

1 **Mercury stable isotope composition of seawater suggests important net**  
2 **gaseous elemental mercury uptake**

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13 atmospheric deposition

**14 Summary**

15 Human exposure to toxic mercury (Hg) is dominated by the consumption of seafood<sup>1,2</sup>. Earth system  
16 models suggest that Hg in marine ecosystems is supplied by Hg(II) deposition, with a 3x smaller  
17 contribution from gaseous Hg(0) uptake, and that photochemical reduction of marine Hg(II) drives  
18 important Hg(0) evasion to the atmosphere<sup>3,4</sup>. Observations of marine Hg(II) deposition and gas  
19 exchange are sparse however<sup>5</sup>, leaving the suggested importance of air-sea exchange<sup>6</sup> unconstrained.  
20 Here we present the first Hg stable isotope measurements of total Hg (tHg) in surface and deep Atlantic  
21 and Mediterranean seawater. We use an isotope mass balance to estimate that sea water tHg can be  
22 explained by the mixing of 41% atmospheric Hg(II) deposition and 59% Hg(0) uptake. In the particulate  
23 Hg (pHg) fraction, which includes phytoplankton at the base of the marine food web, and in a  
24 compilation of marine fish Hg isotope data, we estimate similarly important marine Hg(0) uptake  
25 fractions of 73% and 49%. We observe no photochemical odd Hg isotope anomalies in tHg, which calls  
26 into question the large model Hg(0) evasion flux. Our findings indicate that direct atmospheric Hg(0)  
27 uptake is important and has implications for our understanding of atmospheric Hg dispersal and  
28 marine ecosystem recovery.

**29 Main text**

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 adults<sup>1,2,7</sup>. MMHg is formed  
32 from inorganic mercury (Hg) in the ocean and biomagnifies along marine food webs to high levels<sup>8-10</sup>.  
33 Anthropogenic release of Hg to the atmosphere, land and water bodies outweighs natural release at  
34 least five-fold<sup>11,12</sup>, and is thought to have more than tripled the mercury content of surface ocean  
35 waters<sup>13</sup>. Climate change and overfishing also affect fish MMHg levels, and require detailed models of  
36 Hg cycling to assess future human exposure to Hg<sup>14</sup>. Earth system models of Hg biogeochemical cycling  
37 suggest that atmospheric Hg deposition to the open ocean is dominated by Hg(II) wet deposition (4600  
38 Mg y<sup>-1</sup>) compared to dissolution of gaseous Hg(0) (1700 Mg y<sup>-1</sup>) in a 3:1 ratio<sup>3,4</sup>. Rivers deliver similar  
39 amounts of Hg to the oceans as atmospheric deposition (5500 Mg y<sup>-1</sup>), while only 6% of river Hg is  
40 estimated to reach the open ocean<sup>15</sup>. Models also estimate that, of total deposited Hg, 4600 Mg y<sup>-1</sup> is  
41 re-emitted to the atmosphere by (photo-)chemical and microbial photoreduction of Hg(II) to Hg(0)<sup>3,16</sup>.  
42 Dissolved Hg(0) concentrations in surface waters and atmospheric Hg(0) concentrations are  
43 sporadically measured simultaneously during oceanic cruises<sup>17</sup>, and show variable Hg(0) exchange  
44 fluxes over short time periods and across different ocean basins<sup>18</sup>. The direction and magnitude of the  
45 large air-sea exchange of Hg(0) depends on the parametrization of the Hg(0) exchange velocity in  
46 models<sup>19</sup>. The absence of direct, long-term Hg(0) flux measurements over the ocean and limited

47 observations of Hg(II) wet and dry deposition to oceans therefore provide insufficient constraints for  
48 model validation of sea-air Hg(0) exchange, and Hg(II) deposition fluxes. This in turn hampers our  
49 capability to predict how Hg levels in the Ocean will respond to curbed anthropogenic Hg emissions  
50 under the UN Minamata Convention on Mercury, and to climate change<sup>20-22</sup>.

51 In terrestrial ecosystems, Hg stable isotopes have proven to be instrumental in understanding  
52 the relative importance of Hg(II) and Hg(0) deposition<sup>23-25</sup>. Atmospheric Hg(0) and Hg(II) in rainfall have  
53 different mass-dependent (MDF,  $\delta^{202}\text{Hg}$ ) and mass-independent fractionation (MIF,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$ )  
54 signatures. Even-Hg MIF ( $\Delta^{200}\text{Hg}$ ) is thought to be generated exclusively by upper tropospheric  
55 photochemical reactions<sup>26,27</sup>, and no Hg transformations at the Earth's surface have been shown to  
56 fractionate  $\Delta^{200}\text{Hg}$ .  $\Delta^{200}\text{Hg}$  is therefore considered as a conservative tracer for atmospheric Hg  
57 deposition pathways<sup>24</sup>. Apart from marine biota, the Hg stable isotope composition of total unfiltered  
58 Hg (tHg) has only been measured in coastal seawater of the Canadian Arctic Archipelago, suggesting  
59 that 50% to 80% of tHg originated from coastal erosion and river input<sup>28</sup>. Analysis of particulate Hg  
60 (pHg) isotopes at the tropical Pacific station ALOHA (22°N) suggested that atmospheric deposition of  
61 Hg(II) from rainfall was an important Hg source to the surface ocean<sup>29</sup>. The Hg isotopic composition of  
62 open ocean seawater, characterized by its (sub-)picomolar levels of tHg in all basins<sup>30</sup>, including ocean-  
63 like seas such as the Mediterranean Sea<sup>31</sup>, remains unexplored.

64 In this contribution we develop and apply an ultra-clean pre-concentration method for tHg  
65 isotope analysis of seawater to understand air-sea exchange of Hg. We developed the method on  
66 oligotrophic Mediterranean seawater, and complement the tHg data with samples from the North-  
67 Atlantic Ocean, and with pHg isotope measurements for both basins. We use our new tHg isotope  
68 observations together with published atmospheric Hg(II) and Hg(0) and marine pHg, sediment and fish  
69 Hg isotope data to assess the main pathways of atmospheric Hg deposition to the ocean, and discuss  
70 the plausibility of the large global marine Hg(0) evasion flux.

## 71 **Results and Discussion**

### 72 ***Sea water Hg concentrations, speciation and isotopic composition***

73 Seawater Hg speciation and isotope composition, and procedural standard Hg isotope data are shown  
74 in Tables S3, S4. Mediterranean station K2, 20 km off-shore, is an oligotrophic reference site that was  
75 used for the 2017 GEOTRACES Hg species intercalibration cruise because the typical water masses of  
76 the open Western Mediterranean Sea are present (Figure S1). tHg concentrations at K2 in June 2017,  
77 and Feb and May 2019 (Figure 1a, Table S1, S2) are slightly surface depleted (0.8 pM), and peak at  
78 300m depth (1.1 pM), similar to previous observations in the Western Mediterranean Sea<sup>31,32</sup>. Total

79 methylated Hg (MeHg) concentrations peak at 400-600 m, (43 % of tHg), where oxygen levels reach  
 80 their minimum due to microbial remineralization of particulate organic matter<sup>32</sup>. Surface tHg levels in  
 81 the Bay of Marseille at Endoume pier were higher,  $6.0 \pm 1.1$  pM. In four samples from two Atlantic  
 82 Ocean stations (St21, St38, Figure S1), tHg increased with depth from 0.46 to 0.83 pM and represent  
 83 the mixed layer (5m, 20m), intermediate water (650m), and north-east Atlantic deep water (NEADW,  
 84 3345m)<sup>33</sup>. MeHg in the two Atlantic profiles were similar to Mediterranean station K2 with low levels,  
 85 0.04 pM, at the surface and elevated levels, 0.4 pM, at depth (54 % of tHg). pHg at the Mediterranean  
 86 stations K1, K2 and Julio were low with a mean of  $0.11 \pm 0.06$  pM ( $1\sigma$ ,  $n=16$ ) for the 5-800m depth  
 87 range. Fram Strait pHg in Atlantic Ocean waters of the West-Spitzbergen current had higher pHg levels  
 88 of  $0.31 \pm 0.11$  pM ( $1\sigma$ ,  $n=9$ ).

89 tHg isotope depth profiles for  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  signatures were replicated at station  
 90 K2 during two sampling cruises in February and May 2019 and show reproducible results (Figure  
 91 1).  $\delta^{202}\text{Hg}$  is uniform with depth, with a median value of  $-0.09$  ‰ ( $-0.31$  ‰ to  $0.00$  ‰; median, IQR,  $n$   
 92 = 12). Overall,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  are also near-zero, with median values of  $0.06$  and  $0.01$  ‰  
 93 respectively. The four North-Atlantic Ocean tHg samples show median  $\delta^{202}\text{Hg}$  of  $-0.45$  ‰,  $\Delta^{199}\text{Hg}$  of  
 94  $0.09$  ‰, and  $\Delta^{200}\text{Hg}$  of  $0.06$  ‰, and are therefore similar to Mediterranean waters, even at 3345m depth  
 95 in NEADW. Three independent lines of evidence suggest that the tHg isotope composition of seawater  
 96 is, to first order, a relatively constant feature: 1. The February and May replicate cruises to K2 station  
 97 do not show any large seasonal variation in tHg isotope profiles, 2. The eight replicate samples at the  
 98 Endoume pier (Table S4), covering one diurnal 24 h cycle, do not show any Hg isotope variation, and  
 99 3. The off-shore Mediterranean and Atlantic Ocean tHg isotope signatures are similar.

## 100 pHg isotopes

101 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  $\delta^{202}\text{Hg}$   
 102 was higher in June 2017 by  $1.5$  ‰ at 100-400m depth. In May 2019, the only occasion when tHg and  
 103 pHg isotopes were determined simultaneously at station K2,  $\delta^{202}\text{Hg}$  of pHg was depleted by  $-1.0$  ‰ ( $-$   
 104  $0.8$  ‰ to  $-1.3$  ‰; median and IQR,  $n = 4$ ) relative to tHg (Figure 1). Light isotope enriched pHg may be  
 105 explained by the preferential sorption of light Hg(II) isotopes to particulate organic matter<sup>34</sup>, or by  
 106 preferential bio-uptake of light isotopes by phytoplankton that is part of the particulate pool. pHg  
 107 stable isotopes sampled in 2017 at two stations, Julio and K1, closer to the coast were similar to the  
 108 open sea station (K2) with no clear trends in water depth or distance from the shore (Figure S3). Marine  
 109 sediments, analyzed for station Julio only (700m depth, Table S4), had similar  $\delta^{202}\text{Hg} = -0.75$  ‰  $\pm$   
 110  $0.12$  ‰,  $\Delta^{199}\text{Hg} = 0.04$  ‰  $\pm 0.10$  ‰, and  $\Delta^{200}\text{Hg} = 0.03$  ‰  $\pm 0.06$  ‰ (mean  $\pm 2\sigma$ ,  $n=4$ ) to mean water

111 column pHg (K1, K2, Julio), and were similar to sediment samples taken elsewhere in the  
112 Mediterranean Sea<sup>35,36</sup>.

### 113 **Estimating atmospheric Hg(II) and Hg(0) deposition**

114  $\Delta^{200}\text{Hg}$  has been used successfully as a conservative tracer for atmospheric Hg(0) and Hg(II) wet  
115 deposition in terrestrial ecosystems<sup>23,23,25</sup>. Here we use  $\Delta^{200}\text{Hg}$  to quantify the combined contribution  
116 of Hg(II) wet and dry deposition, and Hg(0) gas exchange to marine tHg and pHg. In doing so, we  
117 exclude other Hg sources such as hydrothermal or river inputs. At Mediterranean station K2, this is  
118 justified by the absence of large rivers draining into the Ligurian Sea, and reflected in the open-ocean  
119 type tHg levels around 1 pM. The Rhône River reaches the Mediterranean, 100 km west of K2, at the  
120 continental shelf of the Gulf of Lions, and is carried further westward away from K2. Similarly, there is  
121 no hydrothermal activity within 500 km from the K2 station. At the Atlantic Ocean stations St21 and  
122 St38, no influence of river<sup>15</sup> or hydrothermal Hg inputs was found<sup>33</sup>.

123 Modern, northern hemispheric Hg(II) wet deposition is characterized by a positive  $\Delta^{200}\text{Hg}$  of  
124 0.16 ‰ (0.11 ‰ to 0.22 ‰; median, IQR, n = 106), for background sites with Hg concentrations < 25  
125 ng L<sup>-1</sup>; Table S1). A new study shows that gaseous atmospheric Hg(II) forms, that are the precursor to  
126 Hg(II) in wet deposition, have the same  $\Delta^{200}\text{Hg}$  as Hg(II) wet deposition in the lower free and middle  
127 troposphere<sup>27</sup>. A recent modeling study evaluated the origin of global Hg(II) wet and dry deposition<sup>37</sup>,  
128 and found that Hg(II) sourced in the upper and middle troposphere constitutes 91% of the annual  
129 global Hg(II) wet deposition flux. The global contribution of the upper and middle troposphere to Hg(II)  
130 dry deposition was 52%. We therefore suggest that the median northern hemisphere rainfall  $\Delta^{200}\text{Hg}$   
131 of 0.17 ‰ is a reasonable estimate of the  $\Delta^{200}\text{Hg}$  of combined wet and dry Hg(II) deposition.  
132 Atmospheric Hg(0), the larger complementary pool, exhibits slightly depleted  $\Delta^{200}\text{Hg}$  of -0.05 ‰ (-  
133 0.08 ‰ to -0.02 ‰; median, IQR, n = 126, for background samples with Hg(0) concentrations < 2 ng m<sup>-3</sup>;  
134 Table S1).

135 All seawater tHg and pHg samples, including published Pacific Ocean pHg<sup>29</sup>, show  $\Delta^{200}\text{Hg}$  values  
136 between those of atmospheric Hg(0) and Hg(II) (Figure 2 & Figure 4A). Based on a  $\Delta^{200}\text{Hg}$  mixing model  
137 (Methods, Eq. 4) we estimate the fraction of Hg(II) wet and dry deposition,  $f_{\text{Hg(II)}}$ , to be 41% (32% to  
138 65%, global median, IQR, n=17) in marine tHg and 27% (13 to 51%, n=61) in pHg. This implies that the  
139 majority, i.e. 59 to 73%, of marine tHg and pHg is derived from direct Hg(0) gas exchange. Current best  
140 model estimates of global Hg(II) deposition and net Hg(0) uptake to the ocean surface are 4600 Mg y<sup>-1</sup>  
141 and 1700 Mg y<sup>-1</sup> respectively<sup>3</sup>. Our marine tHg and pHg isotope observations suggest that the Hg(II)  
142 to Hg(0) net deposition balance is in fact opposite, favoring Hg(0) at the mid-latitude marine stations

143 we investigated. Whereas  $\Delta^{200}\text{Hg}$  informs on the relative proportions of net Hg(II) and Hg(0) deposition,  
144 it cannot independently inform on Hg fluxes in mass per time units. Additional information is therefore  
145 needed to assess which number, 4600 or 1700  $\text{Mg y}^{-1}$ , or both are incorrect. Direct Hg(II) wet and dry  
146 deposition measurements over the ocean are limited. Median Hg(II) wet deposition observed at six  
147 coastal monitoring sites between 2011 and 2015 is  $1.6 \mu\text{g m}^{-2} \text{y}^{-1}$ <sup>5</sup>, suggesting an approximate global  
148 Hg(II) wet deposition of 560  $\text{Mg y}^{-1}$  to oceans. Model Hg(II) wet deposition generally is on the order of  
149 60% of total Hg(II) deposition, the remaining 40% being Hg(II) dry deposition<sup>3</sup>. This suggests that total  
150 Hg(II) deposition to oceans may be closer to 1000  $\text{Mg y}^{-1}$  rather than 4600  $\text{Mg y}^{-1}$ . Applying our  
151 calculated Hg(II)/Hg(0) net deposition ratio of 41%/59%, we suggest that net Hg(0) deposition to  
152 Oceans is then on the order of 1350  $\text{Mg y}^{-1}$ . Our combined marine and atmospheric Hg isotope mass  
153 balance lacks observations in the southern hemisphere. While this adds uncertainty to the global  
154 estimates, we suggest that the global model 3:1 Hg(II) to Hg(0) deposition ratio over oceans is in reality  
155 closer to 1:1.

156 We apply the same  $\Delta^{200}\text{Hg}$  mass balance to published Hg isotope data in northern hemisphere  
157 marine sediments and fish (Table S2). Similar to sea water tHg and pHg, with median  $f_{\text{Hg(II)}}$  of 41% and  
158 27%, global sediments and marine fish  $\Delta^{200}\text{Hg}$  suggest lower than expected  $f_{\text{Hg(II)}}$  of 32% and 51%  
159 respectively. The marine sediment and fish  $\Delta^{200}\text{Hg}$  data cover a much larger geographical range than  
160 our new tHg and pHg data, including South Pacific sediments, and therefore reinforce the idea that  
161 Ocean Hg(0) uptake is a globally important driver of marine ecosystem Hg levels.

## 162 **Photochemical reduction of Hg(II) to Hg(0)**

163 During photoreduction of Hg(II)-organic ligand complexes the magnetic isotope effect separates even  
164 from odd Hg isotopes<sup>38</sup>. Experimental photomicrobial Hg(II) photoreduction in simulated sea water  
165 medium has been shown to lead to negative  $\Delta^{199}\text{Hg}$  in residual aquatic Hg(II)<sup>39</sup>. Here we evaluate  
166 whether the tHg and pHg data show evidence of odd-MIF, in addition to that inherited from  
167 atmospheric deposition sources. We first calculate the excess  $\Delta^{199}\text{Hg}_{\text{exc}}$  in all seawater samples, defined  
168 as the difference between the measured  $\Delta^{199}\text{Hg}$  in a marine sample and the expected  $\Delta^{199}\text{Hg}$ , based  
169 on atmospheric inputs. The expected  $\Delta^{199}\text{Hg}$  was calculated by binary mixing of  $\Delta^{199}\text{Hg}$  in atmospheric  
170 Hg(II) and Hg(0) using the source contributions ( $f_{\text{Hg(II)}}$ ) derived from  $\Delta^{200}\text{Hg}$  (Methods, equations 3-4).  
171 Overall, the  $\Delta^{199}\text{Hg}$  pattern in tHg and pHg of seawater and marine sediments is similar to  $\Delta^{200}\text{Hg}$  and  
172 observed  $\Delta^{199}\text{Hg}$  can largely be explained by a conservative mixing of atmospheric Hg(0) and Hg(II)  
173 deposition (Figure 2B). Atlantic and Mediterranean  $\Delta^{199}\text{Hg}_{\text{exc}}$  was 0.03‰ (0.02 to 0.13‰; median, IQR,  
174  $n = 17$ ) in tHg and 0.01‰ (-0.07‰ to 0.08‰; median, IQR,  $n = 61$ ) in pHg, which is not significant. Very  
175 low  $\Delta^{199}\text{Hg}_{\text{exc}}$  were also found in marine sediments of the Mediterranean Sea (0.09‰, 0.03‰ to

176 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  
177 fish (Table S2) can therefore be predominantly ascribed to photochemical breakdown of MMHg<sup>40</sup>. The  
178 absent diurnal tHg  $\Delta^{199}\text{Hg}$  variation in coastal Mediterranean water, under fully sunlit (175 W m<sup>-2</sup>) and  
179 high wind (10 m s<sup>-1</sup>) conditions favorable of Hg(0) evasion, support slow marine Hg photoreduction.  
180 Given that odd-MIF is one of the hallmarks of aqueous Hg(II) photoreduction, the low to absent  
181  $\Delta^{199}\text{Hg}_{\text{exc}}$ , <0.09‰, in marine tHg, pHg and sediment Hg suggests that the large photoreductive marine  
182 Hg(0) evasion flux of 4600 Mg y<sup>-1</sup> in models is likely overestimated. This notion is also supported by the  
183 absence of seasonal Hg(0) variation in the atmospheric marine boundary layer, in particular in the  
184 ocean dominated southern hemisphere<sup>41</sup>. Figure 4 illustrates (in red) changes in atmosphere-ocean Hg  
185 exchange based on our findings. In order to maintain steady-state in atmospheric Hg inputs and  
186 outputs, we adjust marine Hg emissions to 600 Mg y<sup>-1</sup>, which is 8x lower than the previous estimate  
187 and compatible with the low  $\Delta^{199}\text{Hg}_{\text{exc}}$  observed. Lower atmospheric Hg(II) deposition to and lower  
188 Hg(0) evasion from oceans has profound impacts on the parameterization of Earth system Hg models,  
189 the lifetime of anthropogenic Hg in atmosphere and surface ocean, and consequently the anticipated  
190 recovery of ecosystems following aggressive Hg emission policy.

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207

## 208 **Author contributions**

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

214

## 215 **Methods**

216 The method for tHg in sea water consists of an ultra-clean shipboard sampling and post-cruise sample  
217 processing protocol using a standard stannous chloride ( $\text{SnCl}_2$ ) reduction purge-and-trap method,  
218 based on the USEPA method 1631<sup>42</sup>.

219 **Sampling.** Repeated, daily cruises were undertaken on the RV Antedon II from Marseille (France) to  
220 the nearby (20 km) oligotrophic, off-shore station K2 (42.98 N/5.41 E/ >1500 m-depth) between  
221 14/6/2017 and 21/6/2017, on 27/02/2019 and 22/05/2019. We used an epoxy-painted trace metal  
222 clean carousel, equipped with a conductivity-temperature-depth unit (CTD, Seabird SBE 911plus), and  
223 oxygen sensor (Seabird SBE 43), and 8x 10 L GOFLO trace metal clean bottles (General Oceanics).  
224 Samples were taken at up to 12 depths for Hg species, and at 4 depths for tHg and pHg isotopes,  
225 corresponding to surface waters (5 m), the chlorophyll-maximum (20 m), the oxygen minimum zone  
226 (400 m) and deep (800 m) waters. See SI for salinity, temperature, oxygen and fluorescence data.  
227 Unfiltered seawater was drawn *via* acid-cleaned 6 mm FEP tubing into pre-cleaned 20 L Pyrex glass  
228 bottles with GL45 PFA Teflon caps. Bottles were filled to the 20 L mark, and not to the brim, in order  
229 to preserve a 3 L headspace for purge and trap purposes. Bottles were protected from sunlight and  
230 breaking risk in 70 L plastic barrels (Kruizinga.nl Ref#53-WHV70) by using polyurethane expansive foam  
231 to fit them in the barrels. We anticipate that future use of 20 L polycarbonate carboys are an alternative  
232 option, for safer sampling during rough seas. Unfiltered seawater was drawn from each GOFLO bottle  
233 into acid-cleaned and blank-tested 60 mL FEP Teflon bottles (Nalgene) for tHg and 250 mL PFA Teflon  
234 bottles (Savillex Purillex) for MeHg, MMHg and dissolved gaseous Hg (DGM =  $\text{Hg}^0$  + dimethyl-Hg  
235 (DMHg)) analysis. All sampling was compliant with strict GEOTRACES trace metal clean sampling  
236 procedures<sup>43</sup>. Eight 20 L replicate samples of seawater from the Bay of Marseille were taken every  
237 three hours on 12/11/2019 at the Endoume pier. Seawater is continuously pumped at  $20 \text{ L min}^{-1}$  into  
238 the Mediterranean Institute of Oceanography (MIO) seawater sensing lab (SSL@MM). Samples were  
239 transported to MIO and processed within 24 h. Atlantic Ocean tHg samples were collected during the  
240 GEOVIDE cruise (GEOTRACES-GA01 transect), on board the RV "Pourquoi Pas?" between 15/05/2014  
241 and 30/06/2014. tHg values for GEOVIDE have been published elsewhere<sup>33</sup>.



242 **Particulate Hg.** pHg was sampled using in situ pumps (McLane LV08) at stations K1 (43.10 N, 5.49 E,  
243 700 m depth, 10 km off-shore, continental slope), K2, and Julio (43.13 N, 05.36 E, 100 m-depth, 10 km  
244 off-shore, shelf) in the Mediterranean Sea on 16/06/2017, and at K2 on 22/05/2019; in Fram Strait  
245 Atlantic waters from 21/7/2016 to 1/9/2016 during the FS Polarstern PS100 GRIFF cruise (Geotraces-  
246 GN05 transect). Pre-burnt Millipore 142mm QMA, or GF/F were deployed for 1 - 3 h to collect particles  
247 from 148-792 L of seawater. Filter samples were frozen onboard, shipped frozen to MIO, freeze dried  
248 (Christ Gamma 1-16 LSCplus), and stored in the dark until analysis. Table S4 summarizes all sampling  
249 locations.

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

251 The 20L Mediterranean tHg samples were acidified and oxidized, within 12 h after sampling, at the  
252 MIO laboratory, using 5 mL 0.2 N BrCl (Sigma-Aldrich KBr and KBrO<sub>3</sub> salts) in concentrated bi-distilled  
253 9 N HCl, leading to an initial sample HCl concentration of 0.0023 N. BrCl blanks were analyzed before  
254 addition, as it potentially constitutes the largest single component of the method blank. The volume  
255 of BrCl was optimized by visual inspection of the sample turning slightly yellow, indicating excess BrCl  
256 over reduced seawater components such as dissolved and particulate organic matter (DOC, POC, OM).  
257 We anticipate that the volume of BrCl added, and the time needed to convert all Hg species to labile  
258 Hg(II) forms will depend on the OM levels of seawater elsewhere. Samples were let sit for 12 h, after  
259 which a 60 mL subsample was taken with an acid cleaned, 60 cm long, burette into pre-combusted 60  
260 mL glass vials with acid-washed Teflon-lined caps for tHg concentration analysis. This tHg subsample is  
261 compared to the shipboard 60mL tHg FEP sample and serves to verify that the 20L bottles are neither  
262 contaminated, nor subjected to tHg loss.

263 tHg pre-concentration was started by replacing the GL45 PFA Teflon caps (Savillex) by GL45  
264 two-port PFA Teflon caps (Savillex) to guide 60 cm long 6 mm OD (3 - 4 mm ID) Pyrex bubbling post  
265 with a 1 cm long P3 porosity frit (VitraPOR Micro Filter-Candle, Robuglas, Germany, custom assembled  
266 by Verres Vagner, Toulouse, France). The second port on the GL45 cap hosted a 10 cm long 6 mm OD  
267 FEP tube that was connected with a short piece of 10 mm OD, 4 mm ID silicone tubing to a shorter, 25  
268 cm long, elbowed 6mm OD Pyrex bubbling post, with 1 cm long P2 frit (VitraPOR). The P2 bubbler post  
269 was then inserted into a 60 mL, 20 cm long glass test tube, filled with 6 mL of oxidizing 40 vol% inverse  
270 aqua regia (iAR) solution. The finer P3 bubbler frit inside the bottle leads to abundant small bubbles,  
271 but can technically be replaced by coarser frits. The medium P2 bubbler frit inside the 40% iAR trap is  
272 critical to avoid over pressure and leaks of Hg(0) from the 20 L bottle. All glassware was pre-combusted  
273 at 530°C and Teflon-ware was cleaned by multiple bi-distilled HCl steps in a class 100 clean room.

274 Standard protocols for Hg(II) analysis by SnCl<sub>2</sub> reduction, such as EPA method 1631, use a large  
275 excess of SnCl<sub>2</sub> over Hg(II). While SnCl<sub>2</sub> does not pose a blank issue (purging it removes all Hg traces),  
276 it generates large volumes of toxic waste in each 20 L bottle after pre-concentration. We therefore  
277 tested up to 100x lower levels of anhydrous Sn(II)Cl<sub>2</sub> (Sigma-Aldrich). Hg(II) reduction by Sn(II)  
278 competes however with excess BrCl and natural oxygen present in seawater, i.e. Sn(II) is oxidized by  
279 BrCl and O<sub>2</sub> before it can reduce Hg(II). We therefore neutralized excess BrCl by adding 4 mL of NH<sub>4</sub>.HCl  
280 (4.3 M) and verified disappearance of the yellow color. We then pre-purged (before adding SnCl<sub>2</sub>) the  
281 20 L sample with Hg-free argon at 300 mL min<sup>-1</sup> for 3 h to remove > 90 % of dissolved oxygen. The 40%  
282 iAR solution trap was connected during pre-purging to trap any potential, though unlikely, loss of  
283 gaseous Hg from the sample. Adding SnCl<sub>2</sub> at this point, had however shown abundant precipitation  
284 of a fine white solid, presumably SnCl<sub>2,s</sub>, which we remedied by adding an additional 80 mL volume of  
285 HCl to stabilize Sn(II) in the samples. Sn(II) addition was performed in two ways: i) 125 mL of SnCl<sub>2</sub> was  
286 slowly pumped with a peristaltic pump (Gilson) at 1.25 mL min<sup>-1</sup>, and 1/16" PFA tubing, via the central  
287 bubbling post into the bottle over 2 h; ii) the 125 mL was added instantly *via* the GL45 cap. No  
288 differences in Hg recovery were found between the two. Upon addition of SnCl<sub>2</sub> by pump or in batch,  
289 we purged the 20 L samples for 8 h at 300 mL min<sup>-1</sup>, in order to quantitatively collect sample Hg into  
290 the oxidizing 40% iAR solution trap. At the end of 6 h of pre-concentration, the argon flow was stopped,  
291 and the 40 v% iAR traps removed and diluted with MQ water to 20 v% iAR and stored cold (4°C) in the  
292 dark until analysis.

293 For the Atlantic Ocean tHg samples, a different pre-concentration technique was applied  
294 onboard which is described in detail in the Supporting Information. In brief, 48L samples, stored in  
295 tedlar (Teflon) bags, were pumped at 5mL min<sup>-1</sup>, through an iodated activated carbon (IAC) cartridge  
296 onboard. The IAC sorbent was combusted back on land, at Geosciences Environnement Toulouse  
297 (GET), in a dual tube furnace set-up, and sample Hg(0) trapped in 6 mL 40% iAR. We abandoned this  
298 method due to higher blanks, challenging Hg recoveries from IAC, and slowness of sea water sample  
299 loading (1 week).

### 300 **Procedural blanks and standards**

301 Procedural Hg blanks, representing all laboratory manipulations, cleaning procedures, reagent  
302 additions, and different operators, were determined as follows. Following pre-concentration of a batch  
303 of 8 samples for tHg, the residual Hg-free seawater solution, was conserved in the 20 L bottle, and all  
304 reagents were newly added to 8 bottles as described above. The solutions were then purged, similar  
305 to samples, for 8 hours into newly prepared 6 mL 40% iAR traps. Eight procedural standards were pre-  
306 concentrated in a similar fashion: following blanks, once more all reagents were added to the

307 remaining 20 L of Hg-free seawater solution, and 4 to 8 ng of NIST SRM 3133 Hg was added as internal  
308 standard to each bottle.

### 309 **Particulate Hg concentration analysis**

310 Total particulate Hg (pHg) concentrations were measured on 25 mm stamp-outs, by combustion – cold  
311 vapor atomic absorption spectrometry (CV-AAS, Leco AMA254) equipped with a low level optical cell  
312 at MIO. Certified reference material NRC MESS-3 marine sediment ( $93 \pm 9 \text{ ng g}^{-1}$ ,  $1\sigma$ ) was used for  
313 quality control, with good results in the low,  $<1 \text{ ng Hg}$ , range ( $88 \pm 1 \text{ ng g}^{-1}$ ,  $1\sigma$ ). Remaining filter material  
314 was combusted whole on the dual tube furnace set-up at GET, following published protocols (Sun et  
315 al., 2013). In brief, filters are rolled up, inserted in a 20 mm diameter, 15 cm long quartz tube, which is  
316 plugged from both sides with quartz wool. The sample tube is then inserted in a 140 cm long quartz  
317 tube, housed in two tube furnaces. The first furnace, hosting the sample tube, was heated from room  
318 temperature to  $900 \text{ }^\circ\text{C}$  over 6 h in an  $80 \text{ mL min}^{-1}$  flow of high purity oxygen. The released Hg(0) vapor  
319 and other volatile compounds passed through the 2<sup>nd</sup> pyrolyzing oven, maintained at  $1000^\circ\text{C}$   
320 continuously, and purged into a 40 vol% iAR oxidizing solution trap, that uses an elbowed, fritted, P2  
321 porosity, Pyrex post. GF/F and GF/D filters melt at temperatures  $>530^\circ\text{C}$ , but remain within the quartz  
322 sample tubes, blocked by the quartz wool. Final trapping solutions were diluted to 20%v iAR and stored  
323 cold in the dark until Hg concentration analysis by CV-AFS and Hg isotope analysis by MC-ICPMS.  
324 Reference material NIST SRM1632d coal was used for weekly quality control. Combustion purge and  
325 trapping recovery on samples, assessed by CV-AFS, was  $104 \pm 28\%$ ,  $100 \pm 28\%$ , and  $105 \pm 21\%$  ( $1\sigma$ ) for  
326 the Mediterranean Sea, PS94 and PS100 cruise samples respectively.

### 327 **tHg and Hg species concentration analysis**

328 We added 40  $\mu\text{L}$  of 0.2N BrCl to the 60 FEP Teflon bottles for ambient tHg analysis. Ambient tHg  
329 concentrations in 60 mL FEP Teflon bottle aliquots, in 20 L bottle aliquots before and after pre-  
330 concentration, and in 20% iAR solution traps were all analyzed in duplicate using a custom-made purge  
331 and trap system coupled to a cold vapor atomic fluorescence spectrometry (CV-AFS, Brooks Rand  
332 Model III), either at MIO, at GET, or shipboard<sup>44</sup>. The purge and trap system consists of 100 mL Teflon  
333 batch reactor (VWR), two electromagnetic valves (NResearch), a single gold trap (LECO), all connected  
334 by 1/8 inch FEP tubing to the CV-AFS. Seawater aliquots were 35 mL, and 20% iAR aliquots 100  $\mu\text{L}$ . The  
335 CV-AFS was calibrated in the 1 - 20 pg range using NIST SRM 3133, and the NRC ORMS-5 certified  
336 reference material was always found within 10 % of the certified value ( $26 \pm 1.3 \text{ ng L}^{-1}$ ,  $1\sigma$ ). MeHg,  
337 MMHg, and DGM were analyzed following our published protocols<sup>44</sup>. DMHg was calculated as the  
338 difference of tMeHg and MMHg, and dissolved Hg(0) as the difference of DGM and DMHg. Details are  
339 given in the SI.

340 **Hg isotope analysis**

341 Hg stable isotope ratios of final 20 % iAR trap solutions were measured in duplicate during two sessions  
 342 by cold vapor multi-collector inductively coupled plasma mass spectrometry (CV MC-ICPMS) at the  
 343 Observatoire Midi-Pyrénées, Toulouse<sup>45,46</sup>. We used a CETAC ASX-520 autosampler and HGX-200 CV  
 344 system coupled to a Thermo-Scientific Neptune PLUS, equipped with a  $10^{12} \Omega$  resistor, attributed to  
 345 the  $^{198}\text{Hg}$  isotope in order to improve isotope ratio precision in the 20-50 mV range. Samples and  
 346 standard signals at  $0.25 \text{ ng g}^{-1} \text{ tHg}$  levels were generally 180 mV on the  $^{202}\text{Hg}$  isotope, at a sample  
 347 introduction flow rate of  $0.75 \text{ mL min}^{-1}$ . Thallium was not used as an internal standard, and the 203  
 348 and 205 masses were monitored to survey Hg-hydride interferences (i.e.  $^{202}\text{Hg}^1\text{H}$ , and  $^{202}\text{Hg}^1\text{H}^1\text{H}$ ),  
 349 which were found to be negligible when using standard H-cones.  $^{196}\text{Hg}$  and  $^{204}\text{Hg}$  were not analyzed  
 350 due to low abundance, and cup configuration limitations. MDF of Hg stable isotopes is reported in  
 351 small delta notation ( $\delta$ ) in per mil (‰) deviation from to the reference NIST 3133 Hg standard:

$$352 \quad \delta^{\text{xxx}}\text{Hg} = \left( \frac{{}^{\text{xxx}/198}\text{Hg}_{\text{sample}}}{{}^{\text{xxx}/198}\text{Hg}_{\text{NIST3133}}} - 1 \right) \times 10^3 \quad (1)$$

353 where 'xxx' refers to measured isotope masses: 199, 200, 201, and 202. Mass independent  
 354 fractionation (MIF) is reported in capital delta notation<sup>47</sup>, which is defined as the difference between  
 355 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  
 356 the kinetic MDF law:

$$357 \quad \Delta^{\text{xxx}}\text{Hg} = \delta^{\text{xxx}}\text{Hg} - \text{SF}^{\text{xxx}} \times \delta^{202}\text{Hg} \quad (2)$$

358 where  $\text{SF}^{\text{xxx}}$  is the mass-dependent scaling factor of 0.2520 for  $^{199}\text{Hg}$ , 0.5024 for  $^{200}\text{Hg}$ , and 0.7520 for  
 359  $^{201}\text{Hg}$ <sup>47</sup>.

360 The long-term instrumental precision was assessed through repeated analysis of the UM-Almaden and  
 361 ETH-Fluka Hg standard at  $0.25 \text{ ng g}^{-1}$  during the two analysis sessions (SI Table S4). ETH-Fluka yielded  
 362 values of  $-1.45 \pm 0.20 \text{ ‰}$ ,  $0.07 \pm 0.11 \text{ ‰}$ ,  $0.01 \pm 0.14 \text{ ‰}$ ,  $0.02 \pm 0.09 \text{ ‰}$ ,  $0.00 \pm 0.18 \text{ ‰}$  ( $2\sigma$ ,  $n = 10$ ) for  
 363  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\Delta^{201}\text{Hg}$  respectively, in agreement with published values<sup>48</sup>. UM-Almaden  
 364 standard yielded  $-0.55 \pm 0.16\text{‰}$ ,  $-0.03 \pm 0.11\text{‰}$ ,  $-0.01 \pm 0.03 \text{ ‰}$ ,  $-0.05 \pm 0.23 \text{ ‰}$  ( $2\sigma$ ,  $n = 10$ )  
 365 respectively, in agreement with previously reported values<sup>38</sup>.

366 **pHg and tHg isotope method uncertainty**

367 Mean pre-concentration recoveries for tHg isotope analysis were  $90 \pm 10\%$  ( $1\sigma$ ,  $n=12$ ) at  
 368 Mediterranean station K2,  $93 \pm 18\%$  ( $n=8$ ) at Endoume coastal station, and  $88 \pm 31\%$  ( $n=4$ ) for Atlantic  
 369 Ocean samples. Procedural blanks were  $0.23 \pm 0.08 \text{ ng Hg}$  ( $1\sigma$ ,  $n=4$ ) for the  $\text{SnCl}_2$  pre-concentration  
 370 method, which is  $<10\%$  of tHg in 20L of seawater, e.g. typically 3 - 4 ng of tHg in this study.  $\text{SnCl}_2$  method

371 replication of eight 20L coastal Mediterranean samples (6 pM, analyzed at 1.6 ng g<sup>-1</sup> by MC-ICPMS)  
 372 shows good results with  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  2 $\sigma$  uncertainties of 0.23, 0.16, and 0.06 ‰. NIST  
 373 SRM 3133 procedural standards returned  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\Delta^{201}\text{Hg}$  values of  $0.07 \pm 0.23$  ‰, -  
 374  $0.05 \pm 0.16$  ‰,  $0.00 \pm 0.06$  ‰,  $-0.01 \pm 0.18$  ‰,  $0.02 \pm 0.21$  ‰ and a mean recovery of  $86 \pm 16\%$  (2 $\sigma$ , n  
 375 = 8), suggesting no bias in the method.

376 pHg quality control results on NIST SRM 1632d yielded values of  $-1.75 \pm 0.24$  ‰,  $-0.04 \pm$   
 377  $0.04$  ‰,  $0.00 \pm 0.04$  ‰,  $-0.02 \pm 0.08$  ‰ (2 $\sigma$ , n = 10) for  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  respectively,  
 378 in agreement with published values<sup>45,49</sup>. The 2 $\sigma$  uncertainty on pHg samples was taken to be the larger  
 379 of either replicate sample analysis, procedural standard NIST SRM1632d, or secondary reference  
 380 materials UM-Almaden or ETH-Fluka.

381 Most seawater pHg and tHg samples were analyzed in duplicate on different days. The final 2 $\sigma$   
 382 uncertainties reported for Mediterranean Sea and Atlantic Ocean pHg and tHg samples are the larger  
 383 of the duplicate sample analysis, the 2 $\sigma$  on the eight NIST procedural standards (tHg), the 2 $\sigma$  on the  
 384 ten NIST SRM 1632d standards, or the 2 $\sigma$  of the ETH Fluka or UM-ALmaden standards.

### 385 **Stable isotope data analysis**

386 The fraction of Hg in marine samples derived from atmospheric Hg(II) wet and dry deposition ( $f_{\text{Hg(II)}}$ )  
 387 was calculated using a conservative mixing model as follows:

$$388 \quad \Delta^{200}\text{Hg}_{\text{sample}} = f_{\text{Hg(II)}} \times \Delta^{200}\text{Hg}_{\text{Hg(II)}} + (1 - f_{\text{Hg(II)}}) \times \Delta^{200}\text{Hg}_{\text{Hg(0)}} \quad (3)$$

389 where  $\Delta^{200}\text{Hg}_{\text{sample}}$  represents the median observed value of different marine Hg pools (THg, pHg,  
 390 sediment THg, fish THg),  $\Delta^{200}\text{Hg}_{\text{Hg(II)}}$  and  $\Delta^{200}\text{Hg}_{\text{Hg(0)}}$  the median values of previously published northern  
 391 hemisphere samples for gaseous and rainfall Hg(II), and atmospheric Hg(0), respectively. The excess  
 392  $\Delta^{199}\text{Hg}$  in the different marine Hg pools ( $\Delta^{199}\text{Hg}_{\text{exc}}$ ), representing the  $\Delta^{199}\text{Hg}$  which was produced within  
 393 the marine system, was calculated as follows:

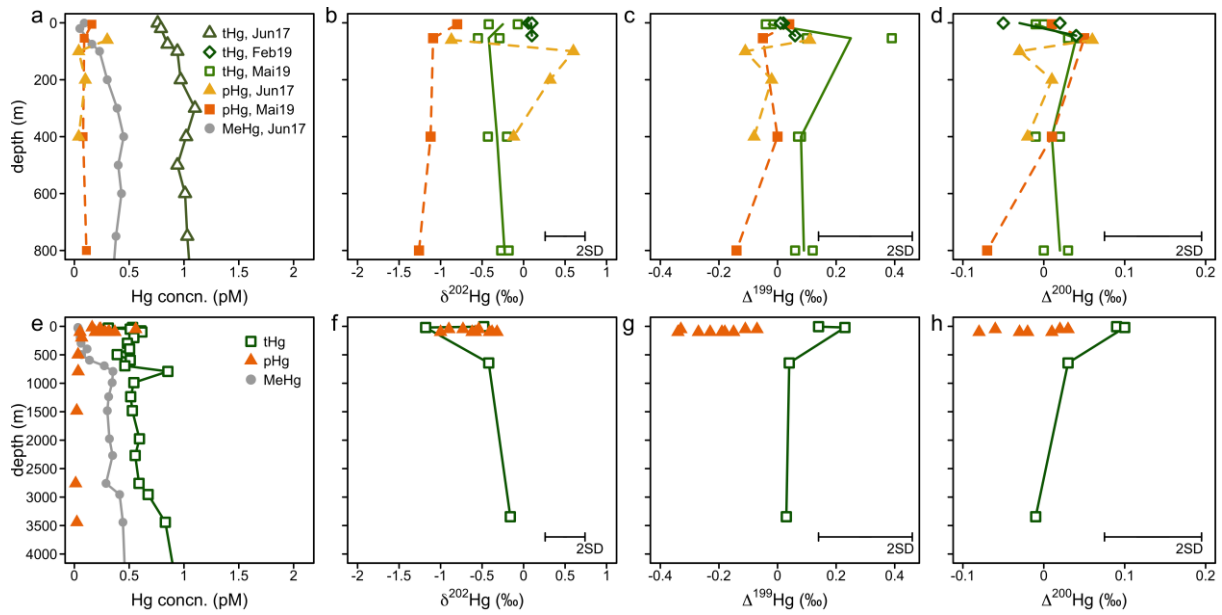
$$394 \quad \Delta^{199}\text{Hg}_{\text{exc}} = \Delta^{199}\text{Hg}_{\text{exc}} - (f_{\text{Hg(II)}} \times \Delta^{199}\text{Hg}_{\text{Hg(II)}} + (1 - f_{\text{Hg(II)}}) \times \Delta^{199}\text{Hg}_{\text{Hg(0)}}) \quad (4)$$

395 where  $f_{\text{Hg(II)}}$  was derived from the  $\delta^{200}\text{Hg}$  of the sample according to eq. 3.

396

397 **Figures**

398



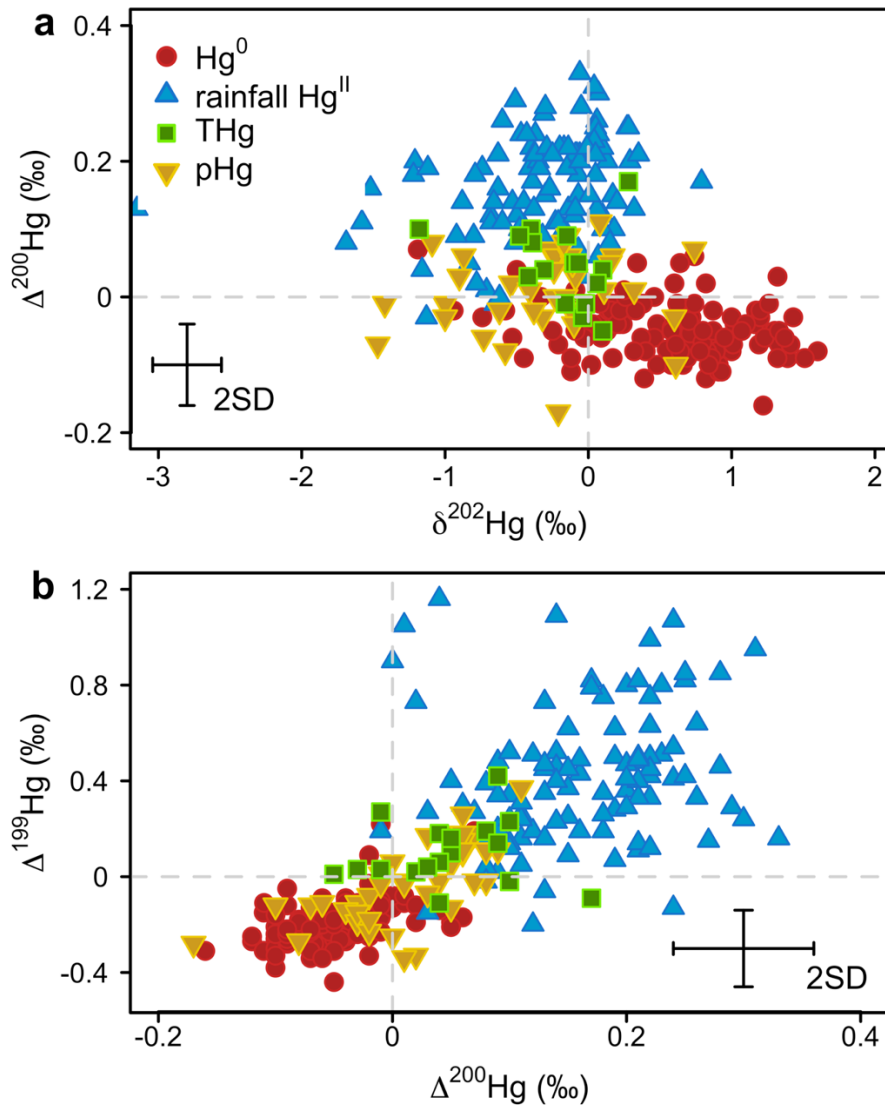
399

400 **Figure 1a-h. Depth profiles of seawater Hg species concentrations and total and particulate Hg stable**  
 401 **isotope composition at station K2 in the Mediterranean Sea (a-d) and the North Atlantic (e-h). a and**  
 402 **e: tHg, pHg, and MeHg concentrations in  $\text{pmol L}^{-1}$  (pM). b and f: mass-dependent fractionation ( $\delta^{202}\text{Hg}$ ),**  
 403 **c and g: odd mass-independent fractionation ( $\Delta^{199}\text{Hg}$ ), d and h: even mass-independent fractionation**  
 404 **( $\Delta^{200}\text{Hg}$ ). Open symbols represent values for tHg and filled symbols pHg. The lines represent averages**  
 405 **of replicate analysis of the same sample. Two standard deviation (2SD) uncertainties on Hg**  
 406 **concentrations are 10%.**

407

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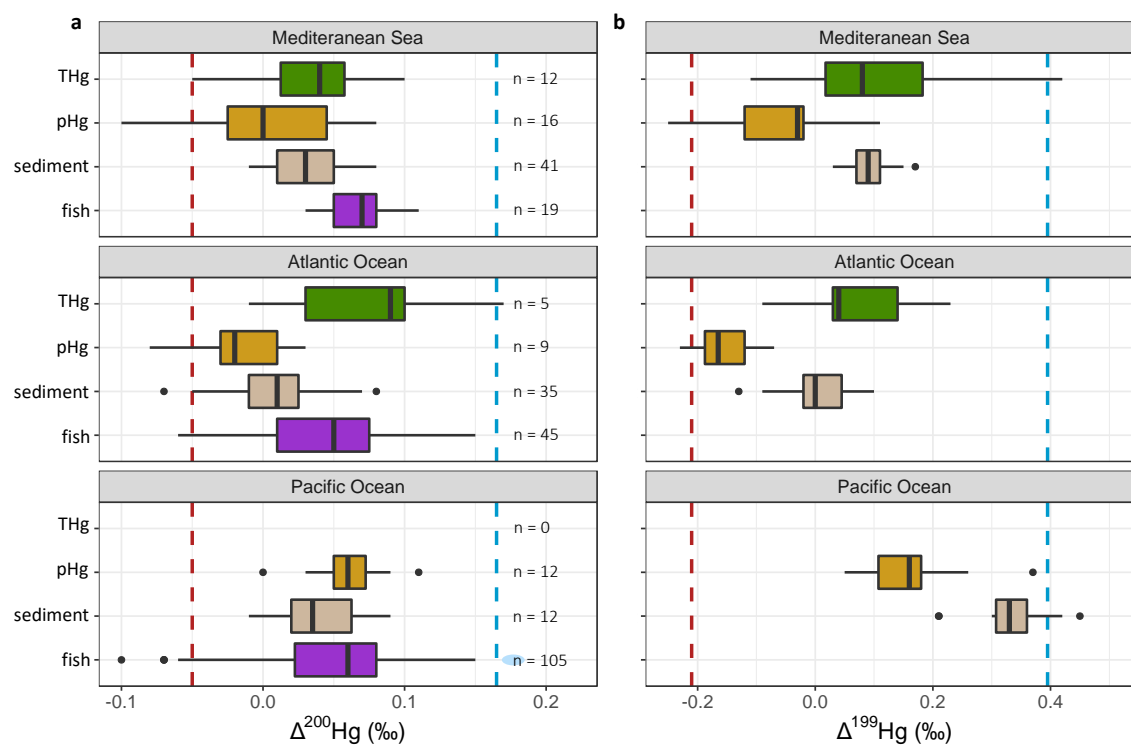


410

411 **Figure 2. Hg stable isotope composition of atmospheric sources (gaseous  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  in rainfall)**  
 412 **and seawater (total (HgT) and particulate (pHg)).** a) even mass independent fractionation ( $\Delta^{200}\text{Hg}$ ) vs.  
 413 mass dependent fractionation ( $\delta^{202}\text{Hg}$ ), and b) odd mass independent fractionation ( $\Delta^{200}\text{Hg}$ ) vs. even  
 414 mass independent fractionation ( $\Delta^{200}\text{Hg}$ ). Values of atmospheric sources are from literature (see Table  
 415 S1), tHg values are from this study, pHg from this study and ref.<sup>29</sup>. Error bars represent the 2SD of  
 416 replicate procedural standards for tHg and pHg.

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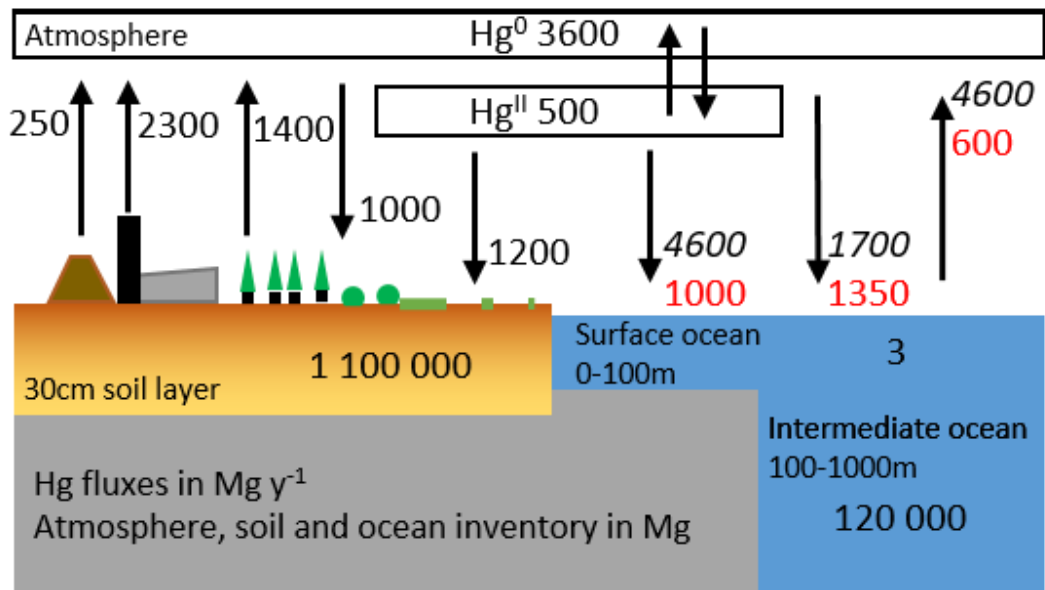


419

420 **Figure 3. Hg stable isotope signatures in different ocean basins of total Hg (tHg) and particulate Hg**  
 421 **(pHg) in seawater, marine sediments and marine fish. a: Even mass-independent signature ( $\Delta^{200}\text{Hg}$ )**  
 422 **and b: Odd mass-independent signature ( $\Delta^{199}\text{Hg}$ ).** tHg values are from this study, pHg from this study  
 423 and from Motta et al. (2019), data for sediments and biota are from literature. The atmospheric  
 424 sources are shown in red for Hg(0) and blue for Hg(II) in rainfall, the dashed line represents the median  
 425 and the shaded area the interquartile range. For fish,  $\Delta^{199}\text{Hg}$  are not shown in this Figure as these  
 426 values are heavily affected by MMHg photo-demethylation (See SI Table S2).

427





428

429 **Figure 4. Global budget of air-sea and air-land exchange.** New Hg isotope based fluxes (Mg  $y^{-1}$ ) are  
 430 shown in red. All other Hg fluxes and atmospheric  $Hg^0$  and  $Hg^{II}$  inventory are from ref.<sup>50</sup>. The upper  
 431 30cm soil and surface (0-100m) and intermediate (100-1000m) ocean inventories are from refs.<sup>11,51</sup>.

432

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562 **Online Supporting Information to:**

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564 **Mercury stable isotope composition of seawater suggests important net**  
565 **gaseous elemental mercury uptake**

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576 **Materials and Methods**577 **Rationale**

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

591 Previous studies have successfully developed methods for large volume (1 - 20 L) pre-  
592 concentration of tHg from natural waters, including rain, snow, ice, lake and coastal seawater. Gratz  
593 et al. (2010) and Sherman et al. (2010) first used continuous cold vapor generation, with  $\text{SnCl}_2$  as a  
594 reductant, to pre-concentrate 1 - 4 L of snow and rainfall samples into small volume (25 mL) 2 % (w/w)  
595 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  
596 pre-concentrate 1 L of rainfall in a 2 L Pyrex bottle, by slow, pumped addition of  $\text{SnCl}_2$ , and identical  
597  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  solution trap <sup>3</sup> and trapping solutions of 40 vol% inverse *aqua regia* (iAR, 4.2 N  $\text{HNO}_3$ ,  
598 1.2 N HCl; <sup>4</sup>). Finally, in Obrist et al. (2017) we scaled up the batch purge and trap method to handle up  
599 to 20 L of snow and rain sample <sup>5</sup>. An alternative method was developed by Chen et al. (2016) using  
600 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  
601 the acidified, 0.1 N HCl, sample is pumped at  $3.5 \text{ mL min}^{-1}$  over 0.5 mL of AG-1-X4 resin. Sorbed Hg is  
602 then eluted with 10 mL of 0.05 % L-cysteine in 0.5 N  $\text{HNO}_3$ , oxidized by BrCl, neutralized with  $\text{NH}_4\text{OH}$   
603 and analyzed by MC-ICPMS. Štok et al. (2015) optimized the anion exchange resin method for  
604 seawater and published the first Hg stable isotope data of coastal seawater (1.5-3.1 pM) from the  
605 Canadian Arctic Archipelago <sup>7</sup>. The latter two methods by Štok et al. (2015) and Obrist et al. (2017)  
606 are capable of handling sample volumes of 20 L or more that are necessary for background level tHg  
607 pre-concentration from seawater (0.4 to 1.5 pM). Our objective was therefore to adapt our existing

608 large volume pre-concentration protocol, based on  $\text{SnCl}_2$  reduction, for rain and snow to seawater. We  
609 optimized the protocol for quantitative pre-concentration yields and low blank levels.

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

611 During pre-concentration the 20L sample bottle is under argon over-pressure in order to generate a  
612 fine stream of bubbles. It is therefore important at the end of pre-concentration, or during  
613 troubleshooting, not to vent the argon supply tube to the 20L sample bottle and release argon  
614 pressure. The reason is that with the 20 L bottle under over-pressure, venting the argon supply tube  
615 results in a sudden pressure drop, and acidified sample solution with  $\text{SnCl}_2$  moving from the 20 L bottle  
616 into the tall bubbler post, possibly all the way to the argon flow regulator, damaging the latter. Worse,  
617 the 40 vol% iAR trap solution is aspirated up into its short bubbler post and into the 20 L bottle,  
618 resulting in the loss of the sample. Using our final optimized Sn addition protocol, each 20 L bottle  
619 contains at the end of a pre-concentration run, 2.5 g of Sn(II), and should be disposed of following local  
620 environmental regulations. If needed, the dissolved Sn(II) concentration can be lowered by hydrogen  
621 peroxide addition, which quantitatively precipitates  $\text{Sn(IV)O}_2$ , that can then be filtered or decanted.  
622 Quantitative oxidation of Sn(II) by hydrogen peroxide also has the advantage that no traces of Sn(II)  
623 remain in the 20 L bottle, which can be acid-cleaned and rinsed with abundant MQ water to receive  
624 the next batch of seawater samples. In this study both sampling and pre-concentration were done in  
625 the same bottle. We expect however that the use of separate bottles, possibly using plastic 20 L  
626 carboys at sea for safety, does not increase blanks.

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

628 We have, over the past years, tested an alternative method for low-level Hg pre-concentration in order  
629 to measure Hg isotopes in sea water. The method uses small 200 mg iodated activated carbon powder  
630 (Brooks Rand) cartridges, over which large volumes (50L) of sea water are pumped at a slow flow rate  
631 of  $5 \text{ ml min}^{-1}$ . Following laboratory recovery and blank testing, we applied the method during the 2014  
632 GEOTRACES Geovides cruise in the North-Atlantic Ocean. Unfiltered seawater was transferred using  
633 clean 6mm FEP tubing from GOFLO bottles into acid washed 50L tedlar bags. A peristaltic pump, with  
634 1.14mm ID (red/red) tygon pump tubing was used to load samples on the IAC traps during 1 week.  
635 Traps were dried for 5 min in a dry high purity argon stream, sealed with silicone stoppers and stored  
636 and transported dry and in the dark to the GET laboratory. The IAC powder was combusted using a  
637 dual tube furnace combustion method<sup>8</sup>. IAC blanks were 0.5 ng Hg per 200mg of IAC traps, and sample  
638 recoveries were  $88 \pm 31\%$ . In hindsight, it has been difficult to fully recover Hg from IAC traps due to  
639 abundant volatile iodine release and transfer to oxidizing solution traps. We recommend that further

640 development of activated carbon based methods use commercial sulfur impregnated activated carbon  
641 (Calgon HGR), which does not have this issue.

642 **MMHg and DMHg analysis**

643 MMHg and DMHg were determined by isotope dilution (ID)- gas chromatography – sector field ICP-  
644 MS (ID-GC-SF-ICPMS) method at the MIO laboratory, following previously published protocols<sup>9</sup>. First  
645 the sum of both species (tMeHg) was quantified on an acidified sample that converts DMHg to MMHg.  
646 A second replicate sample was purged to remove DMHg before acidification, allowing direct  
647 measurement of MMHg. DMHg was calculated by difference, as tMeHg – MMHg. In both sample  
648 aliquots MMHg and inorganic Hg species were extracted after derivatization. In brief, enriched spikes  
649 of <sup>199</sup>iHg and <sup>201</sup>MeHg (ISC Science, Spain) were added to a 115 mL aliquot of the sea water samples.  
650 After 24h of equilibration, pH was adjusted to 3.9 with NH<sub>3</sub> (ULTREX® II Ultrapure Reagent, J.T. Baker,  
651 USA) and a buffer solution made up with acetic acid (glacial, ULTREX® II Ultrapure Reagent, J.T. Baker,  
652 USA) / sodium acetate (J.T. Baker, USA). A solution of 1 % (v:v) sodium tetra propyl borate  
653 (Merseburger Spezialchemikalien, Germany) was made up freshly, under cold conditions and avoiding  
654 contact with atmospheric oxygen. 1 mL of this solution was then added together with 200 µL hexane  
655 (Sigma Aldrich, USA). The glass bottles were hermetically sealed with Teflon-lined caps and vigorously  
656 shaken for 15 minutes. The organic phase was recovered and injected in the GC (Thermo Trace Ultra),  
657 coupled to a sector field ICPMS (Thermo Element XR). Detection limits were 0.005 pM for MMHg, and  
658 0.01 pM for DMHg.

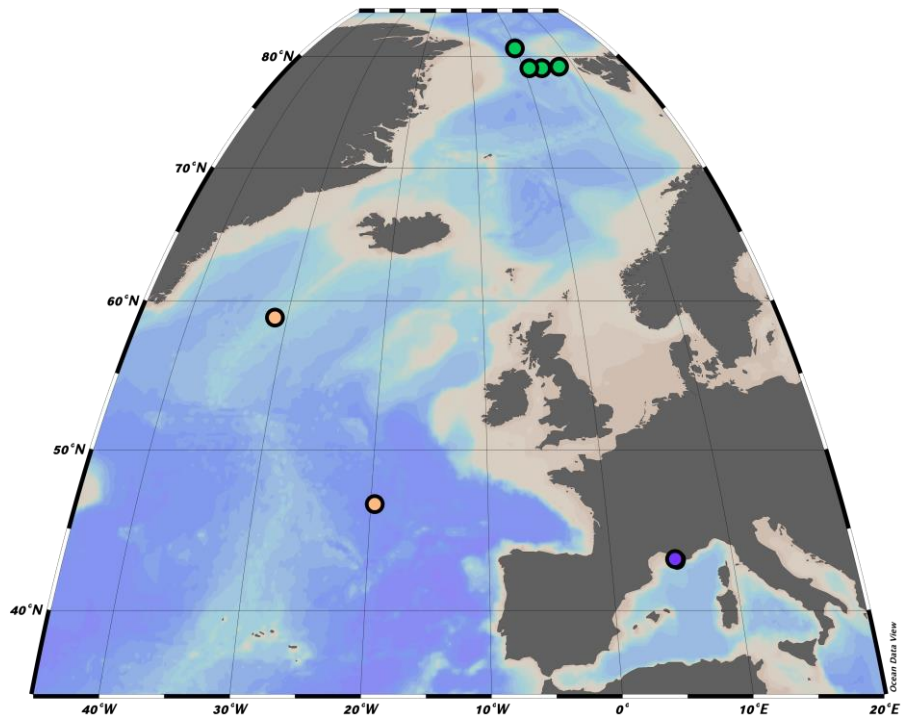
659 Table S1: Summary of Hg stable isotope data used for Figure 2 and calculations. \*sediments considered below 1000m water depth.

Pool	Ocean Basin	n	Hg concn.		Units	$\delta^{202}\text{Hg}$ (‰)		$\Delta^{199}\text{Hg}$ (‰)		$\Delta^{200}\text{Hg}$ (‰)		Reference
			median	IQR		median	IQR	median	IQR	median	IQR	
Hg(II) rainfall		106	13	(9 to 18)	ng/L	-0.30	(-0.63 to 0.03)	0.39	(0.21 to 0.52)	0.16	(0.11 to 0.22)	1,3,4,10–14
Hg(0)		126	1.23	(1.08 to 1.45)	ng/m <sup>3</sup>	0.61	(0.16 to 0.90)	-0.21	(-0.24 to -0.15)	-0.05	(-0.08 to -0.02)	2,4,5,10,15–17
tHg	<b>All samples</b>	17				-0.15	(-0.39 to -0.02)	0.06	(0.02 to 0.18)	0.04	(0.02 to 0.09)	this study
	Med. Sea	12				-0.08	(-0.31 to 0.00)	0.08	(0.02 to 0.18)	0.04	(0.01 to 0.06)	this study
	Atlantic	5				-0.42	(-0.48 to -0.16)	0.04	(0.03 to 0.14)	0.09	(0.03 to 0.10)	this study
pHg	<b>All samples</b>	37				-0.22	(-0.58 to -0.10)	-0.03	(-0.14 to 0.11)	0.01	(-0.02 to 0.06)	this study, <sup>11</sup>
	Med. Sea	16				-0.14	(-0.9 to 0.19)	-0.05	(-0.12 to -0.02)	0.00	(-0.03 to 0.04)	this study
	Atlantic	9				-0.58	(-0.73 to -0.41)	-0.19	(-0.27 to -0.15)	-0.02	(-0.03 to 0.03)	this study <sup>11</sup>
	Pacific	12				-0.13	(-0.22 to -0.1)	0.16	(0.1 to 0.18)	0.06	(0.05 to 0.07)	
sediment	<b>All samples</b>	88	55	(34to 86)	ng/g	-0.82	(-1.21 to -0.45)	0.07	(0.02 to 0.11)	0.02	(0.01 to 0.04)	
	Med. Sea	41	53	(44 to 83)	ng/g	-1.14	(-1.61 to -0.86)	0.09	(0.07 to 0.11)	0.03	(0.01 to 0.05)	This study, <sup>17, 18</sup>
	Atlantic	35	55	(33 to 137)	ng/g	-0.40	(-0.60 to 0.32)	0.00	(-0.02 to 0.05)	0.01	(-0.01 to 0.03)	18,19*
	Pacific	12	52	(20 to 74)	ng/g	-1.58	(-2.5 to -0.5)	0.33	(0.30 to 0.36)	0.04	(0.02 to 0.06)	this study
fish	<b>All samples</b>	169	252	(81 to 1403)	ng/g	0.49	(0.28 to 0.79)	1.72	(1.35 to 1.98)	0.06	(0.03 to 0.08)	
	Med. Sea	19	2950	(2460 to 3826)	ng/g	0.37	(0.29 to 0.47)	1.78	(1.70 to 1.81)	0.07	(0.05 to 0.08)	this study
	Atlantic	45	105	(60 to 190)	ng/g	0.34	(0.26 to 0.45)	1.32	(1.06 to 1.50)	0.05	(0.01 to 0.08)	20,21
	Pacific	105	366	(104 to 747)	ng/g	0.71	(0.35 to 0.89)	1.84	(1.48 to 2.17)	0.06	(0.02 to 0.08)	22–24

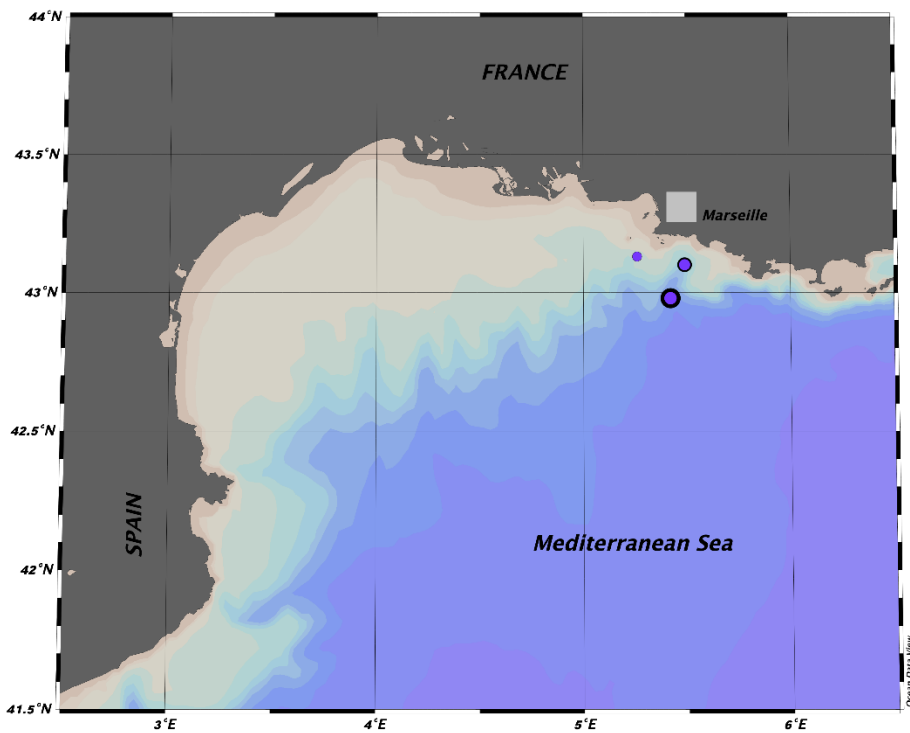
660 Table S2: Modeled contribution of Hg(II) from wet and dry deposition,  $f_{\text{Hg(II)}}$ , and excess  $\Delta^{199}\text{Hg}_{\text{exc}}$  according to Methods Equations 3, 4. Excess  $\Delta^{199}\text{Hg}_{\text{exc}}$   
 661 represents sample  $\Delta^{199}\text{Hg}$  acquired by Hg(II) photoreduction in sea water, in addition to the  $\Delta^{199}\text{Hg}$  inherited from atmospheric Hg deposition.

Pool	Ocean Basin	n	$f_{\text{Hg(II)}}$		$\Delta^{199}\text{Hg}_{\text{exc}}$ (‰)	
			median	IQR	median	IQR
tHg sea water	<b>All samples</b>	17	0.41	(0.32 to 0.65)	0.03	(0.02 to 0.13)
	Med. Sea	12	0.41	(0.29 to 0.50)	0.06	(0.03 to 0.19)
	Atlantic	5	0.65	(0.37 to 0.69)	0.02	(-0.04 to 0.02)
pHg sea water	<b>All samples</b>	37	0.27	(0.13 to 0.51)	0.01	(-0.07 to 0.08)
	Med. Sea	16	0.20	(0.08 to 0.43)	0.02	(-0.08 to 0.05)
	Atlantic	9	0.13	(0.09 to 0.27)	-0.06	(-0.10 to -0.04)
	Pacific	12	0.51	(0.46 to 0.57)	0.07	(0.00 to 0.13)
marine sediment	<b>All samples</b>	88	0.32	(0.28 to 0.41)	0.09	(0.03 to 0.12)
	Med. Sea	41	0.37	(0.28 to 0.47)	0.09	(0.03 to 0.12)
	Atlantic	35	0.28	(0.18 to 0.35)	0.06	(0.02 to 0.10)
	Pacific	12	0.40	(0.32 to 0.52)	0.25	(0.23 to 0.33)
fish	<b>All samples</b>	169	0.51	(0.37 to 0.60)	1.64	(1.28 to 1.92)
	Med. Sea	19	0.55	(0.46 to 0.60)	1.65	(1.56 to 1.72)
	Atlantic	45	0.46	(0.28 to 0.58)	1.29	(1.00 to 1.40)
	Pacific	105	0.51	(0.32 to 0.60)	1.79	(1.47 to 2.08)

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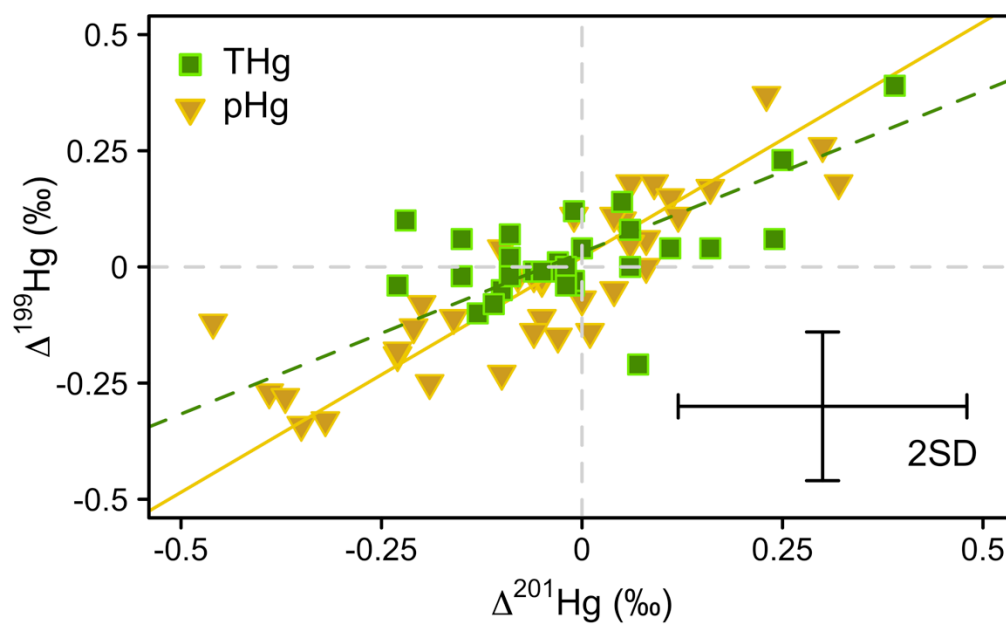


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665 **Figure S1. Top: Sampling locations K1, K2 in the Mediterranean Sea (purple), Atlantic Ocean (yellow)**  
666 **and Fram Strait (green). Bottom: Zoom on the 4 Mediterranean locations, with main station K2 (large**  
667 **purple circle), and pHg station K1 and Julio (small purple circles), and Endoume pier in Marseille Bay**  
668 **(grey square).**

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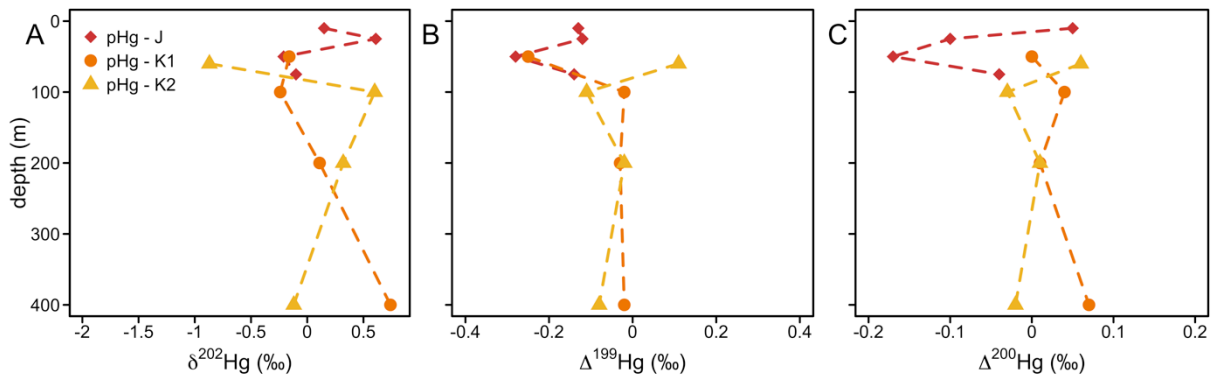


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672 **Figure S2: Scatterplot of odd Hg isotope mass-independent fractionation,  $\Delta^{201}\text{Hg}$  vs.  $\Delta^{199}\text{Hg}$  of all**  
 673 **tHg and pHg seawater data, including the published data by Motta et al. 2019. The dashed line**  
 674 **represents the York regression using IsoplotR<sup>25</sup> for tHg ( $\Delta^{199}\text{Hg} = 0.79(\pm 0.29) \Delta^{201}\text{Hg} + (0.03 \pm 0.04)$ ,**  
 675 **( $\pm$  se), MSWD = 0.2). The solid line represents the York regression for pHg ( $\Delta^{199}\text{Hg} = 1.01(\pm 0.09)$**   
 676  **$\Delta^{201}\text{Hg} + (0.02 \pm 0.02)$ , ( $\pm$  se), MSWD = 1.25). Error bars represent the 2 SD of replicate procedural**  
 677 **standards for tHg and pHg.**

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681 **Figure S3. Depth profile of particulate Hg stable isotope composition at three stations in the**  
 682 **Mediterranean during the June 2017 campaign. A: mass-dependent fractionation ( $\delta^{202}\text{Hg}$ ), B: odd**  
 683 **mass-independent fractionation ( $\Delta^{199}\text{Hg}$ ), C: even mass-independent fractionation ( $\Delta^{200}\text{Hg}$ ).**

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