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1 **Mercury sources and fate in a large brackish ecosystem (the Baltic Sea) depicted by**  
2 **stable isotopes**

3

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13

14 **ABSTRACT**

15 Identifying Hg sources to aquatic ecosystems and processes controlling the levels of monomethylmercury (MMHg)  
16 is critical for developing efficient policies of Hg emissions reduction. Here we measured Hg concentrations and  
17 stable isotopes in sediment, seston and fishes from the various basins of the Baltic Sea, a large brackish ecosystem  
18 presenting extensive gradients in salinity, redox conditions, dissolved organic matter (DOM) composition and  
19 biological activities. We found that Hg mass dependent fractionation (Hg-MDF) values in sediments mostly reflect  
20 a mixing between light terrestrial Hg and heavier industrial sources whereas odd Hg isotope mass independent  
21 fractionation (odd Hg-MIF) reveals atmospheric inputs. Seston presents intermediate Hg-MDF and odd Hg-MIF  
22 values falling between sediments and fish but in the north, high even Hg-MIF values suggests the preferential  
23 accumulation of wet-deposited Hg. Odd Hg-MIF values in fish indicate an overall low extent of MMHg  
24 photodegradation due to limited sunlight exposure and penetration, but also reveals large spatial differences. The  
25 photodegradation extent is lowest in the central basin with recurrent algal blooms due to their shading effect and  
26 highest in the northern, least saline basin with high concentrations of terrestrial DOM. As increased loads of  
27 terrestrial DOM are expected in many coastal areas due to global changes, its impact on MMHg photodegradation  
28 needs to be better understood and accounted for when predicting future MMHg concentrations in aquatic  
29 ecosystems.

30

31 **Keywords:** Hg stable isotopes; Hg sources; MMHg photodegradation; dissolved organic matter.

32 **Synopsis:** Hg stable isotopes helps decipher Hg sources and transformations along gradients in the Baltic Sea and  
33 highlights the importance of terrestrial DOM on the extent of MMHg photodegradation.

34

35

## 36 INTRODUCTION

37 Humans are predominantly exposed to mercury (Hg) through the consumption of seafood products<sup>1</sup>, in which Hg  
38 is mostly present as the neurotoxic compound monomethylmercury (MMHg). Concentrations of MMHg in seafood  
39 depend on the efficiency of MMHg bioconcentration from water to plankton and its bioamplification through food  
40 webs.<sup>2,3</sup> The presence of inorganic Hg (the substrate for MMHg formation) in aquatic ecosystems can be ascribed  
41 to multiple sources: direct atmospheric deposition (dry and wet), watershed runoff and industrial discharges. It is  
42 critical to know the contribution from each source to fish MMHg in a given ecosystem to develop efficient policies  
43 of Hg emissions reduction.<sup>4</sup> The production of MMHg is essentially a biotic process controlled by the interplay  
44 between the activity of specific methylating microorganisms and the bioavailability of inorganic Hg.<sup>5</sup> On the contrary,  
45 the degradation of MMHg can proceed through several biotic and/or abiotic pathways with photodegradation  
46 considered a major sink in the photic zone.<sup>6,7</sup>

47 Over the past two decades, measurements of Hg stable isotopes has emerged as a major tool to advance our  
48 understanding of Hg cycling in the environment. Based on their mass-dependent and mass-independent isotope  
49 fractionation (Hg-MDF and -MIF, respectively), isotopes are useful for both differentiating Hg sources with  
50 contrasted isotopic signatures and informing on the extent, mechanisms and conditions of species transformations.<sup>8</sup>  
51 In soils and sediments, binary or ternary mixing models have been used to discriminate between Hg originating  
52 from contaminated point sources (industrial and/or mining activities with slightly negative Hg-MDF and near zero  
53 Hg-MIF)<sup>9-11</sup> and background Hg sources, i.e. terrestrial inputs with largely negative Hg-MDF and Hg-MIF versus  
54 the atmospheric ones.<sup>12-14</sup> The contribution of atmospheric inputs is however especially difficult to estimate as both  
55 their Hg-MDF and -MIF can be highly variable in background atmosphere but especially when point-source  
56 emissions are involved.<sup>15</sup> Lately the use of even Hg-MIF values ( $\Delta^{200}\text{Hg}$  and to a lesser extent  $\Delta^{204}\text{Hg}$ ) has emerged  
57 to specifically discriminate gaseous Hg inputs,<sup>12,16</sup> as atmospheric  $\text{Hg}^0$  exhibits slightly negative  $\Delta^{200}\text{Hg}$  values  
58 whereas Hg(II) in wet and dry depositions is characterized by slight to large positive values.<sup>16,17</sup>

59 All Hg species undergo numerous reactions in surficial environments, e.g. in the atmosphere, soils, snow and water  
60 column, before being taken up by organisms at the base of food webs but only photochemical reactions specifically  
61 induce large and characteristic Hg-MIF of odd and even isotopes.<sup>18</sup> The  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope has turned out to be  
62 a reliable indicator for the type of reactions involved (Hg(II) photoreduction vs MMHg photodegradation),<sup>19</sup> the  
63 mechanisms causing MIF (magnetic isotope effect vs nuclear volume effect),<sup>20</sup> and the Hg bonding environment

64 including the nature of the Hg ligands and the Hg to ligands ratio.<sup>21-23</sup> Similarly, the even Hg-MIF slopes are  
65 emerging as a new indicator of photochemical reactions occurring in the upper atmosphere.<sup>24,25</sup>

66 Hg stable isotopes are also powerful tracers to examine the environmental controls of MMHg cycling, e.g. its  
67 production depth in aquatic environments or the influence of light transmission and attenuation for its  
68 photodegradation,<sup>26-28</sup> by analyzing high-trophic level organisms that contain predominantly MMHg. They can also  
69 be used as ecological tracers to distinguish populations and provide unique information on animal movements and  
70 their foraging habits within ecosystems.<sup>8,29</sup> One important assumption underlying these studies is the absence of  
71 Hg MIF in organisms after its accumulation. This is in contrast to Hg-MDF that has been shown to occur in higher  
72 organisms, due to MMHg degradation and excretion.<sup>8</sup> Therefore, the MMHg isotopic signature in organisms is  
73 useful to infer the transformations it has undergone, especially its photodegradation that is mainly controlled by  
74 light radiation intensity and penetration as well as the chemical speciation of aqueous MMHg.<sup>30,31</sup>

75 Direct photolysis of MMHg is not possible under environmental conditions in aquatic ecosystems and the presence  
76 of dissolved organic matter (DOM) is required to trigger MMHg photodegradation.<sup>7</sup> Both the concentration and  
77 composition of DOM influence the extent of photodegradation through their effect on light transmission,  
78 production/consumption of reactive oxygen species, and Hg complexation.<sup>32,33</sup> The rates of MMHg  
79 photodegradation increase with dissolved organic carbon (DOC) concentrations till a breaking point (5 – 10 mg L<sup>-</sup>  
80 <sup>1</sup>) after which the reaction is inhibited due to either shading or the scavenging of reactive oxygen species.<sup>27,34,35</sup> The  
81 complexation of MMHg by thiol groups has been found to be key as it weakens the Hg-C bond<sup>36-38</sup> and  
82 photodegradation has been shown to be more efficient when aromatic DOM is involved.<sup>39,40</sup> Accordingly, differences  
83 in MMHg photodegradation rates depending on the size or chemical fraction of DOM have been evidenced<sup>41,42</sup> and  
84 in wetlands and rice fields, higher MMHg losses were related to optical signatures of less labile, humic DOM.<sup>43</sup>

85 However, the effect of DOM quality on the extent of MMHg photodegradation has not been evaluated at large scale  
86 in aquatic ecosystems.

87 In this study, we investigated Hg stable isotopic signature in sediment, seston and fish samples from the various  
88 basins of the Baltic Sea, a semi-enclosed sea with a large freshwater influence and spatial gradients in several key  
89 factors known to influence Hg species transformations and bioaccumulation including salinity, redox conditions,  
90 light, ice cover, presence of algae as well as OM concentration and quality. The salinity, temperature and nutrient  
91 loads are highest in the southern Baltic Sea leading to higher photosynthetic primary production rate and thus to

92 the development of large oxygen depleted areas with a sustained production of MMHg in the anoxic part of the  
93 water column.<sup>44</sup> Because of a lower temperature and larger OM inputs by river discharge in the northern Baltic Sea,  
94 the primary production is lower and the fraction of allochthonous to autochthonous OM is higher, which can impact  
95 both MMHg production, bioavailability and bioaccumulation.<sup>45,46</sup> We combined concentrations and speciation data  
96 with the isotopic signatures observed in the various compartments, trophic levels and spatial origin to provide new  
97 insights into the sources, bioaccumulation and transformations of Hg species in this large brackish ecosystem. We  
98 especially discuss the factors controlling MMHg photodegradation in the various basins and highlight the impact of  
99 the terrestrial DOM gradient on the extent of this reaction.

100

## 101 **EXPERIMENTAL SECTION**

### 102 **Study site, sample collection and ancillary data**

103 Sample types and stations from which sediment, plankton and fish samples were collected are presented in Figure  
104 1 together with our division of the sampling locations into four Baltic Sea basins. Surface sediment samples (0 – 2  
105 cm, n = 29) were obtained from the Swedish Geological Survey archive and were selected from a variety of sites  
106 (coastal vs offshore and contaminated vs pristine) to provide a sufficient spatial coverage and representation of  
107 various sources of Hg. Samples were collected between 1992 and 2007 as part of Sweden's national environmental  
108 monitoring program that takes place every 6<sup>th</sup> year and stored freeze-dried in closed containers. Seston samples  
109 (n = 24) were collected using a 90 µm mesh-size net during field campaigns in July-August 2015 and June-  
110 November 2016 that have been previously described.<sup>44</sup> In short, on cruises in the Baltic Proper and Kattegat,  
111 samples were collected from the upper 20 m of the water column but the net was closed before breaching the  
112 surface to avoid getting filamentous cyanobacteria, often present at the sea surface, in the net. On cruises in the  
113 Bothnian Bay and Sea, samples were collected from the entire water depth at each sampling station (8 - 125 m).  
114 Samples were always transferred from the net to 500 ml HDPE bottles and frozen on board.

115 Herring and cod samples (n = 45, female specimen of 2-5 and 2 years age, respectively) were obtained from the  
116 Swedish Environmental Specimen Bank. They were collected in fall 2013 as part of the Marine Monitoring  
117 Programme for Contaminants in Marine Biota and their length, age, weight as well as their muscle  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$   
118 values were measured.<sup>47</sup> The latter were then corrected for lipids according to equation 1:<sup>48</sup>

$$119 \delta^{13}\text{C}_{\text{norm}} = \delta^{13}\text{C}_{\text{untreat}} - 3.32 + 0.99 \times \text{C:N} \quad \text{eq 1}$$

120 The Baltic herring (*Clupea harengus*) is found in the various basins throughout the Baltic Sea whereas the Atlantic  
121 cod (*Gadus morhua*) is not present in the northern part due to the low salinity. Moreover, there are two distinct  
122 stocks of cod, a western and an eastern one, that partially mix in the southern part of the Baltic Sea.<sup>49</sup> The trophic  
123 levels (TL) of fishes were calculated with equation 2 by matching the  $\delta^{15}\text{N}$  data from the fish with  $\delta^{15}\text{N}$  of mussels  
124 based on areas of collection in the Baltic Sea.

$$125 \text{TL}_{\text{fish}} = (\delta^{15}\text{N}_{\text{fish}} - \delta^{15}\text{N}_{\text{mussels}}) / \text{TLF} + 2 \quad \text{eq 2}$$

126 where TLF is the trophic level fractionation of  $\delta^{15}\text{N}$  and the trophic position of mussels are assumed to be two. We  
127 use a value of 2.4 ‰ for the trophic level fractionation as previously found for the Baltic Sea,<sup>50</sup> and  $\delta^{15}\text{N}$  values for  
128 mussels from previous studies.<sup>47,51</sup>

129 Cumulated PAR and UV irradiance data were obtained from the Swedish Meteorological and Hydrological Institute  
130 (SMHI) and averaged over the period 2012 – 2013. Salinity, secchi depth and concentrations of humic substances  
131 were also obtained from SMHI and are from monthly cruises conducted across the Baltic Sea. When available,  
132 salinity and humic substances were taken from the same station as the fish and when not we used the nearest  
133 available station. Salinity and humic substances were averaged over the top 50 m depth. DOC concentrations were  
134 obtained from Seidel et al.<sup>52</sup>

135

### 136 **Measurements of Hg concentrations and isotopic composition.**

137 HgT concentrations in sediments and some fish were available through the Swedish national environmental  
138 monitoring,<sup>47,53</sup> but seston samples as well as some fish samples for which HgT values were not available were  
139 analyzed with total Hg analyzers (either Leco AMA254 or Milestone DMA-80). MMHg concentrations in sediments,  
140 seston and fish were determined after acidic or basic extraction of freeze-dried samples using species-specific  
141 isotope dilution and (thermal desorption) gas chromatography inductively coupled plasma mass spectrometry  
142 according to established protocols.<sup>54,55</sup> Extraction and/or quantification of Hg total and species concentrations were  
143 validated with various certified reference materials, i.e. IAEA 405, CNRC TORT-2&3, JCR ERM CE-464 and BCR-  
144 414, and NIST SRM-1947.

145 For stable isotopes analysis, sediments and seston samples (0.5 g) were first extracted with a 3:1  $\text{HNO}_3/\text{HCl}$  mixture  
146 for 12 h at 85 °C, then  $\text{H}_2\text{O}_2$  was added and samples were further heated at 85 °C for 12 h. Fish samples (0.2 g)  
147 were extracted for 12 h at 85 °C with a 2:1  $\text{HNO}_3/\text{H}_2\text{O}_2$  mixture. Analyses were carried out with a multicollector-  
148 inductively coupled plasma-mass spectrometer (MC-ICP-MS, Nu Instruments) using either introduction with cold  
149 vapor generation (CVG) or dual amalgamation on gold (DA-Au) using a Tekran 2600 system for low-concentrated  
150 samples.<sup>56</sup> In both cases, a desolvation nebulization system (DSN-100, Nu Instrument) was used to introduce a  
151 certified thallium solution (NIST-SRM-997) for instrumental mass-bias correction using the exponential fractionation  
152 law. We used a standard-sample bracketing system to calculate  $\delta$  values (in ‰) relative to the reference Hg  
153 standard NIST SRM 3133. Reference materials NIST-8610 (UM-Almaden), -1944 and -1947, ERM BCR 414 and



154 CE-464 were used as secondary standards (Table SI-1). Isotopic ratios were calculated by the Linear Regression  
155 Slope (LRS) method for the DA-Au introduction technique as described previously.<sup>56</sup> The common  $\delta$  notation is  
156 used to express the Hg isotopic compositions:

$$\delta^{xxx} \text{Hg} (\text{‰}) = \left[ \frac{\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}}_{\text{sample}}}{\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}}_{\text{NIST 3133}}} - 1 \right] \times 1000$$

157  
158 where xxx can be either 204, 202, 201, 200 or 199 and  $(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{NIST 3133}}$  is the averaged isotopic ratio of the two  
159 bracketing standards. The  $\Delta$  notation is used to express the mass independent fractionation (MIF), calculated as  
160  $\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - \beta_{\text{kin}} \times \delta^{202}\text{Hg}$  where  $\beta_{\text{kin}} = \ln(m_{198}/m_{\text{xxx}})/\ln(m_{198}/m_{202})$ .<sup>57</sup>

161

## 162 RESULTS AND DISCUSSION

163 ***Sedimentary Hg reflects the mixing between terrestrial, industrial and atmospheric sources.*** As sediment  
164 samples were selected to represent both coastal and offshore as well as contaminated and pristine environments,  
165 the range of HgT concentrations is large, from 64 to 10 690 ng g<sup>-1</sup> with a median value of 140 ng g<sup>-1</sup> (interquartile  
166 range (IQR) = 167) (Table SI-2). MMHg concentrations range from 0.1 to 13.6 ng g<sup>-1</sup> and contribute on average 0.7  
167 ± 0.7 % to HgT, similar to other coastal environments and great lakes.<sup>58,59</sup> Our HgT values are overall in agreement  
168 with two recent studies that demonstrated a strong anthropogenic pollution during the second half of the past  
169 century that overall increased Hg concentrations in the Baltic Sea sediments over its pre-industrial background (20  
170 – 50 ng g<sup>-1</sup>)<sup>60</sup> and also led to high Hg concentrations in some local hotspots (industrial and war waste sites).<sup>60,61</sup>  
171  $\delta^{202}\text{Hg}$  in sediments ranges from - 2.3 to - 0.1 ‰ (Table SI-2) and with the exception of 4 outliers, it is linearly and  
172 negatively correlated to 1/HgT (Figure SI-1,  $r^2 = 0.5$ ,  $p\text{-value} = 10^{-4}$ ). This trend indicates mixing between a lighter  
173 Hg end-member with an average  $\delta^{202}\text{Hg}$  value of  $- 2.18 \pm 0.45$  ‰ (calculated for an average background HgT  
174 concentration of 35 ng g<sup>-1</sup>) and a heavier Hg end-member with an average  $\delta^{202}\text{Hg}$  value of  $- 0.55 \pm 0.11$  ‰ (y-  
175 intercept in Figure SI-1), the latter being very similar to the value previously found by Gehrke.<sup>62</sup> Although the data  
176 are relatively scattered, no specific trend is apparent between basins suggesting that both end-members are  
177 relatively homogeneous across the sites investigated. The heavy end-member value is typical of industrial sources  
178 and matches the  $\delta^{202}\text{Hg}$  value reported for cinnabar (HgS)<sup>63</sup> as well as the values previously found in sediments  
179 from polluted sites across Sweden.<sup>10</sup> With respect to their concentrations, the 4 outliers exhibit a much lighter  
180 isotopic composition with  $\delta^{202}\text{Hg}$  values of about - 2.3 ‰ and slightly positive odd-MIF values ( $\Delta^{199}\text{Hg}$  from 0.05 to  
181 0.10 ‰). Their isotopic composition is very similar to those reported for a coastal site polluted by elemental Hg  
182 (exhibiting specifically low  $\delta^{202}\text{Hg}$  values) located in the Bothnian Sea south of these 4 samples.<sup>10</sup> The light end-  
183 member is close to the negative  $\delta^{202}\text{Hg}$  values previously reported for boreal forest soils ( $- 2.6$  to  $- 2.9$  ‰), which  
184 results from the large MDF that occur during uptake and oxidation of atmospheric gaseous Hg by foliage.<sup>64,65</sup> This  
185 MDF is conserved when Hg is transferred to soils and adjacent aquatic ecosystems<sup>66</sup> and the higher  $\delta^{202}\text{Hg}$  values  
186 in sediments compared to soils can reflect both the photoreduction of this terrestrially derived Hg(II) in the water  
187 column<sup>67</sup> and its mixing with heavier Hg inputs, i.e. atmospheric and/or industrial Hg brought in the various basins  
188 by direct deposition, river discharges,<sup>45</sup> and/or sediment redistribution.

189 The range of Hg odd-MIF values in sediments is narrow (Table SI-1,  $\Delta^{199}\text{Hg} = -0.16 - 0.10 \text{ ‰}$ ) as commonly  
190 observed,<sup>18</sup> There is a positive trend between  $\Delta^{199}\text{Hg}$  and  $1/\text{HgT}$  in sediments but it is not significant (Figure SI-1,  
191  $p\text{-value} = 0.35$ ). However, sediments with low Hg content exhibit significantly higher  $\Delta^{199}\text{Hg}$  than values previously  
192 observed in boreal forest soils ( $-0.5$  to  $-0.25 \text{ ‰}$ ), suggesting again mixing with atmospheric Hg (wet and dry) and/or  
193 photoreduction of Hg(II) before its deposition to sediments. The  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope in sediments is indeed  $1.1 \pm$   
194  $0.3$  (not shown,  $r^2 = 0.59$ ,  $p\text{-value} = 3 \cdot 10^{-4}$ ) close to the one imprinted by Hg(II) photoreduction that can occur in the  
195 water column,<sup>19,67</sup> but also in the atmosphere.<sup>25</sup> Regarding Hg even-MIF,  $\Delta^{200}\text{Hg}$  values ranged from  $-0.04$  to  $0.08$   
196  $\text{‰}$  and  $\Delta^{204}\text{Hg}$  from  $-0.22$  to  $0.14 \text{ ‰}$  (Table SI-2, Figure 3), which is also similar to previous observations in  
197 freshwater and coastal sediments.<sup>12,68,69</sup> No significant relationships were found between Hg even-MIF and  
198 concentrations and the data scattering render their interpretations difficult. The discrimination of Hg sources to  
199 sediments is difficult as their Hg isotopic signature results from the mixture of multiple sources and processes  
200 inducing isotopic fractionation. Isotopic signatures of soils and especially atmospheric Hg, for which both Hg-MDF  
201 and  $-$ MIF values can be highly variable, need to be characterized at a regional level before the contribution of each  
202 source of Hg to the Baltic Sea sediments can be better deciphered.

203  
204 **Biota Hg concentrations and MDF are primarily controlled by trophic level.** HgT in seston range from 1.5 to  
205  $60 \text{ ng g}^{-1}$  (d.w., average  $18 \pm 16 \text{ ng g}^{-1}$ ,  $n = 23$ ) with the highest values found at the northernmost, least saline  
206 station Harufjorden ( $31 \pm 16 \text{ ng g}^{-1}$ , Figure SI-2). The percentage of MMHg in seston vary over the full range, from  
207  $0.5$  to  $98 \text{ ‰}$  and averages  $27 \pm 22 \text{ ‰}$  of HgT. In fish muscle, HgT concentrations range from  $34$  to  $530 \text{ ng g}^{-1}$  (d.w.)  
208 and average  $137 \pm 102 \text{ ng g}^{-1}$  to which MMHg contribution is constant at  $93 \pm 3 \text{ ‰}$ . The lowest concentrations are  
209 found in herrings from the Bothnian Sea offshore station ( $48 \pm 12 \text{ ng g}^{-1}$ , Table SI-3) while the highest are found in  
210 cod from the Fladen station ( $312 \pm 135 \text{ ng g}^{-1}$ ) which is explained by the higher trophic level of cod compared to  
211 herring. Overall, the trophic magnification slope determined from our samples is  $0.14 \pm 0.08$  (Figure SI-3a,  $r^2 =$   
212  $0.78$ ), which is similar to the value previously reported for a pelagic food chain from the Baltic Sea,<sup>70</sup> and also in  
213 line with values compiled by Lavoie et al.<sup>2</sup> for a variety of ecosystems (average slope for HgT =  $0.16 \pm 0.11$ ).  
214 With the exception of one outlier ( $\delta^{202}\text{Hg} = -2.47 \text{ ‰}$ ), the  $\delta^{202}\text{Hg}$  values in seston range from  $-1.75$  to  $-0.26 \text{ ‰}$  and  
215 averaged  $-1.1 \pm 0.5 \text{ ‰}$  (1 SD, Figure 2a and Table SI-4). These are very similar to sediments in range and average

216 value ( $-1.2 \pm 0.6 \text{ ‰}$ , 1 SD), which stems from the seston samples being dominated by Hg(II). There is only a weak  
217 relationship between  $\delta^{202}\text{Hg}$  in seston and 1/HgT (Figure SI-4a), reflecting both the presence of MMHg in different  
218 proportions and the fact that seston and sediments do not accumulate Hg(II) with the exact same signature (see  
219 below). As expected, the  $\delta^{202}\text{Hg}$  values in fish are higher ( $-0.29$  to  $0.73 \text{ ‰}$ , Figure 2b) and the range between the  
220 lowest and highest value is smaller ( $1.0 \text{ ‰}$ ) than for seston ( $1.5 \text{ ‰}$ ) and sediments ( $2.2 \text{ ‰}$ ). This reflects a  
221 homogenization (decrease in variability) of the Hg isotopic composition higher up in the food webs with higher  
222 organisms displaying a more integrative MMHg isotopic signature. The average  $\delta^{202}\text{Hg}$  from our fish samples is  
223  $0.27 \pm 0.23 \text{ ‰}$  (1 SD) with the lowest values found in herring from Angskarsklubb ( $-0.08 \pm 0.15 \text{ ‰}$ , 1 SD) whereas  
224 the highest values are found in herring from Fladen and Bothnian Sea offshore ( $0.55 \pm 0.12$  and  $0.51 \pm 0.09 \text{ ‰}$ ,  
225 respectively, 1 SD). Overall,  $\delta^{202}\text{Hg}$  values in biota increase on average by  $0.5 \pm 0.1 \text{ ‰}$  per trophic level (Figure  
226 SI-3b), consistent with values found in the Chinese Bohai Sea.<sup>69</sup> Higher trophic level biota thus accumulates a  
227 higher share of heavier Hg isotopes in MMHg (Figure SI-3c) and variations in  $\delta^{202}\text{Hg}$  among biota are mostly  
228 explained by their trophic level. However, many seston samples from the Bothnian Bay and cod from Fladen are  
229 below this trend revealing the accumulation of isotopically lighter Hg species. For seston from the Bothnian Bay,  
230 we prescribe this to the terrestrial inputs, most important to this basin, carrying lighter Hg isotopes. For cod from  
231 Fladen, they have been shown to have a more pronounced benthic feeding strategy as they live in shallow waters,<sup>71</sup>  
232 and they are therefore likely to accumulate more MMHg originating from sediments, that is less (photo)fractionated,  
233 compared to the pelagic herring and cod from SO Gotland that live in deeper waters.

234

235 ***Odd Hg-MIF in seston reflects in situ photochemical reactions and even Hg-MIF atmospheric Hg sources.***

236  $\Delta^{199}\text{Hg}$  values in seston range from  $-0.04$  to  $2.18 \text{ ‰}$  (Table SI-4) and seston samples are found in intermediate  
237 positions, depending on their trophic level and Hg speciation, between the background sediment and the fish  
238 signatures on the  $\Delta^{199}\text{Hg} - \delta^{202}\text{Hg}$  plot (Figure 2a). Overall, the  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope in seston is  $0.92 \pm 0.11$  (Figure  
239 2c), close to the slope produced by the photoreduction of Hg(II).<sup>19</sup> This results from the predominance of Hg(II) over  
240 MMHg (73 vs 27 % average, respectively) and indicates that most of the Hg present in seston has undergone some  
241 photochemical processing, either Hg(II) photoreduction or MMHg photodegradation. However, the  $\Delta^{199}\text{Hg}$  signal in  
242 seston is also positively albeit weakly correlated to the % MMHg (Figure SI-4b,  $R^2 = 0.50$ ) and negatively to the %

243 Hg(II) (not shown), suggesting that the MIF signal is dominated by the contribution of MMHg in seston of higher  
244 trophic level. The weak correlation between MIF values and % MMHg is likely due to the spatial and seasonal  
245 variability of photochemical processes affecting both MMHg and Hg(II) in the water column before their uptake.  
246 Photochemical reactions are affected by a number of parameters, among which light radiation intensity and  
247 wavelength as well as DOM concentrations are the most important,<sup>30,32,72</sup> and all of them vary both spatially and  
248 temporally across the Baltic Sea (see below).

249 Even Hg-MIF values in sediment, seston and fish are presented in Figure 3. Median  $\Delta^{200}\text{Hg}$  values in seston and  
250 fish are higher than in sediments (0.12, 0.03 and 0.01 ‰, respectively), which is consistent with previous studies  
251 on aquatic invertebrates and fish,<sup>26,27,73-75</sup> but it is particularly noteworthy that several values are above 0.2 ‰ in  
252 seston. Hg isotopic data in phyto- or zooplankton are particularly scarce,<sup>75,76</sup> but the maximum value of 0.58 ‰  
253 observed in our study is to the best of our knowledge the highest reported in such samples. These values are  
254 actually similar to values reported for seawater in the Canadian Arctic<sup>77,78</sup> and higher than many values reported  
255 for precipitations collected at low latitudes in the temperate zone,<sup>65,79-83</sup> with the exception of samples collected in  
256 Peterborough (44 °N) where  $\Delta^{200}\text{Hg}$  reached up 1.2 ‰ in both rain and snow.<sup>17</sup> The median  $\Delta^{200}\text{Hg}$  value is higher  
257 for seston than fish but this could result from a sampling bias as there are fewer seston samples that were not  
258 collected in the same year and their distribution is skewed towards northern stations compared to fish. In seston,  
259 the  $\Delta^{200}\text{Hg}$  values are higher than the  $\Delta^{204}\text{Hg}$  ones and even though not significant, the  $\Delta^{200}\text{Hg}/\Delta^{204}\text{Hg}$  slope (-0.28,  
260  $r^2 = 0.12$ , p-value > 0.05, Figure SI-4c) is very similar to the slopes reported for precipitations and marine biota.<sup>15,16</sup>

261 Our data therefore strengthen previous studies in suggesting that pelagic plankton and invertebrates preferentially  
262 accumulate Hg(II) originating from wet depositions that are characterized by positive  $\Delta^{200}\text{Hg}$  and negative  $\Delta^{204}\text{Hg}$   
263 values,<sup>65,80,84</sup> or MMHg formed from this Hg(II) pool.

264 It has been proposed that even Hg-MIF values in precipitation increases with latitude, implying an upper  
265 atmosphere origin of even-MIF.<sup>82,85</sup> Our data support this (i) as the Baltic Sea is located north of Peterborough  
266 (roughly from 55 to 65 °N) and (ii) because there is an apparent gradient in  $\Delta^{200}\text{Hg}$  average values along the Baltic  
267 Sea, from  $0.06 \pm 0.20$  ‰ in the south, western basin (Kattegat) to  $0.22 \pm 0.20$  ‰ in the northern basin (Bothnian  
268 Bay). The highest even-MIF values are found in the northern basin which can be explained by the fact that (i) deep  
269 stratospheric intrusions are likely more common towards the north as the troposphere height decreases towards

270 the poles,<sup>85</sup> and (ii) snow precipitation is more important in this basin (> 40 % of total precipitations vs 20 % in the  
271 south)<sup>86</sup> and the highest even-MIF values have been reported in snow until now.<sup>17</sup> Similarly to odd-MIF, the  $\Delta^{200}\text{Hg}$   
272 signal in seston is also overall positively (albeit weakly) correlated to the % MMHg (Figure SI-4d,  $R^2 = 0.37$ , p-value  
273 < 0.005), which indicates that at higher trophic levels in the food web the even-MIF signal is eventually dominated  
274 by the contribution of MMHg to total Hg. However, some elevated values are also found in samples with MMHg <  
275 30 %, demonstrating an important contribution of Hg(II) in some cases. Our data suggests that the analysis of  
276 seston is promising to discriminate the contribution of Hg wet deposition to the water column. It seems to be able  
277 to reflect this atmospheric signature at a higher temporal and spatial resolution compared to fish that accumulates  
278 a broader temporal and spatial average MMHg signal or sediments, where it is largely diluted by the terrestrial and  
279 anthropogenic Hg inputs.

280

281 ***Odd Hg-MIF in fish reveals basin-specific MMHg photodegradation patterns.*** Odd Hg-MIF is found in all fish  
282 samples, whatever the fish species or sub-basins, with  $\Delta^{199}\text{Hg}$  ranging from 0.33 to 3.04 ‰ and  $\Delta^{201}\text{Hg}$  from 0.21  
283 to 2.26 ‰ (Figure 2 and Table SI-3). The  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope is  $1.31 \pm 0.02$  (Figure 2c, linear fit, no weighting, p-  
284 value < 0.005, n = 51) when considering all fish samples, which is typical for freshwater fish as it reflects the slope  
285 imprinted during MMHg photodegradation in freshwater with excess DOM compared to MMHg.<sup>18,19,23,27,73,76,87</sup>  
286 However, cod from Fladen present a lower  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  ratio of  $1.08 \pm 0.22$  (n = 5) compared to the other fish  
287 even if their MMHg content is similar (90.9 – 98.6 %). This likely results from both their more pronounced benthic  
288 feeding that lead to the accumulation of both pelagic and benthic MMHg that is less or not photodegraded, and  
289 their migration strategy. It has been evidenced that most individuals from the population in Kattegat (Fladen)  
290 undertake spawning migrations towards the North Sea,<sup>88</sup> and it is well established that a lower slope is imprinted  
291 during MMHg photodegradation in low DOM marine waters.<sup>18,28,29,69,89</sup>

292 There is a good separation of the various fish populations in the  $\delta^{202}\text{Hg} - \Delta^{199}\text{Hg}$  space (Figure 2b), suggesting that  
293 they could be discriminated based on their Hg isotopic signatures as previously demonstrated for juvenile Seabass  
294 at the European scale.<sup>29</sup> This separation stems partly from the multiple Hg sources entering the food web and the  
295 food web structure as discussed above but also from a different degree of MMHg photodegradation between basins  
296 controlled by a combination of environmental factors. There is a clear upward shift from an average  $\Delta^{199}\text{Hg}$  of 0.53

297  $\pm 0.29$  ‰ in herrings from Ostergarnsholm (Baltic Proper) to  $2.58 \pm 0.48$  ‰ in Harufjarden (Bothnian Bay). Contrary  
298 to seston,  $\Delta^{200}\text{Hg}$  values in herring are similar in the northern and central stations (from  $0.03 \pm 0.05$  ‰ for the Baltic  
299 Proper offshore to  $0.08 \pm 0.06$  ‰ for Holmoarna, vs  $-0.01 \pm 0.04$  ‰ for Fladen, Figure 4a). This result demonstrates  
300 that MMHg is formed from an homogenous pool of Hg with respect to atmospheric sources and therefore that the  
301 odd Hg-MIF trends observed are due to differences in MMHg photodegradation rates.

302 The maximum  $\Delta^{199}\text{Hg}$  values found in the Baltic Sea are relatively low compared to values observed in pelagic fish  
303 from other fresh or marine waters (e.g. Lake Baikal, high altitudes Tibetan lakes, North American great Lakes or  
304 the Pacific ocean)<sup>76,90,73,28</sup> that often reach 6 – 7 ‰, sometimes up to 9 ‰, indicating that the extent of MMHg  
305 photodegradation in the Baltic Sea is relatively limited. Based on a MIF enrichment factor of 14.3 ‰,<sup>22,23</sup> we  
306 calculated that the extent of MMHg photodegradation before incorporation into the food web averages 4 - 5 % in  
307 the central Baltic Sea (Baltic Proper), 6 % in the Kattegat and up to 16 % in the northern, less saline basins (Bothnian  
308 Sea and Bay). This limited MMHg photodegradation can be explained by a combination of factors, i.e. the amount  
309 of incident light, its penetration in the water column and the residence time of MMHg in the photic zone. Solar  
310 radiation is about 2-5 times lower in boreal regions compared to temperate or tropical ones and the light penetration  
311 in ice-free water of the Baltic Sea is comparably low. The secchi depth averages 11 m in the south Kattegat strait  
312 to 3 - 5 m in the Bothnian Bay (Figure SI-5a) compared to e.g. about 15 m in the Laurentian Great Lakes<sup>73</sup> and 45  
313 m in the Atlantic and Pacific oceans.<sup>28</sup> The light penetration and residence time of Hg (about one year)<sup>45</sup> are limited  
314 by relatively high concentrations of DOM and/or POM throughout the entire Baltic Sea compared to marine waters  
315 and recurrent “massive” algae blooms that occur especially in the central part of the Baltic Sea, starting with diatoms  
316 and dinoflagellates in spring which are then replaced by filamentous cyanobacteria over the summer.<sup>91</sup> It is  
317 noteworthy that the lowest  $\Delta^{199}\text{Hg}$  values are indeed observed at the Ostergarnsholm and Baltic proper offshore  
318 stations where algae blooms form a thick cover that severely decreases light penetration in the water column but  
319 also likely protects Hg species from light exposure following their internalization. Moreover, light penetration is also  
320 limited by ice cover in the Baltic Sea and this certainly lower the extent of MMHg photodegradation overall,  
321 especially in the northern basins (Bothnian Sea and Bay), as already demonstrated in other northern ecosystems.<sup>92</sup>  
322 The  $\Delta^{199}\text{Hg}$  values in fish presented here are thus likely lower than expected as the maximum ice extents were  
323 above average from 2011 to 2013 (177 000 to 309 000 km<sup>2</sup> compared to an average value of 140 000 km<sup>2</sup> over the

324 past 30 years). On the contrary, values in seston might be higher than expected as ice extents over 2015 – 2016  
325 were lower than average (51 000 to 110 000 km<sup>2</sup>).<sup>93</sup> Finally, production of MMHg in the anoxic parts of the water  
326 column has been previously established in the Baltic Proper basin<sup>44</sup> and deep waters could thus also contribute a  
327 non or less fractionated MMHg to biota. Further studies are required to clarify this point as it was previously found  
328 that turbulent diffusion across the hypoxic-anoxic interface was a likely source of MMHg to the hypoxic zone but  
329 not to normoxic waters where fish spend most of their time.<sup>44</sup>

330

331 **MMHg photodegradation is driven by the terrestrial fraction of DOM.** There is a negative relationship between  
332  $\Delta^{199}\text{Hg}$  in herring and incident light irradiance over the inner Baltic Sea (Kattegat excluded), both with respect to  
333 UV (Figure 4a) and PAR (Figure SI-5a). This trend cannot be explained by light penetration as the secchi depth  
334 overall decreases from south to north and therefore shows no correlation with  $\Delta^{199}\text{Hg}$  (Figure SI-5b&c).<sup>94</sup> The  
335  $\Delta^{199}\text{Hg}$  value in Kattegat is higher than expected from the trend and this is likely the result of the larger irradiance  
336 and deeper light penetration in this basin, about twice that of the others. The negative relationship between  $\Delta^{199}\text{Hg}$   
337 and light penetration in the inner Baltic Sea (Baltic Proper, Bothnian Sea and Bothnian Bay) is a surprising finding  
338 as previous studies have found a positive correlation between the extent of MMHg photodegradation and light  
339 penetration in both fresh and marine waters.<sup>27,28,73</sup> There is also a clear negative correlation of  $\Delta^{199}\text{Hg}$  values with  
340 salinity over the inner Baltic Sea (Figure SI-6a,  $y = -0.5 + 3.7$ ,  $r^2 = 0.9$ , Kattegat excluded) that demonstrates the  
341 importance of freshwater inputs to enhance photodegradation of MMHg along the mixing zone. This increase in  
342  $\Delta^{199}\text{Hg}$  towards the northern, less saline waters, is well explained by the concentration of humic substances (Figure  
343 SI-7a, slope = 0.18,  $r^2 = 0.8$ ), that also increases from an average of  $8.3 \pm 0.2 \mu\text{g L}^{-1}$  in Ostergarnsholm to  $17.5 \pm$   
344  $1.5 \mu\text{g L}^{-1}$  in Harufjarden (while DOC concentrations only increases from 3.5 to 3.9 mg L<sup>-1</sup>, Figure SI-7b).  
345 The contribution of terrestrial DOC to the total DOC in the Baltic Sea has previously been estimated to increase  
346 from about 40 % in the Baltic Proper to 50 % in the Bothnian Sea and up to 80 % in the Bothnian Bay.<sup>95</sup> In this  
347 study from Deutsch et al.,<sup>95</sup>  $\delta^{13}\text{C}$  values in high molecular weight DOM (> 1 kDa) ranged from about -27 to -25 ‰  
348 across the Baltic Proper, Bothnian Sea and Bay basins and were found to be linearly correlated with salinity values  
349 ranging from 2 to 7 psu. Here we find that across the inner Baltic basins,  $\Delta^{199}\text{Hg}$  values in herring are negatively  
350 correlated to the  $\delta^{13}\text{C}$  values measured in the fish themselves, ranging from about -26 to -20 ‰ (Figure 4b,  $y = -$



351 0.38 - 7.36,  $r^2 = 0.81$ ,  $p$ -value < 0.001, regression performed on individual points). The  $\delta^{13}\text{C}$  values also point to  
352 two “sub-populations” of herring in the northern Bothnian Bay (Harufjarden station) with distinct  $\Delta^{199}\text{Hg}$  values  
353 (average  $1.9 \pm 0.1$  and  $2.9 \pm 0.1$  ‰, Figure 4b). This suggests that the gradient in humic substances concentrations  
354 from coastal to open-sea conditions generally observed in the Baltic Sea has a strong impact on the extent of  
355 MMHg photodegradation. Particularly high humic substances concentrations up to  $70 \mu\text{g L}^{-1}$  are observed along  
356 the Bothnian Bay coast (Figure SI-6b). Altogether, the relationships between Hg odd-MIF and salinity,  
357 concentrations of humic substances and  $\delta^{13}\text{C}$  strongly point to the terrestrial fraction of DOC as the key factor  
358 controlling the photodegradation of MMHg along the salinity gradient of this large estuarine ecosystem.

359 To the best of our knowledge, this is the first study to demonstrate at the ecosystem scale that MMHg  
360 photodegradation is enhanced by increasing low concentrations of terrestrial DOM. The importance of low  
361 molecular weight, aromatic DOM for the MMHg photodegradation reaction was previously demonstrated in several  
362 lab or field experiments with addition of model compounds or purified DOM extracts. For example, additions of  
363 fulvic acid up to several ten's of  $\text{mg L}^{-1}$  in natural waters were found to promote the reaction.<sup>38,39,41</sup> On the other  
364 hand, the negative effect of high molecular weight humic acid has been demonstrated with purified extracts,<sup>41</sup> but  
365 also by field studies focused on lakes with high DOC levels.<sup>27,35</sup> These latter studies have overall evidenced a  
366 decrease of the photodegradation extents with increasing DOC concentrations but the tipping point between  
367 enhancement and inhibition remains overall poorly defined. However, it has been suggested that 6 - 7  $\text{mg L}^{-1}$  of  
368 DOC seem to be optimal conditions for MMHg photodegradation in natural waters,<sup>23,34</sup> and here we found it to be  
369 at its highest where the more terrestrial and highest concentrations of DOC are found in the Baltic Sea (i.e. averages  
370 of 16 – 18  $\mu\text{g L}^{-1}$  for humic substances and 3.9  $\text{mg L}^{-1}$  for DOC at Holmoarna and Harufjarden). It gives a new  
371 perspective to the negative relationship previously observed between MMHg and humic OM in the northern Baltic  
372 Sea, which was hypothesized to be caused by a reduced availability of Hg(II) for microbial MMHg formation.<sup>46</sup> Our  
373 findings now strongly suggests that MMHg photodegradation also plays an important role for this negative  
374 relationship. It remains to be tested if terrestrial OM driven photodegradation is an important MMHg sink also in  
375 other types of coastal seas with higher light irradiance and penetration (e.g. in temperate regions). Based on our  
376 results it can be expected that the magnitude of this MMHg sink will increase with the large increased delivery of  
377 terrestrial OM to lakes, rivers and coastal ecosystems expected especially in the world's northern regions with  
378 climate and other global changes. Further studies are thus required to quantitatively assess the impacts of the

379 various OM fractions on MMHg photodegradation, especially the opposing effects of low and high molecular weight  
380 compounds, in order to better predict future MMHg concentrations in water and biota.

381

### 382 **Supporting Information.**

383 Hg isotopic composition of the various reference materials; Hg concentrations and isotopic composition in  
384 sediments from the Baltic Sea;  $\delta^{202}\text{Hg}$  versus  $1/\text{HgT}$  and  $\Delta^{199}\text{Hg}$  versus  $\delta^{202}\text{Hg}$  in sediments from the various basins  
385 of the Baltic Sea; Hg concentrations and isotopic composition in fish from the Baltic Sea; Hg concentrations and  
386 isotopic composition in seston from the Baltic Sea; HgT concentration in seston and fishes versus latitude and  
387 salinity;  $\log_{10}\text{HgT}$  concentrations versus  $\delta^{15}\text{N}$ ,  $\delta^{202}\text{Hg}$  versus trophic level and % MMHg versus trophic level for  
388 all biota samples (seston and fishes);  $\delta^{202}\text{Hg}$  versus  $1/\text{HgT}$ ;  $\Delta^{199}\text{Hg}$  versus % MMHg;  $\Delta^{200}\text{Hg}$  versus  $\Delta^{204}\text{Hg}$  and  
389  $\Delta^{200}\text{Hg}$  versus % MMHg in seston samples from the Baltic Sea;  $\Delta^{199}\text{Hg}$  in herring from the various basins versus  
390 incident PAR irradiance, Secchi depth in the various basins versus incident PAR irradiance and  $\Delta^{199}\text{Hg}$  in herring  
391 from the various basins versus Secchi depth.;  $\Delta^{199}\text{Hg}$  in herring from the various basins as a function of  
392 concentrations of humic substances and DOC.

393

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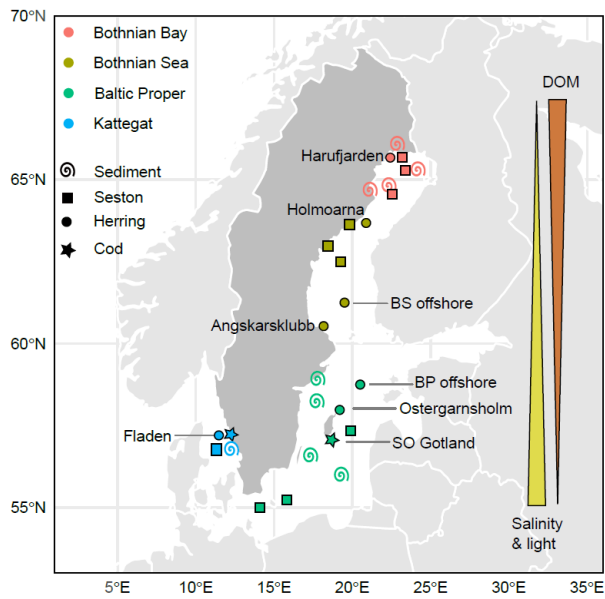
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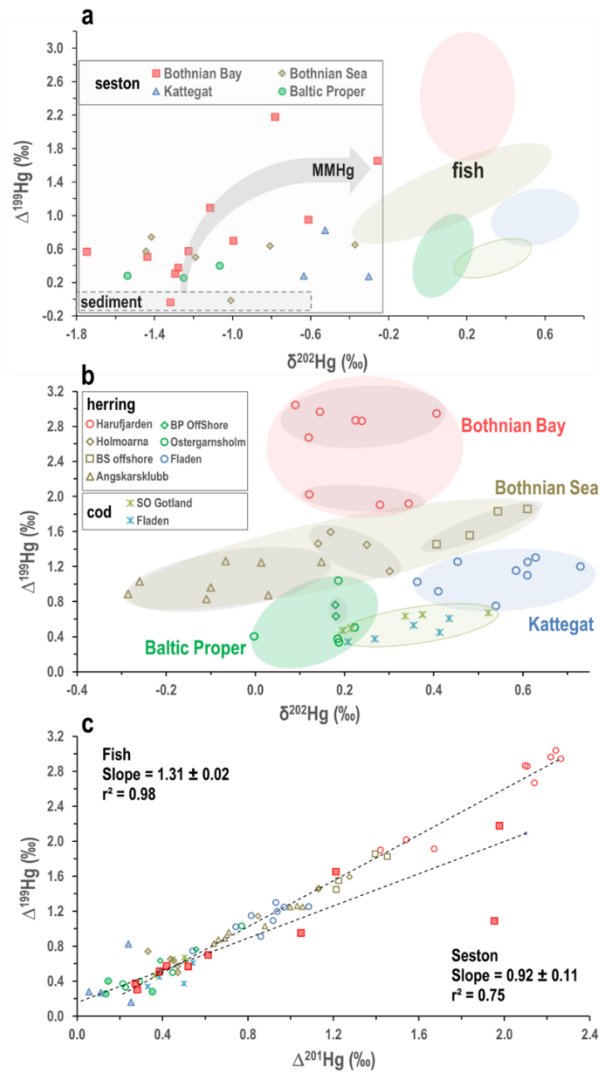


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721 **Figure 1:** Map of the Baltic Sea with the various types of samples analyzed and their location. Specific sampling  
 722 stations are indicated for seston and fishes while several sediment samples were collected at each sediment area  
 723 indicated. There are several latitudinal gradients across the various basins with increases in salinity and light  
 724 irradiation, and decreases in concentration and terrestrial fraction of DOM, from the Bothnian Bay to the Kattegatt.

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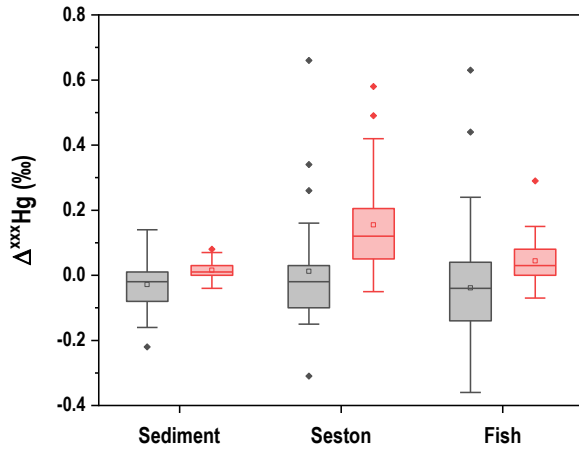


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728 **Figure 2:** (a)  $\Delta^{199}\text{Hg}$  versus  $\delta^{202}\text{Hg}$  in seston (contours of sediments and fish are given for indication); (b)  $\Delta^{199}\text{Hg}$   
 729 versus  $\delta^{202}\text{Hg}$  in fish samples according to their basins, stations and fish species; (c)  $\Delta^{199}\text{Hg}$  versus  $\Delta^{201}\text{Hg}$  in fish  
 730 and seston samples.

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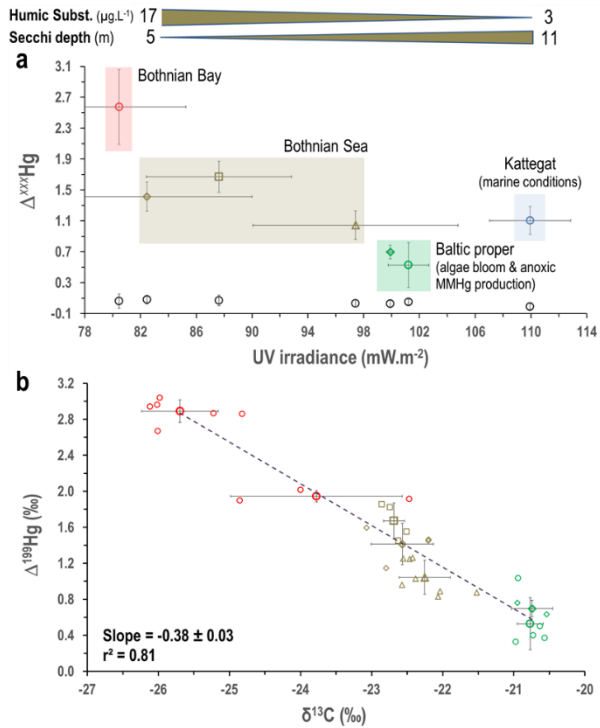


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734 **Figure 3:** Distribution of  $\Delta^{204}\text{Hg}$  (grey boxes) and  $\Delta^{200}\text{Hg}$  (red boxes) in sediment, seston and fish samples.

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738 **Figure 4:** (a)  $\Delta^{199}\text{Hg}$  (color coded) and their corresponding  $\Delta^{200}\text{Hg}$  values (black, open circles) in herrings from  
 739 the various basins of the Baltic Sea versus the average UV irradiance; (b)  $\Delta^{199}\text{Hg}$  in herrings from the various  
 740 basins (same color coding as in panel a) versus  $\delta^{13}\text{C}$ .