

# ***CMAQ Mercury Modeling***

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

- Elemental Mercury ( $\text{Hg}^0$ ): 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 ( $\text{Hg}_p$ ): various condensed Hg compounds and semi-volatile Hg bound to receptive aerosols; two size modes simulated in CMAQ



# ***History of Atmospheric Mercury Modeling with CMAQ***

- 1999: CMAQ-Hg cloud chemistry model developed
- 2000: European Hg model inter-comparison study begins
- 2001: First full-scale version of CMAQ-Hg operational
- 2002: First “evaluation” of full-scale CMAQ-Hg against MDN data
- 2003: European study shows “large differences” between models and observations of oxidized mercury air concentrations
- 2004: New computational efficiencies applied to CMAQ-Hg and a full calendar year (2001) is simulated
- 2005: EPA’s Clean Air Mercury Rule developed using CMAQ-Hg modeling assessments
- 2006: CMAQ-Hg included in Models-3/CMAQ interim code release (expected at the end of February)



# ***CMAQ-Hg: Additions to 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.
- 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.

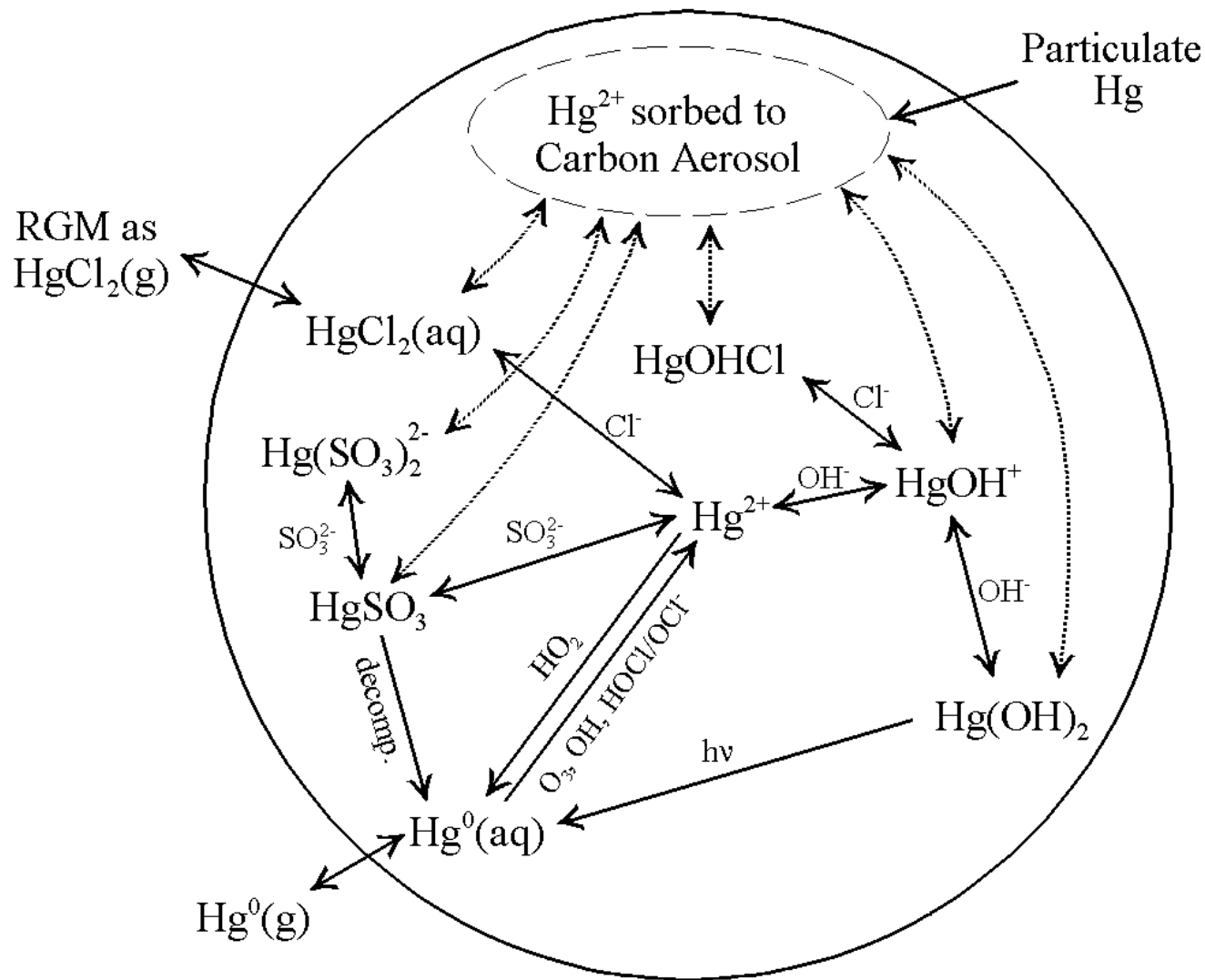


# Current CMAQ Hg Reaction Table *(under consideration)*

No.	Reaction	k or K	Reference
<b>Gaseous-phase reaction of Hg</b>			
RG1	$\text{Hg}_{(g)}^0 + \text{O}_{3(g)} \rightarrow 50\% \text{RGM}, 50\% \text{PHg}$	$2.11 \times 10^{-18} e^{-1256.5/T} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall (1995)
RG1	<b>25 times faster at 295 K?</b>	<b><math>7.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}</math></b>	<b>Pal and Ariya (2004)</b>
RG2	$\text{Hg}_{(g)}^0 + \text{Cl}_{2(g)} \rightarrow \text{RGM}$	$2.6 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya <i>et al.</i> (2002)
RG3	$\text{Hg}_{(g)}^0 + \text{H}_2\text{O}_{2(g)} \rightarrow \text{PHg}$	$8.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Tokos <i>et al.</i> (1998)
RG4	$\text{Hg}_{(g)}^0 + \text{OH}_{(g)} \rightarrow 50\% \text{RGM}, 50\% \text{PHg}$	$7.7 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Pal and Ariya (2004)
new	$\text{Hg}_{(g)}^0 + \text{Cl}_{(g)} \rightarrow \text{products}$	$1.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya <i>et al.</i> (2002)
new	$\text{Hg}_{(g)}^0 + \text{Br}_{2(g)} \rightarrow \text{products}$	$0.9 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya <i>et al.</i> (2002)
new	$\text{Hg}_{(g)}^0 + \text{Br}_{(g)} \rightarrow \text{products}$	$3.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya <i>et al.</i> (2002)
<b>Aqueous-phase reactions of Hg</b>			
RA1	$\text{Hg}_{(aq)}^0 + \text{O}_{3(aq)} \rightarrow \text{Hg}_{(aq)}^{2+} + \text{products}$	$4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Munthe (1992)
RA2	$\text{HgSO}_{3(aq)} \rightarrow \text{Hg}_{(aq)}^0 + \text{products}$	$T \times e^{((31.971 \times T) - 12595)/T} \text{ s}^{-1}$	Van Loon <i>et al.</i> (2000)
RA2	$\text{HgSO}_{3(aq)} \rightarrow \text{Hg}_{(aq)}^0 + \text{SO}_{2(aq)}$	????	Van Loon <i>et al.</i> (2001)
RA3	$\text{Hg}(\text{OH})_{2(aq)} + h\nu \rightarrow \text{Hg}_{(aq)}^0 + \text{products}$	$6.0 \times 10^{-7} \text{ s}^{-1} \text{ (max)}$	Xiao <i>et al.</i> (1994)
RA4	$\text{Hg}_{(aq)}^0 + \text{OH}_{(aq)} \rightarrow \text{Hg}_{(aq)}^{2+} + \text{products}$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen (1997)
RA5	$\text{Hg}_{(aq)}^{2+} + \text{HO}_{2(aq)} \rightarrow \text{Hg}_{(aq)}^0 + \text{products}$	$1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Pehkonen and Lin (1997)
RA5	$\text{Hg}_{(aq)}^{2+} \rightarrow \text{Hg}_{(aq)}^0$ Artifact?	$0 \text{ M}^{-1} \text{ s}^{-1}$	Gardfeldt and Jonsson (2003)
RA6	$\text{Hg}_{(aq)}^0 + \text{HOCl}_{(aq)} \rightarrow \text{Hg}_{(aq)}^{2+} + \text{products}$	$2.09 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen (1998)
RA7	$\text{Hg}_{(aq)}^0 + \text{OCl}_{(aq)} \rightarrow \text{Hg}_{(aq)}^{2+} + \text{products}$	$1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen (1998)
<b>Aqueous-phase chemical equilibria for Hg</b>			
E1	$\text{Hg}^{2+} + \text{SO}_3^{2-} = \text{HgSO}_3$	$2.0 \times 10^{-13} \text{ M}$	Smith and Martell (1976)
E1	<b>Factor of 4.2 decrease?</b>	<b><math>4.8 \times 10^{-14} \text{ M}</math></b>	<b>Van Loon <i>et al.</i> (2001)</b>
E2	$\text{HgSO}_3 + \text{SO}_3^{2-} = \text{Hg}(\text{SO}_3)_2^{2-}$	$4.0 \times 10^{-12} \text{ M}$	Smith and Martell (1976)
E2	<b>Factor of 25 increase?</b>	<b><math>1.0 \times 10^{-10} \text{ M}</math></b>	<b>Van Loon <i>et al.</i> (2001)</b>
E3	$\text{Hg}^{2+} + 2\text{Cl}^- = \text{HgCl}_2$	$1.0 \times 10^{-14} \text{ M}^2$	Lin and Pehkonen (1999)
E4	$\text{Hg}^{2+} + \text{OH}^- = \text{HgOH}^+$	$2.51 \times 10^{-11} \text{ M}$	Smith and Martell (1976)
E5	$\text{HgOH}^+ + \text{OH}^- = \text{Hg}(\text{OH})_2$	$6.31 \times 10^{-12} \text{ M}$	Smith and Martell (1976)
E6	$\text{HgOH}^+ + \text{Cl}^- = \text{HgOHCl}$	$3.72 \times 10^{-8} \text{ M}$	Smith and Martell (1976)



# CMAQ-Hg Cloud Chemistry Mechanism for Mercury



# ***First “Evaluation” of CMAQ-Hg in 2002***

- Calculation efficiencies not yet implemented
- Test periods based on MM5 and mercury emissions data availability
  - April 4 – May 2, 1995
  - June 20 – July 18, 1995
- Static IC/BCs
  - $\text{Hg}^0 = 2 \times 10^{-13}$  (v/v) or  $\sim 1.7$  ng/m<sup>3</sup> @ STP
  - RGM,  $\text{Hg}_p = 2 \times 10^{-15}$  (v/v) or  $\sim 17$  pg/m<sup>3</sup> @ STP
- Oxidation products 100%  $\text{Hg}_p$  for  $\text{O}_3$  and OH reactions (Now 50% RGM & 50%  $\text{Hg}_p$ )
- Kinetic rate constant for OH reaction slightly higher than in current model.

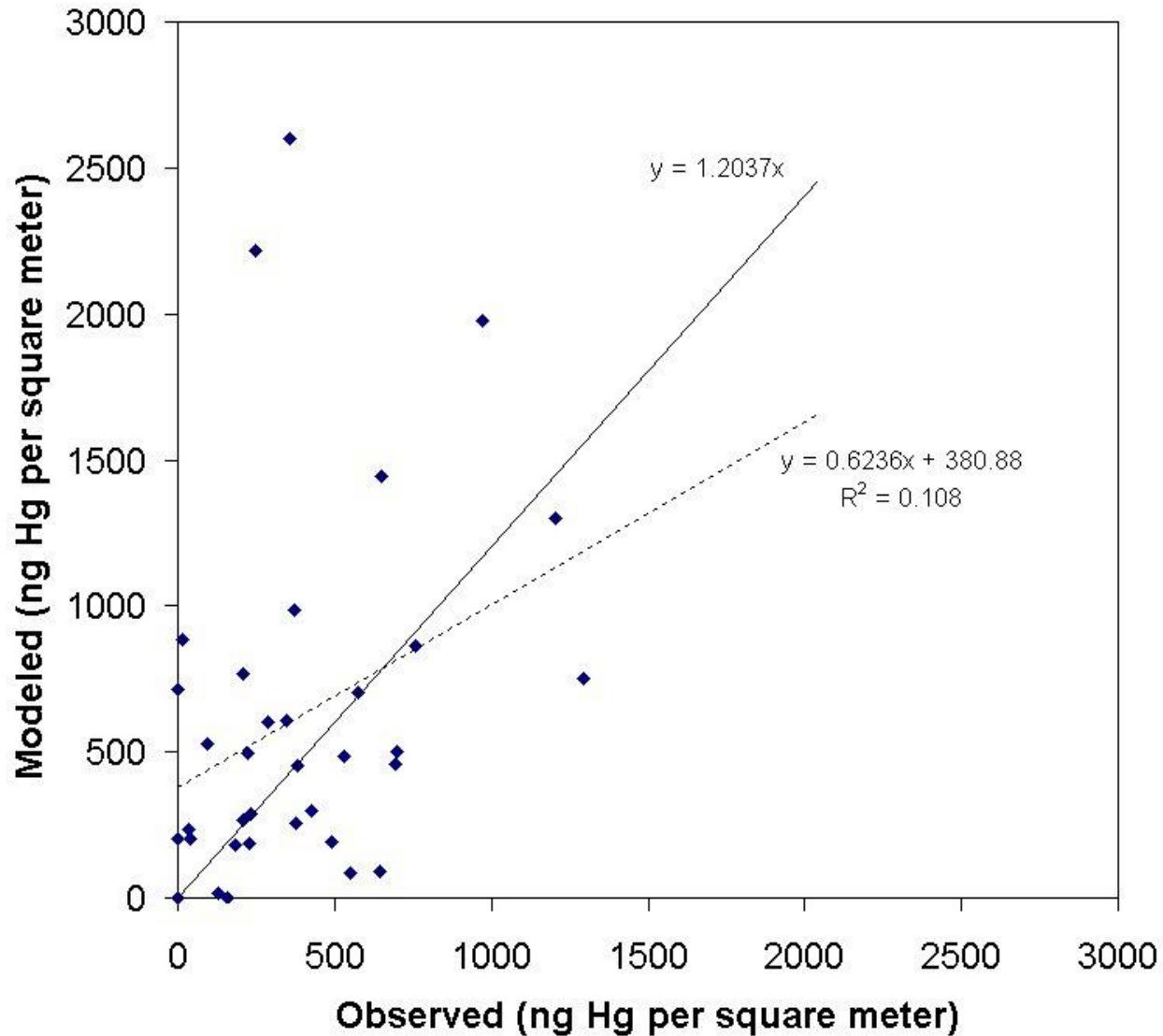




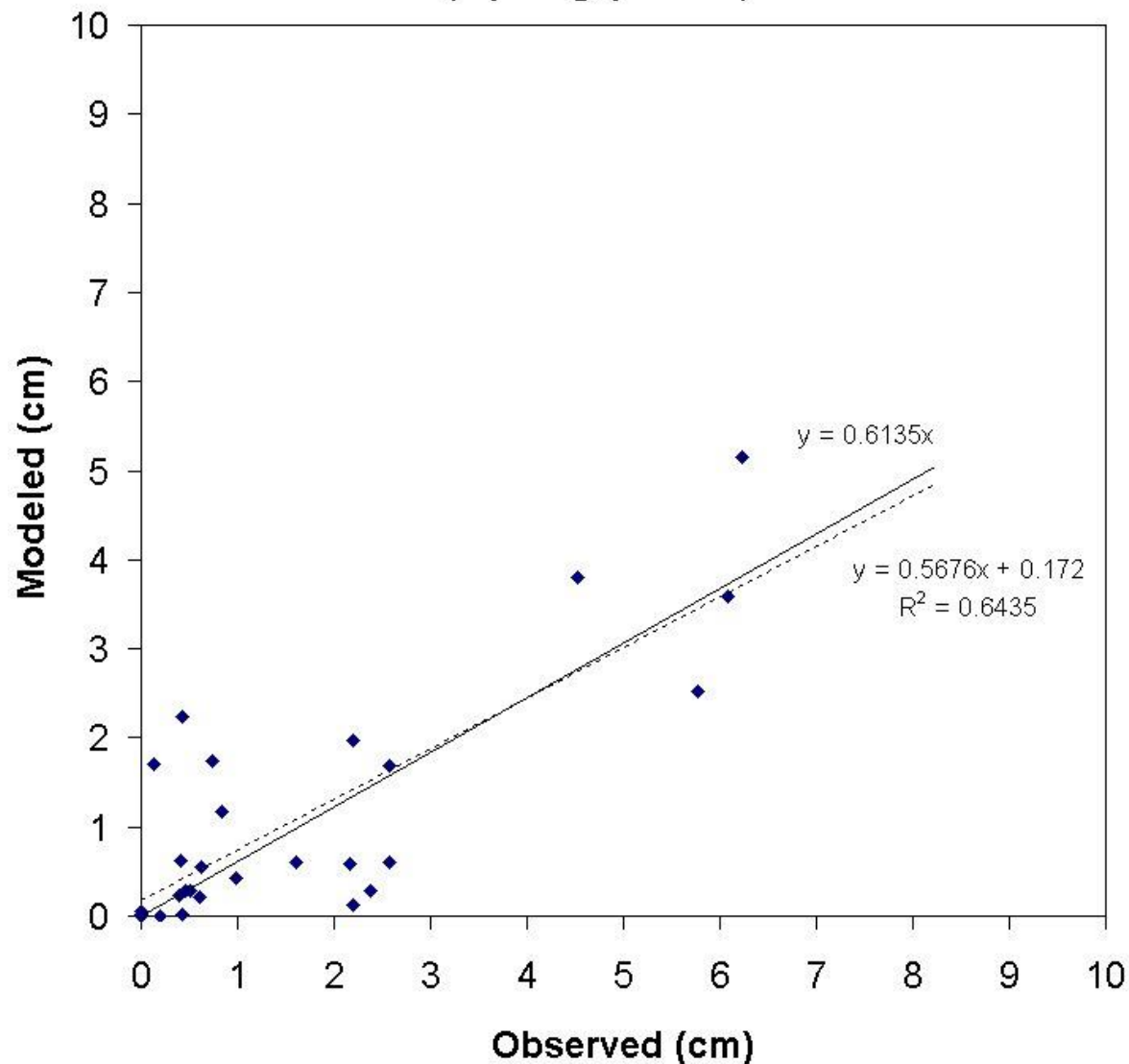




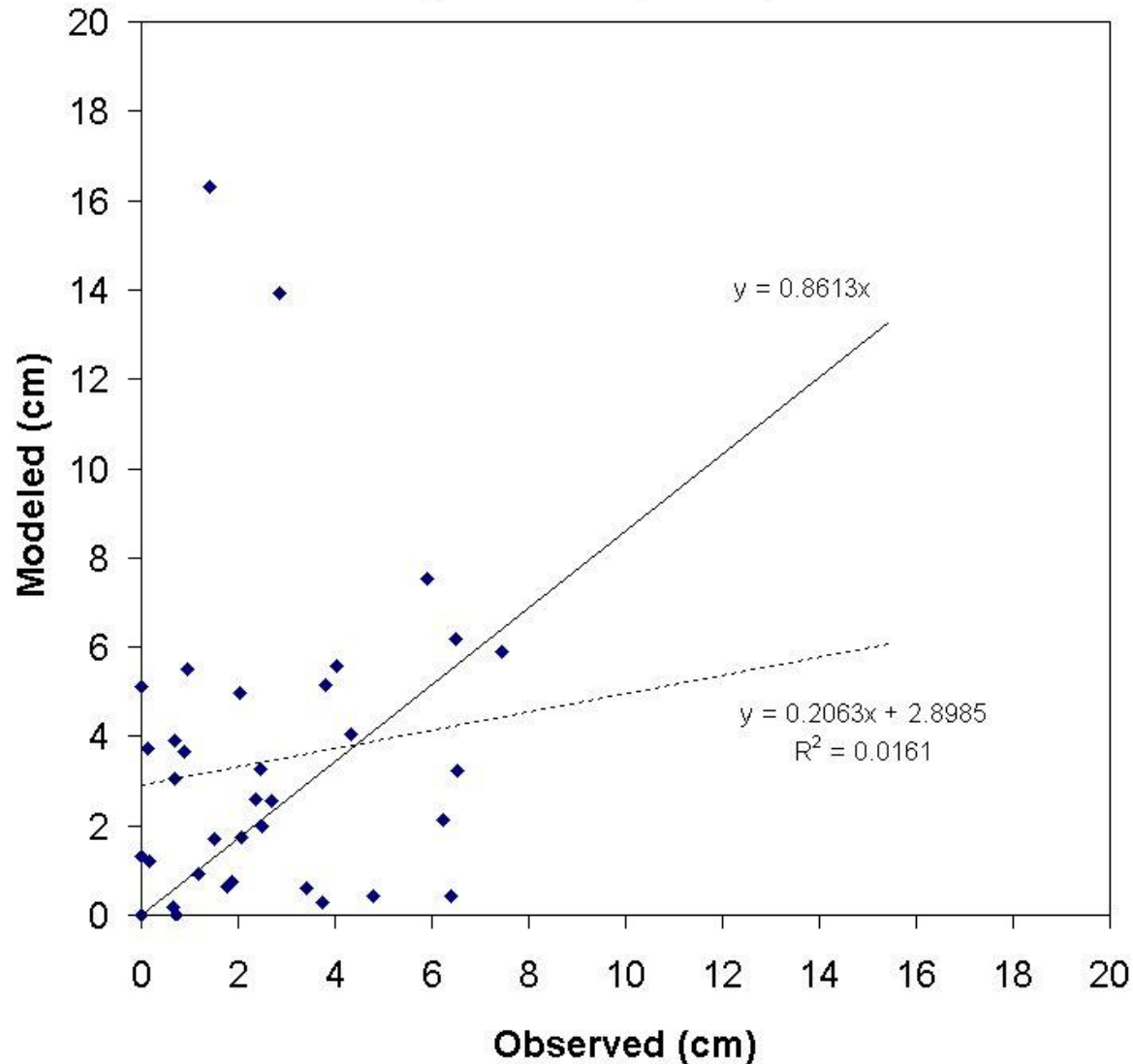
# Modeled vs. Observed Wet Deposition of Hg (Summer period)



# Modeled vs. Observed Precipitation (Spring period)



# Modeled vs. Observed Precipitation (Summer period)



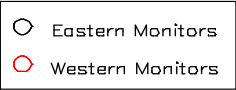
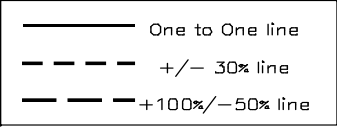
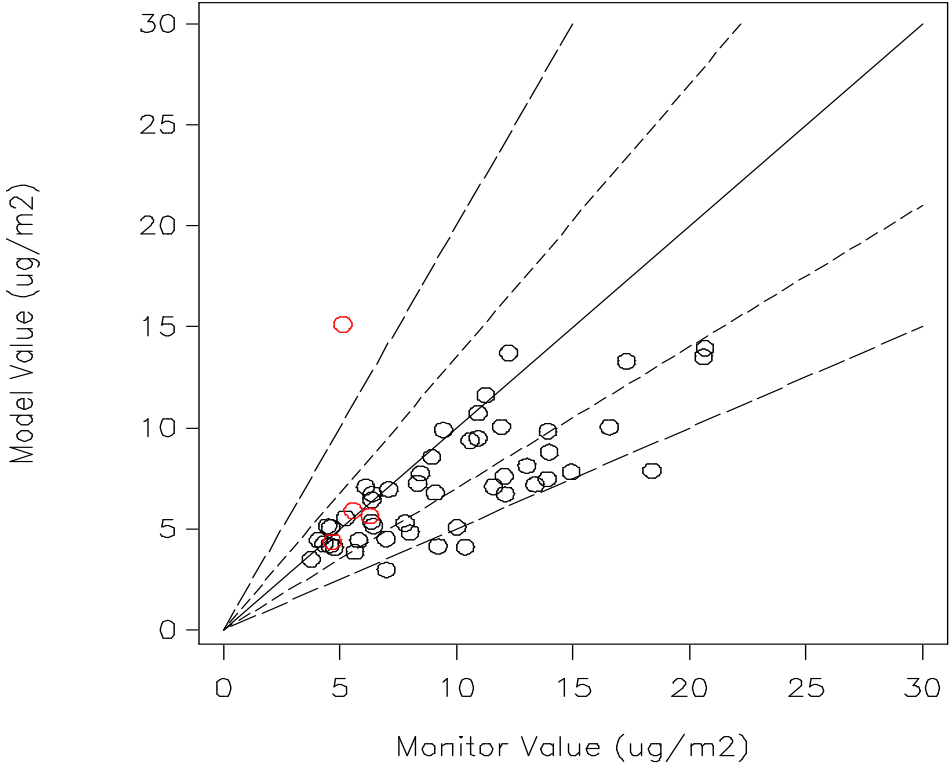
# ***CMAQ-Hg Simulations for the Clean Air Mercury Rule***

- Complete year of 2001 simulated
- IC/BCs from GEOS-CHEM global simulation
  - $\text{Hg}^0$  air concentrations abnormally low
  - RGM,  $\text{Hg}_p$  both within “reasonable” range
- 1999 NEI updated to 2001 for CAMR study
- Oxidation products for  $\text{O}_3$  and OH reactions 50% RGM & 50%  $\text{Hg}_p$  to bring down very high simulated  $\text{Hg}_p$  air concentrations
- Many more MDN sites active in 2001 versus 1995, so testing is more robust than for first evaluation



# CMAQ 2001 Wet Hg Deposition

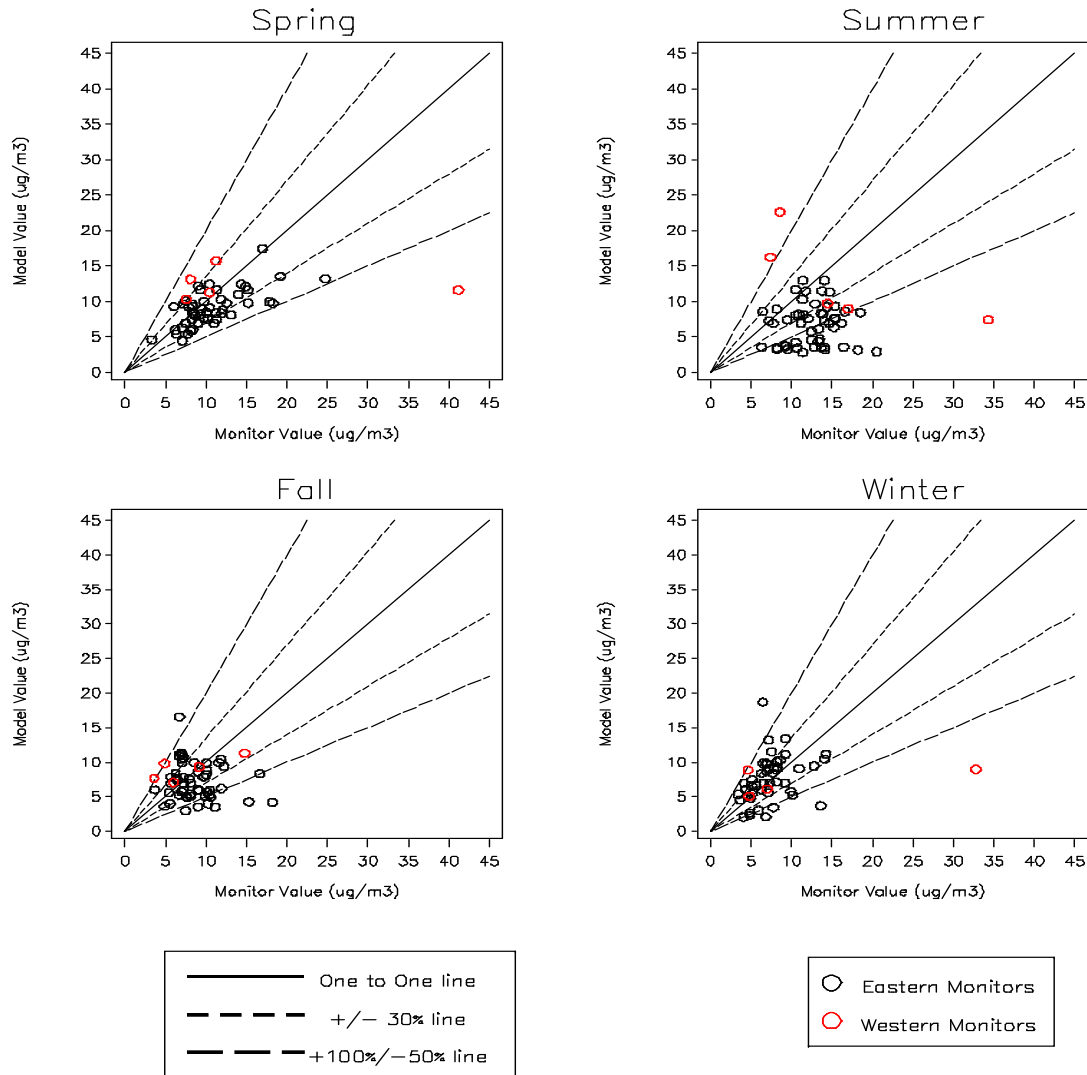
## Annual Deposition



Model Run: Hg\_Annual\_4  
08FEB2005



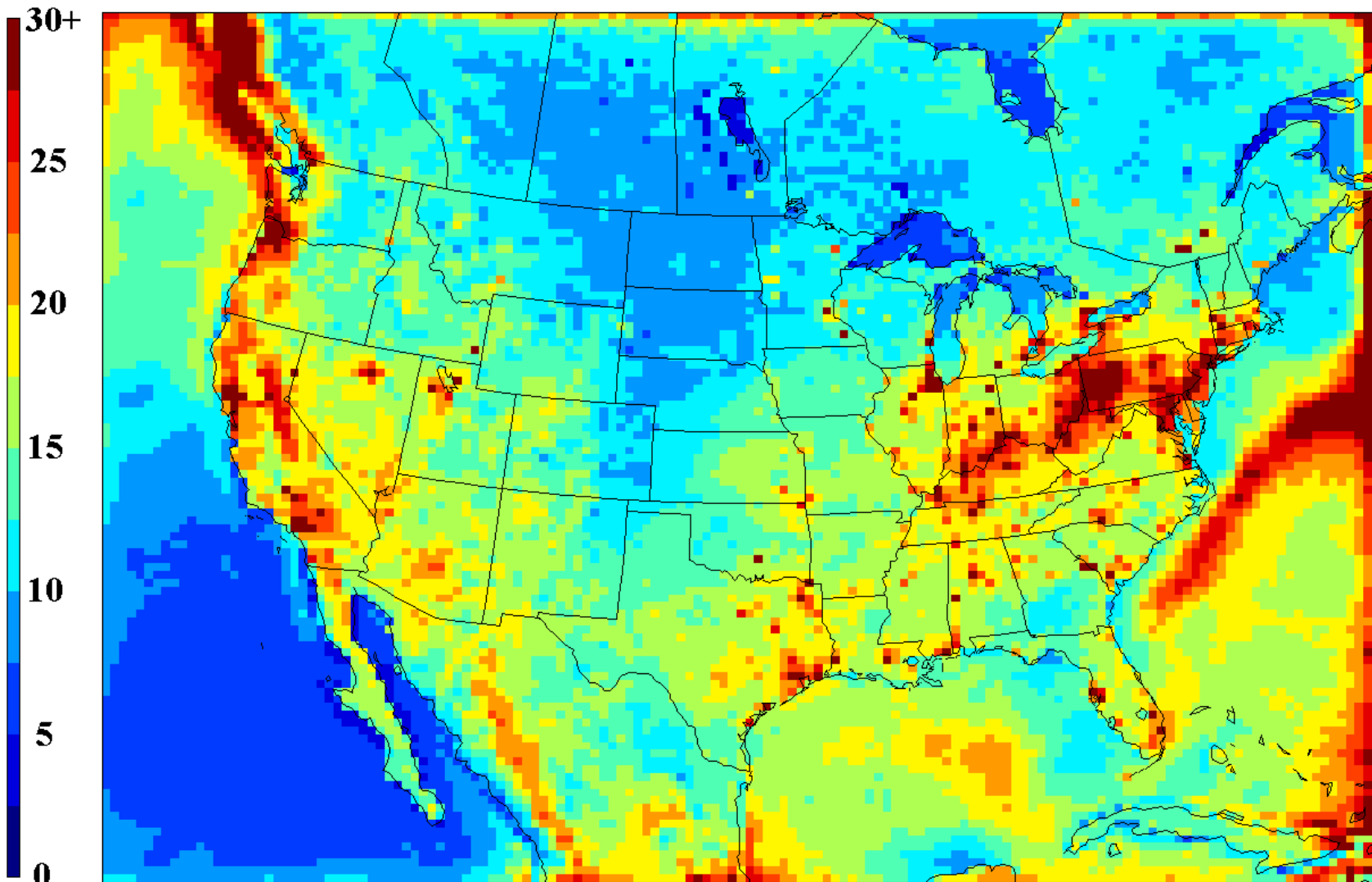
# Wet Hg Concentration MDN vs. CMAQ



Model Run: Hg\_Annual\_4  
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# CMAQ-simulated total mercury deposition for 2001 (micrograms per square meter)



**Base case**



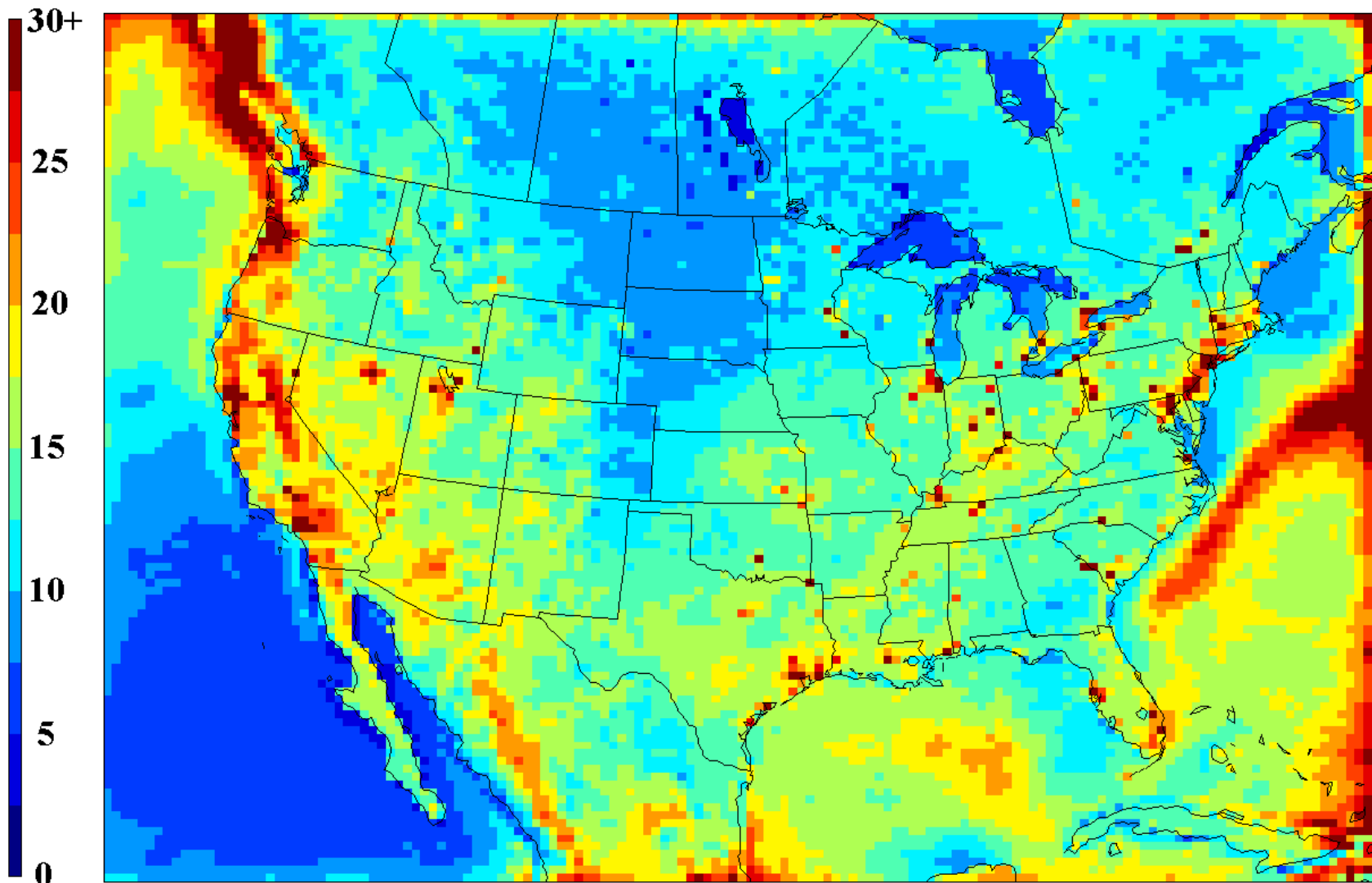
RESEARCH & DEVELOPMENT

*Building a scientific foundation for sound environmental decisions*





# CMAQ-simulated total mercury deposition for 2001 (micrograms per square meter)



**Utility Zero Out**

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# ***General Findings from CAMR Modeling***

- Importance of global background air concentration of  $\text{Hg}^0$  greater than previously indicated due to new gas-phase oxidation reactions and higher kinetic rate constants for existing reactions
- Coal-fired utility boilers contribute less than 5% of total mercury deposition over most areas of the contiguous U.S., but the modeled range is 0.05% to 85.9%
- 144 tons of mercury deposited to the contiguous U.S. in 2001, 23 from all U.S. anthropogenic sources, 11 from coal-fired electric utility boilers.



# ***Recent upgrades to the CMAQ Mercury Model***

- Standard modeling platform for mercury has been updated to CMAQ Version 4.5 (from 4.3).
- Dry deposition of  $\text{Hg}^0$  is now simulated with  $V_d$  estimates computed in MCIP.
- Natural and recycled Hg emissions from geology and vegetation have been added.
- All upgrades are to be included in an interim code release due at the end of February.



# *Future CMAQ-Hg Developments*

- “Natural” Hg emissions will be better characterized with separate treatments for first-time emissions to the mercury cycle and re-emission of previous depositions. This may require an explicit multi-media modeling treatment.
- Chemical and physical reactions of Hg in both air and cloud water are still being identified and described. Kinetic rate constants may be modified and heterogeneous mercury chemistry may need to be added.
- The ability to evaluate the realism of any Hg model is severely limited by a lack of observational data. We need to better define dry deposition of Hg and the concentrations of its various forms throughout the atmosphere before traditional model evaluation can be attempted.



# Research Needs

- The processes controlling the uptake and release of mercury from water bodies, soils, and vegetation need to be understood before our modeling treatments can be believed.
- All important chemical and physical reactions of Hg in air and cloud water must be identified and understood. Kinetic rate constants must be pertinent to atmospheric conditions. Air concentration measurements of specific Hg compounds would be a great help on both points.
- Observational networks are needed for both wet and dry deposition of mercury with at least daily sampling.
- Speciation of industrial emissions must be known and any rapid chemical/physical plume conversions must be identified and understood.



# Disclaimer

*The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.*

