Understanding Hg in the global environment: anthropogenic impacts and atmospheric redox chemistry

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With thanks to: Daniel J. Jacob, Helen M. Amos, and Elsie M. Sunderland

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Mercury
The mercury cycle

ATMOSPHERE

SOIL

LITHOSPHERE

OCEAN
The mercury cycle
The mercury cycle
The mercury cycle
The mercury cycle
The mercury cycle
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Why are atmospheric chemists interested in mercury?

Mass number = 80: \(1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^2 \ 4p^6 \ 4d^{10} \ 4f^{14} \ 5s^2 \ 5p^6 \ 5d^{10} \ 6s^2\)

Mercury’s unique chemical properties

Filled subshells:
- Liquid metal at room temp
- Exists in atmosphere in elemental form like noble gases!
- But can lose its outer two electrons -> biogeochemical cycle
### Mercury’s unique chemical properties

<table>
<thead>
<tr>
<th>Period</th>
<th>Element</th>
<th>Atomic Number</th>
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<tr>
<td>1</td>
<td>H</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Li, Be</td>
<td>3, 4</td>
</tr>
<tr>
<td>3</td>
<td>Na, Mg</td>
<td>11, 12</td>
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<tr>
<td>4</td>
<td>K, Ca</td>
<td>19, 20</td>
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<td>5</td>
<td>Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn</td>
<td>21-30</td>
</tr>
<tr>
<td>6</td>
<td>Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
<td>39-54</td>
</tr>
<tr>
<td>7</td>
<td>Cs, Ba, Fr, Ra</td>
<td>55-88</td>
</tr>
</tbody>
</table>

#### Mass number = 80:

- \( 1s^2 \)  
- \( 2s^2 \)  
- \( 2p^6 \)  
- \( 3s^2 \)  
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- \( 5p^6 \)  
- \( 5d^{10} \)  
- \( 6s^2 \)  

#### Filled subshells:
- Liquid metal at room temp
- Exists in atmosphere in elemental form like noble gases!
- But - can lose its outer two electrons -> biogeochemical cycle
Fish Choices in Connecticut
What’s Safe – What’s Not

Although many fish caught in Connecticut are safe and healthy to eat, some fish from Connecticut waters have dangerous chemicals in them.

If you follow the advice below, you and your family can safely eat fish.

Connecticut Rivers and Lakes – Statewide
Most types of fish may have small amounts of mercury in them. Therefore, the following people should not eat more than one meal a month of fish that are caught in Connecticut rivers and lakes:

- Women who are pregnant
- Women who plan to become pregnant
- Women who are nursing their baby
- Children under six

One exception to this warning is trout. They are safe to eat.

Store Bought Fish
Most fish from the store are safe to eat. Pregnant women, women who plan to become pregnant, nursing mothers and young children should follow these limits:

- Canned Tuna and other commercial seafood:
  - Eat no more than 1-2 meals per week.
  - Choose “Light Tuna” – it has less mercury than the “White” or “Chunk White” Tuna.
  - **DO NOT EAT** Swordfish or Shark – These fish have mercury levels that are too high for women during pregnancy, and nursing mothers.

For more health information call 1-877-458-FISH (3474), or visit this web site: [www.ct.gov/dph/fish](http://www.ct.gov/dph/fish)

For fishing information, call 860-424-3474 or visit this web site: [www.ct.gov/dep/fishing](http://www.ct.gov/dep/fishing)

5/2010
How does Hg end up in fish?
How does Hg end up in fish?

Conversion to methylmercury ([CH$_3$Hg]$^+$) by bacteria

Bioaccumulation of CH$_3$Hg:
- Fish-eating fish: $\times 10^7$
- Insect-eating fish: $\times 10^6$

Mercury concentration
The form of Hg determines its health impact

- **Inorganic Hg** includes:
  - *Quicksilver*
  - 0.01% absorption

- **Hg$^0$** *(inhalation)*
  - ~70% absorption

- **Hg$^{II}$**
  - Avg of 7% absorption *(range 1-17%)*

- **MeHg** *(CH$_3$Hg)*
  - >90% absorption efficiency
  - Primarily a central nervous system toxin
  - Half-life of 50-70 days
  - Chelation not effective
  - Bioaccumulates

Inorganic Hg is more abundant in the environment, but only methylmercury bioaccumulates!
Why is methylmercury so toxic?
Why is methylmercury so toxic?

• Looks like an essential amino acid: passes blood-brain barrier

\[
\text{CH}_3\text{Hg-S-CH}_2\text{-CH-COO}^- \quad \text{NH}_3^+
\]

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- Human exposure is from eating fish
- Greatest health concern is fetal exposure: IQ deficits
- Some evidence of heart disease in adults
We have a problem: major anthropogenic impacts
Mercury has many useful properties

Forms amalgams with silver and gold

Good conductor

Anti-fouling agent
We’ve been using mercury since antiquity
Timescales in the cycle mean historical inputs matter.
Hg emissions take decades to centuries to be sequestered

- Based on best understanding of biogeochemical Hg cycling
- To predict future changes in concentrations from policy action (or climate change), the history of past anthropogenic releases must be accounted for
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Effects of historical emissions on future environmental Hg response

- Same present-day emissions, different past
- Stop all emissions after 2015

Amos et al., 2014, 2015
Effects of historical emissions on future environmental Hg response

**Anthropogenic Emissions**

- Hypothetical profiles:
  - A
  - B
  - C

- Zero after 2015

**Atmosphere**

- **rapid response**
  - independent of emission history

- Pre-anthropogenic level

*Amos et al., 2014, 2015*
Effects of historical emissions on future environmental Hg response

- If historical emissions were decreasing over the last several decades, ocean concentrations will decrease in future when emissions are stopped in 2015

Amos et al., 2014, 2015
Major sources of mined Hg environmental releases

Where Hg is used, and in what products changes with time

Developed world

Developing world

Year (AD)

Mg Hg per year

Other
Explosives/Weapons
Pesticides/Fertilizer
Dyes/Vermilion
Dental
Pharmaceuticals/PCPs
Medical Devices
Wiring/Measuring Devices
Silver/Large-scale gold mining

Batteries
Lamps
Paint
VCM/Other Chemical
ASGM
Chlor-alkali
Major sources of mined Hg environmental releases

Where Hg is used, and in what products changes with time

![Graph showing historical trends in emissions to air from Hg use](Figure 6)

- **Developed world**
- **Developing world**

**Historical trends in emissions to air from Hg use**

- **Explosives/Weapons**
- **Large-scale Gold & Silver Mining**
- **Paint**
- **ASGM**
- **Batteries**

**Where Hg is used, and in what products changes with time**

- **Other**
- **Explosives/Weapons**
- **Pesticides/Fertilizer**
- **Dyes/Vermilion**
- **Dental**
- **Pharmaceuticals/PCPs**
- **Medical Devices**
- **Wiring/Measuring Devices**
- **Silver/Large-scale gold mining**

**year**

**Mg Hg per year**

**Year (AD)**

- 1850
- 1890
- 1930
- 1970
- 2010

**Horowitz et al., 2014**
Commercial Hg sources affect temporal trends of total anthropogenic emissions

- 50% more emissions to air since 1850
- Emissions now thought to have decreased from 1970 - 2000
Confidence in emissions inventory: historical Hg concentrations from ice
Confidence in emissions inventory: historical Hg concentrations from ice

Figure modified from Beal et al. (2015)

Schuster et al., 2002

C) Estimated Primary Anthropogenic Emissions

- Industrial and Mining, Streets et al., 2011
- Commercial, Horowitz et al., 2014
Future global outlook

- Global legally binding mercury treaty
Future global outlook

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North and Central America

total imports of fish, % by continent

UNEP; FAO; Artisanal Gold Council; Mercury Watch
Future global outlook

- Global legally binding mercury treaty

128 signatories 18 ratifications

UNEP; FAO; Artisanal Gold Council; Mercury Watch
Future global outlook

- Global legally binding mercury treaty
- Largest source today (ASGM) is already illegal – but there is hope

128 signatories 18 ratifications

UNEP; FAO; Artisanal Gold Council; Mercury Watch
what happens once Hg gets in the atmosphere?

"The precise chemistry of the mercury in the air is critical to understanding how it is deposited and how it is taken up by plants and animals."

UNITED NATIONS ENVIRONMENT PROGRAMME

Chemicals Branch, DTIE

The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport
Atmospheric redox chemistry plays key role in Hg deposition to the surface.
Atmospheric redox chemistry plays key role in Hg deposition to the surface

Hg(II) → Near-field deposition → Local “hot spot” → atmosphere

Hg(0)
Atmospheric redox chemistry plays key role in Hg deposition to the surface.
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Hg(0) → Hg(II) via Oxidation and Reduction

- Near-field deposition
- Local "hot spot"

Hg(II) → Hg(0) via Reduction

- Long-range transport
- Atmosphere

Hg(0) → Hg(II) via Oxidation

- Far-field deposition
- Foreign countries remote environments
- Surface
Measurement limitations lead to uncertainties in Hg oxidation

- Co-located total Hg(II) measurements are inconsistent
- Exact chemical composition of oxidized Hg in the atmosphere cannot be currently measured
- Very little experimental thermodynamic and kinetic data
- Oxidation may be slow (lifetime of 6 months) and real atmospheric concentrations are on the order of $10^{-13}$ moles Hg/mole of air

We can look to models to fill in the gaps!
Atmospheric chemists search for what oxidizes Hg.
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- OH radical and ozone (O_3) oxidize many other atmospheric gases (e.g., methane), so why not Hg?

- Later theoretical studies show oxidation of Hg(0) by OH or O_3 is endothermic
Atmospheric chemists search for what oxidizes Hg

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Bromine proposed as important atmospheric Hg oxidant

- “Bromine explosion” from photochemistry in saline sea ice surface
- Atmospheric mercury depletion events (AMDEs) and ozone depletion in Arctic spring

- Halogens destroy O₃ - maybe Hg too!
Additional proposed 2\textsuperscript{nd}-step oxidants, NO\textsubscript{2} and HO\textsubscript{2} dominate oxidation mechanism

1) \( \text{Hg}^0 + X + M \rightarrow \text{Hg}X + M \)
2) \( \text{Hg}X + M \rightarrow \text{Hg}^0 + X + M \)
2a) \( \text{Hg}X + X \rightarrow \text{Hg}^0 + X_2 \)
3) \( \text{Hg}X + Y \rightarrow \text{Hg}XY \)

Additional radicals confirmed by Dibble et al. (2012)

\[ X = \text{Br, Cl} \]
\[ Y = \text{Br, OH, HO}_2, \text{NO}_2, \text{BrO, ClO} \]
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Global total Hg oxidation by pathway

- HgBr+NO₂
- HgBr+HO₂
- HgBr+ClO
- HgBr+Br
- HgBr+OH
- HgBr+BrO

GEOS-Chem
Additional proposed 2\textsuperscript{nd}-step oxidants, NO\textsubscript{2} and HO\textsubscript{2} dominate oxidation mechanism

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Global total Hg oxidation by pathway

- \( \text{HgBr} + \text{Cl} \) total
- \( \text{HgBr} + \text{Br} \)
- \( \text{HgBr} + \text{BrO} \)
- \( \text{HgBr} + \text{ClO} \)
- \( \text{HgBr} + \text{NO}_2 \)
- \( \text{HgBr} + \text{HO}_2 \)
Aircraft data can test the modeled total oxidation.

“Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container”

Hg(0) vs Ozone in Stratospheric Air

CARIBIC observations
Model

<table>
<thead>
<tr>
<th>Ozone (ppb)</th>
<th>CARIBIC data courtesy of F. Slemr</th>
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<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
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<tr>
<td>400</td>
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</tr>
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</table>

Hg(0) is oxidized & depleted

~ height into the stratosphere
Changing Hg oxidation changes deposition to the surface

**Hg(0) oxidation rate from different oxidants**

- **Hg+Br Model**
- **Hg+OH/O\(_3\) Model**

![Hg(0) oxidation rate from different oxidants](holmes_et_al_2010)

*Holmes et al., 2010*
Changing Hg oxidation changes deposition to the surface

Hg(II) deposition from different oxidants

Hg+Br

Hg+OH/O₃

Holmes et al., 2010
Changing Hg oxidation changes deposition to the surface

Hg(II) deposition from different oxidants

Hg+Br

Hg+OH/O_3

Holmes et al., 2010
Changing Hg oxidation changes deposition to the surface

**Hg(II) deposition from different oxidants**

- Hg+Br
- Hg+OH/O₃

"Wet" deposition: Hg^{II} not Hg⁰

Need more measurements of Hg(II) deposition in rain water

Hg deposition rain bucket

http://www.eos.unh.edu/

Holmes et al., 2010
What is happening with Hg here in the US?

Hg(II) wet deposition is largely decreasing

Trend, 1990 – 2010
Mercury Deposition Network (MDN) sites

Y. Zhang et al., submitted (PNAS)
What is happening with Hg here in the US?

- Large co-benefits of air pollution controls for other pollutants (acid rain!): Hg(II) very low
- To lower remaining Hg(0) emissions, need Hg-specific controls (ACI = activated carbon injection)
Hg-specific controls needed for further emissions reductions

USEPA “MATS” rule: decades in the making

Earlier in 2015, rule was struck down by Supreme Court, sent back to EPA drawing board

What does this mean for other EPA regulations under the Clean Air Act?
Hg-specific controls needed for further emissions reductions

USEPA “MATS” rule: decades in the making

Cap & Trade (Bush admin.) struck down because of local contamination issue:

Earlier in 2015, rule was struck down by Supreme Court, sent back to EPA drawing board

What does this mean for other EPA regulations under the Clean Air Act?
Take-home messages
• **Unique chemistry of Hg**: volatile elemental form; global pollutant; oxidation determines its solubility and deposition to the surface; methylmercury is especially toxic; and it’s so useful!
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- **Massive anthropogenic signal** in environmental levels historically from Hg use in commercial products & coal emissions
- Today, **small-scale gold mining** is the largest source & global Minamata Convention treaty seeks to regulate sources
Take-home messages

• **Unique chemistry of Hg**: volatile elemental form; global pollutant; oxidation determines its solubility and deposition to the surface; methylmercury is especially toxic; and it’s so useful!

• **Massive anthropogenic signal** in environmental levels historically from Hg use in commercial products & coal emissions

• Today, **small-scale gold mining** is the largest source & global Minamata Convention treaty seeks to regulate sources

• In the US, we have seen **Hg(II) decreases** from other air pollution controls, but we need the **MATS rule** to further decrease Hg(0)
Thank you!

Questions?

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