Mercury cycling between the atmosphere and the ocean and terrestrial systems

Robert Mason
Dept. Marine Sciences, University of Connecticut
Groton, CT 06340

- How important is the ocean in the global cycle? What is the role of oceanic gaseous Hg evasion? Marine boundary layer photochemistry?
- What is the response time of the ocean to changes in atmospheric mercury? What are the most important constraints on oceanic Hg evasion? Is ocean mixing important?
- What is the importance of atmospheric chemistry generally? How well can we model atmospheric processes?
- What are the major controls over Hg exchange at the terrestrial-air interface?
- What is the relationship between inorganic Hg and methylated Hg in the ocean? What is the site for methylation?
Models by Datoor and Larocque (2004) and others have emphasized and examined the importance of anthropogenic emissions in contributing to deposition to the ocean. But what about other processes? How important is oceanic evasion of Hg$^0$ in the global cycle?

But, how important is the ocean and the terrestrial environment as sources of Hg to the atmosphere? How can short-term variations in concentrations of ionic atmospheric Hg, such as shown on the right, be explained?
Redox processes at the air-sea interface

Atmosphere

Hg$^0$ \[\rightarrow\] Hg(II) \[\rightarrow\] Hg$^P$

Deposition both as a gas and particulate

evaporation

Ocean Surface

Hg$^0$ \[\leftrightarrow\] Hg(II) \[\leftrightarrow\] Hg$^0$
Estimates suggest that the concentration of Hg in the atmosphere has increased by about a factor of 3 since industrialization. But has the ocean increased in concentration to the same degree? What is the importance of oceanic evasion? How important are boundary layer atmospheric processes?
Air-Sea Exchange: An important part of the global mercury cycle

- Rate of deposition depends on the concentration and form (solubility for wet deposition; dry deposition rate for gases and particles) of Hg in the atmosphere.
- Mercury is reactive and can be relatively easily converted between its two primary oxidation states in the environment – Hg$^0$ and Hg$^{II}$.
- Hg is very different in its two oxidation states at normal temperature and pressure – Hg$^0$ is a sparingly soluble gas with a low deposition velocity, while Hg$^{II}$ compounds (RGHg) are highly soluble, deposit rapidly from the atmosphere in the gas phase, and interact with particles in the atmosphere, and in water. In the atmosphere, Hg$^0$ is relatively easily oxidized.
- In surface waters, Hg$^{II}$ can be oxidized and Hg$^0$ can be reduced. In water, gas exchange can be an important loss mechanism for Hg$^0$. 
RELATIONSHIP BETWEEN OZONE AND RGHg in the PACIFIC OCEAN MBL

Laurier et al. (2003)
As found by others, there is little relationship between RGHg and pollution indicators. Air masses with low CO and low ozone appear to have the highest RGHg concentrations. Wind speed is also important as there will be higher concentrations during low winds.
Relationship between maximum daily RGHg concentration and midday ozone concentration for various studies

Laurier et al. (in rev)
Measurement and modeling demonstrate the importance of atmospheric oxidation of elemental mercury and of dry deposition of ionic mercury in contributing mercury to the ocean and in influencing the global mercury cycle.

Estimated air-sea exchange fluxes (in Mmol/yr) for two recent global models:

<table>
<thead>
<tr>
<th>Source</th>
<th>Flux (Mason and Sheu, 02)</th>
<th>Flux (Strode et al. (in rev.))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Dep</td>
<td>9.6</td>
<td>7.5</td>
</tr>
<tr>
<td>Dry Dep</td>
<td>5.8</td>
<td>15.3</td>
</tr>
<tr>
<td>Evasion</td>
<td>13</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Reactive gaseous mercury over the North Pacific Ocean

Reactive gaseous mercury over the North Atlantic Ocean

Laurier et al. (in rev)
Location of Sampling Site at CBL
RGHg was low during rainfall indicating their efficient removal by wet deposition. The highest concentrations were found in the afternoon at low wind speed suggestive of in situ formation. However, highest concentrations also appeared to be related to wind direction, and suggestive of a link to winds from the urban-terrestrial reaches.

Laurier et al. (in rev)
Elemental Mercury and Reactive Gaseous Mercury Concentrations at CBL, 11/03-5/04

Laurier et al. (in rev)
General Comments

- Elevated concentrations of Hg\(^0\) are correlated with pollution indicators (e.g. CO).
- Little correlation between elevated Hg\(^0\) and RGHg in a number of studies suggests that pollution is not the only RGHg source.
- Photochemical production of RGHg is important on a global scale. High RGHg concentrations and a diurnal cycle is found over the ocean during low ozone events. In coastal regions, high concentrations and variability (diurnal) is not consistently related to ozone (high or low), pollution indicators, wind direction, etc. Multiple sources, boundary layer changes and in situ production all likely contribute to variability.
- Recent results and modeling studies suggest a depletion in Hg\(^0\) at high elevations, through oxidation to RGHg
Mercury in Ocean Waters and Gas Exchange
<table>
<thead>
<tr>
<th>Location</th>
<th>HgT (pM)</th>
<th>MeHg (fM)</th>
<th>%MeHg</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>South and Eq. Atlantic</td>
<td>0.8 - 2.4</td>
<td>25 - 200</td>
<td>5-10</td>
<td>1</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>2.4 ± 1.6</td>
<td>29 – 160</td>
<td>2-7</td>
<td>2</td>
</tr>
<tr>
<td>North Pacific</td>
<td>1.2 ± 0.9</td>
<td>&lt;50</td>
<td>&lt;4</td>
<td>3</td>
</tr>
<tr>
<td>Equatorial Pacific</td>
<td>0.5-4.0</td>
<td>35 - 670</td>
<td>2-15</td>
<td>4</td>
</tr>
<tr>
<td>Mediterranean</td>
<td>0.5 – 4.0</td>
<td>20 - 460</td>
<td>1 – 35</td>
<td>5-7</td>
</tr>
</tbody>
</table>

Note: HgT: total mercury; MeHg: methylated mercury including MeHg and Me$_2$Hg.

<table>
<thead>
<tr>
<th>Location</th>
<th>DGHg (pM)</th>
<th>Flux (µg m⁻² m⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equatorial Pacific</td>
<td>0.05-0.36</td>
<td>0.7-7</td>
<td>1</td>
</tr>
<tr>
<td>North Pacific</td>
<td>0.13 ± 0.07</td>
<td>0.7-1.8</td>
<td>2</td>
</tr>
<tr>
<td>Equatorial Pacific 2002</td>
<td>0.06 ± 0.03</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>N. Atlantic – summer</td>
<td>0.25-1.25</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>S. Atlantic – summer</td>
<td>1.24 ± 0.81</td>
<td>36</td>
<td>4</td>
</tr>
<tr>
<td>Bermuda</td>
<td>0.08-0.2</td>
<td>2.7</td>
<td>5</td>
</tr>
<tr>
<td>Long Island Sound, USA</td>
<td>0.04-0.55</td>
<td>2.1</td>
<td>6</td>
</tr>
<tr>
<td>Scheldt Estuary, Belgium</td>
<td>0.1-0.65</td>
<td>1.2-2.4</td>
<td>7</td>
</tr>
<tr>
<td>North Sea</td>
<td>0.06-0.8</td>
<td>0.35-6.7</td>
<td>7</td>
</tr>
<tr>
<td>Chesapeake Bay, USA</td>
<td>0.02-0.2</td>
<td>0.8</td>
<td>8</td>
</tr>
<tr>
<td>Lakes/Wetlands</td>
<td>-</td>
<td>0.2-2</td>
<td>9</td>
</tr>
</tbody>
</table>

*Note: As fluxes are mostly from short-term measurements, they are scaled to a monthly rather than yearly basis.*

Atmospheric model – GEOS-Chem tropospheric model version 7 (Selin et al., in review). Pacyna 2000 Inventory; 3 atmospheric species – Hg$^0$, Hg$^{II}$ and Hg-P

Ocean slab model of the mixed layer with three Hg species – Hg$^0$, Hg$^{II}$ and Hg$^{NR}$. Vertical mixing and changing mixed layer depth in model but no horizontal advection

\[
k_p = f(NPP, RAD, z)
\]

\[
k_c = f(NPP)
\]

\[
k_{sink} = f(NPP, \text{ef})
\]

\[
F_{ent} = \text{entainment flux}
\]

\[
F_{diff} = \text{diffusive flux}
\]

\[
F_{up} = \text{upwelling flux}
\]

\[
F_{oa} = \text{evasion flux}
\]

Strode et al. (in rev)
Figure 3: Monthly mean mercury deposition (wet + dry) flux to the ocean (a,b); reduction rate constant, $k_p$ (c,d); and ocean flux, $F_{oa}$ (e,f) for January (left) and July (right). Positive values of $F_{oa}$ indicate that the flux is from the ocean to the atmosphere.
The Importance of Oceanic Evasion in the Global Mercury Cycle

Estimated contribution of ocean evasion of elemental mercury to the total gaseous mercury concentration in the atmospheric boundary layer. Estimate based on the modeling studies of Strode et al. (in review) and Selin et al. (in review)

Figure 7: Percent contribution of ocean emissions to atmospheric surface concentrations of Hg$^0$. Contours shown are between 25% and 55%, with increments of 5%.  
Strode et al. (in rev)
But how important is lateral mixing in Hg distribution and cycling in the upper ocean?

Pacific Ocean  Mason et al. (1994)

<table>
<thead>
<tr>
<th></th>
<th>Fluxes in Mmol/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>net</td>
<td>0.84</td>
</tr>
<tr>
<td>net</td>
<td>1.01</td>
</tr>
<tr>
<td>0.07</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Intermediate Water flowing toward the equator centered around ~800 m

Antarctic Bottom Water

North Atlantic Deep Water formation

Natural and Anthropogenic

\[
\text{Hg}^0 \rightarrow \text{Hg}^{+2} \rightarrow \text{Hg}^{2+} \rightarrow \text{Hg}^{2+} \]

Production and Biological Incorporation

Equator

North Atlantic Deep Water formation
Global Box Model for the Oceans Showing the Major Water Flows. 
*Taken from Kahana et al. (2004)*

### Water Mass and Surface Area

<table>
<thead>
<tr>
<th>Water Mass and Surface Area</th>
<th>Vol (x 10^{16} m^3)</th>
<th>Water Mass and Surface Area</th>
<th>Vol (x 10^{16} m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarctic (&gt;65°S)</td>
<td>1.8 (3%)</td>
<td>Surf. Pac+Ind (30°N-30°S)</td>
<td>4.5 (8%)</td>
</tr>
<tr>
<td>Surface Atl. (35°S-55°N)</td>
<td>1.2 (2%)</td>
<td>North Pac. (&gt;30°N)</td>
<td>5.9 (10%)</td>
</tr>
<tr>
<td>North Atl. (&gt;55°N)</td>
<td>2.6 (5%)</td>
<td>Interm. Pac+Ind (40-65°S)*</td>
<td>30.3 (53%)</td>
</tr>
<tr>
<td>Intermediate Atl. (65-35°S)*</td>
<td>10.8 (19%)</td>
<td><strong>Total</strong></td>
<td><strong>57.1</strong></td>
</tr>
</tbody>
</table>

* At depth these water masses extend under the surface Atl and Pac+Ind masses
Note: a: The total net input is an estimation of the current sources minus the current sinks for each water mass. In addition, the current annual rate of increase in concentration is shown. Mason (unpublished results).

<table>
<thead>
<tr>
<th>Water Mass</th>
<th>Inventory (Mmol)</th>
<th>Total Net Input (Mmol yr⁻¹)</th>
<th>%Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Atlantic</td>
<td>23.7</td>
<td>-0.29</td>
<td>-1.31</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>51.8</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>Intermed. Atlantic</td>
<td>161.6</td>
<td>0.97</td>
<td>0.61</td>
</tr>
<tr>
<td>Surface Pacific+Indian</td>
<td>55.7</td>
<td>0.22</td>
<td>0.40</td>
</tr>
<tr>
<td>North Pacific</td>
<td>73.5</td>
<td>0.20</td>
<td>0.27</td>
</tr>
<tr>
<td>Intemed. Pacific+Indian</td>
<td>364.7</td>
<td>1.35</td>
<td>0.37</td>
</tr>
<tr>
<td>Antarctic</td>
<td>16.2</td>
<td>0.09</td>
<td>0.59</td>
</tr>
<tr>
<td>Total</td>
<td>747.1</td>
<td>2.6</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Both models support the notion that the concentrations of mercury in the surface ocean vary with latitude and with ocean. The box model can be used to estimate the changes that have occurred in the more recent past. The model suggests that the N. Atlantic Ocean is decreasing in concentration and that so far there has been little change in the concentration of Hg in the N. Pacific waters. Filed data support this contention.

<table>
<thead>
<tr>
<th>Ocean Region</th>
<th>Box Model</th>
<th>Strode et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Atlantic</td>
<td>2.0 pM</td>
<td>3.7 pM</td>
</tr>
<tr>
<td>Subtrop. N. Atlantic</td>
<td>2.0 pM</td>
<td>1.6-2.3 pM</td>
</tr>
<tr>
<td>N. Pacific</td>
<td>1.25 pM</td>
<td>1.5 pM</td>
</tr>
<tr>
<td>S. Atlantic</td>
<td>1.5 pM</td>
<td>1.8 pM</td>
</tr>
<tr>
<td>S. Pacific</td>
<td>1.2 pM</td>
<td>1.1 pM</td>
</tr>
</tbody>
</table>

Table S3. Observed and modeled total (Hg$_{aq}$ = Hg$_0$ + Hg$_{aq}$ + Hg$_{aq}$) concentrations from the ocean surface and mixed layer.

<table>
<thead>
<tr>
<th>Location and time period</th>
<th>Observations (pM Hg$_{aq}$)</th>
<th>Standard Model (pM Hg$_{aq}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Atlantic 40°-43°N; 68°-70°W Aug.</td>
<td>2.8</td>
<td>3.7</td>
<td>Gill and Fitzgerald [1987]</td>
</tr>
<tr>
<td>North Pacific 23°-50°N; 142°E-164°W May-June</td>
<td>0.87</td>
<td>1.5</td>
<td>Laurier et al. [2004]</td>
</tr>
<tr>
<td>Bermuda 32°N; 64°W Sept.</td>
<td>0.71</td>
<td>2.3</td>
<td>Mason et al. [2001]; Gill and Fitzgerald [1987]</td>
</tr>
<tr>
<td>Bermuda 32°N; 64°W Dec.</td>
<td>5.5</td>
<td></td>
<td>Mason and Sullivan [1999]</td>
</tr>
<tr>
<td>South Atlantic 33°S-8°N; 20°-49°W May</td>
<td>2.9</td>
<td>1.8</td>
<td>Mason et al. [2001]</td>
</tr>
<tr>
<td>South Pacific 34°-36°S; 163°-173°E Sept.</td>
<td>2.8</td>
<td>1.1</td>
<td>Gill and Fitzgerald [1987]</td>
</tr>
</tbody>
</table>
A: Major Ecosystem Inputs and Outputs of Mercury

Evasion from Soil and Vegetation

Wet Deposition and Dry Deposition of Gaseous and Particulate Hg

Watershed Retention and Transport/Runoff of Hg and CH₃Hg

Bioaccumulation of CH₃Hg

Evasion

B: Major Aquatic Mercury Pathways

Biota

CH₃Hg(II) → demethylation → Hg(II) → reduction → Hg(0) → evasion

CH₃Hg(II) → methylation

Hg(II) → oxidation

Hg(0) → diffusion → resuspension

CH₃Hg(II) → diffusion → resuspension

Burial in Sediments

Mason et al. (2005)
Total Ecosystem Hg Deposition

Wet, Dry, Throughfall, Litterfall,

*Leaf tissue*

Canopy air

Soil

Water

Root tissue

Dry Deposition?
1. Dry deposition to surfaces of particulate Hg and ionic gaseous Hg
2. Net uptake of elemental Hg by vegetation

What does litterfall represent?

Are the terrestrial interactions being adequately modeled?

**NEW INPUTS**
- Particulate/reactive Hg deposition onto canopy
- Stomatal uptake of atmospheric Hg(0)

**FLUX**
- Litterfall
- Throughfall

**FLUX**
- Stomatal uptake of Hg(0) emitted from soils

**RECYCLED INPUTS**
- Hg uptake via roots

*FIGURE 1. Diagrammatic representation of Hg cycling in a forest canopy.*
Dry deposition estimates include the uptake of Hg\(^0\) by vegetation.

*Figure 7.* Estimated dry mercury deposition in \(\mu g \text{ m}^{-2} \text{ y}^{-1}\) to rural areas. Deposition was not estimated for areas with urban or residential land cover. Mercury deposition is likely to be much greater than depicted here in the immediate vicinity of urban areas and emissions sources. The effects of urban and point emissions sources are not well captured by the sparse, rural mercury observation network. Dry mercury deposition may be greater than depicted here in the northern low arctic areas because of seasonal mercury depletion events (Lindberg et al., 2002).
Biological Transformations and Bioaccumulation:

Can we model net mercury methylation and bioaccumulation in ocean waters?
What about Methylmercury? What are its sources and sinks?

Ratio: Pluvial/Fluvial
\[
\begin{align*}
\text{Hg} & \quad \sim 15 \\
\text{MeHg} & \quad \sim 2
\end{align*}
\]

Major source for Hg is the atmosphere

Major source of MeHg is in situ production

But where?
Deep ocean sediments (ala Kraepiel et al., 2003)

Water column in low oxygen environments (ala Mason et al)

Shelf and slope sediments (ala Mason and Fitzgerald et al)
Overall Comments

- Deep ocean sediments as a source of MeHg to fish can only be so if MeHg is highly stable in deeper ocean waters. Available evidence, while limited, suggests that MeHg is degraded fast enough for this to be unlikely.
- Coastal and shelf sediments appear to be important locations of methylation. However, demethylation in both the water column and sediments is occurring. Is the degradation rate slow enough for the MeHg to be transported to the open ocean? “Biotransport” due to migration of fish and fish feeding patterns may be important. Thus, the offshore transport from shelf sediments could be important, as recently shown for Fe.
- While there is little direct evidence for methylation in open ocean waters, mass balance modeling suggests that rates of formation required to sustain measured concentrations are relatively slow and possible.
Summary

• Photochemical reactions are important in controlling the rate of air-sea exchange of Hg by enhancing oxidation of Hg⁰ in the atmosphere, and especially over the ocean, and by mediating the net rate of Hg⁰ formation and evasion from surface waters.

• These reactions determine the next rate of transfer of Hg between the atmosphere and the ocean, and therefore the extent to which anthropogenic inputs have increased ocean Hg concentrations, and MeHg in fish. Current estimates suggest that the ocean is not the major sink for anthropogenic emissions, primarily because of the extensive evasion of Hg⁰ from surface waters.

• Dry deposition of gaseous Hg¹¹ can be as important as wet deposition in contributing Hg to the Earth’s surface.
Below the equatorial Pacific is an extensive region of low oxygen. Samples were collected in this region in 1990. Low oxygen Region <30 µM is ~1 mg/L O₂

Both methylmercury and dimethylmercury were found in the equatorial region in the sub-thermocline, low oxygen waters, but concentrations in the mixed layer were low.

Station #’s reflect a general west to east trend

Mason and Fitzgerald, 1990; 1993
\[ \frac{d[\text{MeHg}]}{dt} = k_m[Hg^{II}] - k_{dm}[\text{MeHg}] \]

Methylation rate a function of dissolved Hg speciation (sulfide, DOC, solid phases), microbial activity and MeHg decomposition rate, which is likely dependent on speciation.
Could the coastal zone be an important source of methylmercury to the ocean? Recent evidence suggests that this is so for iron, and likely so for other compounds released from shelf sediments. Flux estimates suggest that the input of MeHg from shelf sediments could be significant.

So, modeling MeHg production and fate in the ocean will be complex but the information necessary to do this is being accumulated. However, global models do not deal with the ocean “edges” adequately and this is clearly very important for modeling MeHg.

Lam et al. (2006)
FIGURE 6. Schematic diagram of the estimated mass fluxes and pools for native (old) and \(^{202}\)Hg (new) mercury in the experimental U1F catchment at ELA (area = 680 m\(^2\)). All values are in mg; fluxes represent values scaled to the 15-week period from July 13 to October 26, 1999. Ranges are intended to represent levels of uncertainty (see text for description of the vegetation and soil pools).