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1 **Bioconcentration, bioaccumulation and biomagnification of mercury in plankton of the**  
2 **Mediterranean Sea**

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16 the Mediterranean Sea: Biological pump and interactions from regional to global  
17 approaches”

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19 **Revised version**

20  
21 **Highlights**

- 22 - Highest THg bioconcentration was highlighted in picoplankton
- 23 - MMHg biomagnified while THg decreased along the plankton food web
- 24 - MMHg bioaccumulated and biomagnified in zooplankton
- 25 - Highest zooplankton MMHg concentrations were observed in oligotrophic areas

26  
27 **Abstract**

28  
29 Plankton plays a prominent role in the bioaccumulation of mercury (Hg). The MERITE-  
30 HIPPOCAMPE campaign was carried out in spring 2019 along a north-south transect  
31 including coastal and offshore areas of the Mediterranean Sea. Sampling of sea water and  
32 plankton by pumping and nets was carried out in the chlorophyll maximum layer. Two size-  
33 fractions of phytoplankton (0.7–2.7 and 2.7–20 µm) and five of zooplankton (between 60

1 34 and >2000  $\mu\text{m}$ ) were separated, and their total mercury (THg) and monomethylmercury  
2 35 (MMHg) contents were measured. Bioconcentration of THg was significantly higher in the  
3 36 smallest phytoplankton size-fraction dominated by *Synechococcus* spp. The bioaccumulation  
4 37 and biomagnification of MMHg in zooplankton was influenced by size, food sources,  
5 38 biochemical composition and trophic level. MMHg was biomagnified in the plankton food  
6 39 web, while THg decreased toward higher trophic levels. Higher MMHg concentrations were  
7 40 measured in oligotrophic areas. Plankton communities in the Southern Mediterranean Sea  
8 41 had lower MMHg concentrations than those in the Northern Mediterranean Sea. These  
9 42 results highlighted the influence of environmental conditions and trophodynamics on the  
10 43 transfer of Hg in Mediterranean plankton food webs, with implications for higher trophic  
11 44 level consumers.  
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## 22 46 **Keywords**

23 47 Mercury, methylmercury, plankton, trophic transfer, contamination, food web  
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## 27 49 **1. Introduction**

28  
29 50  
30 51 Mercury (Hg), predominantly in its inorganic form, is released to the atmosphere and the  
31 52 ocean from natural and anthropogenic sources, with the latter largely outweighing the  
32 53 former (Outridge et al., 2018). Anthropogenic Hg emissions are thought to have tripled  
33 54 surface ocean Hg levels (Lamborg et al., 2014). Marine apex predator Hg levels are driven  
34 55 by anthropogenic Hg inputs and marine methylmercury (MeHg) production (Medieu et al.  
35 56 2022), yet their relative importance is still poorly constrained (Wang et al. 2019). The  
36 57 relatively small and semi-enclosed Mediterranean Sea receives proportionally more Hg and  
37 58 the sea water MeHg dynamics are well known, making it an ideal case study (Cossa et al.,  
38 59 2022). Microorganisms present in the ocean can convert inorganic Hg into MeHg species  
39 60 (Villar et al., 2020), namely monomethylmercury (MMHg) and dimethylmercury (DMHg).  
40 61 MMHg is a potent neurotoxic which bioaccumulates in organisms with size and age and  
41 62 biomagnifies in food webs, reaching high concentrations in apex predators (Morel et al.,  
42 63 1998). Mediterranean human populations are exposed to high levels of Hg related to higher  
43 64 marine fish consumption, posing a potential health risk (UNEP, 2019; Petrova et al., 2020).  
44 65 This is further exacerbated by the higher fish Hg levels in the Mediterranean Sea, often  
45 66 exceeding regulatory limits (Aston and Fowler, 1985; Storelli and Marcotrigiano, 2001;  
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67 Tseng et al., 2021).

68 Several hypotheses have been proposed to explain the so-called “Mediterranean Hg  
69 anomaly” (Aston and Fowler, 1985; Cossa and Coquery, 2005), mainly attributing the  
70 higher biota Hg levels to enhanced MeHg production. The high methylation capacities  
71 reported in the Mediterranean Sea may enhance MMHg availability to the lower trophic  
72 levels, namely plankton (Cossa and Coquery, 2005, Monperrus et al., 2007; Cossa et al.,  
73 2022). Similarly to the Arctic Ocean, the Mediterranean MeHg maxima are located at  
74 shallow depths in proximity to the phytoplankton habitat, allowing for an efficient uptake  
75 into the food web (Heimbürger et al., 2010, 2015; Cossa et al., 2012). Nevertheless, sea  
76 water Hg concentrations alone cannot explain the “Mediterranean Hg anomaly” observed for  
77 biota (Aston and Fowler, 1985; Cossa and Coquery, 2005). While Hg concentrations have  
78 been extensively observed in Mediterranean higher trophic level biota (Cinnirella et al.,  
79 2019 and references therein), only few studies have been conducted on plankton Hg levels  
80 (Cossa et al., 2012; Chouvelon et al., 2019).

81 Although studies are scarce, plankton organisms are hypothesized to play a key role in the  
82 accumulation and transfer of Hg in the Mediterranean food webs (Cossa and Coquery, 2005;  
83 Harmelin-Vivien et al., 2009; Chouvelon et al., 2018, 2019; Cossa et al., 2022).  
84 Phytoplankton bioconcentrates Hg more than 10,000 times from sea water, which is by far  
85 the largest enrichment step of Hg along the marine food web (Lee and Fisher, 2016).  
86 Mercury bioconcentration has been shown to be related to species and size, with the highest  
87 bioconcentration for smallest phytoplankton cells largely driven by their higher surface-to-  
88 volume ratio (Lee and Fisher, 2016). In the Mediterranean Sea, phytoplankton is mainly  
89 composed of small cells (pico- and nanoplankton) with a low biomass (Leblanc et al., 2018;  
90 Boudriga et al., 2022; Tesán-Onrubia et al., 2023), and a high Hg bioconcentration may thus  
91 be expected (Chouvelon et al., 2018). In addition, the slow-sinking pico- and  
92 nanophytoplankton cells are more prone to remineralization (Guidi et al., 2009) and thus to  
93 providing more Hg for methylation (Heimbürger et al., 2010). Due to technical difficulties,  
94 data on Hg concentrations in small phytoplankton fractions collected in the field remain  
95 scarce to date (Gosnell and Mason, 2015; Gosnell et al., 2017). Zooplankton represents the  
96 link between phytoplankton and higher trophic levels. MMHg bioaccumulates in  
97 zooplankton with size and age mainly because of food uptake (Tsui and Wang, 2004;  
98 Hammerschmidt et al., 2013). A size-based approach has become widely used to study the  
99 structure and functioning of the planktonic compartment (Rau et al., 1990; Rolff, 2000;

100 Carlotti et al., 2008; Hunt et al., 2017). However, taxonomic and groups composition differ  
101 between plankton size-fractions (Boudriga et al., 2023; Fierro-González et al., 2023).  
102 Zooplankton may exhibit different feeding patterns across size-fractions, ranging from  
103 herbivorous to carnivorous, resulting in different Hg exposure (Pućko et al., 2014).  
104 Oligotrophic ecosystems are characterized by lower growth rates, which reduces the  
105 biodilution of Hg in biota (i.e., decrease in Hg with increasing biomass) (Silva et al., 2008;  
106 Cossa et al., 2012; Chauvelon et al., 2018). The relatively warm waters of the Mediterranean  
107 Sea may stimulate Hg-methylating microbes (Bacci et al., 1989; Heimbürger et al. 2010),  
108 likewise increase the metabolic activity of higher trophic levels, and reduce excretion rates  
109 of MMHg (Remen et al., 2015; Maulvault et al., 2016). The biochemical composition of  
110 organisms can influence their physico-chemical affinity for Hg bioaccumulation (Wu and  
111 Wang, 2011; Charette et al., 2021). Overall, little is known about the biological mechanisms  
112 of accumulation of Hg in plankton in the Mediterranean Sea and the influence of species,  
113 size, and biochemical composition of plankton. Moreover, Hg biomagnification in the food  
114 web may be related to food sources but also to trophic structure. The longer food web of  
115 oligotrophic ecosystems (Décima, 2022; Tesán-Onrubia et al., 2023) may increase MMHg  
116 biomagnification (Cossa et al., 2012, 2022). Nevertheless, to date, biomagnification in a  
117 size-fractionated plankton food web has, to our knowledge, never been studied.  
118 The Mediterranean Sea represents a semi-enclosed basin with spatial nutrient gradients and  
119 different sources and concentrations of Hg in sea water (Durrieu de Madron et al., 2011;  
120 Cossa et al., 2022). Spatial variations of Hg concentrations have been shown in both sea  
121 water and sediments (Cossa and Martin, 1991; Horvat et al., 1999; Covelli et al., 2001;  
122 Tessier et al., 2011; Rosati et al., 2020), potentially impacting Hg concentrations in fishes  
123 (Kucuksezgin et al., 2001; Cresson et al., 2015) and at all levels of the food web (Chen et  
124 al., 2008). Gosnell and Mason (2015) hypothesized that the spatial variability of Hg  
125 concentrations in plankton size-fractions is also related to the plankton productivity.  
126 However, in the Mediterranean Sea, no spatially resolved data is available on the Hg content  
127 of plankton.  
128 To investigate the “Mediterranean Hg anomaly” at the base of the pelagic food web,  
129 sampling different plankton size classes remains a challenge, the main technical difficulty  
130 being the collection of large quantities for subsequent chemical analyses. A key feature of  
131 the MERITE-HIPPOCAMPE campaign was the implementation of targeted sampling  
132 strategies for the collection of large quantities of size-fractionated phyto- and zooplankton at

133 the chlorophyll maximum layer (CML). Throughout the MERITE-HIPPOCAMPE cruise,  
134 samples were taken for sea water, different size-fractions of phyto- (0.7–2.7, 2.7–20  $\mu\text{m}$ )  
135 and zooplankton (60–200, 200–500, 500–1000, 1000–2000 and >2000  $\mu\text{m}$ ). Complementary  
136 studies were also conducted on environmental parameters, species or groups composition,  
137 biochemical and stable isotopes composition of the different size-fractions (Boudriga et al.,  
138 2022; Fierro-González et al., 2023; Tesán-Onrubia et al., 2023; Tedetti et al., 2023). The aim  
139 of our study was to investigate the bioconcentration, bioaccumulation and biomagnification  
140 of THg and MMHg in different plankton size classes in contrasted ecoregions of the  
141 Mediterranean Sea.

## 143 2. Material and methods

### 145 2.1 Sampling preparation

147 The MERITE-HIPPOCAMPE cruise took place in the Mediterranean Sea, between April  
148 13th and May 14th 2019, onboard the R/V *Antea* (Fig. 1; Tedetti and Tronczynski, 2019). A  
149 total of 10 stations were sampled in different ecoregions, including coastal sites in the Bay  
150 of Marseille and Toulon (France), in the Gulf of Gabès (Tunisia) and offshore  
151 Mediterranean waters (Table S1). Details on the sampling sites, the hydro-bio-geochemical  
152 context and the sampling techniques are reported in Tedetti et al. (2023).

153 Unfiltered sea water was collected under trace metal clean conditions with a 12 L GOFLO  
154 bottle (General Oceanics). Sea water was filtered through a PFA filter holder (Savillex),  
155 holding a 47 mm diameter glass fiber filter of 0.7  $\mu\text{m}$  porosity (GF/F, Whatman), conserved  
156 in PFA bottles and immediately analyzed. Suspended particulate matter was sampled using  
157 McLane Large Volume Water Transfer System Samplers (WTS6-142LV, 4–8 L  $\text{min}^{-1}$ ), also  
158 called *in situ* pumps. These *in situ* pumps were mounted with bulk and sequential filtration  
159 systems (Bishop et al., 2012), holding 142 mm diameter nylon (20  $\mu\text{m}$ ), GF/D (2.7  $\mu\text{m}$ ) and  
160 GF/F (0.7  $\mu\text{m}$ ) filters, and typically filtered between 169 and 300 L. The glass fiber filters  
161 (GF/D and GF/F, Whatman) were pre-combusted (450°C, 6 h), rinsed, dried and weighed  
162 prior to deployment. The 20  $\mu\text{m}$  nylon filters (Mougel, France) were cleaned (HCl 0.05%  
163 v/v), dried and weighed prior to deployment. After deployment, the filters were stored  
164 folded in half in pre-combusted aluminum foil at  $-20^\circ\text{C}$ .

165 Zooplankton collection was carried out towing a Multinet Plankton Sampler (Midi type with

166 0.25 m<sup>2</sup> opening, Hydro-Bios) at ~2 knots. The obtained bulk sample was consecutively  
167 sieved to obtain the following fractions: 60–200, 200–500, 500–1000, 1000–2000 and  
168 >2000 µm. Samples were stored in cleaned polypropylene tubes and conserved frozen at –  
169 20°C. In the laboratory, filters and zooplankton were freeze-dried before being analyzed.  
170 Overall, 67 samples were collected for THg and MMHg measurements in different fractions.  
171 We collected 10 samples of sea water, 10 samples of each of the following fractions: 0.7–  
172 2.7, 2.7–20, 60–200, 200–500 µm, 9 samples of the 500–1000 µm fraction, 5 samples of the  
173 1000–2000 µm fraction and 3 samples of the >2000 µm fraction.  
174 Dry weight biomass and biochemical content of all the sieved size-fractions were analyzed  
175 and are available in Tesán-Onrubia et al. (2023).

## 177 **2.2 Reagents and standards for Hg analyses**

179 Reagent and standard solutions were prepared in ultrapure water (18 MΩ cm; MilliQ).  
180 Sodium tetraethylborate (Merseburger Spezialchemikalien) solution (1% m/v) was prepared  
181 in ultrapure water and dispensed into 15 mL trace metal grade polypropylene vials (VWR).  
182 The solution was frozen initially and, after thawing, stored at 4°C for up to 3 days. Sodium  
183 acetate buffer solution (2 M) was prepared by diluting glacial acetic acid (J.T. Baker) and  
184 anhydrous sodium acetate (J.T. Baker), which was muffled at 300°C for 3 h prior to making  
185 up the solution. Nitric acid (14 M) and hydrochloric acid (12 M) were bi-distilled in a clean  
186 room under trace metal free conditions.

187 Standard solutions of inorganic Hg (iHg) (0.9 µg L<sup>-1</sup>) and MMHg (0.02 and 1 µg L<sup>-1</sup>) for  
188 plankton analysis were prepared from standard solutions (NIST3133 for iHg and a 1 µg L<sup>-1</sup>  
189 MMHg solution purchased from Brooks Rand Labs, traceable to NIST3133). The standards  
190 were diluted in 0.5% v/v nitric acid and 0.2% v/v hydrochloric acid solution using a  
191 precision balance (Mettler Toledo XS105; d = 0.01 mg).

## 193 **2.3 THg and MMHg in sea water**

195 Filtered dissolved total mercury (dHg) was analyzed on board by cold vapor atomic  
196 fluorescence spectrometry (CV-AFS) immediately after sampling. The mineralization of all  
197 dissolved Hg species was done using an acidic BrCl solution during 20 to 60 min prior to the  
198 analyses. For shipboard analyses, we used a lab-built sample sparging device connected to a

199 Tekran 2500 fluorescence detector and a chromatography package to quantify fluorescence  
200 peaks. For our analyses, a 40 mL aliquot of the digested sample containing its quantitatively  
201 oxidized mercury ( $\text{Hg}^{2+}$ ) was placed in a gas-stripping FEP tube. An excess of  $\text{SnCl}_2$  was  
202 added immediately before closing it to convert all Hg into gaseous elemental Hg,  $\text{Hg}(0)$ . The  
203 sample was sparged in a FEP tube at  $150 \text{ mL min}^{-1}$  for 4 min with Hg-free Ar to exsolve  
204  $\text{Hg}(0)$  and to sweep it toward a gold trap where it was retained. Mercury was thermally  
205 desorbed from the trap and swept by an argon stream into the CV-AFS detector. For dHg  
206 analyses, the daily 4-point external linear calibration curves were verified with an aliquot of  
207 a certified reference material (ORMS-5, National Research Council Canada) that was  
208 analyzed every fifth run. Additional 1-point recalibration curves were acquired when the  
209 instrument's response drifts by more than 5% from the target value of the reference material.  
210 Overall precision and accuracy of dHg measurements, based on repeated analyses of  
211 samples, standards and CRMs, was better than 10%, and limits of quantification attained  
212 during the cruise were better than  $5 \text{ pg L}^{-1}$ , based on repeated analyses of  $4 \text{ pg Hg}^{2+}$ .  
213 Unfiltered MeHg species were analyzed back at the laboratory in samples acidified to 0.5%  
214 v/v with HCl 11N, and stored in FEP bottles without headspace. Acidification converts the  
215 gaseous DMHg to MMHg, and thus the sum of both is measured as MeHg. The general  
216 principles of the hydride generation are as follows. Analyses were carried out by sparging a  
217 40 mL sample aliquot with He while  $\text{NaBH}_4$  was continuously added ( $10 \text{ g L}^{-1}$  pumped at  
218  $0.25 \text{ mL min}^{-1}$ ). The evolved volatiles were retained on a 20 cm long, U-shaped cryogenic  
219 trap and chromatography column (Chromosorb with silicone OV1 at 15%) immersed in  
220 liquid nitrogen. When stripping of the MeHg is completed after 7 min, the trap is removed  
221 from liquid nitrogen and heated. As it progressively warms, the trapped Hg species  
222 including elemental and MeHg are released at different times from the column. Helium and  
223 Hg gases exiting from the outlet of the column then flowed through a 20 cm x 1 mm inner  
224 diameter quartz tube maintained at  $800^\circ\text{C}$ , where Hg species are pyrolyzed to elemental Hg.  
225 The cooled helium and Hg vapor were then directed to a mirrored cell (Hellma, Germany) of  
226 a CV-AFS detector (Tekran 2500).

227 A 2-point external calibration was done at the beginning of each day, and after every 5th  
228 sample to account for potential instrumental drift. Based on the uncertainty of low amounts  
229 of analyte ( $2 \text{ pg Hg}$  as MMHg), the detection limit was  $0.29 \text{ pg Hg}$  as MMHg, in a 40 mL  
230 sample ( $7 \text{ pg L}^{-1}$ ). The dissolved methylmercury (dMeHg) species were calculated by  
231 subtracting the particulate ( $0.7$  to  $20 \mu\text{m}$ ) from the unfiltered fraction.



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## 233 2.4 THg and MMHg in plankton

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235 THg was analyzed in zooplankton size-fractions ( $>60 \mu\text{m}$ ) using atomic absorption  
236 spectrometry (AAS, AMA 254, LECO). The analyzer was equipped with a low-level Hg  
237 optical cell. The certified reference material (MESS-4, National Research Council Canada)  
238 was measured at the beginning and end of the run to verify accuracy. The THg  
239 measurements were always within the certified values and the limit of detection,  
240 corresponding to the blank plus three times the standard deviation, was 23 pg.

241 In contrast to zooplankton, THg and MMHg on digested filters were simultaneously  
242 measured by purge-and-trap gas chromatography pyrolysis atomic fluorescence  
243 spectrometry (PT-GC-Pyr-AFS, MERX-M, Brooks Rand Labs) (Sharif et al., 2013). The  
244 biomass collected on filters was too low for measuring THg in a subsample with a signal  
245 close to the detection limits of the AAS. Secondly, particulate matter may not be evenly  
246 distributed in the filters and may not be suitable for subsampling (Bishop et al., 2012).

247 Filters were digested, and both iHg and MMHg were derivatized and measured  
248 simultaneously. Briefly, filters and zooplankton aliquots between 13 and 190 mg were  
249 digested in 20 and 60 mL, pre-combusted ( $350^\circ\text{C}$ , 5 h) glass vials with 4.57 M nitric acid  
250 (3.5–15 mL) for 12 h at  $60^\circ\text{C}$  (Hammerschmidt and Fitzgerald, 2006). Amber glass vials (60  
251 mL) were filled with ultrapure water and buffered with sodium acetate to pH 4.5–4.9. An  
252 aliquot of the acidic extract (400–800  $\mu\text{L}$ ) was then added. The solution was spiked with iHg  
253 (100 to 400  $\mu\text{L}$ ) and MMHg (10 to 400  $\mu\text{L}$ ) solutions for quantification *via* standard  
254 addition.

255 Finally, we added the derivatizing agent, sodium tetraethylborate ( $\text{NaBeT}_4$ ) and filled the  
256 vial with ultrapure water until a slightly negative meniscus was formed. The cap was  
257 tightened, and the preparation was gently mixed. The samples were measured by PT-GC-  
258 Pyr-AFS. The chromatogram typically contains three peaks, corresponding to different  
259 mercury species: elemental mercury ( $\text{Hg}^0$ ), ethylmethylHg and diethylHg. THg was  
260 calculated as the sum of iHg and MMHg. We followed a standard addition protocol to  
261 estimate THg and MMHg concentrations. The low concentrations and matrix effect  
262 associated with biological samples make standard addition a more reliable analytical  
263 approach than external calibration. For a single sample, five measurements were performed  
264 to construct a regression line. Of the five measurements, two corresponded to sample

265 replicates without addition, and the remaining three to three different volumes of standard  
266 solution. The targeted standard volumes corresponded to between 1 and 5 times the amount  
267 of iHg or MMHg present in the sample. The linear regression between added iHg or MMHg  
268 and the peak height was calculated. The y-intercept of the linear regression was used to  
269 obtain the iHg and MMHg concentrations. The correlation coefficients ( $R^2$ ) ranged from  
270 0.96 to 1.00. The certified reference material (DORM-4, National research council Canada)  
271 was digested and measured similarly to the samples. The measurements corresponded  
272 respectively to 79 and 85% of the THg and MMHg certified concentrations. The limits of  
273 detection for iHg and MMHg were respectively 8 and 0.8 pg.

274 Based on the measurement made during the MERITE-HIPPOCAMPE cruise between  
275 plankton biomass wet and dry weights (% of water in plankton:  $90 \pm 3\%$ ; Tedetti et al.,  
276 2023), a factor of 10 was used to allow comparison of the THg and MMHg concentrations  
277 expressed here on a dry weight basis, with those reported in the literature. Further  
278 experiments were carried out to assess the THg blanks in the filters, which could be due to  
279 the retention of dissolved, colloidal and particulate Hg ( $<0.7 \mu\text{m}$ ) (Table S2). Different  
280 volumes of sea water (10–80 L) were filtered as replicates through three stacked  $0.7 \mu\text{m}$   
281 glass fiber filters (GF/F, 142 mm). THg blanks measured on the 2nd and 3rd filters were not  
282 significantly different ( $H = 1$ ;  $p > 0.05$ ) and represented less than 2% of the particulate  
283 fraction measured on the 1st filter ( $n = 12$ ). We therefore assume that the THg measured on  
284 the filters was representative of the particulate fraction, with a negligible contribution of the  
285 dissolved ( $<0.7 \mu\text{m}$ ) fraction.

## 287 2.5 Data treatment

289 The effect of size-fractions and geographical area on the THg, MMHg and fraction of  
290 MMHg were assessed by means of one-way ANOVA (F) or non-parametric Kruskal-Wallis  
291 (H) tests after testing for normality and homogeneity of variances, followed by appropriate  
292 paired comparison tests, using the software Statistica 12. Principal component analysis  
293 (PCA) was performed using the R software (R Core Team, 2017). The PCA used data from  
294 Tesán-Onrubia et al. (2023) that may influence THg and MMHg in zooplankton: proteins,  
295 carbohydrates, lipids,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , C/N, THg and MMHg in the 0.7–2.7 and 2.7–20  $\mu\text{m}$   
296 fractions, phytoplankton size-fractions biomass, zooplankton size-fractions biomass, and  
297 plankton group composition.

298 The bioconcentration factor of THg and MMHg ( $BCF_{Hg}$ , in  $L\ kg^{-1}$ ) was calculated between  
299 plankton and sea water:

$$BCF_{Hg} = \left( \frac{[Hg]_{Plankton}}{[Hg]_{Seawater}} \right) \times 10^6$$

300 where  $[Hg]_{Plankton}$  is the dry weight concentrations of THg or MMHg on a given size-fraction  
301 (in  $ng\ g^{-1}$ ),  $[Hg]_{sea\ water}$  is the dissolved concentrations of Hg (dHg) or MeHg (dMeHg) in sea  
302 water (in  $pg\ L^{-1}$ ), and  $10^6$  is the unit conversion factor.

303 The trophic magnification factor ( $TMF_{Hg}$ ) of THg and MMHg was calculated within the  
304 planktonic food web as follows:

$$TMF_{Hg} = 10^a$$

$$\text{Log } [Hg]_{Plankton} = \delta^{15}N * a + b$$

307 where  $\log [Hg]_{Plankton}$  is the logarithm of the THg or MMHg concentration in plankton  
308 fractions,  $\delta^{15}N$  is the nitrogen stable isotope in the plankton fraction and  $a$  is the slope of the  
309 linear regression.

### 3. Results and discussion

314 The basis of marine Mediterranean food webs is mainly constituted of pico- (0.7–2.7  $\mu m$ ) and  
315 nanophytoplankton (2.7–20  $\mu m$ ) (Bănaru et al., 2013; 2019). These phytoplankton fractions  
316 are consumed by zooplankton (Hunt et al., 2017; Tesán-Onrubia et al., 2023), which transfer  
317 the organic matter and the associated contaminants up to higher trophic level consumers. THg  
318 and MMHg measurements on the 0.7–2.7 and 2.7–20  $\mu m$  size-fractions are scarce and were  
319 usually only measured on relatively small sea water volumes (Gosnell and Mason, 2015;  
320 Gosnell et al., 2017). In the present study, these analyses were performed on large volume  
321 samples (>150 L), which enabled precise Hg species measurements and complementary  
322 biological and biochemical analyses (Tesán-Onrubia et al., 2023).

#### 3.1 THg and MMHg in phytoplankton

325 A contrasted pattern of the relationship between concentration and size was observed for THg  
326 and MMHg in phyto- and zooplankton size classes (Fig. 2a, 2b, Tables S3, S4). Both THg and

327 MMHg concentrations decreased in phytoplankton with increasing cell size, but the difference  
328 was statistically significant only for THg in the smallest size-fractions ( $86 \pm 32 \text{ ng g}^{-1} \text{ dw}$  in  
329 the  $0.7\text{--}2.7 \mu\text{m}$  fraction, and  $42 \pm 28 \text{ ng g}^{-1} \text{ dw}$  in the  $2.7\text{--}20 \mu\text{m}$  fraction) ( $F = 10.6$ ,  $p =$   
330  $0.005$ ). These values were in the upper range (maxima  $42\text{--}160 \text{ ng g}^{-1} \text{ dw}$ ) of previous  
331 observations obtained on a wide range of phytoplankton fractions (Baeyens et al., 2003;  
332 Hammerschmidt and Fitzgerald, 2006; Beldożska and Kobos, 2018; Cossa et al., 2012;  
333 Hammerschmidt et al., 2013; Gosnell and Mason, 2015; Lamborg et al., 2016; Fox et al.,  
334 2017; Harding et al., 2018). However, our measurements were lower than the maxima ( $420\text{--}$   
335  $740 \text{ ng g}^{-1} \text{ dw}$ ) reported in studies with larger size-fractions (Bargagli et al., 1998), indirect  
336 measurements (Luengen and Flegal, 2009), small volumes of filtered sea water (Gosnell et al.,  
337 2017) and estuaries (Kehrig et al., 2009; Mason et al., 2021, 2023) (Table S5). Mean MMHg  
338 concentrations of  $1.2 \pm 0.7 \text{ ng g}^{-1} \text{ dw}$  and  $0.8 \pm 0.6 \text{ ng g}^{-1} \text{ dw}$  were measured in the  $0.7\text{--}2.7$   
339 and in the  $2.7\text{--}20 \mu\text{m}$  fractions, respectively, and are within the range of previous studies. Our  
340 observations correspond well to MMHg concentration measured in phytoplankton (Baeyens et  
341 al., 2003; Hammerschmidt and Fitzgerald, 2006; Luengen and Flegal 2009; Cossa et al., 2012;  
342 Hammerschmidt et al., 2013; Gosnell and Mason, 2015; Gosnell et al., 2017; Fox et al., 2017;  
343 Harding et al., 2018) but were lower than concentrations modeled for the Mediterranean Sea  
344 ( $2\text{--}15 \text{ ng g}^{-1} \text{ dw}$ ) (Rosati et al., 2022) and for the global ocean ( $12\text{--}185 \text{ ng g}^{-1} \text{ dw}$ ) (Zhang et  
345 al., 2020; Wu et al., 2021).

346 Chouvelon et al. (2019) showed that Hg bioaccumulation in the lowest size-fractions ( $6\text{--}60$   
347  $\mu\text{m}$ ) may be high compared to larger plankton size-fractions. The higher surface-to-volume  
348 ratio (giving a higher contact surface), which increases Hg uptake (Fisher, 1985), may explain  
349 the higher concentrations of THg measured in picoplankton in our study. Small phytoplankton  
350 cells are prevalent in Mediterranean oligotrophic waters and during our sampling survey  
351 (Boudriga et al., 2022). Enhanced concentrations of MeHg have previously been observed in  
352 sea water during pico- and nanoplankton blooms in the Mediterranean Sea (Heimbürger et al.,  
353 2010).

354 Low dissolved Hg (dHg) and MMHg (dMHg) concentrations measured in this study ( $94 \pm 32$   
355  $\text{pg L}^{-1}$  and  $13 \pm 7 \text{ pg L}^{-1}$ , respectively, Table S6) are likely due to enhanced photochemistry  
356 and evasion (Cossa et al., 2009; Sunderland et al., 2009; Heimbürger et al., 2010; Cossa et al.,  
357 2022). The mean  $\text{BCF}_{\text{THg}}$  values in the  $0.7\text{--}2.7$  and  $2.7\text{--}20 \mu\text{m}$  fractions were  $2 \times 10^6 \text{ L kg}^{-1}$   
358  $\text{dw}$  and  $1 \times 10^6 \text{ L kg}^{-1} \text{ dw}$ , respectively, while the mean  $\text{BCF}_{\text{MMHg}}$  values were  $1 \times 10^5 \text{ L kg}^{-1}$   
359  $\text{dw}$  and  $8 \times 10^5 \text{ L kg}^{-1} \text{ dw}$ , respectively (Table S7). Mediterranean phytoplankton of different

360 size classes bioconcentrate THg and MMHg  $10^6$  and  $10^5$  times, respectively, from sea water,  
361 these values being in the upper range of those reported in the literature (Table S5). The mean  
362 THg bioconcentration values observed in this study are >10 times higher than the partitioning  
363 coefficient of suspended particulate matter ( $K_d$ ), generally used in global THg models (Zhang  
364 et al., 2014), which testifies to the need for more accurate regional data. Various studies have  
365 already highlighted the underestimation of  $K_d$ , constraining Hg export fluxes from the surface  
366 and, more broadly, its biogeochemical cycle (Lamborg et al., 2016; Tesán-Onrubia et al.,  
367 2020). It has also been observed that MMHg bioconcentration was promoted under low  
368 dissolved organic carbon concentrations (Schartup et al., 2018).

369 The MERITE-HIPPOCAMPE cruise offered a unique opportunity to couple biological and  
370 contaminant analyses (Tedetti et al., 2023), and explore for the first time the relationships  
371 between the composition of the suspended particles collected, and their THg and MMHg  
372 concentrations. Suspended particles collected on filters were a complex mixture of living and  
373 dead organisms (autotrophic and heterotrophic), also containing detritus and mineral particles.  
374 Tesán-Onrubia et al. (2023) showed that the 0.7–2.7 and 2.7–20  $\mu\text{m}$  size-fractions were  
375 dominated (86% of the total biomass) by two phytoplankton groups: *Synechococcus* spp. (~1  
376  $\mu\text{m}$ ) and nanoeukaryotes (~4  $\mu\text{m}$ ). The two axes of the PCA analysis relating THg and  
377 MMHg concentrations to the size class and group composition of phytoplankton explained  
378 56% of the variability (Fig. S1). Higher THg concentrations were associated with a  
379 dominance of *Prochlorococcus* spp. (~0.5  $\mu\text{m}$ ) in the 0.7–2.7  $\mu\text{m}$  size-fraction, and a  
380 dominance of nanoeukaryotes in the 2.7–20  $\mu\text{m}$  size-fraction. Similarly, higher MMHg  
381 concentrations were related to the dominance of *Synechococcus* spp. in the 0.7–2.7  $\mu\text{m}$  size-  
382 fraction, and to the dominance of *Cryptophyceae* (~6  $\mu\text{m}$ ) in the 2.7–20  $\mu\text{m}$  size-fraction.  
383 These two phytoplankton size-fractions constitute a large part of the diet of zooplankton  
384 organisms between 200 and 1000  $\mu\text{m}$  size, and represent an important source of Hg for  
385 consumers (Tesán-Onrubia et al., 2023).

### 3.2 THg and MMHg in zooplankton

389 THg and MMHg bioaccumulated with size among zooplankton, their concentrations  
390 increasing from 22 to 45  $\text{ng g}^{-1}$  dw, and from 3 to 7  $\text{ng g}^{-1}$  dw, respectively, in 60 to 2000  $\mu\text{m}$   
391 size-fractions (Fig. 2a, 2b, Tables S3, S4). Bioaccumulation of MMHg with zooplankton size  
392 was previously shown in the North Atlantic (Hammerschmidt et al., 2013), while no

393 difference was found for THg in the Mediterranean (Chouvelon et al., 2019). THg and MMHg  
394 concentration values reported here in the Mediterranean zooplankton were comparable to  
395 those observed in other regions (Table S8) (Stern and Macdonald, 2005; Hammerschmidt and  
396 Fitzgerald, 2006; Loseto et al., 2008; Lavoie et al., 2010; Cossa et al., 2012; Hammerschmidt  
397 et al., 2013; Gosnell and Mason, 2015; Gosnell et al., 2017; Harding et al., 2018), but were  
398 lower than those from the Arctic Ocean (Campbell et al., 2005; Foster et al., 2012; Pućko et  
399 al., 2014; Fox et al., 2017) and from one study in the Mediterranean Sea (Buckman et al.,  
400 2018). Our measured MMHg concentrations in zooplankton are in relatively good agreement  
401 with model outputs for the Mediterranean Sea (3–10 ng g<sup>-1</sup> dw) (Rosati et al., 2022) and the  
402 global ocean (1–69 ng g<sup>-1</sup> dw) (Zhang et al., 2020; Wu et al., 2021).

403 Changes in metabolism during an organism's life cycle may impact its MMHg concentration.  
404 Hammerschmidt and Fitzgerald (2006) showed reduced removal and higher uptake rates in  
405 large-size organisms compared to smaller ones. Fierro-González et al. (2023) reported an  
406 increase in carnivory with increasing size of zooplankton, which was also in agreement with  
407 increasing trophic level traced by  $\delta^{15}\text{N}$  (Tesán-Onrubia et al., 2023). The lowest THg and the  
408 highest MMHg concentrations were both measured in the largest size-fraction (>2000  $\mu\text{m}$ )  
409 (Table S3, S4 and S9), as observed in previous studies (Chouvelon et al., 2019).

410 The biochemical composition of zooplankton may also explain the accumulation of THg and  
411 particularly MMHg. MMHg concentrations were significantly correlated with particulate  
412 organic carbon (POC), proteins and lipids in zooplankton ( $R^2 = 0.47$ ,  $p < 0.0001$ ;  $R^2 = 0.18$ ,  $p$   
413  $= 0.009$  and  $R^2 = 0.25$ ,  $p = 0.002$ , respectively). The quantity of these compounds increased  
414 with the size of zooplankton, except for the >2000  $\mu\text{m}$  fraction (Tesan-Onrubia et al., 2023).  
415 The affinity of Hg for POC and proteins is due to the capacity of thiol groups present in  
416 cellular proteins to effectively bind to Hg and MMHg (Ravichandran, 2004; Yoon et al.,  
417 2005; Gosnell and Mason, 2015).

### 3.3 Trophic transfer of THg and MMHg

420 Trophic transfer in the plankton food web was assessed taking into consideration all phyto-  
421 and zooplankton size-fractions. The two smallest size-fractions of phytoplankton (0.7–2.7 and  
422 2.7–20  $\mu\text{m}$ ) presented the highest THg but the lowest MMHg concentrations with respect to  
423 most zooplankton size-fractions ( $H = 23.9$ ,  $p < 0.0001$  and  $H = 30.1$ ,  $p < 0.0001$ , respectively)  
424 (Fig. 2a, 2b, Tables S3, S4). While THg concentrations were related mainly to the effect of  
425 the surface-volume ratio on bioconcentration in phytoplankton, MMHg concentrations were

426 mainly related to predation relationships and biomagnification processes among zooplankton  
427 fractions. Biomagnification was assessed by using the  $\delta^{15}\text{N}$  as a proxy of trophic level (Fig.  
428 3). The logTHg and logMMHg showed respectively negative and positive correlations with  
429  $\delta^{15}\text{N}$  ( $R^2 = 0.1$ ,  $p < 0.05$  and  $R^2 = 0.43$ ,  $p < 0.0001$ , respectively,  $n = 57$ ), indicating a  
430 bioreduction of THg ( $\text{TMF}_{\text{THg}} = 0.9$ ) and a biomagnification of MMHg in the food web  
431 studied ( $\text{TMF}_{\text{MMHg}} = 1.7$ ). In our work, particularly low  $\text{TMF}_{\text{THg}}$  were recorded, indicating a  
432 marked bioreduction of THg within the planktonic food web. Chouvelon et al. (2009) also  
433 observed no THg increase in zooplankton fractions of increasing size, and THg  
434 biomagnification in the food web only when zooplanktivorous fishes were considered. In our  
435 case, when only zooplankton size-fractions  $>60 \mu\text{m}$  were considered, significant positive  
436 correlations were observed for both logTHg and logMMHg and  $\delta^{15}\text{N}$  ( $R^2 = 0.22$ ,  $p < 0.005$   
437 and  $R^2 = 0.39$ ,  $p < 0.0001$ , respectively), thus evidencing the biomagnification of THg  
438 ( $\text{TMF}_{\text{THg}} = 1.3$ ) and a higher biomagnification factor of MMHg ( $\text{TMF}_{\text{MMHg}} = 2.1$ ).  
439 The high proportions of MMHg, exceeding 95% in higher trophic level consumers (UNEP,  
440 2019), as well as the lack of data in the literature regarding primary producers and particularly  
441 pico- and nanoplankton, may explain these differences. The plankton  $\text{TMF}_{\text{MMHg}}$  in our study  
442 showed high values compared to other marine food webs, which also included higher trophic  
443 level organisms (Atwell et al., 1998; Campbell et al., 2005; Al-Reasi et al., 2007; Nfon et al.,  
444 2009; Lavoie et al., 2010, 2013; Cossa et al., 2012; Chouvelon et al., 2018; Harding et al.,  
445 2018; Hilgendorf et al., 2022). Low growth rates, specific to the oligotrophic Mediterranean  
446 Sea, seem to induce higher MMHg biomagnification in planktivorous food webs (Cossa et al.,  
447 2012; Chouvelon et al., 2018). The %MMHg significantly increased between phyto- and  
448 zooplankton groups from a mean of 3% in the  $0.7\text{--}20 \mu\text{m}$  fractions to 23% in the  $>60 \mu\text{m}$   
449 fraction ( $H = 35.8$ ,  $p < 0.0001$ ) (Fig. 2c), highlighting the preferred biomagnification of  
450 MMHg. Inorganic Hg has a lower assimilation efficiency compared to MMHg, while their  
451 efflux rates are similar (Mason et al., 1996; Lawson and Mason, 1998; Lee and Fisher, 2017),  
452 explaining the inverted patterns between food sources and consumers. Inorganic Hg reacts in  
453 the same way as other trace metals (Chen and Folt, 2000; Ho et al., 2007; Chouvelon et al.,  
454 2019; Chifflet et al., 2023). To our knowledge, there is no previous estimation of MMHg  
455 biomagnification in plankton food web considering different size-fractions of phyto- and  
456 zooplankton. The few studies that have explored this point consisted of models for the  
457 Mediterranean Sea (Rosati et al., 2022) and the global ocean (Zhang et al., 2020; Wu et al.,  
458 2021). Without exception, these models indicate bioreduction of MMHg in plankton food

459 webs, mainly composed of herbivorous and omnivorous organisms, and biomagnification  
460 when carnivorous organisms were taken into consideration. Our results suggest the contrary,  
461 biomagnification of MMHg occurs in all plankton consumers, independently of their trophic  
462 position.

463 The trophic transfer efficiency between phytoplankton (0.7–2.7 and 2.7–20  $\mu\text{m}$ ) and  
464 zooplankton size-fractions ( $>60 \mu\text{m}$ ) was assessed by considering the total amounts of THg  
465 and MMHg available in their respective biomasses at the CML (Fig. 4). THg amounts in  
466 phyto- and zooplankton biomass was 15 and 1  $\text{ng m}^{-3}$  of sea water, respectively, while their  
467 respective MMHg contents amounted to 200 and 300  $\text{pg m}^{-3}$ . MMHg is almost 10 times  
468 higher than that modeled in the Mediterranean Sea (Rosati et al., 2022). The trophic transfer  
469 efficiency of THg ranged from 2 to 21% (average 8%), while it was higher for MMHg,  
470 ranging from 11 to 169 %, with an average of 78%. Zooplankton can represent a comparable  
471 or even larger sink of MMHg when compared to phytoplankton. Longer lifespan together  
472 with bioaccumulation can lead to a higher MMHg storage in zooplankton despite their lower  
473 biomass than phytoplankton. The MMHg trophic transfer efficiency estimated here presented  
474 a higher value than the zooplankton daily grazing, which accounted for 2.7 to 27% of the  
475 phytoplankton stock (Fierro-González et al., 2023). Considering daily grazing and Hg  
476 concentrations in phytoplankton and assuming a quantitative assimilation of MMHg,  
477 zooplankton organisms should have grazed for 6 to 13 days to reach the MMHg  
478 concentrations measured in their body. This short integration time suggested that zooplankton  
479 could be a good bioindicator of Hg exposure over days or a few weeks. The results reported  
480 here indicated that MMHg was efficiently biomagnified and transferred along the plankton  
481 food web, in contrast to a rather inefficient transfer of inorganic Hg.

### 483 3.4 Spatial variability of THg and MMHg

484 Dissolved Hg (dHg) concentrations ranged from 50 to 165  $\text{pg L}^{-1}$  at St11 and St4,  
485 respectively. Dissolved MeHg (dMeHg) concentrations ranged from detection limits (7  $\text{pg L}^{-1}$ )  
486 at St1, St9, St11, St17 and St19 to 26  $\text{pg L}^{-1}$  in St3. Both Hg species were comparable to  
487 previous studies in the Mediterranean Sea (Jiskra et al., 2021; Cossa et al., 2022).

488 THg and MMHg concentrations in phytoplankton (0.7–20  $\mu\text{m}$ ) showed strong spatial  
489 variations in the western Mediterranean, with the highest values in the smallest fraction  
490 recorded at St1 (Toulon in the north) and St17 (Gabès in the south) (Table S3 and S4).

491 Volume concentrations of MMHg in the 0.7 to 20  $\mu\text{m}$  fractions (in  $\text{pg L}^{-1}$ ) were significantly



492 correlated to phytoplankton biomass ( $R^2 = 0.49$ ,  $p < 0.001$ ) (Table S10). This highlighted the  
493 influence of the biomass on Hg-uptake at the basis of the plankton food web. Zones with high  
494 biomass of small phytoplankton cells may store a large amount of Hg in phytoplankton,  
495 bioavailable then for grazers and higher trophic level consumers. In addition, inorganic Hg  
496 may represent a substrate for MMHg production.

497 Our results suggested higher THg and especially MMHg differences in zooplankton between  
498 stations than between size-fractions (Fig. 5, Table S3 and S4). The high growth rates and  
499 short life cycles of zooplankton make it a potentially relevant biomonitor for ambient MMHg  
500 concentrations over short periods, as suggested in the previous section. This observation  
501 contrasts with the high variability reported in marine organisms of higher trophic level related  
502 in particular to longer life span and larger home ranges (UNEP, 2019).

503 THg and MMHg concentrations of zooplankton size-fractions available at all stations (60–  
504 200, 200–500 and \*500–1000  $\mu\text{m}$ , \*unavailable for St17) were pooled to test zooplankton  
505 spatial variability that appeared higher for MMHg than for THg (Fig. 5). Significant  
506 differences were reported between stations only for MMHg ( $H = 24.0$ ,  $p = 0.004$ ). Mean  
507 MMHg concentrations differed ten-fold between minimum ( $0.6 \text{ ng g}^{-1} \text{ dw}$ , St17) and  
508 maximum values ( $9.4 \text{ ng g}^{-1} \text{ dw}$ , St1). This highlighted the importance of measuring MMHg  
509 in consumers with lower trophic levels. Zooplankton from northern (St1, 2, 3 and 4) and  
510 offshore (St9, 10 and 11) areas presented higher MMHg concentrations than those from the  
511 southern area (St15, 17 and 19) ( $H = 14.0$ ,  $p = 0.001$ ). A  $\text{TMF}_{\text{MMHg}} < 1$  indicated a  
512 bioreduction of MMHg in zooplankton and consequently a lower exposure to Hg of  
513 zooplankton along the Tunisian coast (St17 and 19). (Fig. 6).

514 The two axes of the PCA analysis, performed between THg, MMHg, POC, C/N, protein,  
515 lipids,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and biomass values in zooplankton per station, explained 57% of the  
516 variability (Fig. S2). Two groups of stations were observed along the first axis: the first group  
517 gathering St1, 2, 9, 10 and 11, and the second one including St3, 4, 15, 17, and 19. The first  
518 group was related to high concentrations in POC, proteins, lipids, THg, MMHg, trophic level  
519 and  $\delta^{15}\text{N}$  in zooplankton, while the second group was correlated with high values of C/N,  $\delta^{13}\text{C}$   
520 and zooplankton biomass. MMHg in zooplankton increased with the trophic level ( $\delta^{15}\text{N}$  may  
521 be used as a proxy). Zooplankton MMHg decreased with increasing amounts of organic  
522 matter, likely because of the affinity of POC, proteins and lipids for Hg. MMHg  
523 concentrations in zooplankton were high in oligotrophic, low productivity areas with low  
524 zooplankton biomass, high trophic level and high POC, protein and lipid content. Under

525 oligotrophic conditions, zooplankton were limited by food resources and, as a result, their  
1 526 biomass and growth rates decreased, and increasing Hg bioaccumulation was observed.  
2  
3 527 Oligotrophic ecosystems also have longer food webs with intermediate consumers (ciliates,  
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5 528 dinoflagellates, microzooplankton, etc.), which may constitute a trophic link between pico-  
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7 529 and nanoplankton, and mesozooplankton, generating additional food steps and probably  
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9 530 increasing the biomagnification processes (Søreide et al., 2006; Kürten et al., 2013).  
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11 531 The negative correlation in zooplankton between MMHg and its biomass may suggest a  
12  
13 532 biodilution with growth in more productive areas. This is probably the case in the Gulf of  
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15 533 Gabès where lower Hg concentrations in planktivorous species were already reported  
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17 534 compared to those in the north-western Mediterranean basin (Aboul-Dahab et al., 1986; Ben  
18 535 Hassine et al., 1990; Joiris et al., 1999). Moreover, in ecosystems where nutrients and  
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20 536 phytoplankton resources are abundant, herbivory is the main food pathway, generating lower  
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22 537 trophic level ecosystems (Sommer et al., 2002) and thus potentially lower Hg concentrations  
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24 538 in consumers.  
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26 539 Coastal areas have been considered to be hotspots for Hg-accumulation due to proximity to  
27 540 sediment and resuspension (Chen et al., 2008). Cossa et al. (2018) showed that MeHg  
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29 541 concentrations in subsurface waters are higher in Mediterranean offshore waters. Although  
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31 542 coastal regions are subjected to additional sources of Hg (submarine groundwater discharge,  
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33 543 rivers and sediments), our results evidenced a lower trophic transfer of Hg in plankton food  
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35 544 webs compared to offshore areas, as also observed by Cossa et al. (2012) in the Gulf of Lion.  
36  
37 545 There is indeed more and more evidence of *in situ* Hg methylation in oxygenated waters of  
38 546 the open ocean (Mason and Fitzgerald, 1990; Blum et al., 2013; Masbou et al., 2015; Villar et  
39  
40 547 al. 2020; Liu et al., 2021), and the Mediterranean Sea (Cossa et al. 2022).  
41  
42 548 However, potential sources of Hg in contaminated areas must be considered as well. Toulon  
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44 549 Bay represents an important hotspot of Hg, containing large amounts in its sediments (Tessier  
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46 550 et al., 2011) and may be responsible for the highest concentrations measured in this study.  
47  
48 551 High concentrations of THg and MMHg have already been recorded in fish and mussels in  
49 552 Toulon Bay (Cresson et al., 2014; Briant et al., 2017).  
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#### 52 554 **4. Conclusions**

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56 556 Few Hg data are currently available for plankton, particularly for MMHg, and they generally  
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58 557 show wide variations. An inappropriate plankton sampling strategy may lead to the collection  
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558 of organisms with a heterogenous size and composition, highly impacting their Hg and  
1 559 MMHg concentrations. We have tried to overcome these limitations with a dedicated  
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3 560 sampling strategy for the acquisition of different phyto- and zooplankton size-classes, the  
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5 561 acquisition of trophic proxies and the collection of sufficient biomass for complementary  
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7 562 biological and chemical analyses.

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9 563 High THg and MMHg bioconcentration values were observed for phytoplankton, with the  
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11 564 highest values for picoplankton. Small phytoplankton cells were the main contributors to  
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13 565 primary production in the Mediterranean waters during our sampling campaign and a major  
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15 566 food source for zooplankton. Phytoplankton THg concentrations were higher overall  
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17 567 compared to the existing literature. Our study implies that phytoplankton in the oligotrophic  
18 568 Mediterranean Sea is an important driver in the biomagnification of MMHg.

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20 569 Although THg accumulation through diet is a widely accepted process, our results show that  
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22 570 THg bioreduces while MMHg bioaccumulates in the plankton food web. Different kinetics of  
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24 571 iHg and MMHg have been evidenced in plankton, supporting the need to analyze both phyto-  
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26 572 and zooplankton, and to relate them to their species/group composition in future studies.

27 573 Biomagnification of MMHg in all plankton consumers was evidenced, independently of their  
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29 574 trophic position. High biomagnification factors were measured compared to previous studies,  
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31 575 suggesting an effective transfer in Mediterranean plankton food webs.

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33 576 Moreover, the biochemical composition of zooplankton, particularly the availability of POC,  
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35 577 proteins and lipids appears to have an important role in MMHg bioaccumulation.

36 578 Spatial variability in MMHg concentrations in zooplankton was important, with ten-fold  
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38 579 differences between areas. Productivity gradients may explain these contrasts. Higher  
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40 580 zooplankton MMHg concentrations were measured in low productive areas offshore. In  
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42 581 contrast, more productive coastal planktonic food webs showed lower zooplankton MMHg  
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44 582 concentrations. Our results suggest a lower impact of Hg on plankton food webs in the less  
45  
46 583 poorly-studied southern Mediterranean Sea, but more observations are needed to corroborate  
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48 584 this. Oligotrophy and plankton trophodynamics were key factors in the transfer of Hg in the  
49 585 Mediterranean Sea, playing probably an important role in the Hg transfer along food webs.

50  
51 586 Our study may thus contribute to explaining the higher Hg levels observed in Mediterranean  
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53 587 apex predators. The impact of climate change is thought to contribute to the increase of the  
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55 588 oligotrophy and the decrease in size of phytoplankton and may thus exacerbate Hg  
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57 589 accumulation in Mediterranean marine food webs in the future. Overall, our study suggests  
58 590 that bioconcentration of MMHg into phytoplankton and subsequent bioaccumulation and

591 biomagnification are by far the most important factors driving higher trophic level MMHg  
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2 592 exposure. As such, the efforts in reducing Hg emissions within the Minamata Convention may  
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4 593 be outweighed by the effects of climate change on the lower marine food web structure.

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595 **Author contribution statement**

596 Conception and design of study: DB, LEHB, FC, MT, JK

597 Acquisition of data: JATO, JK, BT, MT, FC

598 Analysis and/or interpretation of data: JATO, DB, LEHB, MHV, MT, AD, BT, JK

599 Drafting of the manuscript: JATO, DB, LEHB, MHV, MT

600 Revising/editing of the manuscript: JATO, DB, LEHB, MHV, AD, MVL, IGA, JK, BT, FC,

601 MT

602 Project administration and funding acquisition: DB, MT, FC

603

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622 **Supplementary information**

623 Supplementary material related to this article is available online.

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## Figure captions

**Figure 1:** Location of the ten sampling stations of the MERITE-HIPPOCAMPE cruise in the Mediterranean Sea (April-Mai 2019).

**Figure 2:** Boxplot of the concentrations of A) THg, B) MMHg (ng g<sup>-1</sup> dw) and C) %MMHg in the different plankton size-fractions (fractions between 0.7 and 20 µm (green scale) and >60 µm (red scale) for all stations combined. H = Kruskal–Wallis nonparametric test and the associated p-value for the respective Hg species (H = 24, p < 0.0001; H = 36, p < 0.0001 and H = 30, p < 0.0001, respectively). The mean and median values are represented by a cross and a horizontal line, respectively, and the box length is defined as the interquartile range. The minimum and maximum values are represented by whiskers. Mean values with different post-hoc letters are significantly different (p < 0.05).

**Figure 3:** Logarithm of THg (A) and MMHg (B) concentrations in function of δ<sup>15</sup>N (‰) in the different phyto- (green dots) and zooplankton (red dots) size-fractions. The linear regression curve with its equation and the R-square are indicated.

**Figure 4:** Transfer efficiency between phytoplankton (0.7 to 20 µm fractions) and zooplankton (>60 µm fractions) amounts of THg (A) and MMHg (B) (in pg m<sup>-3</sup>) by station. Yellow, orange and red isolines represent transfer efficiencies of 1, 5 and 10% for THg and 10, 50 and 100% for MMHg, respectively.

**Figure 5:** Box plots of A) THg (yellow) and B) MMHg (red) (in ng g<sup>-1</sup> dw) concentrations measured in the 60 to 1000 µm zooplankton size-fractions by station. The mean and median values are represented by a cross and a horizontal line, respectively, and the box length is defined as the interquartile range.

**Figure 6:** Trophic magnification factors of THg (TMF<sub>THg</sub>, in yellow) and MMHg (TMF<sub>MMHg</sub> in red) at the different stations. >1 values indicated biomagnification, while <1 indicated bioreduction.

1114 **Figures**

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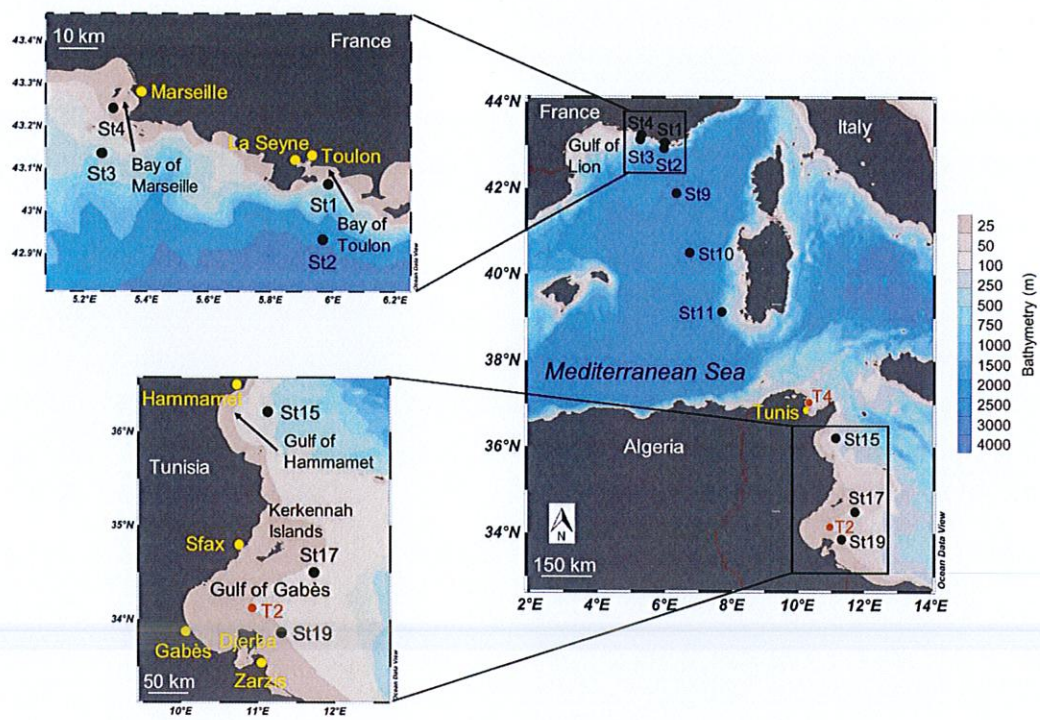
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**Figure 1**



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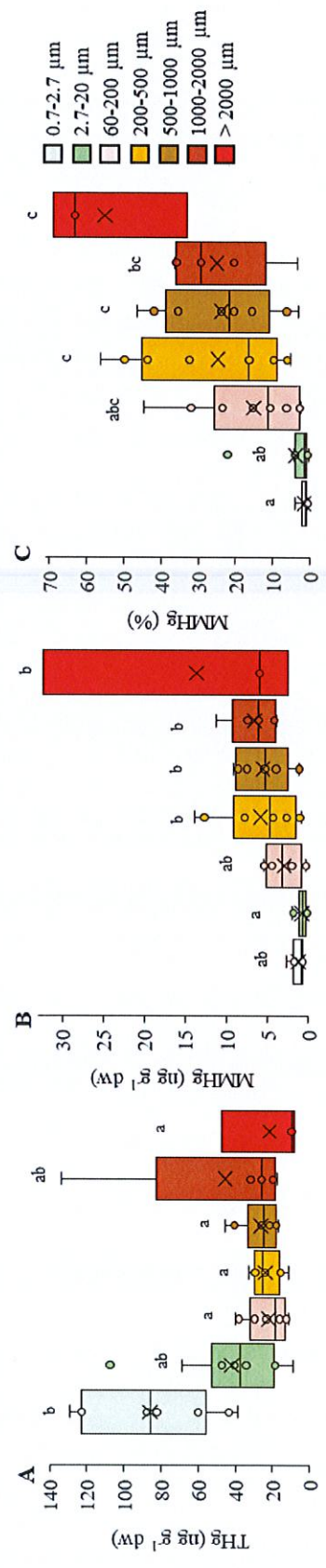
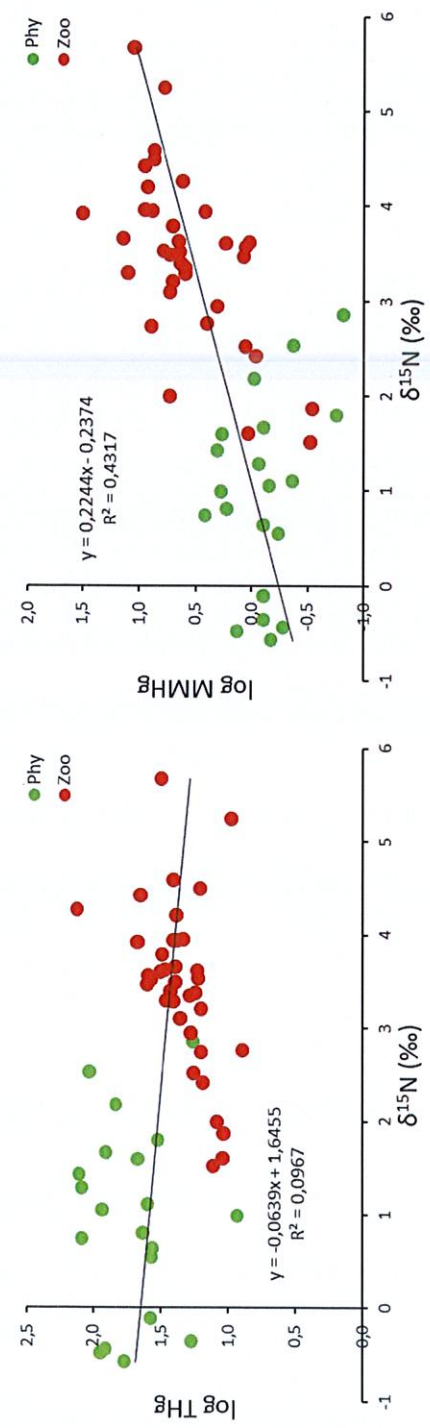


Figure 2



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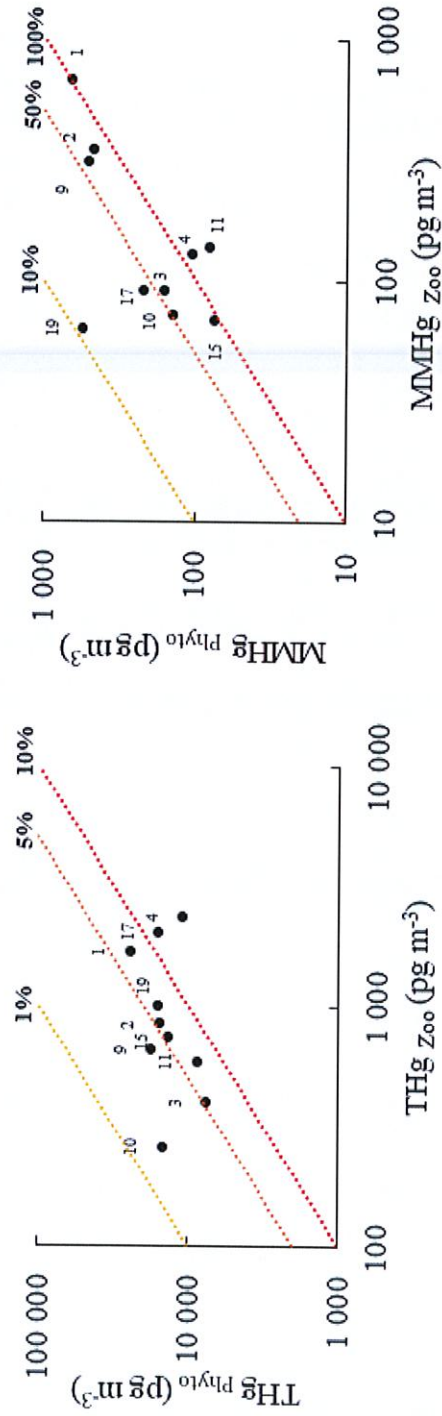


Figure 4



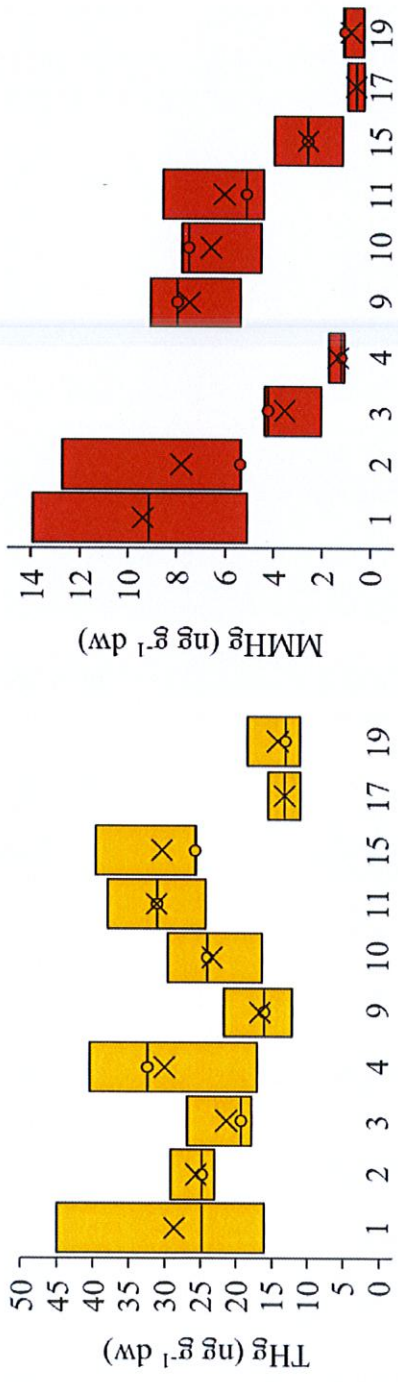


Figure 5



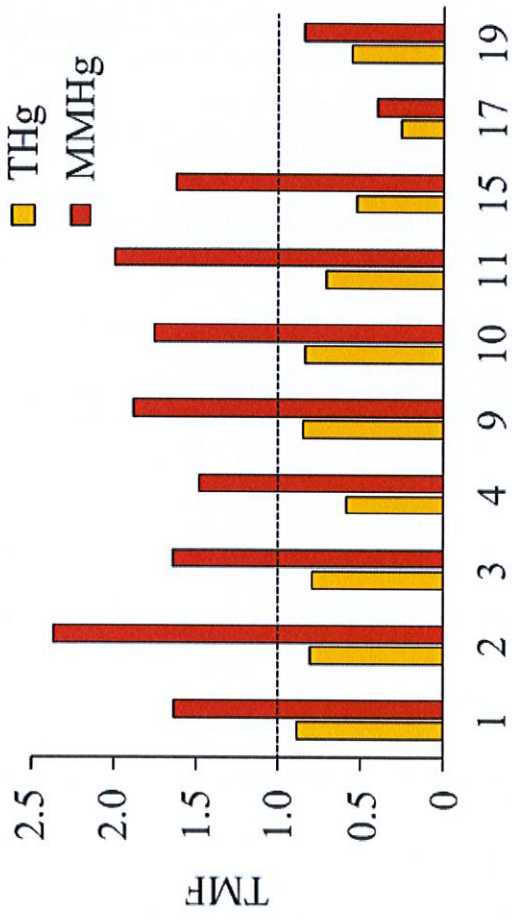
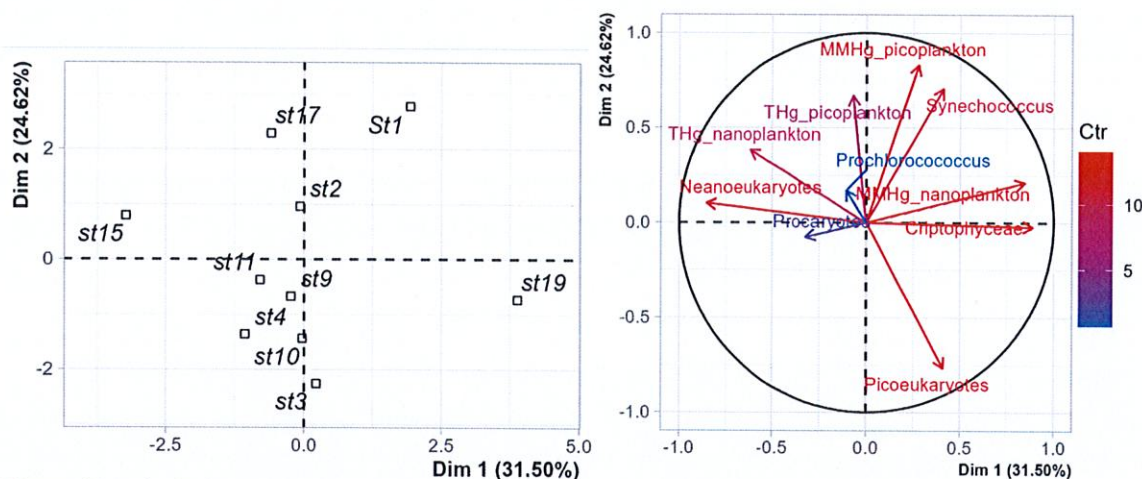


Figure 6

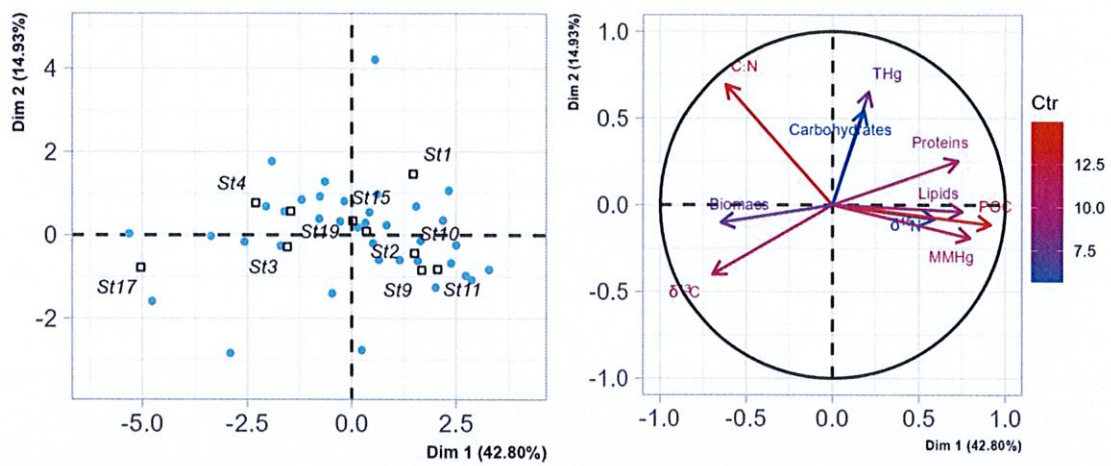
1145 Supplementary information



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1147 **Figure S1:** Principal component analysis of the phytoplankton composition (*Synechococcus* spp.,  
1148 *Prochlorococcus* spp., picoekaryotes, nanoekaryotes and cryptophyceae), THg and MMHg in the 0.7–2.7 and  
1149 2.7–20  $\mu\text{m}$  size-fractions by station. Color gradient indicates the contribution of the variables from blue for low  
1150 contribution to red for high contribution.

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**Figure S2:** Principal component analysis of the biochemical variables (zooplankton biomass,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , C/N, POC, proteins, carbohydrates and lipids), THg and MMHg in zooplankton (60 to 1000  $\mu\text{m}$  fractions) by station. Color gradient indicates the contribution of the variables from blue for low contribution to red for high contribution.

**Table S1.** Main characteristics of the ten sampling stations of the MERITE-HIPPOCAMPE cruise (13 April–14 May 2019) aboard the R/V *Anitea* along a north-south transect in the Mediterranean Sea. The environmental conditions in these stations were detailed in Tedetti et al. (2023).

Station	Location	Latitude (N)	Longitude (E)	Bottom depth (m)	McLane sampling depth (m)	MultiNet sampling depth (m)
St1	Bay of Toulon (north)	43° 03.819'	5° 59.080'	91	20	20
St2	Toulon - Aniharcs (north)	42° 56.020'	5° 58.041'	1770	25	34
St3	Marsaille - Julio (north)	43° 08.150'	5° 15.280'	95	55	58
St4	Bay of Marsaille (north)	43° 14.500'	5° 17.500'	58	31	35
St9	North Balearic Front (offshore)	41° 53.508'	6° 19.998'	2575	20	20
St10	North Balearic Front (offshore)	40° 18.632'	7° 14.753'	2791	50	30
St11	North Balearic Front (offshore)	39° 07.998'	7° 41.010'	1378	40	30
St15	Gulf of Hammamet (south)	36° 12.883'	11° 07.641'	100	40	60
St17	Gulf of Gabès (south)	34° 30.113'	11° 43.573'	50	40	40