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1 **Oceanic mercury concentrations on both sides of the Strait of Gibraltar**  
2 **decreased between 1989 and 2012**

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5 **Abstract**

6 *Mercury (Hg) is a toxic metal that threatens the health of aquatic ecosystems and fish*  
7 *consumers. Its natural cycle has been deeply perturbed by anthropogenic Hg emissions,*  
8 *especially since the start of the Industrial Revolution circa 1850 AD. Anthropogenic Hg*  
9 *emissions from North America and Europe have decreased by a factor of two in the last*  
10 *decades following the implementation of strict regulations. The response of North Atlantic*  
11 *Ocean and Mediterranean waters to this decrease remains poorly documented by field*  
12 *observations. A comparison of results obtained between 1989 and 2012 shows a significant*  
13 *decrease of Hg concentrations in waters on both sides of the Strait of Gibraltar. West of*  
14 *Gibraltar, the Hg decrease ranges from ~35% in the upper North East Atlantic Deep Water*  
15 *to ~50% in the North East Atlantic Central Water. East of Gibraltar, the observed decrease*  
16 *is ~30% in the Western Mediterranean Deep Water. No decrease is observed in the deep*  
17 *Atlantic Ocean layer that formed before the industrial era. Our results strongly substantiate*  
18 *the effectiveness of global anti-pollution policies on Hg contamination in oceanic waters. A*  
19 *consequent decline of Hg bioaccumulation in Northeastern Atlantic and Western*  
20 *Mediterranean pelagic ecosystems is still to be verified.*

21

22 **Keywords:** *Mercury, Mediterranean Sea, Atlantic Ocean, Gibraltar*

23

## 24 1. Introduction

25 Mercury (Hg) is a trace element which affects human health primarily *via* marine fish  
26 consumption (e.g., Fitzgerald et al., 2007). Its toxicity is essentially due to the presence of  
27 methylmercury (MeHg), which biomagnifies up food webs (e.g., Clarkson and Magos, 2006).  
28 In aquatic environments, MeHg is formed by methylation of inorganic Hg by microorganisms  
29 (e.g., Jensen and Jernelöv, 1969; Parks et al., 2013). In the open ocean, although MeHg  
30 formation has been shown in sub-surface seawater and sediments (e.g., Monperrus et al.,  
31 2007; Hollweg et al., 2010; Soerensen et al., 2016), it occurs mainly in the  
32 thermocline/intermediate waters (200-1000 m) where most bacterial organic matter  
33 regeneration occurs (e.g., Mason and Fitzgerald, 1990; Cossa et al., 2009; Blum et al., 2013;  
34 Cossa et al., 2017). Inorganic Hg reaches the thermocline/intermediate waters *via* the  
35 solubility and biological pumps (e.g., Fitzgerald and Lamborg, 2003; Mason et al., 2012;  
36 Lamborg et al., 2016; Semeniuk and Dastoor, 2017). The solubility pump advects Hg with  
37 water circulation, while the biological pump transports Hg to deep water with sinking  
38 biogenic debris after its adsorption/uptake by phytoplankton in the upper reaches of the water  
39 column. At thermocline/intermediate levels, inorganic Hg associated with particulate matter  
40 is partially dissolved during the remineralization of organic matter and used as a substrate by  
41 microorganisms for MeHg synthesis. Since direct atmospheric Hg deposition represents the  
42 principal source of inorganic Hg to the open ocean (e.g., Mason et al., 2012; Sonke et al.,  
43 2013), its rates of deposition and transport to thermocline/intermediate layer depths are, along  
44 with the intensity of microbial activity there, the primary control factors on Hg methylation.  
45 Ultimately, these parameters control the exposition of the base of the aquatic food web to  
46 MeHg levels and thus constrain human contamination from seafood resources.

47 The Hg natural biogeochemical cycle has been disrupted by human activities for  
48 several millennia (e.g., Cooke et al., 2009; Elbaz-Poulichet et al., 2011; Mason et al., 2012).

49 According to Amos et al. (2013), simulations show that the present-day Hg concentration in  
50 the atmosphere is enriched by a factor of 2.6 relative to pre-industrial times (before ~1850  
51 AD) and by a factor of 7.5 relative to natural levels. A recent critical review concludes that  
52 atmospheric Hg concentrations have risen by about 4.5 times above the level prevailing  
53 before 1450 AD (Outridge et al., 2018), and that this increase has driven a 3-fold increase in  
54 the average deposition rates to the Earth's surface, which in turn has elevated Hg levels in  
55 oceanic waters. Mass balance calculations suggest that within the last century Hg increased  
56 by ~200% in the surface ocean, ~25% in subsurface waters, and ~10% in recently formed  
57 deep waters (Mason et al., 2012). Modelling oceanic Hg changes in the last millennium  
58 (Zhang et al., 2014a and b) suggests a Hg increase by a factor of 4.4 in the ocean mixed layer,  
59 whereas the inventory of Hg has increased by 50 and 20% in the thermocline/intermediate  
60 and deep ocean, respectively. Using a different approach, Lamborg et al. (2014a) calculated  
61 that Hg concentrations have increased by 250%, 160% and 10% in surface,  
62 thermocline/intermediate, and deep waters. They argue that these 3 layers contain  
63 respectively 6%, 59% and 35% of total oceanic anthropogenic Hg. These figures are  
64 comparable with the values of 3% in surface, 52% at thermocline/intermediate depths, and  
65 45% for the deep ocean estimated by Zhang et al. (2014b). For their part, Outridge et al.  
66 (2018), in their updated global and oceanic Hg budget, suggest that the oceanic Hg  
67 concentrations increased compared to natural level by a factor of 2.3 in surface waters and by  
68 only 12-25% in deeper layers. In addition, global Hg emissions, as well as the deposition  
69 rates, are geographically heterogeneous, and the time-trends of Hg change in oceanic waters  
70 are consequently geographically dependent (Mason et al., 2012; Lamborg et al. 2014b). For  
71 example, the waters of the Pacific Ocean show a Hg increase at depths between 200 and 1000  
72 m during the last few decades, while such a trend is not observed from measurements for  
73 North Atlantic waters (Mason et al., 2012). Irrespective of the uncertainties of these various

74 estimates, all previously quoted studies converge in establishing that the anthropogenic  
75 emissions of Hg and subsequent oceanic loading have massively increased since the  
76 beginning of the industrial time. These anthropogenic perturbations will persist for years to  
77 centuries depending on the geographical position and oceanic layer concerned. An insight of  
78 the relative persistence of anthropogenic Hg can be derived from the residence times of Hg,  
79 which are roughly < 1 year in the mixed layer (Soerensen et al., 2010), ~120 years in the  
80 thermocline/intermediate layer, and ~2000 years in deep layers (Zhang et al., 2014b).

81         Observations in recent years of Hg concentrations in the atmosphere contrast with the  
82 long-term assessments. Indeed, the Hg concentrations in the troposphere of the northern  
83 hemisphere and the wet deposition have declined by ~35% during the 1990-2010 period  
84 (Prestbo and Gay, 2009; Slemr et al., 2011; Muntean et al., 2014). More specifically, a  
85 temporal decrease of Hg concentrations in the marine boundary layer of the North Atlantic  
86 atmosphere was observed during the same period (Sprovieri et al., 2010; Cole and Steffen,  
87 2010; Mao and Talbot, 2012; Weigelt et al., 2014). Zhang et al. (2016) reviewing the recent  
88 atmospheric data conclude that the decrease in atmospheric elemental Hg ( $\text{Hg}^0$ )  
89 concentrations ranges from 1.2 to 2.1 percent per year at northern midlatitudes, and that wet  
90 deposition fluxes follow these trends. Similar observations for the oceanic waters are lacking  
91 due to the sheer difficulty in obtaining an adequately long time series of quality Hg  
92 concentration data (in both precision and accuracy) Hg concentration data. For an example, a  
93 set of four measurements, obtained between 1980 and 2010, tends to suggest that surface  
94 concentrations in the North Atlantic have decreased since the 1980s (Fig. 4 *in* Driscoll et al.,  
95 2013). These data are obviously limited in their ability to provide a basis for sound  
96 conclusions. For instance, the compilation of a larger dataset collected in the water column of  
97 the North Atlantic Ocean near Bermuda (Fig. 4b *in* Mason et al., 2012) conversely does not  
98 show a clear Hg decrease either at the surface or in intermediate or deep waters when early

99 data (i.e., the samples collected in 1979 that may be poorly validated) are excluded. Mercury  
100 concentrations in the Eastern North Atlantic measured at the beginning of the 2000s (Cossa et  
101 al., 2004) and in 2014 during a GEOTRACES cruise (Cossa et al., 2018a) are difficult to  
102 compare because the data were obtained using different techniques for total Hg  
103 determination. Indeed, the former method (hydride formation) is different from the now  
104 validated bromine oxidation and tin chloride method (see Materials and Methods section)  
105 which is widely used and considered as *the* reference method by research programs and many  
106 national and international agencies. Nevertheless, this comparison suggests a decrease in Hg  
107 concentration in the Mediterranean waters in recent decades, which has also been argued by  
108 Rajar et al. (2007) by using data partially obtained by the hydride technique (Cossa et al.,  
109 1997). Those decreases in the Mediterranean waters are consistent with the decrease of  
110 American and European Hg emissions (Streets et al., 2009; Pirrone et al., 2010). However,  
111 bearing in mind the uncertainty associated with the accuracy of early data, the observed  
112 decreasing trend and its magnitude is questionable. Despite these trends in marine waters  
113 being expected and predicted by modelling (Sunderland and Mason, 2007; Soerensen et al.,  
114 2012), they need to be confirmed by unambiguous field data acquired using consistent  
115 sampling and analytical techniques. Tentatively, a decrease by 30% in Hg concentrations is  
116 observed when using the same sampling procedure and analytical method in the North  
117 Atlantic (GEOTRACES GA-01 transect conducted in June 2014) between a recently formed  
118 core (1-3 years) of the Labrador Sea Water (LSW) and a core of LSW of 20 years old (Cossa  
119 et al. 2018a). Thus, additional field measurements are still clearly needed to actually observe  
120 and confirm the probable but still hypothetical decrease in Hg burden of the North Atlantic  
121 Ocean, both on a regional and seasonal basis. This latter is all the more important since  
122 biological pumping and net Hg deposition rates are geographically variable (Mason et al.,  
123 2012, 2017).

124 The Hg transfer at depth by biological pumping and Hg residence time at  
125 thermocline/intermediate layers of the global ocean (~120 years) suggest that these oceanic  
126 layers are the most suitable for investigating possible effects of changes in Hg deposition  
127 over scale of a century. In addition, the upper layers of the North Atlantic and the entire water  
128 column of the Western Mediterranean are also suitable water masses for studying decadal  
129 environmental changes, since their residence time are of the order of two decades  
130 (Cunningham, 2000; Béthoux et al., 2005, Schneider et al., 2014).

131 In this context, we are herein reporting the results of Hg determinations in the water  
132 column, obtained during oceanographic cruises conducted on both sides of the Strait of  
133 Gibraltar over the last 25 years using similar sampling and analytical techniques. The water  
134 column west of Gibraltar is included in the Subtropical North Atlantic Gyre (STG), which is  
135 one of the main features of North Atlantic circulation, and which anticyclonically links the  
136 Gulf Stream to the North Equatorial Current. The STG is a region where subtropical and  
137 recently ventilated waters mix, leading to an overturning of North Atlantic circulation  
138 (Carracedo Segade et al., 2015). The water column east of Gibraltar, the so-called Alboran  
139 Sea, contains the typical water masses of the Western Mediterranean (Millot et al., 2006;  
140 Garcia-Lafuente et al., 2017) characterized by high salinity values due to evaporation which  
141 exceeds precipitation reaching its maximum, particularly during summer. The Alboran Sea  
142 constitutes the reservoir of Mediterranean outflow to the North Atlantic through the Strait of  
143 Gibraltar. The objective of our study is answering the question: whether or not the decrease in  
144 atmospheric Hg concentrations at northern midlatitudes, at the turn of the century, has had a  
145 measurable impact on the Hg content of the water column of Northeast Atlantic and Western  
146 Mediterranean both sides of the Strait of Gibraltar. We show that a significant decrease in Hg  
147 concentrations occurs, between 1989 and 2012, in the upper and intermediate oceanic waters  
148 on both sides of the Strait of Gibraltar.

## 150 2. Material and Methods

151 Samples were collected during three different cruises, MEDATLANTE-II in September 1989,  
152 ALMOFRONT-I in May 1991, and FENICE in August 2012. The first two cruises were on board  
153 the French research vessel “Jean Charcot” and the FENICE cruise was on board the Italian  
154 research vessel “Urania” of the CNR (National Research Council). Two stations were  
155 occupied west of Gibraltar: Sta. 6A during the MEDATLANTE-II cruise and Sta. 6B during the  
156 FENICE cruise (Fig. 1). Three stations were occupied in the Alboran Sea: Stas. 36, 63 and 65  
157 during the ALMOFRONT-I cruise, and Stas. 4 and 8 during the FENICE cruise.

158 Water samples were collected using the most state-of-the-art techniques for ultra-trace  
159 Hg sampling and analysis that were available at the time of the cruises (Gill and Fitzgerald,  
160 1985; Cossa and Courau, 1990; Mason and Fitzgerald, 1993; Yoon et al., 1996; Lamborg et  
161 al., 2012). During ALMOFRONT-I and MEDATLANTE-II cruises, stainless-steel rosette frame  
162 and hydrowire were deployed with acid-cleaned, Teflon-coated Go-Flo bottles (General  
163 Oceanics), whereas, during FENICE cruise, Niskin bottles (General Oceanics) placed on an  
164 epoxy-coated rosette and hung on a stainless steel hydrowire were used. During all three  
165 cruises, the rosettes were equipped with sensors for salinity, temperature, dissolved oxygen,  
166 and optical transmission. Samples for HgT determinations were treated and measured on  
167 board from sub-samples, using identical procedures in clean lab-vans (Class 100000-ISO8  
168 equipped with Class 100-ISO5 laminar flow hoods). Samples were withdrawn from sampling  
169 bottles into acid-cleaned Teflon bottles (FEP), then stored acidified (Ultrapur HCl, 0.4% v/v)  
170 until analysis, which was always performed within the next 12 hours. In order to determine  
171 operationally defined total mercury (HgT) in the sample, Hg was released from its ligands  
172 and alkyl moieties through oxidation with BrCl. Dissolved, oxidized Hg was reduced to its



173 Hg vapor with an acidic SnCl<sub>2</sub> solution. This technique, initially proposed by Bloom and  
174 Crecelius (1983), is now known as the US-EPA standard method N° 1631 (EPA, 2002). For  
175 our analyses, the Hg vapor is purged using Ar and amalgamated on a gold trap, then released  
176 by thermal desorption into an atomic fluorescence spectrometer (Merlin, PSA in 1989-91,  
177 and Tekran, Model 2500 in 2012). The detailed procedure for 1989-91 analyses is given by  
178 Courau (1983), and by Cossa et al. (2018b) for 2012 analyses. The differences between  
179 cruises are the following: in 1989-91, 125 mL of seawater sample was oxidized with the  
180 bromide present in the seawater by the addition of 0.25 mL of a 0.04 mol L<sup>-1</sup> potassium  
181 permanganate solution, then the Hg was reduced with 1 mL of a 0.05 M SnCl<sub>2</sub> solution. In  
182 2012, the 100mL seawater subsample was oxidized with the addition of 0.1 mL of a 0.2 M  
183 BrCl solution, and Hg reduction was achieved by 0.2 mL of a 1 M SnCl<sub>2</sub> solution. The  
184 detection limit, defined at three times the standard deviation of six blank measurements, was  
185 0.2 pmol L<sup>-1</sup> and 0.1 pmol L<sup>-1</sup> in 1989-91 and 2012, respectively. The reproducibility, defined  
186 as the coefficient of variation of six replicate samples, was 15% in 1989-91, and 12% in  
187 2012. In 2012, the accuracy of Hg measurements was verified using the ORMS-4 certified  
188 reference material (CRM) from the National Research Council of Canada. Our measurements  
189 were always within the confidence limits given for the CRM. No CRM was commercially  
190 available at the time of MEDATLANTE-II and ALMOFRONT-I cruises, but accuracy was  
191 checked using two independent Hg standard solutions. Easily-reducible Hg (often called  
192 “reactive Hg”, HgR) was also systematically measured on board. The data, not reported here,  
193 allowed the calculation of the mean HgR/HgT ratio, which was used to estimate the six  
194 missing HgT values (see SI 1). The quality of the analytical measurements was ensured by  
195 the use of the cleaning procedures for sampling and sample treatment that are recommended  
196 by Gill and Fitzgerald (1985), Mason and Fitzgerald (1993) and more recently by the  
197 GEOTRACES program, and by the rapidity of the onboard determinations after sampling. The

198 capability of the two laboratories (LOV-CNRS and IFREMER) for producing high-quality ultra-  
199 trace measurements is shown by the results of their participation in most of the Hg  
200 intercomparison exercises for the aquatic environments over the last 25 years (e.g., Cossa and  
201 Courau, 1990; Lamborg et al., 2012).

202

### 203 **3. Results and Discussion**

#### 204 ***3.1. Water masses and biogeochemical context***

205 West of Gibraltar, temperature and salinity distributions at Sta. 6A (1989) and Sta. 6B (2012)  
206 are given in SI (Fig. S1a and b). The temperature *versus* salinity (T-S) graphs (Fig. 2) allow  
207 the same water masses to be identified during the two cruises; the presence of these water  
208 masses is well documented in this STG region (e.g., Pérez et al., 2018). Listing them from  
209 surface to bottom: (i) the surface (mixed) layer, (ii) the North East Atlantic Central Water  
210 (NEACW), (iii) the North East Atlantic Deep Water (NEADW) and (iv), at the bottom, the  
211 Lower Deep Water (LDW). The NEACW in the STG is composed of different mode waters  
212 including Mediterranean Water (MW) and Subpolar Mode Waters (SPMW), which both are  
213 clearly identified on the T-S graph in Figure 2 by high and low salinities, respectively  
214 (McCartney, 1992; Tsuchiya et al., 1992). The presence of MW is clearly identified by the  
215 salinity maximum located between 800 and 1250 m (SI, Fig. S1). The salinity variations  
216 along the Sta. 6A profiles testify to the presence of MW escaping the Strait of Gibraltar.  
217 Salinity (herein  $S_p$ ) is defined using the practical salinity scale from rosette sensor data.  
218 Using salinity of 35.5 and 38.5  $S_p$  for the Atlantic and Mediterranean end-members, the  
219 proportions of MW at Sta. 6A varied around 25% in 1989 (MEDATLANTE-II cruise).  
220 According to Yoon et al. (1996), who described zinc distribution from the same cruise, the  
221 salinity maximum (36.37  $S_p$ ) corresponded to 32% of MW. At Sta. 6B occupied during the

222 FENICE cruise (2012), the MW proportion reached 28% at the salinity maximum. There, the  
223 NEADW is underlain by the bottom layer constituted by LDW, which is a warmed Antarctic  
224 Bottom Water (AABW) coming from the Southern Ocean (Fig. 2). This deepest water mass  
225 contains very low chlorofluorocarbon (CFC's) concentrations, which attest for its pre-  
226 industrial atmospheric imprint (Rhein et al., 2002) and a Hg inventory attributable to the Hg  
227 solubility pump. During the MEDATLANTE-II cruise (1989), the soluble reactive phosphorus  
228 (SRP) distribution varied from 0.01 to 1.23  $\mu\text{mol L}^{-1}$  between the surface and 2000 m. The  
229 vertical profiles exhibited the typical pattern for this region with concentrations increasing  
230 rapidly from surface to 500-600 m, then decreasing slightly. The MW was located between  
231 800 and 1200 m (SI, Fig. S2a). At deeper depths, SRP concentrations continued to increase at  
232 slower rates. During the FENICE cruise, at Sta. 6B, nutrient concentrations were not measured.  
233 As a proxy for SRP, we use remineralized phosphate ( $P_{\text{rem}}$ ) calculated from the Apparent  
234 Oxygen Utilization (AOU) divided by a 141 Redfield ratio (Minster and Boulahdid, 1987),  
235 suggesting  $P_{\text{rem}}$  varied from 0.49 to 1.22  $\mu\text{mol L}^{-1}$ . The concentration range and shape of the  
236 vertical profiles (SI, Fig. S2b) were similar during both the 1989 and 2012 cruises, suggesting  
237 that the biogeochemical conditions affecting Hg remobilization remained relatively  
238 unchanged during the 1989-2012 period.

239 In the Western Mediterranean Sea, the following water masses are from top to bottom:  
240 the modified Atlantic waters (MAW), the Levantine Intermediate Water (LIW), the Winter  
241 Intermediate Water (WIW), and the Western Mediterranean Deep Water (WMDW) (Millot et  
242 al., 2006; Garcia-Lafuente et al., 2017). The LIW, identified by a salinity maximum, is  
243 formed in the Eastern Mediterranean basin, while the WIW, identified by a temperature  
244 minimum, is formed along the continental shelf of the North Western Mediterranean basin.  
245 Finally, the WMDW is both the densest and coldest water present in the basin. The  
246 hydrological structures found during the ALMOFRONT-I (1991) and FENICE (2012) cruises

247 were typical of the Alboran Sea (Tintoré et al., 1988; Béthoux et al., 2005). In addition, the  
248 ALMOFRONT-I conditions were given in detail by Prieur and Sournia (1994), who described  
249 the multiple-gyres and frontal structures. Station 4 (2012) was located in the Western Alboran  
250 cyclonic gyre, whereas Stas. 7 (2012) and 36 (1991) were located eastward in the Almeria  
251 cyclonic gyre, and Stas. 63 and 65 (1991) in the Cartagena anticyclonic eddy. Potential  
252 temperature *versus* salinity ( $T_p$ -S) graphs are given in Fig. 3, and  $T_p$  and salinity profiles in  
253 Fig. S3 (SI). The inflowing Atlantic water was located between 0 and 25 m depth with an  
254 average  $S < 37 S_p$ , and MAW was identified down to 100 m ( $S = 37$ - $38 S_p$ ). The WIW ( $S =$   
255  $38.2$ - $38.3 S_p$ ) was found below 125 m down to the maximum of salinity at around 400 m,  
256 which characterized the LIW. The WMDW was located below 900 m depth ( $S = 38.42 S_p$ ).  
257 During the FENICE cruise, the T-S graph of Stas. 4 and 7 exhibited the same hydrological  
258 structure with the presence of MAW, WIW-LIW, and WMDW. In addition, surface  
259 temperatures of 18-25 °C showed the extension of summer surface stratification (FENICE  
260 cruise) that was not observed in spring (ALMOFRONT-I cruise). In the Alboran Sea,  
261 phosphorus concentrations varied from low values in surface waters to  $P_{rem}$  of  $0.5 \mu\text{mol L}^{-1}$  in  
262 1991. In 2012,  $P_{rem}$  also reached  $0.6 \mu\text{mol L}^{-1}$  in deep waters. Vertical dissolved phosphorus  
263 profiles are shown (Fig. S4, SI). The  $P_{rem}$  data obtained in 2012 (FENICE cruise) were  
264 calculated from the AOU divided by a factor of 237, the specific Redfield ratio for the  
265 Western Mediterranean due to the P limitation of this oceanic region (Béthoux et al., 2005).

### 266 **3.2. Mercury distributions**

267 West of Gibraltar, in the Eastern North Atlantic, HgT concentrations measured in 1989 (Sta.  
268 6A) varied from  $0.21$  to  $1.07 \text{ pmol L}^{-1}$  (Fig. 4). They ranged from  $0.21$  to  $0.75 \text{ pmol L}^{-1}$  in the  
269 surface layer, and increased from  $0.21$  at 40 m to  $\sim 1 \text{ pmol L}^{-1}$  at 500 m within the SPMW,  
270 characterized by low temperature and salinity, and by peaking phosphorus levels (Fig. S1 and  
271 S2, SI). Below this depth, the profile showed a small Hg peak between 1000 and 1200 m.

272 This relative maximum corresponds to the water layer (open circles in Fig. 4) where high  
273 salinity and low nutrients indicate the highest proportion of MW (Fig. SI, S1). Below 1200  
274 m, the HgT levels were relatively less variable and ranged between 0.95 and 1.07 pmol L<sup>-1</sup> in  
275 the NEADW and LDW. In comparison, HgT concentrations measured in 2012 (Sta. 6B)  
276 varied within a similar range, from 0.19 to 0.95 pmol L<sup>-1</sup>. However, the concentrations were  
277 clearly lower in the NEACW (Fig. 4). The presence of MW at ~1000 m comes with a small  
278 inflexion in the HgT profile (open circles in Fig. 4). At greater depths (>3000 m), HgT  
279 concentrations, obtained in 1989 and 2012, were converging to a mean value of 0.96 ± 0.04  
280 pmol L<sup>-1</sup> reached within the LDW. Since LDW results from the mixing of AABW with North  
281 Atlantic Deep waters during its northward transit, its relatively high mean HgT concentration  
282 is consistent with the elevated concentrations found recently (2014) in the lower NEADW  
283 during the GEOTRACES GA-01 transect (1.04 ± 0.02 pmol L<sup>-1</sup> according to Cossa et al.,  
284 2018a) and at the source of AABW in the Southern Ocean in 2008 (1.35 ± 0.31 pmol L<sup>-1</sup>)  
285 (Cossa et al., 2011). It can be surprising that, at depth as deep as 2500 m, HgT concentrations  
286 may have changed in a 20-years period. West of Gibraltar, NEADW spread down to 3000 m (Fig.  
287 4). According to García-Ibáñez (2015), the water mass present at 3000 m is composed of 50-60% of  
288 LDW (called by these authors “lower-NEADW” or NEADWL) and similar proportions (20-25%) of  
289 LSW (Labrador Sea water) and ISOW (Island Scotland Outflow water). With a ventilation age of  
290 more than 150 years, NEADWL cannot contain recent anthropogenic Hg from the solubility pump.  
291 Conversely, LSW and ISOW, which are younger than 20 years (Doney et al., 1997), may have  
292 undergone changes in the Hg incorporation within the 1989-2012 period. Furthermore, in the layer of  
293 NEADW between 3000 and 2500 m the proportion of NEADWL is decreasing to 40% and at 2000 m  
294 it is less than 20%, whereas, parallelly, the proportion of the younger LSW is increasing up to 60%.  
295 Thus, a HgT change down to 2500-3000 m, at this place of the Northeast Atlantic Ocean within the  
296 1989-2012 period, is rational.

297 East of Gibraltar, in the Alboran Sea (Fig. 1), HgT concentrations measured in 1991  
298 varied from 1.28 to 2.44 pmol L<sup>-1</sup> in the MAW, with an average of 1.71 pmol L<sup>-1</sup>. They  
299 reached values higher than 2 pmol L<sup>-1</sup> in the WIW, and averaged 1.42 and 1.32 pmol L<sup>-1</sup> in  
300 the LIW and WMDW, respectively (Fig. 5). On the other hand, HgT concentrations measured  
301 in 2012 were clearly lower for the same water masses (0.33 to 0.96 pmol L<sup>-1</sup>). Interestingly  
302 and in contrast to 1991, the lowest values in the subsurface waters were associated with the  
303 MAW probably as results of photoreduction and evaporation of Hg volatile species, whereas  
304 the highest were observed at depth (Fig. 5).

### 305 ***3.3. Time trends in Hg concentrations***

306 Simple calculations can be done to estimate the temporal decrease of HgT concentration from  
307 direct comparison of the vertical profiles obtained in 1989, 1991 and 2012 (Figs. 4 and 5).  
308 West of Gibraltar, the amplitude of the Hg decrease diminished with depth. It ranges from  
309 ~50% in SPMW/NEACW to ~40% in MW/NEACW and ~35% in the upper NEADW. This  
310 last estimate is consistently similar to the 30% decline of Hg mean concentration observed in  
311 the core of LSW during the last 20 years (Cossa et al., 2018a). Below, in the aged LDW, no  
312 HgT change seems to have occurred between 1989 and 2012. East of Gibraltar, the observed  
313 decrease is ~30% in the herein sampled WMDW.

314 Another way to estimate the Hg decrease in the last 20 years that may reveal changes  
315 in the biogeochemical context, is to look at changes in the Hg/nutrient ratios. Indeed, Hg is  
316 thought to exhibit a nutrient-like behaviour in the North Atlantic Ocean (Cossa et al., 2004  
317 and 2018a; Lamborg et al., 2014b; Bowman et al., 2015). This is confirmed by the  
318 statistically significant correlations between Hg and SPR or P<sub>rem</sub> concentrations in both the  
319 1989 and 2012 cruises west of Gibraltar (R<sup>2</sup> = 0.94 and 0.92, respectively, Fig. 6a). The  
320 regression coefficient calculated with 2012 data from Sta. 6B is 0.87 μmol<sub>Hg</sub>/mol<sub>P</sub> based on  
321 an AOU/P<sub>rem</sub> of 141 (Minster and Boulahdid, 1987), and it is 1.05 μmol<sub>Hg</sub>/mol<sub>P</sub> if AOU/P<sub>rem</sub>

322 is 171 according to Lamborg et al. (2014b). This latter value is similar to that obtained for  
323 oceanic water not suspected of containing anthropogenic Hg, namely  $1.02 \pm 0.03$   
324  $\mu\text{mol}_{\text{Hg}}/\text{mol}_{\text{P}}$  (Lamborg et al., 2014b). The regression slope obtained in 1989 was lower ( $0.57$   
325  $\mu\text{mol}_{\text{Hg}}/\text{mol}_{\text{P}}$  based on an  $\text{AOU}/\text{P}_{\text{rem}}$  of 141, or  $0.69 \mu\text{mol}_{\text{Hg}}/\text{mol}_{\text{P}}$  if  $\text{AOU}/\text{P}_{\text{rem}}$  is 171)  
326 reflecting Hg-enrichment in P-poor surface water (Fig. 6a). According to the Lamborg et al.  
327 (2014b) model, this enrichment would be due to anthropogenic Hg since a “pristine  
328 relationship” is characterized by the global relationship for the World Ocean of  $\text{Hg}_{[\text{pmol L}^{-1}]} =$   
329  $1.01 * \text{P}_{\text{rem}[\mu\text{mol L}^{-1}]} - 0.07$  (see discussion in the *Supplementary Information* section in Lamborg  
330 et al.’s paper). The nutrient-like behavior of Hg means that a large fraction of surface Hg is  
331 drawn down to the ocean interior by sinking particles, where it is released as a result of  
332 organic matter microbiological remineralization, according to the well-known biological  
333 pumping/regeneration process (Sigman and Haug, 2006). East of Gibraltar, during the FENICE  
334 cruise in 2012, the Hg *versus*  $\text{P}_{\text{rem}}$  relationships were also statistically significant ( $R^2 = 0.95$   
335 and  $0.76$  at Stas 4 and 7, respectively, Fig. 6b). In contrast, during the ALMOFRONT-I cruise in  
336 1991, the absence of a significant Hg *versus* SRP relationship (Fig. 6b) illustrated the fact  
337 that the major Hg enrichment at Stas. 63-65 was especially elevated in surface waters (Fig.  
338 5). Normalized to common P concentrations, the Hg concentration decrease between 1991  
339 and 2012 in the east of Gibraltar ranges  $\sim 38\%$  for WMDW (for  $\text{P} = 0.6 \mu\text{mol L}^{-1}$ ). West of  
340 Gibraltar, the P-normalized Hg decrease between 1989 and 2012 is  $\sim 30\%$  at 1000 m (for  $\text{P} =$   
341  $1.2 \mu\text{mol L}^{-1}$ ) (i.e., in the MW/NEACW) increasing up to  $>50\%$  in the subsurface water (i.e.,  
342 upper SPMW/NEACW) (for  $\text{P} = 0.6 \mu\text{mol L}^{-1}$ ).

343         It is interesting to note the contrasting situation which exists for deep waters east and  
344 west of Gibraltar. In the Alboran Sea, the Hg decrease is  $30\text{-}38\%$  in  $\sim 20$  years old WMDW  
345 (Bethoux et al., 2005; Schneider et al., 2014), whereas, on the Atlantic side of Gibraltar  
346 Strait, the HgT concentration did not vary in the LDW between 1989 and 2012 (Fig. 4). This

347 is entirely consistent with the pre-industrial age of these deepest oceanic waters. Furthermore,  
348 the Hg decrease between 1989 and 2012 west of Gibraltar appears to be smaller for the oldest  
349 waters (NEADW) than that for younger ones (SPMW/NEACW). This result is consistent  
350 with the smaller decrease (30%) of the anthropogenic Hg fraction modeled in the deep waters  
351 of the North Atlantic at 35°N compared to that modeled at shallower depths (70%) (e.g.,  
352 OFFTRAC-GEOS-Chem model; Zhang et al., 2014b). A minor part of the temporal decline  
353 in Hg concentrations in the intermediate waters of the North Atlantic between 1989 and 2012  
354 might be attributed to the reduced efficiency of the biological pump, since the oceanic  
355 primary production of North and Central Atlantic has slightly (-7%) decreased since the  
356 early 1980s (Gregg et al., 2003). The dramatic drop of Hg concentrations actually observed in  
357 intermediate waters likely reflects the reduction in Hg deposition over the North Atlantic  
358 region over time (Soerensen et al., 2012; Weigelt et al., 2014). Indeed, this trend follows the  
359 temporal decline in Hg emission inventories for the Eastern United States of America since  
360 the mid-1990's years (Zhang et al., 2014b). Such decrease has already been observed in the  
361 North Western Atlantic near Bermuda but in sub-surface waters (Mason et al., 2012;  
362 Lamborg et al., 2014b). Additionally, recent Hg measurements performed in the water  
363 column of the North Eastern Atlantic in 2010 (GA-03 section) and 2014 (GA-01 section)  
364 (Fig. 4; Bowman et al., 2015; Cossa et al., 2018a) indicate, together with our dataset, that Hg  
365 concentrations have been declining between 1989 (Sta. 6A), 2010 (e.g., 0.68-0.89 pmol L<sup>-1</sup> at  
366 Sta. 5) and 2012 (Sta. 6B) in the core of NEADW. Conversely, no significant decrease is  
367 observed between 2012 (Sta. 6B) and 2014 (Sta. 13), since Hg<sub>T</sub> concentration ranges and  
368 distribution at depth were similar at both years (Fig. 4).

369 In the Alboran Sea, sources of Hg are (i) Atlantic waters inflowing the Mediterranean  
370 in surface, (ii) direct atmospheric deposition, and (iii) WIW, LIW and WMDW from the  
371 Western Mediterranean at depth. As discussed above, the Atlantic surface waters, sampled



372 west of Gibraltar, show a decline in their Hg content (>50%) between 1989 and 2012. Thus,  
373 the influx of Hg from the Atlantic toward the Mediterranean is weakening with time. In  
374 addition, Alboran Sea waters are influenced by riverine metal sources (the mine-  
375 contaminated Tinto-Odiel-Huelva riverine system) inflowing the Gulf of Cadiz (van Geen et  
376 al., 1991). In the case of Hg, the concentrations were elevated in those rivers (up to 330 pmol  
377 L<sup>-1</sup> in the Odiel River), and in the surface waters of the Gulf of Cadiz, the average dissolved  
378 Hg concentration was  $2.9 \pm 0.9$  pmol L<sup>-1</sup> in 1997-98 (Cossa et al., 2001). In 2012, during the  
379 2012 FENICE cruise, dissolved Hg concentrations in the Gulf of Cadiz averaged only  $0.55 \pm$   
380  $0.17$  pmol L<sup>-1</sup> (Knoery, unpublished). This decrease in Hg content in the Gulf of Cadiz  
381 surface waters may have contributed to the Hg decrease in the MAW entering the Alboran  
382 Sea. The direct Hg atmospheric deposition on the Alboran Sea has not been estimated.  
383 However, an atmospheric record of CO, O<sub>3</sub> and Hg across the Western Mediterranean and the  
384 Northeastern Atlantic (April 2012) indicates an Hg peak in the troposphere at Gibraltar,  
385 probably due to the densification of maritime traffic and industrialization at the Strait  
386 (Maruszczak et al., unpublished, Fig. S5, SI). At depth, the Hg concentrations in WMDW  
387 have been found to be enriched during the winter water convection occurring in the Gulf of  
388 Lions and the adjacent gyre (Cossa et al., 2018b). The efficiency of the convection, which  
389 governs the Hg export at depth and its further exportation to the adjacent Northeast Atlantic,  
390 is variable from year to year, driven by the intensity of winter cooling of surface water  
391 (Marty and Chiaverini, 2010; Heimbürger et al., 2013; Macias et al., 2018). Furthermore, the  
392 Hg export to the Atlantic (i.e., the “Hg clearing rate” of the Mediterranean Sea) may have  
393 increased since the vertical export flux capacity seems to have increased since 1999 (Marty  
394 and Chiaverini, 2010).

395

396 **Conclusions**

397 Our work reveals that the decrease in atmospheric Hg concentrations, observed at the turn of  
398 the century in northern mid-latitudes, has had a measurable impact on the Hg content of  
399 oceanic waters. We showed that, using identical sampling and analytical techniques during  
400 four oceanographic cruises on both sides of the Strait of Gibraltar, Hg concentrations have  
401 significantly decreased between 1989 and 2012. West of Gibraltar, the Hg decrease ranges  
402 from ~35% in the upper NEADW to ~50% in the NEACW. East of Gibraltar, the observed  
403 decrease is ~30% in the WMDW. In contrast, no change was observed in the deepest waters  
404 (>3000 m) whose ventilation age exceeds 150 years, i.e. waters formed prior the industrial  
405 era. These results corroborate the predicted decreasing Hg concentration trends in North  
406 Atlantic waters (e.g., Sunderland and Mason, 2007) as well as the expected decline in the  
407 Mediterranean Sea (Radjar et al., 2007). Our results suggest that regulations to reduce  
408 anthropogenic Hg emissions, starting with the 1970 US Clean Air Act to the more recent  
409 2017 International Minamata Convention (UNEP, 2013), have had a positive effect on Hg  
410 contamination in parts of the marine environment. Abated anthropogenic Hg emissions  
411 decrease the Hg influx to the marine environment, its subsequent entrapment in the ocean's  
412 interior, and its availability for the formation of the toxic MeHg which biomagnifies through  
413 marine food webs. All other factors governing Hg methylation and bioaccumulation being  
414 equal, our results suggest that Hg bioavailability to Northeastern Atlantic and Western  
415 Mediterranean pelagic ecosystems, including edible fish species, is likely to have decreased  
416 between the two decades straddling the new millennium. A declining-trend in Hg levels in  
417 fish tissue in North American lakes over the period 1972-2016 has recently been  
418 demonstrated (Grieb et al., 2019), but in many cases the temporal trends in aquatic biota do  
419 not parallel changes in atmospheric concentrations and processes other than Hg  
420 concentrations must control MeHg bioaccumulation (Wang et al., 2019). Hence, more

421 information must be gathered to elucidate these complex processes, especially in marine  
422 environments.

423

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662 **Abbreviations**

663 AABW: Antarctic Bottom Water

664 AOU: Apparent oxygen utilization

665 BrCl: Bromine monochloride

666 CFC's: Chlorofluorocarbons

667 CO: Carbon monoxide

668 CRM: Certified reference material

669 FEP: Fluorinated ethylene propylene

670 GEOTRACES: An international study of the marine biogeochemical cycles of trace elements  
671 and their isotopes ([www.geotraces.org](http://www.geotraces.org))

672 Hg: Mercury

673 Hg<sup>0</sup>: Elemental mercury

674 HgR: Reactive or easily reduced mercury

675 HgT: Total mercury

676 HgTUNF: Total mercury in unfiltered samples

677 HgTF: Total mercury in filtered samples

678 LDW: Lower Deep Water

679 LIW: Levantine Intermediate Water

680 LSW: Labrador Sea Water

681 MeHg: Methyl mercury

682 MAW: Modified Atlantic Water

683 MW: Mediterranean Water

684 NEACW: North East Atlantic Central Water

685 NEADW: North East Atlantic Deep Water

686 O<sub>3</sub>: Ozone  
687 OFFTRAC: University of Washington three-dimensional offline ocean tracer model.  
688 ORMS-4: Certified reference material (River water spiked with inorganic mercury).  
689 P: Phosphorus  
690 P<sub>rem</sub>: Remineralized phosphorus  
691 SnCl<sub>2</sub>: Tin chloride  
692 SPMW: Subpolar Mode Water  
693 SRP: Soluble reactive phosphorus  
694 US-EPA: Environmental Protection Agency of the United States of America  
695 WIW: Winter Intermediate Water  
696 WMDW: Western Mediterranean Deep Water

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698 **Figure captions**

699 **Figure 1.** Sampling locations within the North-eastern Atlantic Ocean and Western  
700 Mediterranean during the MEDALANTE-II, ALMOFRONT-I and FENICE cruises. Sta. 6A on  
701 September 5, 1989 (35.6732°N; 13.1588°W, bottom depth 4460 m); Sta. 6B on August 18,  
702 2012 (35.5137°N; 09.1532°W, bottom depth 3610 m); Sta. 36 on April 30, 1991 (36.2231°N;  
703 2.5336°W, bottom 987 m); Sta. 63 on May 3, 1991 (36.2183°N; 1.0733°W, bottom 2601 m);  
704 Sta. 65 on 3 May, 1991 (36.3169°N; 0.5831°W, 2657 m); Sta. 4 on August 16, 2012  
705 (36.4971°N; 4.0356°W, bottom 680 m) ; Sta. 7 on August 15, 2012 (35.9039°N; 2.6943°W,  
706 bottom 990 m). In addition, Sta. 5 (31°N; 22°W, bottom 5175 m) and Sta. 13 (41.3830°N;  
707 13.8877°W, bottom 5350 m) were occupied during the GEOTRACES-GA03 (August 2010) and  
708 GA-01 (June 23, 2014), respectively. Arrows indicate main patterns of oceanic circulation:  
709 Atlantic surface waters entering the Mediterranean Sea through the Gibraltar Strait, Modified  
710 Atlantic Water (MAW) at the surface in the Alboran Sea, and at depth: Levantine  
711 Intermediate Water (LIW), Western Mediterranean Deep Water (WMDW).

712 **Figure 2.** Salinity-Temperature graphs in the water column West of Gibraltar at Stas. 6A and  
713 6B during the MEDATLANTE-II and FENICE cruises. NEACW: North East Atlantic Central  
714 Water; NEADW: North East Atlantic Deep Water; LDW: Lower Deep Water; SPMWs:

715 Subpolar Mode Waters; MW: Mediterranean Water; LSW: Labrador Sea Water; ISOW:  
716 Island Scotland Outflow Water; AABW: Antarctic Bottom Water.

717 **Figure 3.** Salinity-Temperature graphs in the water column East of Gibraltar at Stas. 63, 65, 4  
718 and 7 during the ALMOFRONT-I and FENICE cruises. Modified Atlantic Water; WIW: Winter  
719 Intermediate Water; LIW: Levantine Intermediate Water; WMDW: Western Mediterranean  
720 Deep Water.

721 **Figure 4.** Concentration profiles of total Hg (HgT) West of Gibraltar at Sta. 6A (FENICE  
722 cruise), Sta. 6B (MEDATLANTE-II cruise), Sta. 5 (31°N; 22°W, GEOTRACES GA-03 cruise),  
723 Sta. 13 (41°23'N; 13°53'W, GEOTRACES GA-01 cruise). Open marks correspond to salinity  
724 maxima due to the presence of the maximum proportion ( $\leq 25\%$ ) of Mediterranean waters  
725 (MW) along with the profile. NEACW: North East Atlantic Central Water; NEADW: North  
726 East Atlantic Deep Water; LDW: Lower Deep Water.

727 **Figure 5.** Concentration profiles of total Hg (HgT) east of Gibraltar at Stas. 36, 63 and 65  
728 (ALMOFRONT-I cruise), and Stas. 4 and 7 (FENICE cruise). MAW: Modified Atlantic Water;  
729 WIW: Winter Intermediate Water; LIW: Levantine Intermediate Water; WMDW: Western  
730 Mediterranean Deep Water.

731 **Figure 6.** Relationships between concentrations of total Hg (HgT) and soluble reactive  
732 phosphorus (SRP) or remineralized phosphorus ( $P_{rem}$ ). (a) West of Gibraltar at Stas. 6A and  
733 6B, (b) east of Gibraltar at Stas. 4 and 7.

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1 **Oceanic mercury concentrations on both sides of the Strait of Gibraltar**  
2  
3 **decreased between 1989 and 2012**

3

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6 European Union project), and the European Research Council (ERC-2010-StG-20091028). Thanks are due to P.  
7 Morin and Y. Le Merrer for providing nutrient data, K. Bowman for providing the HgT values at Sta. 5  
8 (GEOTRACES, GA-03 transect), and M. Vautour and A. Mucci for English editing.

Figure

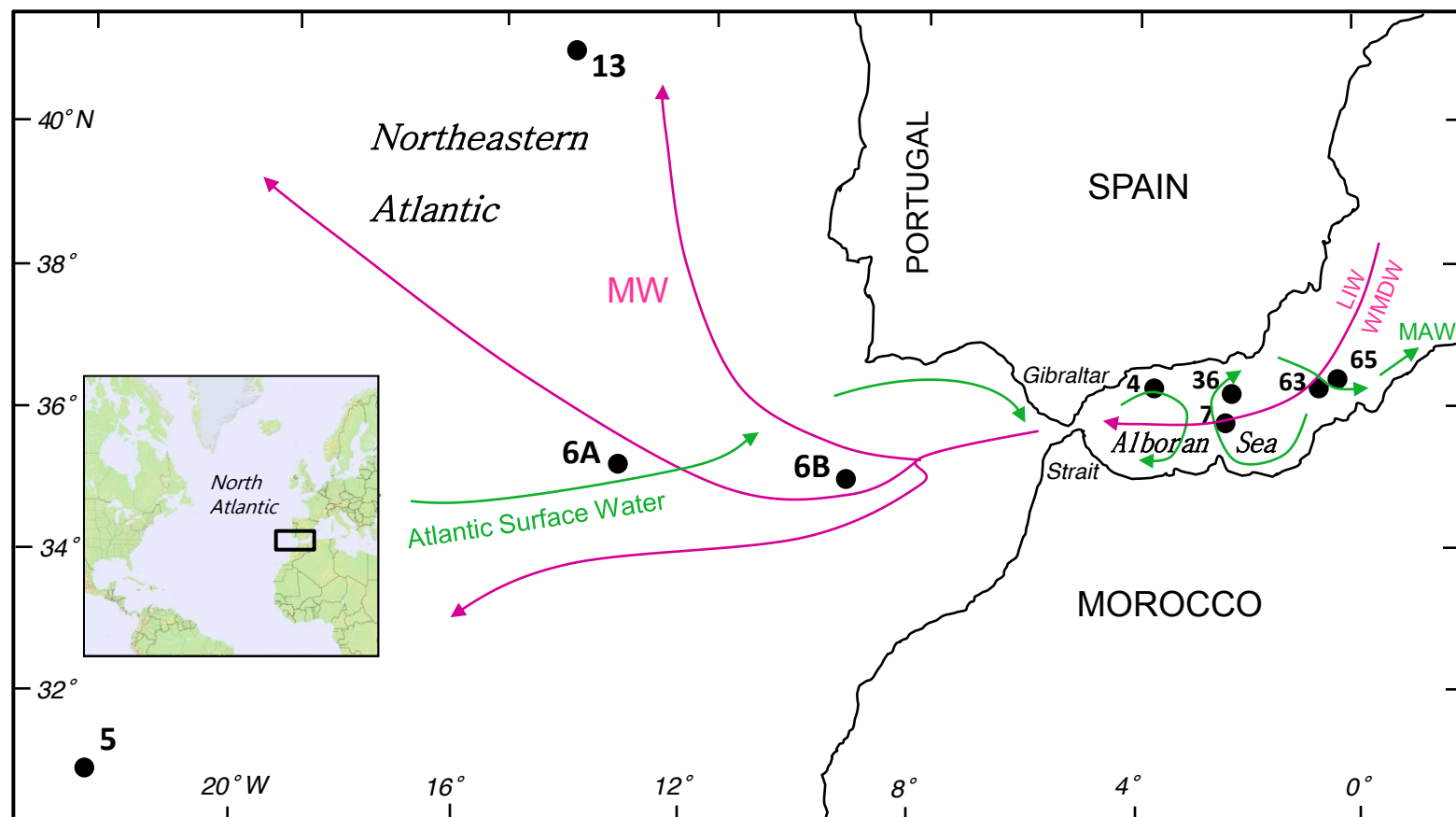


Fig. 1

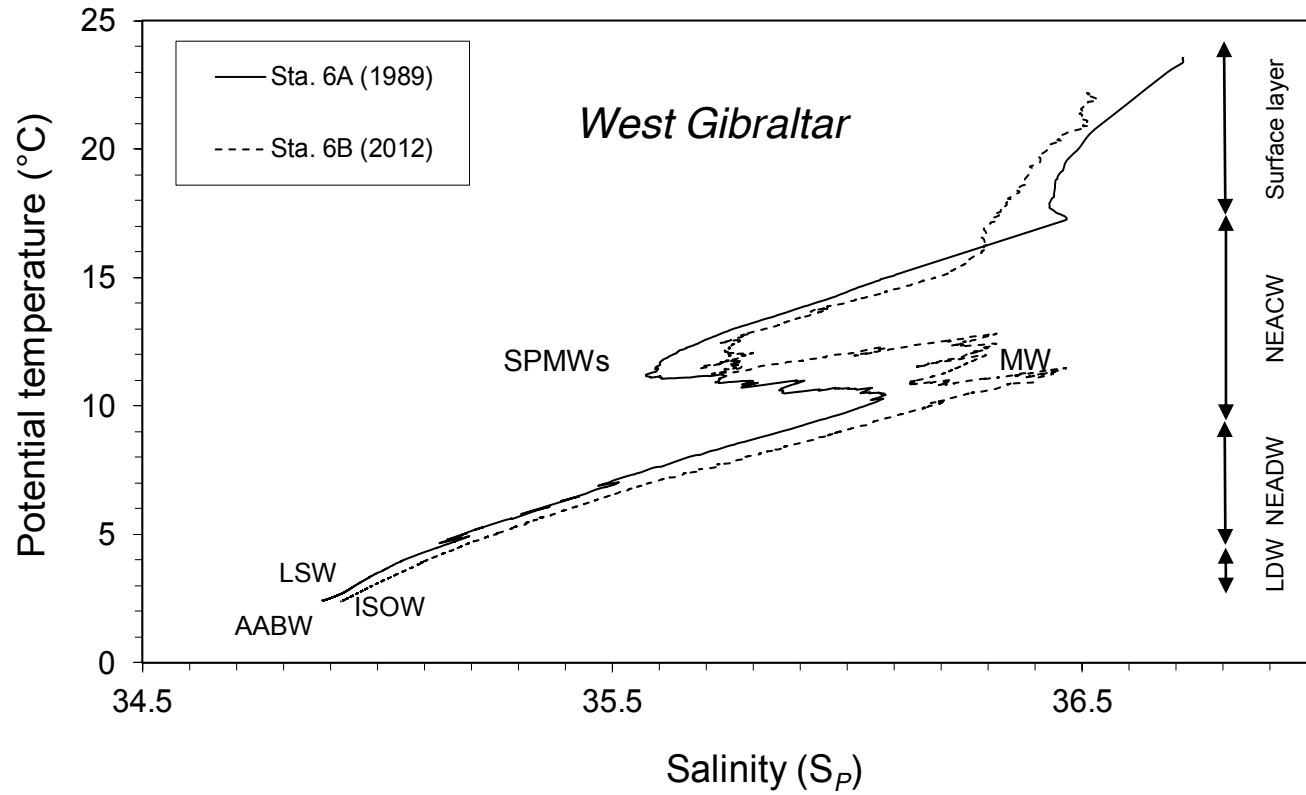


Fig. 2



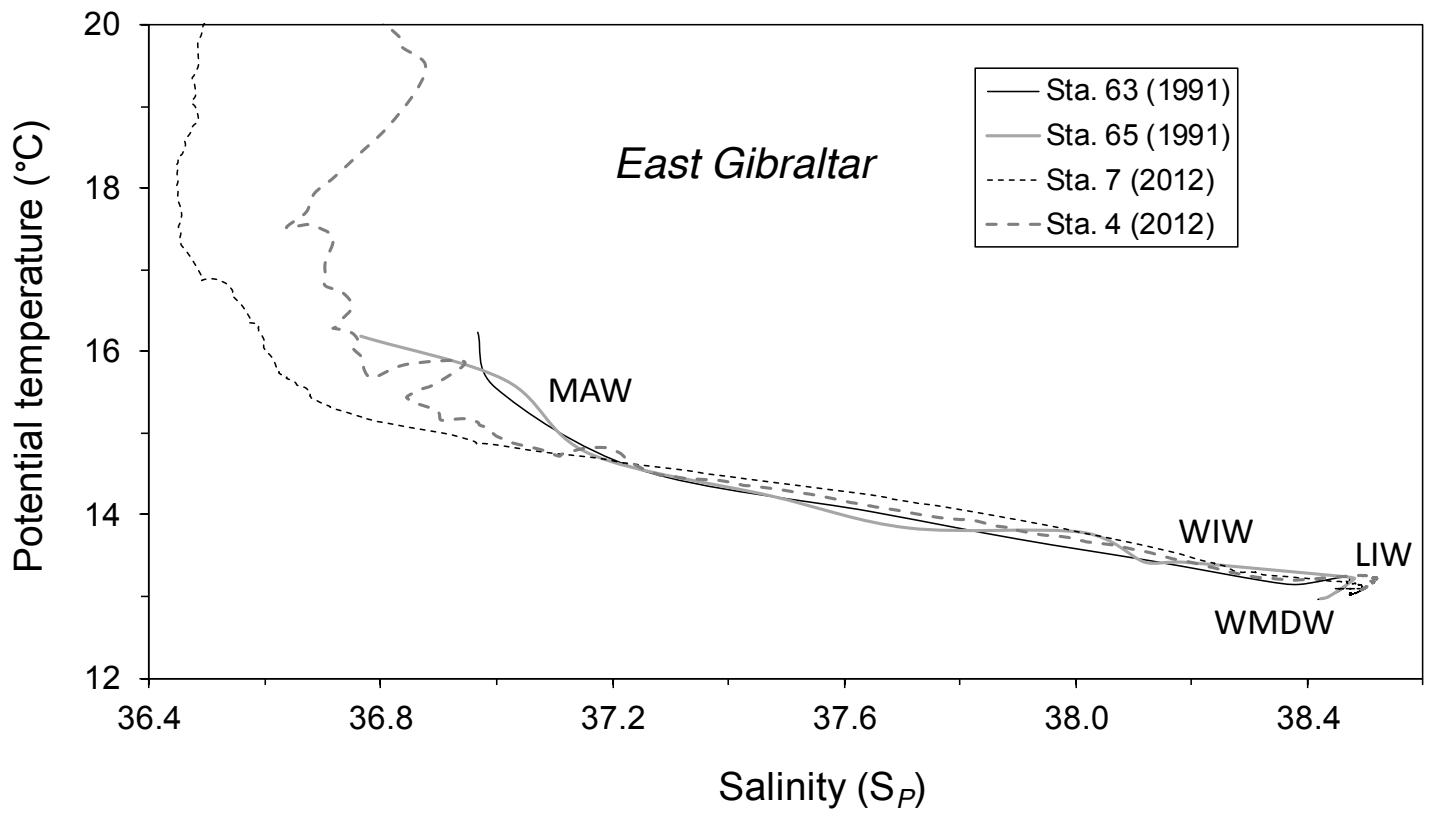


Fig. 3

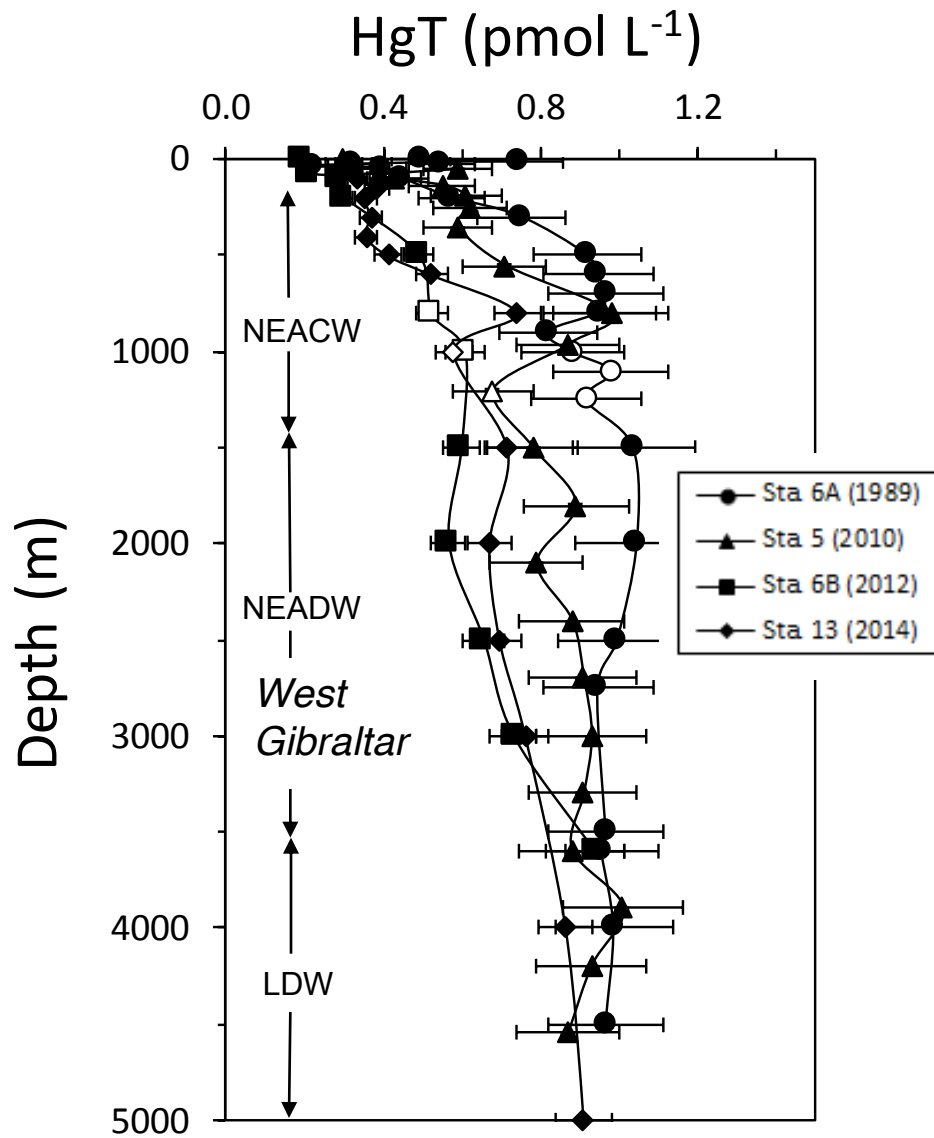


Fig. 4

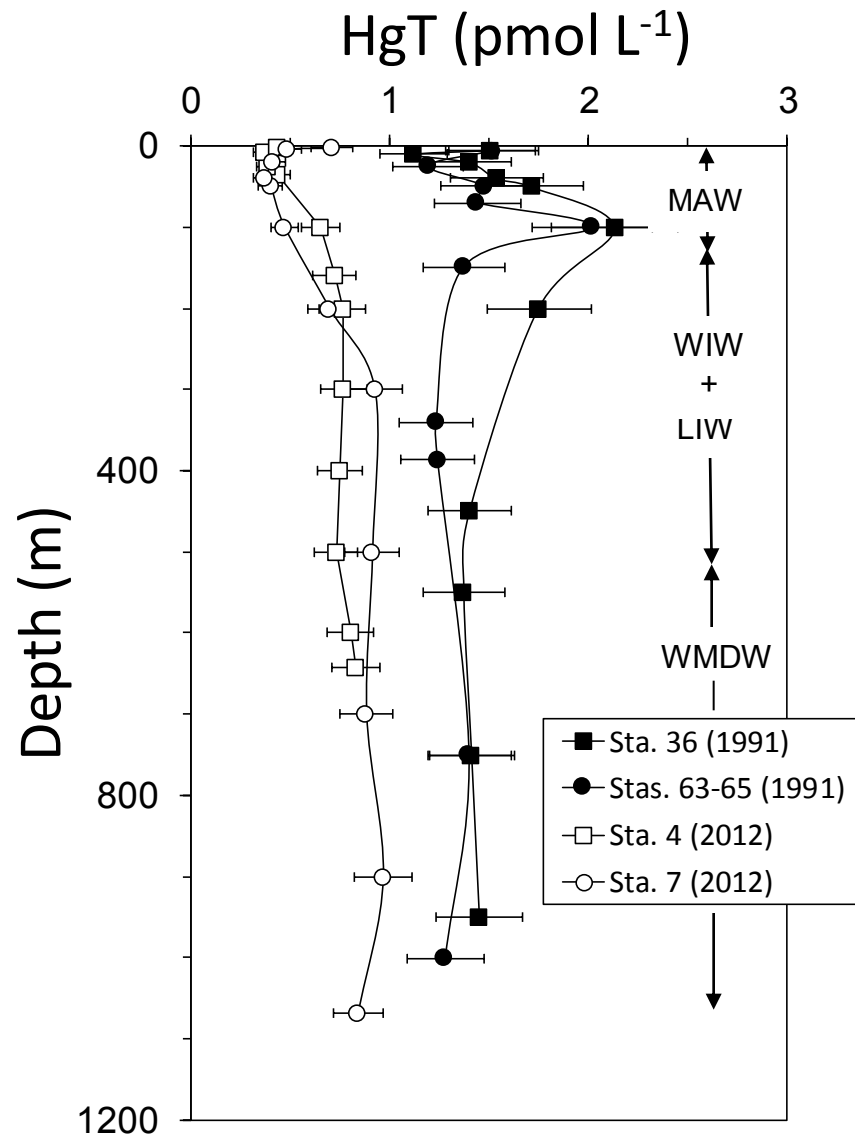


Fig. 5

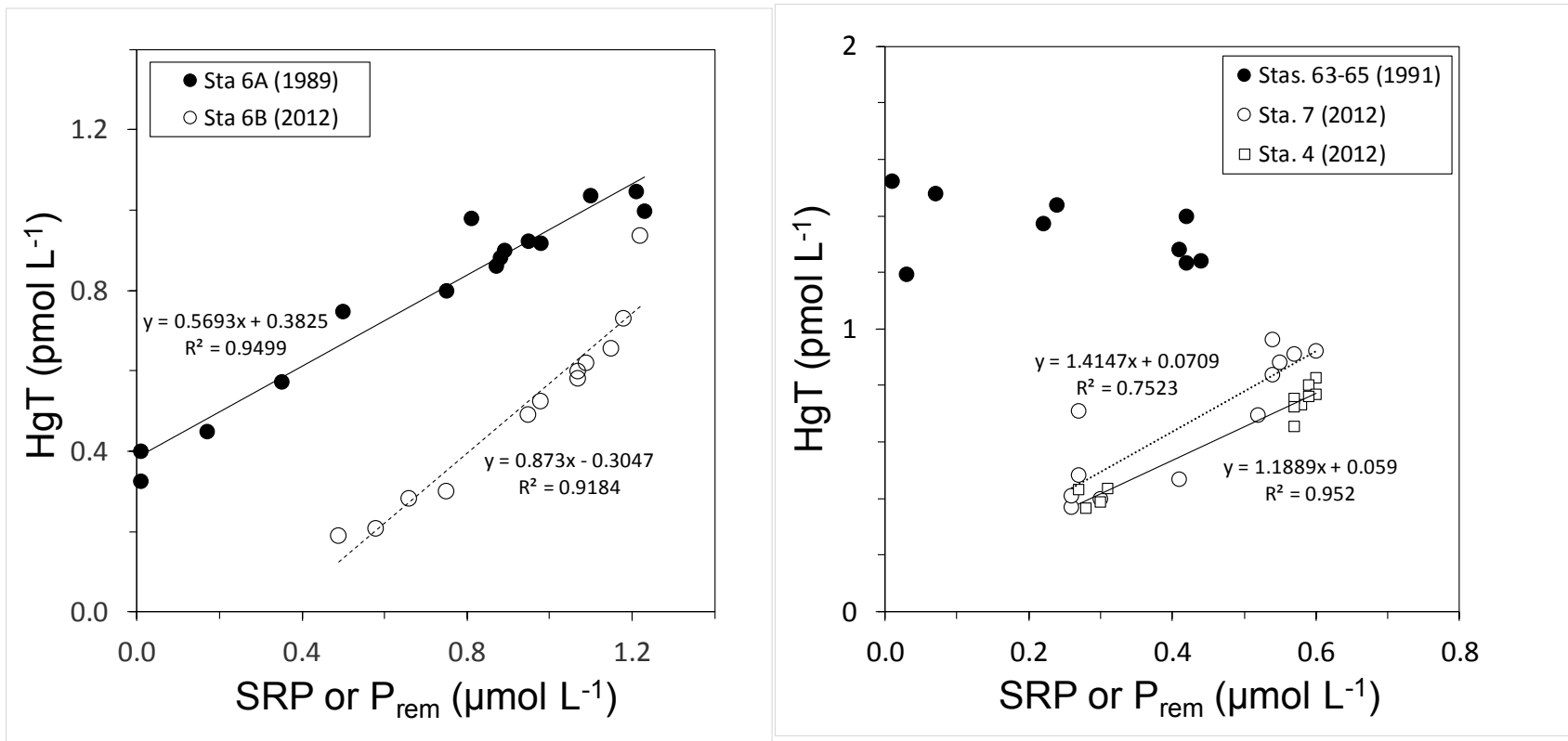
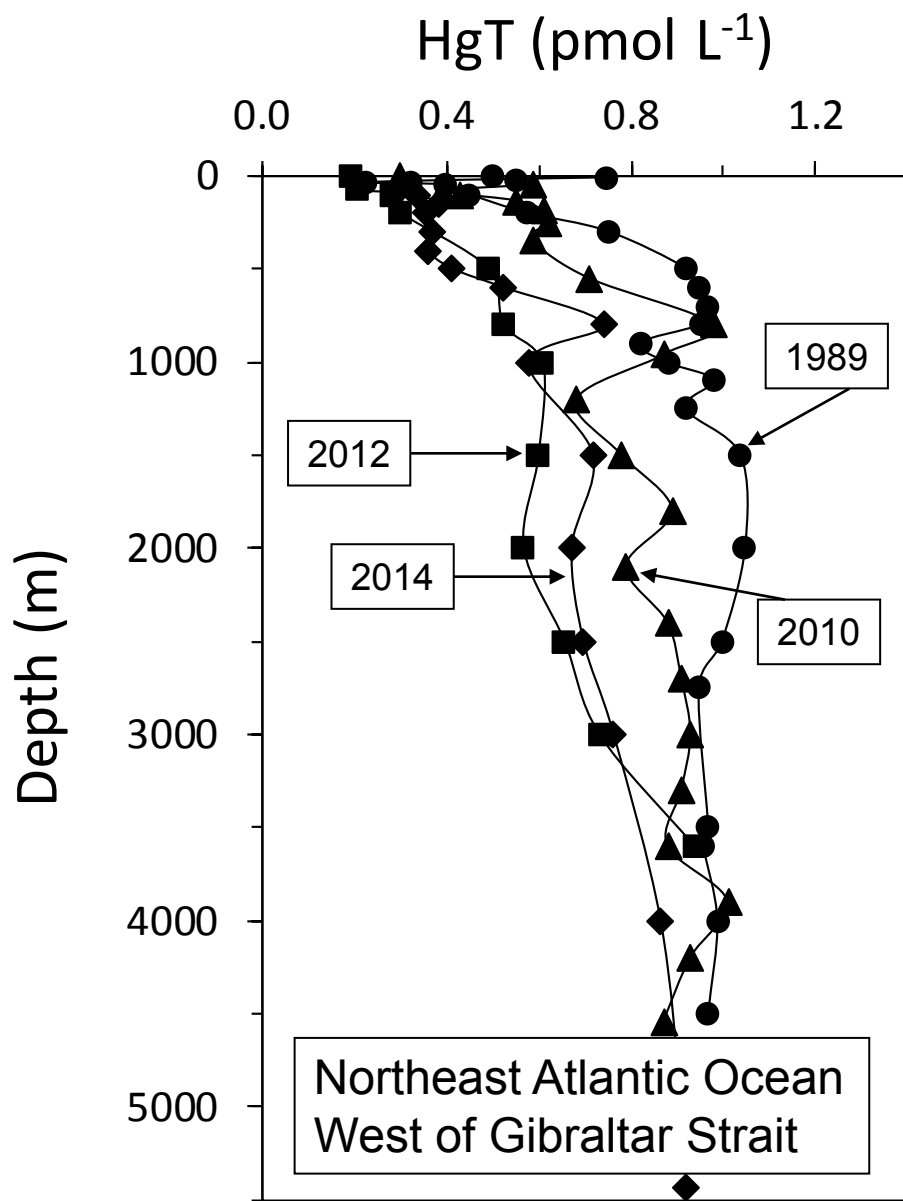


Fig. 6



1 **Supplementary Information**

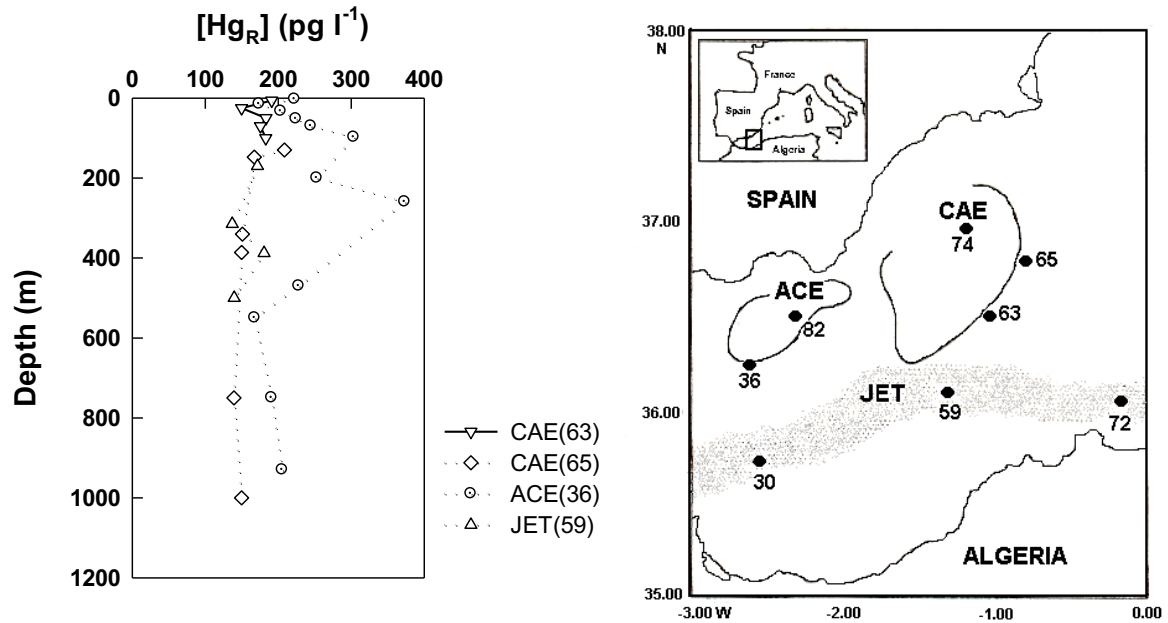
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3 **SI 1.** Easily reducible Hg (HgR) distribution during the Almofront-I cruise in the Alboran Sea (1991).

4 Note that the relationship between HgR and total Hg (HgT) was linear between 200 and 1000 m ( $R^2 =$

5 0.71), with a mean HgR/HgT ratio of 0.45; this ratio was used to extrapolate from HgR six missing

6 HgT concentration values at Sta. 36.

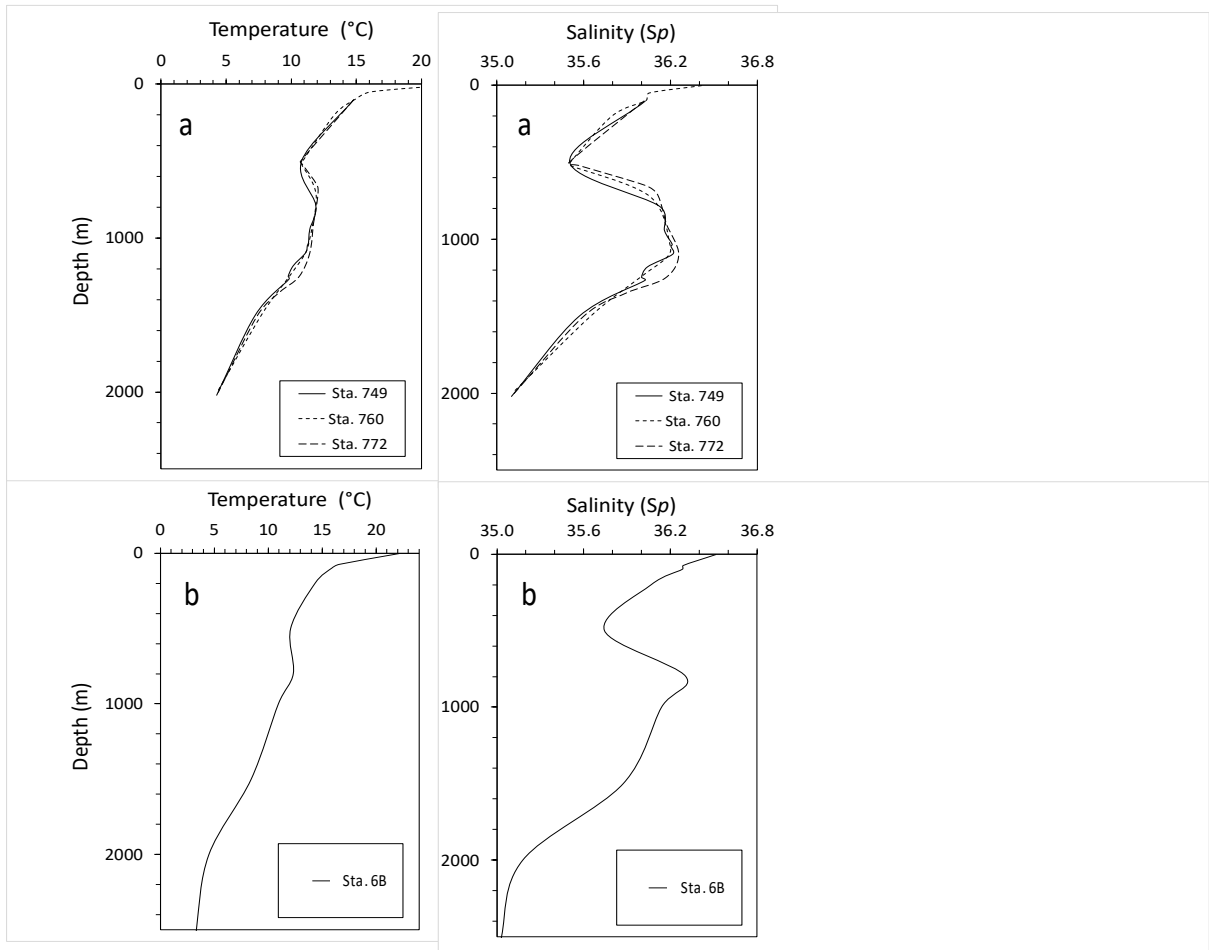


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10 **Figure S1.** West of Gibraltar. Temperature and salinity profiles during the (a) MEDATLANTE-II cruise  
11 (1989) at Stas. 749, 760 and 772 closed to Sta. 6A, and during the (b) FENICE cruise (2012) at Sta 6B.



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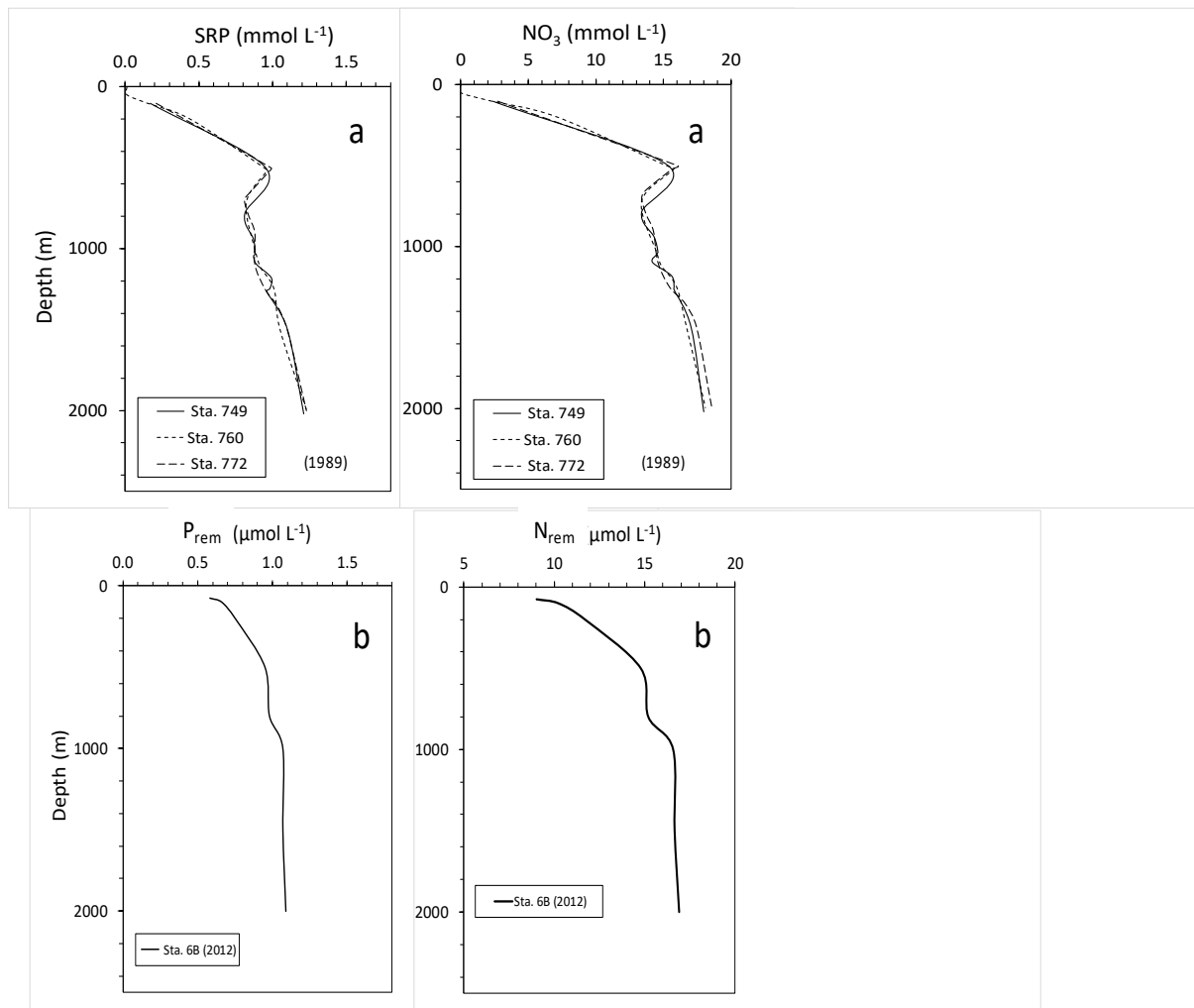
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23 **Figure S2.** West of Gibraltar. Soluble Reactive phosphorus (SRP) and remineralized phosphorus  
24 ( $P_{rem}$ ) and nitrate ( $NO_3$ ) and remineralized nitrogen ( $N_{rem}$ ) profiles during the (a) MEDATLANTE-II  
25 cruise (1989) at Stas. 749, 760 and 772 closed to Sta. 6A, and during the (b) FENICE cruise (2012) at  
26 Sta 6B. The Redfield ratios used for  $P_{rem}/N_{rem}/AOU$  are 1/17/141 according to Minster and Boulhadid  
27 (1987).



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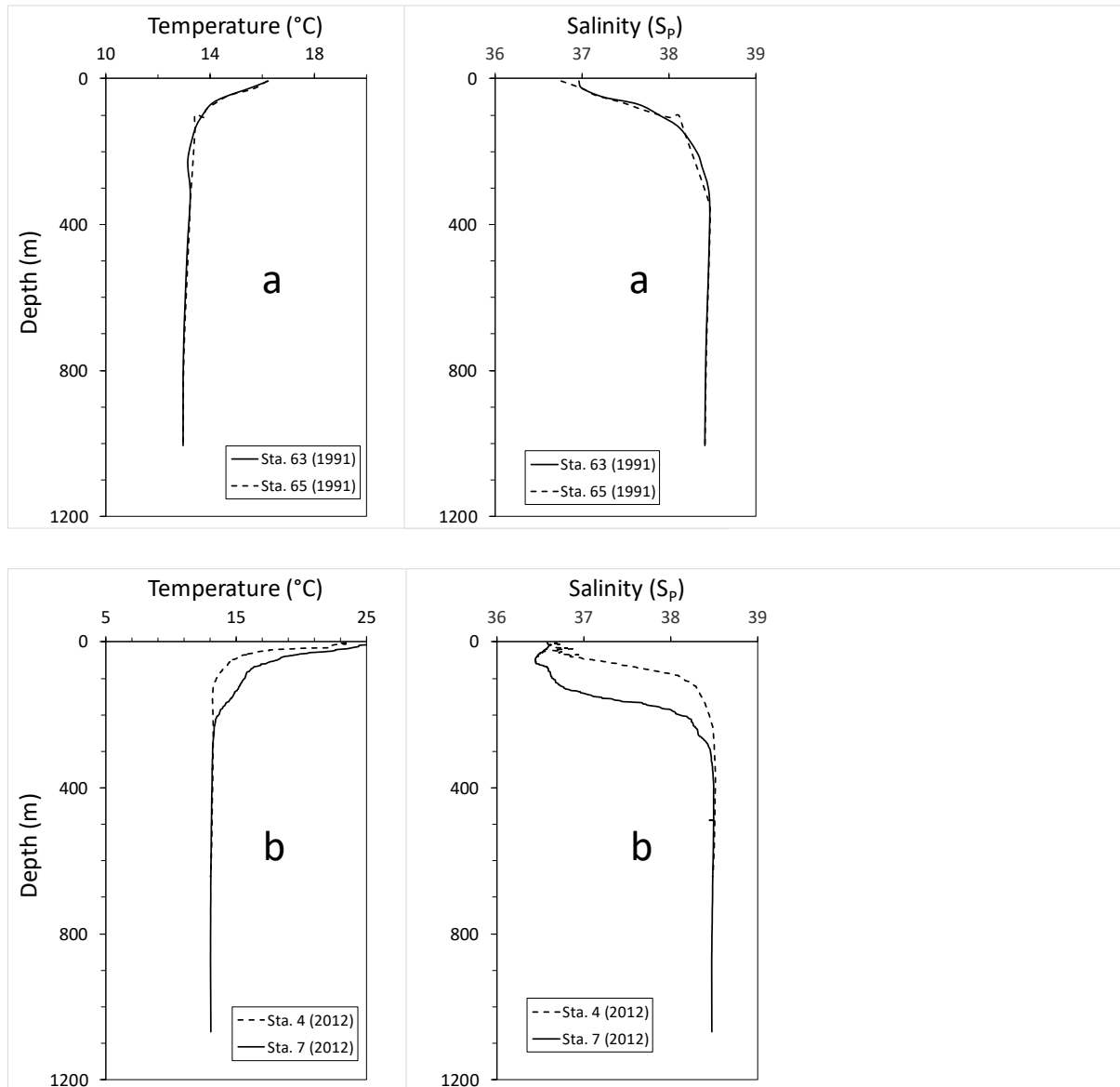
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36 **Figure S3.** East of Gibraltar. Temperature and salinity profiles during the (a) ALMOFRONT-I cruise  
37 (1991) at Stas. 63 and 65, and during the (b) FENICE cruise (2012) at Stas. 4 and 7.

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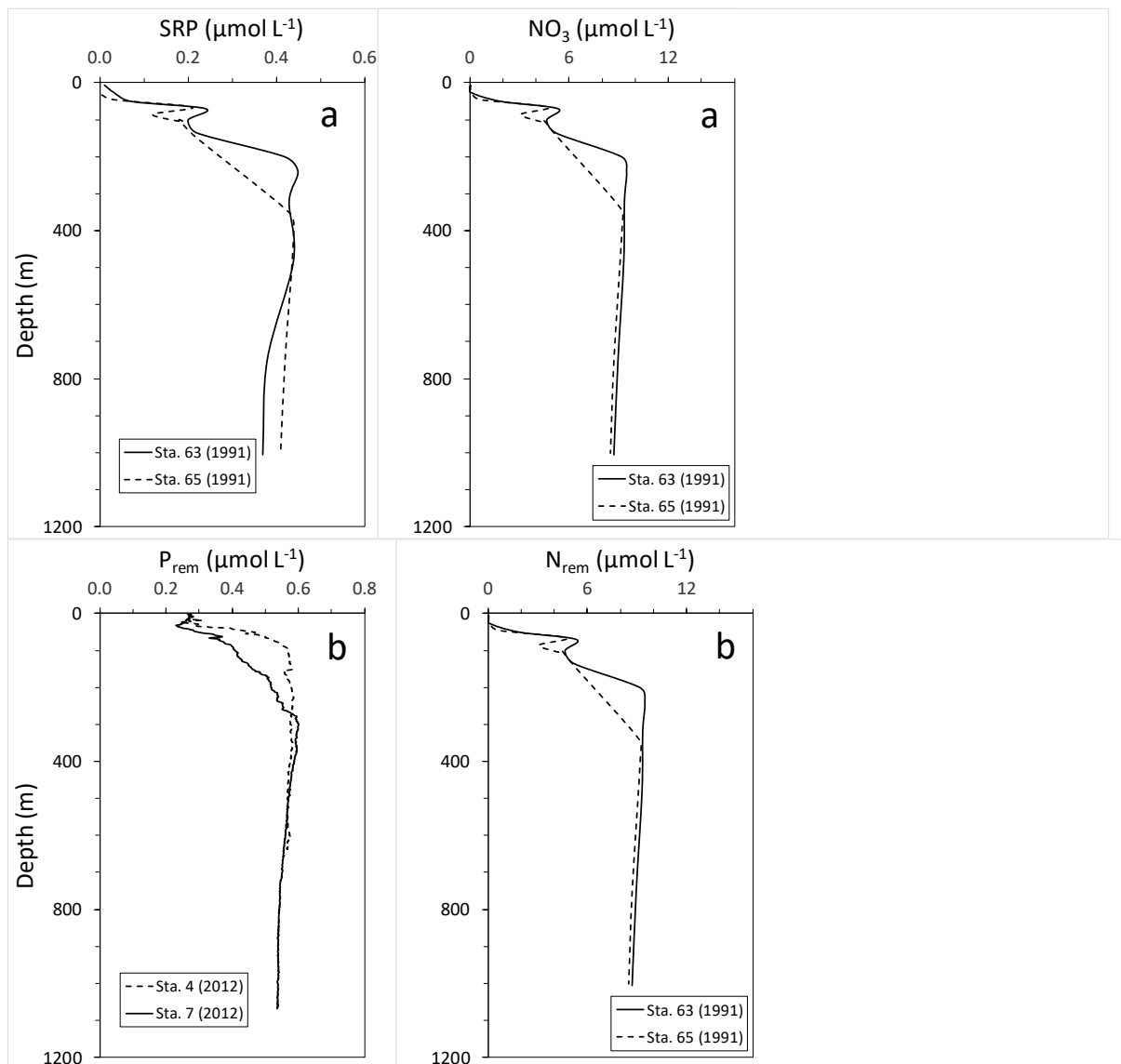
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46 **Figure S4.** East of Gibraltar. Soluble Reactive phosphorus (SRP) and remineralized phosphorus ( $P_{rem}$ )  
47 and nitrate ( $NO_3$ ) and remineralized nitrogen ( $N_{rem}$ ) profiles during the (a) ALMOFRONT-I cruise  
48 (1991) at Stas. 63 and 65, and during the (b) FENICE cruise (2012) at Stas. 4 and 7. The Redfield ratios  
49 used for  $P_{rem}/N_{rem}/AOU$  are 1/22/237 according to Béthoux et al. (2005).

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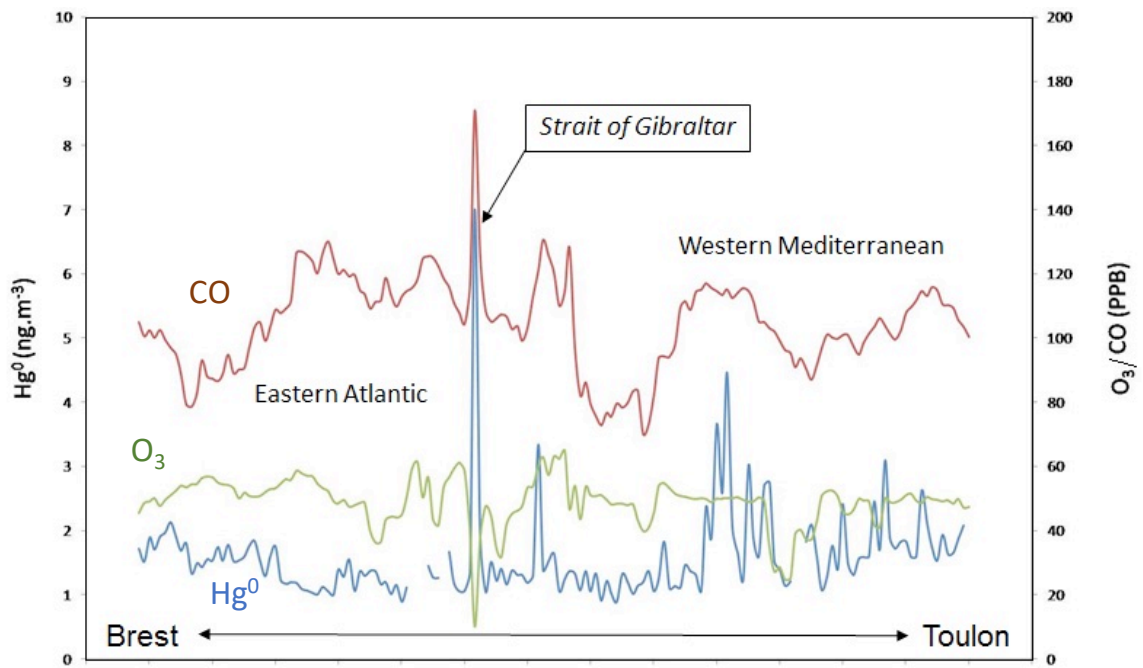
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57 **Figure S5.** Hg concentrations, ozone and carbon monoxide in the atmosphere (10 m above the sea  
58 level) during a transit between Toulon and Brest in April 2012.



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