MERCURY IN THE ATMOSPHERE, BIOSPHERE, AND POLICY SPHERE:
Insights from global modeling

Noelle Eckley Selin
Joint Program on the Science and Policy of Global Change
Center for Global Change Science
Massachusetts Institute of Technology

Rutgers University
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Mercury deposition has increased by 300% since industrialization.

Major anthropogenic source is stationary combustion (coal).

Atmospheric transport and deposition leads to high fish methylmercury.

Ice core from Wyoming [Schuster et al., ES&T 2002]
GLOBAL BIOGEOCHEMICAL CYCLE OF MERCURY

MERCURY: ATMOSPHERIC CHEMISTRY

OH, O₃, Br, other halogens

1.6 ng m⁻³
Hg⁰

1-100 pg m⁻³
Hg²⁺

Atmospheric lifetime 0.5-2 y

In-solution

in-cloud photoreduction

 oxidation

reduction

Wet and Dry Deposition

Soluble

Goal: Use combination of model and measurements to constrain mercury chemistry, transport, and deposition

Measurements: TGM=Total Gaseous Mercury, RGM=Reactive Gaseous Mercury
Annual average concentration at 22 land-based sites:
Measured: 1.58 ± 0.19 ng/m³
Simulated: 1.63 ± 0.10 ng/m³

Ongoing puzzle: Atlantic cruise data (enrichment in North Atlantic from historical emissions?)

[Selin et al. JGR 2007 (atmosphere), Strode et al. GBC 2007 (ocean); Selin et al. GBC 2008 (atm-ocean-land)]
RESEARCH QUESTIONS: OUTLINE

1. What are the oxidation and reduction reactions controlling Hg speciation in the atmosphere?
2. What atmospheric processes control Hg deposition to the United States?
3. How do different sources of mercury affect human exposure?
1. OXIDATION AND REDUCTION PROCESSES

Seasonal variation of TGM is consistent with photochemical oxidation of Hg(0) partially balanced by reduction of Hg(II).

- In most models (including GEOS-Chem) OH is the dominant Hg(0) oxidant.
- But the OH reaction may not occur in the atmosphere [Calvert & Lindberg 2005]

\[
\text{Hg} + \text{OH} \rightarrow \text{HgOH}
\]

\[
\text{HgOH} + \text{O}_2 \rightarrow \text{HgO} + \text{HO}_2
\]

- Could the dominant oxidant be Br? [Holmes et al. 2006] [Selin et al. JGR 2007]
1. CONSTRAINTS FROM TIME SERIES AT OKINAWA

Day-to-day variation of Hg(0) reflects anthropogenic sources.

No correlation between Hg(0) and RGM: evidence that RGM is chemically produced.

Day-to-day variation of RGM is driven by variation in wind speed which affects dry deposition.

RGM shows a diurnal pattern.

[Selin et al. JGR 2007]
1. DIURNAL PATTERN: BR OXIDATION, SEA-SALT UPTAKE

Measured RGM begins to increase earlier in the day than the model.
Production of Br begins earlier than OH.

Evidence for Br oxidation?

Rapid afternoon decline can’t be explained by dry deposition alone.

Uptake onto sea-salt aerosol?

[Selin et al. JGR 2007]
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2. DEPOSITION PATTERNS IN THE UNITED STATES

Why doesn’t the area of highest Hg(II) emission have the highest deposition?

Highest Emission: Ohio River Valley

Highest Deposition: Florida/Gulf Coast

GEOS-Chem captures magnitude and spatial variation of measured wet deposition

We can use the model to gain insights into deposition processes.

[Measurements: Mercury Deposition Network; Model: Selin & Jacob, AE 2008]
2. SEASONAL PATTERNS OF U.S. DEPOSITION

Measurements
GEOS-Chem
North American contribution

- Amplitude of seasonal variation has latitudinal dependence
- GEOS-Chem captures magnitude, amplitude of regional variation
- Contributing factors:
  - Oxidation
  - Inefficient wintertime scavenging
  - Downwelling & convective scavenging from free troposphere

[Measurements: Mercury Deposition Network; Model: Selin & Jacob, AE 2008]
2. HIGH LEVELS OF HG(II) AT ALTITUDE

- Measurements from Mt. Bachelor show elevated RGM over surface levels (higher levels in subsidence at night)
- Murphy et al. [2006] show Hg associated with particles in the upper troposphere
- GEOS-Chem shows increasing Hg(II) with altitude:
  - Source = oxidation from Hg(0) with OH, O3
  - Sinks = Aqueous reduction (dry at altitude), wet and dry deposition (near-surface)
- Supported by aircraft measurements (more to come!) [Selin et al. JGR 2007]
2. SUBSIDENCE BRINGS HG(II) DOWNWARDS

• Hg(II) at higher altitudes will descend where there is subsidence

• High levels of Hg(II) in the model associated with subsidence in the Hadley Cell (subtropical desert regions)

• Potential to affect the surface, but few measurements in these areas!

[Selin et al. GBC 2008]
2. NORTH AMERICAN CONTRIBUTION TO DEPOSITION

Up to 60% of deposition in Midwest/Northeast is from domestic sources

Florida has highest deposition in the U.S., but mostly from non-US sources

Policy implications: Reducing deposition in both Midwest and Southeast will require policy actions on multiple political scales (national and global)

[Selin & Jacob, AE 2008]
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3. CONSTRAINING NATURAL HG: PREINDUSTRIAL MODEL

**Steady state assumption:**
- Soil Hg comes from the atmosphere (for about 90% of land area)
- What goes down, must come up...

**Mean Enrichment:**
3X (from sediment cores)

GEOS-Chem Pre-Industrial Simulation

Soil volatilization:
$F(T, [Hg], \text{solar radiation})$

Evapotranspiration:
$F([Hg], \text{transp. rate})$

Prompt recycling:
Newly-deposited Hg is more easily reduced & emitted than resident Hg

[Selin et al., GBC 2008]

[Hintelmann et al. 2002]
3. EVALUATING MERCURY CYCLE AND LIFETIMES

Hg is very long-lived in the soil, but the surface ocean recycles Hg efficiently

Recycling in the surface ocean more than doubles the effective atmospheric lifetime of Hg

Emitted Hg remains in the land-ocean-atmosphere system for ~3000 y before returning to the sediments.

3. PRESENT VS. PRE-INDUSTRIAL DEPOSITION

- Factor of 3 enrichment on average since pre-industrial times (constrained by sediment core records), but spatial variation
- Historical legacy continues to affect ecosystems through deposition

[Selin et al., GBC 2008]
3. FROM DEPOSITION TO FISH METHYLMERCURY

[Engstrom et al., 2007]
3. FRESHWATER DEPOSITION AND SOURCE ATTRIBUTION

How do sources affect fish methylmercury, and on what timescales?

Northeast U.S.  
24.21 µg m$^{-2}$ y$^{-1}$  
- Pre-industrial + Historical: 32%  
- N. American Anthropogenic: 59%  
- International Anthropogenic: 9%

Southeast U.S.  
34.08 µg m$^{-2}$ y$^{-1}$  
- Pre-industrial + Historical: 11%  
- International Anthropogenic: 23%  
- N. American Anthropogenic: 66%  

SERAFM: Lake model  WASP7: River model  WCS (MLM): Watershed loading  BASS: Aquatic food web  [Knightes et al., in press]

Policy and Timescale Analysis

[Selin et al., PNAS, submitted]
3. FRESHWATER TIMESCALE ANALYSIS

Each ecosystem driven by present-day deposition for 40 years (10-year spin up)

Policy experiment: All Hg is “historical” at t=0. How is anthropogenic signal reflected in fish, and on what timescale?

Regional differences in deposition sources lead to different source attributions (and concentrations) over time

Same deposition, but different ecosystem dynamics lead to very different source attributions (and concentrations) over time

[Note difference in scale!]

Ecosystem A

Ecosystem B

Regional differences in deposition sources lead to different attributions in similar ecosystems

[Selin et al., PNAS, submitted]
3. LOCAL EXPOSURE FROM FRESHWATER FISH

2 x 100 g fish meals/week (60 kg person) @ t=40 y

- **North American anthropogenic**
- **International anthropogenic**
- **Historical+Natural**

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**MeHg intake (ug/kg/day)**

- **WHO intake threshold**
- **EPA Reference Dose**

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**Ecosystems**

- **Ecosystem A**
- **Ecosystem B**

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[Selin et al., PNAS, submitted]
3. ECONOMIC IMPLICATIONS OF POPULATION EXPOSURE

- MIT Emissions Prediction and Policy Analysis (EPPA) model [Paltsev et al., 2005]
- IQ deficits from mercury exposure [Axelrad, 2007] cost 2.5% of income per point lost [Salkever, 1995]
- Calculate additional cost of US emissions for general population (marine) exposure beginning in 2000

Methodology takes into account “indirect” costs of lost investment/savings

Other estimates: $1.3b for US power plants alone (Trasande et al., 2005); $119m-4.9b (Rice et al. 2005)

[Selin et al., in prep.]
ONGOING POLICY CHALLENGES

U.S.:
Clean Air Mercury Rule: establishes “cap and trade” approach to regulating mercury from coal-fired power plants (2005), struck down by courts in 2008

REGIONAL:

GLOBAL:
Global Mercury Assessment (2002): sufficient evidence to warrant international action

**Challenge:** Design effective policies that reduce risk at multiple scales (local to global)

[Selin and Selin, RECIEL, 2006]
FUTURE RESEARCH DIRECTIONS

Compare model with new measurements (including from aircraft) to further constrain redox reactions, transport, gas-particle partitioning

North American Airborne Mercury Experiment (NAAMEX)

Improve understanding of ocean- and land-atmosphere cycling, including possible changes with climate & links to the carbon cycle

Extend exposure work to global scale, and include future energy use scenarios