A Geochemical Perspective on Methylmercury Exposures and Health Risks

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Why are we worried about Hg in the environment?

Should Pregnant Women Eat More Tuna?
By TARA PARKER-POPE  MARCH 2, 2015 3:55 PM  73 Comments

Special report: Can eating the wrong fish put you at higher risk for mercury exposure?
The government wants you to eat more seafood. The key to limiting your risk is choosing the right fish.
Published: August 2014
Methylmercury is a bioaccumulative neurotoxin

Concentrations are $10^6-10^7$ water

- Neurocognitive deficits
- Impaired motor function
- Cardiovascular effects

mercury concentration

water

plankton

small fish

big fish
top predators

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Minamata Convention

- First global agreement on anthropogenic Hg reductions established in 2013
- 128 Signatures, 11 Ratifications (May, 2015)

Mercury and Air Toxics Standards

Protecting our children and communities by limiting emissions of mercury and other air toxics from power plants
Today’s Discussion

• Global biogeochemical Hg cycle
• Anthropogenic Hg sources & trends
• Future trajectories in ocean Hg concentrations
• Use of Hg stable isotopes to better understand human exposures and risks
State-of-the-science understanding ca. 2010

Focused on present day and future

Enrichment
Atmospheric deposition increased 3x (2-5x) since 1850

Isolated systems

atmosphere
land
ocean
The global biogeochemical cycle of mercury
Toolbox of models for capturing global cycling

**ATMOSPHERE**
- GEOS-Chem CTM ([www.geos-chem.org](http://www.geos-chem.org))
- Meteorology from assimilated satellite data (NASA)

**SURFACE OCEAN**
- Smith Downey et al., 2010; Corbitt et al., in-prep.
- Soerensen et al., 2012

**SUBSURFACE OCEAN**
- MITgcm ([http://mitgcm.org](http://mitgcm.org))
- Zhang et al., 2015

**DEEP OCEAN**
- Sunderland & Mason, 2007

**SOIL AND VEGETATION**
- CASA Biogeochemical Carbon Model

**DEEP MINERAL RESERVOIR**
- Selin et al., 2008

Fully coupled biogeochemical box model: Amos et al., 2013
Perturbation analysis reveals timescales of couplings between global reservoirs.

Fate of a unit pulse of Hg to the atmosphere

Amos et al. (2013), GBC; Amos et al. (2014), ES&T
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We’ve been using mercury since antiquity
All-Time Historical Atmospheric Hg Releases

- 350 Gg total release
- 61% 1850-present
- 39% prior to 1850

Streets et al., 2011
All biogeochemical reservoirs have experienced anthropogenic enrichment

Amos et al., 2013
Mercury has lots of useful properties

- Forms amalgams with silver and gold
- Good conductor
- Anti-fouling agent
- Mercury in products

Horowitz et al. (2014)
Global Consumption of Hg in Commercial Applications is well-constrained

Horowitz et al., 2014
Emissions from China and artisanal gold mining drive global trajectory in recent decades

Global Anthropogenic Releases of Hg

Horowitz et al. (2014), ES&T
Explaining measured trends has challenged our understanding of Hg cycling and emissions.

Soeresen et al. (2012); Ebinghaus et al. (2011); Slemr et al. (2011)

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**Marine Boundary Layer**

**North Atlantic**

**South Atlantic**

**Soresen et al. (2012); Ebinghaus et al. (2011); Slemr et al. (2011)**
Global atmospheric Hg emissions from anthropogenic sources in 2010

Source: UNEP, 2013
Artisanal and small-scale gold-mining now the largest global Hg source

Kocman et al., 2015

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Emissions from China and artisanal gold mining drive global trajectory in recent decades

Horowitz et al. (2014), ES&T

Flatter recent trajectory
- ASGM: Muntean’14
- China: Zhang’15

Global Anthropogenic Releases of Hg

Hg releases (Mg a⁻¹)

Year (AD)
Decreased Hg use in products and co-benefits from SO₂ control explain Hg trends

Horowitz’14 inventory with products

Atmospheric Hg⁰ trend, 1990-2010

US utilities Hg⁰ emissions

US wet deposition trend, 1990-2010

Zhang et al. (in prep.)
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More than 90% of U.S. population-wide MeHg exposure is from consumption of marine fish. 

Fraction of U.S. Population-Wide Hg Intake (%)

- Tuna (all): 40%
- Swordfish: 10%
- Pollock: 5%
- Shrimp: 2%
- Cod: 1%
- Crab: 1%
- Salmon (all): 1%
- Anchovies et al.: 1%
- Orange Roughy: 1%
- Halibut: 1%
- Flounders: 1%
- Haddock et al.: 1%
- Grouper et al.: 1%
- Snappers: 1%
- Mackerel: 1%

Fish harvested outside US domestic waters

10%

Sunderland, 2007
Oceans respond rapidly to reductions in anthropogenic emissions

Illustrative response to zero-out of anthropogenic emissions globally in 2015.

Dashed lines = model without coastal sediment sink

Solid lines = updated fully coupled geochemical model

Magnitude of decline sensitive to past emissions and coastal burial
The need for aggressive emission reductions to stabilize ocean Hg is robust to uncertainty

Modeled response to terminating anthropogenic emissions  
(normalized to 2015)

Amos et al. (2015), *ES&T*
Modeled North Pacific seawater and fish concentrations based on anthropogenic emissions

- Range of future concentrations dependent on anthropogenic emissions choices
- Fish MeHg levels track water column concentrations with lag << 10 years

**Total Hg North Pacific Seawater (pM)**

**North Pacific Tuna MeHg (ug/g)**

Sunderland et al., 2013
New Global Inventory for Hg Discharges from Rivers

New Inventory: Rivers: $5400 \pm 2700$ Mg y$^{-1}$
Anthropogenic emissions to the atmosphere~ $2000$ Mg y$^{-1}$

Amos et al. (2014)
High concentrations of bioaccumulative contaminants pose risks for marine fisheries

Modeled contributions of global rivers discharges to seawater mercury concentrations

Source: Zhang et al., 2015 (in-review)
We have developed a generic model for MeHg bioaccumulation in marine ecosystems.

Example: Atlantic Cod (*Gadus morhua*) in the Gulf of Maine

### Temperature Increase

- Baseline (year 2000)
- 1°C temperature increase

### Change in Trophic Structure

- Commercial Fish catch size
- Year 1970 diet
- Year 2000 diet

<table>
<thead>
<tr>
<th>Commercial Fish catch size</th>
<th>Year 1970 diet</th>
<th>Year 2000 diet</th>
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</thead>
<tbody>
<tr>
<td>Temperature Increase</td>
<td></td>
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<tr>
<td>Wet weight (kg)</td>
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<td>Tissue MeHg (ng/g)</td>
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**Biogeochemistry of Global Contaminants**

**Harvard School of Engineering and Applied Sciences**
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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
Ongoing debate about benefits and risks of seafood

**Graph:**
- **Y-axis:** Omega-3 Fatty Acids (EPA + DHA) (g per 100 g of fish)
- **X-axis:** Methylmercury (μg/g)

**Legend:**
- Herring
- Mackerel
- Salmon
- Sardines
- Seabass
- Trout
- Shrimp
- Crabs
- Catfish
- Lobster
- Clams
- Flatfish
- Pollock
- Perch
- Crayfish
- Mussels
- Breaded fish products
- Perch
- Cod
- Oysters
- Mussels
- Scallops

**Graph Title:** Which Fish Should I Eat? Perspectives Influencing Fish Consumption Choices

*Source: Mahaffey et al., 2008*
MeHg Exposure = \[ \sum (\text{Meal Frequency} \times \text{Meal Size} \times \text{Hg in Fish}) \]

Individual Preferences

Environmental Exposure

U.S. individuals consuming > 3 fish meals per week

23% > EPA RfD for MeHg

Li et al., 2015

Hair Hg (ppm)
Many individuals have much less MeHg in their hair than predicted based on their diet.

- Correction applied for species specific over-reporting
- Data quality verified for all surveys
- Individuals with low hair Hg are a mix of ethnicities, genders, and ages from diverse regions in the US
- This pattern has been observed across many studies

Individuals consuming > 3 fish meals per week

1 = perfect agreement model/measured
<1 = underpredict biomarker concentration
>1 = overpredict biomarker concentration

Modeled/measured hair Hg ratio

Number of hair providers

0.3-1 1-3 3-10 10-100 (>100)
Hg stable isotopes provide new information on environmental processes and Hg exposure sources

Example: $^{202}$Hg abundance in nature varies from 29.6 to 29.7 %

Typical measurement precision for $\delta^{202}$Hg is 0.1 – 0.2 ‰
You are what you eat (no MIF change) plus 2‰ MDF

Li et al. (2014)
Demethylation does not explain discrepancy between intake and biomarker Hg levels

\[ \Delta^{199}\text{Hg} (\%) \]

\[ \delta^{202}\text{Hg} (\%) \]

Li et al., 2015, in prep.

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Human activity has substantially enriched Hg in surface reservoirs

Timescales of coupling of the ocean, atmosphere and organic soils range from a few months to millennia

Substantial enrichment of the subsurface ocean in Hg from historic activity

Short term dietary interventions may be possible for altering the assimilation efficiency of MeHg allowing consumption of fish and traditional foods with minimal risk