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ORIGINAL RESEARCH

First Investigation of Seasonal Concentration Behaviors and Sources Assessment of Aliphatic Hydrocarbon in Waters and Sediments from Wadi El Bey, Tunisia

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Abstract

The contents, composition profiles, and sources of aliphatic hydrocarbons were examined in surface sediment and water samples collected from Wadi El Bey, in Tunisia, during different year seasons in 14 stations receiving domestic effluent, industrial discharge, and agricultural drainage wastes. The target substances were analyzed by gas chromatography coupled with mass spectrometric detection (GC/MS). Total concentrations of *n*-alkanes (*n*-C_{14}-*n*-C_{38}) ranged from 0.08 ± 0.01 to 18.14 ± 0.1 µg/L in waters and 0.22 ± 0.04 to 31.9 ± 24.6 µg/g in sediments, while total aliphatic fraction ranged from 0.08 ± 0.01 to 196 ± 140 µg/L in waters and 0.22 ± 0.04 to 1977 ± 1219 µg/g in sediments, which means that almost all sites were affected by hydrocarbon contents in sediments exceeding the recommended limit (100 µg/g). Various diagnostic indices (ADIs) were used to identify the hydrocarbon sources, namely the concentration ratios of individual compounds (*n*-C_{17}/pristane, *n*-C_{18}/phytane, pristane/phytane, *n*-C_{29}/*n*-C_{17}, *n*-C_{31}/*n*-C_{19}) as well as cumulative quantities (Carbon Preference Index, natural *n*-alkanes ratio, terrigenous/aquatic compounds ratio, unresolved complex mixture percentage, low molecular weight vs. high molecular weight homologues, Alkane Proxy and Terrestrial Marine Discriminants). In general, these indexes indicated that the origin of aliphatic hydrocarbons affecting sediments and waters of Wadi El Bey were linked to both biogenic and petrogenic inputs, attesting the impact of plankton and terrestrial plants and of oil contamination, respectively. The average carbon chain length computation (ACL), used to further index the chemical environment, ranged from 25.5 to 31.1 in sediments and 47.9–116 in waters. This finding could depend on the severe disturbances suffered by the ecosystem as a consequence of heavy anthropogenic inputs. Petroleum contamination associated with high eutrophication rates in Wadi El Bey must be strictly controlled, due to possible harmful effects induced on ecosystem and humans.

Petroleum pollution has been a great concern for a long time because of the presence in its composition of a number of chemicals that display mutagenic and carcinogenic toxicity on organisms and humans, including skin and lung cancer (Cheng et al. 1999). Among petroleum hydrocarbons, aliphatic hydrocarbons (AHs) are widespread in the aquatic environement and have incited notable attention worldwide (Ranjbar Jafarabadi et al. 2017a, 2018a, b; Shirneshan et al. 2017; Wang et al. 2018). Aliphtic hydrocarbon is derived from petrogenic and biogenic sources (Commendatore and Esteves 2004; Readman et al. 2002). Petrogenic hydrocarbons are related to pollution and are mostly derived from spills of oil and oil-based products. However, biogenic hydrocarbons originate from the primary production of plants, either terrestrial plants or marine algae and microalgae. Thereby, AHs could be used as molecular tracers to diagnose potential sources and transport mechanisms, as well as to assess the relative importance of terrestrial and aquatic origins for organic matters. Indeed, various indexes were used to descriminate between terrestrial and marine inputs or between petroleum and biogenic inputs, such as carbon preference index (CPI), odd-carbon predominance (OEP), low molecular weight to high molecular weight ratio (LWH/HWH), terrigenous/aquatic ratio (TAR), average chain length (ACL), and aquatic macrophyte proxy

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($P_{\text{mar-aq}}$) (Ficken et al. 2000; Jeng 2006; Méjanelle et al. 2017; Vaezzadeh et al. 2015a, b). The unresolved complex mixture (UCM), UCM/R ratio, isoprenoid pristane and phytane ratio (Pr/Ph), and Pr/n-C_{17} and Ph/n-C_{18} ratios were usually used to evaluate petroleum pollution (Tolosa et al. 2004).

The study of petroleum pollution in Tunisia has been well documented in recent years (Louati et al. 2001; Trabelsi and Driss 2005; Zaghden et al. 2005, 2007; Zrafi et al. 2008, 2013; Zrafi-Nouira et al. 2009; Aloulou et al. 2010; Barhoumi et al. 2013; Zaghden et al. 2014, 2017; Fourati et al. 2017). Most of this work has focused on the marine environment, whereas only a few studies have assessed hydrocarbon contamination in wastewater and associated receiving environments (Khedir-Ghenim et al. 2009; Khadhar et al. 2010; Mzoughi and Chouba 2011; Kessabi et al. 2013). The majority of these studies focused only on PAHs compounds. Therefore, AH often are underestimated and rarely analyzed. Yet their contribution in the contamination of ecosystems is obvious, and their toxic effect is not negligible.

Our work represents the first contribution to the establishment of a database on aliphatic content, composition, and probable origins in one of most important Wadi in Tunisia "Wadi el Bey," which was chosen based on previous studies (Gdara et al. 2017, 2018). In fact, our finding shows that the study area can be classified as highly polluted by PAHs. It is permissible to think that the environmental situation of El Bey Wadi is critical. The potential danger of existing organic pollutants that can be induced by the contamination of the groundwater and the risks related to swimming and fish consumption, because El Bey Wadi carries these discharges toward the Mediterranean Sea (Gulf of Tunis) through Sebkhet El Maleh. However, no data have been assessed about aliphatic hydrocarbons distribution in water and sediment, which encouraged us to complete data related to AHs compounds.

On the other hand, Wadi El Bey is an important Wadi in Tunisia given to its position. In fact, this Wadi is located in the northeast of Tunisia between 36°35′00″–36°42′00″N and 10°28′00″–10°33′00″E. It covers a total area of approximately 664 km^2, which includes several urban agglomerations. Among them, Soliman, Bou Argoub, Grombalia, and Menzel Bouzelfa. In fact, Oued el Bey has become highly polluted, not only because of natural runoff, but also because of domestic effluents, industrial discharges, and agricultural drainage produced in the region. These effluents contain all types of organic and inorganic pollutants. Recently, some researchers have described the pollution status of El Bey Wadi; these studies focused on polycyclic aromatic hydrocarbon, heavy metals, microbiological, and physicochemical pollution (Gdara et al. 2017; Mhamdi et al. 2016; Gasmi et al. 2016).

The objective of the present investigation was to study the data influencing pollution status in the region, in the perspective of obtaining information about their concentrations, distribution patterns, and sources. This kind of information looked very useful for environmental quality management and environmental forensics purposes by considering El Bey Wadi as a good example, which gathers different type of effluents and thus allows to control wastewaters rejected and to propose more severe and detailed legislation for each type of hydrocarbons according to its determined risk.

Materials and Methods

Study Area

The entire hydrographic network consists of El Bey Wadi, the most important river in the governorate of Nabeul (Tunisia), and its major tributaries valley Masri, Tahouna, and el Malah, whose waters are controlled by hillside dams (Fig. 1). The main sources of pollution are industrial effluents (textile, tannery, food industries, etc.), agricultural drainage, urban, and touristic wastewater after or without treatment, domestic sewage along with excreta by humans and various warm-blooded animals, which are directly or indirectly discharged into the river and which will finally be evacuated to Soliman Sebkha and then the sea (ANPE 2007; Ruiz et al. 2006). The direct and permanent dumping of treated and untreated waters in El Bey Wadi exerts an important pressure on quality of the whole river system comprising the wadi, sebkha, and coastal zone. Sewage treatment plants and industrial units located on its banks represent sources of significant punctual pollution affecting water quality in all components of hydro-system. Diffuse pollution of agricultural and natural areas located in the watershed and runoff from urban areas also contribute to deterioration of the quality of these waters.

Sample Collection

The sampling was performed by taking into account the lithological diversity of the basin and the distribution of anthropic activities (urban, agricultural, and industrial discharges). We chose 14 sampling stations (S1–S14) correspondent to the given abbreviation (Table 1). Stations were distributed along El Bey Wadi and its tributaries that reflect the actual characteristics of surface water in the entire study area.

Surface sediments and waters were sampled from El Bey Wadi between 2014 and 2016 during four seasons (November, October, January, February, April, May, June, and August). For each site, two samples per season were

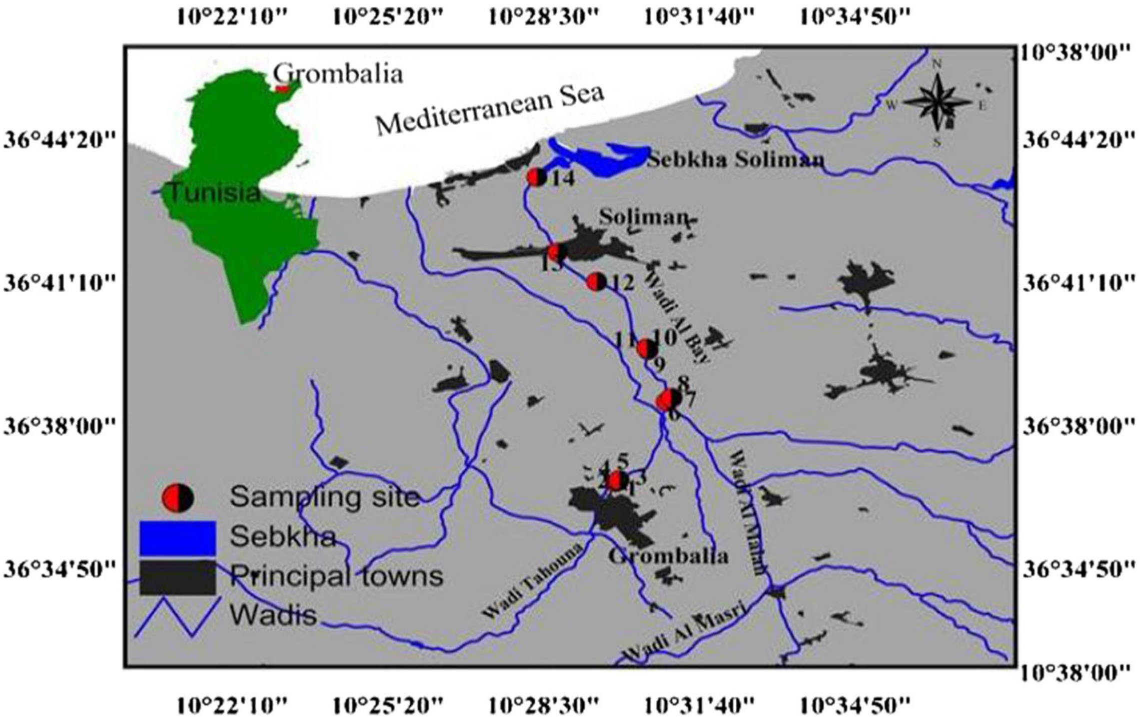


Fig. 1 Sampling location in El Bey Wadi

Table 1 Location and characteristics of sampling stations

Symbol	Code	Stations identification	Latitude	Longitude	Sediment type	Sampling point depth (cm)
S1	ZI-Gr	Discharge of industrial area, Grombalia	36°36′37.18″N	10°29′57.70″E	Grained sand	15
S2	IB-OT	Discharge of beer industry, Wadi Tahouna	36°36′38.52″N	10°29′59.15″E	Fine silt	5
S3	O-NT	Untreated WWTP, Grombalia	36°36′39.00″N	10°30′00.42″E	Grained sand	10
S4	O-T	Treated ONAS, Grombalia (Wadi Tahouna)	36°36′38.70″N	10°30′1.15″E	Fine sand	10
S5	TMM	Tannery discharges, Wadi Tahouna	36°36′40.81″N	10°30′2.16″E	Fine silt	5
S6	OB	Bridge on Wadi El Bey	36°38′24.18″N	10°30′59.70″E	Grained sand	5
S7	Dr-OM	Agricultural drainage, Wadi Maleh	36°38′29.96″N	10°31′6.97″E	Fine silt	5
S8	OM-OB	Bridge on Wadi Maleh, upside of Wadi El Bey	36°38′29.55″N	10°31′5.14″E	Fine sand	15
S9	OB-OBK	Wadi El Bey, upside of WWTP discharges, Beni Khaled	36°39′32.52″N	10°30′37.49″E	Grained silt	15
S10	Dr-BK	Agricultural drainage, Beni Khaled	36°39′34.56″N	10°30′36.75″E	Grained silt	5
S11	O-BK	WWTP discharges, Beni Khaled	36°39′35.18″N	10°30′35.75″E	Fine silt	10
S12	OB-ES	Bridge on Wadi El Bey, Soliman –Grombalia road	36°41′3.39″N	10°29′34.96″E	Fine silt	15
S13	OB-VS	Bridge on Wadi El Bey, Soliman center	36°41′42.51″N	10°28′47.19″E	Fine silt	15
S14	OB-SK	Rejection Wadi El Bey, upside of Sebkha	36°43′22.03″N	10°28′21.94″E	Fine silt	15

collected. The distribution of sampling points according to Global Positioning System is shown in Table 1.

Surface waters were collected by means of 1-L amber glass screw-cap bottle. During the sampling, it is necessary to let a quantity of water overflow and then stop without trapping the air. All boxes and materials used for collection were precombusted, solvent rinsed, and stored in aluminum foil inside Ziplock® bags before use.

Sediment samples were collected using a stainless-steel grab sampler, and the top 15-cm layers were carefully subsampled. The samples are immediately transferred into aluminum box and stored in a cool container to minimize microbial degradation during transport to the laboratory. There, the samples were manually homogenized, lyophilized, filtered through a stainless-steel sieve (200 and 100 µm), and finally stored at 4 °C until analysis. All results of chemical characterization were reported as loads per dry weight units.

Geochemical Characteristics

The particle size distribution was analyzed on fresh material using a Microtrac S3500 Laser diffractometer (provided by NIKKISO.CD.LTD, Osaka, Japan) capable of characterizing matter within the 0.02–2000 µm size interval. Three groups of grain sizes were determined, i.e., < 4 µm (clay), 4–63 µm (silt), and > 63 µm (sand).

To determine total organic carbon (TOC), 1.00 g of dry sediments were weighted and treated with 10 mL of $K_2Cr_2O_7$solution (1N) and 20 mL of H_2SO_4 under the hood. After 30 min, 200 mL of distilled water are added followed by 10 mL of H_3PO_4 and a few drops of diphenylamine. The excess of $K_2Cr_2O_7$ was titrated with $FeSO_4 \cdot 7H_2O$ (1N) under constant stirring until bright green was observed. The organic carbon percent (% C_{org}) was calculated by means of the formula:

$$\%C_{\text{org}} = 4\,(a - b)/(a * P)$$

where a $FeSO_4$ solution volume added to control, b $FeSO_4$ solution volume added to sample, P sample amount in g.

The organic matter content (% OM) was determined using the following formula:

$$\%\text{OM} = 1.724_{*}\%C_{\text{org}}$$

Physicochemical Analysis

Several physicochemical parameters were monitored during this study: temperature, pH, conductivity (CE), dissolved oxygen (O2D), chemical oxygen demand (COD), and biochemical oxygen demand (BOD5) following standard methods (standard methods for the examination of water and wastewater, 1998).

Hydrocarbon Extraction and Clean-Up Through Liquid Chromatography

The analytical procedure applied to extract the hydrocarbon content from waters was a modification of the method described by (Saliot 1989). Total hydrocarbons (TH) in water samples (50 mL) were liquid/liquid-extracted three times for 1 h with 100 mL of pure chloroform, using a separatory funnel. For the sediments, Zrafi et al. (2008) optimized the procedure used for extraction. Twenty grams of dry weight (dw) sediments were extracted in soxhlet with 100 mL of chloroform for 16 h.

The extracts obtained from both sediments and waters were concentrated to 2 mL using a rotary evaporator. Afterwards, the extracts was separated into aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAH), respectively, through liquid chromatography. A column of silica gel was used for this purpose, while pure *n*-hexane (5 mL) and a mixture of *n*-hexane and chloroform (5 mL) (2:1 in volume) were chosen to elute AH and PAH fractions, respectively. After solvent evaporation, AHs were back dissolved in cyclohexane, fortified with a mixture of perdeuterated congeners of analytes, which served as external standards ($C_{14}\,D_{30}$, $C_{16}\,D_{34}$, $C_{20}\,D_{42}$, $C_{24}\,D_{50}$, and $C_{30}\,D_{62}$ *n*-alkanes), and processed through gas chromatography coupled with mass spectrometry (GC–MS).

Gas Chromatography–Mass Spectrometry Analysis

The analytes were detected and quantified using a Trace GC Ultra gas chromatograph equipped with an AS-8000 autosampler and Trace DSQ-II quadrupole mass spectrometer (both from Thermo, Rodano MI, Italy) (Cecinato et al. 2009). The analyte detection was performed in scan mode and data were acquired by a dedicated software (Excalibur). Target compounds were identified by comparing retention times and mass spectrums of GC peaks with those of authentic standard solution. Each analyte was referred to its perdeuterated homologue when present or to the closest internal reference compound in the chromatogram.

Quality Assurance and Quality Control

Before analysis, standard solution of analytes was run to check column performance, peak height and resolution. To ensure quality analyses, standards were injected and analyzed under the same conditions as those used for the samples. Distinct calibration curves, each covering a different range of concentration, were used to quantify the analytes within the linearity range of calibration plot.

In this work, the standard addition graph for all *n*-alkanes in waters and sediments extracted was linear with coefficients of determination (R^2) better than 0.98. LODs for *n*-alkanes congeners (signal to noise ratio = 3) ranged from 0.04 µg/L (*n*-C14) to 0.08 µg/L (*n*-C38). The average recoveries of surrogate standards varied from 81.6 to 92% and were used for the recovery correction calculations.

Determination of Hydrocarbon Indices and Ratios

Aliphatic diagnostic indices and molecular pattern distribution were used to identify the hydrocarbon sources (biogenic or petrogenic) (Table 2).

Table 2 Hydrocarbon molecular diagnostic ratios investigated in this study with typical values from the literature

Diagnostic ratios	Value	Origin	References
R/UCM	< 4	Recent input	Silva et al. (2013)
	> 4	Matured petroleum residues	
Pr/Phy	< 1	Petrogenic origin	Volkman et al. (1992), ten Haven (1996) and Peters et al. (2005)
	$1 < \text{Pr/Phy} < 3$	Sign of oxidizing depositional environment	
	> 1	Biogenic origin	
C17/Pr, C18/Phy	< 1	Biodegraded oils	Tarozo et al. (2010)
	> 1	Recent inputs	
CPI	≈ 1	Petroleum inputs	Petersen et al. (2007) and Commendatore et al. (2012)
	$\text{CPI} < 1$ or > 1	Biogenic sources	
LMW/HMW	< 1	Terrestrial (high plants) origin	Wang et al. (2006)
	> 1	Petroleum origin	
NAR	≈ 0	Petroleum hydrocarbon and crude oil	Mille et al. (2007)
	≈ 1	Marine origin	
TMD	< 0.5	Marine inputs	Yusoff et al. (2012)
	$0.5 < \text{TMD} < 1$	Mixed inputs	
	> 1	Terrestrial plants	
C31/C19	< 0.4	Marine biogenic sources	Fagbote and Olanipekun (2013)
	> 0.4	Land derived hydrocarbon	
Paq	< 0.1	Non-emergent plant input	Ficken et al. (2000)
	$0.1 < \text{Paq} < 0.4$	Emergent marcophytes	
	$0.4 < \text{Paq} < 1$	Submerged/Floating macrophytes	

Statistical Analyses

The concentration data of *n*-alkanes (*n*-C14 to *n*-C38) in waters and sediments were statistically analyzed using *Statistica* software for each station and each season by one-way ANOVA followed by Tukey–Kramer Test. Statistical significance was defined as $P < 0.05$.

PCA was performed on aliphatic hydrocarbon concentrations of wastewaters and sediments with the Varimax rotation method (Hu et al. 2014). Two factors were obtained and the profiles of the factor loadings were used to infer the possible sources of aliphatic hydrocarbons.

Results and Discussion

Sediment Geochemistry

Grain size provides important information about the sediment provenance, depositional conditions, and transport history (Folk and Ward 1957; Blott and Pye 2001). Generally, sediments covering in the studied areas ranged from fine silt to grained sand, mainly biogenic fragments and carbonate aggregates (Fig. 2). The silt fraction was usually predominant, with the exception of S1 (Zi-Gr), S3 (O-NT), S4 (O-T), S6 (OB), and S8 (OM-OB) stations where sediments were overall comprised of sand. The occurrence of fine sediments may be due to the dominance of terrigenous fine grain size sediments and could be explained by the greater depth and the slow water movement. The change of grain size looks as indicative of different erosion and accretion rates, as well as the influence of shell fragments (El Nemer et al. 2013).

TOC in surface sediments from the Wadi el Bey ranged from 1.63 to 3.9% (Fig. 3). The maximums were recorded in S12 (OB-ES) and S14 (OB-SK) stations 3.9% and 3.7%, respectively. This finding could be related to the huge impact of urban and industrial wastewater discharges affecting the two stations, rich of organic matter. The TOC content determined was similar to the Bizerte Lagoon (0.4–3.9%) (Barhoumi et al. 2013). 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).

Regression analysis was performed to investigate possible relationships existing between total aliphatic hydrocarbon contents and TOC percentages (Fig. 3), but no significant correlation was found. The no correlation found between AH and TOC indicate different origins but could highlight a low affinity of AHs toward organic carbon contents at the molecular level. While aliphatic hydrocarbons mainly originate from inputs of anthropogenic emissions, the predominant source of TOC affecting sediments is usually natural (Schumacher 2002; Ouyang et al. 2006; Mirsadeghi et al. 2013). Indeed, the lack of correlation between TOC and hydrocarbon concentrations was reported elsewhere (Cavalcante et al.

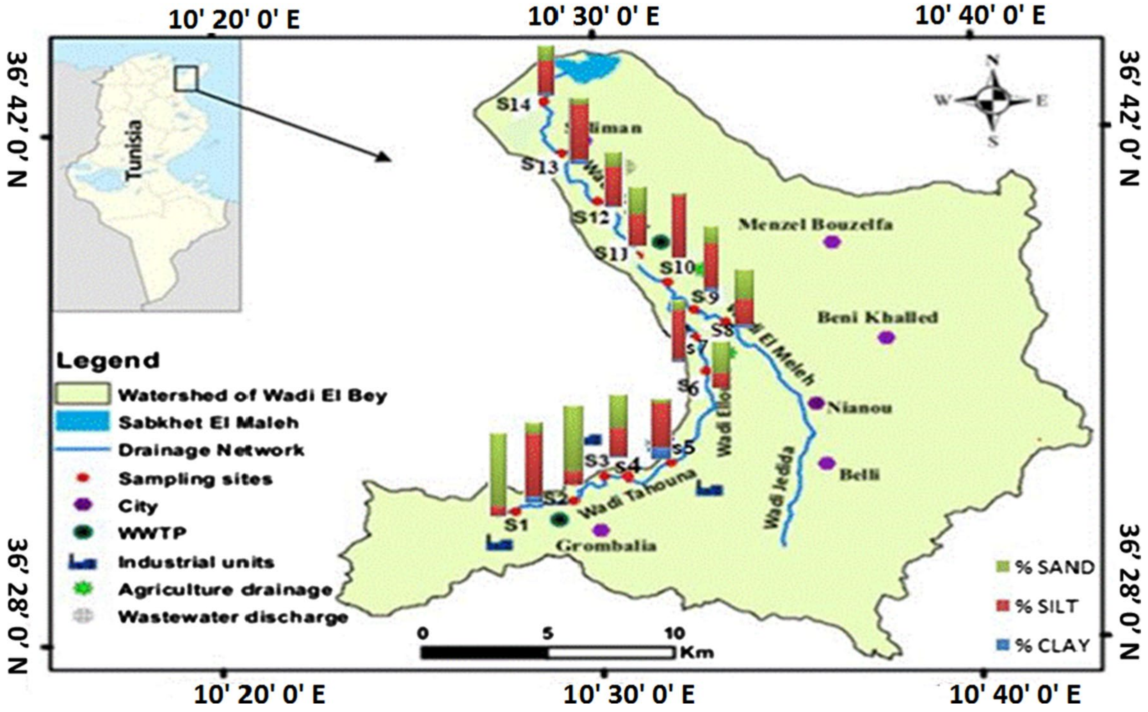
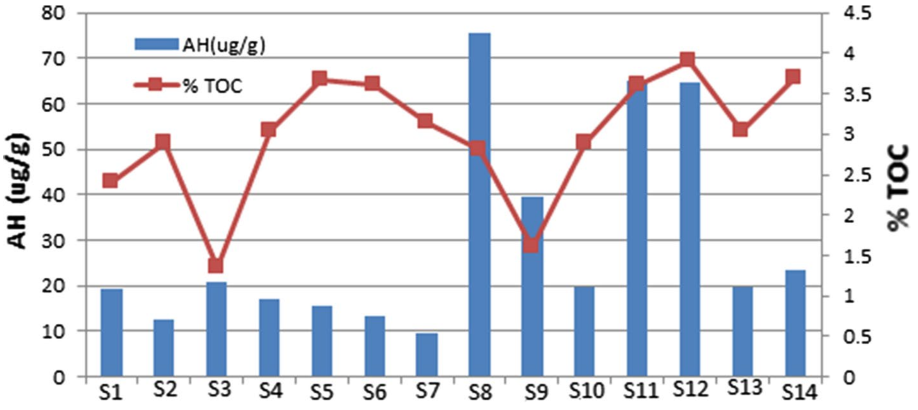


Fig. 2 Percentages of grain size distribution (clay, silt, and sand) in the study area

Fig. 3 Total organic carbon (TOC) and aliphatic hydrocarbon (AH) in sediments of El Bey Wadi



2009; Mirsadeghi et al. 2013; Tam et al. 2001), whilst a link of TOC with levels of hydrocarbons was suggested in other studies (Chen et al. 2012; Huang et al. 2012; Bush and McInerney 2015). It could be inferred that the *n*-alkanes distributions and concentrations in sediments of El Bey Wadi were not controlled by TOC content (correlation coefficient $R^2 = 0.02$, $P = 0.07$, $n = 14$). Besides, no linear relationship was observed between total aliphatic hydrocarbons and the fine fraction amount present in sediments. However, aliphatic hydrocarbons concentrations were generally lower in sites characterized by high percentages of sandy fraction, especially in S1 (ZI-Gr), S2 (IB-OT), and S6 (OB).

Physicochemical Analysis of Wastewater From El Bey Wadi

Physical–chemical parameters, such as temperature, pH, dissolved oxygen (DO), salinity, and organic matter (COD, BOD_5) have been reported to influence biochemical reactions within water systems.

Temperature is among the most important ecological and physical factors heavily influencing both the living and nonliving compartments of the environment, thereby affecting organisms and the functioning of ecosystems (Palamuleni and Mercy 2015). According to Table 3, the average water temperature ranged from 12.3 °C in S10 (Dr-Bk) to 27.1 °C in site S1 (ZI-Gr). S1 (ZI-Gr) is exposed to a

Table 3 Mean values of physicochemical parameters of El Bey Wadi Waters

Stations	Code	T °C	pH	EC (mS/Cm)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)
S1	Zi-Gr	27.1	7.5	7.9	1.8	1180	522
S2	IB-OT	19.2	6.9	6.6	1.5	101.8	35
S3	O-NT	21.8	7.9	4.1	1.7	291	134
S4	O-T	19.1	7.2	3.5	1.6	105.2	32
S5	TMM	20.4	7.1	19.9	1.6	2011	622
S6	OB	19.6	7.9	8.2	1.5	504	198
S7	Dr-OM	16.9	7.8	3.5	1.5	516	119.2
S8	OM-OB	19.5	7.9	9.1	1.9	94.5	41.4
S9	OB-OBK	14.1	7.1	5.2	1.2	390	164.5
S10	Dr-BK	12.3	7.3	6.8	1.3	97.2	23.2
S11	O-BK	13.7	6.9	5.2	1.4	444.8	99.5
S12	OB-ES	18.8	7.8	5.9	1.6	301	99.2
S13	OB-VS	18.2	7.9	6.2	1.5	229	90
S14	OB-SK	18.7	8.1	6.1	1.7	217	123
Tunisian standards (TN-106-02)		25	6.5–8.5	–	–	90	30

thermal pollution that exceeds the maximum permissible value of 25 °C required by the Tunisian standards (TN-106-02). According to Mhamdi et al. (2016) and Taoufik et al. (2017), the site S1 (ZI-Gr) also registered the high temperature level; this is may be due to the water discharge of the Grombalia industrial area that is mainly textile wastewater characterized by high temperature.

Mean pH values of water samples ranged between 6.9 in S2 (IB-OT) and 8.1 S14 (OB-SK), indicating that El Bey Wadi was neutral or slightly alkaline. These values were within the limits of 6.5–8.5 prescribed by WHO and required by Tunisian standards (TN-106-02). A comparison with an earlier report by (Khadhar et al. 2013; Mhamdi et al. 2016; Taoufik et al. 2017) on the same study site showed the same similarities of pH.

In the present study, the EC values ranged from 3.5 mS/cm for samples collected from station (S7) to 19.9 mS/cm for discharge of Grombalia Tannery station (S5). A comparison with the study by Khadhar et al. (2013) and Mhamdi et al. (2016) on the same study area showed some similarities with a maximum EC obtained at site S5 (discharge of Grombalia Tannery). This high value of EC may due to the increase of ions concentration because of the excessive use of agricultural fertilizer.

The standard DO for sustaining aquatic life is 4 mg/L, whereas for drinking purposes it is 6 mg/L. In this study, mean DO values fluctuated between 1.2 mg/L (S9) and 1.8 mg/L (S1). The low values of DO indicate the presence of high organic compounds generated by industrial wastewater (Adebowale et al. 2008).

Mean COD values found in water of El Bey Wadi ranged between 94.5 mg/L (S8) and 2011 mg/L (S5). Tunisian Standard's tolerable limit is of 90 mg/L. These results can be attributed to the high organic content of industrial effluents and insufficiently treated effluents discharged into the El Bey Wadi.

The Tunisian Standard Agency has specified a maximum limit of 30 mg/L for biological oxygen demand (BOD_5) (TN-106-02). This study showed that, apart from site S10 characterized by mean BOD_5 equal to 23 mg/L, all other stations suffered BOD levels exceeding the Tunisian limit. Our results of high levels of COD and BOD are similar to those registered by Mhamdi et al. (2016). High BOD is usually a result of organic pollution, caused by discharges of untreated wastewater from treatment plants and industrial effluents, as well as agricultural runoff.

Spatial and Temporal Distribution of Aliphatic Hydrocarbon and *n*-Alkanes in El Bey Wadi Water and Sediments

The spatial–temporal distribution of aliphatic hydrocarbons and *n*-alkanes (*n*-C14–*n*-C38) in sediments and waters from El Bey Wadi is illustrated in Table 4. Aliphatic hydrocarbons (AHs) of surface water ranging from 0.08 ± 0.01 to 196 ± 139 µg/L. Maximums, namely 196 µg/L and 188 µg/L, were recorded at stations S1 (Discharge of industrial zone—Grombalia) and S9 (Wadi El Bey, upside of WWTP discharges, Beni Khaled), respectively. This could be originated by sewage coming from industrial districts and urban areas insisting in the two stations.

The concentration of total aliphatic hydrocarbons raised during the cold seasons. This could be caused by the high effluent volumes dumped into the El Bey wadi during the

Table 4 Seasonal concentration of total aliphatic hydrocarbon and *n*-alkanes in waters and sediments

Code			Total aliphatic		$\sum$ *n*-Alkanes	
			Sediment (μg/g)	Water (μg/L)	Sediment (μg/g)	Water (μg/L)
S1	ZI-Gr	Au	19.2 ± 12.6	21.6 ± 12.6	1.36 ± 0.63	8.18 ± 3.12
		W	0.35 ± 0.12	70.6 ± 48.6	0.35 ± 0.12	5.17 ± 2.28
		Sp	16.1 ± 11.3	196 ± 139	0.56 ± 0.12	9.09 ± 7.53
		Su	419 ± 275	2.95 ± 2.57	31.9 ± 24.6	2.95 ± 2.57
S2	IB-OT	Au	0.52 ± 0.31	6.41 ± 2.93	0.52 ± 0.31	6.41 ± 2.93
		W	0.62 ± 0.27	0.57 ± 0.28	0.62 ± 0.27	0.57 ± 0.28
		Sp	0.47 ± 0.33	2.64 ± 1.65	0.47 ± 0.33	2.64 ± 1.65
		Su	845 ± 592	1.16 ± 0.98	8.25 ± 2.32	1.16 ± 0.98
S3	O-NT	Au	7.49 ± 5.03	85.1 ± 59.4	0.55 ± 0.17	5.61 ± 3.22
		W	0.34 ± 0.21	1.63 ± 1.32	0.34 ± 0.21	1.63 ± 1.32
		Sp	18.2 ± 15.3	69.7 ± 49.3	1.13 ± 0.56	1.51 ± 0.99
		Su	462 ± 321	16.2 ± 11.3	6.83 ± 1.23	1.10 ± 0.63
S4	O-T	Au	5.99 ± 3.82	36.6 ± 14.4	0.62 ± 0.44	16.2 ± 4.53
		W	7.89 ± 5.31	0.87 ± 0.62	0.38 ± 0.52	0.87 ± 0.62
		Sp	0.63 ± 0.42	5.72 ± 4.52	0.57 ± 0.13	5.75 ± 4.52
		Su	31.9 ± 24.6	19.6 ± 14.4	29.4 ± 14.2	4.23 ± 3.59
S5	TMM	Au	22.5 ± 15.2	18.1 ± 0.32	0.42 ± 0.13	18.1 ± 5.12
		W	21.9 ± 16.3	1.14 ± 0.88	0.39 ± 0.18	1.14 ± 0.88
		Sp	0.68 ± 0.56	1.78 ± 1.13	0.68 ± 0.56	1.82 ± 0.12
		Su	1977 ± 1219	6.45 ± 1.67	19.2 ± 9.72	6.45 ± 1.67
S6	OB	Au	0.53 ± 0.29	7.58 ± 3.62	0.51 ± 0.29	7.58 ± 3.62
		W	16.7 ± 11.5	0.32 ± 0.24	0.46 ± 0.08	0.32 ± 0.24
		Sp	31.9 ± 22.6	0.35 ± 0.12	1.62 ± 1.02	0.35 ± 0.12
		Su	275 ± 232	11.9 ± 8.72	9.92 ± 2.35	2.31 ± 1.89
S7	Dr-OM	Au	0.73 ± 0.41	33.8 ± 21.8	0.73 ± 0.41	4.61 ± 1.32
		W	0.32 ± 0.13	0.94 ± 0.81	0.32 ± 0.13	0.92 ± 0.83
		Sp	0.79 ± 0.64	9.14 ± 8.67	0.79 ± 0.64	9.14 ± 8.67
		Su	13.1 ± 9.41	2.87 ± 2.56	0.85 ± 0.26	2.87 ± 2.56
S8	OM-OB	Au	0.41 ± 0.21	27.92 ± 20.6	0.41 ± 0.21	5.57 ± 4.81
		W	0.48 ± 0.14	0.92 ± 0.82	0.48 ± 0.14	0.92 ± 0.82
		Sp	18.1 ± 12.8	0.35 ± 0.26	18.1 ± 12.1	0.35 ± 0.26
		Su	20.5 ± 16.1	4.46 ± 2.72	20.5 ± 16.1	4.46 ± 2.72
S9	OB-OBK	Au	0.45 ± 0.12	0.91 ± 0.18	0.45 ± 0.12	0.91 ± 0.18
		W	0.36 ± 0.11	0.08 ± 0.01	0.36 ± 0.11	0.08 ± 0.01
		Sp	13.9 ± 9.82	0.69 ± 0.59	13.9 ± 7.51	0.72 ± 0.59
		Su	28.4 ± 24.3	187 ± 132	16.8 ± 5.31	9.25 ± 6.13
S10	Dr-BK	Au	5.14 ± 3.43	8.84 ± 0.02	0.37 ± 0.06	8.82 ± 0.02
		W	5.17 ± 3.38	0.26 ± 0.08	0.42 ± 0.09	0.26 ± 0.08
		Sp	0.42 ± 0.31	0.47 ± 0.24	0.44 ± 0.26	0.47 ± 0.24
		Su	13.2 ± 10.7	3.08 ± 1.34	5.64 ± 2.13	3.08 ± 1.34
S11	O-BK	Au	0.65 ± 1.32	6.21 ± 2.15	0.65 ± 1.32	6.21 ± 2.15
		W	0.47 ± 0.23	0.16 ± 0.09	0.47 ± 0.23	0.16 ± 0.09
		Sp	24.1 ± 9.12	0.37 ± 0.21	24.1 ± 9.12	0.37 ± 0.21
		Su	19.9 ± 8.11	3.51 ± 2.62	19.7 ± 24.6	3.51 ± 2.62
S12	OB-ES	Au	13.4 ± 9.18	121 ± 85.8	0.74 ± 0.22	8.76 ± 6.29
		W	0.22 ± 0.12	0.32 ± 0.14	0.22 ± 0.12	0.32 ± 0.14
		Sp	18.1 ± 12.8	0.36 ± 0.14	1.08 ± 0.31	0.36 ± 0.14
		Su	646 ± 245	2.43 ± 2.07	25.2 ± 2.31	2.43 ± 2.07

Table 4 (continued)

Code			Total aliphatic		$\sum$ *n*-Alkanes	
			Sediment (µg/g)	Water (µg/L)	Sediment (µg/g)	Water (µg/L)
S13	OB-VS	Au	0.73 ± 0.39	22.5 ± 17.2	0.73 ± 0.39	6.31 ± 2.28
		W	1.21 ± 0.71	0.35 ± 0.24	1.21 ± 0.71	0.35 ± 0.24
		Sp	15.1 ± 10.6	0.45 ± 0.25	1.23 ± 0.66	0.45 ± 0.25
		Su	46.6 ± 36.4	3.74 ± 3.41	12.3 ± 12.1	3.74 ± 3.41
S14	OB-SK	Au	0.42 ± 0.11	97.6 ± 69.2	0.42 ± 0.11	5.21 ± 4.26
		W	0.32 ± 0.21	0.52 ± 0.21	0.32 ± 0.21	0.53 ± 0.22
		Sp	18.2 ± 12.87	0.35 ± 0.16	0.44 ± 0.23	0.35 ± 0.16
		Su	192 ± 246	6.33 ± 3.56	9.11 ± 8.64	6.33 ± 3.56

warm period (flow rates ≈ 2 m^3/s in summer and ≈ 0.10 m^3/s in winter). Indeed, hydrological conditions and the strength of pollutant sources are the major factors modulating the AHs concentrations presence in the water bodies. In our case, the contaminants were probably diluted by big water volumes recorded in the hot season, resulting in low AHs concentrations in that year time (Lu et al. 2014).

Compared with reported values from other areas around the world, the concentration of aliphatic hydrocarbons in the El Bey Wadi was much higher than the west coast of the Gulf of Tunis (0.251 µg/L to 1.096 µg/L) (Mzoughi and Chouba 2011), the Xihe River (3.59 µg/L to 21.5 µg/L) (Guo et al. 2006), by contrast AHs were less than Daliao River (13.39 µg/L to 283.62 µg/L) (Guo et al. 2009).

AHs fraction of sediments showed a wide range of concentrations, from 0.22 µg/g ± 0.12 to 1977 ± 1219 µg/g. High concentration of AHs that exceed 100 µg/g is a potential source of contamination (Readman et al. 2002). Table 4 and Fig. 4 show that El Bey Wadi sediments are moderately to highly contaminated. Compared with the literature, total AH were higher than in the Cross River Estuary, Nigeria (0.02–16.84 µg/g) (Oyo-Ita et al. 2010), Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea) (8–174 µg/g) (Zaghden et al. 2017), and comparable to those found in Sfax, Tunisia (16–1729 µg/g) (Zaghden et al. 2007), in Kuching, China (35.6–1466.1 µg/g) (Yusoff et al. 2012), and Baku, Azerbaijan (29–1820 µg/g) (Tolosa et al. 2004); by contrast AHs were lower than in Rio de Janeiro, Brazil (0.81–20,000 µg/g) (Wagener et al. 2012).

The concentrations of Σ*n*-alkanes in waters ranged from 0.08 µg/L ± 0.01 to 18.1 ± 5.12 µg/L. The maximum was recorded in S5 (Tannery discharges, Wadi Tahouna) during

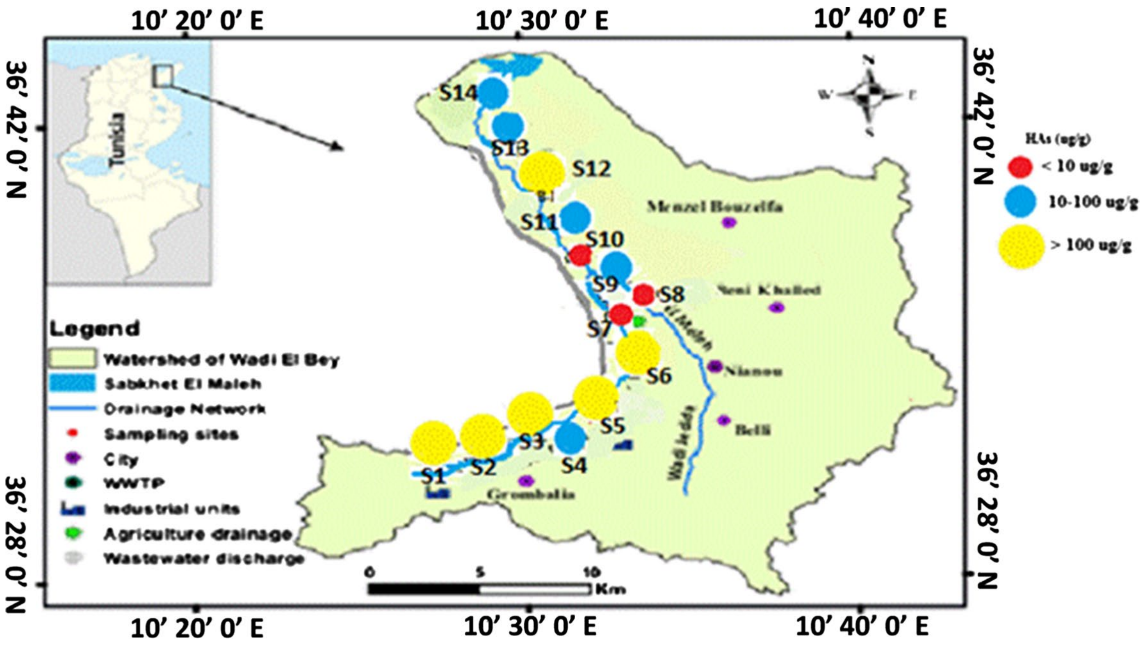


Fig. 4 Contamination status of surface sediments of El Bey Wadi by aliphatic hydrocarbons (Arc-Gis 10.3)

the autumn season and the minimum in S9 (El Bey Wadi-upside of WWTP discharges, Beni Khaled) during the winter. The concentrations of Σ*n*-alkanes decreased from dry to rainy season, possibly due to frequent rains that caused the river water flow and volume increase and the consequent *n*-alkanes dilution. The concentration of *n*-alkanes in El Bey Wadi was lower than that of Shatt Al-Arab River (8.81–35.58 µg/L) and lower than in Yellow River in Henan Sect. (521–5843 µg/L) (Feng et al. 2016) but higher than those registered in central lake China (0.52–6 µg/L (Xiang et al. 2013).

The concentrations of Σ *n*-alkanes in surface sediments showed a wide variability, ranging from 0.22 µg/g ± 0.12 to 31.9 ± 24.6 µg/g. Intersite comparison showed that station 1 (Discharge of industrial area in Grombalia) registered the highest concentration of total *n*-alkanes (31.9 µg/g); this finding probably depended on the high number of industries (> 20) discharging effluents in El Bey Wadi. The *n*-alkanes concentrations were relatively high compared with other locations, such as the Mediterranean Sea (0.41–15.6 µg/g) (Bouzid et al. 2012), the Arc River in France and Beer lagoon (0.56–5.07 µg/g) (Kanzari et al. 2012), Red Sea, Egypt (0.033–0.55 µg/g) (Dalia et al. 2014), Indian Ocean, Indonesia (0.48–1.93 µg/g) (Yazis et al. 2016), Bohai Sea, China (0.88–3.48 µg/g) (Li et al. 2015), and the Atlantic Ocean, Argentina (0.02–1.1 ng/g) (Paletto et al. 2008).

The distribution of aliphatic hydrocarbon and n-alkanes were different in water and sediment samples, fraction of hydrocarbons are under the dissolved phase, which are considered more persistent in water and more toxic (biodisponibilty), whereas the other fraction is under particulate form that will reach the sediment by simple vertical flux (Fig. 5).

Source Identification of *n*-Alkanes in Water and Sediments

Aliphatic diagnostic indices (ADIs) were used to identify hydrocarbon sources, i.e., to discriminate biogenic from petrogenic and marine from terrestrial origin, as well as to estimate the relative degree of biodegradation at sites (Commendatore et al. 2012)

In the present study (Tables 5 and 6), UCM concentrations ranged from "not detected" up to 1958 µg/g in sediments and from "not detected" to 178 µg/L in water samples representing 55% and 62% of the total AHs in water and sediments. The presence of UCM is usually associated with degraded or weathered petroleum residues, because these molecules are resistant to biodegradation and accumulate in sediments (Readman et al. 2002). The ratio between UCM and the sum of *n*-alkanes often is used as diagnostic criteria for anthropogenic contribution to pollution (Silva et al. 2013); rates > 4 indicate the presence of matured petroleum residues, < 4 of recent inputs (Simoneit 1984; Lipiatou and Saliot 1991). In our case, the ratio was < 4 in almost sampling stations with the expectation of S4, S6 (water), and S11 (sediment); this ratio is > 4 and confirms the presence of matured petroleum residues.

The carbon preference index (CPI) is the most common index for determination of the sources of AHs

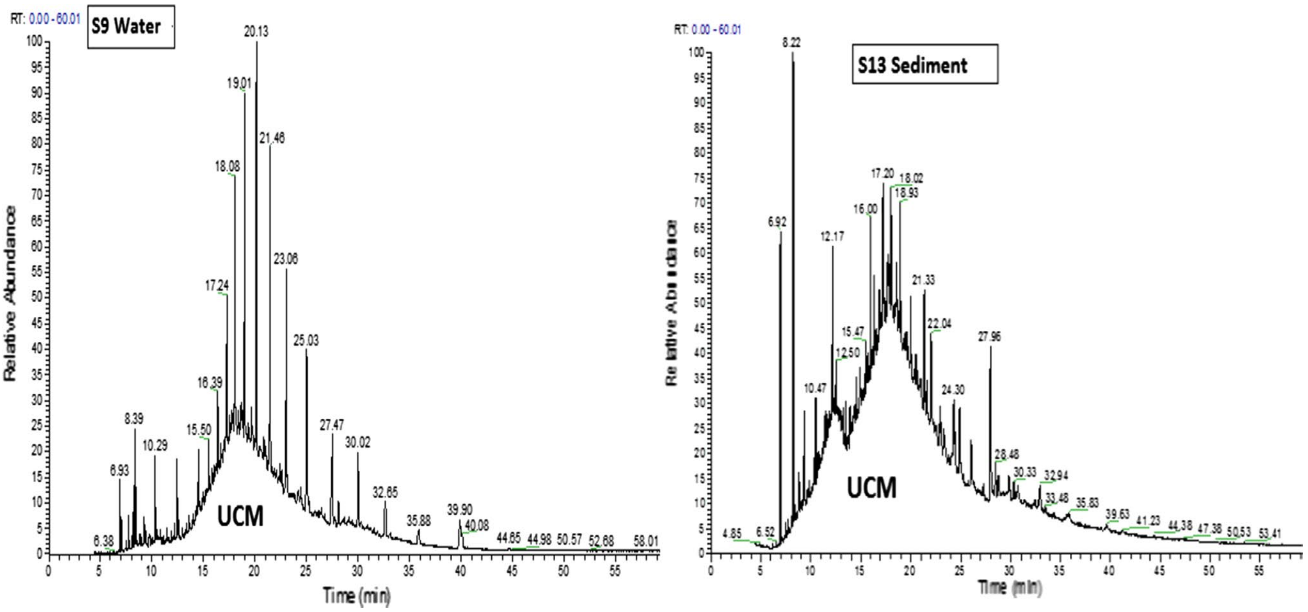


Fig. 5 Capillary column gas chromatograms of non-polar hydrocarbon fraction comprised of *n*-alkanes and UCM in S9 (OB-OBK) in water sample (summer) and in S13 (OB-VS) sediment (spring)

Table 5 Aliphatic diagnostic ratios in sediments from El Bey Wadi

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
	ZI-Gr	IB-OT	O-NT	O-T	TMM	OB	Dr-OM	OM-OB	OB-OBK	Dr-BK	O-BK	OB-ES	OB-VS	OB-SK
UCM														
Au	17.9	ND	6.9	5.3	21.6	ND	ND	ND	ND	4.7	ND	12.6	ND	ND
W	ND	ND	ND	7.5	21.5	16.2	ND	ND	ND	4.1	ND	ND	ND	ND
Sp	15.4	ND	17.4	ND	ND	30.3	ND	ND	ND	ND	ND	17.1	13.8	17.7
Su	389.7	837.3	455.2	ND	1958	266	12.3	ND	11.6	7.6	0.15	621.7	34.3	183.6
Pr/Phy														
Au	0.13	0.24	0.15	ND	0.1	0.17	0.14	0.12	0.95	0.3	0.19	0.11	0.14	0.19
W	0.09	4.01	0.09	0.27	0.1	0.2	ND	0.1	0.14	0.18	ND	ND	ND	0.1
Sp	0.17	0.15	0.25	0.24	0.16	0.23	0.22	ND	ND	0.15	ND	0.13	0.19	0.17
Su	ND	0.71	ND	0.67	0.83	0.36	0.13	0.43	0.17	0.39	0.97	0.64	0.14	0.59
C17/Pr														
Au	1.48	1.04	1.08	ND	1.01	5.9	1.02	1.86	0.85	0.73	1.06	1.23	1.51	1.19
W	1.09	0.26	1.03	0.9	1.01	1.06	ND	2.22	1.44	1.22	ND	ND	2.01	1.3
Sp	1.06	0.95	1.04	1.24	0.98	1.23	1.21	ND	ND	0.99	ND	1.55	1.23	1.4
Su	1.73	5.32	0.01	11.3	6.3	4.12	5.9	4.6	24.2	5.9	3.5	5.3	27.8	2.4
C18/Phy														
Au	2.68	1.67	2.02	ND	1	2.49	1.61	1	2.01	2.52	2.07	1.76	1.92	0.93
W	1.01	6.72	1.06	0.94	1	1	ND	1.02	1.71	2.52	ND	ND	2.7	1.02
Sp	2.3	3.05	4.17	2.95	3.29	2.17	6.37	ND	ND	2.57	ND	2.36	4.23	1.41
Su	ND	36.1	ND	63.1	42.3	28.9	1.38	36	52.5	34.7	23.7	25.1	26.8	6.6
TAR														
Au	3.14	2.88	3.9	2.41	3.6	1.49	3.17	4.69	3.85	2.7	4.5	3.71	2.97	2.85
W	3.01	2.88	3.32	2.47	3.61	6.63	3.1	4.69	2.81	2.4	4.5	27.7	2.63	4.25
Sp	2.71	1.95	2.78	2.11	1.84	2.25	1.78	6.8	4.5	2.5	5.4	2.3	1.6	2.07
Su	2.96	0.64	ND	0.68	1.62	3.69	1	0.5	1.83	0.96	5.12	2.25	0.65	3.92
TMD														
Au	2.09	1.99	2.43	1.73	2.11	1.28	2.03	2.69	2.36	1.88	2.56	2.24	2.05	1.88
W	1.92	1.99	2.01	1.68	2.11	3.17	1.91	2.69	1.91	1.77	2.56	5.29	1.91	2.28
Sp	3.01	2.99	3.15	2.67	1.81	1.99	2.37	5.44	3.27	3.04	4.62	4.82	2.83	3.45
Su	3.21	0.51	ND	1.09	2.45	3.59	1.02	0.7	1.89	0.99	3.93	2.99	0.62	4.9
C31/C19														
Au	1.55	1.18	2.02	0.89	1.47	0.78	1.54	2.83	2.39	1.39	1.97	1.69	1.71	1.44
W	1.44	1.18	1.52	1.24	1.47	3.9	1.46	2.83	1.42	1.23	1.97	ND	1.33	2.26
Sp	3.06	3.17	2.91	2.31	2.1	1.59	1.72	5.1	1.42	3.08	3.34	2.84	2.17	4.27
Su	2.13	ND	ND	ND	ND	20.9	0.55	ND	0.42	1.42	12.7	9.4	1.3	5.6
NAR														
Au	−0.12	−0.03	−0.17	−0.1	−0.04	0.01	−0.2	0.1	−0.3	−0.1	0.02	−0.09	−0.6	−0.01
W	−0.01	−0.03`	−0.01	0.05	−0.04	0.23	−0.8	0.1	−0.7	−0.1	0.03	−0.2	−0.1	0.06
Sp	−0.12	−0.14	−0.14	−0.7	−0.14	−0.1	−0.2	ND	−0.1	ND	−0.2	−0.1	−0.8	−0.9
Su	−0.4	−0.5	−1	−0.2	−0.5	−0.3	0.05	−0.7	−0.5	−0.3	−0.2	−0.3	−0.3	−004
Paq														
Au	0.42	0.28	0.37	0.37	0.42	0.4	0.38	0.44	0.5	0.46	0.53	0.4	0.31	0.3
W	0.42	0.28	0.43	0.4	0.36	0.43	0.38	0.4	0.48	0.46	0.28	0.42	0.31	0.4
Sp	0.42	0.46	0.33	0.40	0.46	0.42	0.48	0.13	0.34	0.38	0.38	0.39	0.48	0.39
Su	0	1	ND	0.59	ND	0.16	0.5	1	0.14	0.91	0.32	0.01	0.84	0.02
LMW/HMW														
Au	0.71	0.4	0.38	0.5	0.3	0.7	0.44	0.23	0.54	0.5	0.47	0.45	0.51	0.31
W	0.29	0.41	0.32	0.45	0.29	0.33	0.32	0.22	0.59	0.83	0.49	0.34	0.71	0.37
Sp	0.65	0.97	1.02	0.88	0.54	0.69	1.35	0.01	0.03	0.61	−0.2	0.72	0.86	0.85

Table 5 (continued)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
	ZI-Gr	IB-OT	O-NT	O-T	TMM	OB	Dr-OM	OM-OB	OB-OBK	Dr-BK	O-BK	OB-ES	OB-VS	OB-SK
Su	0.96	3.57	5.7	3.04	1.3	0.6	0.2	8.04	1.3	1.68	0.8	0.8	3.4	0.5
CPI														
Au	0.91	1.07	0.77	0.74	0.89	1.2	0.82	1.3	0.94	0.78	0.88	0.79	0.74	0.70
W	0.71	0.8	0.7	1.07	0.7	1.47	0.69	1.14	0.80	0.64	0.65	0.62	0.49	1.15
Sp	0.13	0.14	0.09	0.11	0.17	0.14	0.09	0.07	0.08	0.10	0.10	0.11	0.12	0.11
Su	0.4	0.15	0.1	0.18	0.2	0.44	0.34	0.12	0.26	0.33	0.54	0.46	0.22	0.75
ACL														
Au	29	28.6	28.7	28.8	28.6	28.02	29	29.9	29	29	29.1	29.06	28.9	29
W	28.9	28.7	29.06	28.5	28.6	29.03	29	29.2	29	29	29.1	29	28.9	29.05
Sp	29.4	29.72	29.77	29.6	29.7	29.4	29.3	29.6	29.4	29.6	29.1	29.8	29.6	29.7
Su	30.7	25.3	ND	26.8	31.1	30.1	28.4	26.2	29.1	25.5	28.9	30.8	26.1	30.73
%Wax Cn														
Au	6.32	9.88	5.5	2.04	3.36	16.64	1.43	20.5	8.52	0.59	2.59	1.38	2.45	8.27
W	6.7	9.8	8.47	9.05	9.24	23.31	8.27	17.6	7.87	6.05	8.83	9.27	6.05	12.24
Sp	2.98	0.91	2.49	1.66	0.49	2.44	0.82	ND	ND	2.57	3.1	2.44	1.09	5.5
Su	14.35	4.54	0.27	5.8	24.7	15.8	1.56	1.8	22.2	6.3	8.1	19.2	3.4	17.7

(Commendatore et al. 2012; Li et al. 2015; Vaezzadeh et al. 2015a, b; Wang et al. 2015). CPI is defined as the ratio of odd to even carbon numbered *n*-alkanes. CPI values close to 1 are associated to petroleum inputs (Eseme et al. 2006; Petersen et al. 2007), whilst values CPI < 1 or > 1 are indicative of biogenic sources (Commendatore et al. 2012). In the present study, the CPI range of sediments was 0.09–1.15 (Table 5). Most of the sampling stations receive biogenic origin expect of S1 (ZI-Gr) (autumn) and S4 (O-T) (winter) CPI is close to 1 associated to petroleum contamination. As for waters, only in S4 during the winter CPI is close to 1, indicating the predominant of petroleum input.

We also used the Pristane/Phytane ratio as an indicator of biogenic AHs (when > 1) (Cripps 1989; Commendatore and Esteves 2004; Cincinelli et al. 2008). We found Pr/Phy > 1 only in site S2 in winter (Table 5), suggesting the predominance of biogenic sources. The ratios of *n*-alkanes versus isoprenoids (namely *n*-C17/Pr and *n*-C18/Ph) were calculated to draw information about the hydrocarbon origin and the degradation rate of petroleum (Damas et al. 2009; Liu et al. 2012). Because microorganisms generally utilize *n*-alkanes before isoprenoids as an energy source during biodegradation, low values of these ratios (< 1) indicate biodegraded oils, whereas recent input are in accordance with values > 1 (Tarozo et al. 2010). In this study, both *n*-C17/Pr and *n*-C18/Ph exceeded 1 in almost all samples analyzed (waters and sediments), which correspond to degraded petroleum, i.e., recent inputs (Damas et al. 2009). Nonetheless, S9, S10, S12, and S2 stations show a combination of matured petroleum and recent inputs.

The ratio of low to high molecular weight hydrocarbons (LMW/HMW) < 1 indicates the higher plants, aquatic animals, and bacteria sources of *n*-alkanes. It suggests the sources of petroleum sources when close to 1 and indicates the presence of fresh oil source when (LMW/HMW) > 2 (Wang et al. 2011). LMW/HMW rates < 1 were found in sediments from all sites in all year seasons, suggesting the terrestrial (high plants) origin of *n*-alkanes. By contrast in waters the ratios was close to 1, indicating petroleum and plankton as predominant sources (Wang et al. 2006; Sakari et al. 2008), expect for some stations S3 (O-NT), S5 (TMM), S6 (OB), S7 (Dr-OM), S8 (OM-OB), S9 (OB-OBK), S10 (Dr-BK), and 11 (O-BK), LMW/HMW > 2 indicates the presence of fresh oil origin.

The NAR (Natural *n*-Alkane Ratio) represents the proportions between natural and petroleum long chain *n*-alkanes (Mille et al. 2007; Kanzari et al. 2012; Syakti et al. 2013; Asia et al. 2009).

$$\text{NAR} = \sum n\text{-alkanes}(\text{C}19\text{–}32) - 2\sum \text{even}n\text{-alkanes}(\text{C}20\text{–}32) / \sum n\text{-alkanes}(\text{C}19\text{–}32)$$

In petroleum hydrocarbons and crude oils, the NAR ratio is close to zero, whereas in marine or higher terrestrial plants NAR ratio is close to 1. In the present study, the NAR ratio was close to 0, hence indicating that the hydrocarbons were from crude oils sources for most of the studied locations.

Table 6 Aliphatic diagnostic ratios in water samples from El Bey Wadi

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
	ZI-Gr	IB-OT	O-NT	O-T	TMM	OB	Dr-OM	OM-OB	OB-OBK	Dr-BK	O-BK	OB-ES	OB-VS	OB-SK
UCM														
Au	13.4	ND	79.4	20.3	ND	ND	29.2	22.3	ND	0.01	ND	ND	ND	ND
W	65.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sp	187	ND	68.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Su	ND	ND	15.1	15.4	ND	9.65	ND	ND	179	ND	ND	ND	ND	ND
Pr/Phy														
Au	ND	ND	ND	ND	ND	0.52	0.52	1.21	ND	0.81	ND	ND	ND	ND
W	0.19	0.08	0.08	0.08	ND	ND	ND	ND	0.09	0.08	ND	ND	ND	ND
Sp	0.21	0.13	0.13	0.21	0.1	ND	0.21	0.09	0.1	0.08	0.08	0.09	ND	0.08
Su	0.09	0.1	0.25	0.39	0.93	0.15	ND	ND	ND	ND	0.16	0.13	ND	ND
C17/Pr														
Au	ND	ND	ND	ND	ND	1.21	0.88	0.85	0.07	0.88	ND	ND	ND	ND
W	6.46	3.47	4.92	4.54	4.43	5.2	3.12	3.57	ND	3.28	6.6	ND	ND	ND
Sp	28.9	4.93	6.04	27.6	3.8	ND	7.9	2.9	3.75	3.31	4.26	3.43	ND	2.93
Su	0.9	0.82	0.84	0.9	0.75	0.94	ND	ND	4.51	ND	1.65	1.99	ND	ND
C18/Phy														
Au	ND	ND	ND	ND	ND	54.3	30.8	35.5	36.8	ND	47.8	ND	ND	ND
W	3.8	0.9	1.04	0.8	0.82	ND	ND	ND	ND	1.3	1.4	0.46	0.93	0.84
Sp	54.2	25.6	12.9	16.2	43.3	ND	9.91	6.64	15.5	0.62	0.65	0.76	ND	0.75
Su	1.15	1.19	1.57	1.82	22.1	1	ND	ND	ND	ND	5.1	2.4	1.75	ND
TAR														
Au	2.36	3.35	1.79	82.7	1.93	8.33	4.2	3.27	0.69	3.81	9.94	4.29	2.28	2.53
W	33.3	7.66	2.48	9.8	2.46	2.01	1.65	34.5	1.38	5.98	1.29	5.84	5.31	6.09
Sp	5	5.76	8.32	4.75	3.49	1.72	11.7	3.05	2.47	4.24	2.9	7.01	10.8	7.3
Su	3.11	2.32	3.77	2.19	1.27	1.41	1.59	1.53	9.83	2.95	11.1	2.57	1.46	0.95
TMD														
Au	2.31	2.77	1.74	9.43	1.62	6.05	3.11	2.56	0.92	3.02	6.2	3.57	1.93	2.14
W	9.55	0.57	0.67	2.38	0.57	0.24	0.42	2.41	1.31	4.6	1.47	0.46	0.68	0.74
Sp	2.85	2.91	3.31	2.42	2.26	1.24	4.56	2.04	1.91	2.81	2.13	4.06	5.41	3.85
Su	2.26	1.44	2.71	1.87	1.06	1.28	1.32	1.4	6.35	2.6	6.46	1.73	1.03	1.04
C31/C19														
Au	1.99	3.9	3.03	31.4	1.78	8.48	2.37	3.26	0.72	4.08	5.57	4.43	3.63	2.67
W	7.41	2.71	2.06	8.72	1.37	1.17	1.66	14.8	1.61	2.44	1.85	2.44	2.27	2.99
Sp	2.81	1.17	10.3	1.4	2.51	2.1	2.16	1.4	1.52	1.42	1.45	4.62	7.53	3.52
Su	4.03	1.28	3.79	1.3	0.15	1.18	2.02	1.51	0.69	1.05	20.3	2.14	0.71	2.18
NAR														
Au	−0.64	−0.7	−0.7	0.15	−0.5	−0.4	−0.6	−0.3	−0.1	−0.6	−0.6	−0.6	−0.5	−0.6
W	−0.11	0.31	−0.3	−0.1	−0.3	0.54	−0.5	0.07	−0.1	−0.3	−0.2	0.38	0.25	0.16
Sp	−0.35	−0.3	−0.3	−0.1	−0.6	−0.6	−0.1	−0.3	−0.5	−0.3	−0.2	0.04	0.15	−0.1
Su	−0.7	−0.6	−0.4	−0.7	−0.5	−0.7	−0.7	−0.8	−0.3	−0.7	−0.4	−0.7	−0.8	−0.8
Paq														
Au	0.43	0.3	0.35	0.44	0.33	0.16	0.26	0.4	0.52	0.37	0.19	0.31	0.65	0.58
W	0.17	0.42	0.52	0.26	0.55	0.54	0.43	0.44	0.45	0.28	0.53	0.43	0.52	0.5
Sp	0.5	0.41	0.52	0.53	0.28	0.52	0.58	0.55	0.55	0.52	0.49	0.33	0.27	0.53
Su	0.36	0.47	0.31	0.48	0.71	0.45	0.46	0.47	0.29	0.35	0.1	0.44	0.61	0.46
LMW/H MW														
Au	1.6	0.89	1.63	1.16	1.13	0.93	1.71	1.51	0.46	1.12	1.32	1.41	1.37	1.23
W	0.08	1.05	2.26	0.29	2.45	2.19	3.17	0.23	0.84	0.29	0.88	1.16	0.85	0.69
Sp	0.57	1.03	0.71	0.39	5.85	4.66	0.18	2.32	4.49	2.03	2.4	1.18	1.02	0.82

Table 6 (continued)

	S1 ZI-Gr	S2 IB-OT	S3 O-NT	S4 O-T	S5 TMM	S6 OB	S7 Dr-OM	S8 OM-OB	S9 OB-OBK	S10 Dr-BK	S11 O-BK	S12 OB-ES	S13 OB-VS	S14 OB-SK
Su	1.33	1.04	0.85	1.23	1.04	0.97	0.95	1.23	0.46	0.93	0.83	1.21	1.16	1.3
CPI														
Au	0.02	0.03	0.03	0.052	0.06	0.12	0.05	0.04	0.18	0.03	0.07	0.05	0.05	0.03
W	0.9	1.85	0.25	0.97	0.26	2.91	0.15	1.26	0.66	0.58	0.61	2.4	1.58	1.4
Sp	0.41	0.29	0.38	0.76	0.09	0.15	0.93	0.26	0.12	0.25	0.27	0.55	0.69	0.49
Su	0.12	0.19	0.36	0.12	0.23	0.10	0.11	0.10	0.4	0.11	0.28	0.11	0.09	0.08
ACL														
Au	28.5	29	28.9	28.3	29	29.2	28.7	28.6	29.1	28.7	29.1	28.9	28.1	28.7
W	29.7	27.8	27.7	29.2	27.8	28.3	28.8	27.8	29.6	29.1	28.6	28.3	27.6	27.7
Sp	27.7	27.9	27.7	27.5	29.5	28.9	27.5	28.1	28.2	28	28.3	28.8	29.1	27.9
Su	80.1	66.8	51.8	90.1	54.7	88	87	112	47.9	79.4	49.3	87.6	89	91
%Wax Cn														
Au	18.5	21.1	18.4	13.9	14.4	10.7	10.5	15.7	5.74	22.8	11.9	15.3	17.8	22.9
W	12.8	5.51	5.96	10.6	8.13	1.21	6.9	4.53	11.9	20.5	14.9	2.62	2.63	5.37
Sp	5.1	5.57	6.34	5.56	4.89	5.14	4	2.83	1.89	1.87	4.1	13.7	22.1	2.51
Su	19.1	18.1	12.5	21.1	13.5	17.9	24.5	21.6	13.7	16.9	26.8	18.4	23.7	20.6

The relative importance of terrigenous inputs versus aquatic inputs was estimated by means of TMD index (terrestrial vs. marine discriminant) (Syakti et al. 2013; Meyers 2003), which is the ratio of (*n*-C25 + *n*-C27 + *n*-C29 + *n*-C31 + *n*-C33)/(*n*-C15 + *n*-C17 + *n*-C19 + *n*-C21 + *n*-C23). In fact, TMD rates > 1 indicated that terrestrial plants were predominant except for S6 (OB), S7 (Dr-OM), and S12 (OB-ES), where TMD was lower than 0.5 in waters (marine inputs predominant), and for S2 (IB-OT), S8 (OM-OB), and S13 (OB-VS) sediments and S2 (IB-OT), S3 (O-NT) S13 (OB-VS), and S14 (OB-SK) waters (0.5 < TMD < 1.0, i.e., mixed inputs). The *n*-C31/*n*-C19 concentration ratio, which is a source nature index similar to TMD (Yusoff et al. 2012), confirmed our previous findings. The ratio of *n*-C31/*n*-C19 is used to identify the predominance of hydrocarbon input from land or marine source. Values < 0.4 indicate the predominance of marine biogenic sources, whereas numbers > 0.4 show land-derived hydrocarbons (Fagbote and Olanipekun 2013). In this study, all *n*-C31/*n*-C19 ratio rates exceeded 0.4, which indicate terrestrial origin.

Proxy ratio (Paq) indicate the presence of macrophyte inputs from terrestrial plants (Oyo-Ita et al. 2010; Syakti et al. 2013). Values < 0.1 indicate nonemergent plant input. This index was calculated according to the formula (Ficken et al. 2000):

$$\mathrm{Paq} = (\mathrm{C23} + \mathrm{C25})/(\mathrm{C23} + \mathrm{C25} + \mathrm{C29} + \mathrm{C31})$$

Our results shows that Paq ratio are between 0.1 and 0.4 indicate emergent macrophytes. Conversely, those from 0.4 to 1.0 indicate submerged/floating macrophytes.

The plant wax *n*-alkanes percentage (% WNA) was examined to assess the relative importance of biogenic emission. % WNA was calculated according to formula (Simoneit et al. 1991):

$$\%\mathrm{Wax}C_{n=}\left[\sum\left[C_n - 0.5 * \left(C_{n-1} + C_{n+1}\right)\right] \Big/ \sum C_n\right] * 100.$$

Our results shows that in sediment, wax *n*-alkanes range from 0.59 to 23.3 and in waters, wax *n*-alkanes accounted for 2.5% to 26.8%. In fact, high % WNA values indicate high contributions of biogenic sources (Cincinelli et al. 2007; Rogge et al. 1993).

Finally, the average carbon chain length (ACL) was calculated. ACL remains approximately constant in (unpolluted) areas as long as natural inputs do not change with time; by contrast, inputs of petrogenic hydrocarbons decrease the ACL rate (Jeng 2006).

ACL was calculated as follows:

$$\mathrm{ACL}\left(\mathrm{C}_{25} - \mathrm{C}_{33}\right) = \left[25 * \mathrm{C}_{25} + 27 * \mathrm{C}_{27} + 29 * \mathrm{C}_{29} + 31\mathrm{C}_{31} + 33 * \mathrm{C}_{33}\right] / \left[\mathrm{C}_{25} + \mathrm{C}_{27} + \mathrm{C}_{29} + \mathrm{C}_{31} + \mathrm{C}_{33}\right]$$

In El Bey Wadi, ACL lied within the 26–31 intervals for sediments and within 48–116 in waters (Tables 5 and 6). Thus, severe disturbances were detected in the aquatic

Table 7 Pearson correlation matrices (r-values) for the main sediment parameters, taken into account all stations ($n = 13$)

	TOC	n-Alkanes	TAR	NAR	C17/Pr	C18/Phy	R/UCM
n-Alkanes	0.34	–	–	–	–	–	–
TAR	− 0.08	**0.64**	–	–	–	–	–
NAR	− 0.26	0.31	0.17	–	–	–	–
C17/Pr	0.27	**0.57**	0.41	**0.50**	–	–	–
C18/Phy	0.19	**0.59**	0.24	**0.76**	**0.68**	–	–
R/UCM	0.20	**0.61**	0.26	0.27	**0.91**	**0.86**	–
CPI	**0.55**	**0.81**	**0.88**	0.19	0.15	0.25	0.38

Significant correlations ($P < 0.05$) are in bold

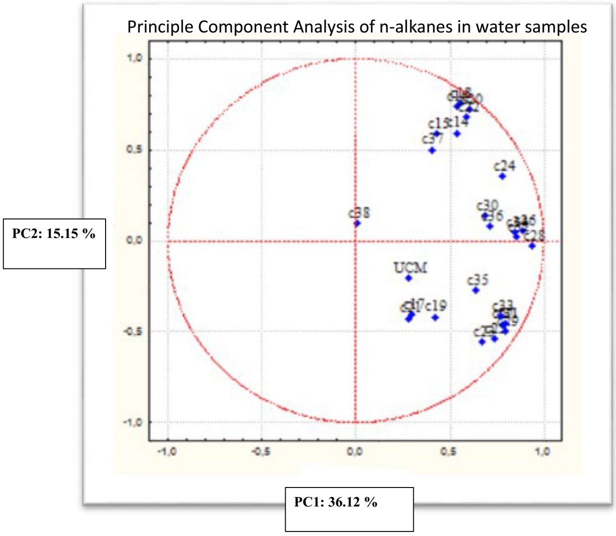


Fig. 6 Principal component analysis (PCA) of n-alkanes and diagnostic ratios in water samples

ecosystems, i.e., heavy anthropogenic inputs interfered with the ACL balance.

Correlation Between Biogeochemical Parameters, *n*-Alkanes, and Indices

In this study, the relationship between the concentrations of n-alkanes, TOC, TAR, NAR, C17/Pr, C18/Phy, R/UCM, and CPI has been analyzed. No correlation between total TOC, n-alkanes, TAR, NAR, C17/Pr, C18/Phy, and R/UCM ($r_{n\text{-alkanes}} = 0.34$, $r_{\mathrm{TAR}} = -0.08$, $r_{\mathrm{NAR}} = -0.26$, $r_{\mathrm{C17/Pr}} = 0.27$, $r_{\mathrm{C18/Phy}} = 0.19$, $r_{\mathrm{R/UCM}} = 0.20$, $P > 0.05$, $n = 13$). No correlation registered between (TAR) and TOC indicated that the dominant source of the organic matter was terrestrial higher plants (Table 7).

The concentrations of n-alkanes is significantly positively correlated with TAR, C17/Pr, C18/Phy, R/UCM, and CPI ($r_{\mathrm{TAR}} = 0.64$, $r_{\mathrm{C17/Pr}} = 0.57$, $r_{\mathrm{C18/Phy}} = 0.59$, $r_{\mathrm{R/UCM}} = 0.61$, $r_{\mathrm{CPI}} = 0.81$, $P < 0.05$, $n = 13$).

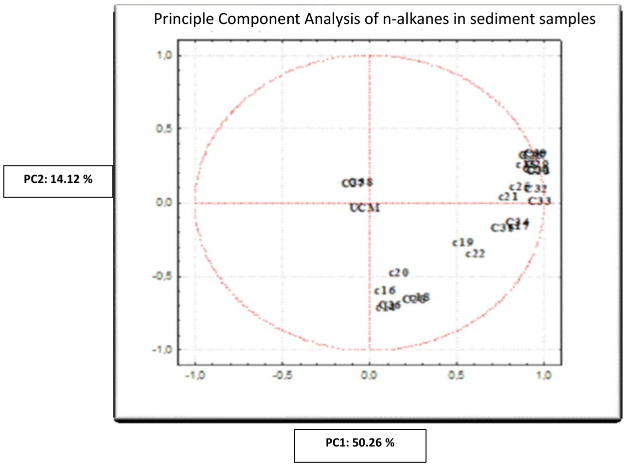


Fig. 7 Principal component analysis (PCA) of n-alkanes and diagnostic ratios in sediment samples

Principal Component Analysis (PCA) of *n*-Alkanes in Sediment and Water

A principal component analysis was used to distinguish between the sampling stations. To assess the sources of n-alkanes determined in this study in waters and sediments of Wadi El Bey, PCA was performed with Statistica6 software to make relatively quantitative analysis for each source of n-alkanes. Five principal components accounting for 75.04% in water and 77.88% in sediment samples of the total variance were extracted from the data set. After varimax rotation, two factors (eigenvalue > 1) were extracted by PCA. The rotated factor loading are listed in Figs. 6 and 7.

For water analysis, the first factors (PC1) explained a total variance of 36.12% in the data. These factors were strongly weighted. The context of low and high molecular weight shows mixed origin and UCM, which is normally associated with petroleum hydrocarbon distribution (Yu et al. 2016). The second factor (PC2) responsible for 15.51% of the total variance was strongly related to even carbon chains, which in water samples were from n-C14-n-C22. It has been suggested that these even light n-alkanes were issued from bacteria and from petroleum-derived inputs (Mille et al. 2007; Harji et al. 2008; Yu et al. 2016). The third factor (PC3) responsible for 8.04% of the total variance was strongly related to odd carbon chain (*n*-C15, *n*-C37), which may be attributed to phytoplankton or higher plant debris (Blumeret al. 1971; Goutx and Saliot 1980). PC4 contributed to 7.86% of the total variance that is related to C18/Pr, C17/C29, CPI, and LMW/HMW, which correspond to petroleum contamination; C17/C29 is associated to terrestrial input. The fifth factor (PC5) is responsible for 7.5% of the total variance and is strongly related to TAR, NAR, and C17/Pr, which indicate a mixed source of crude oils.

For sediments samples, the first factor describes 41.99% of the total variance and mainly represents predominance of long-chain *n*-alkanes and predominance of short-chain *n*-alkanes (Fig. 7). As for the distribution patterns, they showed large contributions from odd carbons (C27, C29, C31). whereas the vascular plants dominated by C27, C29, and C31 *n*-alkanes (Choudhary et al. 2010).

The second factor (PC2) responsible for 14.71% of the total variance was strongly related to even carbon chains, C14-C22, UCM, C17/Pr, and C18/Phy, which reflects petroleum contamination. The third factor (PC3) responsible for 10.30% of the total variance was related to C19 and TAR. Aquatic algae (both micro- and macro-algae) and photosynthetic bacteria are dominated by C19 and TAR to terrestrial origin.

PC4 contributed to 5.63% of the total variance, which was related to C20 and CPI. In this study, CPI value represents petroleum sources.

The fifth factor (PC5) is responsible for 5.25% of the total variance and was related to C37, C38, and LMW/HMW correspond to petroleum inputs. PCA analysis confirmed that *n*-alkanes in waters and sediments of El Bey Wadi were regulated by both biogenic (terrestrial and marine) emission and fresh petroleum contamination, whose relative importance depended on the site.

Pollution Level of El Bey Wadi

The evaluation and monitoring of organic contaminants in the environmental are important objectives (Kouzayha et al. 2011). El Bey Wadi receives a variety of wastewaters from agriculture runoff, industrial, and municipal effluents contain different types of organic pollutants. Among a wide variety of organic pollutants present in water, hydrocarbons, including aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), are among the most widespread organic contaminants found in the aquatic environment. Because of their complementarities, the simultaneous study of AH and PAH constitutes a relevant approach for a more complete estimation of the origin and sources of hydrocarbons as well as their environmental behavior (Bouloubassi and Saliot 1993; Guigue et al. 2011). Recently, some research has described the pollution status of El Bey Wadi. These works were mainly concerned to polycyclic aromatic hydrocarbons assessment (Gdara et al. 2017, 2018). Overall, our results shows that El Bey Wadi is moderate-to-highly impacted by hydrocarbons.

Various diagnostic indices (DRs) were used to identify hydrocarbon sources. These indices indicate that the origin of the aliphatic hydrocarbons affecting the sediments and waters of El Bey Wadiare related to biogenic inputs (plankton and terrestrial plants) and petrogenic (petroleum contamination). For aromatic hydrocarbons, the calculated molecular diagnostic ratios showed pollution by a pyrolytic (car traffic, residential heating, combustion), petrogenic, and mixed origin. According to the ecotoxicological assessment performed, PAHs pose a moderate to high risk for the entire ecosystem (Gdara et al. 2017, 2018). Our results would contribute to understanding the levels and sources of hydrocarbons in El Bey Wadi, directly connected to the Mediterranean Sea. This can provide useful information for human health and water resources protection in this dynamic region of the world.

Conclusions

This study provides the first concentration data and information about the sources of aliphatic hydrocarbons in sediments and waters of 14 stations of El Bey Wadi, which belong to distinct environmental contours, i.e., receive industrial, municipal, and farming wastewaters at different extents. The maximum levels of *n*-alkanes in waters and sediments were found in two stations S1 (ZI-Gr) and S5 (TMM) receiving industrial effluents. Comparison of the concentrations observed with a worldwide survey of aliphatic hydrocarbon loads in rivers showed that El Bey Wadi stations were moderately to highly contaminated. Diagnostic indices (ADIs) used to identify the pollution sources, i.e., *n*-C17/Pr, *n*-C18/Phy, Pr/Phy, C29/C17, C31/C19 ratios, UCM TAR, NAR, LMW/HMW, CPI, Paq, and TMD indexes, showed that aliphatic hydrocarbons in sediments and waters could be linked to mixed biogenic (plankton and terrestrial plant) and petrogenic sources. The low UCM/*n*-alk ratio values indicated that pollution was diluted by natural input. The results of this study can provide a comprehensive baseline reference with regard to aliphatic and *n*-alkanes occurrence in El Bey Wadi ecosystem and background information for further environmental research.

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