

# MODELING THE ATMOSPHERIC FORMATION OF REACTIVE MERCURY IN FLORIDA AND THE GREAT LAKES

## Background

Mercury is one of the most toxic substances in nature and is a potential source of damage in ecosystems, ultimately affecting human health through the food chain. Mercury is introduced to ecosystems through a process that typically involves atmospheric transport and photochemical processing, followed by wet and/or dry deposition.

**Atmospheric mercury** consists of three forms:

- **elemental mercury (Hg<sup>0</sup>)** (with direct emissions, a 1-year atmospheric lifetime and global distribution)
- **reactive mercury (RHG)** (with direct emissions, rapid wet and dry deposition, and a 5-day atmospheric lifetime)
- **particulate mercury (Hgp)** (which rapidly interchanges with RHG).

**Sources of reactive mercury:** Reactive mercury is photochemically produced from Hg<sup>0</sup> through gas-phase and aqueous reactions with OH, O<sub>3</sub>, chlorine, bromine and sulfate. Reactive mercury is also emitted directly into the atmosphere, typically through large point sources.

**Mercury in south Florida:** South Florida has some of the highest wet deposition of mercury to be found in North America. It is unclear to what extent the high deposition rate in south Florida is due to local emission or RHG, and to what extent it is due to photochemical transformation of Hg<sup>0</sup> from the global background.

## Model

Modeling uses a modified version of the Community Model for Air Quality (CMAQ) developed at the University of Michigan.

**Integrated gas- and aqueous-phase photochemistry:** The original CMAQ (Byun and Ching, 1999) calculates gas-phase and aqueous chemistry separately and includes interactions between gas and aqueous phase only on a time scale of 1 hour.

This is replaced with an integrated solution for gas-phase and aqueous chemistry, including rapid exchange between gas and aqueous phases, based on a new solution procedure for photochemical production and loss (Sillman, 1991, Barth et al., 2003).

**The chemical mechanism** includes:

- Gas-phase photochemistry for 120 species and 300 reactions, based on the GEOS-CHEM mechanism (2003 version), expanded to include aromatics and terpenes.

- Aqueous reactions for sulfate and nitrate formation, hydrogen peroxide, O<sub>3</sub>, OH and related radicals, CO<sub>3</sub> and related species, and chlorine (Jacob et al. 1986, Pandis and Seinfeld 1989, Lelieveld et al., 1990, Liu et al. (1997), and Sander and Crutzen, 1996), Bromine is currently being added.

- Gas-phase and aqueous reactions for Hg from Lin et al., 1998a, 1998b, 1999, Pleijel et al. (1995), Gartfeldt et al. (2001), Sommer et al. (2001), Ariya et al., (2002) and Lindberg et al. (2002),

**Model domain:** The model includes the eastern half of the U.S., most of the Gulf of Mexico, and the Atlantic and West Indies as far as 40° W. latitude (See Figure 1). Current results include six vertical layers extending to an altitude of 12 m.

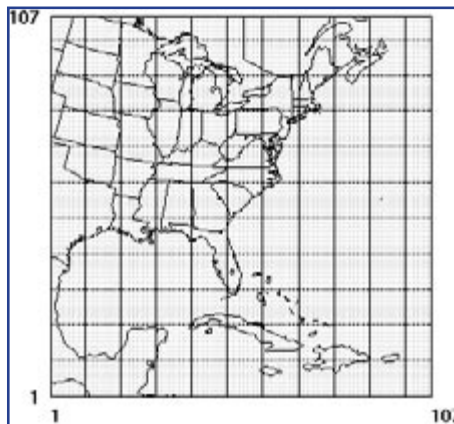


Figure 1. Domain for south Florida model run.

Sanford Sillman<sup>1</sup>, Frank Marsik<sup>1</sup>, Khalid Al-Wali,<sup>1</sup> Matthew S. Landis<sup>2</sup> and Gerald J. Keeler<sup>1</sup>

1. Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, Michigan 48109-2143.  
2. National Environmental Research Laboratory (NERL), Research Triangle Park, NC 27711

## Measurements

Measurements of Hg<sup>0</sup> and RHG were made by aircraft in South Florida during the month of June, 2000, including measurements over rural areas and over the adjacent Atlantic Ocean, at heights up to 4000 m.

## Results

**Variation of RHG with altitude:**

Model results and atmospheric measurements both show higher RHG at altitudes above the boundary layer (>2 km) compared to RHG in the boundary layer.

Model RHG increases from 10 pg/m<sup>3</sup> near the surface to 40 pg/m<sup>3</sup> at 3 km.

Aircraft measurements were made over south Florida and the adjacent Atlantic Ocean throughout the month of June. Measured values below 1 km are 5-40 pg/m<sup>3</sup>, a range that is consistent with measurements. Measurements are 60-250 pg/m<sup>3</sup>. Model values correspond to the lowest range of measurements.

The model does not explain the occasional very high RHG (>200 pg/m<sup>3</sup>) found by the aircraft measurements.

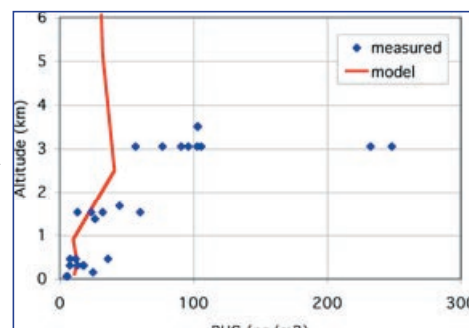


Figure 2. Total reactive mercury (picograms/m<sup>3</sup>) versus altitude (km) from aircraft-based measurements over south Florida and the adjacent Atlantic Ocean during June, 2000 (X's). The solid line shows model values for June 12, 2000

**Spatial variation: regions of high and low RHG:**

Model results at 3 km show significant spatial variation in RHG, with frequent high (40-60 pg/m<sup>3</sup>) and low (5-20 pg/m<sup>3</sup>) values. For the modeled episode, the highest RHG occurs over the Atlantic Ocean (Figure 3).

The pattern of high and low reactive mercury closely corresponds to the pattern of cloudiness (Figure 4). High reactive mercury corresponds to regions without clouds.

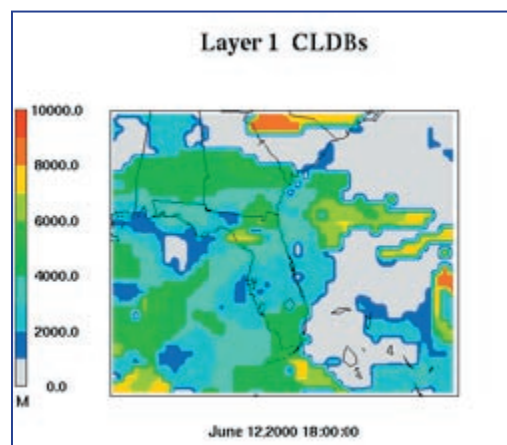


Figure 4. Altitude of the lowest cloud layer (m) over Florida and the adjacent Atlantic Ocean on June 12, 2000. A value of zero represents no clouds

**Impact of photochemical processes:** RHG is produced from Hg<sup>0</sup> primarily through gas-phase chemistry.

Aqueous-phase chemistry acts primarily to convert RHG back to Hg<sup>0</sup>.

This is illustrated with two model scenarios: (i) a scenario which includes gas-phase chemistry only, and (ii) a scenario with no chemistry (emissions, transport and deposition only).

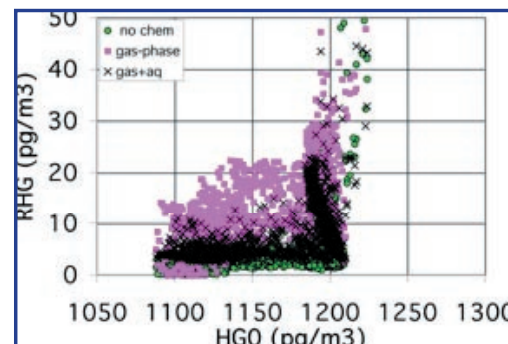


Figure 5. Model correlation between elemental (Hg<sup>0</sup>) and reactive mercury (RHG, both in picograms/m<sup>3</sup>) at 3000 m., Florida and adjacent Atlantic Ocean, June 12, 2000 at 4 pm. The X's represent the standard scenario (including both gas and aqueous chemistry). The pink squares represent a scenario with gas-phase chemistry only. Green circles represent a scenario with no chemistry (emissions, deposition and transport only). Each point represents an individual model location.

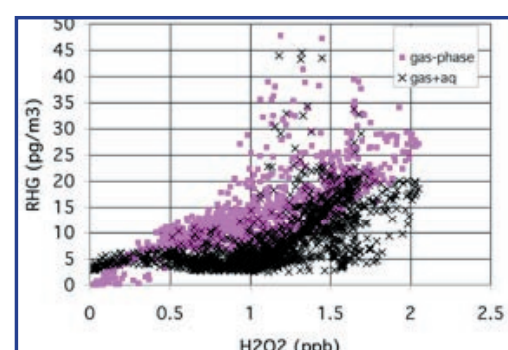


Figure 6. Model correlation between H<sub>2</sub>O<sub>2</sub> (ppb) and reactive mercury (RHG, picograms/m<sup>3</sup>) at 3000 m., Florida and adjacent Atlantic Ocean, June 12, 2000 at 4 pm. The X's represent the standard scenario (including both gas and aqueous chemistry). The pink squares represent a scenario with gas-phase chemistry only.

The correlation between RHG and H<sub>2</sub>O<sub>2</sub> is weaker in the standard scenario (with gas and aqueous chemistry). RHG is removed through aqueous chemistry, and this removal process does not correlate well with H<sub>2</sub>O<sub>2</sub>.

This pattern can be clarified by examining the change in RHG between different model scenarios (Figure 7). The scenario with gas-phase chemistry always has higher RHG than the scenario with no chemistry at all, and the increase in RHG is strongly correlated with model H<sub>2</sub>O<sub>2</sub>. The H<sub>2</sub>O<sub>2</sub> serves as a rough indicator of photochemical activity since the last rain event.

When aqueous chemistry is added to the model, RHG is reduced almost everywhere. Combined gas+aqueous chemistry shows a weaker correlation with H<sub>2</sub>O<sub>2</sub> because the correlation disappears when aqueous chemistry is important.

The scenario with only gas-phase chemistry show much higher RHG than calculations with gas and aqueous chemistry.

The scenario with no chemistry at all shows much lower RHG, demonstrating the importance of chemistry in producing RHG.

However, the highest ambient RHG is virtually identical in scenarios with and without chemistry. This peak ambient RHG (50 pg/m<sup>3</sup>) is associated with direct emissions.

**Correlations between RHG and other species:** No clear correlation is found between RHG and other species (O<sub>3</sub>, SO<sub>x</sub>, CO) in the model.

An ambiguous correlation is found between RHG and H<sub>2</sub>O<sub>2</sub> (Figure 6).

A stronger correlation between RHG and H<sub>2</sub>O<sub>2</sub> appears in the model scenario with only gas-phase chemistry. Here, RHG increases consistently with increasing H<sub>2</sub>O<sub>2</sub>. Locations with the highest RHG are exceptions to this general pattern (possibly because RHG at these locations is emitted directly rather than photochemically produced).

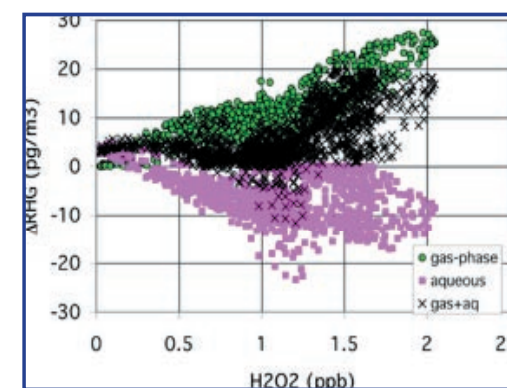


Figure 7. Change in concentration of RHG (picograms/m<sup>3</sup>) associated with various model scenarios, plotted against model H<sub>2</sub>O<sub>2</sub> (ppb) for 3000 m., Florida and the adjacent Atlantic Ocean, on June 12, 2000. The green circles represent the difference between the standard scenario (with gas and aqueous chemistry) and the scenario with gas-phase chemistry only. The pink squares represent the difference between the standard scenario (with gas and aqueous chemistry) and the scenario with no chemistry. The X's represent the difference between the standard scenario and the scenario with no chemistry. Each point represents the difference between values at a single model location.

## Conclusions

Preliminary results suggest that RHG in Florida is affected by both chemical production (derived primarily from global background elemental Hg) and by local direct emission of RHG.

Model results predict higher RHG concentrations at 3000 m. than within the boundary layer. Aircraft measurements in south Florida also showed higher concentrations at higher elevations. However, the increase in RHG with altitude was higher in the measurements than in the model. The model also cannot predict the measured peak RHG (200 pg/m<sup>3</sup>), which was found at 3000 m.

No significant correlations were found between RHG and other species in the model (including SO<sub>x</sub>, NO<sub>y</sub>, O<sub>3</sub> and CO) which might have provided evidence for the source of RHG. A weak correlation was found between RHG and H<sub>2</sub>O<sub>2</sub>. This correlation is associated with photochemical production of RHG, but the correlation is weaker when RHG has been affected by aqueous reactions.

## Future activities and critical issues

The model is being expanded to include (i) Bromine chemistry and (ii) particulate Hg. A future scenario will test for the impact of the reaction of RHG with aqueous HO<sub>2</sub> and with O<sub>2</sub>. This reaction is a major channel for converting RHG back to Hg<sup>0</sup>. Recently Gartfeldt et al. (2003) questioned whether this reaction is valid.

Correlation patterns are being sought that would help to distinguish chemically produced RHG from directly emitted RHG.

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## References

- Ariya, P. A.; Khalizov, A.; Gidas, A., Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Kinetics, Product Studies, and Atmospheric Implications, *J. Phys. Chem. A*, 106 (32): 7310-7320, 2002.
- Barth, M., S. Sillman, R. Hudman, M. Z. Jacobson, C.-H. Kim, A. Monod, J. Liang, Summary of the cloud chemistry modeling intercomparison: Photochemical box model calculation. *J. Geophys. Res.*, 108(D7), 4214, doi:10.1029/2002JD002673, 2003.
- Byun, D. W., and J. K. S. Ching, Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) modeling system, EPA/600/R-99/030, Off. of Res. and Dev., U.S. Environ. Prot. Agency, Washington, DC, 1999.
- Fiore, A., and D. J. Jacob, (2001) *The GEOS-CHEM chemical mechanism version 5-07-8*, Harvard University, Cambridge, MA, USA.
- Gartfeldt, K.; Jonsson, M.; Is Bimolecular Reduction of Hg(II) Complexes Possible in Aqueous Systems of Environmental Importance, *J. Phys. Chem. A*, 107 (22): 4478-4482, 2003.
- Gartfeldt, K., Sommar, J., Stromberg D., Feng X., Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase. *Environment*, 35, 3039-3047, 2001.
- Horowitz, L., J. Liang, G. Gardner, and D. Jacob (1998), Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, *J. Geophys. Res.*, 103(D11), 13,451-13,476.
- Jacob, D. J., Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *Journal of Geophysical Research*, 91, 9807-9826, 1986.
- Khalizov, A. F.; Viswanathan, B.; Larregaray, P.; Ariya, P. A.; A Theoretical Study on the Reactions of Hg with Halogens: Atmospheric Implications, *J. Phys. Chem. A*, 107 (33): 6360-6365, 2003.
- Lelieveld, J. and Crutzen P. J., Influences of cloud photochemical processes on tropospheric ozone. *Nature*, 343, 227-233, 1990.
- Lin, C.-J and Pehkonen S. O., 1998a. Two-phase model of mercury chemistry in the atmosphere. *Atmospheric Environment*, 32(14/15), 2543-2558.
- Lin, C.-J and Pehkonen S. O., 1998b. Oxidation of elemental mercury by aqueous chlorine (HOCl/OCL<sub>2</sub>): implications for tropospheric mercury chemistry. *Journal of Geophysical Research*, 103(D21), 28093-28102.
- Lin, C.J and Pehkonen S. O., 1999. The chemistry of atmospheric mercury: a review. *Atmospheric Environment*, 33, 2067-2079.
- Lindberg, S. E., Steve Brooks, C.-J. Lin, Karen J. Scott, Matthew S. Landis, Robert K. Stevens, Mike Goodsite, and Andreas Richter, Dynamic Oxidation of Gaseous Mercury in the Arctic Troposphere by Polar Sunrise, *Environ. Sci. Tech.*, 36, 1245-1256, 2002.
- Lindqvist, O. and Rodhe H., Atmospheric mercury - a review. *Tellus*, 27B, 136-159, 1985.
- Liu, X., G. Mauersberger and Moeller D., 1997. The effects of cloud processes on the tropospheric photochemistry: an improvement of the EURAD model with a coupled gaseous and aqueous chemical mechanism. *Atmospheric Environment*, 31, 3119-3135.
- Pandis, S. N., and Seinfeld J. H., Sensitivity analysis of a chemical mechanism for aqueous-phase atmospheric chemistry. *Journal of Geophysical Research*, 94, 1105-1126, 1989.
- Pleijel, K. and Munthe J., 1995. Modeling the atmospheric mercury cycle-chemistry in fog droplets. *Atmospheric Environment*, 29(12), 1441-1457.
- Sander, R. and P. J. Crutzen, Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J. Geophys. Res.*, 101, 9121-9138, 1996.
- Sander, R., W. C. Keene, A. A. P. Pszeny, R. Arimoto, G. P. Ayers, E. Baboukas, J. M. Cainey, P. J. Crutzen, R. A. Duce, G. Hönninger, B. J. Huebert, W. Maenhaut, N. Mihalopoulos, V. C. Turekian, and R. Van Dingenen, Inorganic bromine in the marine boundary layer: a critical review. *Atmos. Chem. Phys. Discuss.*, 3, 2963-3050, 2003.
- Sillman, S. A numerical solution to the equations of tropospheric chemistry based on an analysis of sources and sinks of odd hydrogen. *J. Geophys. Res.*, 96, 20735-20744, 1991.
- Sommar, J., Gartfeldt K., Stromberg D., Feng X., A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. *Environment*, 35, 3049-3054, 2001.