Simulations of Atmospheric Mercury with the NOAA HYSPLIT Model

NOAA Air Resources Laboratory, Silver Spring, MD,
http://www.arl.noaa.gov/mercury.php

In collaboration with
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Chuck Patrick, Robert Hughes, Julius Baham, Shelton Swanier,
and other colleagues at Jackson State University

Symposium on Atmospheric Modeling and Application of GIS and Scientific Visualization Technologies for Risk Assessment
July 30-31, 2009, Jackson State University
- Methyl-mercury is a developmental neurotoxin -- risks to fetuses/infants

- Cardiovascular toxicity might be even more significant (CRS, 2005)

- Critical exposure pathway: methylmercury from fish consumption

- Widespread fish consumption advisories

- Uncertainties, but mercury toxicity relatively well understood
  - well-documented tragedies: (a) Minimata (Japan) ~1930 to ~1970; (b) Basra (Iraq), 1971
  - epidemiological studies, e.g., (a) Seychelles; (b) Faroe Islands; (c) New Zealand
  - methylmercury vs. Omega-III Fatty Acids
  - selenium – protective role?

- At current exposures, risk to large numbers of fetuses/infants

+ Wildlife Health Issues e.g., fish-eating birds
Different “forms” of mercury in the atmosphere

Elemental Mercury -- Hg(0)
- most of total Hg in atmosphere
- not very water soluble
- doesn’t easily dry or wet deposit
- upward evasion vs. deposition
- atmos. lifetime approx ~ 0.5-1 yr
- globally distributed

Particulate Mercury -- Hg(p)
- a few percent of total atmos Hg
- not pure particles of mercury
- Hg compounds in/on atmos particles
- species largely unknown (HgO?)
- atmos. lifetime approx 1~ 2 weeks
- local and regional effects
- bioavailability?

Reactive Gaseous Mercury -- RGM
- a few percent of total atmos Hg
- oxidized Hg (HgCl2, others)
- operationally defined
- very water soluble and “sticky”
- atmos. lifetime <= 1 week
- local and regional effects
- bioavailable

Atmospheric methyl-mercury?
Hg from other sources: local, regional & more distant

Reactive halogens in marine boundary layer
→ Enhanced oxidation of Hg(0) to RGM
→ Enhanced deposition

wet and dry deposition to the watershed

Source Attribution for Deposition?
Elemental Mercury -- Hg(0) -- Emissions to the Air

2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada; 1999 Mexican data from inventory prepared by Acosta y Asociados for the Commission for Environmental Cooperation
Reactive Gaseous Mercury – RGM -- Emissions to the Air

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Size/shape of symbol denotes amount of mercury emitted (kg/yr):
- ▲ 5 – 10
- ○ 10 – 50
- △ 50 – 100
- □ 100 – 300
- ◇ 300 – 500
- ▽ 500 – 1000
- ☺ 1000 – 3500

Color of symbol denotes type of mercury source:
- Red: coal-fired power plants
- Green: other fuel combustion
- Blue: waste incineration
- Gray: metallurgical
- Yellow: manufacturing & other
Particulate Mercury -- Hg(p) -- Emissions to the Air

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Total Mercury Emissions to the Air \[ Hg(0) + RGM + Hg(p) \]

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2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada; 1999 Mexican data from inventory prepared by Acosta y Asociados for the Commission for Environmental Cooperation.
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 (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:
Why is emissions speciation information critical?

NOTE: distance results averaged over all directions – Some directions will have higher fluxes, some will have lower.

**Logarithmic**
1965

1970

1975

1980

1985

1990

1995

2000

2005

2010

1970’s - 1990’s: many mercury-cell chlor-alkali plants converted to alternate processes or closed due to regulatory and other pressures.

Clean Air Act Amendments of 1990 – calls for Maximum Achievable Control Technology (MACT) to regulate hazardous air pollutants; *intent is to prohibit emissions trading for these air toxics*

1990’s – Hg emissions from municipal and medical waste incinerators fall dramatically due to:
- closure of some municipal waste incinerators and many medical waste incinerators
- MACT-related pollution control requirements
- reduction in mercury content of waste (e.g., battery legislation)

2002 – Clear Skies Initiative for power plants introduced *(ultimately withdrawn)*

2005 – CAIR (Clean Air Interstate Rule) for power plants (Hg reduced as co-benefit of SO₂ & NOₓ controls)

2005 – EPA meets court-ordered deadline and promulgates CAMR (Clean Air Mercury Rule) for power plants – *based on Hg emissions trading*

“Hot Spot” Controversy -- Many States sue EPA & propose / promulgate more strict regulations

2008 – CAMR and CAIR overturned... What is next?
Direct, Anthropogenic Mercury Emissions in the United States
(data from USEPA)

Estimated Mercury Emissions (tons per year)

- Other categories*
- Gold mining
- Hazardous waste incineration
- Electric Arc Furnaces **
- Mercury Cell Chlor-Alkali Plants
- Industrial, commercial, institutional boilers and process heaters
- Municipal waste combustors
- Medical waste incinerators
- Utility coal boilers

* 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.

Three NOAA sites committed to emerging inter-agency speciated mercury ambient concentration measurement network (comparable to Mercury Deposition Network (MDN) for wet deposition, but for air concentrations).
Atmospheric Mercury Measurement Site at the Grand Bay NERR, MS

view from top of the tower

mercury and trace gas monitoring tower (10 meters)
## Atmospheric Measurements at the Grand Bay NERR

<table>
<thead>
<tr>
<th>Elemental mercury * 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine particulate mercury * 2</td>
</tr>
<tr>
<td>Reactive gaseous mercury * 2</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>Ozone</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>Nitrogen Oxides (NO, NOy)</td>
</tr>
<tr>
<td>Wind speed, Wind Direction</td>
</tr>
<tr>
<td>Temperature, Relative Humidity</td>
</tr>
<tr>
<td>Precipitation Amount</td>
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<tr>
<td>Total Mercury &amp; Methyl Mercury in Precipitation</td>
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<tr>
<td>Trace Metals in Precipitation</td>
</tr>
<tr>
<td>Major Ions in Precipitation</td>
</tr>
</tbody>
</table>

### “Speciated” Atmospheric Mercury Concentrations

Trace gases to help understand and interpret mercury data

### Meteorological Data

WET DEPOSITION: Currently being added, in collaboration with MS DEQ and U.S. EPA
Instrumentation inside the trailer at the Grand Bay NERR site
Can we learn what is needed about atmospheric mercury deposition by making atmospheric measurements alone?

NO...
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:
  - different source regions (local, regional, national, global)
  - different jurisdictions (different states and provinces)
  - anthropogenic vs. natural emissions
  - different source types (power plants, waste incin., smelters...)
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  ...because deposition fields are highly spatially variable, and one can’t measure everywhere all the time...
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- to evaluate potential consequences of future emissions scenarios
Models are not perfect

“...Everyone believes monitoring results except for the person making the measurements... and nobody believes modeling results except for the person doing the modeling...”

How not perfect are they?

Results are encouraging, but difficult to evaluate models due to lack of contemporaneous monitoring and emissions inventory data.

Models are a test of our knowledge...

If they don’t work, fundamental things about our understanding of atmospheric mercury that are wrong or incomplete...

More certain info at a few locations (monitoring) vs. less certain info region-wide (modeling)
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.

Dry and wet deposition of the pollutants in the puff are estimated at each time step.

deposition 1

deposition 2

deposition to receptor

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.
<table>
<thead>
<tr>
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When puffs grow to sizes large relative to the meteorological data grid, they split, horizontally and/or vertically.

Ok for *regional* simulations, but for *global* modeling, puff splitting overwhelms computational resources.
Due to puff splitting, the number of puffs quickly overwhelms numerical resources.

Evolution of Number of Puffs

as a function of MAXPAR and merge parameter multiplication factor

elem emit; growth not stopped; splitting not age-limited; source at lat = 30, long = 105 (China)

In this example, the maximum number of puffs was set to 100,000, so when it got close to that number, the splitting was turned off.

Exponential puff growth
In each test, the number of puffs rises to the maximum allowable within ~ one week.
In the new version of HYSPLIT (4.9), puffs are “dumped” into an Eulerian grid after a specified time (e.g., 96 hrs), and the mercury is simulated on that grid from then on...
**Atmospheric Chemistry**

**Phase Partitioning**

**Wet and Dry Deposition**

**Inputs to Model**

- Meteorology
- Emissions
- Land Use

**Atmospheric Mercury Model**

- Atmospheric Chemistry
- Phase Partitioning
- Wet and Dry Deposition

**Model Outputs**

- Wet and Dry Deposition of different Hg forms to sensitive ecosystems
- Source attribution information for deposition

**Model Evaluation**

- Wet Deposition data
- Speciated ambient concentration data
- Model Inter-comparison
- Model Visualization

*For model evaluation, model inputs must be for the same time period as measurement data.*
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Collaboration with JSU is providing a unique and unprecedented opportunity to evaluate and improve atmospheric mercury models.
We are organizing the initial collaborative work around specific episodes of high concentration of one or more mercury forms.
Thanks!
Extra Slides
Hg from other sources: local, regional & more distant

Series 3300 CEM - Continuous Speciated Mercury Data
Resolution: 2.5 min  Duration: 11 Days

- HgT
- Hg0
- Hg2

Measurement of ambient air concentrations
Measurement of wet deposition
atmospheric deposition to the water surface

Hg(0) → Hg(II) → Hg(p)
Recent RGM concentrations measured at the Grand Bay NERR

Then down for ~2 months due to hurricanes
Atmospheric Mercury Fate Processes

Upper atmospheric halogen-mediated heterogeneous oxidation?

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

Primary Anthropogenic Emissions

Hg(II), ionic mercury, RGM
Elemental Mercury [Hg(0)]
Particulate Mercury [Hg(p)]

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

Natural emissions

Re-emission of previously deposited anthropogenic and natural mercury

Multi-media interface

Wet deposition
Dry deposition
Mercury (Hg) is an element... there is the same amount of mercury on Earth today as there always has been

“natural” Hg cycle – Hg is transported throughout the environment, and chemical transformations interconvert different mercury species

This has always been going on, and there has always been Hg in fish

But, we make some Hg unexpectedly “bioavailable”

Most anthropogenic Hg is “released” as atmospheric emissions:

- Hg in coal is released to the air when coal is burned
- Hg in other fuels is released to the air when they are processed and burned
- Hg in ores is released to the air during metallurgical processes
- Hg in products is released to the air when burned or landfilled after being discarded (e.g., batteries, switches)

Average, current atmospheric Hg deposition is ~3x pre-industrial levels

Evidence suggests that newly deposited Hg is more bioavailable
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
Mercury transformed by bacteria into methylmercury in sediments, soils & water, then bioaccumulates in fish.

Humans and wildlife affected primarily by eating fish containing mercury.

Best documented impacts are on the developing fetus: impaired motor and cognitive skills.

atmospheric deposition to the watershed

atmospheric deposition to the water surface

adapted from slides prepared by USEPA and NOAA
What Do We Need to Know Regarding Atmospheric Mercury?

<table>
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<tbody>
<tr>
<td>Atmospheric deposition*</td>
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<tr>
<td>Source-attribution for deposition</td>
</tr>
<tr>
<td>Deposition for historical periods</td>
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<td>Deposition for alternative future scenarios</td>
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* consistent with the needs of subsequent analyses (e.g., ecosystem modeling) with respect to spatial, temporal, and “species” resolution (e.g., Hg(0) vs. RGM vs. Hg(p))