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ORIGINAL ARTICLE

Evaluation of hydrocarbon pollution in marine sediments of Sfax coastal areas from the Gabes Gulf of Tunisia, Mediterranean Sea

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Abstract The Tunisian environmental legislation that follows the EC Directives requires monitoring of persistent, toxic and bio-accumulated substances commonly considered as hazardous substances. In order to comply with this requirement, samples of sea water, sediment and biota from the urbanized and industrialized coast line of Sfax city are investigated. This study presents the results of petroleum hydrocarbon content, distribution and probable origin (anthropogenic and/or biogenic) in 16 intertidal sediments of Sfax coastal area. Alkane distribution indices and hydrocarbon distribution patterns are used to identify natural and anthropogenic input. Non-aromatic hydrocarbons present a high concentration with a range varying from 180 to 1,400 µg/g of dry sediment. The total concentrations of polycyclic aromatic hydrocarbons (PAHs) varied from 0.41 to 5.6 µg/g dry weight. These concentrations are comparable to other marine areas that receive important inputs. *n*-Alkanes with carbon number ranging from 15 to 35 are identified to be derived from both biogenic and anthropogenic sources in varying proportions. Pristane/phytane ratio shows values lower than 1.4 suggesting the presence of petroleum contamination. This is confirmed by the presence of a large group of unresolved complex mixture and the identification of hopanes with predominant C29 and C30 compounds and steranes with predominance of C27 over C28 and C29 compounds. Ratios of selected PAH concentrations indicate petrogenic and pyrolytic origin of hydrocarbons. Anthropogenic hydrocarbon inputs were more apparent at sites associated with industrial discharges, shipping activities and sewage outfalls.

Keywords Biomarkers · Petroleum contamination · Sediments · Sfax coastal area · South Mediterranean Sea

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Introduction

The Mediterranean Sea is among the most specific and vulnerable marine ecosystem on the earth. It is, therefore, likely that global change will affect this semi-enclosed basin more rapidly and intensively than the world ocean. In fact, many persistent and bio-accumulative chemicals are sources of serious health problems that affect people and the entire ecosystem.

Some authors have demonstrated the negative effects that hydrocarbon has on the ecosystem and, therefore, on marine biodiversity (Clark 1992). However, the presence of hydrocarbons does not necessarily indicate pollution, as these compounds may also have terrestrial (vascular plants) or marine (algae and/or phytoplankton) biogenic origin

(Colombo et al. 1989). Among hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) are a widespread class of environmental pollutants that are carcinogenic and mutagenic. They arise from the incomplete combustion of organic material, especially fossil fuels (pyrolytic origin), from the discharge of petroleum and its products (petrogenic origin) and from the post-depositional transformation of biogenic precursors (diagenetic origin). Terrestrial plant waxes, marine phytoplankton, volcanic eruptions, biomass combustion and natural oil seeps contribute natural inputs of hydrocarbons, including aliphatic and aromatic hydrocarbons (Saliot 2005).

For many decades, industrial, agricultural and urban wastes have been discharged into the Mediterranean Sea via coastal outfalls, rivers and the atmosphere. Consequently, this phenomenon causes a considerable increase in pollution and a progressive degradation of the marine ecosystem (Saliot 2005).

Anthropogenic origin hydrocarbons such as petroleum and its derived products are spilled into the environment as a result of some activities related to oil operation, petroleum transport, harbor activities, domestic and industrial effluents. PAHs have been determined worldwide in many environmental matrices and associated with the toxicity of marine sediment (Volpi Ghirardini et al. 1999; Macias-Zamora et al. 2002; Mai et al. 2002; Maskaoui et al. 2002; Eggleton and Thomas 2004; Illou 1999; Zaghden et al. 2005).

These endocrine-disrupting compounds are persistent in the environment and, therefore, both their accumulation on the sediments and possible remobilization, as well as their uptake by organisms, pose a significant threat of the aquatic life (Zaghden et al. 2007).

Furthermore, hydrocarbons of biogenic origin naturally occur at low concentrations in different substrates, such as water and sediment, and they are part of the natural hydrocarbon baseline of an ecosystem (Volpi Ghirardini et al. 1999). For this reason, it is imperative to investigate the origin and the distribution of hydrocarbons in the aquatic environment. In previous works, the determination of the complex assemblage of these hydrocarbons coming from various sources had been assessed (Macias-Zamora et al. 2002; Mai et al. 2002; Maskaoui et al. 2002; Eggleton and Thomas 2004).

In the south of Tunisia and the Mediterranean Sea, the industrialized region of Sfax, located in Gabes Gulf, is vulnerable and sensible due do its shallow area and its high ecological value characterized by an important biodiversity. Therefore, a lot of work is needed to study these specific systems to understand the common and specific processes taking place there and also to produce a background of information and data that shall be very useful for the sustainable management of this ecosystem (Illou 1999; Zaghden et al. 2005, 2007). This region, second city in Tunisia, is marked by a significant expansion of the urban land, and it also has important industrial and commercial activities. These activities generate an important chemical pollution. The impact of this anthropogenic pressure can be observed in summer with some phenomena of red waters resulting from eutrophication and disequilibrium process. In fact, it is necessary to study and quantify this chronic pollution that affects the coastal and marine ecosystem. As part of an ongoing investigation of Sfax coastal area, we have investigated 16 superficial sediment samples from sites throughout the coast for their hydrocarbon content, distribution and probable origin (anthropogenic and/or biogenic) of hydrocarbon.

Materials and methods

Study area and sampling

The area of this study concerns the coastline of Sfax city located in the southeast of Tunisia in the northern shore of Gabes Gulf (34°44′N, 10°46′E) in the southern Mediterranean Sea (Fig. 1). It is characterized by a shallow area and an important biodiversity with endemic seagrass *Posidonia oceanica*. This area is a sensible model site for hydrocarbon analysis. It is exposed to high entropic pressure due to its commercial harbor and the presence of intense maritime traffic. For many decades, the urban evolution of Sfax city has been marked by a significant expansion of the urban land which is characterized by an important harbor board, a fishing port and industrial activities. The main industries of the region are food processing, olive oil, soap, paint production, chemical and textile industries, pulp factories, metal and phosphate processing.

In this study, intertidal superficial sediment samples are collected from 16 sites that stretch to about 20 km along the coastal area of Sfax city. Eight superficial sediment samples are collected from the northern coast of Sfax and the other eight are collected from the southern coast of Sfax (Fig. 1; Table 1). This area is characterized by a high tide with +1.60 m and a low tide with +0.30 m. Samples are collected manually, at low tide in an area of 40 × 40 cm.

The first centimeter [Surficial sediments (0–5 cm)] of near shore sediments is removed by scraping with a clean spatula.

Chemical analysis

Sediments are freeze-dried immediately after collection. After elimination of largevegetal fragments, sediments are sifted to keep the fine fraction <63 μm. Approximately

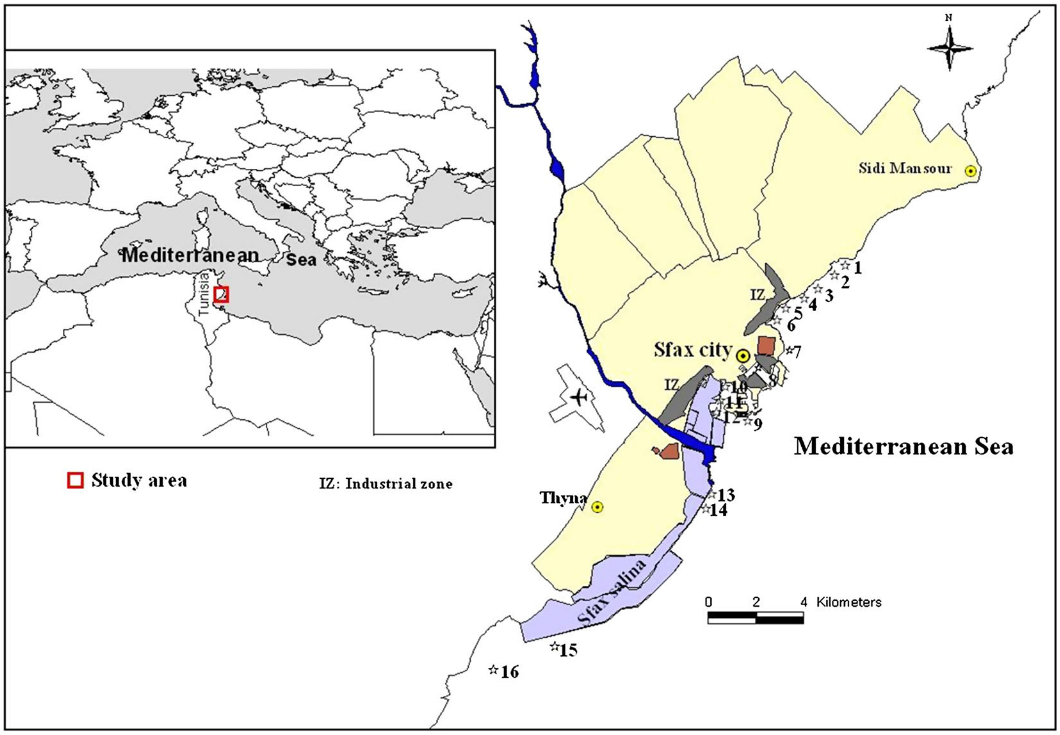

Fig. 1 Map of Sfax coast showing sampling locations

Table 1 Sample site description of Sfax costal area

Sample code	Sample site	Type of sediment
1–3	Northern coastal area of Sfax city, urban area (location name: Sidi Mansour)	Oozy fine grained sediment
4	North channel of Sfax city (run off and urban discharge); channel name: PK4	Fine grained sediment
5, 6	Industrial area	Oozy fine grained sand
7	Industrial area with phosphogypsum discharge (solid waste of fertilizer factory)	Oozy, muddy sediment
8	Commercial port	Muddy sediment
9	Fishing port	Fine grained sand
10–12	10: first site in front of the channel of industrial wastewaters (location name: Sidi Salem).	Oozy, muddy sediment
	11: second site in the front of the channel	
	12: third site in front of the channel	
13, 14	Effluents of urban wastewater station (average: 30,000 m^3/day) and fertilizer factory	Oozy, fine grained sand
15, 16	Southern costal area of Sfax city (location name: Thyna)	Fine-grained sand

30 g of each sediment is used for Soxhlet extraction for 12 h using a mixture of dichloromethane/methanol (2:1 v/v). The extraction of hydrocarbons yield is 90 ± 6 %. The lipid extracts are submitted to adsorption chromatography on a column (2 cm i.d., 20 cm length) filled with florisil (60 mesh). The florisil column elimination of highly polar compounds, resins and extracts obtained after precipitation asphaltenes. This results in a more purified fraction containing a mixture of neutral compounds (total hydrocarbons: alkanes, alkenes and aromatics). Total hydrocarbons are eluted with dichloromethane and polar compounds with methanol.

The amount of total hydrocarbons is determined by gravimetry and by Fourier transformed infrared spectroscopy (FT/IR) using a Nicolet apparatus (Madison, USA). The calibration is performed with the Ashtart crude oil produced in Sfax area and *n*-eicosene. The extract is concentrated by a rotary evaporator and fractioned by silica–alumina gel chromatography using a three-step scheme, providing three fractions:

- Non-aromatics (F1), elution with hexane,
- Aromatics (F2), elution with hexane/dichloromethane 4:1 v/v,
- Polar compounds (F3), elution with methanol.

Therefore, it seems more interesting to use the Soxhlet extractor than the ultrasonic method. Concentrations obtained for all PAHs with the Soxhlet extractor are equivalent to those recommended by IAEA for the reference material IAEA-408 (Mzoughi et al. 2002).

Fractions are evaporated to 150–200 µL under a stream of dry nitrogen. Aliphatic and alicyclic hydrocarbons (F1, data base of this study) are analyzed by a Delsi Model DI 200 gas chromatograph (Perichrom, France). The analysis is performed on a 50-m fused silica column (0.32 mm i.d.) coated with CPSil5-CB (0.25 µm film thickness). Helium at a flow rate of 1.5 mL/min (pressure 0.8 kPa) is used as the carrier gas. The temperature of the column is ramped at 4 °C/min from 70 to 280 °C. Injector and detector temperature is held at 320 °C.

Detection is monitored by flame ionization detector (FID). Hydrocarbons are identified in comparison with retention time by those of known standards of *n*-alkanes ranging from *n*-C14 up to *n*-C35. The structure of several hydrocarbons is confirmed by gas chromatography/mass spectrometry (HP6890-HP5973MSD Agilent Technologies, Wilmington, DE, USA). The GC is used with a 30-m fused-silica column (0.25 mm i.d.) coated with 5 % phenyl methyl siloxane. Helium is used as the carrier gas at a flow rate of 1.4 mL/min. The following temperature program is used: 80–290 °C with ramping at 4 °C/min. The samples are injected in the splitless mode by a temperature injector of 280 °C. Analyses are run in the electron impact mode at 70 eV with a 2.9-s scan time over a 50–550 a.m.u. range resolution. Interpretation of GC/MS spectra is based on mass chromatogram at *m/z*: 191, 217, 218 and 249.

Evaluation indices

Diagnostic techniques such *n*-alkane indices, unresolved complex mixture (UCM) presence and *n*-alkane homologous series are used to help identify potential sources (biogenic and/or anthropogenic) of hydrocarbons. Carbon preference index (CPI) is used to to assess hydrocarbon origin. The carbon predominance index (CPI) represents the relative abundance of odd numbered linear alkanes in front of even numbered linear alkanes. This CPI is around 1 for the first four stations, which characterizes petroleum hydrocarbons (Le Dréau et al. 1997).

$$\mathrm{CPI} = \left(\sum n\mathrm{C17} + n\mathrm{C19} + \cdots + n\mathrm{C27}\right) \Big/ \left(\sum n\mathrm{C16} + n\mathrm{C18} + \cdots + n\mathrm{C26}\right)$$

The CPI has been frequently used as a source indicator of *n*-alkanes in marine sediments (Colombo et al. 1989). It represents the relative abundance of odd-numbered linear alkanes versus even-numbered linear alkanes. *n*-Alkanes derived from terrestrial vascular plant usually have CPI values ranging from 3 to 6, while petrogenic hydrocarbons show CPI values close to 1. Lower CPI indicates microbial sources of hydrocarbons (Blumer et al. 1963). Pristane/phytane (Pr/Ph), *n*-C17/Pr, *n*-C18/Ph and the ratio between unresolved complex mixture over resolved aliphatic hydrocarbons (U/R). For the aromatic fraction, ratios of selected PAH concentration are calculated.

Results and discussion

Extractible organic matter and hydrocarbons

Extractible organic matter (EOM) concentrations vary from 765 to 9,100 µg/g of sediment dry weight (Table 2).

Table 2 Characteristic of extractable organic matter and hydrocarbons in surface sediments of Sfax coastal area

Site and sample code	EOM (µg/g)	THC (µg/g)	THC (%)	NAH (F_1) (µg/g)	CPI	Pr/Ph	U/R
S_1	765	482	63	183	1.01	1.10	N.D
S_2	1,211	830	69	232	1.60	N.D	N.D
S_3	1,853	1,400	76	280	1.00	N.D	N.D
S_4	7,930	2,366	30	946	1.20	N.D	4.43
S_5	3,624	1,715	47	549	1.30	0.50	13.74
S_6	5,310	1,767	32	406	0.90	N.D	N.D
S_7	4,110	1,560	38	297	0.80	N.D	N.D
S_8	4,980	1,800	36	630	1.00	N.D	N.D
S_9	2,886	1,471	51	764	1.14	0.83	9.58
S_{10}	8,343	3,996	48	1,280	1.37	0.60	8.41
S_{11}	9,121	4,087	45	1,406	1.24	0.71	6.80
S_{12}	2,562	1,338	52	788	1.02	0.66	5.15
S_{13}	1,686	882	52	735	0.94	N.D	N.D
S_{14}	1,706	972	57	413	0.96	N.D	N.D
S_{15}	2,033	1,210	60	310	0.90	N.D	N.D
S_{16}	2,976	1,634	55	521	0.89	N.D	N.D

EOM extractable organic matter (µg/g dry weight) evaluated by gravimetry, *THC* total hydrocarbons (µg/g dry weight) evaluated by FT/IR, *THC (%)* total hydrocarbons relative to EOM, *NAH (F_1): NAH (F1)* non-aromatic hydrocarbon (µg/g dry weight) evaluated by FT/IR, *CPI* carbon preference index calculated between *n*-C15 and *n*-C31, *Pr/Ph* ratio of pristane to phytane, *U/R* ratio of unresolved complex mixture (*UCM*) to resolved aliphatic hydrocarbons, *N.D* not determined or not detected

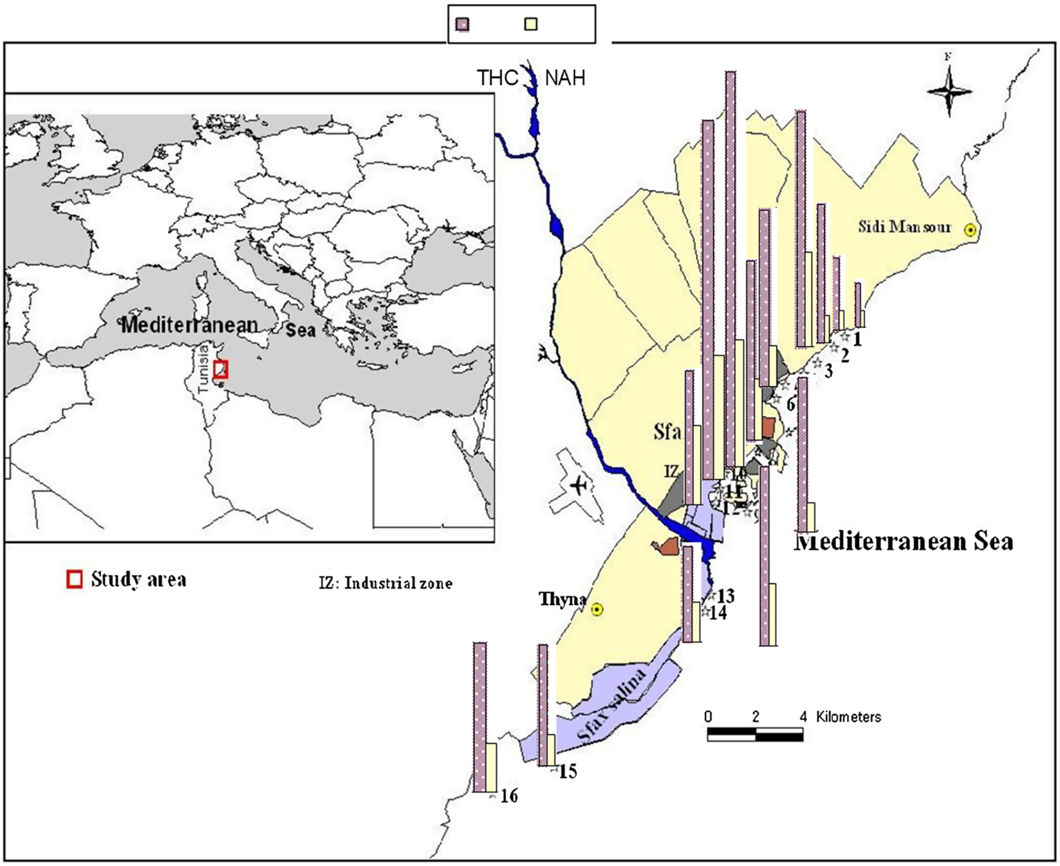

Fig. 2 Total hydrocarbon (*THC*) and non-aromatic hydrocarbon (*NAH*) concentrations of the surface sediment of Sfax coastal area

Total values obtained in this study are considered as the highest level in comparison with many studies of different regions in the world (Eggleton and Thomas 2004; Le Dréau et al. 1997; Maljevic and Balac 2007). The highest values of this area are found in the stations 4, 10 and 11 with an average 8,000 µg/g.

These concentrations correspond, respectively, to the first and second channel of urban and industrial discharge. The second group of concentration values of EOM is found in stations 5, 6, 7 and 8. These stations correspond to the industrial area and harbor port with values varying between 3,000 and 5,000 µg/g of sediment dry weight. The other stations located in the northern and the southern coastal present relatively less concentration of EOM. Therefore, the concentrations of total hydrocarbon (THC) and their relatively concentration to EOM show a significant result. The concentrations of THC are varying between 482 and 4,087 µg/g (Table 2). The low proportion of THC varying between 30 and 50 % of EOM is found in stations 4, 5, 6, 7, 10 and 11 corresponding to the stations with a high concentration of EOM. This is in relation to the sites' location in front of the channel and to the industrial area with important organic discharge. The accumulated pollution has difficult dispersion and dilution in this shallow area. The south area is more polluted than the north area. The highest values are found in front of the southern channel (location name Sidi Salem) with an average of 4,000 µg/g and in front of the northern channel (location name PK4) with 2,366 µg/g.

n-Alkanes and isoprenoid hydrocarbon

Non-aromatic (or aliphatic and alicyclic) hydrocarbons (NAH) present a high concentration with a range varying from 180 to 1,400 µg/g of dry sediment (Table 2). Comparable to the THC, the two channels of Sfax area show the highest values on NAH with an average proportion to THC of around 35 % (Fig. 2). The high proportion (83 %) of NAH to THC is found at station 13 that is characterized by the effluents of urban wastewater and fertilizer factory. These concentrations are generally high compared with other marine areas that receive important anthropogenic inputs such as Hon Kong (Gao et al. 2008), Patagonia, Argentina (Zheng and Richardson 1999), Bay of Fort de France (Commendatore et al. 2000), Tianjin, China (Mille et al. 2006) and Todos os Santos Bay, Brazil (Bixiong et al. 2007).

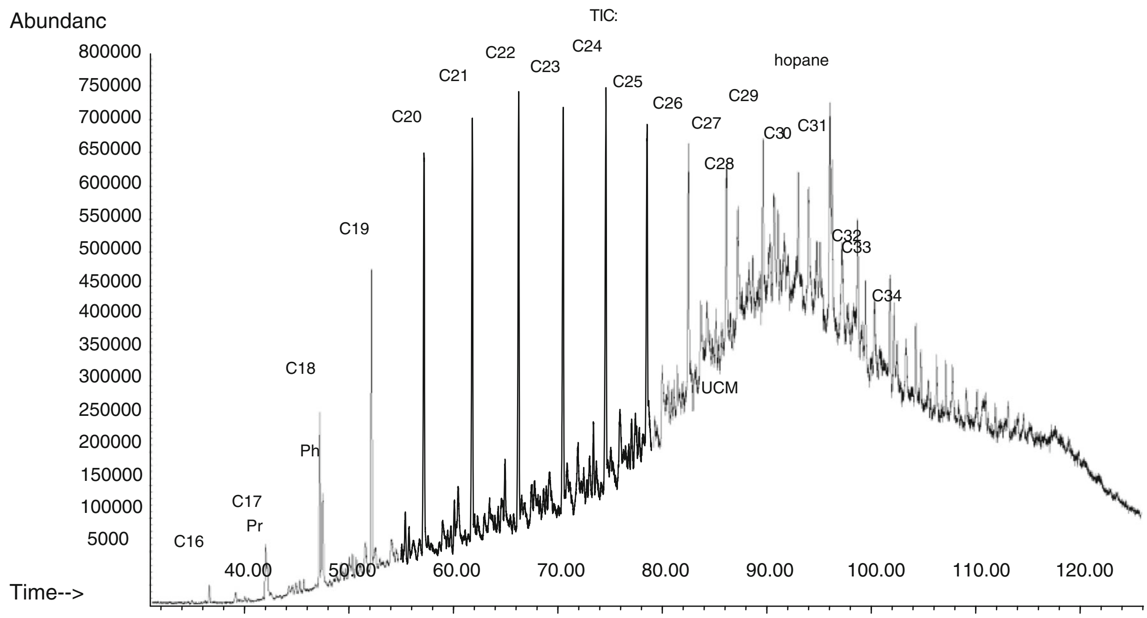

Fig. 3 Gas chromatogram of aliphatic and alicyclic hydrocarbons of surface sediment at site 10. *S* sulfur compound; *Pr* pristine; *Ph* phytane; *C* thiosterane; *UCM* unresolved complex mixture (Zaghden et al. 2007)

GC traces of NAH of samples from Sfax coastal sediments show comparable patterns as illustrated by sample 10 in Fig. 3. The *n*-alkanes range from C15 to C32 without predominance of odd/even carbon numbered chains. Petroleum usually shows a wide distribution range of *n*-alkanes and the even/odd shows no predominance. In contrast, in most plant waxes, odd-chain alkanes are 8–10 times more abundant than even-chain *n*- alkanes (Venturini et al. 2008).

Compared with *n*-alkanes, UCM is more resistant to biodegradation and it has a greater tendency to remain and to accumulate in the environment (Volkman et al. 1992). Unresolved complex mixture/sum of the resolved aliphatic hydrocarbons (U/R) index is used as a criterion to assess the anthropogenic input and to estimate the relative degradation degree. Some researchers suggest that a U/R value $\geq$2 reflects significant contamination by petroleum products (Aboul-Kassim and Simoneit 1995), while others suggest that U/R value >1 can be taken as a threshold of such significant contamination (Simoneit 1986), whereas low values suggest fresh oil presence. The UCM magnitude is related to the degree of anthropogenic contribution. UCM presence is usually associated with petroleum hydrocarbons. It is suggested that UCM can result from bacterial degradation of organic matter (Aboul-Kassim and Williamson 2003). Anyway, the fact that most of the stations of Sfax show U/R higher than 2 indicates a high degree of anthropogenic contribution (Table 2). The CPI index of Sfax sediment ranges between 0.80 and 1.60 (Table 2) and indicates petrogenic hydrocarbons with a highly degraded organic matter (Venkatesan and Kaplan 1982). Therefore, the contribution of uncontaminated sediment and vascular plants ranges from 3 to 6 (Colombo et al. 1989).

Another useful indicator of hydrocarbons' origin is the ratio of isoprenoids pristine and phytane (Pr/Ph). The detection of a large number of aliphatic isoprenoid hydrocarbons in oils, coals, shale and dispersed organic materials is thought to be one of the most important discoveries in petroleum chemistry and organic geochemistry (Simoneit et al. 1991). Pristane and phytane are the two most abundant isoprenoid hydrocarbons and are identified in all samples of this study. These two compounds are considered to originate primarily from the phytyl side chain of chlorophylls during diagenesis. In uncontaminated recent sediments, phytane is practically absent and high pristane content can be derived from zooplankton and some other marine animals (Venturini et al. 2008), leading to the pristane/phytane (Pr/Ph) ratio higher than 1, typically between 3 and 5 (Wang et al. 2006). A Pr/Ph value close to 1 or lower than 1 suggests petroleum contamination (Blumer et al. 1963). The Pr/Ph ratios obtained from Sfax surface sediments are between 0.60 and 1.10 with an average of 0.73 indicating petroleum contaminations (Table 2).

In addition to their use as petroleum contamination markers, the Pr/*n*-C17 and Ph/*n*-C18 ratios are often used to evaluate relative biodegradation of *n*-alkanes (Mai et al. 2002). Comparatively, isoprenoid hydrocarbons are more resistant to biodegradation than *n*-alkanes. High values of

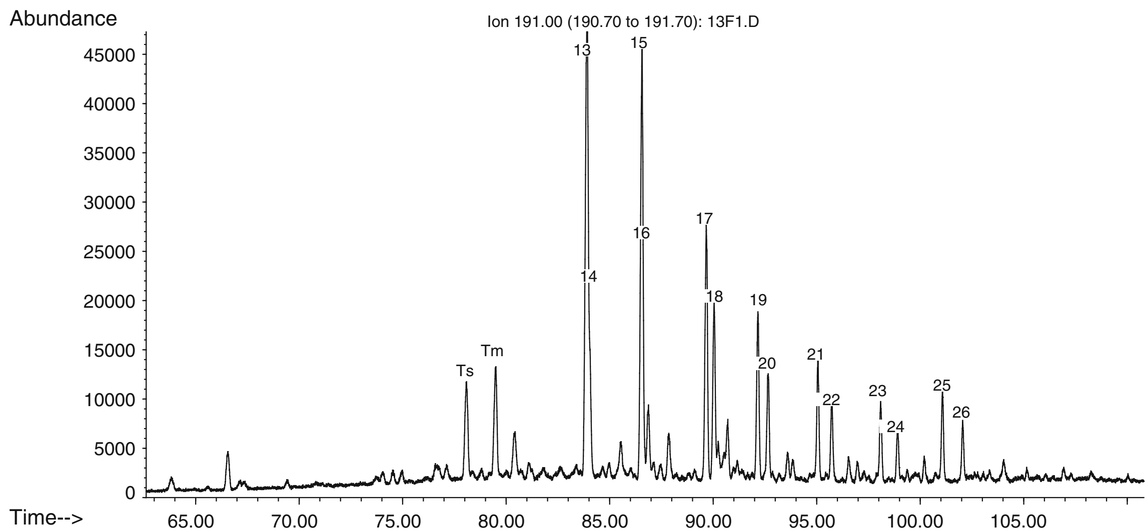

Fig. 4 Mass hromatogram of $m/z = 191$(hopanes) of Sfax sediment at site 10. *Ts* 18α(H)22,29,30-tris-norhopanes; *Tm* 17α(H) 22,29,30-tris-norhopanes; *13* 17α(H), 21β(H), 30-norhopane; *14* 18α(H)-30-norneohopane; *15* 17α(H), 21β(H)-hopane; *16* 17α(H)-30-nor-29-homohopane; *17* 17α(H), 21β(H)-homohopane(22S); *18* 17α(H), 21β(H)-homohopane(22R); *19* 17α(H), 21β(H)-bishomohopane(22S); *20* 17α(H), 21β(H)-bishomohopane(22R); *21* 17α(H), 21β(H)-trishomohopane(22S); *22* 17α(H), 21β(H)-trishomohopane (22R); *23* 17α(H), 21β(H)-tetrakishomohopane(22S); *24* 17α(H), 21β(H)-tetrakishomohopane(22R); *25* 17α(H), 21β(H)-pentakishomohopane(22S); *26* 17α(H), 21β(H)-pentakishomohopane(22R)

these indices suggest the presence of degraded oil, while lower indices suggest low degradation (Steinhauer and Boehm 1992). When hydrocarbon concentrations are also high, lower indices indicate fresh oil inputs (Colombo et al. 1989). Petroleum contamination in Sfax coastal sediments is relatively fresh with both ratios (Pr/*n*-C17 and Ph/*n*-C18) around to 1. These ratios determined in the stations (4, 5, 9, 10 and 11) show values between 0.59 and 0.8 for Pr/*n*-C17 and 0.36 and 1.25 for Ph/*n*-C18. The distribution of Pr/*n*-C17, Ph/*n*-C18 and Pr/Ph ratios for all sample sites shows a common petroleum contamination source in Sfax coastal area (Table 2).

Hopanes and steranes

Alicyclic hydrocarbons are known to be more resistant to biodegradation than aliphatic hydrocarbons. Hopanes and steranes are representatives of these compounds and are considered as petroleum biomarkers. They can be used as source and/or maturity indicators to identify the nature of the fossil materials from which petroleum originates (González-Vila et al. 2003). Such molecules are characterized by their restricted occurrence, source specificity, molecular stability and suitable concentration of analytical detection (Scholz-Böttcher et al. 2008). The majority of the shelf surface sediment yields a complex hopane and sterane. These compounds are converted from corresponding biogenic precursors, and they exist as many stereoisomers with different α/β and/or R/S configurations that have different thermodynamic stability. During sedimentary burial, the thermodynamically unstable isomers are gradually replaced by the 35 geologically stable isomers reaching a known equilibrium point and providing a measure of the maturity of organic matter (Simoneit and Mazurek 1982; Seifert and Moldowan 1986). These processes are a combination of a series of bacteriological actions and low-temperature reactions generally referred to as diagenesis, catagenesis and metagenesis (Simoneit et al. 1991).

Figures 4 and 5 show, respectively, the representative mass fragmentograms of *m/z* 191 (hopane) and 217 (sterane) of non-aromatic hydrocarbon fraction from Sfax surface sediment at site 10. A series of C27–C35 hopanes are identified in all sediment samples. In Sfax surface sediment two hopanes with 29 and 30 carbon atoms with configuration 17α(H), 21β(H) are found as predominant in these series. Hopanes with the 17α, 21β-configuration in the range of 27–35 carbon atoms are characteristic of petroleum because of their greater thermodynamic stability compared with other epimeric series (Peters and Moldowan 1991).

Steranes in sediment or oil are derived from the transformation of biological sterol precursors. In general, C27 and C29 steranes are indicative of algae and higher plant source of organic matter, respectively. So, the ratio of C27/C29 steranes >1 specifies the predominance of organic matter input from marine algae, while when <1 it indicates a preferential higher plant input (Wang et al. 2006; Peters and Moldowan 1993). In Sfax surface sediment, the ratio of C27/C29 is higher than 1 indicating an abundance of organic matter and marine origin of the petroleum products.

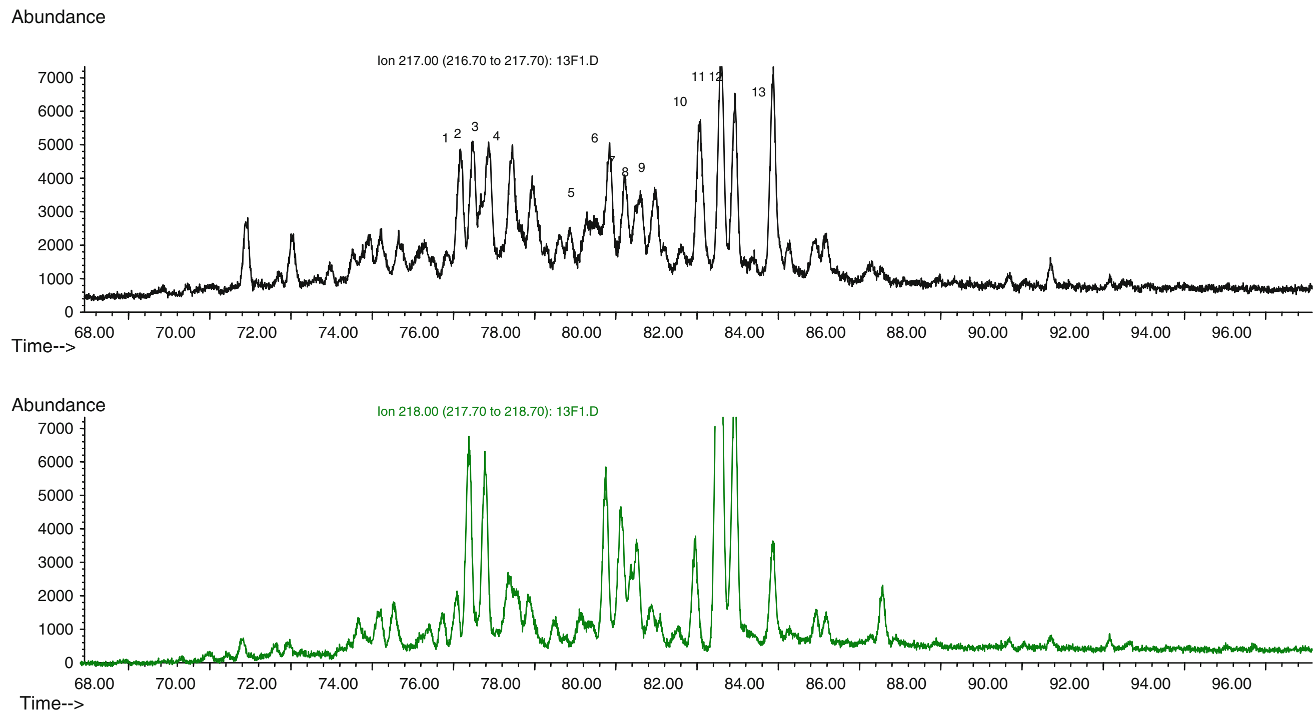

Fig. 5 Mass chromatogram of $m/z = 217$ (steranes) and $m/z = 218$ (diasteranes) of Sfax sediment at site 10. *1* C27ααα-cholestane(20S); *2* C27αββ-cholestane(20R); *3* C27αββ-cholestane(20S); *4* C27ααα-cholestane(20R); *5* C28ααα-ergostane(20S); *6* C28αββ-ergostane (20R); *7* C28αββ-ergostane(20S); *8* C28ααα-ergostane(20R); *9* C29ααα-stigmastane(20S); *10* C29αββ-stigmastane(20R); *11* C29αββ-stigmastane(20S); *12* C29ααα-stigmastane(20R)

Table 3 Individual and total concentrations of the PAHs (ng/g) and ratios for origin identification for the sediments collected in Sfax coastal zone

Site	S_7	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}
Naphthalene	nd	nd	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	89.7	39.2	205.7	19.7	25.5	13.9	9.9	28.5	8.5
∑Methylphenanthrenes	786.4	155.1	681.8	29.5	96.8	98.3	132.8	312.7	101 5
Anthracene	70.5	nd	30.4	nd	nd	nd	nd	32.7	nd
∑Methylanthracenes	296.1	nd	nd	nd	130.2	nd	39	99.7	53.5
Thiophene	300.9	25.1	169.3	12.9	28.4	nd	nd	110.9	22.4
Fluoranthene	251.6	22.8	71.4	15.6	15.2	nd	nd	106.6	56.2
Pyrene	875.9	54.1	56.4	65.6	221.8	82.7	42.5	233.2	127.4
∑Methylpyrene	1,030.5	128.3	258.2	124.5	59.4	23.2	50.5	372.7	126.4
benzo[k]fluoranthene	186.1	50.2	153.9	146.7	32.1	105.7	31.8	121.3	126.8
Chrysene	623.1	63.9	138.6	188.3	302	72.1	50.4	175.1	77.5
∑Methylchrysene	784.1	43.1	128.1	188	nd	nd	81.4	178.6	74.5
Benzo[a]pyrene	nd	113	24.4	60.1	28.1	18.7	42.2	91.2	20.7
Perylene	232	68.9	86.2	52.7	30.8	64.3	22	32.1	51.1
benzo[a]anthracene	nd	nd	nd	nd	nd	36.4	nd	nd	32.9
benzo[ghi]perylene	151.5	46.8	97.6	90.8	14.8	26.2	34	73.5	44.2
Total PAHs	5,608.2	811.3	2,719.8	1,124.9	983.5	907.5	602.5	1,929	955.3
∑Methylphen/phen	8.76	4	3.3	1.5	3.8	7	13.4	11	11.9
∑Methylpyrene/pyre	1.17	2.4	4.6	1.9	0.27	0.28	1.2	1.6	0.99
Fluoranthene/pyrene	0.28	0.59	1.26	0.23	0.07	nd	nd	0.46	0.44

PAH concentrations and compositions

Total PAH concentrations in sediments are reported as the sum of 16 priority PAHs. Ratios of selected PAH concentrations were used to study the possible sources of pollution. The total concentrations of PAH, determined in sediment from the southern coast of Sfax, ranged from 602.5 to 5608.2 ng/g dw (Table 3). Thyna bay and harbor of Sfax city present the highest concentrations in sediments from these sites. The use of ratios between alkyl substituted and unsubstituted PAH homologs provides information about their anthropogenic sources. Generally petrogenic hydrocarbons are characterized by the dominance of alkylated compounds over their parent homologs and by the dominance of low condensed (2–3 rings) PAHs over high condensed (4–6 rings) PAHs (De Luca et al. 2004). Four- and five-ring PAHs were the most abundant compounds in coast line of Sfax city sediments. On average, phenanthrene, fluorene, pyrene and chrysene were the most abundant PAH compounds in coast line of Sfax city, together accounting for 90 % of PAHs at these sites. The discharge of industrial wastewater and the emission of atmospheric particles might be the pyrolytic source in this study area. Values of ratio alkyl-substituted/parent compound are very high ranging from 1.5 to 13.4 for the phenanthrene series and from 0.28 to 1.56 for the pyrene series (Table 3). Thus, PAH compositional patterns and diagnostic ratios reflect a mixture of both petrogenic and pyrolytic sources in most of the sampling sites in sediments of Sfax coastal area.

Conclusions

The study of sediment contamination by hydrocarbons from the coastal area of Sfax indicates that hydrocarbon levels are generally high compared with other maritime areas. Anthropogenic hydrocarbon inputs are more apparent at sites associated with industrial discharges, shipping activities and sewage outfalls. Therefore, the concentrations of total hydrocarbon (THC) non-aromatic hydrocarbon (NAH) and PAH are relatively high near the urban area, whereas the concentrations of these compounds decrease going further from urban area in the north and the south of Sfax city. The sampling sites present CPI values, unresolved complex mixture/resolved aliphatic hydrocarbons (U/R) and pristine to phytane (Pr/Ph) ratios as indicative of petroleum products. Petroleum biomarkers (Hopanes and steranes) indicating higher maturity are found in all analyzed samples confirming the importance of oil inputs and its derivatives in this area. The PAH compositional patterns and diagnostic ratios reflect a mixture of both petrogenic and pyrolytic sources. The present study shows evidence of a common petroleum contamination source in Sfax coastal area. Future studies should include a more exhaustive evaluation of the impact of anthropogenic inputs. In addition, strict regulations are necessary to improve the environmental quality of this region and to avoid the impact of hydrocarbon contamination on fishing activities. This will contribute to the development of management and of control measures to preserve the coastal and marine environment of Gabes Gulf.

References

Aboul-Kassim TAT, Simoneit BRT (1995) Petroleum hydrocarbon fingerprinting and sediment transport assessed by molecular biomarker and multivariate statistical analyses in the Eastern Harbour of Alexandria, Egypt. Mar Poll Bull 30:63–73

Aboul-Kassim TAT, Williamson KJ (2003) Forensic analysis and genetic source partitioning model for portland harbor contaminated sediments. J Environ Infor 1:58–75

Bixiong Y, Zhihuan Z, Ting M (2007) Petroleum hydrocarbon in surficial sediment from rivers and canals in Tianjin, China. Chemosphere 68:140–149

Blumer M, Mullin MM, Thomas DW (1963) Pristane in zooplankton. Science 140:974

Clark RB (ed) (1992) Marine pollution, 3rd edn. Oxford University Press, New York

Colombo JC, Pelletier E, Brochu C, Khalil M, Catoggio JA (1989) Determination of hydrocarbons sources using nalkane and polyaromatic hydrocarbon distribution indexes. Cast study: Rio de la Plata estuary, Argentina. Environ Sci Technol 23:888–894

Commendatore MG, Esteves JL, Colombo JC (2000) Hydrocarbons in coastal sediments of Patagonia, Argentina: levels and probable sources. Mar Poll Bull 40:989–998

De Luca G, Furesi A, Leardi R, Micera G, Panzanelli A, Piu PC, Sanna G (2004) Polycyclic aromatic hydrocarbons (PAHs) assessment in the sediments of the Porto Torres harbor (Northern Sardinia, Italy). Mar Chem 86:15–32

Eggleton J, Thomas KV (2004) A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environ Int 30:973–980

Gao X, Chen S, Long A (2008) Composition and sources of organic matter and its solvent extractable components in surface sediments of a bay under serious anthropogenic influences: Daya Bay, China. Mar Poll Bull 56:1066–1075

González-Vila FJ, Polvillo O, Boski T, Moura D, de Andrés JR (2003) Biomarker patterns in a time-resolved Holocene/terminal Pleistocene sedimentary sequence from the Guadiana river estuarine area (SW Portugal/Spain border). Org Geochem 34:1601–1613

Illou S (1999) Thèse de l'Université de Tunis II, Tunis, Tunisia

Le Dréau Y, Jacquot F, Doumenq P, Guiliano M, Bertrand JC, Mille G (1997) Hydrocarbon balance of a site which had been highly and chronically contaminated by petroleum wastes of a refinery (from 1956 to 1992). Mar Poll Bull 34:456–468

Macias-Zamora JV, Mendoza-Vega E, Villaescusa-Celaya JA (2002) PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, BC, Mexico. Chemosphere 46:459–468

Mai BX, Fu JM, Sheng GY, Kang YH, Lin Z, Zhang G, Min YS, Zeng EY (2002) Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environ Pollut 117:457–474

Maljevic E, Balac M (2007) Determining of mineral oil-petroleum hydrocarbons in river sediments. Desalination 213:135–140
Maskaoui K, Zhou JL, Hong HS, Zhang ZL (2002) Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China. Environ Pollut 118:109–122
Mille G, Guiliano M, Asia L, Malleret L, Jalaluddin N (2006) Sources of hydrocarbons in sediments of the Bay of Fort de France (Martinique). Chemosphere 64:1062–1073
Mzoughi N, Hellal F, Dachraoui M, Villeneuve JP, Cattini C, de Mora SJ et al (2002) Méthodologie de l'extraction des hydrocarbures aromatiques polycycliques. Application a' des sédiments de la lagune de Bizerte (Tunisie). C R Géosci, ISSN: 1631-0713
Peters KE, Moldowan JM (1991) Effects of source, thermal maturity and biodegradation on the distribution and isomerization of homohopanes in petroleum. Org Geochem 17:47–61
Peters KE, Moldowan JM (eds) (1993) The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments. Prentice Hall, Englewood Cliffs
Saliot A (ed) (2005) The Mediterranean Sea. The handbook of environmental chemistry. ISBN 10: 3540250182
Scholz-Böttcher BM, Ahlf S, Vazquez-Gutierre F, Rullkötter J (2008) Sources of hydrocarbon pollution in surface sediments of the Campeche sound, Gulf of Mexico, revealed by biomarker analysis. Org Geochem 39:1104–1108
Seifert WK, Moldowan JM (1986) Use of biological markers in petroleum exploration. In: Johns RB (ed) Biological markers in the sedimentary record. Elsevier, Amsterdam, pp 261–290
Simoneit BRT (1986) Characterization of organic constituents in aerosols in relation to their origin and transport: a review. Int J Environ Anal Chem 23:207–237
Simoneit BRT, Mazurek MA (1982) Organic matter of the troposphere-II natural background of biogenic lipids matter in aerosols over the rural western United States. Atmos Environ 16:2139–2159
Simoneit BRT, Sheng G, Chen X, Fu J, Zhang J, Xu Y (1991) Molecular marker study of extractable organic matter in aerosols from urban areas of China. Atmos Environ 25A:2111–2129
Steinhauer MS, Boehm PD (1992) The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of Alaskan Beaufort sea: implications for detecting anthropogenic hydrocarbon inputs. Mar Environ Res 33:223–253
Venkatesan MI, Kaplan IR (1982) Distribution and transport of hydrocarbons in surface sediments of the Alaskan outer continental shelf. Geochim Cosmochim Ac 46:2135–2149
Venturini N, Muniz P, Biocego MC, Martins CC, Tommasi LR (2008) Petroleum contamination impact on macrobenthic communities under the influence of an oil refinery: integrating chemical and biological multivariate data. Estuar Coast Shelf S 78:457–467
Volkman JK, Holdsworth DC, Neil GP, Bavor HJ Jr (1992) Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. Sci Total Environ 112:203–219
Volpi Ghirardini A, Birkemeyer T, Arizzi Novelli A, Delaney E, Pavoni B, Ghetti PF (1999) An integrated approach to sediment quality assessment: the Venetian lagoon as a case study. Aquat Ecosyst Health Manage 2:435–447
Wang ZD, Fingas M, Yang C, Christensen JH (2006a) Environmental forensics-contaminant specific guide. Academic Press, New York, pp 339–407
Wang Z, Stout SA, Fingas M (2006b) Forensic fingerprinting of biomarkers for oil spill characterization and source identification. Environ Forensics 7:105–146
Zaghden H, Louati A, Kallel M, Elleuch B, Saliot A, Oudot J (2005) Hydrocarbons in surface sediments from the Sfax coastal zone, (Tunisia) Mediterrranean sea. Mar Poll Bull 50:1287–1294
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
Zheng GJ, Richardson BJ (1999) Petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in Hong Kong marine sediments. Chemosphere 38:2625–2632