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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-01847666>**

Submitted on 23 Jul 2018

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

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

Revised version

29 January 2017

## Abstract

The goal of this work is to investigate the spatial distribution and sources of dissolved aliphatic and polycyclic aromatic hydrocarbons (AHs and PAHs), as well as their relationships with a series of biogeochemical parameters (total chlorophyll *a*, phaeopigment *a*, suspended particulate matter, particulate and dissolved organic carbon, and nutrients), in surface coastal waters of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea). Samples were collected off the Northern and Southern coasts of Sfax city, as well as in the Gabès-Ghannouch area, from October-November 2014 and in March 2015. Total dissolved AH and 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. These data suggest that this area has been moderate-to-highly impacted by hydrocarbons compared to other Mediterranean coastal environments. The highest AH concentrations were measured off of the Sfax Northern coast (near Ezzit wadi) and in the Gabès-Ghannouch area, whereas the highest PAH concentrations were recorded in the Sfax Southern coast (near commercial and fishing harbours and the Sidi Salem channel). Analysis of the AH molecular patterns reveals that low molecular weight (LMW) compounds in these samples are 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 activity (in the form of bacteria or algae), and that high molecular weight (HMW) compounds display monomodal distributions centred on *n*-C<sub>25</sub> and *n*-C<sub>26</sub>, which can be attributed to petrogenic inputs. The PAH molecular patterns are characterized by the dominance of LMW (2-3 rings) compounds and their alkylated homologues, which account for  $90 \pm 7\%$  of total PAHs. The observed PAH distribution and isomer ratios thus indicate the presence of major petrogenic contaminations. The concentrations of AHs, PAHs and dissolved organic carbon (DOC) do not correlate with each other, thus demonstrating that these three pools likely originated from different sources and subsequently underwent different processes in the Gulf of Gabès.

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

## 1. Introduction

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

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

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

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

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

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

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

## 2. Materials and Methods

### 2.1. Study area

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

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

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

## 2.2. Sampling

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



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

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

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

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

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

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

*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 analysis quality (Rathburn Chemicals Ltd, Walkerburn, Scotland).

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

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

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

AH and PAH external calibration standards (04071, Fluka and 47543-U, Supelco, among others, purchased from Sigma-Aldrich) were run for peak identification, and sample quantifications were processed using internal standards. Deuterated standard mixtures, which 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 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>), were used to determine procedural recoveries and to quantify hydrocarbons in samples.

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

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

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

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

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

## 2.7. Biogeochemical analyses

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

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

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

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

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 precision of the procedure was  $\leq 2\%$ .

## 2.8. Statistical treatment

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

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

### 3. Results

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

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



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), and SPM ( $10.2 \pm 1.7 \text{ mg L}^{-1}$ ; Fig. 2i), the highest T values ( $26.8 \pm 0.3 ^\circ\text{C}$ ), and the lowest pH values ( $8.0 \pm 0.05$ ) (Table 2). G5 comprises stations from the Gabès-Ghannouch area (S27-S32, S36) (Fig. 1), which are characterized by the lowest  $\text{NO}_2^-$  concentrations ( $\sim 0. \mu\text{M}$ ; Fig. 2a), the lowest salinity values ( $34.7 \pm 2.4$ ), and high DOC concentrations, with the highest value for S30 ( $217.6 \mu\text{M}$ ; Fig. 2g) (Table 2). Finally, G6 includes stations S33 and S34, which are located between the fishing and commercial harbours of the Gabès-Ghannouch area (Fig. 1). They record the highest concentrations of  $\text{Si(OH)}_4$  ( $27.6\text{-}33.4 \mu\text{M}$ ; Fig. 2d) and  $\text{NO}_3^-$  ( $3.2\text{-}4.0 \mu\text{M}$ ; 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* ( $7.7\text{-}8.7 \mu\text{g L}^{-1}$ ; Fig. 2e) (Table 2).

### 3.2. Spatial distribution of dissolved hydrocarbons

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

#### 3.2.1. Group G'1

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

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). When present, *R*/UCM values are all  $> 0.30$  (Table 3). This group exhibits the lowest Pr/Phy ratios, which vary from 0.27 (S3) to 0.36 (S30, S33) (Table 3; Fig. 4b). AH molecular profiles display monomodal distributions centred on *n*-C<sub>25</sub>–*n*-C<sub>26</sub> compounds (Fig. 6a). An equal amount of even and odd carbon numbered *n*-alkanes is also observed, resulting in CPI<sub>15-40</sub> values close to 1 (Table 3; Fig. 4c).

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 ratios range from 0.6 (S3) to 5.5 (S33) but are mainly  $> 2$  (Table 3; Fig. 4e). PAHs<sub>P+A</sub> pattern distributions are marked by the dominance of LMW compounds (2-3 rings) over HMW compounds ( $\geq 4$  rings) (Fig. 7a, f), the former representing  $88 \pm 4\%$  of total PAHs. Naphthalenes (C<sub>2</sub>-Naph  $>$  Naph  $>$  C<sub>3</sub>-Naph  $>$  C<sub>1</sub>-Naph) represent the major compounds, followed by phenanthrenes (C<sub>1</sub>-Phe  $>$  C<sub>2</sub>-Phe  $>$  Phe  $>$  C<sub>3</sub>-Phe). Nevertheless, the heavy compounds C<sub>1</sub>-Pyr and Pyr are also present in significant proportions in these stations ( $6.4 \pm 4.8$  and  $3.8 \pm 3.9\%$ , respectively) (Fig. 7a, f). The Flt/(Flt + Pyr) ratios range from 0.08 to 0.38 (Table 3; Fig. 4f).

### 3.2.2. Group G'2

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

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

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

### 3.2.3. Group G'3

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

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

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

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

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

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

## 4. Discussion

### 4.1. Comparisons with previously published data

#### 4.1.1. Physical and biogeochemical parameters

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

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

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

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

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

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

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

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

micro layer and 3.6-30.7 ng L<sup>-1</sup> in surface waters) (Guitart et al., 2007). However, they are within the same range as those observed in surface waters of the Marseille coastal area ( $\Sigma_{32}$  PAHs<sub>p+A</sub>: 5-162 ng L<sup>-1</sup>) (Guigue et al., 2011), the Rhone delta (France) ( $\Sigma_{80}$  PAHs<sub>p+A</sub>: 15-290 ng L<sup>-1</sup>) (Bouloubassi and Saliot, 1991), and the Venice Lagoon (Italy) ( $\Sigma_{20}$  PAHs<sub>p+A</sub>: 12.4-266.8 ng L<sup>-1</sup>) (Manodori et al., 2006). Our measured concentrations are also lower than those found in the Gulf of Tunis ( $\Sigma_{24}$  PAHs<sub>p+A</sub>: 139-694 ng L<sup>-1</sup> in summer and 150-1008 ng L<sup>-1</sup> in winter) (Mzoughi and Chouba, 2011) and the Saronikos Gulf (Greece) ( $\Sigma_{17}$  PAHs<sub>p+A</sub>: 103-459 ng L<sup>-1</sup>) (Valavanidis et al., 2008). El Nemr and Abd-Allah (2003) also reported higher concentrations of PAHs<sub>p</sub> in surface waters of the Alexandria coast (Egypt) ( $\Sigma_7$  PAHs<sub>p</sub>: 13-120 ng L<sup>-1</sup>). Consequently, these AH and PAH concentration data indicate that the surface coastal waters of the Gulf of Gabès are likely moderately-to-highly contaminated when compared to other Mediterranean regions. Hence concentration levels of hydrocarbons recorded in surface waters of the Gulf of Gabès are not so high compared to other Mediterranean coastal environment despite strong anthropogenic releases. This could be explained by the influence of hydrodynamic conditions, in particular tides. Tides of the Gulf of Gabès, which present the highest amplitude of all the Mediterranean Sea, with the upper Adriatic, may have a role of dispersing hydrocarbons at sea.

## 4.2. Origin and potential sources of dissolved hydrocarbons

### 4.2.1. Group G'1

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 SPM concentrations (data not shown). This could underline a “particle concentration effect” (Zhou et al., 1999). The latter is observed when particle partition coefficient ( $K_p$  or  $K_{oc}$ ) is inversely proportional to particle concentration. The increase in particle concentration is generally associated to an increase in DOC concentration, which may explain this distribution of PAHs towards the dissolved phase (Zhou et al., 1999). However, in our case, the increase in POC/SPM concentrations was not concomitant to an increase in DOC concentrations. Our results thus illustrate the complexity of the relationships between dissolved PAHs, DOC and POC in marine coastal waters.

## 5. Conclusions

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

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

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

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## Figure caption

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

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

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

**Figure 4.** Box-and-whisker plots of main hydrocarbon parameters with regard to the three clusters identified from the hierarchical ascendant classification: a) total resolved *n*-alkanes (*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 are as follow: G'1 (S1-S6, S27-S36), G'2 (S7-S13, S16-S18, S20-S26) and G'3 (S14, S15, S19). The black and red lines represent the median and mean values, respectively.

**Figure 5.** Spatial distribution of dissolved AH and PAH concentrations in the Sfax and Gabès coastal areas. The three groups of stations identified according to the hierarchical ascendant classification applied to hydrocarbon parameters are presented in black (G'1), red (G'2) and 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).

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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

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

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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

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

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1115 **Table 3.** Dissolved aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs): concentrations and ratios.

	$R$ ( $\mu\text{g L}^{-1}$ )	UCM ( $\mu\text{g L}^{-1}$ )	$R/\text{UCM}$	Pr/Phy	CPI <sub>15-40</sub>	MH	$\Sigma_{16}$ PAH ( $\text{ng L}^{-1}$ )	$\Sigma_{19}$ PAH <sub>P</sub> ( $\text{ng L}^{-1}$ )	$\Sigma_{29}$ 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	$n\text{-C}_{25}\text{-C}_{26}$	6.25	6.25	34.84	4.58	<i>nd</i>	0.08
S2	5.34	5.42	0.99	0.34	0.96	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{25}\text{-C}_{26}$	10.39	10.51	17.16	0.63	0.04	0.21
S4	6.31	7.96	0.79	0.34	1	$n\text{-C}_{25}\text{-C}_{26}$	10.66	10.80	19.52	0.81	0.02	0.21
S5	4.93	8.30	0.59	0.33	0.97	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{29}$	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	$n\text{-C}_{16}\text{-C}_{18}$	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	$n\text{-C}_{16}\text{-C}_{18}$	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	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{33}$	3.53	3.63	8.94	1.46	<i>nd</i>	0.51
S14	4.51	7.41	0.61	0.34	0.97	$n\text{-C}_{25}\text{-C}_{26}$	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	$n\text{-C}_{17}\text{-Phy}$	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	$n\text{-C}_{15}\text{-C}_{16}$	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	$n\text{-C}_{29}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{17}\text{-Phy}$	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	$n\text{-C}_{16}\text{-C}_{18}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{16}$	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	$n\text{-C}_{16}$	18.24	19.08	29.26	0.53	0.02	0.84
S27	4.66	12.03	0.39	0.29	0.99	$n\text{-C}_{26}\text{-C}_{25}$	6.63	6.63	37.49	4.66	0.31	0.14
S28	4.53	7.37	0.61	0.35	0.91	$n\text{-C}_{26}\text{-C}_{25}$	6.36	6.36	39.40	5.2	0.62	0.12
S29	4.41	7.32	0.60	0.30	0.96	$n\text{-C}_{26}\text{-C}_{25}$	4.03	4.03	15.48	2.84	<i>nd</i>	0.06
S30	4.92	8.34	0.59	0.36	0.98	$n\text{-C}_{26}\text{-C}_{25}$	6.07	6.07	24.09	2.97	<i>nd</i>	0.19
S31	4.28	8.13	0.53	0.35	0.99	$n\text{-C}_{26}\text{-C}_{25}$	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.

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

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	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	
Σ <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 Σ<sub>29</sub> PAH<sub>P+A</sub> all stations are taken into account (i.e., n = 36).

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