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1 **Mercury stable isotopes constrain atmospheric sources to the Ocean**

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12 **Keywords:** GEOTRACES, marine mercury, Hg stable isotopes, Mediterranean Sea, Atlantic Ocean,
13 atmospheric deposition, gas exchange, emission, invasion, biota, sediment

14

15 **Human exposure to toxic mercury (Hg) is dominated by the consumption of seafood^{1,2}. Earth system**
16 **models suggest that Hg in marine ecosystems is supplied by atmospheric wet and dry Hg(II)**
17 **deposition, with a 3 times smaller contribution from gaseous Hg(0) uptake^{3,4}. Observations of marine**
18 **Hg(II) deposition and Hg(0) gas exchange are sparse however⁵, leaving the suggested importance of**
19 **Hg(II) deposition⁶ ill-constrained. Here we present the first Hg stable isotope measurements of total**
20 **Hg (tHg) in surface and deep Atlantic and Mediterranean seawater and use it to quantify**
21 **atmospheric Hg deposition pathways. We observe overall similar tHg isotope compositions, with**
22 **median $\Delta^{200}\text{Hg}$ signatures of 0.02‰, lying in between atmospheric Hg(0) and Hg(II) deposition end-**
23 **members. We use a $\Delta^{200}\text{Hg}$ isotope mass balance to estimate that seawater tHg can be explained by**
24 **the mixing of 42% (24 to 50 %, median and interquartile range) atmospheric Hg(II) gross deposition**
25 **and 58% (50 to 76 %) Hg(0) gross uptake. We measure and compile additional, global marine Hg**
26 **isotope data including particulate Hg, sediments and biota and observe a latitudinal $\Delta^{200}\text{Hg}$ gradient**
27 **indicating larger ocean Hg(0) uptake at high latitudes. Our findings suggest that global atmospheric**
28 **Hg(0) uptake by the oceans is equal to Hg(II) deposition, which has implications for our**
29 **understanding of atmospheric Hg dispersal and marine ecosystem recovery.**

30 The consumption of seafood exposes humans to mono-methylmercury (MMHg), a toxin known to
31 affect fetal and infant neurodevelopment and cardiovascular disease in adults⁷. MMHg is formed from
32 inorganic mercury (Hg) in the ocean and biomagnifies along marine food webs to high levels⁸⁻¹⁰.
33 Anthropogenic emission of Hg to the atmosphere outweighs natural emission five to ten-fold^{11,12}, and
34 is thought to have more than tripled the Hg content of surface ocean waters¹³. Climate change and
35 overfishing have been suggested to affect marine fish MMHg levels, and require detailed models of Hg
36 cycling to assess future human exposure to Hg¹⁴. Earth system models of Hg biogeochemical cycling
37 suggest that atmospheric Hg deposition to the modern open ocean is dominated by Hg(II) wet and dry
38 deposition (4600 Mg y⁻¹, gross flux) compared to invasion, i.e. ocean uptake, of gaseous Hg(0) (1700
39 Mg y⁻¹, gross flux) in a 3:1 ratio^{3,4} (Extended Data Figure 1). Rivers deliver similar amounts of Hg to
40 coastal oceans (2050 to 5600 Mg y⁻¹)¹⁵⁻¹⁷ as atmospheric deposition, yet only 6% of river Hg is
41 estimated to reach the open ocean⁶. Models also estimate that, of total deposited Hg(0) and Hg(II)
42 forms, 4600 Mg y⁻¹ (gross flux) is re-emitted to the atmosphere by (photo-)chemical and microbial
43 reduction of Hg(II) to Hg(0) and evasion of Hg(0)^{3,18}. The modern ocean is therefore a net sink of Hg
44 (1700 Mg y⁻¹) with respect to the atmosphere (Extended Data Figure 1). Dissolved Hg(0) concentrations
45 in surface waters are sporadically measured, and generally show Hg(0) supersaturation¹⁹⁻²¹, supporting
46 net Hg(0) evasion. The direction and magnitude of the large air-sea exchange of Hg(0) depends on the
47 aqueous Hg(II) reduction and Hg(0) oxidation rates, and the wind driven air-sea Hg(0) exchange velocity
48 in models⁶. The absence of direct, long-term Hg(0) flux measurements over the ocean and limited

49 observations of Hg(II) wet and dry deposition to oceans currently provide insufficient constraints for
50 model validation of air-sea Hg(0) exchange, and Hg(II) deposition fluxes. This in turn hampers our
51 capability to predict how Hg levels in the ocean will respond to curbed anthropogenic Hg emissions
52 under the UN Minamata Convention on Mercury, and to climate change^{12,22}.

53 In terrestrial ecosystems, Hg stable isotopes have proven to be instrumental in understanding
54 the relative importance of Hg(II) and Hg(0) deposition^{23–25}. Atmospheric Hg(0) and Hg(II) in rainfall have
55 different mass-dependent (MDF, $\delta^{202}\text{Hg}$) and mass-independent isotope fractionation (MIF, $\Delta^{199}\text{Hg}$ and
56 $\Delta^{200}\text{Hg}$) signatures. Even-Hg MIF ($\Delta^{200}\text{Hg}$) is thought to be generated exclusively by upper tropospheric
57 and/or stratospheric photochemical reactions^{26,27}. $\Delta^{200}\text{Hg}$ is therefore considered as a conservative
58 tracer for atmospheric Hg deposition pathways²⁸. So far, Hg stable isotopes in total unfiltered Hg (tHg)
59 in seawater have only been measured in coastal seawater of the Canadian Arctic Archipelago,
60 suggesting that 50% to 80% of tHg originated from coastal erosion and river input²⁹. Analysis of
61 particulate Hg (pHg) isotopes at the station ALOHA (22°N) near Hawaii suggested that atmospheric
62 deposition of Hg(II) from rainfall was an important Hg source to the tropical Pacific surface ocean³⁰.

63 In this contribution we develop and apply a method for tHg isotope analysis of open ocean
64 seawater, characterized by its (sub-)picomolar levels of tHg in all basins³¹, to understand atmospheric
65 supply of Hg to the ocean. We use the new Mediterranean and North-Atlantic tHg and pHg isotope
66 observations together with published atmospheric Hg(II) and Hg(0) and marine pHg, sediment and
67 biota Hg isotope data to show that ocean Hg(0) uptake is relatively more important than currently
68 estimated.

69 **Results and Discussion**

70 ***Seawater Hg isotope composition***

71 Oligotrophic Mediterranean station K2, 20 km off-shore (Extended Data Figure 2) showed tHg
72 concentrations in June 2017, February and May 2019 (Figure 1a) that are slightly depleted in surface
73 waters (0.80 pM), and peak at 300 m depth (1.1 pM), similar to previous observations^{32,33}. Total
74 methylated Hg (MeHg) concentrations peak at 400 - 600 m, (43 % of tHg), where oxygen levels reach
75 their minimum due to microbial remineralization of particulate organic matter³³. Surface tHg levels in
76 the Bay of Marseille at Endoume pier were higher with 6.1 pM (4.9 to 6.7 pM, median and interquartile
77 range (IQR), n = 8). In four samples from two Atlantic Ocean stations (St21, St38, Extended Data Figure
78 2), tHg increased with depth from 0.46 to 0.83 pM and represent the mixed layer (5 m, 20 m),
79 intermediate water (650 m), and north-east Atlantic deep water (NEADW, 3345 m)³⁴. MeHg in the two
80 Atlantic profiles were similar to Mediterranean station K2 with low levels, 0.04 pM, at the surface and

81 elevated levels, 0.4 pM, at depth (54 % of tHg). pHg at the Mediterranean stations K1, K2 and Julio
82 were low with a median of 0.10 pM (IQR: 0.08 to 0.15 pM, n = 16) for the 5 - 800 m depth range. Fram
83 Strait pHg in Atlantic Ocean waters of the West-Spitzbergen current had higher pHg levels of 0.28 pM
84 (0.23 to 0.31 pM, median and IQR, n = 9).

85 tHg isotope depth profiles for $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ signatures were replicated at station
86 K2 during two sampling cruises in February and May 2019 and show reproducible results (Figure 1b-
87 d). $\delta^{202}\text{Hg}$ is uniform with depth, with a median value of -0.09 ‰ (IQR: -0.31 to 0.00 ‰, n = 12). Overall,
88 $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ are also near-zero, with median values of 0.06 and 0.01 ‰ respectively. The four
89 North-Atlantic Ocean tHg samples show median $\delta^{202}\text{Hg}$ of -0.45 ‰, $\Delta^{199}\text{Hg}$ of 0.09‰, and $\Delta^{200}\text{Hg}$ of
90 0.06‰, and are therefore similar to Mediterranean waters. pHg isotope data for the Mediterranean
91 Sea (n=19) and Atlantic (n=9) were broadly similar to tHg observations (Figures 1, 2, Supporting
92 Information). Mediterranean sediments, had similar $\delta^{202}\text{Hg}$ = -0.75 ‰ (-0.76 to -0.74 ‰), $\Delta^{199}\text{Hg}$ =
93 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
94 water column pHg, and were similar to sediment samples taken elsewhere in the Mediterranean
95 Sea^{35,36}. Overall, the tHg and pHg $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slopes of 0.8 to 1.0 are indicative of photochemical
96 MIF (Figure S2).

97 ***Atmospheric Hg(II) and Hg(0) deposition***

98 We use $\Delta^{200}\text{Hg}$ to quantify the combined contribution of gross Hg(II) wet and dry deposition, and gross
99 Hg(0) invasion to marine tHg and pHg (Methods, Eq. 3). It is important to clarify that Hg(0) gas exchange
100 is bi-directional (Extended Data Figure 1), i.e. at any time atmospheric gaseous Hg(0) dissolves into the
101 surface microlayer (invasion), and dissolved aqueous Hg(0) evades to the atmosphere. Although
102 generally surface oceans are supersaturated in Hg(0), and gross Hg(0) evasion exceeds gross invasion,
103 the gross Hg(0) invasion flux is substantial, around 1700 Mg y⁻¹ in models, and an important contributor
104 to marine Hg (Extended Data Figure 1). The Hg(II) dry and wet deposition flux is per definition a gross
105 flux. Hg(II) deposition, after reduction to Hg(0) in ocean waters, does however contribute to the large
106 Hg(0) emission flux. We exclude other marine Hg sources such as hydrothermal or river inputs. At
107 Mediterranean station K2, this is justified by the absence of large rivers draining into the Ligurian Sea,
108 and reflected in the open-ocean type tHg levels around 1 pM. The Rhône River reaches the
109 Mediterranean, 100 km west of K2, at the continental shelf of the Gulf of Lions, and is carried further
110 westward away from K2. Similarly, there is no hydrothermal activity within about 1000 km from the
111 K2 station. At the Atlantic Ocean stations St21 and St38, no influence of river³⁷ or hydrothermal Hg
112 inputs was found³⁴.

113 Modern, northern hemispheric Hg(II) wet deposition is characterized by a positive $\Delta^{200}\text{Hg}$ of
114 0.17 ‰ (0.11 ‰ to 0.22 ‰, median and (IQR), $n = 106$), for background sites with Hg concentrations <
115 25 ng L⁻¹; Extended Data Table 1). We also need to consider the $\Delta^{200}\text{Hg}$ of Hg(II) dry deposition,
116 suggested to represent 40% of total atmospheric Hg(II) deposition to oceans³⁸. Aerosol and fog water
117 Hg(II) observations in the marine boundary layer (MBL) and free tropospheric gaseous Hg(II) in Atlantic
118 air masses also have positive but slightly lower $\Delta^{200}\text{Hg}$ of 0.10 ‰ (0.07 to 0.1 ‰; median, IQR, $n = 66$)^{39–}
119 ⁴¹. For end-member mixing calculations we estimated the $\Delta^{200}\text{Hg}$ of combined wet and dry Hg(II)
120 deposition to vary between 0.13 and 0.15 ‰ with latitude (Extended Data Figure 6). Atmospheric
121 Hg(0), the largest Hg pool in the atmosphere, exhibits negative $\Delta^{200}\text{Hg}$ of -0.05 ‰ (-0.08 to -0.03 ‰;
122 median, IQR, $n = 220$, for continental background samples with Hg(0) concentrations < 2 ng m⁻³;
123 Extended Data Table 1). MBL Hg(0) observed at coastal sites and during cruises shows an identical
124 $\Delta^{200}\text{Hg}$ of -0.06 ‰ (-0.08 ‰ to -0.02 ‰, median and IQR, $n = 80$, two-sided t.test, $p = 0.96$)^{39,42,43}.

125 Seawater tHg and pHg samples, including published Pacific Ocean pHg³⁰, show $\Delta^{200}\text{Hg}$ values
126 statistically larger than atmospheric Hg(0) (one-sided t.test, $p < 0.001$) and lower than Hg(II) end-
127 members (one-sided t.test, $p < 0.001$; Figure 2 & Figure 3A). Based on a $\Delta^{200}\text{Hg}$ mixing model (Methods,
128 Eq. 3) we estimate the contribution of Hg(0) uptake, $f_{\text{Hg}(0)}$, to be 58 % (50 to 76 %, median and IQR, $n =$
129 16) to marine tHg and 58 % (39 to 82 %, $n = 61$) to pHg. This implies that the majority, i.e. approximately
130 58% of N-Atlantic and Mediterranean Sea tHg and pHg is derived from direct ocean Hg(0) uptake. We
131 apply the same $\Delta^{200}\text{Hg}$ mass balance to the large body of published Hg isotope data in pelagic marine
132 sediments and pelagic biota ($n = 735$, Extended Data Table 2). Similar to sea water tHg and pHg, global
133 pelagic marine sediments and biota $\Delta^{200}\text{Hg}$ suggest a Hg(0) contribution, $f_{\text{Hg}(0)}$ of 57 % (49 to 65 %, $n =$
134 92) and 40 % (31 to 60 %, $n = 643$), respectively. The marine sediment and biota $\Delta^{200}\text{Hg}$ data cover a
135 much larger geographical range than the tHg and pHg data, including the southern hemisphere, and
136 indicate that, despite net Hg(0) evasion, gross ocean Hg(0) uptake is a globally important driver of
137 marine pelagic ecosystem Hg levels.

138 ***Latitudinal $\Delta^{200}\text{Hg}$ variability***

139 The validity of the $\Delta^{200}\text{Hg}$ mass balance hinges on two important details: 1. the link between
140 aqueous Hg redox transformation rates and the gross or net nature of the Hg(II) deposition and Hg(0)
141 uptake fluxes in the mass balance, and 2. latitudinal variation in marine $\Delta^{200}\text{Hg}$ observations. The
142 current consensus in Hg cycling models is that marine aqueous Hg reduction and oxidation rates are
143 fast^{18,44,45}, leading to global surface ocean oxidation and reduction fluxes of $2.6 \times 10^6 \text{ Mg y}^{-1}$ ⁴⁵, which
144 are 1000-fold larger than Hg deposition and air-sea exchange fluxes. This implies that the contrasting
145 $\Delta^{200}\text{Hg}$ signatures of gross Hg(0) evasion (-0.05 ‰) and gross Hg(II) deposition (+0.14 ‰) will be rapidly

146 homogenized in the surface mixed layer before Hg(0) is partially re-emitted to the atmosphere. The
147 $\Delta^{200}\text{Hg}$ derived Hg(0):Hg(II) deposition ratio therefore represents the gross deposition ratio. Secondly,
148 our new seawater tHg and pHg $\Delta^{200}\text{Hg}$ observations are from 43° – 81°N, where Hg(II) wet deposition
149 is known to be lower than in the northern hemispheric (sub-)tropics (Extended Data Figure 3). We
150 therefore examined current best knowledge on the latitudinal variation of Hg(0) invasion vs Hg(II)
151 deposition by a full latitudinal analysis of marine $\Delta^{200}\text{Hg}$, combined wet and dry Hg(II) deposition flux,
152 atmospheric and dissolved gaseous Hg(0) concentrations, and climatology (indicated by zonal
153 ‘reference model’ in Figure 4). Gross Hg(II) deposition, gross Hg(0) invasion, gross Hg(0) evasion and
154 net Hg(0) evasion, all based on a combination of published observations and models, (Figure 4,
155 Extended Data Figure 5) vary as a function of latitude. Hg(0) invasion is primarily driven by observed
156 atmospheric Hg(0) concentrations and wind speed, and is maximal at mid and high latitudes (Figure
157 4d). Hg(II) deposition is dominated by Hg(II) wet deposition in the sub-tropical northern hemisphere
158 (Figure 4c). We use the Hg(II) deposition and Hg(0) invasion estimates (Figure 4, Extended Data Figure
159 5), together with $\Delta^{200}\text{Hg}$ end-members (Extended Data Figure 6, Extended Data Table 1) to predict the
160 latitudinal marine $\Delta^{200}\text{Hg}$ distribution for the zonal ‘reference model’ (Figure 4a). Due to the
161 asymmetric contributions of Hg(II) deposition and Hg(0) invasion to marine Hg, the predicted marine
162 $\Delta^{200}\text{Hg}$ trend shows a maximum of 0.11 ‰ in the northern hemispheric (sub-)tropics and lower values
163 of 0.02‰ at high latitudes. The observed marine $\Delta^{200}\text{Hg}$ distribution in water, sediments and biota is
164 similar in shape but shifted to lower values compared to the predicted $\Delta^{200}\text{Hg}$ distribution, except
165 between 45 – 65°N (Figure 4a). The $\Delta^{200}\text{Hg}$ observations therefore indicate a relatively larger Hg(0)
166 invasion, or alternatively a smaller Hg(II) deposition contribution to pelagic marine Hg. By integrating
167 the marine $\Delta^{200}\text{Hg}$ observations over latitude and weighting by sea surface area, we estimate a global
168 ocean Hg(0) uptake contribution of 50% (IQR: 34% to 67%). Current best model estimates of global
169 gross Hg(0) uptake and gross Hg(II) deposition at the ocean surface are 1700 Mg y⁻¹ and 4600 Mg y⁻¹
170 respectively.³ Marine Hg isotope observations therefore suggest that gross Hg(0) uptake is equally
171 important as gross Hg(II) deposition in a 1:1 ratio, compared to the Hg cycling model predicted ratio of
172 1:3. The latitudinal $\Delta^{200}\text{Hg}$ data are supported by the alternative even-Hg isotope signature $\Delta^{204}\text{Hg}$,
173 which mirrors $\Delta^{200}\text{Hg}$ (Extended Data Figure 7).

174 The marine $\Delta^{200}\text{Hg}$ composition suggests that our current understanding of the marine Hg
175 budget is incomplete. We consider the most plausible reason for this to be that Hg(II) deposition to
176 oceans is overestimated, either due to bias in coastal Hg(II) wet deposition observations (Figure 4c) by
177 regional continental anthropogenic Hg emission sources, or due to overestimation of marine Hg(II) dry
178 deposition for which no observations exist (Supporting Information text). Alternatively, current Hg(0)
179 air-sea exchange parameterizations (Equations S1-3) could be incomplete, ignoring effects of the

180 surface micro-layer on the Hg(0) gas exchange velocity. In order to fit observed marine $\Delta^{200}\text{Hg}$
181 variability, a 2-3x lower marine Hg(II) deposition or 2-3x higher ocean Hg(0) uptake flux would be
182 required (Figures 4c,d, Extended Data Figure 1; Supporting Information text). In either case, a larger
183 relative contribution of Hg(0) to the oceans would have important impacts on the lifetime of
184 anthropogenic Hg in atmosphere and surface ocean, and consequently on the anticipated recovery of
185 ecosystems following aggressive Hg emission policy.

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207

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314

315 **Author contributions**

316 LEHB, JES, MJ and DP conceived the study. LEHB, MJ, DP, MP, MVP, MMD and JES performed sampling.
317 JES, MJ, and LEHB developed and applied the tHg isotope pre-concentration methods. JES, MJ, JM and
318 JC performed isotope measurements. MMD, MVP, AD, LEHB, MJ, JM, DP, and MT performed additional
319 laboratory work. MJ, JES and LEHB analyzed the data. JES and MJ wrote the draft paper, which was
320 improved by contributions from LEHB and DP, and commented by all authors.

321

322 **Author Information** The authors declare no competing financial interests.

323

324 **Supplementary Information** is available for this paper.

325

326 **Data availability**

327 Hg stable isotope and Hg speciation data that support the findings of this study are available from
328 <https://doi.org/10.5281/zenodo.4740464>

329

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331

333 **Methods**

334 The method for tHg in sea water consists of an ultra-clean shipboard sampling and post-cruise sample
335 processing protocol using a standard stannous chloride (SnCl₂) reduction purge-and-trap method,
336 based on the USEPA method 1631⁴⁶.

337 **Sampling.** Repeated, daily cruises were undertaken on the RV Antedon II from Marseille (France) to
338 the nearby (20 km) oligotrophic, off-shore station K2 (42.98 N / 5.41 E / >1500 m depth) between
339 14/6/2017 and 21/6/2017, on 27/02/2019 and 22/05/2019. We used an epoxy-painted trace metal
340 clean carousel, equipped with a conductivity-temperature-depth unit (CTD, Seabird SBE 911plus), and
341 oxygen sensor (Seabird SBE 43), and 8x 10 L GOFLO trace metal clean bottles (General Oceanics).
342 Samples were taken at up to 12 depths for Hg species, and at 4 depths for tHg and pHg isotopes,
343 corresponding to surface waters (5 m), the chlorophyll-maximum (20 m), the oxygen minimum zone
344 (400 m) and deep (800 m) waters. See SI for salinity, temperature, oxygen and fluorescence data.

345 Unfiltered seawater was drawn *via* acid-cleaned 6 mm FEP tubing into pre-cleaned 20 L Pyrex glass
346 bottles with GL45 PFA Teflon caps. Bottles were filled to the 20 L mark, and not to the brim, in order
347 to preserve a 3 L headspace for purge and trap purposes. Bottles were protected from sunlight and
348 breaking risk in 70 L plastic barrels (Kruizinga.nl Ref#53-WHV70) by using polyurethane expansive foam
349 to fit them in the barrels. We anticipate that future use of 20 L polycarbonate carboys are an alternative
350 option, for safer sampling during rough seas. Unfiltered seawater was drawn from each GOFLO bottle
351 into acid-cleaned and blank-tested 60 mL FEP Teflon bottles (Nalgene) for tHg and 250 mL PFA Teflon
352 bottles (Savillex Purillex) for MeHg, MMHg and dissolved gaseous Hg (DGM = Hg⁰ + dimethyl-Hg
353 (DMHg)) analysis. All sampling was compliant with strict GEOTRACES trace metal clean sampling
354 procedures⁴⁷. Eight 20 L replicate samples of seawater from the Bay of Marseille were taken every
355 three hours on 12/11/2019 at the Endoume pier. Seawater is continuously pumped at 20 L min⁻¹ into
356 the Mediterranean Institute of Oceanography (MIO) seawater sensing lab (SSL@MM). Samples were
357 transported to MIO and processed within 24 h. Atlantic Ocean tHg samples were collected during the
358 GEOVIDE cruise (GEOTRACES-GA01 transect), on board the RV “Pourquoi Pas?” between 15/05/2014
359 and 30/06/2014, similar to the MED Sea but using a 24 bottle trace metal clean carousel. tHg values
360 for GEOVIDE have been published elsewhere⁴⁸.

361 **Particulate Hg.** pHg was sampled using in situ pumps (McLane LV08) at stations K1 (43.10 N, 5.49 E,
362 700 m depth, 10 km off-shore, continental slope), K2, and Julio (43.13 N, 05.36 E, 100 m-depth, 10 km
363 off-shore, shelf) in the Mediterranean Sea on 16/06/2017, and at K2 on 22/05/2019; in Fram Strait
364 Atlantic waters from 21/7/2016 to 1/9/2016 during the FS Polarstern PS100 GRIFF cruise (Geotraces-
365 GN05 transect). Pre-burnt Millipore 142mm QMA, or GF/F were deployed for 1 - 3 h to collect particles
366 from 148-792 L of seawater. Filter samples were frozen onboard, shipped frozen to MIO, freeze dried
367 (Christ Gamma 1-16 LSCplus), and stored in the dark until analysis.

368 **Pre-concentration of tHg from seawater for stable isotope analysis**

369 The 20 L Mediterranean tHg samples were acidified and oxidized, within 12 h after sampling, at the
370 MIO laboratory, using 5 mL 0.2 N BrCl (Sigma-Aldrich KBr and KBrO₃ salts) in concentrated bi-distilled
371 9 N HCl, leading to an initial sample HCl concentration of 0.0023 N. BrCl blanks were analyzed before
372 addition, as it potentially constitutes the largest single component of the method blank. The volume
373 of BrCl was optimized by visual inspection of the sample turning slightly yellow, indicating excess BrCl
374 over reduced seawater components such as dissolved and particulate organic matter (DOC, POC, OM).
375 Samples were let sit for 12 h, after which a 60 mL subsample was taken with an acid cleaned, 60 cm
376 long, burette into pre-combusted 60 mL glass vials with acid-washed Teflon-lined caps for tHg

377 concentration analysis. This tHg subsample is compared to the shipboard 60mL tHg FEP sample and
378 serves to verify that the 20 L bottles are neither contaminated, nor subjected to tHg loss.

379 tHg pre-concentration was started by replacing the GL45 PFA Teflon caps (Savillex) by GL45
380 two-port PFA Teflon caps (Savillex) to guide 60 cm long 6 mm OD (3 - 4 mm ID) Pyrex bubbling post
381 with a 1 cm long P3 porosity frit (VitraPOR Micro Filter-Candle, Robuglas, Germany, custom assembled
382 by Verres Vagner, Toulouse, France). The second port on the GL45 cap hosted a 10 cm long 6 mm OD
383 FEP tube that was connected with a short piece of 10 mm OD, 4 mm ID silicone tubing to a shorter, 25
384 cm long, elbowed 6mm OD Pyrex bubbling post, with 1 cm long P2 frit (VitraPOR). The P2 bubbler post
385 was then inserted into a 60 mL, 20 cm long glass test tube, filled with 6 mL of oxidizing 40 vol% inverse
386 aqua regia (iAR) solution. The medium P2 bubbler frit inside the 40% iAR trap is critical to avoid over
387 pressure and leaks of Hg(0) from the 20 L bottle. All glassware was pre-combusted at 530°C and Teflon-
388 ware was cleaned by multiple bi-distilled HCl steps in a class 100 clean room.

389 Standard protocols for Hg(II) analysis by SnCl₂ reduction, such as EPA method 1631⁴⁶, use a
390 large excess of SnCl₂ over Hg(II). While SnCl₂ does not pose a blank issue (purging it removes all Hg
391 traces), it generates large volumes of toxic waste in each 20 L bottle after pre-concentration. We
392 therefore tested up to 100x lower levels of anhydrous Sn(II)Cl₂ (Sigma-Aldrich). Hg(II) reduction by
393 Sn(II) competes however with excess BrCl and natural oxygen present in seawater, i.e. Sn(II) is oxidized
394 by BrCl and O₂ before it can reduce Hg(II). We therefore neutralized excess BrCl by adding 4 mL of
395 NH₄.HCl (4.3 M) and verified disappearance of the yellow color. We then pre-purged (before adding
396 SnCl₂) the 20 L sample with Hg-free argon at 300 mL min⁻¹ for 3 h to remove > 90 % of dissolved oxygen.
397 The 40% iAR solution trap was connected during pre-purging to trap any potential, though unlikely,
398 loss of gaseous Hg from the sample. Adding SnCl₂ at this point, had however shown abundant
399 precipitation of a fine white solid, presumably SnCl_{2,s}, which we remedied by adding an additional 80
400 mL volume of HCl to stabilize Sn(II) in the samples. Sn(II) addition was performed in two ways: i) 125
401 mL of SnCl₂ was slowly pumped with a peristaltic pump (Gilson) at 1.25 mL min⁻¹, and 1/16'' PFA tubing,
402 *via* the central bubbling post into the bottle over 2 h; ii) the 125 mL was added instantly *via* the GL45
403 cap. No differences in Hg recovery were found between the two. Upon addition of SnCl₂ by pump or
404 in batch, we purged the 20 L samples for 8 h at 300 mL min⁻¹, in order to quantitatively collect sample
405 Hg into the oxidizing 40% iAR trap solution. At the end of 6 h of pre-concentration, the argon flow was
406 stopped, and the 40 v% iAR traps removed and diluted with MQ water to 20 v% iAR and stored cold
407 (4°C) in the dark until analysis.

408 For the Atlantic Ocean tHg samples, a different pre-concentration technique was applied
409 onboard which is described in detail in the Supporting Information. In brief, 48 L samples, stored in

410 Teflon (Tedlar) bags, were pumped at 5 mL min^{-1} , through an iodated activated carbon (IAC) cartridge
411 onboard. The IAC sorbent was combusted back on land, at Geosciences Environnement Toulouse
412 (GET), in a dual tube furnace set-up, and sample Hg(0) trapped in 6 mL 40% iAR. We abandoned this
413 method due to higher blanks, challenging Hg recoveries from IAC, and slowness of sea water sample
414 loading (1 week).

415 **Procedural blanks and standards**

416 Procedural Hg blanks, representing all laboratory manipulations, cleaning procedures, reagent
417 additions, and different operators, were determined as follows. Following pre-concentration of a batch
418 of 8 samples for tHg, the residual Hg-free seawater solution, was conserved in the 20 L bottle, and all
419 reagents were newly added to 8 bottles as described above. The solutions were then purged, similar
420 to samples, for 8 hours into newly prepared 6 mL 40% iAR traps. Eight procedural standards were pre-
421 concentrated in a similar fashion: following blanks, once more all reagents were added to the
422 remaining 20 L of Hg-free seawater solution, and 4 to 8 ng of NIST SRM 3133 Hg was added as internal
423 standard to each bottle.

424 **Particulate Hg concentration analysis**

425 Total particulate Hg (pHg) concentrations were measured on 25 mm stamp-outs, by combustion – cold
426 vapor atomic absorption spectrometry (CV-AAS, Leco AMA254) equipped with a low level optical cell
427 at MIO. Certified reference material NRC MESS-3 marine sediment ($91 \pm 9 \text{ ng g}^{-1}$, 1σ) was used for
428 quality control, with good results in the low, $<1 \text{ ng Hg}$, range ($88 \pm 1 \text{ ng g}^{-1}$, 1σ). Remaining filter material
429 was combusted whole on the dual tube furnace set-up at GET, following published protocols⁴⁹. In brief,
430 filters are rolled up, inserted in a 20 mm diameter, 15 cm long quartz tube, which is plugged from both
431 sides with quartz wool. The sample tube is then inserted in a 140 cm long quartz tube, housed in two
432 tube furnaces. The first furnace, hosting the sample tube, was heated from room temperature to 900°C
433 over 6 h in an 80 mL min^{-1} flow of high purity oxygen. The released Hg(0) vapor and other volatile
434 compounds passed through the 2nd pyrolyzing oven, maintained at 1000°C continuously, and purged
435 into a 40 vol% iAR oxidizing solution trap, that uses an elbowed, fritted, P2 porosity, Pyrex post. GF/F
436 and GF/D filters melt at temperatures $>530^\circ\text{C}$, but remain within the quartz sample tubes, blocked by
437 the quartz wool. Final trapping solutions were diluted to 20%v iAR and stored cold in the dark until Hg
438 concentration analysis by CV-AFS and Hg isotope analysis by MC-ICPMS. Reference material NIST
439 SRM1632d coal was used for weekly quality control. Combustion purge and trapping recovery on
440 samples, assessed by CV-AFS, was $104 \pm 28\%$, $100 \pm 28\%$, and $105 \pm 21\%$ (1σ) for the Mediterranean
441 Sea, PS94 and PS100 cruise samples respectively.

442 **tHg and Hg species concentration analysis**

443 We added 40 μL of 0.2N BrCl to the 60 FEP Teflon bottles for ambient tHg analysis. Ambient tHg
 444 concentrations in 60 mL FEP Teflon bottle aliquots, in 20 L bottle aliquots before and after pre-
 445 concentration, and in 20% iAR solution traps were all analyzed in duplicate using a custom-made purge
 446 and trap system coupled to a cold vapor atomic fluorescence spectrometry (CV-AFS, Brooks Rand
 447 Model III), either at MIO, at GET, or shipboard⁴⁴. The purge and trap system consists of 100 mL Teflon
 448 batch reactor (VWR), two electromagnetic valves (NResearch), a single gold trap (LECO), all connected
 449 by 1/8 inch FEP tubing to the CV-AFS (Brooks Rand Model 3). Seawater aliquots were 35 mL, and 20%
 450 iAR aliquots 100 μL . The CV-AFS was calibrated in the 1 - 20 pg range using NIST SRM 3133, and the
 451 NRC ORMS-5 certified reference material was always found within 10 % of the certified value (26 ± 1.3
 452 ng L^{-1} , 1σ). MeHg, MMHg, and DGM were analyzed following our published protocols⁵⁰. DMHg was
 453 calculated as the difference of MeHg and MMHg, and dissolved Hg(0) as the difference of DGM and
 454 DMHg. Details are given in the SI.

455 **Hg isotope analysis**

456 Hg stable isotope ratios of final 20 % iAR trap solutions were measured in duplicate during two sessions
 457 by cold vapor multi-collector inductively coupled plasma mass spectrometry (CV MC-ICPMS) at the
 458 Observatoire Midi-Pyrénées, Toulouse^{51,52}. We used a CETAC ASX-520 autosampler and HGX-200 CV
 459 system coupled to a Thermo-Scientific Neptune PLUS, equipped with a $10^{12} \Omega$ resistor, attributed to
 460 the ^{198}Hg isotope in order to improve isotope ratio precision in the 10-50 mV range. Samples and
 461 standard signals at 0.25 ng g^{-1} tHg levels were generally 180 mV on the ^{202}Hg isotope, at a sample
 462 introduction flow rate of 0.75 mL min^{-1} . Thallium was not used as an internal standard, and the 203
 463 and 205 masses were monitored to survey Hg-hydride interferences (i.e. $^{202}\text{Hg}^1\text{H}$, and $^{202}\text{Hg}^1\text{H}^1\text{H}$),
 464 which were found to be negligible when using standard H-cones. ^{196}Hg and ^{204}Hg were not analyzed
 465 due to low abundance, and cup configuration limitations. MDF of Hg stable isotopes is reported in
 466 small delta notation (δ) in per mil (‰) deviation from to the reference NIST 3133 Hg standard:

$$467 \quad \delta^{\text{xxx}}\text{Hg} = \left(\frac{{}^{\text{xxx}}\text{Hg}/{}^{198}\text{Hg}}{\text{sample}} / \frac{{}^{\text{xxx}}\text{Hg}/{}^{198}\text{Hg}}{\text{NIST3133}} - 1 \right) \times 10^3 \quad (1)$$

468 where 'xxx' refers to measured isotope masses: 199, 200, 201, and 202. Mass independent
 469 fractionation (MIF) is reported in capital delta notation⁵³, which is defined as the difference between
 470 the measured $\delta^{199}\text{Hg}$, $\delta^{200}\text{Hg}$, and $\delta^{201}\text{Hg}$ values and those predicted for MDF relative to $\delta^{202}\text{Hg}$ using
 471 the kinetic MDF law:

$$472 \quad \Delta^{\text{xxx}}\text{Hg} = \delta^{\text{xxx}}\text{Hg} - \text{SF}^{\text{xxx}} \times \delta^{202}\text{Hg} \quad (2)$$

473 where SF^{xxx} is the mass-dependent scaling factor of 0.2520 for ^{199}Hg , 0.5024 for ^{200}Hg , and 0.7520 for
 474 ^{201}Hg . The long-term instrumental precision was assessed through repeated analysis of the UM-
 475 Almaden and ETH-Fluka Hg standard at 0.25 ng g^{-1} during the two analysis sessions. ETH-Fluka yielded
 476 values of $-1.45 \pm 0.20 \text{ ‰}$, $0.07 \pm 0.11 \text{ ‰}$, $0.01 \pm 0.14 \text{ ‰}$, $0.02 \pm 0.09 \text{ ‰}$, $0.00 \pm 0.18 \text{ ‰}$ (2σ , $n = 10$) for
 477 $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$, and $\Delta^{201}\text{Hg}$ respectively, in agreement with published values⁵⁴. UM-Almaden
 478 standard yielded $-0.55 \pm 0.16\text{‰}$, $-0.03 \pm 0.11\text{‰}$, $-0.01 \pm 0.03 \text{ ‰}$, $-0.05 \pm 0.23 \text{ ‰}$ (2σ , $n = 10$)
 479 respectively, in agreement with previously reported values⁵⁵.

480 **pHg and tHg isotope method uncertainty**

481 Mean pre-concentration recoveries for tHg isotope analysis were $90 \pm 10\%$ (1σ , $n = 12$) at
 482 Mediterranean station K2, $93 \pm 18\%$ ($n=8$) at Endoume coastal station, and $88 \pm 31\%$ ($n = 4$) for Atlantic
 483 Ocean samples. Procedural blanks were $0.23 \pm 0.08 \text{ ng Hg}$ (1σ , $n = 4$) for the SnCl_2 pre-concentration
 484 method, which is $<10\%$ of tHg in 20 L of seawater, e.g. typically 3 - 4 ng of tHg in this study. SnCl_2
 485 method replication of eight 20L coastal Mediterranean samples (6 pM, analyzed at 1.6 ng g^{-1} by MC-
 486 ICPMS) shows good results with $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ 2σ uncertainties of 0.23, 0.16, and 0.06 ‰.
 487 NIST SRM 3133 procedural standards returned $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$, and $\Delta^{201}\text{Hg}$ values of $0.07 \pm$
 488 0.23 ‰ , $-0.05 \pm 0.16 \text{ ‰}$, $0.00 \pm 0.06 \text{ ‰}$, $-0.01 \pm 0.18 \text{ ‰}$, $0.02 \pm 0.21 \text{ ‰}$ and a mean recovery of $86 \pm$
 489 16% (2σ , $n = 8$), suggesting no bias in the method.

490 pHg quality control results on NIST SRM 1632d yielded values of $-1.75 \pm 0.24 \text{ ‰}$, $-0.04 \pm$
 491 0.04 ‰ , $0.00 \pm 0.04 \text{ ‰}$, $-0.02 \pm 0.08 \text{ ‰}$ (2σ , $n = 10$) for $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$ and $\Delta^{201}\text{Hg}$ respectively,
 492 in agreement with published values⁴⁹. The 2σ uncertainty on pHg samples was taken to be the larger
 493 of either replicate sample analysis, procedural standard NIST SRM1632d, or secondary reference
 494 materials UM-Almaden or ETH-Fluka.

495 Most seawater pHg and tHg samples were analyzed in duplicate on different days. The final 2σ
 496 uncertainties reported for Mediterranean Sea and Atlantic Ocean pHg and tHg samples are the larger
 497 of the duplicate sample analysis, the 2σ on the eight NIST procedural standards (tHg), the 2σ on the
 498 ten NIST SRM 1632d standards, or the 2σ of the ETH Fluka or UM-Almaden standards.

499 **Stable isotope data analysis**

500 The fraction of Hg in marine samples derived from atmospheric Hg(0) ($f_{\text{Hg}(0)}$) was calculated using a
 501 binary isotope mixing model as follows:

$$502 \Delta^{200}\text{Hg}_{\text{sample}} = (1 - f_{\text{Hg}(0)}) \times \Delta^{200}\text{Hg}_{\text{Hg(II)}} + f_{\text{Hg}(0)} \times \Delta^{200}\text{Hg}_{\text{Hg(0)}} \quad (3)$$

503 where $\Delta^{200}\text{Hg}_{\text{sample}}$ represents the measured value of the marine sample (THg, pHg, sediment THg, biota
504 THg) or sample group. $\Delta^{200}\text{Hg}_{\text{Hg(0)}}$ and $\Delta^{200}\text{Hg}_{\text{Hg(II)}}$ end-member compositions are based on 392 published
505 data points (Extended Data Table 1). The $\Delta^{200}\text{Hg}_{\text{Hg(II)}}$ end-member composition varies as a function of
506 latitude, between values of 0.13 and 0.15 ‰ due to variable contributions of Hg(II) dry and wet
507 deposition (Extended Data Figure 6). The uncertainty on calculated $f_{\text{Hg(0)}}$ and $f_{\text{Hg(II)}}$ fractions was
508 estimated using a Monte Carlo error propagation approach, taking into account median and IQR in all
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510

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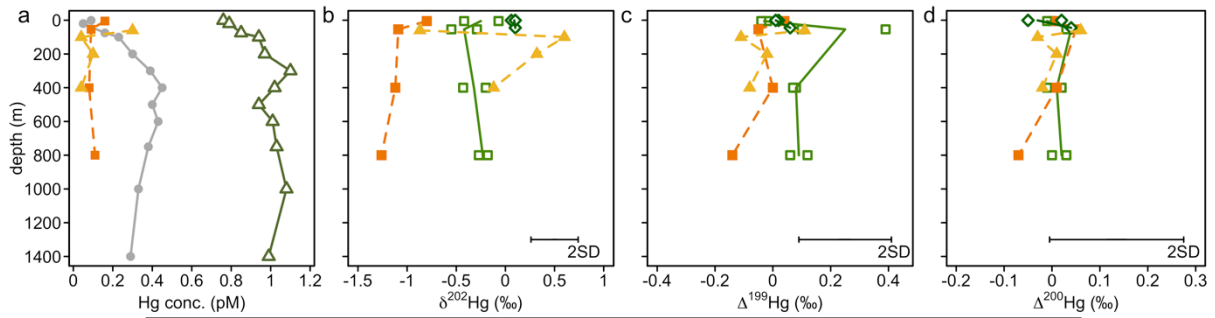
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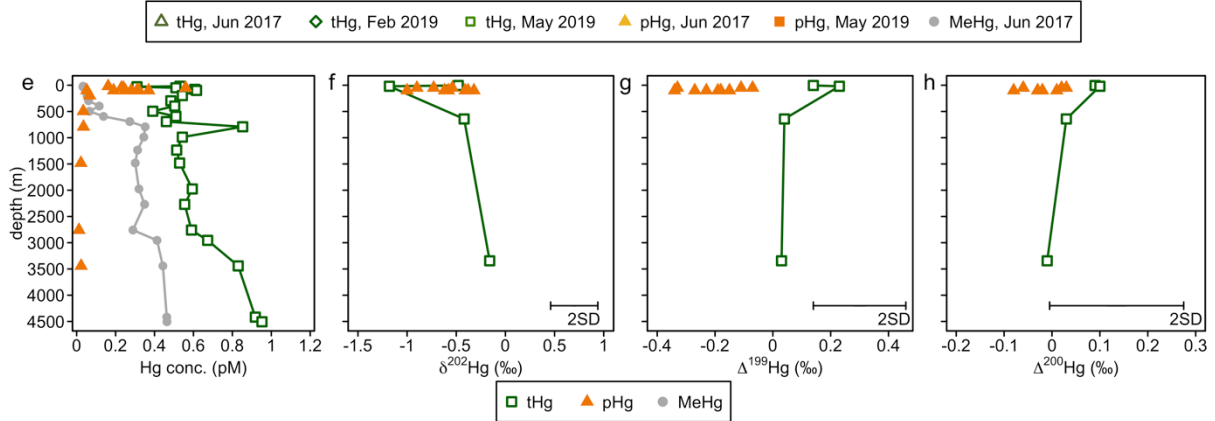
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611 **Figures**



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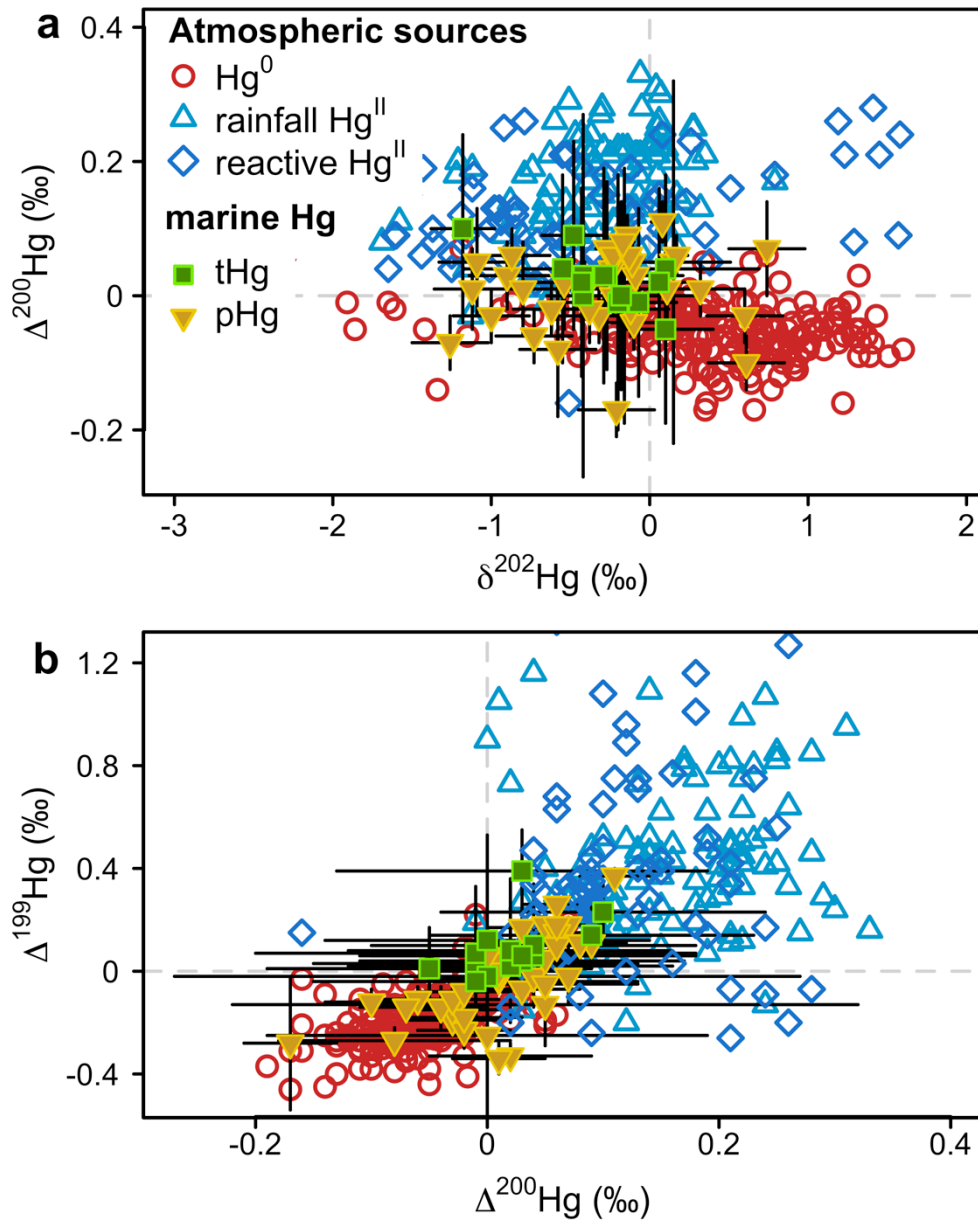


613

614 Figure 1a-h. Depth profiles of seawater Hg species concentrations and total and particulate Hg stable
 615 isotope composition at station K2 in the Mediterranean Sea (a-d) and the North Atlantic (e-h). a) and
 616 e): tHg, pHg, and MeHg concentrations in pmol L⁻¹ (conc. pM). b) and f): mass-dependent fractionation
 617 ($\delta^{202}\text{Hg}$), c) and g): odd mass-independent fractionation ($\Delta^{199}\text{Hg}$), d) and h): even mass-independent
 618 fractionation ($\Delta^{200}\text{Hg}$). Open symbols represent values for tHg and filled symbols pHg. The lines
 619 represent averages of replicate analysis of the same sample. Two standard deviation (2SD)
 620 uncertainties on Hg concentrations are 10%. The North Atlantic profile is a composite profile from two
 621 stations at 47° and 59°N, and the Fram Strait at 79° to 81°N.

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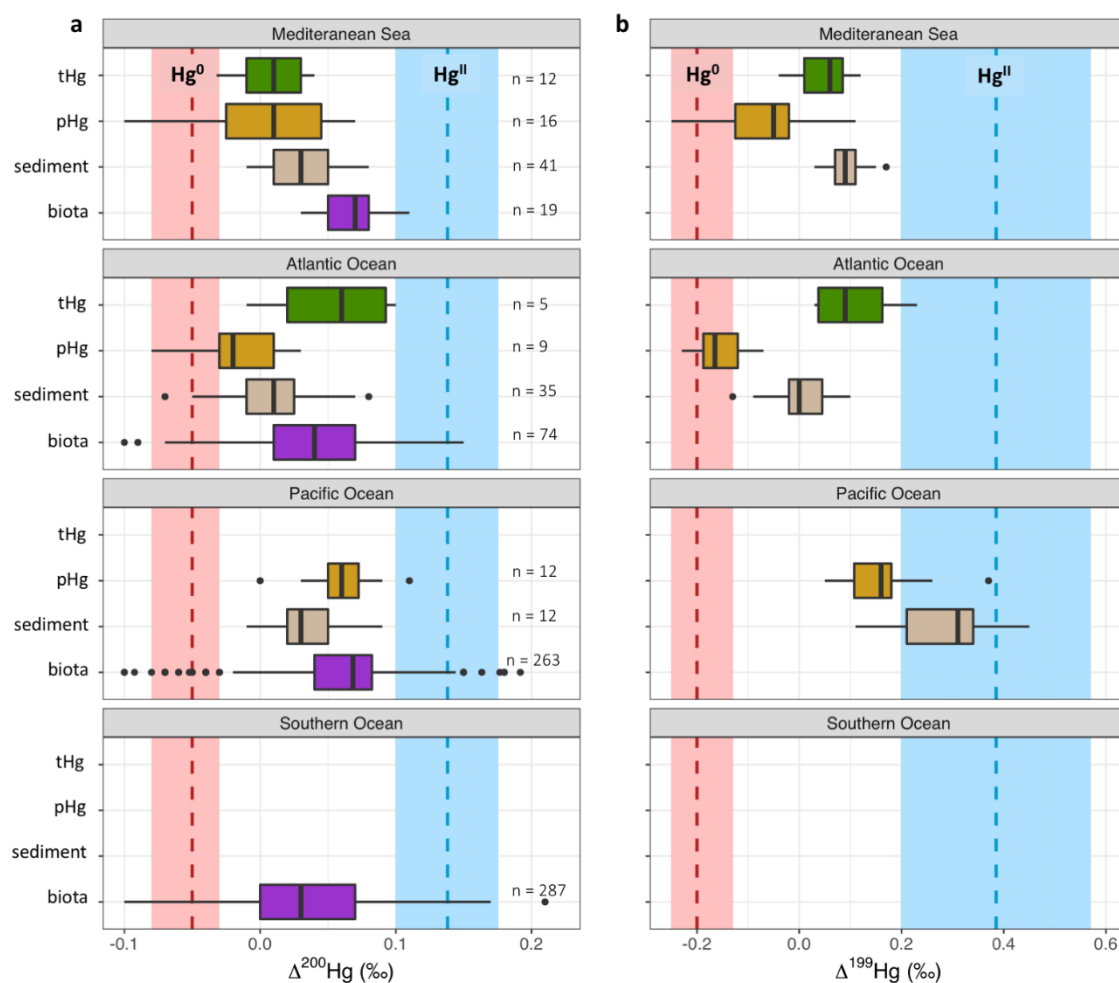


624

625 Figure 2. Hg stable isotope composition of atmospheric Hg deposition sources (gaseous Hg^0) and
 626 Hg^{II} in rainfall), and seawater (total (tHg) and particulate (pHg)). a) even-isotope mass independent
 627 fractionation ($\Delta^{200}\text{Hg}$) vs. mass dependent fractionation ($\delta^{202}\text{Hg}$), and b) odd-isotope mass
 628 independent fractionation ($\Delta^{199}\text{Hg}$) vs. even-isotope mass independent fractionation ($\Delta^{200}\text{Hg}$). Values
 629 of atmospheric sources are from the literature (see Extended Data Table 1), tHg values are from this
 630 study, pHg from this study and ref.³⁰. Error bars represent the two standard deviation (2SD)
 631 uncertainties of individual samples.

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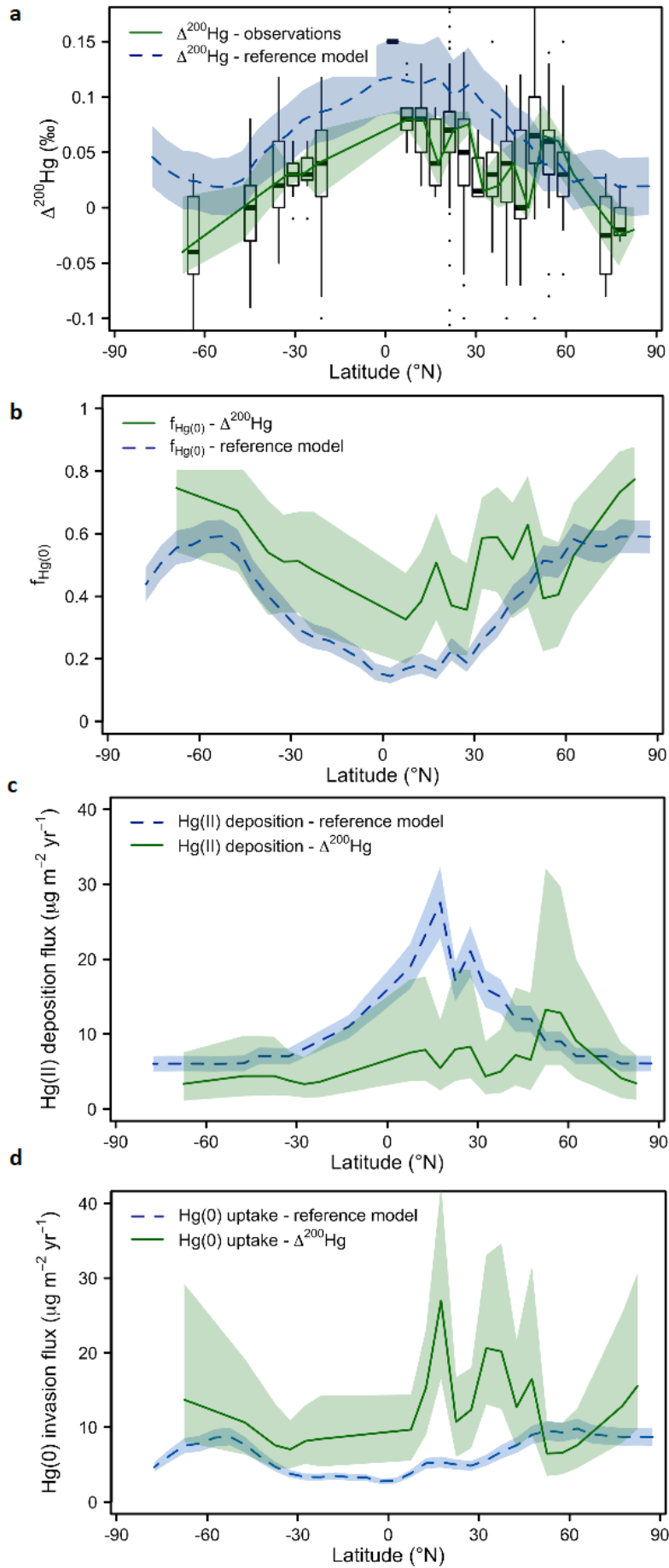
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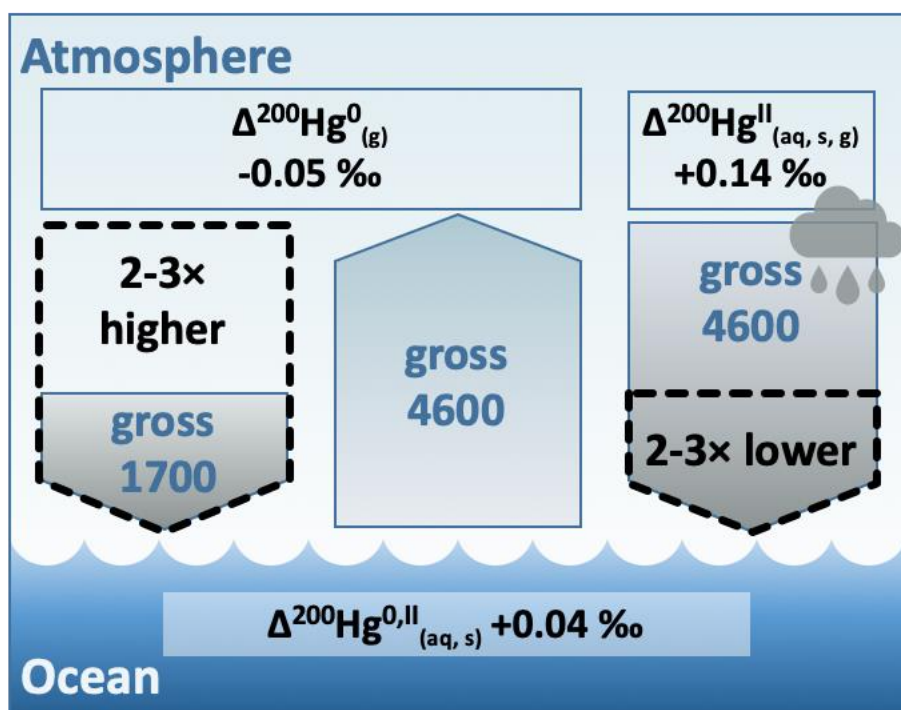
635 Figure 3. Hg stable isotope composition in different ocean basins for total Hg (tHg) and particulate Hg
 636 (pHg) in seawater, marine sediments and marine fish. a) Even-isotope mass-independent signature
 637 ($\Delta^{200}\text{Hg}$) and b) Odd-isotope mass-independent signature ($\Delta^{199}\text{Hg}$). tHg values are from this study, pHg
 638 from this study and from ref.³⁰, data for sediments and biota are from literature (Extended Data Table
 639 1). The atmospheric deposition sources are shown as vertical bars in red for Hg^0 and blue for reactive
 640 and rainfall Hg^{II} , the dashed line represents the mean and the shaded area the interquartile range
 641 (IQR). Marine samples are shown as horizontal boxes, where the bold line represents the median, the
 642 boxes the IQR, the whiskers 1.5 times the IQR and outliers are represented by dots. For biota, $\Delta^{199}\text{Hg}$
 643 are not shown in this Figure as these values are heavily affected by MMHg photo-demethylation.

644



646 Figure 4: Latitudinal variation in atmospheric Hg sources and deposition fluxes to the global Ocean.
647 Zonal 'Reference model' refers to the combination of zonal model and observation derived fluxes; i.e.
648 the gas-exchange model which assimilates atmospheric and dissolved Hg(0) observations, 3D model
649 global Hg(II) dry deposition³, and Hg(II) wet deposition observations (see SI text, Extended Data
650 Figures 3-6). a) Box plot for observed and reference model predicted marine $\Delta^{200}\text{Hg}$ in 5° latitude
651 bins. The bold horizontal line represents the median, the boxes the interquartile range (IQR), the
652 whiskers 1.5 times the IQR and dots are outliers. b) The $\Delta^{200}\text{Hg}$ -derived and reference model derived
653 fraction of ocean Hg(0) uptake relative to total atmospheric Hg deposition. c) The $\Delta^{200}\text{Hg}$ -derived and
654 reference model Hg(II) deposition fluxes. d) The $\Delta^{200}\text{Hg}$ -derived and reference model ocean Hg(0)
655 uptake flux. All fluxes in $\mu\text{g m}^{-2} \text{y}^{-1}$. All lines represent medians and the shaded areas IQR. The green
656 $\Delta^{200}\text{Hg}$ -based curves in panels c) and d) represent the gross Hg(II) deposition and gross Hg(0) invasion
657 needed to reconcile marine $\Delta^{200}\text{Hg}$ observations in panel a), i.e. either lower Hg(II) deposition, or
658 higher ocean Hg(0) uptake (see Supporting Information text).

659

660 **Extended Data Items**

661

662 **Extended Data Figure 1. Summary of marine Hg(II) deposition and Hg(0) air-sea exchange fluxes.**

663 Gross fluxes (solid arrows, Mg y^{-1}) are based on published model estimates³. Hg(0) exchange is bi-

664 directional, meaning that despite surface ocean Hg(0) supersaturation and large Hg(0) evasion, Hg(0)

665 invasion is substantial. Marine $\Delta^{200}\text{Hg}$ signatures of 0.04‰ indicate a relatively more important

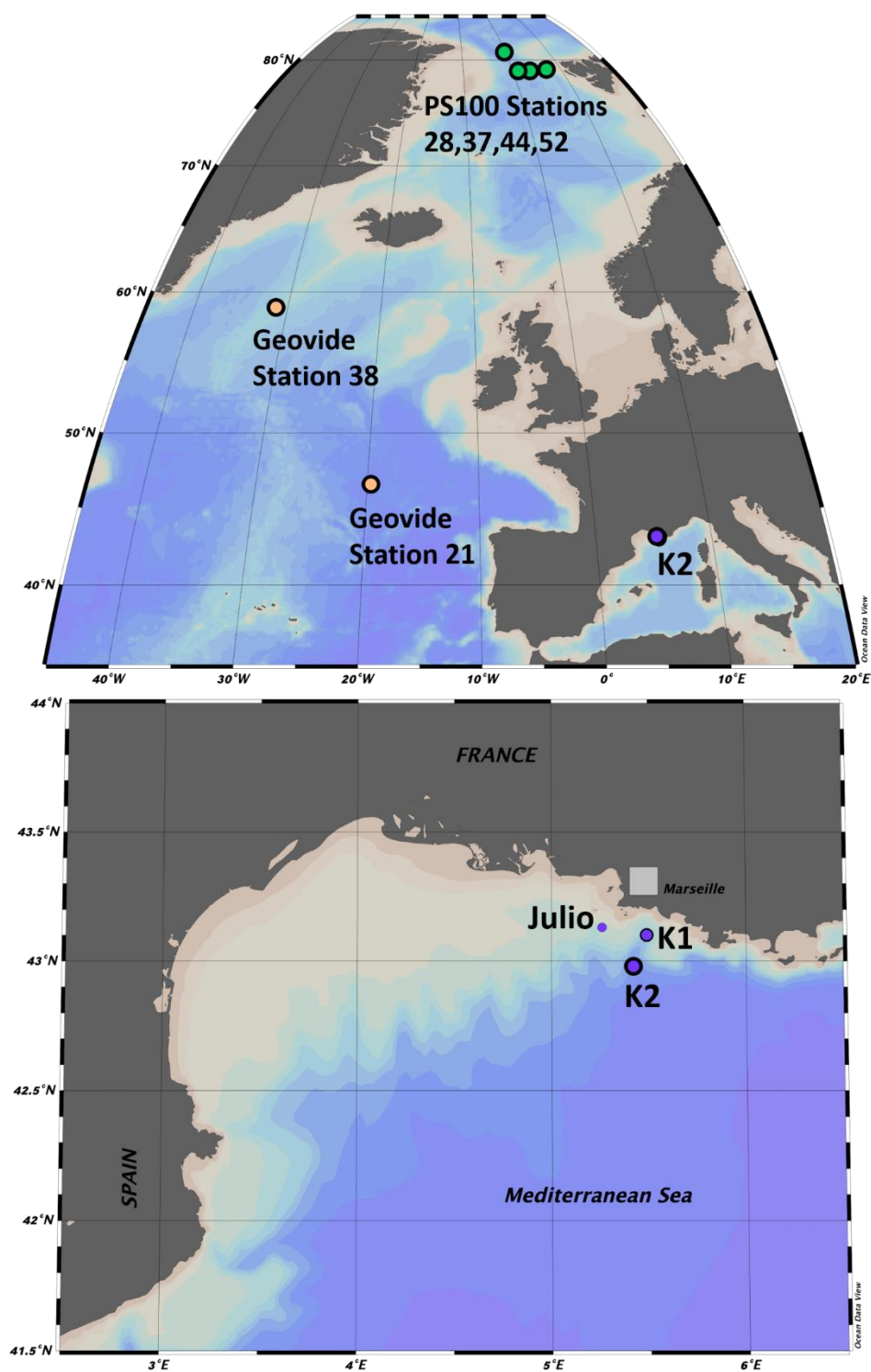
666 contribution of the atmospheric Hg(0) end-member to marine Hg than current 3D models suggest. This

667 indicates that either 3D model Hg(II) deposition is overestimated or that Hg(0) invasion is

668 underestimated (black dotted arrows, indicating 2-3x lower or 2-3x higher fluxes, required to fit $\Delta^{200}\text{Hg}$

669 data).

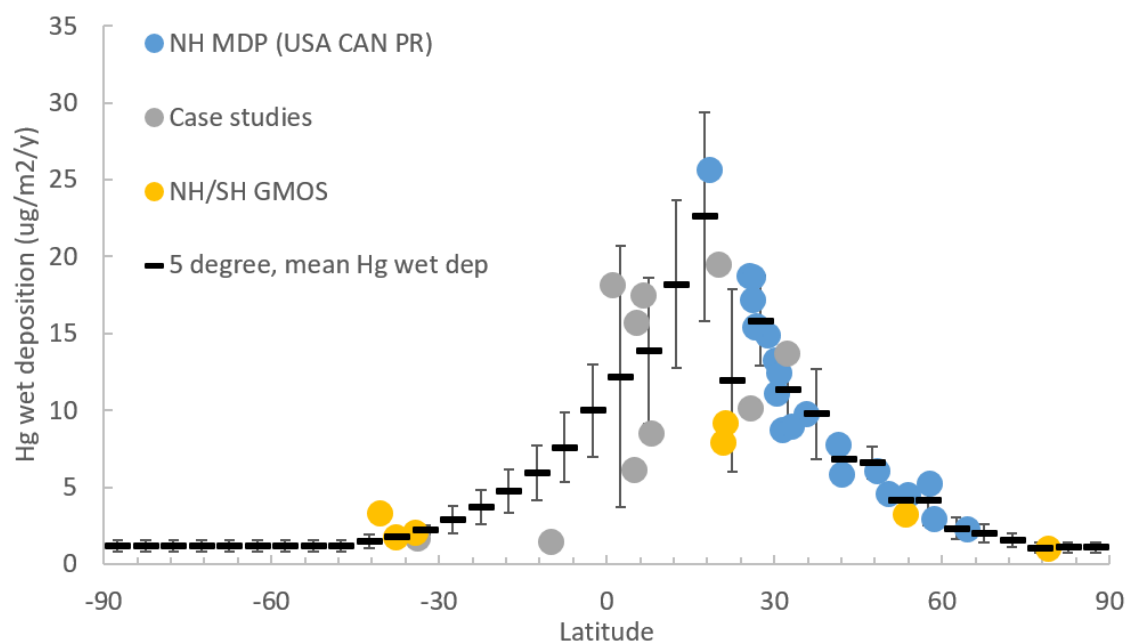
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672 **Extended Data Figure 2. Maps of sampling locations for total and particulate Hg isotopes.** Top:
673 Sampling locations K2 in the Mediterranean Sea (purple), Atlantic Ocean (yellow) and Fram Strait
674 (green). Bottom: Zoom on the 4 Mediterranean locations, with main station K2 (large purple circle),
675 and pHg station K1 and Julio (small purple circles), and Endoume pier in Marseille Bay (grey square).
676 Maps were made with Ocean Data View (Schlitzer, Reiner, Ocean Data View, odv.awi.de, 2021)

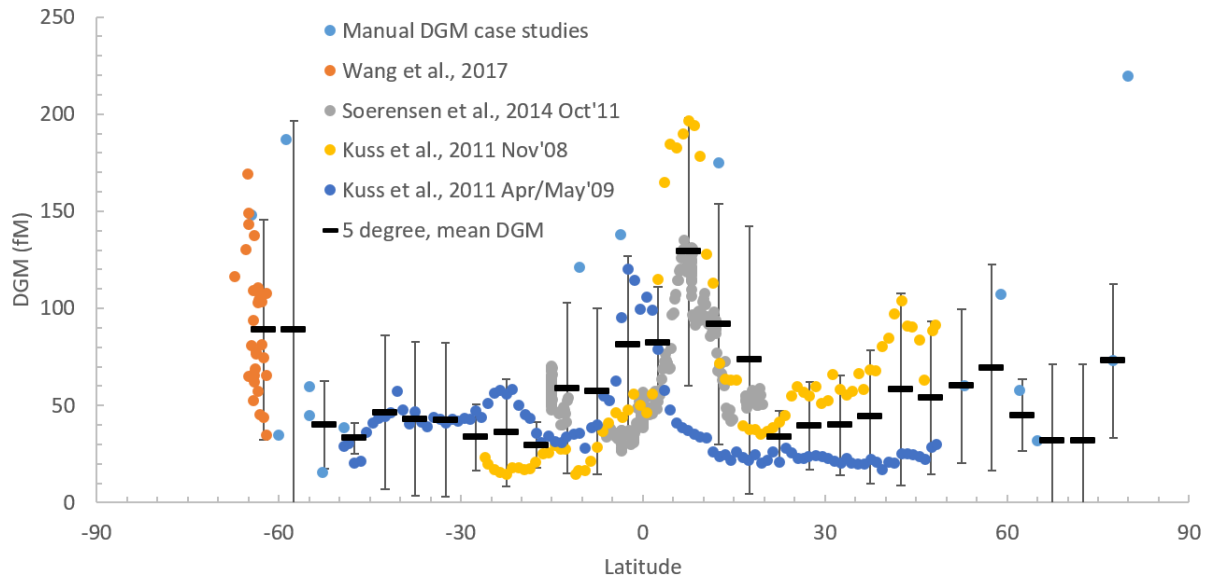
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679 **Extended Data Figure 3. Latitudinal distribution of Hg(II) wet deposition.** Annual mean Hg(II) wet
680 deposition ($\mu\text{g m}^{-2} \text{y}^{-1}$) at oceanic locations in the northern and southern hemispheres (NH, SH), binned
681 in 5° latitude. Mean values (\pm standard deviation, SD) were calculated when sufficient data was
682 available per 5° latitude band, and interpolated using polynomial fitting when no data was available
683 (in which case a mean observed SD of 30% was applied). MDN, mercury deposition network; GMOS,
684 global mercury observation system; USA, CAN, PR, United States of America, Canada, Puerto Rico.

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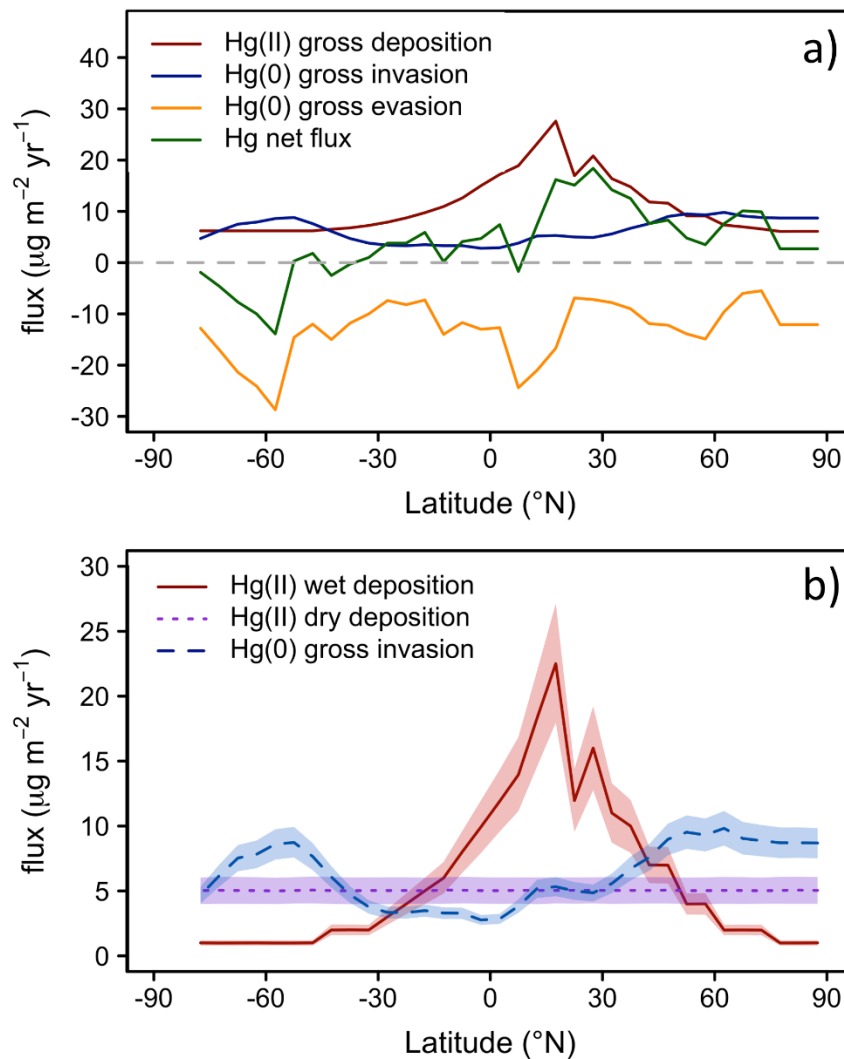


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687 **Extended Data Figure 4. Latitudinal distribution of dissolved gaseous Hg (DGM) concentrations.**

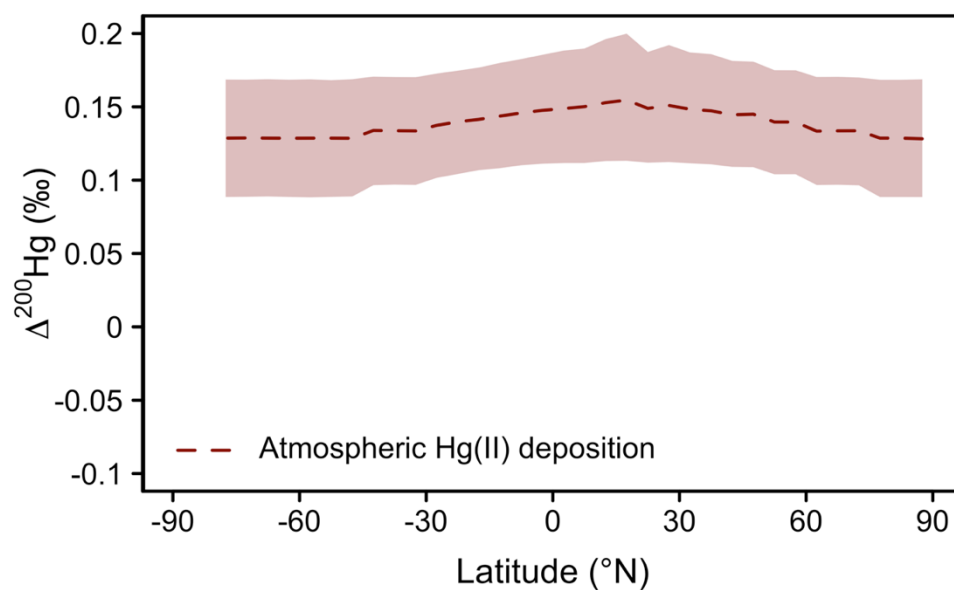
688 Mean (\pm standard deviation) DGM are binned in 5° latitude bands, and equal weight was given to each
 689 study. Polar studies, affected by sea ice show unusually high concentrations (mean 219 fM in the Arctic,
 690 mean 138 fM around Antarctica) for high latitude waters and were excluded in 5° latitude binning
 691 (replaced in calculations by 'open water only' DGM data at 55-60°S and 75-80°N).

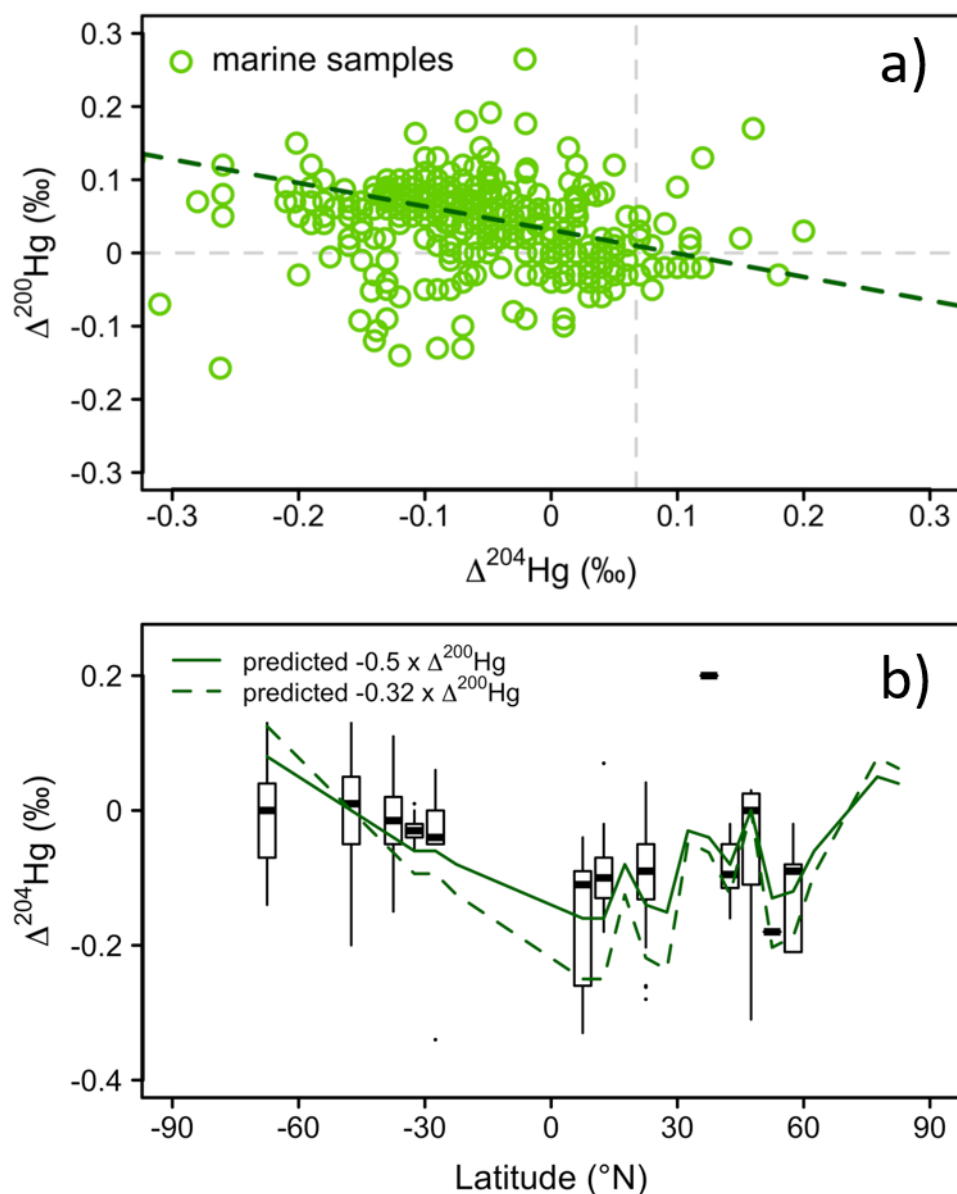
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694 **Extended Data Figure 5. Atmospheric deposition pathways of the zonal 'Reference model'.** a): Marine
 695 Hg(II) gross deposition, Hg(0) gross invasion, Hg(0) gross evasion, and net Hg flux [Hg(II) deposition +
 696 Hg(0) invasion – Hg(0) evasion]; all in $\mu\text{g m}^{-2} \text{yr}^{-1}$ with evasion shown as negative numbers. Hg(0) invasion
 697 is driven by observed atmospheric Hg(0) and wind speed. Hg(II) deposition is dominated by Hg(II) wet
 698 deposition. Hg(0) evasion is driven by DGM concentrations and wind speed. The net Hg evasion trends
 699 shows important net deposition in the northern hemisphere, and net evasion in the southern
 700 hemisphere. b): 'Reference model' Hg gross deposition fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$) as a function of latitude used
 701 in estimating marine $\Delta^{200}\text{Hg}$ in Figure 4a (main text). Hg(II) wet deposition observations as in Extended
 702 Data Figure 3; Hg(II) dry deposition was fixed at 5 $\mu\text{g m}^{-2} \text{yr}^{-1}$, and constrained as 40% of total Hg(II)
 703 deposition³⁸, since no dry deposition observations over oceans exist. Hg(0) invasion (ocean uptake,
 704 same as in top panel) is calculated from the observed inter-hemispheric atmospheric gaseous Hg(0)
 705 gradient³, wind and sea surface temperature (Copernicus), and the latest Hg(0) air-sea gas exchange
 706 model (see SI text).





713

714 **Extended Data Figure 7: Variation of $\Delta^{204}\text{Hg}$ in marine samples.** a) $\Delta^{204}\text{Hg}$ vs $\Delta^{200}\text{Hg}$. The dashed line
715 represents the York regression using IsoplotR⁵⁷ for all marine samples ($\Delta^{200}\text{Hg} = -0.32(\pm 0.06) \Delta^{204}\text{Hg} +$
716 (0.03 ± 0.004) , (\pm se), MSWD = 0.213) b) $\Delta^{204}\text{Hg}$ boxplot for 5° latitudinal intervals. Marine samples are
717 shown in boxes, where the bold horizontal line represents the median, the boxes the interquartile
718 range, the whiskers 1.5 times the IQR and outliers are represented by dots. The solid line represents
719 the predicted $\Delta^{204}\text{Hg}$ based on the observational relationship between $\Delta^{204}\text{Hg}$ and $\Delta^{200}\text{Hg}$ in terrestrial
720 samples by Blum & Johnson, 2017⁵⁸. The dashed line represents the predicted $\Delta^{204}\text{Hg}$ derived from the
721 York regression shown in panel a). $\Delta^{204}\text{Hg}$ data are available for 339 out of 791 marine samples. Note
722 that for pHg and tHg samples presented here, $\Delta^{204}\text{Hg}$ was not measured due to the low abundance of
723 ^{204}Hg isotopes, and unavailability of a second 10^{13} Ohm amplifier.

724 **Extended Data Table 1: Summary of Hg stable isotope data.** *sediments considered below 1000m water depth. ND: not determined.

Pool	Ocean Basin	n	Hg concentration					$\delta^{202}\text{Hg}$ (‰)				$\Delta^{199}\text{Hg}$ (‰)				$\Delta^{200}\text{Hg}$ (‰)				References
			mean	median	p25	p75	units	mean	median	p25	p75	mean	median	p25	p75	mean	median	p25	p75	
Hg(II) rainfall		106	13.2	12.9	9	17.9ng/L	-0.43	-0.30	-0.63	0.03	0.41	0.40	0.21	0.52	0.16	0.17	0.11	0.22	23,24,30,40,59-63	
reactive Hg(II)		66	62.4	56.41	47.8	75.2pg/m ³	-0.40	-0.55	-0.95	0.02	0.36	0.34	0.14	0.51	0.12	0.10	0.07	0.18	27,40,41	
Atmospheric Hg(0)		220	1.38	1.265	1.1	1.57ng/m ³	0.37	0.43	0.09	0.77	-0.19	-0.20	-0.25	-0.13	-0.06	-0.05	-0.08	-0.03	23-25,42,64-66	
tHg	All samples	16	0.82	0.82	0.77	0.88	pM	-0.27	-0.24	-0.42	-0.04	0.08	0.06	0.02	0.11	0.02	0.02	-0.01	0.03	
	Med. Sea	12	0.89	0.83	0.80	1.01	pM	-0.17	-0.19	-0.32	0.07	0.07	0.06	0.01	0.09	0.01	0.01	-0.01	0.03	This study
	Atlantic	4	0.61	0.57	0.51	0.67	pM	-0.56	-0.45	-0.66	-0.36	0.11	0.09	0.04	0.16	0.05	0.06	0.02	0.09	This study
pHg	All samples	36	0.19	0.16	0.09	0.26	pM	-0.28	-0.23	-0.59	-0.10	-0.03	-0.03	-0.14	0.11	0.02	0.02	-0.02	0.06	
	Med. Sea	15	0.11	0.10	0.08	0.15	pM	-0.22	-0.12	-0.84	0.24	-0.06	-0.05	-0.13	-0.02	0.00	0.01	-0.03	0.05	This study
	Atlantic	9	0.31	0.28	0.24	0.32	pM	-0.61	-0.58	-0.73	-0.41	-0.21	-0.19	-0.27	-0.15	-0.02	-0.02	-0.03	0.01	This study
	Pacific	12	ND	ND	ND	ND	pM	-0.12	-0.14	-0.22	-0.11	0.16	0.16	0.11	0.18	0.06	0.06	0.05	0.07	30
sediment	All samples	92	83	52	32	84	ng/g	-0.99	-0.85	-1.21	-0.49	0.10	0.08	0.02	0.11	0.02	0.02	0.01	0.04	
	Med. Sea	40	66	53	44	83	ng/g	-1.28	-1.14	-1.61	-0.86	0.09	0.09	0.07	0.11	0.03	0.03	0.01	0.05	This study, 67,68
	Atlantic	35	119	55	33	137	ng/g	-0.49	-0.40	-0.60	-0.33	0.01	0.00	-0.02	0.05	0.01	0.01	-0.01	0.03	69,70*
	Pacific	17	37	22	12	71	ng/g	-1.34	-0.95	-2.16	-0.66	0.29	0.31	0.21	0.34	0.04	0.03	0.02	0.05	This study
biota	All samples	643	2621	1360	450	3074	ng/g	0.78	0.75	0.31	1.20	1.66	1.60	1.31	1.86	0.04	0.05	0.02	0.08	
	Med. Sea	19	3131	2953	2460	3826	ng/g	0.36	0.37	0.29	0.47	1.76	1.78	1.70	1.82	0.07	0.07	0.05	0.08	This study
	Atlantic	74	1018	190	69	2240	ng/g	0.44	0.36	0.25	0.60	1.51	1.22	0.95	1.49	0.04	0.04	0.01	0.07	71-74
	Pacific	263	943	431	231	766	ng/g	0.45	0.45	0.07	0.85	1.61	1.47	1.13	1.85	0.06	0.07	0.04	0.08	74-80
	S. Ocean	287	3524	2129	930	3962	ng/g	1.20	1.21	0.81	1.55	1.74	1.68	1.55	1.90	0.03	0.03	0.00	0.07	81-84

726 **Extended Data Table 2: Modeled contribution of Hg(II) from wet and dry deposition, $f_{\text{Hg(II)}}$, and excess**
 727 $\Delta^{199}\text{Hg}_{\text{exc}}$ according to Methods Equations 3, 4. Excess $\Delta^{199}\text{Hg}_{\text{exc}}$ represents sample $\Delta^{199}\text{Hg}$ acquired by
 728 Hg(II) photoreduction in sea water, in addition to the $\Delta^{199}\text{Hg}$ inherited from atmospheric Hg deposition.

Pool	Ocean Basin	n	fHg(0)				$\Delta^{199}\text{Hg}_{\text{exc}}$ (‰)			
			mean	median	p25	p75	mean	median	p25	p75
tHg	All samples	16	0.61	0.58	0.50	0.76	0.04	0.00	-0.03	0.12
	Med. Sea	12	0.66	0.64	0.53	0.76	0.06	0.01	-0.03	0.14
	Atlantic	4	0.44	0.38	0.24	0.57	-0.03	-0.04	-0.07	0.00
pHg	All samples	36	0.60	0.58	0.39	0.82	-0.07	-0.05	-0.13	0.01
	Med. Sea	15	0.65	0.64	0.44	0.85	-0.08	-0.04	-0.17	0.00
	Atlantic	9	0.78	0.82	0.61	0.87	-0.15	-0.11	-0.17	-0.07
	Pacific	12	0.40	0.39	0.34	0.43	-0.01	-0.01	-0.08	0.07
sediment	All samples	92	0.58	0.57	0.49	0.65	0.03	0.03	-0.04	0.08
	Med. Sea	40	0.54	0.53	0.43	0.65	0.01	0.02	-0.05	0.05
	Atlantic	35	0.66	0.65	0.55	0.77	-0.01	0.00	-0.05	0.04
	Pacific	17	0.50	0.50	0.45	0.56	0.19	0.17	0.12	0.22
biota	All samples	643	0.47	0.40	0.31	0.60	1.55	1.52	1.19	1.75
	Med. Sea	19	0.35	0.33	0.31	0.39	1.56	1.58	1.50	1.65
	Atlantic	74	0.46	0.40	0.33	0.60	1.48	1.23	0.93	1.45
	Pacific	263	0.42	0.36	0.30	0.50	1.45	1.31	0.96	1.73
	S. Ocean	287	0.52	0.49	0.32	0.67	1.65	1.63	1.47	1.77

729

730

731 **Online Supporting Information to:**

732

733 **Mercury stable isotopes constrain atmospheric sources to the Ocean**

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744

745 **Materials and Methods**

746

747 **Rationale**

748 Total mercury (tHg) concentration in seawater is the sum of several operationally defined species,
749 including dissolved gaseous Hg(0), dissolved gaseous dimethyl-Hg (DMHg), dissolved inorganic Hg(II)
750 compounds, dissolved monomethyl-Hg compounds (MMHg), and particulate-bound Hg(II) and MMHg
751 compounds (pHg). Both concentration and stable isotope analysis of tHg in seawater require the
752 transformation of these compounds to dissolved, labile Hg(II) forms by addition of a strong oxidant
753 such as BrCl, prepared in concentrated HCl. The concomitant oxidation and acidification also inhibits
754 biological activity, stabilizes Hg(II) in solution and minimizes potential losses to sampling container
755 walls or to the atmosphere. Two criteria need to be met for a robust Hg stable isotope analysis of
756 seawater: first, the low-picomolar seawater concentration has to be concentrated to levels suitable
757 for Hg stable isotope analysis (typically 0.2 – 1 ng mL⁻¹ or 1 – 5 nM). This pre-concentration needs to
758 be quantitative in order to avoid Hg isotope fractionation during transfer. Second, the procedural blank

759 of the method needs to be low, ideally below 10% of the total amount of Hg in the sample. Low blank
760 levels rely on ultra-clean sampling at sea, clean sampling vessels and ultra-low Hg levels of reagents
761 used.

762 Previous studies have successfully developed methods for large volume (1 - 20 L) pre-
763 concentration of tHg from natural waters, including rain, snow, ice, lake and coastal seawater. Gratz
764 et al. (2010) and Sherman et al. (2010) first used continuous cold vapor generation, with SnCl₂ as a
765 reductant, to pre-concentrate 1 - 4 L of snow and rainfall samples into small volume (25 mL) 2 % (w/w)
766 oxidizing KMnO₄/H₂SO₄ solution trap^{1,2}. This method was later modified to a batch-reactor set-up to
767 pre-concentrate 1 L of rainfall in a 2 L Pyrex bottle, by slow, pumped addition of SnCl₂, and identical
768 KMnO₄/H₂SO₄ solution trap³ and trapping solutions of 40 vol% inverse *aqua regia* (iAR, 4.2 N HNO₃, 1.2
769 N HCl)⁴. Finally, in Obrist et al. (2017) we scaled up the batch purge and trap method to handle up to
770 20 L of snow and rain sample⁵. An alternative method was developed by Chen et al. (2016) using the
771 AG-1-X4 anion exchange resin to pre-concentrate >40 ng of tHg from freshwater lakes⁶. HgCl₄²⁻ in the
772 acidified, 0.1 N HCl, sample is pumped at 3.5 mL min⁻¹ over 0.5 mL of AG-1-X4 resin. Sorbed Hg is then
773 eluted with 10 mL of 0.05 % L-cysteine in 0.5 N HNO₃, oxidized by BrCl, neutralized with NH₄OH and
774 analyzed by MC-ICPMS. Štok et al. (2015) optimized the anion exchange resin method for seawater
775 and published the first Hg stable isotope data of coastal seawater (1.5-3.1 pM) from the Canadian
776 Arctic Archipelago⁷. The latter two methods by Štok et al. (2015) and Obrist et al. (2017) are capable
777 of handling sample volumes of 20 L or more that are necessary for background level tHg pre-
778 concentration from seawater (0.4 to 1.5 pM). Our objective was therefore to adapt our existing large
779 volume pre-concentration protocol, based on SnCl₂ reduction, for rain and snow to seawater. We
780 optimized the protocol for quantitative pre-concentration yields and low blank levels.

781

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

783 During pre-concentration the 20L sample bottle is under argon over-pressure in order to generate a
784 fine stream of bubbles. It is therefore important at the end of pre-concentration, or during
785 troubleshooting, not to vent the argon supply tube to the 20L sample bottle and release argon
786 pressure. The reason is that with the 20 L bottle under over-pressure, venting the argon supply tube
787 results in a sudden pressure drop, and acidified sample solution with SnCl₂ moving from the 20 L bottle
788 into the tall bubbler post, possibly all the way to the argon flow regulator, damaging the latter. Worse,
789 the 40 vol% iAR trap solution is aspirated up into its short bubbler post and into the 20 L bottle,
790 resulting in the loss of the sample. Using our final optimized Sn addition protocol, each 20 L bottle

791 contains at the end of a pre-concentration run, 2.5 g of Sn(II), and should be disposed of following local
792 environmental regulations. If needed, the dissolved Sn(II) concentration can be lowered by hydrogen
793 peroxide addition, which quantitatively precipitates Sn(IV)O₂, that can then be filtered or decanted.
794 Quantitative oxidation of Sn(II) by hydrogen peroxide also has the advantage that no traces of Sn(II)
795 remain in the 20 L bottle, which can be acid-cleaned (0.1 vol% commercial HCl) and rinsed with
796 abundant MQ water to receive the next batch of seawater samples. In this study both sampling and
797 pre-concentration were done in the same bottle. We expect however that the use of separate bottles,
798 possibly using plastic 20 L carboys at sea for safety, does not increase blanks.

799

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

801 We have, over the past years, tested an alternative method for low-level Hg pre-concentration in order
802 to measure Hg isotopes in sea water. The method uses small 200 mg iodated activated carbon powder
803 (Brooks Rand) cartridges, over which large volumes (50L) of unfiltered, acidified (0.4% v/v HCl) sea
804 water are pumped at a slow flow rate of 5 ml min⁻¹. Following laboratory recovery and blank testing,
805 we applied the method during the 2014 GEOTRACES Geovides cruise in the North-Atlantic Ocean.
806 Unfiltered seawater was transferred using clean 6mm FEP tubing from GOFLO bottles into acid washed
807 50L tedlar bags. A peristaltic pump, with 1.14mm ID (red/red) tygon pump tubing was used to load
808 samples on the IAC traps during 1 week. Traps were dried for 5 min in a dry high purity argon stream,
809 sealed with silicone stoppers and stored and transported dry and in the dark to the GET laboratory.
810 The IAC powder was combusted using a dual tube furnace combustion method⁸. IAC blanks were 0.5
811 ng Hg per 200mg of IAC traps, and sample recoveries were 88 ± 31%. In hindsight, it has been difficult
812 to fully recover Hg from IAC traps due to abundant volatile iodine release and transfer to oxidizing
813 solution traps. We recommend that further development of activated carbon based methods use
814 commercial sulfur impregnated activated carbon (Calgon HGR), which does not have this issue⁹.

815

816 **MMHg and DMHg analysis**

817 MMHg and DMHg were determined by isotope dilution (ID)- gas chromatography – sector field ICP-
818 MS (ID-GC-SF-ICPMS) method at the MIO laboratory, following previously published protocols¹⁰. First
819 the sum of both species (tMeHg) was quantified on an acidified sample that converts DMHg to MMHg.
820 A second replicate sample was purged to remove DMHg before acidification, allowing direct
821 measurement of MMHg. DMHg was calculated by difference, as tMeHg – MMHg. In both sample

822 aliquots MMHg and inorganic Hg species were extracted after derivatization. In brief, enriched spikes
823 of ^{199}iHg and $^{201}\text{MeHg}$ (ISC Science, Spain) were added to a 115 mL aliquot of the sea water samples.
824 After 24h of equilibration, pH was adjusted to 3.9 with NH_3 (ULTREX[®] II Ultrapure Reagent, J.T. Baker,
825 USA) and a buffer solution made up with acetic acid (glacial, ULTREX[®] II Ultrapure Reagent, J.T. Baker,
826 USA) / sodium acetate (J.T. Baker, USA). A solution of 1 % (v:v) sodium tetra propyl borate
827 (Merseburger Spezialchemikalien, Germany) was made up freshly, under cold conditions and avoiding
828 contact with atmospheric oxygen. 1 mL of this solution was then added together with 200 μL hexane
829 (Sigma Aldrich, USA). The glass bottles were hermetically sealed with Teflon-lined caps and vigorously
830 shaken for 15 minutes. The organic phase was recovered and injected in the GC (Thermo Trace Ultra),
831 coupled to a sector field ICPMS (Thermo Element XR). Detection limits were 0.005 pM for MMHg, and
832 0.01 pM for DMHg.

833

834 **pHg isotope results**

835 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 $\delta^{202}\text{Hg}$
836 was higher in June 2017 by 1.5 ‰ at 100 - 400m depth. Only in May 2019 at station K2, tHg and pHg
837 isotopes were determined simultaneously and $\delta^{202}\text{Hg}$ of pHg was depleted by -1.0 ‰ (-0.8 ‰ to -1.3‰;
838 median and (IQR), n = 4) relative to tHg (Figure 1b). Light isotope enriched pHg may be explained by
839 the preferential sorption of light Hg(II) isotopes to particulate organic matter¹¹, or by preferential
840 uptake of light isotopes by phytoplankton that is part of the particulate pool. pHg stable isotopes
841 sampled in 2017 at two stations, Julio and K1, closer to the coast were similar to the open sea station
842 (K2) with no clear trends in water depth or distance from the shore (Figure S1). Marine sediments,
843 analyzed for station Julio only (700 m depth), had similar $\delta^{202}\text{Hg} = -0.75$ ‰ (-0.76 to -0.74 ‰), $\Delta^{199}\text{Hg}$
844 = 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
845 water column pHg (K1, K2, Julio), and were similar to sediment samples taken elsewhere in the
846 Mediterranean Sea^{12,13}.

847

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

849 During photoreduction of Hg(II)-organic ligand complexes the magnetic isotope effect (MIE) may
850 separate even from odd Hg isotopes¹⁴. Experimental photomicrobial Hg(II) reduction in simulated sea
851 water medium has been shown to lead to negative $\Delta^{199}\text{Hg}$ in residual aquatic Hg(II)¹⁵. The sign (positive,
852 negative $\Delta^{199}\text{Hg}$) and magnitude of the MIE is not fully understood, but has been shown to depend on

853 the nature of the Hg-binding ligand (e.g. O or S), the Hg to ligand concentration ratio, and
 854 environmental conditions such as pH^{16,17}. Here, we evaluate whether the tHg and pHg data show
 855 evidence of in situ marine odd-MIF, in addition to that inherited from atmospheric deposition sources.
 856 We first calculate the excess $\Delta^{199}\text{Hg}_{\text{exc}}$ in all seawater samples, defined as the difference between the
 857 measured $\Delta^{199}\text{Hg}$ in a marine sample and the expected $\Delta^{199}\text{Hg}$, based on atmospheric inputs. The
 858 expected $\Delta^{199}\text{Hg}$ was calculated by binary mixing of $\Delta^{199}\text{Hg}$ in atmospheric Hg(II) and Hg(0) using the
 859 source contributions ($f_{\text{Hg(II)}}$) derived from $\Delta^{200}\text{Hg}$ (Methods, equation 3). The excess $\Delta^{199}\text{Hg}$ in the
 860 different marine Hg pools ($\Delta^{199}\text{Hg}_{\text{exc}}$), representing the $\Delta^{199}\text{Hg}$ which was produced within the marine
 861 system, was calculated as follows:

$$862 \quad \Delta^{199}\text{Hg}_{\text{exc}} = \Delta^{199}\text{Hg}_{\text{meas}} - (f_{\text{Hg(II)}} \times \Delta^{199}\text{Hg}_{\text{Hg(II)}} + (1 - f_{\text{Hg(II)}}) \times \Delta^{199}\text{Hg}_{\text{Hg(0)}}) \quad (\text{Eq. S1})$$

863 , 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
 864 marine sediments is similar to $\Delta^{200}\text{Hg}$ and observed $\Delta^{199}\text{Hg}$ can largely be explained by a conservative
 865 mixing of atmospheric Hg(0) and Hg(II) deposition (Figure 2B and 3B). Atlantic and Mediterranean
 866 $\Delta^{199}\text{Hg}_{\text{exc}}$ was 0.03‰ (0.02 to 0.13‰; median, inter quartile range (IQR), n = 17) in tHg and 0.01‰ (-
 867 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
 868 found in marine sediments of the Mediterranean Sea (0.09‰, 0.03‰ to 0.12‰) and the Atlantic
 869 Ocean (0.06‰, 0.02 to 0.10‰). Elevated median $\Delta^{199}\text{Hg}_{\text{exc}}$ of 1.64‰ in marine fish (Extended Data
 870 Table 2) can therefore be predominantly ascribed to photochemical breakdown of MMHg. The absence
 871 of significant odd-MIF in surface seawater does not automatically mean that photoreduction is slow,
 872 or that the MIE is absent. Experimental photoreduction observations on seawater, under
 873 representative conditions, are needed to examine the issue.

874

875 **Observation-based estimates of global marine Hg(II) deposition, and air-sea Hg(0) exchange as a** 876 **function of latitude**

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

885 marine $\Delta^{200}\text{Hg}$ gradient to estimate the ocean Hg(0) uptake flux, or the Hg(II) deposition that is needed
886 to explain the $\Delta^{200}\text{Hg}$ observations.

887 1. Figure S3 (and Figure 4, main text) shows the latitudinal distribution of marine pelagic $\Delta^{200}\text{Hg}$.
888 $\Delta^{200}\text{Hg}$ of marine data at high latitudes ($>60^\circ$, 0.01 ‰ (-0.04 ‰ to 0.03‰); median and IQR, $n= 69$) in
889 both hemispheres are significantly lower ($p<0.001$, one-sided t test), than mid-latitude ($30\text{-}60^\circ$, 0.03 ‰
890 (0.01 ‰ to 0.065‰); median and IQR, $n= 428$), which are significantly lower ($p<0.001$, one-sided t test)
891 than the (sub)tropics ($0\text{-}30^\circ$, 0.07 ‰ (0.04 ‰ to 0.085‰); median and IQR, $n= 275$). This trend suggests
892 that Hg(II) and Hg(0) deposition contributions to pelagic marine waters are variable. The trend also
893 confirms, to first order, that the observed higher $\Delta^{200}\text{Hg}$ (0.06 ‰) in sub-tropical pHg (Motta et al.,
894 2019)¹⁸ and lower pHg $\Delta^{200}\text{Hg}$ in mid-latitude (0.01 ‰) and high latitude (-0.02 ‰) waters (this study)
895 are coherent features that belong to a broader latitudinal trend in marine $\Delta^{200}\text{Hg}$.

896 2. We review Hg(II) wet deposition at remote coastal and island monitoring sites globally, and
897 during a S-Atlantic cruise¹⁹ that collected a large number of rainfall events (Extended Data Figure 3,
898 $n=12,812$). We find a gradual increase from $1.7 \pm 0.9 \mu\text{g m}^{-2} \text{y}^{-1}$ at high latitudes to 6.7 ± 4.0 at mid-
899 latitudes to 15 ± 5 in the (sub-)tropics (mean \pm sd), generally attributed to convective cloud formation
900 and upper tropospheric Hg(II) scavenging²⁰. Whereas the northern hemisphere (NH) (sub-)tropical
901 rainfall Hg(II) maximum is well defined for Mercury Deposition Network (MDN²¹) sites along the coastal
902 N-Atlantic Ocean and Caribbean seas, only limited data is available for the NH Southeast Asian seas^{22,23},
903 the Pacific Ocean at Hawaii¹⁸, the equator^{19,24,25} and the southern hemisphere (SH)^{19,26,27}. Extrapolation
904 of the latitudinal Hg(II) wet deposition trend at marine locations to the global Ocean gives a Hg(II) wet
905 deposition flux of $2561 \pm 768 \text{ Mg y}^{-1}$, assuming the relative standard deviation of 30% observed for
906 individual 5° latitude intervals applies at the global scale. Seasonal Hg(II) dry deposition observations
907 over oceans are inexistent, and must be estimated from 3D Hg models. Model Hg(II) wet deposition
908 generally is on the order of 60% of total Hg(II) deposition, the remaining 40% being Hg(II) dry
909 deposition^{28,29}. For the observed global Hg(II) wet deposition budget of 2561 Mg y^{-1} , Hg(II) dry
910 deposition would then correspond to $1615 \pm 485 \text{ Mg y}^{-1}$. In the absence of observations, we assume
911 Hg(II) dry deposition to be constant as a function of latitude at $5 \mu\text{g m}^{-2} \text{y}^{-1}$, which respects its
912 contribution of 40% to modeled global Hg(II) deposition. The hybrid observational-model estimate
913 (indicated as zonal 'reference model in main text, and Figures 4, Extended Data Figure 5) of global
914 Hg(II) deposition to oceans of $4268 \pm 1280 \text{ Mg y}^{-1}$ is therefore similar to atmospheric Hg(II) deposition
915 of 4600 Mg y^{-1} in Hg cycling models²⁹. Both our zonal 'reference model' and 3D Hg cycling models rely
916 heavily on coastal and continental rainfall observation sites, in particular from the MDN network in N-
917 America. It is therefore possible that the coastal rainfall observations, despite our pre-selection of non-

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

922 3. We review surface Ocean dissolved gaseous Hg (DGM) measurements in order to estimate
 923 mean latitudinal DGM distribution (Extended Data Figure 4), and a DGM observation-based global
 924 marine Hg(0) gross and net emission budget. While DGM technically includes both dissolved gaseous
 925 Hg(0) and DMHg, it is thought to represent mostly Hg(0) due to the low surface ocean DMHg
 926 concentrations. We estimate marine Hg(0) evasion based on marine boundary layer atmospheric
 927 gaseous Hg(0) distribution³⁰. We use latitudinal mean DGM, mean annual sea surface temperature
 928 (SST; 2007-2019; Copernicus product WIND_GLO_PHY_CLIMATE_L4_REP_012_003), wind speed at
 929 10m above sea level (μ_{10} ; 2007-2019; Copernicus product
 930 SST_GLO_SST_L4_NRT_OBSERVATIONS_010_001), and marine boundary layer Hg(0), to calculate
 931 global gross Hg(0) invasion (F_{inv} , Eq S2), gross evasion (F_{ev} , Eq S3) and net Hg(0) evasion (F_{net} , Eq S4) for
 932 5° latitude bands (all in $\text{ng m}^{-2} \text{h}^{-1}$) as follows:

933

$$934 \quad F_{\text{inv}} = K_w \times -C_a/K_H \quad (\text{Eq. S2})$$

$$935 \quad F_{\text{ev}} = K_w \times C_w \quad (\text{Eq. S3})$$

$$936 \quad F_{\text{net}} = K_w \times (C_w - C_a/K_H) \quad (\text{Eq. S4})$$

937

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

941 $\ln(K_H) = 2403.3/T + 6.92$ from Andersson et al. 2008³¹, where T is the SST in degrees Kelvin

942 $K_w = 0.25 \times \mu_{10}^2 (S_{\text{CHg0}}/S_{\text{CCO2}})^{-0.5}$ from Nightingale et al. 2000³², where S_{CHg0} is the Schmidt number for
 943 Hg(0):

$$944 \quad S_{\text{CHg0}} = \nu/D$$

945 where ν 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
946 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
947 Boltzman's constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is SST in Kelvin, all based on Kuss et al. 2009³³.

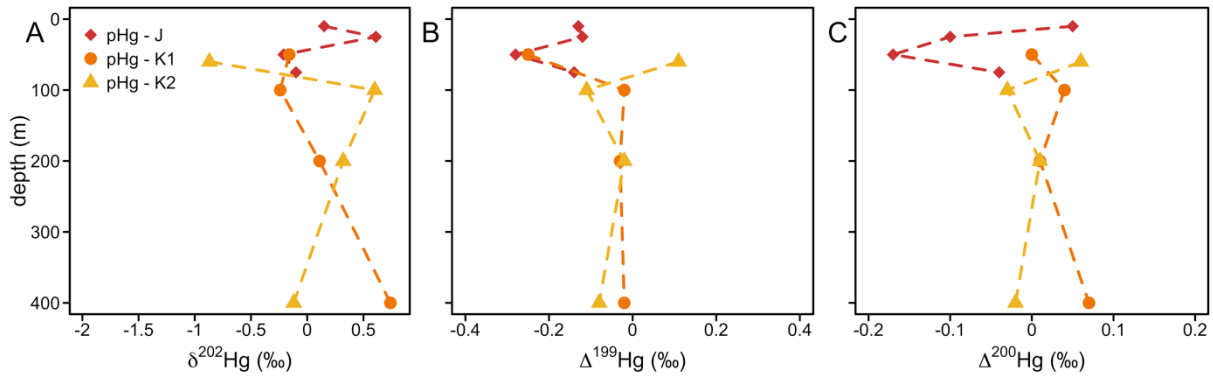
948 Hg(II) deposition, gross Hg(0) invasion, gross Hg(0) evasion and net Hg evasion as a function of latitude
949 are summarized in Extended Data Figure 5 top. Hg(0) invasion is driven by observed atmospheric Hg(0)
950 and wind speed and is maximal at mid and high latitudes. Hg(II) deposition is dominated by Hg(II) wet
951 deposition in the sub-tropical NH. Hg(0) evasion is driven by high DGM concentrations in the
952 (sub-)tropics (Extended Data Figure 3) and by high wind speed at mid and high latitudes. The net Hg
953 evasion trend shows important net deposition in the northern hemisphere, and net evasion in the
954 southern hemisphere, in agreement with 3D Hg cycling models²⁹ and observations³⁴. We use Hg(II) wet
955 deposition, Hg(II) dry deposition and Hg(0) invasion estimates (Extended Data Figure 5 bottom),
956 together with $\Delta^{200}\text{Hg}$ end-members (Extended Data Figure 6, Extended Data Table 1, Equation 3) to
957 calculate an expected latitudinal marine, pelagic $\Delta^{200}\text{Hg}$ distribution (Figure 4a). Expanded
958 uncertainties on $\Delta^{200}\text{Hg}$ are estimated using a Monte Carlo script in R by randomly varying the stated
959 uncertainties on fluxes and end-member $\Delta^{200}\text{Hg}$. Due to the asymmetric latitudinal contributions of
960 Hg(II) deposition and Hg(0) invasion to marine Hg, the expected $\Delta^{200}\text{Hg}$ trend (Figure 4a, main text)
961 shows lower values at high latitudes and maximum, positive values in the NH (sub-)tropics. The
962 observed marine $\Delta^{200}\text{Hg}$ distribution is significantly lower than the predicted $\Delta^{200}\text{Hg}$ distribution,
963 except between 45 – 65°N (Figure 4). Our new tHg $\Delta^{200}\text{Hg}$ observations in the Mediterranean Sea and
964 Atlantic Ocean between 43 – 59°N are therefore coherent with predicted $\Delta^{200}\text{Hg}$. The majority of
965 marine $\Delta^{200}\text{Hg}$ observations, however, are lower than the predicted $\Delta^{200}\text{Hg}$, which leads us to conclude
966 that the contribution of atmospheric Hg(0) to the oceans and to marine biota is underestimated.

967 Although we were not able to measure the $\Delta^{204}\text{Hg}$ in tHg and pHg, due to instrumental
968 limitations (minor isotope, only one 10^{13} Ohm amplifier available and attributed to ^{198}Hg), the large
969 marine biota and sediment data set contains abundant $\Delta^{204}\text{Hg}$ observations. In Extended Data Figure
970 7 we show that these data are consistent with $\Delta^{200}\text{Hg}$ observations in the same marine biota data, and
971 with the $\Delta^{200}\text{Hg}:\Delta^{204}\text{Hg}$ relationship observed in terrestrial samples³⁵.

972 4. Above we used a hybrid approach combining observations of Hg(II) wet deposition and
973 atmospheric Hg(0), and 3D model-based Hg(II) dry deposition and Hg(0) gas-exchange to predict
974 marine $\Delta^{200}\text{Hg}$. The predicted $\Delta^{200}\text{Hg}$ trend is shifted to higher values compared to observed marine
975 $\Delta^{200}\text{Hg}$. Here we discuss why the zonal model, and 3D Hg cycling model predicted Hg(II):Hg(0) gross
976 deposition ratio of 3:1 overestimates Hg(II) deposition to oceans. It is important to understand that
977 $\Delta^{200}\text{Hg}$ does not inform on the absolute magnitude (in $\mu\text{g m}^{-2} \text{y}^{-1}$, or in Mg y^{-1}) of Hg(II) deposition and

978 Hg(0) uptake fluxes. Rather, it informs on the relative Hg(II) and Hg(0) contributions, and therefore
979 constrains the ratio of the marine Hg(II):Hg(0) gross deposition flux. We therefore need to ask which
980 of the two (or both) absolute flux estimates, either per 5° latitude band, or on a global basis, is biased.
981 We have indicated above that the marine Hg(II) wet deposition flux is mostly observed at coastal N-
982 American stations, and only rarely over the open Ocean. Using a fitting approach, minimizing the root
983 mean square error (rmse) between observed and predicted $\Delta^{200}\text{Hg}$, we estimate that Hg(II) wet
984 deposition would need to be approximately half (1252 Mg/y) the current estimate (2561 ± 768 , 1SD)
985 to achieve a good fit (Figure 4d, main text). Note that if marine Hg(II) wet deposition is 100% lower,
986 then automatically Hg(II) dry deposition, fixed at 40% of total Hg(II) deposition also becomes 100%
987 lower. With respect to the GEOS-Chem budget, Hg(II) deposition would need to be lowered 2.7x from
988 4600 to 1700 Mg y⁻¹ in order to achieve a 1:1 Hg(0):Hg(II) gross deposition ratio. We consider that 2-
989 3x times lower Hg(II) deposition is plausible, given the overall uncertainty on observations, and given
990 that the latitudinal coastal Hg(II) wet deposition distribution is asymmetric with higher deposition in
991 NH Hg emission source regions.

992 We can also keep Hg(II) deposition constant, and increase ocean Hg(0) uptake by increasing
993 the gas-transfer velocity, K_w in equations S1-S3, by a factor of 2.3 to achieve an optimum fit between
994 observed and predicted $\Delta^{200}\text{Hg}$ (Figure 4d, main text). In GEOS-Chem, K_w would have to be increased
995 270% to increase Hg(0) evasion from 1700 to 4600 Mg y⁻¹. A 230 - 270% increase in K_w exceeds the
996 typical uncertainty on Hg(0) gas-exchange models which is on the order of 30%^{36,37}. However, since the
997 Hg(0) gas-exchange parameterizations are extrapolated from CO₂, they have not been calibrated
998 against experimental or field observations. In particular the effects of surface ocean micro-layer
999 chemical reactions, for example by consumption of invading Hg(0), could cause underestimation of K_w .
1000 However, there is a caveat in fitting K_w to optimize ocean Hg(0) uptake: gross marine Hg(0) emission
1001 and net marine Hg(0) exchange also depend linearly on K_w (equations S2, S3). A 230% increase in K_w
1002 would result in large global gross marine Hg(0) emission (10900 Mg/y) and large net air-sea Hg(0)
1003 exchange (6500 Mg/y) fluxes. A larger net exchange flux would change the ocean from a net sink in
1004 present Hg cycling models, to a net source, which would have to be balanced by an additional
1005 terrestrial sink to keep the atmosphere in steady state (as observed).

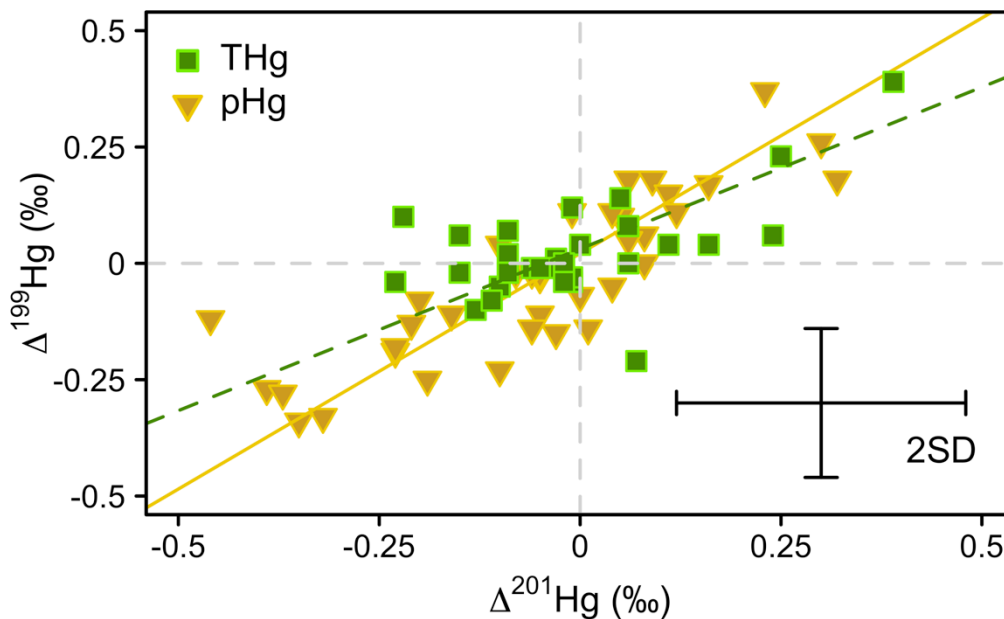


1006

1007 Figure S1. Depth profile of particulate Hg stable isotope composition at three stations in the
 1008 Mediterranean Sea during the June 2017 campaign. A: mass-dependent fractionation ($\delta^{202}\text{Hg}$), B: odd
 1009 mass-independent fractionation ($\Delta^{199}\text{Hg}$), C: even mass-independent fractionation ($\Delta^{200}\text{Hg}$).

1010

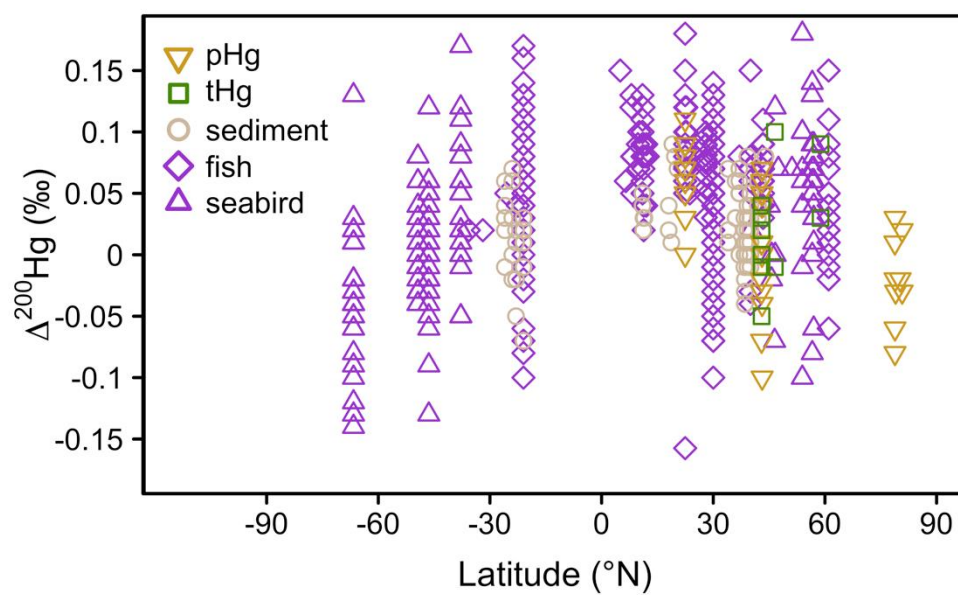
1011



1012

1013 Figure S2: Scatterplot of odd Hg isotope mass-independent fractionation, $\Delta^{201}\text{Hg}$ vs. $\Delta^{199}\text{Hg}$ of all tHg
 1014 and pHg seawater data, including the published data by Motta et al. 2019. The dashed line
 1015 represents the York regression using IsoplotR³⁸ for tHg ($\Delta^{199}\text{Hg} = 0.79(\pm 0.29) \Delta^{201}\text{Hg} + (0.03 \pm 0.04)$, (\pm
 1016 se), MSWD = 0.2). The solid line represents the York regression for pHg ($\Delta^{199}\text{Hg} = 1.01(\pm 0.09)$
 1017 $\Delta^{201}\text{Hg} + (0.02 \pm 0.02)$, (\pm se), MSWD = 1.25). Error bars represent the 2 SD of replicate procedural
 1018 standards for tHg and pHg.

1019



1020

1021 Figure S3: Variation of even-MIF Hg stable isotope composition ($\Delta^{200}\text{Hg}$) in 787 individual marine
 1022 samples resolved by sample type as function of latitude. See Extended Data Table 2 for data sources.

1023

1024

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