The Atmospheric Transport and Deposition of Mercury

Dr. Mark Cohen
NOAA Air Resources Laboratory
Silver Spring, Maryland

Materials assembled for a discussion with the
Baltimore City Department of Law
City Hall, August 25, 2005
The Mercury Problem

- EPA has estimated that 1 out of every 6 children born in the U.S. may have already been exposed *in-utero* to levels of mercury that might cause problems with neurological development.

- There are additional potential mercury-related health hazards to children, adults, and to wildlife.

- Fish-consumption advisories due to mercury contamination are widespread throughout U.S. rivers, lakes, and coastal areas.

- The primary exposure route is through fish consumption.

- Atmospheric deposition is a significant – often the most significant – pathway for mercury loading to aquatic ecosystems.
There are many ways in which mercury is introduced into a given aquatic ecosystem... atmospheric deposition can be a very significant pathway
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
### 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 Mercury Fate Processes

Upper atmospheric halogen-mediated heterogeneous oxidation?

Polar sunrise “mercury depletion events”

Hg(II) reduced to Hg(0) by SO₂ and sunlight

Hg(0) oxidized to dissolved Hg(II) species by O₃, OH, HOCl, OCl⁻

Adsorption/desorption of Hg(II) to/from soot

Vapor phase:
Hg(0) oxidized to RGM and Hg(p) by O₃, H₂O₂, Cl₂, OH, HCl

Primary Anthropogenic Emissions

Natural emissions

Re-emission of previously deposited anthropogenic and natural mercury

Multi-media interface

Wet deposition
Dry deposition

Elemental Mercury [Hg(0)]
Hg(II), ionic mercury, RGM
Particulate Mercury [Hg(p)]
# Atmospheric Chemical Reaction Scheme for Mercury

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GAS PHASE REACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg$^0$ + O$_3$ $\rightarrow$ Hg(p)</td>
<td>3.0E-20</td>
<td>cm$^3$/molec-sec</td>
<td>Hall (1995)</td>
</tr>
<tr>
<td>Hg$^0$ + HCl $\rightarrow$ 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$_2$ $\rightarrow$ 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$_2$ $\rightarrow$ 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 $\rightarrow$ 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$_3$ $\rightarrow$ Hg$^{+2}$</td>
<td>4.7E+7</td>
<td>(molar-sec)$^{-1}$</td>
<td>Munthe (1992)</td>
</tr>
<tr>
<td>Hg$^0$ + OHC $\rightarrow$ Hg$^{+2}$</td>
<td>2.0E+9</td>
<td>(molar-sec)$^{-1}$</td>
<td>Lin and Pehkonen (1997)</td>
</tr>
<tr>
<td>HgSO$_3$ $\rightarrow$ Hg$^0$</td>
<td>T$^<em>$e$^{((31.971</em>T)-12595.0)/T}$ sec$^{-1}$</td>
<td>Van Loon et al. (2002)</td>
<td></td>
</tr>
<tr>
<td>[T = temperature (K)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(II) + HO$_2$C $\rightarrow$ Hg$^0$</td>
<td>$\sim$ 0</td>
<td>(molar-sec)$^{-1}$</td>
<td>Gardfeldt &amp; Jonnson (2003)</td>
</tr>
<tr>
<td>Hg$^0$ + HOCl $\rightarrow$ 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$^{-1}$ $\rightarrow$ Hg$^{+2}$</td>
<td>2.0E+6</td>
<td>(molar-sec)$^{-1}$</td>
<td>Lin and Pehkonen (1998)</td>
</tr>
<tr>
<td>Hg(II) $\leftrightarrow$ Hg(II)$_{\text{soot}}$</td>
<td>9.0E+2</td>
<td>liters/gram; t = 1/hour</td>
<td>eqbrm: Seigneur et al. (1998); rate: Bullock &amp; Brehme (2002).</td>
</tr>
<tr>
<td>Hg$^{+2}$ + h$&lt;$ $\rightarrow$ 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>
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
What is an atmospheric model?

• a computer simulation of the fate and transport of emitted pollutants

• two different types of models
  – Eulerian
  – Lagrangian
In an Eulerian atmospheric model, the atmosphere is divided into a number of cells.

The inputs, outputs, and chemical processes within each cell are simulated.
Dry and wet deposition of the pollutants in the puff are estimated at each time step.

The puff’s mass, size, and location are continuously tracked...

Phase partitioning and chemical transformations of pollutants within the puff are estimated at each time step.

Centerline of puff motion determined by wind direction and velocity.

Initial puff location is at source, with mass depending on emissions rate.

= mass of pollutant (changes due to chemical transformations and deposition that occur at each time step)

Lagrangian Puff Atmospheric Fate and Transport Model

NOAA HYSPLIT MODEL
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.
• In principle, we need do this for each source in the inventory

• But, since there are more than 100,000 sources in the U.S. and Canadian inventory, we need shortcuts…

• Shortcuts described in Cohen et al
  *Environmental Research* 95(3), 247-265, 2004

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.
0.1° x 0.1° subgrid for near-field analysis
0.1° x 0.1° subgrid for near-field analysis

source location
Annual deposition summary for emissions of elemental Hg from a 250 meter high source

Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source:
- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

Source Location

0.1 x 0.1 degree grid

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

Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source:
- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

Source Location

0.1 x 0.1 degree grid

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

Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source:

- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

0.1 x 0.1 degree grid

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Why is emissions speciation information critical?

Logarithmic
Why is emissions speciation information critical?

```
distance range from source (km)
0 - 15 15 - 30 30 - 60 60 - 120 120 - 250
deposition flux (ug/m²-yr) for hypothetical 1 kg/day source
0 10 20 30 40
Hg(II) emit, Hg(0) emit, Hg(p) emit
```

Linear
Why is emissions speciation information critical?

**Logarithmic**

**Linear**
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
Why do we need atmospheric mercury models?

- to get *comprehensive source attribution* information --- we don’t just want to know how much is depositing at any given location, we also want to know where it came from…

- to estimate *deposition over large regions*, …because deposition fields are highly spatially variable, and one can’t measure everywhere all the time…

- to estimate *dry deposition*

- to evaluate *potential consequences* of alternative future emissions scenarios
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
What do atmospheric mercury models need?

- Emissions Inventories
- Meteorological Data
- Scientific understanding of phase partitioning, atmospheric chemistry, and deposition processes
- Ambient data for comprehensive model evaluation and improvement
<table>
<thead>
<tr>
<th>emissions inventories</th>
<th>need all sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>accurately divided into different Hg forms</td>
</tr>
<tr>
<td></td>
<td>temporal variations (e.g. shut downs)</td>
</tr>
<tr>
<td>meteorological data</td>
<td>precipitation not well characterized</td>
</tr>
<tr>
<td>scientific understanding</td>
<td>what is RGM? what is Hg(p)?</td>
</tr>
<tr>
<td></td>
<td>accurate info for known reactions?</td>
</tr>
<tr>
<td></td>
<td>do we know all significant reactions?</td>
</tr>
<tr>
<td></td>
<td>natural emissions, re-emissions?</td>
</tr>
<tr>
<td>ambient data for model evaluation</td>
<td>Mercury Deposition Network (MDN) is great, but:</td>
</tr>
<tr>
<td></td>
<td>also need RGM, Hg(p), and Hg(0) concentrations</td>
</tr>
<tr>
<td></td>
<td>also need data above the surface (e.g., from aircraft)</td>
</tr>
<tr>
<td></td>
<td>also need source-impacted sites (not just background)</td>
</tr>
</tbody>
</table>
Illustrative example of total deposition at a location ~40 km "downwind" of a 1 kg/day RGM source
## Some Challenges Facing Mercury Modeling

| Emissions Inventories | • need *all* sources  
|                       | • accurately divided into *different Hg forms*  
|                       | • *temporal* variations (e.g. shut downs)  
| Meteorological Data | • precipitation not well characterized  
| Scientific Understanding | • what is RGM? what is Hg(p)?  
|                           | • accurate info for known reactions?  
|                           | • do we know all significant reactions?  
|                           | • natural emissions, re-emissions?  
| Ambient Data for Model Evaluation | • Mercury Deposition Network (MDN) is great, but:  
|                                                | • also need RGM, Hg(p), and Hg(0) concentrations  
|                                                | • also need data above the surface (e.g., from aircraft)  
|                                                | • also need source-impacted sites (not just background)  

| emissions inventories                   | • need all sources                           
|                                       | • accurately divided into different Hg forms |
|                                       | • temporal variations (e.g. shut downs)      |
| meteorological data                  | • precipitation not well characterized       |
| scientific understanding              | • what is RGM? what is Hg(p)?               
|                                       | • accurate info for known reactions?         |
|                                       | • do we know all significant reactions?      |
|                                       | • natural emissions, re-emissions?           |
| ambient data for model evaluation     | • Mercury Deposition Network (MDN) is great, but: |
|                                       | • also need RGM, Hg(p), and Hg(0) concentrations |
|                                       | • also need data above the surface (e.g., from aircraft) |
|                                       | • also need source-impacted sites (not just background) |
| emissions inventories | • need *all* sources  
|                       | • accurately divided into *different Hg forms*  
|                       | • *temporal* variations (e.g. shut downs)  |
| meteorological data   | • precipitation not well characterized  |
| scientific understanding | • what is RGM? what is Hg(p)?  
|                         | • accurate info for known reactions?  
|                         | • do we know all significant reactions?  
|                         | • natural emissions, re-emissions?  |
| ambient data for model evaluation | • Mercury Deposition Network (MDN) is great, but:  
|                                    | • also need RGM, Hg(p), and Hg(0) concentrations  
|                                    | • also need data above the surface (e.g., from aircraft)  
|                                    | • also need source-impacted sites (not just background)  |
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
EMEP Model Intercomparison

- Phase II – ambient concentrations
- Phase III – wet and dry deposition

Chesapeake Bay region
EMEP Model Intercomparison

- Phase II – ambient concentrations
- Phase III – wet and dry deposition

Chesapeake Bay region
Measured and Simulated Total Gaseous Mercury at Neuglobsow during the 1995 episode
Comparison of measured vs. modeled TPM
Neuglobsow

- Measured
- Modeled (background = 0)
- Modeled (with background)
Comparison of measured vs. modeled TPM
Aspvreten

- Measured
- Modeled (background = 0)
- Modeled (with background)
Comparison of measured vs. modeled RGM
(comparison for measurement periods only)
☐ EMEP Model Intercomparison

☐ Phase II – ambient concentrations
☐ Phase III – wet and dry deposition

☐ Chesapeake Bay region
Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE_02 during 1996

Cumulative Wet Deposition at MDN_DE_02

- Measured
- Modeled

cumulative deposition (ug Hg/m2)

Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD_13 during 1996

Cumulative Wet Deposition at MDN_MD_13

- Measured
- Modeled
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 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
Summer 2004 Measurement Sites

Baltimore, MD

Washington, DC

Cooperative Oxford Lab
(38.678°N, 76.173°W)

Wye Research and Education Center
(38.9131°N, 76.1525°W)
regional emissions (1999) and sampling sites for summer 2004 Ches Bay Hg study
## Summer 2004 Chesapeake Bay Atmospheric Hg Study
*(June – August 2004)*

<table>
<thead>
<tr>
<th></th>
<th>Oxford</th>
<th>Wye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event-based precipitation samples analyzed for Hg</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Speciated Hg concentrations in ambient air (RGM, Hg(p), Hg⁰)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Ambient concentration of ozone and sulfur dioxide</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>(continuous)</td>
<td>(weekly via AirMON Dry)</td>
</tr>
<tr>
<td>Ambient concentration of carbon monoxide</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Meteorology</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>(via NADP/NTN site)</td>
<td>(via NADP/NTN site)</td>
</tr>
</tbody>
</table>
1. Atmospheric mercury

2. Atmospheric mercury modeling

3. Why do we need atmospheric mercury models?

4. What do atmospheric mercury models need from us?

5. Preliminary model evaluation results

6. Preliminary source-receptor results
Example of Detailed Results: 1999 Results for Chesapeake Bay
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
Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

- Phoenix Services
- Stericycle, Inc.
- Brandon Shores - H.A. Wagner
- Baltimore RESCO
- Chalk Point
- Morgantown
- Yorktown
- NASA Incinerator
- Chesapeake Energy Center
- Norfolk Navy Yard

Fraction of Total Modeled Deposition Contributed by Source:
- 0.1 - 1%
- 1 - 3%
- 3 - 10%
- 10 - 30%
- > 30%
Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay

![Bar chart showing emissions and deposition flux over different distance ranges from the Chesapeake Bay. The x-axis represents distance ranges (0-100 km, 100-200 km, 200-400 km, etc.), while the y-axis represents emissions (metric tons/year) and deposition flux (ug/m²-year). The chart uses red for emissions and blue for deposition flux.]
Preliminary Results for other Maryland Receptors
Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling *(but modeling was not optimized for these receptors!)*
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (national view)
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (regional view)
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (close-up view)
source-attribution — the “big picture”
Natural vs. anthropogenic mercury?

Studies show that anthropogenic activities have typically increased bioavailable Hg concentrations in ecosystems by a factor of 2 – 10

source: USGS, Shuster et al., 2002
Average mercury accumulation rate relative to pre-industrial (1800-1850) accumulation rate in five lakes in Northern Alaska (based on sediment cores)

What is the relative importance of global, national, regional, and local sources?
Data used by EPA to support recent Clean Air Mercury Rule

Mercury Deposition in the U.S.

U.S. Mercury Deposition from All Global Sources

- 2001 Total Deposition: 341.3 tons
- 2001 U.S. Utilities Deposition: 13.5 tons
- 2020 U.S. Utilities Deposition after CAIR and CAMR: 3.9 tons

Source: EPA
the Seigneur et al. (2004) paper shows that, for regions where deposition is high, the impact of local/regional sources is the main cause for these elevated concentrations.

Results from the EPA REMSAD Mercury model

- Based on this modeling approximately half of U.S. mercury deposition is from domestic anthropogenic sources and half is from other sources.
- Domestic sources dominate deposition for large part of Eastern U.S.
- Global sources are dominant in the Western U.S.

Source: slide developed by Anne Pope for the Hg Roundtable conference call April 21, 2005
Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD_13 during 1996

HYSPLIT modeling has shown that in areas of significant local and regional anthropogenic sources, ambient measurements can be explained reasonably well by considering only these local and regional anthropogenic sources.
Source-apportionment answers depend a lot on where you are

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...
What is the relative importance of global, national, regional, and local sources?

*Possible answers are emerging as our understanding improves, but there is no scientific consensus yet...*
Conclusions

Source-attribution information is important

Impacts are episodic & depend on form of mercury emitted

Modeling needed to get source-attribution information

(more!) Monitoring needed for model evaluation & refinement

Many uncertainties but useful model results are emerging – these HYSPLIT model results are being extended to include global & natural emissions, and re-emissions

The question of the relative importance of global vs. national vs. regional vs. local sources is complex – the answer depends on location and on what model one is using...
EXTRA SLIDES
• For each run, simulate fate and transport *everywhere*, but only keep track of impacts on each selected receptor (e.g., Great Lakes, Chesapeake Bay, etc.)

• Only run model for a limited number (~100) of hypothetical, individual unit-emissions sources throughout the domain

• Use spatial interpolation to estimate impacts from sources at locations not explicitly modeled
Spatial interpolation

Impact of source 4 estimated from weighted average of impacts of nearby explicitly modeled sources

Impacts from Sources 1-3 are Explicitly Modeled
• Perform separate simulations at each location for emissions of pure Hg(0), Hg(II) and Hg(p)

[after emission, simulate transformations between Hg forms]

• Impact of emissions mixture taken as a linear combination of impacts of pure component runs on any given receptor
“Chemical Interpolation”

Impact of Source Emitting
30% Hg(0)
50% Hg(II)
20% Hg(p)

\[ 0.3 \times \text{Impact of Source Emitting Pure Hg(0)} \]

\[ + \]

\[ 0.5 \times \text{Impact of Source Emitting Pure Hg(II)} \]

\[ + \]

\[ 0.2 \times \text{Impact of Source Emitting Pure Hg(p)} \]
Standard Source Locations in Maryland region during recent simulation
Why might the atmospheric fate of mercury emissions be essentially linearly independent?

• Hg is present at extremely trace levels in the atmosphere

• Hg won’t affect meteorology (can simulate meteorology independently, and provide results to drive model)

• Most species that complex or react with Hg are generally present at much higher concentrations than Hg

• Other species (e.g. OH) generally react with many other compounds than Hg, so while present in trace quantities, their concentrations cannot be strongly influenced by Hg

• Wet and dry deposition processes are generally 1st order with respect to Hg

• The current “consensus” chemical mechanism (equilibrium + reactions) does not contain any equations that are not 1st order in Hg