Vertical transport of anthropogenic mercury in the ocean

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[1] We investigate the vertical transport of mercury (Hg) within the ocean using a simple box diffusion model to represent vertical water transport coupled with a particulate Hg flux. The particulate flux assumes that the Hg content of marine particles is proportional to the Hg concentration of surface waters via a sorption equilibrium constant, \( K_d \). The model is forced with the observed factor of 3 increase in atmospheric Hg deposition over the industrial era. The modeled vertical profile of oceanic Hg shows a subsurface maximum at ~500 m depth due to remineralization of Hg bound to sinking organic particles, consistent with observations. Model results indicate that surface (top 100 m) concentrations of Hg have increased by 150% since preindustrial times. Over the past 150 years, 280 Mmol of anthropogenic Hg have accumulated in the ocean, representing a 18% increase in the total oceanic Hg content. We find that 36% of the anthropogenic Hg occurs in the top 400 m and only 7% occurs below 1500 m. Over the industrial era, we find that 14% of cumulative anthropogenic emissions have accumulated in the ocean. Our model results show that half of the accumulation of anthropogenic Hg in the ocean is due to sinking on particulates. A sensitivity analysis indicates that the model results are most dependent on the value of \( K_d \).


1. Introduction

[2] The ocean plays a critical role in the biogeochemical cycling of mercury (Hg). Mason and Sheu [2002] estimate that the ocean reservoir contains 1440 Mmol of Hg, compared to the atmospheric reservoir of 25 Mmol, and that ocean emissions contribute approximately one third of the current Hg source to the atmosphere. Anthropogenic perturbation to the global Hg cycle is significant, with historic records in lake sediments indicating a factor of 3 increase in Hg deposition since preindustrial times [Swain et al., 1992; Lamborg et al., 2002].

[3] Oceanic Hg concentrations affect human health through bioaccumulation in fish in the form of methylmercury. Despite its importance to human health, the marine biogeochemistry of Hg remains poorly understood and few observations exist. These observations show large variability across regions and time periods, making anthropogenic impacts difficult to detect [Fitzgerald et al., 2007]. Instead, estimates of past changes in oceanic Hg have relied on simple models. Using a mass balance model separating the ocean into 2 vertical boxes, Mason and Sheu [2002] estimated that anthropogenic activities resulted in a 9% increase in oceanic Hg, with most of this increase occurring in the deep ocean, below 500 m. In a separate study, Lamborg et al., [2002] calculated a 90% increase in the ocean mixed layer (top 100 m), a 20% increase in the thermocline (100–1000 m), and assumed no increase below 1000 m. Their nonsteady state model separated the ocean in two hemispheres and in two vertical boxes. More recently, Sunderland and Mason [2007] examined the evolution of oceanic Hg concentrations for the surface, intermediate, and deep waters in a 14-box model, finding a 25% increase in the surface (0–1500 m) and an 11% increase in the deep ocean (>1500 m). In our previous work, we have coupled a global 3-D atmospheric chemical transport model of mercury (GEOS-Chem) to a slab model of the ocean mixed layer [Strode et al., 2007]. By conducting preindustrial and present-day Hg simulations with GEOS-Chem, Selin et al. [2008] found a 180% increase in ocean mixed layer concentrations.

[4] These studies present a somewhat conflicting picture of how human activities have affected oceanic Hg concentrations. Estimates for the increase in mercury mass in the upper ocean range from < 2% to 200%, and increases in the deep ocean range from 0 to 13%. One issue is that all these studies divide the ocean in 2-4 boxes in the vertical, each assuming different depths.

[5] There is a large body of research on the ocean penetration of other atmospheric gases (CO₂, ¹⁴C, chlorofluorocarbons, tritium) that can serve as analogs to Hg. In particular, the ocean uptake of CO₂ has been studied extensively in order to reproduce trends in atmospheric CO₂
concentrations [e.g., Prentice et al., 2001, and references therein]. Inorganic carbon measurements show that ocean invasion of anthropogenic CO$_2$ has been limited to the top 1500 m of the ocean [Gruber, 1998; Sabine et al., 2004]. Some of the first models used to successfully capture the observed oceanic penetration of $^{14}$C and anthropogenic CO$_2$ were box diffusion models [Oeschger et al., 1975]. These models represent the ocean as a mixed layer box in contact with the atmosphere and an eddy diffusive deep ocean with $\sim$10-40 vertically stacked boxes. In contrast, models with only 2 boxes in the vertical have difficulty reproducing the uptake of anthropogenic CO$_2$ because the deep ocean cannot be accurately represented as a well-mixed box on a 100 year timescale [Siegenthaler and Oeschger, 1978]. Presently, the simple box diffusion models have been replaced by state-of-the-art 3-D Ocean General Circulation Models (OGCM) [e.g., Orr et al., 2001]. Joos et al. [1996] compared the performance of a box diffusion model to an OGCM in representing the penetration of a pulse of anthropogenic CO$_2$. After normalizing by mixed layer depth, they found that the response of the box diffusion model was very close to that of the OGCM. Box diffusion models thus offer a realistic framework to examine global oceanic uptake of anthropogenic CO$_2$ [Joos et al., 1997].

In this work, we use a box diffusion model to examine the anthropogenic perturbation to oceanic Hg over the past 150 years. The model is forced with the observed factor of 3 increase in Hg deposition over the course of the industrial era. Compared to most of the published ocean Hg studies, which have only 2-4 vertical levels, our model provides greater vertical resolution and is thus more adapted to examine vertical transport of Hg into the ocean. We describe the model in section 2. Results are presented in section 3, where we discuss the factors controlling the vertical distribution of Hg in the ocean and examine the penetration of anthropogenic Hg in the ocean. We also explore the sensitivity of our model results to a wide range of parameters to see what values lead to reasonable simulations of the modern surface ocean concentration. Conclusions are presented in section 4.

2. Model Description

We modify the Oeschger et al. [1975] CO$_2$ box diffusion model to represent Hg in the ocean. The Hg model includes a single box representing the surface atmosphere coupled to a box diffusion model of the ocean consisting of 50 vertical layers, each 50 m deep. Vertical transport of dissolved material in this model is parameterized entirely by the eddy diffusion coefficient, $K_v$. The value of this parameter is set by matching data from transient anthropogenic tracers that are presently penetrating the thermocline. Oeschger et al. [1975] demonstrated that a value of $K_v = 1.3 \times 10^{-6}$ m$^2$ s$^{-1}$ was able to capture the main features of the distributions of both natural and bomb-produced $^{14}$C, and we have used this value here. This $K_v$ is similar to vertical eddy diffusion coefficients required in analytical one-dimensional models of the temperature and salinity distribution of the main thermocline of the ocean [Munk, 1966] and is also within the range of depth-independent $K_v$ values ($1.3-2.5 \times 10^{-4}$ m$^2$ s$^{-1}$) used by Joos et al. [1997] in their box diffusion model. These values are about ten times larger than vertical eddy diffusion coefficients predicted from tracer release experiments and temperature microstructure distributions in the thermocline [Ledwell et al., 1993] illustrating that the eddy diffusion coefficients used in the one dimensional models parameterize many different mechanisms that transport water vertically over periods of decades. The model advances in time with a 6 month time step using the Crank-Nicholson numerical scheme for diffusion [Press et al., 1986].

Given the timescales of global ocean transport, we assume little anthropogenic change has occurred over the past 150 years at depths below 2000 m. We thus fix the Hg concentrations at the model’s lower boundary (2500 m) at 1.3 pM, based on deep ocean observations in the Pacific [Sunderland and Mason, 2007]. To reduce boundary condition influence, we will only report results for the top 2000 m of the model.

Mercury exists in several forms within the ocean: dissolved gaseous mercury (Hg$_0^{aq}$), aqueous divalent mercury (Hg$^{II}_{aq}$), several methylated forms (such as CH$_3$Hg and (CH$_3$)$_2$Hg), and particulate mercury [Fitzgerald et al., 2007]. Wet deposition of atmospheric divalent mercury provides a major source of Hg$^{II}_{aq}$ to the ocean. Within the ocean, Hg$^{II}_{aq}$ can become methylated, form organic or inorganic complexes, or undergo reduction to dissolved Hg$^{0}$, commonly called dissolved gaseous mercury (DGM). The aqueous reduction of Hg$^{II}_{aq}$ to Hg$^{0}_{aq}$ combined with the low solubility of Hg$^{0}$, drives an evasion flux of Hg$^{0}$ from the ocean to the atmosphere. In our previous global Hg slab ocean model [Strode et al., 2007], we found that atmospheric deposition provides a 22.8 Mmol yr$^{-1}$ source to the mixed layer. This source is balanced by net evasion to the atmosphere (14.1 Mmol yr$^{-1}$) combined with loss to the deep ocean (8.7 Mmol yr$^{-1}$) from diffusion and particulate sinking.

Our box diffusion model calculates the vertical distribution of dissolved (Hg$^{0}_{aq}$ + Hg$^{II}_{aq}$) and particulate Hg (Hg$^{0}$). Mercury enters the ocean as dissolved Hg through wet and dry deposition, and gas exchange provides a loss of Hg$^{0}_{aq}$ from the ocean to the atmosphere. The measured percent of oceanic mercury as DGM shows large variability. Sunderland and Mason [2007] estimate the fraction of total Hg as Hg$^{0}$ for each ocean basin, with values in the surface ocean ranging from 6% in the Pacific to 13% in the Atlantic. In this study, we average these two values and assume that 9.5% of the dissolved Hg in the surface ocean layer is DGM. In order to calculate gas exchange with the atmosphere. The ocean box diffusion model uses the gas exchange formulation that we have previously described [Strode et al., 2007], with the Henry’s Law constant from Andersson et al. [2008]. We also use the global mean gas exchange velocity ($k_{gw} = 10.7$ cm h$^{-1}$) determined by Strode et al. [2007].

We include vertical transport of Hg via sinking of particulate organic matter composed of dead organisms and detritus, commonly referred to as the biological pump in the context of the carbon cycle. Scavenging of Hg by these organic-rich particles can be a major sink for Hg in the open ocean [Lamborg et al., 2002], but is poorly quantified. We assume that dissolved and particulate mercury are in sorption equilibrium, described with the equilibrium constant $K_d = K_a$ sorbed Hg per sorbent mass/dissolved Hg per water volume
[Meili, 1997; Morel et al., 1998]. In our study, we chose $K_d = 1.2 \times 10^4$ (kg particulate organic carbon)$^{-1}$ in order to obtain concentrations of dissolved Hg in the modern ocean of 0.87 pM, matching the globally averaged mixed layer concentrations we derived from Strode et al. [2007].

Estimates of $K_d$ based on open ocean measurements range from $1.1\times10^5$ (kg total suspended particles)$^{-1}$ in the North Pacific [Mason et al., 1998] to $10^6$ (kg total suspended particles)$^{-1}$ in the Equatorial Pacific [Mason and Fitzgerald, 1993]. If we assume that 52% of organic matter is carbon [Emerson and Hedges, 2008] and that organic matter accounts for ~20% of the suspended material mass in surface ocean waters (top few hundred meters) [Brewer et al., 1980], these observed values lead to a range of $1.1\times10^5$ to $10^7$ (kg particulate organic carbon)$^{-1}$. Meili [1997] and Coquery et al. [1997] report that in lakes, rivers, and estuaries $K_d$ values span an order of magnitude: $10^5$–$10^6$ (kg particulate organic matter)$^{-1}$. The lower values correspond to environments dominated by detrital particles, while the higher values are for detrital organic matter. Converting our assumed $K_d$ to the same units, yields $K_d = 6 \times 10^1$ (kg particulate organic matter)$^{-1}$. Thus our assumed $K_d$ is consistent with the range of observed values. In section 3.3, we will examine the sensitivity of our results to different choices of $K_d$.

We determine the particulate Hg flux by multiplying $K_d$ by the concentration of dissolved Hg and by the organic carbon particulate flux. We use the organic carbon flux parameterization of Antia et al. [2001]: $F_{orgC} = 0.1 \cdot NPP^{0.7} \cdot z^n$, where $NPP$ is net primary productivity (in gC m$^{-2}$ yr$^{-1}$), $z$ is depth (in m), and $n$ is an empirical fit to data. We assume a global NPP value of 148 gC m$^{-2}$ yr$^{-1}$ (53.4 GtC yr$^{-1}$) and set $n$ to −0.7, in between the Atlantic estimate of −0.68 [Antia et al., 2001] and the Pacific estimate of −0.734 [Pace et al., 1987]. This yields $F_{orgC} = 28$ gC$^{-2}$ yr$^{-1}$ (or 10 GtC yr$^{-1}$) at 100 m, consistent with observations of organic carbon export [Emerson and Hedges, 2008]. The net particulate flux of Hg into a given model layer is the difference between the flux at the top and bottom of the layer. We assume this net flux is remineralized within the layer and adds to the total dissolved Hg concentration of the layer. Field observations and laboratory experiments show that the settling velocities of sinking particles are highly variable: 20–200 m d$^{-1}$ [Alldredge and Gotschalk, 1988; Honjo, 1996]. We assume a mean settling velocity of 100 m d$^{-1}$ and calculate the particulate Hg burden in each layer by dividing the particulate flux of Hg out of the layer by this velocity.

Both the mean surface atmospheric concentrations of Hg$^0$ and deposition of Hg to the ocean (in the form of dry and wet deposition of divalent mercury and particulate mercury) are specified using results from the global GEOS-Chem ocean-land-atmosphere mercury simulation [Selin et al., 2007; Strode et al., 2007]. Based on the simulation of Selin et al. [2008], we assume a preindustrial deposition to the ocean of 7.6 Mmol yr$^{-1}$ and 0.5 ng m$^{-3}$ for the atmospheric concentration of Hg$^0$. For the modern-day simulation, these values increase by a factor of 3 to 22.8 Mmol yr$^{-1}$ for deposition and 1.5 ng m$^{-3}$ for Hg$^0$ [Selin et al., 2007]. For simplicity, we assume that both deposition and atmospheric concentrations increase linearly over the 150 years between preindustrial times and present.

The box diffusion model is first run with preindustrial values for Hg deposition and atmospheric Hg$^0$ concentration until it reaches preindustrial steady state. Deposition and atmospheric concentration are then linearly increased to modern levels over 150 years to give the modern, non-steady state marine concentration profile. The Hg content of particulate matter is proportional to the surface ocean Hg concentration and therefore increases over the industrial era, reflecting the greater quantity of Hg available to bind to particles. As we will see, this biological pump represents an effective way for transporting anthropogenic Hg to the thermocline.

We note that our approach of representing the world’s oceans using a 1-D box diffusion model has a number of inherent limitations. In particular, we neglect horizontal variations in a number of factors: atmospheric deposition of Hg to the oceans, temperature (which affects the solubility of Hg$^0$), biological productivity, eddy diffusion, and the shape of the remineralization curve. Furthermore, we do not take into account lateral transport, which can play an important role in controlling the vertical distribution of Hg in the oceans [Sunderland and Mason, 2007; Sunderland et al., 2009]. Despite these limitations, we will show that our idealized modeling approach is a useful framework for examining the roles of vertical diffusion and the biological pump on the penetration of anthropogenic Hg in the ocean.

3. Results and Discussion

3.1. Evolution of the Vertical Distribution of Mercury in the Ocean

Figure 1a shows the increase in dissolved Hg concentrations for the model simulation over the past 150 years at three levels: in the mixed layer, at 250 m, and at 1500 m depth. The modern-day mixed layer concentration of dissolved Hg is 0.87 pM. This value falls within the bounds of observed mixed layer concentrations and matches by design the globally averaged mixed layer concentrations of Strode et al. [2007]. Model results in Figure 1a show that concentrations in the mixed layer increase by 0.55 pM (factor of 2.7 increase) between the preindustrial era and the present as the surface ocean layer equilibrates rapidly with the changing atmospheric input. At 250 m depth, the absolute increase in concentrations is larger (0.75 pM) as a result of transport of Hg on particulates. In contrast, the concentration at 1500 m has increased by only 0.2 pM, because of the slow transport of anthropogenic Hg down to that depth.

Figure 1b illustrates the evolution of the Hg profile from preindustrial to present in 25 year increments. Our initial profile of dissolved Hg, obtained in our steady state preindustrial simulation (blue line on Figure 1b), displays a minimum at the surface because of Hg loss at the surface from particle scavenging and Hg$^0$ evasion to the atmosphere. Organic particles, which are generated at the surface, provide a sink for dissolved Hg. As these particles sink they remineralize at depth providing a net source of dissolved Hg, and thus increasing concentrations with depth. Overall,
this downward particulate flux is balanced by upward diffusion of dissolved Hg.

[19] As atmospheric deposition increase over the industrial era, oceanic Hg concentrations increase. This in turn leads to an increase in particulate-bound Hg flux. The modern-day dissolved Hg profile reaches a maximum of 1.6 pM at 500 m below the surface. This subsurface maximum is due to the vertical penetration of anthropogenic Hg via diffusion and increased particulate transport of Hg.

[20] Several studies have reported a subsurface maximum in total Hg concentration in the thermocline region, which they attributed to Hg release from particulates and/or lateral transport of enriched intermediate waters [Cossa et al., 1992, 2004; Mason et al., 1998, 2001; Mason and Sullivan, 1999; Laurier et al., 2004; Sunderland et al., 2009]. For example, recent profiles of total Hg in the North Pacific Ocean reported by Sunderland et al. [2009] display surface concentrations of 1 pM and a maximum in intermediate waters of ~1.6 pM at 500–600 m depth. Figure 2 compares the present-day modeled depth profile to selected observations from the Atlantic [Dalziel, 1992] and Pacific [Mason and Fitzgerald, 1993; Sunderland et al., 2009]. The model produces a subsurface maximum similar to observations. The observed Atlantic concentrations are generally higher than the Pacific concentrations, with the modeled concentrations lying between the two basins.

3.2. Penetration of Anthropogenic Mercury into the Ocean

[21] Figure 1c displays the depth profile of anthropogenic Hg concentrations, which we calculate by difference between the time-dependent simulation at 150 years and the preindustr-

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Evolution of Hg concentrations from preindustrial times to present in the standard box diffusion model simulation. (a) Increase in concentration with time in the top 50 m (mixed layer) and at 250 and 1500 m depths from preindustrial steady state to the present. (b) Modeled concentration of total dissolved Hg with depth. Colors represent the evolution from preindustrial steady state (initial, blue) to present (150 years, black) in 25 year increments. (c) Present-day concentrations of anthropogenic dissolved Hg obtained by difference between the 150 year profile and preindustrial profile in Figure 1b.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Present-day modeled concentration of dissolved Hg (black line) compared with observed profiles of reactive Hg from the Atlantic [Dalziel, 1992] (blue) and Pacific [Mason and Fitzgerald, 1993] (red). The symbols represent the mean value at each depth, and the error bars represent the minimum and maximum values. Also shown are mean total Hg profiles over the Pacific from Sunderland et al. [2009] (green).
trial simulation. This vertical distribution displays a subsurface maximum due to the downward transport of anthropogenic mercury on particles.

We calculate the mass of preindustrial and present-day Hg in the ocean as a function of depth by assuming a surface area for the ocean of 360 million km². Results for different ocean depths are listed in Table 1. As our model only extends to 2000 m, we estimate the burden below that depth by assuming a constant concentration of 1.3 pM (yielding a total of 840 Mmol of mercury below 2000 m).

When we integrate over the entire ocean, we find that the oceanic Hg burden increases by 280 Mmol between preindustrial times and present, representing an 18% increase. Over that time period in our simulation, anthropogenic emissions have resulted in a cumulative anthropogenic Hg deposition to the ocean of 1140 Mmol. Thus only 25% of the cumulative anthropogenic Hg deposition to the ocean remains in the ocean, while the rest is released back to the atmosphere by air-sea exchange.

Table 1. Oceanic Mercury Mass for the Preindustrial and Modern Time Periods

<table>
<thead>
<tr>
<th>Ocean Depth</th>
<th>Preindustrial (Mmol)</th>
<th>Modern (Mmol)</th>
<th>Anthropogenic Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–100 m</td>
<td>14</td>
<td>35</td>
<td>150%</td>
</tr>
<tr>
<td>100–400 m</td>
<td>78</td>
<td>157</td>
<td>100%</td>
</tr>
<tr>
<td>400–1500 m</td>
<td>432</td>
<td>590</td>
<td>35%</td>
</tr>
<tr>
<td>Below 1500 m</td>
<td>1066</td>
<td>1088</td>
<td>2%</td>
</tr>
<tr>
<td>Entire ocean</td>
<td>1590</td>
<td>1870</td>
<td>18%</td>
</tr>
</tbody>
</table>

*aTotal mercury mass (dissolved + particulate) in our standard simulation.

*bAnthropogenic increase defined as the increase between preindustrial and modern burdens.

(c)We estimate the burden below 2000 m by assuming a constant concentration of 1.3 pM and an average ocean depth of 3790 m (yielding a total of 840 Mmol of mercury below 2000 m).

3.3. Sensitivity Studies

The computational efficiency of the diffusion model makes it ideal for exploring parameter space. Below we examine the sensitivity of our results to assumptions about: particulate sinking, modern and cumulative deposition, the gas exchange coefficient, the particulate-dissolved Hg partitioning coefficient, and the eddy diffusion coefficient.

3.3.1. Particulate Sinking

The standard simulation (described in section 2) includes the effects of both vertical diffusion and particulate remineralization. In order to separate the roles of these two transport modes, we conduct a sensitivity simulation in which the particulate concentration of Hg (and thus the amount of particulate Hg remineralizing at depth) is held fixed at its preindustrial levels. Thus, in this sensitivity simulation vertical transport of anthropogenic Hg is only controlled by diffusion.

Figure 3a shows the resulting vertical profiles for this fixed particulate Hg concentration simulation. The modern-day profile (150 years) shows a gradual increase in concentration with depth, contrary to the pronounced subsurface maximum in the standard simulation (Figure 1b). Surface concentrations are somewhat higher (0.95 pM) compared to the standard simulation (0.87 pM) because less of the anthropogenic Hg deposited from the atmosphere is removed by particle sinking. At depth, Hg concentrations do not increase as much, reaching 1.2 pM at 500 m compared to 1.6 pM in the standard simulation.

This simulation shows the concentration of anthropogenic Hg decreasing with depth (Figure 3b), as transport of anthropogenic Hg is solely controlled by diffusion.
contrast, we find a subsurface maximum in anthropogenic Hg for our standard simulation (Figure 1c). For the fixed particulate Hg concentration simulation, we find a 135 Mmol increase in the ocean Hg burden, a factor of 2 smaller than in the standard simulation. Thus the increasing uptake of Hg in the biological pump over the industrial era, as in our standard simulation, accounts for half of the modeled anthropogenic increase, and represents an effective way of increasing transport of anthropogenic Hg in the ocean interior where it will not be lost by gas exchange.

3.3.2. Modern and Cumulative Deposition

The standard model run assumes that deposition to the ocean increased linearly by a factor of 3 over the last 150 years from 7.6 to 22.8 Mmol yr\(^{-1}\). We conduct sensitivity simulations with a range of modern Hg depositions (15–30 Mmol yr\(^{-1}\)) and a range in the time course of change since the pre-industrial period. In an idealized set of simulations, we are changing the shape of the time-dependent deposition function to be linear, quadratic, cubic, or square root. The square root assumption results in larger cumulative deposition since deposition increases earlier in the industrial era, while the cubic function increases later, resulting in lower cumulative deposition. For a modern deposition value of 22.8 Mmol yr\(^{-1}\), the square root, linear, quadratic and cubic curves lead to cumulative deposition values of 2660, 2280, 1900, and 1710 Mmol, respectively. This corresponds to cumulative anthropogenic deposition values of 1520, 1140, 760, and 570 Mmol.

Figure 4a shows the concentration of Hg in the surface ocean plotted against cumulative anthropogenic deposition for different modern deposition rates. Figure 4a illustrates that surface ocean concentrations are highly sensitive to the rate of modern deposition (concentrations increase by \(\sim 60\%\) for a doubling of modern deposition), but have only a small sensitivity to the cumulative deposition. For a modern deposition value of 22.8 Mmol yr\(^{-1}\), surface concentration increases by only 5% for a 55% increase in cumulative deposition (cyan line). This is consistent with the fast response time of dissolved Hg in the surface ocean, which has a residence time of 7 months [Strode et al., 2007].

Figure 4b shows the sensitivity of ocean Hg concentrations at 500 m depth to cumulative and modern deposition, generated from the same runs as Figure 4a. The lines for different modern deposition values are overlapping in Figure 4b. This indicates that concentrations at 500 m depth are mostly sensitive to the time course of deposition and less sensitive to the modern rate of deposition, because of the time required for Hg to reach this depth. For a doubling in cumulative deposition, Hg concentrations at 500 m depth increase by almost 50%. For a doubling in modern
deposition with the same cumulative deposition, concentrations increase by less than 5%, as shown by the nearly overlapping lines.

3.3.3. Gas Exchange Velocity and Modern Deposition

Since both the gas exchange velocity, \(k_w\), and modern atmospheric deposition to the ocean are uncertain, we use the box diffusion model to explore whether other combinations of \(k_w\) and deposition give realistic surface Hg concentrations. Figure 5 (left) shows the surface concentration of dissolved Hg as a function of the modern deposition rate and a scaling factor applied to \(k_w\) (a scaling factor of 1 corresponds to the standard simulation where \(k_w = 10.7 \text{ cm h}^{-1}\)).

![Figure 4b](https://example.com/figure4b.png)

**Figure 4b.** Mercury concentration at 500 m depth as a function of time-integrated deposition for different values of modern deposition. The model runs are the same as in Figure 4a.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Sensitivity of ocean surface dissolved Hg concentrations (in pM) to (left) deposition and \(k_w\), the gas exchange velocity and (right) to \(K_d\), the dissolved particulate Hg partitioning coefficient and \(K_z\), the eddy diffusion coefficient. The \(k_w\) scale factor represents the scaling applied to the gas exchange velocity used in the standard run. Colors and contours represent total dissolved Hg concentration in pM. The black solid circle marks the parameters used in the standard simulation.
The scaling of $k_w$ can represent either an adjustment of the gas exchange velocity or an altered fraction of total Hg as dissolved gaseous Hg, since the model cannot distinguish these two possibilities.

[32] Figure 5 (left) demonstrates that the surface concentration is sensitive to both deposition and $k_w$. It is possible to maintain a surface concentration of 0.87 pM dissolved Hg with an increase or decrease in $k_w$ provided deposition is increased or decreased concurrently. A smaller value of $k_w$ would provide slower evasion of Hg from the ocean to the atmosphere, but this smaller loss could be balanced by a smaller source from deposition while maintaining realistic surface concentrations.

3.3.4. Eddy Diffusion Coefficient and $K_d$

[33] Figure 5 (right) shows the sensitivity of the surface ocean Hg concentration to the assumed eddy diffusion coefficient $K_z$ and the dissolved particulate partitioning coefficient $K_d$. Increasing $K_z$ leads to faster removal of Hg via particulate sinking from the surface layer, reducing the surface concentration of dissolved Hg. Because of the vertical gradient induced by particulates, diffusion transports dissolved Hg upward from the subsurface maximum to the surface. Thus increasing $K_z$ leads to higher surface concentrations. Increasing $K_d$ also smoothes out the vertical concentration gradient, leading to a lower sensitivity to $K_d$ when $K_z$ is large.

[34] Higher surface concentrations result in a larger loss of Hg from the ocean via gas exchange with the atmosphere. Consequently, the dependence of the ocean burden of anthropogenic Hg on $K_z$ and $K_d$ is opposite that of the surface concentration. Increasing $K_z$ increases the oceanic burden of anthropogenic Hg because Hg is transported more quickly into the ocean interior where it will not be lost by gas exchange. A doubling of $K_d$ leads to a 40% increase in the anthropogenic Hg burden in the ocean (from 280 to 400 Mmol), while a factor of 2 decrease in $K_d$ results in a 20% decrease in the anthropogenic Hg burden.

3.4. Comparison to Previous Studies

[35] Estimates from previous modeling studies for the total Hg oceanic burden increase range from 120 to 270 Mmol [Mason and Sheu, 2002; Lamborg et al., 2002; Sunderland and Mason, 2007; Selin et al., 2008]. Our result (280 Mmol) is thus at the upper end of these studies. Expressed in terms of percentage increase in the oceanic Hg burden our 18% increase is also at the upper end of previous estimates (9–18%).

[36] In the top 100 m of the ocean, we find a 150% increase in the burden of Hg. This is within the range given by previous studies (90–200%). This factor of 2–3 increase is consistent with the limited historical archives of Hg in museum seabird feathers [Monteiro and Furness, 1997].

[37] Our mixed layer burden of total Hg (36 Mmol in the top 100 m) is lower than previous studies (54–64 Mmol). This is likely due to a smaller particulate Hg concentration in our simulation. Our particulate Hg concentration is sensitive to the choice of settling velocity, which varies depending on the size of the particles, so an overestimate in settling velocity could lead to an underestimate in particulate Hg mass in the surface ocean.

[38] There are substantial differences between models in estimates of the distribution of anthropogenic Hg below the ocean mixed layer. The Mason and Sheu [2002] model assumes that less than 5% of the anthropogenic Hg is present at depths shallower than 500 m, with the remaining 95% occurring below 500 m (we find values of 45% and 55%, respectively). Sunderland and Mason [2007] find that 50% of the anthropogenic Hg is above 1500 m and 50% below that depth (we find values of 92% and 8%, respectively). Results from our simulation indicate a much slower penetration of anthropogenic Hg compared to these studies (see Figure 1c and Table 1). However, our results are consistent with the Hg model of Lamborg et al. [2002], who assume that 100% of the anthropogenic Hg is confined to the top 1000 m of the ocean (we find that 76% of anthropogenic Hg is in the top 1000 m).

4. Conclusions

[39] In this paper, we have described the development of a box diffusion model for ocean Hg. The model includes air-sea exchange, atmospheric deposition, and vertical transport of Hg within the ocean due to diffusion and particulate sinking. This simple model framework allows us to investigate the role of vertical transport processes on oceanic Hg distribution in greater detail than previous models. We use this model to explore how the Hg content of the ocean has changed over the past 150 years of the industrial era.

[40] Vertical transport of Hg via sinking particulate organic matter is critical for determining the shape of the Hg profile and the penetration of anthropogenic Hg in the box diffusion model. In our standard simulation, we assume that dissolved and particulate Hg are in sorption equilibrium described with a partitioning constant $K_d$. The amount of Hg bound to particles thus increases over the industrial era, following the increase in dissolved Hg concentration in the mixed layer.

Particulate Hg remineralizes at depth, leading to a subsurface concentration maximum at 500 m in the modern ocean.

[41] Overall, we find an oceanic uptake of anthropogenic Hg emissions of 280 Mmol for the past 150 years in our standard simulation. By conducting a sensitivity simulation where the flux of particulate-bound Hg is kept fixed at preindustrial levels, we find half of the increase in Hg burden over the industrial era is associated with particulate sinking while the other half is due to diffusion. Particulate sinking enhances the ocean uptake of anthropogenic Hg by transporting Hg away from the surface, thus reducing loss to the atmosphere. Our standard model implies that 14% of the anthropogenic Hg emissions have accumulated in the ocean over the industrial era, while the remaining anthropogenic deposition is recycled back to the atmosphere via air-sea exchange.

[42] The box diffusion model predicts that 36% of the anthropogenic Hg occurs in the top 400 m and 93% in the top 1500 m. Our results indicate that mixed layer concentrations of Hg (top 100 m) have increased by 150% since preindustrial times, in the middle of previous estimates (90–200%).

[43] Surface Hg concentrations are sensitive to assumptions about the rate of modern deposition, the gas exchange velocity, the $K_d$ partitioning constant, and the value of the
eddy diffusion coefficient used in the model. Since the surface ocean layer equilibrates rapidly with the atmosphere, it is relatively insensitive to historic deposition rates. In contrast, the thermocline region responds more slowly to changing atmospheric input, and is more sensitive to cumulative deposition over the industrial era.

[44] At present the distribution of Hg in the ocean is poorly constrained by a limited number of observations, which show large variability in time and space [e.g., Laurier et al., 2004; Fitzgerald et al., 2007]. There is a clear need to obtain more systematic observations of speciated vertical Hg profiles for different regions of the ocean. Observations to constrain the partitioning of Hg between dissolved and particulate phases in open ocean environments are particularly important, given the high sensitivity of penetration of anthropogenic Hg to particulate sinking.

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