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## Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton-zooplankton-small pelagic fish marine food web

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1 **Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton-**  
2 **zooplankton-small pelagic fish marine food web**

3

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28

29 **Abstract:**

30 Trace metal contamination in the European sardine and anchovy food web was investigated in the  
31 Gulf of Lions, NW Mediterranean Sea, including seawater and size fractions of plankton. The results  
32 highlighted: i) higher and more variable concentrations in the smaller plankton size classes for all  
33 metals except cadmium; ii) higher concentrations in anchovy versus sardine for all elements except  
34 lead; iii) different patterns of metal bioaccumulation through the food web: cobalt, nickel, copper,  
35 silver, lead and zinc displayed continuously decreasing concentrations (with the exception of increased  
36 zinc in fish only), while mercury concentrations dropped considerably in larger plankton size classes  
37 and rose significantly in fish. Lastly, cadmium concentrations were found to be highest in intermediate  
38 plankton size classes, with very low levels in fish. The need to efficiently characterize the biological  
39 composition of plankton in order to fully identify its role in the mobilization and transfer of metals  
40 was highlighted.

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43 **Keywords:** inorganic elements; seawater; size-classed plankton; *Sardina pilchardus*; *Engraulis*  
44 *encrasicolus*; Mediterranean Sea

45

46 **Highlights:**

47

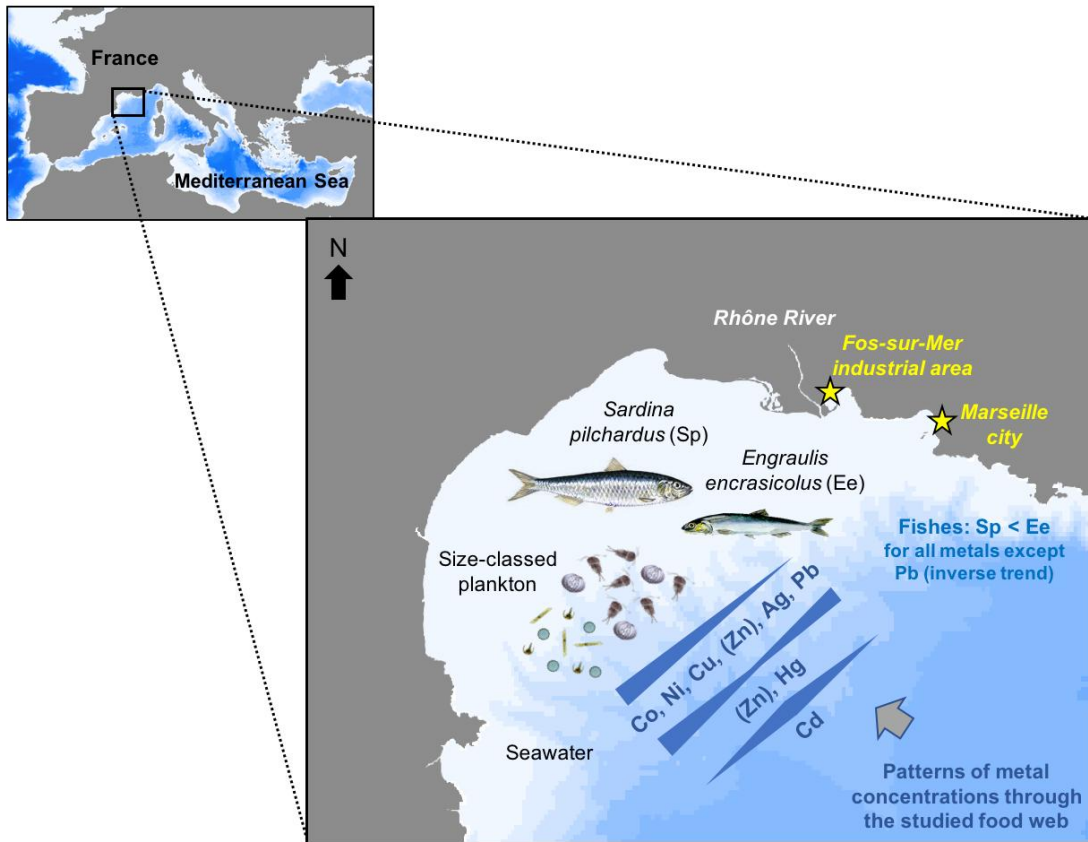
- 48 - Higher concentrations were generally found in water samples from western stations
- 49 - Few or no significant spatial variations were tested or highlighted for biota
- 50 - Contrasted bioaccumulation patterns of trace metals along the food web were found
- 51 - Concentrations differed greatly among size fractions of plankton
- 52 - Anchovy presented higher concentrations than sardine for all metals except Pb

53

54

55 Graphical abstract:

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## 60 1. Introduction

61 Trace metals are released into the environment from both natural sources (e.g. volcanism, soil erosion  
62 and forest fires) and anthropogenic sources (e.g. transport, harbours, industrial activities and major  
63 coastal cities). They reach the ocean through riverine and aeolian fluxes (Mason, 2013). Their  
64 increased use in human activities has led to the contamination of numerous environmental  
65 compartments and, as a result, to environmental levels with a detectable anthropic contribution (Lewis  
66 and Maslin, 2015). Some trace metals have essential biological functions within a narrow range of  
67 optimal concentrations (essential elements), while others have no known biological role (non-essential  
68 elements) and are recognized for their toxic effects on aquatic organisms, even at environmental  
69 concentrations (Mason, 2013).

70 Taxa- and species-specific metal regulation mechanisms (i.e. uptake, storage and/or elimination) have  
71 been described for both essential and non-essential elements (Wang and Rainbow, 2010). Their  
72 transfer between biogeochemical compartments, bioaccumulation in organisms and biomagnification  
73 in food webs depends on their concentrations and speciation in both abiotic (habitat) and biotic (food  
74 sources) environments (Neff, 2002; Rainbow, 2002). Marine organisms are hence exposed and  
75 accumulate contaminants via dissolved and trophic pathways; the latter being the main route for trace  
76 metal intake by medium to high trophic level consumers such as fish (Mathews and Fisher, 2009;  
77 Pouil et al., 2016). Understanding the mechanisms that lead to the bioaccumulation of trace metals in  
78 consumers and the interpretation of their metal burden thus requires good knowledge of feeding habits  
79 and trophic ecology, as well as metal levels in diets.

80 In the Gulf of Lions, in the northwestern (NW) Mediterranean Sea, small pelagic planktivorous fish  
81 such as European sardine (*Sardina pilchardus*) and anchovy (*Engraulis encrasicolus*) are fishery  
82 resources of major economic importance (Palomera et al., 2007). Both species play a major ecological  
83 role in food web functioning (Bănaru et al., 2013) by transferring energy and nutrients from lower  
84 trophic levels (plankton) to upper levels (large pelagic fish, marine mammals and seabirds). In a  
85 broader context of maintaining the functional integrity of ecosystems and associated ecosystem  
86 services, thorough knowledge of global anthropogenic impacts on this pelagic compartment, including  
87 contamination pressures, appears crucial. The Mediterranean Sea is notoriously faced with various  
88 pollution threats, including chemical contamination (Danovaro, 2003; Durrieu de Madron et al., 2011).  
89 Moreover, the UNEP recently highlighted the lack of data on pollutant impacts on Mediterranean  
90 marine ecosystems (UNEP/MAP, 2012). This data may be of particular importance with regards to the  
91 Mediterranean Sea, where contaminant levels observed in predatory species are significantly higher  
92 than in the Atlantic Ocean (Bodiguel et al., 2009; Cossa and Coquery, 2005). Although this difference  
93 may be explained by higher contaminant concentrations in abiotic compartments, it may also be due to  
94 the enhanced ability of Mediterranean pelagic food chains to bioaccumulate certain chemical elements  
95 or substances, as documented for mercury (Chouvelon et al., 2018; Cossa and Coquery, 2005;

96 Harmelin-Vivien et al., 2009). Therefore, contamination in the planktonic compartment must also be  
97 studied in order to properly assess contamination pressures on small pelagic fish.

98 Plankton and, in particular, phytoplankton, forms the first link between abiotic (seawater)  
99 contamination and pelagic fish, hence playing a major role in contaminant transfer into marine food  
100 webs. The contamination dynamics of plankton must therefore be assessed in order to properly  
101 apprehend contaminant bioaccumulation at the secondary trophic levels of small pelagic fish. This  
102 issue remains a challenge and has been relatively poorly-investigated *in-situ*, probably due to the  
103 difficulties in sampling representative fractions of plankton and obtaining sufficient material to  
104 perform trace level chemical analyses. Despite an abundance of studies on the transfer of metals in  
105 upper trophic levels, none address the problem in its entirety from the water column to small pelagic  
106 fish and most consider a limited number of fish organs (muscle, liver and sometimes gonads or gills).  
107 This failure to address wide-ranging food web compartments and analyse contaminants in certain  
108 organs/tissues (with tissue-specific bioaccumulation properties) may constitute a considerable bias  
109 with regards to bioconcentration/bioaccumulation calculations, for which trophic levels must be  
110 considered in their entirety (Gray, 2002; Wang, 2002). As a result, although the biomagnification of  
111 mercury in aquatic ecosystems is undisputed, zinc is sometimes thought to bioaccumulate in fish food  
112 chains (Mathews and Fisher, 2008; Wang, 2002), while conclusions regarding cadmium, lead and  
113 silver differ (Cheung and Wang, 2008; Luoma and Rainbow, 2005; Reinfelder et al., 1998).

114 In this general context, the specific objectives of our study were to: (i) characterize the trace metal  
115 burden of the plankton-sardine-anchovy short food web (including seawater) in the Gulf of Lions, NW  
116 Mediterranean; (ii) assess (whenever possible) the spatial and seasonal variability of this burden;  
117 (iii) identify the potential links between the contamination of anchovies and sardines and their  
118 respective trophic ecology; (iv) define trace metal pattern(s) in terms of bioaccumulation, behavior  
119 and transfer within the studied small pelagic fish food web.

120 Both essential (cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn)) and non-essential elements (silver  
121 (Ag), cadmium (Cd), mercury (Hg), and lead (Pb)) were considered.

122

## 123 **2. Material and Methods**

### 124 *2.1. Study area*

125 The Gulf of Lions (GoL) in the NW Mediterranean Sea is characterized by complex hydrological  
126 dynamics with: (i) a cyclonic Northern Current flowing along the continental slope; (ii) a combination  
127 of wind-driven processes such as coastal upwelling and dense shelf water formation; and  
128 (iii) freshwater dynamics associated with the large Rhône River discharge (Millot, 1999). The Rhône  
129 accounts for the highest mean annual discharge (*ca.* 1700 m<sup>3</sup> s<sup>-1</sup>) into the Western Mediterranean basin

130 (Launay et al., 2019), including 95% of suspended particulate matter (SPM) fluxes to the French  
131 Mediterranean coast (Sadaoui et al., 2016) and 50% of GoL primary production (Lochet and Leveau,  
132 1990). The Mediterranean Sea's very low tidal range allows the Rhône riverine plume to expand  
133 westwards into the GoL (Boudet et al., 2017; Many et al., 2018). This plume is particularly apparent in  
134 the first two meters of the water column (Lorthiois et al., 2012). The influence of SPM from the Rhône  
135 River on both surface water and sediment is observed throughout the western Gulf (Durrieu de  
136 Madron et al., 2000; Espinasse et al., 2014a).

137 Various zooplankton habitats exist in the GoL, characterized by different biological and physical  
138 variables: species composition, size structure, depth, salinity, wind and currents (Espinasse et al.,  
139 2014a). Differences in zooplankton and pelagic fish isotopic signatures and radionuclide  
140 contamination have already been observed in the eastern and the western areas of the GoL (Espinasse  
141 et al., 2014b; Strady et al., 2015a). Phytoplankton and zooplankton communities display conspicuous  
142 seasonal variations in composition and structure, reflected in their respective carbon and nitrogen  
143 isotopic signatures (Bănaru et al., 2013; Espinasse et al., 2014a, 2014b; Harmelin-Vivien et al., 2008).  
144 Phytoplankton spring bloom generally occurs between March and June in the GoL (Alekseenko et al.,  
145 2014).

## 146 2.2. *Seawater and plankton sampling*

147 Seawater and plankton were sampled in May 2010 (spring) and February 2011 (winter) using the RV  
148 "L'Europe" at six to seven stations (depending on the season) along an East-West transect of the GoL  
149 (Fig. 1). As described in previous publications related to this study (Strady et al., 2015a, 2015b; Tiano  
150 et al., 2014), the sampling strategy was adapted to the compartment and size of the sampled  
151 organisms. A chlorophyll *a* (Chl-*a*) concentration profile (measured continuously) was obtained at  
152 each sampling site using a CTD probe fitted with a fluorimeter. Plankton sampling was performed at  
153 the maximum Chl-*a* concentration depth (generally around 10-15m water depth). Seawater for trace  
154 metal analysis was pumped from the surface and at depths of 10, 20, 30, 40 and 50 m using an all-  
155 Teflon tube and surface pump system. The water was pressure-filtered on board through 0.45 µm mesh  
156 pre-cleaned with HNO<sub>3</sub> acid and pre-weighed polycarbonate filters (Nucleopore®) under a clean  
157 laminar flow hood installed in a trace metal-clean van. A sub-sample (~500 mL) of the filtered  
158 seawater was transferred into acid-cleaned Teflon® (FEP) bottles and acidified with ultrapure  
159 (SupraPur® quality from Merck) HCl (0.4%) for further dissolved total Hg analyses. The remaining  
160 filtered seawater (~1L) was transferred into acid-cleaned polyethylene bottles and acidified with  
161 ultrapure HNO<sub>3</sub> (0.1%) for further dissolved trace metal (other than Hg) analyses. Both sub-samples of  
162 filtered seawater were hermetically sealed, double-bagged and stored in the dark at 4° C pending  
163 analytical processing.

164 Plankton was collected by pumping or trawling according to the target size. Small planktonic  
165 organisms were sampled by pumping seawater *in situ* (nominal pumping rate 320 L/min) at the Chl-*a*

166 maximum depth using an 8-cm diameter tube and filtered on board using a series of sieves made out of  
167 plankton net, mesh size 200, 60 and 6  $\mu\text{m}$ . Two small plankton size fractions were thus retained ([6-60  
168  $\mu\text{m}$ ] and [60-200  $\mu\text{m}$ ]). The trawling system was used to collect larger plankton (larger than 200  $\mu\text{m}$   
169 mesh) and towed at a speed of 2-3 knots for around 30 minutes near the Chl-a maximum depth. The  
170 samples were immediately sieved on board in the trace metal laboratory (i.e. clean van) using a sieve  
171 column with four different filter mesh size: 2000, 1000, 500 and 200  $\mu\text{m}$ . All plankton fractions were  
172 kept in acid pre-cleaned polyethylene tubes and frozen at  $-18^{\circ}\text{C}$  on board. They were then freeze-dried  
173 and kept in the dark at room temperature in the laboratory pending analyses.

### 174 2.3. *Fish sampling*

175 European sardines (*S. pilchardus*) and anchovies (*E. encrasicolus*) were collected in July 2010  
176 (summer) during the yearly PELMED pelagic surveys conducted by the French Institute for the  
177 Exploitation of the Sea (Ifremer) and in March 2011 (winter) by professional fishermen, in two areas  
178 of the GoL corresponding to eastern and western plankton stations (Fig. 1). Immediately after  
179 collection, they were identified according to species and sampling area or station, then stored in a  
180 freezer in plastic bags at  $-18^{\circ}\text{C}$ . The fish (sardines:  $n = 280$  individuals in total; anchovies:  $n = 265$   
181 individuals in total) were then dissected in the laboratory in clean and contamination-free conditions.  
182 The sampled tissues/organs included pieces of white muscle, liver, gonads (females only) and  
183 “remaining tissue” (including remaining muscle, skin, head, skeleton, viscera, etc.). They were placed  
184 back in the freezer immediately after dissection. The dissected sardines measured 8.0-13.9 cm in  
185 length; anchovies measured 9.9-13.3 cm in length. In order to collect enough biological material for  
186 analysis, sample pools were constituted according to sampling area/station, species, gender (males vs.  
187 females), and tissue/organ type. For sardines and anchovies, 27 and 23 pools of individuals were  
188 considered respectively, together with 27 and 23 pools of tissues/organs respectively per species. The  
189 pools contained 11 individuals on average. Each pool was homogenised, re-frozen, freeze-dried and  
190 ground into a fine powder using an agate mortar or stainless-steel blade mill (for “remaining tissue”)  
191 pending further chemical analyses. The agate mortar, grinding bowls and stainless-steel blades were  
192 thoroughly washed with milli-Q water after grinding each sample.

### 193 2.4. *Trace metal analyses*

194 Total trace element concentrations in seawater, size-classed plankton and fish tissue were analysed at  
195 the Ifremer LBCM laboratory in Nantes, France. This laboratory regularly performs inter-calibration  
196 studies ([www.quasimeme.org](http://www.quasimeme.org)).

197 Mercury in seawater samples and biological compartments was assessed using a different approach to  
198 the other study metals (Co, Ni, Cu, Zn, Ag, Cd, Pb) in terms of both sample treatment and analytical  
199 techniques. All Hg analyses on seawater were performed within 3 months of sampling using an  
200 Atomic Fluorescence Spectroscopy detector (AFS, Tekran, model 2500<sup>®</sup>) as described in Cossa et al.



201 (2011) coupled to an LBCM-built front end, according to the US-EPA method N°1631 (U.S.  
202 Environmental Protection Agency, 2002). Total Hg in solids (biological compartments) was assessed  
203 by atomic absorption spectrophotometry on aliquots of sample powder (10–50 mg) using an Advanced  
204 Mercury Analyser (ALTEC AMA-254, Altec Ltd), according to the standard operating procedure  
205 described in the US-EPA method N°7473 (U.S. Environmental Protection Agency, 1998).

206 Dissolved seawater concentrations of Co, Ni, Cu, Zn, Ag, Cd and Pb were determined with a  
207 Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS, Thermo Electron  
208 Corporation, Element X Series<sup>®</sup>) on acidified filtrates treated according to an adapted protocol from  
209 Danielsson et al. (1982) and described in detail by Chiffolleau et al. (2002) and Guesdon et al. (2016),  
210 after pre-concentration using a liquid/liquid extraction procedure. Biological compartment samples  
211 were analysed according to an in-laboratory approved method. Briefly, dried samples (~200 mg dry  
212 mass wherever possible) were placed in microwave Teflon<sup>®</sup> bombs and mineralized using a mixture of  
213 ultrapure HNO<sub>3</sub> and HCl acids. The digests were then diluted to 50 mL with milli-Q water. Total  
214 metal concentrations were also determined using Q-ICP-MS.

215 The quality assurance of all metal analyses relied on blank controls and the accuracy and  
216 reproducibility of data relative to the certified reference materials (CRMs) used in each analytical run.  
217 Blank values were systematically below the detection limits and CRM values concurred with certified  
218 concentrations. Details of the CRM analyses are reported in Table S1, together with the limits of  
219 quantification (LOQs) for each metal and each matrix (seawater and biological compartments).

## 220 2.5. *Data treatment and statistical analyses*

221 All data submitted to statistical tests were first checked for normality (through a Shapiro-Wilks test)  
222 and/or homogeneity of variances (Bartlett's test). If these conditions were fulfilled, parametric tests  
223 were then used in the subsequent analyses; otherwise, non-parametric analogues were used. All  
224 statistical tests were performed with the software R version 3.4.3 (R Development Core Team, 2017).  
225 Detailed data per station for seawater (dissolved concentrations) and size-classed plankton are  
226 provided in Supplemental Material (Tables S2 and S3).

227 In order to apprehend variations throughout the water column, trace element concentrations in  
228 seawater (dissolved metals) and salinity were first measured according to sampling depth, station and  
229 season (Figs. 2, 3 and 4, Table S2). Within each season, variations in seawater concentrations were  
230 then assessed by calculating coefficients of variation (Table 1). Non-parametric Spearman correlation  
231 coefficient tests were applied to identify potential relationships between salinity and concentrations of  
232 elements in seawater in the GoL per element and per season, across all stations (Table 2). The  
233 potential enrichment of surface waters in metals (<10 m) versus the remaining water column (i.e. 10-  
234 20 m and ≥20 m) was also tested using parametric ANOVA tests followed by a Tukey's HSD post-hoc  
235 pairwise comparison test, or non-parametric Kruskal-Wallis (KW) tests followed by a multiple

236 comparison test with Holm's adjustment method, per element and per season, across all stations. In  
237 order to assess the effect of season and geography on dissolved trace metal concentrations in the GoL,  
238 parametric Student t-tests or non-parametric Mann-Whitney-Wilcoxon (MWW) tests were performed  
239 per element across all stations to ascertain seasonal variations, and per season to ascertain  
240 geographical variations (Table 3). To avoid bias, the tests used data obtained at 10 to 40 m, i.e. the  
241 depth range at which most sampling was performed, as few samples were collected from surface  
242 waters and at 50 m. Moreover, previous statistical tests revealed no significant differences between the  
243 10-20 m and  $\geq 20$  m depth ranges across all study elements and in either season (see Results).

244 The homogeneity and consistency of biological compartments were first improved by solely taking  
245 into account pools containing all three tissues, i.e. liver, muscle and "remaining tissue" (plus gonads  
246 for females), enabling the calculation of concentrations in "whole organisms" using the following  
247 formula:

248 
$$[\text{Whole organism}] = \frac{([\text{Liver}] * \text{Liver mass}) + [\text{Muscle}] * \text{Muscle mass} + [\text{Remaining tissue}] * \text{Remaining}$$
  
249 
$$\text{tissue mass (+ for females: } [\text{Gonads (for females)}] * \text{Gonad mass)}}}{(\text{Liver mass} + \text{Muscle mass} +$$
  
250 
$$\text{Remaining tissue mass (+ for females: Gonad mass))}$$

251 where "[Tissue/organ]" is the metal concentration determined in the relevant tissue/organ (in  $\text{mg kg}^{-1}$   
252 dry mass), weighted by the mass of each tissue/organ comprising the whole organism or total body  
253 weight (in mg dry mass). Indeed, metal burden (or concentration) values in whole organisms are more  
254 relevant data than concentrations measured in certain tissues/organs in terms of assessing the trophic  
255 transfer of biogeochemical elements between two trophic levels and through food webs (e.g. Cherel et  
256 al., 2005; Lahaye et al., 2005).

257 The statistical procedure adopted for biological compartments was as follows: due to the relatively  
258 low number of samples available per compartment in a given season (Table 4), statistical seasonal  
259 differences and variations among biological compartments could not be tested. Seasonal concentration  
260 variations measured within each compartment were therefore only considered in separate samples  
261 collected in spring (plankton) or summer 2010 (fish) and in winter 2011 (Figs. 5 and 6). Spatial  
262 variations in selected compartments in summer (plankton) and spring (fish) 2010 (i.e. season(s) and  
263 biological compartments with a minimum number of available samples ( $n \geq 4$  per zone), Table 4) were  
264 statistically analysed using Student t-tests or MWW tests (Table 5). In fish species that did not display  
265 any spatial statistical variations (see results), variations according to tissue/organ were tested using  
266 KW tests (Fig. 7) and variations according to gender (for a given tissue/organ) were examined using  
267 Student t-tests or MWW tests (Table 6), using samples collected in summer 2010 only (i.e. with  
268 enough fish samples for statistical tests, Table 4). Variations according to species (for a given  
269 tissue/organ except gonads) were also tested using Students t-tests or MWW tests (Table 7) using fish  
270 collected in summer 2010.

271 Finally, bioaccumulation factors (BAFs) were calculated for each biological compartment of the  
272 considered theoretical food web (different plankton size fractions and fish species) and each trace  
273 element, according to the following equation of Griboff et al. (2018):

$$274 \text{ BAF} = C_{ssbo}/C_{sw}$$

275 whereby  $C_{ssbo}$  is the element concentration in biological organisms at steady state (in  $\text{mg kg}^{-1}$  dry  
276 mass), and  $C_{sw}$  is the element concentration in seawater (in  $\text{mg L}^{-1}$ ). As planktonic organisms and fish  
277 live at different depths throughout the day and throughout their lifecycle, selected seawater  
278 concentrations included all of the sampled water column (Fig. 8, Table S2). Finally, the correlation  
279 between BAFs calculated for the different metals (Table S5) was tested using non-parametric  
280 Spearman correlation coefficient tests and seasonal differences (per element) were tested using  
281 Student-t tests or MWW tests.

282

### 283 3. Results

#### 284 3.1. Metals in seawater (dissolved metals)

285 Spatial and temporal variations of dissolved trace metal concentrations were recorded in the GoL.  
286 Larger fluctuations occurred in spring for all elements except Pb, as indicated by higher coefficients of  
287 variation in spring (Table 1). Variations in dissolved trace metal concentrations were also analyzed  
288 according to depth, from the surface to 50 m in both seasons (Figs. 3 and 4). Surface waters (<10 m  
289 depth) were significantly enriched in Co, Ni, Cu and, to a lesser extent, in Zn in spring (i.e. no  
290 statistical difference between the <10 m and 10-20 m depth ranges for Zn, but statistical difference  
291 between the <10 m and  $\geq 20$  m depth ranges) and in Zn alone in winter (ANOVA or KW tests followed  
292 by post-hoc multiple comparison tests,  $p < 0.05$ ). Mean concentrations of all considered elements (Co,  
293 Ni, Cu, Zn) did not differ between the 10-20 m and  $\geq 20$  m depth ranges in either season (post-hoc  
294 multiple comparison tests,  $p > 0.05$ ). No significant differences in the three other study elements (Cd,  
295 Hg and Pb) were observed according to depth in either season (ANOVA or KW tests followed by  
296 post-hoc multiple comparison tests,  $p > 0.05$ ). Cobalt and Ni were significantly negatively correlated  
297 with salinity in both seasons (Table 2), while Cu and Zn were significantly negatively correlated with  
298 salinity in spring only, and Cd and Pb were significantly positively correlated with salinity in winter  
299 only. No correlation with salinity was observed for Hg in spring (Table 2).

300 Higher mean concentrations of Co and Cu were determined in the water column (10-40 m depth) in  
301 spring (MWW tests,  $p = 0.008$  and  $p = 0.026$  respectively), with higher mean concentrations of Cd in  
302 winter ( $p < 0.001$ ), while no seasonal differences were observed for Ni, Zn and Pb (MWW tests, all  
303  $p > 0.05$ ). In both seasons, significantly higher dissolved concentrations of Co and Ni were determined  
304 in the western part of the GoL, with higher concentrations of Pb in the eastern part (Table 3). Higher

305 concentrations of Cd and Cu were also determined in the western part of the GoL in spring, but not in  
306 winter. No spatial differences were observed for Zn and Hg and no clear pattern emerged at a station  
307 level (Figs. 3 and 4; Table S2).

### 308 3.2. *Metals in size-classed plankton*

309 Overall, fraction size appeared to be a major factor in trace metal concentration variations measured in  
310 plankton (Table 4, Figs. 5 and 6). The highest values of all metals (Co, Ni, Cu, Zn, Ag, Hg and Pb),  
311 except Cd, were found in the smallest size fraction [6-60  $\mu\text{m}$ ] and, to a lesser extent, in [60 - 200  $\mu\text{m}$ ].  
312 These two size fractions also displayed the greatest concentration variability. The highest  
313 concentrations of Cd were determined in intermediate size fractions [200-500  $\mu\text{m}$ ], [500-1000  $\mu\text{m}$ ]  
314 and [1000-2000  $\mu\text{m}$ ]. The lowest concentrations of all metals were generally recorded in the largest  
315 size fraction [ $>2000$   $\mu\text{m}$ ], especially in spring (Table 4, Figs. 5 and 6). Mean concentrations of trace  
316 metals in plankton were generally more variable in spring than in winter (Figs. 5 and 6). In the four  
317 compartments in which spatial differences could be tested (i.e. [6-60  $\mu\text{m}$ ], [60-200  $\mu\text{m}$ ]; sardines and  
318 anchovies collected in spring (plankton size fractions) or summer 2010 (fish), Table 5), no variations  
319 in Co, Ni, Cu, Zn or Ag were observed. However, significant spatial differences in Cd, Hg and Pb  
320 were revealed in the [60-200  $\mu\text{m}$ ] size fraction only, with significantly higher mean concentrations in  
321 plankton in the eastern part of the GoL (Table 5).

### 322 3.3. *Metals in fish*

323 Trace metal analyses and statistical tests were performed on fish collected in summer 2010 (i.e. season  
324 with sufficient samples) in order to appreciate variations according to zone, tissue/organ, gender and  
325 species. Spatial variations were investigated separately for each species considering whole individuals  
326 and no significant differences were revealed (Table 5). Conversely, trace metal concentrations in  
327 tissues/organs were significantly different in the two species, with identical patterns observed in both  
328 anchovies and sardines (Table 6, Fig. 7). The highest concentrations of all elements except Ni and Zn  
329 were systematically found in the liver and the lowest concentrations in muscle (except Hg). The  
330 highest concentrations of Ni and Zn were found in female gonads in both fish species, with higher  
331 values in sardines than anchovies (Fig. 7). Variations according to gender were tested separately on  
332 the basis of tissues/organs and species (Table 6). In sardines, significant gender-related variations were  
333 only found in Ag in “remaining tissue”, with females showing slightly lower Ag concentrations than  
334 males. These variations were more conspicuous in anchovies: females displayed significantly lower  
335 liver concentrations of all metals except Ni (Cu, Zn, Ag, Cd, Hg and Pb) versus males and  
336 significantly lower concentrations of Cu in whole individuals (Table 6).  
337 Finally, significantly higher mean concentrations of Ni, Cu, Zn, Ag, Cd and Hg were found in  
338 anchovy “remaining tissue” or whole individuals versus sardines (Table 7, Figs. 5 and 6). Significantly  
339 higher concentrations of Ni, Cu, Cd and Hg were also found in anchovy liver versus sardine and

340 significantly higher concentrations of Ni and Hg were found in anchovy muscle versus sardine.  
341 Among the trace elements analysed, the only exception was hence Pb, which was found in higher  
342 concentrations in sardines across all tissue types (Table 7).

### 343 3.4. Bioaccumulation factors (BAFs)

344 Bioaccumulation factors (BAFs) were calculated for each plankton fraction and fish species in both  
345 seasons, taking into account dissolved metal concentrations measured throughout the sampled water  
346 column (Fig. 8; Table S4). BAF variation patterns in the food web were fairly similar for given metals  
347 regardless of season, but differed among metals (Fig. 8; Table S4). The highest BAFs were obtained  
348 on the two smallest fractions [6-60  $\mu\text{m}$ ] and [60-200  $\mu\text{m}$ ] for all metals except Cd. Four BAF profiles  
349 were differentiated using Spearman rank correlation coefficient tests. Firstly, Co, Ni, Cu and Pb were  
350 significantly correlated, with Spearman rank correlation coefficients ( $r$ ) varying from 0.909 to 0.986  
351 (Table S5). All four elements exhibited similar profiles, with a continuous BAF decrease along the  
352 food web from the smallest phytoplankton fraction [6-60  $\mu\text{m}$ ] up to fish (Fig. 8). Secondly, Zn BAFs  
353 were also significantly correlated with Co, Ni, Cu and Pb BAFs, but with lower  $r$  values (from 0.579  
354 to 0.700). The Zn profile was similar to those of Co, Ni, Cu and Pb in plankton, but increased slightly  
355 in fish: this pattern was particularly apparent when BAF was expressed in log (Fig. 8; Table S4).  
356 Thirdly, Hg displayed a particular BAF profile, with a strong decrease in plankton according to size,  
357 particularly between phytoplankton [6 - <200  $\mu\text{m}$ ] and zooplankton [200 to >2000  $\mu\text{m}$ ] and a sharp  
358 increase in both fish species (Fig. 8). Lastly, Cd exhibited a completely different BAF profile, which  
359 was not significantly correlated with any other element (Table S4). Cadmium was the only metal to  
360 show the highest values in zooplankton [200 to >2000  $\mu\text{m}$ ] rather than small phytoplankton size  
361 classes [6 - <200  $\mu\text{m}$ ], with low BAF values in fish too (Fig. 8; Table S4).

362 Seasonal differences were highlighted in some compartments, with slightly higher BAFs in winter for  
363 Co, Cu, Zn and Pb, in particular Co in the smallest fractions and Cu, Zn and Pb in the intermediate  
364 fractions (Table S4). However, no significant seasonal variations in the study elements were found  
365 across compartments (Student-t tests or MWW tests,  $p < 0.05$ ), except for Zn (MWW test,  $p = 0.015$ ),  
366 which showed a higher mean BAF value in winter (*ca.* 773 00  $\pm$  144 000 dm) than in spring  
367 (plankton) and summer (fish) (*ca.* 570 000  $\pm$  375 000 dm).

368

## 369 4. Discussion

370 Our study enabled the characterization of trace metal burdens in seawater, plankton and two major  
371 small pelagic fish species from the GoL in the NW Mediterranean Sea. A consistent and original  
372 database was obtained on trace metal contamination in the study area, including its short, small pelagic  
373 fish food web, hence reinforcing available data on radionuclides and rare earth elements (Strady et al.,

374 2015a, 2015b). This geographical area is of major economic and ecological importance and has been  
375 widely investigated in recent years, in particular in the aim of understanding the potential drivers of  
376 change observed in the small pelagic fish community (e.g. [Brosset et al., 2017, 2016, 2015, 2015](#); [Le  
377 Bourg et al., 2015](#); [Van Beveren et al., 2017, 2016](#)). However, thorough information on the chemical  
378 contamination of pelagic compartments (from seawater to pelagic fish) by trace elements was lacking.

#### 379 *4.1. Variability of metals in seawater and vertical distribution patterns*

380 Although a relatively large number of trace metal studies on the Mediterranean Sea were performed in  
381 the 1980s and 1990s (see [Yoon et al., 1999](#)), recent dissolved trace metal measurements remain scarce  
382 (however, see [Battuello et al., 2016](#) and [Heimbürger et al., 2011](#) for recent data reported in the  
383 northwestern Mediterranean Sea). Overall, surface and sub-surface (i.e. 0-15 m depth) concentrations  
384 determined in the GoL versus the range of surface metal concentrations reported in recent decades in  
385 the Mediterranean Sea (see [Heimbürger et al., 2011](#); [Lacan et al., 2006](#); [Morley et al., 1990](#); [Riso et  
386 al., 1994](#); [Yoon et al., 1999](#); [Zeri and Voutsinou-Taliadouri, 2003](#)) are as follows: (i) in the same range  
387 for Zn, (ii) in the same range or higher for Ni, Cu, Cd, Pb, and (iii) higher than previously-reported for  
388 Co and Hg. However, in direct comparison with a recent study in the northwestern Mediterranean Sea  
389 (Ligurian Sea), the seawater concentrations we measured in the GoL were lower than those reported  
390 by Battuello et al. (2016).

391 Dissolved trace metal concentrations in Mediterranean surface waters are generally higher than in the  
392 Atlantic Ocean (Boyle et al., 1985; Morley et al., 1997), mainly due to atmospheric inputs (including  
393 Saharan dust events and European anthropogenic emissions) and riverine outflows on the continental  
394 shelves ([Durrieu de Madron et al., 2011](#) and references therein). In the Mediterranean Sea, surface-  
395 enriched concentrations of Co, Cu, Ni and Zn, along with their significant negative correlations with  
396 salinity, suggest that concentrations are influenced by the Rhône River plume, as already demonstrated  
397 in the GoL (e.g. [Radakovitch et al., 2008](#); [Cossa et al., 2017](#)). However, as this pattern of surface-  
398 enriched waters is only observed for essential elements (Co, Cu, Ni and Zn) and not non-essential  
399 elements (Cd, Hg and Pb), we cannot exclude a potential uptake by plankton in surface waters  
400 ([Battuello et al., 2016](#)).

401 Below the surface, significantly higher concentrations of most elements (Co, Ni, Cu and Cd) were  
402 observed in the western area of the GoL; only Pb showed higher concentrations in the eastern area.  
403 This spatial variation is mainly due to the dynamics of the Rhône River plume, which is generally  
404 directed westward by the Northern Current and prevailing winds ([Gangloff et al., 2017](#)) and to the  
405 existence of small rivers to the West ([Sadaoui et al., 2016](#)). Our study revealed that Co, Ni, Cu and Zn  
406 were more concentrated in surface desalinated waters, in particular in spring. The East-West influence  
407 of Rhône river water inputs in the GoL has already been demonstrated with regards to particulate  
408 organic matter and sediment transfer ([Durrieu de Madron et al., 2000](#)). In contrast, the higher  
409 dissolved Pb concentrations we found in the eastern area of the GoL are coherent with the results of

410 Strady et al. (2015a), which recorded higher  $^{210}\text{Pb}$  concentrations in the eastern area. As Pb did not  
411 display any relationship with depth and salinity, its concentration is probably linked to the industrial  
412 and urban activities of the nearby city of Marseille and town of Fos-sur-Mer, together with inputs from  
413 the Rhône River. Dissolved Pb concentrations were indeed significantly higher at St1 and St10  
414 adjacent to Marseille (Fig. 1) than at other stations.

415 In our study, seasonal variations in dissolved element concentrations were limited to Cd (higher in  
416 winter), Co and Cu (higher in spring). No seasonal-dependent variations in Ni, Zn and Pb were  
417 observed in the water column (10-40 m depth), in contrast to the study of Battuello et al. (2016),  
418 which found high seasonal variations in Ni and Zn in the Ligurian Sea, allocated to bioaccumulation  
419 by zooplankton and changes in the abundance of zooplankton taxa. In the GoL, the lack of seasonal  
420 variations in dissolved element concentrations in seawater, in particular in Ni and Zn, but also Pb, may  
421 be due to the predominant role of highly variable river and atmospheric contaminant inputs  
422 (Desboeufs et al., 2018; Dumas et al., 2015; Sadaoui et al., 2016).

#### 423 4.2. *Variability of metal concentrations in size-classed plankton*

424 Recent data on trace metal concentrations in plankton in the Mediterranean Sea are also relatively  
425 scarce (however, see Battuello et al., 2016; Rossi and Jamet, 2008; Strady et al., 2015a, 2015b for  
426 recent data reported in the northwestern Mediterranean Sea) in comparison to the numerous  
427 Mediterranean Sea studies conducted in the 1980s (see in Roméo et al., 1992). Different plankton  
428 species are known to show significant variations in terms of metal bioaccumulation (Battuello et al.,  
429 2017; Bhattacharya et al., 2014; Levy et al., 2008). Therefore, variations in metal concentrations  
430 among plankton size fractions are probably related to their specific composition.

431 As indicated by (Espinasse et al., 2014b) and Strady et al. (2015a), the plankton composition of our  
432 samples (i.e. same samples as cited authors) was related to the size of the considered fraction: the two  
433 smallest fractions [6-60  $\mu\text{m}$ ] and [60-200  $\mu\text{m}$ ] were mainly composed of phytoplankton and detritus  
434 (detritus decreased with particle size). The larger fractions [200-500  $\mu\text{m}$ ], [500-1000  $\mu\text{m}$ ] and [1000-  
435 2000  $\mu\text{m}$ ] were mainly composed of copepods and crustacean larvae of increasing size. The largest  
436 fraction [ $>2000$   $\mu\text{m}$ ] consisted mainly of large gelatinous organisms (salps, siphonophores, pteropods,  
437 chaetognaths), with some copepods and euphausiids (Espinasse et al., 2014b; Strady et al., 2015a).

438 The marked ability of most metals to be adsorbed onto small particles (dead or alive, organic or  
439 inorganic) may partly explain the highest values we observed in the smallest size fractions (i.e. higher  
440 surface/volume ratio hence higher potential for metal adsorption and absorption). Moreover, sorption  
441 processes can vary widely according to microalgae species (e.g. Levy et al., 2008 for Cu); this may  
442 also explain the highly-varied concentrations observed in the smallest fractions composed of  
443 phytoplankton and detritus. Alternatively, the relatively-high Cd, Zn and, to a lesser extent, Ag  
444 contents found in intermediate size fractions could be related to predominant copepods. Previous  
445 studies have documented that the assimilation of these metals by copepods depends on their prey and

446 is particularly efficient when copepods feed on protozoa rather than phytoplankton (Twining and  
447 Fisher, 2004). This is due to the fact that Cd, Zn and Ag occur in higher proportions in the cytoplasmic  
448 fraction of protozoan cells, and are therefore more easily assimilated by consumers (Reinfelder et al.,  
449 1998; Reinfelder and Fisher, 1991). Our sampling campaign did not allow an assessment of protozoa  
450 proportions in the various fractions, but the study results clearly highlight Cd, Zn and Ag  
451 biomagnification in part of the trophic chain, as suspected by Reinfelder et al. (1998). Finally, the low  
452 concentrations we observed in the largest size fraction [ $>2000\ \mu\text{m}$ ] could be related to a predominance  
453 of gelatinous organisms, which concentrate metals less efficiently than crustaceans (Roméo et al.,  
454 1992), together with a possible “bio-dilution effect” due to size. Cadmium, Cu, Pb and Zn  
455 concentrations recorded in salps and copepods sampled in the Mediterranean Sea in the 1980s  
456 (e.g. Krishnaswami et al., 1985; Roméo et al., 1992) were in the same range as in our study fractions  
457 ( $>2000\ \mu\text{m}$ ] and [200-500  $\mu\text{m}$ ], respectively). However, Co, Ni, Cu, Zn, Cd and Pb concentrations  
458 reported in zooplankton ( $>300\ \mu\text{m}$ ) collected from the Ligurian Sea (Battuello et al., 2016) were far  
459 lower than those found in corresponding fractions in the GoL ([200-500  $\mu\text{m}$ ], [500-1000  $\mu\text{m}$ ] and  
460 [1000-2000  $\mu\text{m}$ ]). As decreased metal concentrations in zooplankton (versus phytoplankton) can be  
461 partly explained by the possible excretion of metals through faecal pellets (Rossi and Jamet, 2008),  
462 metal concentration patterns observed in the various plankton size fractions are likely to depend on  
463 both their size and species composition. While increasing cell and organism size is probably the main  
464 driver behind decreasing direct sorption process (ad- and ab-sorption) in phytoplankton, the diet,  
465 physiological characteristics and detoxification mechanisms the different zooplankton species  
466 (Battuello et al., 2017) are probably of prime importance in explaining the metal concentrations found  
467 in our zooplankton samples (corresponding to the  $>200\ \mu\text{m}$  plankton fractions according to Espinasse  
468 et al., 2014b and Strady et al., 2015a).

#### 469 4.3. *Variability of metal concentrations in fish*

470 Trace metal concentrations measured in anchovies and sardines collected in the GoL allowed us to  
471 pinpoint bioaccumulation variations according to geographical zone, organ/tissue (i.e. organotropism),  
472 gender and species. Seasonal-dependant variations could not be tested. Broadly, (i) no spatial  
473 differences were recorded (considering whole individuals); (ii) liver showed the highest concentrations  
474 (except for Zn and, to a lesser extent, Ni), while muscle showed the lowest concentrations (except for  
475 Hg); (iii) few gender-related differences were observed (more so in anchovies than sardines), with  
476 lower concentrations in females when significant; (iv) concentrations in reconstructed whole  
477 individuals were correlated with concentrations in “remaining tissue” comprising the majority of body  
478 mass; (v) anchovies were generally more contaminated by all metals except Pb in comparison to  
479 sardines (inverse trend).

480 The highest concentrations of most metals in liver versus muscle is a well-documented pattern,  
481 especially in fish (Durrieu et al., 2005; Le Croizier et al., 2018; Metian et al., 2013; Pouil et al., 2017),



482 due to the direct role of the liver in metal storage and/or detoxification further to trace element  
483 incorporation, in particular through the trophic pathway/diet (Roesijadi, 1992; Siscar et al., 2014;  
484 Wang and Rainbow, 2010). Conversely, the relatively high concentrations of Hg (versus other metals)  
485 observed in muscle may be due to its high affinity with muscular protein sulfhydryl groups (-SH)  
486 (e.g. Bloom, 1992). The high Zn concentrations recorded in female gonads are probably due to its vital  
487 role in fish gonad development (Fletcher and King, 1978). Finally, on the organism scale, the liver  
488 represented less than 2% of wet body mass on average in the studied small pelagic fish species, while  
489 “remaining tissue” (including remaining muscle, viscera, gills, kidneys, bones, skin, etc.) accounted  
490 for 85-95% of body mass. Therefore, whole (reconstructed) organisms showed very similar metal  
491 concentrations to “remaining tissue”.

492 Dietary exposure is widely considered as the main route for contaminant incorporation and  
493 assimilation (both inorganic and organic) in consumers such as fish (Fisk et al., 2001; Mathews and  
494 Fisher, 2009; Wang, 2002). However, no differences in anchovy diet according to gender were  
495 reported in the GoL by Pethybridge et al. (2014), or by Karachle and Stergiou (2014) in another area  
496 of the Mediterranean Sea (Aegean Sea), suggesting that the contaminant variations we found are  
497 probably not related to differing diets. Other factors such as substantial contaminant elimination  
498 through reproduction (i.e. through spawning by female anchovy) may explain gender-related  
499 variations in anchovies; this topic has been well-documented in terms of organic contaminants in fish  
500 (Bodiguel et al., 2009). However, similar variations were not reported in sardines, while variations in  
501 anchovies were mainly found in liver. This probably indicates poor elimination of trace metals versus  
502 organic contaminants by small pelagic female fish during reproduction, as already suggested for large  
503 pelagic fish such as tuna (Chouvelon et al., 2017).

504 Variations in metal concentrations found in the two study fish species may also be due to differing in  
505 trophic ecologies (trophic level, prey preferences, etc.). Both anchovies and sardines were recently  
506 shown to have dietary overlaps in the GoL, with the main targeted prey being small copepods such as  
507 *Microsetella*, *Oncaea* and *Corycaeidae* copepods (Le Bourg et al., 2015). However, sardine have a  
508 more diverse, temporally variable and seasonally-specific feeding strategy than anchovies (Le Bourg  
509 et al., 2015; Pethybridge et al., 2014), confirming that the two species do not feed on exactly the same  
510 food sources or at the same trophic level in the GoL (Costalago et al., 2014, 2012). Moreover,  
511 anchovies tend to feed on the continental shelf and in the western GoL, whereas sardines remain  
512 nearer the coast and feed more in the eastern area (Le Bourg et al., 2015; Saraux et al., 2014). Sardines  
513 can also capture smaller prey than anchovies (Blaxter and Hunter, 1982; Costalago et al., 2014, 2012).  
514 The differing trophic ecologies of anchovies and sardines can hence account, at least in part, for the  
515 variations observed in trace metal concentrations: each species probably feeds on planktonic prey  
516 species affected by different levels of contamination.

517 Finally, differences in body condition and/or proximate composition could also explain some of the  
518 variations observed in the two fish species, although these parameters were not analysed in our study.

519 Indeed, recent studies have demonstrated that variations in metal content may be attributable to the  
520 specific proximate composition (i.e. proteins, lipids, ash content) of fish species (e.g. Marval-León et  
521 al., 2014; Sofoulaki et al., 2018). This is due to the fact that most metals, including all the trace  
522 elements studied here, have a high affinity with the cysteine amino-acid of certain proteins, such as  
523 metallothioneins (e.g. Capdevila et al., 2012). Similarly, certain organic pollutants have a well-known  
524 high affinity with lipids (e.g. Munsch et al., 2016). Sardines have a far higher total lipid content than  
525 anchovies in the GoL (Pethybridge et al., 2014), although specific lipid content may vary according to  
526 season. If a lower lipid content theoretically corresponds to a higher protein content, this could  
527 explain, at least in part, the higher metal concentrations measured in anchovies versus sardines.  
528 However, it does not explain the exception we observed for Pb. Nonetheless, in direct comparison, our  
529 results were similar to those found by Sofoulaki et al. (2018) on individuals collected from six Greek  
530 sites (Mediterranean Sea), with higher levels of most of the study trace elements observed in  
531 anchovies versus sardines, with the exception of Pb (i.e. same as the inverse trend found in our study).

#### 532 4.4. *Patterns of metal bioaccumulation in the study food web (BAFs)*

533 Field-based bioaccumulation factors (BAFs) were calculated as a ratio of chemical concentration in  
534 organisms versus seawater (e.g. DeForest et al., 2007; Gobas et al., 2009), using the dissolved metal  
535 concentrations measured throughout the sampled water column. Patterns of BAFs calculated on the  
536 basis of dissolved concentrations measured at 10-15 m depth only (i.e. plankton sampling depth) were  
537 rigorously identical (results not shown), confirming the probable night and day migration of organisms  
538 in the water column, at least at the sampling depths (0-50 m).

539 The higher BAFs observed in the two smallest plankton fractions were probably linked to two factors:  
540 firstly, the higher surface/volume ratio of small versus large cells/organisms, which may enhance  
541 dynamic metal sorption processes and secondly, the relatively-large proportion of detritus in these  
542 fractions (Strady et al., 2015a), which may efficiently adsorb metals onto their large, particle-specific  
543 surface area. Most metals showed a decreasing BAF in higher chains of the food web, from phyto- to  
544 zooplankton, then fish. Only two metals among those considered, Zn and particularly Hg, showed  
545 increased BAF values in fish. This pattern is coherent with the well-known biomagnifying properties  
546 of Hg through food webs, especially in its methylated forms (Chen et al., 2008; Cossa et al., 2012).  
547 The slight increase in Zn BAF in fish is also consistent with the biomagnifying potential of Zn in  
548 marine fish food chains (Wang, 2002). Conversely, the higher Cd bioaccumulation we observed in  
549 zooplankton fractions (mainly composed of copepods and crustacean larvae) versus fish may be linked  
550 to efficient copepod Cd assimilation (Twining and Fisher, 2004) and the ability of crustaceans to  
551 accumulate high quantities of Cd in their exoskeleton (Sarkar et al., 2016).

552 Generally speaking, the BAFs calculated in our study were lower than those calculated in the Ligurian  
553 Sea (NW Mediterranean Sea) by Battuello et al. (2016), probably due to the significant differences in  
554 dissolved metal concentrations found in the two studies (see above). Moreover, field BAFs tend to be

555 inversely-related to exposure concentrations (DeForest et al., 2007), i.e. lower when seawater  
556 concentrations are higher in the field. This could also explain BAF differences in studies performed in  
557 environments with potentially different contamination levels and hence the differences in our results in  
558 the GoL versus those of Battuello et al. (2016) in the Ligurian Sea.

559

#### 560 4.5. *Synthesis on the seawater-plankton-fish continuum*

561 When adequate material was available for statistical testing, slightly higher metal concentrations were  
562 found in seawater samples from western stations (especially below the surface and with the exception  
563 of Pb) and in biological compartment samples from eastern stations (i.e. for the [60-200 µm] fraction,  
564 and for Cd, Hg and Pb only). The slightly higher seawater concentrations found at western stations  
565 may be due to the influence of small river outflows in this area combined with the Rhône River plume,  
566 which is directed westward by the Northern Current and prevailing winds (Gangloff et al., 2017;  
567 Sadaoui et al., 2016). The inverse spatial trend observed in some biological compartments (i.e. higher  
568 concentrations at eastern part when significant) should be confirmed by testing larger numbers of  
569 samples per compartment, in particular plankton. The role of Rhône River loads on the overall  
570 contaminant burden of GoL organisms has already been reported with regards to radionuclides such as  
571 <sup>210</sup>Po (Strady et al., 2015a) and organic contaminants such as Polychlorinated biphenyls (PCBs) in  
572 plankton (Alekseenko et al., 2018). Small pelagic planktivorous fish in the eastern areas of the GoL  
573 are therefore probably affected by more prevalent/efficient exposure to chemical contamination via  
574 trophic pathways (i.e. plankton). However, this hypothesis should be supported by an additional  
575 experimental design for metals.

576 No common patterns were established for essential elements (Co, Ni, Cu, Zn) or non-essential  
577 elements (Ag, Cd, Hg, Pb). Instead, our results showed different metal uptake/level fingerprints in the  
578 GoL for the different study elements, with: (i) Co, Cu, Ni, Pb and, to a lesser extent, Zn and Ag,  
579 displaying the highest concentrations in the smallest investigated plankton fractions ([6-60 µm] and  
580 [60-200 µm]). Metal levels decreased considerably in intermediate plankton sizes and, finally, in fish  
581 (with the exception of Zn); (ii) Hg, which also displayed high concentrations in the smallest plankton  
582 fractions, far lower levels in intermediate fractions and enhanced concentrations in fish; and (iii) Cd,  
583 which showed higher bioaccumulation in intermediate zooplankton fractions versus both the smallest  
584 phytoplankton fractions and fish. These findings are globally consistent with studies previously  
585 conducted in other areas, which have reported general trends of lower metal concentrations in larger  
586 plankton (e.g. Ho et al., 2007), and/or in phyto- versus zooplankton (e.g. Rossi and Jamet, 2008),  
587 probably corresponding to small versus large plankton fractions according to the composition of our  
588 size fractions as described by Espinasse et al. (2014b) and Strady et al. (2015a). Only Hg has been  
589 documented as biomagnifying in upper trophic levels such as small planktivorous pelagic fishes  
590 (e.g. Cossa et al., 2012; Nfon et al., 2009). However, as fish live far longer than planktonic organisms,

591 they are exposed to contaminants over a longer period: this may also explain the peculiar trend found  
592 for Hg and, to a lesser extent, Zn. Indeed, as previously stated, Hg is notoriously poorly-excreted by  
593 organisms over time versus other trace metals (Maulvault et al., 2016; Wang and Wong, 2003).  
594 Finally, the analysis of different fish tissues revealed that metal concentrations in whole organisms  
595 and, to a lesser extent, liver, reflect potential differences between fish species more accurately than  
596 muscle tissue.

#### 597 4.6. Future work and prospects

598 First and foremost, further studies on the topic of trace metal bioaccumulation and trophic transfer in  
599 planktonic compartments and pelagic food webs in general would greatly enhanced by a better  
600 biological-chemical coupling of the various parameters analysed on each sample. Where possible, this  
601 should include: (i) a thorough identification of the taxonomic composition of each plankton size  
602 fraction analysed for contaminants and (ii) the systematic analysis of indirect tracers of autotrophic  
603 and heterotrophic components of these fractions, together with their average trophic level  
604 (e.g. analysis of stable carbon and nitrogen isotopes, fatty acid profiles). This would improve our  
605 interpretation of concentrations determined in plankton fractions; (iii) assessment of metal fractions  
606 adsorbed/absorbed onto/into plankton (i.e. using chelating agents) to improve our understanding of  
607 metal fractions that are actually “bioaccumulated” in plankton; iv) assessment of insoluble versus  
608 soluble metal fractions in plankton, or subcellular compartmentalization, to better assess which metal  
609 fractions are actually available to upper trophic levels. Regarding fish, further studies on this topic  
610 would also be largely improved by an analysis of proximate composition and biological/trophic  
611 parameters using the same samples studied for contaminants. Moreover, our analyses of the various  
612 body parts showed that whole individuals more accurately reflect differences in “global” metal  
613 contamination among species within a food web. In terms of larger species, which are difficult to  
614 analyze whole, our results suggest liver as an alternative tissue for Ni, Cu, Cd, Hg and Pb analysis  
615 and/or muscle for Ni, Zn, Hg and Pb analysis.

616 More broadly, future studies on this topic would be improved by (i) fine-tuning research on the  
617 smallest plankton size, i.e. <60 µm; (ii) analysing the physical-chemical form of metals, which  
618 determines their bioavailability, transfer and bioaccumulation in organisms and food webs  
619 (e.g. methylated forms for Hg); (iii) comparing eco-regions with different trophic functioning,  
620 e.g. oligotrophic vs. mesotrophic areas, or areas subject to different anthropogenic pressures. This  
621 would enable a better consolidation of the processes we observed in terms of contaminant  
622 bioaccumulation in plankton and transfer to upper trophic levels.

623

624

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639

640

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**Table 1:** Mean concentrations  $\pm$  standard deviation (in  $\text{ng L}^{-1}$ ) of dissolved trace metals in seawater from the Gulf of Lions, in spring 2010 (N = 27) and winter 2011 (N = 28), with the range of values indicated into brackets. CV = Coefficient of variation (in %).

	Co	Ni	Cu	Zn	Cd	Hg	Pb
Spring 2010	13 $\pm$ 5 (7-30) CV = 41	236 $\pm$ 32 (205-374) CV = 13	203 $\pm$ 72 (137-488) CV = 36	256 $\pm$ 160 (144-894) CV = 63	11 $\pm$ 2 (9-18) CV = 19	0.65 $\pm$ 0.32 (0.41-1.79) CV = 50	29 $\pm$ 9 (21-60) CV = 32
Winter 2011	9 $\pm$ 2 (7-13) CV = 16	231 $\pm$ 14 (205-253) CV = 6	172 $\pm$ 37 (126-323) CV = 21	202 $\pm$ 40 (140-297) CV = 20	13 $\pm$ 2 (10-16) CV = 14	— — —	29 $\pm$ 11 (20-75) CV = 39

**Table 2:** Results of the Spearman correlation coefficient (r) tests and associated probability (p-value) between concentrations of dissolved elements in seawater and salinity in the Gulf of Lions (N = 27 for each metal in spring 2010; N = 28 in winter 2011). Significant correlations are in bold.

		Co	Ni	Cu	Zn	Cd	Hg	Pb
Spring 2010	r	-0.859	-0.816	-0.754	-0.549	-0.372	0.205	0.232
	r <sup>2</sup>	0.738	0.666	0.569	0.301	0.138	0.042	0.054
	p-value	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>0.003</b>	0.056	0.325	0.245
Winter 2011	r	-0.577	-0.593	-0.289	-0.301	0.488	—	0.651
	r <sup>2</sup>	0.333	0.352	0.084	0.091	0.238	—	0.424
	p-value	<b>0.001</b>	<b>&lt;0.001</b>	0.136	0.120	<b>0.008</b>	—	<b>&lt;0.001</b>

**Table 3:** Results of the Student t-tests (t) or of the Mann-Whitney-Wilcoxon tests (W) and associated probability (p-values) for the statistical comparison of dissolved trace metal concentrations between East and West parts in the Gulf of Lions (N = 21 in spring 2010; N = 20 in winter 2011). Only the data corresponding to the depths 10-40 m were considered here (see section 2.5). E = East; W = West. Significant differences are in bold.

		Co	Ni	Cu	Zn	Cd	Hg	Pb
Spring 2010	t or W	(W) 4	(t) -5.5	(W) 19	(W) 32	(t) -3.7	(W) 69.5	(W) 87
	p-value	<b>&lt;0.001</b>	<b>&lt;0.001</b>	0.012	0.129	0.002	0.137	0.018
		<b>E &lt; W</b>	<b>E &lt; W</b>	<b>E &lt; W</b>	E = W	<b>E &lt; W</b>	E = W	<b>E &gt; W</b>
Winter 2011	t or W	(W) 17	(t) -5.8	(W) 27	(t) -0.9	(t) 1.9	—	(W) 74
	p-value	0.016	<b>&lt;0.001</b>	0.115	0.374	0.075	—	0.047
		<b>E &lt; W</b>	<b>E &lt; W</b>	E = W	E = W	E = W	—	<b>E &gt; W</b>

**Table 4:** Trace metal concentrations (in mg kg<sup>-1</sup> dry mass) determined in biological compartments (size-classed plankton and fish), reported per element type (essential vs. non-essential), per season (spring (plankton) or summer (fish) 2010 vs. winter 2011) and per sampling zone (East vs. West). Values are mean ± standard deviation (SD). N = number of stations (for size-classed plankton) or number of pools of individuals (for fish), for which total metal concentrations could be determined within each area and at each season. Nd = Not determined.

	N	Essential elements				Non-essential elements			
		Co Mean ± SD	Ni Mean ± SD	Cu Mean ± SD	Zn Mean ± SD	Ag Mean ± SD	Cd Mean ± SD	Hg Mean ± SD	Pb Mean ± SD
<b>Spring or Summer 2010 - East</b>									
6-60 µm	4	6.7 ± 2.8	45.4 ± 4.2	58.8 ± 11.1	293 ± 72	0.56 ± 0.37	0.37 ± 0.16	0.570 ± 0.513	44.0 ± 15.1
60-200 µm	4	4.3 ± 3.0	22.2 ± 8.9	30.0 ± 11.6	142 ± 30	0.43 ± 0.36	0.61 ± 0.18	0.365 ± 0.535	38.9 ± 14.3
200-500 µm	3	0.22 ± 0.06	1.9 ± 0.5	7.0 ± 0.5	154 ± 14	0.14 ± 0.03	0.89 ± 0.08	0.037 ± 0.017	0.93 ± 0.09
500-1000 µm	3	0.24 ± 0.05	2.1 ± 0.5	8.1 ± 2.2	172 ± 18	0.16 ± 0.04	0.99 ± 0.01	0.042 ± 0.026	0.96 ± 0.46
1000-2000 µm	3	0.30 ± 0.07	3.4 ± 1.7	8.7 ± 2.5	186 ± 55	0.19 ± 0.05	1.0 ± 0.1	0.043 ± 0.023	1.3 ± 0.5
> 2000 µm	3	0.34 ± 0.19	1.8 ± 0.7	4.6 ± 2.2	63 ± 41	0.10 ± 0.04	0.36 ± 0.18	0.024 ± 0.019	1.3 ± 0.6
Sardine (Wh*)	8	Nd	0.52 ± 0.17	4.8 ± 0.7	85 ± 6	0.02 ± 0.00	0.06 ± 0.01	0.130 ± 0.036	0.21 ± 0.04
Anchovy (Wh*)	8	Nd	0.77 ± 0.11	5.9 ± 0.6	116 ± 17	0.03 ± 0.01	0.12 ± 0.03	0.275 ± 0.039	0.14 ± 0.04
<b>Spring or Summer 2010 - West</b>									
6-60 µm	4	4.7 ± 1.1	65.6 ± 40.5	41.9 ± 31.9	439 ± 115	0.74 ± 0.74	0.38 ± 0.15	0.049 ± 0.039	72.4 ± 90.9
60-200 µm	4	3.5 ± 1.8	17.2 ± 6.8	20.3 ± 16.0	76 ± 54	0.11 ± 0.04	0.14 ± 0.04	0.031 ± 0.021	17.4 ± 5.9
200-500 µm	4	0.53 ± 0.15	3.0 ± 0.6	7.2 ± 1.9	114 ± 43	0.13 ± 0.04	0.58 ± 0.14	0.013 ± 0.009	2.4 ± 0.6
500-1000 µm	3	0.50 ± 0.25	3.0 ± 1.1	7.2 ± 0.7	138 ± 9	0.14 ± 0.02	0.49 ± 0.06	0.014 ± 0.007	2.8 ± 2.2
1000-2000 µm	4	0.54 ± 0.28	2.8 ± 1.1	6.3 ± 1.2	102 ± 20	0.11 ± 0.03	0.36 ± 0.10	0.015 ± 0.007	2.3 ± 1.4
> 2000 µm	4	0.36 ± 0.23	1.8 ± 0.9	3.3 ± 1.9	41 ± 33	0.06 ± 0.03	0.16 ± 0.13	0.008 ± 0.008	1.3 ± 0.8
Sardine (Wh*)	16	Nd	0.54 ± 0.11	5.1 ± 0.8	90 ± 12	0.02 ± 0.01	0.06 ± 0.01	0.141 ± 0.038	0.23 ± 0.07
Anchovy (Wh*)	11	Nd	0.65 ± 0.15	5.8 ± 0.7	123 ± 11	0.03 ± 0.01	0.11 ± 0.02	0.236 ± 0.054	0.13 ± 0.02
<b>Winter 2011 - East</b>									
6-60 µm	2	8.6 ± 0.4	44.0 ± 6.5	35.2 ± 13.0	158 ± 0	0.26 ± 0.07	0.14 ± 0.04	1.318 ± 1.459	53.2 ± 11.5
60-200 µm	2	1.8 ± 0.8	38.1 ± 29.9	27.9 ± 6.2	305 ± 92	0.20 ± 0.04	1.0 ± 0.3	0.264 ± 0.283	33.6 ± 14.2
200-500 µm	3	0.43 ± 0.14	4.4 ± 0.8	25.0 ± 16.4	198 ± 45	0.15 ± 0.02	1.2 ± 0.1	0.068 ± 0.007	9.2 ± 7.8
500-1000 µm	3	0.62 ± 0.49	5.9 ± 2.8	13.6 ± 2.3	218 ± 89	0.17 ± 0.05	0.92 ± 0.18	0.067 ± 0.011	22.5 ± 31.2
1000-2000 µm	2	0.39 ± 0.04	4.2 ± 1.3	18.6 ± 7.0	186 ± 60	0.16 ± 0.08	0.77 ± 0.02	0.063 ± 0.015	8.0 ± 3.1
> 2000 µm	1	0.95	6.9	9.1	137	0.14	0.78	0.042	11.0
Sardine (Wh*)	2	Nd	0.66 ± 0.10	4.8 ± 0.7	131 ± 5	0.02 ± 0.00	0.07 ± 0.01	0.290 ± 0.054	0.46 ± 0.0
Anchovy (Wh*)	1	Nd	0.66	6.3	131	0.05	0.11	0.371	0.17
<b>Winter 2011 - West</b>									
6-60 µm	3	7.5 ± 1.0	66.8 ± 18.7	42.8 ± 19.5	200 ± 40	0.31 ± 0.04	0.28 ± 0.12	0.115 ± 0.025	74.4 ± 45.1
60-200 µm	3	2.3 ± 0.5	27.2 ± 14.9	16.6 ± 3.1	126 ± 7	0.15 ± 0.02	0.65 ± 0.26	0.046 ± 0.011	13.6 ± 5.2
200-500 µm	3	0.28 ± 0.05	2.4 ± 0.7	10.8 ± 1.0	125 ± 8	0.13 ± 0.03	1.0 ± 0.1	0.040 ± 0.005	0.95 ± 0.30
500-1000 µm	3	0.30 ± 0.10	2.5 ± 0.3	9.7 ± 0.3	129 ± 10	0.14 ± 0.02	0.82 ± 0.14	0.038 ± 0.003	1.5 ± 1.1
1000-2000 µm	2	0.37 ± 0.03	4.0 ± 1.1	12.8 ± 1.4	122 ± 4	0.17 ± 0.01	0.61 ± 0.14	0.040 ± 0.003	2.5 ± 0.6
> 2000 µm	3	1.1 ± 0.4	5.5 ± 3.8	16.3 ± 6.5	107 ± 71	0.11 ± 0.06	0.43 ± 0.29	0.031 ± 0.021	8.6 ± 5.4
Sardine (Wh*)	1	Nd	0.84	6.3	121	0.02	0.06	0.335	0.62
Anchovy (Wh*)	3	Nd	0.64 ± 0.07	5.7 ± 0.4	134 ± 16	0.03 ± 0.01	0.10 ± 0.01	0.379 ± 0.066	0.13 ± 0.03

\*Wh = whole individuals (reconstructed data).



**Table 5:** Results of the statistical tests for the differences between zones for the biological compartments: [6-60  $\mu\text{m}$ ], [60-200  $\mu\text{m}$ ], sardine and anchovy (whole individuals), collected in spring (plankton) or summer 2010 (fish). This corresponded to season(s) and biological compartments with a minimum number of samples ( $n \geq 4$  per zone) for testing the spatial differences (see Table 4). Results are reported per element type (essential vs. non-essential) and per biological compartment. Significant differences are in bold and the results and p-values of the statistical tests performed (Student t-tests (t) or Mann-Whitney-Wilcoxon (W) tests) are indicated (with \*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$ ).

Biological compartment	Differences between zones	Biological compartment	Differences between zones
<b>Essential elements</b>		<b>Non-essential elements</b>	
<b>Co</b>		<b>Ag</b>	
6-60 $\mu\text{m}$	t = 1.4; p = 0.224; East = West	6-60 $\mu\text{m}$	t = -0.4; p = 0.677; East = West
60-200 $\mu\text{m}$	t = 0.4; p = 0.670; East = West	60-200 $\mu\text{m}$	t = 1.8; p = 0.127; East = West
Sardine (Wh*)	—	Sardine (Wh*)	W = 61; p = 0.840; East = West
Anchovy (Wh*)	—	Anchovy (Wh*)	W = 58; p = 0.229; East = West
<b>Ni</b>		<b>Cd</b>	
6-60 $\mu\text{m}$	t = -1.0; p = 0.359; East = West	6-60 $\mu\text{m}$	W = 6; p = 0.663; East = West
60-200 $\mu\text{m}$	t = 0.9; p = 0.402; East = West	60-200 $\mu\text{m}$	<b>t = 5.2; p = 0.002***; East &gt; West</b>
Sardine (Wh*)	W = 45.5; p = 0.269; East = West	Sardine (Wh*)	W = 62.5; p = 0.949; East = West
Anchovy (Wh*)	t = 1.9; p = 0.077; East = West	Anchovy (Wh*)	W = 52; p = 0.518; East = West
<b>Cu</b>		<b>Hg</b>	
6-60 $\mu\text{m}$	t = 1.0; p = 0.356; East = West	6-60 $\mu\text{m}$	t = 2.0; p = 0.090; East = West
60-200 $\mu\text{m}$	t = 1.0; p = 0.367; East = West	60-200 $\mu\text{m}$	<b>W = 15.5; p = 0.042*; East &gt; West</b>
Sardine (Wh*)	W = 49; p = 0.375; East = West	Sardine (Wh*)	W = 46.5; p = 0.294; East = West
Anchovy (Wh*)	t = 0.2; p = 0.868; East = West	Anchovy (Wh*)	t = 1.8; p = 0.093; East = West
<b>Zn</b>		<b>Pb</b>	
6-60 $\mu\text{m}$	t = -2.2; p = 0.074; East = West	6-60 $\mu\text{m}$	W = 10; p = 0.686; East = West
60-200 $\mu\text{m}$	W = 13; p = 0.200; East = West	60-200 $\mu\text{m}$	<b>t = 2.8; p = 0.032*; East &gt; West</b>
Sardine (Wh*)	t = -1.2; p = 0.250; East = West	Sardine (Wh*)	W = 50.5; p = 0.424; East = West
Anchovy (Wh*)	t = -1.2; p = 0.262; East = West	Anchovy (Wh*)	t = 0.6; p = 0.564; East = West

\*Wh = whole individuals (reconstructed data).

**Table 6:** Trace metal concentrations (in mg kg<sup>-1</sup> dry mass) determined in the different tissues of fish collected in summer 2010, reported per element type (essential vs. non-essential) and per fish species (sardine vs. anchovy). Values are mean ± standard deviation (SD), and N = number of pools of individuals considered for organotropism (i.e. metal concentrations in the different tissues). For each tissue, the results of the statistical tests for gender differences (females (F) vs. males (M)) are also given. To test gender differences, only pools of individuals whose sex could be determined were considered (i.e. F vs. M; no consideration of pools of sexually undetermined (U) individuals). Also, as no spatial differences were evidenced for fish during the summer season (see Table 5), individuals from the different zones were combined. Significant differences are in bold, and only the p-values of the statistical tests performed (Student t-test or Mann-Whitney-Wilcoxon test) are indicated (with \* p <0.05; \*\* p <0.01; \*\*\* p <0.001).

Essential elements	Ni		Cu		Zn			
	Mean ± SD	Differences between sexes	Mean ± SD	Differences between sexes	Mean ± SD	Differences between sexes		
<b>Sardine</b> (N= 24 / F: n= 9, M: n= 7; U: n= 8)								
Gonads (F)	2.9 ± 4.3	—	3.6 ± 1.3	—	481 ± 149	—		
Liver	0.41 ± 0.29	F = M (p=0.077)	9.7 ± 3.2	F = M (p=0.314)	115 ± 19	F = M (p=0.935)		
Muscle	0.09 ± 0.02	F = M (p=0.322)	1.9 ± 0.3	F = M (p=0.623)	48 ± 12	F = M (p=0.535)		
Remaining tissue	0.56 ± 0.14	F = M (p=0.560)	5.2 ± 0.9	F = M (p=0.841)	91 ± 11	F = M (p=0.470)		
Whole*	0.53 ± 0.13	F = M (p=0.686)	5.0 ± 0.8	F = M (p=0.791)	88 ± 11	F = M (p=0.620)		
<b>Anchovy</b> (N= 19 / F: n= 9, M: n= 9; U: n= 1)								
Gonads (F)	0.71 ± 0.32	—	4.3 ± 0.4	—	168 ± 18	—		
Liver	0.64 ± 0.29	F = M (p=0.077)	11.8 ± 2.1	<b>F &lt; M (p=0.012*)</b>	127 ± 23	<b>F &lt; M (p=0.001**)</b>		
Muscle	0.12 ± 0.04	F = M (p=0.770)	2.1 ± 0.5	F = M (p=0.508)	46 ± 13	F = M (p=0.114)		
Remaining tissue	0.77 ± 0.17	F = M (p=0.246)	6.2 ± 0.7	F = M (p=0.145)	129 ± 15	F = M (p=0.367)		
Whole*	0.70 ± 0.15	F = M (p=0.528)	5.8 ± 0.6	<b>F &lt; M (p=0.035*)</b>	120 ± 14	F = M (p=0.052)		
Non-essential elements	Ag		Cd		Hg		Pb	
	Mean ± SD	Differences between sexes	Mean ± SD	Differences between sexes	Mean ± SD	Differences between sexes	Mean ± SD	Differences between sexes
<b>Sardine</b> (N= 24 / F: n= 9, M: n= 7; U: n= 8)								
Gonads (F)	0.03 ± 0.01	—	0.12 ± 0.04	—	0.104 ± 0.040	—	0.17 ± 0.20	—
Liver	0.10 ± 0.10	F = M (p=0.260)	0.46 ± 0.15	F = M (p=0.981)	0.270 ± 0.091	F = M (p=0.710)	0.23 ± 0.06	F = M (p=0.884)
Muscle	0.02 ± 0.01	F = M (p=0.815)	0.004 ± 0.003	F = M (p=0.439)	0.179 ± 0.059	F = M (p=0.481)	0.05 ± 0.01	F = M (p=1.000)
Remaining tissue	0.02 ± 0.01	<b>F &lt; M (p=0.038*)</b>	0.06 ± 0.01	F = M (p=0.817)	0.134 ± 0.035	F = M (p=0.676)	0.24 ± 0.07	F = M (p=0.593)
Whole*	0.02 ± 0.01	F = M (p=0.069)	0.06 ± 0.01	F = M (p=0.753)	0.138 ± 0.037	F = M (p=0.690)	0.23 ± 0.07	F = M (p=0.710)
<b>Anchovy</b> (N= 19 / F: n= 9, M: n= 9; U: n= 1)								
Gonads (F)	0.08 ± 0.02	—	0.17 ± 0.04	—	0.102 ± 0.019	—	0.04 ± 0.01	—
Liver	0.10 ± 0.05	<b>F &lt; M (p=0.004**)</b>	0.91 ± 0.25	<b>F &lt; M (p=0.017*)</b>	0.704 ± 0.197	<b>F &lt; M (p=0.012*)</b>	0.15 ± 0.06	<b>F &lt; M (p=0.008**)</b>
Muscle	0.01 ± 0.01	F = M (p=0.458)	0.01 ± 0.00	F = M (p=0.514)	0.268 ± 0.067	F = M (p=0.863)	0.04 ± 0.02	F = M (p=0.513)
Remaining tissue	0.03 ± 0.01	F = M (p=0.773)	0.12 ± 0.03	F = M (p=0.686)	0.248 ± 0.052	F = M (p=0.934)	0.15 ± 0.04	F = M (p=0.348)
Whole*	0.03 ± 0.01	F = M (p=0.362)	0.12 ± 0.02	F = M (p=0.780)	0.252 ± 0.051	F = M (p=0.727)	0.14 ± 0.03	F = M (p=0.660)

\*Whole = whole individuals (reconstructed data).

**Table 7:** Results of the statistical tests for the differences between species for the fish collected in summer 2010. The results are reported per element type (essential vs. non-essential) and per fish tissue (except gonads, collected from females only). Significant differences are in bold and the results and p-values of the statistical tests performed (Student t-tests (t) or Mann-Whitney-Wilcoxon (W) tests) are indicated (with \* p < 0.05; \*\* p < 0.01; \*\*\* p < 0.001).

Tissue/organ	Differences between species	Tissue/organ	Differences between species
<b>Essential elements</b>		<b>Non-essential elements</b>	
<b>Ni</b>		<b>Ag</b>	
Liver	<b>W = 103; p = 0.002**;</b> S < A	Liver	W = 201; p = 0.514; S = A
Muscle	<b>t = -2.6; p = 0.014*;</b> S < A	Muscle	W = 255.5; p = 0.453; S = A
Remaining tissue	<b>t = -4.4; p &lt; 0.001***;</b> S < A	Remaining tissue	<b>W = 50.5; p &lt; 0.001***;</b> S < A
Whole*	<b>t = -3.8; p &lt; 0.001***;</b> S < A	Whole*	<b>W = 71; p &lt; 0.001***;</b> S < A
<b>Cu</b>		<b>Cd</b>	
Liver	<b>W = 105.5; p = 0.003**;</b> S < A	Liver	<b>W = 20; p &lt; 0.001***;</b> S < A
Muscle	W = 148.5; p = 0.053; S = A	Muscle	W = 168; p = 0.094; S = A
Remaining tissue	<b>t = -4.0; p &lt; 0.001***;</b> S < A	Remaining tissue	<b>W = 3; p &lt; 0.001***;</b> S < A
Whole*	<b>t = -3.7; p &lt; 0.001***;</b> S < A	Whole*	<b>W = 1; p &lt; 0.001***;</b> S < A
<b>Zn</b>		<b>Hg</b>	
Liver	t = -1.9; p = 0.066; S = A	Liver	<b>t = -9.6; p &lt; 0.001***;</b> S < A
Muscle	W = 259.5; p = 0.448; S = A	Muscle	<b>t = -4.7; p &lt; 0.001***;</b> S < A
Remaining tissue	<b>W = 13; p &lt; 0.001***;</b> S < A	Remaining tissue	<b>t = -8.3; p &lt; 0.001***;</b> S < A
Whole*	<b>W = 21; p &lt; 0.001***;</b> S < A	Whole*	<b>t = -8.6; p &lt; 0.001***;</b> S < A
		<b>Pb</b>	
		Liver	<b>W = 375; p &lt; 0.001***;</b> S > A
		Muscle	<b>W = 313.5; p = 0.032*;</b> S > A
		Remaining tissue	<b>W = 420; p &lt; 0.001***;</b> S > A
		Whole*	<b>W = 430; p &lt; 0.001***;</b> S > A

\*Whole = whole individuals (reconstructed data).

## **Figure captions**

**Fig. 1:** Location of sampling sites in the Gulf of Lions (northwestern Mediterranean Sea). Black squares = seawater and plankton sampling stations; dotted circles = pelagic fish sampling areas; dashed line = separation between the eastern and western areas (East, West) considered in this study.

**Fig. 2:** Vertical profiles of seawater salinity determined at each station sampled in spring 2010 and winter 2011. Data are expressed in practical salinity unit (psu). The depth range of plankton samples (i.e. 10-15 m depth) is indicated. E = East; W = West.

**Fig. 3a:** Vertical profiles of (dissolved) seawater concentrations (in  $\text{ng. L}^{-1}$ ) of Co, Ni, Cu and Zn (i.e. essential metals) determined at each station sampled in spring 2010 (left panel) and winter 2011 (right panel). The depth range of plankton samples (i.e. 10-15 m depth) is indicated. E = East; W = West.

**Fig. 4:** Vertical profiles of (dissolved) seawater concentrations (in  $\text{ng. L}^{-1}$ ) of Hg, Cd and Pb (i.e. non-essential metals) determined at each station sampled in spring 2010 (left panel) and winter 2011 (right panel). The depth range of plankton samples (i.e. 10-15 m depth) is indicated. E = East stations; W = West.

**Fig. 5:** Boxplots of concentrations (in  $\text{mg kg}^{-1}$  dry mass) of Co, Ni, Cu and Zn (i.e. essential metals) determined in the various biological compartments, reported per element and per season (spring (plankton) or summer (fish) 2010 (blue boxes) vs. winter 2011 (red boxes)). Stations are combined. Boxplots for fish are enlarged in the upper right corner. The box length represents the interquartile, the bar length represents the range and the horizontal lines in bold are median values.

**Fig. 6:** Boxplots of concentrations (in  $\text{mg kg}^{-1}$  dry mass) of Ag, Cd, Hg and Pb (i.e. non-essential metals) determined in the various biological compartments, reported per element and per season (spring (plankton) or summer (fish) 2010 (blue boxes) vs. winter 2011 (red boxes)). Stations are combined. Boxplots for fish are enlarged in the upper right corner. The box length represents the interquartile, the bar length represents the range and the horizontal lines in bold are median values.

**Fig. 7:** Histograms of trace metal concentrations (in  $\text{mg kg}^{-1}$  dry mass) determined in different tissues (i.e. organotropism) of fish collected in summer 2010, reported per element (essential (left panel) vs. non-essential elements (right panel)) and per fish species (sardine vs. anchovy). Values are mean  $\pm$  SD per tissue.  $N = 24$  and  $N = 19$  for each sardine and anchovy tissue type, respectively (except gonads, collected from females only,  $N = 9$  for each species). The results of statistical tests to ascertain concentration variations among tissue types are also indicated (with numbers for sardines, and letters for anchovies). An identical number or letter indicates that tissue concentrations were not significantly different within a species (i.e. results of the post-hoc multiple comparison test with Holm adjustment method after a Kruskal-Wallis test, at  $\alpha = 0.05$ ). F = Females; RT = Remaining Tissue.

**Fig. 8:** Plots of mean bioaccumulation factors (BAFs) calculated per element type (essential vs. non-essential), reported per season (spring (plankton) or summer (fish) 2010 vs. winter 2011) and per biological compartment. Concentrations used for calculations were  $\text{mg L}^{-1}$  for seawater and  $\text{mg kg}^{-1}$  dry mass for biological compartments. Top panel = BAF values  $\times 10^3$ ; Bottom panel = log-transformed BAF values. For exact values see Table S4 (Supplemental Material). S = Sardine; A = Anchovy.

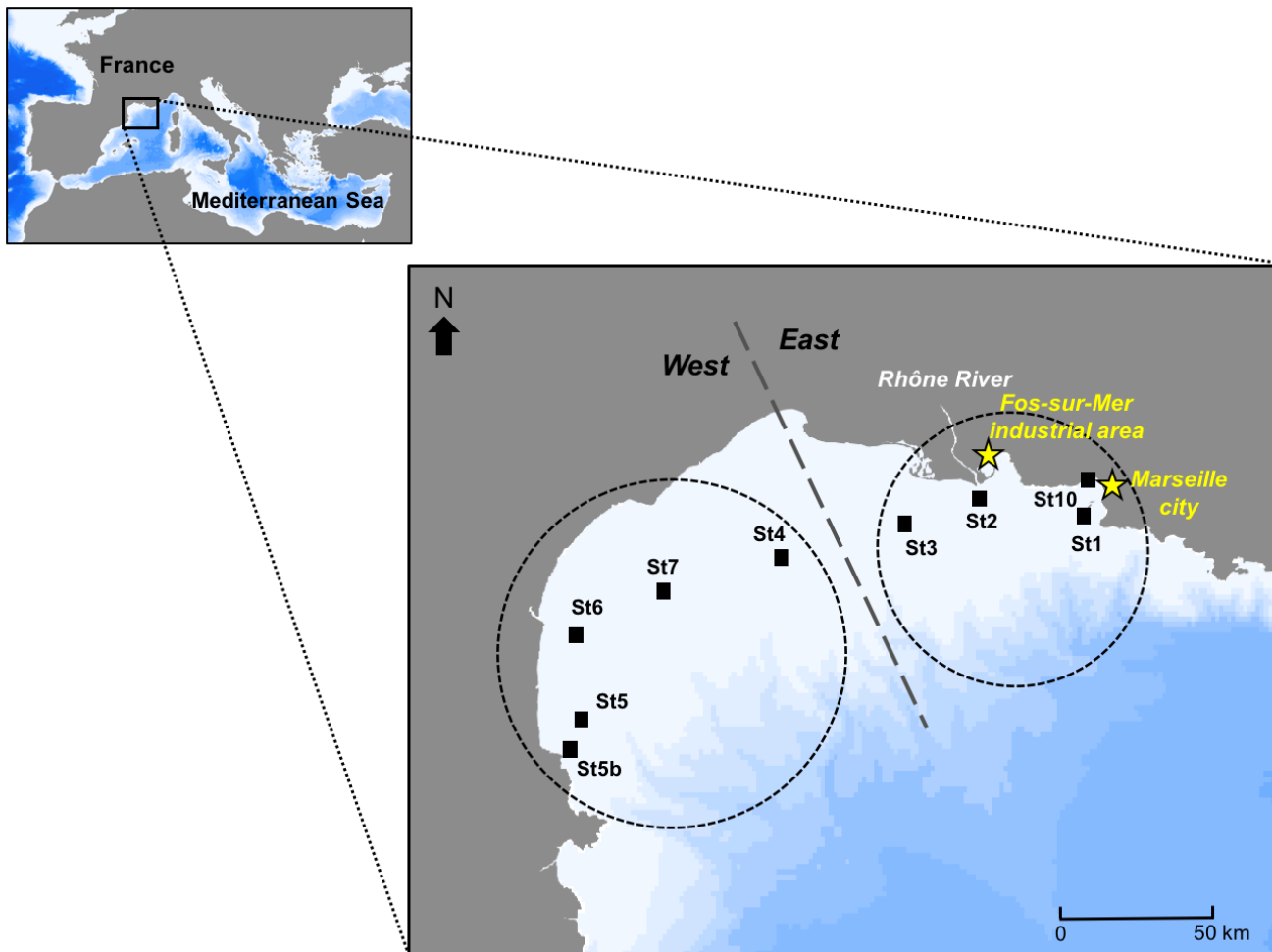
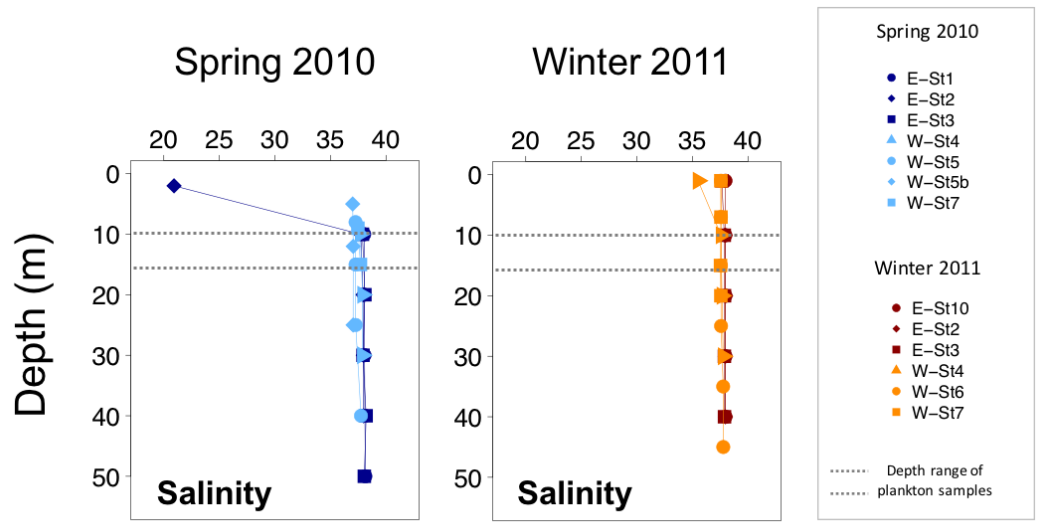


Fig. 1



**Fig. 2**

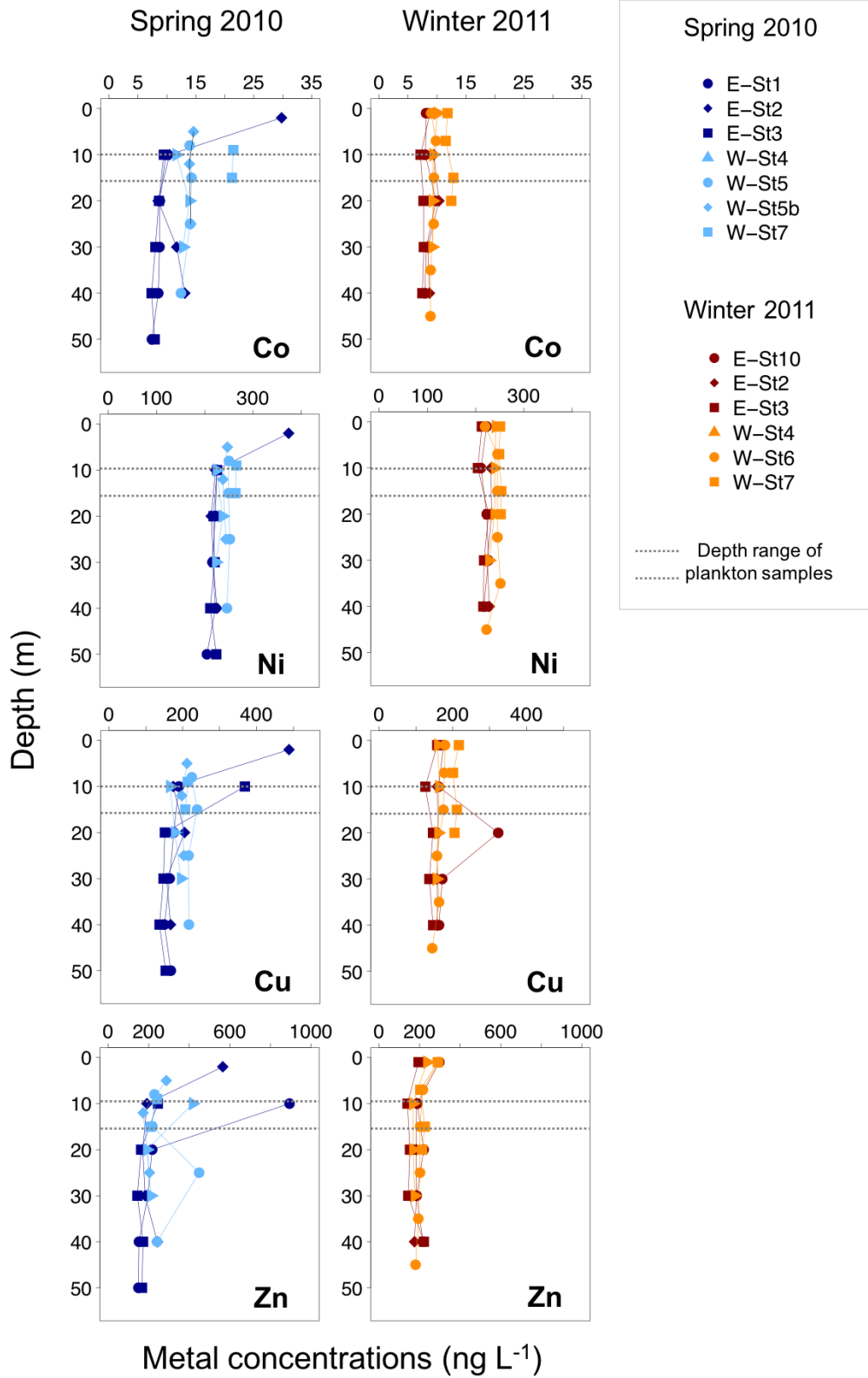


Fig. 3

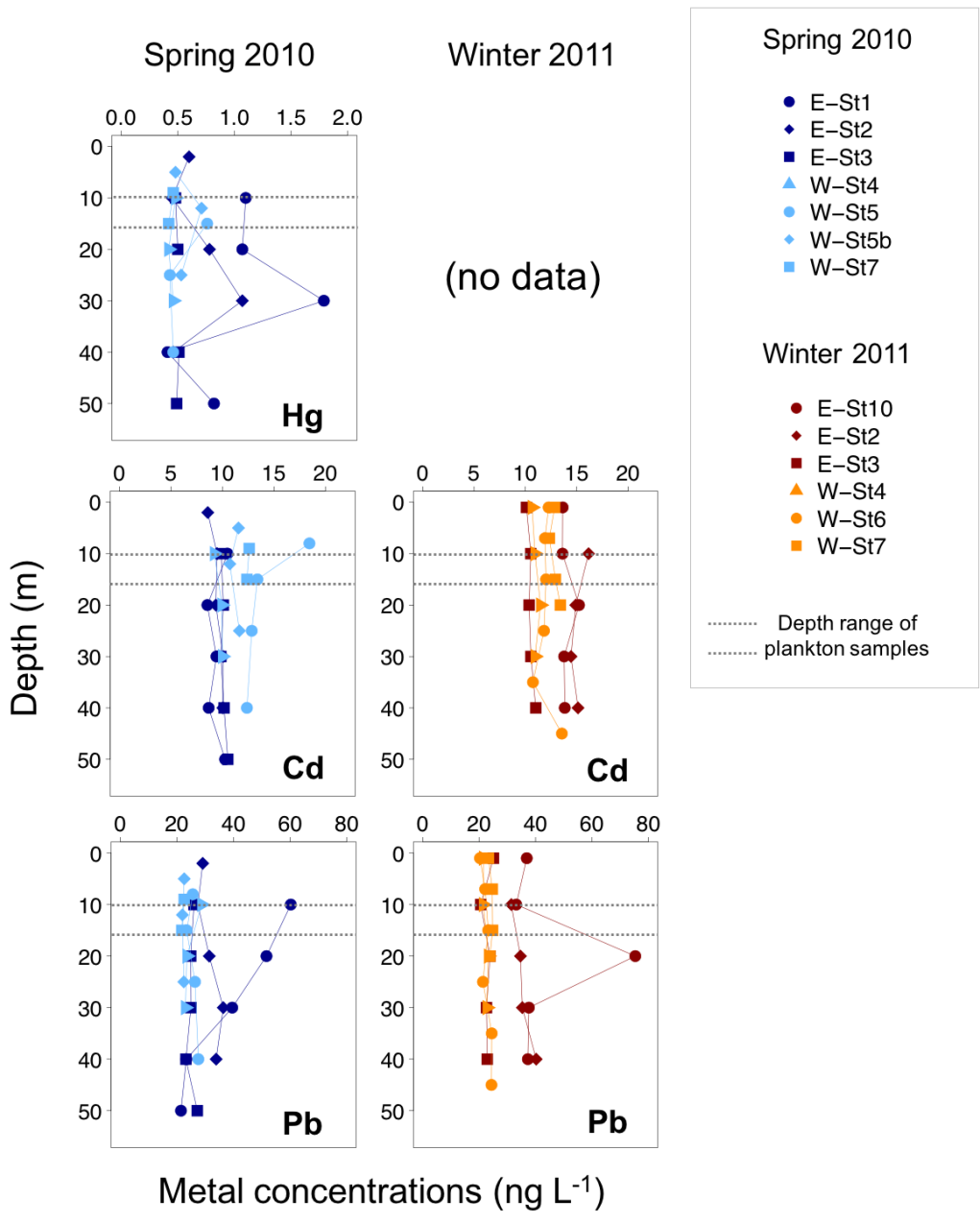
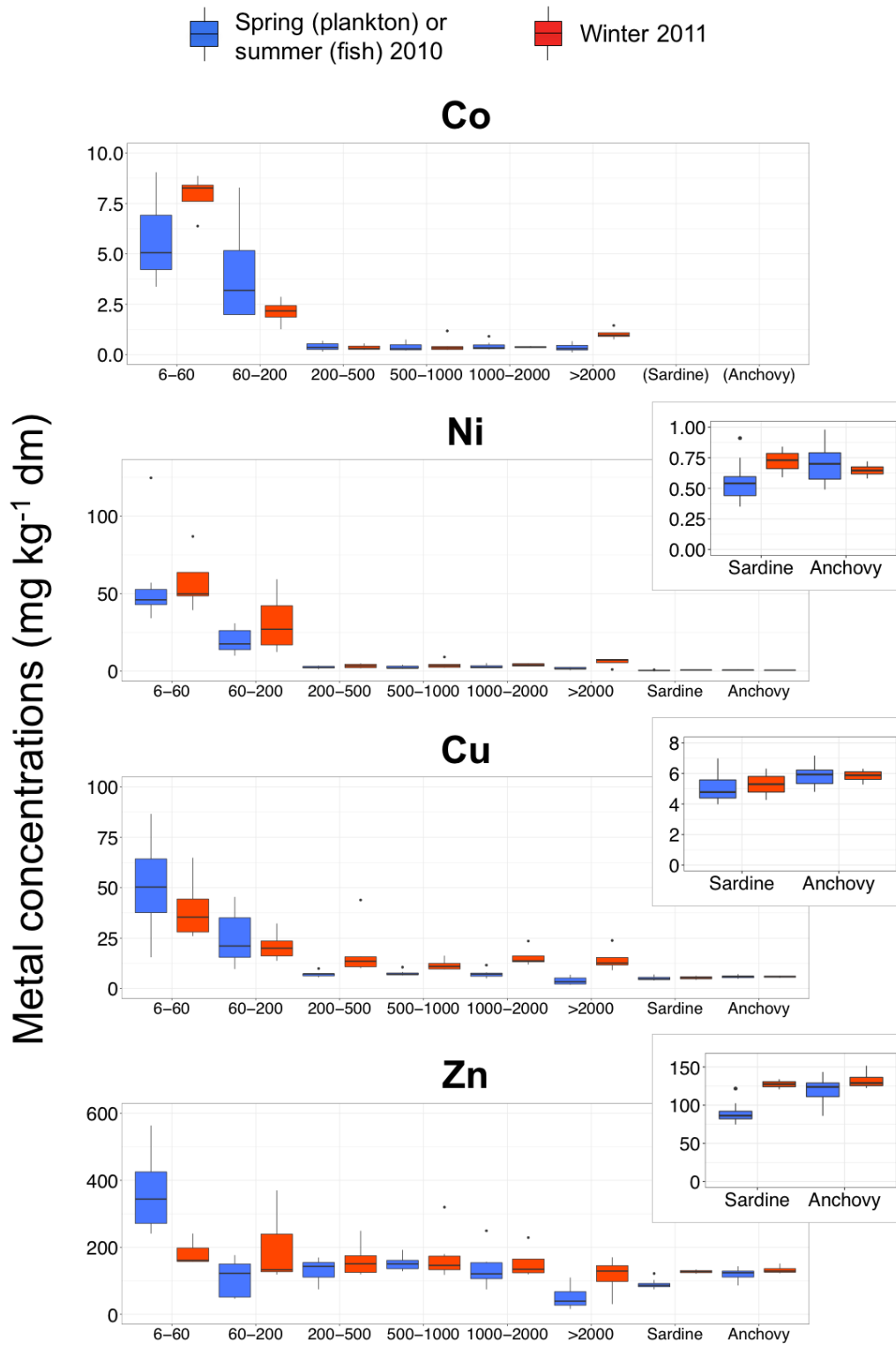


Fig. 4





**Fig. 5**

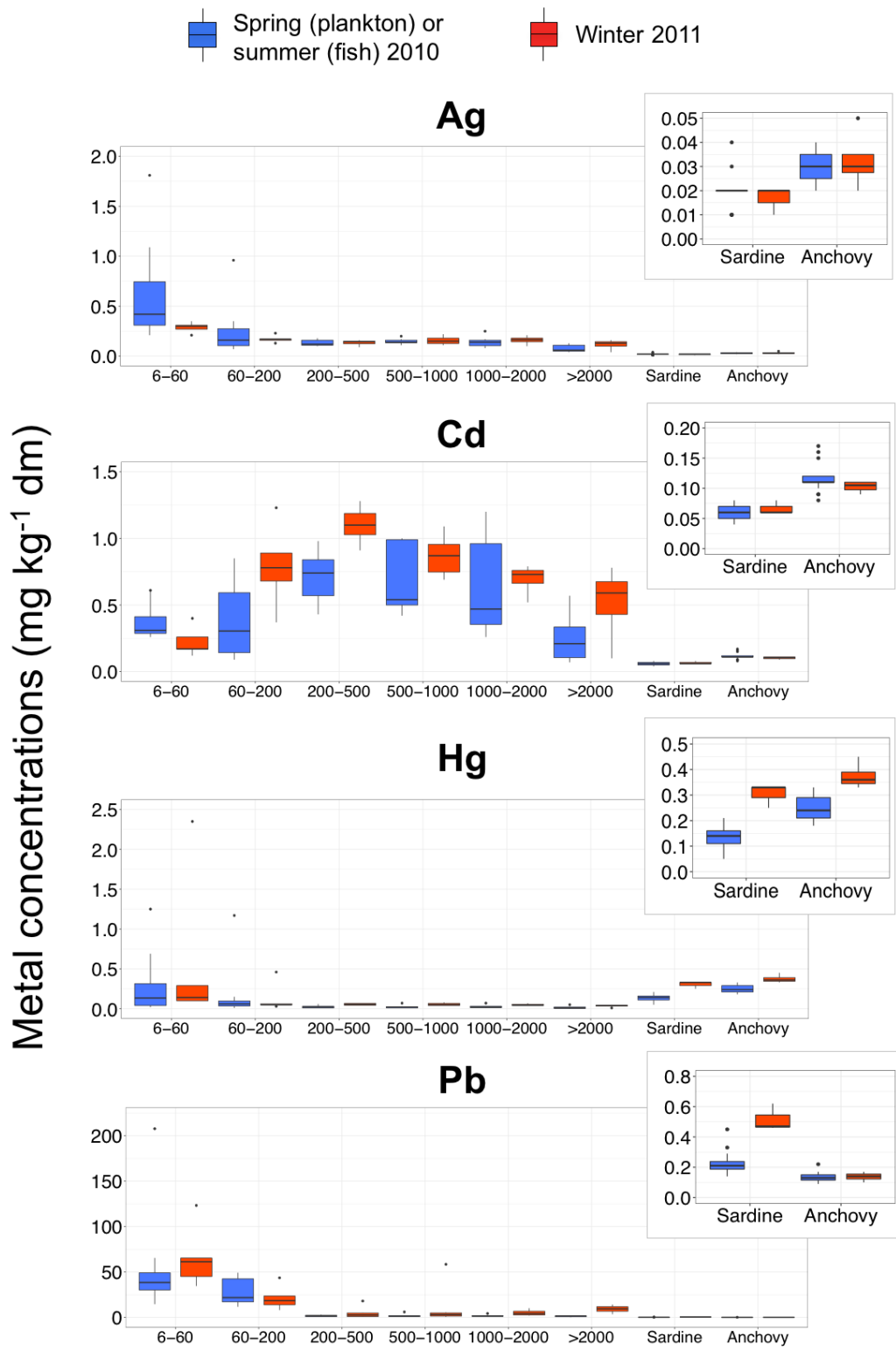


Fig. 6

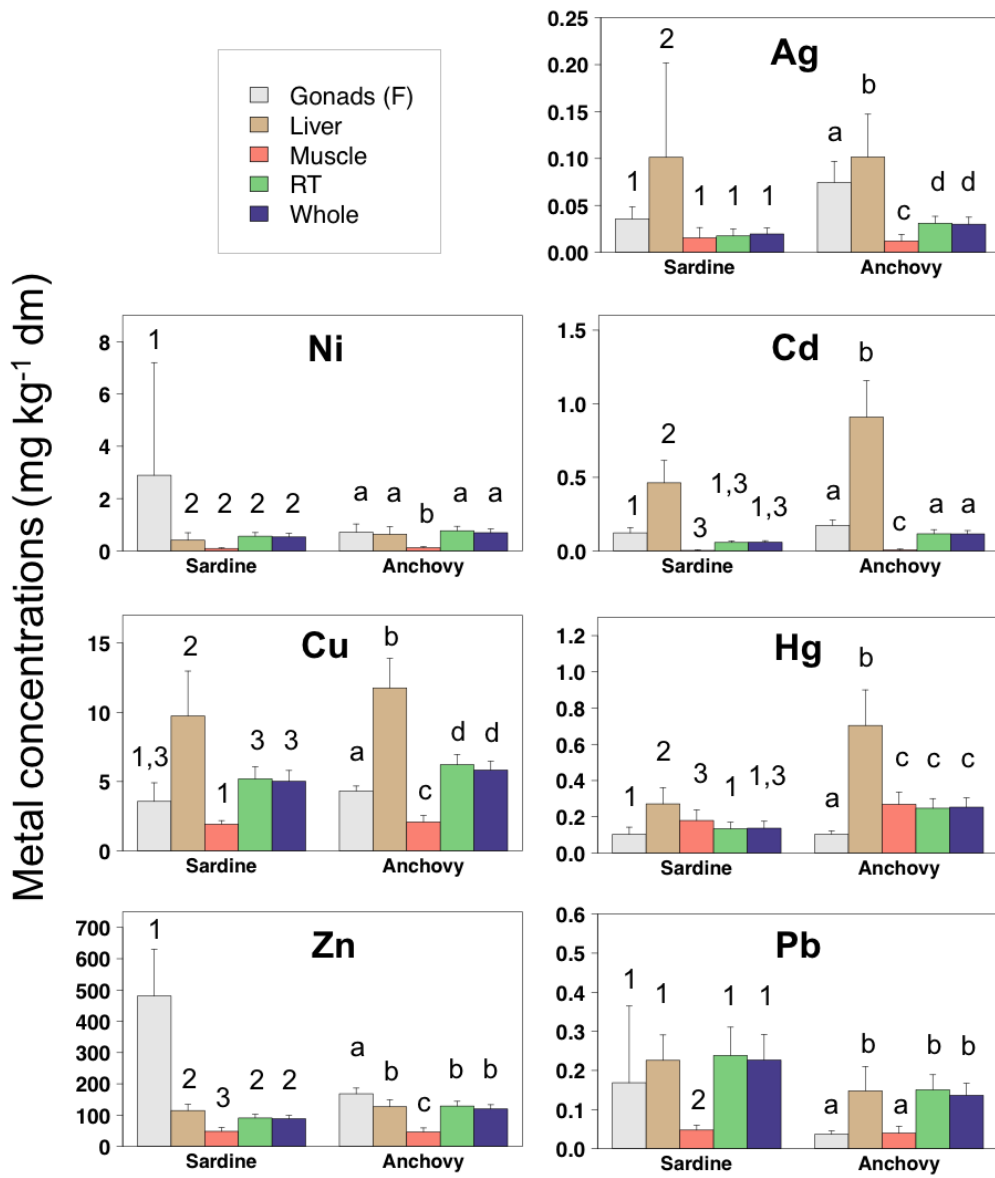
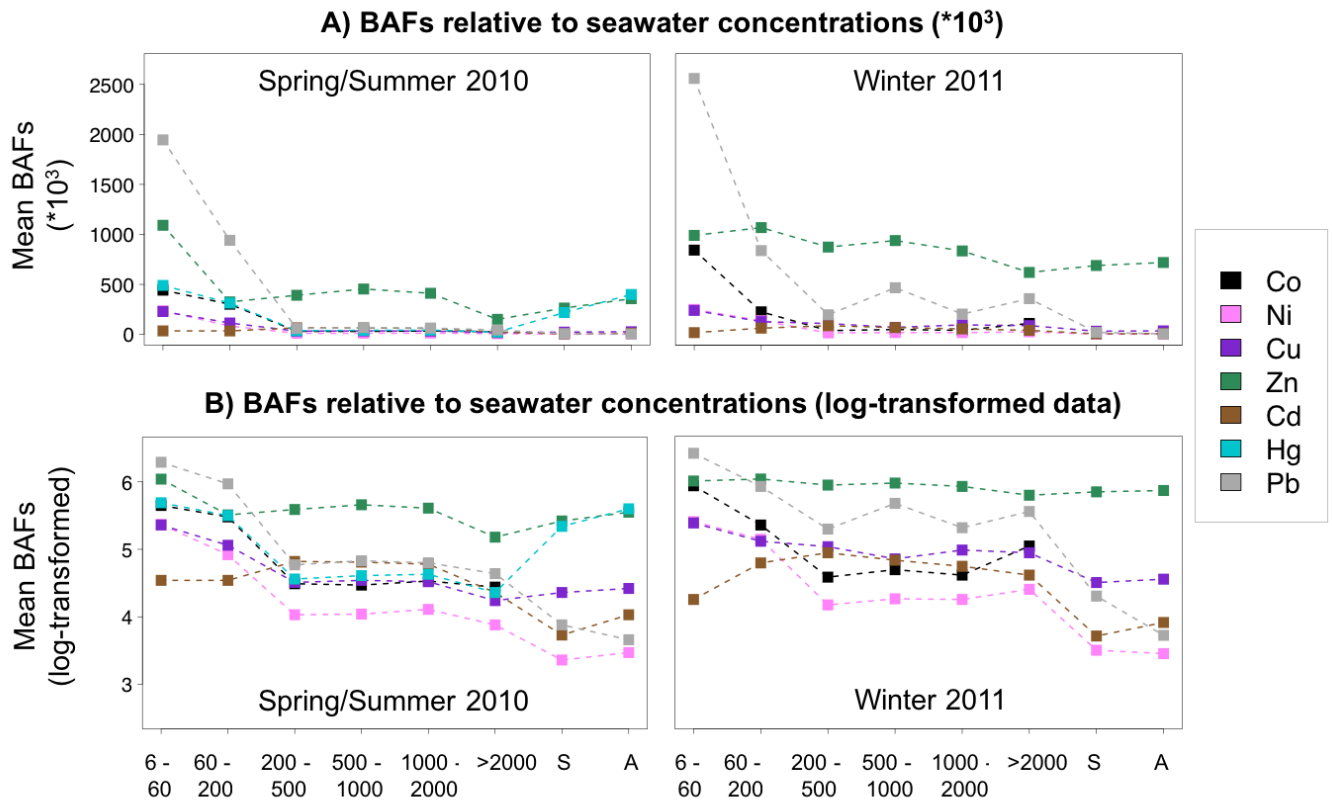


Fig. 7



**Fig. 8**

## Supplemental Material

**Table S1:** Results obtained for certified reference materials (CRMs) used in trace metal analyses. Values are means  $\pm$  standard deviation (SD), in ng L<sup>-1</sup> for seawater and mg kg<sup>-1</sup> dry mass for biological compartments. The limits of quantification (LOQ, in italics) and the recovery rate (in %, in bold) are also indicated. The symbol “—” appears when the element was not determined nor quantified in the samples. Nc = CRM not certified for the element.

		Essential elements				Non-essential elements			
		Co	Ni	Cu	Zn	Ag	Cd	Hg	Pb
<b>Seawater</b>									
	<i>LOQ (ng L<sup>-1</sup>):</i>	<i>0.2</i>	<i>0.001</i>	<i>0.01</i>	<i>0.01</i>	—	<i>0.1</i>	<i>0.075</i>	<i>0.4</i>
ORMS-4 (lake water, National Research Council Canada/NRCC)	Measured value	—	—	—	—	—	—	22.68 $\pm$ 0.04	—
	Certified value	—	—	—	—	—	—	22.0 $\pm$ 1.6	—
	<b>RR (%)</b>	—	—	—	—	—	—	<b>103</b>	—
CASS-5 (seawater, NRCC)	Measured value	83.1 $\pm$ 2.0	0.304 $\pm$ 0.005	0.36 $\pm$ 0.01	0.67 $\pm$ 0.03	—	20.9 $\pm$ 1.4	—	9.9 $\pm$ 0.9
	Certified value	93	0.32 $\pm$ 0.02	0.37 $\pm$ 0.03	0.70 $\pm$ 0.07	—	21 $\pm$ 2	—	11 $\pm$ 2
	<b>RR (%)</b>	<b>89</b>	<b>95</b>	<b>97</b>	<b>96</b>	—	<b>100</b>	—	<b>90</b>
<b>Biological compartments</b>									
	<i>LOQ (mg kg<sup>-1</sup> dm):</i>	<i>0.25</i>	<i>0.13</i>	<i>1.25</i>	<i>12.5</i>	<i>0.03</i>	<i>0.03</i>	<i>0.015</i>	<i>0.03</i>
BCR-414 (plankton, JRC-European Commission/EC)	Measured value	—	—	—	—	—	—	0.259 $\pm$ 0.001	—
	Certified value	—	—	—	—	—	—	0.276 $\pm$ 0.018	—
	<b>RR (%)</b>	—	—	—	—	—	—	<b>94</b>	—
SRM-2976 (mussel tissue, National Institute of Standards and Technology/NIST)	Measured value	—	—	—	—	—	—	0.058 $\pm$ 0.006	—
	Certified value	—	—	—	—	—	—	0.061 $\pm$ 0.004	—
	<b>RR (%)</b>	—	—	—	—	—	—	<b>95</b>	—
IAEA-142 (mussel homogenate, International Atomic Energy Agency)	Measured value	—	—	—	—	—	—	0.127 $\pm$ 0.006	—
	Certified value	—	—	—	—	—	—	0.126 $\pm$ 0.007	—
	<b>RR (%)</b>	—	—	—	—	—	—	<b>101</b>	—
BCR-422 (cod muscle, JRC-EC)	Measured value	—	—	—	—	—	—	0.543 $\pm$ 0.003	—
	Certified value	—	—	—	—	—	—	0.559 $\pm$ 0.016	—
	<b>RR (%)</b>	—	—	—	—	—	—	<b>97</b>	—
BCR-CRM 278 R (mussel tissue, JRC-EC)	Measured value	0.33 $\pm$ 0.01	(Nc)	8.98 $\pm$ 0.13	79.1 $\pm$ 1.7	(Nc)	0.343 $\pm$ 0.013	—	1.95 $\pm$ 0.04
	Certified value	0.34*	(Nc)	9.45 $\pm$ 0.13	83.1 $\pm$ 1.7	(Nc)	0.348 $\pm$ 0.007	—	2.00 $\pm$ 0.04
	<b>RR (%)</b>	<b>98</b>	(Nc)	<b>95</b>	<b>95</b>	(Nc)	<b>99</b>	—	<b>98</b>
DORM-3 (fish protein, NRCC)	Measured value	(Nc)	1.30 $\pm$ 0.10	14.9 $\pm$ 0.4	49.2 $\pm$ 0.4	0.03 $\pm$ 0.01	0.30 $\pm$ 0.01	—	0.34 $\pm$ 0.08
	Certified value	(Nc)	1.28 $\pm$ 0.24	15.5 $\pm$ 0.63	51.3 $\pm$ 3.1	0.04*	0.29 $\pm$ 0.02	—	0.395 $\pm$ 0.050
	<b>RR (%)</b>	(Nc)	<b>101</b>	<b>96</b>	<b>96</b>	<b>70</b>	<b>104</b>	—	<b>86</b>
DOLT-3 (dogfish liver, NRCC)	Measured value	(Nc)	3.17 $\pm$ 0.59	31.7 $\pm$ 0.0	89.4 $\pm$ 0.9	1.21 $\pm$ 0.01	19.0 $\pm$ 0.0	—	0.32 $\pm$ 0.01
	Certified value	(Nc)	2.72 $\pm$ 0.35	31.2 $\pm$ 1.0	86.6 $\pm$ 2.4	1.20 $\pm$ 0.07	19.4 $\pm$ 0.6	—	0.319 $\pm$ 0.045
	<b>RR (%)</b>	(Nc)	<b>116</b>	<b>102</b>	<b>103</b>	<b>101</b>	<b>98</b>	—	<b>100</b>

\* Indicative value on the certificate.



<b>St7</b>	9	37.5	21	265	214	241	13	0.46	23	<b>St7</b>	1	37.6	12	251	217	290	13	(Nd)	23
	15 <sup>#</sup>	37.7	21	264	207	209	12	0.42	22		7	37.6	12	249	201	203	12	(Nd)	25
	<b>Mean*</b>		<b>21</b>	<b>264</b>	<b>210</b>	<b>225</b>	<b>12</b>	<b>0.44</b>	<b>22</b>		15 <sup>#</sup>	37.5	13	253	211	226	13	(Nd)	25
											20	37.6	12	252	205	213	13	(Nd)	24
											<b>Mean*</b>		<b>12</b>	<b>251</b>	<b>208</b>	<b>233</b>	<b>13</b>	<b>(Nd)</b>	<b>24</b>

\* Data used for the calculations of mean BAFs including dissolved metal concentrations measured throughout the sampled water column (Fig. 6, Tables S4 and S5).

# Data used for the calculations of mean BAFs including dissolved concentrations measured at 10-15 m depth only (i.e. plankton sampling depth; results not shown).

**Table S3:** Detailed trace metal concentrations (in mg kg<sup>-1</sup> dry mass) determined in size-classed plankton, reported per season (spring 2010 vs. winter 2011), per sampling zone (East vs. West) and per station. Ns/d = Not sampled/not determined.

Spring 2010										Winter 2011									
	Size class (µm)	Co	Ni	Cu	Zn	Ag	Cd	Hg	Pb		Size class (µm)	Co	Ni	Cu	Zn	Ag	Cd	Hg	Pb
<b>East</b>										<b>East</b>									
<b>St1</b>	6-60	3.4	45.6	73.3	256	1.09	0.60	1.248	65.5	<b>St10</b>	6-60	8.9	48.6	44.4	158	0.30	0.12	2.350	61.4
	60-200	2.0	13.9	45.4	142	0.96	0.60	1.165	49.3		60-200	2.4	17.0	23.6	240	0.17	0.78	0.464	43.7
	200-500	0.15	1.3	7.3	142	0.18	0.82	0.056	0.88		200-500	0.28	3.6	43.9	167	0.12	1.2	0.074	5.2
	500-1000	0.21	1.8	10.6	192	0.20	0.99	0.072	1.5		500-1000	0.29	4.5	11.9	180	0.12	1.1	0.071	5.5
	1000-2000	0.28	5.3	11.6	249	0.25	1.2	0.069	1.9		1000-2000	0.36	5.1	23.5	229	0.10	0.79	0.073	10.2
> 2000	0.24	1.6	6.9	110	0.13	0.57	0.045	1.6	> 2000	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	
<b>St2</b>	6-60	9.0, 9.1*	41.5, 51.2*	47.8, 52.9*	241, 277*	0.31, 0.32*	0.26, 0.28*	0.156, 0.188*	32.0, 35.0*	<b>St2</b>	6-60	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)
	60-200	5.0, 8.3 *	29.0, 30.9 *	21.5, 32.1*	103, 148*	0.16, 0.35*	0.42, 0.59*	0.060, 0.151*	18.2, 40.9*		60-200	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)
	200-500	0.25	2.0	7.3	150	0.14	0.86	0.030	0.87		200-500	0.56	5.1	15.8	249	0.15	1.3	0.068	18.1
	500-1000	0.21	1.9	6.6	160	0.13	1.0	0.031	0.59		500-1000	1.2	9.1	16.3	320	0.19	0.94	0.076	58.5
	1000-2000	0.25	2.2	7.3	157	0.17	0.98	0.030	0.91		1000-2000	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)
> 2000	0.56	2.5	4.4	46	0.11	0.32	0.018	1.7	> 2000	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)		
<b>St3</b>	6-60	5.5	43.3	61.3	399	0.52	0.35	0.687	43.6	<b>St3</b>	6-60	8.3	39.4	26.0	158	0.21	0.17	0.286	45.1
	60-200	2.0	15.1	20.7	177	0.25	0.85	0.083	47.4		60-200	1.3	59.3	32.3	370	0.23	1.2	0.064	23.6
	200-500	0.27	2.3	6.4	170	0.11	0.98	0.024	1.0		200-500	0.46	4.7	15.2	178	0.16	1.1	0.061	4.1
	500-1000	0.29	2.6	7.2	162	0.15	0.99	0.024	0.81		500-1000	0.38	4.0	12.7	154	0.22	0.73	0.055	3.5
	1000-2000	0.38	2.7	7.1	151	0.15	0.94	0.029	1.1		1000-2000	0.42	3.3	13.7	144	0.21	0.75	0.052	5.8
> 2000	0.22	1.3	2.5	34	0.06	0.21	0.008	0.61	> 2000	0.95	6.9	9.1	137	0.14	0.78	0.042	11.0		
<b>West</b>										<b>West</b>									
<b>St4</b>	6-60	6.2	34.1	23.2	372	0.21	0.29	0.105	42.0	<b>St4</b>	6-60	8.4	63.7	64.9	241	0.35	0.26	0.144	123
	60-200	5.7	25.2	43.8	156	0.16	0.19	0.057	25.2		60-200	2.9	27.0	16.2	133	0.17	0.68	0.052	18.5
	200-500	0.69	3.6	7.3	143	0.11	0.64	0.025	2.2		200-500	0.26	2.0	10.5	134	0.14	1.0	0.046	1.0
	500-1000	0.68	4.1	7.1	128	0.17	0.53	0.024	2.2		500-1000	0.25	2.3	10.0	132	0.15	0.80	0.041	1.1
	1000-2000	0.59	2.5	5.0	74	0.08	0.26	0.020	1.5		1000-2000	0.35	4.7	11.8	125	0.16	0.71	0.042	2.1
> 2000	0.67	2.6	3.4	39	0.05	0.08	0.019	1.9	> 2000	1.4	7.9	12.6	170	0.16	0.64	0.049	14.3		
<b>St5</b>	6-60	3.7	57.1	42.4	316	0.63	0.31	0.037	25.3	<b>St6</b>	6-60	6.4	86.9	35.4	198	0.27	0.17	0.098	34.6
	60-200	2.0	10.0	17.1	46	0.11	0.15	0.015	11.8		60-200	1.9	42.2	20.0	127	0.16	0.89	0.052	8.2
	200-500	0.36	2.2	5.5	75	0.10	0.50	0.007	1.7		200-500	0.24	3.2	10.1	122	0.09	0.91	0.038	0.62
	500-1000	0.30	2.0	8.2	135	0.14	0.54	0.010	1.3		500-1000	0.23	2.9	9.6	118	0.11	0.69	0.036	0.72
	1000-2000	0.34	2.1	5.8	101	0.12	0.47	0.008	1.5		1000-2000	0.39	3.2	13.8	119	0.17	0.52	0.038	2.9
> 2000	0.11	0.63	1.9	16	0.05	0.13	0.002	0.28	> 2000	0.97	7.5	23.8	121	0.12	0.54	0.037	8.0		
<b>St5b</b>	6-60	4.6	125	86.6	564	1.81	0.61	0.017	208	<b>St7</b>	6-60	7.6	49.9	28.0	161	0.31	0.40	0.103	65.4
	60-200	2.1	13.5	10.7	47	0.07	0.09	0.014	14.1		60-200	2.2	12.4	13.8	119	0.13	0.37	0.033	14.1
	200-500	0.47	3.3	6.2	80	0.12	0.43	0.006	2.6		200-500	0.33	1.8	11.9	119	0.15	1.1	0.037	1.2



	500-1000	0.26	2.1	6.7	137	0.14	0.47	0.010	1.7		500-1000	0.41	2.3	9.6	138	0.15	0.96	0.036	2.8
	1000-2000	0.31	2.1	6.4	112	0.14	0.42	0.021	1.9		1000-2000	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)	(Ns/d)
	> 2000	0.37	2.4	6.0	89	0.11	0.35	0.008	2.0		> 2000	0.76	1.1	12.6	30	0.04	0.10	0.008	3.5
<b>St7</b>	6-60	4.4	46.5	15.5	504	0.31	0.31	0.036	14.6										
	60-200	4.2	20.0	9.7	53	0.09	0.12	0.038	18.6										
	200-500	0.61	2.9	9.9	159	0.18	0.74	0.013	3.1										
	500-1000	0.75	3.7	6.9	150	0.11	0.42	0.010	6.1										
	1000-2000	0.91	4.3	8.0	121	0.09	0.29	0.010	4.4										
	> 2000	0.30	1.6	2.0	20	0.04	0.07	0.002	1.1										

\* Exceptionally, two samples were collected and analyzed for this fraction at this station.

**Table S4:** Mean bioaccumulation factors (BAFs) calculated per element type (essential vs. non-essential), reported per season (spring (plankton) or summer (fish) 2010 vs. winter 2011) and per biological compartment. Concentrations used for calculations were in mg L<sup>-1</sup> for seawater (including dissolved concentrations of all the sampled water column), and mg kg<sup>-1</sup> dry mass for biological compartments (plankton and fish). Nd = Not determined.

BAFs relative to dry mass	Essential elements				Non-essential elements		
	Co	Ni	Cu	Zn	Cd	Hg	Pb
<b>Spring or Summer 2010</b>							
6-60 µm	428 761	232 173	248 653	1 444 604	34 243	511 885	2 129 335
60-200 µm	292 479	82 453	124 069	430 540	34 118	327 532	1 030 065
200-500 µm	29 901	10 552	35 195	517 921	64 622	38 071	64 557
500-1000 µm	28 892	10 911	37 593	600 977	64 151	42 800	73 827
1000-2000 µm	32 648	12 621	36 062	544 352	59 165	44 219	69 376
> 2000 µm	26 415	7 537	19 057	199 331	22 456	24 119	48 085
Sardine (Wh*)	(Nd)	2 232	24 748	348 582	5 324	227 948	8 259
Anchovy (Wh*)	(Nd)	2 913	28 766	472 684	10 495	417 278	4 996
<b>Winter 2011</b>							
6-60 µm	842 765	248 766	230 584	909 054	17 824	(Nd)	2 307 768
60-200 µm	225 671	136 122	122 738	980 543	62 693	(Nd)	755 432
200-500 µm	37 841	14 651	103 889	801 698	87 353	(Nd)	176 687
500-1000 µm	48 845	18 175	67 760	861 720	68 785	(Nd)	420 605
1000-2000 µm	40 434	17 562	91 127	766 240	54 884	(Nd)	183 254
> 2000 µm	109 873	25 221	84 257	569 031	40 781	(Nd)	322 338
Sardine (Wh*)	(Nd)	3 117	30 693	632 459	5 211	(Nd)	18 040
Anchovy (Wh*)	(Nd)	2 788	33 841	660 097	8 238	(Nd)	4 785

\*Wh = whole individuals (reconstructed data).

**Table S5:** Spearman rank order correlation coefficients (r) between mean metal BAFs calculated for the pelagic food web analyzed in the Gulf of Lions. Significant correlations at  $p < 0.05$  are indicated in bold characters.

	Co	Ni	Cu	Zn	Cd	Hg	Pb
Co	—						
Ni	<b>0.986</b>	—					
Cu	<b>0.909</b>	<b>0.926</b>	—				
Zn	<b>0.608</b>	<b>0.621</b>	<b>0.700</b>	—			
Cd	-0.406	0.403	0.394	0.318	—		
Hg	<b>0.943</b>	0.310	0.524	0.333	-0.357	—	
Pb	<b>0.972</b>	<b>0.982</b>	<b>0.918</b>	<b>0.579</b>	0.403	0.238	—