

## **MODELS FOR THE FORMATION AND TRANSPORT OF REACTIVE MERCURY: RESULTS FOR FLORIDA, THE NORTHEASTERN U.S. AND THE ATLANTIC OCEAN**

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## **ABSTRACT**

A photochemistry/transport model has been developed for elemental and reactive mercury (Hg) in the atmosphere and used to simulate events in the eastern U.S. and adjacent Atlantic Ocean. Results are compared to aircraft measurements in south Florida. The model is a modified form of CMAQ with a new solver for integrated gas-phase and aqueous chemistry, including O<sub>3</sub> and precursors, sulfates, chlorine and bromine. The model predicts episodic high reactive Hg (up to 200 pg m<sup>-3</sup>) over the Atlantic Ocean, corresponding to cloud-free periods. Aircraft measurements in South Florida show similar elevated Hg. Reactive Hg is formed photochemically from elemental Hg (Hg(0)) in the gas phase, while aqueous reactions convert reactive Hg back to Hg(0). The model predicts that reactive Hg and Hg(0) will be positively correlated if reactive Hg results from direct emissions and negatively correlated when reactive Hg is produced by photochemistry. The model also predicts that reactive Hg is enhanced by regional pollution events with high O<sub>3</sub>.

## **INTRODUCTION**

Reactive mercury (Hg(II)) in the atmosphere represents both a significant environmental problem and a challenge in terms of science. Elevated levels of Hg(II) are sometimes

associated with direct emissions from localized sources, but can also be produced by photochemical conversion from elemental mercury (Hg(0)). Hg(0) also has direct emissions as its ultimate source, but its atmospheric lifetime (>20 days) is long enough to allow global-scale transport. Total gaseous mercury (TGM) is affected by gas-phase and aqueous photochemical reactions that involve a wide range of species (O<sub>3</sub>, OH, Cl, Br and sulfates).

Here, we present results from a model for atmospheric transport of TGM and related species. The model is a modified version of the Community Model for Air Quality (CMAQ)<sup>1</sup> that includes an integrated solution of gas- and aqueous-phase chemistry. The model has been exercised for 15 days in June 2000 for a domain that includes the eastern U.S., the Gulf of Mexico and large parts of the Atlantic Ocean. Results are compared with aircraft-based measurements in south Florida by the U.S. Environmental Protection Agency.

We have also used the model to predict the impact of atmospheric processes on Hg(II) formation in three different regions: Florida, the northeast and Great Lakes regions of the U.S. The predicted model sensitivities are also linked to correlations between ambient Hg(II) and various species (including Hg(0), H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>). The species correlations are important because they provide a basis for evaluating the accuracy of model predictions concerning the sources of Hg(II).

## **METHODS**

### **Model**

The study uses a modified version of the Community Model for Air Quality (CMAQ)<sup>1</sup> to represent the photochemistry and transport of TGM. The model includes the photochemistry and transport of all major gas-phase species (O<sub>3</sub>, OH, reactive nitrogen, volatile organics) and gas and aerosol versions of sulfates, nitrates, reactive chlorine and bromine (including aqueous chemistry). Wet and dry deposition are included.

The modification to CMAQ includes a new solver for combined gas- and aqueous-phase photochemistry in place of the original CMAQ solvers. The original CMAQ uses separate solutions for gas-phase and aqueous-phase chemistry over one-hour time periods. Interactions between the gas and aqueous phase on time scales smaller than one hour are not included in the calculation.

We have replaced both the gas-phase and aqueous chemistry modules with an integrated solver for gas and aqueous chemistry developed by Sillman<sup>2</sup>. The new module solves the reverse-Euler equations for gas-phase and aqueous chemistry. It uses an iterative solution for summed production and loss of odd hydrogen radicals in place of the standard matrix inversion in order to derive an efficient solution in terms of computation time. The combined gas-aqueous solution calculates gas-aqueous exchange including diffusion limitations and accounts for non-uniform distribution of species within aqueous droplets using methods and approximations developed by Lelieveld and Crutzen<sup>3</sup>.

The remainder of the model uses standard features of the CMAQ modeling package, including the Fifth Generation Pennsylvania State University/National Center for Atmospheric Research (NCAR) Mesoscale Model (MM5) version 3.6 for meteorology and the Sparse Matrix Operator Kernel Emission (SMOKE) for emissions processing.

## Model chemistry

The model chemistry includes a comprehensive list of gas-phase and aqueous reactions for Hg(0) and Hg(II), derived from Lin<sup>4,5,6</sup>, Pleijel<sup>7</sup>, Gartfeldt<sup>8</sup>, Sommer<sup>9</sup>, Ariya<sup>10</sup>, Lindberg<sup>11</sup> and Khalizov<sup>12</sup>, including interactions between mercury, chlorine, bromine and sulfates.

The model also includes aqueous reactions for sulfates, nitrates, hydrogen peroxide, O<sub>3</sub>, and OH and related radicals. The model also includes chlorine and bromine chemistry<sup>13,14</sup>.

Gas-phase photochemistry includes representation of O<sub>3</sub>, reactive nitrogen, CO and a wide range of organics, including organic nitrates and volatile organics from anthropogenic and biogenic sources. The gas-phase chemistry is based on an extended version of the GEOS-CHEM mechanism<sup>15</sup>, which is widely used in global-scale modeling. The extensions include chemistry of aromatics. We have not used the standard mechanisms for urban photochemistry such as CB4 or SAPRC because these methods are not suitable for rural or remote conditions.

Listings of reactions and reaction rates are available at <http://www-personal.engin.umich.edu/~sillman/publications.htm>.

## Emissions

Mercury emissions were derived from EPA's 1999 version 3 Hazardous Air Pollutants (HAP) (<http://www.epa.gov/ttn/chief/net/1999inventory.html#final3haps>). The inventory includes area, point, onroad and non-road mobile sources. While this inventory has no mercury species for the onroad and nonroad mobile sources, the emissions of Hg(0) and Hg(II) and particulate mercury (Hg(p)) are all included for other source categories.

Emissions for other species (NO<sub>x</sub>, volatile organics, sulfates) were derived from the 1999 National Emission Inventory (NEI), version 2 and 3.

## Initial and boundary conditions

Model initial and boundary conditions include Hg(0)=1.6 ng m<sup>-3</sup> and Hg(II)=0.6 pg m<sup>-3</sup>. The latter assumption insures that Hg(II) in the model is almost entirely generated by internal model emissions and photochemistry rather than transported from the outside.

Other initial and boundary conditions include: 40 ppb O<sub>3</sub> (varying with altitude); 0.03 ppb NO<sub>x</sub>; 0.01 ppb Cl<sub>2</sub> and 0.01 ppt Br<sub>2</sub>; and 0.01 ppt HBr<sup>14</sup>. NaCl is represented by assuming an equivalent gas-phase concentration of 0.1 ppb.

## Measurements

Measurements of Hg(0) and Hg(II) 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. These measurements were obtained using collocated Tekran Model 2537A Mercury Analyzers for Hg(0) (with soda and lime traps to prevent collection of Hg(II)) and manual KCl-coated annular denuders for Hg(II).

## Events and model domain

The model domain (see Figure 1, next section) includes the eastern half of the U.S. and adjacent parts of Canada, most of the Gulf of Mexico, and large parts of the Atlantic

Ocean. The domain extends from 15 to 50 degrees North latitude and 55 to 105 degrees West longitude. The large model domain insures that calculations for both Florida and the Great Lakes include photochemical evolution for several days during transport. The model uses coarse horizontal and vertical resolution (36x36 km horizontal; six vertical layers).

The model has been exercised for June 6-14 and June 21-26, 2000, with the first two days of the calculation regarded as spin-up. These time periods include five days for which aircraft measurements in south Florida are available (June 9, 12, 14, 25 and 26). These days also represent a wide variety of meteorological conditions. They include the two days with the highest measured reactive mercury (June 12 and 14), events with significant ozone formation in the eastern U.S. (June 14), events with transport to Florida from the northern U.S. (June 9) and transport from the Atlantic Ocean (June 12, 14, 25 and 26).

## RESULTS AND DISCUSSION

### Model Results -- Reactive Mercury

Model results (Figure 1) show elevated concentrations of Hg(II) forming at 3000 m. altitude. Elevated Hg(II) is especially noteworthy over the Atlantic Ocean, with concentrations above  $100 \text{ pg m}^{-3}$ .

The elevated Hg(II) is intermittent and episodic in nature rather than uniform. Patches of high and low Hg(II) appear in the model predictions, and the regions of high Hg(II) are typically 300-500 km in spatial extent. The patches of high Hg(II) move with the atmospheric circulation, so that individual locations experience intermittent high and low Hg(II).

The elevated Hg(II) is associated with cloud-free regions and with cloud-free periods in the model back-trajectory. Hg(II) accumulates in an air mass as a result of gas-phase photochemistry that converts Hg(0) to Hg(II). The process of gas-phase conversion is relatively slow ( $>20$  day lifetime for Hg(0)). When an air mass encounters a cloud, aqueous chemistry results in a net conversion of Hg(II) back to Hg(0). This conversion process is relatively rapid ( $< 1$  day). Hg(II) is also removed from clouds through wet-deposition processes.

As a result, the regions of low Hg(II) in Figure 1 correspond to either cloudy regions or to locations in which air has recently been processed by clouds. The regions of highest Hg(II) correspond to air that has been subject to gas-phase photochemistry for an extended period of time without any processing by clouds.

In order to identify this photochemical processing in the model, we have added a model tracer for gas-phase photochemical activity. The tracer is produced during each time step in proportion to the gas-phase concentration of OH and is removed very rapidly by aqueous chemistry in cloud droplets, as well as by wet deposition. The tracer is regarded as being highly soluble (with the same Henry's law coefficient as mercuric oxide, HgO). Effectively, the tracer represents cumulative exposure to OH (in ppb-hours) since the air was last subject to aqueous-phase processing by cloud droplets. Hg(II) in the model is strongly correlated with this tracer.

# Layer 4 RGMa

a=CCTM\_e1aCONC.e1e

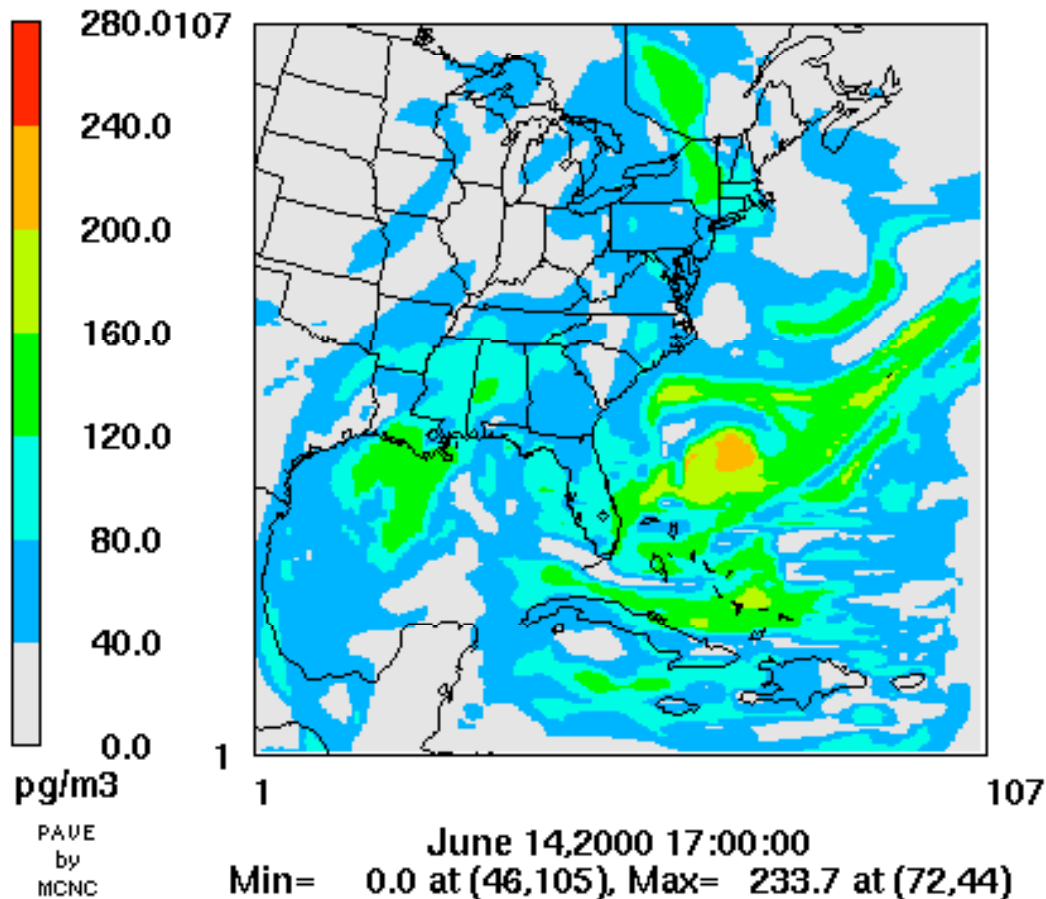


Figure 1. Concentrations of Hg(II) ( $\text{pg m}^{-3}$ ) in the model at 3000 m. altitude for the full model horizontal domain. Results are for 5 pm, June 14, 2000. The colors represent the following concentration intervals: grey, 0-40  $\text{pg m}^{-3}$ ; dark blue, 40-80  $\text{pg m}^{-3}$ ; light blue, 80-120  $\text{pg m}^{-3}$ ; green, 120-160  $\text{pg m}^{-3}$ ; light green, 160-200  $\text{pg m}^{-3}$ ; orange, 200-240  $\text{pg m}^{-3}$ ; red, 240-280  $\text{pg m}^{-3}$ .

## Comparison with Measurements in South Florida

Figures 2 and 3 show a comparison between ambient Hg(II) in the model and measurements obtained during the June, 2000 USEPA airplane flights.

Results show that the model is consistent with measurements in many aspects, although there are also significant discrepancies. Hg(II) increases with altitude from 0 to 3 km in

both the model and in the measured ensemble. The rate of increase vs. altitude is steeper for the ensemble of measurements than for the model, but the comparison is not extensive enough to show whether this is a consistent trend. Individual vertical profiles of Hg(II) in the model sometimes show a complex layered pattern, reflecting cloud layers at various elevations, but this can not be compared to the single layer measurement data.

A direct comparison between model and measured values (paired in time and space) is possible for an ensemble of nine measurements over five days (see Figure 3). For this ensemble the range of model and measured values are similar (15-126  $\text{pg m}^{-3}$  modeled, 8-248  $\text{pg m}^{-3}$  measured). The major discrepancy is the large underestimate by the model in comparison with the highest measured Hg(II) (232 and 248  $\text{pg m}^{-3}$  on June 12 and 14, compared to 87 and 126  $\text{pg m}^{-3}$  modeled). However, the model domain includes Hg(II) up to 233  $\text{pg m}^{-3}$  on these days over the Atlantic Ocean near Florida (see Figure 1).

In terms of EPA performance statistics for the ensemble of nine measurements, the model shows a normalized bias of +0.13 and a normalized gross error of 0.77. This is somewhat misleading because the normalized discrepancy is dominated by a single measurement with very low Hg(II) (7  $\text{pg m}^{-3}$  measured, 36  $\text{pg m}^{-3}$  modeled). If this measurement is omitted the resulting normalized bias is -0.32 and the normalized gross error is 0.40.

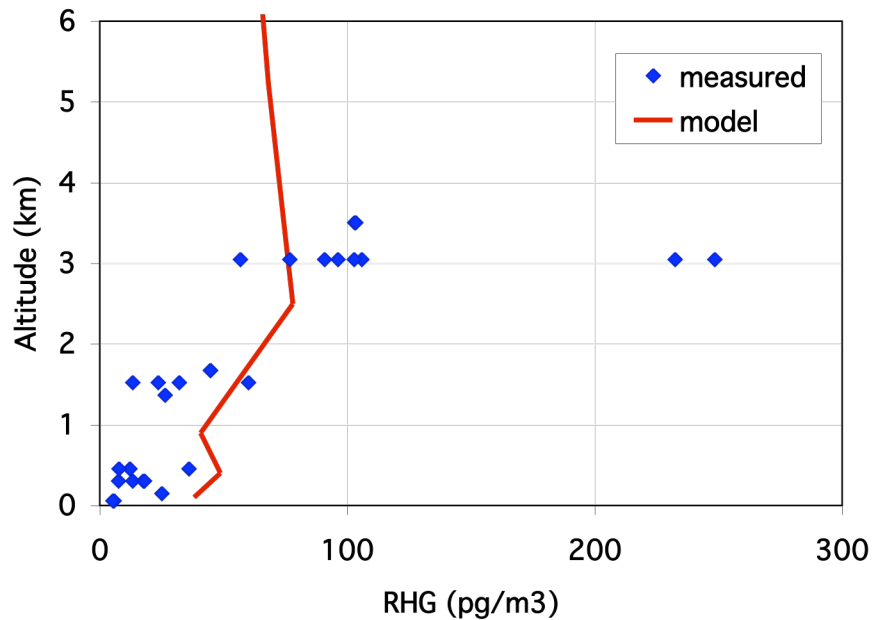


Figure 2. Measured Hg(II) ( $\text{pg m}^{-3}$ ) versus altitude (km) from aircraft measurements over south Florida and the adjacent Atlantic Ocean during June, 2000 (points). The line represents model Hg(II) versus altitude, based on an average of model results during the afternoon on the five days (June 9, 12, 14, 25 and 26) that coincide with measurements.

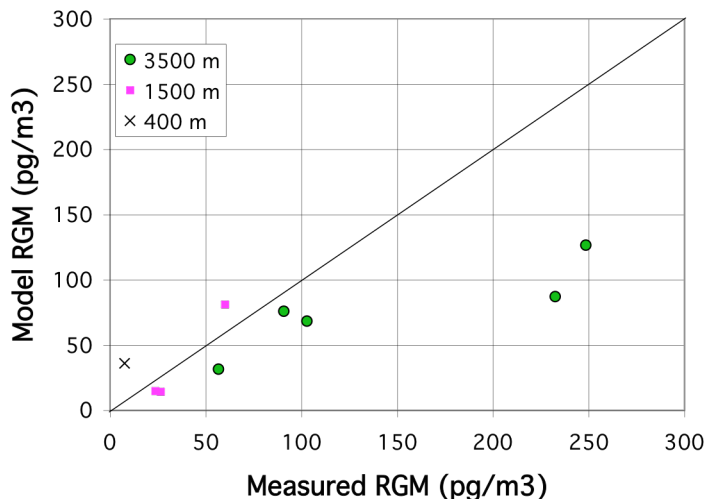


Figure 3. Model versus measured Hg(II) ( $\text{pg m}^{-3}$ ) paired in time and space for June 9, 12, 14, 25 and 26. Results are sorted by altitude: 3000-3500 m (circles); 1400-1700 m (squares) and 0-400 m (X's).

### Model Sensitivity

Results for model sensitivity are presented in the form of predicted correlations between Hg(II) and other species for different model scenarios. This format is used because the correlation between species provides a basis for testing critical model predictions versus measurements. The correlations have been selected to represent the species most closely associated with the model sensitivity test. Results are shown for three model sub-domains: (1) South Florida (including south and central Florida and the adjacent Atlantic Ocean and Gulf of Mexico); (2) The northeast corridor (extending from Boston to Washington and including the adjacent Atlantic Ocean and rural areas in Pennsylvania, New York and New England; and (3) the Great Lakes (including locations within 200 km of a line extending from Chicago to Cleveland).

#### *Correlation between Hg(II) and Hg(0)*

The predicted correlation between Hg(II) and elemental mercury (Hg(0)) shows a different pattern in Florida as opposed to the northeast corridor (Figure 4). The model predicts that Hg(II) and Hg(0) anticorrelate in Florida, but in the northeast corridor Hg(II) and Hg(0) generally increase together.

As will be shown below, Hg(II) and Hg(0) anticorrelate when most of the Hg(II) is produced photochemically by conversion from Hg(0). Hg(II) and Hg(0) correlate when Hg(II) is associated with direct emissions.

These correlation patterns change from day to day, and are also different at different altitudes. In particular, Hg(II) vs. Hg(0) may either correlate or anticorrelate in the northeast corridor and in the Great Lakes on individual days.

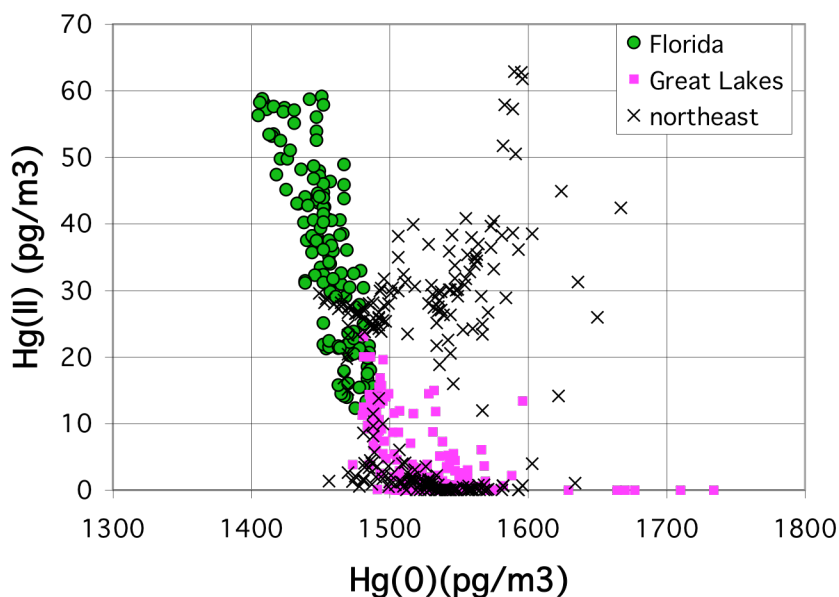


Figure 4. Model Hg(II) versus Hg(0) ( $\text{pg m}^{-3}$ ) at 5 pm, June 12, 2000, 100 m. altitude, in Florida (circles), the Great Lakes (squares), and the northeast corridor (X's).

### ***Sensitivity to Background Hg(0) and to Hg Chemistry***

When background Hg(0) is set to zero, the resulting Hg(II) is much lower in most of the model domain. This is especially noticeable in Florida (Figure 5). However, in the northeast corridor the model still shows elevated Hg(II), which is apparently associated with direct emissions.

A model scenario with all photochemical reactions involving Hg(0) and Hg(II) removed (not shown here) gives results that are very similar to the model scenario with zero background Hg(0).



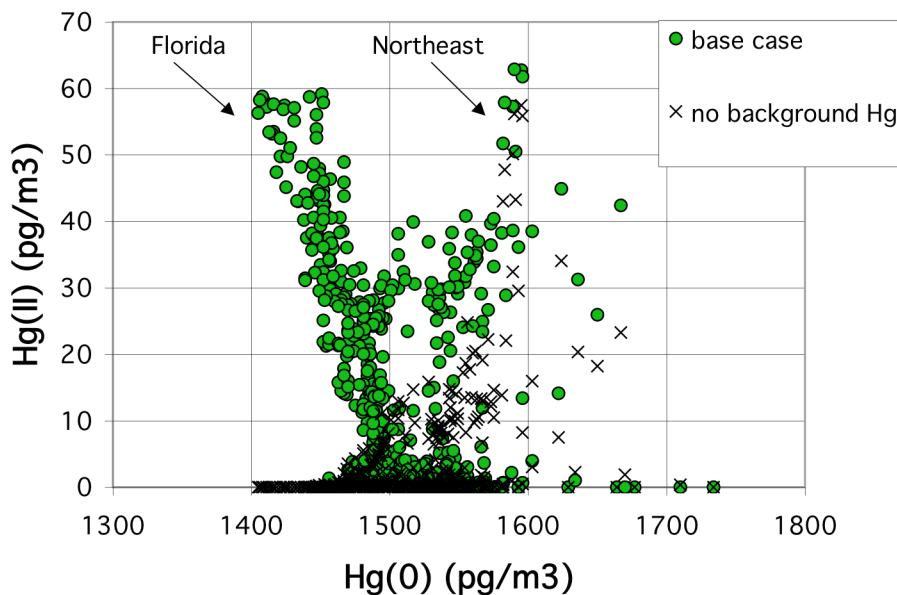


Figure 5. Model Hg(II) versus Hg(0) ( $\text{pg m}^{-3}$ ) at 5 pm, June 12, 2000, 100 m. altitude, in Florida, the Great Lakes and the northeast corridor. Circles represent the model base case. X's represent a scenario with initial and background Hg(0) set to zero.

### ***Sensitivity to Direct Emission of Hg(II) and Hg(0)***

When the initial model scenario is repeated with all direct emission of Hg(II) and Hg(0) within the model domain set to zero (Figure 6), there is little change in ambient Hg(II) in south Florida. The Hg(II) in Florida in this model is almost entirely the result of photochemical conversion from background Hg(0).

Results for the northeast corridor are different. Locations in the northeast with high ambient Hg(II) are predicted to show large reductions in Hg(II) when direct emission is set to zero.

It should be underscored that the predicted impact of direct emissions of either Hg(0) or Hg(II) in the model is strongly influenced by the coarse model resolution. The 35x35 km resolution sharply underestimates the effect of local point sources and as such, our current modeling framework is best applied to the investigation of regional Hg(0) and Hg(II) transport, transformation and fate. We are currently developing model scenarios with fine grid resolution that will be more appropriate for use in the investigation of potential local source impacts.

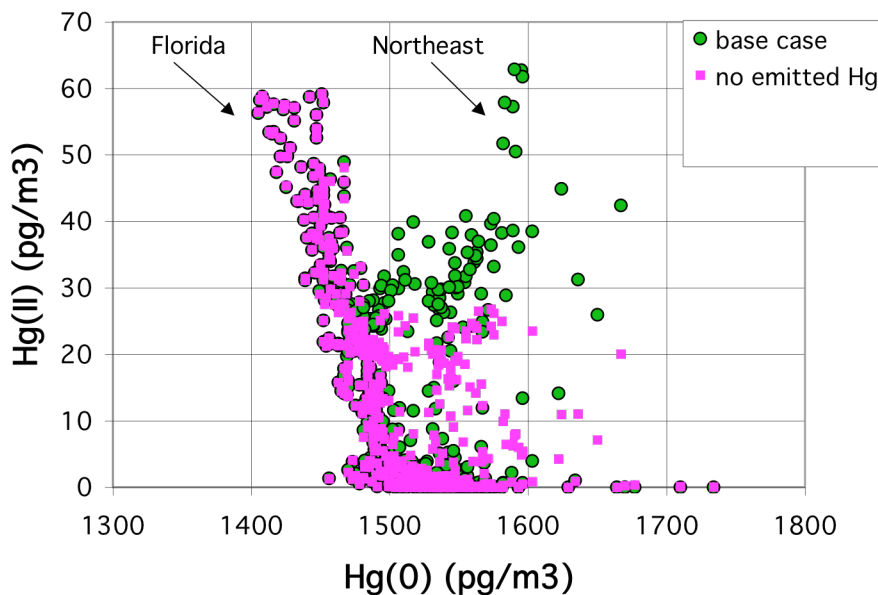


Figure 6. Model Hg(II) versus Hg(0) ( $\text{pg m}^{-3}$ ) at 5 pm, June 12, 2000, 100 m. altitude, in Florida, the Great Lakes and the northeast corridor. Circles represent the model base case. Squares represent a scenario with zero direct emission of Hg(II) and Hg(0).

### ***Hg(II) and O<sub>3</sub>***

Model results suggest that the ambient concentration of Hg(II) is significantly affected by ozone formation during region-wide pollution events. This is illustrated by results from June 14, 2000, an event that included elevated O<sub>3</sub> throughout the Midwest and Great Lakes region in the model.

Figure 7 compares results from the model base case with results from a model scenario with a 99% reduction in both anthropogenic VOC and NO<sub>x</sub> throughout the model domain. The reduced NO<sub>x</sub> and VOC creates a scenario with zero enhancement of ozone due to region-wide pollution sources. Surface O<sub>3</sub> remains below 50 ppb throughout the model domain in this scenario. Direct emission of Hg(II) and Hg(0) remained the same in both scenarios.

Results show little change in ambient Hg(II) in Florida, which did not have elevated O<sub>3</sub> in the model base case. In the Great Lakes region Hg(II) is reduced by approximately 50% in the scenario with near-zero NO<sub>x</sub> and VOC.

The model base case also predicts a strong correlation between ambient Hg(II) and O<sub>3</sub> in the Great Lakes region. This correlation between Hg(II) and O<sub>3</sub> is apparently related to the prediction that Hg(II) is sensitive to ozone precursors.

The sensitivity of Hg(II) to O<sub>3</sub> is almost certainly due to the reaction between Hg(0) and O<sub>3</sub> to form HgO. This is one of the most important sources of conversion from Hg(0) to

Hg(II). Because the rate of this reaction is slow, the relation between Hg(II) and O<sub>3</sub> is likely to occur mainly during region-wide events in which elevated O<sub>3</sub> persists for several days. Localized peaks in O<sub>3</sub> associated with a narrowly confined plume are less likely to lead to elevated Hg(II).

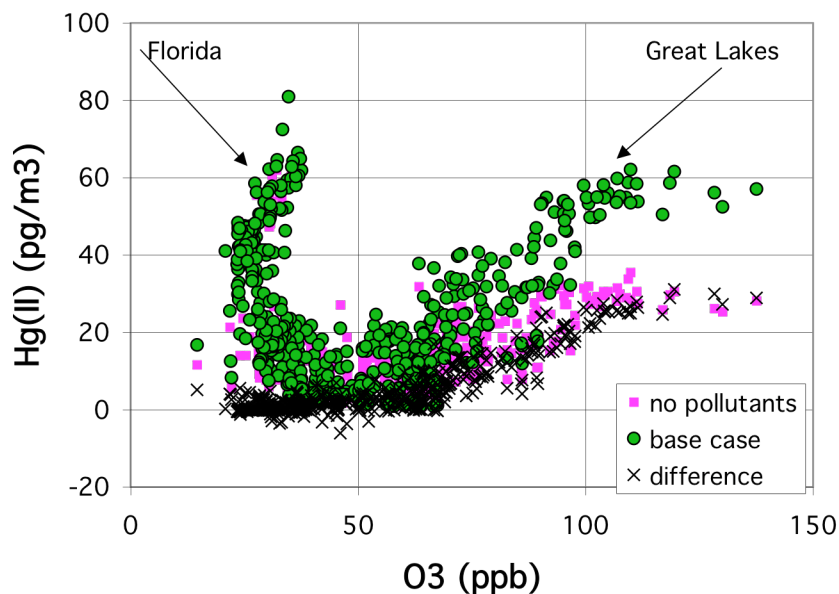


Figure 7. Model Hg(II) ( $\text{pg m}^{-3}$ ) versus O<sub>3</sub> (ppb) at 5 pm, June 14, 2000, 100 m. altitude in Florida, the Great Lakes and the northeast corridor. Circles represent the model base case. Squares show Hg(II) in a model scenario with a 99% reduction in emissions of anthropogenic NO<sub>x</sub> and VOC throughout the model domain, plotted against O<sub>3</sub> from the model base case. The X's represent the difference in Hg(II) between the two scenarios.

### *Sensitivity to Chemistry*

The model results described here are critically dependent on the assumed photochemistry of Hg(II) and Hg(0). One of the more uncertain aspects of this chemistry involves the aqueous reaction of Hg(II) with aqueous HO<sub>2</sub> and O<sub>2</sub><sup>-</sup>. Gartfeld and Jonsson<sup>16</sup> have challenged the viability of this reaction.

We have repeated the initial model scenario without these reactions. Results show that ambient Hg(II) would be 30% higher if these reactions were removed. The role of photochemical conversion from Hg(0) to Hg(II) would be somewhat more important in this case. The reaction of Hg(II) with aqueous HO<sub>2</sub> and O<sub>2</sub><sup>-</sup> is responsible for most of the aqueous conversion from Hg(II) to Hg(0). If this reaction were removed, the aqueous reactions would have little effect on Hg(II). The processing of Hg(0) and Hg(II) in the

atmosphere would be dominated by gas-phase photochemistry and by wet and dry deposition only, unless additional aqueous and/or aerosol reactions were added.

### **Species Correlations as Evidence for the Sources of Hg(II)**

Model correlations between ambient species are important because they provide a way to evaluate specific model predictions concerning the sources of atmospheric Hg(II).

As described above, the predicted correlation between Hg(II) and Hg(0) provides a possible way to identify the sources of ambient Hg(II). Hg(II) and Hg(0) are expected to correlate positively when ambient Hg(II) is affected by local emissions, which usually include simultaneous emission of Hg(II) and Hg(0). Hg(II) and Hg(0) are expected to anticorrelate when Hg(II) is produced primarily by photochemical conversion of Hg(0) to Hg(II).

However, there is some uncertainty in this interpretation. The aircraft measurements in South Florida show that Hg(II) and Hg(0) anticorrelate, and this might be interpreted as validation of model predictions for this region. However, the measurements also show an anticorrelation between Hg(II) and TGM (equal to the sum of measured Hg(II) and Hg(0)). The model does not predict an anticorrelation between Hg(II) and total Hg. The measured anticorrelation therefore represents a process that is not captured by the model, and should not be interpreted as evidence for photochemical conversion from Hg(II) to Hg(0). As an example, one process not specifically addressed is the potential role of gas-particle interaction involving Hg(II) during transport. Further research is needed to clarify what information can be obtained from the Hg(II)-Hg(0) correlation.

A correlation between Hg(II) and SO<sub>2</sub> might be used as evidence for direct emissions as the source of Hg(II). When models predict that Hg(II) is sensitive to direct emissions, they also show a positive correlation between Hg(II) and SO<sub>2</sub>. Some caution is needed here also because a positive correlation between Hg(II) and SO<sub>2</sub> can occur if Hg(II) is sensitive to anthropogenic O<sub>3</sub>.

A correlation between ambient Hg(II) and H<sub>2</sub>O<sub>2</sub> might be interpreted as evidence that Hg(II) is being produced by photochemical conversion from Hg(0) rather than by direct emissions. Photochemical conversion of Hg(0) to Hg(II) is accompanied by production of H<sub>2</sub>O<sub>2</sub>, and removal of Hg(II) and H<sub>2</sub>O<sub>2</sub> through wet deposition also occur simultaneously. Model results predict a correlation between Hg(II) and H<sub>2</sub>O<sub>2</sub> in South Florida, where Hg(II) is associated with photochemistry, but not in the northeast, where Hg(II) is associated with direct emissions (see Figure 8). However, there is considerable day-to-day variation in the predicted correlation between Hg(II) and H<sub>2</sub>O<sub>2</sub>.

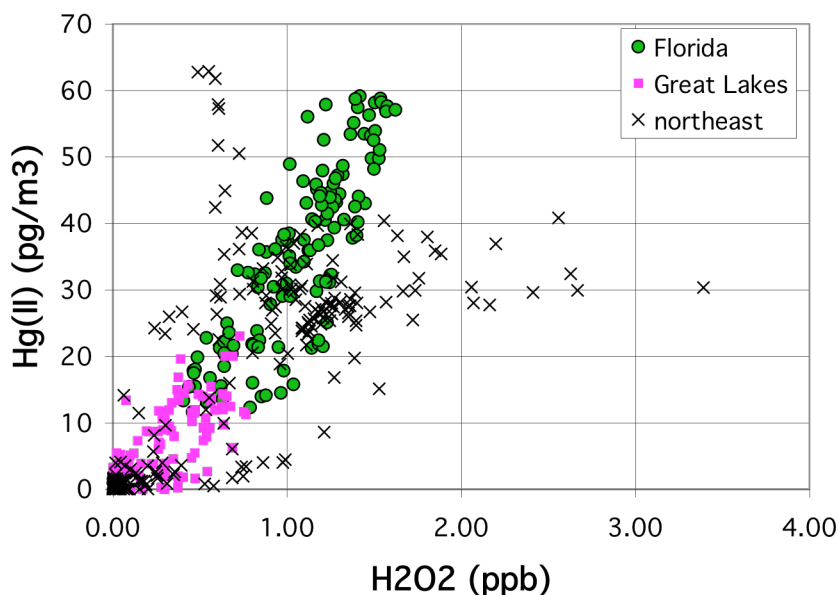


Figure 8. Model Hg(II) ( $\text{pg m}^{-3}$ ) versus  $\text{H}_2\text{O}_2$  (ppb) at 5 pm, June 12, 2000, 100 m altitude, in Florida (circles), the Great Lakes (squares), and the northeast corridor (X's).

## CONCLUSIONS

We have shown results from a model for the photochemistry and transport of Hg(0) and Hg(II) in the eastern U.S. and adjacent Atlantic Ocean, focusing on three regions: southern Florida, the northeast corridor of the U.S. and Great Lakes region. Our modeling results have been compared with U.S. EPA aircraft-based measurements of Hg(0) and Hg(II) in south Florida. Results from both model and measurements show that elevated ambient concentrations of Hg(II) can form over the Atlantic Ocean and that these elevated concentrations are intermittent in nature and form during cloud-free periods. Clouds and the resulting aqueous chemistry convert Hg(II) back to Hg(0). Modeled ambient reactive mercury is the same magnitude as measured in south Florida (bias -0.33, gross error 0.41).

While our coarse model resolution is more appropriate for addressing issues of regional mercury transport, transformation and fate, this current application of the model does predict that direct emission of Hg(II) is more important as a source of Hg(II) in the northeast and Great Lakes regions than in Florida. Photochemical conversion from Hg(0) is an important source of reactive mercury in all locations, but is especially important in Florida. The model also predicts that Hg(II) concentrations are increased as a result of elevated  $\text{O}_3$  associated with region-wide pollution events.

We have also investigated correlations among ambient species that might be used to evaluate the relative importance of local emissions and photochemistry as sources of Hg(II). When photochemical conversion is the main source of Hg(II) in the model, the

model predicts an anticorrelation between Hg(II) and Hg(0) and a positive correlation between Hg(II) and H<sub>2</sub>O<sub>2</sub>. When local emissions are the main source of Hg(II) the model predicts positive correlations between Hg(II) and Hg(0) and between Hg(II) and sulfate. When Hg(II) is affected by production of O<sub>3</sub> from anthropogenic sources the model predicts a positive correlation between Hg(II) and O<sub>3</sub>. These correlations may provide the basis for measurement-based evaluation of model predictions in future studies.

## ACKNOWLEDGEMENTS

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