Atmospheric Mercury: Emissions, Transport/Fate, Source-Receptor Relationships

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Atmospheric Mercury: Sources, Transport/Fate, Source-Receptor Relationships

1. Mercury in the Environment

2. Atmospheric Emissions

3. Atmospheric Fate & Transport

4. Atmospheric Modeling

5. Source-Receptor Relationships
   a. Receptor-based
   b. Source-based
      - single source
      - entire inventory

6. Summary
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6. Summary
Many waterbodies throughout the U.S. have fish consumption advisories due to high mercury levels.

Significant numbers of people are currently being exposed to levels of mercury that may cause adverse effects –

- in the general population, 1 out of every 6 children born in the U.S. has already been exposed in-utero to levels of mercury that may cause neuro-developmental effects;
- in some sub-populations, fish consumption & mercury exposure may be higher.

Fish consumption is the most important mercury exposure pathway for most humans and wildlife.

For many aquatic ecosystems, much of the mercury loading comes directly or indirectly through the atmospheric pathway...
There are many ways in which mercury is introduced into a given aquatic ecosystem... atmospheric deposition can be a very significant pathway.
many policy-relevant questions regarding mercury

- Relative importance of different loading pathways? (e.g. atmospheric deposition, industrial discharge, etc?)
- Relative importance of natural vs. anthropogenic contamination?
- Relative importance of different source regions? (e.g., how much from local, regional, national, global…)
- Relative importance of current vs. past loadings?
- Have these answers changed over time? How will they change in the future?
- How are these answers different for different ecosystems?
- Which sources should be regulated, and to what extent?
- Is “emissions trading” workable and ethical?
- Is the recently promulgated Clean Air Mercury Rule a reasonable approach?
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, Schuster et al., 2002
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Global natural and anthropogenic emissions of mercury. Estimates taken/inferred from Lamborg et al. (2002). All values are in metric tons per year, and are for ~1990.

Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere, 2000

Total Hg, point sources + distributed sources, 0.5° grid

Total anthropogenic mercury emissions
(\(\text{kg per 0.5° grid cell}\))

- < 0.25
- 0.25 - 1.00
- 1.00 - 5.00
- 5.00 - 10.00
- 10.00 - 50.00
- 50.00 - 100.00
- 100.00 - 500.00
- 500.00 - 1000.00
- 1000.00 - 5000.00
- 5000.00 - 10000.00
- > 10000.00 (max 19125)

unprojected (geographic)

citation:

S. Wilson (AMAP), F. Steenhuisen (Arctic Centre, RuG), J. Pacyna (NILU)

There were big reported changes in emissions between 1990 and 1999, but when did these occur? And when did they occur for individual facilities?

* Data for Lime Manufacturing are not available for 1990.
** Data for Electric Arc Furnaces are not available for 1999. The 2002 estimate (10.5 tons) is shown here.
Some Current Emissions Inventory Challenges

- Re-emissions of previously deposited anthropogenic Hg
- Emissions speciation [at least among Hg(0), Hg(II), Hg(p); more specific species if possible]
- Reporting and harmonization of source categories
- Mobile source emissions?
- Enough temporal resolution to know when emissions for individual point sources change significantly

Note: Hg continuous emissions monitors now commercially available
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### Three “forms” of atmospheric mercury

<table>
<thead>
<tr>
<th>Form</th>
<th>Description</th>
</tr>
</thead>
</table>
| **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”

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

Elemental Mercury [Hg(0)]

Hg(II), ionic mercury, RGM

Particulate Mercury [Hg(p)]

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

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

Wet deposition

Dry deposition
## Atmospheric Chemical Reaction Scheme for Mercury

<table>
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<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$_3$ → Hg(p)</td>
<td>3.0E-20</td>
<td>cm$^3$/molec-sec</td>
<td>Hall (1995)</td>
</tr>
<tr>
<td>Hg$^0$ + HCl → 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$_2$ → 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$_2$ → 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 → 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$_3$ → Hg$^{+2}$</td>
<td>4.7E+7</td>
<td>(molar-sec)$^{-1}$</td>
<td>Munthe (1992)</td>
</tr>
<tr>
<td>Hg$^0$ + OHC → Hg$^{+2}$</td>
<td>2.0E+9</td>
<td>(molar-sec)$^{-1}$</td>
<td>Lin and Pehkonen (1997)</td>
</tr>
<tr>
<td>HgSO$_3$ → Hg$^0$</td>
<td>T$^<em>$e$^{(31.971</em> T)-12595.0/T}$ sec$^{-1}$</td>
<td>[T = temperature (K)]</td>
<td>Van Loon et al. (2002)</td>
</tr>
<tr>
<td>Hg(II) + HO$_2$C → Hg$^0$</td>
<td>~0</td>
<td>(molar-sec)$^{-1}$</td>
<td>Gardfeldt &amp; Jonnson (2003)</td>
</tr>
<tr>
<td>Hg$^0$ + HOCl → 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$^{-1}$ → Hg$^{+2}$</td>
<td>2.0E+6</td>
<td>(molar-sec)$^{-1}$</td>
<td>Lin and Pehkonen (1998)</td>
</tr>
<tr>
<td>Hg(II) ↔ 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$^{+2}$ + $h$ ↔ 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>
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6. Summary
1. Models are mathematical and/or conceptual descriptions of real-world phenomena

- They are necessarily a simplification – the real world is very complicated

- *Hopefully* the most important aspects are treated sufficiently well…
The Role and Potential Value of Models

2. Models and measurements are inextricably linked

- Most models are created only after extensive measurement data are collected and studied
- Models are based on the data in one form or another
- In almost all cases, models must be continually “ground-truth’ed” against actual measurements – (definitely the case with current atmospheric mercury models)
3. Models are potentially valuable for:

- Examining large-scale scenarios that cannot easily be tested in the real world
- Interpreting measurements (e.g., filling in spatial and temporal gaps between measurements)
- Providing Source-Receptor Information (maybe the only way to really get this...)
4. Models are a test of our collective knowledge

- They attempt to synthesize everything important that we know about a given system

- If a model fails, it means that we may not know everything we need to know…
5. Whether we like it or not, models are used in developing answers to most information necessary for environmental policy decisions…

- EFFECTS (e.g., on human and wildlife health)
- CAUSES (e.g., environmental fate and transport of emitted substances)
- COSTS (e.g. for remediation)
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.
What is an atmospheric model?

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

- two different types of models
  - Eulerian
  - Lagrangian
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
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.

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.

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

Centerline of puff motion determined by wind direction and velocity.
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.
## EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

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<th>Stage II</th>
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<th>Conclusions</th>
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<td>Chemistry</td>
<td>Hg⁰</td>
<td>Hg(p)</td>
<td>RGM</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Wet Dep</td>
<td>Dry Dep</td>
</tr>
</tbody>
</table>

### Total Particulate Mercury (pg/m³) at Neuglobsow, Nov 1-14, 1999

![Graphs comparing measured and model predictions for particulate mercury levels over time](chart.png)
Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE_02 during 1996
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Source-receptor information can be estimated using either *receptor-based* or *source-based* techniques.
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Summer 2004 NOAA ARL Hg Measurement Sites

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

Wye Research and Education Center
(38.9131°N, 76.1525°W)

Baltimore, MD
Washington, DC
Measured Atmospheric Concentrations at Oxford MD, Summer 2004

Highest measured RGM

- RGM
Concentrations Measured at Oxford, MD

O3, CO/10 (ppbv); RGM, FPM (pg/m^3)

SO2 (ppbv); GEM (ng/m^3)

Julian Decimal Day

O3, CO/10 (ppbv); RGM, FPM, SO2, GEM
Oxford July 2, 2004 Peak Concentration in RGM

1999 RGM Emissions (kg/yr)
- 0 - 50
- 50 - 100
- 100 - 200
- 200 - 400
- 400 - 600
- 600 - 1000

Type of Emissions Source
- coal-fired electricity generation
- waste incineration
- manufacturing
- metallurgical
- other fuel combustion

BackTrajectory Starting Height = 1000 m

BackTrajectory Starting Height = 500 m

BackTrajectory Starting Height = 100 m
Oxford July 3, 2004 -- one day after Peak Concentration in RGM

1999 RGM Emissions (kg/yr)
- 0 - 50
- 50 - 100
- 100 - 200
- 200 - 400
- 400 - 600
- 600 - 1000

Type of Emissions Source
- coal-fired electricity generation
- waste incineration
- manufacturing
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- other fuel combustion

Back Trajectory Starting Height = 1000 m
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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)
$1^\circ \times 1^\circ$ grid over entire modeling domain
Results tabulated on a 1° x 1° grid over model domain

Daily values for each grid square will be shown as “ug/m²-year” as if the deposition were to continue at that particular daily rate for an entire year.

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

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

And now for the movie…
Illustrative example of total deposition at a location ~40 km "downwind" of a 1 kg/day RGM source

- Daily value
- Weekly average
0.1° x 0.1° subgrid for near-field analysis
Annual deposition summary for emissions of elemental Hg from a 250 meter high source

Annual Deposition Flux
(ug/m²-yr)
originating 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)
Annual deposition summary for emissions of particulate Hg from a 250 meter high source

Source Location

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
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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

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Estimated Speciation Profile for 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

Very uncertain for most sources

Fraction of Total Hg Emissions

- Ionic
- Particulate
- Elemental
Why is emissions speciation information critical?

Logarithmic

NOTE: distance results averaged over all directions –
Some directions will have higher fluxes, some will have lower
Why is emissions speciation information critical?

![Graph showing deposition flux (ug/m²-yr) for a hypothetical 1 kg/day source over different distance ranges from the source. The graph compares Hg(II) emit, Hg(0) emit, and Hg(p) emit.]
Why is emissions speciation information critical?

**Logarithmic**

**Linear**
Wet + Dry Deposition: ISC (Kansas City)
for emissions of different mercury forms from different stack heights

Calculated from data used to produce Appendix A of USEPA (2005): Clean Air Mercury Rule (CAMR) Technical Support Document: Methodology Used to Generate Deposition, Fish Tissue Methylmercury Concentrations, and Exposure for Determining Effectiveness of Utility Emissions Controls: Analysis of Mercury from Electricity Generating Units
HYSPLIT 1996

ISC: 1990-1994

Different Time Periods and Locations, but Similar Results
The fraction deposited and the deposition flux are both important, but they have very different meanings...

The fraction deposited nearby can be relatively “small”, but the area is also small, and the relative deposition flux can be very large...

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
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Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling (but modeling was not optimized for these receptors!)

Total Hg emissions (kg/year):
- 0 - 100
- 100 - 300
- 300 - 500
- 500 - 700
- 700 - 1000
- 1000 - 1300
- 1300 - 7000

Legend:
- Red: Coal-Fired Electricity Generation
- Blue: Waste Incineration
- Gray: Metallurgical
- Yellow: Manufacturing
- Green: Other Fuel Combustion
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)
Some CMAQ results, used in the development of the CAMR rule, courtesy of Russ Bullock, EPA
CMAQ-simulated total mercury deposition for 2001
(micrograms per square meter)

Utility Zero Out
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Summary

- Models needed for source-receptor and other info
- At present, many model uncertainties & data limitations
- Measurements needed to develop, evaluate & improve models
- Some useful model results appear to be emerging
- Future is much brighter because of increased coordination between measurer’s and modelers! Thanks Mark Castro!
Thanks!

For more information on this research: http://www.arl.noaa.gov/ss/transport/cohen.html