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## Persistent Organic Pollutants Burden, Trophic Magnification and Risk in a Pelagic Food Web from Coastal NW Mediterranean Sea

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1 **Persistent organic pollutants burden, trophic magnification and risk in a pelagic**  
2 **food web from coastal NW Mediterranean Sea**

3  
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23 **Abstract**

24 The storage capacity, trophic magnification and risk of sixty-two POPs have been  
25 evaluated in a well-characterized pelagic food web (eleven trophic levels) from an  
26 impacted area in NW Mediterranean Sea. Our results show the high capacity of the  
27 planktonic compartment for the storage of polybrominated diphenyl ethers (PBDEs) and  
28 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), consistent with their  
29 estimated low trophic magnification factors (TMF) of 0.2-2.0 (PBDEs) and of 0.3-1.1  
30 (PCDD/Fs).  $\Sigma$ PBDEs dominated in the zooplankton size-class 200-1000 $\mu$ m (~330 ng g<sup>-1</sup>  
31 lw, median), whereas  $\Sigma$ PCDD/Fs accumulated preferentially in phytoplankton size-  
32 class 0.7-200 $\mu$ m (875 pg g<sup>-1</sup> lw, median). In contrast, polychlorinated biphenyls (PCBs)  
33 were preferentially bioaccumulated in the higher trophic levels (six fish species and two  
34 cephalopods) with TMFs=0.8-3.9, reaching median concentrations of 4270 and 3140 ng  
35 g<sup>-1</sup> lw ( $\Sigma$ PCBs) in Atlantic bonito (*Sarda sarda*) and chub mackerel (*Scomber colias*),  
36 respectively. For these edible species, the estimated weekly intakes of dioxin-like POPs  
37 for humans based on national standards overpassed the EU tolerable weekly intake.  
38 Moreover, the concentrations of non-dioxin like PCBs in *S. sarda* were above the EU  
39 maxim levels in foodstuffs, pointing to a risk. No risk evidence was found due to  
40 consumption of all other edible species studied, also for PBDEs. The integrated burden  
41 of POPs in the food web reached ~ 18  $\mu$ g g<sup>-1</sup> lw, representing a dynamic stock of toxic  
42 organic chemicals in the study area. We show that the characterized food web could be a  
43 useful and comprehensive ‘bioindicator’ of the chemical pollution status of the study area,  
44 opening new perspectives for the monitoring of toxic chemicals in NW Mediterranean  
45 coastal waters.

46

47 **Keywords:** Environmental exposure, bioaccumulation, flame retardants, dioxins, PCBs,  
48 fish, cephalopods, plankton

49

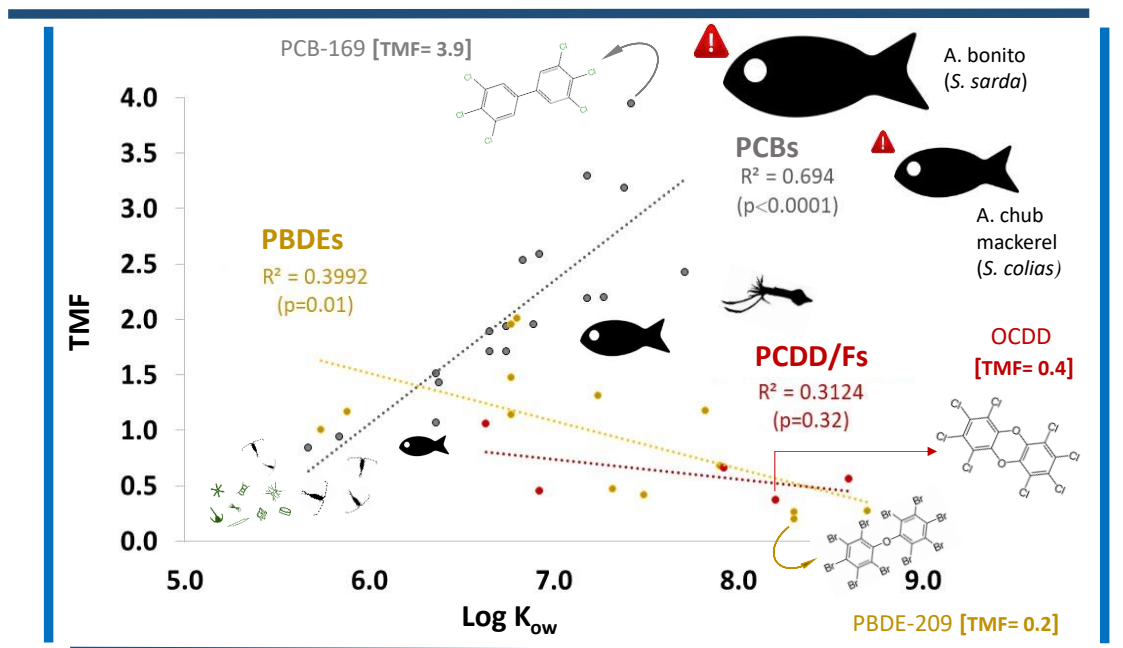
50 **Synopsis:** The integrated burden of POPs in a pelagic food web (eleven trophic levels) in  
51 coastal NW Mediterranean Sea reached  $\sim 18 \mu\text{g g}^{-1}$  lw. A potential risk for humans mostly  
52 due to exposure to dioxin-like POPs *via* consumption of Atlantic bonito and chub  
53 mackerel was found.

54

55

## 56 Abstract Graphic

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## 63 1. Introduction

64

65 The chemical contamination of the marine environment is a global and transversal issue  
66 with important ecological and socio-economic implications, yet not well quantified nor  
67 efficiently managed.<sup>1,2</sup> Populations living in coastal areas, as well as marine organisms,

68 are exposed to multiple sources of chemical contamination, particularly in semi-enclosed  
69 environments such as the Mediterranean Sea. The Mediterranean is a sensitive  
70 environment with the particularity of being a hotspot of both marine biodiversity (up to  
71 18% of the world's marine diversity) and chemical contamination (e.g. organic and  
72 inorganic contaminants, plastic debris).<sup>3-5</sup> Among the contaminants impacting this  
73 marine environment, persistent organic pollutants (POPs) and related chemicals are well  
74 documented in non-biotic compartments<sup>6-10</sup> and different marine organisms.<sup>5,8,11-17</sup> POPs  
75 are organic contaminants of major concern due to their high toxicity, long-range transport  
76 and bioaccumulation potential, and their high resistance to degradation.<sup>18</sup> Even if these  
77 toxic chemicals have been banned by international regulations, such as the Stockholm  
78 Convention on POPs (SC), their ubiquity in the marine environment many years after  
79 their release may still pose potential risks.

80 Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated  
81 biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are widespread POPs  
82 with different environmental sources. While PCDD/Fs can occur as unintentional by-  
83 products in a number of industrial processes and domestic heating<sup>19,20</sup>, PCBs are legacy  
84 industrial chemicals used in many applications (e.g. lubricants, transformers, oil  
85 additives).<sup>21</sup> Major primary sources for these two families of legacy POPs are considered  
86 under control in most parts of the world today.<sup>22</sup> However, ongoing primary releases from  
87 diffuse sources such as open fires and uncontrolled waste incineration, urban/industrial  
88 centres, as well as secondary sources such as net re-emissions from environmental  
89 reservoirs are still possible.<sup>21,22</sup> PBDEs were mostly used (and are still in some regions)  
90 as flame retardants<sup>23</sup> and, in contrast to PCDD/Fs and PCBs, have been only recently  
91 restricted at global scale by the SC.<sup>24</sup> These chemicals constitute complex mixtures in the  
92 environment to which marine organisms and humans are exposed. Their accurate

93 determination in the biotic compartment represents a very important first step to  
94 apprehend potential risks. However, despite the fact that POPs are often measured in  
95 organisms from different trophic levels (TLs), these organisms do not always belong to  
96 the same food web, making it difficult to properly investigate their trophic magnification,  
97 subsequent risks and more generally the environmental status of marine waters, as  
98 requested by the European Marine Strategy Framework Directive.<sup>25</sup>

99

100 Here, we report results for PCDD/Fs, PCBs, and PBDEs in 26 biotic samples consisting  
101 of phyto- and zooplankton, six fish species and two cephalopods, all belonging to the  
102 same trophic web from an impacted coastal area, the Bay of Marseille, in the NW  
103 Mediterranean Sea. The overall aims of this work were: (1) to characterize a pelagic food  
104 web representative of the coastal NW Mediterranean, including species consumed by  
105 humans, which could help the monitoring and assessment of chemical pollution in the  
106 area; (2) to determine the burden and storage capacity of a cocktail of 62 toxic organic  
107 chemicals in the selected food web; (3) to assess their potential trophic magnification,  
108 exposure to humans and risks *via* consumption of fishery products.

109

## 110 **2. Materials and Methods**

111

### 112 *2.1. Study area*

113 Samples were collected in the Bay of Marseille in the south of France (NW Mediterranean  
114 Sea) (Figure S1). This bay is highly impacted by multiple contamination sources, such as  
115 the Marseille sewage treatment plant, with its outlet (WWTP Cortiou) located around 10  
116 km south-east of the sampling site,<sup>26</sup> and the port, industry, agriculture and tourism, in  
117 particular. The Bay of Marseille is naturally influenced by high solar radiation,<sup>27</sup>

118 intrusions of the Northern Current on the shelf,<sup>28</sup> and occasionally by intrusions of the  
119 Rhone river plume and the coastal Huveaune River, giving rise to episodic high inputs of  
120 particle and dissolved organic matter.<sup>29-31</sup> Inputs of a wide diversity of POP families and  
121 related organic contaminants of emerging concern have been reported in the area coming  
122 from the Rhone River,<sup>32-36</sup> the Marseille WWTP at Cortiou and the Huveaune,<sup>35,37-39</sup>  
123 and the atmosphere.<sup>10</sup> Marine organisms and pelagic food webs in the Bay of Marseille  
124 are certainly exposed to those contaminants (Figure S1).

125

## 126 2.2. Sampling

127 Phyto- and zooplankton samples were collected at the Solemio station (43.24°N; 5.29°E,  
128 Figure S1) on 15th March 2017 on board the RV ANTEDON II. Phytoplankton and  
129 suspended particulate matter (mostly microphytoplankton and detritus particles) were  
130 obtained by filtering ~60 L of surface water collected with an inner lining Teflon GoFlo  
131 12 L bottle through ten pre-combusted 47mm glass fiber filters (GFFs, 0.7 µm) and  
132 treated as one sample. Zooplankton was vertically sampled, from 0 to 50 m depth, using  
133 a zooplankton net of 150 µm mesh, and then sequentially separated by using stainless  
134 steel sieves. Due to the limited amount of sampled material, the various fractions were  
135 pooled together into two overall size classes ('Z1': 200-1000µm, and 'Z2': >2000 µm)  
136 for POPs analyses. However, all zooplankton size-classes were considered for the food  
137 web structure determination (Figure S2). Their groups and species as well as biochemical  
138 composition are detailed elsewhere.<sup>40</sup> Teleosts and cephalopods were sampled by  
139 professional fishers in the Bay of Marseille near Solemio and specimens were acquired  
140 in the Marseille fish market on the same day. Sampled species were: (1) the planktivorous  
141 fish bogue (*Boops boops*, Linnaeus, 1758); (2) the mesopredators *Trachurus trachurus*  
142 (Linnaeus, 1758), *Trachurus mediterraneus* (Steindachner, 1868), *Scomber colias*

143 (Gmelin, 1789), the European hake (*Merluccius merluccius*, Linnaeus, 1758), and the  
144 cephalopod squid *Illex coindetii* (Vérany, 1839), *Todarodes sagittatus* (Lamarck, 1798),  
145 and (3) the top predator Atlantic bonito (*Sarda sarda*, Bloch, 1793). All these fish and  
146 cephalopods are commonly caught by local fisheries and consumed in the region. Three  
147 individuals of different size were considered by species, except for the cephalopod *T.*  
148 *sagittatus* for which only one specimen was available. In the laboratory, the fresh  
149 organisms were cleaned, measured and weighed (Table S1). Plankton analyses were made  
150 on the entire individuals, while dorsal muscle was sampled for teleosts and mantle for  
151 squid. Dissection was done on a clean glass table strictly avoiding contact with plastics  
152 or any other material which could be a source of organic matter. All the samples were  
153 then frozen at -20°C, freeze-dried and ground into a homogenized fine powder prior to  
154 analyses (see text S1 for details). We acknowledge that the overall contaminant transfer  
155 in the food web will be dictated by the consumption of the entire prey individuals in the  
156 ecosystem. However, the choice of the sampling in this study concerned only the muscle  
157 for cephalopods and fishes as generally represents the major contaminant exposure route  
158 for humans, therefore enabling a risk assessment (section 3.5). Further analyses in higher  
159 lipid-rich organs such as the liver and gonads may reveal a higher total POP burden and  
160 a potentially higher biomagnification.

161

### 162 2.3. Stable isotope and biochemical analyses

163 Three replicates were performed on phytoplankton and zooplankton size classes, while  
164 the three individuals of teleosts and cephalopods were considered as replicates for  $\delta^{13}\text{C}$ ,  
165  $\delta^{15}\text{N}$ , %C, %N, and total lipid analyses. Stable isotope measurements were performed  
166 with a continuous-flow isotope-ratio mass spectrometer coupled to an elemental analyzer  
167 in LIENSs Laboratory, La Rochelle University (France). Details for total lipid



168 determinations are presented in Text S1. For fish samples,  $\delta^{13}\text{C}$  values were corrected for  
169 the effects of lipids when the  $\text{C/N} > 3.5$ .<sup>41</sup> TLs were estimated using the zooplankton 200-  
170 300  $\mu\text{m}$  size class (composed mostly of small herbivorous copepods) as 'baseline' with  
171 trophic position defined as 2.<sup>40,42</sup> A classical enrichment factor of 3.4‰ between prey  
172 and predator was applied except for the top predator *S. sarda* for which a value of 2.4‰  
173 was used<sup>43</sup> (See Text S1 for all details).

174

#### 175 2.4. POPs analysis

176 All samples were freeze-dried and zooplankton and fish samples homogenized by using  
177 a ball mill mounting stainless steel cells. The corresponding amounts of sample (0.14-  
178 0.25 g dw, Table S1) were spiked with  $^{13}\text{C}$ -labeled standards of PCDD/Fs, PCBs, and  
179 PBDEs prior to Soxhlet extraction (24h) with a n-hexane: DCM (9:1) mixture. Extracts  
180 were rota-evaporated and cleaned-up using the automated sample preparation system  
181 DEXTech+.<sup>14</sup> The six indicator PCBs (IDPCBs), the eight mono-*ortho* dioxin-like PCBs  
182 (DLPCBs) and PBDEs (27 congeners) were collected in a first fraction, while the  
183 seventeen 2,3,7,8-substituted PCDD/Fs along with the four non-*ortho* DLPCBs were  
184 obtained in a second fraction, summing up a total of 62 POPs. Final extracts were rota-  
185 evaporated to  $\sim 1$  mL, transferred to vials, and dried under a gentle nitrogen steam.  
186 Fractions were reconstituted in a few microliters of the respective PCDD/F, PCB, and  
187 PBDE  $^{13}\text{C}$ -labeled injection standards prior to instrumental analysis. Quantification was  
188 carried out by isotopic dilution according to 1613 US EPA method<sup>44</sup> on a gas  
189 chromatograph (Trace GC ultra, Thermo Fisher Scientific) coupled to a high-resolution  
190 mass spectrometer (DFS, Thermo Fisher Scientific). Details can be found in Text S1.

#### 191 2.5. Quality assurance / quality control (QA/QC)

192 Field blanks for phytoplankton samples (n=2), consisting of baked GFFs which were  
193 placed in the freeze-dryer and then processed with the samples, were performed.  
194 Analytical laboratory blanks (n=6) accounting for all the sample processing steps were  
195 also performed. After sampling, GFFs were wrapped in aluminium foil again and stored  
196 in the dark at -20°C. Laboratory blank levels were generally low for the three POP classes  
197 compared to their concentrations in the samples, averaging from not detected (n.d) to 25  
198 pg (PCBs), from n.d. to 0.13 pg (PCDD/Fs), and from n.d. to 7 pg (PBDEs) depending  
199 on the congener and sample (Table S3). Laboratory blanks showed lower or similar levels  
200 to field blanks, so no contamination occurred during sampling, storage and analysis.  
201 Results were blank-corrected by subtracting the average field and laboratory blanks  
202 values for phytoplankton and the rest of samples, respectively. Chromatographic peaks  
203 were only considered when the ratio between the two monitored ions was within  $\pm 15\%$   
204 of the theoretical value, and the signal-to-noise (S/N) ratio  $> 3$  (limit of detection, LOD).  
205 Limits of quantification (LOQs) corresponded to  $S/N \geq 10$ . Calibration curves were daily  
206 checked. Median LODs (n=26) ranged from 0.2 to 2.3 pg (PCBs), from 0.1 to 0.8 pg  
207 (PCDD/Fs) and from 0.3 to 14.0 pg (PBDEs) depending on the compound and sample  
208 (Table S4). Median method recoveries varied from 60 to 111 % (PCBs), from 79 to 102  
209 % (PCDD/Fs) and from 61 to 102 % (PBDEs) (Table S5). Results were corrected by  
210 recoveries.

## 211 2.6. *Data analysis*

212 Non-parametric tests (Kruskal–Wallis and Wilcoxon rank-sum) were used in order to  
213 investigate significant differences among pollutant levels. The effect of multiple  
214 comparisons was considered by applying the false discovery rate method. Non-detected  
215 values were imputed to the LOD/2 to run these tests (Text S2 and Table S6). The software  
216 employed was STATA/SE 16.1. However, the concentration sums presented in sections

217 3.3.1 and 3.3.2 consider only the detected values, and the concentrations expressed as  
218 World Health Organization-toxic equivalents (WHO<sub>05</sub>-TEQ) presented in section 3.5 for  
219 DLPOPs are reported as upper bound values (i.e. the n.d values were substituted by the  
220 corresponding LODs before the blank correction) to facilitate their comparison with  
221 available threshold values. The sample BB-1 was excluded from the data set for PBDEs  
222 due to suspected specific contamination. Trophic magnification factors (TMFs) for  
223 individual POPs were calculated using the slope ( $m$ ) of the linear regression between the  
224  $\log_{10}$  of the lipid-normalized contaminant concentration in the food web organisms and  
225 their corresponding TLs (calculated as indicated above)<sup>45, 46</sup> (section 3.4.). For PBDEs  
226 and PCDD/Fs, which exhibited more n.d values, only congeners with >30% detection  
227 frequency and detected in at least 7 different TLs were considered for the TMF  
228 calculation. In order to derive the estimated weekly intake (EWI) of DLPOPs and  $\Sigma$ PBDEs  
229 (section 3.5.), the weekly consumption data for France for demersal (*M. merluccius*) and  
230 pelagic (rest of species) fish and cephalopod (222, 132 and 9.2 g/week, respectively)<sup>47</sup>  
231 were multiplied by the WHO<sub>05</sub>-TEQ (PCDD/Fs + DLPCBs) and the  $\Sigma$ PBDEs (only  
232 detected values) concentration, respectively, measured in the corresponding species and  
233 divided by 70 Kg (average human bodyweight, bw), as previously described.<sup>15</sup> Risk  
234 quotients (R), were calculated as the concentration in the sample, and its corresponding  
235 EWI, to threshold values, legally binding or not, derived by international authorities to  
236 protect humans consuming fishery products and aquatic ecosystems.

237

### 238 **3. Results and discussion**

239

#### 240 **3.1. Food web characterization**

241 The stable isotope ratios of the species and size classes analysed in the Bay of Marseille  
242 pelagic food web are presented in Figure S2A and Table S7. Both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are

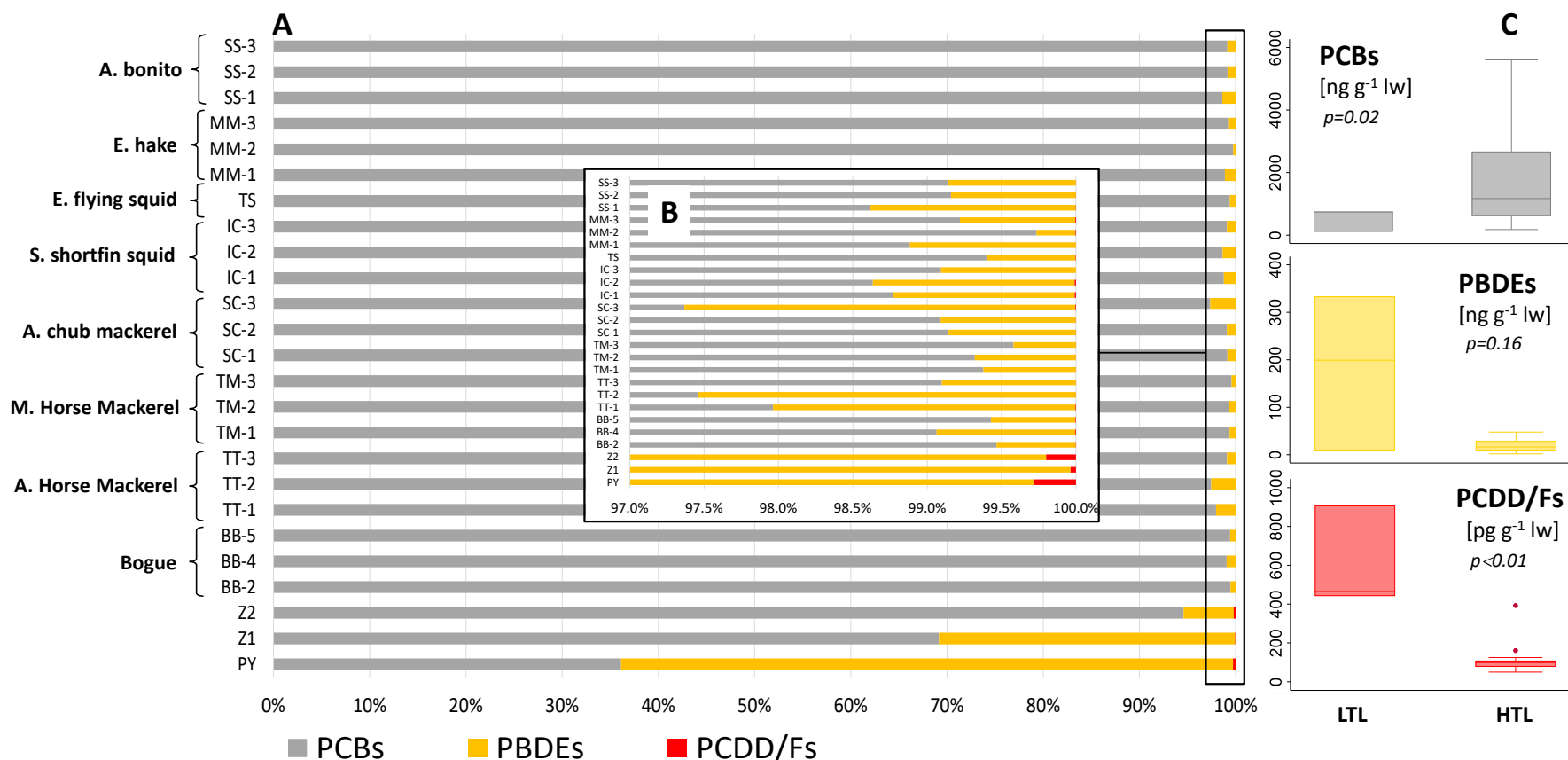
243 significantly different between species and/or size classes (Kruskal-Wallis,  $p < 0.0001$ ).  
244 Zooplankton  $> 2000 \mu\text{m}$  mainly constituted of gelatinous organisms has the lowest stable  
245 isotope ratios related to their filter feeding regime based on small pico ( $0.2\text{-}2 \mu\text{m}$ ) and  
246 nano ( $2\text{-}20 \mu\text{m}$ ) phytoplankton. These small size classes of phytoplankton are supposed  
247 to be the main source of the zooplankton food web in the North-Western Mediterranean  
248 area <sup>48</sup> but they could not be sampled for this study in sufficient quantities for POPs  
249 analyses. Particles issued from the Cortiou WWTP with low stable isotope ratios are also  
250 susceptible to be consumed by the different zooplankton size classes and decrease their  
251 stable isotope ratios during particulate rain or hydrodynamic conditions. <sup>26,42</sup> Micro-  
252 phytoplankton size class may represent the prey of many planktivorous fish such as *B.*  
253 *boops*, and all the juveniles of the studied fishes and squid. Herbivorous zooplankton  $200\text{-}$   
254  $300 \mu\text{m}$  had also low stable isotope value and were considered as baseline for the  
255 estimation of the TL of the other consumer groups. The  $\delta^{15}\text{N}$  ratios increased between  
256 low TL groups (phyto- and zooplankton) and high TL groups (fish and squid,  $\text{TL} > 3$ )  
257 consistent with their TL position (Figure S2B/Table S7). Predators such as the fish *S.*  
258 *sarda* and squid *T. sagittatus* showed the highest stable isotope ratios related to their  
259 high TL (5.3 and respectively 4.2).

260

### 261 3.2. Distribution of POPs and storage capacity in the food web

262 Overall, PCBs exhibited a high detection frequency (DF) of 73-100% for most congeners  
263 (Figure S3), and dominated total POP concentrations from zooplankton to top predators,  
264 accounting for 69% to around 100% of the  $\Sigma\text{POPs}$  (Figure 1A). PBDEs showed a  
265 generally lower DF with most congeners in the range 0-60%, although a certain number  
266 of congeners such as BDEs-28, -47, -49, -71, -99, -100 and -154 were highly detected  
267 (DF= 84-100%). PBDEs dominated only in phytoplankton, reaching 64% of total POPs

268 concentrations, while accounting for 0.3 – 31% of the total contaminant stock in the rest  
269 of the samples. PCDD/Fs levels were below LODs in many cases and DF was mostly in  
270 the range 0-40% and only 2,3,7,8-TCDF (88 %) and 1,2,3,4,6,7,8-HpCDD (96%) were  
271 highly present. The contribution of PCDD/Fs to the total POPs burden in the studied food  
272 web was minor, representing < 0.5% of the total POPs. These contaminants accumulated  
273 preferentially in the lowest trophic levels (LTL) like PBDEs (Figure 1B). LTL,  
274 considered as the planktonic compartment (i.e. phytoplankton 0.7-200  $\mu\text{m}$ , zooplankton  
275 200-1000  $\mu\text{m}$  and zooplankton > 2000  $\mu\text{m}$ ), seemed to play a predominant role driving  
276 the food web burden and storage capacity of  $\Sigma$ PBDEs and  $\Sigma$ PCDD/Fs exhibiting 12-fold  
277 and 5-fold higher median concentration than in higher trophic levels (HTL), respectively  
278 (Figure 1C). This trend was followed by individual PBDEs and PCDD/Fs too (Figure S4-  
279 S5) showing similar or significantly higher ( $p < 0.01-0.04$ , Kruskal-Wallis) median  
280 concentrations in LTL. In contrast, the  $\Sigma$ PCB burden in the food web may be dominated  
281 mostly by HTL showing a significantly 9-fold higher median concentration ( $p = 0.02$ ,  
282 Kruskal-Wallis) than the LTL (Figure 1B). Individual PCB congeners generally followed  
283 the same trend except for CBs-28 and -52, which exhibited similar or significantly higher  
284 median concentrations ( $p = 0.03$ , Kruskal-Wallis) in LTL as PBDEs and PCDD/Fs (Figure  
285 S6). In other words, the lipid-normalized cumulative concentrations of PBDEs and  
286 PCDD/Fs in the phytoplankton and the two zooplankton size classes were similar or  
287 significantly higher than the cumulative concentrations of the 21 fish and 2 cephalopod  
288 individuals studied, pointing to the high capacity of the planktonic compartment for the  
289 accumulation and storage of these two POPs families. In contrast, fishes and cephalopods  
290 represent efficient biotic storage compartments for PCBs.

292  
293

294 **Figure 1.** POPs relative burden in the food web (A) with a zoom showing the higher % of PCDD/Fs found in the planktonic compartment (B), and box plots (C) of the lipid  
 295 normalized total concentrations of  $\Sigma\text{PCBs}$ ,  $\Sigma\text{PBDEs}$  ( $\text{ng g}^{-1} \text{lw}$ ) and  $\Sigma\text{PCDD/Fs}$  ( $\text{pg g}^{-1} \text{lw}$ ) in the lowest trophic levels (LTL) considered as the planktonic compartment for  
 296 the purpose of this comparison (i.e. *PY*=phytoplankton 0.7-200  $\mu\text{m}$ , *Z1*=zooplankton 200-1000  $\mu\text{m}$  and *Z2*=zooplankton > 2000  $\mu\text{m}$ ,  $n=3$ ) and the higher trophic levels (HTL)  
 297 considered as the other organisms from the food web (fishes and cephalopods,  $n=22$ ) Kruskal-Wallis test p-value. *BB*=*B. boops*; *TT*=*T. trachurus*; *TM*=*T. mediterraneus*;  
 298 *SC*=*S. colias*; *IC*=*I. coindetii*; *TS*=*T. sagittatus*; *MM*=*M. merluccius*; *SS*=*S. sarda*.

### 299 3.3. Environmental concentrations and patterns

300

#### 301 3.3.1. Overall concentrations

302  $\sum_{18}$ PCB concentrations varied from 3.3 to 496 ng g<sup>-1</sup> dw (from 113 to ~5600 ng g<sup>-1</sup> lipid  
303 weight - lw) in the different individuals from the studied food web. The total PCB load  
304 was dominated by  $\sum_{10}$ PCBs, accounting for 83-92% of  $\sum_{18}$ PCBs with concentrations  
305 ranging from 3.0 to 454 ng g<sup>-1</sup> dw (~100 to 5130 ng g<sup>-1</sup> lw).  $\sum_{DL}$ PCBs represented only  
306 between 8 and 17% of the total PCBs with levels between 0.3 and 42 ng g<sup>-1</sup> dw (13 to 470  
307 ng g<sup>-1</sup> lw).  $\sum_{26}$ PBDE concentrations varied from 0.08 to 25 ng g<sup>-1</sup> dw (1.0 to 333 ng g<sup>-1</sup>  
308 lw) whereas three orders of magnitude lower  $\sum_{17}$ PCDD/F concentrations were measured,  
309 ranging from 0.3 to 110 pg g<sup>-1</sup> d.w (3.4 to 875 pg g<sup>-1</sup> lw). Results for individual PCBs,  
310 PBDEs and PCDD/Fs in each sample are presented in Tables S8-10. In addition, in order  
311 to facilitate data comparability, POPs concentrations are also expressed on a wet weight  
312 (ww) basis (Table S11).

313

#### 314 3.3.2. Levels and patterns in the different organisms

315 Although concentrations of a number of POPs, mostly PCBs and PBDEs, were found  
316 significantly different among the different TLs in a first data analysis ( $p < 0.0-0.04$ ,  
317 Kruskal-Wallis) (Table S6), when comparing by pairs of TLs (Wilcoxon rank-sum test)  
318 and correcting by the effect of multiple comparisons (section 2.6, Text S2), these  
319 differences were not statistically significant. These analyses are certainly hampered by  
320 the limited amount of data. However, some trends are worth discussing. Although some  
321 bioaccumulation was observed in the 200-1000  $\mu$ m zooplankton for the sum of PCBs, the  
322 species exhibiting the highest median  $\sum_{18}$ PCB concentration was the Atlantic bonito (*S.*  
323 *sarda*) (4270 ng g<sup>-1</sup> lw), presenting the highest position in the food web (i.e TL=5.3),

324 followed by the Atlantic chub mackerel (*S. colias*) (3140 ng g<sup>-1</sup> lw). The European flying  
 325 squid (*T. sagittatus*) and the Mediterranean horse mackerel (*T. mediterraneus*) were also  
 326 among the highest concentrations with 2670 ng g<sup>-1</sup> lw (only one sample) and 2280 ng g<sup>-1</sup>  
 327 lw (Table 1). Similar trends were found for individual PCBs, except for CB-28 and -52  
 328 which accumulated preferentially in the planktonic compartments with no clear trends in  
 329 the other TLs (Figure S7). A consistent PCB pattern was observed in the whole food web,  
 330 with PCB-153 as the most abundant congener in all TLs (27-42% of the median  
 331  $\sum_{18}\text{PCBs}$ ), except for the TL 1 (phytoplankton) where PCB-101 and -52 were more  
 332 abundant. The predominance of PCBs-101 and -52 has been reported in the dissolved  
 333 water phase in other NW Mediterranean coastal areas.<sup>49</sup> Likely their preferential  
 334 bioconcentration at the very first TLs could explain this differential pattern found in  
 335 phytoplankton. PCB-118 was the most abundant DLPCBs contributing ~53 – 74% of the  
 336 median  $\sum_{\text{DL}}\text{PCBs}$  (Figure S8).

337

338 **Table 1.** Median concentrations (only detected values) of indicator, dioxin-like, and total PCBs ( $\sum_{\text{ID}}\text{PCBs}$ ,  
 339  $\sum_{\text{DL}}\text{PCBs}$ ,  $\sum_{18}\text{PCBs}$ , respectively), total PBDEs ( $\sum_{26}\text{PBDEs}$ ) and total PCDD/Fs ( $\sum_{17}\text{PCDD/Fs}$ ) in the  
 340 different trophic levels of the food web under study. Values are expressed in dry, wet and lipid weights  
 341 (dw, ww, lw, respectively). Concentrations are in ng g<sup>-1</sup> except for PCDD/Fs (pg g<sup>-1</sup>).

342

Median concentrations*	$\sum_{\text{ID}}\text{PCB}$			$\sum_{\text{DL}}\text{PCB}$			$\sum_{18}\text{PCB}$			$\sum_{26}\text{PBDEs}$			$\sum_{17}\text{PCDD/Fs}$		
	[ng g <sup>-1</sup> ]			[ng g <sup>-1</sup> ]			[ng g <sup>-1</sup> ]			[ng g <sup>-1</sup> ]			[pg g <sup>-1</sup> ]		
Foodweb Species	dw	ww	lw	dw	ww	lw	dw	ww	lw	dw	ww	lw	dw	ww	lw
<i>Phytoplankton (0.7-200 μm)</i>	12.5	2.5	99.2	1.7	0.3	13.8	14.2	2.8	113.0	25.0	5.0	199.0	109.9	22.0	874.6
<i>Zooplankton (200-1000 μm)</i>	39.3	7.9	653.0	5.7	1.1	95.4	45.1	9.0	748.3	20.1	4.0	333.3	23.7	4.7	393.4
<i>Zooplankton (&gt;2000 μm)</i>	3.0	0.6	112.7	0.3	0.1	12.9	3.3	0.7	125.6	0.2	0.04	6.9	7.0	1.4	265.9
<i>Boops boops</i>	38.4	9.2	629.4	6.2	1.5	102.2	44.7	10.7	732.3	0.5	0.1	5.3	2.1	0.5	28.8
<i>Trachurus trachurus</i>	55.7	11.1	858.5	5.6	1.1	79.2	61.3	12.3	937.6	1.0	0.2	19.5	0.7	0.1	9.2
<i>Trachurus mediterraneus</i>	180.2	36.0	2023.4	18.9	3.8	256.0	200.3	40.1	2279.4	0.8	0.2	15.6	0.9	0.2	16.2
<i>Scomber colias</i>	203.0	58.9	2734.2	19.1	5.5	286.4	222.1	64.4	3140.8	1.9	0.6	28.7	2.6	0.8	38.8
<i>Merluccius merluccius</i>	36.8	8.8	538.1	3.9	0.9	45.9	41.1	9.9	584.0	0.3	0.08	4.8	1.6	0.4	23.8
<i>Illex coindetii</i>	69.3	16.6	1229.4	8.1	2.0	155.5	77.5	18.6	1384.9	0.8	0.2	14.9	6.2	1.5	152.2
<i>Todarodes sagittatus</i>	181.8	43.6	2355.8	24.4	5.9	316.3	206.2	49.5	2672.1	1.2	0.3	16.1	6.5	1.6	84.5
<i>Sarda sarda</i>	444.0	106.5	3903.9	41.6	10.0	367.5	485.7	116.6	4271.4	4.2	1.0	37.1	3.9	0.9	43.3

343

\*only one sample was available for phytoplankton, the two zooplankton size classes and the cephalopod *Todarodes sagittatus*

344



345 Median  $\Sigma_{26}$ PBDE concentrations clearly dominated in the 200-1000 $\mu$ m zooplankton  
346 ( $\sim 330$  ng g<sup>-1</sup> lw) and phytoplankton (199 ng g<sup>-1</sup> lw), whereas  $\Sigma_{17}$ PCDD/Fs accumulated  
347 preferentially in phytoplankton (875 pg g<sup>-1</sup> lw) followed by 200-1000  $\mu$ m zooplankton  
348 ( $\sim 390$  pg g<sup>-1</sup> lw). The  $\Sigma$ PBDE predominance in zoo- and phytoplankton was driven by  
349 the higher contribution of BDE-209 (70-75% of the detected  $\Sigma$ PBDEs). The high  
350  $\Sigma_{17}$ PCDD/F levels found in the LTL were driven by the higher abundance of  
351 octachlorodibenzo-p-dioxin (OCDD) accounting for the 64-80% of the detected  
352  $\Sigma$ PCDD/Fs (Figure S9). Indeed, the predominant of OCDD/Fs in zooplankton has been  
353 reported in other marine food webs.<sup>50</sup> Both BDE-209 and OCDD are highly hydrophobic  
354 POPs with log octanol-water partition coefficients (log  $K_{ow}$ ) of 8.7 and 8.2, respectively,  
355 indicating high partition potential on hydrophobic components such as lipids or organic  
356 carbon-rich particles. The combination of the following factors may explain this  
357 observation: The 200-1000  $\mu$ m plankton size classes in the study area, mostly composed  
358 of copepods, have been reported to have a high concentration of protein and lipid.<sup>40</sup>  
359 Moreover, the composition of smallest size class (0.7–200  $\mu$ m) is dominated by  
360 microphytoplankton and detritus (mostly from the Marseille WWTP effluents and Rhone  
361 inputs), and small copepod stages<sup>26,40,42</sup>, providing active surfaces for the accumulation of  
362 highly hydrophobic contaminants. A previous study showed important atmospheric  
363 inputs of particle-bound PBDEs ( $\sim 550$  ng m<sup>-2</sup> y<sup>-1</sup>) and PCDD/Fs ( $\sim 15$  ng m<sup>-2</sup> y<sup>-1</sup>) in the  
364 area, also with a clear predominance of BDE-209 and OCDD in the atmospheric particle  
365 patterns.<sup>10</sup> This atmospheric loading may constitute a relatively constant and direct source  
366 of these congeners to surface waters, facilitating their way to the LTL of the food web.  
367 Regarding HTLs, *S. sarda* and *S. colias* presented the highest  $\Sigma$ PBDE median  
368 concentrations of 37 and 29 ng g<sup>-1</sup> lw, respectively, followed by *T. trachurus*, *T. sagittatus*  
369 and, *T. mediterraneus* exhibiting median concentrations in the range 16-20 ng g<sup>-1</sup> lw

370 (Table 1). Although individual PBDEs generally followed this trend too (Figure S10),  
371 some differences were found in the PBDE patterns. In the group of species showing  
372 higher  $\Sigma$ PBDE median concentrations (i.e. *S. sarda*, *S. colias*, *T. trachurus*, *T.*  
373 *mediterraneus*, and *T. sagittatus*), the PBDE pattern was characterized mostly by the  
374 predominance of BDE-47 and -100 (32-46% and 13-31% of the detected  $\Sigma$ PBDEs,  
375 respectively) and a lower contribution of PBDE-209 (4-16% of the detected  $\Sigma$ PBDEs)  
376 (Figure S11A). The predominance of these congeners, particularly BDE-47, has been  
377 reported for other marine organisms.<sup>14,17,51</sup> Furthermore, the patterns in *M. merluccius*  
378 and *I. coindetii*, two out of the three species showing the lowest median values, showed  
379 a more even relative distribution of BDE-47 and BDE-209, accounting for the 24-32 and  
380 32-39% of the detected  $\Sigma$ PBDEs, respectively (Figure S11B). These are piscivorous and  
381 invertivorous species feeding mainly on pelagic species. Interestingly, the pattern found  
382 in *B. boops* showed a similar BDE-209 contribution as *M. merluccius* and *I. coindetii* but  
383 lower relative contribution of BDE-47 and higher % of BDE-99, resembling instead that  
384 of phytoplankton and 200-1000 $\mu$ m zooplankton (Figure S11B,C). The fact that *B. boops*  
385 is essentially zooplanktivorous<sup>40</sup> could partially explain this pattern. The 200-1000 $\mu$ m  
386 zooplankton have been reported as the zooplankton class-size with the highest energy  
387 content in the study area, making it preferable prey for zooplanktivorous fish such as the  
388 bogue.<sup>40</sup> However, a differential metabolic capacity of *B. boops* could also contribute to  
389 the observed pattern. Species-specific differences in metabolic rates of PBDE in fish has  
390 been already reported.<sup>52</sup> A higher median BDE-99/BDE-100 ratio (reported as an  
391 indicator of fish capacity to metabolize PBDEs)<sup>49, 53</sup> for *B. boops* (0.9) was observed in  
392 comparison to the combined ratio for *M. merluccius* and *I. coindetii* (0.2), suggesting a  
393 less efficient capacity of *B. boops* to metabolize PBDEs. For comparison, the  $\Sigma$ PBDE  
394 concentrations in HTL organisms in this study (0.02-1.0 ng g<sup>-1</sup>ww, Table S11B) were

395 similar or slightly lower to those reported in fish from other Mediterranean locations.  
396 Values ranging from 0.07 to 3.4 ng g<sup>-1</sup> ww were measured in wild fish from the Adriatic,  
397 Ionian and Tyrrhenian Seas (E Mediterranean)<sup>17</sup> and average concentrations ranging from  
398 ~1.0 to 3.9 ng g<sup>-1</sup> ww were reported for fish and seafood collected in Valencian markets  
399 (Spain, NW Mediterranean)<sup>54</sup>. The fact that the authors of these studies reported the upper  
400 bound concentrations and that other fish species were also studied could explain an  
401 important part of the concentration variability.

402  
403 Regarding HTL,  $\Sigma$ PCDD/Fs accumulated preferentially in the cephalopods exhibiting  
404 median concentrations of 152 and 84 pg g<sup>-1</sup> lw in the Southern shortfin squid (*I. coindetii*)  
405 and European flying squid (*T. sagittatus*), respectively. The pattern in these organisms  
406 was characterized by a predominance of OCDD (around 50% of the detected  $\Sigma$ PCDD/Fs)  
407 and was quite similar to that of the planktonic compartment (Figure S12A). Individual  
408 congeners followed the same concentrations trend, except for 2,3,7,8-TDCF which also  
409 accumulated in *S. colias*, *B. boop*, *S. sarda* and *T. trachurus* (Figures S13), as reflected  
410 too in their respective patterns (Figure S12B) with this congener accounting from ~60 to  
411 76% (median) of the detected  $\Sigma$ PCDD/Fs. *M. merluccius* and *T. mediterraneus* showed a  
412 comparable contribution of 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TDCF, and OCDFs  
413 representing 30-40% of the detected  $\Sigma$ PCDD/Fs depending on the congener and species  
414 (Figure S12C).

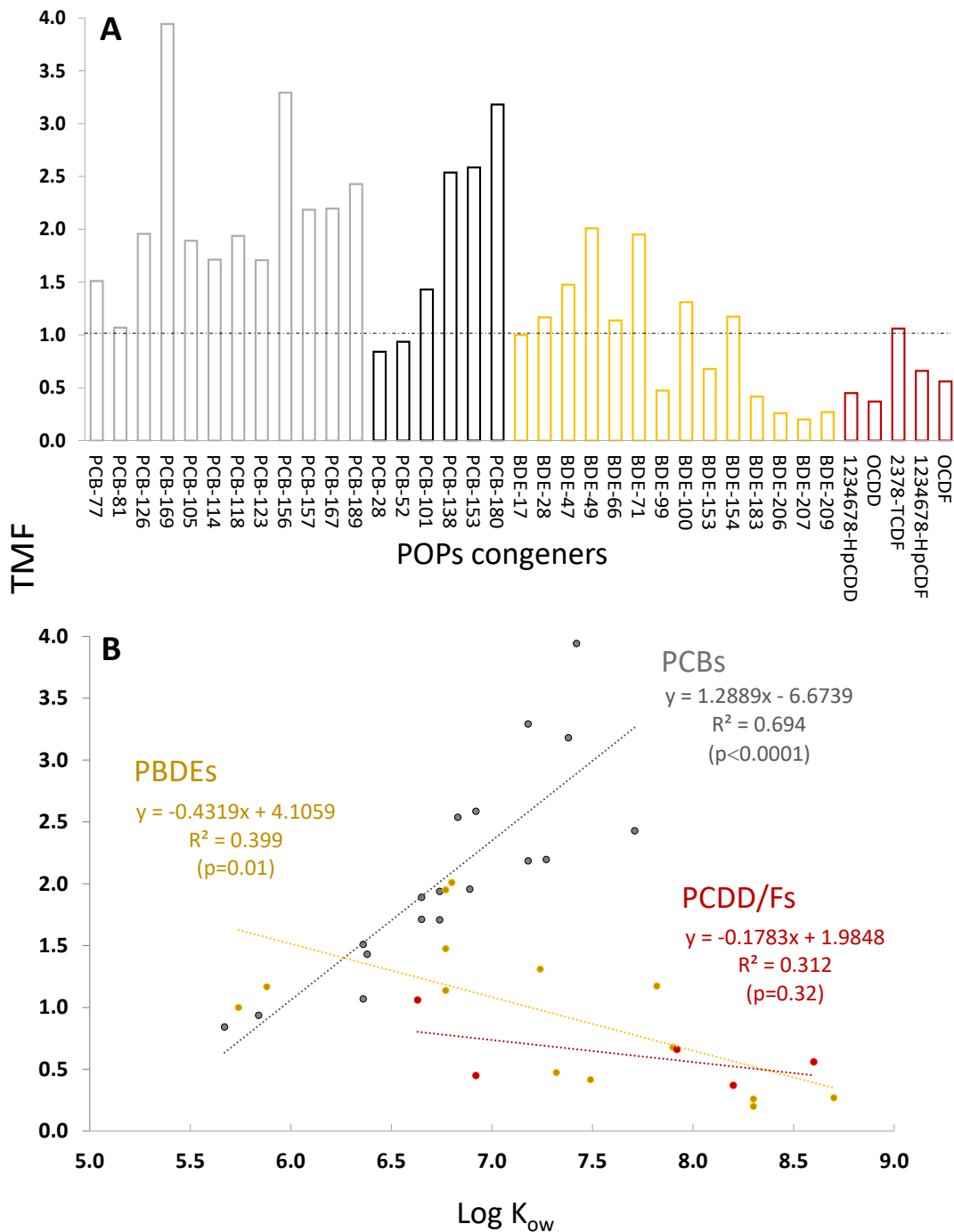
415

#### 416 3.4. Trophic magnification

417

418 TMFs were calculated for the eighteen PCBs, fourteen PBDEs and five PCDD/Fs (Figure  
419 S14, Table S12). The majority of POPs (60%) with calculated TMFs bioamplified

420 (TMF>1), 32% biodiluted (TMF<1) and the remaining 8% exhibited no apparent tendency  
 421 (TMF~1)<sup>45</sup> (Figure 2A).



422

423 **Figure 2.** Trophic magnification factors (TMFs) for individual PCBs, PBDEs and PCDD/Fs (A) and their  
 424 relationship with the POP's log K<sub>ow</sub> (B) for the NW Mediterranean Sea food web. Only congeners with DF  
 425 > 30% and expanding at least along 7 different TLs were considered. The horizontal dotted line indicates  
 426 TMF=1. Light and dark grey, yellow and red indicates DLPCBs, IDPCBs, PBDEs and PCDD/Fs,  
 427 respectively. The standard errors and confidence intervals of the slopes used to derive the TMFs can be  
 428 consulted in Table S12.

429

430 PCBs showed the highest biomagnification potential (>80% congeners with  $TMF > 1$ ) with  
431  $TMFs$  ranging from 1.4 (PCB-101) to 3.9 (PCB-169). Our results indicate that even if  
432 PCB-153, one of the most studied PCBs in aquatic organisms, exhibited a lipid-  
433 normalized concentration of 4-5 orders of magnitude higher than PCB-169 and PCB-126  
434 (Table S8), its estimated trophic magnification potential ( $TMF_{CB-153} = 2.6$ ) is around 35%  
435 weaker than that for PCB-169 and only 24% higher than that of PCB-126 ( $TMF = 1.9$ ).  
436 PCBs-126 and -169 are indeed the most toxic  $DLPCBs$  (toxic equivalent factor,  $TEFs = 0.1$   
437 and 0.03, respectively).<sup>55</sup> This may have implications for the appropriate environmental  
438 exposure assessment to the most toxic PCBs in the study area, which may be overlooked  
439 by only studying the most abundant PCBs, which is often the case, and warrants further  
440 research. Only PCB-28 ( $TMF = 0.8$ ) and -52 ( $TMF = 0.9$ ) did not biomagnify, consistent  
441 with their higher abundance in the food web LTL (section 3.3.2). A significant positive  
442 correlation ( $R^2 = 0.69$ ,  $p < 0.0001$ ) was found between the  $TMF_{PCBs}$  and the  $\log K_{ow}$  (Figure  
443 2B) confirming the general higher trophic magnification for the more hydrophobic PCBs  
444 in this Mediterranean food web, as previously reported for other aquatic ecosystems<sup>46</sup>.  
445 This biomagnification potential is consistent too with the higher PCB concentrations  
446 generally found in the Atlantic bonito (Tables 1, S7 and Figure S7).

447

448 In contrast to PCBs, only 50% of PBDE congeners biomagnified, exhibiting generally  
449 lower  $TMFs$  ranging from 1.1 (BDE-66) to 2.0 (BDE-49). The other congeners showed a  
450 trophic dilution in the food web with  $TMFs$  varying from 0.2-0.7 (Figure 2A, Table S12).  
451 A negative significant correlation ( $R^2 = 0.40$ ,  $p = 0.01$ ) was found for  $TMF_{PBDEs}$  and the  $\log$   
452  $K_{ow}$  indicating a lack of biomagnification of the heaviest PBDEs like BDE-206, 207 and  
453 209 among others (Figure 2B), consistent with their higher predominance in the  
454 planktonic compartment. It is worth mentioning that no or little trophic magnification

455 (0.5 < TMF < 1.5) was found for most of the PBDEs considered in the European Quality  
456 Standard for PBDEs (i.e. BDE-28, -47, -99, -100, -153, -154) in fishes (EQS<sub>biota</sub>)<sup>56</sup>.  
457 Moreover, a generic biomagnification factor (BMF) of 5 is used for those PBDEs to cover  
458 their biomagnification from lower trophic levels to fish species<sup>57</sup>, which is much higher  
459 than our field-derived TMFs. PCDD/Fs showed TMFs ranging from 0.4 to 1.1 indicating  
460 mostly trophic dilution, with a non-significant negative correlation ( $R^2=0.31$ ,  $p=0.32$ )  
461 between  $TMF_{PCDD/Fs}$  and  $\log K_{ow}$ . This lack of significant correlation with  $\log K_{ow}$  has  
462 also been reported in other aquatic food webs.<sup>58</sup> Similarly to PBDEs, a  $BMF=10$  is  
463 considered for PCDD/Fs and  $DL$ -PCBs to account for their biomagnification in aquatic  
464 food webs<sup>59</sup>, which is much higher than the TMFs measured in this study. These fact  
465 raises the importance of using site and food web specific biomagnification values in order  
466 to perform a more reliable site-specific risk assessment instead of applying generic default  
467 values.

468

469 Overall, our results indicate that the POPs biomagnification in the studied food web is  
470 strongly congener and species dependent. The fact that POPs congeners with similar  $K_{ow}$   
471 showed distinct bioaccumulation patterns, particularly the more hydrophobic PCBs,  
472 PBDEs and PCD/Fs indicated that lipophilicity was not the only factor explaining their  
473 trophic magnification. This differential behaviour has also been reported in other aquatic  
474 food webs.<sup>58</sup> Indeed, the interplay of the specific contaminant bioavailability and  
475 metabolic transformation may have driven their final biomagnification. The observed  
476 trophic dilution of higher hydrophobic PBDEs in wild fish could be mostly attributed to  
477 the metabolic debromination of HMW PBDEs as previously reported.<sup>52</sup> However, the  
478 biodilution of higher hydrophobic PCDD/Fs, exhibiting negligible metabolization rates

479 in most cases, may be better explained by a reduced membrane permeability due to their  
480 larger molecular size compared to the lower chlorinated congeners.<sup>50</sup>

481

482 Field-derived TMFs for the studied POPs in marine food webs are scarce in the literature  
483 for comparison. In addition, TMFs in marine systems have been reported to be highly  
484 variable and a number of factors such as type, structure and length of the food web and  
485 the site study specificities and season of the year, may have an important influence on the  
486 final TMF value<sup>60,61</sup>. Therefore, the comparability of TMFs must be carefully interpreted.  
487 TMFs of 1.3 and 1.2 were reported for PCB-153 and BDE-47, respectively, in a study  
488 conducted in the Gulf of Lion during the period 2004-2006 and in a shorter foodweb<sup>60</sup>.  
489 These values are slightly lower than those calculated for the same contaminants in this  
490 study ( $TMF_{PCB-153} = 2.6$  and  $TMF_{BDE-47} = 1.5$ ). The fact that we studied a longest food  
491 web, including a higher top predator (*A. bonito*), could explain our higher values. TMFs  
492 within the same range were reported for a pelagic food web in the western Scheldt estuary  
493 (Netherlands)<sup>62</sup> for BDE-28, -47, and -100. This work highlighted too the trophic dilution  
494 of BDE-209 with a very similar TMF of 0.2. However, they found BDE-99  
495 biomagnifying ( $TMF=2.4$ ) in their studied food web, while a  $TMF=0.5$  was found for the  
496 same congener in our study. The reported predominance of BDE-99 in the western  
497 Scheldt estuary organisms<sup>62</sup>, likely linked to historical local sources, could explain this  
498 difference, since this congener was not predominant in our food web. TMFs for PCBs  
499 and PBDEs within the same range were reported for a pelagic food web in coastal Atlantic  
500 Ocean<sup>63</sup>. However, our TMFs for these two families of POPs were generally lower than  
501 the average ( $\pm$  standard deviation) TMFs reported for a global compilation also including  
502 fresh water ecosystems, which ranged from  $1.7 \pm 1.1$  to  $8.1 \pm 6.9$  for PCBs and from  $0.3$   
503  $\pm 0.3$  to  $3.2 \pm 1.9$  for PBDEs<sup>61</sup>, although a large variability was reported too (Figure S15).

504 To the best of our knowledge, we report here the first field-derived TMFs for PCDD/Fs  
 505 in a Mediterranean food web, which are very similar to those reported in other aquatic  
 506 ecosystems<sup>61</sup> (Figure S15).

507

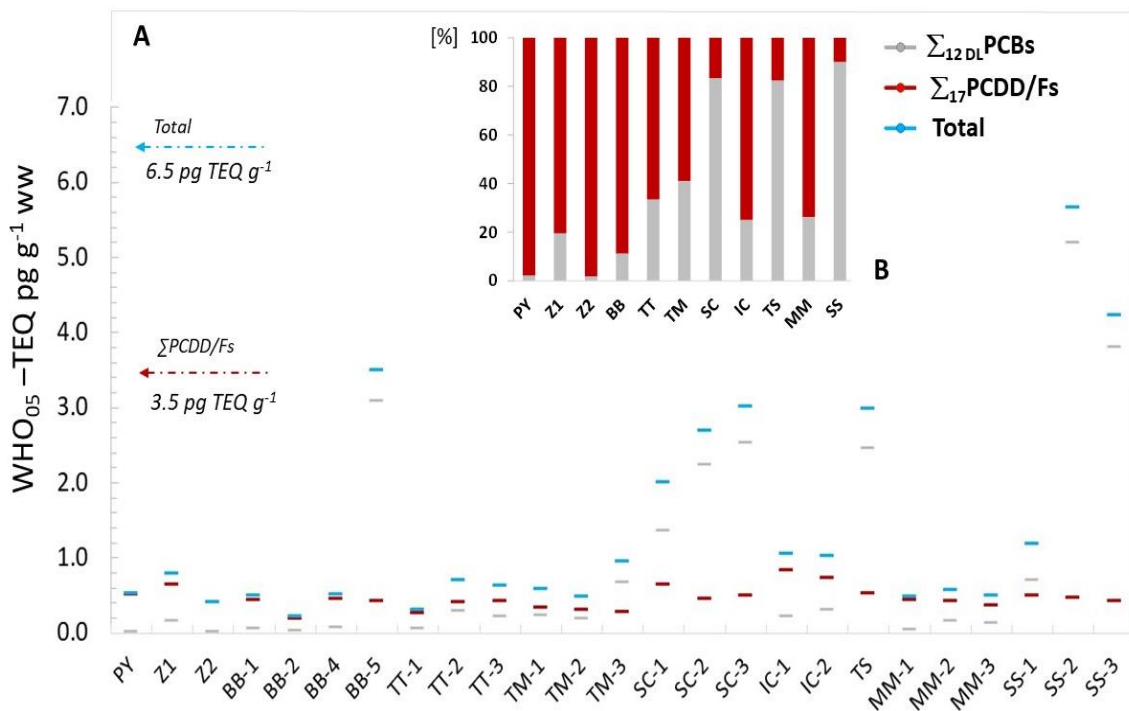
### 508 3.5.Toxicity potential and risk assessment

509

#### 510 3.5.1. *DL*POPs

511 Concentrations expressed as upper bound WHO<sub>05</sub>-TEQ were derived for *DL*PCBs and the  
 512 2,3,7,8-PCDD/Fs in the food web organisms using the latest available TEFs<sup>55</sup> in order to  
 513 study their toxicity potential against humans. Concentrations ranged 0.008 - 5.2 and 0.2  
 514 – 0.8 WHO<sub>05</sub> TEQ pg g<sup>-1</sup> ww for  $\Sigma_{DL}PCBs$  and  $\Sigma_{17}PCDD/Fs$ , respectively, resulting in  
 515 TEQ<sub>Total</sub> ( $\Sigma_{29}$ dioxin-like POPs) of 0.2-5.7 pg g<sup>-1</sup> ww (Figure 3A, Table S13).

516



517

518 **Figure 3.** Calculated WHO<sub>05</sub>-TEQ (pg g<sup>-1</sup> ww) in all samples from the pelagic food web in coastal NW  
 519 Mediterranean Sea (A) and median relative contribution (%) of  $\Sigma_{12DL}PCBs$  (grey) and  $\Sigma_{17}PCDD/Fs$  (red)  
 520 to the total WHO<sub>05</sub>-TEQ (PCBs+PCDD/Fs) in blue (B), except for PY, Z1, Z2 and TS, which are single  
 521 values. The horizontal dotted lines show the EU concentration thresholds in sea foodstuffs and wild fish  
 522 (see text for details). PY=phytoplankton 0.7-200  $\mu m$ ; Z1=zooplankton 200-1000  $\mu m$ ; Z2=zooplankton >  
 523 2000 BB=*B. boops*; TT=*T. trachurus*; TM=*T. mediterraneus*; SC=*S. colias*; IC=*I. coindetii*; TS=*T.*  
 524 *sigittatus*; MM=*M. merluccius*; SS=*S. sarda*.

525



526 The species *S. sarda*, *T. sagittatus* and *S. colias* exhibited the highest median TEQ<sub>Total</sub>  
527 values of 4.2, 3.0, and 2.7 pg g<sup>-1</sup> ww, respectively (Table S13). These TEQs were driven  
528 by the predominant contribution of DLPCBs (82-90%) in those species (Figure 3B).  
529 Median TEQ<sub>Total</sub> values in the remaining trophic levels varied from 0.4 to 1.1 pg g<sup>-1</sup> ww.  
530 PCDD/Fs exhibited a generally higher contribution (53-98%) on these species, except for  
531 some isolated samples such as BB-5 and TM-3, which show a higher concentration of  
532 PCB-126, increasing the relative contribution of  $\sum_{DLPCBs}$  TEQ on those samples. The  
533  $\sum_{DLPCB}$  TEQ concentrations measured in the studied food web were within the range or  
534 higher than those reported for other fish species in the Mediterranean. For example, levels  
535 of 0.4-1.2 (*Sardina pilchardus*), 0.08-0.4 (*Engraulis encrasicolus*) and 0.07-0.27 (*B.*  
536 *boops*) TEQ pg g<sup>-1</sup> ww have been recently reported.<sup>14</sup> Our concentrations in fish samples,  
537 excluding those of the top predator Atlantic bonito, ranged from 0.02 to 3.1 TEQ pg g<sup>-1</sup>  
538 ww for  $\sum_{DLPCB}$ , with values varying from 0.05 to 3.1 TEQ pg g<sup>-1</sup> ww for *B. boops*. Our  
539  $\sum_{DLPCB}$  TEQ values were also higher than those reported for chub mackerel (*Scomber*  
540 *japonicas*) (0.002 -0.008 TEQ pg g<sup>-1</sup> ww) and horse mackerel (*T. trachurus*) (0.004 –  
541 0.016 TEQ pg g<sup>-1</sup> ww) caught in the Adriatic Sea.<sup>64</sup> For comparison, our  $\sum_{DLPCB}$  levels  
542 in *T. trachurus* varied from 0.05 to 0.3 TEQ pg g<sup>-1</sup> ww (Table S13). A recent study  
543 measured dioxin-like POPs in Mediterranean bluefin tuna (*Thunnus thynnus*), reporting  
544 0.7 and 1.9 TEQ pg g<sup>-1</sup> ww for  $\sum_{DLPCB}$  and  $\sum_{PCDD/Fs}$ , respectively.<sup>65</sup> Our results in  
545 the Atlantic bonito ranged from 0.7 to 5.2 and from 0.4 – 0.5 TEQ pg g<sup>-1</sup> ww for  $\sum_{DLPCB}$   
546 and  $\sum_{PCDD/Fs}$ , respectively. However, the concentrations reported for the bluefin tuna  
547 were lower bound values (non-detected values were considered as zero). These  
548 comparisons are only indicative due to the associated variability related to the different  
549 species considered, sampling year and season and the quantification strategies adopted in  
550 each specific study.

551 At European level, two pieces of legislation, Commission Regulation 1259/2011<sup>66</sup> and  
552 Directive 2013/39/EU<sup>56</sup>, set a maximum level for DLPOPs in seafood and marine  
553 organisms aiming at protecting human health *via* consumption of fishery products (but  
554 also aquatic top predators from secondary poisoning for the EQS<sub>biota</sub>). A threshold level  
555 of 6.5 pg TEQ g<sup>-1</sup> ww for the  $\sum_{17}\text{PCDD/Fs} + \sum_{12}\text{DLPCBs}$  in fish muscle and fishery  
556 products, and wild fish (EQS<sub>Biota</sub>) is established. In addition, regulation 1259/2011 also  
557 set a threshold value of 3.5 pg TEQ g<sup>-1</sup> ww for  $\sum_{17}\text{PCDD/Fs}$  only. The concentrations  
558 measured in the various species considered did not exceed any of these thresholds,  
559 although certain *S. sarda* and *S. colias* individuals (i.e. SS-2-3 and SC-3) approached the  
560 6.5 pg TEQ g<sup>-1</sup> ww threshold for total DLPOPs (Figure 3A) with risk quotients (R) between  
561 0.5 and 0.9 (R>1 indicating risk) (Table S14). The DLPOPs EWIs considering fish and  
562 cephalopod consumption data in French population (section 2.6) were calculated for each  
563 sample and varied from 0.1 to 11 pg TEQ Kg<sup>-1</sup> bw week<sup>-1</sup>. All individuals of *S. colias* and  
564 *S. sarda* exceeded the tolerable weekly intake (TWI) of 2 pg TEQ Kg<sup>-1</sup> bw week<sup>-1</sup> set by  
565 the European Food Safety Authority<sup>67</sup> with R values ranging from 1.1-5.3 and 1.9-2.8 for  
566 *S. sarda* and *S. colias*, respectively (Table S14). The major contributors to the EWI and  
567 subsequent risk for humans associated with the consumption of *S. colias* and *S. sarda*  
568 were DLPCBs, particularly PCB-126.

569 Moreover, Directive 1259/2011 sets a maximum level (75 ng g<sup>-1</sup> ww) for the sum of the  
570 six non-dioxin-like PCBs in seafood, also referred as IDPCB in this work. The  $\sum_{\text{ID}}\text{PCB}$   
571 concentrations in the studied food web were for most samples below that threshold (Table  
572 S11), varying from 0.6 to 59 ng g<sup>-1</sup> ww. However, some *S. colias* individuals again  
573 approached the threshold (R=0.8 for SC-1-2) and two out three samples of the top  
574 predator *S. sarda* (i.e. SS-2-3) exceeded it with concentrations between 106-109 ng g<sup>-1</sup>  
575 ww (R=1.4, Table S14) pointing to a risk for humans to non-dioxin-like PCBs due to

576 consumption of this last species. It has been reported that non-dioxin-like PCBs, which  
577 are weak aryl hydrocarbon receptor agonists, can modulate the overall toxic potency of  
578 2,3,7,8-TCDD and related compounds<sup>55</sup> and therefore their co-occurrence cannot exclude  
579 cumulative effects including synergic harmful effects.

580

### 581 3.5.2. PBDEs

582 Regarding PBDEs, the EQS<sub>Biota</sub> of 0.0085 ng g<sup>-1</sup> ww (as  $\Sigma_6$ PBDEs including BDE-28,-  
583 47,-99,-100,-153,-154) based on human toxicity<sup>56</sup> was used for a first risk evaluation.  
584 This threshold value was exceeded in every single individual in all TLs (Table S14),  
585 indicating a risk for humans consuming the edible species, again pointing to *S. sarda*  
586 (R=54-97) and *S. colias* (R=15-65) as the most 'risky' fish. However, some authors argue  
587 that the existing EQS<sub>Biota</sub> for PBDEs is extremely low leading to environmental  
588 concentrations exceeding the threshold value in most study cases.<sup>51,68</sup> Moreover, for  
589 OSPAR assessment, there are still questions on the reliability and appropriateness of  
590 some of the thresholds set as EQS<sub>biota</sub>, based on human protection, to support  
591 environmental assessment. It has been recently proposed to adopt the Canadian Federal  
592 Environmental Quality Guidelines (FEQGs) based only on wildlife protection.<sup>69</sup>  
593 Comparing our concentrations with the proposed FEQGs, which have been set for a  
594 number of individual PBDE congeners (i.e BDE-28, 47, 99, 100, 153, 154, 183 and 209),  
595 there is no indication of apparent risk (Table S15). However, it should be noted that the  
596 FEQGs are derived for whole organisms, and PBDE were measured in muscle in this  
597 study. The  $\Sigma$ PBDEs EWI in France ranged from 0.02 to 1.9 ng Kg<sup>-1</sup> bw week<sup>-1</sup>, the highest  
598 value corresponding to *S. sarda*, followed by *S. colias* (0.7-1.2 ng Kg<sup>-1</sup> bw week<sup>-1</sup>). For  
599 comparison, an average estimated intake of 0.14 ng Kg<sup>-1</sup> bw d<sup>-1</sup> via fish and seafood  
600 consumption for adults has been reported for Valencia (Spain) in the NW Mediterranean

601 Sea<sup>54</sup>, corresponding well with our higher end estimate (0.17 ng Kg<sup>-1</sup> bw d<sup>-1</sup>). There is no  
602 TWI for  $\Sigma$ PBDE to the best of our knowledge, but the US Agency for Toxic Substances  
603 and Disease Registry and the US Environmental Protection Agency have established  
604 acute/sub-chronic Minimal Risk Levels<sup>70</sup> and chronic oral reference doses<sup>71</sup>, respectively,  
605 for some of the most abundant PBDE congeners (i.e BDE-47, BDE-99, BDE-153, BDE-  
606 209). These health standards ranged from 3 to 7000 ng Kg<sup>-1</sup> bw d<sup>-1</sup> depending on the  
607 congener, showing that there is no risk associated with these congeners for humans  
608 consuming these Mediterranean fishery products.

609

610 Our study demonstrates that the edible species Atlantic bonito (*S. sarda*) and Atlantic  
611 chub mackerel (*S. colias*) bioaccumulated the highest concentrations of POPs which may  
612 pose a risk for humans consuming these species caught and /or marketed in the Gulf of  
613 Lion (NW Mediterranean Sea) mostly due to DLPOPs exposure. The cephalopods  
614 southern shortfin squid (*I. coindetti*) and European flying squid (*T. sagittatus*) showed a  
615 high potential for the accumulation of PCDD/Fs, however no indications of risk can be  
616 observed according to our evaluation. An in-depth review of available thresholds for  
617 PBDEs concentration in biota and the determination of tolerable daily intakes for more  
618 congeners are urgently needed to provide a more comprehensive risk assessment. We  
619 consider the calculated EWI as a lower-end estimate of their total exposure, since their  
620 intake through other food items is not considered and external exposure routes were not  
621 accounted for in this evaluation. For example, the reported median outdoor inhalation  
622 intake in the study area for DLPOPs (0.028 pg TEQ Kg<sup>-1</sup> bw week<sup>-1</sup>) and  $\Sigma$ PBDEs (0.015  
623 ng Kg<sup>-1</sup> bw week<sup>-1</sup>) could range up between 0.4 - 1.3% and 0.8-2.1 % their respective total  
624 intakes. These results warrant further research on the overall intake rates of the three POP  
625 families by humans and their cumulative risks in this impacted region of NW

626 Mediterranean Sea. Our results would be highly valuable to set up-to-date and comparable  
627 concentration thresholds in biota considering trophic level normalization as  
628 recommended by EU guidance<sup>72</sup> and OSPAR.<sup>73</sup> Besides, the characterized food web, as  
629 a whole, may be a useful and site-specific comprehensive ‘bioindicator’ of the chemical  
630 pollution status, representing a dynamic stock of toxic organic chemicals in the study  
631 area. A lower-end estimation of its integrated POPs burden in the study season, calculated  
632 considering the sum of the median concentrations in all TLs, reached  $\sim 18 \mu\text{g g}^{-1} \text{lw}$ . This  
633 value could be considered a benchmark for further studies using the same food web,  
634 opening new perspectives for the monitoring of toxic chemicals in Mediterranean coastal  
635 waters.

636

637

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651

652 **Supporting information available**

653

654 Additional data and details on the sampling and analytical procedures, QA/QC,  
655 concentration of individual congeners, TMFs among others are available free of charge  
656 via the Internet at <http://pubs.acs.org/>

657

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