



**HAL**  
open science

## Sources and spatial distribution of dissolved aliphatic and polycyclic aromatic hydrocarbons in surface coastal waters of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea)

Rania Fourati, Marc Tedetti, Catherine Guigue, Madeleine Goutx, Nicole Garcia, Hatem Zaghden, Sami Sayadi, Boubaker Elleuch

### ► To cite this version:

Rania Fourati, Marc Tedetti, Catherine Guigue, Madeleine Goutx, Nicole Garcia, et al.. Sources and spatial distribution of dissolved aliphatic and polycyclic aromatic hydrocarbons in surface coastal waters of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea). *Progress in Oceanography*, 2018, 163, pp.232-247. 10.1016/j.pocean.2017.02.001 . hal-01847666

**HAL Id: hal-01847666**

**<https://hal.science/hal-01847666v1>**

Submitted on 23 Jul 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Sources and spatial distribution of dissolved aliphatic and polycyclic aromatic**  
2 **hydrocarbons in surface coastal waters of the Gulf of Gabès (Tunisia, Southern**  
3 **Mediterranean Sea)**

4

5 Rania Fourati<sup>1</sup>, Marc Tedetti<sup>2\*</sup>, Catherine Guigue<sup>2</sup>, Madeleine Goutx<sup>2</sup>, Nicole Garcia<sup>2</sup>, Hatem  
6 Zaghden<sup>3</sup>, Sami Sayadi<sup>3</sup>, Boubaker Elleuch<sup>1</sup>

7

8 <sup>1</sup> Laboratoire Eau-Energie et Environnement, ENIS, Université de Sfax, BP 1173, 3038 Sfax,  
9 Tunisie

10 <sup>2</sup> Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute  
11 of Oceanography (MIO) UM 110, 13288, Marseille, France

12 <sup>3</sup> Laboratoire des Bioprocédés Environnementaux, Centre de Biotechnologie de Sfax, Route  
13 de Sidi Mansour km 6, PO Box 1177, 3018 Sfax, Tunisie

14

15 \* Corresponding author: marc.tedetti@mio.osupytheas.fr; Phone: + 33 (0)4 86 09 05 27;

16 Fax: + 33 (0)4 91 82 96 41

17

18 For submission to Progress in Oceanography to the special issue MERMEX as a full research  
19 article

20

21 Revised version

22 29 January 2017

23

24

25

26 **Abstract**

27       The goal of this work is to investigate the spatial distribution and sources of dissolved  
28 aliphatic and polycyclic aromatic hydrocarbons (AHs and PAHs), as well as their  
29 relationships with a series of biogeochemical parameters (total chlorophyll *a*, phaeopigment  
30 *a*, suspended particulate matter, particulate and dissolved organic carbon, and nutrients), in  
31 surface coastal waters of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea). Samples  
32 were collected off the Northern and Southern coasts of Sfax city, as well as in the Gabès-  
33 Ghannouch area, from October-November 2014 and in March 2015. Total dissolved AH and  
34 PAH concentrations ranged from 0.02 to 6.3  $\mu\text{g L}^{-1}$  and from 8.9 to 197.8  $\text{ng L}^{-1}$ , respectively.  
35 These data suggest that this area has been moderate-to-highly impacted by hydrocarbons  
36 compared to other Mediterranean coastal environments. The highest AH concentrations were  
37 measured off of the Sfax Northern coast (near Ezzit wadi) and in the Gabès-Ghannouch area,  
38 whereas the highest PAH concentrations were recorded in the Sfax Southern coast (near  
39 commercial and fishing harbours and the Sidi Salem channel). Analysis of the AH molecular  
40 patterns reveals that low molecular weight (LMW) compounds in these samples are  
41 dominated by *n*-C<sub>16</sub>, *n*-C<sub>17</sub> and *n*-C<sub>18</sub>, which suggests that these samples feature high biogenic  
42 activity (in the form of bacteria or algae), and that high molecular weight (HMW) compounds  
43 display monomodal distributions centred on *n*-C<sub>25</sub> and *n*-C<sub>26</sub>, which can be attributed to  
44 petrogenic inputs. The PAH molecular patterns are characterized by the dominance of LMW  
45 (2-3 rings) compounds and their alkylated homologues, which account for  $90 \pm 7\%$  of total  
46 PAHs. The observed PAH distribution and isomer ratios thus indicate the presence of major  
47 petrogenic contaminations. The concentrations of AHs, PAHs and dissolved organic carbon  
48 (DOC) do not correlate with each other, thus demonstrating that these three pools likely  
49 originated from different sources and subsequently underwent different processes in the Gulf  
50 of Gabès.

51

52 **Keywords:** Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, Gulf of Gabès,  
53 Mediterranean Sea, anthropogenic signatures, biogenic inputs.

54

## 55 **1. Introduction**

56

57 Hydrocarbons, including aliphatic hydrocarbons (AHs) and polycyclic aromatic  
58 hydrocarbons (PAHs), are among the most ubiquitous organic compounds in marine  
59 environments (Lipiatou and Saliot, 1991a; Roose and Brinkman, 2005; Dachs and Méjanelle,  
60 2010). AHs, which may be defined as straight chained, branched, or cyclic non-aromatic, are  
61 herein considered to be comprise a series of resolved compounds (*R*), including linear *n*-  
62 alkanes (*n*-C<sub>x</sub>) and two branched *n*-alkanes (isoprenoids), pristane (Pr) and phytane (Phy), as  
63 well as unresolved complex mixture (UCM). While AHs have several biogenic sources,  
64 including higher plant waxes, marine phyto- and zoo-plankton, bacteria and diagenetic  
65 transformations (Cripps, 1989; Rieley et al., 1991; Volkman et al., 1992; Wang et al., 1999),  
66 their anthropogenic sources mainly comprise unburned petroleum/oils (Mazurek and  
67 Simoneit, 1984; Bouloubassi and Saliot, 1993; Wang et al., 1997; Readman et al., 2002).

68 PAHs consist of two or more fused benzene rings and are composed of parent  
69 compounds and their alkylated homologues. They are synthesized during the formation of oil  
70 (petrogenic PAHs), during the incomplete combustion of fossil fuels and biomass (pyrogenic  
71 PAHs) (Wang et al., 1999; Wurl and Obbard, 2004; Pampanin and Sydnes, 2013), and  
72 biologically produced in soils by woody plants and termites or in oceanic environments  
73 through microbial degradation of organic matter (Chen et al., 1998; Wilcke et al., 2002).  
74 Petrogenic PAHs encompass low molecular weight (LMW) 2-3 ring compounds and their  
75 alkylated homologues, whereas pyrogenic PAHs encompass high molecular weight (HMW)

76 4-6 ring compounds with a low proportion of alkylated derivatives (Neff, 1979; Wang et al.,  
77 1999). PAHs, which are deleterious to living organisms (Kennish, 1992; Samanta et al.,  
78 2002), have long been recognized as high-priority contaminants by both the European Union  
79 (Official Journal of the EU 24/08/2013, Directive 2013/39/EU) and the United States  
80 Environmental Protection Agency (US EPA, 40 CFR Part 423, Appendix A to Part 423).

81 The Mediterranean Sea has long been considered to be one of the most polluted seas in  
82 the world (Hinrichsen, 1990; UNEP/MAP, 2012). It is believed that anthropogenic AHs and  
83 PAHs released from urban, industrial, and agricultural activities may enter Mediterranean  
84 waters through rivers (Lipiatou and Saliot, 1991b; Tolosa et al., 1996), surface runoffs,  
85 effluents (Guigue et al., 2011), atmospheric deposition (Castro-Jiménez et al., 2012) and sea-  
86 based or shipping-related activities (Tsapakis et al., 2010; Tornero and Hanke, 2016). Because  
87 of their low solubility in water, AHs and PAHs are considered to be preferentially associated  
88 with particles in coastal marine waters (May et al., 1978; Gustafsson et al., 1997; Adhikari et  
89 al., 2015). Therefore, most of studies dealing with hydrocarbons in the Mediterranean Sea  
90 have focused on sediments and particles, whereas relatively little work has studied the  
91 dissolved phase of the water column (Dachs and Méjanelle, 2010; The Mermex group, 2011).

92 However, the dissolved phase is considered as a significant compartment for  
93 hydrocarbon dynamics in the ocean. First, some studies have shown that the concentrations of  
94 hydrocarbons, mostly PAHs, in the dissolved phase are equal to or higher than those in the  
95 particulate phase of coastal and open ocean waters (Bouloubassi and Saliot, 1991; Tedetti et  
96 al., 2010; Berrojalbiz et al., 2011; Guigue et al., 2011; 2015). Second, dissolved PAHs in  
97 surface waters represent a relevant compartment to investigate the dynamics of air-water  
98 fluxes (González-Gaya et al., 2016). Third, dissolved hydrocarbons become bioconcentrated  
99 by passive diffusion and respiration and are thus more bioavailable for marine biota than are  
100 particulate hydrocarbons, for which bioaccumulation by ingestion occurs within a smaller

101 variety of organisms (i.e. filter feeders) (Tilseth et al., 1984; Akkanen et al., 2012). Finally, in  
102 the dissolved phase, hydrocarbons are subjected to a variety of processes, such as  
103 volatilization (*via* air-water gas exchanges) (Guitart et al., 2010; González-Gaya et al., 2016),  
104 biodegradation (Jiménez et al., 2011; Sauret et al., 2016), phototransformation (Al-Lihaibi,  
105 2003; King et al., 2014) and complexation with dissolved organic matter (DOM) (Sabbah et  
106 al., 2004; Kim and Kwon, 2010), which may in turn modify their bioavailability and thus  
107 modify their fate in marine waters (Berrojalbiz et al., 2011; Adhikari et al., 2015).

108         The Gulf of Gabès (Southeastern Tunisia) is one of the most productive ecosystems of  
109 the Mediterranean Sea and is the main fishing area of Tunisia (Jabeur et al., 2000; Bel Hassen  
110 et al., 2009; D'Ortenzio and Ribera d'Alcalà, 2009; The Mermex group, 2011). At the same  
111 time, the coastal zone of the Gulf of Gabès has been strongly affected by anthropogenic  
112 activity due to the recent significant expansion of the population and the intensification of  
113 industrial and agricultural activities. These anthropogenic inputs can be attributed to  
114 contributions from great urban centres (i.e., Sfax and Gabès cities), fishing and commercial  
115 harbours, several phosphoric acid production plants, municipal landfills and wastewater  
116 effluents, and industrial and agricultural waste issued from the production and storage of olive  
117 oil, chemical products, textiles, soap and paint (Aloulou et al., 2012). The Gulf of Gabès has  
118 thus recently become a site of growing interest for investigations of contaminants. Numerous  
119 studies have reported the levels of hydrocarbons in sediments (Aloulou et al., 2010; Amorri et  
120 al., 2011; Louati et al., 2001; Zaghdien et al., 2005; 2007; 2014). Nonetheless, to our  
121 knowledge, no data concerning the distribution of dissolved hydrocarbons in surface waters of  
122 this ecosystem currently exist. Therefore, the overall objective of this work is to evaluate, for  
123 the first time, the origins and spatial distributions of dissolved AHs and PAHs, along with  
124 several biogeochemical parameters, in the surface waters of the Sfax and Gabès coastal areas.

125

126

## 127 **2. Materials and Methods**

128

### 129 **2.1. Study area**

130 The Gulf of Gabès, located in the Southeastern region of Tunisia (within the Southern  
131 Mediterranean Sea), extends from the city of Chebba (35°14'N, 11°09'E) to the Tunisian-  
132 Libyan border (33°10'N, 11°34'E) and encompasses the Kerkennah and Djerba islands (Fig.  
133 1). It is characterized by several unique geomorphologic, climatic and oceanographic  
134 conditions. First, the tidal range is one of the highest within the Mediterranean Sea, due to the  
135 width (~ 250 km) and very low slope of its continental shelf (Sammari et al., 2006; Hattour et  
136 al., 2010). Second its basin is very shallow: in some areas, the water depth does not exceed a  
137 few meters over a distance of several kilometres, thus making the Gulf of Gabès very  
138 sensitive to atmospheric changes (Hattab et al., 2013) and inducing weak currents, high  
139 temperatures (14-29 °C) and high salinities (38-40) in surface waters (Hamdi et al., 2015).  
140 The climate in the Gulf of Gabès is arid to semiarid (i.e., dry and sunny) with strong easterly  
141 winds (INM, 2008), resulting in severe aeolian erosion and the transportation of Saharan dusts  
142 into the sea (Jedoui, 1980; Bouaziz et al., 2003). Finally, the Gulf of Gabès is one of the most  
143 productive areas of the Mediterranean Sea [with a total chlorophyll *a* concentration (TChl *a*)  
144 that can reach 20 µg L<sup>-1</sup>] and accounts for 65% of all Tunisian fish production (Jabeur et al.,  
145 2000; Bel Hassen et al., 2009; D'Ortenzio and Ribera d'Alcalà, 2009; DGPA, 2010; The  
146 Mermex group, 2011). Because the Gulf of Gabès is an essential region for the Tunisian  
147 economy, this coastal area has been strongly influenced by anthropogenic activity from  
148 various urban, industrial and agricultural outputs for many decades. These activities are  
149 particularly pronounced in the two largest cities of the Gulf, Sfax and Gabès (Fig. 1).

150 Sfax (34°43'N, 10°46'E; Fig. 1) is the second-largest city in Tunisia (with 730,000  
151 inhabitants) and represents its economic centre. The Sfax Northern coast (which extends from  
152 the commercial harbour to Ezzit wadi and beyond; Fig. 1) was recently restored through the  
153 *Taparura* project. This area features the outlet of the rainwater drain channel (“PK4”), the  
154 outlet of the Ezzit wadi, and the “Poudrière” industrial zone (Fig. 1). The Sfax Southern coast  
155 extends from the commercial harbour to the southern boundary of the Salina/Thyna  
156 agglomeration and contains the “SIAPE” phosphoric acid industry (Fig. 1). Near this industry  
157 are also the Thyna municipal landfill and the “ONAS” wastewater treatment plant (WWTP).  
158 SIAPE washing water, the WWTP effluent, and the municipal landfill leaching waters are  
159 released into the sea through a channel that joins the El Hakmouni wadi eastward of the  
160 WWTP. Moreover, the Sfax Southern coast encompasses several industrial zones, including  
161 “Madagascar”, the fishing harbour and “Sidi Salem” (Fig. 1).

162 The Gabès-Ghannouch area (33°56'N, 10°03'E; Fig. 1) contains approximately 130,000  
163 inhabitants and is characterized by important industrial and harbour activities. The “GCT-  
164 Gabès” phosphoric acid industry is situated along the commercial harbour. This area also  
165 houses a thermal power plant in the commercial harbour zone, petrochemical and off-shore  
166 petroleum infrastructures, and industries related to agribusiness, building materials, energy  
167 production and textiles. The El-Tine and Gabès wadis receive a variety of urban, industrial  
168 and agricultural wastes (Fig. 1) (see Text S1 for complete description of Sfax and Gabès  
169 coastal areas).

170

## 171 **2.2. Sampling**

172 Thirty-six stations were sampled in the coastal areas of Sfax (October 2014 and March  
173 2015) and Gabès cities (November 2014) (Fig. 1; Table 1). For each transect, the most coastal  
174 station was located approximately 100 m (S1, S5, S8, S14, S15, S19) or 300 m (S12, S16,



175 S22, S25, S27, S30, S33, S35) from land. With the exception of S1-S2, S5-S6, and S8-S9,  
176 which were sampled from a distance of 200 m, all stations were located at 1000 m intervals  
177 along each transect (Fig. 1; Table 1). Sampling was performed on board the vessel  
178 “*Taparura*” between 10:30 am and 3:30 pm (18 and 23 October 2014), 8:30 am and 12:30 pm  
179 (13 November 2014), and 14 pm and 16.30 pm (8 March 2015). This sampling occurred  
180 around high tide and under calm sea and sunny conditions (18 and 23 October, 13 November  
181 2014) or in cloudy weather (8 March 2015). Seawater samples were collected at a depth of ~  
182 0.1 m using 4-L Nalgene<sup>®</sup> polycarbonate bottles (ThermoFisher Scientific, Waltham, USA),  
183 which were opened below the water surface to avoid sampling of the surface microlayer.  
184 Before their use, these bottles were extensively washed with 1 M hydrochloric acid (HCl) and  
185 ultrapure water (i.e., Milli-Q water from Millipore system, final resistivity: 18.2 MΩ cm<sup>-1</sup>).  
186 They were then rinsed three times with each respective sample before being filled and placed  
187 in a cold and dark area after collection. On board, *in situ* measurements of temperature,  
188 salinity and pH were obtained using measuring cells with the TetraCon<sup>®</sup> 4-electrode system  
189 and a refractometer (WTW, Weilheim, Germany). Temperature and salinity data are not  
190 available for stations S1, S5, S8, S14, S15 and S19 (see data in Table 2).

191

### 192 **2.3. Filtration, handling and storage of samples**

193 Once in the laboratory, samples were immediately filtered under low vacuum conditions  
194 (< 50 mm Hg) through pre-combusted (500 °C, 4 h) GF/F (~ 0.7 μm) glass fibre filters (25 or  
195 47 mm diameter, Whatman, Fisher Scientific, Illkirch, France) using glassware filtration  
196 systems. To analyse dissolved hydrocarbons (AHs and PAHs), 2 L of samples were filtered  
197 through 47-mm diameter GF/F filters. Filtered samples were then stored in 2.5 L amber glass  
198 bottles with 50 mL of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at 4 °C, in the dark, before undergoing  
199 solvent extraction (see §2.4). It should be noted that these filters were also used for particulate

200 hydrocarbon analyses, but these results are not presented in this study. For analyses of TChl *a*  
201 and phaeopigment *a* (Phaeo *a*), 250-300 mL of samples were filtered through 25-mm  
202 diameter GF/F filters. Filters were stored in Nunc<sup>®</sup> cryogenic vials (Dutscher, Brumath,  
203 France) at -20 °C until analysis. For analyses of suspended particulate matter (SPM) and  
204 particulate organic carbon (POC), between 250 and 1100 mL of sample, depending on their  
205 station of origin, were both filtered with pre-weighted 25-mm diameter GF/F filters. After this  
206 filtration, filters were dried at 60 °C for 24 h and stored in Petrislides MilliPore<sup>®</sup> (Saint-Louis,  
207 USA) until analysis. Filtered seawater issued from this SPM and POC filtration was  
208 transferred in 100-mL Schott<sup>®</sup> glass bottles (Fisher Scientific) and in 60-mL HDPE bottles for  
209 nutrient and dissolved organic carbon (DOC) analyses, respectively. Glass and HDPE bottles  
210 were stored at -20 °C until analysis. Nutrient, TChl *a*, Phaeo *a*, SPM, and POC analyses were  
211 not conducted for samples obtained from S1, S5, S8, S14, S15 and S19, whereas DOC  
212 analyses were not performed on samples from stations S1, S5 and S14 (see analytical  
213 procedures in § 2.7 and data in Table 2).

214

#### 215 **2.4. Hydrocarbon extraction, purification and instrumental analysis**

216 Dissolved hydrocarbons in the < 0.7 µm size fraction were extracted from seawater  
217 using liquid-liquid extraction with CH<sub>2</sub>Cl<sub>2</sub> (2 x 50 mL per litre), according to the procedure of  
218 Guigue et al. (2011; 2014; 2015). These extracts were then concentrated by using a rotary  
219 evaporator before changing the solvent to *n*-hexane. Hexane extracts were then purified to  
220 separate the hydrocarbon fraction from more polar compounds. Extracts were fractionated  
221 within a 500 mg silica column (Silica gel extra pure, Merck, Darmstadt, Germany), which had  
222 previously been activated at 500 °C for 4 h and then partially deactivated with ultrapure water  
223 (2% w/w). AHs and PAHs were eluted together using 2 mL of *n*-hexane followed by 3 mL of

224 *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1 v/v) (Guigue et al., 2014; 2015). All solvents were of organic trace  
225 analysis quality (Rathburn Chemicals Ltd, Walkerburn, Scotland).

226 Purified hydrocarbon fractions (AHs + PAHs) were analysed by a gas chromatograph-  
227 mass spectrometer (GC-MS) (5977A Series GC/MSD System, Agilent Technologies, Santa  
228 Clara, USA) running at an ionization energy of 70 eV for a *m/z* range of 50-400, and using  
229 the selected ion monitoring (SIM) mode. The GC-MS used helium at a flow rate of 1.2  
230 mL/min as a carrier gas and an HP-5 MS column (30 m x 0.25 mm x 0.25 μm, J&W  
231 Scientific, Agilent Technologies). The injector (used in splitless mode) and detector  
232 temperatures were set at 270 and 320 °C, respectively. The non-linear temperature program  
233 used for the column was as follow: 70 °C for 3 min, 15 °C/min (ramp 1) to 150 °C, and then 7  
234 °C/min (ramp 2) to a final temperature of 320 °C, held for 10 min. The identification and  
235 quantification of hydrocarbons in samples and calibrations were performed in SIM mode  
236 (Guigue et al., 2014; 2015).

237

## 238 **2.5. Quality assurance/Quality control**

239 During the experiments and analyses, gloves were worn and care was taken to avoid  
240 contamination. All the glassware was washed with 1 M HCl and ultrapure water before being  
241 baked at 500 °C for 4 h. All materials that could not be baked were washed with 1 M HCl and  
242 ultrapure water and dried at room temperature.

243 AH and PAH external calibration standards (04071, Fluka and 47543-U, Supelco,  
244 among others, purchased from Sigma-Aldrich) were run for peak identification, and sample  
245 quantifications were processed using internal standards. Deuterated standard mixtures, which  
246 were introduced in samples prior to extraction (*n*-C<sub>16</sub>-*d*<sub>34</sub>, *n*-C<sub>24</sub>-*d*<sub>50</sub>, *n*-C<sub>36</sub>-*d*<sub>74</sub> for AHs, and  
247 Naph-*d*<sub>8</sub>, Phe-*d*<sub>10</sub>, Per-*d*<sub>12</sub> for PAHs) and prior to injection (Ace-*d*<sub>10</sub>, Flu-*d*<sub>10</sub> and Chrys-*d*<sub>12</sub>),  
248 were used to determine procedural recoveries and to quantify hydrocarbons in samples.

249 Average recoveries of  $n\text{-C}_{16}\text{-}d_{34}$ ,  $n\text{-C}_{24}\text{-}d_{50}$  and  $n\text{-C}_{36}\text{-}d_{74}$  were 93% for each standard, while  
250 those of Naph- $d_8$ , Phe- $d_{10}$ , Per- $d_{12}$  were 51, 71, and 84%, respectively. These procedural  
251 recoveries, which include the processes of extraction, evaporation, and purification, do not  
252 take into account the potential losses of HMW dissolved hydrocarbons by sorption onto  
253 polycarbonate bottles during the few hours between the sampling and filtration steps, which  
254 are very difficult to quantify in natural samples (Delle Site, 2001). Blanks were run for the  
255 entire procedure, including extraction, solvent concentration, and purification. The total mass  
256 of all AH and PAH compounds measured in these procedural blanks represented on average  
257 19 and 4% of the total mass of all AH and PAH compounds measured in these samples,  
258 respectively. For AHs, the procedural blank was mainly due to  $n\text{-C}_{23}$ ,  $n\text{-C}_{24}$ ,  $n\text{-C}_{30}$ , and  $n\text{-C}_{32}$ .  
259 All concentration values were blank- and recovery-corrected. Detection limits of the method  
260 used for individual compounds varied from 1 to 30  $\text{pg L}^{-1}$  in water.

261

## 262 **2.6. Determination of hydrocarbon indices and ratios**

263 For AHs, we determined the concentration of resolved compounds ( $R$ ) (i.e.,  $n$ -alkanes  
264 from  $n\text{-C}_{15}$  to  $n\text{-C}_{40}$ , including Pr and Phy) and the concentration of the UCM by integrating  
265 the hump (if present) using the mean response factors of the resolved compounds. Biogenic  
266 AHs were distinguished from petrogenic AHs mainly by relying on their molecular pattern  
267 distribution and then by determining several ratios and indices. First, we used the  $R/UCM$   
268 ratio as an indicator of recent petroleum contamination (when  $> 0.3$ ) or severe degraded  
269 petroleum contamination (when  $< 0.05$ ) (Simoneit and Mazurek, 1982; Commendatore and  
270 Esteves, 2004; Asia et al., 2009; Commendatore et al., 2012). We also used the Pr/Phy ratio  
271 as an indicator of biogenic AHs (when  $> 1$ ) (Cripps, 1989; Commendatore and Esteves, 2004;  
272 Cincinelli et al., 2008). However, due to the controversial origin of these isoprenoids, it is not  
273 relevant to employ this ratio as an indicator of petrogenic AHs (when it is  $< 1$ ). Finally, we

274 used the carbon preference index ( $CPI_{15-40}$ ), computed as the odd/even ratio in the  $n-C_{15}-n-$   
275  $C_{40}$  range, as an indicator of biogenic AHs ( $CPI_{15-40} > 1$  or  $< 1$ ) or AHs issued from petroleum  
276 contaminations ( $CPI_{15-40} \sim 1$ ) (Commendatore et al., 2012).

277 We quantified 29 PAH compounds ( $\sum_{29} PAHs_{-P+A}$ ) in these samples. These include 19  
278 parent PAHs ( $PAHs_{-P}$ ), which are naphthalene (Naph), acenaphthylene (Acy), acenaphthene  
279 (Ace), fluorene (Flu), dibenzothiophene (DBT), phenanthrene (Phe), anthracene (Ant),  
280 fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene [BaA], chrysene (Chr),  
281 benzo[b]fluoranthene [BbF], benzo[k]fluoranthene [BkF], benzo[a]pyrene [BaP],  
282 benzo[e]pyrene [BeP], perylene (Per), dibenzo[a,h]anthracene [DA], benzo[g,h,i]perylene  
283 [BP] and indeno[1,2,3-cd]pyrene [IP]. We also quantified 10 alkylated homologues ( $PAHs_{-A}$ ),  
284 including methyl ( $C_1$ ), dimethyl ( $C_2$ ) and trimethyl ( $C_3$ ) of Naph and Phe, and  $C_1$  and  $C_2$  of  
285 Flu and Pyr. Petrogenic and pyrogenic PAHs were discriminated mainly by relying on their  
286 molecular pattern distribution and then by determining selected ratios (Lipiatou and Saliot,  
287 1991; Budzinski et al., 1997; Mille et al., 2007). First, we used the ratio between alkylated  
288 homologues and parent compounds (Alk/Par); generally, petrogenic PAHs are characterized  
289 by the dominance of alkylated homologues over their parent compounds ( $Alk/Par > 1$ ),  
290 whereas the inverse pattern is observed for pyrogenic PAHs (Youngblood and Blumer, 1975).  
291 Second, we used the  $Ant/(Ant + Phe)$  and  $Flt/(Flt + Pyr)$  ratios, as indicators of pyrogenic ( $>$   
292  $0.1$  and  $> 0.5$ , respectively) or petrogenic PAHs ( $< 0.1$  and  $< 0.4$ , respectively) (Budzinski et  
293 al., 1997; Yunker et al., 2002; Asia et al., 2009; Li et al., 2015). It is worth noting that all  
294 these ratios and indices have to be used with precaution since hydrocarbon presence patterns  
295 may be substantially modified by many processes.

296

## 297 **2.7. Biogeochemical analyses**

298 Nutrients, such as nitrites ( $\text{NO}_2^-$ ), nitrates ( $\text{NO}_3^-$ ), phosphates ( $\text{PO}_4^{3-}$ ), and silicates  
299  $[\text{Si}(\text{OH})_4]$  were analysed using the automated colorimetric method described in Aminot and  
300 K  rouel (2007). To obtain reproducible nutrient measurements, we used standards and  
301 compared their results to those of commercial products (OSIL Ltd, Havant, UK). The  
302 detection limits of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  were 0.05, 0.05, and 0.02  $\mu\text{M}$ , respectively.

303 TChl *a* and Phaeo *a* were analysed using the fluorescence method following a methanol  
304 extraction (Raimbault et al., 2004). Five mL of methanol (RP Prolabo, VWR France,  
305 Fontenay sous Bois, France) were added to the filter, and, after 30 minutes of extraction in the  
306 dark at 4   C, a fluorescence measurement was performed using a fluorometer from model 10  
307 Turner Designs (Sunnyvale, USA) equipped with the Welschmeyer kit to avoid Chl *b*  
308 interference (Welschmeyer, 1994). As the monochromatic fluorescence method cannot  
309 separate divinyl chlorophyll from chlorophyll, results are given in terms of total Chl *a* (TChl  
310 *a*) concentrations, representing the sum of Chl *a* and divinyl Chl *a*. The blank “methanol +  
311 filter” was close to zero, yielding a very low detection limit of approximately 0.01  $\mu\text{g L}^{-1}$ .  
312 Calibrations were made using a pure Sigma Chl *a* standard. We applied the acidification  
313 method to determine Phaeo *a* concentrations (Raimbault et al., 2004).

314 After spending 24 h in the desiccator, filters were reweighed on the same balance, and  
315 the SPM concentration was calculated as the difference between the filter weight before and  
316 after sample filtration, normalised to the filtration volume (Neukermans et al., 2012). POC  
317 was then determined with an AutoAnalyser II Technicon (New York, USA) using the wet-  
318 oxidation procedure established by Raimbault et al. (1999). The POC detection limit was 0.50  
319  $\mu\text{M}$ .

320 To determine DOC, samples were acidified with orthophosphoric acid and analysed  
321 using a TOC-5000 total carbon analyser (Shimadzu, Kyoto, Japan) (Sohrin and Semp  r  ,  
322 2005). Average TOC concentrations in Deep Atlantic Water and low carbon water reference

323 standards were  $43 \pm 2 \mu\text{M C}$ ,  $n = 24$  and  $1 \pm 0.3 \mu\text{M C}$ ,  $n = 24$ , respectively. The analytical  
324 precision of the procedure was  $\leq 2\%$ .

325

## 326 **2.8. Statistical treatment**

327 Colour maps of dissolved AH and PAH concentrations were performed using Ocean  
328 Data View (ODV) software version 4.6.5 (Schlitzer, R., <http://odv.awi.de>, 2014.). The spatial  
329 interpolation/gridding of data was conducted using Data-Interpolating Variational Analysis  
330 (DIVA) (Barth et al., 2010; Troupin et al., 2012). Because all variables (except pH) displayed  
331 non-normal distributions and high-amplitude values (Joliffe, 1986), it was preferable to use  
332 Spearman's rank-order correlation over Pearson's correlation. Hierarchical ascendant  
333 classification (HAC) was used to find homogenous groups of individuals (stations) within the  
334 dataset, with respect to selected variables. These groups (or clusters) present a low within-  
335 variability and are different than others (displaying high between-variability). The  
336 dissimilarity measurement between clusters was based on Ward's method, which uses squared  
337 Euclidean distance. Variable values were centred and reduced beforehand. Two different  
338 HAC were then applied: one on physical and biogeochemical parameters (i.e., T, salinity, pH,  
339  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Si(OH)}_4$ , TChl *a*, Phaeo *a*, SPM, POC, DOC) and the other one on selected  
340 hydrocarbon parameters (i.e., *R*, Pr/Phy,  $\text{CPI}_{15-40}$ , for AHs,  $\sum_{29} \text{PAHs}_{\text{P+A}}$ , Alk/Par, Flt/(Flt +  
341 Pyr) for PAHs). Clusters (groups) issued from these HAC were represented in the form of  
342 box-and-whisker plots. Principal component analysis (PCA) was also applied to these  
343 hydrocarbon variables, based on Spearman's rank-order correlation matrix. Normality tests  
344 (including Shapiro-Wilk, Jarque-Bera and Kolmogorov-Smirnov tests), Spearman's rank-  
345 order correlation matrices, HAC, and PCA were performed using XLSTAT 2013.5.01 (a  
346 Microsoft Excel add-in program), while box-and-whisker plots were completed with

347 StatView 5.0. The significance threshold for these different analyses and tests was set at  $p <$   
348 0.05.

349

### 350 **3. Results**

351

#### 352 **3.1. Spatial distribution of physical and biogeochemical parameters**

353 Physical and biogeochemical parameters are reported in Table 2. Applying HAC to this  
354 dataset reveals the presence of six groups of stations (G1-G6; Fig. 1; Fig. 2a-i). The first  
355 group (G1) includes stations S2 and S6, which are located on the Sfax Northern coast, in front  
356 of Ezzit wadi and between Ezzit wadi and PK4 channel, respectively (Fig. 1). These stations  
357 are characterized by the highest observed POC (245 and 208  $\mu\text{M}$ , respectively; Fig. 2h) and  
358 SPM concentrations (44 and 59  $\text{mg L}^{-1}$ , respectively; Fig. 2i), as well as the highest measured  
359 salinity values ( $\sim 42.0$ ), and high TChl *a* (16  $\mu\text{g L}^{-1}$  in S2; Fig. 2e), Phaeo *a* (3.5  $\mu\text{g L}^{-1}$  in S6;  
360 Fig. 2f) and DOC concentrations (181  $\mu\text{M}$  in S2; Fig. 2g) (Table 2). G2 includes all other  
361 stations from the Sfax Northern coast (S3, S4, S7, S9-S13) as well as station S35 from the  
362 Gabès-Ghannouch area (Fig. 1). This group is marked by the lowest observed  $\text{PO}_4^{3-}$  ( $10.4 \pm$   
363  $2.3 \mu\text{M}$ ; Fig. 2c), TChl *a* ( $3.7 \pm 1.4 \mu\text{g L}^{-1}$ ; Fig. 2e), and Phaeo *a* concentrations ( $1.3 \pm 0.6 \mu\text{g}$   
364  $\text{L}^{-1}$ ; Fig. 2f) (Table 2). G3 encompasses stations S16 (in front of the fishing harbour), S20 (in  
365 front of the Sidi Salem channel) and S22 (in front of the El Maou wadi) on the Sfax Southern  
366 coast (Fig. 1). These stations yield the highest measured concentrations of  $\text{NO}_2^-$  ( $0.8 \pm 0.1$   
367  $\mu\text{M}$ ; Fig. 2a),  $\text{PO}_4^{3-}$  ( $107.5 \pm 22.0 \mu\text{M}$ ; Fig. 2c), TChl *a* ( $27.8 \pm 13.5 \mu\text{g L}^{-1}$ ; Fig. 2e), Phaeo *a*  
368 ( $6.8 \pm 3.4 \mu\text{g L}^{-1}$ ; Fig. 2f), and DOC ( $194.8 \pm 10.7 \mu\text{M}$ ; Fig. 2g), as well as high  
369 concentrations of  $\text{NO}_3^-$ , POC, and SPM (Fig. 2b, h, i; Table 2). Therefore, it is likely that  
370 these three stations were subjected to intense eutrophication. G4 includes the remaining  
371 stations from the Sfax Southern coast (S17, S18, S21, S23-S26) (Fig. 1), which are marked by



372 the lowest concentrations of  $\text{Si(OH)}_4$  ( $3.1 \pm 1.4 \mu\text{M}$ ; Fig. 2d), POC ( $30.7 \pm 12.8 \mu\text{M}$ ; Fig. 2h),  
373 and SPM ( $10.2 \pm 1.7 \text{ mg L}^{-1}$ ; Fig. 2i), the highest T values ( $26.8 \pm 0.3 \text{ }^\circ\text{C}$ ), and the lowest pH  
374 values ( $8.0 \pm 0.05$ ) (Table 2). G5 comprises stations from the Gabès-Ghannouch area (S27-  
375 S32, S36) (Fig. 1), which are characterized by the lowest  $\text{NO}_2^-$  concentrations ( $\sim 0. \mu\text{M}$ ; Fig.  
376 2a), the lowest salinity values ( $34.7 \pm 2.4$ ), and high DOC concentrations, with the highest  
377 value for S30 ( $217.6 \mu\text{M}$ ; Fig. 2g) (Table 2). Finally, G6 includes stations S33 and S34, which  
378 are located between the fishing and commercial harbours of the Gabès-Ghannouch area (Fig.  
379 1). They record the highest concentrations of  $\text{Si(OH)}_4$  ( $27.6\text{-}33.4 \mu\text{M}$ ; Fig. 2d) and  $\text{NO}_3^-$  ( $3.2\text{-}$   
380  $4.0 \mu\text{M}$ ; Fig. 2b), as well as high concentrations of  $\text{PO}_4^{3-}$  ( $35.9\text{-}42.0 \mu\text{M}$ ; Fig. 2c) and TChl *a*  
381 ( $7.7\text{-}8.7 \mu\text{g L}^{-1}$ ; Fig. 2e) (Table 2).

382

### 383 **3.2. Spatial distribution of dissolved hydrocarbons**

384 Dissolved total AH and PAH concentrations and ratios are reported in Table 3. HAC  
385 and PCA applied to the main hydrocarbon variables from these tables reveal the presence of  
386 three groups of stations (G'1-G'3). These three groups are represented by PCA (Fig. 3) (HAC  
387 dendrogram not shown), in the form of box-and-whisker plots (Fig. 4) and colour maps (Fig.  
388 5). AH and PAH molecular profiles are shown in Fig. 6 and Fig. 7, respectively. Stations  
389 displaying similar molecular profiles were grouped together. Below, we describe the  
390 hydrocarbon content of each of these three HAC/PCA groups.

391

#### 392 **3.2.1. Group G'1**

393 Group G'1 includes the northernmost stations of Sfax (S1-S6) and all stations from the  
394 Gabès-Ghannouch region (S27-S36) (Fig. 1, 3, 5). These stations are characterized by the  
395 highest *R* concentrations, including Pr and Phy, with an average of  $4.7 \pm 0.7 \mu\text{g L}^{-1}$  (Table 3;  
396 Fig. 3, 4a, 5). UCM is present in all stations, except S3 and S6, with concentrations varying

397 from 5.42 (S2) to 14  $\mu\text{g L}^{-1}$  (S34), representing  $63.4 \pm 5.7\%$  of the total AH pool (Table 3).  
398 When present, *R/UCM* values are all  $> 0.30$  (Table 3). This group exhibits the lowest Pr/Phy  
399 ratios, which vary from 0.27 (S3) to 0.36 (S30, S33) (Table 3; Fig. 4b). AH molecular profiles  
400 display monomodal distributions centred on *n-C<sub>25</sub>-n-C<sub>26</sub>* compounds (Fig. 6a). An equal  
401 amount of even and odd carbon numbered *n*-alkanes is also observed, resulting in  $\text{CPI}_{15-40}$   
402 values close to 1 (Table 3; Fig. 4c).

403 Concentration of  $\sum_{29} \text{PAHs}_{\text{P+A}}$  was  $29.7 \pm 12.1 \text{ ng L}^{-1}$  (Table 3; Fig. 3, 4d, 5). Alk/Par  
404 ratios range from 0.6 (S3) to 5.5 (S33) but are mainly  $> 2$  (Table 3; Fig. 4e).  $\text{PAHs}_{\text{P+A}}$  pattern  
405 distributions are marked by the dominance of LMW compounds (2-3 rings) over HMW  
406 compounds ( $\geq 4$  rings) (Fig. 7a, f), the former representing  $88 \pm 4\%$  of total PAHs.  
407 Naphthalenes ( $\text{C}_2\text{-Naph} > \text{Naph} > \text{C}_3\text{-Naph} > \text{C}_1\text{-Naph}$ ) represent the major compounds,  
408 followed by phenanthrenes ( $\text{C}_1\text{-Phe} > \text{C}_2\text{-Phe} > \text{Phe} > \text{C}_3\text{-Phe}$ ). Nevertheless, the heavy  
409 compounds  $\text{C}_1\text{-Pyr}$  and  $\text{Pyr}$  are also present in significant proportions in these stations ( $6.4 \pm$   
410  $4.8$  and  $3.8 \pm 3.9\%$ , respectively) (Fig. 7a, f). The  $\text{Flt}/(\text{Flt} + \text{Pyr})$  ratios range from 0.08 to  
411 0.38 (Table 3; Fig. 4f).

412

### 413 **3.2.2. Group G'2**

414 Group G'2 contains the southernmost stations of the Sfax North coast (S7-S13) as well  
415 as most stations from the Sfax Southern coast (S16-S18, S20-S26) (Fig. 1, 3, 5). These  
416 stations are distinguished by the lowest *R* concentrations ( $0.13 \pm 0.25 \mu\text{g L}^{-1}$ ) and the absence  
417 of UCM (Table 3; Fig. 3, 4a, 5). Pr/Phy ratios vary from 0.51 (S7) to 2.43 (S21) but are  
418 mainly  $> 1$  (Table 3; Fig. 4b). AH molecular profiles also vary within this group. S7 and S11  
419 reveal distributions similar to those of G'1 stations (i.e., monomodal distribution centred on  
420 the *n-C<sub>25</sub>-n-C<sub>26</sub>* range) (Fig. 6a) and do not display any odd-to-even carbon-numbered  
421 dominance ( $\text{CPI}_{15-40} \sim 1$ ) (Fig. 3, 4c). The molecular profiles of S8 and S17 are marked by a

422 regular distribution of *n*-alkanes in the *n*-C<sub>15</sub>–*n*-C<sub>38</sub> range, with the maximal abundance of *n*-  
423 C<sub>29</sub> (Fig. 6c) resulting in a slight odd-to-even carbon-numbered predominance (CPI<sub>15-40</sub> = 1.3  
424 and ~1, respectively) (Fig. 3, 4c). A bimodal distribution of *n*-alkanes is observed at S26 and  
425 S13, in which light compounds are centred on *n*-C<sub>16</sub> (S26) or *n*-C<sub>15</sub> (S13) and heavy  
426 compounds are centred on *n*-C<sub>28</sub> (S26) or *n*-C<sub>33</sub> (S13) (Fig. 6d,e). In contrast, the molecular  
427 profiles of stations S9, S10, S12, S16, S18 and S20-S25 also display monomodal distributions  
428 but feature a strong even-to-odd predominance within the *n*-C<sub>16</sub>–*n*-C<sub>22</sub> range (Fig. 6f). This  
429 trend results in low CPI<sub>15-40</sub> values (0.11-0.89), with *n*-C<sub>16</sub> being the major compound,  
430 followed by *n*-C<sub>18</sub> (Table 3; Fig. 3, 4c). Globally, CPI<sub>15-40</sub> values for this group are < 1 (Table  
431 3, Fig. 4c).

432 G'2 stations record PAH concentrations similar to those of G'1 stations, with  $\sum_{29}$  PAHs.  
433 P<sub>+A</sub> of  $28.9 \pm 16.2$  ng L<sup>-1</sup> (Table 3; Fig. 3, 4d, 5). Alk/Par ratios are lowest in G'2, ranging  
434 from 0.25 to 2.25 (but mainly falling between 1 and 2) (Table 3; Fig. 3, 4e). PAH molecular  
435 profiles reveal the predominance of LMW compounds (Fig. 7a-e), as LMW compounds  
436 represent  $89.2 \pm 8.2\%$  of all total PAHs. Naphthalenes are the dominant compounds, followed  
437 by phenanthrenes (Fig. 7a-e). Heavy compounds are also present in these stations, with C<sub>1</sub>-  
438 Pyr and Pyr in S7, Flt in S8, Flt and Chr in S21-S26 (Fig. 7a, b, e). Flt/(Flt + Pyr) ratios are  
439 the highest in this group, with values exceeding 0.5, except at S7 and S11 (Table 3; Fig. 3,  
440 4f).

441

### 442 3.2.3. Group G'3

443 Group G'3 comprises only three stations from the Sfax Southern coast: S14, S15 and  
444 S19 (Fig. 1, 3, 5). *R* concentration is high in S14 ( $4.5 \mu\text{g L}^{-1}$ ) and low in S15 and S19 ( $0.04$   
445 and  $0.03 \mu\text{g L}^{-1}$ , respectively) (Table 3; Fig. 3, 4a, 5). S14 displays a molecular distribution  
446 similar to those of G'1 stations (i.e., monomodal distribution centred on the *n*-C<sub>25</sub>–*n*-C<sub>26</sub>

447 range), with UCM present at a concentration of  $7.4 \mu\text{g L}^{-1}$ , representing 62.2% of total AHs  
448 (Table 3; Fig. 6a). Stations S15 and S19 exhibit different molecular profiles, with an almost  
449 regular distribution from  $n\text{-C}_{15}$  to  $n\text{-C}_{36}$  and the slight emergence of  $n\text{-C}_{17}$  and Phy (Table 3;  
450 Fig. 3, 6b). Within these three stations, Pr/Phy are low (0.34-0.48) and equal amounts of  
451 even- and odd-carbon-numbered  $n$ -alkanes can be found (CPI  $\sim 1$ ) (Table 3; Fig. 4b, c).

452 These stations contain the highest recorded PAH concentrations, with  $175.8 \pm 20.7 \text{ ng}$   
453  $\text{L}^{-1}$  (Table 3; Fig. 3, 4d, 5). Molecular profile of the PAHs reveals the predominance of LMW  
454 compounds (Fig. 7d), as inferred by the presence of the highest Alk/Par ratios ( $6.6 \pm 0.6$ )  
455 (Table 3; Fig. 3, 4e). The LMW compounds represent  $97.6 \pm 0.3\%$  of all total PAHs.  
456 Naphthalenes are the dominant compounds, followed by phenanthrenes and fluorenes,  
457 whereas the HMW compounds are almost undetectable (Fig. 7d). The Flt/(Flt + Pyr) ratios are  
458 among the lowest measured values (0.08-0.13; Table 3; Fig. 3, 4f).

459 Additionally, we can also use the cross plot of Ant/(Ant + Phe) *versus* Flt/(Flt + Pyr)  
460 ratios to distinguish different origins of PAHs (Yunker et al., 2002, 2015), as shown in Fig. 8.  
461 Most stations reveal mixed origins of PAHs. All stations in G'3 and G'1 yield Ant/(Ant +  
462 Phe)  $> 0.1$  and Flt/(Flt + Pyr)  $< 0.4$  (mixed origin), except S2, S3, S4, S6, which are strictly of  
463 petrogenic origin. In contrast, G'2 stations record Ant/(Ant + Phe)  $< 0.1$  and Flt/(Flt + Pyr)  $>$   
464  $0.5$  (mixed origin), except S8, which has a pyrogenic origin, and S7 and S11, which are  
465 strictly of petrogenic origin. Therefore, the clustering of the highly contaminated G'1 + G'3  
466 stations in an area where Flt/(Flt + Pyr)  $< 0.4$  along with the clustering of the less  
467 contaminated G'2 group (displaying more degraded hydrocarbons) in an area where  
468 Ant/Ant+Phe  $< 0.1$ , very likely suggests that PAHs have different origins in G'1 + G'3 than  
469 they do in G'2.

470

### 471 **3.3. Correlation between biogeochemical parameters and dissolved hydrocarbons**

472 Table 4 displays the Spearman's rank-order correlation matrix for biogeochemical  
473 parameters and dissolved hydrocarbons. *R* concentration is significantly negatively correlated  
474 with T ( $r = -0.68$ ,  $n = 30$ ,  $p < 0.05$ ) and significantly positively correlated with  $\text{Si(OH)}_4$   
475 concentration ( $r = 0.56$ ,  $n = 30$ ,  $p < 0.05$ ). The concentration of  $\sum_{29} \text{PAHs}_{\text{-P+A}}$  shows a  
476 significant negative correlation with pH ( $r = -0.47$ ,  $n = 30$ ,  $p < 0.05$ ) and significant positive  
477 correlation with concentrations of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Si(OH)}_4$  and TChl *a* ( $r = 0.39$ - $0.66$ ,  $n = 30$ ,  $p <$   
478  $0.05$ ). Neither *R* concentrations nor  $\sum_{29} \text{PAHs}_{\text{-P+A}}$  concentrations are correlated to DOC  
479 concentrations ( $r = 0.01$ - $0.20$ ,  $n = 30$ ,  $p > 0.05$ ). No significant relationship was found  
480 between *R* and  $\sum_{29} \text{PAHs}_{\text{-P+A}}$  concentrations ( $r = -0.07$ ,  $n = 36$ ,  $p > 0.05$ ), suggesting that AHs  
481 and PAHs in this coastal area are decoupled. Evidence for this decoupling can also be seen in  
482 results of the PCA, in which AH and PAH variables are located on principal component 1  
483 (PC1) and principal component 2 (PC2), respectively, thus underscoring their absence or very  
484 low correlation (Fig. 3). TChl *a* concentrations are significantly positively correlated to those  
485 of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Si(OH)}_4$ , Phae *a*, SPM, POC and DOC ( $r = 0.40$ - $0.70$ ,  $n = 30$ ,  $p < 0.05$ ). This  
486 underlines the strong coupling between phytoplankton biomass, nutrients and the organic  
487 carbon pool (Table 4). The absence of any correlation between POC and DOC concentrations,  
488 as well as the positive correlation observed between DOC and SPM concentrations, suggest  
489 the presence of slightly different sources of particulate and dissolved organic carbon in the  
490 surface waters.

491

492

## 493 **4. Discussion**

494

### 495 **4.1. Comparisons with previously published data**

496

497 **4.1.1. Physical and biogeochemical parameters**

498 Measured temperature and pH values in this study, which range from 18.0-27.3 °C and  
499 7.90-8.30, respectively (Table 2), are within the same order of magnitude as those reported in  
500 other studies in the Gulf of Gabès (Drira et al., 2014; 2016; Rekik et al., 2014) and in the  
501 Western Mediterranean basin (Pujo-Pay et al., 2011). Salinity, however, displays a wider  
502 range (32-42) than has been observed by previous works in this coastal area (i.e., 36-40 by  
503 Drira et al., 2016). This is likely because stations in this study are located closer to the coast  
504 and are thus more influenced by terrestrial freshwater inputs for the lower values and by a  
505 thinner water column subjected to greater evaporation for the higher ones.

506  $\text{NO}_2^-$  concentrations measured here (0.00-0.90  $\mu\text{M}$ ; Table 2) are similar to those already  
507 reported in these coastal waters (0.01-0.83  $\mu\text{M}$ ), whereas  $\text{NO}_3^-$  and  $\text{Si}(\text{OH})_4$  concentrations  
508 (0.01-4.0 and 1.4-33.4  $\mu\text{M}$ , respectively; Table 2) are lower than previously reported values  
509 (1.2-13.4 and 2.6-55.2  $\mu\text{M}$ , respectively) (Rekik et al., 2013; Drira et al., 2016).  $\text{PO}_4^{3-}$   
510 concentrations measured here (5.5-120.3  $\mu\text{M}$ ; Table 2) are higher than those that have  
511 previously been recorded in this area (0.1-39.7  $\mu\text{M}$ ) (Rekik et al., 2012, 2013; Drira et al.,  
512 2016). The highest  $\text{PO}_4^{3-}$  concentrations are found in the Sfax Southern coast (G3 group:  
513 stations S16, S20, S22; Fig. 1, 2c; Table 2) and can be attributed, in part, to the release of  
514 phosphogypsum from the SIAPE industry, which is known to be enriched in  $\text{PO}_4^{3-}$ , as well as  
515 to the release of domestic and industrial wastes from the Sidi Salem channel. The lowest  
516  $\text{PO}_4^{3-}$  concentrations are observed mainly in the Sfax Northern coast (G2 group; Fig. 1, 2c;  
517 Table 2), where phosphoric acid activities have not occurred for several years.

518 TChl *a* concentrations measured in the present work (1.7-40.7  $\mu\text{g L}^{-1}$ ; Table 2) are  
519 higher than those previously found in the same coastal waters (0.0-25.6  $\mu\text{g L}^{-1}$ ) (Rekik et al.,  
520 2013; 2014), while our SPM concentrations (8.3-59.4  $\text{mg L}^{-1}$ ; Table 2) are on the same order

521 of magnitude ( $0.7-30 \text{ mg L}^{-1}$ ) (Katlane et al., 2013) and lower than those measured in the  
522 Northern coast of Sfax ( $14-434 \text{ mg L}^{-1}$ ) (Rekik et al., 2014).

523 Therefore, these data suggest that this coastal area is characterized by an enrichment in  
524  $\text{PO}_4^{3-}$ , TChl *a*, POC, DOC and SPM concentrations compared to other Mediterranean systems  
525 (The Mermex group; Pujol-Pay et al., 2011; Karydis and Kitsiou, 2012).  $\text{PO}_4^{3-}$  anthropogenic  
526 inputs from various industrial sources have led to the eutrophication (or the enhancement of  
527 biological production) of these coastal waters (Ben Mustapha et al., 1999; Drira et al., 2014;  
528 2016). The high variability in concentrations from station to station may be related not only to  
529 different anthropogenic input contributions, but also to the complex bathymetry and  
530 hydrodynamics of this area.

531

#### 532 ***4.1.2. Dissolved *n*-alkane and PAH concentrations***

533 Compared to PAHs, only a few studies have investigated dissolved *n*-alkanes in marine  
534 waters. Dissolved total *R* concentrations (*n*- $\text{C}_{15}$ -*n*- $\text{C}_{40}$  with Pr and Ph<sub>y</sub>) determined here in the  
535 surface waters of the Sfax and Gabès coastal areas ( $0.02$  to  $6.3 \text{ } \mu\text{g L}^{-1}$ ; Table 3) yield higher  
536 values than those recorded in surface waters of the Marseille coastal area (Northwestern  
537 Mediterranean Sea, France) ( $0.04-0.58 \text{ } \mu\text{g L}^{-1}$ ) (Guigue et al., 2011; 2014), in offshore surface  
538 waters of the Northwestern Mediterranean Sea ( $0.7-2.4 \text{ } \mu\text{g L}^{-1}$ ) (Marty and Saliot, 1976) and  
539 in surface waters of the Gulf of Tunis (Tunisia) ( $0.25-1 \text{ } \mu\text{g L}^{-1}$ ; Mzoughi and Chouba, 2011).

540 Dissolved total PAH concentrations measured here in the surface waters of the Sfax and  
541 Gabès coastal areas, i.e.,  $8.9-197.8 \text{ ng L}^{-1}$  for  $\sum_{29} \text{PAHs}_{\text{-P+A}}$  and  $3.6-56.4 \text{ ng L}^{-1}$  for  $\sum_{19} \text{PAHs}_{\text{-P}}$ ,  
542 are high compared to those reported in the Western Mediterranean ( $\sum_{16} \text{PAHs}_{\text{-P+A}}$ :  $0.4-2.2$   
543  $\text{ng L}^{-1}$  and  $\sum_{19} \text{PAHs}_{\text{-P+A}}$ :  $0.16-0.8 \text{ ng L}^{-1}$ ) and the Eastern Mediterranean ( $\sum_{19} \text{PAHs}_{\text{-P+A}}$ :  
544  $0.16-8.8 \text{ ng L}^{-1}$ ) (Dachs et al., 1997; Berrojalbiz et al., 2011), as well as in coastal waters of  
545 Barcelona (Spain) and Banyuls-sur-Mer (France) ( $\sum_{15} \text{PAHs}_{\text{-P+A}}$ :  $2.5-41.7 \text{ ng L}^{-1}$  in surface

546 micro layer and 3.6-30.7 ng L<sup>-1</sup> in surface waters) (Guitart et al., 2007). However, they are  
547 within the same range as those observed in surface waters of the Marseille coastal area ( $\sum_{32}$   
548 PAHs<sub>p+A</sub>: 5-162 ng L<sup>-1</sup>) (Guigue et al., 2011), the Rhone delta (France) ( $\sum_{80}$  PAHs<sub>p+A</sub>: 15-  
549 290 ng L<sup>-1</sup>) (Bouloubassi and Saliot, 1991), and the Venice Lagoon (Italy) ( $\sum_{20}$  PAHs<sub>p+A</sub>:  
550 12.4-266.8 ng L<sup>-1</sup>) (Manodori et al., 2006). Our measured concentrations are also lower than  
551 those found in the Gulf of Tunis ( $\sum_{24}$  PAHs<sub>p+A</sub>: 139-694 ng L<sup>-1</sup> in summer and 150-1008 ng  
552 L<sup>-1</sup> in winter) (Mzoughi and Chouba, 2011) and the Saronikos Gulf (Greece) ( $\sum_{17}$  PAHs<sub>p+A</sub>:  
553 103-459 ng L<sup>-1</sup>) (Valavanidis et al., 2008). El Nemr and Abd-Allah (2003) also reported  
554 higher concentrations of PAHs<sub>p</sub> in surface waters of the Alexandria coast (Egypt) ( $\sum_7$  PAHs<sub>p</sub>:  
555 13-120 ng L<sup>-1</sup>). Consequently, these AH and PAH concentration data indicate that the  
556 surface coastal waters of the Gulf of Gabès are likely moderately-to-highly contaminated  
557 when compared to other Mediterranean regions. Hence concentration levels of hydrocarbons  
558 recorded in surface waters of the Gulf of Gabès are not so high compared to other  
559 Mediterranean coastal environment despite strong anthropogenic releases. This could be  
560 explained by the influence of hydrodynamic conditions, in particular tides. Tides of the Gulf  
561 of Gabès, which present the highest amplitude of all the Mediterranean Sea, with the upper  
562 Adriatic, may have a role of dispersing hydrocarbons at sea.

563

## 564 **4.2. Origin and potential sources of dissolved hydrocarbons**

565

### 566 **4.2.1. Group G'1**

567 AH and PAH concentrations and ratios ( $R/UCM > 0.3$ ;  $CPI \sim 1$  and  $Alk/Par > 2$ )  
568 indicate the presence of recent and chronic petrogenic contaminations (Simoneit and  
569 Mazurek, 1982; Wang et al., 1999; Commendatore and Esteves, 2004; Commendatore et al.,  
570 2012). Additionally, the cross plot and occurrence of Pyr and C<sub>1</sub>-Pyr suggest, for many of



571 these stations, a contribution of pyrogenic (combustion) sources (Fig. 7, 8). AH profiles  
572 display a molecular distribution very close to that recorded for classic heavy fuels or residuals  
573 used as marine diesel and for industrial power generation (Wang and Fingas, 2003). This  
574 observed high proportion of alkylated homologues was also reported in Sfax surficial  
575 sediments by Zaghden et al. (2014). The hydrocarbon contamination found in the  
576 northernmost stations of Sfax and in the Gabès-Ghannouch stations may have several sources,  
577 especially wadis, uncontrolled discharges, and harbour activities. The Ezzit wadi, which may  
578 transport various uncontrolled domestic, industrial, and agricultural wastes, would thus  
579 represent a significant source of petrogenic hydrocarbons for the Northern coast of Sfax.  
580 Within the Gabès coastal area, the main sources of hydrocarbons include industrial discharges  
581 (from the thermal power plant), commercial and fishing harbours (by means of oil spills,  
582 ballast water, shipping, and air emissions) and wadis (El-Tine and Gabès wadis) (Fig. 1).  
583 Despite the weak correlation between biogeochemical and hydrocarbon individual  
584 parameters, this observed G'1 station contamination is supported by the presence of  
585 widespread anthropisation occurring in the northernmost Sfax stations (G1) and in the Gabès-  
586 Ghannouch area (G5 + G6 stations).

587

#### 588 **4.2.2. Group G'2**

589 This group is characterized by a range of diverse AH profiles, from the most petrogenic  
590 distribution (S7, S11, close to G'1 profiles; Fig. 3, 6a) to increasingly biogenic origin markers  
591 (away from G'1 profiles, Fig. 3, 6c-f). The emergence of odd *n*-alkanes *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, *n*-C<sub>29</sub>, *n*-  
592 C<sub>33</sub> may be attributed to phytoplankton or higher plant debris lysis (Douglas and Eglinton,  
593 1966; Blumer et al., 1971; Goutx and Saliot, 1980), as well as the suspected presence of  
594 small-size phytoplankton cells (picophytoplankton). Since micro and macro algae are  
595 abundant in the Gulf of Gabès (Bel Hassen et al., 2008; Drira et al., 2014; Rekik et al., 2014),

596 this assumption seems plausible. Even *n*-alkanes can be attributed to microbial activities such  
597 as bacteria, fungi and yeast (Elias et al., 1997). Stations S9, S10, S12, S16, S18, S20-25,  
598 which yield the lower CPI, exhibit higher abundances of these microbial signatures (Fig. 3,  
599 6f). The hypothesised biogenic signatures of AHs within this group are supported by the  
600 presence of Pr/Phy ratios  $> 1$  (Fig. 4b, c). Also, the relatively low concentration levels of AHs  
601 and PAHs, associated with low Alk/Par values (compared to the two other groups), suggest at  
602 these sites less petrogenic inputs, and, at the same time, more pronounced weathering  
603 processes, very likely through biodegradation. Indeed, it has been shown that the bacterial  
604 degradation of PAHs could lead to a depletion of alkylated PAHs compared to their non  
605 alkylated counterparts (Vila et al., 2010; Jiménez et al., 2011).

606

#### 607 ***4.2.3. Group G'3***

608 This group is mainly characterized by the highest PAH concentrations, LMW PAH  
609 abundances, and Alk/Par values associated with CPI  $\sim 1$ , which indicate the importance of  
610 local petrogenic inputs. These stations were sampled in March 2015 close to the coast and  
611 were thus likely affected by anthropogenic inputs from Sidi Salem channel as well as by  
612 fishing and commercial harbours located in the Southern coast of Sfax. The Sidi Salem  
613 channel contains, among other things, untreated wastewater from slaughter-house, whose  
614 flow rate is estimated at  $55 \text{ m}^3 \text{ day}^{-1}$ , sludge from the WWTP, and pretreated wastewaters of  
615 various industries (DGQEV, 2008). Therefore, all these inputs may substantially contribute to  
616 the PAH content in this area.

617

#### 618 ***4.2.4. Differences between Sfax and Gabès environments***

619 In the Sfax region, we observe a combination of petrogenic inputs (G'1, G'3) and  
620 biogenic sources (G'2), as well as the occurrence of weathering processes which are

621 supported by the decrease in both AH and PAH concentrations and Alk/Par ratio off of the  
622 coast (G'2: S1-S3/S4, S5-S7, S8-S11, S12-S13, S16-S18, S19-S26). Even though these  
623 weathering processes seem to be driven by biodegradation (Vila et al., 2010; Jiménez et al.,  
624 2011), we cannot exclude other processes such as volatilisation (Jiménez et al., 2012),  
625 photodegradation (King et al., 2014) and particle sequestration (Dachs et al., 2002). These  
626 biogenic AHs and weathering processes are not observed in the Gabès-Ghannouch region; we  
627 assume that this is due to either the recurrence of larger releases in Gabès, with continuous  
628 and direct discharge of phosphogypsum into the sea, or to a particular ecosystem in Sfax that  
629 is more suitable for the biodegradation of hydrocarbons. Measurements of bacterial  
630 abundance, diversity and activities in these two ecosystems should thus be considered as  
631 complements to hydrocarbon analysis in future studies. Moreover, in the Sfax waters, we did  
632 not observe coupling between the hydrocarbon and biogeochemical contents, whereas  
633 hydrocarbons in the Gabès-Ghannouch area (G'1 stations) are associated with biogeochemical  
634 groups G5 and G6, which exhibit the highest measured values of silica. These data may thus  
635 reflect the influence of terrigenous inputs (Gabès and El-Tine wadis), chronic releases or  
636 spills/plumes (harbour activities, phosphogypsum releases).

637

#### 638 ***4.2.5. Inputs of PAHs from particles***

639 For each of the three hydrocarbon groups, the cross plot shows the superposition of  
640 pyrogenic inputs in addition to the widespread existence of petrogenic sources (Fig. 8). This  
641 pyrogenic component probably reflects the influence of either high suspended matter contents  
642 or of the proximity of sediment. Given the dynamics of the area, we may assume that we are  
643 not in a particle-dissolved equilibrium position and thus that rearrangements may occur in  
644 cases of environmental disturbance (Dong et al., 2015). Dissolved PAHs found here in surface  
645 waters may partially originate from surficial sediments. Indeed, in these very shallow waters,

646 exchanges between sediment and the water column are exacerbated. Studies carried out on  
647 surficial sediments of the Sfax coastal area have demonstrated that phenanthrenes (especially  
648 alkylated homologues) are among the most abundant PAHs (Zaghden et al., 2007; 2014).  
649 Consequently, some LMW PAHs recorded in surface waters may be released from sediments,  
650 either by the resuspension of particulate matter or by passive diffusion. This process of  
651 partitioning between the two matrixes (water and sediment) is highly related to the  
652 octanol/water partition coefficients ( $K_{ow}$ ) of PAHs, as well as to the organic carbon content in  
653 sediment that controls this partitioning through a linear free energy relationship (Zhou and  
654 Maskaoui, 2003).

655

#### 656 **4.3. PAH partitioning in the dissolved phase**

657 DOC is considered as one of the most important factors controlling the partitioning of  
658 hydrocarbons in the dissolved phase. Although we record high DOC concentrations in these  
659 coastal waters, no linear correlation is found between DOC and dissolved  $\sum_{29}$  PAHs<sub>P+A</sub>  
660 concentrations ( $r = 0.01$ ,  $n = 30$ ,  $p > 0.05$ ). In addition, no linear correlation is observed  
661 between individual PAH and DOC concentrations, except for Ace (data not shown). This lack  
662 of correlation between DOC and dissolved PAHs may reflect different sources for these two  
663 pools in surface waters of the Gulf of Gabès, but also their low affinity at the molecular level.  
664 Therefore, a fraction of dissolved LMW PAHs in this area could be under freely form (i.e.,  
665 not complexed to dissolved organic matter), which is in agreement with their physico-  
666 chemical properties (relatively low  $K_{ow}$  and high solubility) (Shi et al., 2007). Besides,  
667 significant negative linear relationships are found between individual PAH concentrations and  
668 their respective  $K_{ow}$  values (data not shown), which suggests that the molecular distribution  
669 pattern observed, i.e., dominance of LMW PAHs in all samples, is driven by the hydrophobic  
670 character of compounds. Interestingly, significant positive correlations are detected between

671 several dissolved PAHs (C<sub>2</sub>-Naph, C<sub>3</sub>-Naph, Ace, Flu, C<sub>1</sub>-Flu, C<sub>2</sub>-Flu and DBT) and POC or  
672 SPM concentrations (data not shown). This could underline a “particle concentration effect”  
673 (Zhou et al., 1999). The latter is observed when particle partition coefficient (K<sub>p</sub> or K<sub>oc</sub>) is  
674 inversely proportional to particle concentration. The increase in particle concentration is  
675 generally associated to an increase in DOC concentration, which may explain this distribution  
676 of PAHs towards the dissolved phase (Zhou et al., 1999). However, in our case, the increase  
677 in POC/SPM concentrations was not concomitant to an increase in DOC concentrations. Our  
678 results thus illustrate the complexity of the relationships between dissolved PAHs, DOC and  
679 POC in marine coastal waters.

680

## 681 **5. Conclusions**

682

683 While some works have already reported hydrocarbon levels in surficial sediments of  
684 the Sfax coastal area (Zaghden et al., 2007; 2014), this present study represents to our  
685 knowledge the first assessment of concentrations of dissolved hydrocarbons (28 AHs and 29  
686 PAHs) in surface waters of the Gulf of Gabès (in the Sfax and Gabès coastal areas), and their  
687 associations with biogeochemical parameters. Overall, these areas are moderate-to-highly  
688 impacted by hydrocarbons and show a relatively high eutrophication level compared to other  
689 Mediterranean coastal environments. The highest hydrocarbon concentrations can be  
690 attributed to recent petrogenic sources from industrial, domestic and harbour activities.  
691 Interestingly, biogenic AHs and signatures of weathering processes are found in Sfax, but not  
692 in Gabès, with lower hydrocarbon contents and decreasing Alk/Par ratios off the coast.  
693 Concentrations in AHs, PAHs, and DOC do not correlated with each other, thus highlighting  
694 that these three pools have different sources and are then submitted to different processes in  
695 the Gulf of Gabès. Despite these relatively high DOC concentrations, dissolved PAHs do not

696 seem to show an affinity towards dissolved organic matter. These results demonstrate that the  
697 dissolved phase can provide very interesting information about the dynamics of PAHs in  
698 coastal waters. Further investigations should take into consideration the particulate organic  
699 matter of water column to obtain a global view of PAH dynamics in coastal waters of the Gulf  
700 of Gabès.

701

702 *Acknowledgements.* We are grateful to the “Institut de Recherche pour le  
703 Développement” (IRD) for providing scholarship to R. Fourati through the “Allocations de  
704 Recherche pour une Thèse au Sud” (ARTS) program. This thesis was also supported by the  
705 Tunisian Ministry of Higher Education and Scientific Research. This work was conducted in  
706 the framework of the IRD Action South project “MANGA” and the IRD French-Tunisian  
707 International Joint Laboratory (LMI) “COSYS-Med”. This study was carried out as a part of  
708 the WP3 C3A-Action MERMEX/MISTRALS and is a contribution to the international  
709 SOLAS, IMBER and LOICZ projects. We warmly thank Z. Drira from the laboratory of  
710 Biodiversity and Aquatic Ecosystems (Faculty of Sciences, University of Sfax) as well as H.  
711 Sahnoun and T. Omar for their technical help during cruises. We thank the core parameter  
712 analytical platform (PAPB) of the Mediterranean Institute of Oceanography (MIO) for  
713 performing biogeochemical analyses as well as R. Sempéré for the use of the Agilent GC-MS.  
714 We acknowledge two anonymous reviewers for their relevant comments and corrections.

715

716

717

718

719

720

721 **References**

- 722 Adhikari, P.L., Maiti, K., Overton, E., 2015. Vertical fluxes of polycyclic aromatic  
723 hydrocarbons in the northern Gulf of Mexico. *Mar. Chem.*, 168, 60-68.
- 724 Akkanen, J., Tuikka, A., Kukkonen, J.V.K., 2012. On the borderline of dissolved and  
725 particulate organic matter: Partitioning and bioavailability of polycyclic aromatic  
726 hydrocarbons. *Ecotoxicol. Environ. Saf.* 78, 91–98.
- 727 Al-Lihaibi, S.S., 2003. Photo-oxidation products of petroleum hydrocarbons in the Eastern  
728 Red Sea coastal waters. *Environ. Inter.* 28, 573–579.
- 729 Aloulou, F., Elleuch, B., Kallel, M., 2012. Benthic foraminiferal assemblages as pollution  
730 proxies in the northern coast of Gabes Gulf, Tunisia. *Environ. Monit. Assess.* 184, 777–95.
- 731 Aloulou, F., Kallel, M., Dammak, M., Elleuch, B., Saliot, A., 2010. Even-numbered n-  
732 alkanes/n-alkenes predominance in surface sediments of Gabes Gulf in Tunisia. *Environ.*  
733 *Earth Sci.* 61, 1–10.
- 734 Aminot A., K erouel R., 2007. Dosage automatique des nutriments dans les eaux marines :  
735 m ethodesen flux continu. Ed. Ifremer, M ethodes d’analyse en milieu marin 188p.
- 736 Amorri, J., Geffroy-Rodier, C., Boufahja, F., Mahmoudi, E., Aissa, P., Ksibi, M., Ambl es, A.,  
737 2011. Organic matter compounds as source indicators and tracers for marine pollution in a  
738 western Mediterranean coastal zone. *Environ. Sci. Pollut. Res.* 18, 1606–1616.
- 739 Asia, L., Mazouz, S., Guiliano, M., Doumenq, P., Mille, G., 2009. Occurrence and  
740 distribution of hydrocarbons in surface sediments from Marseille Bay (France). *Mar.*  
741 *Pollut. Bull.* 58, 443–451.
- 742 Barth, A., Alvera Azcarate, A., Troupin, C., Ouberdous, M., Beckers, J.-M., 2010. A web  
743 interface for griding arbitrarily distributed in situ data based on Data-Interpolating  
744 Variational Analysis (DIVA). *Adv. Geosci.* 28, 29–37.
- 745 Bel Hassen, M., Drira, Z., Hamza, a., Ayadi, H., Akrouf, F., Issaoui, H., 2008. Summer

746 phytoplankton pigments and community composition related to water mass properties in  
747 the Gulf of Gabes. *Estuar. Coast. Shelf Sci.* 77, 645–656.

748 Bel Hassen, M., Drira, Z., Hamza, a., Ayadi, H., Akrouf, F., Messaoudi, S., Issaoui, H.,  
749 Aleya, L., Bouaïn, A., 2009. Phytoplankton dynamics related to water mass properties in  
750 the Gulf of Gabes: Ecological implications. *J. Mar. Syst.* 75, 216–226.

751 Ben Mustapha, K., Hattour, A., Mhetli, M., El Abed, A., Tritar. B., 1999. Bionomie des  
752 étages infra et circalittoral du golfe de Gabès. *Bull. Inst. Natl. Sci. Tech. Mer (Tunisie)* 26,  
753 5–48.

754 Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro-Jiménez, J., Wollgast, J., Ghiani,  
755 M., Hanke, G., Zaldivar, J.M., 2011. Biogeochemical and physical controls on  
756 concentrations of polycyclic aromatic hydrocarbons in water and plankton of the  
757 Mediterranean and Black Seas. *Global Biogeochem. Cycles* 25, 1–14.

758 Blumer, M., Guillard, R.R.L., Chase, T., 1971. Hydrocarbons of marine phytoplankton. *Mar.*  
759 *Biol.* 8, 183.

760 Bouaziz, S., Jedoui, Y., Barrier, E., Angelier, J., 2003. Néotectonique affectant les dépôts  
761 marins tyrrhéniens du littoral sud-est tunisien: implications pour les variations du niveau  
762 marin. *C. R. Géosci.* 335, 247–254.

763 Bouloubassi, I., Saliot, A., 1991. Composition and sources of dissolved and particulate PAH  
764 in surface waters from the Rhone delta (NW Mediterranean). *Mar. Pollut. Bull.* 22, 588–  
765 594.

766 Bouloubassi, I., Saliot, A., 1993. Investigation of anthropogenic and natural organic inputs in  
767 estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanol. Act.* 16,  
768 145–161.



769 Budzinski, H., Jones, I., Bellocq, J., Pierard, C., Garrigues, P., 1997. Evaluation of sediment  
770 contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar. Chem.*  
771 58, 85–97.

772 Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., Dachs, J., 2012. Polycyclic aromatic  
773 hydrocarbons (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and  
774 decoupling with settling fluxes in the water column. *Environ. Pollut.* 166, 40–47.

775 Chen, J., Henderson, G., Grimm, C.C., Lloyd, S.W., Laine, R.A., 1998. Termites fumigate  
776 their nests with naphthalene. *Nature* 392, 558.

777 Cincinelli, A., Martellini, T., Bittoni, L., Russo, A., Gambaro, A., Lepri, L., 2008. Natural and  
778 anthropogenic hydrocarbons in the water column of the Ross Sea (Antarctica). *J. Mar.*  
779 *Syst.* 73, 208–220.

780 Commendatore, M.G., Esteves, J.L., 2004. Natural and anthropogenic hydrocarbons in  
781 sediments from the Chubut River (Patagonia, Argentina). *Mar. Pollut. Bull.* 48, 910–918.

782 Commendatore, M.G., Nievas, M.L., Amin, O., Esteves, J.L., 2012. Sources and distribution  
783 of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay  
784 (Tierra del Fuego, Patagonia, Argentina). *Mar. Environ. Res.* 74, 20–31.

785 Cripps, G.C., 1989. Problems in the identification of anthropogenic hydrocarbons against  
786 natural background levels in the Antarctic. *Antart. Sci.* 1, 307–312.

787 Dachs, J., Bayona, J.M., Raoux, C., Albaigés, J., 1997. Spatial distribution, vertical profiles  
788 and budget of polycyclic aromatic hydrocarbons in western Mediterranean. *Env. Sci.*  
789 *Technol.* 31, 682–688.

790 Dachs, J., Lohman, R., Ockenden, W.A., Méjanelle, L., Eisenrich, S., Jones, K.C., 2002.  
791 Oceanic biogeochemical controls on global dynamics of persistent organic pollutants.  
792 *Environ. Sci. Technol.* 36, 4229–4237.

793 Dachs, J., Méjanelle, L., 2010. Organic pollutants in coastal waters, sediments, and biota: A

794 relevant driver for ecosystems during the anthropocene? *Estuaries and Coasts* 33, 1–14.

795 Delle Site, A., 2001. Factors affecting sorption of organic compounds in natural sorbent/water  
796 systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem*, 31, 187.

797 Dong, J., Xia, X., Wang, M., Lai, Y., Zhao, P., Dong, H., Zhao, Y., Wen, J., 2015. Effect of  
798 water-sediment regulation of the Xiaolangdi Reservoir on the concentrations,  
799 bioavailability, and fluxes of PAHs in the middle and lower reaches of the Yellow River. *J.*  
800 *Hydrol.* 527, 101–112.

801 Douglas, A.G., Eglinton, G., 1966. Distribution of Alkanes, in *Comparative Phytochemistry*.  
802 Academic Press: New York, 57–77.

803 DGEQV (Direction Générale de l'Environnement et de la Qualité de Vie), 2008. Etude de  
804 dépollution et de réhabilitation des côtes sud de Sfax. Phase-1: Inventaire et caractérisation  
805 des sources de pollution. Note de synthèse. COMETE Engineering, Code 26079, pp. 67.

806 DGPA, 2010. Direction Générale de Pêche et de l'Aquaculture. Annuaire des statistiques de  
807 pêche de Tunisie. D.G.P.A., 144 pp.

808 D'Ortenzio, F., d'Alcalà, M.R., 2009. On the trophic regimes of the Mediterranean Sea: A  
809 satellite analysis. *Biogeosciences* 6, 139–148.

810 Drira, Z., Elloumi, J., Guermazi, W., Bel Hassen, M., Hamza, A., Ayadi, H., 2014. Seasonal  
811 changes on planktonic diatom communities along an inshore-offshore gradient in the Gulf  
812 of Gabes (Tunisia). *Acta Ecol. Sin.* 34, 34–43.

813 Drira, Z., Chaari, D., Kmiha-Megdiche, S., Sahnoun, H., Hammami, A., Allouche, N.,  
814 Tedetti, M., Ayadi, H., 2016. Assessment of anthropogenic inputs in the surface waters of  
815 the southern coastal area of Sfax during Spring (Tunisia, Southern Mediterranean Sea).  
816 *Marine Pollution Bulletin*, 104, 355-363.

817 Elias, V.O., 1997. Even N-Alkane Predominances on the Amazon Shelf and A Northeast  
818 Pacific Hydrothermal System. *Naturwissenschaften* 84, 415–420.

819 El Nemr, A., Abd-Allah, A.M. a, 2003. Contamination of polycyclic aromatic hydrocarbons  
820 (PAHs) in microlayer and subsurface waters along Alexandria coast, Egypt. *Chemosphere*  
821 52, 1711–6.

822 González-Gaya, B., Fernández-Pinos, M.C., Morales, L., Méjanelle, L., Abad, E., Piña, B.,  
823 Duarte, C.M., Jiménez, B., Dachs, J., 2016. High atmosphere – ocean exchange of  
824 semivolatile aromatic hydrocarbons. *Nat. Geosci.* 9, 438–442.

825 Goutx, M., and Saliot, A., 1980. Relationship between dissolved and particulate fatty acids  
826 and hydrocarbons, chlorophyll and zooplankton biomass in Villefranche Bay,  
827 Mediterranean Sea. *Mar. Chem.* 8, 299–318.

828 Gustafsson, O., Gschwend, P.M., Buesseler, K.O., 1997. Using  $^{234}\text{Th}$  disequilibria to estimate  
829 the vertical removal rates of polycyclic aromatic hydrocarbons from the surface ocean.  
830 *Mar. Chem.* 57, 11–23.

831 Guigue, C., Tedetti, M., Giorgi, S., Goutx, M., 2011. Occurrence and distribution of  
832 hydrocarbons in the surface microlayer and subsurface water from the urban coastal marine  
833 area off Marseilles, Northwestern Mediterranean Sea. *Mar. Pollut. Bull.* 62, 2741–2752.

834 Guigue, C., Tedetti, M., Ferretto, N., Garcia, N., Méjanelle, L., Goutx, M., 2014. Spatial and  
835 seasonal variabilities of dissolved hydrocarbons in surface waters from the Northwestern  
836 Mediterranean Sea: results from one year intensive sampling. *Sci. Total Environ.* 466-467,  
837 650–62.

838 Guigue, C., Bigot, L., Turquet, J., Tedetti, M., Ferretto, N., Goutx, M., Cuet, P., 2015.  
839 Hydrocarbons in a coral reef ecosystem subjected to anthropogenic pressures (La Réunion  
840 Island, Indian Ocean). *Environ. Chem.*, 12, 350–365.

841 Guitart, C., García-Flor, N., Bayona, J.M., Albaigés, J., 2007. Occurrence and fate of  
842 polycyclic aromatic hydrocarbons in the coastal surface microlayer. *Mar. Pollut. Bull.* 54,  
843 186–194.

844 Guitart, C., García-Flor, N., Miquel, J.C., Fowler, S.W., Albaigés, J., 2010. Effect of the  
845 accumulation of polycyclic aromatic hydrocarbons in the sea surface microlayer on their  
846 coastal air–sea exchanges. *J. Mar. Sys.* 79, 210–217.

847 Hamdi, I., Denis, M., Bellaaj-Zouari, A., Khemakhem, H., Bel Hassen, M., Hamza, A.,  
848 Barani, A., Bezac, C., Maalej, S., 2015. The characterisation and summer distribution of  
849 ultraphytoplankton in the Gulf of Gabès (Eastern Mediterranean Sea, Tunisia) by using  
850 flow cytometry. *Cont. Shelf Res.* 93, 27–38.

851 Hattab, T., Ben Rais Lasram, F., Albouy, C., Romdhane, M.S., Jarboui, O., Halouani, G.,  
852 Cury, P., Le Loc’h, F., 2013. An ecosystem model of an exploited southern Mediterranean  
853 shelf region (Gulf of Gabes, Tunisia) and a comparison with other Mediterranean  
854 ecosystem model properties. *J. Mar. Syst.* 128, 159–174.

855 Hattour, M.J., Sammari, C., Ben Nassrallah, S., 2010. Hydrodynamique du golfe de Gabès  
856 déduite à partir des observations de courants et de niveaux. *Rev. Paralia* 3, 3.1–3.12.

857 Hinrichsen, D., 1990. Our common seas: Coasts in crisis. Earthscan Publications, London, in  
858 association with United Nations Environment Programme, Nairobi, 184 pp.

859 Institut National de la Météorologie de Tunisie (INM), 2008. Données climatiques et  
860 statistiques annuelles des vents. *Rapports Annuels (1981–2004)*, 118pp.

861 Jabeur, C., Gobert, B., Missaoui, H., 2000. Typologie de la flottille de pêche côtière dans le  
862 golfe de Gabès (Tunisie). *Aquat. Living Resour.* 13, 421–428.

863 Jedoui, Y., 1980. Etude hydrologique et sédimentologique d’une lagune en domaine  
864 méditerranéen: Le bahiret el Boughrara (Tunisie). PhD thesis. Université de Bordeaux I,  
865 190 pp.

866 Jiménez, N., Viñas, M., Guiu-Aragonés, C., Bayona, J., Albaigés, J., Solanas, A., 2011.  
867 Polyphasic approach for assessing changes in an autochthonous marine bacterial

868 community in the presence of *Prestige* fuel oil and its biodegradation potential. Appl.  
869 Microbiol. Biotechnol., 91, 823–834.

870 Joliffe, I.T., 1986. Principal component analysis. Springer-Verlag, p. 271.

871 Karydis, M., Kitsiou, D., 2012. Eutrophication and environmental policy in the Mediterranean  
872 Sea: A review. Environ. Monit. Assess. 184, 4931–4984.

873 Katlane, R., Nechad, B., Ruddick, K., Zargouni, F., 2013. Optical remote sensing of turbidity  
874 and total suspended matter in the Gulf of Gabes. Arab. J. Geosci. 6, 1527–1535.

875 Kennish, M.J., 1992. Poly-nuclear aromatic hydrocarbons. Ecology of estuaries:  
876 anthropogenic effects. Boca Raton: CRC Press, p. 133–181.

877 Kim, S.-J., Kwon, J.-H., 2010. Determination of partition coefficients for selected PAHs  
878 between water and dissolved organic matter. Clean – Soil, Air, Water, 38, 797–802.

879 King, S.M., Leaf, P.A., Olson, A.C., Ray, P.Z., Tarr, M.A., 2014. Photolytic and  
880 photocatalytic degradation of surface oil from the Deepwater Horizon spill. Chemosphere,  
881 95, 415–422.

882 Li, Y., Li, P., Ma, W., Song, Q., Zhou, H., Han, Q., Diao, X., 2015. Spatial and temporal  
883 distribution and risk assessment of polycyclic aromatic hydrocarbons in surface seawater  
884 from the Haikou Bay, China. Mar. Pollut. Bull. 92, 244–251.

885 Lipiatou, E., Saliot, A., 1991a. Fluxes and transport of anthropogenic and natural polycyclic  
886 aromatic-hydrocarbons in the western Mediterranean Sea. Mar. Chem. 32, 51–71.

887 Lipiatou, E., Saliot A., 1991b. Hydrocarbon contamination of the Rhone delta and western  
888 Mediterranean Sea. Mar. Pollut. Bull. 22, 297–304.

889 Louati, A., Elleuch, B., Kallel, M., Saliot, A., Dagaut, J., Oudot, J., 2001. Hydrocarbon  
890 contamination of coastal sediments from the Sfax area (Tunisia), Mediterranean Sea. Mar.  
891 Pollut. Bull. 42, 444–451.

892 Manodori, L., Gambaro, a., Piazza, R., Ferrari, S., Stortini, a. M., Moret, I., Capodaglio, G.,

893 2006. PCBs and PAHs in sea-surface microlayer and sub-surface water samples of the  
894 Venice Lagoon (Italy). *Mar. Pollut. Bull.* 52, 184–192.

895 Marty, J.C., Saliot, A., 1976. Hydrocarbons (normal alkanes) in the surface microlayer of  
896 seawater. *Deep. Res. Oceanogr. Abstr.* 23, 863–873.

897 May, W.E., Wasik, S.P., Freeman, H.F., 1978. Determination of the solubility behavior of  
898 some polycyclic aromatic hydrocarbons in water. *Anal. Chem.* 50, 997–1000.

899 Mazurek, M.A., Simoneit, B.R.T., 1984. Characterization of biogenic and petroleum-derived  
900 organic matter in aerosols over remote rural and urban areas. In: L.H. Keith (Ed.).  
901 Identification and Analysis of Organic Pollutants in Air. Ann Arbor Science/Butterworth.  
902 Boston. pp. 353–370.

903 Mille, G., Asia, L., Guiliano, M., Malleret, L., Doumenq, P., 2007. Hydrocarbons in coastal  
904 sediments from the Mediterranean sea (Gulf of Fos area, France). *Mar. Pollut. Bull.* 54,  
905 566–575.

906 Mzoughi, N., Chouba, L., 2011. Distribution and partitioning of aliphatic hydrocarbons and  
907 polycyclic aromatic hydrocarbons between water, suspended particulate matter, and  
908 sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *J. Environ. Monit.*  
909 13, 689–698.

910 Neff, J.M., 1979. Polycyclic aromatic hydrocarbons in the aquatic environment sources, fates  
911 and biological effects. Applied Science Publishers, LTD, London, p. 262.

912 Neukermans, G., Ruddick, K., Loisel, H., Roose, P., 2012. Optimization and quality control  
913 of suspended particulate matter concentration measurement using turbidity measurements.  
914 *Limnol. Oceanogr. Methods*, 10, 1011–1023.

915 Pampanin, D.M., Sydnese, M.O., 2013. Polycyclic Aromatic Hydrocarbons a Constituent of  
916 Petroleum: Presence and Influence in the Aquatic Environment. In *Hydrocarbon*, V.  
917 Kutcherov (Ed.), ISBN: 978-953-51-0927-3, InTech.

918 Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.F., Goyet, C.,  
919 Moutin, T., Prieur, L., 2011. Integrated survey of elemental stoichiometry (C, N, P) from  
920 the western to eastern Mediterranean Sea. *Biogeosciences* 8, 883–899.

921 Raimbault, P., Diaz, F., Pouvesle, W., Boudjellal, B., 1999. Simultaneous determination of  
922 particulate forms of organic carbon, nitrogen and phosphorus collected on filters, using a  
923 semi-automatic wet-oxidation method. *Marine Ecology Progress Series*, 180, 289–295.

924 Raimbault, P., Lantoiné, F., Neveux, J., 2004. Dosage rapide de la chlorophylle a et des  
925 phéopigments a par fluorimétrie après extraction au méthanol. Comparaison avec la  
926 méthode classique d'extraction à l'acétone. *Océanis*, 30, 189–205.

927 Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.-P., Catinni, C., Mee,  
928 L.D., 2002. Petroleum and PAH contamination of the Black Sea. *Mar. Pollut. Bull.* 44, 48–  
929 62.

930 Rekik, A., Drira, Z., Guermazi, W., Elloumi, J., Maalej, S., Aleya, L., Ayadi, H., 2012.  
931 Impacts of an uncontrolled phosphogypsum dumpsite on summer distribution of  
932 phytoplankton, copepods and ciliates in relation to abiotic variables along the near-shore of  
933 the southwestern Mediterranean coast. *Mar. Pollut. Bull.* 64, 336–46.

934 Rekik, A., Denis, M., Aleya, L., Maalej, S., Ayadi, H., 2013. Spring plankton community  
935 structure and distribution in the north and south coasts of Sfax (Tunisia) after north coast  
936 restoration. *Mar. Pollut. Bull.* 67, 82–93.

937 Rekik, A., Denis, M., Dugenne, M., Barani, A., Maalej, S., Ayadi, H., 2014. Seasonal  
938 distribution of ultraphytoplankton and heterotrophic prokaryotes in relation to abiotic  
939 variables on the north coast of Sfax after restoration. *Mar. Pollut. Bull.* 84, 280–305.

940 Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., 1991. The biogeochemistry of Ellesmere  
941 Lake, UK-I: source correlation of leaf wax inputs to the sedimentary lipid record. *Org.*  
942 *Geochem.* 17, 901–912.

943 Roose, P., Brinkman, U.A.Th., 2005. Monitoring organic microcontaminants in the marine  
944 environment: principles, programmes and progress. *Trends Anal. Chem.* 24, 897–926.

945 Sabbah, I., Rebhun, M., Gerstl, Z., 2004. An independent prediction of the effect of dissolved  
946 organic matter on the transport of polycyclic aromatic hydrocarbons. *J. Contam. Hydrol.*,  
947 75, 55–70.

948 Samanta, S.K., Singh, O.V., Jain, R.K., 2002. Polycyclic aromatic hydrocarbons:  
949 environmental pollution and bioremediation. *Trends Biotechnol.* 20, 243–248.

950 Sammari, C., Koutitonsky, V.G, Moussa, M., 2006. Sea level variability and tidal resonance  
951 in the Gulf of Gabes, Tunisia. *Continental Shelf Res.* 26, 338–350.

952 Sauret, C., Tedetti, M., Guigue, C., Dumas, C., Lami, R., Pujo-Pay, M., Conan, P., Goutx, M.,  
953 Ghiglione, J.-F. (2016). Influence of PAHs among other coastal environmental variables  
954 on total and PAH-degrading bacterial communities. *Environ. Sci. Pollut. Res.*

955 Shi, Z., Tao, S., Pan, B., Liu, W.X., Shen, W.R., 2007. Partitioning and source diagnostics of  
956 polycyclic aromatic hydrocarbons in rivers in Tianjin, China 146, 492–500.

957 Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere-II.\* Natural  
958 background of biogenic lipid matter in aerosols over the rural western United States.  
959 *Atmos. Environ.* 16, 2139–2159.

960 Sohrin, R., and Sempéré R., 2005. Temporal variation in total organic carbon in the Northeast  
961 Atlantic in 2000–2001, *J. Geophys. Res.* 110, C10S90.

962 Tedetti, M., Guigue, C., Goutx, M., 2010. Utilization of a submersible UV fluorometer for  
963 monitoring anthropogenic inputs in the Mediterranean coastal waters. *Mar. Pollut. Bull.* 60,  
964 350–362.

965 Tilseth, S., Solberg, T.S., Westrheim, K., 1984. Sublethal effects of the water-soluble fraction  
966 of Ekofisk oil on the early larval stages of cod (*Gadus morhua* L.). *Mar. Environ.*  
967 *Res.*, 11, 1–16.



968 The MerMex Group, 2011. Marine ecosystems responses to climatic and anthropogenic  
969 forcings in the Mediterranean. *Prog. Oceanogr.* 91, 97–166.

970 Tolosa, M., Bayona, O.M., Albaigés, O., 1996. Aliphatic and polycyclic aromatic  
971 hydrocarbons and sulfur/oxygen derivatives in Northwestern Mediterranean sediments:  
972 Spatial and temporal variability, fluxes, and budgets. *Environ. Sci. Technol.* 30, 2495–  
973 2503.

974 Tornero, V., Hanke, G., 2016. Chemical contaminants entering the marine environment from  
975 sea-based sources: A review with a focus on European seas. *Mar. Pollut. Bull.* 112, 17–38.

976 Troupin, C., Barth, A., Sirjacobs, D., Ouberdous, M., Brankart, J.-M., Brasseur, P., Rixen, M.,  
977 Alvera Azcarate, A., Belounis, M., Capet, A., Lenartz, F., Toussaint, M.-E., & Beckers, J.-  
978 M., 2012. Generation of analysis and consistent error fields using the Data Interpolating  
979 Variational Analysis (Diva). *Ocean Model.* 52–53, 90–101.

980 Tsapakis, M., Dakanali, E., Stephanou, E.G., Karakassis, I., 2010. PAHs and n-alkanes in  
981 Mediterranean coastal marine sediments: Aquaculture as a significant point source. *Journal*  
982 *of Environmental Monitoring* 12, 958–963.

983 UNEP/MAP, 2012. State of the Mediterranean Marine and Coastal Environment,  
984 UNEP/MAP–Barcelona Convention, Athens.

985 Valavanidis, A., Vlachogianni, T., Triantafillaki, S., Dassenakis, M., Androutsos, F.,  
986 Scoullou, M., 2008. Polycyclic aromatic hydrocarbons in surface seawater and in  
987 indigenous mussels (*Mytilus galloprovincialis*) from coastal areas of the Saronikos Gulf  
988 (Greece). *Estuar. Coast. Shelf Sci.* 79, 733–739.

989 Vila, J., Nieto, J.M., Mertens, J., Springael, D., Grifoll, M., 2010. Microbial community  
990 structure of a heavy fuel oil-degrading marine consortium: linking microbial dynamics  
991 with polycyclic aromatic hydrocarbon utilization. *FEMS Microbiol. Ecol.* 73, 349–362.

992 Volkman, J.K., Holdsworth, D.G., Neil, G.P., Bavor Jr., H.J., 1992. Identification of natural  
993 anthropogenic and petroleum hydrocarbons in aquatic sediments. *Sci. Tot. Environ.* 112,  
994 203–219.

995 Wang, Z., Fingas, M., Landriault, M., Sigouin, L., Feng, Y., Mullin, J., 1997. Using  
996 systematic and comparative analytical data to identify the source of an unknown oil on  
997 contaminated birds. *J. Chromatogr. A* 775, 251–265.

998 Wang, Z., Fingas, M., Page, D.S., 1999. Oil spill identification. *J. Chromatogr. A* 843, 369–  
999 411.

1000 Wang, Z., Fingas, M. V., 2003. Development of oil hydrocarbon fingerprint and identification  
1001 techniques. *Mar. Pollut. Bull.* 47, 423–452.

1002 Welschmeyer, N.A., 1994. Fluorometric analysis of chlorophyll *a* in the presence of  
1003 chlorophyll *b* and pheopigments. *Limnol. Ocean.* 39, 1985–1992.

1004 Wilcke, W., Krauss, M., Amelung, W., 2002. Carbon isotope signature of polycyclic aromatic  
1005 hydrocarbons (PAHs): evidence for different sources in tropical and temperate  
1006 environments? *Environ. Sci. Technol.* 36, 3530–3535.

1007 Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a  
1008 unique habitat for marine organisms. *Mar. Pollut. Bull.* 48, 1016–1030.

1009 Youngblood, W.W., Blumer, M., 1975. Polycyclic aromatic hydrocarbons in the environment:  
1010 Homologous series in soils and recent marine sediments. *Geochim. Cosmochim. Acta* 188,  
1011 53–55.

1012 Yunker, M.B., Backus, S.M., Graf Pannatier, E., Jeffries, D.S., Macdonald, R.W., 2002.  
1013 Sources and significance of alkane and PAH hydrocarbons in Canadian arctic rivers.  
1014 *Estuar. Coast. Shelf Sci.* 55, 1–31.

1015 Yunker, M.B., Macdonald, R.W., Ross, P.S., Johannessen, S.C., Dangerfield, N., 2015.  
1016 Alkane and PAH provenance and potential bioavailability in coastal marine sediments

1017 subject to a gradient of anthropogenic sources in British Columbia, Canada. *Org.*  
1018 *Geochem.* 89-90, 80–116.

1019 Zaghden, H., Kallel, M., Louati, A., Elleuch, B., Oudot, J., Saliot, A., 2005. Hydrocarbons in  
1020 surface sediments from the Sfax coastal zone, (Tunisia) Mediterranean Sea. *Mar. Pollut.*  
1021 *Bull.* 50, 1287–94.

1022 Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A., 2007. Sources and distribution of  
1023 aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea.  
1024 *Mar. Chem.* 105, 70–89.

1025 Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A., Sayadi, S., 2014. Evaluation of  
1026 hydrocarbon pollution in marine sediments of Sfax coastal areas from the Gabes Gulf of  
1027 Tunisia, Mediterranean Sea. *Environ. Earth Sci.* 72, 1073–1082.

1028 Zhou, J.L., Fileman, T.W., Evans, S., Donkin, P., Readman, J.W., Mantoura, R.F.C.,  
1029 Rowland, S., 1999. The partition of fluoranthene and pyrene between suspended particles  
1030 and dissolved phase in the Humber Estuary: A study of the controlling factors. *Sci. Total*  
1031 *Environ.* 243–244, 305–321.

1032 Zhou, J.L., Maskaoui, K., 2003. Distribution of polycyclic aromatic hydrocarbons in water  
1033 and surface sediments from Daya Bay, China. *Environ. Pollut.* 121, 269–81.

1034  
1035  
1036  
1037  
1038  
1039  
1040  
1041

1042 **Figure caption**

1043

1044 **Figure 1.** Location of the study stations in the coastal areas of Sfax and Gabès cities, in the  
1045 Gulf of Gabès (Southeastern Mediterranean Sea, Tunisia). The detailed characteristics of the  
1046 stations are given in Table 1. The six groups of stations (G1-G6) identified according to the  
1047 hierarchical ascendant classification applied to biogeochemical parameters are presented with  
1048 different colours.

1049 **Figure 2.** Box-and-whisker plots of biogeochemical parameters with regard to the six clusters  
1050 identified from the hierarchical ascendant classification: a)  $\text{NO}_2^-$ , b)  $\text{NO}_3^-$ , c)  $\text{PO}_4^{3-}$ , d)  
1051  $\text{Si(OH)}_4$ , e) TChl *a*, f) Phaeo *a*, g) SPM, h) POC and i) DOC concentrations. The six clusters  
1052 are as follow: G1 (S2, S6), G2 (S3, S4, S7, S9-S13), G3 (S16, S20, S22), G4 (S17, S18, S21,  
1053 S23-S26), G5 (S27-S32; S36) and G6 (S33, S34). The black and red lines represent the  
1054 median and mean values, respectively.

1055 **Figure 3.** Principal component analysis (PCA) of hydrocarbons dataset: a) correlation circle  
1056 and b) projections of samples on the first factorial plane (PC1 *versus* PC2).

1057 **Figure 4.** Box-and-whisker plots of main hydrocarbon parameters with regard to the three  
1058 clusters identified from the hierarchical ascendant classification: a) total resolved *n*-alkanes  
1059 (*R*), b) Pr/Phy, c)  $\text{CPI}_{15-40}$ , d)  $\sum_{29} \text{PAH}_{\text{P+A}}$ , e) Alk/Par and f) Flt/(Flt + Pyr). The three clusters  
1060 are as follow: G'1 (S1-S6, S27-S36), G'2 (S7-S13, S16-S18, S20-S26) and G'3 (S14, S15,  
1061 S19). The black and red lines represent the median and mean values, respectively.

1062 **Figure 5.** Spatial distribution of dissolved AH and PAH concentrations in the Sfax and Gabès  
1063 coastal areas. The three groups of stations identified according to the hierarchical ascendant  
1064 classification applied to hydrocarbon parameters are presented in black (G'1), red (G'2) and  
1065 blue (G'3). Ocean Data View software version 4.6.5, Schlitzer, R., <http://odv.awi.de>, 2014.

1066 **Figure 6.** Relative abundances of dissolved AHs (%) for stations a) S1-S7, S11, S14, S27-  
1067 S36, b) S15, S19, c) S8, S17, d) S26, e) S13 and f) S9, S10, S12, S16, S18, S20-S25.

1068 **Figure 7.** Relative abundances of dissolved PAHs (%) for stations a) S1-S7, b) S8, c) S9-S13,  
1069 d) S14-S20, e) S21-S26 and f) S27-S36.

1070 **Figure 8.** PAH cross-plot between Flt/(Flt + Pyr) and Ant/(Ant + Phe) ratios. Stations S1,  
1071 S13, S29-S31, S35 and S36, for which Ant was not detected, are not represented.

1072 **Table 1.** Characteristics of the study stations in the coastal areas of Sfax and Gabès cities, in the Gulf of Gabès (Southeastern Mediterranean Sea,  
 1073 Tunisia).

1074

Stations	Area	Position	Date of sampling	Site depth (m)	Sampling depth (m)
S1	Northern Sfax, in front of Ezzit wadi	34°45'34.20"N, 10°48'30.06"E	08/03/2015	0.5	0.1
S2	Northern Sfax, in front of Ezzit wadi	34°45'29.31"N, 10°48'38.11"E	23/10/2014	0.9	0.1
S3	Northern Sfax, in front of Ezzit wadi	34°45'04.18"N, 10°49'05.26"E	23/10/2014	1.2	0.1
S4	Northern Sfax, in front of Ezzit wadi	34°44'40.06"N, 10°49'30.42"E	23/10/2014	1.8	0.1
S5	Northern Sfax, in front of Taparura fishing harbour	34°45'16.47"N, 10°47'55.98"E	08/03/2015	0.5	0.1
S6	Northern Sfax, in front of Taparura fishing harbour	34°45'12.08"N, 10°48'01.54"E	23/10/2014	2	0.1
S7	Northern Sfax, in front of Taparura fishing harbour	34°44'50.57"N, 10°48'33.99"E	23/10/2014	2	0.1
S8	Northern Sfax, in front of PK4 channel	34°44'57.08"N, 10°47'20.72"E	08/03/2015	0.5	0.1
S9	Northern Sfax, in front of PK4 channel	34°44'48.13"N, 10°47'28.79"E	23/10/2014	1.2	0.1
S10	Northern Sfax, in front of PK4 channel	34°44'25.94"N, 10°48'02.75"E	23/10/2014	2	0.1
S11	Northern Sfax, in front of PK4 channel	34°44'06.98"N, 10°48'30.00"E	23/10/2014	1	0.1
S12	Northern Sfax, in front of buried phosphogypsum	34°44'11.50"N, 10°47'17.78"E	23/10/2014	2	0.1
S13	Northern Sfax, in front of buried phosphogypsum	34°43'54.81"N, 10°47'49.23"E	23/10/2014	2	0.1
S14	Southern Sfax, in front of commercial harbour	34°43'15.18"N, 10°46'55.91"E	08/03/2015	0.5	0.1
S15	Southern Sfax, between commercial and fishing harbours	34°42'53.31"N, 10°46'36.94"E	08/03/2015	0.5	0.1
S16	Southern Sfax, in front of fishing harbour	34°42'33.58"N, 10°46'10.56"E	18/10/2014	3	0.1
S17	Southern Sfax, in front of fishing harbour	34°42'13.32"N, 10°46'43.64"E	18/10/2014	5	0.1
S18	Southern Sfax, in front of fishing harbour	34°41'55.94"N, 10°47'17.71"E	18/10/2014	9	0.1
S19	Southern Sfax, in front of Sidi Salem channel/industrial zone	34°42'32.34"N, 10°45'22.38"E	08/03/2015	0.5	0.1
S20	Southern Sfax, in front of Sidi Salem channel/industrial zone	34°42'15.90"N, 10°45'54.53"E	18/10/2014	1	0.1
S21	Southern Sfax, in front of Sidi Salem channel/industrial zone	34°41'58.75"N, 10°46'30.02"E	18/10/2014	6	0.1
S22	Southern Sfax, in front of El Maou wadi/SIAPE phosphogypsum area	34°41'35.05"N, 10°45'25.26"E	18/10/2014	1	0.1
S23	Southern Sfax, in front of El Maou wadi/SIAPE phosphogypsum area	34°41'22.70"N, 10°46'01.65"E	18/10/2014	8	0.1
S24	Southern Sfax, in front of El Maou wadi/SIAPE phosphogypsum area	34°41'08.60"N, 10°46'37.37"E	18/10/2014	6.2	0.1
S25	Southern Sfax, in front of El Hakmouni wadi/SIAPE phosphogypsum area	34°40'40.42"N, 10°45'00.41"E	18/10/2014	4	0.1
S26	Southern Sfax, in front of El Hakmouni wadi/SIAPE phosphogypsum area	34°40'25.81"N, 10°45'37.67"E	18/10/2014	5.5	0.1
S27	Gabès, in front of El-Tine wadi	33°56'17.26"N, 10°05'09.35"E	13/11/2014	5.5	0.1
S28	Gabès, in front of El-Tine wadi	33°56'25.23"N, 10°05'47.31"E	13/11/2014	8.5	0.1
S29	Gabès, in front of El-Tine wadi	33°56'32.81"N, 10°06'25.37"E	13/11/2014	10	0.1
S30	Gabès, in front of commercial harbour and phosphogypsum discharges	33°55'03.65"N, 10°06'25.72"E	13/11/2014	8	0.1
S31	Gabès, in front of commercial harbour and phosphogypsum discharges	33°55'16.48"N, 10°07'01.99"E	13/11/2014	9.5	0.1

S32	Gabès, in front of commercial harbour and phosphogypsum discharges	33°55'27.79"N, 10°07'36.81"E	13/11/2014	10	0.1
S33	Gabès, between commercial and fishing harbours	33°54'24.48"N, 10°06'37.27"E	13/11/2014	2.8	0.1
S34	Gabès, between commercial and fishing harbours	33°54'37.77"N, 10°07'13.43"E	13/11/2014	8	0.1
S35	Gabès, in front of fishing harbour and Gabès wadi	33°53'50.15"N, 10°07'20.52"E	13/11/2014	7.5	0.1
S36	Gabès, in front of fishing harbour and Gabès wadi	33°54'06.24"N, 10°07'55.26"E	13/11/2014	10.5	0.1

---

1075

1076

1077

1078

1079

1080

1081

1082

1083

1084

1085

1086

1087

1088

1089

1090

1091

1092

1093

1094 **Table 2.** Physical and biogeochemical parameters.

1095

Stations	T (°C)	Salinity	pH	NO <sub>2</sub> <sup>-</sup> (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	PO <sub>4</sub> <sup>3-</sup> (μM)	Si(OH) <sub>4</sub> (μM)	TChl <i>a</i> (μg L <sup>-1</sup> )	Phae <i>a</i> (μg L <sup>-1</sup> )	SPM (mg L <sup>-1</sup> )	POC (μM)	DOC (μM)
S1	<i>nd</i>	<i>Nd</i>	8.30	<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>
S2	21.0	42	8.11	0.24	0.11	6.2	8.5	16.1	2.8	43.6	244.8	180.8
S3	21.8	42	8.19	0.06	0.06	7.5	6.1	5.7	1.7	16.5	53.2	148.3
S4	21.0	42	8.14	0.10	0.09	7.8	6.0	5.3	0.6	13.4	43.5	144.9
S5	<i>nd</i>	<i>Nd</i>	8.12	<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>
S6	21.5	42	8.06	0.07	0.18	9.7	8.1	6.0	3.4	59.4	207.6	139.7
S7	22.0	40	8.21	0.04	0.12	8.6	5.1	2.3	0.6	9.7	30.3	129.1
S8	<i>nd</i>	<i>Nd</i>	8.17	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	106.7
S9	22.5	42	8.11	0.05	0.26	11.6	4.1	2.9	1.4	17.6	66.5	122.2
S10	22.6	40	8.14	0.03	0.13	10.0	4.0	1.7	0.7	23.3	28.2	122.1
S11	22.0	38	8.14	0.07	0.17	9.4	6.9	3.1	2.2	25.8	101.8	135.2
S12	23.2	42	8.01	0.07	0.50	14.7	4.3	4.1	2.0	16.4	45.3	146.8
S13	21.5	40	8.00	0.07	0.29	11.9	3.1	2.9	0.6	15.7	23.6	124.1
S14	<i>nd</i>	<i>Nd</i>	8.08	<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>
S15	<i>nd</i>	<i>Nd</i>	8.22	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	115.0
S16	26.7	40	8.02	0.68	1.50	120.0	13.4	40.7	9.7	27.1	177.5	190.9
S17	26.5	40	8.03	0.00	0.06	17.4	2.5	7.7	3.8	11.8	49.4	127.3
S18	27.3	40	7.94	0.01	0.07	5.5	1.4	2.0	0.4	10.6	14.9	107.3
S19	<i>nd</i>	<i>Nd</i>	8.19	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	132.1
S20	26.9	40	8.06	0.90	1.76	120.3	7.3	29.0	7.8	32.2	168.2	186.6
S21	26.5	38	8.00	0.23	0.86	24.0	3.2	8.7	2.4	13.0	42.4	126.3
S22	26.9	32	8.11	0.66	1.20	82.1	7.2	13.8	3.0	19.5	77.0	206.9
S23	26.8	38	8.00	0.15	0.45	6.4	2.8	2.8	0.8	9.0	24.7	126.2
S24	26.9	40	7.90	0.01	0.09	10.2	2.3	3.2	1.0	8.3	17.0	121.1
S25	26.7	35	7.90	0.35	1.31	14.5	5.3	3.9	2.5	10.1	30.5	126.2
S26	26.8	38	7.94	0.16	0.47	12.0	4.6	4.9	1.9	8.8	35.7	117.4
S27	22.0	36	7.97	0.02	0.89	18.7	13.1	6.1	1.7	17.0	34.1	137.4
S28	22.0	35	7.99	0.01	0.31	14.9	11.2	5.7	1.7	19.5	34.6	110.6
S29	21.0	32	8.14	0.00	0.01	6.8	2.6	3.0	0.7	18.7	24.5	112.9
S30	20.0	32	8.08	0.00	0.97	19.9	15.2	7.1	1.1	21.8	36.8	217.6



S31	20.0	34	8.00	0.00	0.14	14.1	7.9	6.7	1.2	22.7	39.1	124.3
S32	21.0	35	8.02	0.00	0.01	15.0	8.1	8.1	2.1	22.2	45.1	122.8
S33	18.0	36	7.97	0.00	4.00	42.1	33.4	7.7	1.4	19.5	46.2	110.6
S34	18.0	38	8.02	0.03	3.22	35.9	27.6	8.7	1.6	19.3	54.8	118.9
S35	18.0	40	8.13	0.00	0.39	12.1	6.6	5.0	1.5	21.9	36.8	127.8
S36	18.0	39	8.13	0.00	1.47	21.8	14.9	6.5	1.6	18.8	54.4	187.1

1096 *nd*: not determined.  $\text{NO}_2^-$ : nitrites;  $\text{NO}_3^-$ : nitrates;  $\text{PO}_4^{3-}$ : phosphates;  $\text{Si(OH)}_4$ : silicates; TChl *a*: total chlorophyll *a*; Phae *a*: phaeopigment *a*;  
1097 POC: particulate organic carbon; SPM: suspended particulate matter; DOC: dissolved organic carbon.

1098

1099

1100

1101

1102

1103

1104

1105

1106

1107

1108

1109

1110

1111

1112

1113

1114

**Table 3.** Dissolved aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs): concentrations and ratios.

	$R$ ( $\mu\text{g L}^{-1}$ )	UCM ( $\mu\text{g L}^{-1}$ )	$R/UCM$	Pr/Phy	CPI <sub>15-40</sub>	MH	$\sum_{16}$ PAH ( $\text{ng L}^{-1}$ )	$\sum_{19}$ PAH <sub>P</sub> ( $\text{ng L}^{-1}$ )	$\sum_{29}$ PAH <sub>P+A</sub> ( $\text{ng L}^{-1}$ )	Alk/Par	Ant/ (Ant + Phe)	Flt/ (Flt + Pyr)
S1	4.46	7.95	0.56	0.32	0.99	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	6.25	6.25	34.84	4.58	<i>nd</i>	0.08
S2	5.34	5.42	0.99	0.34	0.96	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	12.73	12.98	27.88	1.15	0.05	0.21
S3	5.88	<i>Np</i>	<i>nd</i>	0.27	1.05	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	10.39	10.51	17.16	0.63	0.04	0.21
S4	6.31	7.96	0.79	0.34	1	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	10.66	10.80	19.52	0.81	0.02	0.21
S5	4.93	8.30	0.59	0.33	0.97	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	7.58	7.58	37.67	3.97	0.78	0.10
S6	3.84	<i>Np</i>	<i>nd</i>	0.36	0.98	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	7.90	8.08	18.14	1.24	0.03	0.20
S7	1.09	<i>Np</i>	<i>nd</i>	0.51	1.09	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	10.89	11.08	20.23	0.83	0.04	0.19
S8	0.033	<i>Np</i>	<i>nd</i>	1.02	1.30	<i>n</i> -C <sub>29</sub>	14.50	14.50	45.21	2.12	0.75	0.91
S9	0.030	<i>Np</i>	<i>nd</i>	1.13	0.31	<i>n</i> -C <sub>16</sub> -C <sub>18</sub>	8.38	8.64	24.58	1.84	0.05	0.57
S10	0.021	<i>Np</i>	<i>nd</i>	0.97	0.49	<i>n</i> -C <sub>16</sub> -C <sub>18</sub>	3.69	3.79	9.86	1.6	0.07	0.58
S11	0.144	<i>Np</i>	<i>nd</i>	0.79	0.93	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	4.44	4.50	9.73	1.16	0.08	0.40
S12	0.045	<i>Np</i>	<i>nd</i>	1.06	0.41	<i>n</i> -C <sub>16</sub>	16.67	17.45	53.70	2.08	0.04	0.55
S13	0.053	<i>Np</i>	<i>nd</i>	1.51	0.97	<i>n</i> -C <sub>33</sub>	3.53	3.63	8.94	1.46	<i>nd</i>	0.51
S14	4.51	7.41	0.61	0.34	0.97	<i>n</i> -C <sub>25</sub> -C <sub>26</sub>	19.52	19.52	156.82	7.03	0.80	0.13
S15	0.044	<i>Np</i>	<i>nd</i>	0.43	0.94	<i>n</i> -C <sub>17</sub> -Phy	25.65	25.65	197.83	6.71	0.79	0.10
S16	0.041	<i>Np</i>	<i>nd</i>	1.57	0.89	<i>n</i> -C <sub>15</sub> -C <sub>16</sub>	7.66	8.08	26.25	2.25	0.08	0.56
S17	0.094	<i>Np</i>	<i>nd</i>	1.73	0.86	<i>n</i> -C <sub>29</sub>	5.68	6.00	19.41	2.23	0.05	0.53
S18	0.16	<i>Np</i>	<i>nd</i>	1.51	0.11	<i>n</i> -C <sub>16</sub>	7.42	7.71	19.84	1.57	0.03	0.61
S19	0.035	<i>Np</i>	<i>nd</i>	0.48	0.99	<i>n</i> -C <sub>17</sub> -Phy	24.90	24.90	172.76	5.94	0.78	0.08
S20	0.25	<i>Np</i>	<i>nd</i>	0.90	0.14	<i>n</i> -C <sub>16</sub> -C <sub>18</sub>	7.79	8.29	25.97	2.13	0.05	0.49
S21	0.034	<i>Np</i>	<i>nd</i>	2.43	0.59	<i>n</i> -C <sub>16</sub>	19.65	20.33	37.29	0.83	0.03	0.88
S22	0.077	<i>Np</i>	<i>nd</i>	1.25	0.33	<i>n</i> -C <sub>16</sub>	13.59	14.30	37.85	1.65	0.04	0.78
S23	0.038	<i>Np</i>	<i>nd</i>	1.64	0.53	<i>n</i> -C <sub>16</sub>	18.84	19.21	30.13	0.57	0.02	0.85
S24	0.026	<i>Np</i>	<i>nd</i>	1.76	0.52	<i>n</i> -C <sub>16</sub>	9.98	10.40	22.79	1.19	0.03	0.74
S25	0.032	<i>Np</i>	<i>nd</i>	1.66	0.42	<i>n</i> -C <sub>16</sub>	53.73	56.37	70.60	0.25	0.04	0.86
S26	0.045	<i>Np</i>	<i>nd</i>	1.85	0.62	<i>n</i> -C <sub>16</sub>	18.24	19.08	29.26	0.53	0.02	0.84
S27	4.66	12.03	0.39	0.29	0.99	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	6.63	6.63	37.49	4.66	0.31	0.14
S28	4.53	7.37	0.61	0.35	0.91	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	6.36	6.36	39.40	5.2	0.62	0.12
S29	4.41	7.32	0.60	0.30	0.96	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	4.03	4.03	15.48	2.84	<i>nd</i>	0.06
S30	4.92	8.34	0.59	0.36	0.98	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	6.07	6.07	24.09	2.97	<i>nd</i>	0.19
S31	4.28	8.13	0.53	0.35	0.99	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	4.23	4.23	16.56	2.91	<i>nd</i>	0.09

S32	4.44	7.89	0.56	0.34	0.98	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	6.37	6.37	29.24	3.6	0.38	0.15
S33	3.61	6.53	0.55	0.36	0.98	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	7.33	7.33	47.42	5.47	0.40	0.17
S34	5.08	14.03	0.36	0.31	0.95	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	9.38	9.38	56.79	5.05	0.22	0.38
S35	4.38	7.47	0.59	0.32	0.99	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	5.09	5.09	20.45	3.02	<i>nd</i>	0.10
S36	3.91	7.05	0.55	0.31	0.98	<i>n</i> -C <sub>26</sub> -C <sub>25</sub>	7.25	7.25	33.10	3.56	<i>nd</i>	0.18

1116 *np*: not present; *nd*: not determined. *R*: total resolved *n*-alkanes from *n*-C<sub>15</sub> to *n*-C<sub>40</sub> including two isoprenoids, pristane (Pr) and phytane (Phy); UCM:  
1117 unresolved complex mixture; CPI<sub>15-40</sub>: carbon preference index:  $\sum \text{odd } n\text{-alkanes } n\text{-C}_{15}\text{-}n\text{-C}_{40} / \sum \text{even } n\text{-alkanes } n\text{-C}_{15}\text{-}n\text{-C}_{40}$ ; MH: major hydrocarbons.  $\sum_{16}$   
1118 PAH: sum of the 16 priority PAHs listed by EPA;  $\sum_{19}$  PAH<sub>p</sub>: sum of 19 parent PAHs;  $\sum_{29}$  PAH<sub>p+A</sub>: sum of 29 parent and alkylated PAHs; Alk/Par: sum of  
1119 alkylated PAHs/sum of parent PAHs; Ant: anthracene; Phe: phenanthrene; Flt: fluoranthene; Pyr: pyrene.

1120

1121

1122

1123

1124

1125

1126

1127

1128

1129

1130

1131

1132

1133

1134

1135

1136 **Table 4.** Spearman's rank-order correlation matrix for biogeochemical parameters and dissolved hydrocarbons (n = 30).

1137

	T (°C)	Salinity	pH	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Si(OH) <sub>4</sub>	TChl <i>a</i>	Phae <i>a</i>	SPM	POC	DOC	<i>R</i>
Salinity	0.09												
pH	-0.35	0.32											
NO <sub>2</sub> <sup>-</sup>	<b>0.54</b>	0.30	-0.04										
NO <sub>3</sub> <sup>-</sup>	0.00	-0.26	-0.30	0.31									
PO <sub>4</sub> <sup>3-</sup>	-0.03	<b>-0.37</b>	-0.25	0.03	<b>0.74</b>								
Si(OH) <sub>4</sub>	<b>-0.56</b>	-0.24	0.07	-0.06	<b>0.54</b>	<b>0.53</b>							
TChl <i>a</i>	-0.18	-0.16	-0.05	0.17	<b>0.41</b>	<b>0.70</b>	<b>0.65</b>						
Phae <i>a</i>	0.23	0.04	-0.07	<b>0.47</b>	0.32	<b>0.50</b>	0.33	<b>0.69</b>					
SPM	-0.18	0.29	0.36	0.34	0.27	0.36	<b>0.56</b>	<b>0.69</b>	<b>0.72</b>				
POC	<b>-0.39</b>	0.00	<b>0.37</b>	0.01	0.15	0.25	<b>0.63</b>	<b>0.49</b>	<b>0.41</b>	<b>0.64</b>			
DOC	-0.03	0.23	<b>0.45</b>	<b>0.38</b>	0.24	0.25	0.36	<b>0.46</b>	<b>0.45</b>	<b>0.56</b>	0.35		
<i>R</i>	<b>-0.68</b>	-0.06	0.33	-0.32	-0.16	-0.06	<b>0.56</b>	0.35	-0.08	0.22	0.32	0.20	
∑ <sub>29</sub> PAH <sub>P+A</sub>	0.09	-0.30	<b>-0.47</b>	0.22	<b>0.66</b>	<b>0.55</b>	<b>0.39</b>	<b>0.40</b>	0.34	0.15	-0.15	0.01	-0.07*

1138 Significant correlations ( $p < 0.05$ ) are in bold. Stations S1, S5, S8, S14, S15 and S19 are not included in these correlations (absence of biogeochemical  
 1139 parameter measurements). \* For the correlation between *R* and ∑<sub>29</sub> PAH<sub>P+A</sub> all stations are taken into account (i.e., n = 36).

1140

1141

1142

1143

1144

1145

1146

1147