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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 µg 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 $\delta^{13}C$ 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, $CaCO_3$ and $\delta^{13}C$) 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 km^2 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, $\delta^{13}C$, 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*-C_{24}-d_{50} for AHs and p-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 °C, dried with magnesium sulphate and filtered on a pre-combusted glass fiber filter of porosity 4 µm. 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 °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 m × 0.25 mm × 0.25 µm, 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 °C, respectively. The initial column temperature was held for 2 min at 60 °C, next ramped at 25 °C min^{-1} (ramp 1) to 100 °C and then at 2 °C min^{-1} (ramp 2) to a final temperature of 310 °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 CH_3OH and CH_2Cl_2 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, CH_3OH and CH_2Cl_2. 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 CH_2Cl_2 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*-C_{15} to *n*-C_{34} and two isoprenoids, pristane (Pr, C_{19}) and phytane (Phy, C_{20}), 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*-C_{17}/Pr and *n*-C_{18}/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*-C_{15}-*n*-C_{24} and *n*-C_{25}-*n*-C_{34} (CPI_{15-24} and CPI_{25-34}), 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*-C_{27} + *n*-C_{29} + *n*-C_{31}) to short-chain *n*-alkanes (*n*-C_{15} + *n*-C_{17} + *n*-C_{19}), as index of the relative importance of terrestrial (higher plants) and aquatic (algae, phyto-and zoo-plankton) 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 (∑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: ∑LMW/∑HMW, ∑MePhe/Phe, ∑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, $CaCO_3$ and $\delta^{13}C$

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.

$\delta^{13}C$, given in ‰, is the ratio of stable isotopes $^{13}C/^{12}C$. It was determined on OC (acidified) sub-samples using the following formula: $[(^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{standard} - 1] \times 1000$, where $(^{13}C/^{12}C)_{standard}$ corresponds to the isotopic ratio of the international standard Pee Dee Belemnite (PDB), and $(^{13}C/^{12}C)_{sample}$ 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; $\delta^{13}C$, *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 $\delta^{13}C$

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 ~ 11.7% in the Sfax harbor (R201) and, quite surprisingly, in the Sfax-Kerkennah channel (R107) (Table 3; Fig. 2a). High values of ~ 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 $CaCO_3$ 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 $CaCO_3$ in surficial sediments is related to marine organisms. In our case, the two mains contributors of $CaCO_3$ would be benthic foraminifera and green seaweeds (Aloulou et al., 2012). The highest $\delta^{13}C$ 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 $\delta^{13}C$ 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 ($\delta^{13}C$) is useful to distinguish between marine and terrestrial sources of sedimentary organic matter. Marine organic matter typically has $\delta^{13}C$ values between –22 and –20‰, whilst terrestrial organic matter (C_3 land plants) has an average $\delta^{13}C$ 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*-C_{15} to *n*-C_{34} + Pr and Phy) ranged from 8.1-14.2 µg g^{-1} sed. dw in the Sfax-Kerkennah channel (R102, R105-R107, R208, R209) to 173.9 µg g^{-1} sed. dw in the Sfax harbor (R201). High values were also recorded in the Sfax-Kerkennah channel (45.7 µg g^{-1} sed. dw, R104) and the Kerkennah harbor (72.1 µg g^{-1} sed. dw, R111) (Table 3; Fig. 2c). These *R* concentrations (8.1- 173.9 µg 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 (Tukey), concentrations did not exceed 10 µg 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 Aliağa Bay (Turkey), maximal concentrations were comprised between 10 and 57 µg 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 µg 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 µg g^{-1} sed. dw (sediments collected in 2003). Finally, Amori et al. (2011) observed concentrations that were largely higher, i.e. 3,886 µg 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 175-245 ng g^{-1} sed. dw in the Sfax-Kerkennah channel (R109, R209, R208) and 10,769 ng g^{-1} sed. dw in the Sfax harbor (R201), with concentrations > 1,000 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 (175-10,769 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 ng g^{-1} 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 ng g^{-1} 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; Zaghden 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 Aliağa Bays (Turkey), Rovinj coastal area and Rijeka Bay (Croatia), maximal concentrations were much higher than 10,000 ng g^{-1} 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 Zaghden et al. (2007) for the same area (113-10,720 ng g^{-1} 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 mg g^{-1} and < 60 µg g^{-1} sed. dw, respectively), while high ratios were found in coastal stations outside the channel (> 10 mg g^{-1} and > 500 µg g^{-1} 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 ($r = 0.73\text{-}0.81$, $p < 0.05$, $n = 20$). 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 ($r = 0.66\text{-}0.88$, $p < 0.05$, $n = 19$) (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* ($r = -0.08\text{-}0.21$, $p > 0.05$, $n = 18$), 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 ng g^{-1} 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 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*-C_{16}, *n*-C_{18} and, in a lesser extent, *n*-C_{20} were the dominant compounds over the whole range *n*-C_{15}-*n*-C_{34} apart from the coastal stations R101-R103, the Kerkennah harbor area (R110, R111) and the Sfax harbor (R201), in which *n*-C_{31} and *n*-C_{33} were the major compounds. The predominance of even light *n*-alkanes *n*-C_{16}, *n*-C_{18} and *n*-C_{20} 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*-C_{17}/Pr and *n*-C_{18}/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 Archaebacteria, such as methanogens (Volkman et al., 1992). It has been proposed that Pr/Phy < 1 could be taken as an indicator of petroleum origin and/or highly reducing (anoxic, hypersaline) depositional environments. 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 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 Zaghden et al. (2007) in the same area. The *n*-C_{18}/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*-C_{18}/Phy decreased (~ 1.7 in R201 and R202) (Table 3), which reflected the presence of more degraded AHs. The *n*-C_{17}/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*-C_{18}/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 ∑MePyr (in R101, R104, R110, R111, R207, R203, R201), ∑MePhe (in R102, R106, R107, R204) or Chr and/or ∑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, ∑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 ∑LMW/∑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 ∑LMW/∑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 (∑LMW/∑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 ∑LMW/∑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, ∑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, ∑MePyr/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 µg g^{-1} sed. dw) and PAH concentrations (> 10,000 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 $\delta^{13}C$ 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 ($\delta^{13}C$ in ‰), c) the concentration in total *n*-alkanes (*R* in µg g^{-1} sed. dw), d) the concentration in total (∑17) PAHs (in ng g^{-1} sed. dw), e) the *R*/TOC ratio (in mg g^{-1}) and f) the PAH/TOC ratio (in µg 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 ∑MeNap; 3-ring compounds: Phe, ∑MePhe, Ant, ∑MeAnt; 4-ring compounds: Flt, Pyr, ∑MePyr, BaA, Chr, ∑MeChr; 5-ring compounds: BkF, BaP, Per; 6-ring compounds: BgP.

Figure 4. Cross plot of ∑LMW/∑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.

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

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 *Posidonia*
R102		34°47’56”N, 10°54’00”E	1.1	Meadows of *Posidonia*
R103		34°47’19”N, 10°54’30”E	1.7	Meadows of *Posidonia*
R104	Channel	34°46’00”N, 10°54’57”E	7.6	Muddy sand
R105	Channel	34°45’05”N, 10°55’25”E	9.5	Dense meadows of *Posidonia*
R106	Channel	34°44’08”N, 10°55’50”E	8.5	Sandy with *Posidonia*
R107	Channel	34°43’08”N, 10°56’20”E	5.5	Dense meadows of *Posidonia*
R108		34°42’10”N, 10°56’48”E	2.8	Dense meadows of *Posidonia*
R109		34°41’10”N, 10°57’18”E	1	Dense meadows of *Posidonia*
R110		34°40’19”N, 10°57’43”E	0.8	Muddy sand
R111	Kerkennah harbor	34°39’26”N, 10°58’00”E	2.7	Sandy with *Posidonia*
R210	Channel	34°40’19”N, 10°56’05”E	7	Sandy
R209	Channel	34°40’52”N, 10°55’05”E	9	Meadows of *Posidonia*
R208	Channel	34°41’25”N, 10°54’00”E	15.7	Meadows of *Posidonia*
R207	Channel	34°41’48”N, 10°52’55”E	20	Meadows of *Posidonia*
R205	Channel	34°42’15”N, 10°50’28”E	7.3	Muddy sand
R204	Channel	34°42’23”N, 10°49’15”E	8.5	Muddy sand
R203	Channel	34°42’31”N, 10°48’00”E	7.9	Muddy sand
R202		34°42’39”N, 10°46’50”E	4	Muddy sand
R201	Sfax harbor	34°42’46”N, 10°46’05”E	4.5	Muddy sand

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

Hydrocarbons	Ratios	Hydrocarbon origin		References
AHs		Recent/less degraded	Degraded	
	UCM/*R*	-	> 3-4	Simoneit and Mazurek (1982); Mazurek and Simoneit (1984); Asia et al. (2009)
	n-C_{17}/Pr	> 1	< 1	
	n-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)

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 carbonate ($CaCO_3$) and total organic carbon (TOC), isotopic signature of organic carbon ($\delta^{13}C$ in ‰), and concentrations in total *n*-alkanes (*R* in µg g^{-1} sed. dw) and associated molecular diagnostic ratios (UCM/*R*, CPI, Pr/Phy, *n*-C_{17}/Pr, *n*-C_{18}/Phy, TAR) in the fraction < 63 µm of surficial sediments (0-1 cm) collected along the Sfax-Kerkennah channel (Southeast Tunisia, Southern Mediterranean Sea).

	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
$CaCO_3$ (%)	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
$\delta^{13}C$ (‰)	-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
***R* (µg 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/*R*	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
CPI_{15-24}	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
CPI_{25-34}	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
***n*-C_{17}/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
***n*-C_{18}/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

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.

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

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

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 surficial sediments (0-1 cm) collected along the Sfax-Kerkennah channel (Southeast Tunisia, Southern Mediterranean Sea).

	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
∑MeNap	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
∑MePhe	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
∑MeAnt	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
∑MePyr	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
∑MeChr	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
∑17 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
∑LMW/∑HMW	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
∑MePhe/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
∑MePyr/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

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 Ameur 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 Banuyls-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)
	Aliağa 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 homogues 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**	**$CaCO_3$**	**$\delta^{13}C$**	***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			
$\delta^{13}C$	-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**	**$CaCO_3$**	**$\delta^{13}C$**	***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			
$\delta^{13}C$	-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**	**CaCO3**	**$\delta^{13}C$**	***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			
$\delta^{13}C$	-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**	**$CaCO_3$**	**$\delta^{13}C$**	***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				
$CaCO_3$	**0.78**	-0.46	-0.56	-0.13	-0.11			
$\delta^{13}C$	**-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	
∑17 PAHs	-0.15	0.16	0.04	0.48	0.18	0.14	0.05	0.07

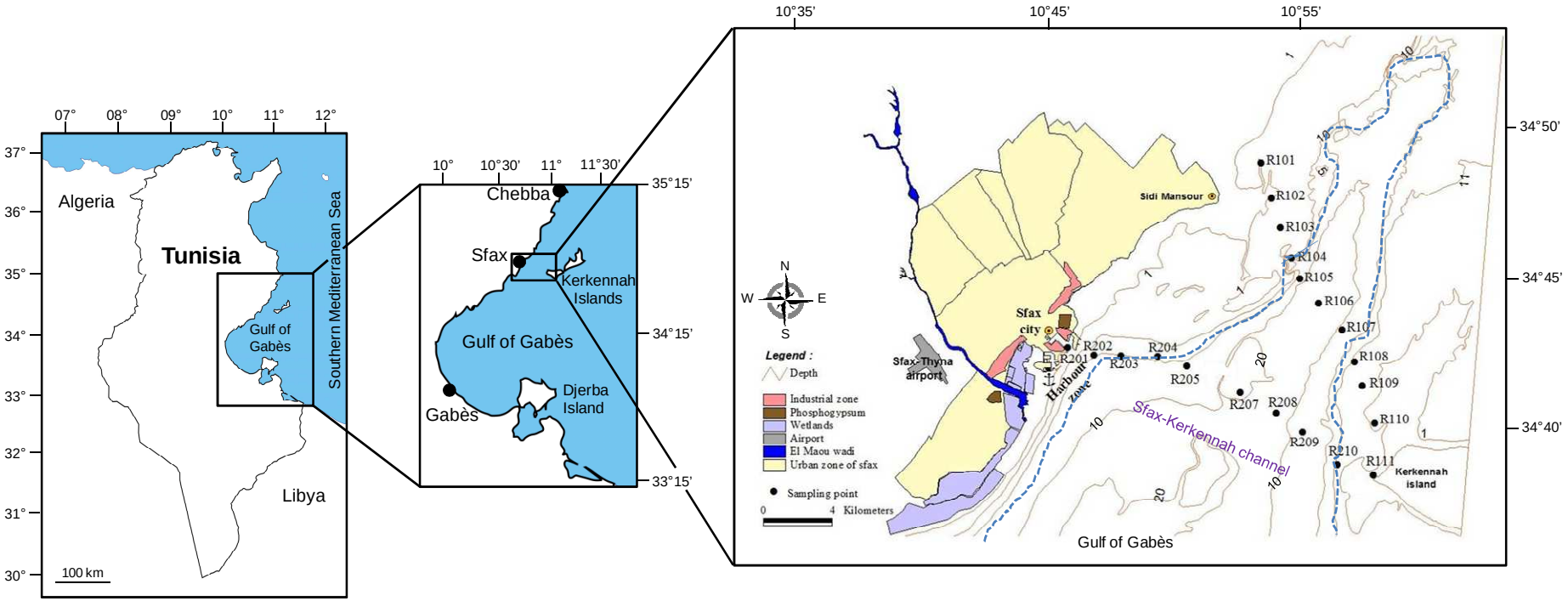
Algeria
Tunisia
Libya
Southern Mediterranean Sea
Gulf of Gabès
100 km
Chebba
Sfax
Kerkennah Islands
Djerba Island
Gabès
Gulf of Gabès
Sfax city
Sfax-Thyna airport
Harbour zone
Sidi Mansour
Sfax-Kerkennah channel
Kerkennah island
Gulf of Gabès
Legend :
Depth
Industrial zone
Phosphogypsum
Wetlands
Airport
El Maou wadi
Urban zone of sfax
Sampling point
Kilometers

Figure 1

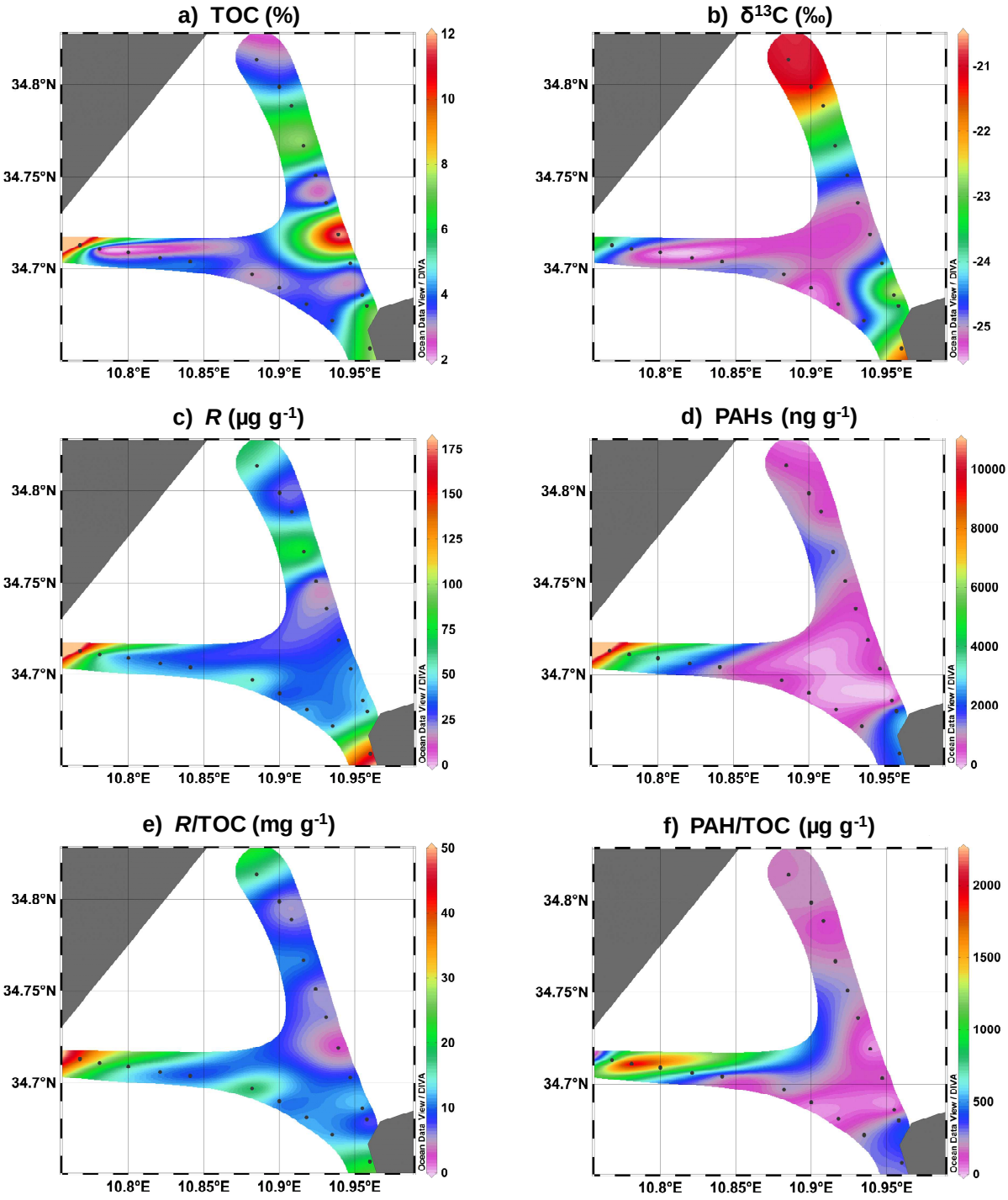
a) TOC (%)
b) δ13C (‰)
c) R (µg g-1)
d) PAHs (ng g-1)
e) R/TOC (mg g-1)
f) PAH/TOC (µg g-1)
34.8°N
34.75°N
34.7°N
10.8°E
10.85°E
10.9°E
10.95°E
Ocean Data View / DIVA

Figure 2

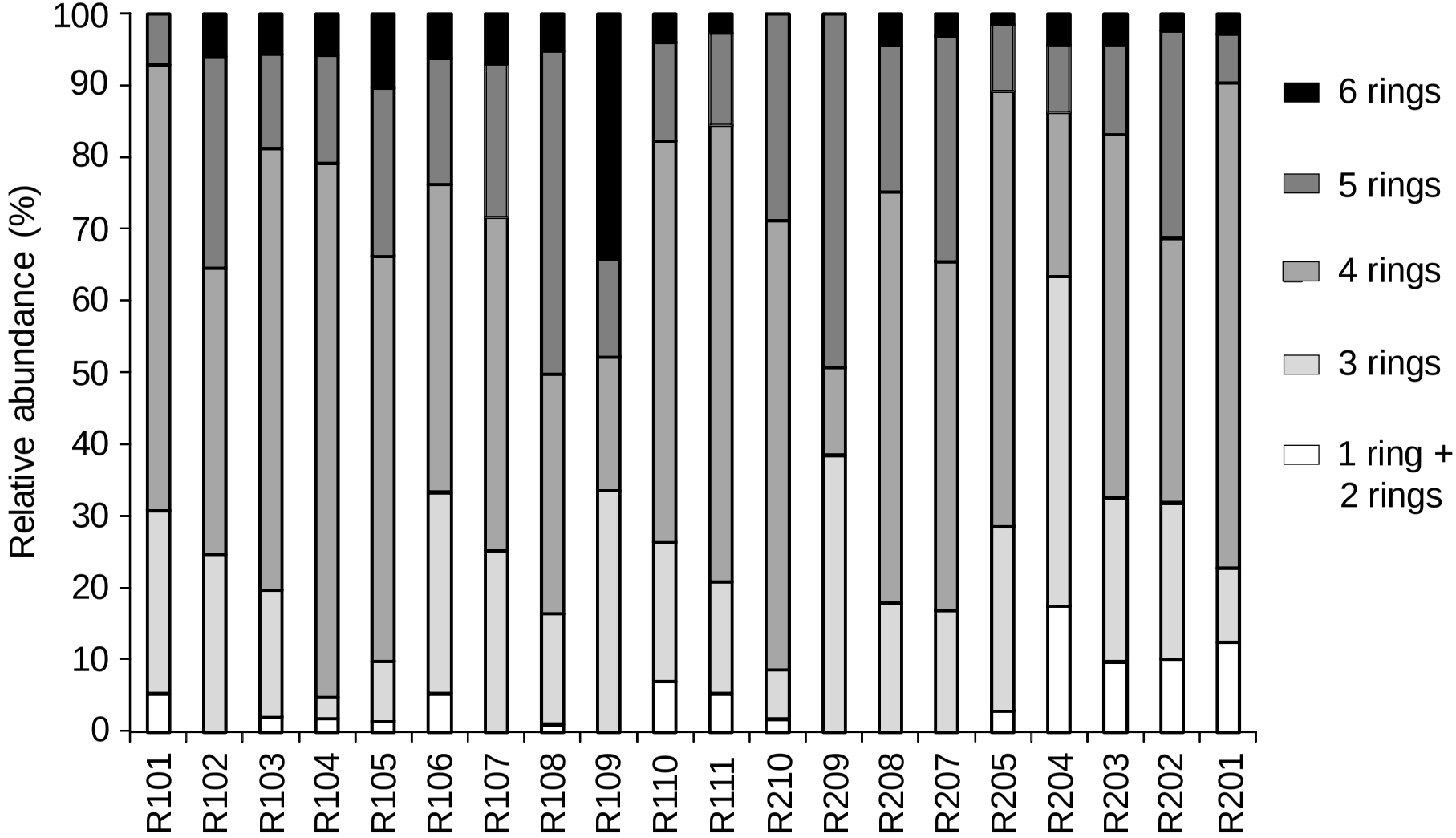
Relative abundance (%)
100
90
80
70
60
50
40
30
20
10
0
R101
R102
R103
R104
R105
R106
R107
R108
R109
R110
R111
R210
R209
R208
R207
R205
R204
R203
R202
R201
6 rings
5 rings
4 rings
3 rings
1 ring +
2 rings

Figure 3

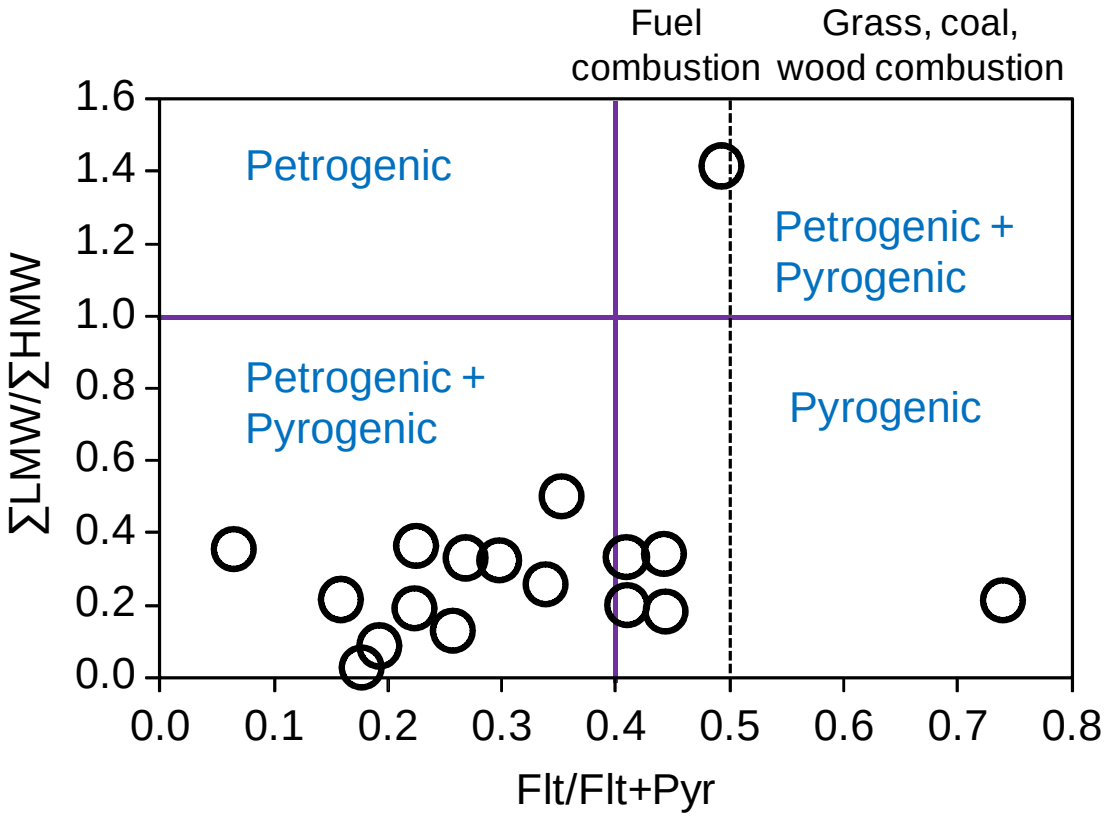
Fuel combustion
Grass, coal, wood combustion
Petrogenic
Petrogenic + Pyrogenic
Petrogenic + Pyrogenic
Pyrogenic
ΣLMW/ΣHMW
Flt/Flt+Pyr
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Figure 4