New Science Implementation in CMAQ-Hg: Test over a Continental United States Domain

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Atmospheric Mercury

	Elemental (GEM)	Divalent (RGM, DAM, PHg)
Primary Source	Emissions	Emission, Products of Hg(0)
Abundance	> 95%	< 5 %
Phase	Gas	Gas, aqueous, solid
Water Solubility	Low (0.3 μM)	High (a few mM)
Henry's Constant	0.11 M/atm	$10^4 – 10^7$ M/atm
Lifetime	0.5 - 2 years	Days - Weeks
Transport	Long Range	Relatively short
Background Concentration	1~4 ng/m^3	Up to 900 pg/m^3 (RGM) 0.025~0.5 nM (DAM)

What makes Hg unique?

- Very small concentrations (often in sub-ppt levels) compared to criterion air pollutants
- Its “gaseous” forms have little human health concerns
- Has multiple chemical forms with diverse properties
- Has “its own” chemistry cycle – does not affect other air pollutants significantly
- Concurrent atmospheric processes involving multiple pollutants affect its transport and deposition
- Transformation occurs in multiple phases in the atmosphere
- Both dry and wet depositions cause problems
- Analytically challenging to measure
- Cycling in the environment

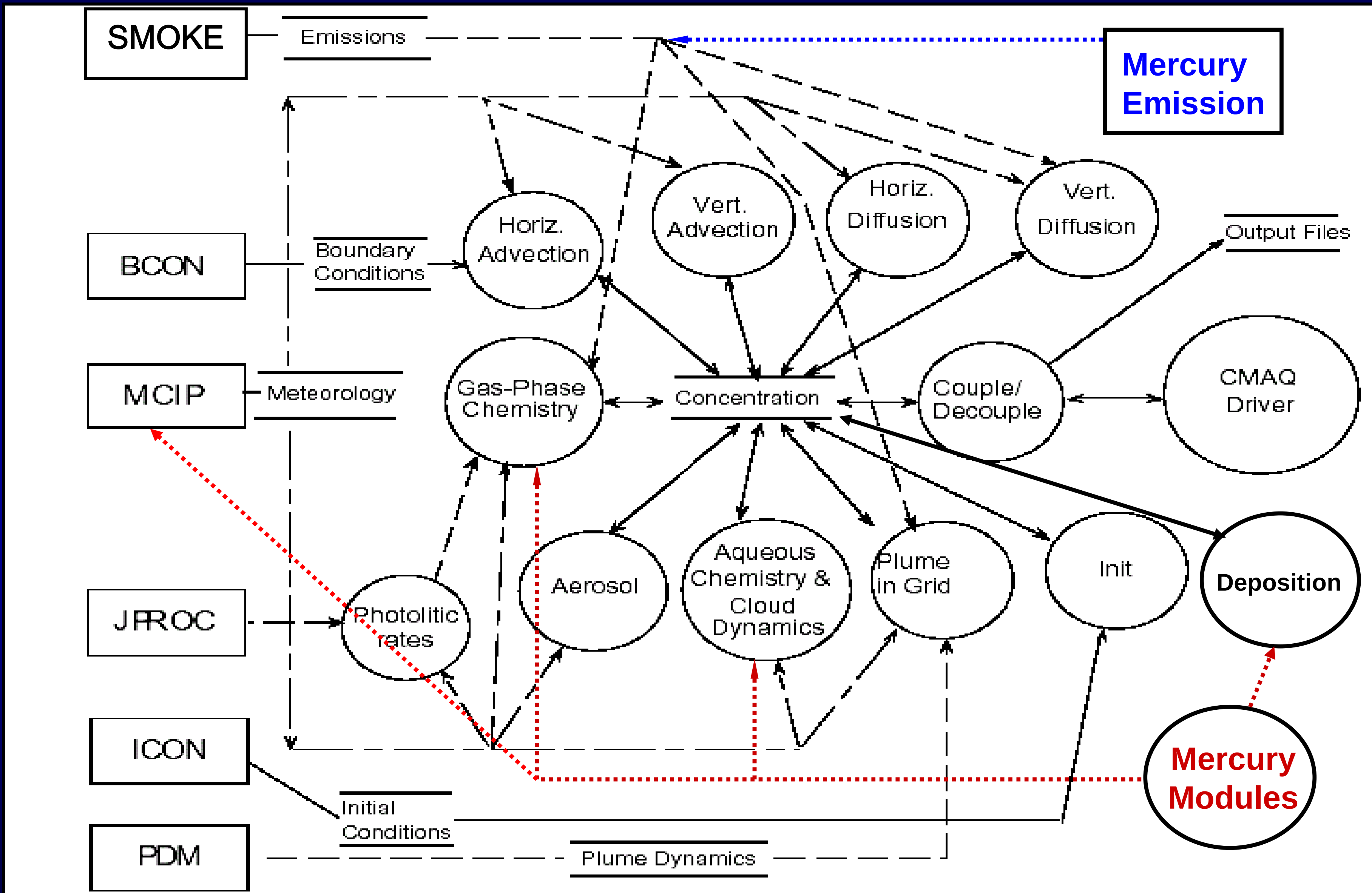
Modeling Atmospheric Hg

- **The Emission**
  - Anthropogenic sources
  - Natural sources
  - Re-emissions?

The Transport – as determined by the advection and diffusion treatment in air quality models.

- **The Transformation**
  - Gaseous phase – oxidation & product speciation
  - Aqueous phase – oxidation, reduction and sorption
  - Interfacial transfer – scavenging and evaporation
- **The Deposition**
  - Dry deposition – GEM, RGM, PHg
  - Wet deposition – Aqueous Hg(II)

CMAQ-Hg Model



CMAQ-Hg (Bullock & Brehme, 2002)

Emission	Anthropogenic (Point & Area)	Veg./re-emission needed
Gas Chemistry	O_3, Cl_2, H_2O_2, and OH, PHg as the oxidation product by OH and O_3	New kinetics available & speciation need revision
Aq. Chemistry	Ox: O_3, OH, HOCl, and OCl^-	Speciation controlled
	Red: $HgSO_3$, $Hg(OH)_2$+hv, HO_2	Speciation controlled
Aq. Speciation	SO_3^{2-}, Cl^-, OH^-	Major ligands considered but assume constant Cl^-
Aq. Sorption	Sorption of Hg(II) to ECA, bi-directional non-eq. kinetics w/ linear sorption isotherm	High sorption constant, no impact based on current formulation
Dry Deposition	V_{dep} of HNO_3 for RGM deposition	No Hg^0 deposition. RGM deposition likely too high
	V_{dep} of I,J modes for PHg deposition	As sulfate deposition
Wet Deposition	Dissolved and Sorbed $Hg(II)_{aq}$	By precipitation & aqueous concentration

Science Issues in CMAQ-Hg

- Impact of emission natural/re-emission unclear.
- Widely varied kinetic data reported for same mechanisms (e.g., gaseous Hg^0 oxidation by O_3 and OH; aqueous reduction of Hg(II) by sulfite).
- Uncertain reaction product distribution of gaseous oxidation (e.g., RGM or PHg?).
- Extrapolation of laboratory results may not be appropriate (e.g., aqueous reduction of Hg(II) by HO_2, gaseous oxidation of Hg^0 by OH and O_3).
- Deposition velocity for both GEM and RGM not treated rigorously.
- Revision needed for sorption scheme in the aqueous phase (cloud water).

Sensitivity Cases

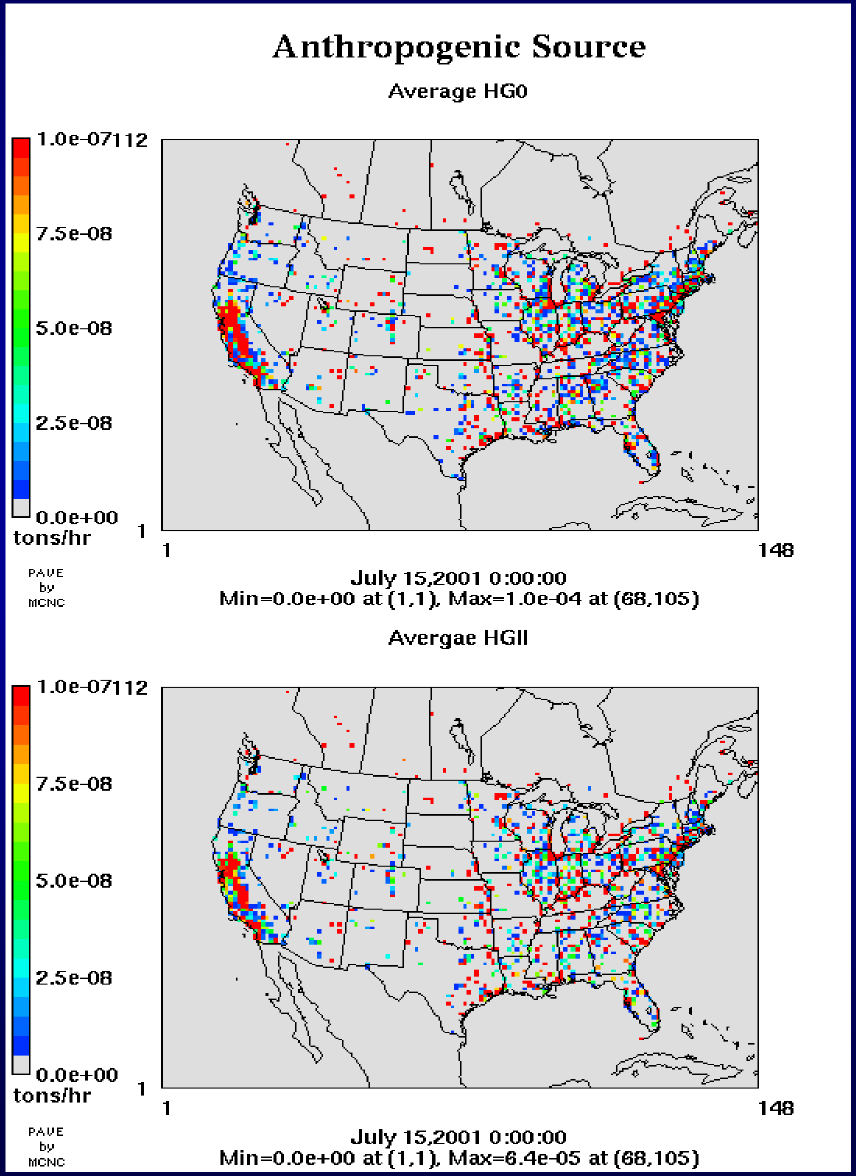
- Case 1: CMAQ-Hg as in Bullock & Brehme (2002)
- Case 2: include vegetative/natural emission in mercury emission inventory
- Case 3: incorporate dry deposition schemes for elemental mercury and RGM (as $HgCl_2$)
- Case 4: speciate mercury oxidation products to reactive gaseous mercury (RGM)
- Case 5: incorporate new aqueous sorption scheme based on new sorption isotherm
- Case 6: combine the modifications of Cases 2-5

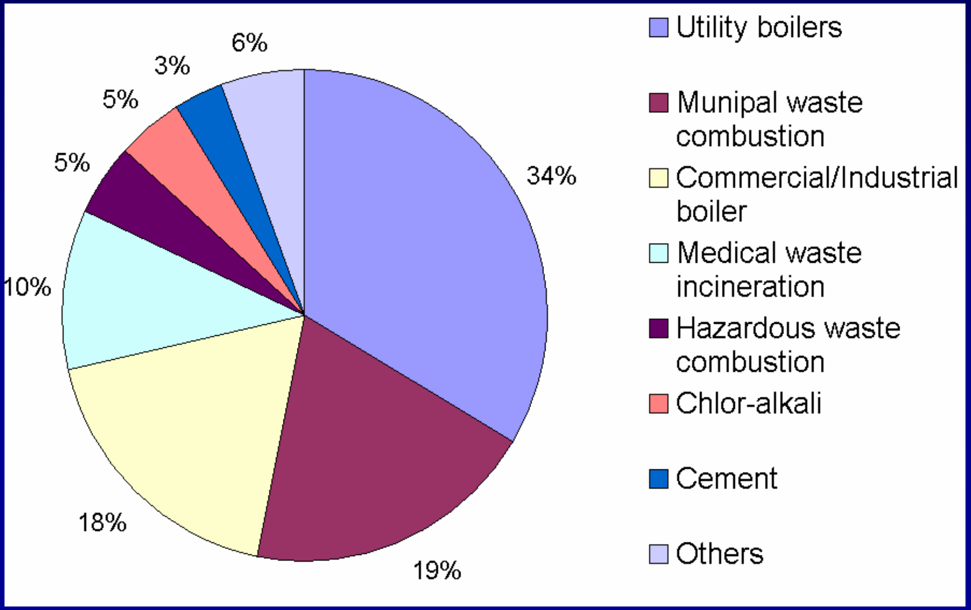
Parameter of interest: wet/dry deposition of mercury

Simulation Details

- Modeling periods: January and July 2001
- Meteorology: 2001 USEPA 36-km MM5 fields in CONUS domain
- Vertical structure: model top 10,000 Pa, 25 layers collapsing into 14 layers
- Emission inventory: NEI99 final Version 3, mercury speciation EI based on Walcek *et al*. (2003); natural / vegetative emission based on Lin *et al*. (2005)
- Chemistry: CB4 + updated mercury mechanisms (Lin and Pehkonen, 1999; Lin *et al*., 2005)
- Dry deposition: based on Wesley scheme (1989) with updated formulation for GEM and RGM
- Initial and boundary conditions: assumed typical background concentrations for GEM, RGM and PHg

Anthropogenic Mercury Emission Inventory



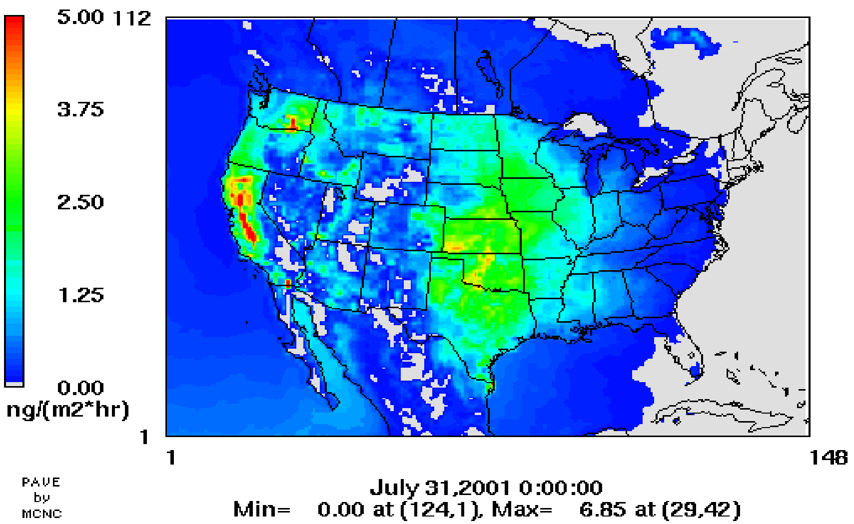


Anthropogenic Mercury Emission
Total Annual Emission: 142 tons
Hg(0) Emission: 78 tons
Hg(II) Emission: 50 tons
Particulate Hg Emission: 14 tons

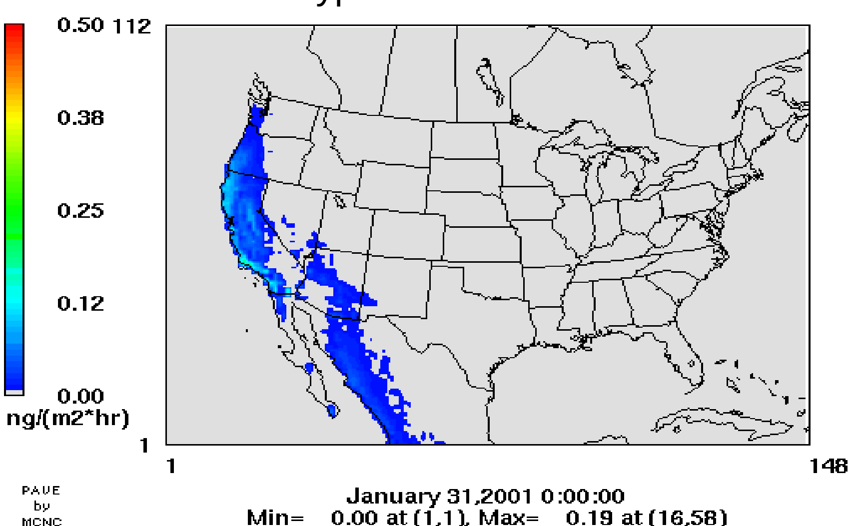
Based on NEI99 Final Version 3

Natural Mercury Emission Inventory

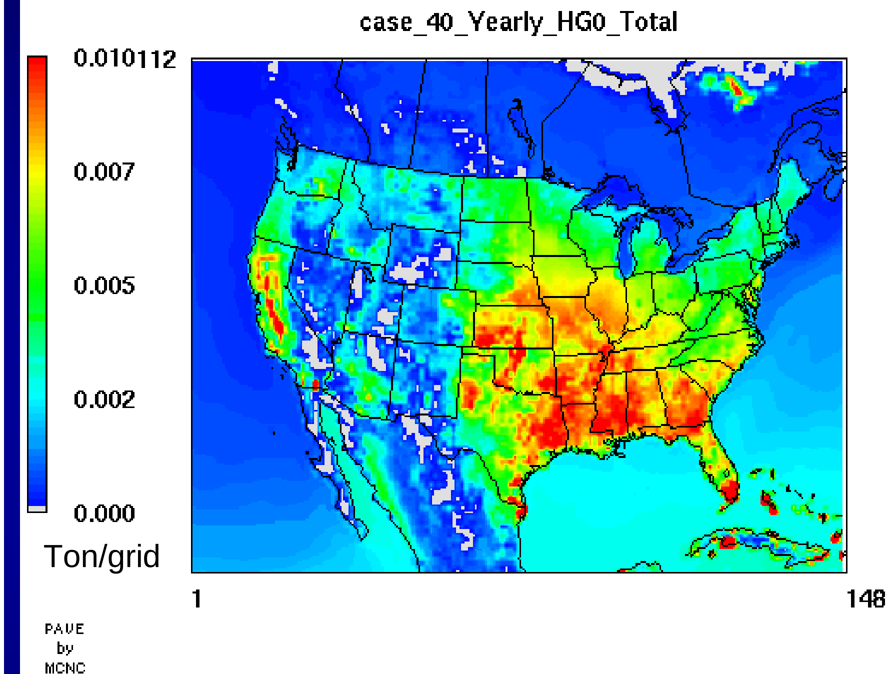
Typical Summer Emission



Typical Winter Emission



case_40_Yearly_HG0_Total



Annual Natural Emission:

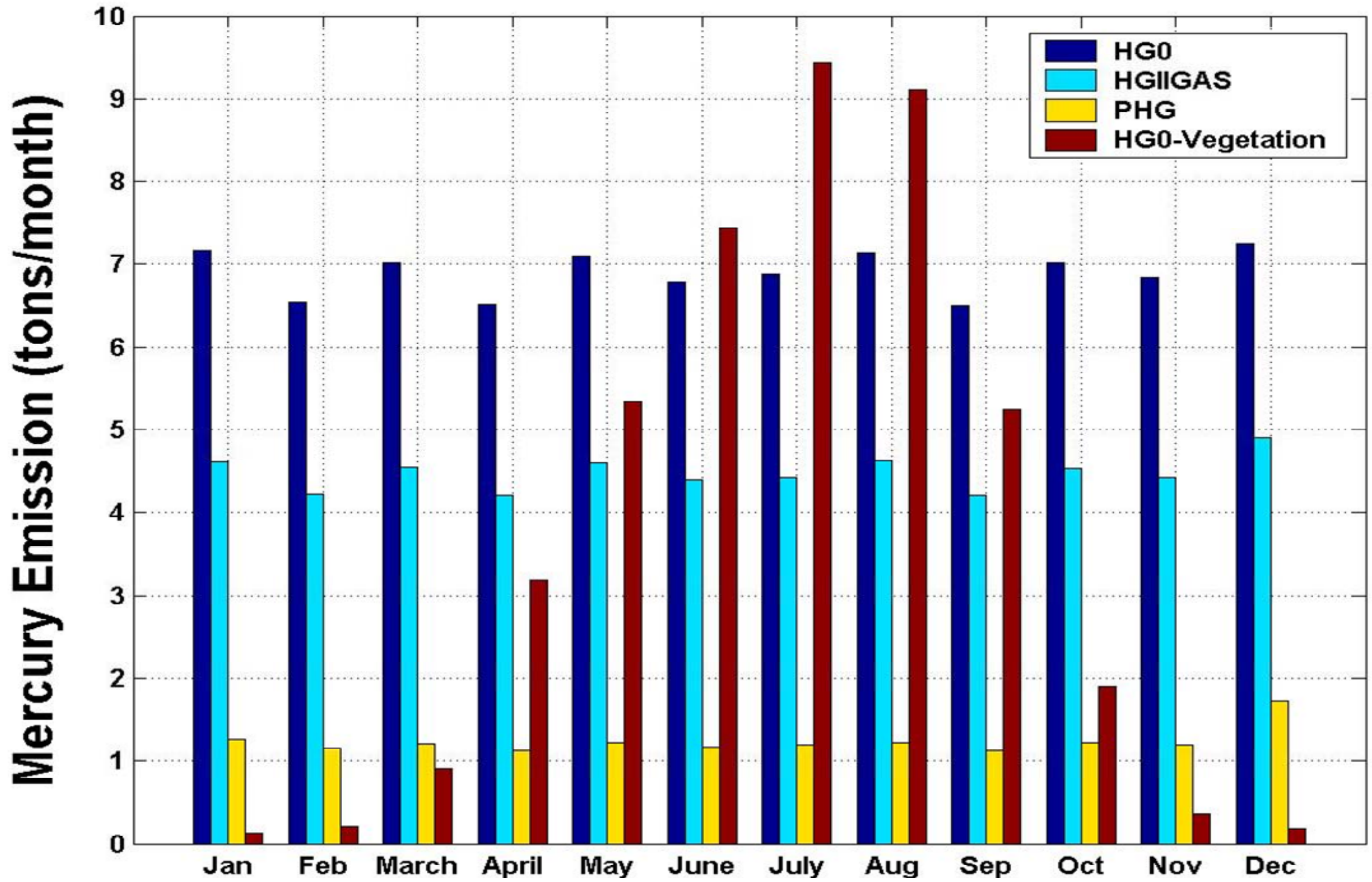
Lower Limit = 31 tons

"Best" Available Estimate = 44 tons

Upper Limit = 136 tons

(Lin et al., 2005)

Anthropogenic vs. Natural*



Anthropogenic Hg Emission based on EPA NEI99 Final Version 3.

*: in the Continental United States.

$F_{dry} = V_d \times C_g$

Mercury Deposition

- Dry Deposition (Based on Wesley Scheme)

$$F_{dry} = -V_d \times C_g$$

$$V_d = (R_a + R_b + \boldsymbol{R_c})^{-1} + V_g$$

$$R_c = \left(\frac{1}{r_{sx} + r_{mx}} + \frac{1}{r_{lux}} + \frac{1}{r_{dc} + r_{clx}} + \frac{1}{r_{ac} + r_{gsx}}\right)^{-1}$$

- Wet Deposition

$$F_{wet} = P \times [Hg^{2+}]_{aq,total}$$

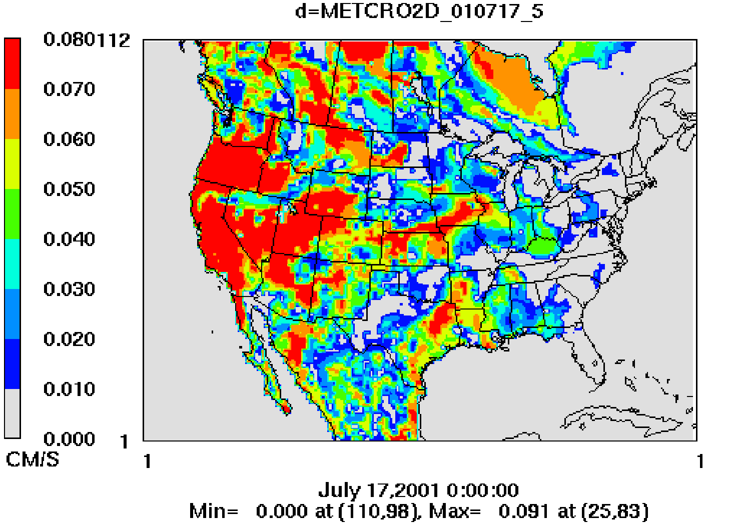
Hg V_{dep} Implementation - R_c

Terms	Formulation	Description	Remarks
r_{dc}	$100[1 + 1000(G + 10)^{-1}](1 + 1000\theta)^{-1}$	- Buoyant convection resistance	
r_{sx}	$r_s D_{H2O}/D_x$, where $r_s = r_i\{1 + [200(G + 0.1)^{-1}]^2\}\{400[T_s(40 - T_s)]^{-1}\}$	- Stomatal resistance for substance x	RGM : $D_{RGM} = 0.086$ cm²/s; $D_{H2O}/D_{RGM} = 2.53$ GEM : $D_{GEM} = 0.1194$ cm²/s; $D_{H2O}/D_{GEM} = 1.82$
r_{clx}	$[k_H/(10^5 r_{clS}) + f_0/r_{clO}]^{-1}$	- Lower canopy resistance	RGM : K_H=2.8x10⁶ M atm⁻¹ ($HgCl_2$) K_H=2.7x10¹² M atm⁻¹ (HgO) f_0(RGM) = **0.1 or 1.0** GEM : K_H = 0.139 M atm⁻¹, f_0(GEM) = **10^{-5}**
r_{gsx}	$[k_H/(10^5 r_{gsS}) + f_0/r_{gsO}]^{-1}$	- Ground surf. resistance	
r_{mx}	$(k_H/3000 + 100\, f_0)^{-1}$	- Mesophyll resistance	
r_{lux}	$r_{lu}\,(10^{-5}\,k_H + f_0)^{-1}$	- Leaf cuticular resist.	
	$[1/(3r_{lu}) + 10^{-7}\,k_H + f_0/r_{luO}]^{-1}$	- Dew or rain correction	
r_{luS}	100	- Leaf cuticular, SO_2 (Dew)	
	$[1/5000 + 1/(3r_{lu})]^{-1}$	- Rain correction	
r_{luO}	$[1/3000 + 1/(3r_{lu})]^{-1}$	- Leaf cuticular, O_3 (Dew)	
	$[1/1000 + 1/(3r_{lu})]^{-1}$	- Rain correction	

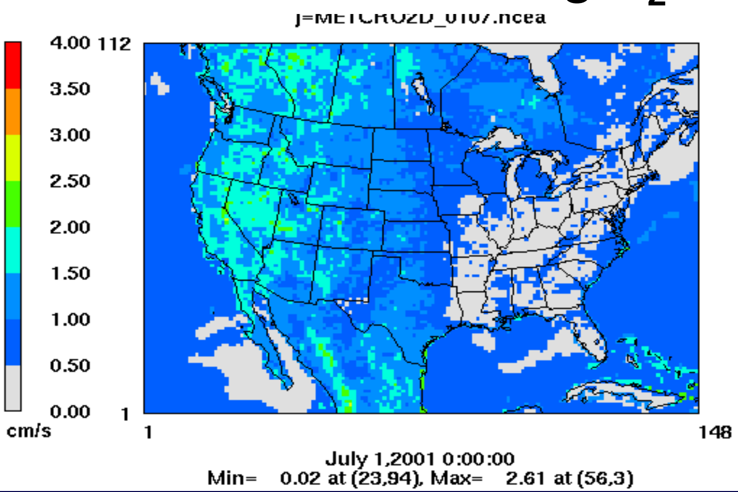
Note: r_i, r_{lu}, r_{clS}, r_{clO}, r_{ac}, r_{gsS}, r_{gsO} are parameters depending on land uses and seasons

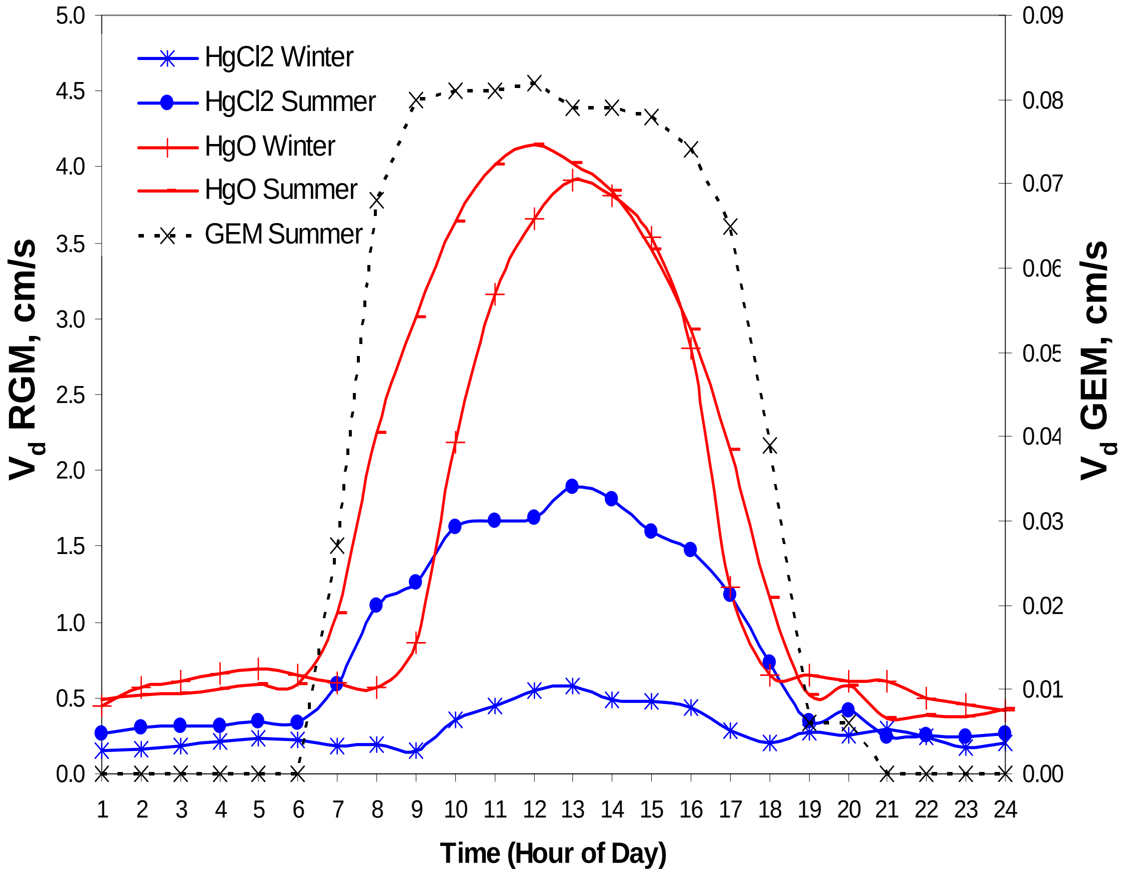
Hg Dry Deposition Velocity

GEM



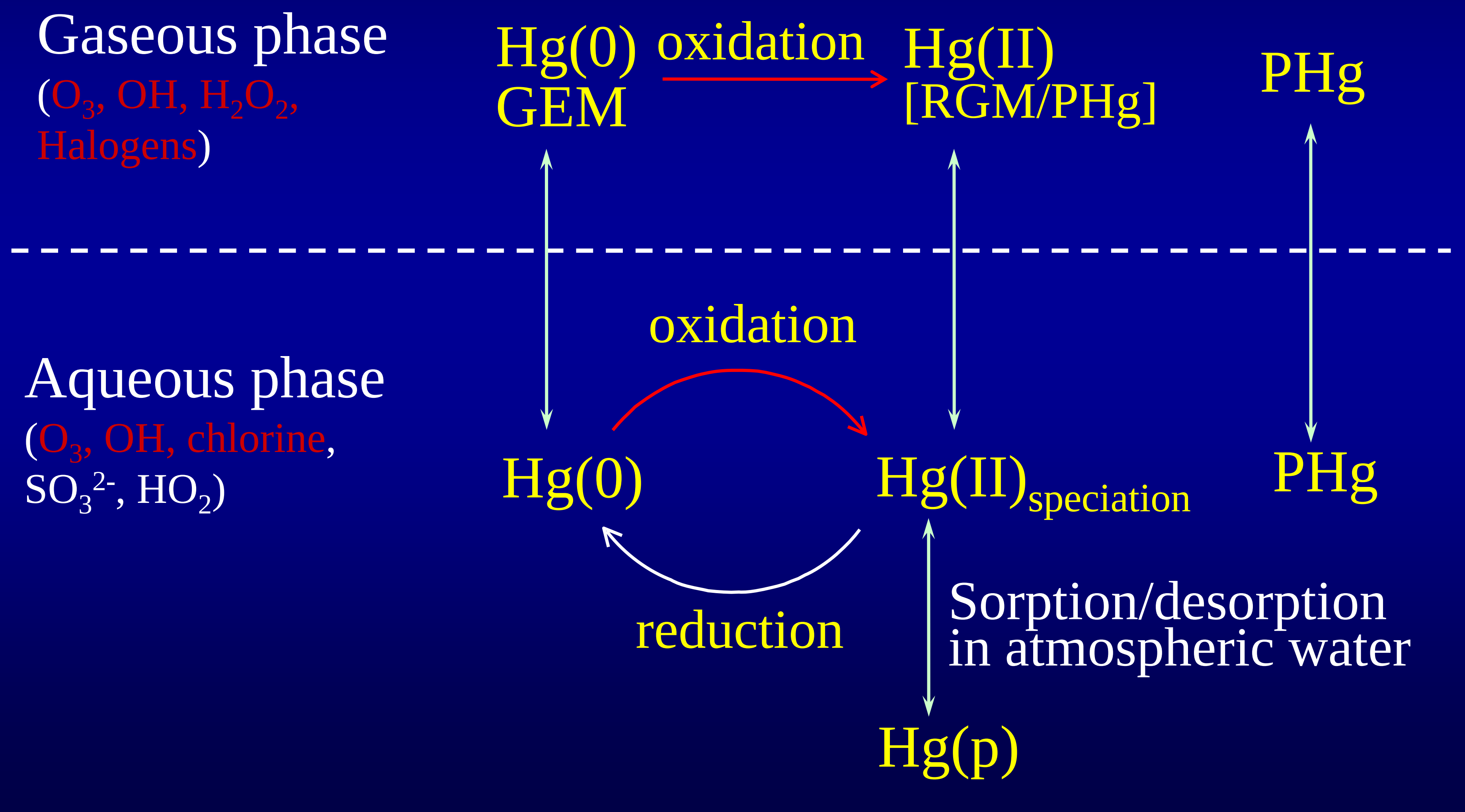
RGM – as $HgCl_2$





Average V_d in Domain

Simplified Hg Chemistry Scheme



Reaction Kinetics

Reaction	Rate constant	Type	
$Hg^0_{(g)} + O_{3(g)} \longrightarrow$ RGM/PHg $+ O_{2(g)}$	$3\text{-}75\times10^{-20}$ cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(aq)} + O_{3(aq)} + 2\,H^+ \rightarrow Hg^{2+}_{(aq)} + H_2O + O_2$	4.7×10^7 M^{-1} s^{-1}	Ox	AQ
$Hg^0_{(g)} + {}^{\bullet}OH_{(g)} \longrightarrow$ RGM/PHg + Products	8.7×10^{-14} cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(aq)} + {}^{\bullet}OH_{(aq)} \longrightarrow Hg^{2+}_{(aq)}$ + Products	2.0×10^9 M^{-1} s^{-1}	Ox	AQ
$Hg^0_{(aq)} + HOCl_{(aq)} \longrightarrow Hg^{2+}_{(aq)} + Cl^- + OH^-$	2.09×10^6 M^{-1}s^{-1}	Ox	AQ
$Hg^0_{(aq)} + OCl^-_{(aq)} \xrightarrow{H^+} Hg^{2+}_{(aq)} + Cl^- + OH^-$	1.99×10^6 M^{-1}s^{-1}	Ox	AQ
$Hg^0_{(g)} + H_2O_{2(g)} \longrightarrow$ RGM/PHg + products	8.5×10^{-19} cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(g)} + Cl_{2(g)} \longrightarrow$ RGM + products	$2.6\text{-}4.8\times10^{-18}$cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(g)} + Br_{2(g)} \longrightarrow$ RGM + products	9×10^{-17} cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(g)} + Cl_{(g)} \longrightarrow$ RGM + products	1.0×10^{-11} cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(g)} + Br_{(g)} \longrightarrow$ RGM + products	3.2×10^{-12} cm^{3}molec^{-1}s^{-1}	Ox	G
$Hg^0_{(g)} + BrO_{(g)} \longrightarrow$ RGM + products	1.5×10^{-14} cm^{3}molec^{-1}s^{-1}	Ox	G
$HgSO_{3(aq)} \longrightarrow Hg^0_{(aq)}$ + products	$T\exp(31.971-(12595/T))s^{-1}$	Red	AQ
$Hg(OH)_{2(aq)}$ + UV $\longrightarrow Hg^0_{(aq)}$ + products	3×10^{-7} s^{-1}, midday 60^{o}N	Red	AQ
$Hg(II)_{(aq)} + HO_2{}^{\bullet}{}_{(aq)} \rightarrow Hg^+_{(aq)} + O_2 + H^+$	1.7×10^4 M^{-1} s^{-1}	Red	AQ

Hg Sorption Implementation

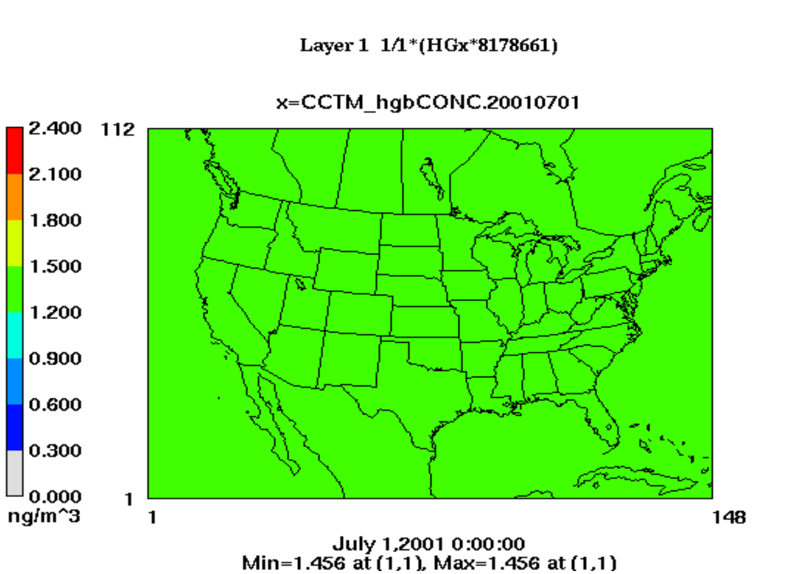
$$[Hg^{2+}]_{aq,total} = (1 + K_a[APM]_{aq})[Hg_D^{2+}]_{aq}$$

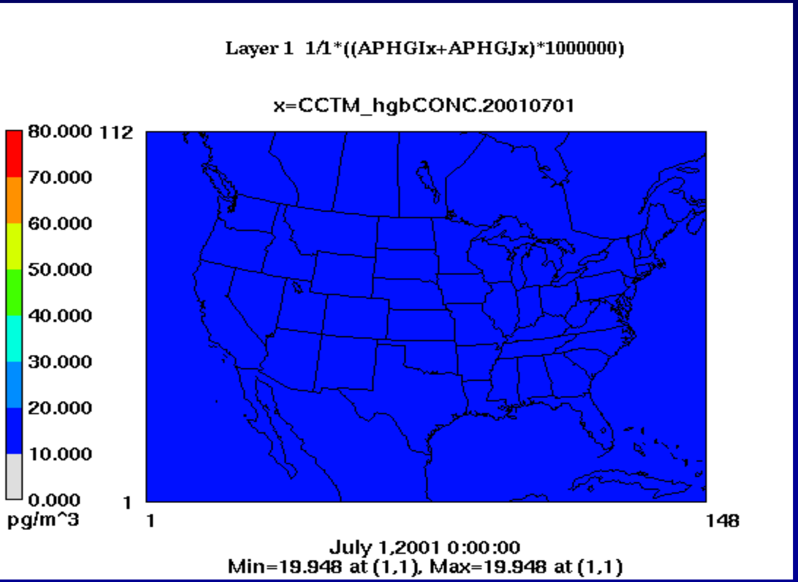
Sources	Xiao & Thomas (2004)	Budinova et al. (2003)	Sanchez-Polo & Rivera-Utrilla (2002)	Manohar et al (2002)	Karabulut et al. (2001)	Seigneur et al. (1998)	Yin et al. 1997
Sorbents	Activated carbon, 0.002 g/mL	Furfural-based carbon, 0.0002 g/mL	Ozonated activated carbon, Φ=500-800 μm, pH_{pzc}: 2.6-8.8, 0.002 g/mL	Clay (Φ=0.096 mm, As= 71.3 m^2/g, porosity:=0.39 ml/g, ρ=1.39 g/ml, cation exchange capacity: 2.3 meq/g, pH_{pzc}: 3.4, 0.002 g/mL	Coal (Lignite), 65 mesh ASTM, 1 g/mL	Atmospheric particulate matter, Φ < 62 μm, 20 mg/L	15 Soil types (sand-loam), Φ < 2 mm., 0.01 g/mL
Hg Conc.	$Hg(NO_3)_2$: 48 - 4173 mM	$HgCl_2$: 10 - 40 mg/L	50 mg/L Hg(II)	25-1000 mg/L Hg(II)	10 - 100 ppm Hg(II)	THg: 1.67 ng/L	$Hg(NO_3)_2$: 1.0×10^{-7} ~ 1.1×10^{-4} M
Solution Conditions	T: 25 °C, pH: 1.97 - 3.90	pH: 2.0 - 5.0	T: 25 °C, pH: 2.0 - 12.0	T: 30 - 60 °C, pH: 4.0 - 8.0	T=25 ± 2 °C, pH: 2.0 - 6.0	pH: 3.1 - 6.1	T=25 ± 2 °C, pH=4.9-6.5. I = 0.001-0.1 M $NaNO_3$
Sorption Model[(1)]	q_{max}: 1.06 - 1.37 mmol g^{-1}, K_{ads}: 1.82 - 7.87 L $mmol^{-1}$	q_{max}: 134 - 174 mg/g, K_{ads}^{-1}: 0.11 - 1.40 mg/L	q_{max}: 38.61 - 62.11 mg/g, K_{ads}: 0.06 - 0.57 L/mg	q_{max}: 46.02 - 70.32 mg/g, K_{ads}: 0.037 - 0.123 l/mg	q_{max}: 2.03 mg/g, K_{ads}^{-1}: 9.81 mg/L	--	Log K_{ads}: 5.16 - 5.97 L mol^{-1}, q_{max}: 3.73 - 12.80 μmol g^{-1}
Ka, L/g[(2)]	1.93 - 10.78	124 - 1,218	2-11	1.7 - 8.6	0.21	3 - 91	0.54 - 10.26

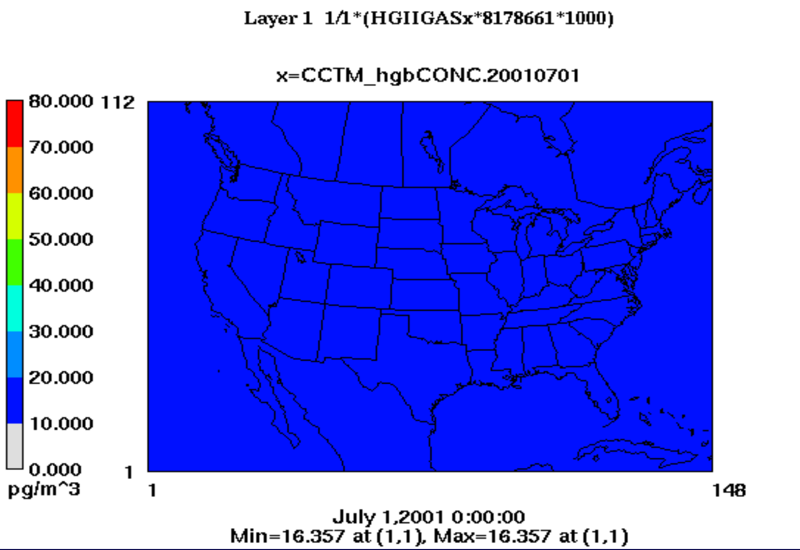
(1) All the sorption models are based on Langmuir isotherm except Seigneur et al. (1998).
(2) The K_a (as shown in Equation 1) values are calculated from the linear range of the Langmuir isotherm using the sorption parameters reported in the sorption models.

Lin *et al.*, 2005

ICONs & BCONs





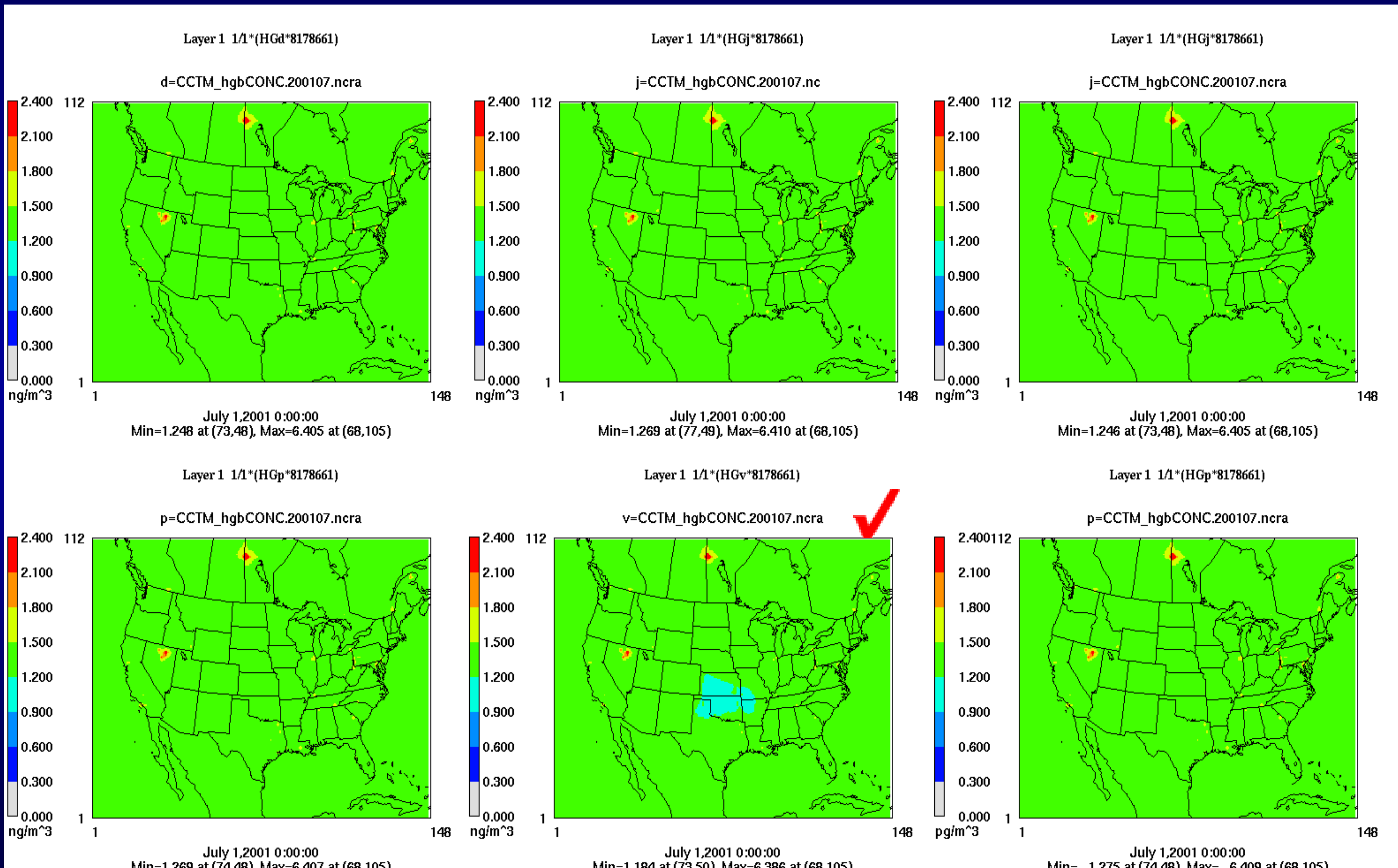


σ layer	*0.98*	*0.93*	*0.84*	*0.60*	*0.30*	*0.00*
HG (ppmv)	1.78 E-07	1.77 E-07	1.76 E-07	1.75 E-07	1.74 E-07	1.73 E-07
HGIIGAS (ppmv)	2.00 E-09	3.00 E-09	4.00 E-09	5.00 E-09	6.00 E-09	7.00 E-09
APHGI (μg/m³)	9.97 E-06	9.48 E-06	8.98 E-06	6.98 E-06	4.49 E-06	1.49 E-06
APHGJ (μg/m³)	9.97 E-06	9.48 E-06	8.98 E-06	6.98 E-06	4.49 E-06	1.49 E-06

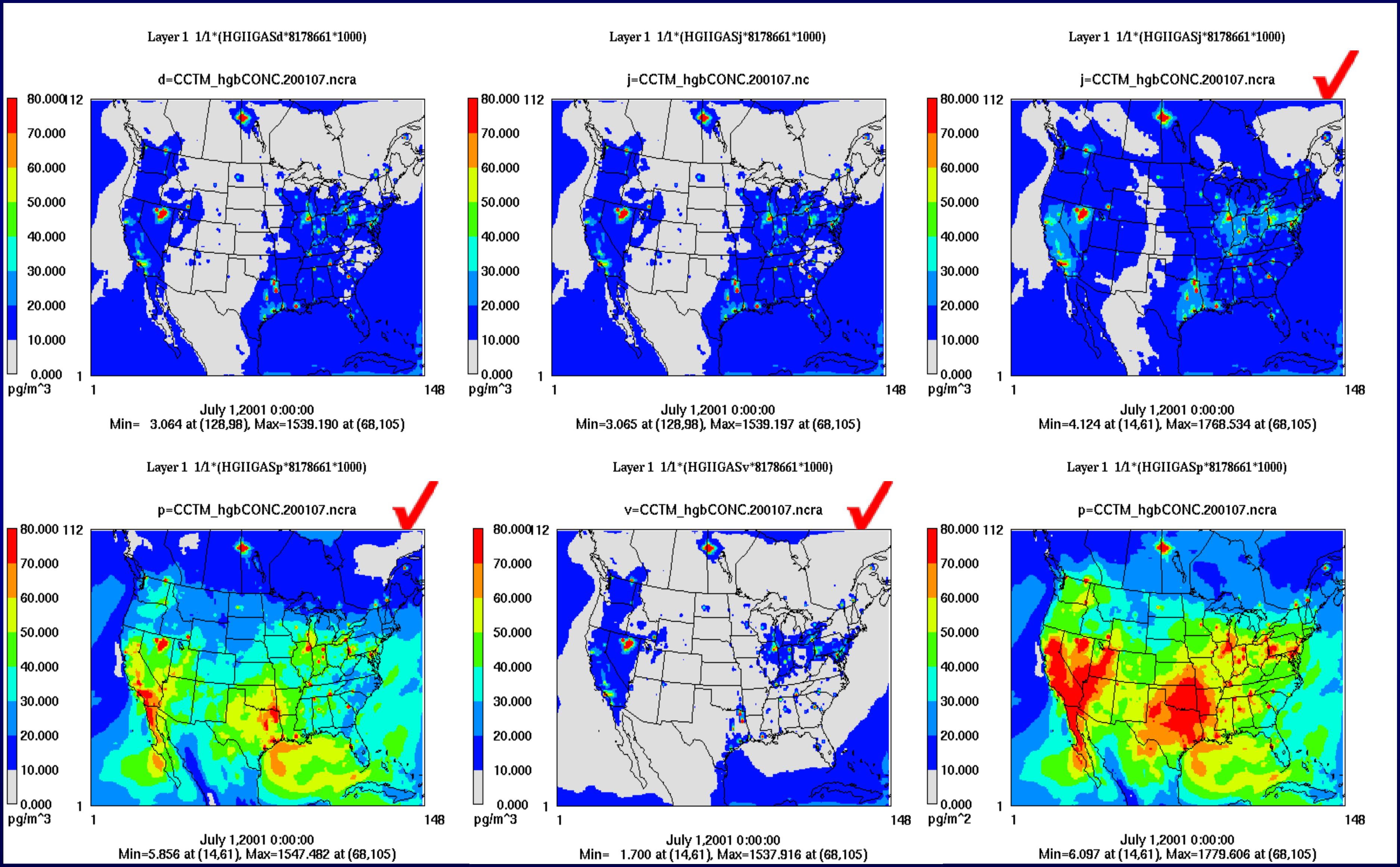
Simulation Results (July 2001)

Case 1 (Bullock & Brehme, 2002)	**Case 2** **(veggie/natural EI)**	**Case 3** **(Dry deposition)**
Case 4 **(Oxidation products)**	**Case 5** ✓ **(Sorption modification)**	**Case 6** **(All combined)**

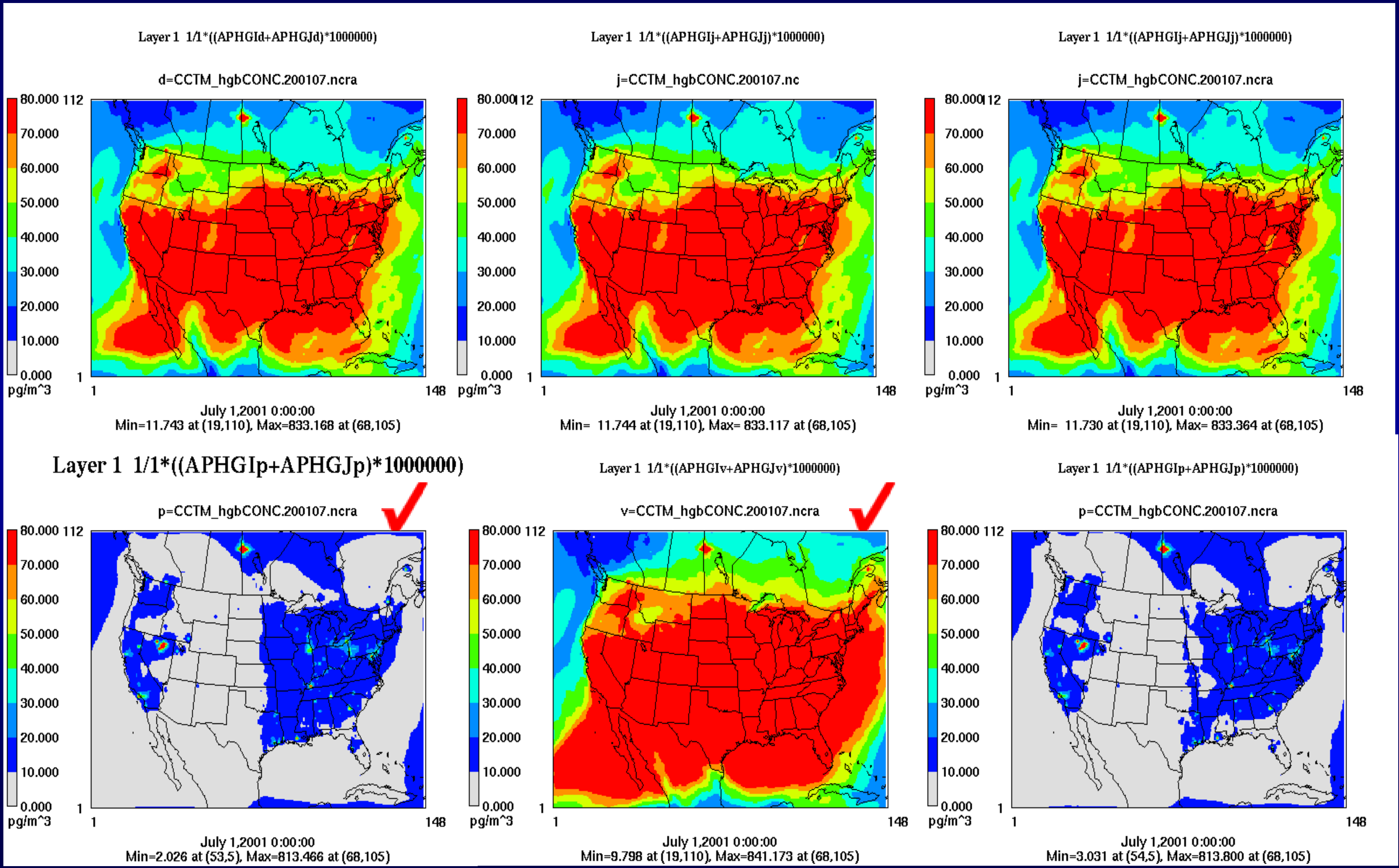
GEM Concentrations



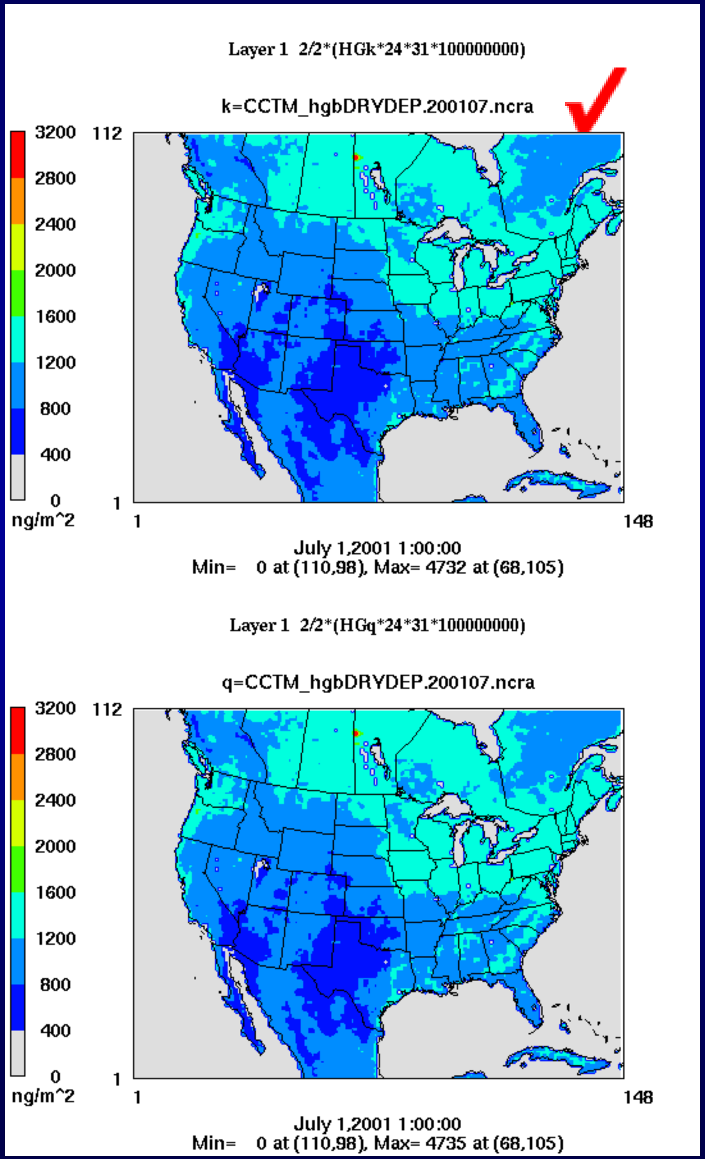
RGM Concentrations



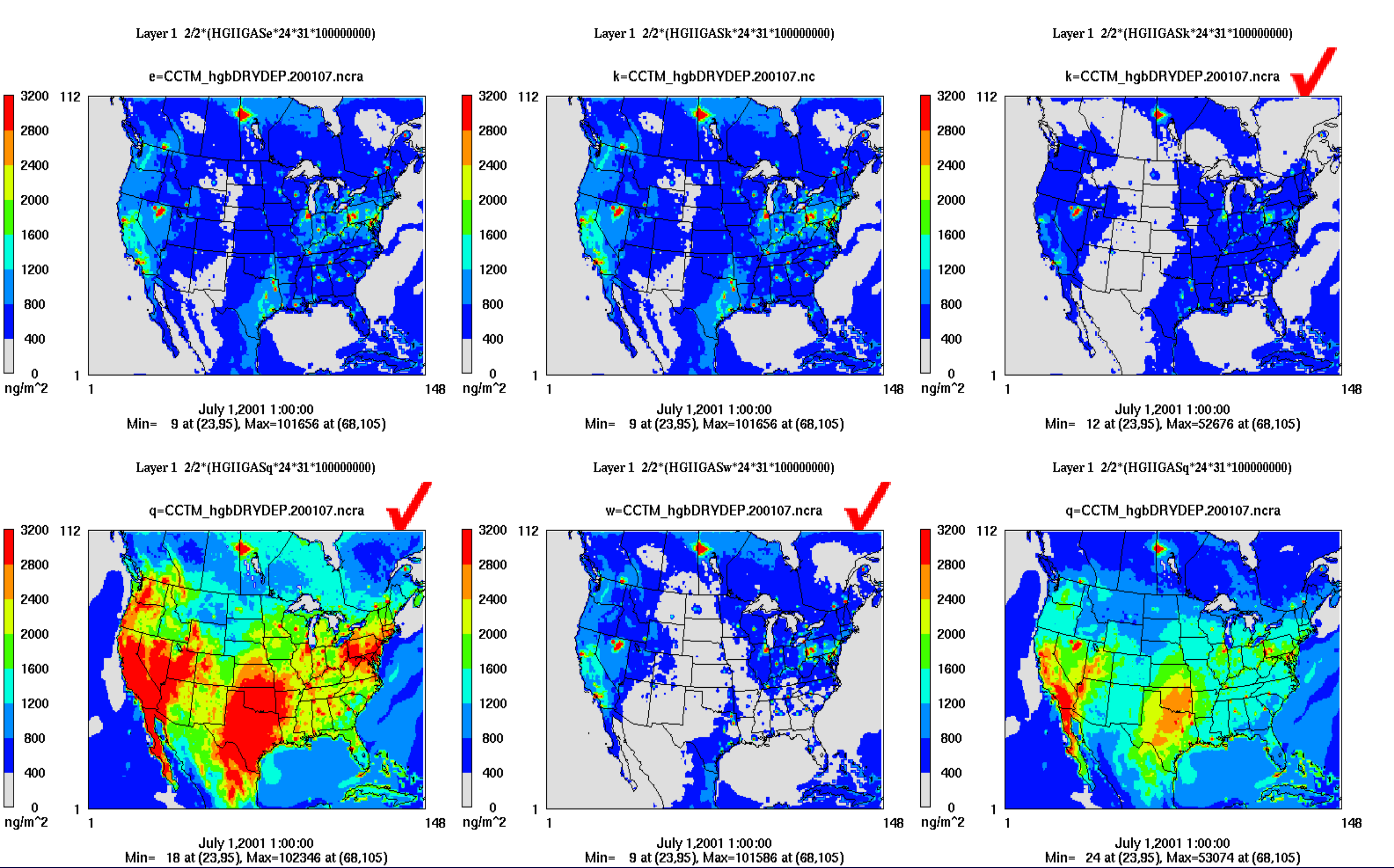
PHg Concentrations



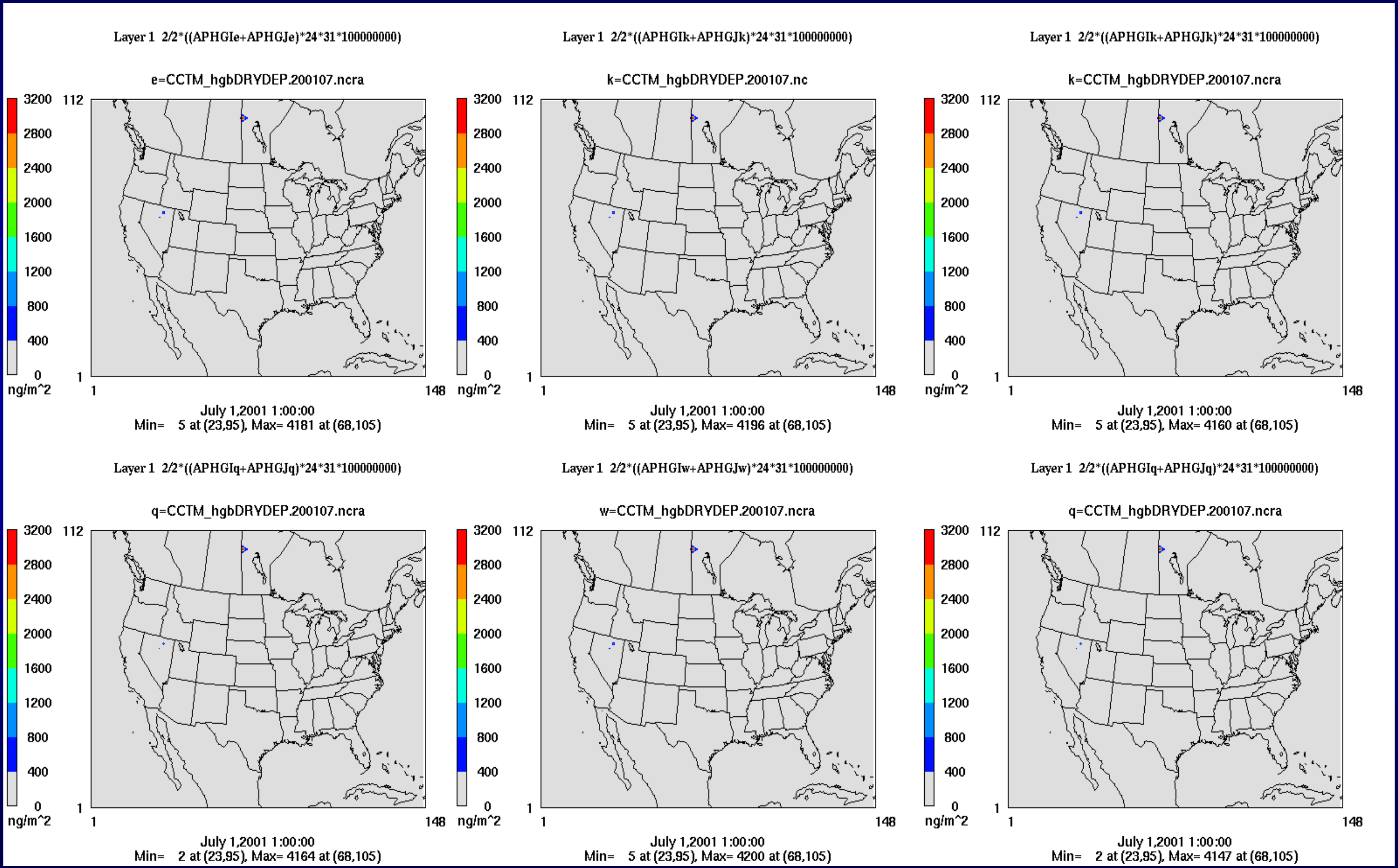
GEM Dry Deposition



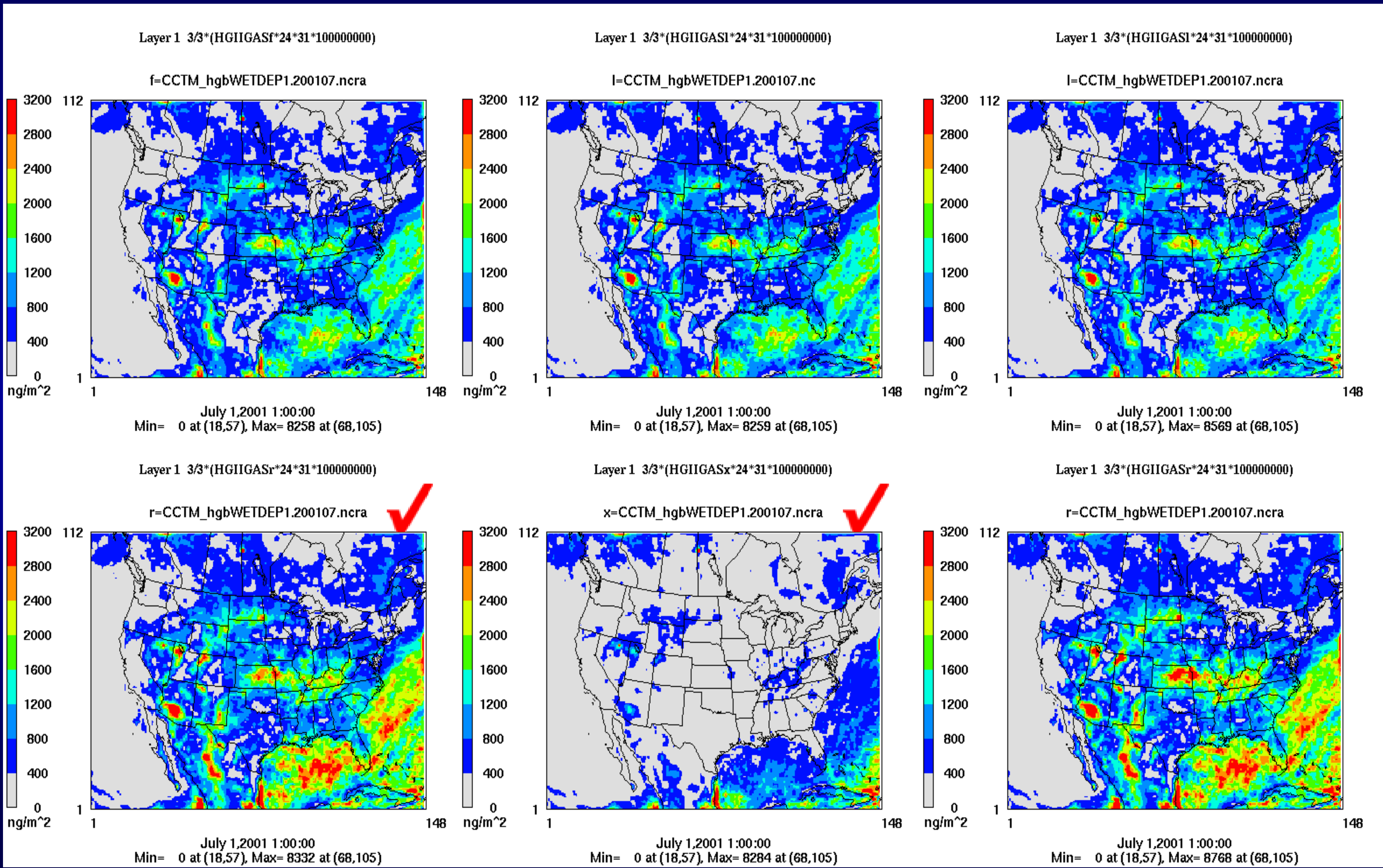
RGM Dry Deposition



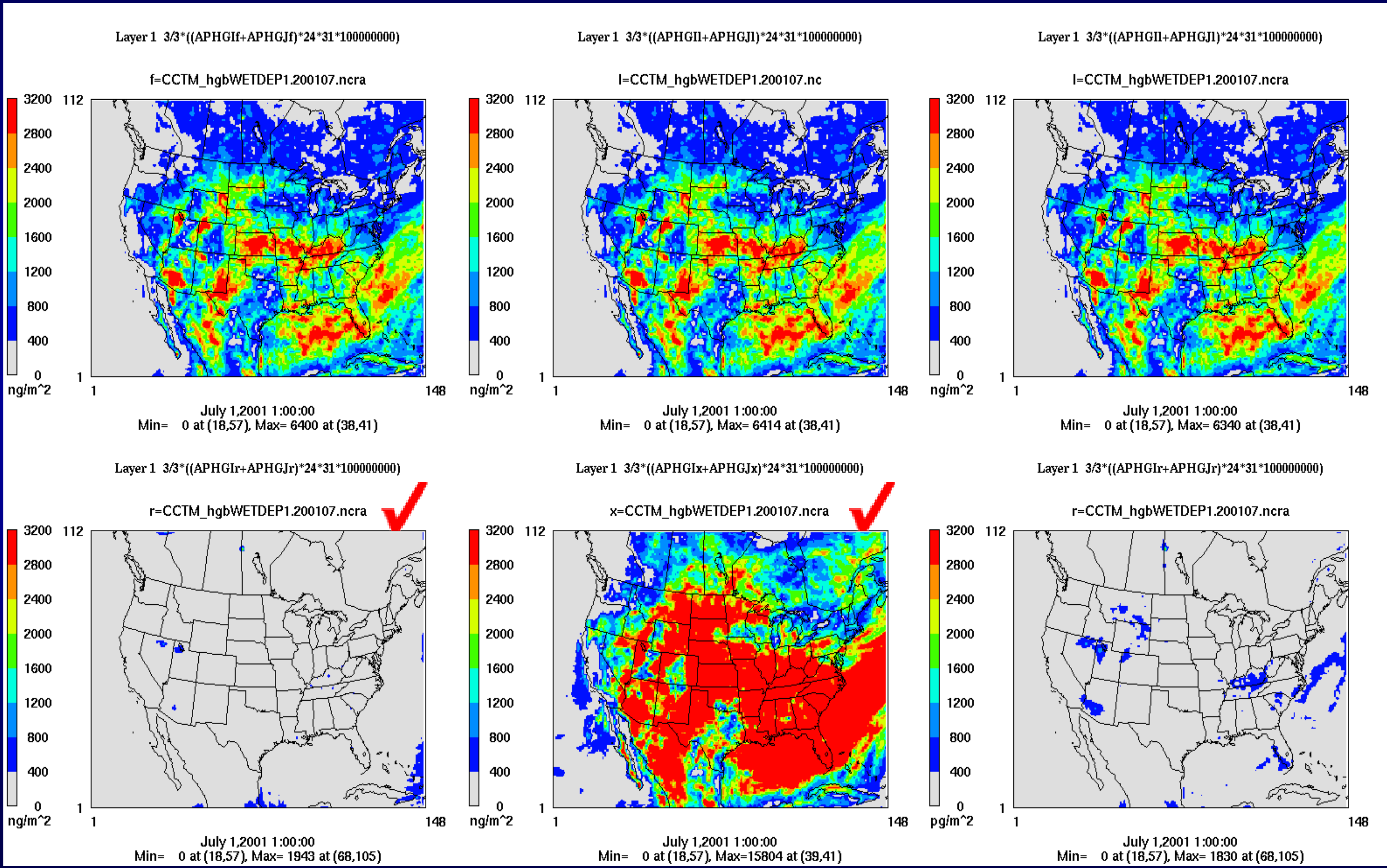
PHg Dry Deposition



RGM Wet Deposition



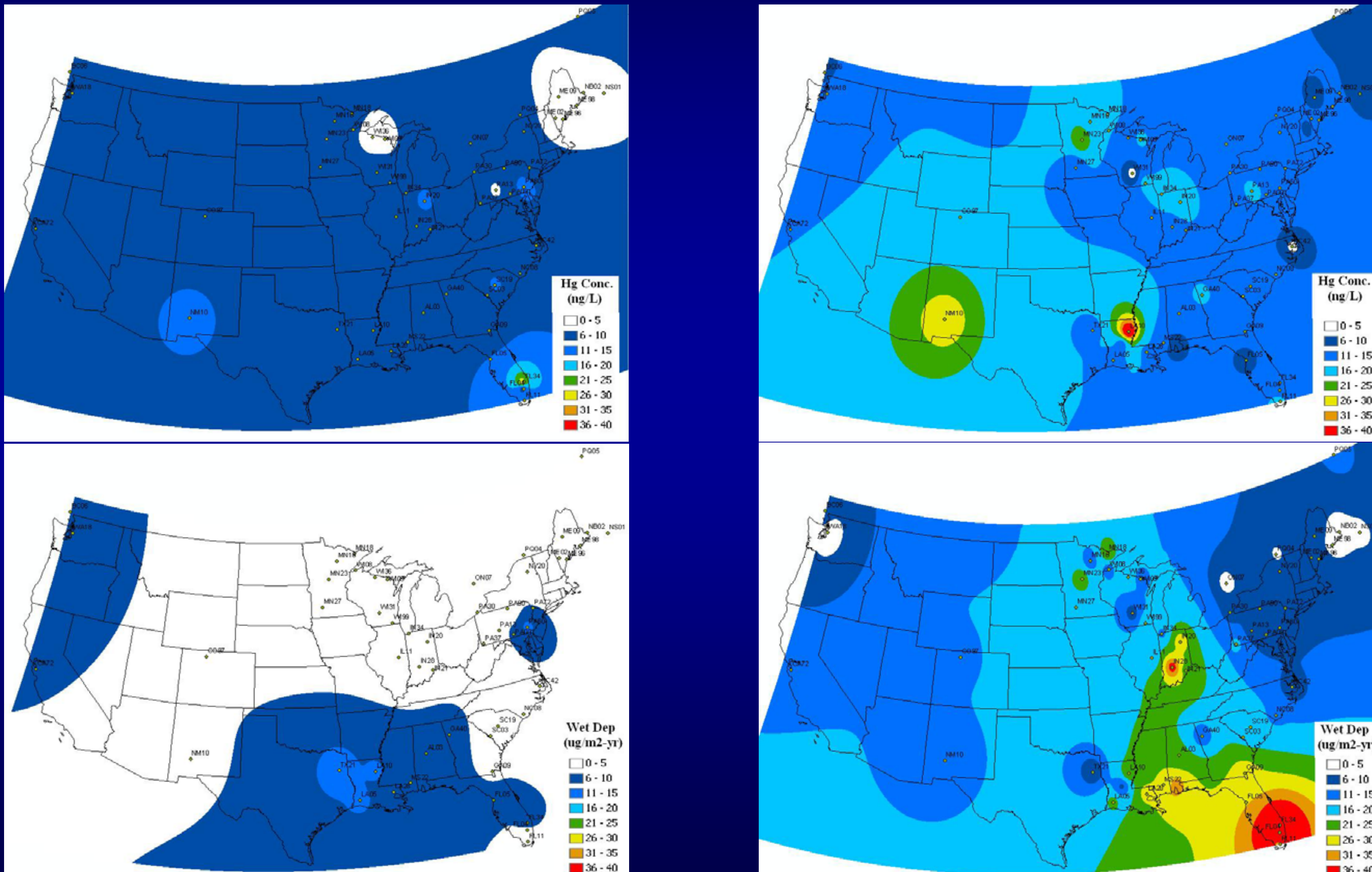
PHg Wet Deposition



Mercury Deposition Network

- National network
- Started in 1995 at 13 sites
- Currently 89 active sites
- Monitors wet deposition of Hg and Me-Hg
- Weekly data in precipitation
- Weekly aqueous Hg concentrations
- Operated by Frontier Geosciences

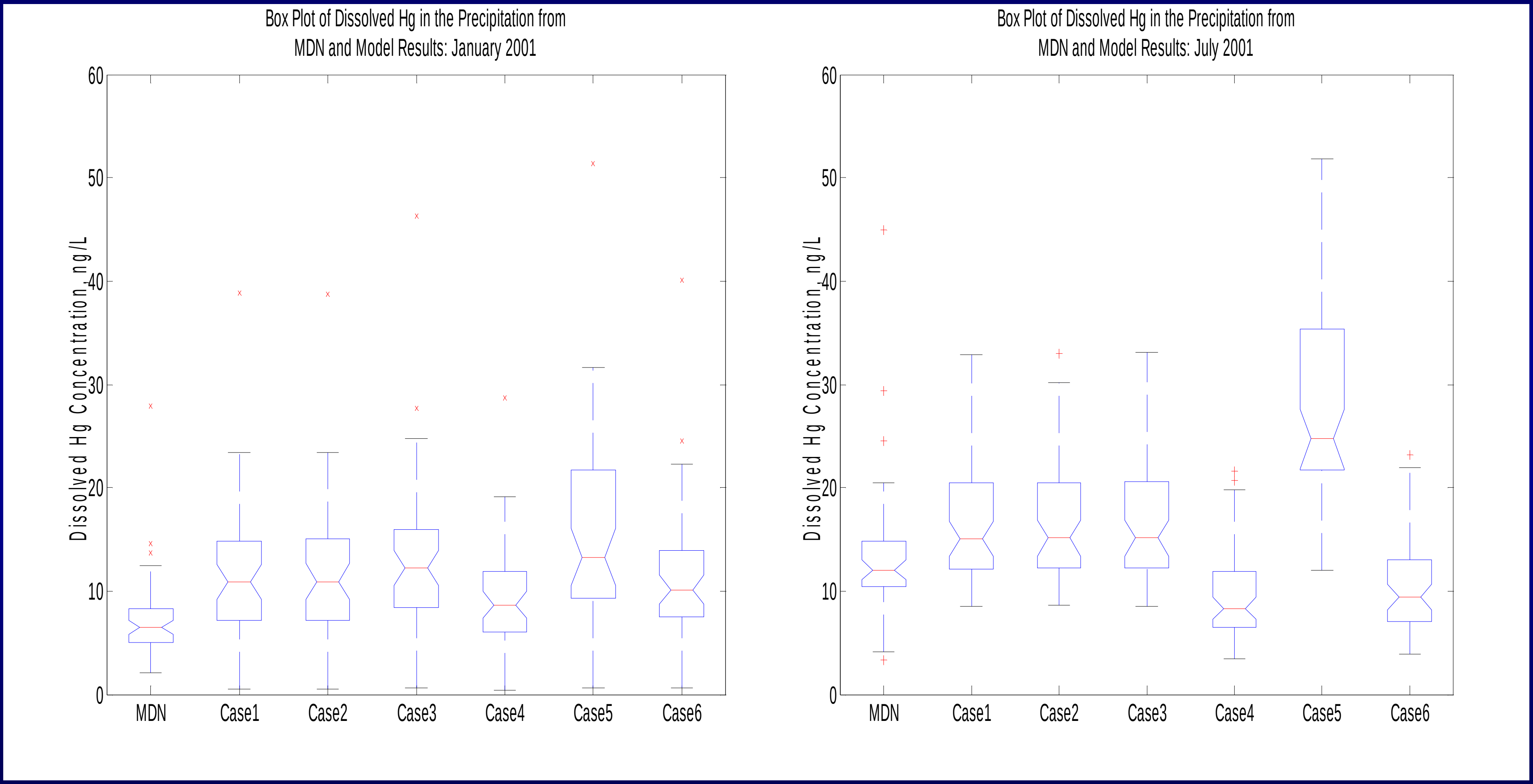
Interpolated Aqueous Concentration Wet Deposition of Hg from MDN Data



January 2001

July 2001

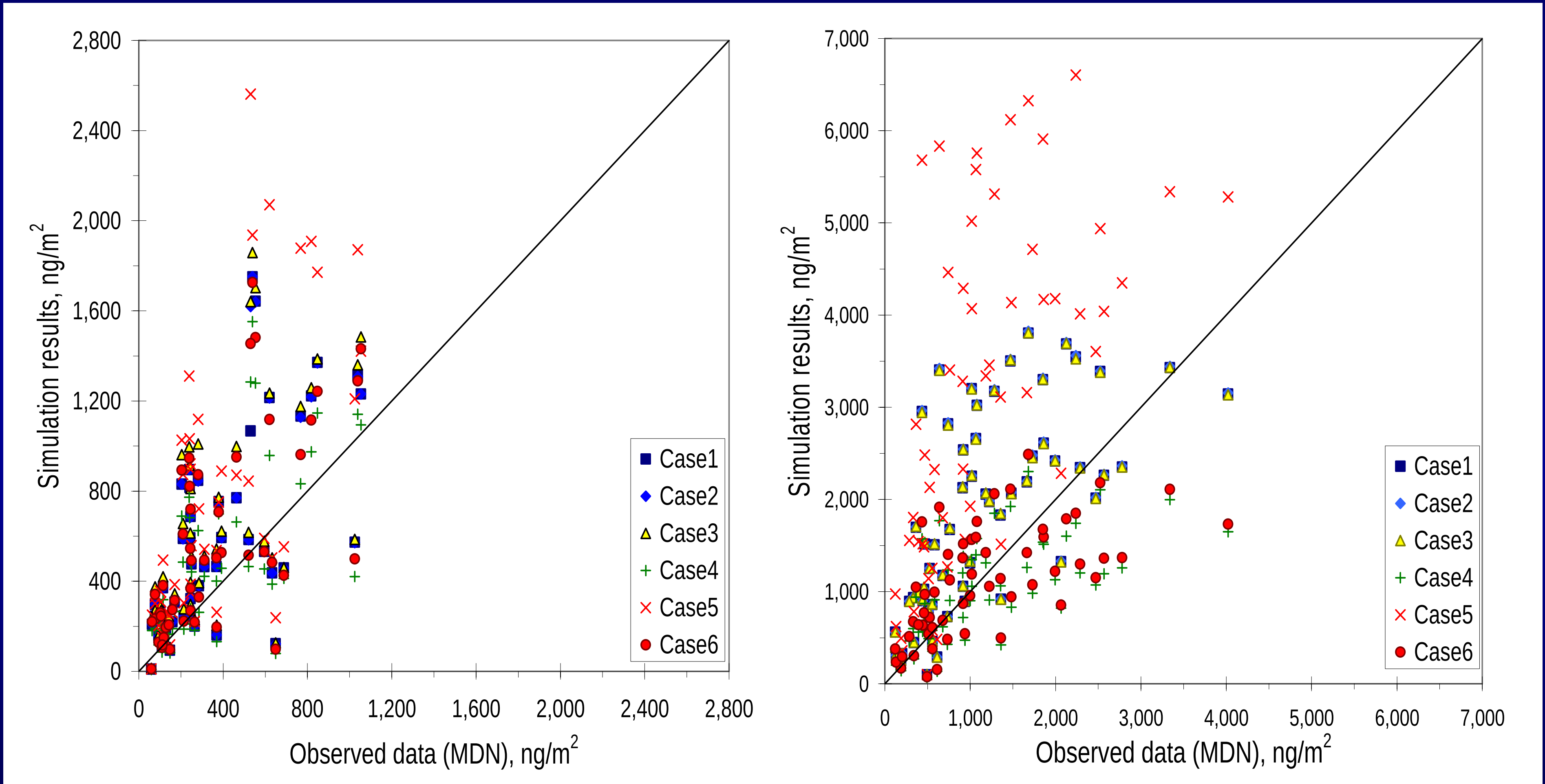
Model Verification – Aqueous Conc.



January 2001

July 2001

Model Verification – Wet Deposition



January 2001 **July 2001**

Key Conclusions

- Mercury emission does not significantly change total ambient Hg concentration except near major point sources.
- Photochemical activities enhance mercury deposition.
- Atmospheric deposition (wet and dry) is forced mainly by chemistry except near major point sources.
- Vegetative Hg emission does not contribute significantly to Hg deposition, instead, it only slightly increases the concentration of GEM.
- The speciation of oxidized mercury products (RGM vs. PHg) has a strong effect on the relative concentration of RGM and PHg as well as their deposition intensity.
- Sorption/desorption equilibrium strongly affects the composition of deposited mercury in wet deposition. More experimental data are needed for further implementation.
- The science update development in this study shows improvement over the original CMAQ-Hg model.