Smoke stack to stomach: the role of atmospheric chemistry in mercury exposure

Christopher Holmes (Harvard)

Daniel Jacob, Bess Corbitt, Anne Soerensen, Elsie Sunderland (Harvard)

Rob Mason (UConn)
Dan Jaffe (U. Washington)
Mercury exposure in U.S diet

- Tuna (all)
- Swordfish
- Pollock
- Shrimp
- Cod
- Crab
- Salmon (all)
- Anchovies et al.
- Orange Roughy
- Halibut
- Flounders
- Haddock et al.
- Grouper et al.
- Snappers
- Mackerel

Fraction of population-wide Hg intake

2003: 2,362 Advisories

States with mercury consumption advisories

Sunderland 2007
Spectrum of health effects

Children IQ Deficits
EPA’s RfD (2000)

- From fetal exposures above MeHg RfD

Adult Cardiovascular Effects

- From any fetal MeHg exposures
- Male consumers of non-fatty freshwater fish with high MeHg
- Male fish consumers
- All fish consumers

~6% of U.S. women of child-bearing age exceed RfD

Decreasing Credibility

Rice and Hammitt 2005
Anthropogenic impact

**Mercury in Wyoming ice core**

- Mt St Helens (1980 AD)
- Industrialization (circa 1880-present)
- WWII manufacturing (circa 1940-45 AD)
- Krakatau (1883 AD)
- Gold Rush (circa 1850-84 AD)
- "Unknown"
- Tambora (1815 AD)
- Pre-industrial

Year (AD) vs. Total mercury (ng/L)

**Mercury in Arctic wildlife**

- Beluga teeth
- Gyrfalcon feather
- Human teeth
- Perigrine falcon feather
- Polar bear hair
- Ringed seal teeth

Historic proportion of present vs. Year

Schuster et al. 2002

Dietz et al. 2009
Anthropogenic impact

Mercury in Wyoming ice core

Schuster et al. 2002

Mercury concentration in moose teeth (Michigan UP)

Vucetich et al. 2009
Mercury exposure pathway

**Anthropogenic Source**

<table>
<thead>
<tr>
<th>Source</th>
<th>Mg/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary Combustion</td>
<td>1400</td>
</tr>
<tr>
<td>Gold production</td>
<td>400</td>
</tr>
<tr>
<td>Incineration</td>
<td>170</td>
</tr>
<tr>
<td>Non-Fe metals</td>
<td>160</td>
</tr>
<tr>
<td>Cement</td>
<td>140</td>
</tr>
<tr>
<td>Other</td>
<td>220</td>
</tr>
</tbody>
</table>

*Pirrone et al. 2008*

**Atmospheric transport**

**Emissions**

\[ Hg^0, Hg^{II} \]

**Deposition**

**Methylation**

**Biomagnification Factor**

**Diet**

**Water**

MeHg 1 1,600,000 6,800,000

*USEPA, 1999*
Atmospheric Hg cycle

GEOS-Chem Hg simulation
Holmes et al., in prep.
Figure 3. Evolution of knowledge of atmospheric Hg chemistry over the last several decades.

Atmospheric redox

Many "successful" models based on this mechanism:
CMAQ (Bullock et al. 2000), GEOS-Chem (Selin et al. 2007), HYSPLIT Hg (Cohen et al. 2004), AER-CTM-Hg (Seigneur et al. 2004) ...
Our overall knowledge of the chemistry of atmospheric Hg has improved significantly, but major uncertainties remain, which affect our ability to predict source-receptor relations.

Atmospheric redox - updated

Gas phase

Hg(0) → Hg(II) (oxidation)

OH & O₃ (fast)
Br & BrO (very fast)

Hg(II) → Hg(p) (adsorption)

Hg(p) → Hg(0) (reduction in plumes?)

Aqueous phase

Hg(0) → Hg(II) (oxidation)

OH, O₃, Cl₂

Hg(II) → Hg(p) (dissolution)

Hg(p) → Hg(0) (adsorption to PM)

SO₂, HO₂?

unknown chemical composition!
call it “RGM”, “TGM”

Lindberg et al. 2007
updated following Hynes et al. 2008
Evidence for Hg+Br reaction

Spitzbergen O₃ and Hg⁰ depletion events

Hg depletion events discovered in 1995 (Schroeder et al. 1998)

Strong O₃-Hg⁰ correlation shows common chemical mechanism

Alert O₃, Br₂ and BrCl

O₃ depletions studied since 1980s

Halogen oxidation measured and modeled extensively

Spicer et al. 2002

Goodsite et al. 2004
Hg+Br could be globally important

Halocarbons (e.g. CH₃Br, CHBr₃)
Sea-salt aerosol

Br mixing ratio

Br from pTOMCAT - Yang et al., 2005

Chance et al. 1998
Salawitch et al. 2005
Hg+Br could be globally important

Halocarbons (e.g. CHBr₃)
Sea-salt aerosol

Br mixing ratio

Hg⁰ Lifetime

Global lifetime due to Hg-Br reaction:

\[ \tau_{Hg^0} = 200 \ (160-510) \text{ days} \]

Holmes et al., 2006
Field evidence for Hg+Br

Antarctic subsidence events

Neumayer Station - Temme et al., 2003

Aerosol-bound Hg, Br, and I correlation near the tropopause

PALMS on WB-57 - Murphy et al., 2006
Consistent diurnal cycles at all sites
- Fast morning rise
- Midday peak
- Fast decline in afternoon
- Amplitudes 1-3X mean

-Not caused by diurnal entrainment!

Holmes et al. 2009
Marine boundary layer model

Free troposphere

Marine boundary layer

$Hg^0$ $\xrightarrow{O_3, \text{Br, Cl, OH}}$ $Hg(\text{II})$

$Z_{MBL}$

Entrainment

Dry & Wet Deposition

Sea salt aerosol

Holmes et al. 2009
Box model simulations

Diurnal amplitudes consistent with 0.5-1 ppt BrO, 3 x 10^4 cm^-3 Cl

Halogen model simulates peak timing better than Hg+OH model

Holmes et al. 2009
Hg$^{II}$ budget

Hg+Br is a major or dominant source

Entrainment is a large term, but poorly known

Hg+O$_3$ could be smaller than shown

Aerosols are the dominant sink

80-90% of Hg$^{II}$ in the MBL enters the ocean

Sources
- Entrainment
- Hg+O$_3$
- Hg+Cl
- Hg+Br

Sinks
- Ventilation
- Sea salt aerosols
- Dry deposition

Flux, pg m$^{-3}$ d$^{-1}$

Okinawa

Pacific midlatitudes

Pacific subtropics

Holmes et al. 2009
Global model---alternative hypotheses

1. Hg+Br simulation

2. Hg+OH/O₃ simulation

Adjust reduction to match mean NH TGM, then
Compare both against
• global spatial gradients
• seasonal cycles
GEOS-Chem Hg simulation

- 3-D 4x5° resolution, 47 layers
- Assimilated meteorology (GEOS-5 2004-2009)
- 2-D Surface ocean (Strode et al. 2007)
- 2-D Soil and vegetation (Selin et al. 2008)
- Anthropogenic emissions from Streets et al. (2009)
- Archived oxidants: Br, OH, O₃
- Simplified sea-salt aerosol exchange

Holmes et al. in prep
Sensitivity tests

1. Hg+Br simulation

\[
\begin{align*}
\text{Hg}^0 & \xrightarrow{k_1} \text{HgBr} \xrightarrow{k_2} \text{Hg}^0 \\
\text{HgBr} & \xrightarrow{k_3} \text{HgBrX}
\end{align*}
\]

2. Hg+OH/O_3 simulation

\[
\text{Hg}^0 \xrightarrow{\text{OH}} \xrightarrow{\text{O}_3} \text{Hg}^{\text{II}}
\]

Adjust reduction to match mean NH TGM, then
Compare both against
• global spatial gradients
• seasonal cycles
Global Br distribution

Logo Combo stratosphere:
CH$_3$Br, Halons (CF$_2$Br$_2$, CF$_3$Br,
CF$_2$ClBr, CF$_3$CFBr$_2$)

pTOMCAT troposphere:
CH$_3$Br, Biogenics (CHBr$_3$, CH$_2$Br$_2$,
CH$_2$ClBr, CHClBr$_2$, CHCl$_2$Br)

GMI: Strahan et al. 2007
pTOMCAT: Yang et al. 2008
Surface total gaseous mercury

Major features:
- Anthropogenic emissions drive variability
- Enigmatic cruise data (Soerensen et al. 2010)

Hg+Br model

Holmes et al. in prep

$R^2 = 0.87$ at terrestrial sites
Interhemispheric gradient

Our result:
• Both oxidants give realistic gradient
• Hg+Br closer to land stations
Our result:

• Both oxidants give realistic seasonal cycle
• Arctic sites consistent with 100% reemission from snow
Antarctic subsidence events

Neumayer Station - Temme et al., 2003

Observations

Model

\[ \Delta Hg^0/\Delta O_3 \]

\[ \Delta RGM/\Delta O_3 \]

slope, \( \mu \text{mol m}^{-1} \)

-11

-6

0

3

Observed range

* Hg+Br model

Hg+OH/O_3 model

Neumayer Station - Temme et al., 2003
ARCTAS

Satellites routinely show extensive BrO in March and April, DC-8 never observed > 5ppt
ARCTAS Hg\textsuperscript{0}

Model simulates mean strat. oxidation, but not extremes

Fairbanks

Surface depletion very similar to observations

Hg data - Bob Talbot, UNH
Holmes et al. in prep
Source attribution

Hg Dry Deposition

Large dry dep. contribution
few observations
Hg$^0$ dep. mainly balanced by emission

Hg Wet Deposition

Wet dep. overprediction:
Scavenging at cold T?
Gas-aerosol partitioning?

Hg Total Deposition

Large domestic contribution in industrial region
Overall 20% due to US emissions

US Anthropogenic Emissions (%)

Holmes et al. in prep
Outlook for reducing mercury exposure

• Limited domestic U.S. control over Hg deposition, but emission cuts do help

• Managing other pollutants and nutrients might help

• Ocean deposition sensitive to oxidant, fish accumulation models should be reevaluated