CMAQ Modeling of Atmospheric Mercury

CMAQ Model Peer Review – December 17, 2003

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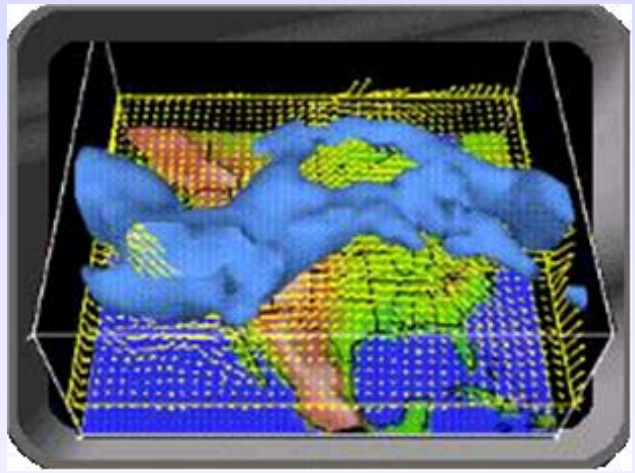
* On assignment to the National Exposure Research Laboratory, U.S. EPA



Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy

Physicochemical Species of Mercury Added to the Standard CMAQ

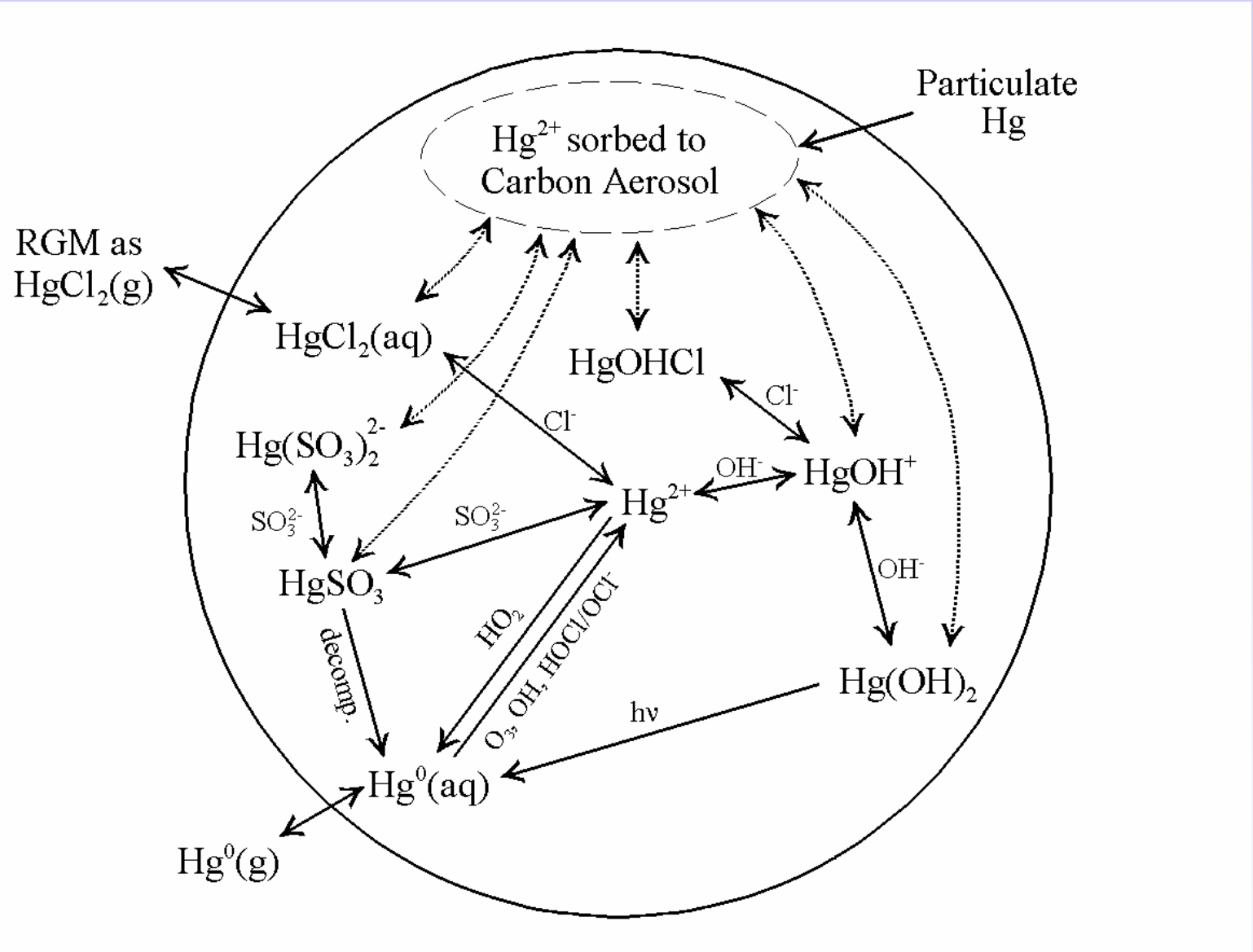
- Elemental Mercury (Hg^0)– Mildly reactive gas; sparingly soluble in water; subject to very long range transport throughout the entire atmosphere
- Reactive Gaseous Mercury (RGM) – Common term for unspecified gaseous compounds; water soluble and chemically reactive; readily deposited to water, soils and vegetation by wet and dry atmospheric processes
- Particulate Mercury (PHg)– Unspecified condensed compounds and RGM adsorbed to receptive aerosols; morphology rather uncertain at this time

What are RGM and PHg really?

- RGM is thought to be primarily $HgCl_2$ based on vapor pressure and water solubility data, but could also include small fractions of other compounds.
- PHg is thought to be HgO, HgS and other low vapor pressure compounds plus more volatile compounds (maybe even Hg^0) adsorbed to carbon-rich aerosols.
- No practical air-sampling technology exists to measure the specific compounds comprising either of these species. Thus, CMAQ uses these generalized species for the gaseous-phase.

However, for the aqueous phase, the CMAQ-Hg employs a much more definite mercury speciation.

Aqueous Mercury Chemistry Mechanism for CMAQ-Hg



Hg reactions and rate constants in the CMAQ-Hg model

No.	Reaction	k or K	Reference
Gaseous-phase reaction of Hg			
RG1	$Hg^0_{(g)} + O_{3(g)} \rightarrow PHg$	3.0×10^{-20} cm^3 molec^{-1} s^{-1}	Hall (1995)
RG2	$Hg^0_{(g)} + Cl_{2(g)} \rightarrow RGM$	4.8×10^{-18} cm^3 molec^{-1} s^{-1}	Calhoun and Prestbo (2001)
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	$Hg^0_{(g)} + OH_{(g)} \rightarrow PHg$	8.7×10^{-14} cm^3 molec^{-1} s^{-1}	Sommar *et al.* (2001)
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)
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)
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)
E2	$HgSO_3 + SO_3^{2-} \rightleftharpoons Hg(SO_3)_2^{2-}$	4.0×10^{-12} M	Smith and Martell (1976)
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)

† Rate constant for RA3 is scaled to the cosine of solar zenith angle

Sorption of Aqueous Hg^{2+} Complexes

- Based on work of Seigneur et al. (1998)
- $[Hg^{2+}_S] = K_S[Hg^{2+}_D]$ at equilibrium
- $K_S = 900$ L g^{-1} elemental carbon
- Sorption/desorption time constant = 1 h
- PHg $\rightarrow$ Hg^{2+}_S and RGM $\rightarrow$ Hg^{2+}_D at start of cloud chemistry time split
- $Hg^{2+}_S \rightarrow$ PHg and $Hg^{2+}_D \rightarrow$ RGM at end of cloud chemistry time split

Feedback effects of the Hg chemistry?

- Air concentrations for the Hg species:
  - $Hg^0 \sim 10^{-13}$ (mol/mol)
  - RGM and PHg $\sim 10^{-15}$ (mol/mol)
- Aqueous concentrations are many orders of magnitude less than the standard CMAQ species with which they react.
- Feedback effect was 10^{-4} or less for all criteria pollutants in initial testing.
- For efficiency, Hg chemistry is computed separately with no feedback to standard species.

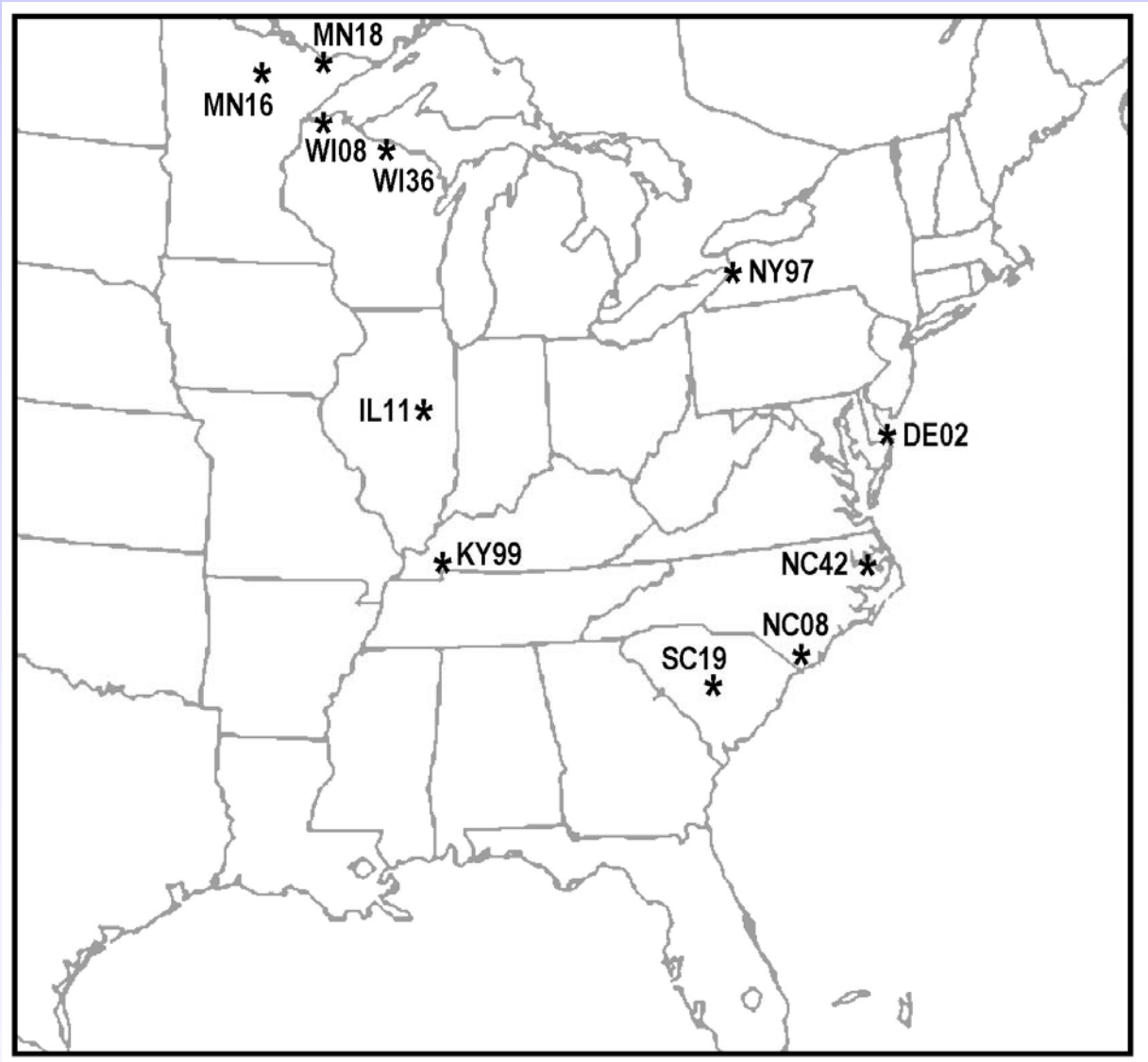
For a more complete description of the CMAQ modifications for atmospheric mercury simulation:

Bullock, O.R., Jr., Brehme, K. A., 2002. Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results. *Atmospheric Environment* **36**, 2135-2146.

Testing the accuracy of the CMAQ-Hg Model

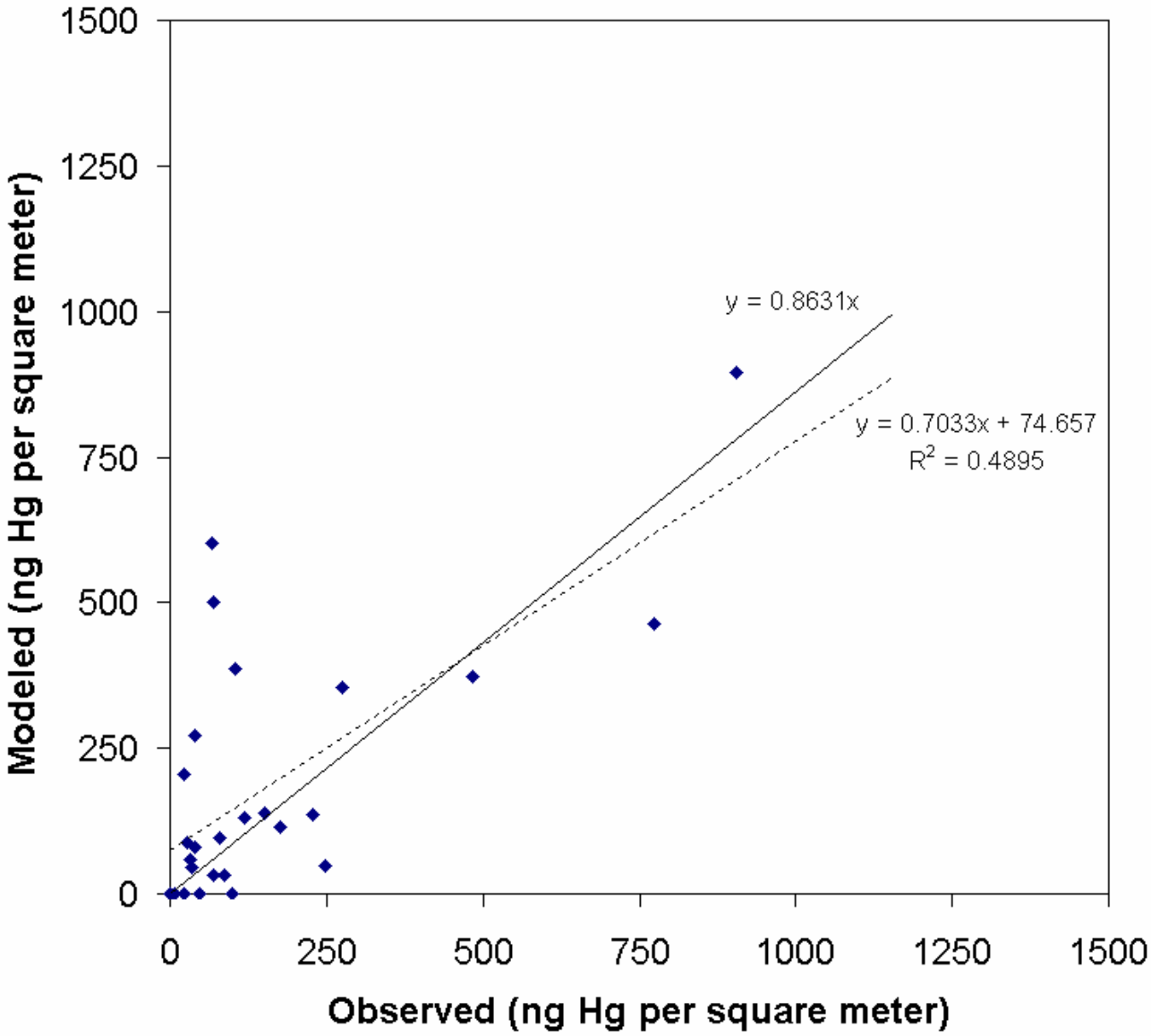
- CMAQ-Hg simulations performed for two four-week test periods in 1995 (April 4 – May 2 and June 20 – July 18)
- Model resolution – Horizontal: 36 km Vertical: 21 layers
- MM5-derived meteorological inputs already available
- Ozone, sulfur, nitrogen, PM emissions already available
- Mercury emissions data for 1995 from the U.S. EPA's Mercury Study Report to Congress (published 1997)
- Simulated wet deposition of mercury compared to ***weekly*** observations from the Mercury Deposition Network

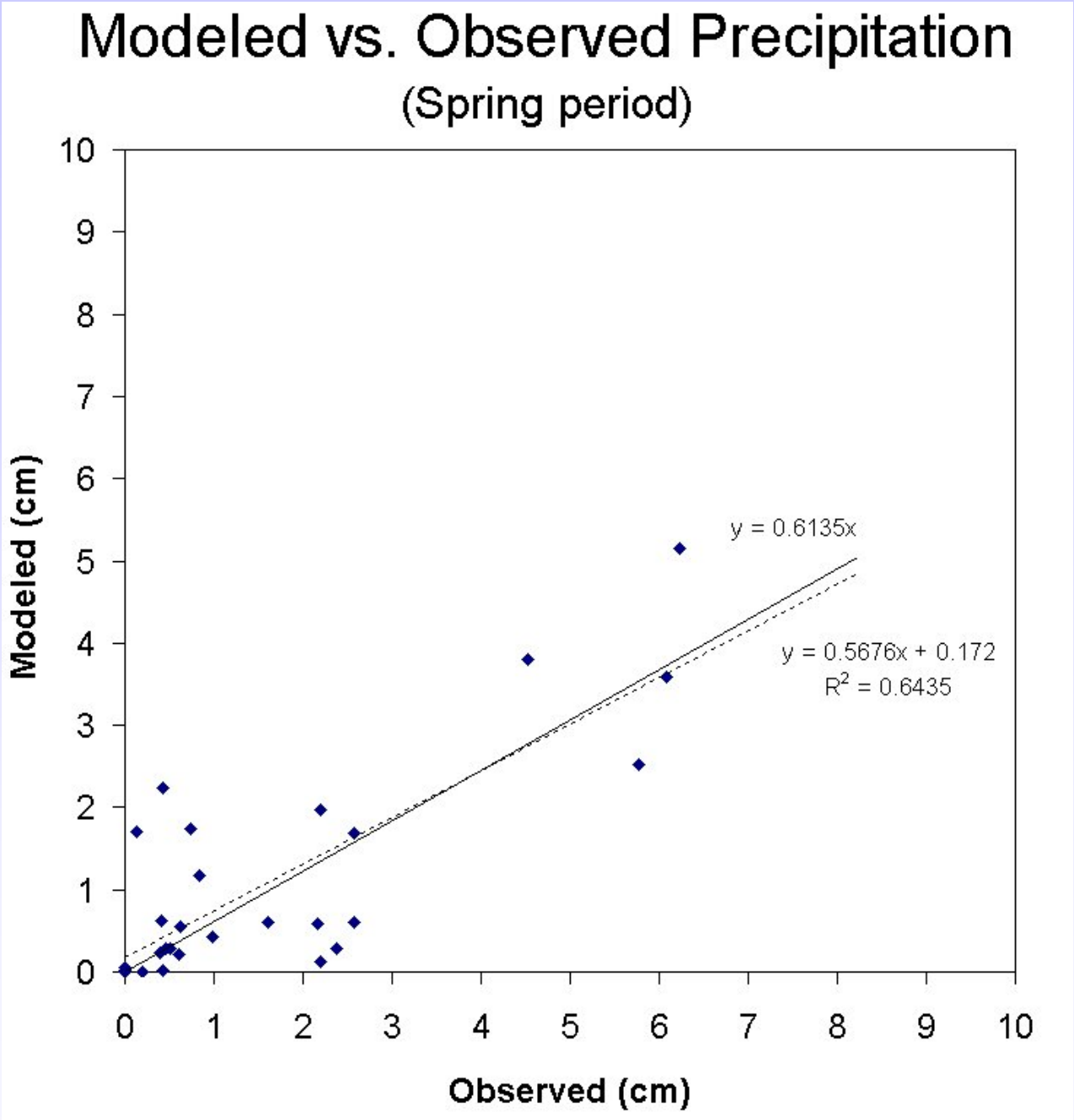
CMAQ-Hg Model Testing Domain



Modeled vs. Observed Wet Deposition of Hg

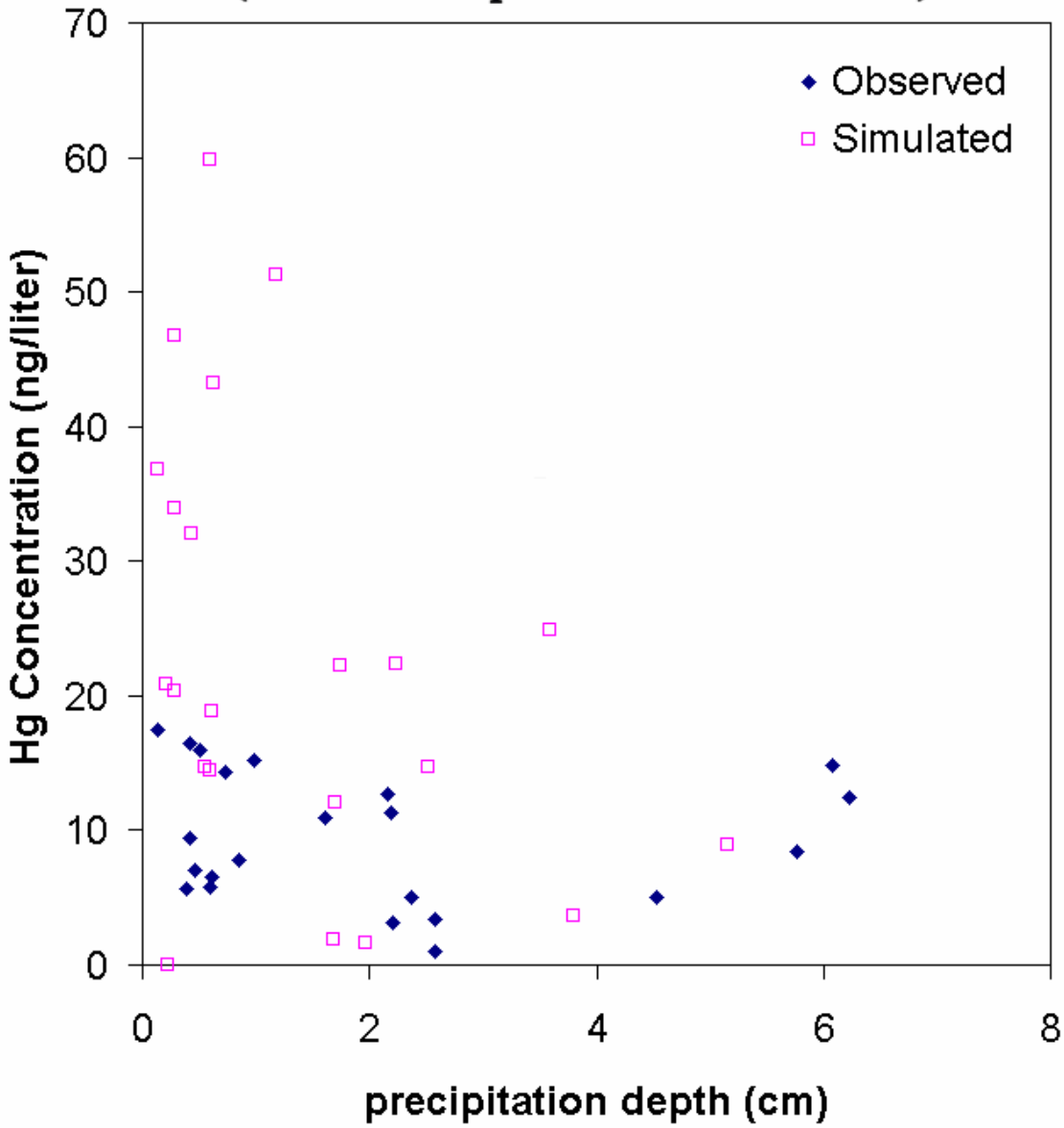
(all MDN samples for 4/4/95 - 5/2/95)




Modeled vs. Observed Precipitation
(Spring period)
Modeled (cm)
Observed (cm)
y = 0.6135x
y = 0.5676x + 0.172
R2 = 0.6435
0
1
2
3
4
5
6
7
8
9
10

Hg Concentration vs. Precipitation Depth

(all MDN samples for 4/4/95 - 5/2/95)



Model Intercomparison in Europe

- *Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury* organized by the Meteorological Synthesizing Center – East (MSC-East) in Moscow, Russia.
- Stage I: Various starting conditions were used in 48-hour test simulations of a closed cloud/fog volume. (results compared among the models)
- Stage II: Full-scale model simulations of two 15-day episodes over central Europe were performed. Comparisons were made to air concentration observations at five sites.
- Stage III (ongoing): One-year simulations with comparison to observed air concentrations (~8 sites) and wet depositions (~8 sites) in Europe.

Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe **EMEP**

Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

Stage I. Comparison of chemical modules for mercury transformations in a cloud/fog environment

A.Ryaboshapko, I.Ilyin, R.Bullock, R.Ebinghaus, K.Lohman, J.Munthe, G.Petersen, C.Segneur, I.Wangberg

Technical Report 2/2001

September 2001

Available on-line at
http://www.msceast.org/publications.html

Meteorological Synthesizing Centre - EAST

Convention on Long-Range Transboundary Air Pollution

emep

Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe

TECHNICAL REPORT 1/2003 June 2003

Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

Stage II. Comparison of modeling results with observations obtained during short-term measuring campaigns

Technical Report 1/2003

A. Ryaboshapko, R. Artz, R. Bullock, J. Christensen, M. Cohen, A. Dastoor, D. Davignon, R. Draxler, R. Ebinghaus, I. Ilyin, J. Munthe, G. Petersen, D. Syrakov

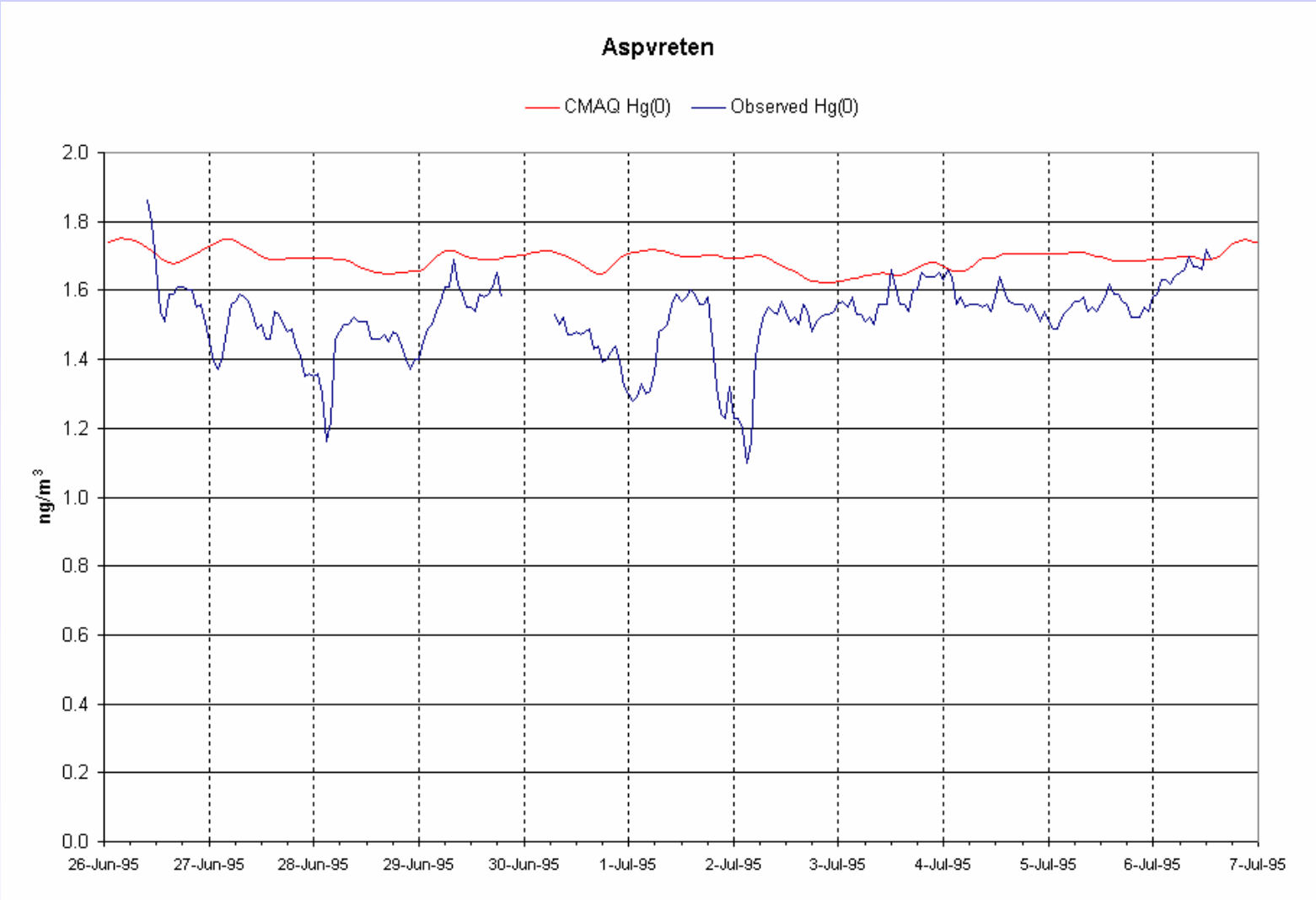
Available on-line at
http://www.msceast.org/publications.html

msc-e

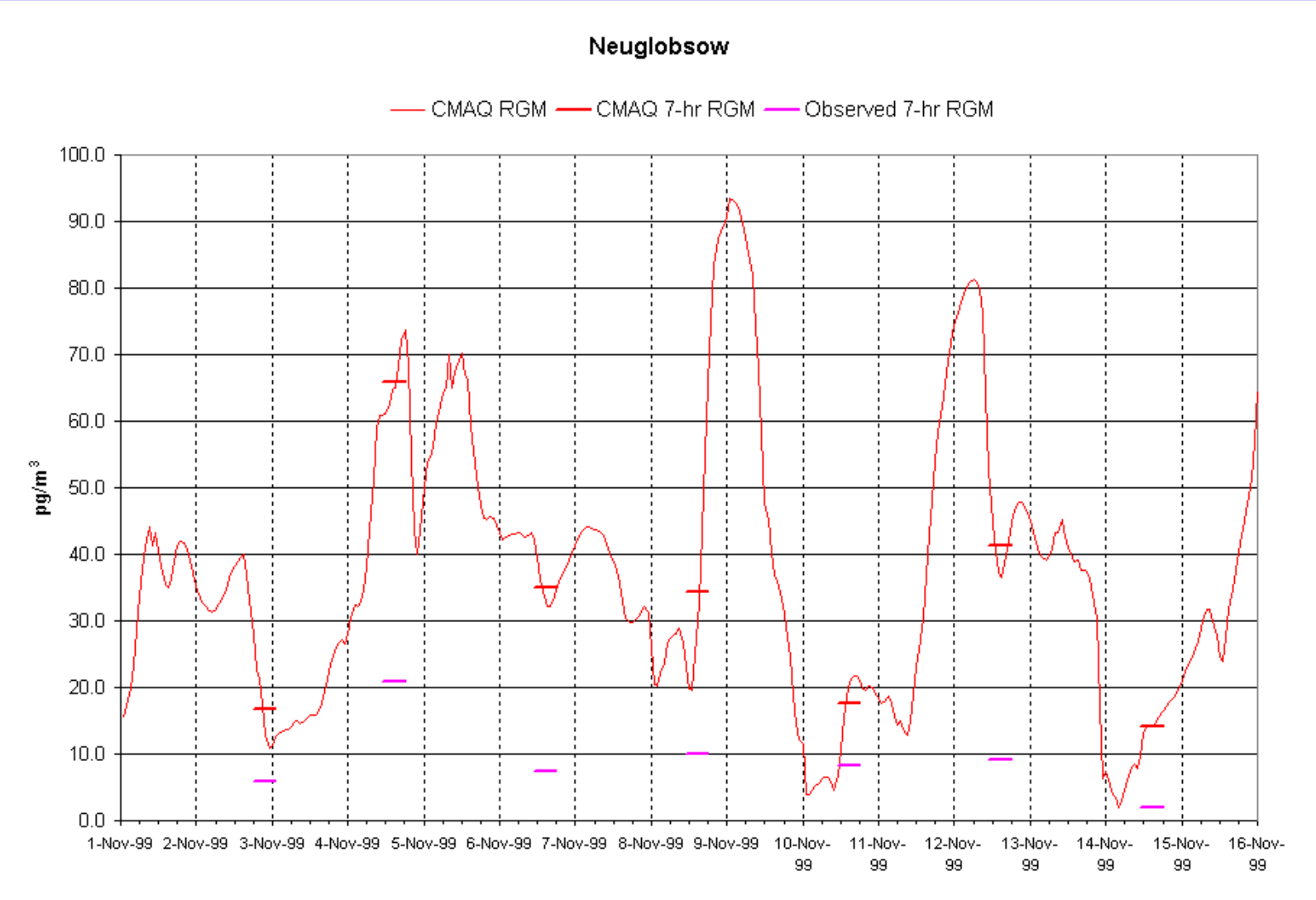
Stage 2: CMAQ-Hg European Domain

With the Mercury Over Europe observation sites

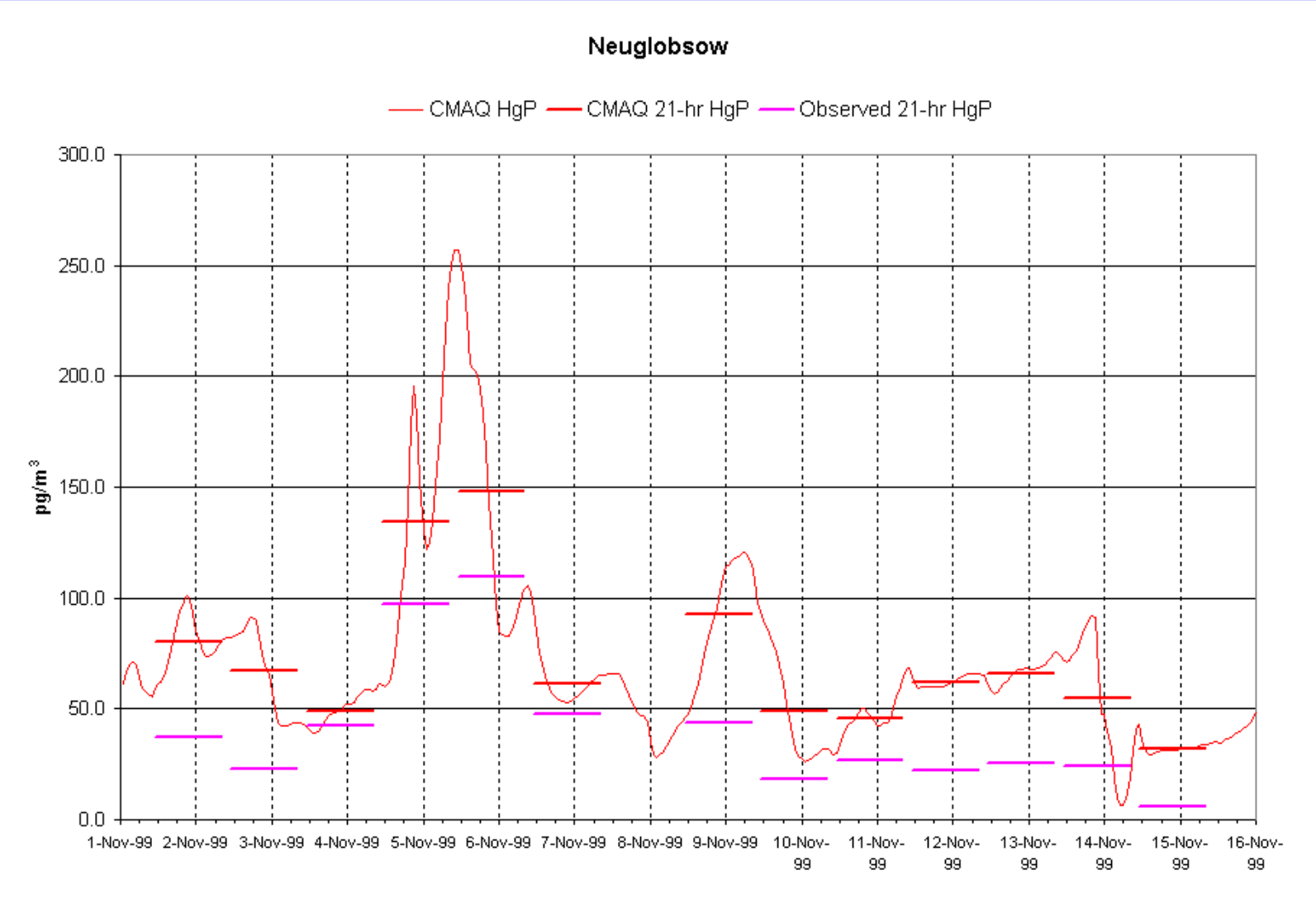
Simulated and Observed Hg^0 for Aspvreten, Sweden



Simulated and Observed RGM for Neuglobsow, Germany



Simulated and Observed TPM for Neuglobsow, Germany



Concluding Remarks

- CMAQ-Hg cloud chemistry model is based on the same set of chemical and physical reactions used in most other state-of-the-science models. However, additional reactions will likely be identified and characterized in the future.
- The cloud model produces total-Hg concentrations that are within the range of values observed in weekly samples of precipitation, but event-based precipitation samples and samples of actual cloud water are lacking.
- Full-scale model results for wet deposition are strongly dependent on the accuracy of the precipitation definition.
- Model accuracy for Hg wet deposition is comparable to that seen in RADM acid rain modeling in the mid-1980's; reasonably accurate in cool seasons, but poor accuracy for warm-season convective precipitation.
- How can we test for accuracy of dry deposition?