



Natural and anthropogenic sources of extractable organic matter in sediments from the coastal zone of the Arabian Gulf in Saudi Arabia

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Abstract

Surface sediment samples from the Arabian Gulf coast of Saudi Arabia were collected by Van Veen grab sampler to identify the characteristics, distribution, and levels and to discriminate between natural and anthropogenic sources of the total extractable organic matter (TEOM). The dried and sieved sediments were extracted with a dichloromethane/methanol mixture for analysis by gas chromatography-mass spectrometry. The TEOM included *n*-alkanes ($353.9 \pm 283.8 \text{ ng.g}^{-1}$), *n*-alkanols ($283.2 \pm 296.1 \text{ ng.g}^{-1}$), fatty acid methyl esters ($245.2 \pm 353.7 \text{ ng.g}^{-1}$), hopanes ($100.7 \pm 158.2 \text{ ng.g}^{-1}$), steranes ($58.5 \pm 96.3 \text{ ng.g}^{-1}$), triterpenoids ($18.9 \pm 21.1 \text{ ng.g}^{-1}$), steroids ($15.3 \pm 17.0 \text{ ng.g}^{-1}$), polycyclic aromatic hydrocarbons (PAHs) ($0.48 \pm 1.19 \text{ ng.g}^{-1}$), as well as an unresolved complex mixture (UCM = $1633 \pm 3151 \text{ ng.g}^{-1}$) and petrochemicals ($343.1 \pm 424.2 \text{ ng.g}^{-1}$). The major sources of these TEOM compound groups were anthropogenic (petroleum and petrochemical) and natural (lipids from higher plants, marine material, and microbiota) inputs. Anthropogenic contaminants from petroleum products ranged from 46.6 to 85.6% of the TEOM, whereas petrochemicals varied from 10.7 to 40.6%. The biogenic influx from terrestrial vegetation ranged from 5.7 to 19.3%, and marine biotic sources varied from 11.1 to 37.5%. The continuous accumulation of anthropogenic contaminants will ultimately affect the critical habitats of this marine coastal region. This provides a basis for further studies to understand human and developmental activities on input delivery, deposition processes, distribution, and biogeochemical alteration of organic matter in the coastal zones of the Arabian Gulf. Such studies are important for the sustainable development and protection of these key regional habitats.

Keywords Arabian Gulf · TEOM · UCM · GC–MS

Introduction

The Arabian Gulf is a major source region for crude oil and an important shipping pathway for oil tankers. Its tropical marine habitats have been recognized by international

organizations for their conversation, scientific, economic, and recreational values (Sheppard et al. 1992, 2010; Vogt 1995, 1996; George and John 1999; Qurban et al. 2011; Almahasheer 2018; Cusack et al. 2018). The need for conservation and protection arises from the rapid developmental activities in the region, with the concomitant introduction of a range of pollutants and the unplanned use of these habitats (Burt 2014; Burt and Bartholomew 2019). Petroleum exploitation and transport have been of particular concern in these coastal marine systems because of the obvious and detrimental short-term effects, although there is also evidence of subtle long-term consequences (Sadiq and McCain 1993; Burt et al. 2008; Issa and Vempatti 2018). However, it should be noted that there are considerable difficulties in distinguishing the subtle long-term effects of petroleum or any other pollution under field conditions due to the natural variability in ecosystems.

Previous studies have indicated that the main sources of contaminants in the Arabian Gulf are inputs from

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urbanization and tourism activities and from oil and industrial production activities (Vaughan et al. 2019). Much of the petroleum contaminants in the Arabian Gulf region are due to onshore and offshore oilfields, discharges from refineries and shipping traffic, petrochemical plants, regional recurrent wars, and possibly natural oil seeps (PME/UNEP 1989; Sadiq and McCain 1993; Michel et al. 1993; Soliman et al. 2019). The degree of oil pollution of shorelines around the Arabian Gulf has been a serious problem along major sections of the Gulf (Al-Arfaj and Alam 1993; Literathy 1993; Reynolds 1993; Massoud et al. 1998; Issa and Vempatti 2018; Soliman et al. 2019). Runoff from rivers and fallout of air particulate matter transported by wind are other major sources of organic components to the Arabian Gulf (Rushdi et al. 2009, 2010, 2014a, b). The Shatt al-Arab River, which is about 200 km in length, is the main river discharging into the Gulf. It deposits copious amounts of silt into the coastal zone of the northern part of the Gulf (Talling 1980; DouAbul et al. 1988), which ultimately introduces different amounts and types of organic and inorganic materials to the upper part of the Gulf (Rushdi et al. 2010, 2018). Dust storm episodes are ubiquitous on the Arabian Peninsula and extend offshore to impact the Arabian seas (Rushdi et al. 2017, 2019a). A wide variety of materials of different chemical compositions are introduced to oceanic ecosystems by atmospheric dust and fine aerosol components (Simoneit 1977, 1978, 2006).

Organic compositions and components of sediments are commonly applied to discriminate the various sources of chemical compounds (e.g., Rushdi and Simoneit 2002a, b; Birgel et al. 2004; Gogou and Stephanou 2004; Hopmans et al. 2004; Boot et al. 2006; Rushdi et al. 2006a, b, c, 2009). Source correlation of sediment organic matter has usually been utilized to distinguish specific inputs from point sources (Rushdi and Simoneit 2002a, b; Stiehl et al. 2005; Boot et al. 2006; Jaffé et al. 2006; Rushdi et al. 2019a, b).

Different organic sources will have different impacts on the biogeochemistry and biodiversity of the aquatic environment depending on the chemical components and levels of inputs. Most of the previous research on organic matter (OM) in the Gulf has focused mainly on oil pollution (Sadiq and McCain 1993; Zhao et al. 2015; Al-Saad et al. 2017; Marzooq et al. 2019). However, we still do not know the different fractions of natural and anthropogenic OM sources and their contributions to this coastal zone environment. Therefore, the objectives of this work are to characterize the compositions, levels, and distribution of the total extractable organic matter (TEOM) and to assess its sources in the surface sediments of the eastern coast of Saudi Arabia. This is based on key parameters and molecular marker analysis. Also, we will evaluate the possible impacts of these organic inputs on the habitats of this coastal ecosystem.

Study area

The coast of Saudi Arabia has about a 777 km shoreline from the Kuwait border to Salawa Bay at the border of Qatar (Fig. 1). The major ecosystems along this coastal zone include seagrasses, coral reefs, mangroves, saltmarshes, sabkha, rocky shores, and landfills (Price 1993; Price et al. 1991; Barth 2001). These habitats are important for maintaining the biological diversity of the marine environment of the region and providing precious natural and economic resources such as nursery areas for a variety of commercially important marine organisms. The coastal zone is also a significant fishery resource for the region, especially for shrimp (Price 1979, 1982; Burt and Bartholomew 2019; Vaughan et al. 2019).

Experimental procedures

Sampling

Shallow surface sediments were collected by Van Veen samplers from the Arabian Gulf along the coastal zone of Saudi Arabia, where twelve sites were selected for sample collection (Fig. 1). The location names, coordinates, and water depths of the selected sites, which ranged from 0.2 to 20.3 m, are listed in Table 1. The sites were divided into nearshore and offshore locations from Al-Khafji in the north to Al-Uqair in the south. About 35 g of each wet sediment subsample was taken, dried at room temperature, ground with mortar and pestle, and sieved to obtain < 125 μm fine particles.

Extraction

The extraction method was the same procedure as that described by Rushdi et al. (2014a, b). About 15 g of each dried and ground sample was extracted three times using ultrasonic agitation for a 15 min period each with 20 mL of dichloromethane (DCM) and 10 mL of methanol (MeOH). The extraction was carried out in a 150 mL precleaned beaker. A filtration unit with an annealed glass fiber filter (Whatman, GF/A filters, particle retention = 1.6 μm) was used to separate the sediment particles from the extract. We first concentrated the filtrate on a rotary evaporator and then reduced it to a volume of about 50 μL by a stream of dry nitrogen gas. The volume of the extract was then adjusted to 100 μL exactly by the addition of DCM:MeOH (2:1, v:v).

Instrumental analysis

Instrumental analysis by gas chromatography-mass spectrometry (GC-MS) was performed by an Agilent 6890 gas

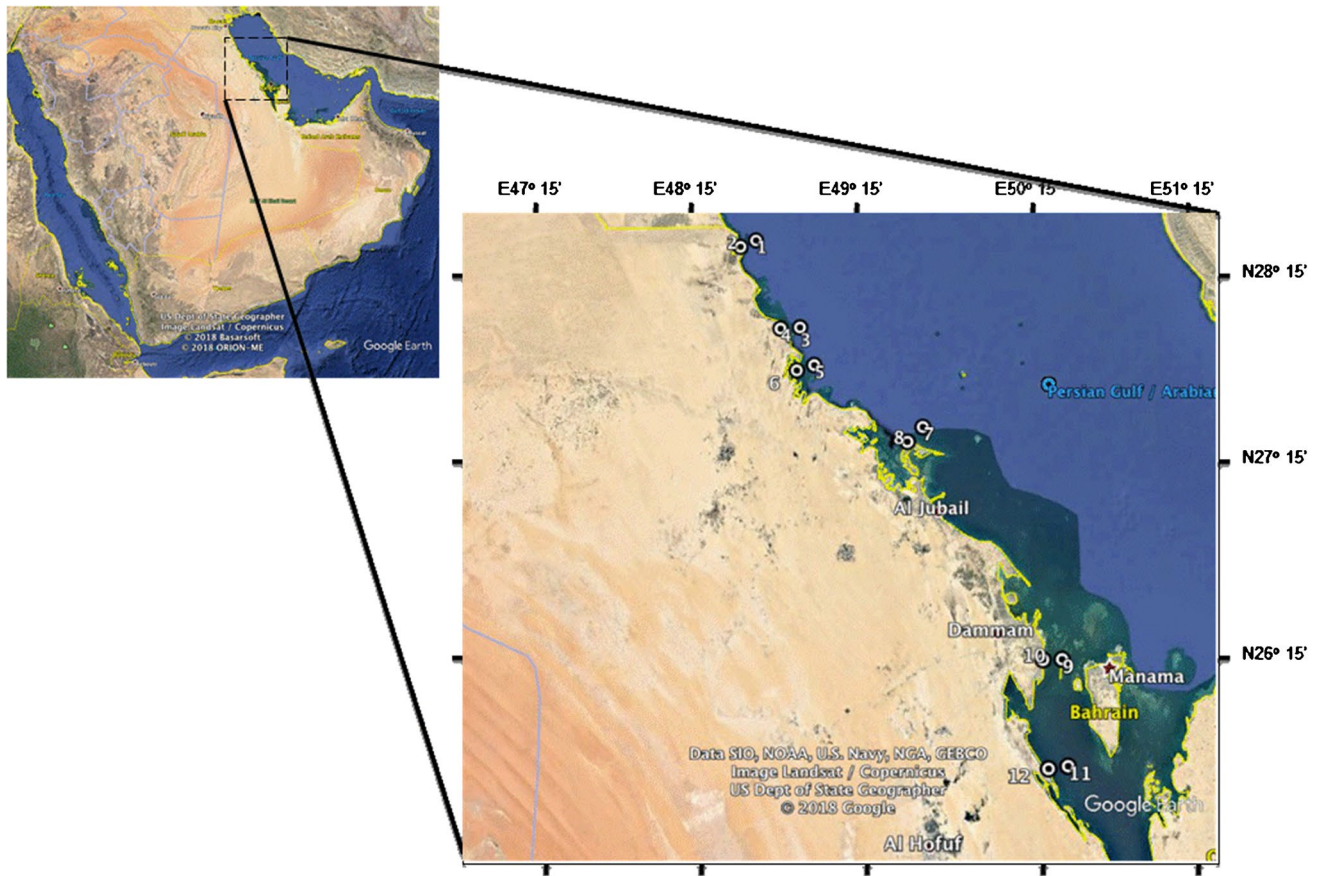


Fig. 1 Map showing the locations of sampling sites along the coastal zone of the Arabian Gulf in Saudi Arabia

Table 1 Stations, location names, coordinates, and water depths of the sampling sites along the Arabian Gulf coast of Saudi Arabia

Station ^a	Location name	Latitude (°E)	Longitude (°N)	Water depth (m)
S1	Al-Khafji	28.4531	48.6222	20.3
S2	Al-Khafji	28.4172	48.5303	6.1
S3	Saffaniyah	27.9912	48.8561	3.2
S4	Saffaniyah	27.9637	48.7756	7.8
S5	Tanjib	27.7665	48.9731	3.1
S6	Tanjib	27.6937	48.8725	1.2
S7	Khursaniyah	27.4379	49.5942	11.2
S8	Khursaniyah	27.9637	49.7756	1.2
S9	Dammam	26.2669	50.3306	1.1
S10	Dammam	26.2663	50.2253	0.2
S11	Al-Uqair	25.7563	50.3383	10.5
S12	Al-Uqair	25.7454	50.2325	6.4

^aOdd number = offshore stations and even numbers = near shore stations

chromatography coupled to a 5973MSD operated in the electron impact mode at 70-eV ion source energy. The gas chromatography (GC) was fitted with a 30 m × 0.25 mm fused capillary column coated with 0.25-µm film thickness

DB-5MS (Agilent). Helium was the carrier gas at a constant flow rate of 1.3 ml.min⁻¹ (split ratio = 1:1.2), and the samples were injected in the splitless mode (splitless time of 30 s). The GC was temperature programmed from 65

(2-min initial hold) to 310 °C at 6 °C min⁻¹ (isothermal for 20-min final time). The MS was operated in the electron impact mode at 70-eV ion source energy and scanned from 50 to 650 dalton at 1.27 scan s⁻¹. Mass spectrometric data were acquired and processed using the GC–MS ChemStation software (NIST98-library) data system.

Before analysis by GC–MS, we derivatized an aliquot (50 µL) of each total extract with a silylating reagent [N,O-bis(trimethylsilyl)trifluoroacetamide, BSTFA, Pierce Chemical Co.] to replace the H in hydroxyl groups with a trimethylsilyl [(CH₃)₃Si, i.e., TMS] group for better GC resolution of polar compounds. Each sample was injected splitless with an injector temperature of 300 °C.

Identification and quantification

The identifications of *n*-alkanes, hopanes, steranes, polycyclic aromatic hydrocarbons (PAHs), plasticizers (mainly phthalates), fatty acid methyl esters (FAME), fatty alcohols, sterols, triterpenoids are based primarily on their key ion pattern and mass spectra (i.e., fragmentograms *m/z* 85, 191, 217/218, 128/178/202/228/252/276/300, 177, 149, 87, 103, and 189, respectively) and gas chromatographic retention times that were compared with those of external standards. Other anthropogenic compounds were identified from their mass spectra. Quantification was performed from the total ion current (TIC) GC profiles using the external standard method with authentic compounds of each homologous series (Rushdi et al. 2006a, b, 2014a, b).

The external standards, which are shown in Figure SM-1, were from Sigma-Aldrich and included *n*-alkanes (nC₁₀–nC₄₀; total concentration = 500 ng.µL⁻¹), standard mixture (phenanthrene = 14 ng.µL⁻¹, methyl hexadecanoate = 16 ng.µL⁻¹, nonadecane-2-one = 12 ng.µL⁻¹, and tetracosane = 14 ng.µL⁻¹), chrysene-d-12 (100 ng.µL⁻¹), cholesterol (248 ng.µL⁻¹), friedelin (584 ng.µL⁻¹), and hexamethylbenzene (25 ng.µL⁻¹). We assessed the limit of detection (LoD) and limit of quantification (LoQ) the same way with the samples. The least-square method was used to fit the concentrations of the different standards versus their relative responses, and the correlations were significant with correlation coefficients ($R^2 = 0.91–0.98$). The LODs were 0.05–0.8 ng.µL⁻¹ for *n*-alkanes, 0.2–2.0 ng.µL⁻¹ for PAHs (chrysene), 0.2–2.7 ng.µL⁻¹ for friedelin, 0.01–0.01 ng.µL⁻¹ for cholesterol. The software SPSS 16.0 (IBM-Statistical Package for Social Science, version 16.0) was used to treat the data.

We calculated the average response factors for each compound, and the peak areas of the compounds derived from the TIC trace were used for their quantifications. The integration parameters were selected from ChemStation integrator with an initial threshold of 10. Relative ion counts were converted to compound mass using the area counts of

the external standards determined under the same instrumental operating conditions. The following formula: $[C_{(s)} (\text{ng/g}) = C_{st} (\text{ng.}\mu\text{L}) \cdot V_{inj,st} (\mu\text{L}) \cdot A_s (\text{count}) \cdot V_{TEXT} (\mu\text{L})] / [A_{st} (\text{count}) \cdot V_{inj,s} (\mu\text{L}) \cdot wt_{sed} (\text{g})]$ was used to calculate the concentration of each compound; where *C*, *A*, *V*, and *wt* are concentration, count, volume, and weight; the subscripts *s*, *st*, *inj*, and *sed* represent the sample, standard injected, and sediment, respectively.

Recovery blank and quality control

Fiber filters and sediment samples were spiked with *n*-tetracosane-d50 to test the recoveries, which were 92.8% and 72.9%, respectively. The measured concentrations were corrected accordingly. Both procedural blanks for sediments and solvents were analyzed and quantified to make sure there were no significant background interferences. We performed blank extracts with patches of three samples throughout the entire chemical analysis.

The technical accuracy of the research was one of the main considerations throughout this study and included sample collection, analytical methods, chemistry, geochemical interpretation, and biomarker tracer determination.

Results and discussion

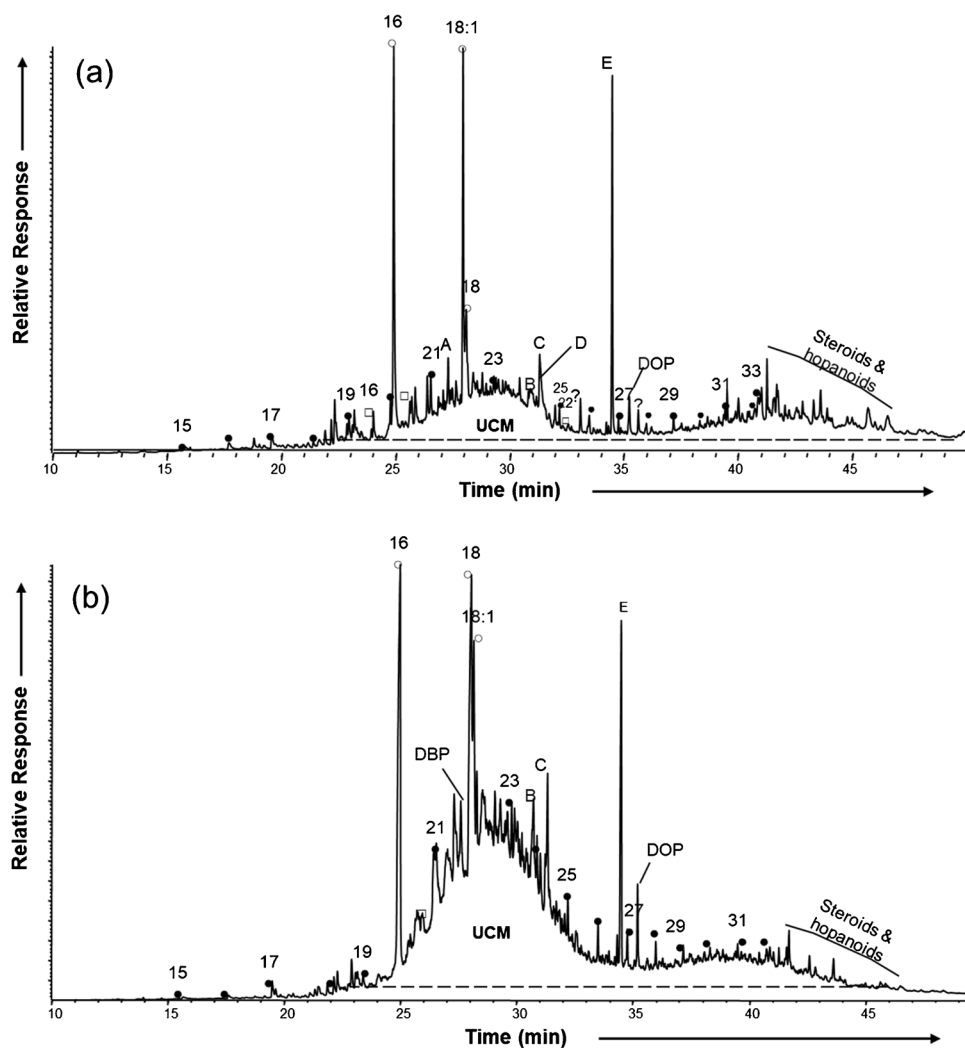
Examples of the main features of the GC–MS data and the major compounds in the total extractable organic matter (TEOM), identified in the sediment extracts are shown in Fig. 2. The TEOM included lipids from both natural and anthropogenic sources. The major natural organic compounds consisted of wax *n*-alkanes, fatty acid methyl esters, and *n*-alkanols, steroids, and triterpenoids. The anthropogenic compounds included *n*-alkanes, hopane and sterane biomarkers, PAHs, miscellaneous petrochemicals, and a UCM.

The presence, characteristics, and distribution patterns of the different compounds of TEOM from environmental samples can be used to classify their sources (Simoneit 1977, 1984, 1985; Bouloubassi et al. 2001; Rushdi et al. 2010, 2014a, b, 2017, 2018, 2019a). Therefore, known sources and mixtures of compounds in the environment can be compared. Accordingly, the TOEM compounds are reported and discussed here in order to define the sources of natural and anthropogenic inputs.

n-Alkanes

The dominant *n*-alkanes were in the range of C₁₃ to C₃₅ with maximum (C_{max}) concentrations at lower molecular weights mainly at pentadecane, heptadecane, eicosane, docosane, or

Fig. 2 GC–MS total ion current traces of total extracts from nearshore sediment samples of **a** station 2 (Al-Khafji) and **b** station 8 (Dammam), showing the major organic compounds (as TMS) (● *n*-alkanes, ○ methyl *n*-alkanoates, □ *n*-alkanols, DBP = dibutyl phthalate, DOP = dioctyl phthalate, A = 2,4-dioctyl phenol, B = 2-mercaptobenzothiazole, C = diethylene glycol-*p*-(1,1,3,3-tetramethylbutyl)phenol, D = *N*-phenylbenzenesulfonamide, and E = 2,2'-methylenebis[6-(*t*-butyl)-4-methyl]phenol. The numbers indicate the carbon chain length



tetracosane ($C_{\max} = 15, 17, 20, 22, \text{ or } 24$). The total concentrations ranged from 61 to 1080 $\text{ng}\cdot\text{g}^{-1}$ dry weight (dw) with a mean of $354 \pm 284 \text{ ng}\cdot\text{g}^{-1}$ (Table 2). The lowest concentration was observed for the sediment from station 8 (Al-Jubail conservation area) and the highest from station 10 (near Dammam). The odd-numbered *n*-alkanes were dominant over the entire range for some samples and the carbon preference index ($\text{CPI}_{(o/e)}$, Mazurek and Simoneit 1984) has been calculated using the following equation:

$$\text{CPI}_{(o/e)} = \frac{\sum C_{i(o)}}{\sum C_{i(e)}} \quad (1)$$

where $\sum C_{i(o)}$ and $\sum C_{i(e)}$ are the total concentrations of odd- and even-numbered *n*-alkanes, respectively. The $\text{CPI}_{(o/e)}$ values for the entire range varied from 0.75 to 3.42 (mean 1.63 ± 0.79). Pristane and phytane were not detected in any sample.

n-Alkanes are mainly derived from biogenic and anthropogenic sources and occur in all ecosystems. Their presence and distribution patterns are useful in assessing their sources

and preservation conditions in the environment. The CPI and C_{\max} parameters of the most abundant *n*-alkane in the homologous series provide critical information about their sources and characteristics. Another useful parameter is the unresolved-to-resolved compound ratio (U:R), which can be applied to confirm the sources of hydrocarbons (Simoneit 1977, 1978, 2002; Mazurek and Simoneit 1984).

The different C_{\max} of the *n*-alkanes of these samples, mainly at 15, 17, 21, and 22 (Table 2) indicated that major sources were from marine biota, including algae and bacteria and petroleum input (Gelpi et al. 1970; Meyers 1997; Bouloubassi et al. 2001). The $\text{CPI}_{(o/e)}$ was used to assess the contribution of biogenic versus anthropogenic inputs (Scalan and Smith 1970; Simoneit 1989), where a high value (> 3.0) indicates a major input from terrestrial plants and a low value (~ 1.0) indicates that the major source is petroleum residues. The range has been divided into C_{13} – C_{24} for marine inputs and C_{25} – C_{35} for a higher plant wax contribution. The low range (C_{13} – C_{24}) $\text{CPI}_{(o/e)}$ values vary from 0.70 to 8.83 with an average of 2.15 ± 2.31 (Table 2) and indicate a

Table 2 The concentrations, distribution, and organic geochemical parameters of the various lipid compounds in sediments from the coastal zone of the Arabian Gulf in Saudi Arabia

Stations	1	2	3	4	5	6	7	8	9	10	11	12	Mean	SD
n-Alkanes														
Range	13–33	14–33	14–35	16–35	15–33	13–35	15–33	16–33	14–33	14–33	15–33	14–33		
C (max)	15	22	22	21	22	15	22	17	17	24	21	17		
Concentration (ng/g)	227	381	578	63	345	573	177	61	166	1080	316	280	353.9	283.8
CPI	1.48	0.89	0.75	1.46	1.25	1.18	0.98	2.29	1.54	2.65	3.42	1.69	1.63	0.79
(<i>o/e</i>) _(14–35)														
CPI	3.49	1.38	0.94	1.46	1.20	2.06	0.94	1.55	1.22	0.78	1.62	2.35	1.51	0.75
(<i>o/e</i>) _(25–35)														
CPI (<i>o/e</i>) (13–24)	0.97	0.75	0.70	1.46	1.26	1.00	0.99	2.58	1.65	8.83	4.14	1.47	2.26	2.40
T (14–24)/ (25–35)	2.18	2.90	4.45	2.48	4.52	4.75	4.50	4.42	4.13	2.43	6.23	2.23	3.77	1.29
Terrestrial n-alkanes														
Concentration	35.0 (15.4%)	23.7 (6.2%)	7.0 (1.2%)	5.4 (8.5%)	13.7 (4.0%)	35.2 (6.1%)	2.5 (1.4%)	4.0 (6.5%)	7.4 (4.5%)	15.6 (1.4%)	17.7 (5.6%)	38.5 (13.8%)	17.1 (6.2%)	13.1 (4.5%)
Marine algae n-alkanes														
Concentration	9.7 (4.3%)	20.6 (5.4%)	23.8 (4.1%)	4.0 (6.2%)	41.0 (11.9%)	33.4 (5.8%)	27.9 (15.5%)	19.9 (32.5%)	21.9 (13.2%)	101.4 (9.4%)	66.6 (21.1%)	33.7 (12.1%)	33.7 (11.8%)	26.6 (8.3%)
Marine bacteria n-alkanes														
Concentration (ng/g)	2.6 (1.2%)	2.0 (0.5%)	6.7 (1.1%)	0.8 (1.2%)	0	0	3.2 (1.8%)	0	0	0	0	0	1.3 (0.5%)	2.1 (0.7%)
Petroleum n-alkanes														
Concentration (ng/g)	179.4 (79.1%)	336.7 (87.9%)	547.2 (93.6%)	53.9 (84.1%)	289.9 (84.1%)	504.3 (88.0%)	146.7 (81.4%)	37.3 (61.0%)	137.0 (82.4%)	963.0 (89.2%)	231.7 (73.3%)	207.6 (74.2%)	302.9 (81.5%)	261.3 (8.8%)
Methyl n-alkanoxates														
Range	14–26	14–28	14–28	14–26	14–28	14–28	14–28	14–27	14–30	14–26	14–20	14–26		
C _{max}	18	16	16	16	16	16	16	16	16	16	16	16		
Concentration (ng/g)	728.3	210.9	279.0	31.8	134.6	48.3	111.2	12.5	58.1	1179.1	129.9	18.1	245.2	353.7
CPI(<i>o/e</i>)	28.4	60.4	92.0	15.7	36.0	3.8	24.1	6.1	11.7	199.1	250.4	4.7	61.0	77.9
Terrestrial inputs (ng/g)	19.8	3.0	3.7	1.3	3.6	6.0	7.0	1.2	4.1	17.2	0.6	3.0	5.9	5.9
Marine inputs (ng/g)	708.4	207.9	275.3	30.5	131.0	42.3	104.2	11.3	54.0	1162.0	129.3	15.1	239.3	333.5
Terrestrial/marine ratio	0.028	0.014	0.013	0.042	0.027	0.141	0.067	0.106	0.076	0.015	0.005	0.200	0.061	0.058
n-alkanols														
Range	14–32	14–32	14–32	14–32	14–32	14–32	14–32	14–32	14–32	14–32	14–32	14–32		
C _{max}	30	28	28	28	28	28	28	28	28	28	28	28		

Table 2 (continued)

Stations	1	2	3	4	5	6	7	8	9	10	11	12	Mean	SD
Concentration (ng/g)	378.7	191.8	231.4	36.0	210.3	210.6	97.6	35.0	138.5	1173.2	494.5	200.6	278.5	310.6
CPI (e/o)	7.2	8.6	6.4	8.9	6.9	11.4	7.3	15.0	6.5	11.4	10.9	13.6	9.5	2.8
Terrestrial inputs (ng/g)	249.6	123.2	148.2	24.5	137.5	138.9	65.7	24.0	92.3	775.9	323.0	139.5	193.6	216.0
Marine inputs (ng/g)	129.1	68.7	83.2	11.6	72.7	71.7	31.8	11.0	46.2	397.3	171.5	61.1	84.8	94.6
Terrestrial/marine ratio	1.93	1.79	1.78	2.11	1.89	1.94	2.07	2.17	2.00	1.95	1.88	2.28	1.98	0.14
Hopane biomarkers														
Range	27–35	27–35	27–35	27–33	27–35	27–35	27–33	27–32	27–33	27–35	27–35	ND	ND	
C _{max}	30	30	30	30	30	30	30	29,30	30	31	0	0	0	
Concentration (ng/g)	360	96	58	7	60	96	27	3	10	491	0	0	100.7	158.2
C ₃₁ S/(R+S)	0.66	0.63	0.61	0.66	0.68	0.67	0.60	0.60	0.58	0.67			0.64	0.04
C ₃₂ S/(R+S)	0.34	0.41	0.32	0.44	0.49	0.38	0.46	0.35	0.37	0.79			0.43	0.14
Steranes														
Range	27–29	ND	ND	ND	27–29	27–29	27–29	27–29	27–29	27–29	27–29	ND	ND	
C _{max}	28				27	29	29	29	29	27	27	27	27	
Concentration (ng/g)	63.7				40.8	16.8	6.7	2.0	5.5	290.7	42.0	0	58.5	96.3
C ₂₇ S/(R+S)	0.79				0.38	0.52	0.39	0.34	0.56	0.67	0.56		0.53	0.16
C ₂₉ S/(R+S)	0.68				0.75	0.71	0.59	0.54	0.51	0.54	0.49		0.59	0.10
Steroids														
Range	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	27–29	
C _{max}	29	29	29	29	29	29	29	29	29	29	29	29	29	
Concentration (ng/g)	20.8	10.1	12.6	1.6	11.5	11.8	4.8	1.4	7.4	64.5	26.0	11.2	15.3	17.0
Terrestrial vascular plants	14.3	6.9	8.7	1.1	8.0	8.1	3.3	1.0	5.1	44.4	17.9	7.9	10.5	11.7
Marine biota	6.5	4.1	4.0	0.4	3.6	5.0	1.6	0.5	2.7	18.1	10.1	3.8	5.03	4.89
Terrestrial/marine	2.21	1.79	2.36	3.37	2.27	1.96	2.66	2.40	2.16	2.47	1.88	2.37	2.32	0.42
Triterpenoids														
Concentration (ng/g)	25.7	12.5	15.6	1.9	14.3	14.6	6.0	1.7	9.1	79.8	32.1	13.6	18.9	21.1
Plasticizers/petrochemicals														
Concentration (ng/g)	424.5	375.5	375.0	30.8	368.1	232.5	111.4	27.2	145.0	2798.7	784.8	217.0	490.9	756.2

Table 2 (continued)

Stations	1	2	3	4	5	6	7	8	9	10	11	12	Mean	SD
PAHs														
Concentration (ng/g)	3.87	1.86	0	0	0	0	0	0	0	0	0	0	0.48	1.19
Fla/(Fla+Py) ratio	0.55	0.59												
UCM														
Concentration (ng/g)	2285	1367	569	51	1588	563	203	91	14	11,388	1019	462	1633	3151
U:R	1.61	1.29	0.58	0.10	0.67	0.17	0.34	0.17	0.03	1.50	0.13	0.26	0.57	0.58
U:nC _B	51	31	19	5	29	8	7	4	0	97	12	6	22.5	27.8

ND, not detected

mixture of both marine plants, bacterial residues, and petroleum inputs are major in these sediments. Except for station 10, nearshore to Damman, its $CPI_{(13-24)} = 8.83$ is comparatively high due to dominant input from coastal marine algae. The $CPI_{(o/e)}$ values for the C_{25} – C_{35} range vary from 0.78 to 3.49 (mean 1.51 ± 0.75) and indicate that higher plant wax and petroleum are sources of these *n*-alkanes. The $CPI_{(o/e)}$ values for the entire *n*-alkane range (C_{13} – C_{35}) of these samples of 0.74–3.42 (mean 1.63 ± 0.79 , Table 2), also confirm a mixture of natural and anthropogenic sources. The lowest $CPI_{(o/e)}$ values are observed for station 2 ($CPI_{(o/e)} = 0.89$, near shore of Al-Khafji), station 3 ($CPI_{(o/e)} = 0.74$, offshore Saf-faniyah) and station 7 ($CPI_{(o/e)} = 0.98$, Khursaniyah), indicating that petroleum is the major source of *n*-alkanes for these locations.

To estimate the relative input from different sources, the concentrations of terrestrial plant wax *n*-alkanes (i.e., C_{27} , C_{29} , C_{31} , C_{33}) were calculated according to Simoneit et al. (1991a) and found to range from 2.5 to 38.5 ng.g^{-1} (mean $17.1 \pm 13.1 \text{ ng.g}^{-1}$, Table 2). We have used the same method to estimate the natural *n*-alkane (NA_x) contributions of marine algae (i.e., total of C_{15} , C_{17} , and C_{19}) and bacteria (total of C_{16} , C_{18} , and C_{20}) by the following equation:

$$NA_x = C_i - (C_{i-1} + C_{i+1})/2 \quad (2)$$

where C_i is the C_{max} of *n*-alkanes and C_{i-1} and C_{i+1} are the carbon numbers before and after the C_i . Thus, the concentrations of *n*-alkanes from marine algae and bacteria ranged from 4.0 to 101.4 ng.g^{-1} (mean $33.7 \pm 26.6 \text{ ng.g}^{-1}$) and from 0.0 to 6.7 ng.g^{-1} (mean $1.3 \pm 2.1 \text{ ng.g}^{-1}$), respectively.

Accordingly, the contributions from both marine and terrestrial natural sources range from 10.2 to 117.0 ng.g^{-1} (mean $52.1 \pm 29.6 \text{ ng.g}^{-1}$), and for *n*-alkanes from fossil fuel sources 53.9 to 936.0 ng.g^{-1} (mean $302.9 \pm 261.3 \text{ ng.g}^{-1}$, Table 2). Apparently, the major source of *n*-alkanes on the eastern coast of Saudi Arabia is crude oil and petroleum by-products. This is shown by the significant correlation ($R^2 = 0.99$) between petroleum *n*-alkanes and the total *n*-alkanes of the samples (Fig. 3d). The insignificant correlations between marine bacterial and terrestrial plant *n*-alkanes versus total *n*-alkanes ($R^2 = 0.0$ and 0.4, respectively; Fig. 3b, c) confirm that both bacterial and terrestrial inputs are not major in the sediments. The marine plant inputs have some contribution to *n*-alkanes of the sediments as indicated by the relatively significant correlation ($R^2 = 0.59$) between marine *n*-alkanes and total *n*-alkanes (Fig. 3a). The concentrations of *n*-alkanes from the Arabian Gulf coast sediments were about the same as concentrations in other contaminated coastal zones, such as Jiaozhou Bay, Qingdao, China (500 – 8200 ng.g^{-1} ; Wang et al. 2006). These concentrations were much lower compared to those reported from the Niger Delta, Nigeria

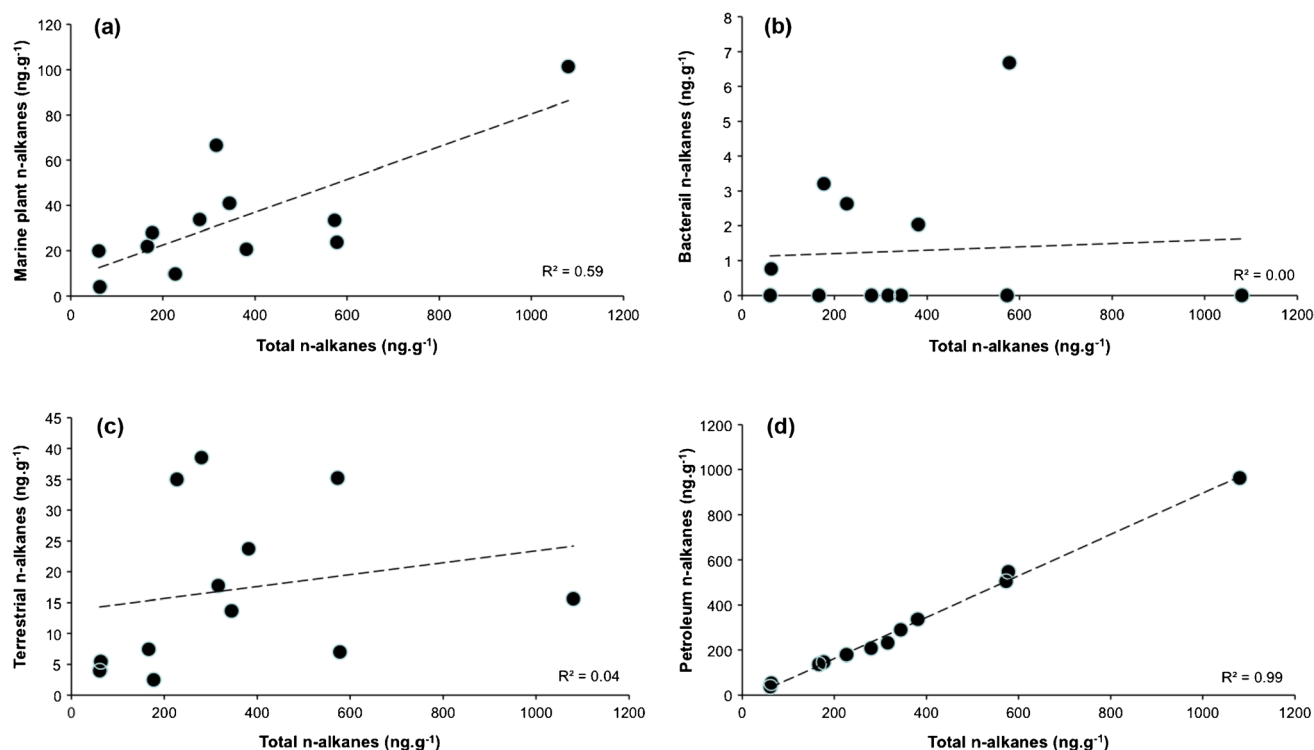


Fig. 3 The relationships between various sources of n-alkanes to total n-alkanes in the sediment samples from the coastal zone of the Arabian Gulf

(20–16,840 ng.g⁻¹ dw; Oyo-Ita et al. 2010), Patagonia, San Jorge Gulf (0–13,047 ng.g⁻¹; Commendatore et al. 2000), and Santos, SP, Brazil (170–107,800 ng.g⁻¹; Medeiros and Bicego 2004).

The percentages of anthropogenic n-alkanes from petroleum inputs on the eastern coast of Saudi Arabia ranged from 61 at station 8 to 94% at station 3 (mean $82 \pm 9\%$, Table 2). The natural n-alkane percentages ranged from 4 at stations 1 and 3 to 33% at station 8 (mean $12 \pm 8\%$) from marine algae, and from 1 at stations 3, 7, and 10 and 15% at station 1 (mean $6 \pm 5\%$) from terrestrial plants. The n-alkanes from bacterial sources were 0.0% at many stations to 1.8% at station 7. This indicates that petroleum by-products and marine algae are the major sources of n-alkanes in this coastal zone, followed by terrestrial plant wax and marine bacteria.

Fatty acids and alcohols

The methyl n-alkanoates (i.e., fatty acid methyl esters), were not detected in the sample blank and evidently, they were esterified natural fatty acids during sample preparation and extraction. Their concentrations in the sediment samples ranged from 13 to 728 ng.g⁻¹ (mean 245 ± 354 ng.g⁻¹). The

highest concentration was detected at station 1 and the lowest at station 8. The series from C₁₄ to C₃₀ had a C_{max} at 16 as acid, and an even-to-odd carbon preference indices (CPI_(e/o)) from 3.8 at station 6 to > 100 at stations 11 and 12 (mean 61.0 ± 77.9 , Tables 2 and SM-1). The total n-alkanol concentrations ranged from 35 to 1137 ng.g⁻¹ (mean 283 ± 296 ng.g⁻¹), where the lowest and highest concentrations were also observed at stations 8 and 10, respectively. The C_{max} was at 28 or 30, and the CPI_(e/o) ranged from 6.4 to 15.0 (mean 9.5 ± 2.8 , Table 2).

Methyl n-alkanoates are generally of natural origin or may be formed by transesterification in the extraction solvent from fatty acids or wax esters present. Their sources are similar to n-alkanoic acids from terrestrial vegetation, marine phytoplankton, microbial mats, and bacteria. The n-alkanoic acids from terrestrial plants are characterized by even carbon numbered homologs > C₂₀, whereas those from algae, plankton, and diatoms are characterized by also even carbon-numbered and branched homologs < C₂₀ (Simoneit 1978; Perry et al. 1979; Volkman et al. 1980; Kharlamenko et al. 1995; Budge and Parrish 1998). n-Alkanoic acids from bacterial mats are characterized by odd carbon-numbered and branched homologs < C₂₀ (Volkman et al. 1980; Rajendran et al. 1993; Harvey and Marko 1997; Parrish

et al. 2000; Oyo-Ita and Oyo-Ita 2012; Yang et al. 2014). Accordingly, we treated all fatty acids $> C_{20}$ as inputs from terrestrial sources, and all $< C_{20}$ from marine inputs. The contributions of terrestrial inputs ranged from 1.2 at station 8 to 19.8 ng.g⁻¹ at station 1 (mean 5.9 ± 5.9 ng.g⁻¹), whereas the marine contributions ranged from 11.3 at station 8 to 1162 ng.g⁻¹ at station 10 (mean 239 ± 334 ng.g⁻¹). The ratios of terrestrial/marine were small (0.061 ± 0.059 , Table 2), indicating that the dominant sources of fatty acids in these sediments were from marine biota, where the high values of CPI_(e/o) (61 ± 78) confirmed that they were mainly from marine algae and planktonic diatoms but not bacteria.

The occurrence of *n*-alkanols in the environment with C_{max} at 28, 30, or 32 and a strong even carbon-numbered predominance confirmed an input of terrestrial plant wax from tropical to semitropical environments (Simoneit 1977, 1978, 1989; Mudge 2005; Rushdi et al. 2006b; Treignier et al. 2006). Here, the high concentrations of *n*-alkanols with C_{max} at 28 or 30 and CPI_(e/o) > 4 support that the main source of these compounds is a terrestrial wax plant (Table 2). Also, the presence of the short-chain ($< C_{20}$) homologs are reported as markers of microbial sources (Bianchi 2007; Robinson et al. 1984). The ratios of terrestrial/marine *n*-alkanols in these sediments were relatively high (1.98 ± 0.14 , Table 2), indicating that the major source was terrestrial plant wax.

Hopane and sterane biomarkers

The occurrence of hopanes and or steranes in the environment indicates contamination from petroleum residues (e.g., Simoneit 1984; Simoneit et al. 1991b; Medeiros et al. 2005; Rushdi et al. 2016). Both hopane and sterane biomarkers were detected in the sediment samples, except for stations 11 and 12. The hopanes ranged from C₂₇ to C₃₅ with C_{max} at 30, 29, or 31 and concentrations from 0.0 to 491 ng.g⁻¹ (mean 101 ± 158 ng.g⁻¹, Table 2). The maximum concentration was found for station 10. Hopanes are usually resistant to degradation and alteration in the environment (Simoneit et al. 2009); thus, they are used to validate contamination by petroleum or coal in the environment (Peters and Moldowan 1993). The hopanes in the sediment samples had a dominance of the thermodynamically stable 17 α (H),21 β (H) epimers, C_{max} at 30, and minor 17 β (H), 21 α (H)-hopanes (Table 2). These epimeric configurations occur in crude oils and mature sedimentary rocks and are derived from the diagenetic interconversion of the 17(H),21(H)-hopane precursors of bacterial origins (Peters and Moldowan 1993). The distribution of the hopanes ranged from C₂₇ to C₃₅ for the α,β -series, with the homologs $> C_{30}$ present as the typically mature C-22 *R/S* pairs (Simoneit 1984; Simoneit et al. 1990).

Commonly, the hopane distributions from petroleum and engine exhaust show higher 22*S* hopane concentrations

relative to the corresponding 22*R* epimers (Simoneit 1984, 1985). The C₃₁ and C₃₂ *S/(S+R)* ratios of the extended hopanes ranged from 0.58 to 0.68 (mean 0.64 ± 0.04) and from 0.32 to 0.79 (mean 0.43 ± 0.14), respectively (Table 2). These values are in the range of mature crude oil and petroleum hydrocarbons (Peters and Moldowan 1993; Rushdi and Simoneit 2002a, b), and therefore confirm that petroleum is the source of the hopanes in sediments.

Sterane hydrocarbons are rarely found in gasoline or diesel fuels and are introduced into the environment from petroleum spills or lubricants in emissions of vehicular engines (Abas and Simoneit 1996; Rushdi et al. 2016). Ship-washing discharges, refinery activities, and municipal wastewaters are additional inputs of petroleum components to marine sediments (Laws 1993; Rushdi et al. 2014b). Thus, steranes are useful in confirming biomarker indicators for pollution by oil-related products in the marine environment (e.g., Moldowan et al. 1986; Aboul-Kassim and Simoneit 1996; Barakat et al. 1999). Steranes were also detected in the sediment samples, with dominant amounts of the C₂₇ and C₂₈ homologs. Their concentrations were significantly lower than those of the hopanes, ranging from 0.0 for stations 2–4 to 12 to 291 ng.g⁻¹ for station 10 (mean 58.4 ± 96.3 ng.g⁻¹, Table 2). The homologs comprised mainly the 5 $\alpha,14\alpha,17\beta$ and minor 5 $\alpha,14\alpha,17\alpha$ configurations, both occurring as 20*S* and 20*R* epimers. The *S/(S+R)* ratio of sterane epimerization at C-20 for C₂₇ was 0.34 to 0.67 (mean 0.53 ± 0.16), and for C₂₉ from 0.49 to 0.75 (mean 0.59 ± 0.10 , Table 2). These values indicated that the steranes were derived from petroleum sources.

Steroids and triterpenoids

The steroids and triterpenoids were also major components of the TEOM in these sediments (Fig. 2). The steroid concentrations ranged from 1.4 to 64.5 ng.g⁻¹ (mean 15.3 ± 17.1 ng.g⁻¹). The highest concentration was at station 10 and the lowest at station 8. They ranged from C₂₇ (cholesterol) to C₂₉ (sitosterol) with a C_{max} at 29.

Steroids occur in all ecosystems and are derived from the tissues of both fauna and flora (Akihisa et al. 1991). They have been used to classify the sources and identify the fate of organic matter in the environment (Volkman et al. 1981; Mudge and Norris 1997; Duan 2000; Rushdi et al. 2006b; Tolosa et al. 2014; Wisniewski et al. 2014). The major sterols in terrestrial plant lipids are campesterol, stigmasterol, and sitosterol (Moreau et al. 2002; Volkman et al. 2008), whereas the highest sterol in animal lipids and some phytoplankton and aquatic microbes is cholesterol (Volkman 1986; Bouloubassi et al. 1997; Voet and Voet 2004; Rampen et al. 2010). Brassicasterol, dinosterol, fucosterol, and minor cholesterol are dominant sterols in marine algae, diatoms, and dinoflagellates (Volkman and Smittenberg 2017 and

references therein). The presence of campesterol, stigmasterol, and sitosterol in these samples supports an origin from terrestrial vascular higher plant sources (Barbier et al. 1981; Simoneit et al. 1983; Volkman 1986; Moreau et al. 2002; Volkman et al. 2008), whereas the occurrence of brassicasterol, dinosterol, and fucosterol is interpreted as input from marine biota (Bouloubassi et al. 1997; Volkman 1986; Rampen et al. 2010). The contributions of steroids from terrestrial vascular plants ranged from 1.0 at station 8 to 45.9 ng.g⁻¹ at station 10 (mean 10.6 ± 12.1 ng.g⁻¹). The steroid component from marine biota (i.e., algae, diatoms, and fauna) ranged from 0.4 at station 8 to 18.6 ng.g⁻¹ at station 10 (mean 4.7 ± 5.0 ng.g⁻¹, Table SM-1). Terrestrial higher plant detritus was the major source of steroids in these sediments as indicated by the elevated ratios of terrestrial/marine steroids, ranging from 1.79 to 3.37 (mean 2.32 ± 0.42).

The triterpenoids in these sediments were mainly tetrahymanol, tetrahymanone, and 17β(H), 21β(H)-bishomohopan-32-ol (Table SM-1) and ranged from 1.7 to 79.8 ng.g⁻¹ (18.9 ± 21.1 ng.g⁻¹, Table 2). The presence of these triterpenoids in the samples indicated a microbial origin, where the protozoan *Tetrahymena pyriformis* is considered to be the major source of tetrahymanol (Mallory et al. 1963; Holz and Conner 1973), excluding minor other sources. Therefore, tetrahymanol and its derivative tetrahymanone confirm that marine biota is an input of sedimentary organic detritus (Venkatesan 1989). The 17β(H), 21β(H)-bishomohopan-32-ol is a known compound in sediments of aquatic environments as an early diagenetic product from bacteriohopanepolyol demonstrating oxidation or bacterial reworking of microbial organic detritus (Ourisson et al. 1979; Brassell et al. 1983).

Plasticizers and other petrochemicals

Plasticizers and other petrochemicals were significant components of these sediments (Fig. 2, Table 2). The major plasticizers included di-isobutyl phthalate (DiBP), dibutyl phthalate (DBP), and dioctyl phthalate (DOP). The petrochemicals were 2,4-dioctylphenol (CAS 1807–29-0), 2-mercaptobenzothiazole (CAS 149–30-4), diethylene glycol *p*-(1,1,3,3-tetramethylbutyl)phenol (a Triton-X), *N*-phenylbenzenesulfonate (CAS 1678–25-7), and 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (Advastab 405, CAS 119–47-1). Their total concentrations ranged from 27 to 2799 ng.g⁻¹ (mean 491 ± 756 ng.g⁻¹) of the TEOM. The antioxidant Advastab 405 was a major compound and ranged from 0.00 to 334 ng.g⁻¹, with a maximum level at station 10 (Table SM-1). The major plasticizer was DOP ranging from 14 to 662 ng.g⁻¹ (Table SM-1).

Elevated levels of phthalates have been detected in atmospheric total suspended particles (TSP) collected from the region (Rushdi et al. 2017). A recent study reported high

concentrations of phthalates, non-phthalates (adipates and mellitates), phenyl phosphates, and polychlorinated biphenyls in atmospheric suspended particles from the Dhahran area in Saudi Arabia (Rushdi et al. 2022). The region is known as the largest industrial complex for the petrochemical and plastic industry in the Middle East (Picó et al. 2021) and is a major source of plasticizers, flame retardants, and pesticides in the regional environment (Rushdi et al. 2017; Saini et al. 2019). Littering is another source of these POPs (persistent organic pollutants) in the environment. Accordingly, the obvious sources of the plasticizer compounds in the Gulf coastal zones are emissions and spillage from the regional petrochemical industry, as well as leaching from plastic debris. These TSP plasticizers transported by wind and those leached from plastic debris in the coastal environment eventually accumulate in marine biota (Vered et al. 2019; Jebara et al. 2021; Sala et al. 2022; Hidalgo-Serrano et al. 2022) and can transfer across different trophic levels (Farrell and Nelson 2013; Setälä et al. 2014). Further studies are needed to investigate the plasticizer levels in marine organisms and their toxicity effects.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) were detected only in the sediments from the stations near Al-Khafji. The total concentrations were 1.86 ng.g⁻¹ and station 2 to 3.87 ng.g⁻¹ at station 1 (Table 2). The major PAHs detected in these sediments included fluoranthene, pyrene, benzo[*g,h,i*]fluoranthene, cyclopenta[*c,d*]pyrene, benzo[*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, and perylene (Table SM-1). The concentrations were in the range measured at other locations of the Gulf (Soliman et al. 2014, 2019; Gevao et al. 2016). The absence of low molecular weight aromatic and alkyl aromatic hydrocarbons (i.e., alkylnaphthalenes and phenanthrene/alkylphenanthrenes) is likely due to their removal as a result of their high volatility and water solubility (Kawka and Simoneit 1990). The summertime high temperature in the region causes considerable loss of PAHs, especially low molecular weight PAHs (Soliman et al. 2019). Also, the sediment properties and the water current direction affect the levels of PAHs in the Gulf, where higher concentrations have been reported in the semi-enclosed area such as bays and harbors (Gevao et al. 2016; Soliman et al. 2019).

The ratio of fluoranthene/(fluoranthene + pyrene) has been used to differentiate between petrogenic and combustion sources, where a low value (<0.4) indicates petroleum inputs and a high value (>0.5) implies combustion sources (Rogge et al. 1993; Yunker et al. 2002, 2012). Here the ratios were >0.5, similar to the values obtained

by others (Gevao et al. 2016; Soliman et al. 2019) and confirming that these PAHs were from combustion.

Unresolved complex mixture (UCM)

The UCM consists of branched and cyclic compounds above the baseline and under the envelope of the resolved compounds (Fig. 2). The UCM concentrations ranged from 14 at station 9 to 11,388 ng.g⁻¹ at station 10 (mean 1633 ± 3151 ng.g⁻¹, Table 2). The ratio U:R (UCM-to-resolved compound concentrations, Mazurek and Simoneit 1984) ranged from 0.03 to 1.61 (mean 0.57 ± 0.58). The lowest ratio was found offshore of Dammam (station 9) and the highest offshore of Al-Khafji (station 1). High levels of UCM were detected mainly in the semi-enclosed area, locales close to oil production, and near seaports such as Al-Khafji town in the north (stations 1 and 2) and Dammam city (stations 10 and 11). These locales are less affected by water currents, resulting in additional accumulation of organic matter in sediments.

The major sources of the UCM (Fig. 2) are oil spills and/or fossil fuel utilization (Simoneit 1984, 1985; Tolosa et al. 2004; Harji et al. 2008). The presence of a narrow UCM is distinctive for a gasoline source, whereas a broader UCM is exhibited by the input of diesel or lubricant oils, and both envelopes can be derived from refined crude oil (Simoneit 1984, 1985). Hydrocarbons from higher plants have no UCM (Simoneit and Mazurek 1982). Microbial detritus can produce a UCM with a C_{max} at 19–22 under an anaerobic condition (Simoneit et al. 1979). The UCM derived exclusively from fossil fuel utilization was evaluated as a ratio of UCM to biogenic (marine and terrestrial) n-alkanes (U:nC_B ratio) to assess the level of oil and petroleum contamination, where high values of the ratio suggest contamination by biodegraded petroleum residues (Peters and Moldowan 1993; Rushdi et al. 2014b). The U:nC_B ratio ranged from 0 to 97 (mean 23 ± 28 , Table 2) and a value > 3 was considered to be contaminated. Obviously, all sites were contaminated, except station 9 (offshore of Dammam), and the most polluted were the nearshore of Dammam city (station 10) and offshore of Al-Khafji (stations 1 and 2).

Station similarities and anthropogenic versus natural sources

The data of the related compound groups in TEOM were examined by principal component analysis (PCA), using Varimax rotation to examine the similarities between the different stations. Two significant components (C1 and C2) were identified by the PCA output explaining 94.62% of the variance at an eigenvalue of > 1 (Table SM-2, Fig. SM-2).

We used factor loadings of > 0.75 for each component. The C1 revealed a variance of 81.54% with S10, S5, S1, and S2 suggesting that they had similar sources of organic matter. The variance of C2 was 13.08% with S9, S4, S3, S7, and S6 indicating that their organic matter sources were likely comparable but have been modified by physicochemical processes. These include wind and current directions and speeds, sediment deposition rates, oxygen concentration, and microbes at surface sediments (Hedges and Oades 1997; Zonneveld et al. 2010; Zakem et al. 2021).

Obviously, the contributions of anthropogenic versus natural biogenic sources of TEOM varied and depended on the locations of the sampling stations (Fig. 4). The estimated anthropogenic sources of n-alkanes ranged from 61 to 94% (mean $82 \pm 9\%$), whereas the terrestrial biogenic sources ranged from 1.2 to 15.2% (mean $6.2 \pm 4.5\%$), and the marine biota sources ranged from 5.2 to 32.5% (mean $12.3 \pm 8.1\%$) (Fig. 4a). For TEOM (based on n-alkanes, hopanes, steranes, PAHs, plasticizers, and UCM), the anthropogenic sources were from 56.1 to 84.9% (mean $72.7 \pm 8.7\%$), and the marine biogenic components were 9.4 to 24.1% (mean $16.7 \pm 5.7\%$) and 4.9–19.7% (mean $10.9 \pm 4.6\%$) for terrestrial and marine sources. The ternary plots of both n-alkanes and TEOM showed that anthropogenic inputs were dominant in this coastal zone, followed by marine and minor terrestrial higher plant contributions (Fig. 4). The results confirmed that marine traffic, crude oil industry, and human-related activities are the major detrital anthropogenic organic matter source and pollutants in this region. The low input from natural terrestrial sources (i.e., vegetation) to these sediments is attributed to the arid region with low vegetation around this coastal zone.

Environmental effects

Certain coastal areas are defined as critical habitats (Ray 1976; IUCN 1983; Dugan 1990) because they are productive locales providing breeding, feeding, nursing, or nesting places for marine organisms (Sheppard et al. 1992; Burt 2014). These critical habitats include fauna and flora sites (e.g., rocky shores), nesting locales for turtles and nursery floor for crustaceans (e.g., sandy beaches), as well as nursery grounds for shrimp (e.g., mangrove stands) (Vaughan et al. 2019). The ecosystems of the Arabian Gulf coastal zone including benthic macroalgae, mangrove stands, coral reefs, and seagrasses are very important sources of nutrients in the region (Ogden and Gladfelter 1983; Crossland et al. 1987). For example, benthic macroalgal productivity is significantly greater than of both microalgae and phytoplankton (Valiela et al. 1997).

The environmental effects of pollution from petroleum, plasticizers, and other petrochemicals on these critical

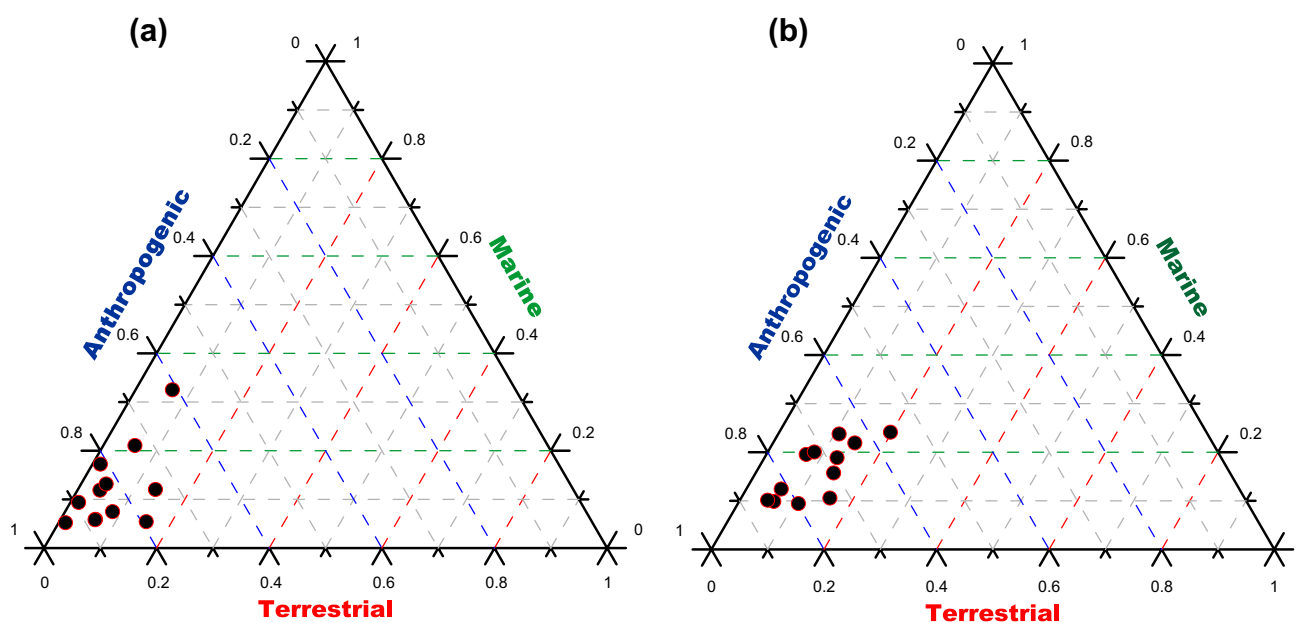


Fig. 4 Ternary diagrams showing the distributions of the terrestrial, marine and anthropogenic sources of **a** *n*-alkanes and **b** total extractable organic matter (TEOM) in the sediments from the coastal zone of the Arabian Gulf

habitats of the region are detrimental and expected (Al-Hurban 2013). Benthic species and largely their early life stages such as eggs and larvae are susceptible to such toxic waste. Coastal spawning and nursery floors are adversely affected by the presence of oil pollutants (Basson et al. 1977; Price 1979, 1982). Petroleum product inputs from oil transfer docks, oil refineries, oil tankers, and sewage treatment plants likely distress the coastal ecosystems and associated groups of species (Loya 1975; Rinkevich and Loya 1979; Dicks 1987). Studies have shown that the presence of petroleum reduced colonization in reefs (Dicks 1987); nevertheless, there is no concrete evidence that the reefs have declined due to oil pollution in the region (IUCN/UNEP 1985). The petroleum pollution effects on coral reefs and marine coastal ecosystems need further study. The inorganic nutrients exchange with dissolved organic matter (DOM) and particulate organic matter (POM), as well as animal migrations, can also be affected by the presence and elevated levels of organic pollutants (IUCN 1983; Por and Dor 1984).

Conclusions

The total solvent-extractable organic matter (TEOM) of the sediments from the Arabian Gulf coast of Saudi Arabia has been characterized using GC–MS techniques. The analyses showed that anthropogenic and biogenic sources both contributed to their organic matter contents.

The presence of UCM, *n*-alkanes with CPI ~ 1, steranes, and hopanes from petroleum production and utilization in the region such as offshore oilfields, discharges from refineries and tanker traffic, and the possibility of natural oil seeps, are the major sources of TEOM. The anthropogenic sources of compounds from petroleum, its products, and plastic waste accumulation comprised $72.7 \pm 8.7\%$ of the TEOM. The abundance of anthropogenic organic compounds in the sediments of the Arabian Gulf coast depended on the location of the sampling site and the types of regional urban activities. Thus, the environmental effects of anthropogenic organic matter on the critical habitats of the coastal Arabian Gulf are possible and need more investigation.

The natural sources of organic compounds including *n*-alkanes (in part), *n*-alkanols, *n*-alkanoic acids, steroids, and triterpenoids are mostly from marine biota at $21.8 \pm 9.4\%$ of TEOM. The terrestrial detritus from higher plant influx to the TEOM is $16.7 \pm 5.7\%$.

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Declarations

Competing interests The authors declare no competing interests.

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