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Origin and distribution of hydrocarbons and organic matter in the surficial sediments of the Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea)

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ABSTRACT

We investigated the origin and distribution of aliphatic and polycyclic aromatic hydrocarbons (AHs and PAHs) and organic matter (OM) in surficial sediments of the Sfax-Kerkennah channel in the Gulf of Gabès (Tunisia, Southern Mediterranean Sea). TOC, AH and PAH concentrations ranged 2.3–11.7%, 8–174 $\mu\text{g g}^{-1}$ sed. dw and 175–10,769 ng g^{-1} sed. dw, respectively. The lowest concentrations were recorded in the channel (medium sand sediment) and the highest ones in the Sfax harbor (very fine sand sediment). AHs, PAHs and TOC were not correlated for most of the stations. TOC/N and $\delta^{13}\text{C}$ values revealed a mixed origin of OM with both marine and terrestrial sources. Hydrocarbon molecular composition highlighted the dominance of petrogenic AHs and the presence of both petrogenic and pyrogenic PAHs, associated with petroleum products and combustion processes. This work underscores the complex distribution patterns and the multiple sources of OM and hydrocarbons in this highly anthropogenized coastal environment.

Keywords: Sediment, hydrocarbons, organic matter, Sfax, Gulf of Gabès, Mediterranean Sea.

1. Introduction

The study of the composition of coastal sediments represents one of the main pathways to highlight the level and source of contamination within marine ecosystems. Indeed, sediments are receptacles for a wide variety of organic contaminants emitted from land and which reach the sedimentary layer through their adsorption onto particles in the water column. In addition, sediments may accumulate biogenic particulate material issued from surface waters and thus may provide fruitful information about autochthonous biological activity of marine ecosystems.

Hydrocarbons, including aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs), are abundant components of the organic material in coastal sediments (Volkman et al., 1992; Gogou et al., 2000), PAHs being among the most ubiquitous organic contaminants in the marine environment (Louati et al., 2001; Roose and Brinkman, 2005). AHs, which may be of biogenic or anthropogenic origin, consist of a series of resolved *n*-alkanes (*R*) and of unresolved complex mixture (UCM). Their biogenic sources include terrestrial 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; Mille et al., 2007), whereas their anthropogenic sources comprise essentially unburned petroleum/oils (Mazurek and Simoneit, 1984; Bouloubassi and Saliot, 1993; Wang et al., 1997; Readman et al., 2002; Zaghden et al., 2005).

Parent PAHs and their alkylated homologues (i.e. mono-, di-, tri- or tetra-methyl PAHs) may be also of biogenic or anthropogenic origin. PAHs 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), and biologically produced in soils from woody plants, termites or from the microbial transformation of organic matter

(Chen et al., 1998; Wilcke et al., 2002). Petrogenic PAHs consist of low molecular weight (LMW) 2-3 ring compounds with a high proportion of alkylated homologues, while pyrogenic PAHs comprise high molecular weight (HMW) 4-6 ring compounds with a low proportion of alkylated derivatives (Neff, 1979). PAHs are known to be harmful to living organisms, with reprotoxic, carcinogenic and mutagenic effects (Kennish, 1992). Therefore, they are recognized for a long time as highly priority contaminants by various international organizations: 8 PAHs are included in the list of the 45 priority regulated substances by the European Union (Official Journal of the EU 24/08/2013, Directive 2013/39/EU) and 16 PAHs are included in the list of 126 priority regulated substances by the US Environmental Protection Agency (US EPA, 40 CFR Part 423, Appendix A to Part 423).

Hence, hydrocarbons (AH and PAHs) in sediments may originate from numerous sources including petroleum inputs, incomplete combustion of fuels (PAHs), forest and grass fires (PAHs), biosynthesis by marine and terrestrial organisms, and early diagenetic transformation processes (UNEP/IOC/IAEA, 1992; Clark, 1997; Readman et al., 2002).

Anthropogenic hydrocarbons are introduced into marine waters mainly *via* the direct discharge of crude oil and petroleum products during sea-based activities (spills from tankers, platforms and pipelines, ballast water discharge, drilling...) or *via* industrial and urban wastes (fuel combustion, traffic exhaust emissions, varied spills) routed by rivers, surface runoffs, effluents and the atmosphere (Wang et al., 1999; Wurl and Obbard, 2004; Dachs and Méjanelle, 2010). Thus, investigating the concentrations and molecular composition of hydrocarbons in surficial sediments allows for a better understanding of the levels and sources of anthropogenic contaminations and of the origin (marine *versus* terrestrial) of natural organic matter in coastal waters (Budzinski et al., 1997).

The Gulf of Gabès (Southeast Tunisia, Southern Mediterranean Sea) presents two major characteristics. First, it is one of the most productive coastal environments of the

Mediterranean Sea due to nutrient availability and the main fishing area of the Tunisian coasts (Jabeur et al., 2001; Bel Hassen et al., 2009; D'Ortenzio and Ribera d'Alcalà, 2009; The Mermex group, 2011). Second, the Gulf of Gabès is submitted to very high anthropogenic pressures, especially around Sfax city, the second largest city in Tunisia and the one with the most important fishing and harbor activities. In this highly urbanized and industrialized area, organic contaminants are issued from a multitude of sources (Illou, 1999; Serbaji, 2000; Louati, 2003). However, the studies dealing with the assessment of the hydrocarbon levels in the surficial sediments of the Gulf of Gabès/Sfax coastal area remain few compared to those conducted in the Northwestern Mediterranean Sea. They have really begun in the 2000's with the first reports of concentrations in AHs (Louati et al., 2001; Zaghden et al., 2005; Elloumi et al., 2008; Aloulou et al., 2010; Amorri et al., 2011), in PAHs (Kessabi et al., 2013), and in both AHs and PAHs (Zaghden et al., 2007; 2014). Interestingly, the AH and PAH concentrations found in the surficial sediments of the Sfax coastal area are rather located in the upper range of those recorded for the whole Mediterranean Sea.

The main objectives of this study were 1) to determine the contents in several biogeochemical parameters (C/H/N/S, TOC, CaCO₃ and $\delta^{13}\text{C}$) and in hydrocarbons (AHs and PAHs) in surficial sediments of the Sfax-Kerkennah channel and to compare these contents to those recorded in other regions of the Mediterranean Sea. 2) To assess the spatial distribution of these parameters in relation to the Sfax-Kerkennah channel geomorphology/bathymetry and to examine the degree of correlation between these parameters, especially between TOC, AHs and PAHs. 3) To evaluate the origin (marine *versus* terrestrial *versus* anthropogenic) of organic matter and hydrocarbons regarding molecular/isotopic ratios and indices.

2. Material and methods

2.1. Study area

This study was conducted in the coastal area between the Sfax city and the Kerkennah Islands, in the Northern part of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea) (Fig. 1). The Gulf of Gabès, located in the Southeast of Tunisia, extends from the city of Chebba (35°14'N, 11°09'E) to the Tunisian-Libyan border (33°10'N, 11°34'E) and shelters the Kerkennah Islands in the Northeast and Djerba Island in the Southeast. The climate in the Gulf of Gabès is arid to semiarid, i.e. dry (average annual precipitation: 210 mm) and sunny with strong easterly winds (INM, 2008), resulting in a severe aeolian erosion and the transport of Saharan dusts into the sea (Jedoui, 1980; Bouaziz et al., 2003). The gulf is characterized by a wide continental shelf (~ 250 km) with a very low slope and an important network of channels and wadis. Hence, its basin is very shallow, with in some areas, a water depth not exceeding 1 m over several kilometres. Also, in the Gulf of Gabès, the tide is semidiurnal and one of the highest in the Mediterranean Sea, with a maximum range of approximately 2.3 m at spring low tides (Sammari et al., 2006). The sediment of the gulf is rich in organic matter and principally composed of sand with a high density of plants (Ben Othman, 1973). The Gulf of Gabès is an important nursery for several species of fish and accounts for 65% of the Tunisian fish production (DGPA, 2010). These favourable geomorphologic and climatic conditions have led to the development of one of the most extensive marine habitats of seagrass *Posidonia oceanica*.

Sfax (34°43'N, 10°46'E; Fig. 1), with a population of about 730,000 inhabitants distributed over about 20,000 ha, represents the second largest city and the second economic pole in Tunisia. Sfax is heavily industrialized with important fishing and harbor activities. Its main industrial activity domains are phosphates, chemical products, textiles, olive oil, food, soap and paint. Therefore, the sources of pollution in the Sfax coastal zone are numerous: atmospheric depositions, ship traffic, fishery activities, rivers, wadis, wild landfills, municipal

sewage effluents and industrial wastewaters, especially those coming from the storage of crude oil, phosphogypsum and olive oil wastes at the coast (Ben Mustapha et al., 1999; Louati et al., 2001). The Kerkennah Islands (34°42'N, 11°11'E; Fig. 1), which include the two principal islands Gharbi and Chergui, are situated ~ 20 km offshore Sfax. They have an area of 160 km² and are low-lying being no more than 13 m above the sea level. These islands are characterized by a -10 m isobath few kilometers away from the shoreline and by a lithology dominated by smooth rocks (Katlane et al., 2014). Since there is neither industrial activity nor urban concentration in the Kerkennah Islands, the latter are much less submitted to anthropogenic pressures than the Sfax coastal area.

The Sfax-Kerkennah channel is an underwater channel, Northeast-Southwest oriented, which cut the shelf at depths higher than 20 m. It allows for conducting the ferry boat crossings Sfax-Kerkennah (Fig. 1). Bottom sediments are largely composed of sand, muddy sand and shell-sand with a high density of plants. This structure extends from the beaches up to about 20 m depth. Muddy sands are the most widespread sediment of the Sfax shelf. This sediment is the substrate of mixed *Cymodocea* and *Posidonia* meadows. In some places (southern Kerkennah), areas with gravel or concretions of calcareous algae are distinguished. At the Kerkennah islands, the shelf is characterized by the presence of sandy shoals.

2.2. Sampling, storage, sieving and granulometric analysis of samples

Twenty stations were sampled in January 2005 at low tide on board a vessel from the Fishing Professional Training Centre of Sfax. Stations were located along two transects: one between the North of Sfax - Sidi Mansour area (station R101) and the Kerkennah harbor (station R111), and the other one between the Kerkennah harbor and the Sfax harbor (station R201) (Fig. 1; Table 1). Stations R104-R107 and R203-R210, displaying depths from > 5 to 20 m, were comprised within the Sfax-Kerkennah channel, whereas stations R101-R103,

R108-R111, R201 and R202, with depths < 5 m, were positioned outside the channel (Table 1). At each station, surficial sediments (0-1 cm) were collected by professional divers. Surficial sediments were transferred into pre-combusted (450 °C, 6 h) glass bottles and stored on board in the dark in the cold (~ 6 °C).

Back in the laboratory, samples were immediately frozen at -20 °C. They were maintained frozen for few days and then freeze dried. Afterwards, each sediment sample (200 g) was dry sieved sequentially during 30 min, using an electric shaker, through twenty AFNOR standard stainless steel screens of mesh sizes ranging from 4 mm to 50 µm (Aloulou et al., 2012). Before sieving, stainless steel forceps were used to remove vegetal fragments from sediment samples. The percentages of sediment mass corresponding to each particle size were determined. Grain Size Analyzer (GSA) software was used to establish granulometric curves and to derive the parameters describing the grain size distribution, i.e. the index of mean trend, expressed by the mean of the size (M_z), and the index of classification, expressed by the standard deviation of the size (σ). M_z and σ are given in unit ϕ , where $\phi = -\log_2 D/D_0$ (D_0 being a reference diameter and D the diameter of the particle in mm) (Folk and Ward, 1957; Blott and Pye, 2001; Ghannem et al., 2011). All chemical analyses (hydrocarbons, elemental composition, organic carbon, calcium carbonate, $\delta^{13}\text{C}$, see below) were performed on the fraction < 63 µm, which represents the fraction of silts and clays.

2.3. Extraction, purification and GC-FID/MS analysis of hydrocarbons

Sediment samples (around 5 g dry weight of the fraction < 63 µm) were transferred into a pre-combusted glass tube, in which were also added 30 ml of a dichloromethane (CH_2Cl_2)/methanol (CH_3OH) (3:1 v/v) solvent mixture, deuterated (internal) standard mixtures ($n\text{-C}_{24}\text{-}d_{50}$ for AHs and $p\text{-terphenyl-}d_{14}$ for PAHs) and activated copper to remove sulphurs. Extraction was carried out in an ultrasonic bath for 15 min. The sediment was then

isolated from the lipid extract by centrifugation (3500 rpm for 10 min). The entire extraction procedure (ultrasounds and centrifugation) was repeated 3 times. The extracts (supernatants) were combined and concentrated with a rotary evaporator at $T < 30\text{ }^{\circ}\text{C}$, dried with magnesium sulphate and filtered on a pre-combusted glass fiber filter of porosity $4\text{ }\mu\text{m}$. The remaining solvent was changed to *n*-hexane (Ke et al., 2004; Bouloubassi et al., 2006; Parinos et al., 2013).

Hexane-solubilised extracts were purified to separate AHs and PAHs (hydrocarbon fraction) from more polar compounds. The extracts were fractionated on a column (6 mm i.d.) filled with 400 mg of silica gel (extra pure Merck 60), beforehand Soxhlet extracted with CH_2Cl_2 , activated 1 h at $150\text{ }^{\circ}\text{C}$ and partially deactivated with 4% water by weight. The AH fraction was first eluted with 3 ml *n*-hexane, followed by the elution of the PAH fraction with 9 ml hexane/toluene (9:1 v/v). Finally, purified extracts were concentrated to 150-200 μl with a rotary evaporator and a gentle stream of nitrogen.

Analyses of hydrocarbons (AHs and PAHs) were performed with a Delsi DI 200 gas chromatograph coupled with a flame ionisation detector (GC-FID) (Perichrom, France) (Zaghden et al., 2007; 2014). The GC-FID was equipped with a DB-5 MS fused-silica capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$, J&W Scientific, Agilent Technologies, USA) and used helium as a carrier gas at a flow rate of 1.5 ml min^{-1} . The injector (used in splitless mode) and detector temperatures were 250 and $320\text{ }^{\circ}\text{C}$, respectively. The initial column temperature was held for 2 min at $60\text{ }^{\circ}\text{C}$, next ramped at $25\text{ }^{\circ}\text{C min}^{-1}$ (ramp 1) to $100\text{ }^{\circ}\text{C}$ and then at $2\text{ }^{\circ}\text{C min}^{-1}$ (ramp 2) to a final temperature of $310\text{ }^{\circ}\text{C}$, which was held for 10 min. With each set of samples to be analysed, AH and PAH calibration standards were run for peak identification and quantification. Compounds were identified mainly by their retention times. To confirm the structure of several hydrocarbons, some samples were also analysed using a HP 6890 gas chromatograph coupled with a HP 5973 MSD mass spectrometer (GC-MS)

(Agilent Technologies, Wilmington DE, USA), equipped with a DB-5 MS fused-silica capillary column coated with 5% phenyl methyl siloxane (Zaghden et al., 2007; 2014). Helium was used as a carrier gas. The injector temperature and column temperature program were the same than those used for the GC-FID. GC-MS analyses were run in the electron impact mode at 70 eV with a 0.6 scan s⁻¹ time over a 50-550 atomic mass unit (amu) range resolution.

2.4. Quality assurance and quality control of hydrocarbon analyses

During the procedures described above, nitrile gloves were worn and care was taken to avoid contaminations. All the glassware was cleaned with ultrapure water (Milli-Q water from Millipore system, final resistivity: 18.2 MΩ cm⁻¹ at 25 °C, pH ~ 5), combusted at 450 °C during 6 h and finally cleaned with CH₃OH and CH₂Cl₂ before use. The precision glassware, which could not be baked, was cleaned in a bath of sulfochromic acid for at least 4 h, and then rinsed with ultrapure water, CH₃OH and CH₂Cl₂. All the (Teflon-lined) caps were wrapped with Teflon tape for the storage of samples. All organic solvents were of trace-analysis quality (Merck, Darmstadt, Germany) and were further distilled before use. Silica and magnesium sulphate were purified by soxhlet extraction with CH₂Cl₂ for 24 h and then dried in the oven.

Deuterated (internal) standards mixtures (04071, Fluka, and 47543-U, Supelco) were introduced before ultrasonic treatment to assess the recoveries of the analytical procedure (including extraction, evaporation and purification processes). The latter were on average > 75% for the different AHs and PAHs investigated. Calibration (external) standards (04071, Fluka, and 47543-U, Supelco) as well as procedural and solvent blanks were run with each set of samples to check for contamination and for quantification. Calibration curves were constructed for all target hydrocarbons analysed except for the alkylated PAHs, which were

quantified with their parent-compound calibration curves. For the different hydrocarbons, the detection limits ranged from 0.01 to 0.5 ng g⁻¹. Instrumental reproducibility, evaluated from samples R110 and R207, was on average ± 10%. All the concentration values, given in ng g⁻¹ (PAHs) or µg g⁻¹ (AHs) sediment dry weight (sed. dw), were blank- and recovery-corrected.

2.5. Determination of individual hydrocarbons and molecular diagnostic ratios

For AHs, we determined the concentrations of resolved *n*-alkanes (*R*), including linear *n*-alkanes from *n*-C₁₅ to *n*-C₃₄ and two isoprenoids, pristane (Pr, C₁₉) and phytane (Phy, C₂₀), and the concentrations of UCM. We computed different ratios and indices allowing to distinguish biogenic AHs (issuing from biological activity) and petrogenic AHs (coming from uncombusted petroleum): 1) the UCM/*R* ratio as indicator of the presence of degraded petroleum products (when > 3-4) (Simoneit and Mazurek, 1982; Mazurek and Simoneit, 1984). 2) The Pr/Phy ratio as indicator of biogenic AHs (when >> 1), even though values < 1 do not necessarily reflect the presence of petrogenic AHs (Cripps, 1989; Commendatore and Esteves, 2004; Cincinelli et al., 2008). 3) The *n*-C₁₇/Pr and *n*-C₁₈/Phy ratios as indicators of degraded (when < 1) or less degraded or relatively fresh AHs (when > 1) (Mille et al., 2007; Asia et al., 2009). 4) The carbon preference index, the ratio of odd to even carbon-numbered *n*-alkanes, in the ranges *n*-C₁₅-*n*-C₂₄ and *n*-C₂₅-*n*-C₃₄ (CPI₁₅₋₂₄ and CPI₂₅₋₃₄), which are indicators of crude oil/petrogenic AHs (when ~ 1) or biogenic AHs (when >> or << 1) (Eglinton and Hamilton, 1967; Rieley et al., 1991; Wang et al., 1999; Harji et al., 2008). 5) The terrigenous/aquatic ratio (TAR), the ratio between the concentrations of long-chain *n*-alkanes (*n*-C₂₇ + *n*-C₂₉ + *n*-C₃₁) to short-chain *n*-alkanes (*n*-C₁₅ + *n*-C₁₇ + *n*-C₁₉), as index of the relative importance of terrestrial (higher plants) and aquatic (algae, phyto- and zooplankton) materials (Bourbonniere and Meyers, 1996; Mille et al., 2007) (Table 2).

Concerning PAHs, we investigated the concentrations of 17 PAHs: 12 parent PAHs, namely naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), thiophene (Thi), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), perylene (Per) and benzo[g,h,i]perylene (BgP), and 5 alkylated homologues, i.e. the sums of mono-, di- and tri-methyl compounds (Σ Me) of the five target compounds Nap, Phe, Ant, Pyr and Chr. Thi is a 1-ring sulfur heterocyclic compound. Naph and its alkylated homologues are 2-ring compounds. Phe, Ant and their alkylated homologues are 3-ring compounds. These 2-3 ring compounds represent low molecular weight (LMW) PAHs. Flt, Pyr, BaA, Chr and alkylated homologues of Pyr and Chr are 4-ring compounds. BkF, BaP and Per are 5-ring compounds, whereas BgP is a 6-ring compound. These 4-6 ring compounds represent high molecular weight (HMW) PAHs. We determined several ratios allowing to differentiate petrogenic PAHs and pyrogenic PAHs (issuing from the incomplete combustion of fossil fuels), PAHs from fuel combustion and those from the combustion of grass, coal or wood, and PAHs from traffic emissions and PAHs from non-traffic emissions: Σ LMW/ Σ HMW, Σ MePhe/Phe, Σ MePyr/Pyr, Flt/Flt+Pyr and BaP/BgP (Yunker et al., 2002; Brändli et al., 2008; Tobiszewski and Namieśnik, 2012; Katsoyiannis and Breivik, 2014) (Table 2).

2.6. Analysis of C/H/N/S, TOC, CaCO₃ and $\delta^{13}\text{C}$

Several parameters were measured on sub-samples of freeze-dried and homogenized sediments (fraction < 63 μm). Content in total carbon, hydrogen, nitrogen and sulphur (C/H/N/S) was determined using a SC-144 LECO Elemental Analyzer at combustion temperatures of 1050 (C, H, N) or 1350 °C (S) in oxygen (C, H, S) or helium (N) atmosphere. For total organic carbon (TOC) determination, sediment sub-samples were acidified with 1 N HCl and oven dried at 60 °C. This procedure (acidification and drying) was repeated twice in

order to remove inorganic carbon. Then, sub-samples were run in the Elemental Analyzer the same way as for total carbon. Two replicates of each sample were run for these elemental analyses. Content in calcium carbonate (CaCO_3) was estimated as the difference between total carbon and TOC contents. Concentrations in C, H, N, S, TOC and CaCO_3 are expressed in percentages (%) for 1 g sed. dw.

$\delta^{13}\text{C}$, given in ‰, is the ratio of stable isotopes $^{13}\text{C}/^{12}\text{C}$. It was determined on OC (acidified) sub-samples using the following formula: $[(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1] \times 1000$, where $(^{13}\text{C}/^{12}\text{C})_{\text{standard}}$ corresponds to the isotopic ratio of the international standard Pee Dee Belemnite (PDB), and $(^{13}\text{C}/^{12}\text{C})_{\text{sample}}$ to the isotopic ratio measurements of sediment sub-samples conducted by using an elemental analyzer coupled to an isotopic ratio mass spectrometer (EA-IRMS).

2.7. Statistical analyses

Ocean Data View (ODV) software version 4.6.5 (Schlitzer, R., <http://odv.awi.de>, 2014.) was employed for the spatial representation of TOC; $\delta^{13}\text{C}$, R and PAH concentrations as well as R/TOC and PAH/TOC ratios. The spatial interpolation/gridding of data was performed using Data-Interpolating Variational Analysis (DIVA) (Barth et al., 2010; Troupin et al., 2012). Pearson correlation matrices were performed using XLSTAT 2011.2.05 (Microsoft Excel add-in program). The significance threshold was set at $p < 0.05$.

3. Results and discussion

3.1. Granulometry and content in C/H/N/S, TOC, CaCO_3 and $\delta^{13}\text{C}$

Mean grain size (M_z) ranged from 4 to 3 ϕ (i.e. 62.5-125 μm ; very fine sand) in stations R104, R111, R201, from 3 to 2 ϕ (i.e. 125-250 μm ; fine sand) in stations R101-R103, R106,

R108-R110, R202, R210, and from 2 to 1 ϕ (i.e. 250-500 μm ; medium sand) in stations R105, R107, R203-R209 (Table 3). The index of classification (σ) was comprised between 2 and 1 ϕ for all stations, which reflected poorly sorted sands (Table 3). Therefore, the granulometric distribution was closely related to the bathymetry and geomorphology of the Sfax-Kerkennah channel. The fact that sediments were essentially constituted of sand is in accordance with the hydrodynamic properties of this intertidal area where the combined action of waves and tide prevent the deposition of the finest fraction along with promoting a sandy facies (Aloulou et al., 2012). Apart from stations R104, R106 and R210, which were situated at the border of or within the channel, fine and very fine sands were found outside the channel, i.e. in the most coastal and the shallowest stations, including harbors (Fig. 1; Tables 1, 3). In contrast, medium sand was observed in the deepest stations, in the area where the channel is the widest. In this zone, fines particles, coming from the North-East South-West-oriented current, cannot reach the bottom and are transported further southward (Fig. 1; Tables 1, 3).

The content in C, H, N and S ranged from 7.9 (R202) to 14.6% (R201), from 0.57 (R202) to 1.91% (R201), from 0.19 (R203, R202) to 1.23% (R201) and from 0.10 (R107) to 1.33% (R201), respectively (Table 3). The highest percentages were thus recorded in the Sfax harbor (R201) and the lowest ones close to the Sfax harbor (R203, R202) or in the Sfax-Kerkennah channel (R107). The C content was comparable to that determined in surficial sediments of Moroccan coastal waters (Southern Mediterranean Sea), i.e. 1.3-15.1% (Pavoni et al., 2003). In contrast, the N and S contents were much higher than those reported for these Moroccan waters or in the Todos os Santos Bay, Brazil (0.01-0.3 and < 0.01-1.3%, respectively) (Pavoni et al., 2003; Venturini et al., 2004).

The TOC content varied between ~ 2.3 (R203, R202) and $\sim 11.7\%$ in the Sfax harbor (R201) and, quite surprisingly, in the Sfax-Kerkennah channel (R107) (Table 3; Fig. 2a). High values of $\sim 7.2\%$ were observed in the Kerkennah harbor (R111) and the Sfax-

Kerkennah channel (R104) (Table 3; Fig. 2a). The TOC content determined here was higher than that found in the surficial sediments of the Northeastern (0.02-2.4%) and Northwestern (0.35-6.2%) Mediterranean Sea (Lipiatou and Saliot, 1991a; Benlahcen et al., 1997; Kucuksezgin et al., 2013) and the Bizerte Lagoon (0.4-3.9%) (Barhoumi et al., 2014). Nonetheless, it was lower than that recorded in the Abu Qir Bay (Egyptian coasts), where it reached up to 20% (El Deeb et al., 2007). Our quite high TOC concentrations were very likely related to the enhanced marine productivity (eutrophication) of this coastal area due to diverse nutrient inputs (Bel Hassen et al., 2009; D'Ortenzio and Ribera d'Alcalà, 2009; The Mermex group, 2011).

The TOC/N ratio ranged from 9.4 (R201) to 56.6 (R107) (Table 3), which was higher than that measured in the surficial sediments from the Northwestern Mediterranean Sea (~ 7) (Charles et al., 2012), the Northern Adriatic (3-37) (Guerra, 2012; Acquavita et al., 2014) and the Todos os Santos Bay, Brazil (8.8-27.6) (Venturini et al., 2004). The TOC/N ratio may provide information about the origin of organic matter. A high TOC/N ratio (> 20) reveals rather a terrestrial origin of organic matter due to the low N percentage in the higher vegetation (Muller, 1977; Emerson and Hedges, 1988; Meyers, 1994). On the other hand, a low TOC/N ratio (5-7) implies a marine origin (plankton or seaweeds) (Muller 1979; Monoley and Field, 1991; Meyers, 1994). In our case, TOC/N ratio was comprised between 9.4 (R201) and 18 (R110) for almost all the stations, which suggested a mixed origin with both autochthonous marine and terrestrial sources. For station R111 (22.3) and above all R107 (56.6), the high ratio was in favour of a dominance of the terrestrial origin of organic matter. The TOC/S ratio varied between 2.6 (R202) and 118.9 (R107) (Table 3) and was more important than that observed in Todos os Santos Bay (2.8-13.6) (Venturini et al., 2004). Except in station R202, the TOC/S ratio was > 2.8, which put forward the occurrence of oxic conditions in the surficial sediments of the Sfax-Kerkennah channel (Leventhal, 1983; Berner,

1989). It is worth noting that the high TOC/N and TOC/S ratios observed in R107 were due to an elevated TOC content relative to low N and S concentrations (Table 3).

The content in CaCO₃ was minimal (~ 40%) in the Sfax-Kerkennah channel (R104) and the Sfax harbor (R201), and maximal (~ 95.6%) on the Sidi Mansour-Kerkennah transect (R105, R108) (Table 3). This content was on average higher than that recorded in surficial sediments of Todos os Santos Bay, Brazil (0-93.2%) (Venturini et al., 2004) and Athens coastal area, Greece (24-86.3%) (Kapsimalis et al., 2014). The presence of CaCO₃ in surficial sediments is related to marine organisms. In our case, the two main contributors of CaCO₃ would be benthic foraminifera and green seaweeds (Aloulou et al., 2012). The highest $\delta^{13}\text{C}$ signature was found in R101 (-20.9‰). It decreased from R101 to R107 (-25.1‰) and increased from R107 to R111 (-22.2‰). Then, the $\delta^{13}\text{C}$ signature tended to decrease to reach -25.5‰ in R203. It finally slightly increased towards R201 (-24.0‰) (Table 3; Fig. 2b). Carbon isotopic ratio ($\delta^{13}\text{C}$) is useful to distinguish between marine and terrestrial sources of sedimentary organic matter. Marine organic matter typically has $\delta^{13}\text{C}$ values between -22 and -20‰, whilst terrestrial organic matter (C₃ land plants) has an average $\delta^{13}\text{C}$ value of -27‰ (Meyer, 1994). It thus appears that our sediments displayed overall a mixed origin with a stronger marine fingerprint in stations R101-R103, R109 and R111 (Table 3; Fig. 2b).

3.2. Concentrations in hydrocarbons, comparison with other regions of the Mediterranean and Sediment Quality Guidelines

Total *R* concentration (sum of *n*-C₁₅ to *n*-C₃₄ + Pr and Phy) ranged from 8.1-14.2 $\mu\text{g g}^{-1}$ sed. dw in the Sfax-Kerkennah channel (R102, R105-R107, R208, R209) to 173.9 $\mu\text{g g}^{-1}$ sed. dw in the Sfax harbor (R201). High values were also recorded in the Sfax-Kerkennah channel (45.7 $\mu\text{g g}^{-1}$ sed. dw, R104) and the Kerkennah harbor (72.1 $\mu\text{g g}^{-1}$ sed. dw, R111) (Table 3; Fig. 2c). These *R* concentrations (8.1- 173.9 $\mu\text{g g}^{-1}$ sed. dw) were quite high compared to

those reported in the surficial/surface sediments from other regions of the Mediterranean Sea (Table 4). Indeed, for the sediments from Abu Qir Bay (Egypt), Gulf of Lions, Gulf of Fos-sur-mer, Berre lagoon (France), Gulf of Trieste (Italy), Catalan coast (Spain), Cretan Sea (Greece) and Coastal Aegean Sea (Turkey), concentrations did not exceed $10 \mu\text{g g}^{-1}$ sed. dw (Lipiataou and Saliot, 1991b; Tolosa et al., 1996; Gogou et al., 2000; El Deeb et al., 2007; Mille et al., 2007; Gonul and Kucuksezgin, 2012; Kanzari et al., 2012; Bajt, 2014; Mandalakis et al., 2014) (Table 4). In the Gulf of Tunis, Khniss coast (Tunisia), Tangier coastal zone (Morocco), Rhône delta (France), Patroklos and Sitia areas (Greece) and Aliğa Bay (Turkey), maximal concentrations were comprised between 10 and $57 \mu\text{g g}^{-1}$ sed. dw (Lipiatou and Saliot, 1991b; Tsapakis et al., 2010; Mzoughi and Chouba, 2011; Bouzid et al., 2012; Neşer et al., 2012; Zrafi et al., 2013) (Table 4). In Sfax ponds (Tunisia) and Eastern harbour of Alexandria (Egypt), maximal concentrations were 128 and $143 \mu\text{g g}^{-1}$ sed. dw, respectively (Aboul-Kassim and Simoneit, 1995; Elloumi et al., 2008). In the Sfax coastline (Tunisia), close to our study area, Zaghden et al. (2007) found concentrations reaching up to $430 \mu\text{g g}^{-1}$ sed. dw (sediments collected in 2003). Finally, Amori et al. (2011) observed concentrations that were largely higher, i.e. $3,886 \mu\text{g g}^{-1}$ sed. dw., in Gabès, Kettana and Al-Zar coastline (Tunisia). Hence, this comparison underscores that *n*-alkane concentrations in the surficial/surface sediments of the Tunisian coasts, particularly of the Gulf of Gabès, were among the highest measured in the Mediterranean Basin (Table 4).

Total PAH concentration (sum of 17 PAHs) varied between $175\text{-}245 \text{ ng g}^{-1}$ sed. dw in the Sfax-Kerkennah channel (R109, R209, R208) and $10,769 \text{ ng g}^{-1}$ sed. dw in the Sfax harbor (R201), with concentrations $> 1,000 \text{ ng g}^{-1}$ sed. dw recorded in the Sfax-Kerkennah channel (R104) and in the vicinity of Sfax (R204, R203, R202) and Kerkennah (R110, R111) harbors (Table 5; Fig. 2d). These total PAH concentrations ($175\text{-}10,769 \text{ ng g}^{-1}$ sed. dw) mirror a moderate to very high pollution level according to the pollution level classification proposed

by Baumard et al. (1998) (Table 5) and were situated in the mid-range of those reported in the surficial/surface sediments from other regions of the Mediterranean Sea (Table 6). Actually, for the sediments from Bizerte lagoon, Khniss coast (Tunisia), Al Hoceïma coastal area (Morocco), Bay of Banuyls-sur-mer (France), Chioggia and Ancona coastal zones (Italy), Cretan Sea (Greece), Candarli Gulf (Turkey) and Cilician Basin (Cyprus), concentrations did not exceed $1,000 \text{ ng g}^{-1} \text{ sed. dw}$ (Magi et al., 2002; Pavoni et al., 2003; Trabelsi and Driss, 2005; Charles et al., 2012; Kucuksezgin et al., 2012, 2013; Zrafi et al., 2013; Barhoumi et al., 2014; Mandalakis et al., 2014) (Table 6). Also, in the Sfax, Luza, Sousse, Jarzouna-Bizerte coastal areas, Gulf of Tunis (Tunisia), Abu Qir Bay (Egypt), Rhône Delta, Port Vendres harbor (France), Gulf of Trieste (Italy) and coastal Aegean Sea (Turkey), maximal concentrations were comprised between $1,000$ and $< 10,000 \text{ ng g}^{-1} \text{ sed. dw}$ (Bouloubassi and Saliot, 1993; Baumard et al., 1998; Khairy et al., 2009; Zrafi-Nouira et al., 2010; Mzoughi and Chouba, 2011; Gonul and Kucuksezgin, 2012; Kessabi et al., 2013; Bajt, 2014; Zaghdén et al., 2014) (Table 6). Nevertheless, in Egypt coastal areas, Lazaret Bay, Gulf of Fos-sur-mer (France), Taranto Gulf, Coastal Ligurian Sea, Venice Lagoon, Naples harbor (Italy), Santander Bay, Catalonia coast (Spain), Gulf of Corinth, North Evoikos and Saronikos Gulfs, Drapetsona-Keratsini coastal zone (Greece), Izmit and Aliğa Bays (Turkey), Rovinj coastal area and Rijeka Bay (Croatia), maximal concentrations were much higher than $10,000 \text{ ng g}^{-1} \text{ sed. dw}$ (La Rocca et al., 1996; Benlahcen et al., 1997; Eljarrat et al., 2001; Viguri et al., 2002; Bertolotto et al., 2003; Bihari et al., 2006; Tolun et al., 2006; Mille et al., 2007; Sprovieri et al., 2007; Annicchiarico et al., 2011; Alebic-Juretic, 2011; Barakat et al., 2011; Botsou and Hatzianestis, 2012; Neşer et al., 2012; Kapsimalis et al., 2014) (Table 6). It should be noticed that our total PAH concentrations were similar to those recorded by Zaghdén et al. (2007) for the same area ($113\text{-}10,720 \text{ ng g}^{-1} \text{ sed. dw}$) (sediments collected in 2003).

Sediment quality guidelines (SQGs) are used to assess the contamination level of marine and estuarine sediments (Long et al. 1995; Barhoumi et al., 2014). Long et al. (1995) proposed two guideline values, an effects range low (ERL) and an effects range median (ERM) to determine the sediment quality. Our PAH concentrations were thus compared to these ERL and ERM values (Table 7). Total PAH concentrations in all stations were below ERL, except in R202 (close to Sfax harbor) and R201 (Sfax harbor) where they were comprised between ERL and ERM. At the level of individual compounds, concentrations in Nap, BaA and BaP were below ERL in all stations, while concentrations in Phe, Ant, Flt and Chr were below ERL or between ERL and ERM depending on the stations. Concentration in Pyr was > ERM in R201 (Table 7). Consequently, PAH concentrations in surficial sediments in this Sfax-Kerkennah channel area may be harmful for marine biota mainly in the Sfax harbor.

3.3. Sediment geochemistry and relationships between hydrocarbons and biogeochemical parameters

Stations displaying high C, H, N, S, TOC, *R* and PAH contents were the Sfax (R201) and Kerkennah (R111) harbors as well as station R104 (in the channel), and, in a lesser extent, station R110 (close to Kerkennah harbor; outside the channel). Except R110 (fine sand), these stations were characterized by very fine sand (Tables 3, 5; Fig. 2a, c, d), which may be linked to the relatively high PAH levels encountered. Indeed, PAHs are known to be mainly adsorbed onto very fine particles because of their higher specific surface area (Xia and Wang, 2008). TOC/N and $\delta^{13}\text{C}$ values emphasized a mixed (marine and terrestrial) origin of organic matter (Tables 3; Fig. 2b), while the hydrocarbon levels suggested significant anthropogenic inputs in this sites. In the Sfax and Kerkennah harbors, anthropogenic inputs were rather evident with ship traffic and petroleum wastes. Nevertheless, specific

anthropogenic sources were less obvious in station R104. The latter was located in a cuvette that might receive particular industrial wastewaters. In general, sediments with high organic carbon content contained high PAH concentrations (Barhoumi et al., 2014). However, station R107 (in the channel) presented a high TOC concentration and, in the meantime, low *R* and PAH levels compared to those of stations R201, R111 and R104. R107 was also typified by medium sand and by a terrestrial fingerprint of the organic matter with regard to its TOC/N and $\delta^{13}\text{C}$ values. An inverse pattern was observed in stations R202-R204 with high *R* and PAH concentrations and a very low TOC content. TOC/N and $\delta^{13}\text{C}$ showed a marine and terrestrial origin of organic matter (Tables 3, 5; Fig. 2a-d). These stations, located outside (R202) or at the channel border (R203-204), were very likely under the influence of anthropogenic (PAH) inputs from the Sfax harbor and city. All other stations of the channel (R105, R106, R205-R210) as well as stations R108 and R109 (outside the channel) were characterized by fine or medium sand and presented the lowest *R* and PAH concentrations, a low TOC content, a high CaCO_3 content and TOC/N and $\delta^{13}\text{C}$ values revealing both marine and terrestrial organic matter (Tables 3, 5; Fig. 2a-d). These sites were thus much less impacted by anthropogenic inputs. This was due to their relative greater distance from the coast and their higher bathymetry as well as to the North-East South-West-oriented current crossing the channel, which transports the finest particles further southward.

As mentioned above, strong decoupling occurred between hydrocarbon and TOC contents depending on the stations, especially for R107. As seen from Fig. 2e, f, the *R*/TOC and PAH/TOC ratios were not constant: low ratios were observed inside the channel ($< 8 \text{ mg g}^{-1}$ and $< 60 \mu\text{g g}^{-1} \text{ sed. dw}$, respectively), while high ratios were found in coastal stations outside the channel ($> 10 \text{ mg g}^{-1}$ and $> 500 \mu\text{g g}^{-1} \text{ sed. dw}$, respectively). When taken into account all stations ($n = 20$), significant positive linear correlations appeared between total *R* concentration and C, H, N, S and TOC contents ($r = 0.49-0.93$, $p < 0.05$, $n = 20$), and between

total PAH concentration and H, N and S contents ($r = 0.73-0.81$, $p < 0.05$, $n = 20$). A significant correlation was also found between total R and PAH concentrations ($r = 0.85$, $p < 0.05$, $n = 20$) (Table 8). When removing station R107 from the dataset, for which the decoupling between hydrocarbons and TOC was very pronounced (this station appeared as outlier when plotting the data), correlations between R , PAHs and TOC clearly increased ($r = 0.66-0.88$, $p < 0.05$, $n = 19$) (Table 8). However, when station R201 (i.e. the station showing “extreme” hydrocarbon concentrations) was also excluded in addition to R107, the degree of correlation between parameters dropped: PAHs were not correlated anymore to TOC and R ($r = -0.08-0.21$, $p > 0.05$, $n = 18$), whereas the correlation between the two latter substantially decreased ($r = 0.68$, $p < 0.05$, $n = 18$) (Table 8). Finally, when eliminating R107 and all stations with total PAH concentration $> 1000 \text{ ng g}^{-1} \text{ sed. dw}$ (i.e. R201, R104, R110, R111, R202-R204), the correlation between R and TOC disappeared as well ($r = -0.02$, $p > 0.05$, $n = 12$) (Table 8). This correlation study shows that the significant correlations occurring between R , PAHs and TOC were almost merely due to the “extreme” station R201. Therefore, the distribution and concentrations of R , PAHs and TOC were decoupled in the surficial sediments of the Sfax-Kerkennah channel. R and PAHs were very likely more influenced by specific inputs rather than by organic matter content. The absence of significant linear relationship between PAH and TOC concentrations or between R and PAH concentrations in surficial/surface sediments were also reported for the Bizerte Lagoon (Tunisia), Marano and Grado Lagoons (Italy) and Egyptian coastal areas (El Nemr et al., 2013; Aquavita et al., 2014; Barhoumi et al., 2014). Moreover, Simpson et al. (1996) proposed that PAH and TOC concentrations in sediments are significantly correlated solely in greatly contaminated sites where total PAH concentrations $> 2,000 \text{ ng g}^{-1}$, which is in accordance with our results.

3.4. Composition and sources of hydrocarbons

The UCM/R ratio was > 3 for stations R106, R111 (Kerkennah harbor), R201 (Sfax harbor), R202, R208-R210 (Sfax-Kerkennah channel) (Table 3), which reflects the presence of degraded petroleum products in these stations (Simoneit and Mazurek, 1982; Guigue et al., 2011; Parinos et al., 2013). CPI_{15-24} was < 1 for all the stations, except for the Sfax harbor (R201) where it was close to 1 (Table 3). This shows the predominance of even carbon number in short chain *n*-alkanes. Indeed, *n*-C₁₆, *n*-C₁₈ and, in a lesser extent, *n*-C₂₀ were the dominant compounds over the whole range *n*-C₁₅-*n*-C₃₄ apart from the coastal stations R101-R103, the Kerkennah harbor area (R110, R111) and the Sfax harbor (R201), in which *n*-C₃₁ and *n*-C₃₃ were the major compounds. The predominance of even light *n*-alkanes *n*-C₁₆, *n*-C₁₈ and *n*-C₂₀ in sediments is not so common albeit it has been observed for instance in sediments from the Arabian Gulf (Grimalt et al., 1985), the Gulf of Fos-sur-mer (Mille et al., 2007) and the Taihu Lake, China (Yu et al., 2016). It has been suggested that these even light *n*-alkanes were issued from bacteria, but also fungi, and yeast species, and from petroleum-derived inputs (Mille et al., 2007; Harji et al. 2008; Yu et al., 2016). CPI_{25-34} displayed values > 3 for stations R101-R110 and R208 (Table 3). This underscored the presence of AHs from mixed petroleum and biogenic (terrestrial higher plant debris) sources, the latter having a higher contribution (Rieley et al., 1991; Harji et al., 2008). In contrast, for almost all the stations from the Kerkennah-Sfax city transect, CPI_{25-34} was < 3 (Table 3), which emphasised an increase in the contribution of petroleum inputs (Mille et al., 2007; Guigue et al., 2011). TAR was > 1 in most of stations, being comprised between 1.2 and 2.8, with high values of 6.6 and 10.4 detected in R102 and R103. TAR was ~ 1.0 in stations R106 and R205 and < 1 in R104, R107, R202 and R207 (Table 3). Hence, this ratio mirrored the higher contribution of terrestrial higher plants compared to aquatic material (algae, phyto- and zoo-plankton).

Ratios involving Pr and Phy (Pr/Phy, *n*-C₁₇/Pr and *n*-C₁₈/Phy) have to be taken with extreme caution because these branched alkanes have multiple origins and are sensitive to

diagenetic conditions and thermal maturity (Peters et al., 2005). They are both derived from the phytol side chain of chlorophyll *a*, either under reducing conditions (Phy) or oxidizing conditions (Pr). They are thus abundant in weathered crude oils. However, Pr can also originate from zooplankton, and Phy from Archaeobacteria, such as methanogens (Volkman et al., 1992). It has been proposed that $\text{Pr/Phy} < 1$ could be taken as an indicator of petroleum origin and/or highly reducing (anoxic, hypersaline) depositional environments. $\text{Pr/Phy} > 3$ may reflect the presence of biogenic AHs, while Pr/Phy between 1 and 3 may be the sign of oxidizing depositional environments (Volkman et al., 1992; ten Haven, 1996; Peters et al., 2005). Here, we found $\text{Pr/Phy} < 1$ for all the stations, except R110, R201, R208 and R209, which presented values comprised between 1.19 and 2.85 (Table 3). These Pr/Phy values (< 3) underlined the absence of biogenic AHs. Although no significant correlation was found between Pr/Phy ratio or Phy concentration and % S (data not shown), we may assume that the relatively high sulphur content in these sediments (underscoring the occurrence of anoxic conditions) contributed to the relatively low Pr/Phy values observed, in addition to the petroleum signature. These results are in agreement with those from Zaghdien et al. (2007) in the same area. The $n\text{-C}_{18}/\text{Phy}$ ratio was > 1 for all the stations. Values comprised between 2 and 5 were observed for a majority of stations, whereas higher values (6-9) were found in stations R107, R205, R209, R210 (Table 3). Interestingly, the highest value was detected in R107 suggesting a very recent hydrocarbon input that could be related to the relatively high TOC concentration found in this station. In the Sfax harbor area, $n\text{-C}_{18}/\text{Phy}$ decreased (~ 1.7 in R201 and R202) (Table 3), which reflected the presence of more degraded AHs. The $n\text{-C}_{17}/\text{Pr}$ ratio, which showed values around 1 for several stations from coastal areas and the Sfax-Kerkennah channel, did not follow the same trend than the $n\text{-C}_{18}/\text{Phy}$ ratio (Table 3). Its interpretation seems thus more complicated. This analysis of AH ratios and indices suggests the presence of both petrogenic and biogenic materials, the petrogenic fingerprint being more

accentuated in the harbor areas and in the Kerkennah-Sfax city transect compared to North of Sfax-Kerkennah transect.

Concerning PAHs, the most abundant compounds were \sum MePyr (in R101, R104, R110, R111, R207, R203, R201), \sum MePhe (in R102, R106, R107, R204) or Chr and/or \sum MeChr (in R103, R105, R210, R205), which accounted on average for 20% of total PAHs (Table 5). Per (35%), BgP (34%), BaP (30%), Flt (17%) and BkF (19%) dominated in R108, R109, R209, R208 and R202, respectively. Nap, \sum MeNap, Ant and BaA were not detected, except in R103, R209, R204, R203 and/or R202 (Table 5). High proportions of alkylated Pyr and Phe in the Sfax sediments have already been pointed out by Zaghden et al. (2007; 2014). Hence, PAH molecular profiles illustrated the predominance of 4-ring compounds apart from stations R204 (dominance of 3 rings), R108, R209 (dominance of 5 rings) and R109 (dominance of 6 rings) (Fig. 3).

Fig. 4 presents the cross plot of \sum LMW/ \sum HMW *versus* Flt/Flt+Pyr ratios for the different samples, except stations R106, R209 and R210, for which Flt/Flt+Pyr could not be determined. Most of the stations (R101-R105, R107, R109-R111, R205, R201) displayed \sum LMW/ \sum HMW ratio < 1 and Flt/Flt+Pyr ratio < 0.4 , which highlighted both petrogenic and pyrogenic sources of PAHs. In station R204, the inverse pattern (\sum LMW/ \sum HMW > 1 and Flt/Flt+Pyr < 0.4), suggested this mixed source as well. On the contrary, stations R108, R202, R203, R207 and R208 presented \sum LMW/ \sum HMW ratio < 1 and Flt/Flt+Pyr ratio > 0.4 , putting forward the dominance of the pyrogenic source (Soclo et al., 2000; Yunker et al., 2002; Li et al., 2006; Zhang et al., 2008). R108, R202, R203 and R207 had Flt/Flt+Pyr ratio < 0.5 , which might be attributed to fuel combustion. R208, with Flt/Flt+Pyr ratio of 0.74, was distinguished by a contribution of grass, coal, and/or wood combustion (De La Torre-Roche et al., 2009; Fig. 4; Table 2). On the other side, \sum MePhe/Phe ratio was > 2 with the exception of stations R109 and R210, which implied the dominance of the petrogenic source (Prahl and

Carpenter 1983; Garrigues et al., 1995). In the same way, $\sum\text{MePyr}/\text{Pyr}$ was > 1 apart from R107, R205 and R203, underscoring the petrogenic fingerprint (Zaghden et al., 2007; 2014). At last, BaP/BgP was > 0.6 , except for R103, R109 and R201. This could reflect traffic emissions (Katsoyiannis et al., 2007; Table 2). Consequently, from these different indices and ratios, it appears that the Sfax-Kerkennah channel area was characterized by various petrogenic and pyrogenic sources of PAHs, with no clear trend highlighted between coastal stations (outside the channel) and stations inside the channel.

4. Conclusion

This study investigated the origin and distribution of hydrocarbons (AHs and PAHs) and organic matter in the surficial sediments of the Sfax-Kerkennah channel. Sediments, mainly composed of sand, displayed a grain size distribution in relation with the geomorphology, bathymetry and hydrodynamic properties of the Sfax-Kerkennah channel. Fine and very fine sands were generally found outside the channel (coastal stations and harbors), whereas medium sand was observed within the channel (deepest stations). Compared to other regions of the Mediterranean Sea, we recorded high TOC concentrations ($> 11\%$), quite high R (up to $174 \mu\text{g g}^{-1}$ sed. dw) and PAH concentrations ($> 10,000 \text{ ng g}^{-1}$ sed. dw). According to Baumard et al. (1998), PAH pollution was moderate to very high in the Sfax-Kerkennah channel. Moreover, with regard to sediment quality guidelines (Long et al., 1995), the pyrene concentration in the Sfax harbor sediment may be detrimental for marine ecosystems. In the Sfax and Kerkennah harbors as well as in stations R104 and R110, we found high contents in C, H, N, S, TOC, R and PAHs. Except for station R110, these high contents were associated with very fine sand. In contrast, most of the stations located within the channel were characterized by fine or medium sand and by low TOC, R and PAH concentrations.

Nevertheless, by examining in details the degree of correlation between parameters, we put forward that *R*, PAHs and TOC were actually decoupled for most of the stations. This suggested that hydrocarbons were very likely more influenced by specific inputs rather than by organic matter content in the surficial sediments of the Sfax-Kerkennah channel. TOC/N and $\delta^{13}\text{C}$ values revealed a mixed origin of organic matter with both autochthonous marine and terrestrial sources. Index and ratio diagnostic emphasized the dominance of petrogenic origin of *n*-alkanes (relatively to biogenic origin) and the presence of both petrogenic and pyrogenic PAHs. AH ratios revealed the presence of both biogenic and petrogenic materials, the petrogenic fingerprint being more important and more degraded in the harbor areas and in the Kerkennah-Sfax city transect. However, PAH diagnostic did not reveal any clear relationship between the geographical repartition of stations and the molecular composition/origin of hydrocarbons. This work underscores the complex distribution patterns and the multiple sources (marine, terrestrial, anthropogenic) of organic matter and hydrocarbons in the Gulf of Gabès. Also, further investigations should consider the molecular composition of hydrocarbons in the water column (particulate and dissolved phases) for a global view of organic pollutant dynamics in coastal waters of the Gulf of Gabès.

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Figure captions

Figure 1. Location of the study stations along the Sfax-Kerkennah channel, in the Northern part of the Gulf of Gabès (Southeast Tunisia, Southern Mediterranean Sea). The blue dotted line delimited the Sfax-Kerkennah channel area. The detailed characteristics of the stations are provided in Table 1.

Figure 2. Spatial distribution of a) the concentration in TOC (in % for 1 g sed. dw), b) the isotopic signature of organic carbon ($\delta^{13}\text{C}$ in ‰), c) the concentration in total *n*-alkanes (*R* in $\mu\text{g g}^{-1}$ sed. dw), d) the concentration in total ($\Sigma 17$) PAHs (in ng g^{-1} sed. dw), e) the *R*/TOC ratio (in mg g^{-1}) and f) the PAH/TOC ratio (in $\mu\text{g g}^{-1}$) in surficial sediments of the Sfax-Kerkennah channel (Ocean Data View software version 4.6.5, Schlitzer, R., <http://odv.awi.de>, 2014.).

Figure 3. Distribution pattern of PAHs in the surficial sediments of the Sfax-Kerkennah channel. 1-ring compound: Thi; 2-ring compounds: Nap and ΣMeNap ; 3-ring compounds: Phe, ΣMePhe , Ant, ΣMeAnt ; 4-ring compounds: Flt, Pyr, ΣMePyr , BaA, Chr, ΣMeChr ; 5-ring compounds: BkF, BaP, Per; 6-ring compounds: BgP.

Figure 4. Cross plot of $\Sigma\text{LMW}/\Sigma\text{HMW}$ versus Flt/Flt+Pyr ratios for the different samples, except stations R106, R209 and R210, for which Flt/Flt+Pyr could not be determined.

1 **Table 1.** Characteristics of the study stations, located along the Sfax-Kerkennah channel in the Northern part of the Gulf of
 2 Gabès (Southeast Tunisia, Southern Mediterranean Sea), and sampled in January 2005.

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| Station | Area | Position | Depth of the water column (m) | Type of bottom | |
|---------|------------------------------|------------------------|-------------------------------|-----------------------------------|----|
| R101 | North of Sfax - Sidi Mansour | 34°48'52"N, 10°53'05"E | 1 | Dense meadows of <i>Posidonia</i> | 4 |
| R102 | | 34°47'56"N, 10°54'00"E | 1.1 | Meadows of <i>Posidonia</i> | 5 |
| R103 | | 34°47'19"N, 10°54'30"E | 1.7 | Meadows of <i>Posidonia</i> | 6 |
| R104 | Channel | 34°46'00"N, 10°54'57"E | 7.6 | Muddy sand | 7 |
| R105 | Channel | 34°45'05"N, 10°55'25"E | 9.5 | Dense meadows of <i>Posidonia</i> | 8 |
| R106 | Channel | 34°44'08"N, 10°55'50"E | 8.5 | Sandy with <i>Posidonia</i> | 9 |
| R107 | Channel | 34°43'08"N, 10°56'20"E | 5.5 | Dense meadows of <i>Posidonia</i> | 10 |
| R108 | | 34°42'10"N, 10°56'48"E | 2.8 | Dense meadows of <i>Posidonia</i> | 11 |
| R109 | | 34°41'10"N, 10°57'18"E | 1 | Dense meadows of <i>Posidonia</i> | 12 |
| R110 | | 34°40'19"N, 10°57'43"E | 0.8 | Muddy sand | 13 |
| R111 | Kerkennah harbor | 34°39'26"N, 10°58'00"E | 2.7 | Sandy with <i>Posidonia</i> | 14 |
| R210 | Channel | 34°40'19"N, 10°56'05"E | 7 | Sandy | 15 |
| R209 | Channel | 34°40'52"N, 10°55'05"E | 9 | Meadows of <i>Posidonia</i> | 16 |
| R208 | Channel | 34°41'25"N, 10°54'00"E | 15.7 | Meadows of <i>Posidonia</i> | 17 |
| R207 | Channel | 34°41'48"N, 10°52'55"E | 20 | Meadows of <i>Posidonia</i> | 18 |
| R205 | Channel | 34°42'15"N, 10°50'28"E | 7.3 | Muddy sand | 19 |
| R204 | Channel | 34°42'23"N, 10°49'15"E | 8.5 | Muddy sand | 20 |
| R203 | Channel | 34°42'31"N, 10°48'00"E | 7.9 | Muddy sand | 21 |
| R202 | | 34°42'39"N, 10°46'50"E | 4 | Muddy sand | 22 |
| R201 | Sfax harbor | 34°42'46"N, 10°46'05"E | 4.5 | Muddy sand | |

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23 **Table 2.** Hydrocarbon molecular diagnostic ratios investigated in this study with typical values from the literature. Adapted from Tobiszewski
 24 and Namieśnik (2012) and Katsoyiannis and Breivik (2014).

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| Hydrocarbons | Ratios | Hydrocarbon origin | | References |
|--------------|--------------------------------|---------------------------|-----------------------------|---|
| | | Recent/less degraded | Degraded | |
| AHs | UCM/R | - | > 3-4 | Simoneit and Mazurek (1982); Mazurek and Simoneit (1984); Asia et al. (2009) |
| | <i>n</i> -C ₁₇ /Pr | > 1 | < 1 | |
| | <i>n</i> -C ₁₈ /Phy | > 1 | < 1 | |
| | | Biogenic | Petrogenic | |
| | Pr/Phy | >> 1 | - | Rieley et al. (1991); Wang et al. (1999); Commendatore and Esteves (2004); Harji et al. (2008) |
| | CPI ₁₅₋₂₄ | >> or << 1 | ~ 1 | |
| | CPI ₂₅₋₃₄ | >> or << 1 | ~ 1 | |
| | | Terrestrial higher plants | Algae, phyto-, zoo-plankton | |
| | TAR | > 1 | < 1 | Bourbonniere and Meyers (1996); Mille et al. (2007) |
| | PAHs | | Petrogenic | Pyrogenic |
| ∑LMW/∑HMW | | > 1 | < 1 | Soclo et al. (2000); Zhang et al. (2008) |
| ∑MePhe/Phe | | > 2 | < 2 | Prahl and Carpenter (1983); Garrigues et al. (1995) |
| ∑MePyr/Pyr | | > 1 | < 1 | Zaghden et al. (2007; 2014) |
| Flt/Flt+Pyr | | < 0.4 | > 0.4 | Yunker et al. (2002); Li et al. (2006) |
| | | Fuel combustion | Grass/coal/wood combustion | |
| Flt/Flt+Pyr | | 0.4-0.5 | > 0.5 | De La Torre-Roche et al. (2009) |
| | | Non-traffic emissions | Traffic emissions | |
| BaP/BgP | < 0.6 | > 0.6 | Katsoyiannis et al. (2007) | |

26 **Table 3.** Granulometric parameters (Mz and σ in unit ϕ), percentages (for 1 g sediment dry weight) of elemental constituents (C, H, N, S), calcium
 27 carbonate (CaCO₃) and total organic carbon (TOC), isotopic signature of organic carbon ($\delta^{13}\text{C}$ in ‰), and concentrations in total *n*-alkanes (*R* in $\mu\text{g g}^{-1}$
 28 sed. dw) and associated molecular diagnostic ratios (UCM/*R*, CPI, Pr/Phy, *n*-C₁₇/Pr, *n*-C₁₈/Phy, TAR) in the fraction < 63 μm of surficial sediments (0-
 29 1 cm) collected along the Sfax-Kerkennah channel (Southeast Tunisia, Southern Mediterranean Sea).

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| | R101 | R102 | R103 | R104 | R105 | R106 | R107 | R108 | R109 | R110 | R111 | R210 | R209 | R208 | R207 | R205 | R204 | R203 | R202 | R201 |
|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Mz (ϕ) | 3 to 2 | 3 to 2 | 3 to 2 | 4 to 3 | 2 to 1 | 3 to 2 | 2 to 1 | 3 to 2 | 3 to 2 | 3 to 2 | 4 to 3 | 3 to 2 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 3 to 2 | 4 to 3 |
| σ (ϕ) | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 | 2 to 1 |
| C (%) | 9.3 | 10.3 | 11.1 | 13.0 | 12.1 | 11.8 | 11.9 | 12.6 | 12.7 | 12.7 | 12.7 | 12.3 | 12.7 | 11.7 | 11.6 | 12.1 | 10.8 | 9.4 | 7.9 | 14.6 |
| H (%) | 0.73 | 0.73 | 0.99 | 1.22 | 0.64 | 0.62 | 0.60 | 0.76 | 0.67 | 0.73 | 0.75 | 0.71 | 0.71 | 0.65 | 0.61 | 0.75 | 0.65 | 0.58 | 0.57 | 1.91 |
| N (%) | 0.30 | 0.32 | 0.39 | 0.49 | 0.23 | 0.22 | 0.21 | 0.28 | 0.29 | 0.35 | 0.32 | 0.27 | 0.27 | 0.23 | 0.21 | 0.26 | 0.22 | 0.19 | 0.19 | 1.23 |
| S (%) | 0.54 | 0.62 | 0.67 | 0.61 | 0.47 | 0.50 | 0.10 | 0.52 | 0.44 | 0.48 | 0.60 | 0.75 | 0.42 | 0.31 | 0.37 | 0.41 | 0.31 | 0.29 | 0.84 | 1.33 |
| TOC (%) | 3.2 | 4.0 | 5.5 | 7.3 | 3.5 | 3.5 | 11.9 | 4.5 | 3.9 | 6.3 | 7.2 | 3.8 | 3.7 | 3.2 | 2.9 | 4.0 | 3.5 | 2.5 | 2.2 | 11.6 |
| TOC/N | 10.8 | 12.5 | 14.0 | 14.9 | 15.2 | 15.7 | 56.6 | 16.0 | 13.3 | 18.0 | 22.3 | 14.0 | 13.6 | 13.7 | 13.8 | 15.3 | 15.7 | 13.3 | 11.4 | 9.4 |
| TOC/S | 6.0 | 6.5 | 8.1 | 12.0 | 7.4 | 6.9 | 118.9 | 8.6 | 8.8 | 13.1 | 11.9 | 5.0 | 8.7 | 10.2 | 7.8 | 9.7 | 11.2 | 8.7 | 2.6 | 8.7 |
| CaCO₃ (%) | 48.8 | 57.9 | 52.5 | 40.0 | 95.8 | 91.6 | 51.6 | 95.4 | 84.6 | 90.1 | 76.9 | 88.3 | 72.7 | 71.6 | 67.9 | 79.7 | 70.8 | 63.3 | 53.1 | 41.0 |
| $\delta^{13}\text{C}$ (‰) | -20.9 | -21.2 | -22.4 | -23.7 | -24.6 | -25.1 | -25.1 | -24.4 | -22.7 | -23.6 | -22.2 | -24.7 | -25.2 | -25.4 | -25.0 | -25.0 | -25.4 | -25.5 | -24.8 | -24.0 |
| <i>R</i> ($\mu\text{g g}^{-1}$) | 29.4 | 14.2 | 22.8 | 45.7 | 10.3 | 8.1 | 14.1 | 18.7 | 23.5 | 24.2 | 72.1 | 18.1 | 12.7 | 10.2 | 33.5 | 15.7 | 15.9 | 16.8 | 20.6 | 173.9 |
| UCM/<i>R</i> | 1.6 | 1.5 | 0.9 | 2.7 | 2.0 | 3.1 | 2.5 | 2.3 | 1.9 | 1.9 | 3.8 | 3.5 | 4.6 | 4.8 | 1.2 | 2.7 | 2.8 | 2.9 | 5.7 | 5.0 |
| CPI₁₅₋₂₄ | 0.59 | 0.38 | 0.35 | 0.33 | 0.35 | 0.38 | 0.34 | 0.24 | 0.36 | 0.39 | 0.40 | 0.41 | 0.72 | 0.65 | 0.64 | 0.30 | 0.33 | 0.28 | 0.70 | 0.96 |
| CPI₂₅₋₃₄ | 4.3 | 3.9 | 5.8 | 3.9 | 3.8 | 4.7 | 2.2 | 5.2 | 5.1 | 4.8 | 2.5 | 2.3 | 2.0 | 4.3 | 2.9 | 3.0 | 2.4 | 2.0 | 1.7 | 1.8 |
| Pr/Phy | 0.36 | 0.59 | 0.73 | 0.49 | 0.68 | 0.39 | 0.91 | 0.64 | 0.43 | 1.19 | 0.29 | 0.70 | 2.85 | 1.47 | 0.39 | 0.73 | 0.82 | 0.35 | 0.64 | 1.23 |
| <i>n</i>-C₁₇/Pr | 4.5 | 0.7 | 1.3 | 4.9 | 1.1 | 4.3 | 3.1 | 1.5 | 4.3 | 1.0 | 5.2 | 3.9 | 1.1 | 1.5 | 3.1 | 3.5 | 1.3 | 3.0 | 3.0 | 1.4 |
| <i>n</i>-C₁₈/Phy | 3.0 | 3.2 | 4.5 | 5.4 | 3.7 | 4.1 | 9.0 | 4.1 | 4.7 | 4.7 | 3.2 | 7.5 | 6.3 | 4.1 | 2.5 | 7.3 | 3.9 | 4.0 | 1.8 | 1.7 |
| TAR | 2.1 | 6.6 | 10.4 | 0.9 | 1.7 | 1.0 | 0.5 | 1.8 | 1.4 | 2.8 | 1.7 | 1.2 | 1.2 | 1.5 | 0.8 | 1.0 | 1.6 | 1.5 | 0.8 | 1.2 |

31 ϕ from 4 to 3, 3 to 2 and 2 to 1 corresponds to the size range of 62.5-125, 125-250 and 250-500 μm , respectively.

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36 **Table 4.** Comparison of total *n*-alkane concentrations (*R* in $\mu\text{g g}^{-1}$ sed. dw) in surficial/surface sediments from different regions of the
 37 Mediterranean Sea.

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| Country | Site | Number of samples/sites | <i>n</i> -alkanes analyzed | Range ($\mu\text{g g}^{-1}$ sed. dw) | Reference |
|---------|--|-------------------------|---|---------------------------------------|----------------------------------|
| Tunisia | Gulf of Gabès, Sfax-Kerkennah channel | 20 | <i>n</i> -C ₁₅ - <i>n</i> -C ₃₄ | 8.1-174 | This study |
| | Gulf of Gabès, Sfax coastline and Kerkennah channel | 18 | <i>n</i> -C ₁₂ - <i>n</i> -C ₃₄ | 2.2-430 | Zaghden et al. (2007) |
| | Gulf of Gabès, Gabès, Kettana, Al-Zar coastline | 9 | <i>n</i> -C ₁₄ - <i>n</i> -C ₃₇ | 21-3,886 | Amorri et al. (2011) |
| | Sfax ponds | 5 | <i>n</i> -C ₁₃ - <i>n</i> -C ₃₀ | 27-128 | Elloumi et al. (2008) |
| | Gulf of Tunis (Rades, Goulette, Sidi Bou Saïd harbors) | 12 | <i>n</i> -C ₁₀ - <i>n</i> -C ₃₄ | 1.8-10 | Mzoughi and Chouba (2011) |
| | Khniss Coast | 12 | <i>n</i> -C ₉ - <i>n</i> -C ₃₂ | 9.7-36.1 | Zrafi et al. (2013) |
| Morocco | Tangier coastal zone | 10 | <i>n</i> -C ₁₅ - <i>n</i> -C ₃₈ | 0.4-15.6 | Bouزيد et al. (2012) |
| Egypt | Eastern harbour of Alexandria | 15 | <i>n</i> -C ₁₃ - <i>n</i> -C ₃₅ | 7-143 | Aboul-Kassim and Simoneit (1995) |
| | Coastal areas (bays, estuaries and harbors) | 31 | <i>n</i> -C ₇ - <i>n</i> -C ₃₄ | 0.09-9.1 | El Nemr et al. (2007) |
| | Coastal areas (bays, estuaries and harbors) | 10 | <i>n</i> -C ₇ - <i>n</i> -C ₃₄ | 0.5-1.6 | El Nemr et al. (2013) |
| | Abu Qir Bay | 20 | <i>n</i> -C ₁₀ - <i>n</i> -C ₃₄ | 0.06-0.6 | El Deeb et al. (2007) |
| France | Rhône delta | 6 | <i>n</i> -C ₁₂ - <i>n</i> -C ₃₄ | 10.1-27.1 | Lipiatou and Saliot (1991b) |
| | Gulf of Lions and Central Western Mediterranean | 5 | <i>n</i> -C ₁₂ - <i>n</i> -C ₃₄ | 1.4-2.5 | Lipiatou and Saliot (1991b) |
| | Gulf of Fos-sur-mer | 11 | <i>n</i> -C ₁₄ - <i>n</i> -C ₃₂ | 0.5-6.9 | Mille et al. (2007) |
| | Berre Lagoon | 2 | <i>n</i> -C ₁₄ - <i>n</i> -C ₃₄ | 1.4-3.6 | Kanzari et al. (2012) |
| Italy | Gulf of Trieste | 8 | <i>n</i> -C ₁₄ - <i>n</i> -C ₃₄ | 2.0-4.9 | Bajt (2014) |
| Spain | Ebro shelf and slope, Catalan coast | 5 | <i>n</i> -C ₁₄ - <i>n</i> -C ₄₀ | 0.3-1.1 | Tolosa et al. (1996) |
| Greece | Patroklos and Sitia areas | 15 | <i>n</i> -C ₁₁ - <i>n</i> -C ₃₅ | 1.6-32.3 | Tsapakis et al. (2010) |
| | Cretan Sea | 10 | <i>n</i> -C ₁₅ - <i>n</i> -C ₄₀ | 0.08-0.90 | Gogou et al. (2000) |
| | Cretan Sea | 52 | <i>n</i> -C ₁₇ - <i>n</i> -C ₄₁ | 0.22-3.8 | Mandalakis et al. (2014) |
| Turkey | Aliğa Bay (Aegean Sea) | 15 | <i>n</i> -C ₁₀ - <i>n</i> -C ₃₄ | 0.34-56.5 | Neşer et al. (2012) |
| | Coastal Aegean Sea | 12 | <i>n</i> -C ₁₂ - <i>n</i> -C ₃₅ | 0.25-2.4 | Gonul and Kucuksezgin (2012) |

39 **Table 5.** Concentrations in polycyclic aromatic hydrocarbons (PAHs in ng g⁻¹ sed. dw) and associated molecular diagnostic ratios in the fraction < 63 μm of
 40 surficial sediments (0-1 cm) collected along the Sfax-Kerkennah channel (Southeast Tunisia, Southern Mediterranean Sea).

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| | R101 | R102 | R103 | R104 | R105 | R106 | R107 | R108 | R109 | R110 | R111 | R210 | R209 | R208 | R207 | R205 | R204 | R203 | R202 | R201 |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Nap | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | 56.1 | bld | 43.1 | bld |
| ΣMeNap | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | 79.7 | bld | 42.7 | bld |
| Phe | 8.9 | 39.2 | 13.9 | 10.9 | 13.8 | 9.9 | 11.9 | 9.9 | 35.2 | 38.5 | 35.8 | 19.7 | 12.6 | 9.8 | 12.7 | 25.5 | 205.7 | 79.5 | 63.6 | 179.4 |
| ΣMePhe | 78.9 | 155.2 | 98.3 | 29.9 | 39.7 | 93.9 | 89.6 | 30.0 | 47.0 | 247.9 | 314.7 | 29.5 | 59.7 | 21.6 | 102.8 | 96.6 | 457.5 | 401.9 | 497.9 | 940.1 |
| Ant | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | 15.0 | bld | bld | bld | 169.3 | bld | 151.7 | bld |
| ΣMeAnt | 58.8 | bld | bld | bld | 19.7 | 49.0 | bld | 62.2 | bld | 104.7 | bld | 13.0 | bld | bld | bld | 130.2 | 198.4 | 283.9 | 251.5 | bld |
| Thi | 30.1 | bld | 12.9 | 25.1 | 12.9 | 28.8 | bld | 6.6 | bld | 140.9 | 118.4 | 15.6 | bld | bld | bld | 28.5 | 258.2 | 324.2 | 362.7 | 1344 |
| Flt | 25.2 | 22.8 | 15.6 | 53.1 | 15.6 | bld | 27.3 | 22.3 | 5.3 | 126.6 | 100.6 | bld | bld | 29.4 | 69.4 | 15.2 | 54.6 | 251.7 | 396.6 | 601.8 |
| Pyr | 87.6 | 54.1 | 82.7 | 248.2 | 65.6 | 42.5 | 74.7 | 28.1 | 9.8 | 248.2 | 350.3 | 65.6 | 14.0 | 10.4 | 100.2 | 221.8 | 56.4 | 364.6 | 500.9 | 1752 |
| ΣMePyr | 103.1 | 128.3 | 87.8 | 297.7 | 124.5 | 60.5 | 58.4 | 42.5 | 19.6 | 387.9 | 412.2 | 120.5 | bld | 19.6 | 126.2 | 57.4 | 102.7 | 434.6 | 412.9 | 2675 |
| BaA | bld | bld | 26.4 | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | bld | 71.9 | bld | bld |
| Chr | 62.3 | 63.9 | 72.1 | 190.6 | 188.3 | 50.5 | 27.2 | 50.2 | 11.0 | 190.6 | 249.5 | 188.3 | 13.9 | 29.1 | 34.3 | 302.0 | 138.6 | 248.3 | 171.3 | 1246 |
| ΣMeChr | 78.2 | 43.8 | 105.7 | 239.0 | 100.0 | 81.5 | bld | 75.6 | bld | 178.6 | 313.6 | 188.0 | bld | 11.3 | bld | bld | 159.8 | 326.8 | 162.9 | 993.7 |
| BkF | 18.6 | 50.2 | bld | bld | 94.9 | 31.8 | 26.3 | 24.8 | 7.9 | 136.5 | 74.3 | 146.7 | bld | 7.9 | 49.9 | 32.2 | 126.1 | 144.6 | 853.7 | bld |
| BaP | bld | 113.0 | 18.7 | 101.7 | 60.1 | 42.2 | 18.5 | 39.8 | 8.8 | 101.7 | 119.3 | 60.1 | 68.3 | 8.8 | 38.4 | 30.8 | bld | 144.5 | 192.0 | 113.9 |
| Per | 22.7 | 68.9 | 64.3 | 107.3 | 49.9 | 21.9 | 41.5 | 232.0 | 16.7 | 40.3 | 92.8 | 52.7 | 43.6 | 18.9 | 125.7 | 28.2 | 86.2 | 129.5 | 241.5 | 620.5 |
| BgP | bld | 46.7 | 36.2 | 80.5 | 90.8 | 34.1 | 28.4 | 34.1 | 83.9 | 80.5 | 60.6 | bld | bld | 7.8 | 21.2 | 14.8 | 97.6 | 147.6 | 105.9 | 303.1 |
| Σ17 PAHs | 574.4 | 786.1 | 634.6 | 1384 | 875.8 | 546.6 | 403.8 | 658.0 | 245.2 | 2023 | 2242 | 899.7 | 227.1 | 174.5 | 680.8 | 983.2 | 2247 | 3354 | 4451 | 10769 |
| ΣLMW/ΣHMW | 0.37 | 0.33 | 0.22 | 0.03 | 0.09 | 0.42 | 0.34 | 0.19 | 0.50 | 0.26 | 0.20 | 0.08 | 0.62 | 0.22 | 0.20 | 0.36 | 1.42 | 0.34 | 0.35 | 0.13 |
| ΣMePhe/Phe | 8.9 | 4.0 | 7.1 | 2.7 | 2.9 | 9.5 | 7.5 | 3.0 | 1.3 | 6.4 | 8.8 | 1.5 | 4.7 | 2.2 | 8.1 | 3.8 | 2.2 | 5.1 | 7.8 | 5.2 |
| ΣMePyr/Pyr | 1.2 | 2.4 | 1.1 | 1.2 | 1.9 | 1.4 | 0.8 | 1.5 | 2.0 | 1.6 | 1.2 | 1.8 | nd | 1.9 | 1.3 | 0.3 | 1.8 | 1.2 | 0.8 | 1.5 |
| Flt/Flt+Pyr | 0.22 | 0.30 | 0.16 | 0.18 | 0.19 | nd | 0.27 | 0.44 | 0.35 | 0.34 | 0.22 | nd | nd | 0.74 | 0.41 | 0.06 | 0.49 | 0.41 | 0.44 | 0.26 |
| BaP/BgP | nd | 2.42 | 0.52 | 1.26 | 0.66 | 1.24 | 0.65 | 1.17 | 0.10 | 1.26 | 1.97 | nd | nd | 1.13 | 1.81 | 2.08 | nd | 0.98 | 1.81 | 0.38 |

42 bld: below detection limit; nd: not determined.

Table 6. Comparison of total PAH concentrations (in ng g⁻¹ sed. dw) in surficial/surface sediments from different regions of the Mediterranean Sea.

| Country | Site | Number of samples/sites | Number of PAHs analyzed | Range (ng g ⁻¹ sed. dw) | Pollution level ^a | Reference |
|---------|--|-------------------------|-------------------------|------------------------------------|------------------------------|-------------------------------|
| Tunisia | Gulf of Gabès, Sfax-Kerkennah channel | 20 | 17 | 175-10,769 | Moderate to very high | This study |
| | Gulf of Gabès, Sfax coastline and Kerkennah channel | 18 | 17 | 113-10,720 | Moderate to very high | Zaghden et al. (2007) |
| | Gulf of Gabès, Sfax coastline | 9 | 16 | 811-5,608 | Moderate to very high | Zaghden et al. (2014) |
| | Gulf of Tunis (Rades, Goulette, Sidi Bou Saïd harbors) | 12 | 22 | 363-7,026 | Moderate to very high | Mzoughi and Chouba (2011) |
| | Jarzouna-Bizerte coastal area | 4 | 17 | 916-3,146 | Moderate to high | Zrafi-Nouira et al. (2010) |
| | Coasts of Sfax, Luza, Khniss and Sousse | 4 | 14 | 160-1,990 | Moderate to high | Kessabi et al. (2013) |
| | Ghar El Melh Lagoon | 12 | 17 | 40-655 | Low to moderate | Ben Ameer et al. (2010) |
| | Bizerte Lagoon | 6 | 16 | 2-537 | Low to moderate | Louiz et al. (2008) |
| | Bizerte Lagoon | 10 | 16 | 83-447 | Low to moderate | Trabelsi and Driss (2005) |
| | Bizerte Lagoon | 18 | 14 | 17-394 | Low to moderate | Barhoumi et al. (2014) |
| | Khniss coast | 12 | 17 | 7-15 | Low | Zrafi et al. (2013) |
| Morocco | Al Hoceïma coastal area (effluent outfall and harbor) | 22 | - | 15-551 | Low to moderate | Pavoni et al. (2003) |
| Egypt | Coastal areas (bays, estuaries and harbors) | 26 | 16 | 3.5-14,100 | Low to very high | Barakat et al. (2011) |
| | Coastal areas (bays, estuaries and harbors) | 31 | 16 | 88-6,338 | Low to very high | El Nemr et al. (2007) |
| | Coastal areas (bays, estuaries and harbors) | 10 | 15 | 209-1,020 | Moderate to high | El Nemr et al. (2013) |
| | Abu Qir Bay | 20 | 16 | bld-2,660 | Low to high | Khairy et al. (2009) |
| | Abu Qir Bay | 20 | 11 | 69-1,464 | Low to high | El Deeb et al. (2007) |
| France | Lazaret Bay | 5 | 14 | 1440-48,090 | High to very high | Benlahcen et al. (1997) |
| | Rhône Delta | 15 | 9 | 1070-6,330 | High to very high | Bouloubassi and Saliot (1993) |
| | Port Vendres harbor | 2 | 14 | 150-6,900 | Moderate to very high | Baumard et al. (1998) |
| | Gulf of Fos-sur-mer | 11 | 13 | 34-13,780 | Low to very high | Mille et al. (2007) |
| | Berre Lagoon | 2 | 16 | 334-853 | Moderate | Kanzari et al. (2012) |
| | Bay of Banyuls-sur-mer | 2 | 10 | 21-23 | Low | Charles et al. (2012) |
| Italy | Taranto Gulf | 10 | 16 | 28,918-262,446 | Very high | Annicchiarico et al. (2011) |
| | Coastal Ligurian Sea | 12 | 16 | 2875-26,247 | High to very high | Bertolotto et al. (2003) |
| | Venice Lagoon | 6 | 6 | 65-48,000 | Low to very high | La Rocca et al. (1996) |
| | Naples harbor | 189 | 16 | 9-31,774 | Low to very high | Sprovieri et al. (2007) |

| | | | | | | |
|---------|--|----|----|-------------|-----------------------|--------------------------------|
| | Gulf of Trieste | 8 | 16 | 214-4,416 | Moderate to high | Bajt (2014) |
| | Marano and Grado Lagoons | 28 | 16 | 50-1,026 | Low to high | Acquavita et al. (2014) |
| | Gulf of Trieste | 17 | 22 | 35-682 | Low to moderate | Notar et al. (2001) |
| | Chioggia and Ancona coastal zones | 23 | 16 | 24-500 | Low to moderate | Magi et al. (2002) |
| Spain | Barcelona harbor | 2 | 14 | 1,700-8,400 | Moderate to very high | Baumard et al. (1998) |
| | Barcelona harbor | 20 | 16 | 300-10,320 | Moderate to very high | Martínez-Lladó et al. (2007) |
| | Santander Bay | 17 | 16 | 20-344,600 | Low to very high | Viguri et al. (2002) |
| | Catalonia coast | 45 | 16 | 13-16,700 | Low to very high | Eljarrat et al. (2001) |
| | Cap Salou, Cap Roig | 2 | 14 | 5-840 | Low to moderate | Baumard et al. (1998) |
| Greece | Gulf of Corinth, North Evoikos and Saronikos Gulfs | 41 | 21 | 115-26,633 | Moderate to very high | Botsou and Hatzianestis (2012) |
| | Drapetsona–Keratsini coastal zone | 12 | 26 | 929-18,907 | Moderate to very high | Kapsimalis et al. (2014) |
| | Patroklos and Sitia areas | 15 | 14 | 2.1-181 | Low to moderate | Tsapakis et al. (2010) |
| | North Aegean Sea | 6 | 21 | 44-166 | Low to moderate | Papadopoulou and Samara (2002) |
| | Cretan Sea | 10 | 25 | 15-162 | Low to moderate | Gogou et al. (2000) |
| | Cretan Sea | 52 | 64 | 9-60 | Low | Mandalakis et al. (2014) |
| Turkey | Izmit Bay | 9 | 14 | 118-11,435 | Moderate to very high | Tolun et al. (2006) |
| | Aliğa Bay (Aegean Sea) | 15 | 24 | 70-20,940 | Low to very high | Neşer et al. (2012) |
| | Coastal Aegean Sea | 12 | 19 | 74-2,170 | Low to high | Gonul and Kucuksezgin (2012) |
| | Candarli Gulf | 18 | 12 | bld-405 | Low to moderate | Kucuksezgin et al. (2012) |
| Croatia | Northern Adriatic (Rovinj coastal area) | 8 | 16 | 32-13,681 | Low to very high | Bihari et al. (2006) |
| | Northern Adriatic (Rijeka Bay) | 83 | 16 | 5-12,532 | Low to very high | Alebic-Juretic (2011) |
| Cyprus | Cilician Basin | 19 | 15 | 5-271 | Low to moderate | Kucuksezgin et al. (2013) |

^a The pollution levels are those defined by Baumard et al. (1998): low, 0-100 ng g⁻¹; moderate, 100-1,000 ng g⁻¹; high, 1,000-5,000 ng g⁻¹; very high, > 5,000 ng g⁻¹; bld: below detection limit.

Table 7. Concentration ranges of PAHs in surficial sediments of the Sfax-Kerkennah channel (Southeast Tunisia, Southern Mediterranean Sea) and toxicity guidelines (in ng g⁻¹ sed. dw); SQG: Sediment Quality Guidelines; ERL: Effects Range Low; ERM: Effects Range Median.

| | SQG ^a | | Concentration range (this study) | Stations | Stations | Stations |
|--------------|------------------|--------|-------------------------------------|--|------------------------|----------|
| | ERL | ERM | | < ERL | ERL-ERM | > ERM |
| Nap | 160 | 2,100 | bld-136 ^b | All | - | - |
| Phe | 240 | 1,500 | 31-1,120 ^b | R101-R109, R205-R210 | R110, R111, R201-204 | - |
| Ant | 85 | 1,100 | bld-403 ^b | R101-R109, R111, R201, R207-R210 | R110, R202-R205 | - |
| Flt | 600 | 5,100 | bld-602 | All except R201 | R201 | - |
| Pyr | 665 | 2,600 | 14-4,426 ^b | R101-R110, R204-R210 | R111, R202, R203 | R201 |
| BaA | 261 | 1,600 | bld-72 | All | - | - |
| Chr | 384 | 2,800 | 11-2240 ^b | R101-R103, R105-R110, R202, R204-R210 | R104, R111, R201, R203 | - |
| BkF | na | na | bld-854 | - | - | - |
| BaP | 430 | 1600 | bld-192 | All | - | - |
| Per | na | na | 17-621 | - | - | - |
| BgP | na | na | bld-303 | - | - | - |
| ∑LMW | 552 | 3,160 | 31-1,167 ^b | R101-R111, R205-R210 | R201-R204 | - |
| ∑HMW | 1,700 | 9,600 | 140-8,306 ^b | R101-R110, R204-R210 | R111, R201-R203 | - |
| ∑PAHs | 4,022 | 44,792 | 175-10,769 ^b | All except R201, R202 | R201, R202 | - |

^a SQGs values are taken from Long et al. (1995); ^b Concentrations taking into account alkylated homologues of the parent PAH (∑Me): for Nap, Phe, Ant, Pyr and Chr; bld: below detection limit.

Table 8. Pearson correlation matrices (r values) for the main sediment parameters, taken into account all stations (n = 20) or excluding station R107 (n = 19), stations R107 and R201 (n = 18) and stations R107, R201, R104, R110, R111, R202-R204 (n = 12). Significant correlations (p < 0.05) are in bold.

| n = 20 | C | H | N | S | TOC | CaCO ₃ | δ ¹³ C | R |
|-------------------|--------------|--------------|--------------|-------------|-------------|-------------------|-------------------|-------------|
| H | 0.55 | | | | | | | |
| N | 0.55 | 0.97 | | | | | | |
| S | 0.21 | 0.76 | 0.79 | | | | | |
| TOC | 0.58 | 0.63 | 0.64 | 0.27 | | | | |
| CaCO ₃ | 0.24 | -0.50 | -0.44 | -0.31 | -0.40 | | | |
| δ ¹³ C | -0.08 | 0.20 | 0.20 | 0.31 | 0.10 | -0.26 | | |
| R | 0.49 | 0.88 | 0.93 | 0.76 | 0.63 | -0.43 | 0.19 | |
| ∑17 PAHs | 0.17 | 0.73 | 0.81 | 0.75 | 0.44 | -0.41 | -0.06 | 0.85 |
| n = 19 | C | H | N | S | TOC | CaCO ₃ | δ ¹³ C | R |
| H | 0.56 | | | | | | | |
| N | 0.55 | 0.97 | | | | | | |
| S | 0.25 | 0.78 | 0.81 | | | | | |
| TOC | 0.69 | 0.91 | 0.90 | 0.70 | | | | |
| CaCO ₃ | 0.25 | -0.55 | -0.49 | -0.45 | -0.34 | | | |
| δ ¹³ C | -0.08 | 0.18 | 0.19 | 0.26 | 0.27 | -0.32 | | |
| R | 0.49 | 0.88 | 0.93 | 0.78 | 0.88 | -0.47 | 0.18 | |
| ∑17 PAHs | 0.17 | 0.73 | 0.81 | 0.77 | 0.66 | -0.46 | -0.08 | 0.85 |
| n = 18 | C | H | N | S | TOC | CaCO ₃ | δ ¹³ C | R |
| H | 0.38 | | | | | | | |
| N | 0.42 | 0.94 | | | | | | |
| S | -0.21 | 0.31 | 0.35 | | | | | |
| TOC | 0.60 | 0.76 | 0.85 | 0.24 | | | | |
| CaCO ₃ | 0.53 | -0.45 | -0.37 | -0.24 | -0.06 | | | |
| δ ¹³ C | -0.09 | 0.36 | 0.57 | 0.41 | 0.41 | -0.35 | | |
| R | 0.21 | 0.41 | 0.48 | 0.25 | 0.68 | -0.29 | 0.44 | |
| ∑17 PAHs | -0.57 | -0.21 | -0.23 | 0.24 | -0.08 | -0.26 | -0.19 | 0.21 |

| n = 12 | C | H | N | S | TOC | CaCO₃ | δ¹³C | R |
|-------------------------|--------------|-------------|-------------|----------|------------|-------------------------|------------------------|----------|
| H | -0.20 | | | | | | | |
| N | -0.34 | 0.90 | | | | | | |
| S | -0.26 | 0.54 | 0.63 | | | | | |
| TOC | 0.10 | 0.90 | 0.82 | 0.55 | | | | |
| CaCO₃ | 0.78 | -0.46 | -0.56 | -0.13 | -0.11 | | | |
| δ¹³C | -0.74 | 0.43 | 0.73 | 0.47 | 0.30 | -0.65 | | |
| R | -0.35 | 0.19 | 0.25 | 0.09 | -0.02 | -0.49 | 0.42 | |
| Σ17 PAHs | -0.15 | 0.16 | 0.04 | 0.48 | 0.18 | 0.14 | 0.05 | 0.07 |

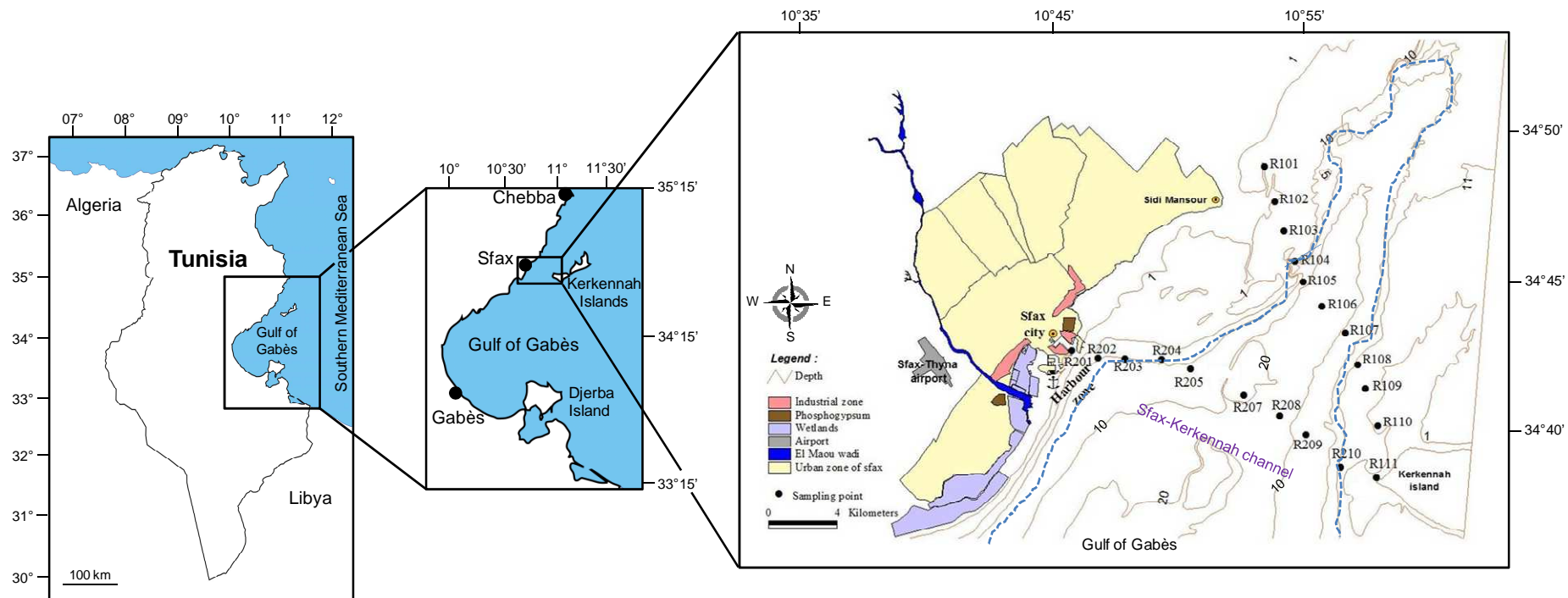


Figure 1

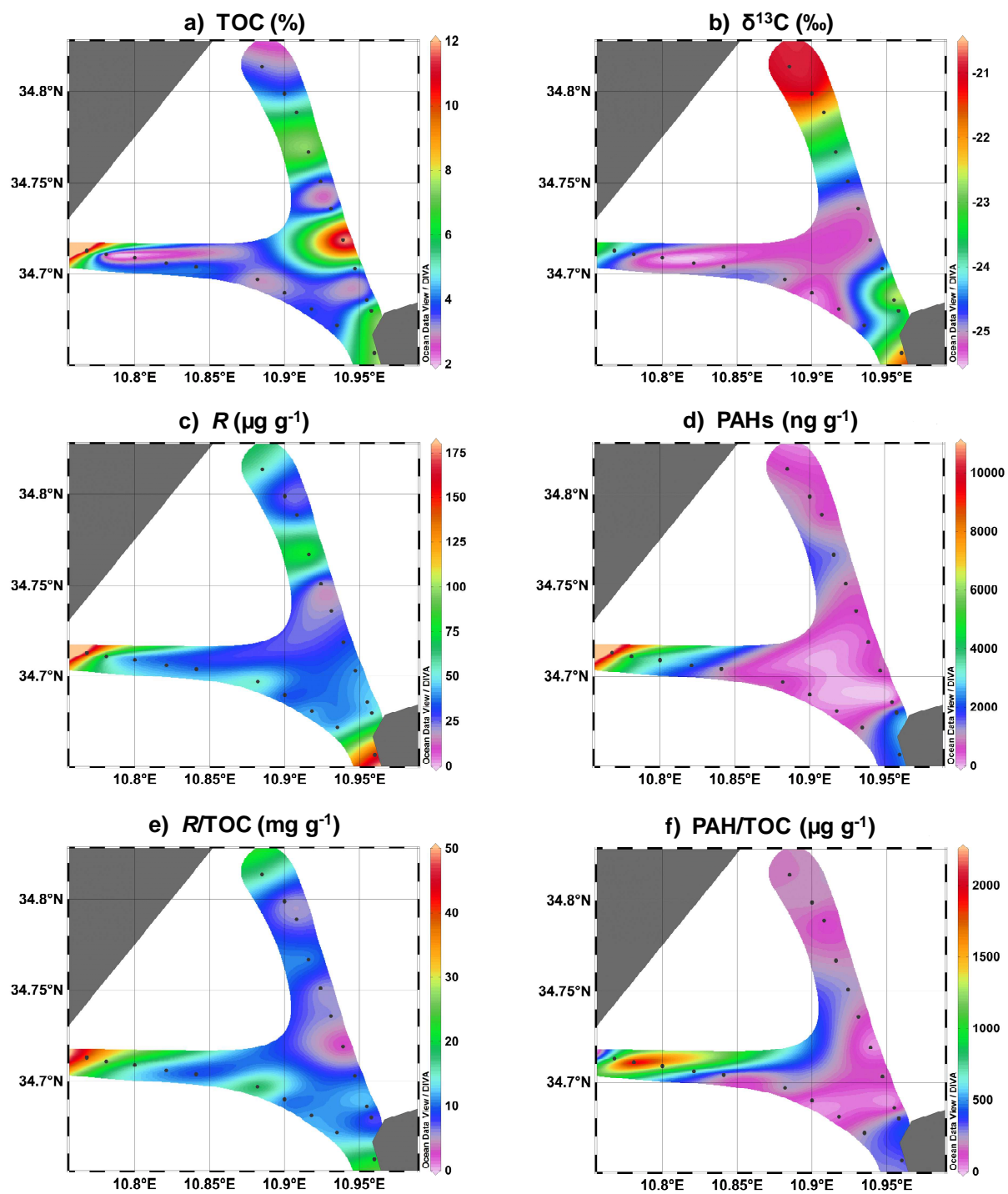


Figure 2

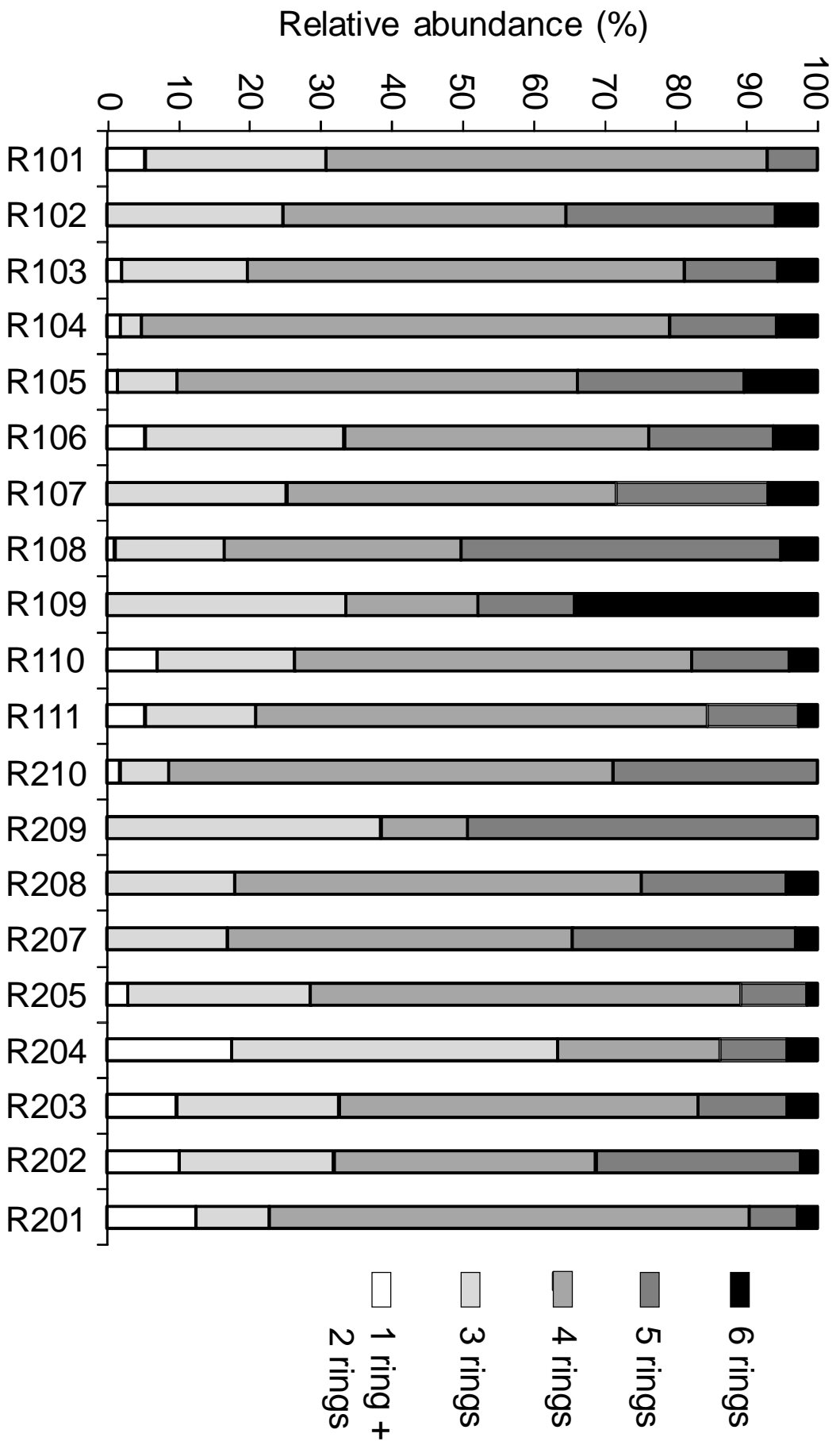


Figure 3

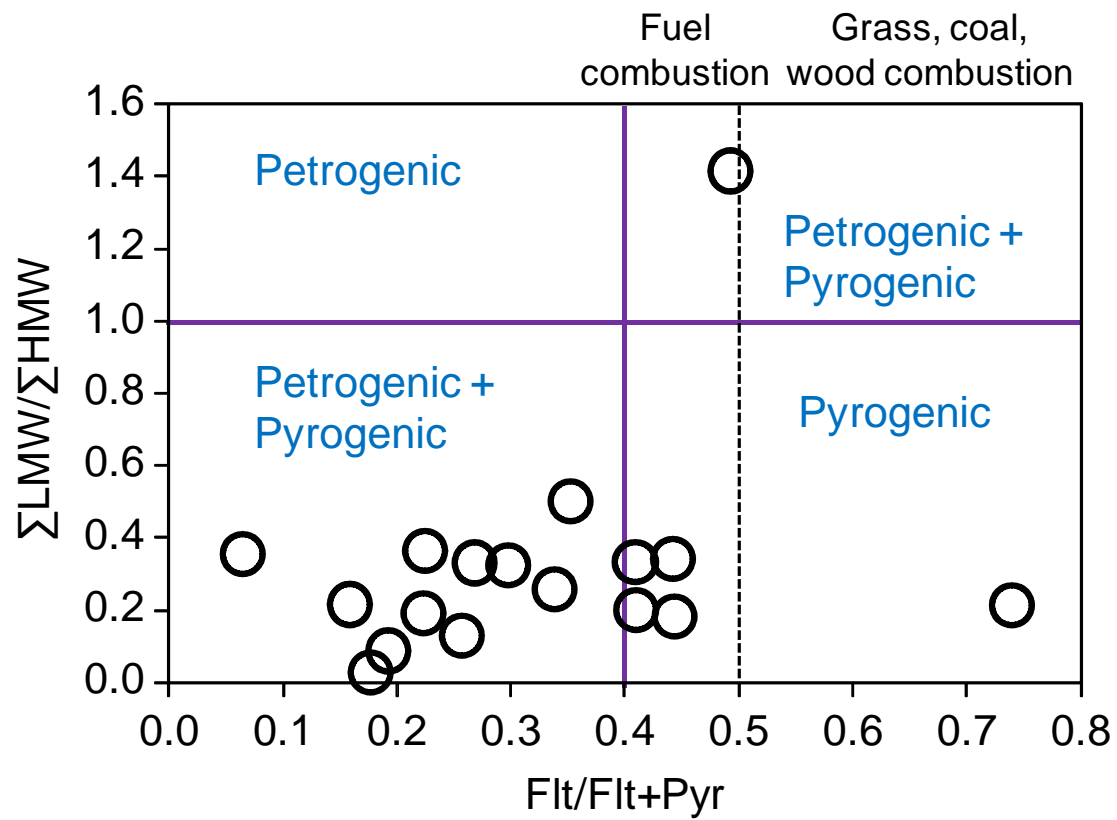


Figure 4