Atmospheric Fate and Transport of Mercury: Where does the mercury in mercury deposition come from?

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(revised version, January 2005)
• Fish consumption is the most important exposure pathway for most humans and wildlife

• For many (but not all) aquatic ecosystems, much of the loading comes directly or indirectly through the atmospheric pathway...

For the atmospheric pathway:

- How much of the mercury in atmospheric mercury deposition comes from local, regional, national, continental, and global sources?

- How important are different source types?
We currently face key policy decisions regarding regulation of Hg emissions:

- what difference will regulating U.S. coal-fired power plants make?
- is emissions trading workable (and ethical)?
- how deep should emissions reductions be?
## Three “forms” of atmospheric mercury

| **Elemental Mercury: Hg(0)** | • ~ 95% of total Hg in atmosphere  
  • *not* very water soluble  
  • long atmospheric lifetime (~ 0.5 - 1 yr); globally distributed |
|-------------------------------|--------------------------------------------------------------------------------------------------|
| **Reactive Gaseous Mercury (“RGM”)** | • a few percent of total Hg in atmosphere  
  • oxidized mercury: Hg(II)  
  • HgCl₂, others species?  
  • somewhat operationally defined by measurement method  
  • *very* water soluble  
  • short atmospheric lifetime (~ 1 week or less);  
  • more local and regional effects |
| **Particulate Mercury (Hg(p))** | • a few percent of total Hg in atmosphere  
  • not pure particles of mercury…  
    (Hg compounds associated with atmospheric particulate)  
  • species largely unknown (in some cases, may be HgO?)  
  • moderate atmospheric lifetime (perhaps 1~ 2 weeks)  
  • local and regional effects  
  • bioavailability? |
Atmospheric Fate Processes for Hg

- **Primary Anthropogenic Emissions**
  - Elemental Mercury: Hg(0)
  - Reactive Gaseous Mercury: RGM
  - Particulate Mercury: Hg(p)

- **Dry and Wet Deposition**

- **Hg(0) oxidized to RGM** by O₃, H₂O₂, Cl₂, OH, HCl
  - Adsorption/desorption of Hg(II) to/from soot
  - Re-emission of natural AND previously deposited anthropogenic mercury

- **Hg(II) reduced to Hg(0) by SO₂**

- **Polar sunrise “mercury depletion events”**

- **Upper atmospheric halogen-mediated heterogeneous oxidation?**

- **“DRY” (low RH) ATMOSPHERE:**
  - Hg(0) oxidized to RGM by O₃, H₂O₂, Cl₂, OH, HCl

- **Br**

- **Adsorption/desorption of Hg(II) to/from soot**
Atmospheric Chemical Reaction Scheme for Mercury

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Units</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td><strong>GAS PHASE REACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(^0) + O(_3) &lt;(\rightarrow) Hg(p)</td>
<td>3.0E-20</td>
<td>cm(^3)/molec-sec</td>
<td>Hall (1995)</td>
</tr>
<tr>
<td>Hg(^0) + HCl &lt;(\rightarrow) HgCl(_2)</td>
<td>1.0E-19</td>
<td>cm(^3)/molec-sec</td>
<td>Hall and Bloom (1993)</td>
</tr>
<tr>
<td>Hg(^0) + H(_2)O(_2) &lt;(\rightarrow) Hg(p)</td>
<td>8.5E-19</td>
<td>cm(^3)/molec-sec</td>
<td>Tokos et al. (1998) (upper limit based on experiments)</td>
</tr>
<tr>
<td>Hg(^0) + Cl(_2) &lt;(\rightarrow) HgCl(_2)</td>
<td>4.0E-18</td>
<td>cm(^3)/molec-sec</td>
<td>Calhoun and Prestbo (2001)</td>
</tr>
<tr>
<td>Hg(^0) + OHC &lt;(\rightarrow) Hg(p)</td>
<td>8.7E-14</td>
<td>cm(^3)/molec-sec</td>
<td>Sommar et al. (2001)</td>
</tr>
<tr>
<td><strong>AQUEOUS PHASE REACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(^0) + O(_3) &lt;(\rightarrow) Hg(^+2)</td>
<td>4.7E+7</td>
<td>(molar-sec(^{-1}))</td>
<td>Munthe (1992)</td>
</tr>
<tr>
<td>Hg(^0) + OHC &lt;(\rightarrow) Hg(^+2)</td>
<td>2.0E+9</td>
<td>(molar-sec(^{-1}))</td>
<td>Lin and Pehkonen (1997)</td>
</tr>
<tr>
<td>HgSO(_3) &lt;(\rightarrow) Hg(^0)</td>
<td>T(\times)e((31.971\times T-12595.0)/T) sec(^{-1})</td>
<td>Van Loon et al. (2002)</td>
<td></td>
</tr>
<tr>
<td>Hg(II) + HO(_2)C &lt;(\rightarrow) Hg(^0)</td>
<td>~ 0</td>
<td>(molar-sec(^{-1}))</td>
<td>Gardfeldt &amp; Jonnson (2003)</td>
</tr>
<tr>
<td>Hg(^0) + HOCl &lt;(\rightarrow) Hg(^+2)</td>
<td>2.1E+6</td>
<td>(molar-sec(^{-1}))</td>
<td>Lin and Pehkonen (1998)</td>
</tr>
<tr>
<td>Hg(^0) + OCl(^-1) &lt;(\rightarrow) Hg(^+2)</td>
<td>2.0E+6</td>
<td>(molar-sec(^{-1}))</td>
<td>Lin and Pehkonen (1998)</td>
</tr>
<tr>
<td>Hg(II) &lt;(\leftrightarrow) Hg(II) (_{\text{soot}})</td>
<td>9.0E+2</td>
<td>liters/gram; t = 1/hour</td>
<td>eqlbrm: Seigneur et al. (1998) rate: Bullock &amp; Brehme (2002).</td>
</tr>
<tr>
<td>Hg(^{+2}) + h &lt;(\leftrightarrow) Hg(^0)</td>
<td>6.0E-7</td>
<td>(sec(^{-1})) (maximum)</td>
<td>Xiao et al. (1994); Bullock and Brehme (2002)</td>
</tr>
</tbody>
</table>
Figure 1. Lagrangian Puff Air Transport and Deposition Model

- Mass of pollutant: decreases as destruction and deposition occur each time step.
- Puff’s mass, size, and location continually tracked.
- Centerline of puff motion determined by wind direction and velocity.
- Photolytic and chemical transformation of pollutant also estimated at each time step.
- Initial puff location is at source, with initial mass & size.
- Total deposition from a puff during a given time step is calculated from the sum of the estimated dry and wet deposition of gas and particle-phase material, based on pollutant cons. in the puff, the local weather, and the nature of the surface.
- Deposition 1, deposition 2, deposition to lake.
Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).

Each released puff is advected and dispersed, and the pollutant within the puff is transformed and deposited.
1. The impact of any given mercury emissions source on any receptor is highly variable

- extreme spatial and temporal variations

- Think about the weather and then add all the chemistry and physics of mercury’s interactions with the “weather”
$1^\circ \times 1^\circ$ grid over entire modeling domain
Results tabulated on a $1^\circ \times 1^\circ$ grid over model domain.

Daily variations in total deposition flux arising from a hypothetical 1 kg/day source of Hg(II) (250 m effective stack height).

Daily values for May 1996 will be shown (julian days 121-151).

Daily values for each grid square will be shown as “ug/m$^2$-year” as if the deposition were to continue at that particular daily rate for an entire year.

And now for the movie…
2. The impact of any given mercury emissions source on any receptor is highly dependent on the “type” of mercury emitted

- Elemental mercury - $\text{Hg}^0$ - is not readily dry or wet deposited, and its conversion to ionic Hg or Hg(p) is relatively slow

- Particulate mercury – Hg(p) - is moderately susceptible to dry and wet deposition

- Ionic mercury – also called Reactive Gaseous Mercury or RGM – is easily dry & wet deposited

- Current questions regarding conversion of RGM to $\text{Hg}^0$ in plumes...
Example simulation of the atmospheric fate and transport of mercury emissions:

- hypothetical 1 kg/day source of RGM, Hg(p) or Hg(0)
- source height 250 meters
- results tabulated on a 1° x 1° receptor grid
- annual results (1996)
For emissions of Hg(0)

annual deposition
(ug/m2-year)
for 1 kg/day source
(250 m effective
stack height)

- 0 - 0.000001
- 0.000001 - 0.00001
- 0.00001 - 0.0001
- 0.0001 - 0.001
- 0.001 - 0.01
- 0.01 - 0.1
- 0.1 - 1
- 1 - 3.5

Kilometers
For emissions of Hg(p)
For emissions of Hg(II)

annual deposition
(ug/m²-year)
for 1 kg/day source
(250 m effective
stack height)

0 - 0.000001
0.000001 - 0.00001
0.00001 - 0.0001
0.0001 - 0.001
0.001 - 0.01
0.01 - 0.1
0.1 - 1
1 - 3.5
Estimated Speciation Profile for 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

Very uncertain for most sources

[Bar chart showing speciation profile for various sources with red for Ionic, black for Particulate, and blue for Elemental]
Estimated 1999 U.S. Atmospheric Anthropogenic Mercury Emissions
Each type of source has a very different emissions speciation profile

Even within a given source type, there can be big differences – depending on process type, fuels and raw materials, pollution control equipment, etc.
3. There can be large local and regional impacts from any given source

- same hypothetical 1 kg/day source of RGM
- source height 250 meters
- exactly the same simulation, but results tabulated on a $0.1^\circ \times 0.1^\circ$ receptor grid
- overall results for an entire year (1996)
0.1° x 0.1° subgrid for near-field analysis
0.1° x 0.1° subgrid for near-field analysis
Annual deposition summary for emissions of elemental Hg from a 250 meter high source

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Annual deposition summary for emissions of particulate Hg from a 250 meter high source

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Annual deposition summary for emissions of ionic Hg from a 250 meter high source

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Deposition flux within different distance ranges from a hypothetical 1 kg/day source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Deposition flux within different distance ranges from a hypothetical 1 kg/day source

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Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Deposition flux within different distance ranges from a hypothetical 1 kg/day source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
4. At the same time, medium to long range transport can’t be ignored
Fraction deposited within concentric regions away from a hypothetical source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Cumulative fraction deposited within different distances from a hypothetical source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Cumulative fraction deposited out to different distance ranges from a hypothetical source

- Hg(II) emit, 250 m
- Hg(p) emit, 250 m
- Hg(0) emit, 250 m

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Ionic Hg emitted from different source heights

Cumulative fraction deposited out to different distance ranges from a hypothetical source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Cumulative fraction deposited out to different distance ranges from a hypothetical source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
Cumulative fraction deposited out to different distance ranges from a hypothetical source

Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data
5. There are a lot of sources…

- Large spatial and temporal variations
- Each source emits mercury forms in different proportions
- A lot of different sources can contribute significant amounts of mercury through atmospheric deposition to any given receptor
6. Getting the source-apportionment information we all need is difficult

- With measurements alone, generally impossible

- Coupling measurements with back-trajectory analyses yields only a little information

- Comprehensive fate and transport modeling – “forward” from emissions to deposition – holds the promise of generating detailed source-receptor information
7. There are a lot of uncertainties in current comprehensive fate and transport models

- atmospheric chemistry of mercury
- concentrations of key reactants
- meteorological data (e.g., precipitation)
- mercury emissions (amounts & speciation profile)
- data for evaluation are scarce...
8. Nevertheless, many models seem to be performing reasonably well, i.e., are able to explain a lot of what we see
Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD_13 during 1996
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

Some HYSPLIT Results from MSC-East Hg Model Intercomparison Study

Comparison of measured vs. modeled TPM
Zingst

- Red: Measured
- Green: Modeled (background = 0)
- Blue: Modeled (with background)

Day (1999):
- 11/01
- 11/02
- 11/03
- 11/04
- 11/05
- 11/06
- 11/07
- 11/08
- 11/09
- 11/10
- 11/11
- 11/12
- 11/13
- 11/14
- 11/15
- 11/16

Concentration (pg/m3):
- 0
- 20
- 40
- 60
- 80
- 100
- 120
9. A model does not have to be perfect in order to be useful

- Often, most decisions just require qualitatively reasonable results

- And realistically, most if not all data and information used in decision-making has uncertainties (e.g., public health impacts, economic impacts)

- So, we shouldn’t demand perfection of models
10. To get the answers we need, we need to use both monitoring and modeling -- together.

Modeling needed to help interpret measurements and estimate source-receptor relationships.

Monitoring needed to develop models and to evaluate their accuracy.
11. **MDN is GREAT!…but there are some big gaps in atmospheric monitoring – making it very difficult to evaluate and improve models**

- We desperately need national MDN-like network to measure ambient air concentrations of Hg0, Hg(p), and RGM, with readily available data.

- What is RGM? What is Hg(p)?

- Both “background/regional” and near-source measurements needed…

- Measurements at different heights in the atmosphere
Dry Deposition?

- Dry deposition is important, and difficult – if not impossible – to measure reliably with current techniques…

- Essentially all dry deposition estimates made currently are made by applying models

- National ambient network of speciated ambient measurements will help to evaluate and improve models of dry deposition
Source-Apportionment

where does the mercury in mercury deposition come from?
Source-apportionment answers depend on

- **where** you are, and
- **when** you are

(and the effects of deposition will be different in each ecosystem)
For areas **without large emissions sources**

- the deposition may be relatively low,
- but what deposition there is may largely come from natural and global sources

For areas **with large emissions sources**

- the deposition will be higher
- and be more strongly influenced by these large emissions sources...
Mercury deposition at selected receptors arising from 1999 base-case emissions from anthropogenic sources in the United States and Canada (IPM coal fired plants are large coal-fired plants in the U.S. only)
Example of modeling results: Chesapeake Bay
Modeling the atmospheric transport and deposition of mercury to the Great Lakes

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Abstract

A special version of the NOAA HYSPLIT 4 model that produced results and provided estimates of the contributions of the atmospheric mercury deposition to the Great Lakes is described. The model was validated for model evaluation and the Great Lakes region and with independent measurements. Contributions from the Great Lakes and other ecosystems to atmospheric mercury deposition are assessed. Published by Elsevier Inc.

Keywords: Mercury; Atmospheric deposition; Great Lakes

Mercury contamination in the Great Lakes and other ecosystems is increasingly being recognized as a serious environmental concern. The distribution of mercury in the environment is through volatilization, and significant portions of the generally low levels of mercury are believed to be consuming toxicologically significant levels of mercury (e.g., National Research Council, 2000). Historical discharges, e.g., from pulp and paper production using the mercury-cell process or consumption, have caused large accumulations of mercury in the Great Lakes. Published by Elsevier Inc.

Note: Volume 95(3) is a Special Issue: "An Ecosystem Approach to Health Effects of Mercury in the St. Lawrence Great Lakes", edited by David O. Carpenter.
Modeling Methodology

- Modeling domain: North America
- U.S. and Canadian anthropogenic sources
- Natural emissions, Re-emissions, & Global sources not included
- 1996 meteorology (180 km horizontal resolution)
- Model evaluation: 1996 emissions and 1996 monitoring data
- Results: using 1999 emissions
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)
Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

Fraction of Total Modeled Deposition Contributed by Source:
- 0.1 - 1%
- 1 - 3%
- 3 - 10%
- 10 - 30%
- > 30%

Legend:
- Coal-Fired Electricity Generation
- Other Fuel Combustion Activities
- Waste Incineration
- Smelters and other Metallurgical
- Manufacturing and Other

Chesapeake Bay

0 500 Kilometers
Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay
Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay

Distance Range from Chesapeake Bay (km)

Emissions (metric tons/year)

Deposition Flux (ug/m2-year)
Emissions and deposition arising from emissions within different distance ranges

Fraction emitted and deposited from different distance ranges

Cumulative fraction emitted and deposited from different distance ranges

Distance Range from the Chesapeake Bay (km)
Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay

- Phoenix Services
- Brandon Shores
- Stericycle Inc.
- Morgantown
- Chalk Point
- NASA Incinerator
- Hampton/NASA Incin.
- Chesapeake Energy Ctr.
- Chesterfield
- Yorktown
- INDIA RIVER
- Roxboro
- BALTIMORE RESCO
- H.A. Wagner
- Norfolk Navy Yard
- Montour
- Keystone
- BMWNC
- Homer City
- Mt. Storm
- Belews Creek
- Harford Co. Incin.
- Harrisburg Incin.
- Harford Co. Incin.
Summer 2004 Chesapeake Bay Atmospheric Hg Study  
(June – August 2004)

• NOAA Cooperative Oxford Lab: *Bob Wood*

• NOAA Air Resources Lab Atmospheric Turbulence and Diffusion Division (ATDD): *Steve Brooks*

• NOAA Air Resources Lab HQ Division: *Winston Luke, Paul Kelley, Mark Cohen, Richard Artz*

• NOAA Chesapeake Bay Office: *Maggie Kerchner*

• Frontier GeoSciences: *Bob Brunette, Gerard van der Jagt, Eric Prestbo*

• Univ. of MD Wye Res. and Educ. Center: *Mike Newall*
regional emissions (1999) and sampling sites for summer 2004 Ches Bay Hg study
## Summer 2004 Chesapeake Bay Atmospheric Hg Study  
*(June – August 2004)*

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<tr>
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<th>Oxford</th>
<th>Wye</th>
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<tbody>
<tr>
<td>Event-based precipitation samples analyzed for Hg</td>
<td>✔️</td>
<td>✔️</td>
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<tr>
<td>Speciated Hg concentrations in ambient air (RGM, Hg(p), Hg$^0$)</td>
<td>✔️</td>
<td>✔️</td>
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<tr>
<td>Ambient concentration of ozone and sulfur dioxide</td>
<td>✔️</td>
<td>✔️</td>
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<tr>
<td>(via CASTNet)</td>
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<td>(via NADP site)</td>
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<tr>
<td>Ambient concentration of carbon monoxide</td>
<td>✔️</td>
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<td>Meteorology</td>
<td>✔️</td>
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<td>(via NADP site)</td>
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<tr>
<td>Major ions in precipitation</td>
<td></td>
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<td>(via NADP site)</td>
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</table>
Conclusions

- Source-attribution information is important
- Impacts are episodic & depend on form of mercury emitted
- Modeling needed to get source-attribution information
- (more!) Monitoring for model evaluation & refinement
- Models don’t have to be perfect to give useful information
- Many uncertainties but useful model results are emerging
- Many opportunities exist for improvements in modeling/monitoring integrated approaches to develop source-attribution information

(and States can play a key role in developing critical emissions & monitoring information)
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