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### ► To cite this version:

Catherine Guigue, Javier Angel Tesán-Onrubia, Léa Guyomarc'H, Daniela Bănaru, François Carlotti, et al.. Hydrocarbons in size-fractionated plankton of the Mediterranean Sea (MERITE-HIPPOCAMPE campaign). *Marine Pollution Bulletin*, 2023, 194 (Part B), pp.115386. 10.1016/j.marpolbul.2023.115386 . hal-04248925

**HAL Id: hal-04248925**

**<https://hal.science/hal-04248925v1>**

Submitted on 31 Oct 2023

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1 **Hydrocarbons in size-fractionated plankton of the Mediterranean Sea (MERITE-**  
2 **HIPPOCAMPE campaign)**

3

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16 For submission to Marine Pollution Bulletin – Special issue “*Plankton and Contaminants in*  
17 *the Mediterranean Sea: Biological pump and interactions from regional to global*  
18 *approaches*”

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20 Revised version, 1 August 2023

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27 **Abstract**

28 Aliphatic and polycyclic aromatic hydrocarbons (AHs and PAHs, respectively) were  
29 analyzed in the dissolved fraction ( $< 0.7 \mu\text{m}$ ) of surface water and in various  
30 particulate/planktonic size fractions (0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$ ) collected at  
31 the deep chlorophyll maximum, along a North-South transect in the Mediterranean Sea in  
32 spring 2019 (MERITE-HIPPOCAMPE campaign). Suspended particulate matter, biomass,  
33 total chlorophyll *a*, particulate organic carbon, C and N isotopic ratios, and lipid biomarkers  
34 were also determined to help characterizing the size-fractionated plankton and highlight the  
35 potential link with the content in AHs and PAHs in these size fractions.  $\Sigma_{28}\text{AH}$  concentrations  
36 ranged 18-489  $\text{ng L}^{-1}$  for water, 3.9-72  $\mu\text{g g}^{-1}$  dry weight (dw) for the size fraction 0.7-60  $\mu\text{m}$ ,  
37 and 3.4-55  $\mu\text{g g}^{-1}$  dw for the fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$ . AH molecular  
38 profiles revealed that they were mainly of biogenic origin.  $\Sigma_{14}\text{PAH}$  concentrations were 0.9-  
39 16  $\text{ng L}^{-1}$  for water, and  $\Sigma_{27}\text{PAH}$  concentrations were 53-220  $\text{ng g}^{-1}$  dw for the fraction 0.7-60  
40  $\mu\text{m}$  and 35-255  $\text{ng g}^{-1}$  dw for the three higher fractions, phenanthrene being the most abundant  
41 compound in planktonic compartment. Two processes were evidenced concerning the PAH  
42 patterns, the bioreduction, i.e., the decrease in concentrations from the small size fractions  
43 (0.7-60 and 60-200  $\mu\text{m}$ ) to the higher ones (200-500  $\mu\text{m}$  and 500-1000  $\mu\text{m}$ ), and the  
44 biodilution, i.e., the decrease in concentrations in plankton at higher suspended matter or  
45 biomass, especially for the 0.7-60 and 60-200- $\mu\text{m}$  size fractions. We estimated the biological  
46 pump fluxes of  $\Sigma_{27}\text{PAHs}$  below 100-m depth in the Western Mediterranean Sea at  $15 \pm 10 \text{ ng}$   
47  $\text{m}^{-2} \text{ day}^{-1}$ , which is comparable to those previously reported in the South Pacific and Indian  
48 Ocean.

49

50 **Key words:** Hydrocarbons, PAHs, plankton, size fractions, bioaccumulation, Mediterranean  
51 Sea

## 52 **1. Introduction**

53

54 Hydrocarbons, in particular polycyclic aromatic hydrocarbons (PAHs), are among the  
55 most widespread organic pollutants in the marine environment (Hylland, 2006; Duran and  
56 Cravo-Laureau, 2016; Ben Othman et al., 2023). PAHs are considered to be almost  
57 exclusively of anthropogenic origin, possibly coming from crude oil or its derivatives  
58 (petrogenic PAHs) or from the combustion of fossil fuels and biomass (pyrogenic PAHs)  
59 (Wang et al., 1999; Yunker et al., 2002; Stogiannidis and Laane, 2015). Aliphatic  
60 hydrocarbons (AHs), which also represent an important class of hydrocarbons in the marine  
61 environment, can be of anthropogenic (petroleum) and biogenic (terrestrial or marine) origin  
62 (Volkman et al., 1992; Bouloubassi and Saliot, 1993; Love et al., 2021). PAHs are listed as  
63 priority pollutants by various international organizations (US-EPA, 2012; EU-Directive,  
64 2013) due to their deleterious effects on living organisms (Honda and Suzuki, 2020). Thus,  
65 for many years, PAHs, and to a lesser extent AHs, have been studied in different matrices of  
66 the marine ecosystems, such as surface sediments (Mille et al., 2007; Zaghden et al., 2017;  
67 Mandić et al., 2018), the dissolved phase of water (Guigue et al., 2014; Adhikari et al., 2015;  
68 Tong et al., 2019), suspended particles (Bouloubassi et al., 2006; Mzoughi and Chouba, 2011;  
69 Rocha and Rocha, 2021), surface microlayer (Stortini et al., 2009; Guitart et al., 2010; Guigue  
70 et al., 2011), and biota, especially macro-organisms (Baumard et al., 1998; Tolosa et al.,  
71 2005; Pirsaeheb et al., 2018).

72 The incorporation and transfer of PAHs within marine food webs is known to induce  
73 major disturbances of ecosystems, and to have negative impacts on the exploitation of marine  
74 resources and habitats, socio-economic activities, and human health (Islam and Tanaka, 2004;  
75 Balcioglu, 2016; Romero et al., 2018). However, even though the concentrations of PAHs in  
76 upper food webs has been quite well documented so far, they have been much less

77 investigated in plankton, i.e., the first trophic levels of pelagic marine ecosystems. Yet,  
78 plankton, which includes phytoplankton (mostly unicellular photosynthetic autotrophic  
79 organisms), zooplankton (heterotrophic eukaryotes), and bacterioplankton (heterotrophic  
80 prokaryotes), is recognized as a key gateway and playing a major role in the transfer of  
81 contaminants from water to upper food webs ([Berrojalbiz et al., 2011](#); [Tiano et al., 2014](#); [Tao  
82 et al., 2018](#); [Chouvelon et al., 2019](#); [Tedetti et al., 2023](#)).

83         Given their high surface area/volume ratio and the subsequent large areas of exchanges,  
84 phytoplankton cells display high bioconcentration capacities (bioconcentration referring to the  
85 accumulation of contaminants in a given organism relative to surrounding water by direct  
86 absorption from the latter) ([Martin and Knauer, 1973](#); [Fan and Reinfelder, 2003](#); [Heimbürger  
87 et al., 2010](#); [Chouvelon et al., 2019](#)). Assuming partition equilibrium processes between the  
88 cells and the surrounding water ([Frouin et al., 2013](#)), the bioconcentration of organic  
89 contaminants in phytoplankton may be directly related to their octanol-water partitioning  
90 coefficient (Log  $K_{ow}$ ), i.e., their degree of hydrophobicity (the higher the Log  $K_{ow}$ , the  
91 greater the contaminant bioconcentration) ([Swackhamer and Skoglund, 1993](#); [Nizzetto et al.,  
92 2012](#); [Li et al., 2020](#)), and to the size of the phytoplankton species (the smaller the cell size,  
93 the greater the contaminant bioconcentration) ([Fan and Reinfelder, 2003](#)). On the other side,  
94 bioaccumulation processes in zooplankton (bioaccumulation referring to the accumulation of  
95 contaminants in a given organism relative to surrounding water by both direct absorption from  
96 water and the consumption of contaminated prey) are made complex by 1) the influence of  
97 trophic interactions and transfers between phytoplankton and zooplankton and within  
98 zooplanktonic compartment, and 2) the removal processes of contaminants implemented by  
99 these organisms, including metabolization, passive release and excretion ([Berrojalbiz et al.,  
100 2009](#); [Tiano et al., 2014](#); [Aleksenko et al., 2018](#); [Tao et al., 2018](#); [Li et al., 2020](#)). Ultimately,  
101 all these processes, which can act concurrently in the same or opposite directions, makes it

102 difficult to understand and predict the pattern of contaminant concentrations within the  
103 planktonic food web (Nizzetto et al., 2012; Strady et al., 2015; Alekseenko et al., 2018;  
104 Castro-Jiménez et al., 2021; Li et al., 2021).

105 Recently, some works have focused on the bioaccumulation of PAHs in the planktonic  
106 compartment (here and below the term bioaccumulation includes bioconcentration for  
107 simplicity, the latter being a direct form of bioaccumulation) (Berrojalbiz et al., 2009, 2011;  
108 Tao et al., 2017a, b, 2018; González-Gaya et al., 2019). These have provided a very  
109 interesting insight of the PAH bioaccumulation pattern within the plankton and showed a link  
110 between this bioaccumulation and the surrounding biogeochemical parameters. Nevertheless,  
111 in these studies, plankton has been generally taken as an entire compartment, without any  
112 separation into size fractions. Furthermore, the lipid content was not taken into account, even  
113 though, due to their hydrophobic nature, lipids represent a major matrix contributing to the  
114 bioaccumulation of the organic contaminants within marine and planktonic organisms  
115 (Mackay and Fraser, 2000; Arnot and Gobas, 2006; Lee et al., 2006; Tesán-Onrubia et al.,  
116 2023).

117 In this context, the objectives of the present work were to **1)** determine the contents in  
118 hydrocarbons (AHs and PAHs) in the dissolved fraction ( $< 0.7 \mu\text{m}$ ) of surface water and in  
119 various particulate/planktonic size fractions (0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$ ) from  
120 sampling in the deep chlorophyll maximum (DCM), along a North-South transect in the  
121 Mediterranean Sea during the MERITE-HIPPOCAMPE campaign. For these different size  
122 fractions, suspended particulate matter (SPM), biomass, total chlorophyll *a* (TChl*a*),  
123 particulate organic carbon (POC), C and N isotopic ratios ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) and lipid biomarkers  
124 were also determined. **2)** Evaluate the spatial variations (between stations) and the  
125 distributions within the planktonic size fractions of these parameters (mainly AHs, PAHs,  
126 POC, lipids), as well as the correlations between them. **3)** Investigate the concentration

127 patterns and bioaccumulation of PAHs within plankton according to the size fraction, trophic  
128 level, organic carbon partitioning and biomass. **4)** Assess, *via* the estimation of hydrocarbon  
129 vertical fluxes, the role of Mediterranean plankton as biological pump for hydrocarbons.

130

## 131 **2. Material and Methods**

132

### 133 **2.1. Study area**

134 The MERITE-HIPPOCAMPE cruise took place in spring 2019 (from April 13 to May  
135 14), aboard the R/V *Antea*, along a North-South transect in the Mediterranean Sea, from the  
136 French coast (La Seyne-sur-Mer, Northwestern Mediterranean) to the Gulf of Gabès in  
137 Tunisia (Southeastern Mediterranean). Leg 1 (13-28 April) covered the southward transect,  
138 between La Seyne-sur-Mer and Tunis, with sampling of stations St2, St4, St3, St10 and St11.  
139 Leg 2 (30 April-14 May) included the end of the southward transect (from Tunis to the Gulf  
140 of Gabès), and the return trip back northward to La Seyne-sur-Mer, with sampling of stations  
141 St15, St17, St19, St9 and St1 (Fig. 1a, b) (Tedetti and Tronczynski, 2019; Tedetti et al.,  
142 2023). The ten stations were chosen according to criteria of physical, biological and  
143 biogeochemical conditions and level of anthropogenic pressures, as well as the location of  
144 bloom areas and ecoregions of the Mediterranean (see full description in Tedetti et al., 2023).

145

### 146 **2.2. Sampling, filtration, sieving and conditioning**

147 At each station, a conductivity-temperature-depth probe (CTD; Seabird SBE 911*plus*)  
148 equipped with a TChl*a* fluorescence sensor (Chelsea ctg) was deployed over the depth range  
149 0-250 m (or 0-bottom when depth was < 250 m) to identify the DCM. For each station, the  
150 sampling depth ranges in the DCM are reported Table S1.

151           2.2.1. *In situ* filtration. Two McLane *in situ* pumps (WTS6-142LV, 4-8 L min<sup>-1</sup>) were  
152 used to collect high amounts of particles/plankton in the DCM. Each pump was mounted with  
153 a regular 142-mm filter holder for hosting a pre-combusted (450 °C, 6 h), pre-weighted 142-  
154 mm diameter glass fiber (GF/F) filter (Whatman). The holder was covered with a sock-type  
155 pre-filter of 60- $\mu$ m pore size, so as to collect on the filters the size fraction 0.7-60  $\mu$ m. Both  
156 pumps were deployed at the same time by the ship's Moon-Pool on the hydrographic cable to  
157 reach the DCM. At the DCM, the pumping lasted 40-60 min, so that ~ 250 L of seawater was  
158 passed over each GF/F filter. Back on board, the filters were recovered and dried. One filter  
159 was used for the analysis of SPM and hydrocarbons, while the other filter was dedicated to  
160 SPM, TChla, POC, and  $\delta^{13}\text{C}/\delta^{15}\text{N}$ . Before drying, this second filter was also rinsed with ultra-  
161 pure water to remove residues of the seawater salts. Finally, the GF/F filters were placed in  
162 glass boxes and stored at -18 °C on board and then in the laboratory before analysis. It should  
163 be noted that molecular lipid analyzes were not conducted on these filters/size fraction 0.7-60  
164  $\mu$ m.

165           2.2.2. *Plankton sampling*. Multiple Plankton Sampler (Midi type, Hydro-Bios), here  
166 referred to as "MultiNet", was used to collect plankton in the DCM. The MultiNet was made  
167 of 5 individual opening and closing nets with 0.25-m<sup>2</sup> aperture, 60- $\mu$ m mesh size, and cod  
168 ends of 60- $\mu$ m mesh size, as well as two flowing meters to measure the volume of water  
169 filtered by the nets, a CTD sensor and a TChla fluorometer. The MultiNet was deployed  
170 horizontally in the DCM from the rear of the ship *via* the electromechanical cable. The  
171 Multinet position was maintained stable at the defined depth by means of a V-fin deflector, a  
172 helicoidal bucket connector gathering the cod ends, a controlled vessel speed, and real-time  
173 control of its position from the on board desk unit. Once the five nets were filled, the  
174 MultiNet was brought on board, the cod ends rinsed out with local seawater, and their content



175 transferred into pre-cleaned 10-L HDPE bottles. The device was then returned to the water as  
176 many times as necessary until sufficient quantities of plankton were obtained.

177 In the on board clean lab container, plankton was then fractionated on a column of five  
178 stainless steel sieves (60, 200, 500, 1000 and 2000- $\mu\text{m}$  mesh size) by wet-sieving with GF/F  
179 filtered seawater previously retrieved from ASTI pump/in-line filtration system and stored in  
180 a stainless steel jerry can (see section 2.2.3). The planktonic size fractions recovered on the  
181 stainless-steel sieves (i.e., 60-200, 200-500, 500-1000, 1000-2000 and  $> 2000 \mu\text{m}$ ) were  
182 shared out for the different analyzes. For the analyzes of hydrocarbons, lipids, POC and  
183  $\delta^{13}\text{C}/\delta^{15}\text{N}$ , each size fraction was transferred into two pre-combusted 150-mL amber glass  
184 flasks. It is worth noting that the quantities obtained for the size fractions 1000-2000 and  $>$   
185 2000  $\mu\text{m}$  were not sufficient enough for PAH analyzes. Hence, only the fractions 60-200,  
186 200-500 and 500-1000  $\mu\text{m}$  are exploited in the present work. The glass flasks were stored at -  
187 18 °C on board and then in the laboratory before analysis.

188 *2.2.3. Water sampling and in-line filtration.* Seawater was sampled at ~ 5-20-m  
189 depth, depending on the stations, with a pneumatically-operated Teflon ASTI pump (model  
190 PFD2) set up on board, connected to Teflon tubing, which was weighted down and immersed  
191 with the hydrology gallows. The pump was connected to a clean dry air supply. The seawater  
192 brought on board in the Teflon tubing was then filtered in-line onto a pre-combusted GF/F  
193 142-mm filter using a Teflon filtration holder. The seawater filtered through GF/F was stored  
194 in two stainless steel jerry cans of 20 L each. The seawater of the first jerry can was used  
195 exclusively for sieving the plankton collected with the MultiNet. The seawater of the second  
196 jerry can was amended with 50 mL of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) for subsequent analyzes of  
197 dissolved ( $< 0.7 \mu\text{m}$ ) AHs and PAHs. This jerry can was stored at ~ 20 °C on board and then  
198 in the laboratory before analysis. Before filling the jerry cans, several liters of filtered  
199 seawater were thrown away.

200

## 201 **2.3. Analysis**

202 **2.3.1. SPM, Biomass.** SPM was measured on the size fraction 0.7-60  $\mu\text{m}$  by  
203 weighing, with a precision balance, the tare, the entire (142-mm GF/F) filters before filtration,  
204 and the entire filters, wet and dry (freeze dried), after filtration, taking into account the  
205 volumes of water filtered with the McLane pumps (Tesán-Onrubia et al., 2023). Dry-weight  
206 biomasses of the size fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$  were determined after  
207 drying samples on pre-weighed GF/F filters (60 °C, 24 h) and then re-weighed with a  
208 precision balance, taking into consideration the volumes of water filtered by the MultiNet  
209 (Fierro-González et al., 2023). The contributions of zooplankton, phytoplankton and detritus  
210 components to the total weighted biomass were estimated according to Fierro-González et al.  
211 (2023). SPM is expressed in  $\text{mg L}^{-1}$ , and biomass concentrations in  $\mu\text{g}$  (or  $\text{mg}$ ) dry weight  
212 (dw)  $\text{L}^{-1}$ .

213 **2.3.2. TChla, POC,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ .** The determination of TChla concentration on the  
214 size fraction 0.7-60  $\mu\text{m}$  was performed on a 22-mm diameter aliquot of the 142-mm GF/F  
215 filter by fluorescence method after methanol (MeOH) extraction according to Welschmeyer  
216 (1994) and Raimbault et al. (2004). TChla concentration is expressed in  $\mu\text{g L}^{-1}$ . POC  
217 concentration and  $\delta^{13}\text{C}/\delta^{15}\text{N}$  were determined on the size fractions 0.7-60 to 500-1000  $\mu\text{m}$ .  
218 POC samples, i.e., 22-mm diameter aliquots of the freeze dried 142-mm GF/F filters (0.7-60  
219  $\mu\text{m}$ ) and ~ 1 mg of the freeze dried plankton material (60-200 to 500-1000  $\mu\text{m}$ ), were  
220 analyzed using the persulfate wet-oxidation procedure according to Raimbault et al. (1999).  
221 For the fraction 0.7-60  $\mu\text{m}$ , POC concentration is expressed either in  $\text{mg L}^{-1}$  or in  $\text{mg g}^{-1}$  dw  
222 (when normalized by SPM). For the fractions 60-200 to 500-1000  $\mu\text{m}$ , POC concentration is  
223 expressed in  $\text{mg g}^{-1}$  dw. Concerning  $\delta^{13}\text{C}/\delta^{15}\text{N}$  samples, the SPM collected on the GF/F filters  
224 were scraped off with a scalpel, whereas plankton fractions were ground to fine powder.

225 Samples were then acidified (for  $\delta^{13}\text{C}$ ) or not (for  $\delta^{15}\text{N}$ ) and analyzed using an elemental  
226 analyzer (Flash EA 2000, Thermo Scientific<sup>®</sup>) coupled with a continuous flow isotope ratio  
227 mass spectrometer (Delta V Plus, Thermo Scientific<sup>®</sup>) (see details in [Tesán-Onrubia et al.,](#)  
228 [2023](#)). Isotope compositions are expressed in ‰ as deviations from the standard reference  
229 materials ( $\text{N}_2$  in air for  $\delta^{15}\text{N}$  and Vienna Pee Dee Belemnite for  $\delta^{13}\text{C}$ ).

230 **2.3.3. Lipid biomarkers.** Lipid biomarkers were determined on the size fractions 60-  
231 200 to 500-1000  $\mu\text{m}$ . For each fraction, ~ 10 mg of freeze dried plankton were mixed with 15  
232 mL MeOH and reduced with excess sodium borohydride ( $\text{NaBH}_4$ ). This process was  
233 conducted to reduce any hydroperoxides in samples ([Galeron et al., 2015](#)), which are known  
234 to induce autoxidative damage of some lipids during the hot saponification step.  
235 Saponification was carried out on each reduced sample. After  $\text{NaBH}_4$  reduction, water and  
236 potassium hydroxide (KOH) were added and the mixture directly saponified by refluxing.  
237 After cooling, the contents of the flask were acidified with hydrochloric acid (HCl) to pH 1,  
238 and extracted 3 times with 30-mL  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  extracts were dried over  
239 anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated to give the total lipid extract.  
240 These latter were derivatized by dissolution in 300  $\mu\text{L}$   
241 pyridine/bis(trimethylsilyl)trifluoroacetamide (BSTFA, Supelco) (2:1, v/v) and silylated.  
242 After evaporation to dryness under a stream of  $\text{N}_2$ , the derivatized residue was dissolved in  
243 hexane/BSTFA (2:1, v/v) to avoid desilylation and analyzed using gas chromatography-  
244 electron ionization quadrupole time of flight mass spectrometry (GC-QTOF). Individual fatty  
245 acids, fatty alcohols and sterols were identified and quantified using an Agilent 7890B/7200  
246 GC-QTOF System (Agilent Technologies, France) according to [Rontani et al. \(2017\)](#). It  
247 should be noticed that the polyunsaturated fatty acid concentrations must be regarded as  
248 minimal values because they might have been affected by oxidative losses occurring during

249 the 2-year storage of samples at -18 °C before analysis. Concentrations of individual and total  
250 lipid biomarkers (fatty acids, fatty alcohols and sterols) are expressed in mg g<sup>-1</sup> dw.

251       **2.3.4. Hydrocarbons.** Twenty-eight AHs, i.e., a series of *n*-alkanes from *n*-C<sub>15</sub> to *n*-C<sub>40</sub>  
252 and two isoprenoids, pristane (Pr) and phytane (Phy), were determined in this study.  
253 Unresolved complex mixture (UCM) was not detected or negligible in our samples. For  
254 PAHs, we determined the concentrations of 17 parent PAHs, namely naphthalene (Nap),  
255 acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), dibenzothiophene (DBT),  
256 phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[*a*]anthracene  
257 (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF),  
258 benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BP),  
259 indeno[1,2,3-*cd*]pyrene (IndP), as well as the concentrations of methylated derivatives  
260 (methyl- = C1-, dimethyl- = C2-, trimethyl- = C3-) of the five compounds Nap (C1, C2, C3),  
261 Flu (C1, C2), DBT (C1, C2), Phe/Ant (C1, C2) and Flt/Pyr (C1), which lead to a total of 27  
262 PAHs (or groups of PAHs). AHs and PAHs were determined on the dissolved fraction (< 0.7  
263 μm) of seawater, as well as on the size fractions 0.7-60, 60-200, 200-500 and 500-1000 μm.  
264 For the fractions > 0.7 μm, samples (entire GF/F filters and plankton) were freeze dried for  
265 24-96 h, then spiked with a multi-standard mixture containing surrogate standards for AHs  
266 (C<sub>16</sub>-*d*<sub>34</sub>, C<sub>24</sub>-*d*<sub>50</sub> and C<sub>36</sub>-*d*<sub>74</sub>) and PAHs (Nap-*d*<sub>8</sub>, Flu-*d*<sub>10</sub>, Phe-*d*<sub>10</sub>, Flt-*d*<sub>10</sub> and BaP-*d*<sub>12</sub>), and  
267 extracted with CH<sub>2</sub>Cl<sub>2</sub> using accelerated solvent extraction (ASE 350, Dionex, Thermo  
268 Scientific) with the following procedure: 150 °C, 110 bars, 3 cycles of 10 min, 100% of  
269 rinsing and purging for 60 s (Guigue et al., 2017; Fourati et al., 2018a). For the fraction < 0.7  
270 μm, samples, i.e., 20 L of filtered seawater with 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, were spiked with the  
271 multi-standard mixture and extracted by liquid-liquid extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 × 60 mL per  
272 liter) according to Guigue et al. (2014) and Fourati et al. (2018b). All CH<sub>2</sub>Cl<sub>2</sub> extracts were  
273 concentrated and solvent was exchanged by *n*-hexane. Extracts were reduced to ~ 1 mL, and

274 cleaned with a silica-alumina column (10 mm i.d., made of glass) packed from bottom to top  
275 with 1-3 g deactivated alumina (by 3% ultra-pure water w/w), 1-3 g activated silica, and 1 g  
276 dehydrated Na<sub>2</sub>SO<sub>4</sub>, depending on the quantity of extracted matter. First, the sorbents were  
277 conditioned with 20 mL *n*-hexane, then the extract was deposited on the top of the column  
278 and both AHs and PAHs were eluted with 50-mL *n*-hexane:CH<sub>2</sub>Cl<sub>2</sub> (9:1 v/v). This was  
279 followed by solvent reduction to 200-500 µL, and deuterated mixtures for AHs (C<sub>19</sub>-*d*<sub>40</sub> and  
280 C<sub>30</sub>-*d*<sub>62</sub>) and PAHs (Ace-*d*<sub>10</sub>, Ant-*d*<sub>10</sub>, Pyr-*d*<sub>10</sub>, Chr-*d*<sub>12</sub> and Per-*d*<sub>12</sub>) were spiked as internal  
281 standards before analysis.

282 AHs and PAHs were analyzed separately by gas chromatography (Trace ISQ, Thermo  
283 Electron) equipped with a mass spectrometry (MS) detector operating at an ionization energy  
284 of 70 eV, with hydrogen (1.2 mL min<sup>-1</sup>) as carry gas. The capillary column (HP-5MS, Agilent  
285 Technologies, USA) was 30 m in length with an internal diameter of 0.25 mm and a film  
286 thickness of 0.25 µm. The injector (used in splitless mode) and detector temperatures were  
287 250 and 320 °C, respectively. The column temperature was initially held at 70 °C for 3 min,  
288 increased to 150 °C at 15 °C min<sup>-1</sup>, then increased to 320 °C at 7 °C min<sup>-1</sup> and finally held for  
289 10 min. AHs and PAHs were identified and quantified in full scan and selected ion  
290 monitoring (SIM) modes simultaneously using two distinct methods (Guigue et al., 2011,  
291 2014, 2017). All solvents and chemicals used were of high purity grade. Σ AHs and Σ PAHs  
292 represented the sum of the targeted AH and PAH compounds, respectively. Concentrations of  
293 dissolved AHs and PAHs are expressed in ng L<sup>-1</sup>. Concentrations of AHs and PAHs for the  
294 fractions > 0.7 µm are expressed in µg g<sup>-1</sup> dw and ng g<sup>-1</sup> dw, respectively.

295 The quality control procedures were strictly followed throughout the whole sampling  
296 and laboratory treatments. They included control/validation of GC-MS calibration and tuning,  
297 laboratory and field blanks, method limit of detection/quantification (LODs/LOQs), as well as  
298 surrogate recoveries. Field and laboratory blanks were prepared, processed and analyzed in

299 the same manner as the real samples. LOQs ranged from 30 to 100  $\text{pg L}^{-1}$  and from 10 to 50  
300  $\text{pg L}^{-1}$  in water for AHs and PAHs, respectively. They ranged from 0.3 to 1  $\text{ng g}^{-1}$  and from  
301 0.1 to 0.5  $\text{ng g}^{-1}$  in plankton for AHs and PAHs, respectively. Blank values were below LODs  
302 or LOQs and surrogate recoveries were  $> 75$  and  $> 70\%$  for AHs and PAHs, respectively. All  
303 the concentrations reported here were not neither blank- nor recovery-corrected.

304

## 305 **2.4. Data handling**

306 To fully compare our PAH concentrations in the planktonic size fractions with those in  
307 literature, we estimated the concentrations of individual PAHs (and of POC) in the entire size  
308 fraction 60-1000  $\mu\text{m}$  by summing the concentrations of individual PAHs (and of POC) in the  
309 fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$ , each of these concentrations being weighted  
310 (multiplied) by the contribution of the biomass of the given fraction to the total biomass of the  
311 fraction 60-1000  $\mu\text{m}$  ( $f_{\text{Biomass}} = \text{biomass of the given fraction} / \text{biomass 60-1000 } \mu\text{m}$ ).

312 According to [González-Gaya et al. \(2019\)](#), we estimated the biological pump fluxes of  
313 PAHs, i.e., the vertical fluxes of PAHs exported in depth through the biological pump process  
314 (in  $\text{ng m}^{-2} \text{day}^{-1}$ ), for the Western basin of the Mediterranean Sea. For this, we normalized the  
315 PAH concentrations in the size fraction 60-1000  $\mu\text{m}$  at each station (in  $\text{ng g}^{-1} \text{dw}$ ) by the  
316 corresponding organic carbon (OC) content (in  $\text{g C g}^{-1} \text{dw}$ ). Then, we averaged these OC-  
317 normalized PAH concentrations (in  $\text{ng g}^{-1} \text{C dw}$ ), and multiplied this obtained mean  
318 concentration by the vertical settling flux of POC (in  $\text{g C m}^{-2} \text{day}^{-1}$ ) below 100-m depth for  
319 the Western Mediterranean Sea estimated by [Guyennon et al. \(2015\)](#), where POC is defined  
320 as being fueled by the natural mortality of the largest organisms (mesozooplankton, diatoms  
321 and ciliates) and by the excretion of fecal pellets and sloppy feeding by mesozooplankton.  
322 This calculation was performed for total PAHs (sum of our 27 parent and alkylated

323 compounds;  $\Sigma_{27}$ PAHs) but also for Phe alone, which was the dominant PAH in the planktonic  
324 fractions.

325 The partition coefficient between particulate matter and water ( $K_D$  in  $L\ kg^{-1}$ ) was  
326 calculated for seven individual PAHs (the ones present both in water and  
327 particulate/planktonic phases, namely Nap, Flu, Phe, Flt, Pyr, BaA and Chr) in each size  
328 fraction (0.7-60, 60-200, 200-500, 500-1000 and 60-1000  $\mu m$ ) as  $(C_P / C_W) \times 1000$  where  $C_P$   
329 is the concentration of the given PAH in the given size fraction in  $ng\ g^{-1}\ dw$ , and  $C_W$  is the  
330 concentration of the PAH in the dissolved phase (size fraction  $< 0.7\ \mu m$ ) in  $ng\ L^{-1}$ . The  
331 partition coefficient between organic carbon and water ( $K_{OC}$  in  $L\ kg^{-1}$ ) was then determined  
332 for the seven individual PAHs in each size fraction as  $K_D / f_{OC}$  where  $f_{OC}$  is the contribution of  
333 the OC mass (in g) to the total matter mass (in g) for a given size fraction ( $f_{OC} = POC$  in  $mg\ g^{-1}\ dw / 1000$ ).  
334

335 According to the previous works by [Berrojalbiz et al. \(2011\)](#) and [González-Gaya et al.](#)  
336 [\(2019\)](#), we assume that the relationships between SPM or biomass concentration in a given  
337 size fraction and the concentration of individual PAHs in this size fraction can be  
338 approximated by a power function of the form:  $C_P = aSPM^{-m}$  or  $aBiomass^{-m}$  where  $a$  is the  
339 constant and  $m$  the slope of the regression. In the present study, the Log  $K_{OC}$  and slope ( $m$ )  
340 values were exploited to highlight the influence of plankton on the PAH bioaccumulation.

341

## 342 **2.5. Statistics**

343 Statistical analyzes were performed using XLSTAT software (version 2021.1.1).  
344 Student's parametric test (t-test) was used to determine significant differences between the  
345 means of two groups, i.e., the mean concentrations in two size fractions over the 10 stations.

346

## 347 **3. Results and Discussion**

348

### 349 **3.1. TChl<sub>a</sub>, POC and SPM/biomass**

350 In the size fraction 0.7-60  $\mu\text{m}$  sampled from the DCM, TChl<sub>a</sub>, POC and SPM  
351 concentrations followed substantially the same spatial distribution (Fig. 2a; Table S1), and  
352 were thus significantly positively correlated with each other ( $r = 0.70-0.93$ ,  $n = 10$ ,  $p < 0.05$ ).  
353 The lowest concentrations were found at two southern coastal stations, St17 and St15. Low  
354 values were also recorded at St3 and St11. The highest concentrations were observed at the  
355 offshore station St9. High values were also found at two coastal stations, St19 and St1 (Fig.  
356 2a; Table S1).

357 These results are in accordance with the observations by Tedetti et al. (2023) who  
358 highlighted that St9 displayed the highest contents in silicates [ $\text{Si}(\text{OH})_4$ ] and nitrates ( $\text{NO}_3^-$ ),  
359 and the highest concentrations in POC and TChl<sub>a</sub> in the size fraction  $> 0.7 \mu\text{m}$  in the DCM  
360 compared to the other stations. The high levels of TChl<sub>a</sub> in St9 during the sampling period  
361 were also confirmed from satellite data (Tedetti et al., 2023). Indeed, St9, situated at the  
362 boundary of the Ligurian consensus region (Ayata et al., 2018) in the deep convection area,  
363 benefited from a relatively intense phytoplankton bloom in late March 2019 (still visible in  
364 May), consecutive to a pronounced winter convection process (Margirier et al., 2020; Bosse et  
365 al., 2022). In line with our results, Tedetti et al. (2023) also reported high concentrations in  
366  $\text{Si}(\text{OH})_4$  and phosphates ( $\text{PO}_4^{3-}$ ), as well as TChl<sub>a</sub> and POC in the fraction  $> 0.7 \mu\text{m}$  at St19.  
367 This enrichment could be related to nutrient inputs and the subsequent stimulation of  
368 phytoplankton activity from Saharan dust deposition event that occurred in the south of the  
369 Gulf of Gabès during sampling. Such Saharan dust deposition events have been already  
370 reported and recognized to provide nutrients in this area (Béjaoui et al., 2019). Apart from St9  
371 and St19, the fraction 0.7-60  $\mu\text{m}$  exhibited higher TChl<sub>a</sub>, POC and SPM contents for the  
372 northern stations (St1-St4) than for the offshore and southern stations (St10-St17) (Fig. 2a),



373 which is consistent with their positioning in terms of bloom-condition areas and consensus  
374 regions defined by [D'Ortenzio and d'Alcalà \(2009\)](#) and [Ayata et al. \(2018\)](#).

375 The highest biomasses of the size fractions 60-200 to 500-1000  $\mu\text{m}$  recovered from the  
376 DCM sampling were determined at the southern (St17, St19) and northern (St4, St1) coastal  
377 stations. The lowest ones were recorded at St3 and St10 ([Fig. 2b](#); [Table S1](#)). The fractions 60-  
378 200 and 200-500  $\mu\text{m}$  contributed the most to the total biomass (37 and 41% on average,  
379 respectively), while the contribution of the fraction 500-1000  $\mu\text{m}$  was smaller (22% on  
380 average) ([Fig. 2b](#); [Table S1](#)).

381 The spatial distribution pattern of the biomasses of the size fractions 60-200 to 500-  
382 1000  $\mu\text{m}$  ([Fig. 2b](#)) did not really correspond to that of the SPM of the fraction 0.7-60  $\mu\text{m}$  ([Fig.](#)  
383 [2a](#)). According to [Fierro-González et al. \(2023\)](#) and [Tesán-Onrubia et al. \(2023\)](#), the biomass  
384 of the fractions 60-200 and 200-500  $\mu\text{m}$  was dominated by detritus and phytoplankton, which  
385 represented on average 68.8% (fraction 60-200  $\mu\text{m}$ ) and 59.2% (fraction 200-500  $\mu\text{m}$ ) of the  
386 total biomass (against 31.2 and 40.8% for zooplankton, respectively). An inverse pattern was  
387 found for the fraction 500-1000  $\mu\text{m}$  whose biomass was dominated by zooplankton (69.8% on  
388 average). Zooplankton was mainly composed of copepods, which accounted for 48.9, 91.9  
389 and 69.7% of total zooplankton in the fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$ ,  
390 respectively ([Fierro-González et al., 2023](#); [Tesán-Onrubia et al., 2023](#)). Compared to the other  
391 stations, the fraction 60-200  $\mu\text{m}$  at St4 was enriched in phytoplankton, while the fractions 60-  
392 200 and 200-500  $\mu\text{m}$  at St17 were enriched in detritus.

393 The POC concentrations in the fractions 60-200 to 500-1000  $\mu\text{m}$  were the highest in the  
394 three offshore stations (St9-St11) and at the coastal station St1. They were the lowest at the  
395 coastal stations St17, St4 and St3 ([Fig. 2c](#); [Table S1](#)). The low POC levels at St17 could be  
396 related to the high proportion of detritus within the biomass at this site. The POC  
397 concentrations were generally the highest for the fraction 200-500  $\mu\text{m}$ , and the lowest for the

398 60-200  $\mu\text{m}$ . The POC concentrations of the three size fractions were quite well correlated  
399 with each other ( $r = 0.87\text{-}0.91$ ,  $n = 9\text{-}10$ ,  $p < 0.05$ ). However, the latter were not at all  
400 correlated with the those of the 0.7-60- $\mu\text{m}$  fraction, as seen from Fig. 2a, c.

401

### 402 3.2. Lipids

403 Concentrations of total lipid biomarkers in the planktonic fractions 60-200 to 500-1000  
404  $\mu\text{m}$  from the DCM are shown in Fig. 3. Concentrations of individual compounds are also  
405 presented in Table S2. Concentration of total ( $\Sigma_{39}$ ) lipids (= concentrations of  $\Sigma_{25}$ fatty acids +  
406  $\Sigma_8$ fatty alcohols +  $\Sigma_6$ sterols) ranged from 3.5  $\text{mg g}^{-1}$  dw (equivalent to 0.35%) at St2, fraction  
407 500-1000  $\mu\text{m}$  to 35.6  $\text{mg g}^{-1}$  dw (equivalent to 3.6%) at St9, fraction 200-500  $\mu\text{m}$  (Fig. 3a).

408 The highest  $\Sigma_{39}$ lipid concentrations were recorded in the three offshore stations St9-St11, as  
409 well as in the southern coastal stations St15 and St19, while the lowest ones were found at  
410 St17 and St3 (Fig. 3a).  $\Sigma_{39}$ lipid concentrations in the three fractions were significantly  
411 positively correlated with each other ( $r = 0.79\text{-}0.86$ ,  $n = 9\text{-}10$ ,  $p < 0.05$ ) and no significant  
412 difference was detected between the mean concentrations of the three fractions over the 10  
413 stations (t-test,  $p > 0.05$ ). The distribution of  $\Sigma_{39}$ lipid concentrations throughout stations and  
414 fractions was very close to that of POC (Fig. 2c). Logically, a significant positive relationship  
415 appeared between  $\Sigma_{39}$ lipid and POC concentrations when considering the fractions 60-200 to  
416 500-1000  $\mu\text{m}$  ( $r = 0.69$ ,  $n = 29$ ,  $p < 0.05$ ) (Fig. S1a). This underlines the strong link between  
417 the lipid and POC contents in the planktonic compartment. Interestingly, our  $\Sigma_{39}$ lipid  
418 concentrations (determined by GC-MS) were compared to those obtained by colorimetric  
419 method by Tesán-Onrubia et al. (2023) on the same samples. Both were rather well correlated  
420 ( $r = 0.75$ ,  $n = 29$ ,  $p < 0.05$ ) albeit the colorimetric method gave slightly higher concentrations  
421 (Fig. S1b).

422 The  $\Sigma_{39}$ lipid concentrations we measured here in the three fractions (0.35-3.6%) were  
423 quite low compared to works by [Båmstedt \(1986\)](#) who found up to 61% lipid in some  
424 copepod species from temperate areas. However, they were of the same order of magnitude as  
425 a previous study conducted in the Mediterranean waters ( $3.0 \pm 2.8\%$ ; [Tiano et al., 2014](#)).  
426 According to [Lee et al. \(2006\)](#), the plankton that has a year-round low-level supply of food  
427 available do not accumulate lipid reserves. This is in agreement with the oligotrophic  
428 character of the Mediterranean waters along with poor seasonality of food supply for  
429 plankton. In addition, even though zooplankton is known to have a higher content in lipids  
430 than phytoplankton, the occurrence of phytoplankton and detritus in addition to zooplankton  
431 species (mainly copepods) in each of our size fractions tended to lower their lipid content  
432 ([Tesán-Onrubia et al., 2023](#)), as for St17 where the high proportion of detritus was  
433 accompanied by a very low lipid content.

434 Concentrations of  $\Sigma_{25}$ fatty acids,  $\Sigma_8$ fatty alcohols and  $\Sigma_6$ sterols represented  $80 \pm 7.9\%$ ,  
435  $15 \pm 8.6\%$  and  $5.0 \pm 2.5\%$  of the  $\Sigma_{39}$ lipid concentration, respectively ([Fig. 3b-d](#)). The  
436 distribution of  $\Sigma_{25}$ fatty acid concentrations throughout stations and fractions ([Fig. 3b](#)) was  
437 very similar to that of  $\Sigma_{39}$ lipid concentrations. While the distribution of  $\Sigma_6$ sterol  
438 concentrations ([Fig. 3d](#)) followed also quite well those of  $\Sigma_{39}$ lipids and  $\Sigma_{25}$ fatty acids, the  
439 distribution of  $\Sigma_8$ fatty alcohol concentrations ([Fig. 3c](#)) was rather different from the three  
440 others. Overall, as for  $\Sigma_{39}$ lipids and  $\Sigma_{25}$ fatty acids, the highest  $\Sigma_8$ fatty alcohol and  $\Sigma_6$ sterol  
441 concentrations were measured in St9-St11, followed by St15, St19 and St1 ([Fig. 3c, d](#)).

442 The prevalence of 16:0, 14:0, 18:1w9, 18:0 and 16:1w7 compounds for fatty acids, and  
443 of 16:0 and 14:0 compounds for fatty alcohols ([Table S2](#)) reflected the overall dominance of  
444 the carnivorous/omnivorous zooplankton ([Lee et al., 2006](#)). Nevertheless, some indicators  
445 allowed us to point out substantial differences between stations. Indeed, some phytoplankton  
446 (organisms or detrital matter) biomarkers, such as 16:1w7/18:1w9 and 16:1w7/16:0 fatty acid

447 ratios and the relative abundance of phytol among the fatty alcohols, were abundant at St4 and  
448 St17 (Fig. S2a-c). This could be related to the much higher contributions of phytoplankton  
449 and detritus found within the total biomass for the fractions 60-200 to 500-1000  $\mu\text{m}$  at these  
450 two stations (Fierro-González et al., 2023; Tesán-Onrubia et al., 2023). These phytoplankton  
451 biomarkers revealed more pronounced signatures of diatoms and/or organisms feeding on  
452 phytoplankton residues (Falk-Petersen et al., 1981, 1982; Sargent and Falk-Petersen, 1981;  
453 Tolosa et al., 2004). Zooplankton biomarkers were also used: the relative abundance of 22:1,  
454 20:5 and 22:6 fatty acids. The latter were higher in offshore stations, especially at St11 in the  
455 fraction 500-1000  $\mu\text{m}$ , and St15 (Fig. S3a-c). They could highlight together the presence of  
456 herbivorous zooplankton feeding on diatoms (Kates and Volcani, 1966; Harrington et al.,  
457 1970; Graeve 1993; Lee et al., 2006). Indeed, according to Fierro-González et al. (2023),  
458 there was a high % (in biomass) of large crustaceans which could be euphausiids, actually  
459 potential consumers of diatoms, in the fractions 500-100 and 1000-2000  $\mu\text{m}$  at St11 and St15.  
460 Moreover, according to the taxonomy results (M. Pagano personal communication), the % (in  
461 number) of herbivorous filter feeders (large calanides of the Calanus type) over the entire  
462 water column was the highest at these two stations, especially St11.

463       Among sterols, cholesterol (Cholest-5-en-3 $\beta$ -ol) was the dominant compound ( $63.5 \pm$   
464  $6.5\%$ ) followed by Cholesta-5,22E-dien-3 $\beta$ -ol ( $14.4 \pm 6.5\%$ ) (Table S2). These % are in  
465 agreement with previous values found in crustaceans from the Northern Adriatic Sea  
466 (Serrazanetti et al., 1989). The concentrations of cholesterol were low, in accordance with the  
467 overall low lipid content. This may be due not only to the composition of the zooplankton  
468 diet, but also to the absence in these organisms of biochemical mechanisms capable of  
469 converting into cholesterol some of the most diffused sterols in the marine environment  
470 (Serrazanetti et al., 1989).

471

### 472 **3.3. Hydrocarbons**

#### 473 **3.3.1. AH distribution**

474 In seawater, dissolved  $\Sigma_{28}\text{AH}$  concentrations varied from 18 ng L<sup>-1</sup> (St10) to 489 ng L<sup>-1</sup>  
475 (St1) (Fig. S4a; Table S3). The highest values were recorded at St1, St9, St11, and at the  
476 Tunisian coasts (St15-St19), and were associated with monomodal molecular profiles in the  
477 range *n*-C<sub>22</sub>-*n*-C<sub>36</sub> without predominance of odd over even carbon numbered *n*-alkanes, which  
478 reflected anthropogenic inputs from uncombusted oil-derived products (Fig. S4b)  
479 (Bouloubassi and Saliot, 1993; Wang et al., 1997). The lower concentrations recorded at St2-  
480 St4 and St10 were associated with bimodal molecular profiles exhibiting, in the range *n*-C<sub>24</sub>-  
481 *n*-C<sub>36</sub>, anthropogenic input residues, and in the range *n*-C<sub>15</sub>-*n*-C<sub>24</sub>, the peculiar abundance of  
482 *n*-C<sub>16</sub> and *n*-C<sub>18</sub> linked to microorganism contribution (bacteria, fungi, yeast) and their action  
483 on algal detritus (Fig. S4c) (Elias et al., 1997). These molecular profiles have been already  
484 observed in the dissolved phase of variably anthropogenic-stressed marine coastal areas  
485 (Guigue et al., 2014).

486 In the fraction 0.7-60  $\mu\text{m}$ ,  $\Sigma_{28}\text{AH}$  concentrations varied from 3.9  $\mu\text{g g}^{-1}$  dw (St9) to 104  
487  $\mu\text{g g}^{-1}$  dw (St11) (Fig. 4a; Table S4). The molecular profiles were dominated by *n*-C<sub>15</sub> and *n*-  
488 C<sub>17</sub> (Fig. 4b), indicative of phytoplanktonic contribution linked to high primary production  
489 (Blumer et al., 1971; Goutx and Saliot, 1980). Despite these predominant biological  
490 fingerprints, no correlation was found between *n*-C<sub>15</sub> or *n*-C<sub>17</sub> and TChl<sub>a</sub> concentrations ( $r = -$   
491 0.12 to 0.23,  $n = 19$ ,  $p > 0.05$ ). *n*-pentadecane (*n*-C<sub>15</sub>) has been shown to be produced by  
492 cyanobacteria, mainly in the lower euphotic zone, and rapidly consumed by heterotrophic  
493 prokaryotes in the ocean (Love et al., 2021). This could explain the absence of correlation  
494 between *n*-C<sub>15</sub> and TChl<sub>a</sub> concentrations.

495 In the fractions 60-200 to 500-1000  $\mu\text{m}$ ,  $\Sigma_{28}\text{AH}$  concentrations ranged from 3.4  $\mu\text{g g}^{-1}$   
496 dw (St17, 60-200  $\mu\text{m}$ ) to 55  $\mu\text{g g}^{-1}$  dw (St11, 500-1000  $\mu\text{m}$ ) (Fig. 4c; Table S4). While  $\Sigma_{28}\text{AH}$

497 concentrations in these three fractions were significantly positively correlated with each other  
498 ( $r = 0.62-0.88$ ,  $n = 9-10$ ,  $p < 0.05$ ), they were all weakly correlated with that of the fraction  
499  $0.7-60 \mu\text{m}$  ( $r = 0.24-0.64$ ,  $n = 9-10$ ,  $p < 0.05$  or  $> 0.05$ ). No significant difference was  
500 detected between the mean concentrations of the four fractions over the 10 stations (t-test,  $p >$   
501  $0.05$ ). Interestingly,  $\Sigma_{28}\text{AH}$  concentration was significantly positively correlated to  $\Sigma_{39}\text{lipid}$   
502 and POC concentrations only in the fraction  $60-200 \mu\text{m}$  ( $r = 0.62-0.65$ ,  $n = 10$ ,  $p < 0.05$ ).

503 Pristane was one of the main compounds within the low molecular weight range ( $< n-$   
504  $\text{C}_{22}$ ) (Fig. 4d; Table S4), which is in line with the presence of zooplankton, especially the  
505 dominance of copepods (Blumer et al., 1963). Indeed, the high values of pristane in the  
506 fractions  $200-500$  and  $500-1000 \mu\text{m}$  at St11 (Table S4) coincided with very high proportions  
507 of zooplankton (Fierro-González et al., 2023). Also, the abundance of  $n\text{-C}_{15}$  and  $n\text{-C}_{17}$   
508 revealed the presence of phytoplanktonic residues (Fig. 4d), although no significant  
509 correlation was observed with these two latter biomarkers and the 16:1w7 diatom biomarker  
510 ( $r = -0.28$  to  $0.16$ ,  $n = 29$ ,  $p > 0.05$ ) (Blumer et al., 1971). The high molecular weight  
511 compounds ( $> n\text{-C}_{22}$ ) displayed the predominance of odd over even carbon numbered  
512 compounds ( $n\text{-C}_{27}$ ,  $n\text{-C}_{29}$ ,  $n\text{-C}_{31}$ ,  $n\text{-C}_{33}$ ) (Fig. 4d; Table S4), illustrating the presence of  
513 terrigenous higher plant debris in the samples (Douglas and Eglinton, 1966). It is unlikely that  
514 these debris were ingested by the organisms. It seems more likely that they were part of some  
515 allochthonous detritus collected along with zooplankton as observed by imagery analyzes  
516 (Fierro-González et al., 2023). Moreover, a background series of  $n$ -alkanes with no  
517 predominance of odd over even compounds was visible and may originate from  
518 anthropogenic inputs with minor occurrence. These results (AH concentrations and their  
519 molecular profiles in plankton) are in good agreement with previous studies from neighboring  
520 areas (Serrazanetti et al., 1989, 1991; Salas et al., 2006).

521 This class of compounds is very useful to better assess the sources of hydrocarbons in  
522 planktonic organisms. Nevertheless, the dominance of biogenic signatures observed here  
523 makes AH biomarkers not very explanatory in the study of the bioaccumulation of  
524 hydrocarbons.

525

### 526 **3.3.2 PAH distribution**

527 In seawater, the dissolved  $\Sigma_{14}$ PAH concentrations ranged from 0.9 ng L<sup>-1</sup> (St11) to 16  
528 ng L<sup>-1</sup> (St4) (Fig. S5a; Table S5). The concentrations were quite low (< 5 ng L<sup>-1</sup>) and the  
529 methylated derivatives were not really identifiable, except at St4 (Fig. S5b, c). At this station,  
530 the concentration reached 16 ng L<sup>-1</sup> due to significant inputs of C1-, C2- and C3-Nap (Fig.  
531 S5c). The 2-3 ring PAHs were the major compounds representing  $71 \pm 16\%$  of the total  
532 PAHs, which is in accordance with their lower hydrophobicity (Fig. S5b, c; Table S5). The  
533 quite low levels of concentrations along with the highly altered methylated derivatives at  
534 almost all sites reflected remote or aged (weathered/photo- and bio-degraded) inputs, except  
535 at St4, where local and recent moderate petrogenic inputs were suspected (Wang and Fingas,  
536 1995; Chifflet et al., 2023).

537 In the fraction 0.7-60  $\mu\text{m}$ , the  $\Sigma_{27}$ PAH concentrations ranged from 53 ng g<sup>-1</sup> dw (St9) to  
538 ~ 220 ng g<sup>-1</sup> dw (St3 and St11) (Fig. 5a; Table S6). The PAH profiles in the fraction 0.7-60  
539  $\mu\text{m}$  (Fig. 5b) were different from those found in water (Fig. S5b, c), the 2-3 ring PAHs being  
540 less abundant ( $49 \pm 9\%$  of total PAHs) and the 4-6 ring PAHs more abundant (Fig. 5b), which  
541 is consistent with previous studies on particles in the Mediterranean Sea (Dachs et al., 1997;  
542 Marti et al., 2001). However, as for PAHs in water (Fig. S5b, c), the methylated derivatives  
543 were not well visible in this fraction and suspected to be highly degraded. Hence, the PAH  
544 profiles in the fraction 0.7-60  $\mu\text{m}$  might be explained by a high microbial degradation which  
545 rather affected LMW PAHs, especially methylated derivatives (Lipiatou et al., 1993; Dachs et

546 [al., 1997](#)). Another explanation could be inputs of atmospheric aerosols or from sediments  
547 ([Chifflet et al., 2023](#)), which are important sources of pyrogenic PAHs (HMW PAHs with a  
548 low proportion of methylated derivatives) ([Lipiatou et al., 1997](#)), but the lack of 5-6 ring  
549 compounds suggests that these inputs were minor.

550 In the fractions 60-200 to 500-1000  $\mu\text{m}$ , the  $\Sigma_{27}\text{PAH}$  concentrations ranged from 35 ng  
551  $\text{g}^{-1}$  dw (St19, 200-500  $\mu\text{m}$ ) to 255 ng  $\text{g}^{-1}$  dw (St1, 60-200  $\mu\text{m}$ ) ([Fig. 5c](#); [Table S6](#)). The lowest  
552  $\Sigma_{27}\text{PAH}$  concentrations were found at St9, St17 and St19 ([Fig. 5c](#)). Two of them, St9 and  
553 St19, showed the highest TChl*a* concentrations. These two stations displayed a particular  
554 biogeochemical context with regard to the other stations, as explained in [section 3.1](#).  $\Sigma_{27}\text{PAH}$   
555 concentrations in these three fractions were rather well positively correlated with each other ( $r$   
556 = 0.50-0.73,  $n = 9-10$ ,  $p < 0.05$  or  $> 0.05$ ), but not significantly correlated with that in the  
557 fraction 0.7-60  $\mu\text{m}$  ( $r = 0.14-0.55$ ,  $n = 9-10$ ,  $p > 0.05$ ). The mean  $\Sigma_{27}\text{PAH}$  concentration of the  
558 fraction 60-200  $\mu\text{m}$  was significantly higher than those of the fractions 200-500 and 500-1000  
559  $\mu\text{m}$  ([Fig. 5c](#)) (t-test,  $p < 0.05$ ).  $\Sigma_{27}\text{PAH}$  concentration was significantly positively correlated to  
560  $\Sigma_{28}\text{AH}$  concentration only in the fraction 0.7-60  $\mu\text{m}$  ( $r = 0.84$ ,  $n = 10$ ,  $p < 0.05$ ), while  
561  $\Sigma_{27}\text{PAH}$  concentrations were not correlated with  $\Sigma_{39}\text{lipid}$  and POC concentrations whatever  
562 the size fraction. The PAH molecular profiles in the three fractions, i.e., dominance ( $80 \pm$   
563 12%) of the 2-3 ring compounds (parents and methylated), especially Phe, and very low  
564 abundance of the 4-6 ring compounds ([Fig. 5d](#)), were in agreement with those reported by  
565 [Salas et al. \(2006\)](#) and [Berrojalbiz et al. \(2011\)](#).

566

#### 567 **3.4. Comparison of plankton PAH concentrations and biological pump** 568 **fluxes of PAHs**

569 It is important to note that comparisons of our concentrations/fluxes of PAHs and  
570 individual Phe (the dominant PAH in our study and also in most of previously works) with



571 those reported in the literature should be taken with caution since the methodologies for  
572 sampling/separations of planktonic fractions, the planktonic size fractions, analyzes of PAHs  
573 and the number of PAHs analyzed are not the same. Despite these limitations, these  
574 comparisons still allow us to situate our data in relation to those obtained formerly.

575 The  $\Sigma_{27}$ PAH and Phe concentrations in plankton we determined here in the Western  
576 Mediterranean Sea were globally lower than those measured in the Western and Eastern  
577 Mediterranean Sea (Berrojalbiz et al., 2011), and in the Atlantic, Pacific and Indian Oceans  
578 (González-Gaya et al., 2019), when taking into account maximal and mean values (see data in  
579 Table 1). Salas et al. (2006) also found higher concentrations in the Galician coast (NW  
580 Spain) after the Prestige oil spill (353-2035 ng g<sup>-1</sup> dw; not reported in Table 1). However,  
581 when considering minimal and median values, our  $\Sigma_{27}$ PAH concentrations were very close to  
582 those of other oceanic areas, and our Phe concentrations were even slightly higher (Table 1).

583 From the vertical settling flux of POC (in Table 1) and OC-normalized PAH  
584 concentrations (not in Table 1), we estimated the biological pump fluxes of  $\Sigma_{27}$ PAHs and Phe  
585 below 100-m depth in the Western Mediterranean Sea at  $15 \pm 10$  and  $4 \pm 2$  ng m<sup>-2</sup> day<sup>-1</sup>,  
586 respectively (Table 1). González-Gaya et al. (2019) found mean biological pump fluxes of  
587  $\Sigma_{64}$ PAHs and Phe below the surface mixed layer depth of 172 and 23 ng m<sup>-2</sup> day<sup>-1</sup> in the North  
588 Atlantic, 91 and 6 ng m<sup>-2</sup> day<sup>-1</sup> in the South Atlantic, 55 and 7 ng m<sup>-2</sup> day<sup>-1</sup> in the North  
589 Pacific, 14 and 1 ng m<sup>-2</sup> day<sup>-1</sup> in the South Pacific, and 22 and 2 ng m<sup>-2</sup> day<sup>-1</sup> in the Indian  
590 Ocean (Table 1). Therefore, our biological pump fluxes were lower than those in the Atlantic  
591 and North Pacific but comparable to those in the South Pacific and Indian Ocean. From our  
592 results, the annual biological pump flux of  $\Sigma_{27}$ PAHs for the whole Western Mediterranean Sea  
593 would be of  $5274 \pm 3467$  kg yr<sup>-1</sup>.

594

595 **3.5. Concentration patterns and bioaccumulation of PAHs within plankton**

596 It is important to note that only seven parent PAHs (Nap, Flu, Phe, Flt, Pyr, BaA and  
597 Chr) were found both in water and all particulate/planktonic size fractions (Table S7). They  
598 were thus selected to investigate the concentration patterns and bioaccumulation of PAHs  
599 within plankton (see below).

### 600 **3.5.1. Concentration pattern with the size fraction and trophic level**

601 The concentrations of  $\Sigma_7$ PAHs and  $\Sigma_6$ PAHs (without Phe) significantly decreased from  
602 the fractions 0.7-60 or 60-200  $\mu\text{m}$  to the fractions 200-500 or 500-1000  $\mu\text{m}$  (t-test,  $p < 0.05$ )  
603 (Fig. 6a, b), highlighting the bioreduction process of PAHs within the planktonic food web,  
604 i.e., decreasing concentration with increasing organism size/trophic level. The fact that the  
605 highest concentrations were found in the smallest fraction (0.7-60  $\mu\text{m}$ ) is in agreement with  
606 recent observations (Berroralbiz et al., 2011; Tao et al., 2018; González-Gaya et al., 2019)  
607 and related to the strong capacity of small cells to bioaccumulate contaminants due to their  
608 high surface/volume ratio (Fan and Reinfelder, 2003; Heimbürger et al., 2010; Chauvelon et  
609 al., 2019). Fig. 7 shows the concentrations in relation with the trophic levels, given by  $\delta^{13}\text{C}$   
610 and  $\delta^{15}\text{N}$ . It appears that the fraction 0.7-60  $\mu\text{m}$  was trophically decoupled from the three  
611 other ones. In other words, the bioaccumulation of PAHs in the upper 60-200- $\mu\text{m}$  fraction  
612 would not take place by trophic transfer from the 0.7-60- $\mu\text{m}$  fraction but rather by water.  
613 Then, considering the trophic proximity between the fractions 60-200, 200-500 and 500-1000  
614  $\mu\text{m}$ , it is possible that besides transfer from water, the PAHs were also transferred by  
615 ingestion/diet between these three fractions (Fig. 7a, b). The overall bioreduction observed  
616 along the planktonic food web would be due to the fact that when going up in the trophic  
617 levels, even if there was trophic transfer of PAHs, the processes of absorption directly by the  
618 water would have been less and less effective and the removal processes of PAHs (such as  
619 depuration or metabolization) likely more effective, which ultimately would have led to this  
620 decrease of PAH concentrations within the planktonic food web.

621 Phe presented a different pattern from the other compounds, with the highest  
622 concentrations mainly found in the fraction 60-200  $\mu\text{m}$  (Fig. 6c; Fig. 7c). Phe was the most  
623 abundant compound representing for all sites 14, 51, 48 and 41% of  $\Sigma_7\text{PAHs}$  in the fractions  
624 0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$ , respectively. Berrojalbiz et al. (2011) also  
625 reported Phe (and alkylated homologues) as dominant compound in particles and plankton  
626 along a West-East transect in the Mediterranean Sea. In the present work, the peculiar Phe  
627 bioaccumulation in the fraction 60-200  $\mu\text{m}$ , systematically observed at all stations (see Table  
628 S6), is intriguing. It could originate from a biogenic production within the collected plankton,  
629 as already suggested by Nizzetto et al. (2008). However, since there were no correlations  
630 between Phe concentrations, neither with POC, TChl $a$ , nor lipids (in both fractions 0.7-60 and  
631 60-200  $\mu\text{m}$ ) ( $r = -0.33$  to  $-0.04$ ,  $n = 20$ ,  $p > 0.05$ ), this suggests that even if this process had  
632 occurred, it would have been minor and hidden within the complex dynamics of Phe in  
633 plankton. Another explanation for the Phe bioaccumulation in the 60-200- $\mu\text{m}$  fraction could  
634 be that this compound was less subjected to depuration/metabolization processes than the  
635 other compounds and than in the other fractions.

636

### 637 **3.5.2. Water-OC partitioning and influence of biomass**

638 For each fraction at each station, the water-particulate matter coefficients ( $K_D$  in  $\text{L kg}^{-1}$ ),  
639 then the water-organic carbon partition coefficients ( $K_{OC}$  in  $\text{L kg}^{-1}$ ) were calculated for the 7  
640 targeted PAHs (Tables S7-S9). It should be noticed that  $K_D$  and  $K_{OC}$  values were determined  
641 using dissolved PAH concentrations measured in surface waters (at  $\sim 5$ -20-m depth  
642 depending on stations) and particulate/plankton PAH concentrations measured in the DCM (at  
643  $\sim 20$ -60 depth depending on the stations). Despite these depth discrepancies, and the possible  
644 differences in the dissolved PAH concentrations between surface waters and the DCM, the  
645 use of  $K_{OC}$  as determined here remains very likely more suitable and reflects the PAH

646 biogeochemistry much better than the use of  $K_{OW}$  that are theoretical values provided under  
647 partition equilibrium conditions (these equilibrium conditions certainly did not prevail in the  
648 water at the time of sampling). Consistent with the concentration patterns,  $\text{Log } K_{OC}$  values  
649 clearly decreased with the size fractions, which confirms the higher PAH bioaccumulation in  
650 the smaller size fractions (Fig. 8a). Moreover, for each individual compound and each station,  
651 the PAH concentrations in size fractions ( $\text{ng g}^{-1} \text{ dw}$ ) were plotted against the plankton  
652 biomass concentrations ( $\text{mg dw L}^{-1}$ ). For most of PAHs and size fractions (except 500-1000  
653  $\mu\text{m}$ ), the concentrations decreased with biomass, following a power function equation  $[\text{PAH}]$   
654  $= a[\text{Biomass}]^{-m}$  (Fig. 8b; Table S10), reinforcing the results presented above (Fig. 6, 7). This  
655 highlights the biodilution process, which reflects the decrease in PAH concentrations with  
656 plankton biomass (Berrojalbiz et al., 2011; Nizzetto et al., 2012; Everaert et al., 2015;  
657 Morales et al., 2015; Ding et al., 2021).

658 The  $-m$  slope values originating from the power function equations were further  
659 examined because they are indicative of the influence level of the SPM or biomass load on the  
660 PAH concentration (Berrojalbiz et al., 2011). As for  $\text{Log } K_{OC}$ , the  $-m$  values noticeably  
661 decreased with the size fraction (Fig. 8b), which illustrates once again the more important role  
662 of the smaller fractions in the bioaccumulation of PAH, as well as the biodilution process.  
663 These  $m$  values were then plotted against  $\text{Log } K_{OC}$ . Finally, a positive significant relationship  
664 was found between “ $-m$ ” and the  $\text{Log } K_{OC}$  for the 7 PAHs and the different size fractions (0.7-  
665 60 to 500-1000  $\mu\text{m}$ , as well as 60-1000  $\mu\text{m}$ ) (Fig. S6; Table S11). Such a linear relationship  
666 highlighted the strong link between the PAH bioaccumulation and the impact of the  
667 planktonic biomass on the PAH concentrations in plankton, implying also the biological  
668 pump process for the PAHs. González-Gaya et al. (2019) observed the same type of  
669 relationship between  $-m$  slope and  $\text{Log } K_{OW}$ . Tao et al. (2018) also reported a decrease in the  
670 PAH concentration along with phyto- and zooplankton biomass, but without any obvious

671 linear relationship between Log  $K_{ow}$  et -m. The present results show that through the  
672 bioaccumulation process, the plankton, and in particular its smallest fractions, plays a key role  
673 in the PAH cycling in the Mediterranean Sea. Besides, biotransformation/degradation is  
674 another essential fate for PAHs in the ocean. This biological reworking has already been  
675 reported by [González-Gaya et al. \(2019\)](#), who observed a linear negative relationship between  
676 Log  $K_{ow}$  and -m for some LMW PAHs. In our study, the biological removal was very likely  
677 present, especially in the fraction 60-200  $\mu\text{m}$ , for which we also found a negative linear  
678 relationship between Log  $K_{oc}$  et -m for the LMW HAPs, as well as the low abundance of  
679 methylated derivatives.

680

#### 681 **4. Conclusion**

682

683 In this study, we determined the hydrocarbon (AH and PAH) content in water and size-  
684 fractionated plankton to help characterizing the bioaccumulation of these compounds at the  
685 water-plankton interface in the Western Mediterranean Sea. Zooplankton was mainly  
686 composed of copepods and its low lipid content was in accordance with the oligotrophic  
687 character of the Mediterranean waters, along with poor seasonality of food supply for  
688 plankton. Concerning AHs, anthropogenic inputs were recorded in water at all sites, even  
689 though these inputs were masked in plankton by major biogenic signatures. Regarding PAHs,  
690 profiles in water and in the 0.7-60- $\mu\text{m}$  size fraction were quite similar but distinct from those  
691 in zooplankton, highlighting differences in the bioaccumulation processes. The peculiar  
692 bioaccumulation of Phe in the 60-200  $\mu\text{m}$  is intriguing and could be related to reduced  
693 metabolization/depuration processes. We also demonstrate the strong PAH bioaccumulation  
694 in the 0.7-60- $\mu\text{m}$  fraction (relative to water), followed by a limited transfer to higher size  
695 fractions, ultimately underscoring a bioreduction process along the planktonic food web.

696 Furthermore, the biodilution process (the decrease in concentration at higher SPM/biomass)  
697 was evidenced for the fractions 0.7-60 and 60-200  $\mu\text{m}$ . Finally, our results point out the key  
698 role of the smallest size fractions of plankton in the PAH cycling in the Mediterranean Sea.

699

## 700 **Data availability**

701 All data from this paper is stored in the MISTRALS-SEDOO database  
702 (<https://mistrals.sedoo.fr/MERITE/>) and will be made publicly accessible once all the articles  
703 related to the MERITE-HIPPOCAMPE cruise are published. In the meantime, data can be  
704 obtained upon request from the corresponding author.

705

## 706 **Author contribution statement**

707 All the authors participated in the MERITE-HIPPOCAMPE project and design of the  
708 manuscript.

709 *Conception and design of study:* C.G., J.A.T.-O., D.B., F.C., M.P., S.C., J.T., M.T.

710 *Acquisition of data:* C.G., J.A.T.-O., L.G., D.B., F.C., M.P., S.C., D.M., L.C., M.T.

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717

## 718 **Acknowledgments**

719 The MERITE-HIPPOCAMPE project was initiated and funded by the cross-disciplinary  
720 *Pollution & Contaminants* axis of the CNRS-INSU MISTRALS program (joint action of the

721 MERMEX-MERITE and CHARMEX subprograms). The project also received financial  
722 support from the IRD French-Tunisian International Joint Laboratory (LMI) COSYS-Med.  
723 The MERITE-HIPPOCAMPE cruise was organized and supported by the French  
724 Oceanographic Fleet (FOF), CNRS/INSU, IFREMER, IRD, the Tunisian Ministry of  
725 Agriculture, Water Resources and Fisheries, and the Tunisian Ministry of Higher Education  
726 and Scientific Research. The project also benefited from additional funding by IFREMER, by  
727 the MIO Action Sud and Transverse Axis programs (CONTAM Transverse Axis), by the IRD  
728 Ocean Department, and by the CONTAMPUMP project (ANR JCJC #19-CE34-0001-01). We  
729 are grateful to the captains and crew of the R/V *Antea* for their help and assistance during the  
730 cruise. Various MIO platforms also provided valuable support: the Service Atmosphère-Mer  
731 (SAM), the Plateforme Analytique de Chimie des Environnements Marins (PACEM platform)  
732 and the Plateforme Microscopie et Imagerie (MIM platform). We warmly thank J.-F. Rontani  
733 for his expertise on lipid biomarkers. Finally, we acknowledge two Reviewers for their  
734 relevant and helpful comments.

735

### 736 **Supplementary information**

737       Supplementary material related to this article is available online at: xxx

738

739

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## 1127 **Figure caption**

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1129 **Figure 1. a)** Location of the ten stations (black circles) investigated during the MERITE-  
1130 HIPPOCAMPE cruise (13 April-14 May 2019) along a North-South transect in the  
1131 Mediterranean Sea on board the R/V *Antea*, and **b)** cruise track with the position of the  
1132 stations. St2, St4, St3, St10 and St11 were sampled during leg 1 (13-28 April; from La Seyne-  
1133 sur-Mer to Tunis), whereas St15, St17, St19, St9 and St1 were sampled during leg 2 (30  
1134 April-14 May; from Tunis to Gulf of Gabès, and then return to La Seyne-sur-Mer). See the  
1135 detailed description of stations in [Tedetti et al. \(2023\)](#).

1136

1137 **Figure 2. a)** Concentrations of total chlorophyll *a* (TChl*a*, in  $\mu\text{g L}^{-1}$ ), suspended particulate  
1138 matter (SPM, in  $\text{mg L}^{-1}$ ) and particulate organic carbon (POC, in  $\text{mg L}^{-1}$ ) in the size fraction  
1139 0.7-60  $\mu\text{m}$ , **b)** total biomass (in  $\mu\text{g dw L}^{-1}$ ) (see [Fierro-González et al., 2023](#), this cumulates  
1140 phytoplankton, zooplankton and detritus biomasses), and **c)** concentration of POC (in  $\text{mg g}^{-1}$   
1141 dw) in the planktonic size fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$ , sampled at the deep  
1142 chlorophyll maximum (DCM). All measurements are presented for the 10 stations. For POC,  
1143 sample St17 500-1000  $\mu\text{m}$  is not available.

1144  
1145 **Figure 3.** Concentrations of total lipid biomarkers (in  $\text{mg g}^{-1}$  dw) in the planktonic size  
1146 fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$  recovered from the deep chlorophyll maximum  
1147 (DCM) at the 10 stations: **a)**  $\Sigma_{39}$ lipids (=  $\Sigma_{25}$ fatty acids +  $\Sigma_8$ fatty alcohols +  $\Sigma_6$ sterols), **b)**  
1148  $\Sigma_{25}$ fatty acids, **c)**  $\Sigma_8$ fatty alcohols and **d)**  $\Sigma_6$ sterols. Sample St17 500-1000  $\mu\text{m}$  is not available.

1149  
1150 **Figure 4.** Concentrations of total aliphatic hydrocarbons ( $\Sigma_{28}$ AHs, in  $\mu\text{g g}^{-1}$  dw) in the  
1151 particulate/planktonic size fractions **a)** 0.7-60  $\mu\text{m}$  and **c)** 60-200, 200-500 and 500-1000  $\mu\text{m}$ ,  
1152 recovered from the deep chlorophyll maximum (DCM) at the 10 stations, and mean relative  
1153 abundances of individual AHs (in %) for the 10 stations in the fractions **b)** 0.7-60  $\mu\text{m}$  and **d)**  
1154 60-200, 200-500 and 500-1000  $\mu\text{m}$ .  $\Sigma_{28}$ AHs =  $\Sigma n\text{-C}_{15-n}\text{-C}_{40}$ , Pr, Phy (28 compounds).

1155  
1156 **Figure 5.** Concentrations of total polycyclic aromatic hydrocarbons ( $\Sigma_{27}$ PAHs, in  $\text{ng g}^{-1}$  dw)  
1157 in the particulate/planktonic size fractions **a)** 0.7-60  $\mu\text{m}$  and **c)** 60-200, 200-500 and 500-1000  
1158  $\mu\text{m}$ , recovered from the deep chlorophyll maximum (DCM) at the 10 stations, and mean  
1159 relative abundances of individual PAHs (in %) for the 10 stations in the fractions **b)** 0.7-60  
1160  $\mu\text{m}$  and **d)** 60-200, 200-500 and 500-1000  $\mu\text{m}$ .  $\Sigma_{27}$ PAHs =  $\Sigma$  Nap–BP (27 compounds).

1161



1162 **Figure 6.** Concentrations (in  $\text{ng g}^{-1}$  dw) of **a)**  $\Sigma_7\text{PAHs}$  (= Nap + Flu + Phe + Flt + Pyr + BaA  
1163 + Chr), **b)**  $\Sigma_6\text{PAHs}$  (= Nap + Flu + Flt + Pyr + BaA + Chr), and **c)** Phe, for all 10 stations in  
1164 the particulate/planktonic size fractions 0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$  recovered  
1165 from the deep chlorophyll maximum (DCM). Letters **a)** and **b)** indicate significant differences  
1166 between the means of the distributions (t-test;  $p < 0.05$ ).

1167

1168 **Figure 7.** Concentrations (in  $\text{ng g}^{-1}$  dw) of **a)**  $\Sigma_7\text{PAHs}$  (= Nap + Flu + Phe + Flt + Pyr + BaA  
1169 + Chr), **b)**  $\Sigma_6\text{PAHs}$  (= Nap + Flu + Flt + Pyr + BaA + Chr), and **c)** Phe, with regard to the C  
1170 and N isotopic ratios ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , in ‰) for all 10 stations in the particulate/planktonic  
1171 size fractions 0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$  recovered from the deep chlorophyll  
1172 maximum (DCM).

1173

1174 **Figure 8.** Distribution of **a)** Log  $K_{\text{OC}}$  and **b)** slope value (-m) in the particulate/planktonic size  
1175 fractions 0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$  recovered from the deep chlorophyll  
1176 maximum (DCM). The letters **a)**, **b)** and **c)** indicate significant differences between the means  
1177 of the distributions (t-test;  $p < 0.05$ ). Log  $K_{\text{OC}}$  and -m were determined in each fraction, at the  
1178 10 stations, for each of the 7 PAHs (Nap, Flu, Phe, Flt, Pyr, BaA, Chr). For each size fraction,  
1179 the value m is the slope of the regression (power function) between the SPM/biomass  
1180 concentration (in  $\text{mg L}^{-1}$  dw) and the concentration of the given PAH (in  $\text{ng g}^{-1}$  dw) for the 10  
1181 stations. Examples of SPM/biomass *versus* PAH power relationships and associated -m values  
1182 are presented for Phe for each size fraction. The detailed regression parameters of the power  
1183 functions for the 7 PAHs, including m values, are found in [Table S10](#).

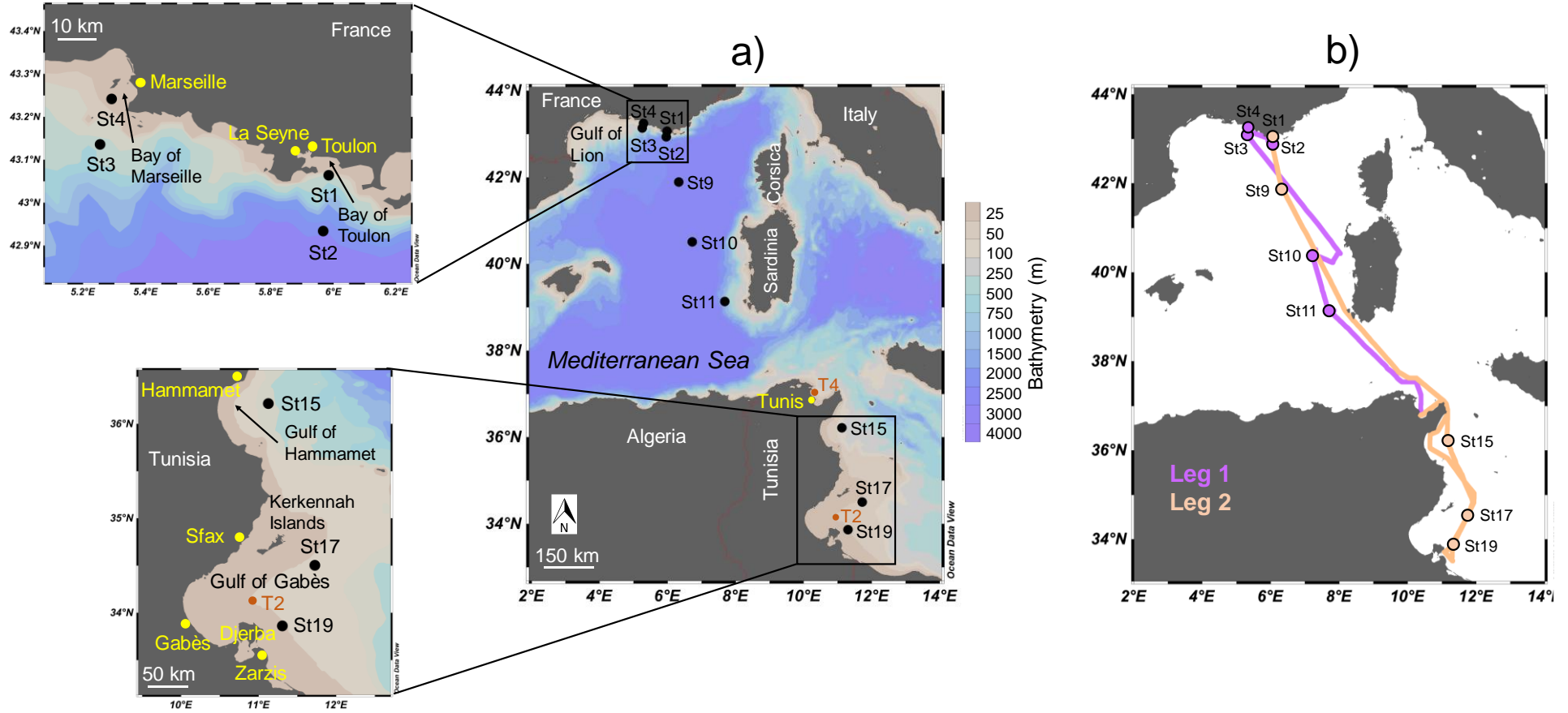
1184 **Table 1.** Comparison of plankton PAH concentrations and biological pump fluxes of PAHs determined here for the Western Mediterranean Sea  
 1185 (over our ten stations) with those reported previously in the same and other oceanic areas. We present the data for total PAHs (sum of individual  
 1186 compounds) and individual phenanthrene.  
 1187

		This study <sup>a, b</sup>	Berrojalbiz et al. (2011) <sup>c, d</sup>	González-Gaya et al. (2019) <sup>d, e</sup>				
		Western Med. Sea	Western and Eastern Med. Sea	North Atlantic	South Atlantic	North Pacific	South Pacific	Indian Ocean
Plankton total PAH concentration (ng g <sup>-1</sup> dw)	Min	40	57	18	13	11	40	15
	Max	163	1903	790	1300	7700	360	440
	Median	102	na	180	88	37	110	45
	Mean ± SD	96 ± 41	na	250 ± 230	280 ± 350	590 ± 2000	140 ± 120	130 ± 130
Plankton Phe concentration (ng g <sup>-1</sup> dw)	Min	12	9	2	1	1	5	2
	Max	39	235	120	120	1035	33	59
	Median	26	na	8	7	4	8	6
	Mean ± SD	25 ± 10	77 ± na	30 ± 39	18 ± 28	78 ± 280	11 ± 11	13 ± 15
POC vertical flux (mg C m <sup>-2</sup> day <sup>-1</sup> )	Mean	27 <sup>f</sup>	na	39 <sup>g</sup>	37 <sup>g</sup>	57 <sup>g</sup>	58 <sup>g</sup>	46 <sup>g</sup>
Biological pump flux of total PAHs (ng m <sup>-2</sup> day <sup>-1</sup> )	Min	5	na	na	na	na	na	na
	Max	39	na	na	na	na	na	na
	Median	15	na	na	na	na	na	na
	Mean ± SD	15 ± 10	na	172 ± na	91 ± na	55 ± na	14 ± na	22 ± na
Biological pump flux of Phe (ng m <sup>-2</sup> day <sup>-1</sup> )	Min	1	na	na	na	na	na	na
	Max	7	na	na	na	na	na	na
	Median	4	na	na	na	na	na	na
	Mean ± SD	4 ± 2	na	23 ± na	6 ± na	7 ± na	1 ± na	2 ± na

1188 *na*: not available; Phe: phenanthrene; POC: particulate organic carbon; <sup>a</sup> Total PAHs = sum of 27 compounds ( $\Sigma_{27}$ PAHs); <sup>b</sup> The plankton fraction corresponds  
 1189 to the size fraction 60-1000  $\mu$ m; <sup>c</sup> Total PAHs = sum of 19 compounds ( $\Sigma_{19}$ PAHs); <sup>d</sup> The plankton fraction corresponds to the size fraction > 50  $\mu$ m; <sup>e</sup> Total  
 1190 PAHs = sum of 64 compounds ( $\Sigma_{64}$ PAHs); <sup>f</sup> Vertical settling flux of POC below 100-m depth for the western Mediterranean Sea estimated by [Guyennon et al. \(2015\)](#),  
 1191 where POC is defined as being fueled by the natural mortality of the largest organisms (mesozooplankton, diatoms and ciliates) and by the excretion of  
 1192 fecal pellets and sloppy feeding by mesozooplankton; <sup>g</sup> Vertical settling flux of POC from the surface mixed layer due to phytoplankton and to zooplankton-  
 1193 associated pellets estimated from [Siegel et al. \(2014\)](#)'s global climatology.

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Figure 1

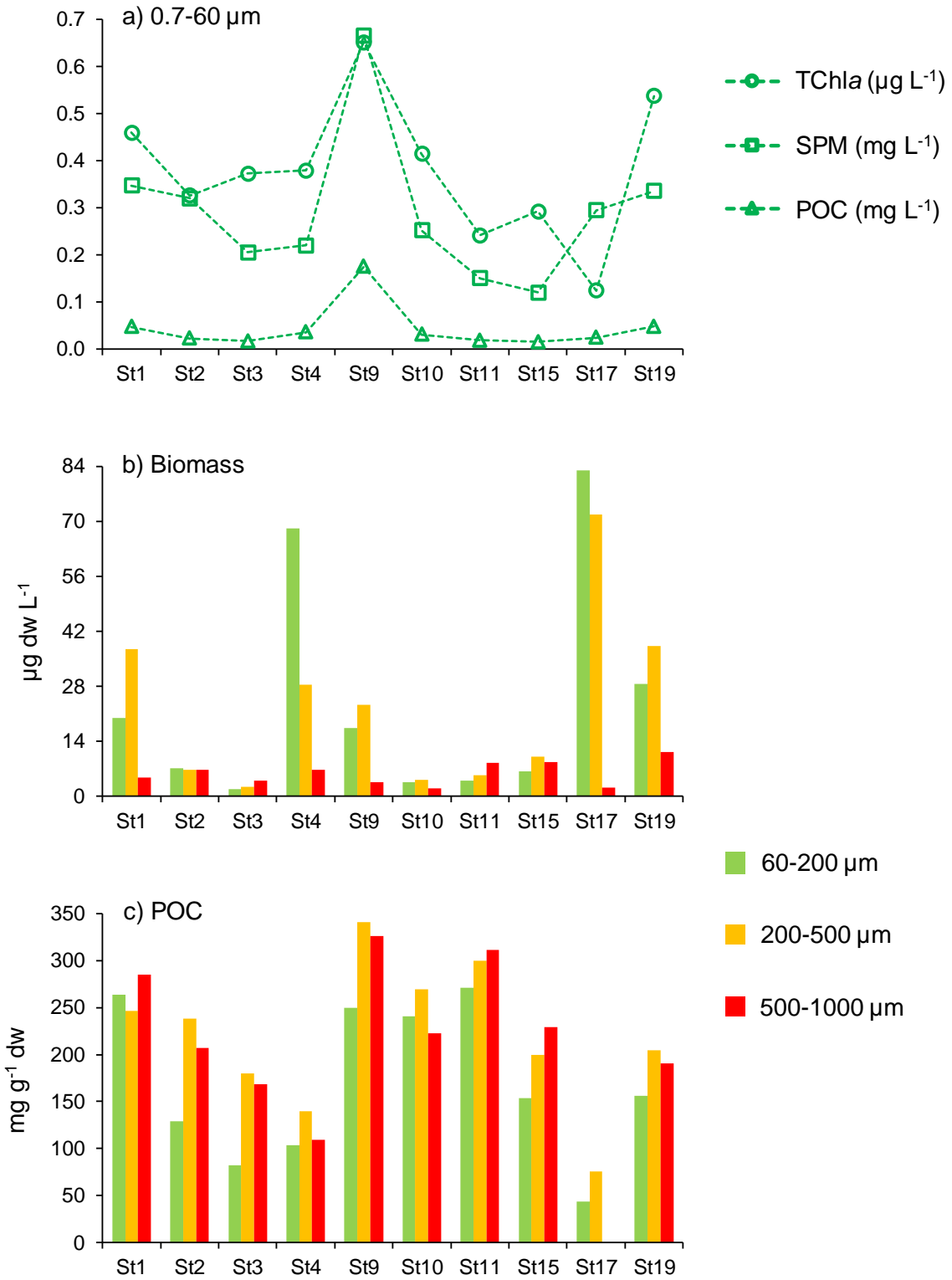


Figure 2

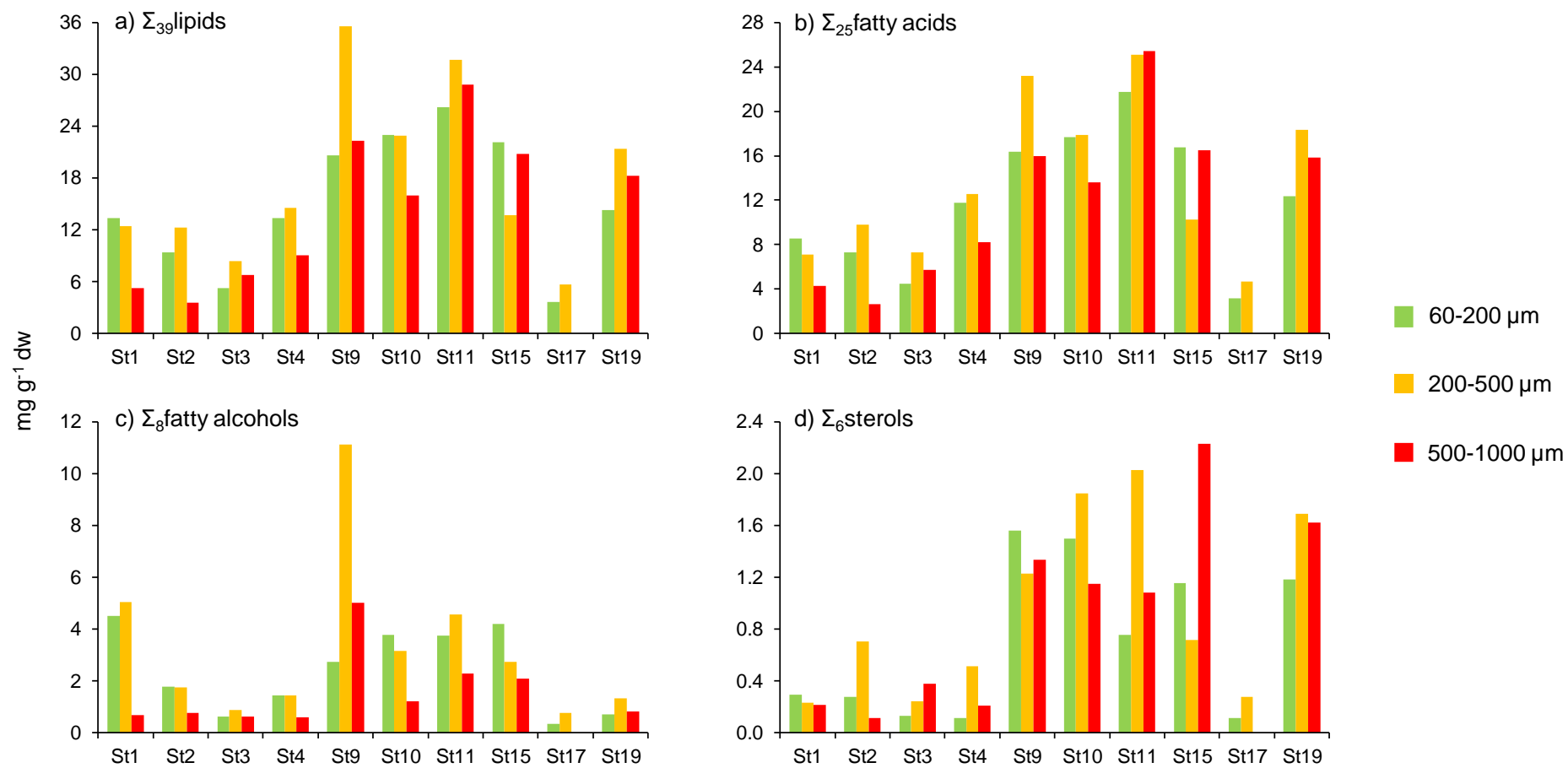


Figure 3

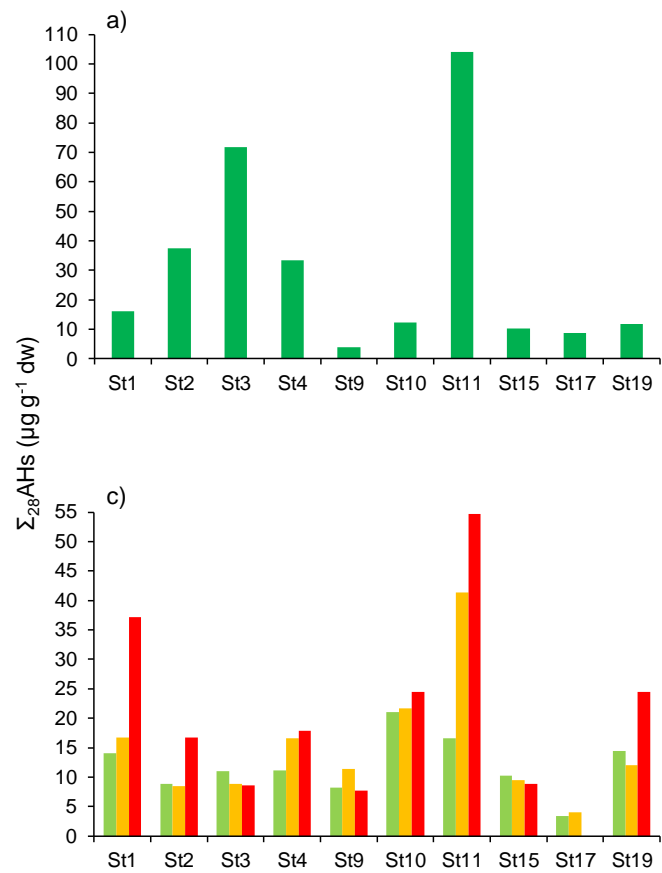


Figure 4

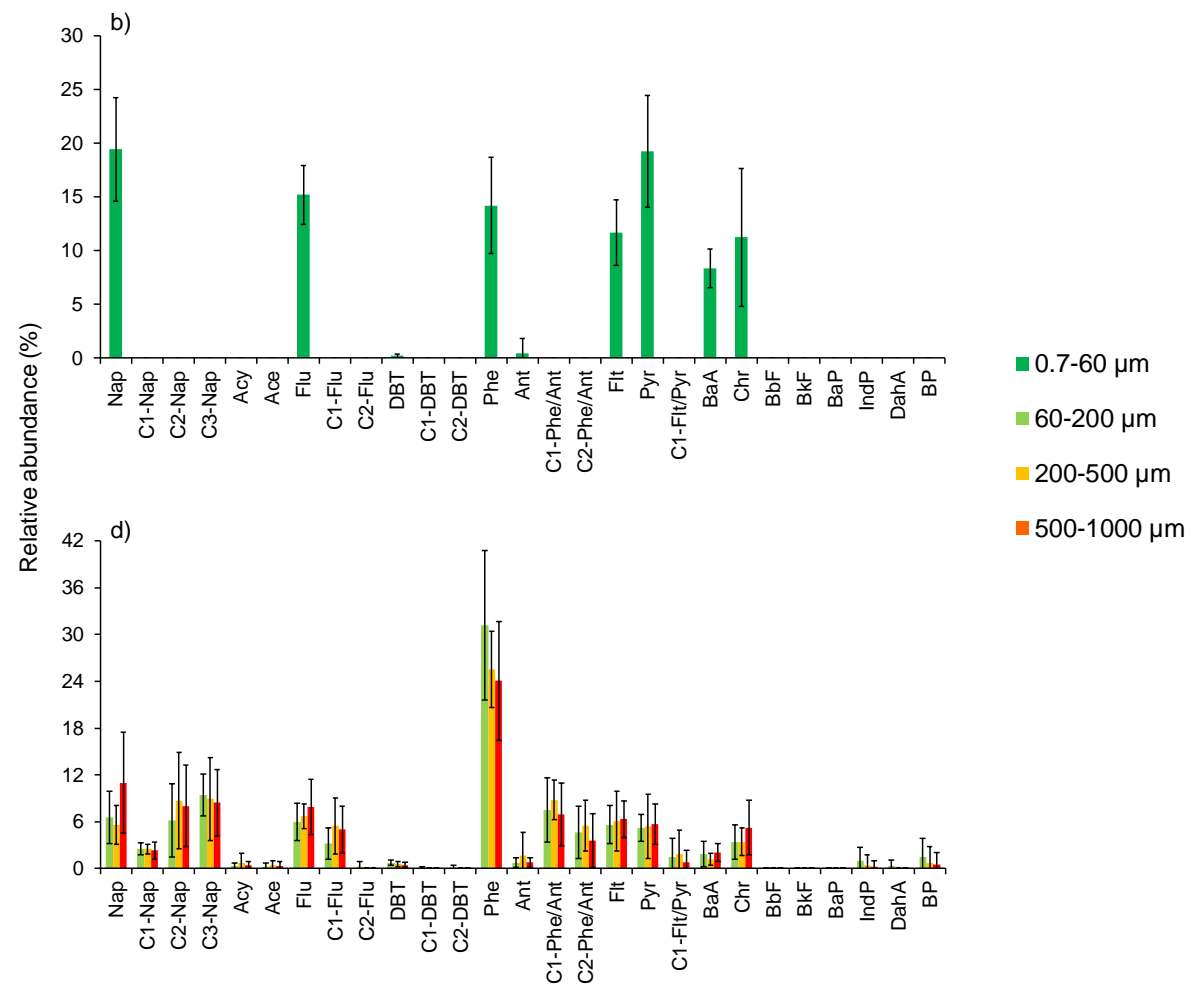
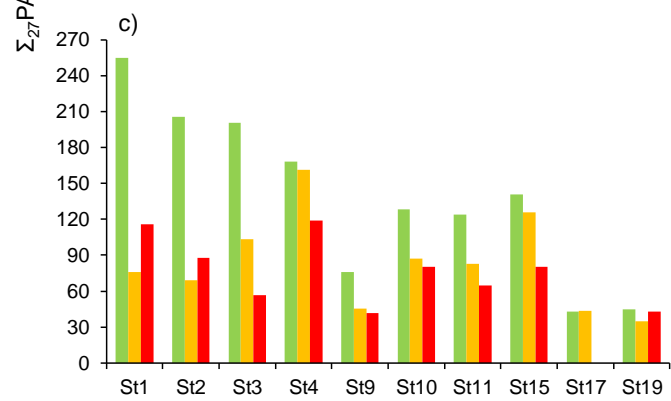
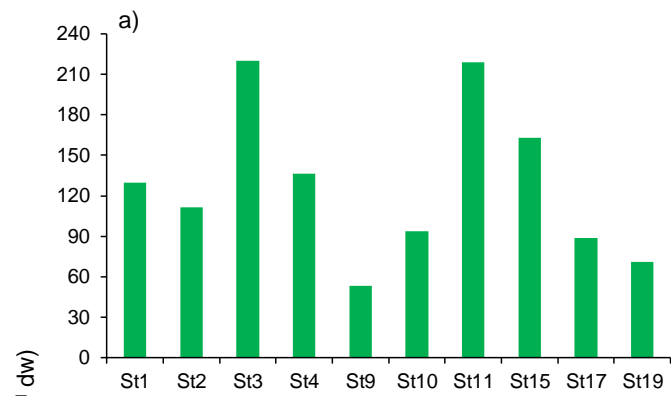


Figure 5

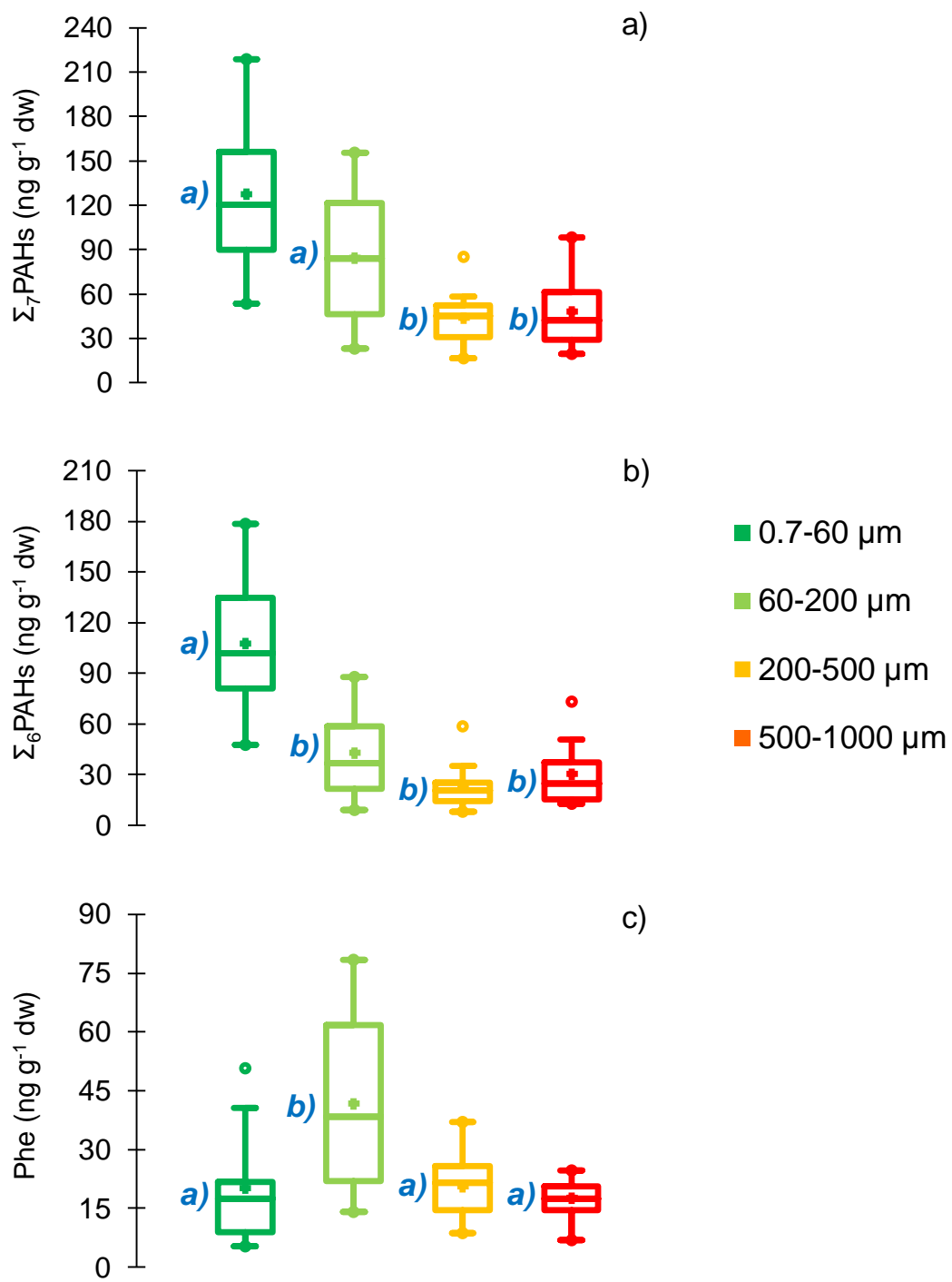
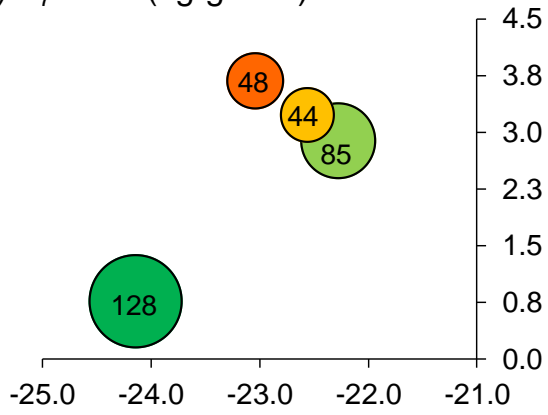


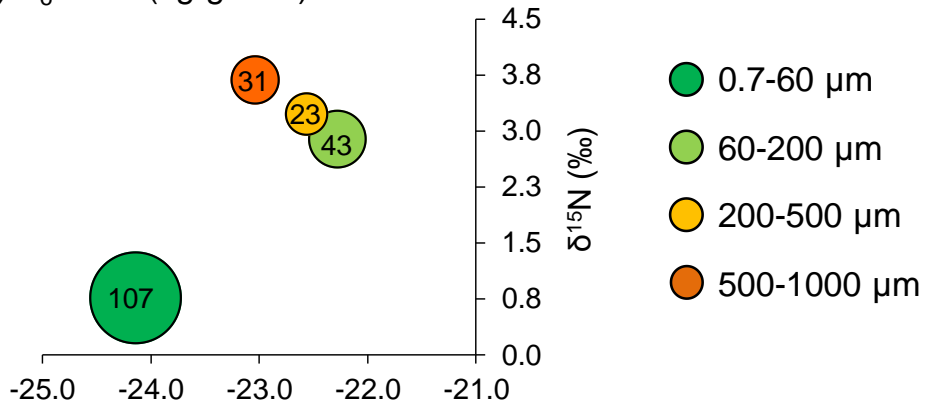
Figure 6



a)  $\Sigma_7\text{PAHs}$  ( $\text{ng g}^{-1}$  dw)



b)  $\Sigma_6\text{PAHs}$  ( $\text{ng g}^{-1}$  dw)



c) Phe ( $\text{ng g}^{-1}$  dw)

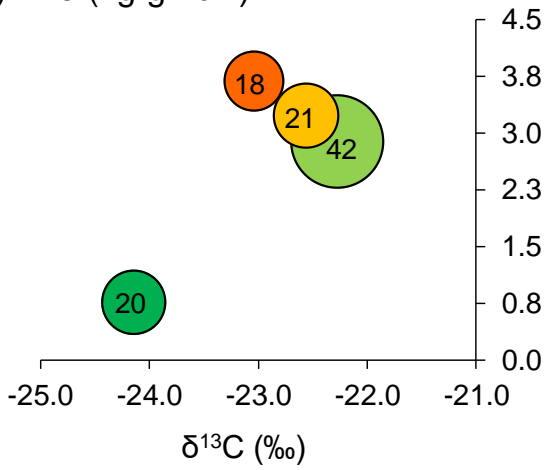
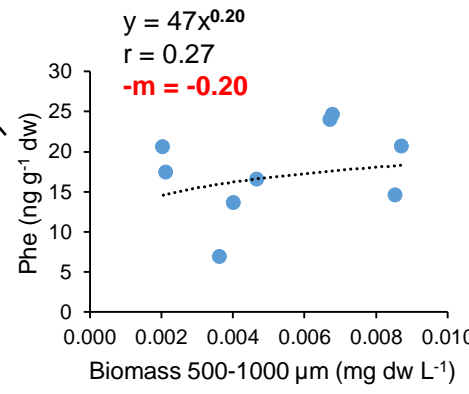
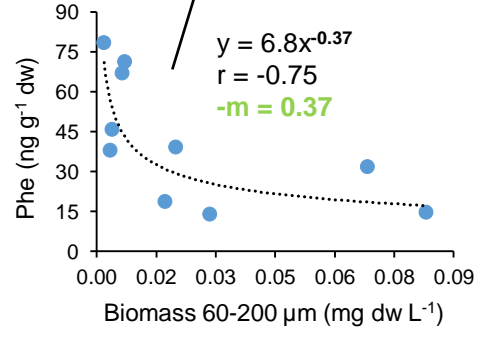
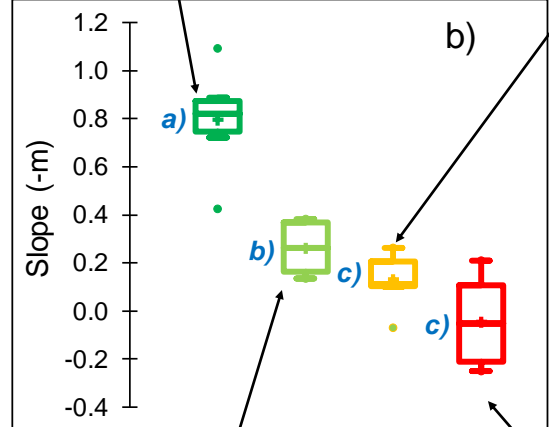
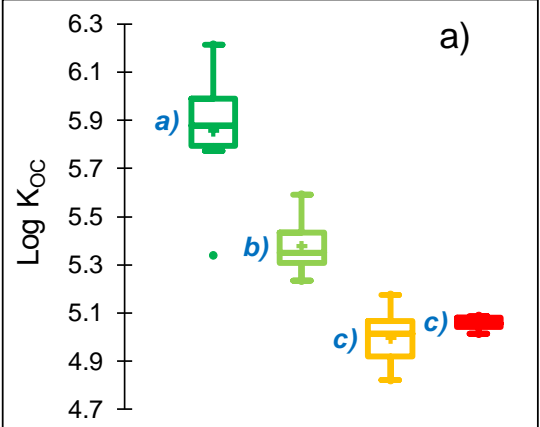
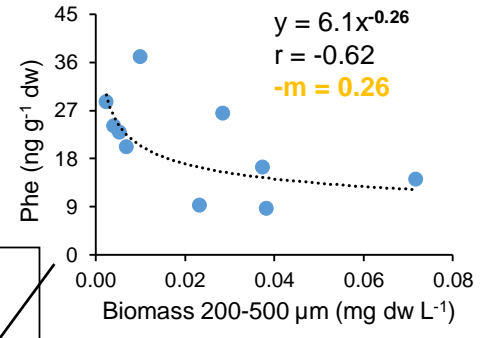
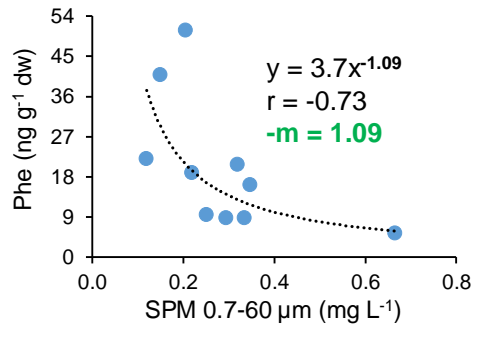


Figure 7



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Figure 8

**Hydrocarbons in size-fractionated plankton of the Mediterranean Sea (MERITE-  
HIPPOCAMPE campaign)**

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**Supplementary Material**

The supplementary material contains 26 pages, and includes 11 tables and 6 figures.

**Table S1.** Biogeochemical parameters measured in the different particulate/planktonic size fractions (0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$ ) recovered from the deep chlorophyll maximum (DCM) at the 10 stations.

			St1	St2	St3	St4	St9	St10	St11	St15	St17	St19
Sampling depth range in the DCM (m)			20-24	25-53	53-58	13-35	20	40-60	30-58	60-68	37-46	30-46
Parameter	Unit	Size fraction ( $\mu\text{m}$ )										
<b>TChla</b>	$\mu\text{g L}^{-1}$	0.7-60	0.46	0.33	0.37	0.38	0.65	0.41	0.24	0.29	0.12	0.54
<b>SPM</b>	$\text{mg L}^{-1}$	0.7-60	0.35	0.32	0.21	0.22	0.67	0.25	0.15	0.12	0.29	0.34
<b>Biomass</b>	$\mu\text{g dw L}^{-1}$	60-200	20.0	7.1	1.9	68.3	17.3	3.5	3.9	6.4	83.1	28.5
		200-500	37.4	6.8	2.3	28.5	23.3	4.1	5.4	10.0	71.8	38.2
		500-1000	4.7	6.7	4.0	6.8	3.6	2.0	8.6	8.7	2.1	11.2
		Tot 60-1000	62.1	20.6	8.2	103.5	44.2	9.6	17.9	25.2	157.0	77.9
<b>POC</b>	$\text{mg L}^{-1}$	0.7-60	0.047	0.022	0.016	0.035	0.175	0.030	0.018	0.014	0.024	0.048
		$\text{mg g}^{-1} \text{ dw}$	0.7-60	134.5	67.3	78.3	159.5	261.8	118.6	121.7	120.6	80.9
	60-200		263.4	129.4	81.9	103.5	249.8	240.3	271.5	153.7	43.5	156.0
	200-500		246.4	238.0	179.6	139.4	341.0	269.8	299.9	199.6	75.9	204.7
	500-1000		284.9	207.1	168.5	109.7	326.2	222.8	311.4	228.9	<i>na</i>	190.5
	%	0.7-60	13.5	6.7	7.8	15.9	26.2	11.9	12.2	12.1	8.1	14.2
		60-200	26.3	12.9	8.2	10.4	25.0	24.0	27.1	15.4	4.4	15.6
		200-500	24.6	23.8	18.0	13.9	34.1	27.0	30.0	20.0	7.6	20.5
500-1000		28.5	20.7	16.9	11.0	32.6	22.3	31.1	22.9	<i>na</i>	19.1	
<b><math>\delta^{13}\text{C}</math></b>	‰	0.7-60	-24.5	-24.8	-23.6	-23.2	-24.2	-24.6	-24.1	-25.1	-23.7	-23.6
		60-200	-22.8	-22.7	-21.7	-20.5	-22.7	-22.8	-22.9	-22.8	-21.8	-22.3
		200-500	-23.9	-23.9	-23.0	-21.5	-23.2	-23.7	-24.0	-23.4	-17.4	-21.8
		500-1000	-23.4	-23.8	-22.7	-22.2	-22.9	-23.3	-23.4	-22.7	<i>na</i>	-23.1
<b><math>\delta^{15}\text{N}</math></b>		0.7-60	1.8	0.9	0.1	2.1	-1.3	0.4	0.9	1.6	0.8	0.3
		60-200	3.2	3.1	2.9	3.6	2.0	3.6	3.5	3.6	1.9	1.5
		200-500	3.7	3.3	3.4	3.6	2.7	3.9	3.8	3.9	2.4	1.6
		500-1000	4.4	3.5	3.4	3.5	3.9	4.5	4.2	3.3	<i>na</i>	2.5

*na*: not available; TChla: total chlorophyll *a*; SPM: suspended particulate matter; Biomass: total biomass including the biomasses of zooplankton, phytoplankton and detritus (see [Fierro-González et al., 2023](#)); POC: particulate organic carbon;  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ : C and N stable isotopic ratios.

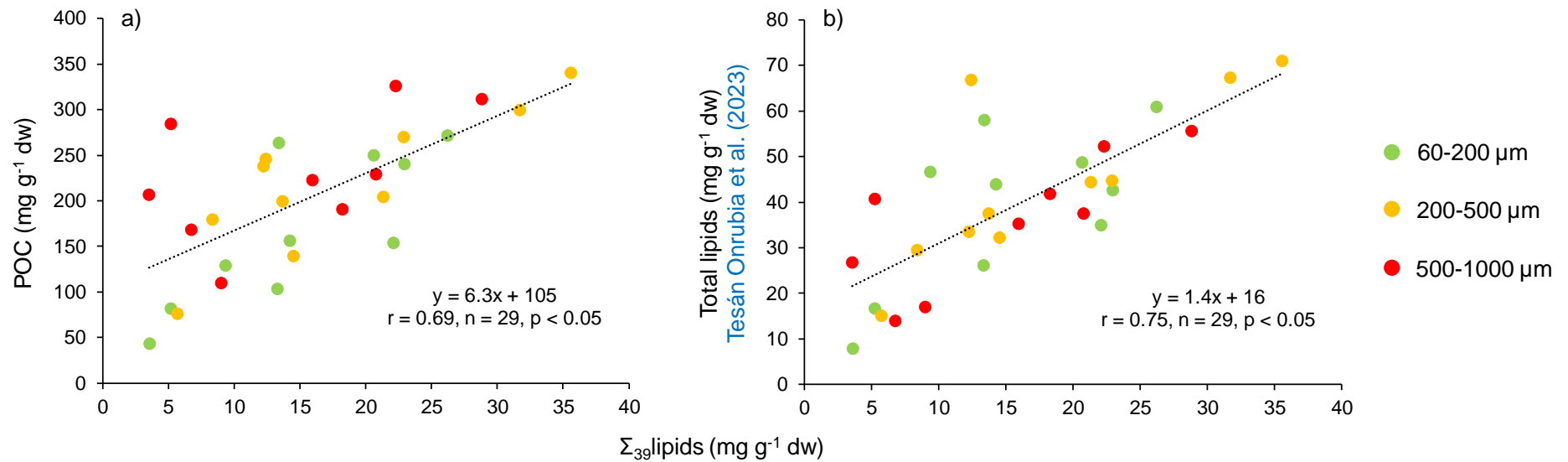
**Table S2.** Concentrations (in mg g<sup>-1</sup> dw) of individual and total lipid biomarkers (fatty acids, fatty alcohols and sterols) in the planktonic size fractions 60-200, 200-500 and 500-1000 µm recovered from the DCM at the 10 stations.

Size fraction (µm)	St1			St2			St3			St4			St9		
	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000
<b>Σ<sub>39</sub>lipids (mg g<sup>-1</sup> dw)</b>	13.4	12.4	5.21	9.36	12.3	3.53	5.22	8.37	6.72	13.3	14.5	9.01	20.7	35.6	22.3
<b>Σ<sub>25</sub>fatty acids (mg g<sup>-1</sup> dw)</b>	8.58	7.13	4.30	7.32	9.80	2.65	4.46	7.27	5.74	11.8	12.6	8.21	16.4	23.2	16.0
14:0	1.61	1.12	0.76	1.07	1.08	0.51	0.58	0.86	0.81	4.28	3.73	2.24	1.99	1.86	1.58
i15:0	0.07	0.05	0.03	0.05	0.06	0.02	0.05	0.06	0.06	0.05	0.07	0.04	0.10	0.14	0.12
a15:0	0.04	0.03	0.02	0.03	0.04	0.01	0.02	0.03	0.03	0.03	0.04	0.03	0.06	0.07	0.05
15:0	0.16	0.14	0.12	0.15	0.21	0.07	0.11	0.17	0.16	0.18	0.21	0.15	0.26	0.31	0.35
16:0	4.53	3.60	2.23	3.95	4.92	1.31	2.15	3.83	3.03	3.50	4.46	2.90	8.21	10.2	8.18
16:1ω7	0.32	0.30	0.16	0.25	0.55	0.15	0.13	0.23	0.18	1.77	1.54	1.06	0.48	0.53	0.37
16:1ω11	0.08	0.07	0.03	0.05	0.05	0.02	0.02	0.03	0.02	0.09	0.09	0.06	0.17	0.14	0.08
br17:0	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
i17:0	<i>nd</i>	<i>nd</i>	0.01	<i>nd</i>	0.02	<i>nd</i>	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.03
a17:0	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.03	<i>nd</i>	0.02	0.02	0.02	0.02	0.02	0.01	<i>nd</i>	0.06	<i>nd</i>
17:0	0.02	0.14	0.08	0.14	0.22	0.05	0.07	0.17	0.13	0.08	0.13	0.07	0.41	0.51	0.46
18:0	0.51	0.44	0.24	0.59	0.88	0.16	0.45	0.80	0.60	0.58	0.79	0.54	1.28	2.12	1.43
18:1ω9	0.90	0.95	0.41	0.75	1.19	0.23	0.59	0.64	0.35	0.54	0.71	0.42	1.67	5.31	2.04
18:1ω7	0.15	0.16	0.11	0.13	0.24	0.08	0.09	0.15	0.11	0.29	0.32	0.26	0.37	0.45	0.34
18:2	0.05	0.07	0.06	0.04	0.11	0.01	0.04	0.05	0.04	0.07	0.08	0.06	0.20	0.17	0.12
18:4	<i>nd</i>	<i>nd</i>	0.01	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.00	0.00	<i>nd</i>	0.01	<i>nd</i>	<i>nd</i>	0.14	0.13	0.07
20:0	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	0.04	<i>nd</i>	0.03	0.03	0.03	0.03	0.05	0.03	0.08	0.14	0.04
20:1	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.02	0.04	<i>nd</i>	0.03	0.04	0.04	0.04	0.07	0.03	0.07	0.12	0.10
20:5	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	0.02	0.02	0.08	0.06	0.07	0.11	0.12	0.09
22:0	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	0.01	0.03	0.05	0.02	0.05	0.07	0.03
22:1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.00	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01
22:6	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	0.02	0.02	0.02	0.02	0.04	0.19	0.22	0.13
24:1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.07	<i>nd</i>	<i>nd</i>	0.01	0.02	<i>nd</i>	0.02	0.01	0.13	0.28	0.22
Phytanic acid	0.13	0.07	0.03	0.08	0.06	0.02	0.04	0.06	0.05	0.07	0.11	0.08	0.23	0.12	0.08

Isomeric dihydroxy 16:0	<i>nd</i>	0.00	<i>nd</i>	<i>nd</i>	0.00	<i>nd</i>	<i>nd</i>	0.00	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.05	0.14	0.10	0.03
<b>Σ<sub>8</sub>fatty alcohols (mg g<sup>-1</sup> dw)</b>	4.52	5.04	0.69	1.77	1.75	0.76	0.62	0.86	0.61	1.43	1.44	0.59	2.73	11.1	5.01
14:0	0.77	0.13	0.03	0.27	0.04	0.03	0.09	0.04	0.05	0.22	0.15	0.04	0.28	0.15	0.09
16:0	3.48	4.64	0.54	1.33	1.56	0.47	0.37	0.70	0.41	0.62	0.77	0.25	2.17	10.1	4.28
16:1	0.01	0.00	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	<i>nd</i>	0.01	0.02	0.03	0.01	<i>nd</i>	0.01	<i>nd</i>
18:0	0.21	0.19	0.04	0.10	0.08	0.03	0.05	0.06	0.03	0.11	0.12	0.07	0.16	0.63	0.28
18:1	0.01	0.08	0.02	0.05	0.05	0.04	0.03	0.03	0.03	0.04	0.05	0.03	0.08	0.24	0.13
20:1	<i>nd</i>	<i>nd</i>	0.02	<i>nd</i>	<i>nd</i>	0.09	0.03	0.00	0.03	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.08
22:1	<i>nd</i>	<i>nd</i>	0.02	<i>nd</i>	<i>nd</i>	0.09	0.03	0.02	0.03	<i>nd</i>	0.04	0.01	<i>nd</i>	0.06	0.14
Phytol	0.03	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.41	0.28	0.18	0.04	<i>nd</i>	<i>nd</i>
<b>Σ<sub>6</sub>sterols (mg g<sup>-1</sup> dw)</b>	0.30	0.23	0.22	0.28	0.71	0.11	0.13	0.24	0.38	0.12	0.52	0.21	1.56	1.23	1.34
24-Norcholesta-5,22E-dien-3β-ol	0.01	<i>nd</i>	<i>nd</i>	0.02	0.03	<i>nd</i>	0.01	0.01	0.02	<i>nd</i>	0.02	0.01	0.06	0.05	0.03
5α-Cholestan-3β-ol	0.03	0.01	0.01	0.02	0.04	0.01	0.02	0.02	0.04	0.01	0.04	0.01	0.12	0.08	0.06
Cholesta-5,22E-dien-3β-ol	0.05	0.04	0.02	0.04	0.10	0.02	0.02	0.03	0.06	0.04	0.12	0.05	0.17	0.13	0.12
Cholest-5-en-3β-ol	0.18	0.16	0.16	0.17	0.45	0.08	0.07	0.15	0.21	0.06	0.29	0.13	0.99	0.82	1.01
Cholesta-5,24-dien-3β-ol	0.02	0.01	0.01	0.01	0.03	<i>nd</i>	<i>nd</i>	0.01	0.01	<i>nd</i>	0.02	0.01	0.17	0.12	0.09
24-Methylcholesta-5,22E-dien-3β-ol	0.01	0.01	0.01	0.01	0.05	0.01	0.01	0.02	0.04	<i>nd</i>	0.03	0.01	0.06	0.03	0.03
	<b>St10</b>			<b>St11</b>			<b>St15</b>			<b>St17</b>			<b>St19</b>		
Size fraction (μm)	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000	60-200	200-500	500-1000
<b>Σ<sub>39</sub>lipids (mg g<sup>-1</sup> dw)</b>	23.0	22.9	16.0	26.2	31.7	28.8	22.1	13.7	20.8	3.60	5.69	<i>na</i>	14.3	21.4	18.3
<b>Σ<sub>25</sub>fatty acids (mg g<sup>-1</sup> dw)</b>	17.7	17.9	13.6	21.7	25.1	25.5	16.7	10.3	16.5	3.14	4.66	<i>na</i>	12.4	18.3	15.8
14:0	2.08	2.14	1.44	2.76	3.13	2.01	2.38	1.38	1.73	0.74	1.13	<i>na</i>	1.38	2.80	2.01
i15:0	0.16	0.17	0.12	0.20	0.20	0.16	0.14	0.08	0.10	0.02	0.04	<i>na</i>	0.16	0.20	0.16
a15:0	0.08	0.09	0.08	0.10	0.10	0.08	0.09	0.03	0.05	0.02	0.02	<i>na</i>	0.04	0.09	0.05
15:0	0.31	0.36	0.32	0.42	0.42	0.45	0.37	0.21	0.32	0.07	0.11	<i>na</i>	0.26	0.43	0.41
16:0	7.32	8.07	6.35	9.28	10.1	9.51	7.05	4.35	7.61	1.18	1.80	<i>na</i>	6.58	9.26	8.20
16:1ω7	0.59	0.59	0.59	0.77	0.77	0.88	1.19	0.61	1.09	0.47	0.55	<i>na</i>	0.47	0.60	0.57
16:1ω11	0.08	0.09	0.08	0.14	0.13	0.11	0.10	0.05	0.07	0.03	0.03	<i>na</i>	0.06	0.12	0.11
br17:0	0.02	0.04	0.02	0.04	0.04	0.05	0.03	0.03	0.04	0.00	<i>nd</i>	<i>na</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
i17:0	0.04	0.06	0.05	0.06	0.08	0.09	0.05	0.04	0.09	0.02	0.02	<i>na</i>	0.06	0.07	0.06
a17:0	0.07	0.07	0.06	0.06	0.07	0.05	0.05	0.04	0.05	0.01	0.01	<i>na</i>	0.04	0.05	0.04

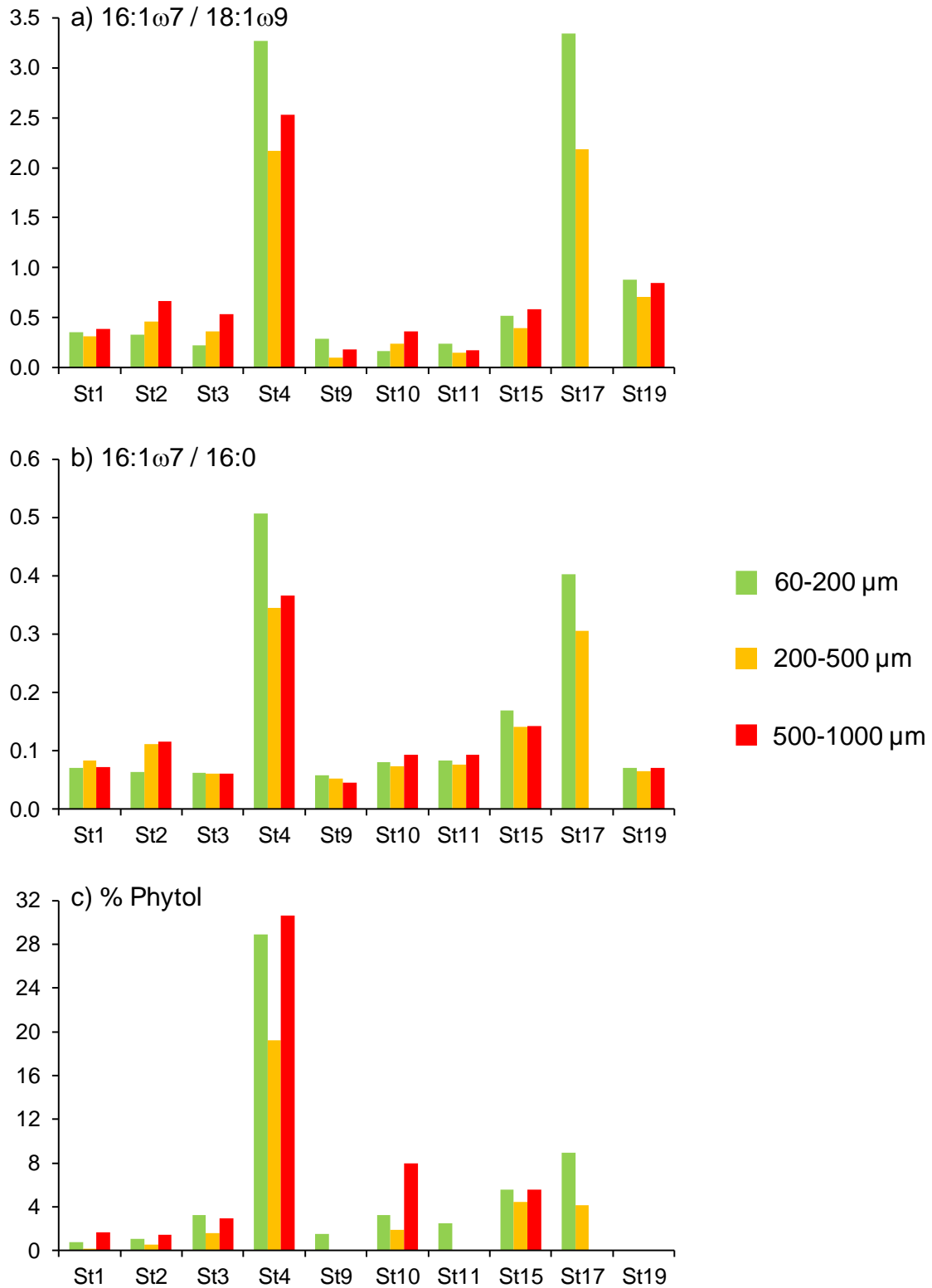
17:0	0.38	0.47	0.31	0.45	0.48	0.51	0.32	0.22	0.37	0.05	0.08	na	0.35	0.06	0.44
18:0	1.37	1.77	1.18	1.65	1.91	1.75	1.07	0.79	1.25	0.22	0.35	na	1.48	2.61	1.98
18:1 $\omega$ 9	3.67	2.44	1.62	3.18	5.16	5.12	2.30	1.55	1.87	0.14	0.25	na	0.53	0.85	0.68
18:1 $\omega$ 7	0.33	0.40	0.30	0.42	0.46	0.47	0.47	0.30	0.60	0.07	0.08	na	0.25	0.28	0.27
18:2	0.14	0.13	0.09	0.36	0.31	0.51	0.19	0.08	0.18	0.03	0.03	na	0.11	0.10	0.10
18:4	0.10	0.10	0.07	0.16	0.13	0.13	0.09	0.05	0.09	nd	nd	na	0.05	0.06	0.05
20:0	0.11	0.11	0.07	0.10	0.12	0.20	0.08	0.07	0.10	nd	0.02	na	0.07	0.15	0.12
20:1	0.09	0.10	0.10	0.16	0.27	0.16	0.13	0.08	0.15	nd	0.02	na	0.06	0.09	0.05
20:5	0.07	0.10	0.07	0.29	0.17	0.73	0.09	0.05	0.21	0.01	0.02	na	0.03	0.08	0.05
22:0	0.05	0.04	0.07	0.08	0.09	0.12	0.05	0.03	0.08	0.02	0.02	na	0.05	0.11	0.06
22:1	nd	nd	0.08	0.09	0.13	0.66	0.11	0.05	0.09	nd	nd	na	nd	nd	nd
22:6	0.13	0.13	0.14	0.47	0.29	1.18	0.16	0.06	0.18	0.01	0.02	na	0.06	0.10	0.05
24:1	0.16	0.19	0.15	0.20	0.37	0.26	0.08	0.06	0.08	0.00	nd	na	0.07	0.12	0.11
Phytanic acid	0.12	0.11	0.08	0.19	0.15	0.15	0.11	0.06	0.10	0.04	0.04	na	0.05	0.07	0.06
Isomeric dihydroxy 16:0	0.24	0.12	0.16	0.10	0.06	0.11	0.05	nd	nd	nd	nd	na	0.14	0.04	0.20
<b><math>\Sigma_8</math>fatty alcohols (mg g<sup>-1</sup> dw)</b>	<b>3.78</b>	<b>3.15</b>	<b>1.20</b>	<b>3.75</b>	<b>4.58</b>	<b>2.29</b>	<b>4.20</b>	<b>2.72</b>	<b>2.08</b>	<b>0.35</b>	<b>0.76</b>	<b>na</b>	<b>0.72</b>	<b>1.31</b>	<b>0.82</b>
14:0	1.12	0.34	0.09	1.68	0.38	0.26	1.50	0.47	0.17	0.04	0.07	na	0.09	0.23	0.09
16:0	2.06	2.44	0.75	1.71	3.83	1.67	2.03	1.85	0.94	0.20	0.54	na	0.44	0.83	0.49
16:1	0.02	0.01	0.02	0.02	0.01	0.01	0.05	0.02	0.04	0.01	0.01	na	0.03	0.03	0.03
18:0	0.23	0.17	0.07	0.14	0.23	0.13	0.19	0.15	0.13	0.06	0.07	na	0.12	0.16	0.12
18:1	0.24	0.13	0.10	0.11	0.13	0.15	0.15	0.12	0.12	0.01	0.02	na	0.04	0.07	0.10
20:1	nd	nd	0.03	nd	nd	nd	nd	nd	0.17	nd	nd	na	nd	nd	nd
22:1	nd	nd	0.05	nd	nd	0.07	0.04	nd	0.39	nd	nd	na	nd	nd	nd
Phytol	0.12	0.06	0.10	0.09	nd	nd	0.23	0.12	0.12	0.03	0.03	na	nd	nd	nd
<b><math>\Sigma_6</math>sterols (mg g<sup>-1</sup> dw)</b>	<b>1.50</b>	<b>1.85</b>	<b>1.15</b>	<b>0.75</b>	<b>2.03</b>	<b>1.08</b>	<b>1.16</b>	<b>0.72</b>	<b>2.23</b>	<b>0.11</b>	<b>0.28</b>	<b>na</b>	<b>1.18</b>	<b>1.69</b>	<b>1.62</b>
24-Norcholesta-5,22E-dien-3 $\beta$ -ol	0.06	0.04	0.04	0.03	0.08	0.03	0.04	0.04	0.11	0.00	0.01	na	0.04	0.00	0.05
5 $\alpha$ -Cholestan-3 $\beta$ -ol	0.14	0.11	0.10	0.09	0.16	0.08	0.09	0.05	0.07	0.02	0.04	na	0.09	0.10	0.07
Cholesta-5,22E-dien-3 $\beta$ -ol	0.20	0.22	0.16	0.10	0.25	0.13	0.18	0.11	0.21	0.02	0.04	na	0.12	0.15	0.14
Cholest-5-en-3 $\beta$ -ol	0.95	1.31	0.70	0.42	1.30	0.70	0.67	0.42	1.67	0.06	0.16	na	0.75	1.18	1.20
Cholesta-5,24-dien-3 $\beta$ -ol	0.06	0.08	0.04	0.07	0.11	0.07	0.08	0.03	0.06	0.01	0.01	na	0.07	0.11	0.06
24-Methylcholesta-5,22E-dien-3 $\beta$ -ol	0.09	0.09	0.10	0.03	0.13	0.07	0.10	0.07	0.11	0.01	0.02	na	0.12	0.15	0.10

na: not available; nd: not detected;  $\Sigma_{39}$ lipids =  $\Sigma_{25}$ fatty acids +  $\Sigma_8$ fatty alcohols +  $\Sigma_6$ sterols;  $\Sigma_{25}$ fatty acids =  $\Sigma$  14:0–isomeric dihydroxy 16:0 (25 compounds);  $\Sigma_8$ fatty alcohols =  $\Sigma$  14:0–phytol (8 compounds);  $\Sigma_6$ sterols =  $\Sigma$  24-Norcholesta-5,22E-dien-3 $\beta$ -ol–24-Methylcholesta-5,22E-dien-3 $\beta$ -ol (6 compounds).

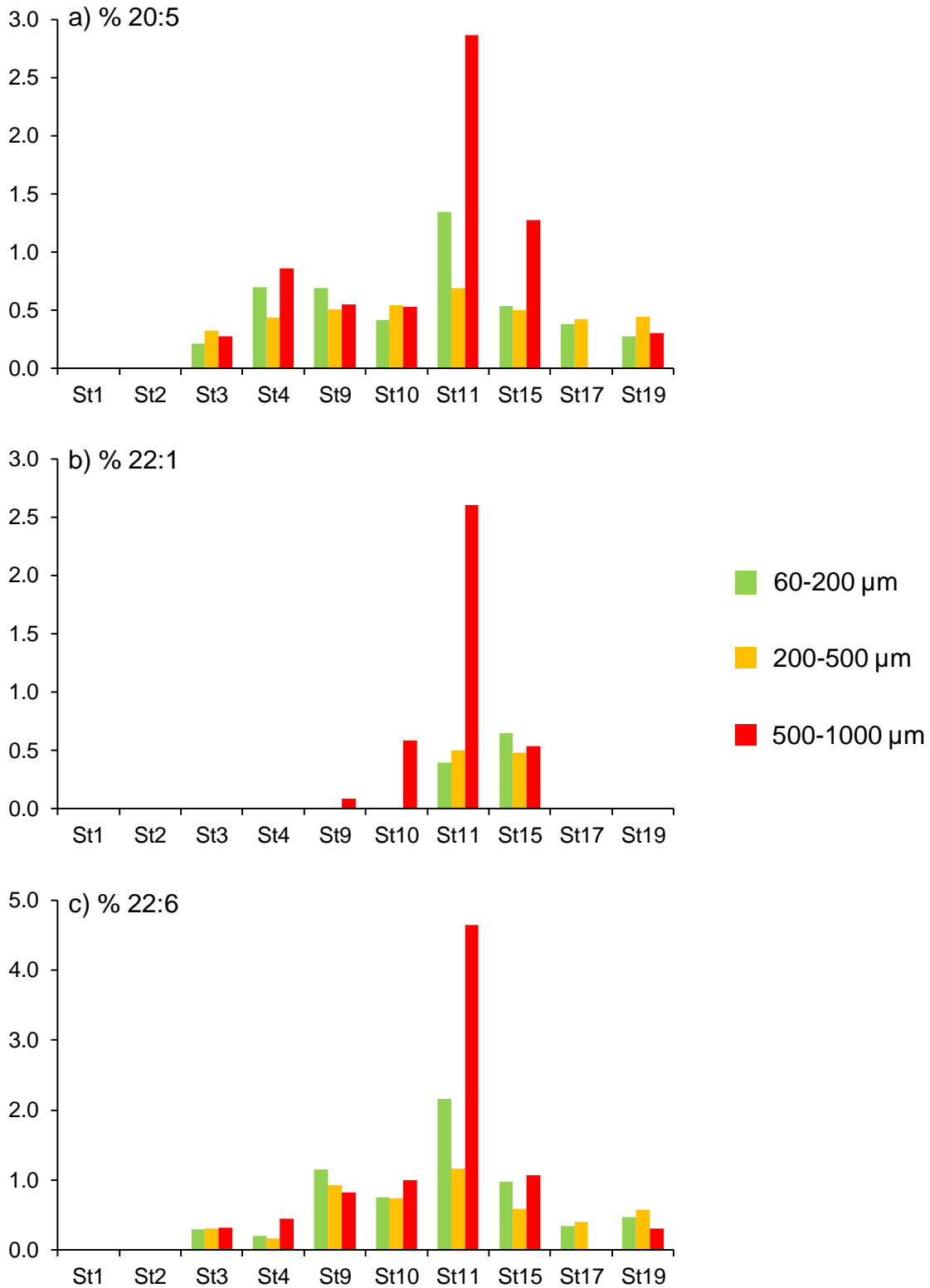


**Figure S1.** Relationships between the concentration of  $\Sigma_{39}\text{lipids}$  (=  $\Sigma_{25}\text{fatty acids}$  +  $\Sigma_8\text{fatty alcohols}$  +  $\Sigma_6\text{sterols}$ ; in mg g<sup>-1</sup> dw) measured in the present study (horizontal axis), and **a)** the concentration of POC (in mg g<sup>-1</sup> dw) measured in the present study and **b)** the concentration of total lipids (in mg g<sup>-1</sup> dw) determined by [Tésan Onrubia et al. \(2023\)](#) using a global method (vertical axes), on the same planktonic size fractions (60-200, 200-500 and 500-1000  $\mu\text{m}$ ) recovered from the DCM at the 10 stations.





**Figure S2.** Phytoplankton biomarkers in the planktonic size fractions 60-200, 200-500 and 500-1000  $\mu$ m, recovered from the DCM at the 10 stations: **a)** the ratio of fatty acids 16:1 $\omega$ 7/18:1 $\omega$ 9, **b)** the ratio of fatty acids 16:1 $\omega$ 7/16:0, and **c)** the relative abundance of phytol within fatty alcohols (in %).

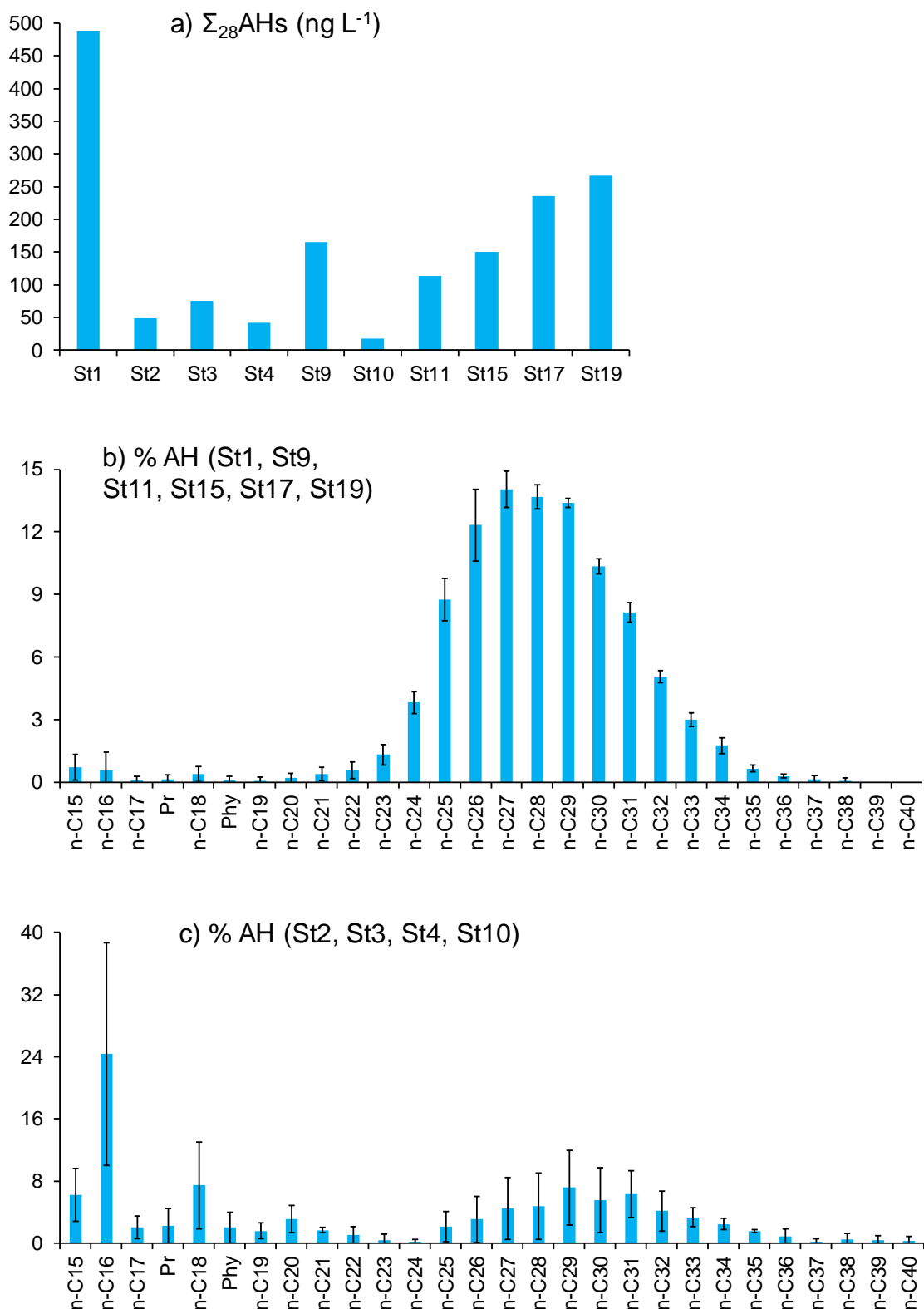


**Figure S3.** Zooplankton biomarkers in the planktonic size fractions 60-200, 200-500 and 500-1000 μm, recovered from the DCM at the 10 stations: relative abundances of **a)** 20:5, **b)** 22:1 and **c)** 22:6 within fatty acids (in %).

**Table S3.** Concentrations (in ng L<sup>-1</sup>) of individual and total aliphatic hydrocarbons (AHs) in the dissolved phase (< 0.7 μm) of water collected at 5-20-m depth at the 10 stations.

	St1	St2	St3	St4	St9	St10	St11	St15	St17	St19
<i>n</i> -C <sub>15</sub>	1.3	1.9	1.5	1.9	3.0	1.8	1.1	1.2	0.8	0.5
<i>n</i> -C <sub>16</sub>	<i>nd</i>	6.2	4.5	8.3	<i>nd</i>	7.3	2.6	0.9	0.3	0.9
<i>n</i> -C <sub>17</sub>	<i>nd</i>	0.2	0.1	1.4	0.3	0.4	<i>nd</i>	0.7	<i>nd</i>	0.1
Pr	<i>nd</i>	<i>nd</i>	0.5	0.9	<i>nd</i>	0.8	<i>nd</i>	0.7	<i>nd</i>	0.8
<i>n</i> -C <sub>18</sub>	<i>nd</i>	1.3	1.3	2.6	<i>nd</i>	2.4	1.0	1.1	1.1	0.6
Phy	0.6	<i>nd</i>	0.8	0.9	<i>nd</i>	0.7	<i>nd</i>	0.6	<i>nd</i>	0.4
<i>n</i> -C <sub>19</sub>	<i>nd</i>	0.2	<i>nd</i>	0.9	<i>nd</i>	0.4	<i>nd</i>	0.6	<i>nd</i>	0.1
<i>n</i> -C <sub>20</sub>	<i>nd</i>	0.7	0.3	1.2	<i>nd</i>	0.9	0.4	0.9	0.1	0.5
<i>n</i> -C <sub>21</sub>	1.0	1.0	0.2	0.6	<i>nd</i>	0.3	0.9	1.2	0.8	0.7
<i>n</i> -C <sub>22</sub>	2.1	1.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.2	1.1	1.6	1.3	0.9
<i>n</i> -C <sub>23</sub>	7.6	0.6	<i>nd</i>	<i>nd</i>	0.5	<i>nd</i>	1.6	2.5	3.8	3.6
<i>n</i> -C <sub>24</sub>	22	0.3	0.8	<i>nd</i>	5.0	<i>nd</i>	4.0	5.6	9.3	11
<i>n</i> -C <sub>25</sub>	51	1.8	3.5	1.2	13	<i>nd</i>	9.7	11	22	23
<i>n</i> -C <sub>26</sub>	73	2.8	6.7	1.4	19	<i>nd</i>	12	17	33	31
<i>n</i> -C <sub>27</sub>	68	2.8	8.5	3.2	24	<i>nd</i>	15	22	31	40
<i>n</i> -C <sub>28</sub>	67	4.0	9.2	2.5	24	<i>nd</i>	15	20	31	38
<i>n</i> -C <sub>29</sub>	66	5.6	9.9	3.3	23	0.4	15	20	31	36
<i>n</i> -C <sub>30</sub>	49	4.5	8.4	2.6	18	0.2	12	15	24	29
<i>n</i> -C <sub>31</sub>	37	4.7	6.8	2.2	14	0.7	10	12	19	21
<i>n</i> -C <sub>32</sub>	23	3.4	4.8	1.5	8.9	0.3	5.8	7.3	13	13
<i>n</i> -C <sub>33</sub>	13	2.3	3.1	1.1	5.7	0.5	3.7	4.1	7.4	7.5
<i>n</i> -C <sub>34</sub>	5.4	1.6	2.1	0.9	3.6	0.4	2.3	2.4	4.5	4.5
<i>n</i> -C <sub>35</sub>	2.6	0.9	1.2	0.6	1.5	0.3	0.9	0.8	1.7	1.4
<i>n</i> -C <sub>36</sub>	1.2	0.4	0.5	0.8	0.7	<i>nd</i>	0.4	0.3	0.8	0.6
<i>n</i> -C <sub>37</sub>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.3	0.7	<i>nd</i>	<i>nd</i>	0.1	0.7	0.3
<i>n</i> -C <sub>38</sub>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.6	0.5	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.3
<i>n</i> -C <sub>39</sub>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.5	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>40</sub>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.4	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<b>Σ<sub>28</sub>AHs</b>	<b>489</b>	<b>48</b>	<b>75</b>	<b>42</b>	<b>165</b>	<b>18</b>	<b>113</b>	<b>150</b>	<b>235</b>	<b>267</b>

*nd*: not detected; Pr: pristane; Phy: phytane; Σ<sub>28</sub>AHs = Σ *n*-C<sub>15</sub>-*n*-C<sub>40</sub>, Pr, Phy (28 compounds).



**Figure S4.** a) Concentrations of total aliphatic hydrocarbons ( $\Sigma_{28}\text{AHs}$ , in ng L<sup>-1</sup>) at the 10 stations, and b) mean relative abundances of individual AHs (in %) for stations St1, St9, St11, St15, St17, St19 and c) stations St 2, St3, St4, St10, for the dissolved phase (< 0.7  $\mu\text{m}$ ) of water collected at 5-20-m depth.  $\Sigma_{28}\text{AHs} = \Sigma n\text{-C}_{15}\text{-}n\text{-C}_{40}$ , Pr, Phy (28 compounds).

**Table S4.** Concentrations (in  $\mu\text{g g}^{-1}$  dw) of individual and total aliphatic hydrocarbons (AHs) in the particulate/planktonic size fractions 0.7-60, 60-200, 200-500 and 500-1000  $\mu\text{m}$  recovered from the DCM at the 10 stations.

Size fraction ( $\mu\text{m}$ )	St1				St2				St3				St4				St9			
	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000
<i>n</i> -C <sub>15</sub>	11	0.7	1.8	1.2	16	1.9	3.2	5.4	9.2	1.5	1.9	1.8	5.0	0.3	0.5	0.8	2.1	0.5	0.2	0.1
<i>n</i> -C <sub>16</sub>	0.5	0.1	0.1	0.1	1.2	0.0	0.1	0.2	1.7	0.1	0.1	0.0	0.4	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.3	0.1	0.1	<i>nd</i>
<i>n</i> -C <sub>17</sub>	1.4	0.4	0.4	0.4	4.6	0.4	0.3	0.7	7.2	0.4	0.5	0.1	2.2	0.3	0.3	0.1	0.3	0.2	0.1	0.1
Pr	0.2	0.9	2.5	2.0	1.6	3.7	2.6	3.1	6.9	2.1	1.5	0.4	1.1	1.3	1.5	1.0	<i>nd</i>	0.2	0.3	0.4
<i>n</i> -C <sub>18</sub>	0.3	<i>nd</i>	<i>nd</i>	0.1	1.9	<i>nd</i>	<i>nd</i>	0.1	8.9	<i>nd</i>	<i>nd</i>	1.7	0.6	0.1	0.1	0.1	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>
Phy	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	1.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	5.5	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.4	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>19</sub>	0.1	0.1	0.1	0.1	1.6	<i>nd</i>	<i>nd</i>	0.1	7.3	<i>nd</i>	0.1	<i>nd</i>	0.7	0.2	0.4	0.1	0.1	0.1	0.1	<i>nd</i>
<i>n</i> -C <sub>20</sub>	<i>nd</i>	0.1	<i>nd</i>	0.1	1.1	0.1	<i>nd</i>	0.1	4.6	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.2	0.1	0.1	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>21</sub>	0.1	0.2	0.2	0.2	0.6	0.1	0.1	0.1	1.8	0.1	0.1	0.1	0.4	0.1	0.2	0.2	<i>nd</i>	0.1	0.1	0.1
<i>n</i> -C <sub>22</sub>	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.2	0.7	0.1	0.1	0.1	0.7	0.1	0.2	0.2	<i>nd</i>	0.1	0.1	<i>nd</i>
<i>n</i> -C <sub>23</sub>	0.1	0.4	0.6	0.9	0.4	0.2	0.1	0.4	0.4	0.2	0.2	0.4	1.7	0.2	0.4	0.6	<i>nd</i>	0.3	0.4	0.2
<i>n</i> -C <sub>24</sub>	0.1	<i>nd</i>	0.1	0.2	0.5	0.2	0.1	0.3	0.7	0.3	0.2	0.1	2.0	0.2	0.2	0.3	<i>nd</i>	0.2	0.2	0.1
<i>n</i> -C <sub>25</sub>	0.3	0.8	1.4	2.6	0.7	0.2	0.2	0.6	1.4	0.5	0.4	0.4	2.4	0.5	0.8	1.3	0.1	0.9	1.0	0.6
<i>n</i> -C <sub>26</sub>	0.1	0.3	<i>nd</i>	0.3	0.8	0.2	0.1	0.3	2.3	0.6	0.4	0.2	2.3	0.3	0.6	0.5	<i>nd</i>	0.2	0.2	0.1
<i>n</i> -C <sub>27</sub>	0.3	2.8	2.5	10	0.8	0.5	0.5	1.5	2.5	1.0	0.9	0.8	2.4	1.6	2.5	4.4	0.1	2.6	2.4	2.0
<i>n</i> -C <sub>28</sub>	0.1	0.3	<i>nd</i>	0.5	0.7	0.2	0.1	0.3	2.3	0.6	0.4	0.3	1.8	0.7	0.9	0.6	<i>nd</i>	0.1	0.2	0.1
<i>n</i> -C <sub>29</sub>	0.4	3.1	2.6	10	0.9	0.4	0.3	1.0	2.3	1.0	0.7	0.9	2.2	1.5	2.2	2.3	0.4	0.3	2.5	1.8
<i>n</i> -C <sub>30</sub>	0.2	0.2	0.2	0.2	0.5	0.1	0.1	0.3	1.7	0.7	0.4	0.2	1.6	0.8	1.2	0.6	0.1	0.2	0.1	0.1
<i>n</i> -C <sub>31</sub>	0.3	1.9	1.6	4.2	0.7	0.4	0.2	0.8	1.6	0.9	0.5	0.6	2.1	1.2	1.8	1.9	0.1	1.7	1.6	0.9
<i>n</i> -C <sub>32</sub>	0.1	0.0	0.3	0.2	0.4	0.1	0.0	0.3	1.1	0.4	0.3	0.1	1.0	0.5	0.6	0.3	<i>nd</i>	0.1	0.1	0.1
<i>n</i> -C <sub>33</sub>	0.1	1.7	1.1	3.1	0.4	0.1	0.2	0.7	0.8	0.3	0.3	0.3	0.9	0.4	1.2	1.8	<i>nd</i>	0.1	1.6	0.9
<i>n</i> -C <sub>34</sub>	<i>nd</i>	0.1	0.2	0.1	0.3	<i>nd</i>	0.1	0.1	0.5	0.1	<i>nd</i>	<i>nd</i>	0.5	0.2	0.2	0.1	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>35</sub>	<i>nd</i>	<i>nd</i>	0.3	0.3	0.2	<i>nd</i>	<i>nd</i>	0.2	0.3	0.1	<i>nd</i>	<i>nd</i>	0.5	0.1	0.2	0.2	<i>nd</i>	0.2	0.2	0.1
<i>n</i> -C <sub>36</sub>	<i>nd</i>	<i>nd</i>	0.2	<i>nd</i>	0.2	<i>nd</i>	<i>nd</i>	0.0	0.2	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.2	0.1	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>37</sub>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.1	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.1	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>38</sub>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>39</sub>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<i>n</i> -C <sub>40</sub>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
<b><math>\Sigma_{28}\text{AHs}</math></b>	<b>16</b>	<b>14</b>	<b>17</b>	<b>37</b>	<b>38</b>	<b>8.9</b>	<b>8.5</b>	<b>17</b>	<b>72</b>	<b>11</b>	<b>8.9</b>	<b>8.6</b>	<b>33</b>	<b>11</b>	<b>17</b>	<b>18</b>	<b>3.9</b>	<b>8.2</b>	<b>11</b>	<b>7.7</b>

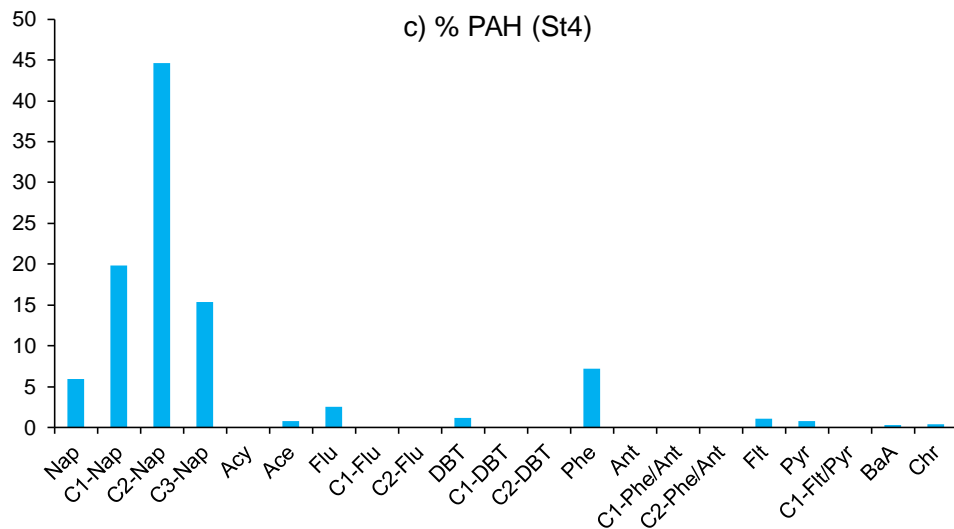
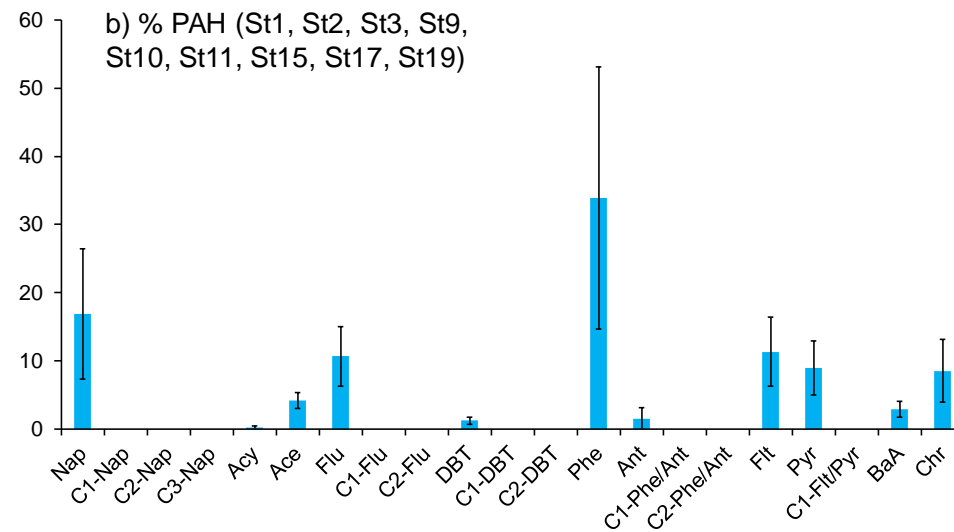
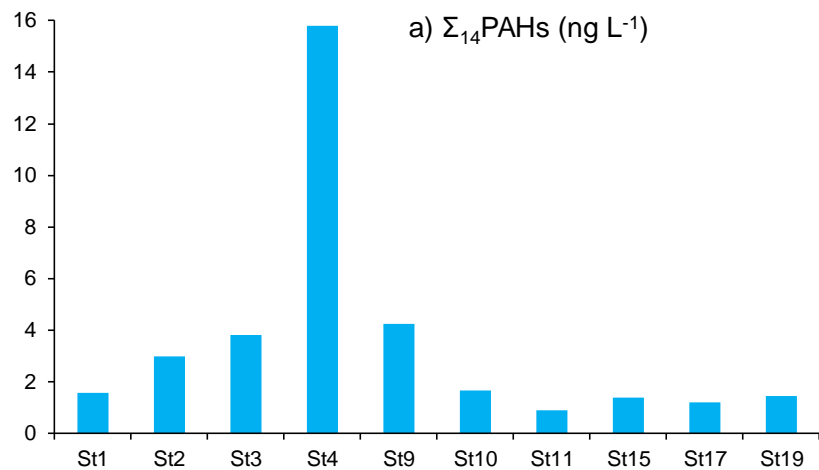
	St10				St11				St15				St17				St19			
Size fraction ( $\mu\text{m}$ )	0.7- 60	60- 200	200- 500	500- 1000	0.7- 60	60- 200	200- 500	500- 1000	0.7- 60	60- 200	200- 500	500- 1000	0.7- 60	60- 200	200- 500	500- 1000	0.7- 60	60- 200	200- 500	500- 1000
<i>n</i> -C <sub>15</sub>	7.0	1.3	1.9	1.8	11.9	1.4	1.6	2.3	3.7	1.7	2.3	1.9	5.6	0.5	0.7	na	8.3	0.6	0.5	1.1
<i>n</i> -C <sub>16</sub>	0.5	0.1	0.2	0.1	1.7	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.2	nd	nd	na	0.3	0.1	nd	nd
<i>n</i> -C <sub>17</sub>	1.5	0.7	2.1	1.2	10.8	3.5	2.8	3.0	1.9	0.5	1.4	1.0	0.7	0.3	0.3	na	0.3	0.2	0.2	0.4
Pr	0.2	1.0	4.3	4.2	5.4	3.6	32.9	45	0.1	0.9	1.8	3.1	0.1	1.0	1.5	na	0.6	4.4	2.9	6.9
<i>n</i> -C <sub>18</sub>	0.3	nd	0.1	0.1	6.0	0.1	nd	nd	0.2	nd	0.1	0.1	0.1	nd	nd	na	0.2	nd	0.1	nd
Phy	0.1	nd	nd	nd	3.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	0.1	nd	nd	nd
<i>n</i> -C <sub>19</sub>	0.2	0.1	0.2	0.1	4.1	0.2	0.1	0.1	nd	nd	nd	nd	nd	nd	nd	na	0.2	0.1	0.1	0.1
<i>n</i> -C <sub>20</sub>	0.0	0.1	0.1	0.0	2.2	0.1	nd	nd	0.0	0.1	0.0	0.1	nd	nd	nd	na	nd	nd	nd	nd
<i>n</i> -C <sub>21</sub>	0.1	0.2	0.2	0.1	1.4	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	nd	nd	na	0.1	0.1	0.1	0.1
<i>n</i> -C <sub>22</sub>	0.1	0.1	0.1	0.1	1.0	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	nd	nd	na	nd	0.1	0.1	0.1
<i>n</i> -C <sub>23</sub>	0.1	0.4	0.4	0.4	2.3	0.2	0.1	0.1	0.2	0.2	0.1	0.2	0.1	nd	0.1	na	0.1	0.1	0.2	0.4
<i>n</i> -C <sub>24</sub>	0.1	0.2	0.2	0.2	3.3	0.2	0.1	0.1	0.3	0.1	0.1	0.1	0.1	nd	0.1	na	0.1	0.2	0.3	0.8
<i>n</i> -C <sub>25</sub>	0.1	0.8	0.8	1.0	6.9	0.4	0.3	0.3	0.4	0.4	0.3	0.3	0.3	0.1	0.1	na	0.1	0.3	0.6	1.3
<i>n</i> -C <sub>26</sub>	0.1	0.4	0.3	0.4	6.7	0.3	0.2	0.3	0.3	0.2	0.1	0.2	0.1	0.1	0.1	na	0.1	0.2	0.5	1.3
<i>n</i> -C <sub>27</sub>	0.2	2.0	1.8	2.8	10	0.7	0.4	0.5	0.4	0.7	0.4	0.3	0.3	0.1	0.1	na	0.1	0.6	0.8	1.9
<i>n</i> -C <sub>28</sub>	0.1	0.4	0.3	0.5	5.8	0.2	0.1	0.2	0.3	0.3	0.1	0.1	0.1	0.1	0.1	na	0.1	0.2	0.4	1.0
<i>n</i> -C <sub>29</sub>	0.3	4.0	3.0	4.8	7.3	1.5	0.8	0.9	0.4	1.4	0.7	0.5	0.3	0.2	0.2	na	0.3	2.0	1.3	2.9
<i>n</i> -C <sub>30</sub>	0.2	0.6	0.3	0.4	3.7	0.2	0.2	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.1	na	0.1	0.3	0.3	0.7
<i>n</i> -C <sub>31</sub>	0.2	5.1	3.0	4.2	5.3	2.3	1.0	1.0	0.5	2.2	0.7	0.4	0.3	0.3	0.3	na	0.3	3.2	1.8	3.5
<i>n</i> -C <sub>32</sub>	0.2	0.5	0.3	0.3	1.7	0.2	0.0	0.1	0.2	0.1	0.1	0.1	0.1	0.0	0.0	na	0.1	0.3	0.3	0.5
<i>n</i> -C <sub>33</sub>	0.2	1.8	1.0	1.2	1.6	0.8	0.3	0.3	0.1	0.5	0.2	0.1	0.1	0.1	0.1	na	0.1	1.1	0.7	1.1
<i>n</i> -C <sub>34</sub>	0.1	0.2	0.1	0.1	0.6	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	0.1	0.1	0.2
<i>n</i> -C <sub>35</sub>	0.1	0.8	0.7	0.2	0.4	0.2	0.1	0.1	nd	0.1	0.1	nd	nd	nd	nd	na	0.2	0.2	0.2	0.2
<i>n</i> -C <sub>36</sub>	0.1	nd	nd	nd	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	0.1	0.1
<i>n</i> -C <sub>37</sub>	0.1	0.1	0.3	nd	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	0.4	0.1
<i>n</i> -C <sub>38</sub>	0.1	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
<i>n</i> -C <sub>39</sub>	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
<i>n</i> -C <sub>40</sub>	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
<b><math>\Sigma_{28}\text{AHs}</math></b>	<b>12</b>	<b>21</b>	<b>22</b>	<b>24</b>	<b>104</b>	<b>17</b>	<b>41</b>	<b>55</b>	<b>10</b>	<b>10</b>	<b>9.4</b>	<b>8.8</b>	<b>8.8</b>	<b>3.4</b>	<b>4.0</b>	<b>na</b>	<b>12</b>	<b>14</b>	<b>12</b>	<b>25</b>

na: not available; nd: not detected; Pr: pristane; Phy: phytane;  $\Sigma_{28}\text{AHs} = \Sigma n\text{-C}_{15}\text{-}n\text{-C}_{40}$ , Pr, Phy (28 compounds).

**Table S5.** Concentrations (in ng L<sup>-1</sup>) of individual and total polycyclic aromatic hydrocarbons (PAHs) in the dissolved phase (< 0.7 μm) of water collected at 5-20-m depth at the 10 stations.

	St1	St2	St3	St4	St9	St10	St11	St15	St17	St19
Nap	0.29	0.69	0.24	0.93	0.11	0.44	0.06	0.34	0.18	0.41
C1-Nap	<i>nd</i>	<i>nd</i>	<i>nd</i>	3.13	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
C2-Nap	<i>nd</i>	<i>nd</i>	<i>nd</i>	7.06	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
C3-Nap	<i>nd</i>	<i>nd</i>	<i>nd</i>	2.43	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
Acy	0.01	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.01	0.01
Ace	0.08	0.10	0.12	0.12	0.08	0.09	0.04	0.06	0.06	0.06
Flu	0.27	0.26	0.21	0.40	0.14	0.23	0.09	0.16	0.15	0.19
DBT	0.01	0.07	0.03	0.18	0.03	0.02	0.02	0.01	0.01	0.01
Phe	0.43	1.06	0.91	1.14	3.52	0.46	0.33	0.34	0.28	0.32
Ant	0.03	<i>nd</i>	0.07	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	0.05	0.03	0.06
Flt	0.17	0.34	0.82	0.17	0.13	0.15	0.13	0.14	0.15	0.12
Pyr	0.10	0.29	0.65	0.12	0.10	0.13	0.09	0.12	0.12	0.12
BaA	0.05	0.04	0.13	0.05	0.04	0.03	0.04	0.05	0.05	0.05
Chr	0.10	0.13	0.62	0.06	0.09	0.11	0.08	0.12	0.18	0.11
<b>Σ<sub>14</sub>PAHs</b>	<b>1.5</b>	<b>3.0</b>	<b>3.8</b>	<b>16</b>	<b>4.2</b>	<b>1.7</b>	<b>0.9</b>	<b>1.4</b>	<b>1.2</b>	<b>1.4</b>
<b>Σ<sub>7</sub>PAHs</b>	<b>1.4</b>	<b>2.8</b>	<b>3.6</b>	<b>2.9</b>	<b>4.1</b>	<b>1.6</b>	<b>0.8</b>	<b>1.3</b>	<b>1.1</b>	<b>1.3</b>
LMW PAHs (%)	73	73	42	97	92	74	61	69	59	73
HMW PAHs (%)	27	27	58	3	8	26	39	31	41	27

*nd*: not detected; C1: methyl; C2: di-methyl; C3: tri-methyl; Σ<sub>14</sub>PAHs = Σ Nap–Chr (14 compounds); Σ<sub>7</sub>PAHs = Σ Nap, Flu, Phe, Flt, Pyr, BaA, Chr; LMW: low molecular weight, i.e., 2-3 rings; HMW: high molecular weight, i.e., 4-6 rings.



**Figure S5.** a) Concentrations of total polycyclic aromatic hydrocarbons ( $\Sigma_{14}$ PAHs, in ng L<sup>-1</sup>) at the 10 stations, and b) mean relative abundances of individual PAHs (in %) for stations St1, St2, St3, St9, St10, St11, St15, St17, St19 and c) station St4 only, for the dissolved phase (< 0.7  $\mu$ m) of water collected at 5-20-m depth.  $\Sigma_{14}$ PAHs =  $\Sigma$  Nap–Chr (14 compounds).



**Table S6.** Concentrations (in ng g<sup>-1</sup> dw) of individual and total polycyclic aromatic hydrocarbons (PAHs) in the particulate/planktonic size fractions 0.7-60, 60-200, 200-500 and 500-1000 µm recovered from the DCM at the 10 stations.

Size fraction (µm)	St1				St2				St3				St4				St9			
	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000
Nap	18	8.0	2.9	13	25	31	7.0	7.0	36	14	5.6	3.6	20	6.2	7.8	18	11	3.9	2.1	5.2
C1-Nap	nd	4.5	1.3	2.9	nd	8.1	2.1	1.7	nd	5.0	2.4	1.2	nd	3.9	5.1	4.7	nd	1.5	0.9	1.5
C2-Nap	nd	16	4.4	8.1	nd	18	2.0	5.9	nd	18	14	7.8	nd	nd	nd	nd	nd	6.4	4.0	5.9
C3-Nap	nd	16	0.2	6.1	nd	17	5.4	5.9	nd	16	12.5	5.8	nd	10.3	14	10	nd	6.4	4.0	5.8
Acy	nd	1.8	3.1	1.4	nd	nd	nd	nd	nd	0.9	0.4	0.3	nd	nd	1.2	0.8	nd	0.5	0.2	nd
Ace	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.5	0.4	nd
Flu	14	4.3	3.4	7.6	20	19	5.5	6.9	38	15	4.9	2.2	18	5.5	14	11	9.7	3.1	2.7	2.3
C1-Flu	nd	6.8	3.6	4.0	nd	7.5	4.5	4.5	nd	7.9	7.8	4.0	nd	4.9	4.4	3.0	nd	3.6	2.9	2.1
C2-Flu	nd	5.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DBT	0.6	2.1	nd	0.5	nd	nd	nd	nd	nd	1.9	0.8	0.4	0.5	0.8	1.1	0.0	0.2	0.4	0.1	0.2
C1-DBT	nd	1.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C2-DBT	nd	2.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Phe	16	39	16	17	21	71	20	24	51	79	29	14	19	32	26	25	5.3	19	9.1	6.8
Ant	nd	1.7	nd	1.3	nd	nd	7.0	0.0	10	3.8	1.1	0.5	nd	2.1	1.9	2.4	nd	0.7	0.4	0.3
C1-Phe/Ant	nd	16	6.0	8.1	nd	nd	2.6	8.7	nd	9.1	6.9	4.7	nd	17	14	0.0	nd	6.9	5.1	4.0
C2-Phe/Ant	nd	12	nd	4.0	nd	nd	nd	nd	nd	5.7	5.1	2.9	nd	9.0	12	0.0	nd	4.8	2.8	1.4
Flt	23	24	12	9.3	7.0	14	4.3	8.3	22	10	5.1	3.4	17	16	13	12	6.6	3.4	3.4	2.1
Pyr	31	21	12	8.6	19	12	5.2	7.3	41	8.4	3.6	2.4	14	13	11	12	13	2.9	1.6	1.1
C1-Flt/Pyr	nd	17	6.1	4.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	7.8	5.6	0.0	nd	2.2	3.0	1.2
BaA	9.0	14	0.3	3.6	8.2	2.9	1.1	1.6	11	2.5	1.3	0.6	14	5.9	4.9	4.7	4.4	2.3	0.4	0.7
Chr	19	17	4.8	8.2	12	5.1	2.6	6.1	12	3.9	3.0	3.5	35	13	8.9	16	3.5	3.0	2.4	1.2
BbF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BkF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IndP	nd	8.2	nd	2.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	7.3	6.9	nd	2.1	nd	nd
DahA	nd	6.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.7	nd	nd	nd	nd	nd
BP	nd	8.6	nd	5.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	11.5	11	nd	2.4	nd	nd
<b>Σ<sub>27</sub>PAHs</b>	<b>130</b>	<b>255</b>	<b>76</b>	<b>116</b>	<b>111</b>	<b>206</b>	<b>69</b>	<b>88</b>	<b>220</b>	<b>201</b>	<b>104</b>	<b>57</b>	<b>136</b>	<b>168</b>	<b>162</b>	<b>119</b>	<b>53</b>	<b>76</b>	<b>45</b>	<b>42</b>
<b>Σ<sub>7</sub>PAHs</b>	<b>129</b>	<b>127</b>	<b>51</b>	<b>67</b>	<b>111</b>	<b>155</b>	<b>46</b>	<b>61</b>	<b>211</b>	<b>133</b>	<b>52</b>	<b>29</b>	<b>136</b>	<b>91</b>	<b>85</b>	<b>98</b>	<b>53</b>	<b>37</b>	<b>22</b>	<b>19</b>
LMW PAHs	37	55	54	64	59	83	81	73	61	88	83	81	41	55	62	63	48	76	76	85
HMW PAHs	63	45	46	36	41	17	19	27	39	12	17	19	59	45	38	37	52	24	24	15

	St10				St11				St15				St17				St19			
Size fraction (µm)	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000	0.7-60	60-200	200-500	500-1000
Nap	23	8.9	3.0	8.2	64	5.5	4.0	3.0	29	11	2.9	4.3	15	2.7	3.8	na	13	2.9	2.7	11
C1-Nap	nd	2.4	2.0	1.9	nd	2.2	1.6	1.4	nd	4.1	2.7	1.4	nd	1.5	1.6	na	nd	1.1	0.9	nd
C2-Nap	nd	8.4	14	6.7	nd	10	9.1	7.4	nd	0.0	17	8.8	nd	nd	nd	na	nd	6.2	5.5	nd
C3-Nap	nd	19	0.0	6.3	nd	12	13	8.5	nd	17	16	8.6	nd	5.1	4.2	na	nd	4.0	4.9	nd
Acv	nd	1.2	0.6	0.7	nd	0.5	0.2	0.2	nd	nd	0.6	0.2	nd	nd	nd	na	nd	nd	nd	nd
Ace	nd	nd	nd	nd	nd	nd	1.0	0.9	nd	nd	1.8	1.1	nd	nd	nd	na	nd	0.6	0.3	nd
Flu	14	7.7	5.6	7.1	41	6.8	4.8	4.5	20	12	8.5	4.8	13	3.1	4.2	na	11	2.9	2.5	6.9
C1-Flu	nd	6.3	9.3	4.9	nd	7.8	7.8	7.0	nd	4.1	8.2	3.9	nd	nd	nd	na	nd	nd	nd	nd
C2-Flu	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
DBT	0.2	0.8	0.7	0.3	nd	1.1	0.5	0.3	0.6	1.9	1.0	0.5	nd	0.4	0.3	na	0.2	0.4	0.3	0.4
C1-DBT	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
C2-DBT	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
Phe	9.4	38	24	21	41	46	23	15	22	67	37	21	8.7	15	14	na	8.7	14	8.6	17
Ant	nd	1.2	1.1	0.6	nd	1.4	0.6	0.4	nd	nd	1.3	0.7	nd	nd	nd	na	nd	0.3	0.1	0.0
C1-Phe/Ant	nd	9.9	10	6.7	nd	5.4	7.2	6.8	nd	9.3	9.8	7.0	nd	6.0	5.4	na	nd	5.7	3.3	0.0
C2-Phe/Ant	nd	6.0	5.9	3.1	nd	4.5	3.6	3.6	nd	0.0	11	8.6	nd	4.8	4.0	na	nd	3.5	2.6	0.0
Flt	9.1	7.3	4.8	4.9	20	7.2	2.6	2.3	24	5.2	3.6	3.2	11	1.4	1.7	na	9.0	1.1	1.0	2.0
Pyr	21	5.9	3.1	4.4	24	4.8	1.6	1.4	31	8.3	2.6	4.0	19	2.1	3.1	na	18	1.4	1.0	2.7
C1-Flt/Pyr	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
BaA	7.6	1.3	0.8	1.0	18	1.9	0.6	0.6	19	0.0	1.3	0.9	7.3	0.3	0.4	na	6.9	0.3	0.3	1.5
Chr	9.4	4.1	2.9	2.7	11	4.4	1.6	1.8	18	2.1	2.0	2.0	15	0.9	0.9	na	4.3	0.5	0.5	1.0
BbF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
BkF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
BaP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
IndP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
DahA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
BP	nd	nd	nd	nd	nd	2.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
<b>Σ<sub>27</sub>PAHs</b>	<b>94</b>	<b>128</b>	<b>87</b>	<b>80</b>	<b>219</b>	<b>124</b>	<b>83</b>	<b>65</b>	<b>163</b>	<b>141</b>	<b>126</b>	<b>81</b>	<b>89</b>	<b>43</b>	<b>44</b>	<b>na</b>	<b>71</b>	<b>45</b>	<b>35</b>	<b>43</b>
<b>Σ<sub>7</sub>PAHs</b>	<b>94</b>	<b>73</b>	<b>44</b>	<b>49</b>	<b>219</b>	<b>76</b>	<b>38</b>	<b>28</b>	<b>163</b>	<b>105</b>	<b>58</b>	<b>40</b>	<b>89</b>	<b>25</b>	<b>28</b>	<b>na</b>	<b>71</b>	<b>23</b>	<b>17</b>	<b>42</b>
LMW PAHs	50	85	87	84	66	84	92	90	43	89	92	87	41	89	86	na	47	93	92	83
HMW PAHs	50	15	13	16	34	16	8	10	57	11	8	13	59	11	14	na	53	7	8	17

na: not available; nd: not detected; C1: methyl; C2: di-methyl; C3: tri-methyl; Σ<sub>27</sub>PAHs = Σ Nap–BP (27 compounds); Σ<sub>7</sub>PAHs = Σ Nap, Flu, Phe, Flt, Pyr, BaA, Chr; LMW: low molecular weight, i.e., 2-3 rings; HMW: high molecular weight, i.e., 4-6 rings.

**Table S7.** Summary of SPM, biomass, POC and individual PAH concentration data for the particulate/planktonic size fractions 0.7-60, 60-200, 200-500, 500-1000  $\mu\text{m}$ , but also 60-1000  $\mu\text{m}$ , recovered from the DCM at the 10 stations.

	Size fractions ( $\mu\text{m}$ )	Biomass (mg dw L <sup>-1</sup> ) or SPM (mg L <sup>-1</sup> )	f <sub>Biomass</sub>	POC (mg g <sup>-1</sup> dw)	f <sub>oc</sub>	ng L <sup>-1</sup> for < 0.7 $\mu\text{m}$ , ng g <sup>-1</sup> dw for other fractions						
						Nap	Flu	Phe	Flt	Pyr	BaA	Chr
<b>St1</b>	< 0.7	na	na	na	na	0.29	0.27	0.43	0.17	0.10	0.05	0.10
	0.7-60	0.347	na	134.5	0.135	18.0	13.6	16.1	22.8	31.2	9.0	18.7
	60-200	0.020	0.3	263.4	0.263	8.0	4.3	39.1	23.8	20.5	13.7	17.4
	200-500	0.037	0.6	246.4	0.246	2.9	3.4	16.3	12.0	11.9	0.3	4.8
	500-1000	0.005	0.1	284.9	0.285	13.3	7.6	16.5	9.3	8.6	3.6	8.2
60-1000	0.062	1.0	254.8	0.255	5.3	4.0	23.6	15.6	14.4	4.8	9.1	
<b>St2</b>	< 0.7	na	na	na	na	0.69	0.26	1.06	0.34	0.29	0.04	0.13
	0.7-60	0.320	na	67.3	0.067	25.3	19.6	20.7	7.0	18.5	8.2	12.2
	60-200	0.007	0.3	129.4	0.129	31.2	19.0	71.2	13.9	12.1	2.9	5.1
	200-500	0.007	0.3	238.0	0.238	7.0	5.5	20.1	4.3	5.2	1.1	2.6
	500-1000	0.007	0.3	207.1	0.207	7.0	6.9	23.9	8.3	7.3	1.6	6.1
60-1000	0.021	1.0	190.7	0.191	15.3	10.6	38.9	8.9	8.3	1.9	4.6	
<b>St3</b>	< 0.7	na	na	na	na	0.24	0.21	0.91	0.82	0.65	0.13	0.62
	0.7-60	0.210	na	78.3	0.078	36.3	38.1	50.8	22.2	40.6	11.2	11.6
	60-200	0.002	0.2	81.9	0.082	14.0	15.4	78.5	10.2	8.4	2.5	3.9
	200-500	0.002	0.3	179.6	0.180	5.6	4.9	28.5	5.1	3.6	1.3	3.0
	500-1000	0.004	0.5	168.5	0.169	3.6	2.2	13.5	3.4	2.4	0.6	3.5
60-1000	0.008	1.0	152.0	0.152	6.5	5.9	32.5	5.4	4.1	1.2	3.4	
<b>St4</b>	< 0.7	na	na	na	na	0.93	0.4	1.14	0.17	0.12	0.05	0.06
	0.7-60	0.220	na	159.5	0.159	19.7	17.5	18.8	16.5	14.4	14.0	34.9
	60-200	0.068	0.7	103.5	0.104	6.2	5.5	31.7	16.4	13.2	5.9	12.6
	200-500	0.028	0.3	139.4	0.139	7.8	13.5	26.4	12.5	10.9	4.9	8.9
	500-1000	0.007	0.1	109.7	0.110	18.2	11.4	24.6	12.0	11.6	4.7	15.5
60-1000	0.104	1.0	113.8	0.114	7.4	8.1	29.8	15.0	12.5	5.5	11.8	
<b>St9</b>	< 0.7	na	na	na	na	0.11	0.14	3.52	0.13	0.1	0.04	0.09
	0.7-60	0.670	na	261.8	0.262	10.5	9.7	5.3	6.6	13.2	4.4	3.5
	60-200	0.017	0.4	249.8	0.250	3.9	3.1	18.7	3.4	2.9	2.3	3.0
	200-500	0.023	0.5	341.0	0.341	2.1	2.7	9.1	3.4	1.6	0.4	2.4
	500-1000	0.004	0.1	326.2	0.326	5.2	2.3	6.8	2.1	1.1	0.7	1.2
60-1000	0.044	1.0	304.2	0.304	3.1	2.8	12.7	3.3	2.1	1.2	2.6	
<b>St10</b>	< 0.7	na	na	na	na	0.44	0.23	0.46	0.15	0.13	0.03	0.11
	0.7-60	0.250	na	118.6	0.119	23.1	14.3	9.4	9.1	20.5	7.6	9.4
	60-200	0.003	0.4	240.3	0.240	8.9	7.7	37.9	7.3	5.9	1.3	4.1
	200-500	0.004	0.4	269.8	0.270	3.0	5.6	24.0	4.8	3.1	0.8	2.9
	500-1000	0.002	0.2	222.8	0.223	8.2	7.1	20.5	4.9	4.4	1.0	2.7
60-1000	0.010	1.0	249.1	0.249	6.3	6.7	28.3	5.7	4.4	1.0	3.3	
<b>St11</b>	< 0.7	na	na	na	na	0.06	0.09	0.33	0.13	0.09	0.04	0.08
	0.7-60	0.150	na	121.7	0.122	64.2	40.5	40.7	20.4	24.3	17.6	11.3
	60-200	0.004	0.2	271.5	0.271	5.5	6.8	45.9	7.2	4.8	1.9	4.4
	200-500	0.005	0.3	299.9	0.300	4.0	4.8	22.8	2.6	1.6	0.6	1.6

	500-1000	0.009	0.5	311.4	0.311	3.0	4.5	14.5	2.3	1.4	0.6	1.8
	60-1000	0.018	1.0	299.1	0.299	3.9	5.1	23.9	3.5	2.2	0.9	2.4
<b>St15</b>	< 0.7	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	0.34	0.16	0.34	0.14	0.12	0.05	0.12
	0.7-60	0.120	<i>na</i>	120.6	0.121	28.6	19.7	22.0	24.0	31.0	18.8	18.4
	60-200	0.006	0.3	153.7	0.154	10.5	12.0	66.9	5.2	8.3	<i>na</i>	2.1
	200-500	0.010	0.4	199.6	0.200	2.9	8.5	37.0	3.6	2.6	1.3	2.0
	500-1000	0.009	0.3	228.9	0.229	4.3	4.8	20.6	3.2	4.0	0.9	2.0
	60-1000	0.025	1.0	198.1	0.198	5.3	8.1	38.9	3.9	4.5	0.8	2.0
<b>St17</b>	< 0.7	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	0.18	0.15	0.28	0.15	0.12	0.05	0.18
	0.7-60	0.290	<i>na</i>	80.9	0.081	15.0	13.1	8.7	10.7	18.9	7.3	15.1
	60-200	0.083	0.5	43.5	0.044	2.7	3.1	14.5	1.4	2.1	0.3	0.9
	200-500	0.072	0.5	75.9	0.076	3.8	4.2	14.0	1.7	3.1	0.4	0.9
	500-1000	0.002	0.0	<i>na</i>	0.000	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>
	60-1000	0.157	1.0	57.7	0.058	3.2	3.6	14.1	1.5	2.6	0.4	0.9
<b>St19</b>	< 0.7	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	0.41	0.19	0.32	0.12	0.12	0.05	0.11
	0.7-60	0.340	<i>na</i>	141.9	0.142	13.4	10.7	8.7	9.0	17.6	6.9	4.3
	60-200	0.029	0.4	156.0	0.156	2.9	2.9	14.0	1.1	1.4	0.3	0.5
	200-500	0.038	0.5	204.7	0.205	2.7	2.5	8.6	1.0	1.0	0.3	0.5
	500-1000	0.011	0.1	190.5	0.191	10.8	6.9	17.3	2.0	2.7	1.5	1.0
	60-1000	0.078	1.0	184.9	0.185	3.9	3.3	11.8	1.2	1.4	0.5	0.6

*na*: not available.

$f_{\text{Biomass}}$ : contribution of the biomass of a given size fraction to the total biomass of the fraction 60-1000  $\mu\text{m}$  (i.e.,  $f_{\text{Biomass } x} = \text{biomass fraction } x / \text{biomass } 60\text{-}1000 \mu\text{m}$ ), with biomass 60-1000  $\mu\text{m} = \text{biomass } 60\text{-}200 \mu\text{m} + \text{biomass } 200\text{-}500 \mu\text{m} + \text{biomass } 500\text{-}1000 \mu\text{m}$ .

$f_{\text{OC}}$ : contribution of the OC mass (in g) to the total matter mass (in g) for a given size fraction (i.e.,  $f_{\text{OC}} = \text{POC in mg g}^{-1} \text{ dw} / 1000$ ).

Concentrations of POC and individual PAHs in the size fraction 60-1000  $\mu\text{m}$  were calculated by summing the concentrations of POC/PAH in the fractions 60-200, 200-500 and 500-1000  $\mu\text{m}$ , each of these concentrations being weighted (multiplied) by the corresponding  $f_{\text{Biomass}}$  value.

**Table S8.** Partition coefficient between particulate matter and water ( $K_D$  in  $L\ kg^{-1}$ ) and  $\log K_D$  for the 7 individual PAHs in each particulate/planktonic size fraction (0.7-60, 60-200, 200-500, 500-1000 and 60-1000  $\mu m$ ) and station.

	Size fractions ( $\mu m$ )	$K_D$ ( $L\ kg^{-1}$ )							$\log K_D$						
		Nap	Flu	Phe	Flt	Pyr	BaA	Chr	Nap	Flu	Phe	Flt	Pyr	BaA	Chr
<b>St1</b>	0.7-60	61968	50402	37546	133838	311743	180191	186903	4.79	4.70	4.57	5.13	5.49	5.26	5.27
	60-200	27589	16089	90814	140275	205392	274689	173735	4.44	4.21	4.96	5.15	5.31	5.44	5.24
	200-500	9828	12537	37820	70311	118644	5214	48387	3.99	4.10	4.58	4.85	5.07	3.72	4.68
	500-1000	45902	28186	38282	54476	86145	71473	82200	4.66	4.45	4.58	4.74	4.94	4.85	4.91
	60-1000	18260	14858	54904	91627	144104	96901	91261	4.26	4.17	4.74	4.96	5.16	4.99	4.96
<b>St2</b>	0.7-60	36609	75278	19529	20684	63624	204506	93689	4.56	4.88	4.29	4.32	4.80	5.31	4.97
	60-200	45212	73198	67132	40743	41854	72886	39568	4.66	4.86	4.83	4.61	4.62	4.86	4.60
	200-500	10146	21025	18963	12569	17848	27888	19819	4.01	4.32	4.28	4.10	4.25	4.45	4.30
	500-1000	10112	26496	22549	24554	25330	39204	46882	4.00	4.42	4.35	4.39	4.40	4.59	4.67
	60-1000	22158	40704	36652	26149	28527	47018	35442	4.35	4.61	4.56	4.42	4.46	4.67	4.55
<b>St3</b>	0.7-60	151402	181259	55817	27024	62409	86410	18700	5.18	5.26	4.75	4.43	4.80	4.94	4.27
	60-200	58158	73373	86227	12394	12911	19161	6264	4.76	4.87	4.94	4.09	4.11	4.28	3.80
	200-500	23466	23460	31367	6262	5549	10291	4771	4.37	4.37	4.50	3.80	3.74	4.01	3.68
	500-1000	14877	10256	14874	4152	3625	4582	5674	4.17	4.01	4.17	3.62	3.56	3.66	3.75
	60-1000	27090	28257	35665	6611	6268	9488	5553	4.43	4.45	4.55	3.82	3.80	3.98	3.74
<b>St4</b>	0.7-60	21168	43669	16528	96979	120318	279300	582278	4.33	4.64	4.22	4.99	5.08	5.45	5.77
	60-200	6636	13871	27774	96459	109872	117408	210352	3.82	4.14	4.44	4.98	5.04	5.07	5.32
	200-500	8399	33723	23161	73713	90808	98657	148349	3.92	4.53	4.36	4.87	4.96	4.99	5.17
	500-1000	19537	28604	21574	70335	96549	94223	259076	4.29	4.46	4.33	4.85	4.98	4.97	5.41
	60-1000	7969	20296	26098	88489	103755	110729	196512	3.90	4.31	4.42	4.95	5.02	5.04	5.29
<b>St9</b>	0.7-60	95270	68960	1493	50734	132374	110649	39342	4.98	4.84	3.17	4.71	5.12	5.04	4.59
	60-200	35853	21900	5322	25968	28505	57125	33596	4.55	4.34	3.73	4.41	4.45	4.76	4.53
	200-500	19084	19166	2576	26267	16184	10828	26720	4.28	4.28	3.41	4.42	4.21	4.03	4.43
	500-1000	47133	16105	1925	16116	10509	17476	13828	4.67	4.21	3.28	4.21	4.02	4.24	4.14
	60-1000	27946	19982	3595	25313	20528	29460	28343	4.45	4.30	3.56	4.40	4.31	4.47	4.45

<b>St10</b>	0.7-60	52540	62279	20510	60652	157676	254108	85776	4.72	4.79	4.31	4.78	5.20	5.41	4.93
	60-200	20289	33631	82380	48585	45451	44561	37710	4.31	4.53	4.92	4.69	4.66	4.65	4.58
	200-500	6842	24396	52248	31807	23638	26642	26065	3.84	4.39	4.72	4.50	4.37	4.43	4.42
	500-1000	18656	30738	44642	32334	33982	32109	24520	4.27	4.49	4.65	4.51	4.53	4.51	4.39
	60-1000	14207	29077	61501	37973	33709	34270	29938	4.15	4.46	4.79	4.58	4.53	4.53	4.48
<b>St11</b>	0.7-60	1069630	450076	123387	157163	269475	438959	141026	6.03	5.65	5.09	5.20	5.43	5.64	5.15
	60-200	92396	75597	138982	55169	52831	46976	55423	4.97	4.88	5.14	4.74	4.72	4.67	4.74
	200-500	66860	53573	69056	19705	17609	14275	20606	4.83	4.73	4.84	4.29	4.25	4.15	4.31
	500-1000	49587	49642	44022	17633	15897	14987	22986	4.70	4.70	4.64	4.25	4.20	4.18	4.36
	60-1000	64228	56554	72511	26545	24568	21838	29436	4.81	4.75	4.86	4.42	4.39	4.34	4.47
<b>St15</b>	0.7-60	84002	123336	64712	171305	258611	376558	153414	4.92	5.09	4.81	5.23	5.41	5.58	5.19
	60-200	30812	74703	196819	37477	68844	na	17260	4.49	4.87	5.29	4.57	4.84	na	4.24
	200-500	8393	53192	108873	25889	21841	25581	16829	3.92	4.73	5.04	4.41	4.34	4.41	4.23
	500-1000	12633	29775	60603	23024	33464	17750	16592	4.10	4.47	4.78	4.36	4.52	4.25	4.22
	60-1000	15576	50540	114513	27846	37849	16346	16856	4.19	4.70	5.06	4.44	4.58	4.21	4.23
<b>St17</b>	0.7-60	83560	87018	31093	71024	157840	146655	83961	4.92	4.94	4.49	4.85	5.20	5.17	4.92
	60-200	14794	20698	51923	9088	17663	6351	4730	4.17	4.32	4.72	3.96	4.25	3.80	3.67
	200-500	21283	27846	49855	11467	26234	8756	5032	4.33	4.44	4.70	4.06	4.42	3.94	3.70
	500-1000	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	60-1000	17559	23683	50268	10051	21340	7364	4804	4.24	4.37	4.70	4.00	4.33	3.87	3.68
<b>St19</b>	0.7-60	32747	56337	27095	75145	146679	138735	39072	4.52	4.75	4.43	4.88	5.17	5.14	4.59
	60-200	7098	15390	43658	9115	11776	6363	4416	3.85	4.19	4.64	3.96	4.07	3.80	3.65
	200-500	6464	13385	26780	8743	8199	6837	4486	3.81	4.13	4.43	3.94	3.91	3.83	3.65
	500-1000	26428	36095	54197	17081	22413	29267	8729	4.42	4.56	4.73	4.23	4.35	4.47	3.94
	60-1000	9560	17377	36894	10076	11548	9881	5069	3.98	4.24	4.57	4.00	4.06	3.99	3.70

na: not available.

$K_D$  in a given size fraction (in  $L\ kg^{-1}$ ) was calculated as  $(C_P / C_W) \times 1000$  where  $C_P$  is the concentration in the given size fraction (0.7-60, 60-200, 200-500, 500-1000 or 60-1000  $\mu m$ ) in  $ng\ g^{-1}\ dw$ , and  $C_W$  is the concentration in the dissolved phase (size fraction  $< 0.7\ \mu m$ ) in  $ng\ L^{-1}$  (see concentration values in [Table S7](#)).

**Table S9.** Partition coefficient between particulate organic carbon and water ( $K_{oc}$  in  $L\ kg^{-1}$ ) and  $\log K_{oc}$  for the 7 individual PAHs in each particulate/planktonic size fraction (0.7-60, 60-200, 200-500, 500-1000 and 60-1000  $\mu m$ ) and station.

	Size fractions ( $\mu m$ )	$K_{oc}$ ( $L\ kg^{-1}$ )							$\log K_{oc}$						
		Nap	Flu	Phe	Flt	Pyr	BaA	Chr	Nap	Flu	Phe	Flt	Pyr	BaA	Chr
<b>St1</b>	0.7-60	460668	374689	279118	994947	2317478	1339528	1389425	5.66	5.57	5.45	6.00	6.37	6.13	6.14
	60-200	104753	61088	344818	532618	779864	1042985	659666	5.02	4.79	5.54	5.73	5.89	6.02	5.82
	200-500	39882	50870	153465	285307	481430	21158	196344	4.60	4.71	5.19	5.46	5.68	4.33	5.29
	500-1000	161111	98931	134364	191204	302359	250863	288511	5.21	5.00	5.13	5.28	5.48	5.40	5.46
	60-1000	71668	58317	215492	359625	565591	380325	358190	4.86	4.77	5.33	5.56	5.75	5.58	5.55
<b>St2</b>	0.7-60	544172	1118977	290285	307460	945751	3039907	1392659	5.74	6.05	5.46	5.49	5.98	6.48	6.14
	60-200	349441	565739	518858	314903	323486	563330	305815	5.54	5.75	5.72	5.50	5.51	5.75	5.49
	200-500	42629	88340	79678	52811	74993	117177	83274	4.63	4.95	4.90	4.72	4.88	5.07	4.92
	500-1000	48817	127917	108860	118539	122289	189270	226335	4.69	5.11	5.04	5.07	5.09	5.28	5.35
	60-1000	116218	213486	192237	137151	149619	246607	185889	5.07	5.33	5.28	5.14	5.17	5.39	5.27
<b>St3</b>	0.7-60	1932978	2314155	712623	345014	796789	1103212	238747	6.29	6.36	5.85	5.54	5.90	6.04	5.38
	60-200	710302	896119	1053109	151376	157686	234022	76500	5.85	5.95	6.02	5.18	5.20	5.37	4.88
	200-500	130691	130660	174696	34874	30906	57318	26572	5.12	5.12	5.24	4.54	4.49	4.76	4.42
	500-1000	88273	60852	88254	24633	21508	27187	33664	4.95	4.78	4.95	4.39	4.33	4.43	4.53
	60-1000	178195	185871	234598	43486	41231	62414	36528	5.25	5.27	5.37	4.64	4.62	4.80	4.56
<b>St4</b>	0.7-60	132741	273843	103643	608138	754497	1751447	3651377	5.12	5.44	5.02	5.78	5.88	6.24	6.56
	60-200	64104	133993	268299	931804	1061367	1134174	2032019	4.81	5.13	5.43	5.97	6.03	6.05	6.31
	200-500	60238	241861	166114	528673	651276	707567	1063960	4.78	5.38	5.22	5.72	5.81	5.85	6.03
	500-1000	178166	260857	196749	641429	880487	859272	2362657	5.25	5.42	5.29	5.81	5.94	5.93	6.37
	60-1000	70029	178362	229349	777627	911784	973070	1726916	4.85	5.25	5.36	5.89	5.96	5.99	6.24
<b>St9</b>	0.7-60	363924	263421	5701	193802	505661	422670	150284	5.56	5.42	3.76	5.29	5.70	5.63	5.18
	60-200	143511	87660	21304	103943	114097	228659	134477	5.16	4.94	4.33	5.02	5.06	5.36	5.13
	200-500	55964	56205	7553	77028	47460	31755	78358	4.75	4.75	3.88	4.89	4.68	4.50	4.89
	500-1000	144472	49366	5900	49400	32212	53567	42386	5.16	4.69	3.77	4.69	4.51	4.73	4.63
	60-1000	91876	65691	11818	83219	67489	96851	93180	4.96	4.82	4.07	4.92	4.83	4.99	4.97

<b>St10</b>	0.7-60	443056	525175	172952	511461	1329629	2142808	723320	5.65	5.72	5.24	5.71	6.12	6.33	5.86
	60-200	84431	139949	342812	202181	189140	185436	156926	4.93	5.15	5.54	5.31	5.28	5.27	5.20
	200-500	25363	90433	193676	117905	87623	98759	96619	4.40	4.96	5.29	5.07	4.94	4.99	4.99
	500-1000	83737	137966	200373	145130	152524	144120	110055	4.92	5.14	5.30	5.16	5.18	5.16	5.04
	60-1000	57025	116708	246848	152412	135298	137552	120162	4.76	5.07	5.39	5.18	5.13	5.14	5.08
<b>St11</b>	0.7-60	8790529	3698855	1014031	1291613	2214626	3607490	1158992	6.94	6.57	6.01	6.11	6.35	6.56	6.06
	60-200	340341	278463	511941	203214	194604	173037	204152	5.53	5.44	5.71	5.31	5.29	5.24	5.31
	200-500	222956	178647	230279	65711	58719	47601	68714	5.35	5.25	5.36	4.82	4.77	4.68	4.84
	500-1000	159212	159389	141344	56615	51042	48120	73804	5.20	5.20	5.15	4.75	4.71	4.68	4.87
	60-1000	214702	189051	242391	88736	82127	73001	98398	5.33	5.28	5.38	4.95	4.91	4.86	4.99
<b>St15</b>	0.7-60	696518	1022653	536565	1420401	2144309	3122278	1272055	5.84	6.01	5.73	6.15	6.33	6.49	6.10
	60-200	200476	486051	1280589	243839	447930	na	112302	5.30	5.69	6.11	5.39	5.65	na	5.05
	200-500	42054	266527	545532	129722	109436	128180	84325	4.62	5.43	5.74	5.11	5.04	5.11	4.93
	500-1000	55199	130105	264806	100604	146222	77560	72498	4.74	5.11	5.42	5.00	5.17	4.89	4.86
	60-1000	78642	255181	578188	140595	191104	82533	85109	4.90	5.41	5.76	5.15	5.28	4.92	4.93
<b>St17</b>	0.7-60	1032441	1075161	384173	877555	1950225	1812018	1037395	6.01	6.03	5.58	5.94	6.29	6.26	6.02
	60-200	339793	475388	1192589	208734	405686	145862	108647	5.53	5.68	6.08	5.32	5.61	5.16	5.04
	200-500	280379	366838	656778	151058	345594	115350	66296	5.45	5.56	5.82	5.18	5.54	5.06	4.82
	500-1000	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	60-1000	304082	410144	870539	174068	369568	127522	83192	5.48	5.61	5.94	5.24	5.57	5.11	4.92
<b>St19</b>	0.7-60	230824	397097	190980	529667	1033887	977889	275405	5.36	5.60	5.28	5.72	6.01	5.99	5.44
	60-200	45495	98644	279833	58425	75483	40786	28306	4.66	4.99	5.45	4.77	4.88	4.61	4.45
	200-500	31570	65375	130801	42704	40044	33392	21910	4.50	4.82	5.12	4.63	4.60	4.52	4.34
	500-1000	138704	189442	284452	89649	117631	153609	45814	5.14	5.28	5.45	4.95	5.07	5.19	4.66
	60-1000	51715	94001	199576	54504	62468	53453	27421	4.71	4.97	5.30	4.74	4.80	4.73	4.44

na: not available.

$K_{OC}$  in a given size fraction (in  $L\ kg^{-1}$ ) was calculated as  $K_D / f_{OC}$  in the corresponding fraction (0.7-60, 60-200, 200-500, 500-1000 or 60-1000  $\mu m$ ) (see values of  $K_D$  in [Table S8](#) and values of  $f_{OC}$  in [Table S7](#)).

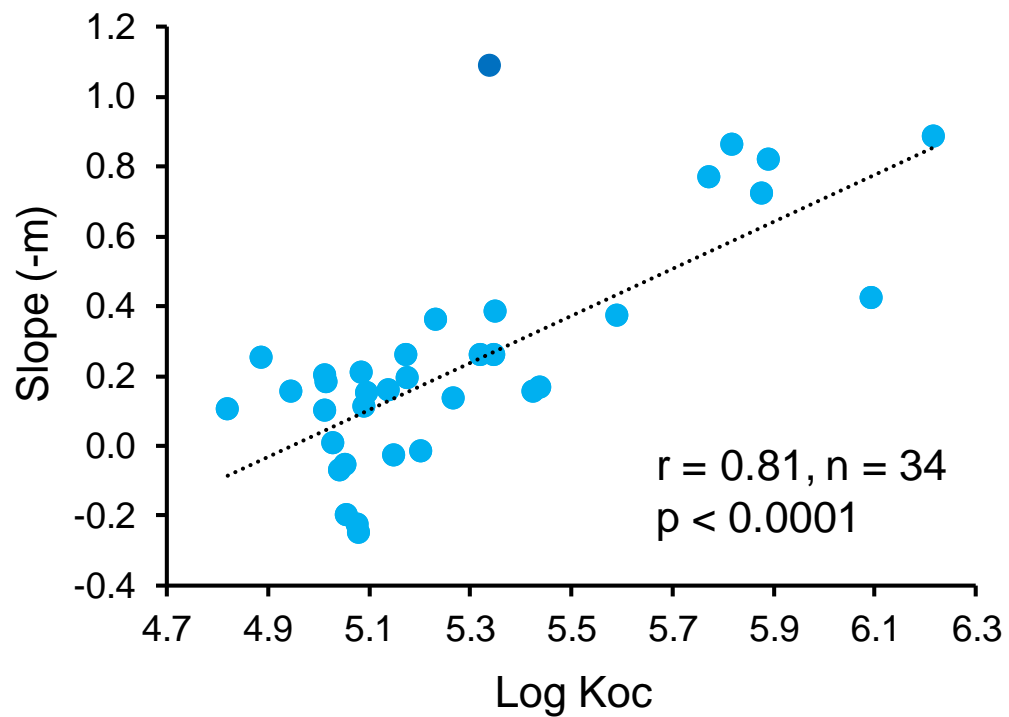


**Table S10.** Nonlinear regression parameters (power function) between SPM (in mg L<sup>-1</sup>) or biomass (in mg dw L<sup>-1</sup>; horizontal axis) and PAH concentration (C<sub>p</sub> in ng g<sup>-1</sup> dw; vertical axis) for each particulate/planktonic size fraction (0.7-60, 60-200, 200-500, 500-1000 and 60-1000 μm) and individual PAH; The power functions are of the form:  $y = ax^{-m}$  (i.e.,  $C_p = aSPM^{-m}$  or  $aBiomass^{-m}$ ). The number of samples n correspond to the stations. Power functions for Phe are shown Fig. 8.

	Size fractions (μm)	Constant (a)	Slope (-m)	Coefficient of correlation (r)	Number of samples (n)	Probability (p)
<b>Nap</b>	0.7-60	6.98	0.863	- 0.79	10	< 0.05
	60-200	1.44	0.362	- 0.62	10	< 0.05
	200-500	2.42	0.106	- 0.27	10	> 0.05
	500-1000	6.61	0.008	- 0.01	9	> 0.05
	60-1000	2.91	0.181	- 0.38	10	> 0.05
<b>Flu</b>	0.7-60	6.65	0.723	- 0.72	10	< 0.05
	60-200	1.18	0.384	- 0.72	10	< 0.05
	200-500	3.05	0.111	- 0.25	10	> 0.05
	500-1000	19.10	- 0.249	0.24	9	> 0.05
	60-1000	2.77	0.195	- 0.44	10	> 0.05
<b>Phe</b>	0.7-60	3.70	1.091	- 0.73	10	< 0.05
	60-200	6.81	0.373	- 0.75	10	< 0.05
	200-500	6.11	0.261	- 0.62	10	< 0.05
	500-1000	46.86	- 0.200	0.27	9	> 0.05
	60-1000	9.75	0.260	- 0.58	10	< 0.05
<b>Flt</b>	0.7-60	4.72	0.769	- 0.72	10	< 0.05
	60-200	1.93	0.262	- 0.33	10	> 0.05
	200-500	2.56	0.100	- 0.15	10	> 0.05
	500-1000	1.50	0.202	- 0.16	9	> 0.05
	60-1000	2.74	0.160	- 0.19	10	> 0.05
<b>Pyr</b>	0.7-60	12.29	0.423	- 0.57	10	< 0.05
	60-200	2.85	0.166	- 0.25	10	> 0.05
	200-500	4.48	- 0.071	0.10	10	> 0.05
	500-1000	4.86	- 0.054	0.23	9	> 0.05
	60-1000	4.46	- 0.014	0.12	10	> 0.05
<b>BaA</b>	0.7-60	2.92	0.886	- 0.94	10	< 0.05
	60-200	0.97	0.157	- 0.17	9	> 0.05
	200-500	0.26	0.254	- 0.33	10	> 0.05
	500-1000	4.09	- 0.226	0.16	9	> 0.05
	60-1000	1.37	- 0.026	0.03	10	> 0.05
<b>Chr</b>	0.7-60	3.84	0.821	- 0.58	10	< 0.05
	60-200	1.88	0.134	- 0.16	10	> 0.05
	200-500	1.17	0.154	- 0.22	10	> 0.05
	500-1000	1.07	0.209	- 0.12	9	> 0.05
	60-1000	1.69	0.153	- 0.16	10	> 0.05

**Table S11.** Mean values of Log  $K_D$  and Log  $K_{OC}$ , and slope (-m) of the power function between SPM or biomass and PAH concentration for each particulate/planktonic size fraction (0.7-60, 60-200, 200-500, 500-1000 and 60-1000  $\mu\text{m}$ ) and individual PAHs. Mean Log  $K_D$  and Log  $K_{OC}$  were determined over the 10 stations from Log  $K_D$  and Log  $K_{OC}$  values reported in [Tables S8](#) and [S9](#), respectively. Slope values are also reported [Table S10](#).

	Size fractions ( $\mu\text{m}$ )	Mean Log $K_D$	Mean Log $K_{OC}$	Slope (-m)
<b>Nap</b>	0.7-60	4.895	5.818	0.863
	60-200	4.402	5.233	0.362
	200-500	4.130	4.820	0.106
	500-1000	4.366	5.029	0.008
	60-1000	4.277	5.016	0.181
<b>Flu</b>	0.7-60	4.955	5.877	0.723
	60-200	4.520	5.351	0.384
	200-500	4.402	5.092	0.111
	500-1000	4.418	5.081	- 0.249
	60-1000	4.437	5.177	0.195
<b>Phe</b>	0.7-60	4.414	5.337	1.091
	60-200	4.760	5.591	0.373
	200-500	4.485	5.175	0.261
	500-1000	4.393	5.056	- 0.200
	60-1000	4.580	5.320	0.260
<b>Flt</b>	0.7-60	4.851	5.773	0.769
	60-200	4.517	5.348	0.262
	200-500	4.324	5.014	0.100
	500-1000	4.350	5.013	0.202
	60-1000	4.400	5.140	0.160
<b>Pyr</b>	0.7-60	5.170	6.093	0.423
	60-200	4.608	5.439	0.166
	200-500	4.353	5.043	- 0.071
	500-1000	4.390	5.053	- 0.054
	60-1000	4.463	5.202	- 0.014
<b>BaA</b>	0.7-60	5.292	6.215	0.886
	60-200	4.593	5.426	0.157
	200-500	4.197	4.887	0.254
	500-1000	4.414	5.077	- 0.226
	60-1000	4.410	5.149	- 0.026
<b>Chr</b>	0.7-60	4.966	5.889	0.821
	60-200	4.436	5.267	0.134
	200-500	4.257	4.947	0.154
	500-1000	4.423	5.086	0.209
	60-1000	4.356	5.095	0.153



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**Figure S6.** Linear relationship between the mean Log Koc and slope (-m) values (reported in Table S11) for all the particulate/planktonic size fractions, i.e., 0.7-60, 60-200, 200-500, 500-1000 and 60-1000  $\mu\text{m}$ , and the 7 PAHs (Nap, Flu, Phe, Flt, Pyr, BaA, Chr). The darker blue dot is not taken into account in the linear regression.

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