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**Supplementary information**

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**Mercury stable isotopes constrain  
atmospheric sources to the ocean**

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## Online Supporting Information to:

### Mercury stable isotopes constrain atmospheric sources to the Ocean

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## Materials and Methods

### Rationale

Total mercury (tHg) concentration in seawater is the sum of several operationally defined species, including dissolved gaseous Hg(0), dissolved gaseous dimethyl-Hg (DMHg), dissolved inorganic Hg(II) compounds, dissolved monomethyl-Hg compounds (MMHg), and particulate-bound Hg(II) and MMHg compounds (pHg). Both concentration and stable isotope analysis of tHg in seawater require the transformation of these compounds to dissolved, labile Hg(II) forms by addition of a strong oxidant such as BrCl, prepared in concentrated HCl. The concomitant oxidation and acidification also inhibits biological activity, stabilizes Hg(II) in solution and minimizes potential losses to sampling container walls or to the atmosphere. Two criteria need to be met for a robust Hg stable isotope analysis of seawater: first, the low-picomolar seawater concentration has to be concentrated to levels suitable for Hg stable isotope analysis (typically 0.2 – 1 ng mL<sup>-1</sup> or 1 – 5 nM). This pre-concentration needs to be quantitative in order to avoid Hg isotope fractionation during transfer. Second, the procedural blank of the method needs to be low, ideally below 10% of the total amount of Hg in the sample. Low blank levels rely on ultra-clean sampling at sea, clean sampling vessels and ultra-low Hg levels of reagents used.

Previous studies have successfully developed methods for large volume (1 - 20 L) pre-concentration of tHg from natural waters, including rain, snow, ice, lake and coastal seawater. Gratz et al. (2010) and Sherman et al. (2010) first used continuous cold vapor generation, with  $\text{SnCl}_2$  as a reductant, to pre-concentrate 1 - 4 L of snow and rainfall samples into small volume (25 mL) 2 % (w/w) oxidizing  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  solution trap<sup>1,2</sup>. This method was later modified to a batch-reactor set-up to pre-concentrate 1 L of rainfall in a 2 L Pyrex bottle, by slow, pumped addition of  $\text{SnCl}_2$ , and identical  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  solution trap<sup>3</sup> and trapping solutions of 40 vol% inverse *aqua regia* (iAR, 4.2 N  $\text{HNO}_3$ , 1.2 N  $\text{HCl}$ )<sup>4</sup>. Finally, in Obrist et al. (2017) we scaled up the batch purge and trap method to handle up to 20 L of snow and rain sample<sup>5</sup>. An alternative method was developed by Chen et al. (2016) using the AG-1-X4 anion exchange resin to pre-concentrate >40 ng of tHg from freshwater lakes<sup>6</sup>.  $\text{HgCl}_4^{2-}$  in the acidified, 0.1 N  $\text{HCl}$ , sample is pumped at  $3.5 \text{ mL min}^{-1}$  over 0.5 mL of AG-1-X4 resin. Sorbed Hg is then eluted with 10 mL of 0.05 % L-cysteine in 0.5 N  $\text{HNO}_3$ , oxidized by  $\text{BrCl}$ , neutralized with  $\text{NH}_4\text{OH}$  and analyzed by MC-ICPMS. Štok et al. (2015) optimized the anion exchange resin method for seawater and published the first Hg stable isotope data of coastal seawater (1.5-3.1 pM) from the Canadian Arctic Archipelago<sup>7</sup>. The latter two methods by Štok et al. (2015) and Obrist et al. (2017) are capable of handling sample volumes of 20 L or more that are necessary for background level tHg pre-concentration from seawater (0.4 to 1.5 pM). Our objective was therefore to adapt our existing large volume pre-concentration protocol, based on  $\text{SnCl}_2$  reduction, for rain and snow to seawater. We optimized the protocol for quantitative pre-concentration yields and low blank levels.

### **Pre-concentration troubleshooting, Sn waste disposal and bottle cleaning**

During pre-concentration the 20L sample bottle is under argon over-pressure in order to generate a fine stream of bubbles. It is therefore important at the end of pre-concentration, or during troubleshooting, not to vent the argon supply tube to the 20L sample bottle and release argon pressure. The reason is that with the 20 L bottle under over-pressure, venting the argon supply tube results in a sudden pressure drop, and acidified sample solution with  $\text{SnCl}_2$  moving from the 20 L bottle into the tall bubbler post, possibly all the way to the argon flow regulator, damaging the latter. Worse, the 40 vol% iAR trap solution is aspirated up into its short bubbler post and into the 20 L bottle, resulting in the loss of the sample. Using our final optimized Sn addition protocol, each 20 L bottle contains at the end of a pre-concentration run, 2.5 g of  $\text{Sn(II)}$ , and should be disposed of following local environmental regulations. If needed, the dissolved  $\text{Sn(II)}$  concentration can be lowered by hydrogen peroxide addition, which quantitatively

precipitates  $\text{Sn(IV)O}_2$ , that can then be filtered or decanted. Quantitative oxidation of  $\text{Sn(II)}$  by hydrogen peroxide also has the advantage that no traces of  $\text{Sn(II)}$  remain in the 20 L bottle, which can be acid-cleaned (0.1 vol% commercial HCl) and rinsed with abundant MQ water to receive the next batch of seawater samples. In this study both sampling and pre-concentration were done in the same bottle. We expect however that the use of separate bottles, possibly using plastic 20 L carboys at sea for safety, does not increase blanks.

### **Alternative, activated carbon based pre-concentration method for sea water**

We have, over the past years, tested an alternative method for low-level Hg pre-concentration in order to measure Hg isotopes in sea water. The method uses small 200 mg iodated activated carbon powder (Brooks Rand) cartridges, over which large volumes (50L) of unfiltered, acidified (0.4% v/v HCl) sea water are pumped at a slow flow rate of  $5 \text{ ml min}^{-1}$ . Following laboratory recovery and blank testing, we applied the method during the 2014 GEOTRACES Geovides cruise in the North-Atlantic Ocean. Unfiltered seawater was transferred using clean 6mm FEP tubing from GOFLO bottles into acid washed 50L tedlar bags. A peristaltic pump, with 1.14mm ID (red/red) tygon pump tubing was used to load samples on the IAC traps during 1 week. Traps were dried for 5 min in a dry high purity argon stream, sealed with silicone stoppers and stored and transported dry and in the dark to the GET laboratory. The IAC powder was combusted using a dual tube furnace combustion method<sup>8</sup>. IAC blanks were 0.5 ng Hg per 200mg of IAC traps, and sample recoveries were  $88 \pm 31\%$ . In hindsight, it has been difficult to fully recover Hg from IAC traps due to abundant volatile iodine release and transfer to oxidizing solution traps. We recommend that further development of activated carbon based methods use commercial sulfur impregnated activated carbon (Calgon HGR), which does not have this issue<sup>9</sup>.

### **MMHg and DMHg analysis**

MMHg and DMHg were determined by isotope dilution (ID)- gas chromatography – sector field ICP-MS (ID-GC-SF-ICPMS) method at the MIO laboratory, following previously published protocols<sup>10</sup>. First the sum of both species (tMeHg) was quantified on an acidified sample that converts DMHg to MMHg. A second replicate sample was purged to remove DMHg before acidification, allowing direct measurement of MMHg. DMHg was calculated by difference, as tMeHg – MMHg. In both sample aliquots MMHg and inorganic Hg species were extracted after derivatization. In brief, enriched spikes of  $^{199}\text{iHg}$  and  $^{201}\text{MeHg}$  (ISC Science, Spain) were added to a 115 mL aliquot of the sea water samples. After 24h of equilibration, pH

was adjusted to 3.9 with  $\text{NH}_3$  (ULTREX® II Ultrapure Reagent, J.T. Baker, USA) and a buffer solution made up with acetic acid (glacial, ULTREX® II Ultrapure Reagent, J.T. Baker, USA) / sodium acetate (J.T. Baker, USA). A solution of 1 % (v:v) sodium tetra propyl borate (Merseburger Spezialchemikalien, Germany) was made up freshly, under cold conditions and avoiding contact with atmospheric oxygen. 1 mL of this solution was then added together with 200  $\mu\text{L}$  hexane (Sigma Aldrich, USA). The glass bottles were hermetically sealed with Teflon-lined caps and vigorously shaken for 15 minutes. The organic phase was recovered and injected in the GC (Thermo Trace Ultra), coupled to a sector field ICPMS (Thermo Element XR). Detection limits were 0.005 pM for MMHg, and 0.01 pM for DMHg.

### **pHg isotope results**

At station K2, pHg  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  were similar in June 2017 and May 2019 at all depths, while  $\delta^{202}\text{Hg}$  was higher in June 2017 by 1.5 ‰ at 100 - 400m depth. Only in May 2019 at station K2, tHg and pHg isotopes were determined simultaneously and  $\delta^{202}\text{Hg}$  of pHg was depleted by -1.0 ‰ (-0.8 ‰ to -1.3‰; median and (IQR),  $n = 4$ ) relative to tHg (Figure 1b). Light isotope enriched pHg may be explained by the preferential sorption of light Hg(II) isotopes to particulate organic matter<sup>11</sup>, or by preferential uptake of light isotopes by phytoplankton that is part of the particulate pool. pHg stable isotopes sampled in 2017 at two stations, Julio and K1, closer to the coast were similar to the open sea station (K2) with no clear trends in water depth or distance from the shore (Figure S1). Marine sediments, analyzed for station Julio only (700 m depth), had similar  $\delta^{202}\text{Hg} = -0.75$  ‰ (-0.76 to -0.74 ‰),  $\Delta^{199}\text{Hg} = 0.05$  ‰ (0.04 to 0.05 ‰) and  $\Delta^{200}\text{Hg} = 0.03$  ‰ (0.00 to 0.06 ‰) (median and (IQR),  $n = 4$ ) to mean water column pHg (K1, K2, Julio), and were similar to sediment samples taken elsewhere in the Mediterranean Sea<sup>12,13</sup>.

### **Sea water $\Delta^{199}\text{Hg}$ and photochemical reduction of Hg(II) to Hg(0)**

During photoreduction of Hg(II)-organic ligand complexes the magnetic isotope effect (MIE) may separate even from odd Hg isotopes<sup>14</sup>. Experimental photomicrobial Hg(II) reduction in simulated sea water medium has been shown to lead to negative  $\Delta^{199}\text{Hg}$  in residual aquatic Hg(II)<sup>15</sup>. The sign (positive, negative  $\Delta^{199}\text{Hg}$ ) and magnitude of the MIE is not fully understood, but has been shown to depend on the nature of the Hg-binding ligand (e.g. O or S), the Hg to ligand concentration ratio, and environmental conditions such as pH<sup>16,17</sup>. Here, we evaluate whether the tHg and pHg data show evidence of in situ marine odd-MIF, in addition to that inherited from atmospheric deposition sources. We first calculate the excess  $\Delta^{199}\text{Hg}_{\text{exc}}$  in all

seawater samples, defined as the difference between the measured  $\Delta^{199}\text{Hg}$  in a marine sample and the expected  $\Delta^{199}\text{Hg}$ , based on atmospheric inputs. The expected  $\Delta^{199}\text{Hg}$  was calculated by binary mixing of  $\Delta^{199}\text{Hg}$  in atmospheric  $\text{Hg(II)}$  and  $\text{Hg(0)}$  using the source contributions ( $f_{\text{Hg(II)}}$ ) derived from  $\Delta^{200}\text{Hg}$  (Methods, equation 3). The excess  $\Delta^{199}\text{Hg}$  in the different marine Hg pools ( $\Delta^{199}\text{Hg}_{\text{exc}}$ ), representing the  $\Delta^{199}\text{Hg}$  which was produced within the marine system, was calculated as follows:

$$\Delta^{199}\text{Hg}_{\text{exc}} = \Delta^{199}\text{Hg}_{\text{meas}} - (f_{\text{Hg(II)}} \times \Delta^{199}\text{Hg}_{\text{Hg(II)}} + (1 - f_{\text{Hg(II)}}) \times \Delta^{199}\text{Hg}_{\text{Hg(0)}}) \quad (\text{Eq. S1})$$

, where  $\Delta^{199}\text{Hg}_{\text{meas}}$  is the measured value. Overall, the  $\Delta^{199}\text{Hg}$  pattern in tHg and pHg of seawater and marine sediments is similar to  $\Delta^{200}\text{Hg}$  and observed  $\Delta^{199}\text{Hg}$  can largely be explained by a conservative mixing of atmospheric  $\text{Hg(0)}$  and  $\text{Hg(II)}$  deposition (Figure 2B and 3B). Atlantic and Mediterranean  $\Delta^{199}\text{Hg}_{\text{exc}}$  was 0.03‰ (0.02 to 0.13‰; median, inter quartile range (IQR),  $n = 17$ ) in tHg and 0.01‰ (-0.07‰ to 0.08‰; median, IQR,  $n = 61$ ) in pHg, which is not significant. Very low  $\Delta^{199}\text{Hg}_{\text{exc}}$  were also found in marine sediments of the Mediterranean Sea (0.09‰, 0.03‰ to 0.12‰) and the Atlantic Ocean (0.06‰, 0.02 to 0.10‰). Elevated median  $\Delta^{199}\text{Hg}_{\text{exc}}$  of 1.64‰ in marine fish (Extended Data Table 2) can therefore be predominantly ascribed to photochemical breakdown of MMHg. The absence of significant odd-MIF in surface seawater does not automatically mean that photoreduction is slow, or that the MIE is absent. Experimental photoreduction observations on seawater, under representative conditions, are needed to examine the issue.

### **Observation-based estimates of global marine $\text{Hg(II)}$ deposition, and air-sea $\text{Hg(0)}$ exchange as a function of latitude**

In order to assess potential latitudinal bias in the global  $\Delta^{200}\text{Hg}$  mass balance (main text), which for tHg and pHg is mostly based on northern hemisphere mid-latitude  $\Delta^{200}\text{Hg}$  observations (43°-81°N), we perform in this section a full 5 degree zonal analysis of marine  $\Delta^{200}\text{Hg}$ , rainfall  $\text{Hg(II)}$ , dissolved gaseous  $\text{Hg(0)}$ , climatology and calculated  $\text{Hg(0)}$  invasion, and evasion fluxes as a function of latitude. The analysis is based on 1. A review of marine aqueous, pelagic biota and pelagic sediment  $\Delta^{200}\text{Hg}$ , 2. A review of the latitudinal distribution of  $\text{Hg(II)}$  wet deposition, 3. A review of gross  $\text{Hg(0)}$  invasion (i.e. ocean uptake), which allows us to estimate, by mass balance, an expected  $\Delta^{200}\text{Hg}$  gradient which we compare to observed marine  $\Delta^{200}\text{Hg}$ , and 4. A reversed mass balance where we use the observed marine  $\Delta^{200}\text{Hg}$  gradient to estimate the ocean  $\text{Hg(0)}$  uptake flux, or the  $\text{Hg(II)}$  deposition that is needed to explain the  $\Delta^{200}\text{Hg}$  observations.

1. Figure S3 (and Figure 4, main text) shows the latitudinal distribution of marine pelagic  $\Delta^{200}\text{Hg}$ .  $\Delta^{200}\text{Hg}$  of marine data at high latitudes ( $>60^\circ$ ,  $0.01\text{ ‰}$  ( $-0.04\text{ ‰}$  to  $0.03\text{ ‰}$ ); median and IQR,  $n=69$ ) in both hemispheres are significantly lower ( $p<0.001$ , one-sided t test), than mid-latitude ( $30\text{--}60^\circ$ ,  $0.03\text{ ‰}$  ( $0.01\text{ ‰}$  to  $0.065\text{ ‰}$ ); median and IQR,  $n=428$ ), which are significantly lower ( $p<0.001$ , one-sided t test) than the (sub)tropics ( $0\text{--}30^\circ$ ,  $0.07\text{ ‰}$  ( $0.04\text{ ‰}$  to  $0.085\text{ ‰}$ ); median and IQR,  $n=275$ ). This trend suggests that Hg(II) and Hg(0) deposition contributions to pelagic marine waters are variable. The trend also confirms, to first order, that the observed higher  $\Delta^{200}\text{Hg}$  ( $0.06\text{ ‰}$ ) in sub-tropical pHg (Motta et al., 2019)<sup>18</sup> and lower pHg  $\Delta^{200}\text{Hg}$  in mid-latitude ( $0.01\text{ ‰}$ ) and high latitude ( $-0.02\text{ ‰}$ ) waters (this study) are coherent features that belong to a broader latitudinal trend in marine  $\Delta^{200}\text{Hg}$ .

2. We review Hg(II) wet deposition at remote coastal and island monitoring sites globally, and during a S-Atlantic cruise<sup>19</sup> that collected a large number of rainfall events (Extended Data Figure 3,  $n=12,812$ ). We find a gradual increase from  $1.7 \pm 0.9\text{ }\mu\text{g m}^{-2}\text{ y}^{-1}$  at high latitudes to  $6.7 \pm 4.0$  at mid-latitudes to  $15 \pm 5$  in the (sub-)tropics (mean  $\pm$  sd), generally attributed to convective cloud formation and upper tropospheric Hg(II) scavenging<sup>20</sup>. Whereas the northern hemisphere (NH) (sub-)tropical rainfall Hg(II) maximum is well defined for Mercury Deposition Network (MDN<sup>21</sup>) sites along the coastal N-Atlantic Ocean and Caribbean seas, only limited data is available for the NH Southeast Asian seas<sup>22,23</sup>, the Pacific Ocean at Hawaii<sup>18</sup>, the equator<sup>19,24,25</sup> and the southern hemisphere (SH)<sup>19,26,27</sup>. Extrapolation of the latitudinal Hg(II) wet deposition trend at marine locations to the global Ocean gives a Hg(II) wet deposition flux of  $2561 \pm 768\text{ Mg y}^{-1}$ , assuming the relative standard deviation of 30% observed for individual  $5^\circ$  latitude intervals applies at the global scale. Seasonal Hg(II) dry deposition observations over oceans are inexistent, and must be estimated from 3D Hg models. Model Hg(II) wet deposition generally is on the order of 60% of total Hg(II) deposition, the remaining 40% being Hg(II) dry deposition<sup>28,29</sup>. For the observed global Hg(II) wet deposition budget of  $2561\text{ Mg y}^{-1}$ , Hg(II) dry deposition would then correspond to  $1615 \pm 485\text{ Mg y}^{-1}$ . In the absence of observations, we assume Hg(II) dry deposition to be constant as a function of latitude at  $5\text{ }\mu\text{g m}^{-2}\text{ y}^{-1}$ , which respects its contribution of 40% to modeled global Hg(II) deposition. The hybrid observational-model estimate (indicated as zonal ‘reference model in main text, and Figures 4, Extended Data Figure 5) of global Hg(II) deposition to oceans of  $4268 \pm 1280\text{ Mg y}^{-1}$  is therefore similar to atmospheric Hg(II) deposition of  $4600\text{ Mg y}^{-1}$  in Hg cycling models<sup>29</sup>. Both our zonal ‘reference model’ and 3D Hg cycling models rely heavily on coastal and continental rainfall observation sites, in particular from the MDN network in N-America. It is therefore possible that the coastal rainfall observations, despite our pre-selection

of non-urban remote sites, are biased high by regional anthropogenic Hg(II) emissions. Consequently the marine Hg(II) deposition budget discussed here (Extended Data Figure 3) may therefore be biased high, which we argue (in the main text discussion) is a potential reason for the  $\Delta^{200}\text{Hg}$ -based underestimation of Hg(0) to the marine Hg budget in 3D Hg cycling models.

3. We review surface Ocean dissolved gaseous Hg (DGM) measurements in order to estimate mean latitudinal DGM distribution (Extended Data Figure 4), and a DGM observation-based global marine Hg(0) gross and net emission budget. While DGM technically includes both dissolved gaseous Hg(0) and DMHg, it is thought to represent mostly Hg(0) due to the low surface ocean DMHg concentrations. We estimate marine Hg(0) evasion based on marine boundary layer atmospheric gaseous Hg(0) distribution<sup>30</sup>. We use latitudinal mean DGM, mean annual sea surface temperature (SST; 2007-2019; Copernicus product WIND\_GLO\_PHY\_CLIMATE\_L4\_REP\_012\_003), wind speed at 10m above sea level ( $\mu_{10}$ ; 2007-2019; Copernicus product SST\_GLO\_SST\_L4\_NRT\_OBSERVATIONS\_010\_001), and marine boundary layer Hg(0), to calculate global gross Hg(0) invasion ( $F_{\text{inv}}$ , Eq S2), gross evasion ( $F_{\text{ev}}$ , Eq S3) and net Hg(0) evasion ( $F_{\text{net}}$ , Eq S4) for 5° latitude bands (all in  $\text{ng m}^{-2} \text{h}^{-1}$ ) as follows:

$$F_{\text{inv}} = K_w \times -C_a/K_H \quad (\text{Eq. S2})$$

$$F_{\text{ev}} = K_w \times C_w \quad (\text{Eq. S3})$$

$$F_{\text{net}} = K_w \times (C_w - C_a/K_H) \quad (\text{Eq. S4})$$

where  $C_w$  is the surface sea water DGM concentration ( $\text{ng m}^{-3}$  sea water),  $C_a$  is the air Hg(0) concentration ( $\text{ng m}^{-3}$  air),  $K_H$  is the dimensionless Henry's law constant, and  $K_w$  is the Hg(0) gas transfer velocity ( $\text{m h}^{-1}$ ):

$\ln(K_H) = 2403.3/T + 6.92$  from Andersson et al. 2008<sup>31</sup>, where  $T$  is the SST in degrees Kelvin  
 $K_w = 0.25 \times \mu_{10}^2 (Sc_{\text{Hg0}}/Sc_{\text{CO2}})^{-0.5}$  from Nightingale et al. 2000<sup>32</sup>, where  $Sc_{\text{Hg0}}$  is the Schmidt number for Hg(0):

$$Sc_{\text{Hg0}} = \nu/D$$

where  $\nu$  is the kinematic viscosity ( $\text{cm}^2 \text{s}^{-1}$ ) =  $0.027 \times e^{(-0.025 \times T')}$  with  $T'$  the SST temperature in degrees Celsius, and  $D$ , the diffusivity of Hg(0) in sea water ( $\text{cm}^2 \text{s}^{-1}$ ) =  $0.02293 \times e^{-(17760 \text{ J/mol})/RT}$ , where  $R$  is the Boltzman's constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is SST in Kelvin, all based on Kuss et al. 2009<sup>33</sup>.

Hg(II) deposition, gross Hg(0) invasion, gross Hg(0) evasion and net Hg evasion as a function of latitude are summarized in Extended Data Figure 5 top. Hg(0) invasion is driven by observed atmospheric Hg(0) and wind speed and is maximal at mid and high latitudes. Hg(II) deposition is dominated by Hg(II) wet deposition in the sub-tropical NH. Hg(0) evasion is driven by high DGM concentrations in the (sub-)tropics (Extended Data Figure 3) and by high wind speed at mid and high latitudes. The net Hg evasion trend shows important net deposition in the northern hemisphere, and net evasion in the southern hemisphere, in agreement with 3D Hg cycling models<sup>29</sup> and observations<sup>34</sup>. We use Hg(II) wet deposition, Hg(II) dry deposition and Hg(0) invasion estimates (Extended Data Figure 5 bottom), together with  $\Delta^{200}\text{Hg}$  end-members (Extended Data Figure 6, Extended Data Table 1, Equation 3) to calculate an expected latitudinal marine, pelagic  $\Delta^{200}\text{Hg}$  distribution (Figure 4a). Expanded uncertainties on  $\Delta^{200}\text{Hg}$  are estimated using a Monte Carlo script in R by randomly varying the stated uncertainties on fluxes and end-member  $\Delta^{200}\text{Hg}$ . Due to the asymmetric latitudinal contributions of Hg(II) deposition and Hg(0) invasion to marine Hg, the expected  $\Delta^{200}\text{Hg}$  trend (Figure 4a, main text) shows lower values at high latitudes and maximum, positive values in the NH (sub-)tropics. The observed marine  $\Delta^{200}\text{Hg}$  distribution is significantly lower than the predicted  $\Delta^{200}\text{Hg}$  distribution, except between 45 – 65°N (Figure 4). Our new tHg  $\Delta^{200}\text{Hg}$  observations in the Mediterranean Sea and Atlantic Ocean between 43 – 59°N are therefore coherent with predicted  $\Delta^{200}\text{Hg}$ . The majority of marine  $\Delta^{200}\text{Hg}$  observations, however, are lower than the predicted  $\Delta^{200}\text{Hg}$ , which leads us to conclude that the contribution of atmospheric Hg(0) to the oceans and to marine biota is underestimated.

Although we were not able to measure the  $\Delta^{204}\text{Hg}$  in tHg and pHg, due to instrumental limitations (minor isotope, only one  $10^{13}$  Ohm amplifier available and attributed to  $^{198}\text{Hg}$ ), the large marine biota and sediment data set contains abundant  $\Delta^{204}\text{Hg}$  observations. In Extended Data Figure 7 we show that these data are consistent with  $\Delta^{200}\text{Hg}$  observations in the same marine biota data, and with the  $\Delta^{200}\text{Hg}:\Delta^{204}\text{Hg}$  relationship observed in terrestrial samples<sup>35</sup>.

4. Above we used a hybrid approach combining observations of Hg(II) wet deposition and atmospheric Hg(0), and 3D model-based Hg(II) dry deposition and Hg(0) gas-exchange to predict marine  $\Delta^{200}\text{Hg}$ . The predicted  $\Delta^{200}\text{Hg}$  trend is shifted to higher values compared to observed marine  $\Delta^{200}\text{Hg}$ . Here we discuss why the zonal model, and 3D Hg cycling model predicted Hg(II):Hg(0) gross deposition ratio of 3:1 overestimates Hg(II) deposition to oceans. It is important to understand that  $\Delta^{200}\text{Hg}$  does not inform on the absolute magnitude (in  $\mu\text{g m}^{-2} \text{ y}^{-1}$ , or in  $\text{Mg y}^{-1}$ ) of Hg(II) deposition and Hg(0) uptake fluxes. Rather, it informs on the relative Hg(II) and Hg(0) contributions, and therefore constrains the ratio of the marine

Hg(II):Hg(0) gross deposition flux. We therefore need to ask which of the two (or both) absolute flux estimates, either per 5° latitude band, or on a global basis, is biased. We have indicated above that the marine Hg(II) wet deposition flux is mostly observed at coastal N-American stations, and only rarely over the open Ocean. Using a fitting approach, minimizing the root mean square error (rmse) between observed and predicted  $\Delta^{200}\text{Hg}$ , we estimate that Hg(II) wet deposition would need to be approximately half (1252 Mg/y) the current estimate ( $2561 \pm 768$ , 1SD) to achieve a good fit (Figure 4d, main text). Note that if marine Hg(II) wet deposition is 100% lower, then automatically Hg(II) dry deposition, fixed at 40% of total Hg(II) deposition also becomes 100% lower. With respect to the GEOS-Chem budget, Hg(II) deposition would need to be lowered 2.7x from 4600 to 1700 Mg y<sup>-1</sup> in order to achieve a 1:1 Hg(0):Hg(II) gross deposition ratio. We consider that 2-3x times lower Hg(II) deposition is plausible, given the overall uncertainty on observations, and given that the latitudinal coastal Hg(II) wet deposition distribution is asymmetric with higher deposition in NH Hg emission source regions.

We can also keep Hg(II) deposition constant, and increase ocean Hg(0) uptake by increasing the gas-transfer velocity,  $K_w$  in equations S1-S3, by a factor of 2.3 to achieve an optimum fit between observed and predicted  $\Delta^{200}\text{Hg}$  (Figure 4d, main text). In GEOS-Chem,  $K_w$  would have to be increased 270% to increase Hg(0) evasion from 1700 to 4600 Mg y<sup>-1</sup>. A 230 - 270% increase in  $K_w$  exceeds the typical uncertainty on Hg(0) gas-exchange models which is on the order of 30%<sup>36,37</sup>. However, since the Hg(0) gas-exchange parameterizations are extrapolated from CO<sub>2</sub>, they have not been calibrated against experimental or field observations. In particular the effects of surface ocean micro-layer chemical reactions, for example by consumption of invading Hg(0), could cause underestimation of  $K_w$ . However, there is a caveat in fitting  $K_w$  to optimize ocean Hg(0) uptake: gross marine Hg(0) emission and net marine Hg(0) exchange also depend linearly on  $K_w$  (equations S2, S3). A 230% increase in  $K_w$  would result in large global gross marine Hg(0) emission (10900 Mg/y) and large net air-sea Hg(0) exchange (6500 Mg/y) fluxes. A larger net exchange flux would change the ocean from a net sink in present Hg cycling models, to a net source, which would have to be balanced by an additional terrestrial sink to keep the atmosphere in steady state (as observed).

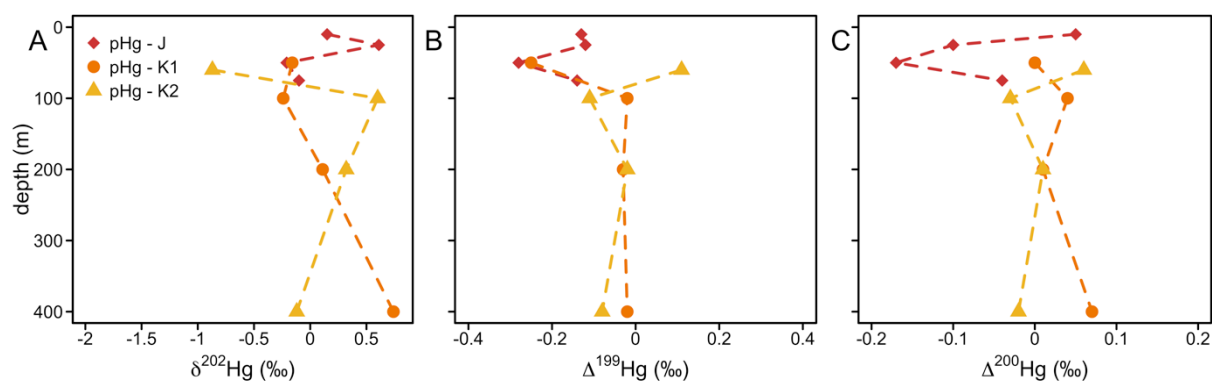


Figure S1. Depth profile of particulate Hg stable isotope composition at three stations in the Mediterranean Sea during the June 2017 campaign. A: mass-dependent fractionation ( $\delta^{202}\text{Hg}$ ), B: odd mass-independent fractionation ( $\Delta^{199}\text{Hg}$ ), C: even mass-independent fractionation ( $\Delta^{200}\text{Hg}$ ).

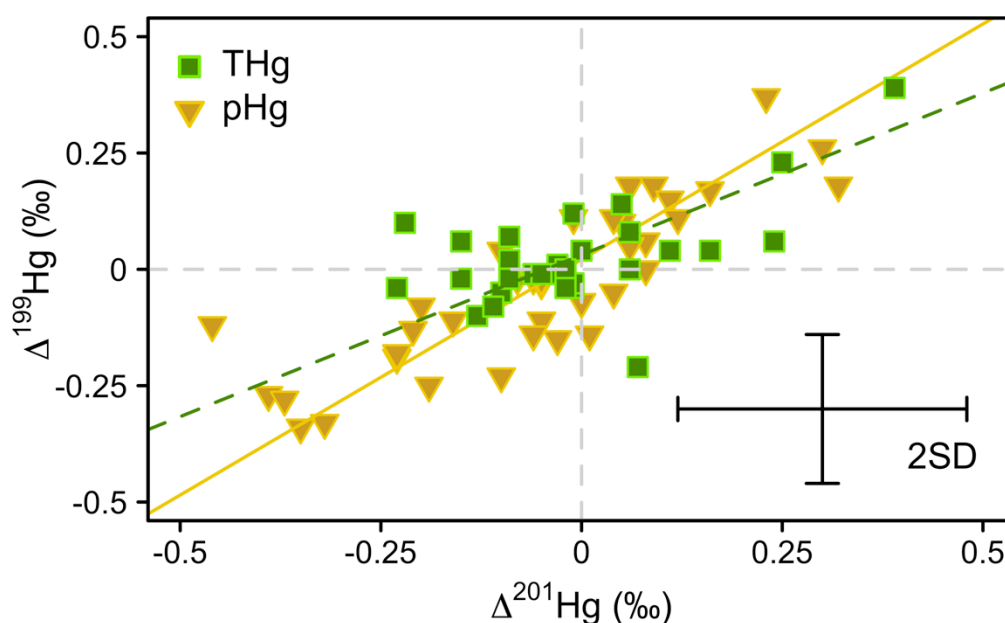


Figure S2: Scatterplot of odd Hg isotope mass-independent fractionation,  $\Delta^{201}\text{Hg}$  vs.  $\Delta^{199}\text{Hg}$  of all tHg and pHg seawater data, including the published data by Motta et al. 2019. The dashed line represents the York regression using IsoplotR<sup>38</sup> for tHg ( $\Delta^{199}\text{Hg} = 0.79(\pm 0.29) \Delta^{201}\text{Hg} + (0.03 \pm 0.04)$ , ( $\pm$  se), MSWD = 0.2). The solid line represents the York regression for pHg ( $\Delta^{199}\text{Hg} = 1.01(\pm 0.09) \Delta^{201}\text{Hg} + (0.02 \pm 0.02)$ , ( $\pm$  se), MSWD = 1.25). Error bars represent the 2 SD of replicate procedural standards for tHg and pHg.

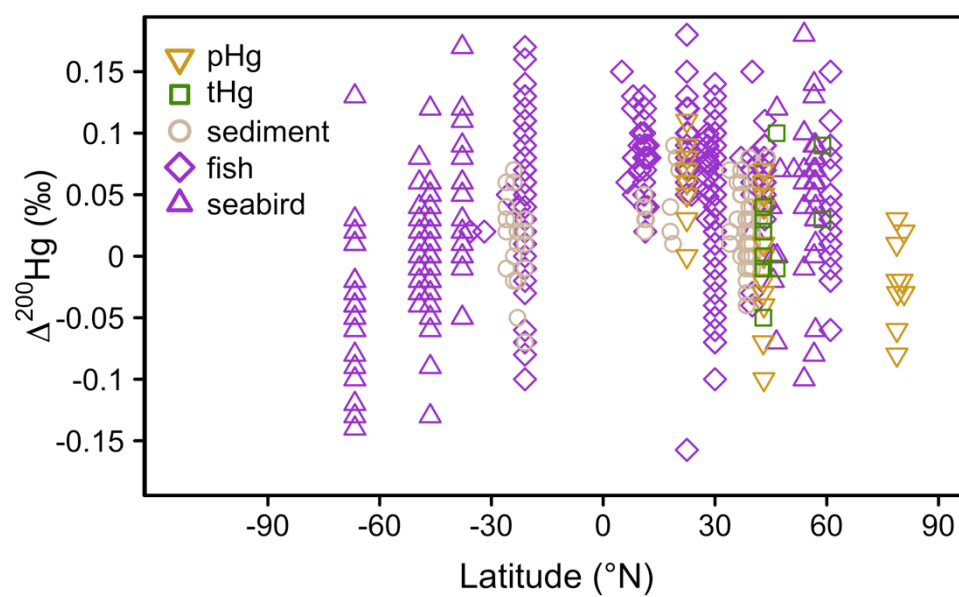


Figure S3: Variation of even-MIF Hg stable isotope composition ( $\Delta^{200}\text{Hg}$ ) in 787 individual marine samples resolved by sample type as function of latitude. See Extended Data Table 2 for data sources.

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