A New Global Simulation of Mercury Air-Sea Exchange for Evaluating Impacts on Marine Boundary Layer Concentrations

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Data sources for observations shown in Figures 2 and 4 in the main text:

Data sources for Figure 2 “Modeling results for 2008 atmospheric deposition to the global oceans, surface ocean fluxes, and aqueous Hg concentrations” are as follows: Atlantic (1-4); Pacific (5-8); Arctic (9, 10); Mediterranean (11). We omitted outliers in Hg⁰ observations from two cruises in the Atlantic Ocean in the 1990s due to an apparent contamination problem (2, 3).

Data sources for Figure 4 “Modeled seasonal mean marine boundary layer Hg⁰ concentrations and relative contributions of oceanic emissions” are as follows for cruise observations: (12-18).
Section I: Supplemental Results

Figure S1. Modeled seasonal surface water Hg\(^0\) saturation values for 2008. The degree of saturation indicates the direction of the flux across the air-sea interface. Less than 100% indicates net deposition and greater than 100% indicates net evasion of Hg\(^0\).
Figure S2. Seasonal variability in modeled oceanic Hg$^0$ evasion for 2008.
Figure S3. Comparison of monthly modeled (2008) and observed (various years) total inorganic Hg concentrations. Data sources are as follows: Pacific (5-7, 19-21); Atlantic Ocean (1-3, 21); Arctic Ocean (9).

Figure S4. Comparison of monthly modeled (2008) and observed (various years) seawater Hg\(^0\) concentrations. Pacific Ocean: (5, 8, 19, 22); Atlantic Ocean (2, 11); Arctic Ocean: (9).
Figure S5. Modeled contribution of oceanic Hg$^0$ emissions to marine boundary Hg$^0$ concentrations.
Figure S6. Conceptual diagram of model resolution, subsurface ocean compartments and specified intermediate seawater Hg concentrations.
Table S1. Model differential equations

\[ \frac{dM_{\text{Hg}(0)}}{dt} \text{ Change in Hg}^0 \text{ mass over time (}dt\text{)} = \frac{M_{\text{dep}}}{dt} + \frac{M_{\text{up}}}{dt} - \frac{M_{\text{ent}}}{dt} - \frac{M_{\text{oa}}}{dt} + \frac{k_{\text{ox}}}{dt} + \frac{k_{\text{r}}}{dt} \]

\[ \frac{dM_{\text{Hg}(II)}}{dt} \text{ Change in Hg}^{\text{II}} \text{ mass over time (}dt\text{)} = \frac{M_{\text{dep}}}{dt} + \frac{M_{\text{up}}}{dt} - \frac{M_{\text{ent}}}{dt} - \frac{M_{\text{sink}}}{dt} + \frac{k_{\text{ox}}}{dt} + \frac{k_{\text{r}}}{dt} \]

- \text{Model time step (}s^{-1}\text{)}
- \text{Deposition of Hg to the ocean surface (}kg\text{)}
- \text{Mass of mercury species introduced or removed due to deep convection or shoaling of the mixed-layer (}kg\text{)}
- \text{Wind-driven mass transfer of mercury species due to Ekman pumping (}kg\text{)}
- \text{Mass of Hg}^0 \text{ evaded from the ocean to the atmosphere (}kg\text{)}
- \text{Flux of Hg}^{\text{II}} \text{ lost from mixed layer with sinking particles (}kg\text{)}
- \text{Reservoir of Hg}^0 \text{ in the surface mixed layer (}kg\text{)}
- \text{Reservoir of Hg}^{\text{II}} \text{ in the surface mixed layer (}kg\text{)}
- \text{Hg}^0 \text{ oxidation rate (}s^{-1}\text{)}
- \text{Reduction rate of reducible pool of Hg}^{\text{II}} (\text{unitless})
- \text{Hg}^{\text{II}} \text{ fraction in the dissolved phase (}{}\text{)}$
- \text{Reducible fraction of the filtered Hg}^{\text{II}} \text{ pool (}{}\text{)}$

Table S2. Particle associated mercury reservoirs and fluxes.

- \text{Hg}^{\text{II}} \text{ mass in the particulate phase (}kg\text{)}
- \text{Seawater partition coefficient for Hg}^{\text{II}} \text{ (}L \text{ kg}^{-1}\text{)}
- \text{Concentration of suspended particles (}kg \text{ L}^{-1}\text{)}
- \text{Mixed layer depth (}m\text{)}
- \text{Water surface area (}m^2\text{)}
- \text{Integrated water column pigment content (}mg \text{ m}^{-2}\text{)}
- \text{Carbon to chlorophyll a ratio (}{}\text{)}$
- \text{Conversion for wet weights of planktonic biomass (}{}\text{)}$
- \text{Organic carbon flux out of the mixed layer (}mg \text{ C m}^{-2} \text{ d}^{-1}\text{)}$
- \text{Net primary productivity (}mg \text{ C m}^{-2} \text{ d}^{-1}\text{)}$
- \text{Exponent describing relationship between declines in organic carbon flux due to mineralization in the water column with depth (}{}\text{)}$
- \text{Mass of Hg}^{\text{II}} \text{ sorbed to particles (}kg\text{)}$
- \text{Hg}^p \text{ to organic carbon ratio in the mixed layer (}{}\text{)}$
- \text{Mass of Hg}^p \text{ lost from the mixed layer due to particle sinking (}kg\text{)}$

\[ M_{\text{Hg}(p)} (kg) \text{ Hg}^{\text{II}} \text{ mass in the particulate phase} \]

\[ K_D (L \text{ kg}^{-1}) \text{ Seawater partition coefficient for Hg}^{\text{II}} \]

\[ SPM (kg \text{ L}^{-1}) \text{ Concentration of suspended particles} \]

\[ MLD (m) \text{ Mixed layer depth} \]

\[ A_w (m^2) \text{ Water surface area} \]

\[ OC_{\text{tot}} (mg \text{ m}^{-2}) \text{ Standing stock of organic carbon in mixed layer} \]

\[ Chl_{\text{tot}} (mg \text{ m}^{-2}) \text{ Integrated water column pigment content} \]

\[ C:Chla \text{ (unitless) Carbon to chlorophyll a ratio} \]

\[ wetwt \text{ (unitless) Conversion for wet weights of planktonic biomass} \]

\[ J_{\text{orgC}} (mg \text{ C m}^{-2} \text{ d}^{-1}) \text{ Organic carbon flux out of the mixed layer} \]

\[ NPP (mg \text{ C m}^{-2} \text{ d}^{-1}) \text{ Net primary productivity} \]

\[ n \text{ (unitless) Exponent describing relationship between declines in organic carbon flux due to mineralization in the water column with depth} \]

\[ M_{\text{Hg}(p)} (kg) \text{ Mass of Hg}^{\text{II}} \text{ sorbed to particles} \]

\[ \text{Hg}^p \text{ to organic carbon ratio in the mixed layer} \]

\[ M_{\text{sink}} (kg) \text{ Mass of Hg}^p \text{ lost from the mixed layer due to particle sinking} \]
Method used for estimating suspended particulate matter concentrations

No global data sets on SPM concentrations in the ocean mixed layer are available. We therefore estimate SPM concentrations in the surface mixed layer based on the standing biomass in the water column derived from MODIS satellite chlorophyll a ($Chl \ a, \ mg \ m^{-3}$) concentrations (http://oceancolor.gsfc.nasa.gov/ftp.html) for the year 2003. We calculate the water column integrated pigment content within the euphotic layer ($Chl_{tot}, \ mg \ m^{-2}$) based on the statistical fits for subsurface algal productivity in the ocean developed by Morel and Berthon (29) and updated by Uitz et al. (30).

These equations are as follows:

1. STRATIFIED WATERS

For stratified waters in low and mid latitude stations, where $Chl_{sat} \leq 1.0 \ mg \ m^{-3}$

$$Chl_{tot} = 36.1 \ Chl_{a}^{0.357}$$

For stratified waters in low and mid latitude stations, where $Chl_{sat} \geq 1.0 \ mg \ m^{-3}$

$$Chl_{tot} = 37.7 \ Chl_{a}^{0.615}$$

2. WELL-MIXED WATERS

For well-mixed waters at high latitudes:

$$Chl_{tot} = 42.1 \ Chl_{sat}^{0.538}$$

Waters are defined as well-mixed if $z_{eu}/MLD < 1$
Conversely, if $z_{eu}/MLD > 1$ then the waters are considered stratified.

Where,

$z_{eu}$ is the euphotic depth and is defined as the depth where the PAR irradiance is 1% of its value at the surface.

$MLD$ (m) is the mixed layer depth derived from de Boyer Montegut et al. (25) from the National Oceanographic Data Center (NODE), World Ocean Circulation Experiment (WOCE) database, and the ARGO program (available: http://www.locean-ipsl.upmc.fr/~cdblod/mld.html)

$Chl_{tot}$ and $z_{eu}$ are calculated iteratively in the model to determine whether waters are stratified or well mixed and the appropriate equations for $Chl_{tot}$.

$z_{eu}$ is derived as a function of $Chl_{tot}$ by Morel and Maritorena (31):

$$z_{eu} = 912 \ Chl_{tot}^{-0.839} \text{ when } 10 \ m < z_{eu} < 102 \ m \text{ and } Chl_{tot} > 13.65 \ mg \ m^{-2}$$

$$z_{eu} = 426.3 \ Chl_{tot}^{-0.547} \text{ when } 102 \ m < z_{eu} < 180 \ m \text{ and } Chl_{tot} < 13.65 \ mg \ m^{-2}$$
We calculate the standing stock of organic carbon ($OC_\text{tot}$, mg m$^{-2}$) from the integrated water column pigment content ($Chl_\text{tot}$, mg m$^{-2}$) by assuming a constant C:Chl a ratio of 80:1 based on Wetzel et al. (26). This is a simplification of real biological processes in the ocean where the C:Chla ratios are known to vary as a function of light limitation, depth, and phytoplankton growth rates among other factors (32).

$$OC_\text{tot} = Chl_\text{tot} \cdot C : Chl_a$$

We approximate the concentration of suspended particles in each model grid cell from wet weights of planktonic biomass that are derived by assuming that organic carbon is 50% of the dry weight and the dry weight is 20% of the weight for phytoplankton, resulting in an overall conversion factor of 10 mg wet weight: mg carbon (33). This results in an overall conversion factor of 10 mg wet weight: mg carbon.

$$SPM = 10^3 \left( OC_\text{tot} \cdot \text{wetwt} \cdot A_w \right) / MLD$$

Although the majority of particles in open ocean environments are living and dead planktonic biomass, we allow for up to an additional 10% increase in $SPM$ to account for allochthonous abiotic particles such as mineral dust (34).
### Table S3. Redox reactions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ox1}$ (s$^{-1}$)</td>
<td>Photo-oxidation rate constant</td>
<td>$6.6 \times 10^{-6} \cdot RAD_{\pi}$ (24)</td>
</tr>
<tr>
<td>$k_{ox2}$ (s$^{-1}$)</td>
<td>Dark oxidation rate constant</td>
<td>$1.0 \times 10^{-7}$ (35, 36)</td>
</tr>
<tr>
<td>$k_{red1}$ (s$^{-1}$)</td>
<td>Photolytic reduction rate constant</td>
<td>$1.7 \times 10^{-4} \cdot RAD_{\pi}$ (24)</td>
</tr>
<tr>
<td>$k_{bio}$ (s$^{-1}$)</td>
<td>Biotic reduction rate constant</td>
<td>$4.5 \times 10^{-8} \cdot NPP$ (24)</td>
</tr>
<tr>
<td>$RAD_{\pi}$ (W m$^{-2}$)</td>
<td>Average shortwave radiation intensity in the mixed layer</td>
<td>$\int_{0}^{MLD} RAD$ (W m$^{-2}$)</td>
</tr>
<tr>
<td>$\int_{0}^{MLD} RAD$ (W m$^{-2}$)</td>
<td>Total local shortwave radiation penetration in the mixed layer</td>
<td>$\frac{1}{x_2 - x_1} \cdot RAD \left[ e^{\eta x_1} - e^{\eta x_2} \right]$</td>
</tr>
<tr>
<td>RAD (W m$^{-2}$)</td>
<td>Total shortwave radiation intensity</td>
<td>GEOS-5 meteorology</td>
</tr>
<tr>
<td>$x_1$ (m)</td>
<td>Surface depth</td>
<td>0 m</td>
</tr>
<tr>
<td>$x_2$ (m)</td>
<td>Bottom depth</td>
<td>MLD</td>
</tr>
<tr>
<td>$\eta$ (m$^{-1}$)</td>
<td>Extinction coefficient for radiation</td>
<td>$\eta_{water} + \eta_{Chla} C_{Chl} + \eta_{DOC} C_{DOC}$</td>
</tr>
<tr>
<td>$\eta_{water}$ (m$^{-1}$)</td>
<td>Extinction coefficient for water</td>
<td>450 nm (vis) = 0.0145</td>
</tr>
<tr>
<td>$\eta_{Chla}$ (m$^{-1}$)</td>
<td>Extinction coefficient for pigments</td>
<td>450 nm (vis) = 31</td>
</tr>
<tr>
<td>$C_{Chla}$ (mg L$^{-1}$)</td>
<td>Average concentration of Chl a in mixed layer</td>
<td>$(Chl_{tot} \cdot A_{w}) / MLD$</td>
</tr>
<tr>
<td>$\eta_{DOC}$ (mg L$^{-1}$)</td>
<td>Extinction coefficient for dissolved organic carbon (DOC)</td>
<td>450 nm (vis) = 0.654</td>
</tr>
<tr>
<td>$C_{DOC}$ (mg L$^{-1}$)</td>
<td>Concentration of DOC in water column</td>
<td>$1.5 \cdot (NPP_i / NPP_{globalavg})$ (38)</td>
</tr>
<tr>
<td>$NPP_i$ (gC m$^{-2}$ d$^{-1}$)</td>
<td>NPP in model grid cell</td>
<td>2003 MODIS satellite data (27)</td>
</tr>
<tr>
<td>$NPP_{avg}$</td>
<td>Global average NPP</td>
<td>global NPP/ocean surface area</td>
</tr>
</tbody>
</table>
### Table S4. Gas exchange parameterization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Equation/Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{oa}$ (kg)</td>
<td>Air-sea exchange of Hg$^0$ for each model time step ($dt$, s$^{-1}$)</td>
<td>$(10^{-12} F_v \cdot A_w)dt / 3600$</td>
</tr>
<tr>
<td>$F_v$ (ng m$^{-2}$ hr$^{-1}$)</td>
<td>Hg$^0$ air-sea exchange flux</td>
<td>$F_v = K_w (C_w - C_a / H'(T))$</td>
</tr>
<tr>
<td>$C_w$ (ng m$^{-3}$)</td>
<td>Concentration of Hg$^0$ in seawater</td>
<td>See differential equations</td>
</tr>
<tr>
<td>$C_a$ (ng m$^{-3}$)</td>
<td>Concentration of Hg$^0$ in air</td>
<td>GEOS-Chem atmospheric simulation</td>
</tr>
<tr>
<td>$H'(T)$</td>
<td>Temperature dependent dimensionless Henry’s law constant</td>
<td>$\ln H’ = (-2403.3 \frac{T}{T^2} + 6.92)$</td>
</tr>
<tr>
<td>$K_w$ (m hr$^{-1}$)</td>
<td>Water-side mass transfer coefficient for steady winds</td>
<td>$A_w = u_{10} (Sc / Sc_{CO_2})^{-0.5}$</td>
</tr>
<tr>
<td>A (unitless)</td>
<td>Constant based on the Weibull distribution of wind speeds over oceans</td>
<td>0.25</td>
</tr>
<tr>
<td>$u_{10}$ (m s$^{-1}$)</td>
<td>Wind speed normalized to 10 m above sea surface</td>
<td>GEOS-5 data</td>
</tr>
<tr>
<td>$Sc_{CO_2}$</td>
<td>Schmidt number for CO$_2$</td>
<td>$0.11T^{-2} - 6.16T' + 644.7$ (42)</td>
</tr>
<tr>
<td>$T'$ (°C)</td>
<td>Water temperature</td>
<td>GEOS-5</td>
</tr>
<tr>
<td>$Sc_{Hg(0)}$</td>
<td>Schmidt number for Hg(0)</td>
<td>$\nu / D$</td>
</tr>
<tr>
<td>$\nu$ (cm$^2$ s$^{-1}$)</td>
<td>Kinematic viscosity</td>
<td>$N/\rho = 0.017e^{(-0.025T')}$</td>
</tr>
<tr>
<td>$N$ (cP)</td>
<td>Viscosity of water</td>
<td>See text</td>
</tr>
<tr>
<td>$\rho$ (mg cm$^{-3}$)</td>
<td>Seawater density</td>
<td></td>
</tr>
<tr>
<td>$D$ (cm$^2$ s$^{-1}$)</td>
<td>Diffusivity (Wilke-Chang (43) method)</td>
<td>$7.4 \times 10^{-8} (\phi_w M_w)^{1/2} / N V_B^{0.6}$</td>
</tr>
<tr>
<td>$M_w$ (g mol$^{-1}$)</td>
<td>Molecular weight of water</td>
<td>18.0</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>Water temperature in Kelvin</td>
<td>GEOS-5 data</td>
</tr>
<tr>
<td>$V_B$ (cm$^3$ mol$^{-1}$)</td>
<td>Molal volume of mercury at its normal boiling temperature</td>
<td>12.74</td>
</tr>
<tr>
<td>$\phi_w$</td>
<td>Solvent association factor introduced to define the effective molecular weight of the solvent with respect to the diffusion process</td>
<td>2.26 (44)</td>
</tr>
</tbody>
</table>

#### Aqueous Viscosity

Loux (45) provides the following relationship for estimating aqueous viscosity as a function of aqueous temperature between 0-20°C:

\[
(8) \log(N) = \frac{1301}{(998.333 + 8.1855(T' - 20) + 0.00585(T' - 20)^2)} - 3.30233
\]

For water temperatures 20-100°C:

\[
(9) \log(N_{T'}/N_{20}) = \frac{1.3272(20 - T') - 0.001053(T' - 20)^2}{T' + 105}
\]

Where $N_{20} =$ aqueous viscosity at 20°C.
References Cited:


