species) of Atmospheric Mercury added to CMAQ

- **Elemental Mercury (Hg^0):** mildly reactive gas (in most cases); sparingly soluble in water; subject to very long range transport throughout the entire atmosphere
- **Reactive Gaseous Mercury (RGM):** operational term for gaseous Hg compounds that are water soluble and/or chemically reactive; readily deposited to water, soils and vegetation by wet and dry processes
- **Particulate Mercury (PHg):** various condensed Hg compounds and semi-volatile Hg bound to receptive aerosols; Aitken and accumulation modes simulated in CMAQ

Atmospheric Mercury Modeling

State of the Science

- Industrial Hg emissions are well-defined for certain source types in the developed nations. Natural & recycled Hg emissions are poorly defined for simulation modeling purposes.
- Chemical and physical reactions of Hg in both air and cloud water are still being identified and described by the scientific community. Note, some reactions previously believed to be important are now being dismissed as analytical artifacts.
- Certain phenomena of mercury behavior have been observed which seem to contradict current emissions and/or chemical kinetics data. (e.g., high concentrations of RGM aloft and on mountain tops)
- The ability to evaluate the fidelity of any model is severely limited by the lack of observation. We cannot yet define the sources and sinks of atmospheric Hg with sufficient completeness to confidently test model accuracy and completeness. (e.g., deposition: wet, but no dry)

Mercury Emission Inventories

- U.S. EPA's National Emission Inventory (NEI) now contains mercury, but speciation information comes from special data set relevant to specific sources or source types. Other industrialized nations have developed similar inventories for anthropogenic Hg.
- Various global inventories of anthropogenic Hg emissions have been developed, but estimates for the developing nations remain uncertain.
- Estimates of Hg emission flux from oceans, lakes, land surfaces and volcanoes have been made, but the recycling process is poorly understood so the anthropogenic fraction of these fluxes from water and land is uncertain.

Atmospheric Mercury Modeling at NOAA/EPA

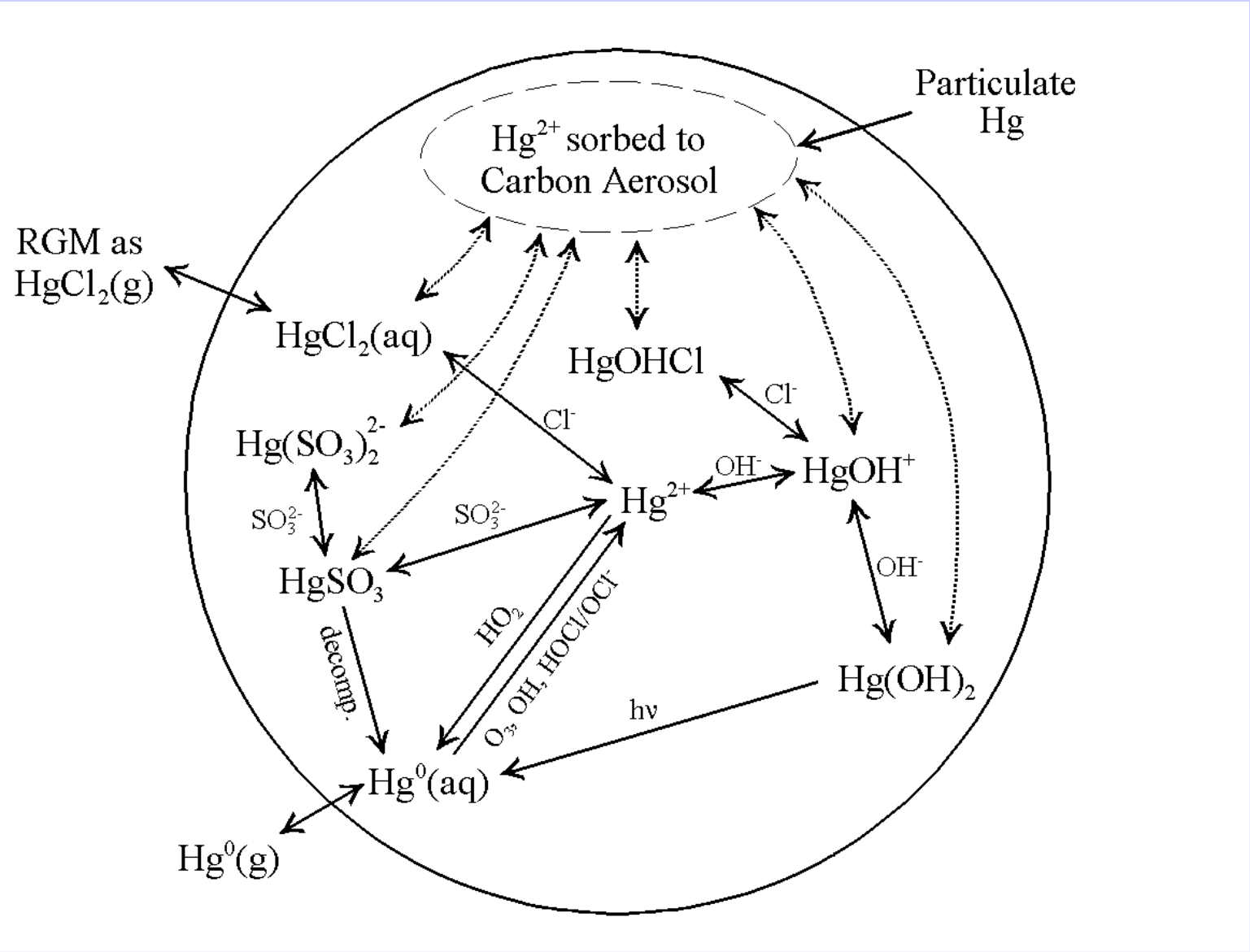
CMAQ-Hg from the standard CMAQ modeling system

- **Emissions:** Special point and non-point industrial emission inventories for Hg and rough estimates of molecular chlorine emissions from saline water bodies are processed by the Sparse Matrix Operator Kernel Emissions (SMOKE) module.
- **Gaseous Chemistry:** Hg(0), RGM and Cl_2 are added to the Carbon-Bond IV gas-phase chemical mechanism where oxidation of Hg(0) can form RGM and/or PHg (in the Aitken mode). Cl_2 is photolyzed by sunlight and effectively destroyed.
- **Aqueous Chemistry:** Special version of AQCHEM is used to add the simulation of a Hg redox system with compound-specific reactions and Hg(II) sorption to particles. Total dissolved Hg(II) in water and RGM in air are partitioned using the Henry's Law constant for $HgCl_2$.
- **Deposition:** Wet deposition of Hg treated just like standard species. Dry deposition (V_d) of PHg is based on elemental carbon aerosol. V_d of RGM is based on nitric acid surrogate. V_d of Hg(0) = 0.

Current CMAQ Hg Reaction Table (under consideration)

No.	Reaction	k or K	Reference
Gaseous-phase reaction of Hg			
RG1	$Hg^0_{(g)} + O_{3(g)} \rightarrow$ 50% RGM, 50% PHg	$2.11 \times 10^{-18} e^{-1256.5/T}$ cm^3 $molec^{-1}$ s^{-1}	Hall (1995)
RG1	25 times faster at 295 K?	7.5×10^{-19} cm^3 $molec^{-1}$ s^{-1}	Pal and Ariya (2004)
RG2	$Hg^0_{(g)} + Cl_{2(g)} \rightarrow$ RGM	2.6×10^{-18} cm^3 $molec^{-1}$ s^{-1}	Ariya *et al.* (2002)
RG3	$Hg^0_{(g)} + H_2O_{2(g)} \rightarrow$ PHg	8.5×10^{-19} cm^3 $molec^{-1}$ s^{-1}	Tokos *et al.* (1998)
RG4	$Hg^0_{(g)} + OH_{(g)} \rightarrow$ 50% RGM, 50% PHg	7.7×10^{-14} cm^3 $molec^{-1}$ s^{-1}	Pal and Ariya (2004)
new	$Hg^0_{(g)} + Cl_{(g)} \rightarrow$ products	1.0×10^{-11} cm^3 $molec^{-1}$ s^{-1}	Ariya *et al.* (2002)
new	$Hg^0_{(g)} + Br_{2(g)} \rightarrow$ products	0.9×10^{-16} cm^3 $molec^{-1}$ s^{-1}	Ariya *et al.* (2002)
new	$Hg^0_{(g)} + Br_{(g)} \rightarrow$ products	3.2×10^{-12} cm^3 $molec^{-1}$ s^{-1}	Ariya *et al.* (2002)
Aqueous-phase reactions of Hg			
RA1	$Hg^0_{(aq)} + O_{3(aq)} \rightarrow Hg^{2+}_{(aq)} +$ products	4.7×10^7 M^{-1} s^{-1}	Munthe (1992)
RA2	$HgSO_{3(aq)} \rightarrow Hg^0_{(aq)} +$ products	$T \times e^{((31.971 \times T) - 12595)/T}$ s^{-1}	Van Loon *et al.* (2000)
RA2	$HgSO_{3(aq)} \rightarrow Hg^0 \cdot SO_{2(aq)}$	????	Van Loon *et al.* (2001)
RA3	$Hg(OH)_{2(aq)} + h\nu \rightarrow Hg^0_{(aq)} +$ products	6.0×10^{-7} s^{-1} (max)	Xiao *et al.* (1994)
RA4	$Hg^0_{(aq)} + OH_{(aq)} \rightarrow Hg^{2+}_{(aq)} +$ products	2.0×10^9 M^{-1} s^{-1}	Lin and Pehkonen (1997)
RA5	$Hg^{2+}_{(aq)} + HO_{2(aq)} \rightarrow Hg^0_{(aq)} +$ products	1.1×10^4 M^{-1} s^{-1}	Pehkonen and Lin (1997)
RA5	$Hg^{2+}_{(aq)} \rightarrow Hg^0_{(aq)}$ Artifact?	0 M^{-1} s^{-1}	Gardfeldt and Jonsson (2003)
RA6	$Hg^0_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{2+}_{(aq)} +$ products	2.09×10^6 M^{-1} s^{-1}	Lin and Pehkonen (1998)
RA7	$Hg^0_{(aq)} + OCl^-_{(aq)} \rightarrow Hg^{2+}_{(aq)} +$ products	1.99×10^6 M^{-1} s^{-1}	Lin and Pehkonen (1998)
Aqueous-phase chemical equilibria for Hg			
E1	$Hg^{2+} + SO_3^{2-} \rightleftharpoons HgSO_3$	2.0×10^{-13} M	Smith and Martell (1976)
E1	Factor of 4.2 decrease?	4.8×10^{-14} M	Van Loon *et al.* (2001)
E2	$HgSO_3 + SO_3^{2-} \rightleftharpoons Hg(SO_3)_2^{2-}$	4.0×10^{-12} M	Smith and Martell (1976)
E2	Factor of 25 increase?	1.0×10^{-10} M	Van Loon *et al.* (2001)
E3	$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$	1.0×10^{-14} M^2	Lin and Pehkonen (1999)
E4	$Hg^{2+} + OH^- \rightleftharpoons HgOH^+$	2.51×10^{-11} M	Smith and Martell (1976)
E5	$HgOH^+ + OH^- \rightleftharpoons Hg(OH)_2$	6.31×10^{-12} M	Smith and Martell (1976)
E6	$HgOH^+ + Cl^- \rightleftharpoons HgOHCl$	3.72×10^{-8} M	Smith and Martell (1976)

CMAQ-Hg Cloud Chemistry Mechanism for Mercury

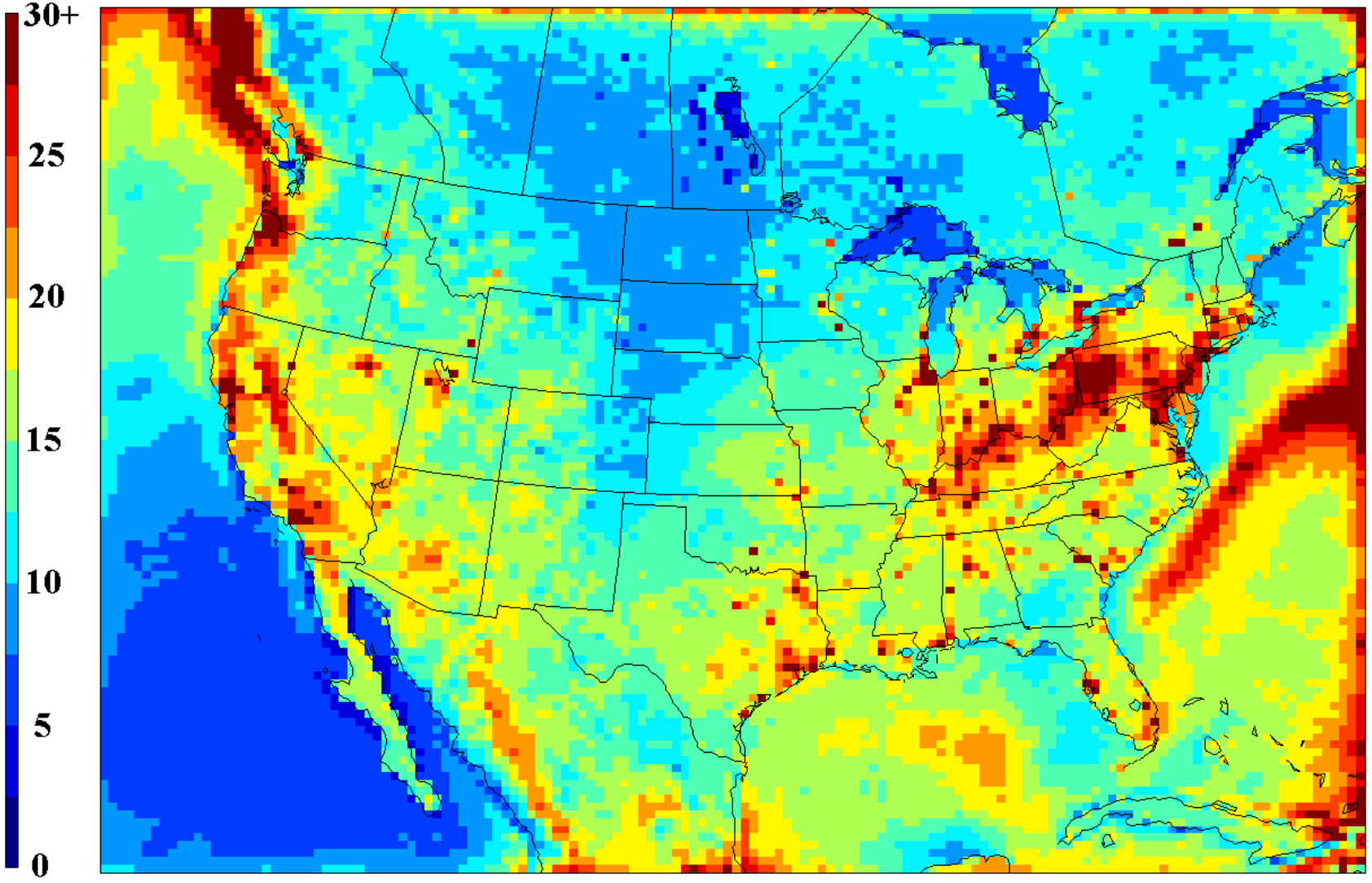


CMAQ-Hg: Regulatory Modeling

- **Ongoing work with OAQPS related to the Clean Air Mercury Rule (CAMR)**
  - CMAQ-Hg simulations: 2001 base, 2001 zero-out, 2010 & 2020 (base, control, and zero-out)
  - Implement and test various mercury chemical kinetics configurations
  - Test CMAQ-Hg results against EPA/NERL's source-apportionment work in Steubenville, Ohio
  - Testing IC/BC data sources for mercury (GEOS-CHEM vs. static values used for European intercomparison)
  - Investigating high RGM and Hg_P concentrations simulated from Hg oxidation in regional oxidant plumes

CMAQ-simulated total mercury deposition for 2001

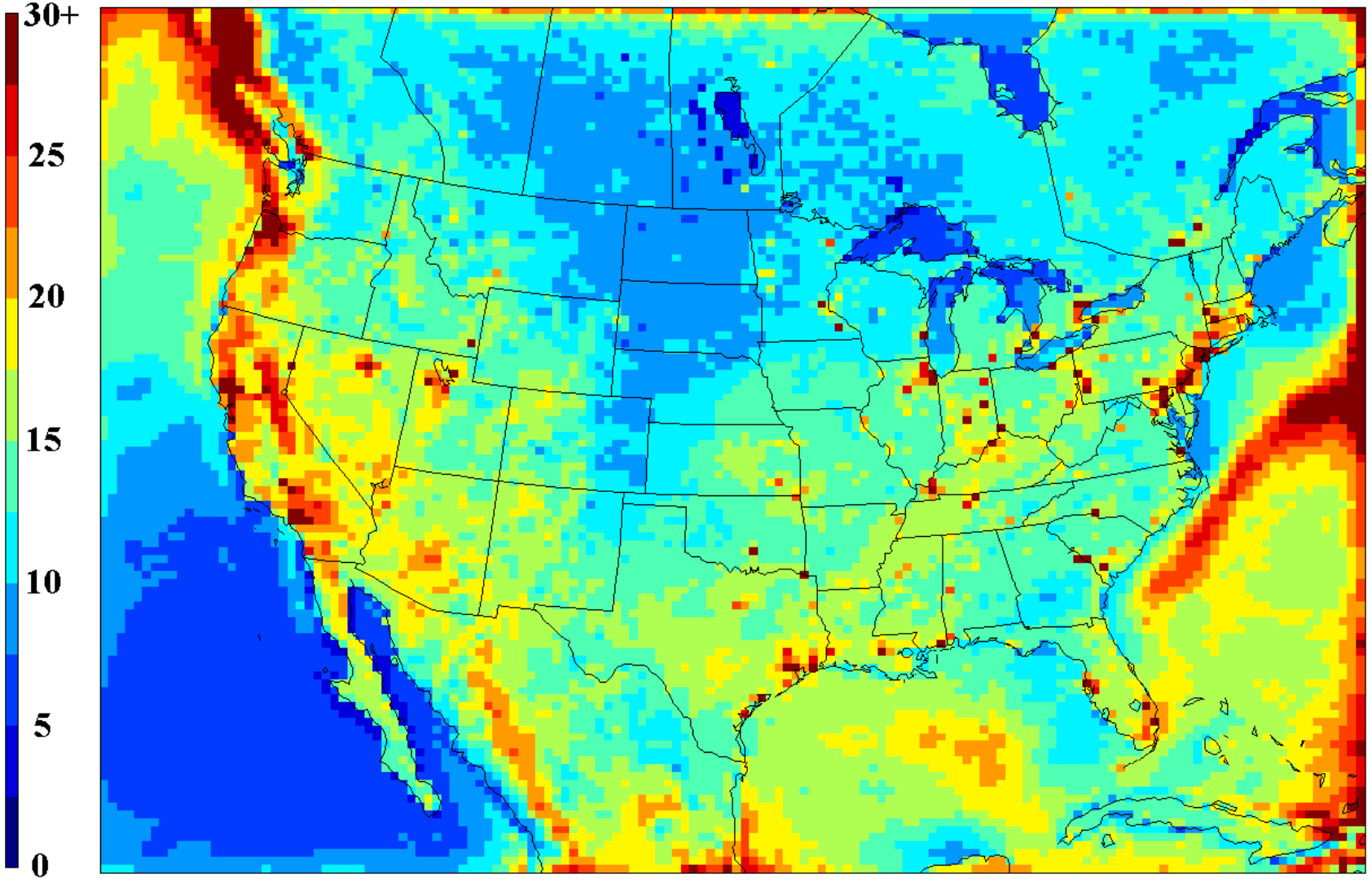
(micrograms per square meter)



Base case

CMAQ-simulated total mercury deposition for 2001

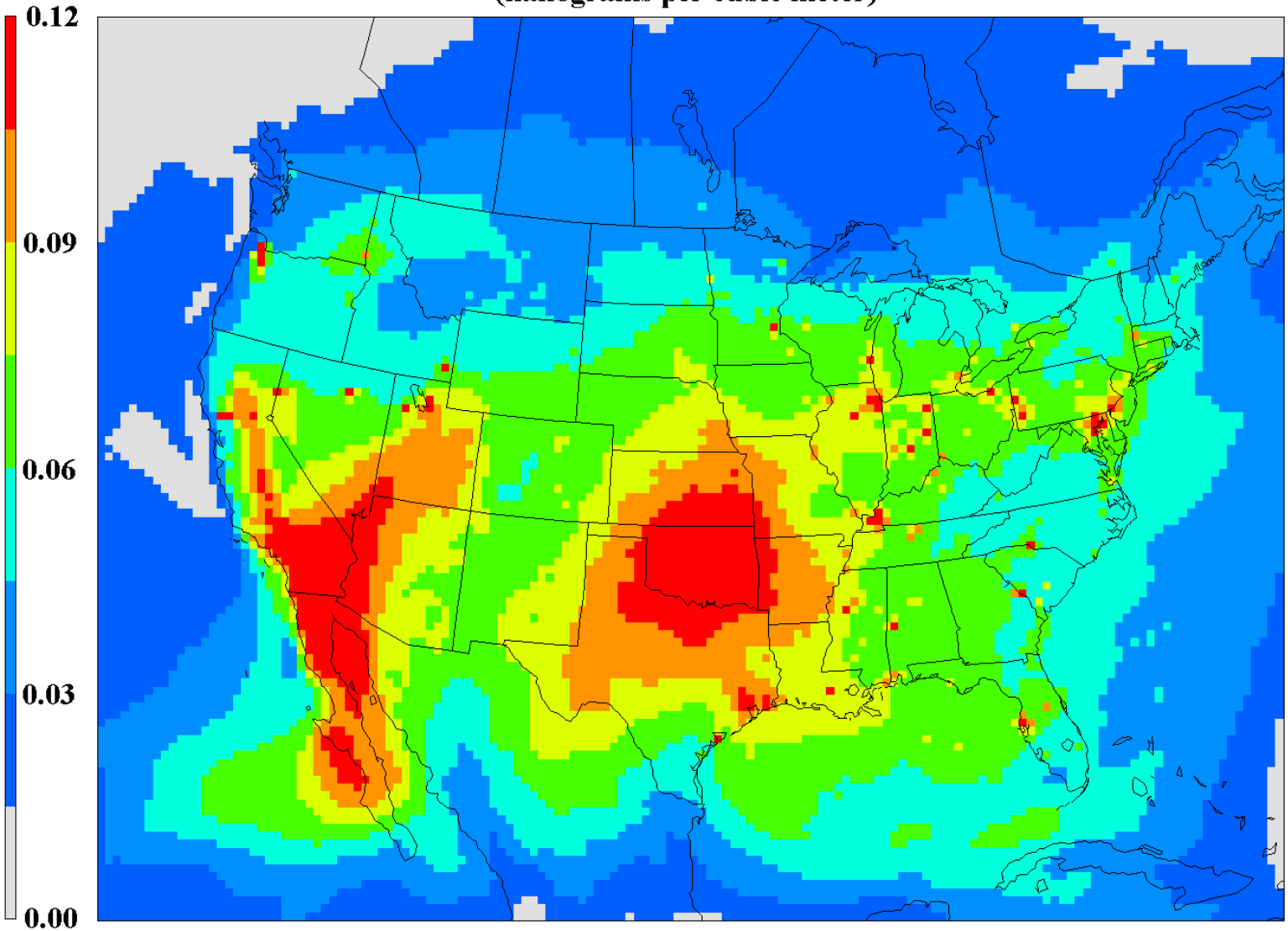
(micrograms per square meter)



Utility Zero Out

July 2001 Average Particulate Hg Air Concentration - Base Case

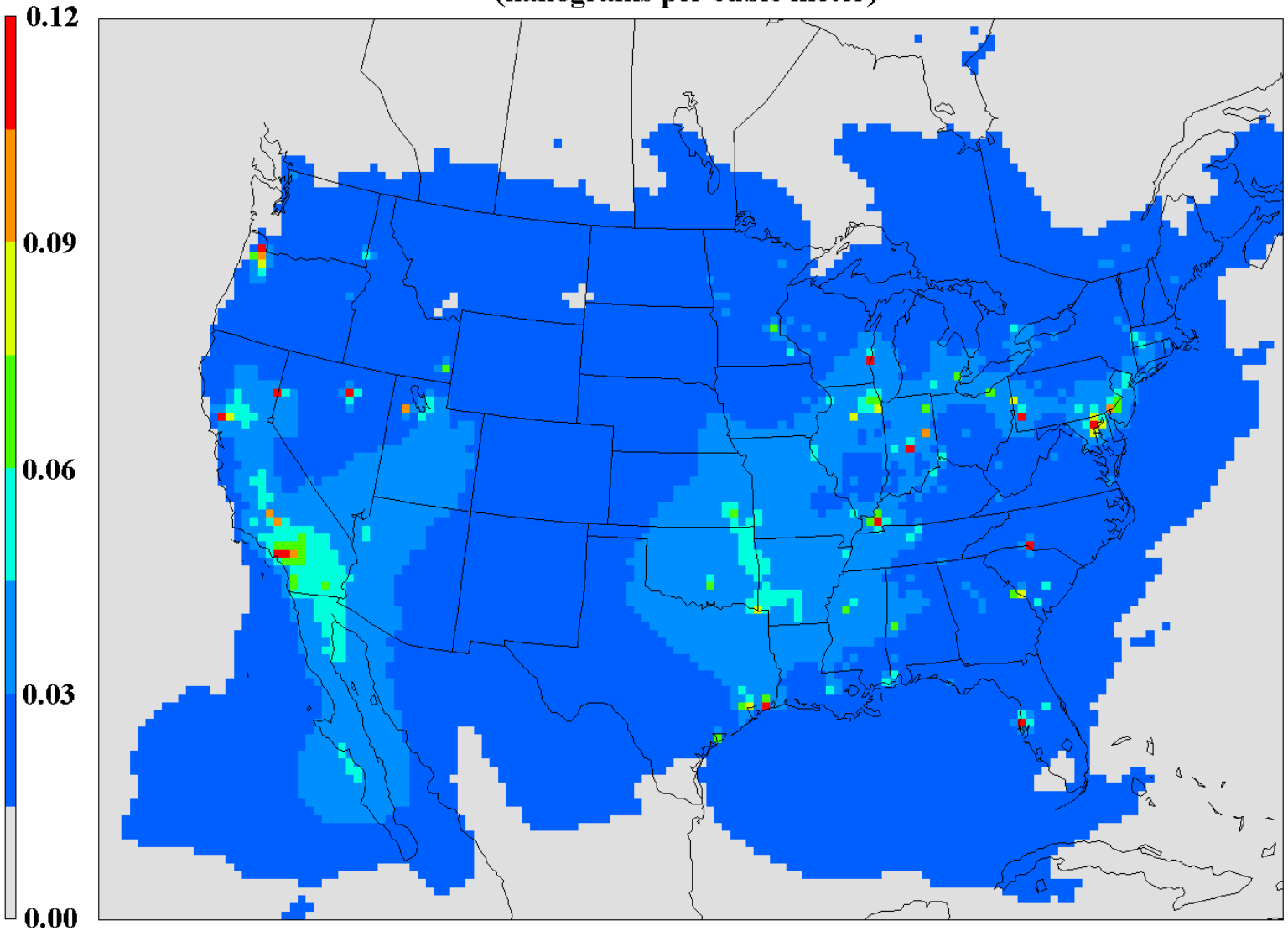
(nanograms per cubic meter)



Layer 1

July 2001 Average Particulate Hg Air Concentration - No RG4

(nanograms per cubic meter)



Layer 1

Mercury Model Intercomparison

(trying to make sense of it all)

- **MSC-East Mercury Model Intercomparison in Europe**
  - Full-scale model simulations of 1999 (or parts thereof)
  - Seven models applied from 6 different nations
  - All models used the same mercury emission inventory
  - Comparisons to observed air concentrations of Hg(0), RGM and PHg
  - Comparisons between models
  - Most models within a factor of two of observations (based on monthly averages)
  - Generally poor agreement with daily-average RGM measurements
  - Wide variation among models in their derived source-receptor relationships

North American Mercury Model Intercomparison Study (NAMMIS)

- Modeling Participants: EPA/ORD, EPA/OW, EPA/OAR, AER-EPRI, Environment Canada, Harvard University
- NYSDEC will perform all model results comparison/evaluation
- Develop three IC/BC sets from three separate global models: GRAHM (Env. Canada), CTM (AER) and GEOS-CHEM (Harvard Univ.)
- Same regional model domains (covering most of North America)*
- All regional models to use these same IC/BC files*
- All regional models to use the same MM5-derived meteorology*
- All regional models to use the same Hg emission inventory
- All regional models to use the same criteria pollutant emission inventory to simulate reactants (where applicable)*
- Hg emission control scenarios may also be simulated (additional runs?)
- Status: IC/BCs from global models complete, regional models being applied

** Improved constraint as compared to European intercomparison study*

Development of next version of CMAQ-Hg

- Next CMAQ-Hg to be based on CMAQ 4.5 as released in September 2005
- Dry deposition velocity of RGM explicitly calculated based on its molecular diffusivity and reactivity
- Dry deposition of Hg(0) to be simulated
- Emission of Hg(0) from natural processes to be simulated (largely anthropogenic Hg)
- Adoption of new chemical kinetic rates?????

CMAQ-Hg: Future Emphasis

- Monitor chemical kinetics research and update model accordingly, including revised rate constants and new reactions and reactants
- Expand CMAQ-Hg chemical mechanism options
- Obtain better speciation in mercury emission inventories and inventories for more nations
- Consider natural and recycled mercury emissions as part of a multi-media modeling strategy
- Advocate for more complete observational networks with specialized measurements to support model development and evaluation

Guiding Principle for Model Development

The greatest obstacle to discovery is not ignorance - it is the illusion of knowledge.

Daniel J. Boorstin (1914-2004)

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