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

Hatem Zaghden, Marc Tedetti, Sami Sayadi, Mohamed Moncef Serbaji,
Boubaker Elleuch, Alain Saliot

► To cite this version:

Hatem Zaghden, Marc Tedetti, Sami Sayadi, Mohamed Moncef Serbaji, Boubaker Elleuch, et al.. Origin and distribution of hydrocarbons and organic matter in the surficial sediments of the Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea). *Marine Pollution Bulletin*, 2017, 117 (1-2), pp.414 - 428. 10.1016/j.marpolbul.2017.02.007 . hal-01622004

HAL Id: hal-01622004

<https://hal-amu.archives-ouvertes.fr/hal-01622004>

Submitted on 20 Apr 2018

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

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

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

Hatem Zaghden^{a,b*}, Marc Tedetti^c, Sami Sayadi^b, Mohamed Moncef Serbaji^d, Boubaker Elleuch^e, Alain Saliot^a

^a Laboratoire d'Océanographie et du Climat; Expérimentation et Approches Numériques LOCEAN, UMR CNRS 7159, CNRS/IRD/UPMC/MNHN, Université Pierre et Marie Curie, Case courrier 100, 4 Place Jussieu, 75252 Paris Cedex 05, France

^b Laboratoire des Bioprocédés Environnementaux, Pôle d'Excellence Régional AUF (PER-LBP), Centre de Biotechnologie de Sfax, BP, 1177, 3018 Sfax, Tunisia

^c Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute of Oceanography (MIO) UM 110, 13288, Marseille, France

^d Study and management of coastal and urban environments, National School of Engineers of Sfax, University of Sfax, Soukra, 3038 Sfax, Tunisia

^e Laboratoire Eau-Energie-Environnement (Lab 3E), Université de Sfax, ENIS, BP W 3038, Sfax, Tunisia

* Corresponding author: hatem.zaghden@gmail.com; Phone: +216 74 874 452;

Fax: +216 74 874 452

For submission to Marine Pollution Bulletin as a full length research paper

Final version, 20 January 2017

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; Zaghdien 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; Zaghdien 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 (Zaghdien 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 ($35^{\circ}14'N$, $11^{\circ}09'E$) to the Tunisian-Libyan border ($33^{\circ}10'N$, $11^{\circ}34'E$) 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 ($34^{\circ}43'N$, $10^{\circ}46'E$; 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 $\pm 10\%$. All the concentration values, given in ng g⁻¹ (PAHs) or $\mu\text{g g}^{-1}$ (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 $> 3\text{--}4$) (Simoneit and Mazurek, 1982; Mazurek and Simoneit, 1984). 2) The Pr/Phy ratio as indicator of biogenic AHs (when $\gg 1$), 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 $\gg$ or $\ll 1$) (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 CaCO_3 was minimal ($\sim 40\%$) in the Sfax-Kerkennah channel (R104) and the Sfax harbor (R201), and maximal ($\sim 95.6\%$) 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 main contributors of CaCO_3 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 (C_3 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 $n\text{-C}_{15}$ to $n\text{-C}_{34}$ + Pr and Phy) ranged from $8.1\text{-}14.2\ \mu\text{g g}^{-1}$ 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 ($8.1\text{-}173.9\ \mu\text{g g}^{-1}$ 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 $10 \mu\text{g g}^{-1} \text{ sed. dw}$ (Lipiatou 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 $57 \mu\text{g g}^{-1} \text{ sed. dw}$ (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 $143 \mu\text{g g}^{-1} \text{ sed. dw}$, respectively (Aboul-Kassim and Simoneit, 1995; Elloumi et al., 2008). In the Sfax coastline (Tunisia), close to our study area, Zaghdien et al. (2007) found concentrations reaching up to $430 \mu\text{g g}^{-1} \text{ sed. dw}$ (sediments collected in 2003). Finally, Amori et al. (2011) observed concentrations that were largely higher, i.e. $3,886 \mu\text{g g}^{-1} \text{ sed. dw}$, 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 $175\text{-}245 \text{ ng g}^{-1} \text{ sed. dw}$ in the Sfax-Kerkennah channel (R109, R209, R208) and $10,769 \text{ ng g}^{-1} \text{ sed. dw}$ in the Sfax harbor (R201), with concentrations $> 1,000 \text{ ng g}^{-1} \text{ sed. dw}$ 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 ($175\text{-}10,769 \text{ ng g}^{-1} \text{ sed. dw}$) 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; Zaghdien 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 Aliaga 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 Zaghdien 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 ($r = 0.49\text{-}0.93$, $p < 0.05$, $n = 20$), 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 Σ MePyr (in R101, R104, R110, R111, R207, R203, R201), Σ MePhe (in R102, R106, R107, R204) or Chr and/or Σ 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, Σ 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 Zaghdien 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 Σ LMW/ Σ 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 Σ LMW/ Σ 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 (Σ LMW/ Σ 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 Σ LMW/ Σ 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, Σ 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, $\Sigma\text{MePyr}/\text{Pyr}$ 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.

Acknowledgements. We acknowledge the service central d'analyses du CNRS (Vernaison, France). We are grateful to Pr. J.-L. Reyss (LSCE, UMR CEA-CNRS 1572, France) for providing access to CHN and isotope ratio equipment. We warmly thank A. Lorre for her help and assistance for OC and $\delta^{13}\text{C}$ analyses. One anonymous Reviewer is acknowledged for his relevant comments and corrections. This work was conducted in part in the framework of the IRD French-Tunisian International Joint Laboratory "LMI COSYS-Med".

References

- Aboul-Kassim, T.A.T., Simoneit, B.R.T., 1995. Petroleum hydrocarbon fingerprinting and sediment transport assessed by molecular biomarker and multivariate statistical analyses in the Eastern Harbour of Alexandria, Egypt. *Mar. Pollut. Bull.* 30, 63–73.
- Acquavita, A., Falomo, J., Predonzani, S., Tamberlich, F., Bettoso, N., Mattassi, G., 2014. The PAH level, distribution and composition in surface sediments from a Mediterranean Lagoon: The Marano and Grado Lagoon (Northern Adriatic Sea, Italy). *Mar. Pollut. Bull.* 81, 234–241.
- Alebic-Juretic, A., 2011. Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006. *Mar. Pollut. Bull.* 62, 863–869.
- Aloulou, F., Elleuch, B., Kallel, M., 2012. Benthic foraminiferal assemblages as pollution proxies in the northern coast of Gabes Gulf, Tunisia. *Environ. Monit. Assess.* 184, 777–795.
- Aloulou, F., Kallel, M., Dammak, M., Elleuch, B., Saliot, A., 2010. Even-numbered *n*-alkanes/*n*-alkenes predominance in surface sediments of Gabes Gulf in Tunisia. *Environ. Earth Sci.* 61, 1–10.
- Amorri, J., Geffroy-Rodier, C., Boufahja, F., Mahmoudi, E., Aïssa, P., Ksibi, M., Amblès, A., 2011. Organic matter compounds as source indicators and tracers for marine pollution in a western Mediterranean coastal zone. *Environ. Sci. Pollut. Res. Int.* 18, 1606–1616.
- Annicchiarico, C., Buonocore, M., Cardellicchio, N., Di Leo, A., Giandomenico, S., Spada, L., 2011. PCBs, PAHs and metal contamination and quality index in marine sediments of the Taranto Gulf. *Chem. Ecol.* 27, 21–32.
- Asia, L., Mazouz, S., Guiliano, M., Doumenq, P., Mille, G., 2009. Occurrence and distribution of hydrocarbons in surface sediments from Marseille Bay (France). *Mar. Pollut. Bull.* 58, 443–451.

- Bajt, O., 2014. Aliphatic and Polycyclic Aromatic Hydrocarbons in Gulf of Trieste Sediments (Northern Adriatic): Potential Impacts of Maritime Traffic. *Bull. Environ. Contam. Toxicol.* 93, 299–305.
- Barakat, A.O., Mostafa, A., Wade, T.L., Sweet, S.T., El Sayed, N.B., 2011. Distribution and characteristics of PAHs in sediments from the Mediterranean coastal environment of Egypt. *Mar. Pollut. Bull.* 62, 1969–1978.
- Barhoumi, B., LeMenach, K., Devier, M.H., Ben Ameer, W., Etcheber, H., Budzinski, H., Cachot, J., Driss, M.R., 2014. Polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Bizerte Lagoon, Tunisia: levels, sources, and toxicological significance. *Environ. Monit. Assess.* 186, 2653–2669.
- Barth, A., Alvera Azcarate, A., Troupin, C., Ouberdous, M., Beckers, J.-M., 2010. A web interface for gridding arbitrarily distributed in situ data based on Data-Interpolating Variational Analysis (DIVA). *Adv. Geosci.* 28, 29–37.
- Baumard, P., Budzinski, H., Michon, Q., Garrigues, P., Burgeot, T., Bellocq, J., 1998. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuar. Coast. Shelf Sci.* 47, 77–90.
- Ben Ameer, W., Trabelsi, S., Driss, M.R., 2010. Polycyclic aromatic hydrocarbons in superficial sediments from Ghar El Melh Lagoon, Tunisia. *Bull. Environ. Contam. Toxicol.* 85, 184–189.
- Ben Mustapha, K., Hattour, A., Mhetli, M., El Abed, A., Tritar, B., 1999. Bionomie des étages infra et circalittoral du golfe de Gabès. *Bull. Inst. Natl. Sci. Tech. Mer (Tunisie)* 26, 5–48.
- Benlahcen, K.T., Chaoui, A., Budzinski, H., Bellocq, J., Garrigues, P.H., 1997. Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Mar. Pollut. Bull.* 34, 298–316.

- Ben Othman, S., 1973. Le sud tunisien (golfe de Gabès) : Hydrologie, sédimentologie, flore et faune. PhD thesis. Université de Tunis, 166 pp.
- Berner, R.A., 1989. Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Paleogeogr. Paleoclimatol. Paleoecol.* 75, 97–122.
- Bertolotto, R.M., Ghioni, F., Frignani, M., Alvarado-Aguilar, D., Bellucci, L.G., Cuneo, C., Picca, M.R., Gollo, E., 2003. Polycyclic aromatic hydrocarbons in surficial coastal sediments of the Ligurian Sea. *Mar. Pollut. Bull.* 46, 907–913.
- Bihari, N., Fafandel, M., Hamer, B., Kralj-Bilen, B., 2006. PAH content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, Northern Adriatic, Croatia. *Sci. Tot. Environ.* 366, 602–611.
- Blott, S.J., Pye, K., 2001. GRADISTAT: a grain size distribution and statistics package for the analysis of unconsolidated sediments. *Earth Surf. Process. Landf.* 26, 1237–1248.
- Blumer, M., Mullin, M.M., Thomas, D.W., 1963. Pristane in zooplankton. *Science* 140, 974.
- Botsou, F., Hatzianestis, I., 2012. Polycyclic aromatic hydrocarbons (PAHs) in marine sediments of the Hellenic coastal zone, eastern Mediterranean: levels, sources and toxicological significance. *J. Soils Sediments* 12, 265–277.
- Bouaziz, S., Jedoui, Y., Barrier, E., Angelier, J., 2003. Néotectonique affectant les dépôts marins tyrrhéniens du littoral sud-est tunisien: implications pour les variations du niveau marin. *C. R. Géosci.* 335, 247–254.
- Bouloubassi, I., Saliot, A., 1993. Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanol. Act.* 16, 145–161.

- Bouloubassi, I., Méjanelle, L., Pete, R., Fillaux, J., Lorre, A., Point, V., 2006. PAH transport by sinking particles in the open Mediterranean Sea: a 1 year sediment trap study. *Mar. Pollut. Bull.* 52, 560–571.
- Bourbonniere, R.A., Meyers, P.A., 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnol. Oceanogr.* 41, 352–359.
- Bouزيد, S., Raissouni, A., Khannous, S., El Arrim, A., Bouloubassi, I., Saliot, A., Er-Raioui, H., 2012. Distribution and origin of aliphatic hydrocarbons in surface sediments of strategical areas of the western moroccan mediterranean sea. *Open Environ. Pollut. Toxicol. J.* 3, 13–22.
- Brändli, R.C., Bucheli, T.D., Ammann, S., Desaulles, A., Keller, A., Blum, F., Stahel, W.A., 2008. Critical evaluation of PAH source apportionment tools using data from the Swiss soil monitoring network. *J. Environ. Monit.* 10, 1278–1286.
- Budzinski, H., Jones, I., Bellocq, J., Pierard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar. Chem.* 58, 85–97.
- Charles, F., Nozais, C., Pruski, A.M., Bourgeois, S., Méjanelle, L., Vétion, G., Rivière, B., Coston-Guarini, J., 2012. Ecodynamics of PAHs at a peri-urban site of the French Mediterranean Sea. *Environ. Pollut.* 171, 256–264.
- Chen, J., Henderson, G., Grimm, C.C., Lloyd, S.W., Laine, R.A., 1998. Termites fumigate their nests with naphthalene. *Nature* 392, 558.
- Cincinelli, A., Martellini, T., Bittoni, L., Russo, A., Gambaro, A., Lepri, L., 2008. Natural and anthropogenic hydrocarbons in the water column of the Ross Sea (Antarctica). *J. Mar. Syst.* 73, 208–220.
- Clark, R.B., 1997. *Marine Pollution*. fourth ed. Claredon Press, Oxford, p. 270.

- Commendatore, M.G., Esteves, J.L., 2004. Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). *Mar. Pollut. Bull.* 48, 910–918.
- Cripps, G.C., 1989. Problems in the identification of anthropogenic hydrocarbons against natural background levels in the Antarctic. *Antarctic Sci.* 14, 307–312.
- Dachs, J., Méjanelle, L., 2010. Organic Pollutants in Coastal Waters, Sediments, and Biota: A Relevant Driver for Ecosystems During the Anthropocene? *Estuar. Coasts* 33, 1–14.
- De La Torre-Roche, R.J., Lee, W.-Y., Campos-Díaz, S.I., 2009. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. *J. Hazard. Mater.* 163, 946–958.
- DGPA, 2010. Direction Générale de Pêche et de l’Aquaculture. *Annuaire des statistiques de pêche de Tunisie*. D.G.P.A., 144 pp.
- D’Ortenzio, F., d’Alcalà, M.R., 2009. On the trophic regimes of the Mediterranean Sea: A satellite analysis. *Biogeosciences* 6, 139–148.
- Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* 3, 621–634.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- Eljarrat, E., Caixach, J., Rivera, J., De Torres, M., Ginebreda, A., 2001. Toxic potency assessment of non- and mono-ortho PCBs, PCDDs, PCDFs, and PAHs in northwest Mediterranean sediments (Catalonia Spain). *Environ. Sci. Technol.* 35, 3589–3594.
- Elloumi, J., Guermazi, W., Ayadi, H., Bouaïn, A., Aleya, L., 2008. Detection of Water and Sediments Pollution of An Arid Saltern (Sfax, Tunisia) by Coupling the Distribution of Microorganisms With Hydrocarbons. *Water Air Soil Pollut.* 187, 157–171.
- El Deeb, K.Z., Said, T.O., El Naggar, M.H., Shreadah, M.A., 2007. Distribution and Sources of Aliphatic and Polycyclic Aromatic Hydrocarbons in Surface Sediments, Fish and

- Bivalves of Abu Qir Bay (Egyptian Mediterranean Sea). *Bull. Environ. Contam. Toxicol.* 78, 373–379.
- El Nemr, A., Said, T.O., Khaled, A., El Sikaily, A., Abd-Allah, A.M.A., 2007. The distribution and sources of polycyclic aromatic hydrocarbons in surface sediments along the Egyptian Mediterranean coast. *Environ. Monit. Assess.* 124, 343–359.
- El Nemr, A., El-Sadaawy, M.M., Khaled, A., Draz, S.O., 2013. Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments of the Mediterranean: assessment and source recognition of petroleum hydrocarbons. *Environ. Monit. Assess.* 185, 4571–4589.
- Folk, R.L., Ward, W.C., 1957. Brazos River bar: a study in the significance of grain size parameters. *J. Sedimentary Petrol.* 27, 3–26.
- Garrigues, P., Budzinski, H., Manitz, M.P., Wise, S.A., 1995. Pyrolytic and petrogenic inputs in recent sediments: a definitive signature through phenanthrene and chrysene compound distribution. *Polycyclic Aromat. Compd.* 7, 275–284.
- Ghannem, N., Azri, C., Serbaji, M.M., Yaich C., 2011. Spatial Distribution of Heavy Metals in the Coastal Zone of “Sfax-Kerkennah” Plateau, Tunisia. *Environ. Progr. Sustain. Ener.* 30, 21–233.
- Gogou, A., Bouloubassi, I., Stephanou, E.G., 2000. Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. *Mar. Chem.* 68, 265–282.
- Gonul, L.T., Kucuksezgin, F., 2012. Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments from the Eastern Aegean: assessment and source recognition of petroleum hydrocarbons. *Environ. Sci. Pollut. Res.* 19, 31–41.
- Grimalt, J., Albaiges, J., Al Saad, H.T., Douabul, A.A.Z., 1985. n-Alkane distributions in surface sediments from the Arabian Gulf. *Naturwissenschaften* 72, 35–37.

- Guerra, R., 2012. Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls and Trace Metals in Sediments from a Coastal Lagoon (Northern Adriatic, Italy). *Water Air Soil Pollut.* 223, 85–98.
- Guigue, C., Tedetti, M., Giorgi, S., Goutx, M., 2011. Occurrence and distribution of hydrocarbons in the surface microlayer and subsurface water from the urban coastal marine area off Marseilles, Northwestern Mediterranean Sea. *Mar. Pollut. Bull.* 62, 2741–2752.
- Harji, R.R., Yvenat, A., Bhosle, N.B., 2008. Sources of hydrocarbons in sediments of the Mandovi estuary and the Marmugoa harbour, west coast of India. *Environ. Int.* 34, 959–965.
- Illou, S., 1999. Impact des rejets telluriques d'origines domestiques et industrielles sur les environnements côtiers : cas du littoral nord de la ville de Sfax (Tunisie). Ph.D. thesis, Faculté des Sciences de Tunis.
- Institut National de la Météorologie de Tunisie (INM), 2008. Données climatiques et statistiques annuelles des vents. *Rapports Annuels (1981–2004)*, 118pp.
- Jedoui, Y., 1980. Etude hydrologique et sédimentologique d'une lagune en domaine méditerranéen: Le bahiret el Boughrara (Tunisie). PhD thesis. Université de Bordeaux I, 190 pp.
- Kanzari, F., Syakti, A.D., Asia, L., Malleret, L., Mille, G., Jamoussi, B., Abderrabba, M., Doumenq, P., 2012. Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc river and the Berre lagoon, France. *Environ. Sci. Pollut. Res.* 19, 559–576.
- Kapsimalis, V., Panagiotopoulos, I.P., Talagani, P., Hatzianestis, I., Kaberi, H., Rousakis, G., Kanellopoulos, T.D., Hatiris, G.A., 2014. Organic contamination of surface sediments in

- the metropolitan coastal zone of Athens, Greece: Sources, degree, and ecological risk. Mar. Pollut. Bull. 80, 312–324.
- Katlane, R., Bergès, J.-C., Beltrando, G., Zargouni, F., 2014. Recent dynamics of submerged shoals and channels around the Kerkennah archipelago (Tunisia) from LANDSAT TM and MODIS. Proceedings for the 2nd Inter. Conf. Water resources and wetlands, 11-13 Sept, Tulcea (Romania), p. 361-365.
- Katsoyiannis, A., Breivik, K., 2014. Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. Environ. Pollut. 184, 488–494.
- Katsoyiannis, A., Terzi, E., Cai, Q.-Y., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? Chemosphere 69, 1337–1339.
- Ke, L., Wong, Y.S., Tam, N.F.Y., 2004. Determination of polycyclic aromatic hydrocarbons in mangrove sediments: Comparison of two internal standard surrogate methods and quality-control procedures. Int. J. Environ. An. Ch. 84, 661–675.
- Kennish, M.J., 1992. Poly-nuclear aromatic hydrocarbons. Ecology of estuaries: anthropogenic effects. Boca Raton: CRC Press, p. 133–181.
- Kessabi, K., Annabi, A., Hassine, A.I., Bazin, I., Mnif, W., Said, K., Messaoudi, I., 2013. Possible chemical causes of skeletal deformities in natural populations of *Aphanius fasciatus* collected from the Tunisian coast. Chemosphere 90, 2683–2689.
- Khairy, M.A., Kolb, M., Mostafa, A.R., EL-Fiky, A., Bahadir, M., 2009. Risk assessment of polycyclic aromatic hydrocarbons in a Mediterranean semi-enclosed basin affected by human activities (Abu Qir Bay, Egypt). J. Hazard Mater. 170, 389–397.

- Kucuksezgin, F., Pazi, I., Gonul, L.T., 2012. Marine organic pollutants of the Eastern Aegean: Aliphatic and polycyclic aromatic hydrocarbons in Candarli Gulf surficial sediments. *Mar. Pollut. Bull.* 64, 2569–2575.
- Kucuksezgin, F., Pazi, I., Gonul, L.T., Duman, M., 2013. Distribution and sources of polycyclic aromatic hydrocarbons in Cilician Basin shelf sediments (NE Mediterranean). *Mar. Pollut. Bull.* 71, 330–335.
- La Rocca, C., Conti, L., Crebelli, R., Crochi, B., Iacovella, N., Rodriguez, F., Turrio-Baldassarri, L., Di Domenico, A., 1996. PAHs content and mutagenicity of marine sediments from the Venice lagoon. *Ecotoxicol. Environ. Safety* 33, 236–245.
- Leventhal, J.S., 1983. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. *Geochim. Acta.* 47, 133–137.
- Li, G., Xia, X., Yang, Z., Wang, R., Voulvoulis, N., 2006. Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ. Pollut.* 144, 985–993.
- Lipiatou, E., Saliot, A., 1991a. Fluxes and transport of anthropogenic and natural polycyclic aromatic-hydrocarbons in the western Mediterranean Sea. *Mar. Chem.* 32, 51–71.
- Lipiatou, E., Saliot A., 1991b. Hydrocarbon contamination of the Rhone delta and western Mediterranean Sea. *Mar. Pollut. Bull.* 22, 297–304.
- Lipiatou, E., Tolosa, I., Simo, R., Bouloubassi, I., Dachs, J., Marti, S., Sicre, M.A., Bayona, J.M., Grimalt, J.O., Saliot, A., Albaigés, J., 1997. Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea. *Deep Sea Res. Part 2 Top. Stud. Oceanogr.* 44, 881–905.
- Liu, Y., Ling, C.N., Zhao, J.F., Huang, Q.H., Zhu, Z.L., Gao, H.W., 2008. Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environ. Pollut.* 154, 298–305.

- Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects with ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manage.* 19, 81–97.
- Louati, A., 2003. Etude de la contamination par hydrocarbures des sédiments de la région de Sfax (Tunisie). Phd Thesis. Université de Sfax et de Université Pierre et Marie Curie. Paris, 139 pp.
- Louati, A., Elleuch, B., Kallel, M., Oudot, J., Saliot, A., Dagaut, J., 2001. Hydrocarbon contamination of coastal sediments from the Sfax area (Tunisia), Mediterranean Sea. *Mar. Pollut. Bull.* 42, 445–452.
- Louiz, I., Kinani, S., Gouze, M.E., Ben-Attia, M., Menif, D., Bouchonnet, S., Porcher, J.M., Ben-Hassine, O.K., Aït-Aïssa, S., 2008. Monitoring of dioxin-like, estrogenic and anti-androgenic activities in sediments of the Bizerta lagoon (Tunisia) by means of in vitro cell-based bioassays: contribution of low concentrations of polynuclear aromatic hydrocarbons (PAHs). *Sci. Tot. Environ.* 402, 318–329.
- Magi, E., Bianco, R., Ianni, C., Di Carro, M., 2002. Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environ. Pollut.* 119, 91–98.
- Mandalakis, M., Polymenakou, P.N., Tselepides, A., Lampadariou, N., 2014. Distribution of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and organochlorinated pollutants in deep-sea sediments of the southern Cretan margin, eastern Mediterranean Sea: A baseline assessment. *Chemosphere* 106, 28–35.
- Martínez-Lladó, X., Gibert, O., Martí, V., Díez, S., Romo, J., Bayona, J.M., De Pablo, J., 2007. Distribution of polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in Barcelona harbour sediments and their impact on benthic communities. *Environ. Pollut.* 149, 104–113.

- Mazurek, M.A., Simoneit, B.R.T., 1984. Characterization of biogenic and petroleum-derived organic matter in aerosols over remote rural and urban areas. In: L.H. Keith (Ed.). *Identification and Analysis of Organic Pollutants in Air*. Ann Arbor Science/Butterworth. Boston. pp. 353–370.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 144, 289–302.
- Mille, G., Asia, L., Guiliano, M., Malleret, L., Doumenq, P., 2007. Hydrocarbons in coastal sediments from the Mediterranean sea (Gulf of Fos area, France). *Mar. Pollut. Bull.* 54, 566–575.
- Monoley, C.L., Field, J.G., 1991. Modelling carbon and nitrogen flows in a microbial plankton community, In: P.C. Reid et al. (Ed.), *Protozoa and their role in marine processes*, Springer, 443–474.
- Muller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effects of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* 41, 765–776.
- Muller, P.J., Stress, E., 1979. Productivity, sedimentation rate and sedimentary carbon content in the oceans, 1- Organic carbon preservation. *Deep Sea Res.* 26A, 1347–1362.
- Mzoughi, N., Chouba, L., 2011. Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *J. Environ. Monit.* 13, 689–698.
- Neff, J.M., 1979. Polycyclic aromatic hydrocarbons in the aquatic environment sources, fates and biological effects. Applied Science Publishers, LTD, London, p. 262.

- Neşer, G., Kontas, A., Unsalan, D., Altay, O., Darılmaz, E., Uluturhan, E., Küçüksezgin, F., Tekoğul, N., Yercan, F., 2012. Polycyclic aromatic and aliphatic hydrocarbons pollution at the coast of Aliğa (Turkey) ship recycling zone. *Mar. Pollut. Bull.* 64, 1055–1059.
- Notar, M., Leskovšek, H., Faganeli, J., 2001. Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. *Mar. Pollut. Bull.* 42, 36–44.
- Papadopoulou, D., Samara, C., 2002. Polycyclic aromatic hydrocarbon contamination and Lumistox (R) solvent extract toxicity of marine sediments in the North Aegean Sea, Greece. *Environ. Toxicol.* 17, 556–566.
- Parinos, C., Gogou, A., Bouloubassi, I., Pedrosa-Pàmies, R., Hatzianestis, I., Sànchez-Vidal, A., Rousakis, G., Velaoras, D., Krokos, G., Lykousis, V., 2013. Occurrence, sources and transport pathways of natural and anthropogenic hydrocarbons in deep-sea sediments of the eastern Mediterranean Sea. *Biogeosciences* 10, 6069–6089.
- Pavoni, B., Mecozzi, M., Berto, D., Ausili, A., Romano, E., Amici, M., Zharova, N., Amato, E., 2003. Environmental pollutants and organic carbon content in sediments from an area of the Moroccan Mediterranean Coast. *Toxicol. Environ. Chem.* 84, 53–67.
- Peters, K.E., Watters, C.C., Moldown, J.W., 2005. *The Biomarker Guide*, 2nd edn. Cambridge University Press, Cambridge UK.
- Prahl, F.G., Carpenter, R., 1983. Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediments. *Geochim. Cosmochim. Acta* 47, 1013–1023.
- Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.-P., Catinni, C., Mee, L.D., 2002. Petroleum and PAH contamination of the Black Sea. *Mar. Pollut. Bull.* 44, 48–62.

- Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., 1991. The biogeochemistry of Ellesmere Lake, UK-I: source correlation of leaf wax inputs to the sedimentary lipid record. *Org. Geochem.* 17, 901–912.
- Roose, P., Brinkman, U.A.Th., 2005. Monitoring organic microcontaminants in the marine environment: principles, programmes and progress. *Trends Anal. Chem.* 24, 897–926.
- Sadouni-Barbedette, N., 2002. Contribution à l'étude de la biogéochimie de la mer Noire nord-ouest: approche par les biomarqueurs. Thèse de l'Université Pierre et Marie Curie, Paris, p. 235.
- Sammari, C., Koutitonsky, V.G, Moussa, M., 2006. Sea level variability and tidal resonance in the Gulf of Gabes, Tunisia. *Continental Shelf Res.* 26, 338–350.
- Serbaji, M.N., 2000. Utilisation d'un S.I.G. multi-sources pour la compréhension et la gestion intégrée de l'écosystème côtier de la région de Sfax (Tunisie). Ph.D. Thesis, University of Tunis II, p. 227.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere–II.* Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16, 2139–2159.
- Simpson, C.D., Mosi, A.A., Cullen, W.R., Reimer, K.J., 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. *Sci. Total Environ.* 181, 265–278.
- Soclo, H.H., Garrigues, P.H., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar. Pollut. Bull.* 40, 387–396.
- Sporstol, S., Gjøs, N., Lichtenthaler, R.G., Gustaren, K.O., Urdal, K., Orelid, F., Skel, J., 1983. Source identification of aromatic hydrocarbons in sediments using GC/MS. *Environ. Sci. Technol.* 17, 282–286.

- Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbor (southern Italy). *Chemosphere* 67, 998–1009.
- ten Haven, H.L., 1996. Applications and limitations of Mango's light hydrocarbon parameters in petroleum correlation studies. *Org. Geochem.* 24, 957–976.
- The MerMex Group, 2011. Marine ecosystems responses to climatic and anthropogenic forcings in the Mediterranean. *Prog. Oceanogr.* 91, 97–166.
- Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119.
- Tolosa, M., Bayona, O.M., Albaigés, O., 1996. Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in Northwestern Mediterranean sediments: Spatial and temporal variability, fluxes, and budgets. *Environ. Sci. Technol.* 30, 2495–2503.
- Tolun, L., Martens, D., Okay, O.S., Schramm, K.W., 2006. Polycyclic aromatic hydrocarbon contamination in coastal sediments of the Izmit Bay (Marmara Sea): case studies before and after the Izmit Earthquake. *Environ. Int.* 32, 758–765.
- Trabelsi, S., Driss, M.R., 2005. Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. *Mar. Pollut. Bull.* 50, 344–359.
- Troupin, C., Barth, A., Sirjacobs, D., Ouberdous, M., Brankart, J.-M., Brasseur, P., Rixen, M., Alvera Azcarate, A., Belounis, M., Capet, A., Lenartz, F., Toussaint, M.-E., & Beckers, J.-M., 2012. Generation of analysis and consistent error fields using the Data Interpolating Variational Analysis (Diva). *Ocean Model.* 52–53, 90–101.

- Tsapakis, M., Dakanali, E., Stephanou, E.G., Karakassis, I., 2010. PAHs and n-alkanes in Mediterranean coastal marine sediments: aquaculture as a significant point source. *J Environ Monit.* 12, 958–963.
- UNEP/IOC/IAEA. 1992. Determination of petroleum hydrocarbons in sediments. Reference Methods for Marine Pollution Studies 20, UNEP, 75 pp.
- Venturini, N., Tommasi, L.R., Bicego, M.C. and Martins, C.C., 2004. Characterization of the Benthic Environment of a Coastal Area Adjacent to an Oil Refinery, Todos os Santos Bay (NE-Brazil). *Brazilian Journal of Oceanography* 52, 39–50.
- Viguri, J., Verde, J., Irabien, A., 2002. Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay. Northern Spain. *Chemosphere* 48, 157–165.
- Volkman, J.K., Holdsworth, D.G., Neil, G.P., Bavor Jr., H.J., 1992. Identification of natural anthropogenic and petroleum hydrocarbons in aquatic sediments. *Sci. Tot. Environ.* 112, 203–219.
- Wang, Z., Fingas, M., Landriault, M., Sigouin, L., Feng, Y., Mullin, J., 1997. Using systematic and comparative analytical data to identify the source of an unknown oil on contaminated birds. *J. Chromatogr. A* 775, 251–265.
- Wang, Z., Fingas, M., Page, D.S., 1999. Oil spill identification. *J. Chromatogr. A* 843, 369–411.
- Wilcke, W., Krauss, M., Amelung, W., 2002. Carbon isotope signature of polycyclic aromatic hydrocarbons (PAHs): evidence for different sources in tropical and temperate environments? *Environ. Sci. Technol.* 36, 3530–3535.
- Witt, G., Trost, E., 1999. Polycyclic aromatic hydrocarbon (PAHs) in sediment of the Baltic Sea and of the German coastal waters. *Chemosphere* 38, 1603–1614.

- Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. *Mar. Pollut. Bull.* 48, 1016–1030.
- Xia, X., Wang, R., 2008. Effect of sediment particle size on polycyclic aromatic hydrocarbon biodegradation: importance of the sediment-water interface. *Environ. Toxicol. Chem.* 27, 119–125.
- Yu, Y., Li, Y., Guo, Z., Zou, H., 2016. Distribution and sources of n-alkanes in surface sediments of Taihu Lake, China. *Archives of Environmental Protection* 42, 49–55.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A., 2007. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea. *Mar. Chem.* 105, 70–89.
- Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A., Sayadi, S., 2014. Evaluation of hydrocarbon pollution in marine sediments of Sfax coastal areas from the Gabes Gulf of Tunisia, Mediterranean Sea. *Environ. Earth. Sci.* DOI 10.1007/s12665-013-3023-6.
- Zaghden, H., Louati, A., Kallel, M., Elleuch, B., Saliot, A., Oudot, J., 2005. Hydrocarbons in surface sediments from the Sfax coastal zone, (Tunisia) Mediterranean Sea. *Mar. Pollut. Bull.* 50, 1287–1294.
- Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., Wang, X., 2008. Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ. Pollut.* 153, 594–601.
- Zrafi-Nouira, I., Safi, N.M.D., Bahri, R., Mzoughi, N., Aissi, A., Ben Abdennebi, H., Saidane-Mosbahi, D., 2010. Distribution and Sources of Polycyclic Aromatic

Hydrocarbons around a Petroleum Refinery Rejection Area in Jarzouna-Bizerte (Coastal Tunisia). *Soil and Sediment Contamination: An International Journal* 19, 292–306.

Zrafi, I., Hizem, L., Chalhmi, H., Ghrabi, A., Rouabhia, M., Saidane-Mosbahi, D., 2013.

Aliphatic and Aromatic Biomarkers for Petroleum Hydrocarbon Investigation in Marine Sediment. *J. Pet. Sci. Res.* 2, 145–155.

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.

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 <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		34°46'00"N, 10°54'57"E	7.6	Muddy sand	7
R105		34°45'05"N, 10°55'25"E	9.5	Dense meadows of <i>Posidonia</i>	8
R106		34°44'08"N, 10°55'50"E	8.5	Sandy with <i>Posidonia</i>	9
R107		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	
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	

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).
25

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)
	<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	
	ΣLMW/ΣHMW	> 1	< 1	Soclo et al. (2000); Zhang et al. (2008)
	ΣMePhe/Phe	> 2	< 2	
	ΣMePyr/Pyr	> 1	< 1	Zaghden et al. (2007; 2014)
	Flt/Flt+Pyr	< 0.4	> 0.4	
		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 ($\delta^{13}\text{C}$ in ‰), and concentrations in total *n*-alkanes (*R* in $\mu\text{g g}^{-1}$ 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 (0-1 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
$\delta^{13}\text{C}$ (‰)	-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

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.

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.

38

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)
	Khniiss 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	Bouzid 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).

41

	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 Salot (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)
	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 < ERL	Stations ERL-ERM	Stations > ERM
	ERL	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	-	-	-
ΣLMW	552	3,160	31-1,167 ^b	R101-R111, R205-R210	R201-R204	-
ΣHMW	1,700	9,600	140-8,306 ^b	R101-R110, R204-R210	R111, R201-R203	-
ΣPAHs	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 (ΣMe): 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	
Σ17 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	
Σ17 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	
Σ17 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 2

Figure 3

Figure 4