

Sources of Organic Tracers in Atmospheric Dust, Surface Seawater Particulate Matter and Sediment of the Red Sea

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Abstract

This chapter discusses the various input sources of extractable organic matter (EOM) compounds to the Red Sea. These are based on geochemical analyses of atmospheric dust, surface seawater particulate matter and sediment samples collected from the Gulf of Aqaba and the coasts of the Gulf of Suez, Saudi Arabia and Yemen. The samples were extracted with a dichloromethane/methanol mixture and analyzed by gas chromatography-mass spectrometry (GC-MS). The EOM compounds (lipids) in the samples are diverse and include *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, methyl *n*-alkanoates, steroids, petroleum hydrocarbons and plasticizers. The steroids and *n*-alkanoic acids were major components of the surface seawater particulate matter samples, whereas petroleum hydrocarbons were major compounds in coastal sediments. Based on the results of the different samples, the main input sources of these lipids were from: (1) natural autochthonous microbiota (plankton and bacteria) as indicated by the presence of cholesterol and brassicasterol in the different surface seawater particulate matter and sediment samples; (2) natural allochthonous material origins from terrestrial plant detritus transported

by dust as shown by the distributions of *n*-alkanoic acids, *n*-alkanols and phytosterols; and (3) anthropogenic sources (mainly petroleum) from regional oil production activities, oil tankers or shipping activities as revealed by the *n*-alkane distribution pattern and the presence of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons, with hopane and sterane biomarkers. Future studies of the organic and inorganic biogeochemistry on the water column, coastal areas and dust transported to the Red Sea are needed to characterize the various regional sources, transformation, and diagenetic processes of the organic matter en route to this marine environment.

Introduction

The Red Sea is a semi-enclosed body of water that lies between 30°N and 12°30'N, and is about 1932 km long and 280 km wide (Morcos 1970; Head 1987; Rasul et al. 2015). The boundary between the Red Sea and the Gulf of Aden is the narrow southern Strait of Bab-el-Mandab (~29 km in width). The total surface area of the Red Sea is estimated to range between 438×10^3 and 450×10^3 km², and the volume between 215×10^3 and 251×10^3 km³ with an average depth of about 491 m (Morcos 1970; Head 1987; Anderson and Dyrssen 1994). The Red Sea is a shallow sea with the shallowest shelves extending in the southern part. The maximum depth of the basin is 2850 m (Edwards and Head 1987).

The major external sources of organic and inorganic components to the Red Sea are from atmospheric particulate matter transported by wind, and coastal human development activities with minimal riverine input. The dust belt (African and Asian low-latitude deserts) impacting the region is the largest source of dust on Earth (Pye and Tsoar 1987; Prospero et al. 1987; Arimoto et al. 1997; Husar et al. 2001; Tratt et al. 2001; Reid and Maring 2003; Haywood et al. 2003;

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Uno et al. 2005; Laurent et al. 2008). Dust storm episodes are common on the African Sahara and Arabian Peninsula, and extend to impact the Arabian seas including the Red Sea (Kalenderski et al. 2013; Prakash et al. 2015). The strongest dust storms occur in summer time when vast amounts of dust are lofted into the atmosphere from arid and semi-arid lands in northern Africa and the Arabian Peninsula, respectively. Human activities can increase dust loadings and enlarge the extent of the dust sources (Savoie et al. 1987; Tegen et al. 1996; Pilcher 1999; Ashbaugh et al. 2003). Atmospheric dust and fine aerosol components introduce a wide variety of materials with different chemical compositions to marine systems (Simoneit 1977, 1978, 2006; Chase et al. 2006). These components include organic and inorganic substances depending upon the types of sources. For example, organic compounds (e.g., hydrocarbons, fatty acids, triterpenoids, steroids, saccharides and plasticizers,) and trace and heavy metals (e.g., lead, zinc, copper, chromium, cadmium, nickel, aluminum, lithium, and iron) as well as major elements (silicon, potassium, sodium, magnesium, and calcium), were found in dust leachates collected from the Red Sea (Saad and Kandeel 1988; Chester et al. 1993; Chen et al. 2006, 2008; Romankevich 2013, Elfadly et al. 2016; Ahmed et al. 2016, 2017a, b). Analyses of bottom sediments from the Red Sea indicate the presence of lithogenic and biogenic components from desert sources (Stein et al. 2007). Furthermore, during a desert storm event, dust and fine particle mass loadings can change by orders of magnitude in a matter of hours (Tindale and Pease 1999). These loading variations are also associated with changes in the chemical components of the dusts and fine particles, which are due to the transit of the dust plumes over developed regions that add pollutants and other atmospheric constituents (Pawar et al. 2015; Chen et al. 2008). The transport of these dust and fine particles to coastal and offshore locales affects the biological activities and biogeochemical element cycles in the marine environment (Paytan et al. 2009). The annual deposition of dust to the Red Sea, associated with the major dust storms, is estimated to be about 6 Mt (Prakash et al. 2015). The dust storms bring nutrients to marine ecosystems of the Red Sea, especially those of the oligotrophic northern Red Sea.

Storm runoff from wadis (dry river beds) and human activities are other significant sources of natural and anthropogenic organic and inorganic components to the region (Gheith and Sultan 2002; El-Taher and Madkour 2011). As a result of the high dispersion of sediments by wadis, the terrestrial organic matter content of the associated marine deposits can be significant. Biogenic organic matter from primary and secondary marine production is also a major source of organic compounds to Red Sea sediments (Sanders and Morgan 1989; Weisse 1989; Raitsos et al.

2013; Qurban et al. 2014). The main sources of anthropogenic organic matter to the Red Sea are inputs from urbanization, tourism activities, and from oil and industrial production activities (Ahmed et al. 2016, 2017a, b). Much of these anthropogenic organic compound inputs are due to discharges from refineries, petrochemical plants, regional fuel emissions and possibly natural oil seeps (Dicks 1987; PERSGA/SAP 2001a, b; Rushdi et al. 2009, 2010; Elfadly et al. 2016; Ahmed et al. 2016, 2017a, b). The degree of oil pollution of shorelines around the Red Sea was identified as a serious problem along major sections of the coastal zones (Dicks 1987; Rushdi et al. 2010).

The main objectives of this chapter are to show the characteristics of the extractable organic matter (EOM) of dust deposition, surface seawater particulate matter and coastal sediments in order to elucidate the sources of organic matter to the Red Sea. This is based on key parameters and molecular marker analysis of the samples from the Gulf of Aqaba, and sediment samples from the Gulf of Suez and coastal zones of Saudi Arabia and Yemen.

Methodology

Sample Collection

Fourteen dust, surface seawater particulate matter (SSPM) and sediment samples from different parts of the Red Sea were collected for organic geochemical study. The samples were from the Gulf of Aqaba, the Gulf of Suez and coastal zones of Saudi Arabia and Yemen (Fig. 4.1). The dust samples were collected between August 2003 and November 2004 using a Total Suspended Particle High Volume Sampler (TSP-HVS) located at the northwest coast of the Gulf of Aqaba (Fig. 4.1). Quartz filters (47 mm in diameter) were used to collect dust after combustion at 450 °C for 5 h and stored in pre-extracted aluminum foil until sampling. Samples were taken at least once a week over a 24 h period with an air flow of 2.4–2.7 m³ h⁻¹. The TSP-HVS samples were kept frozen until analysis. SSPM samples were collected at two stations (X and Y, Fig. 4.1) in the Gulf of Aqaba, using GO-FLO bottles, and at additional stations where only surface-water was sampled using a peristaltic pump. Sampling procedures were described in detail in Chase et al. (2006) and Chen et al. (2008). Briefly, water samples were filtered through quartz filters (47 mm diameter) to retain the particulate matter. Surface sediment samples from the Gulf of Suez were collected with an Ekman grab sampler along an off-shore transect south of Ras Abu el-Darag at back-reef (station I) and reef flat (station II) locations (Fig. 4.1). The sediment samples from the coastal zone of Saudi Arabia and

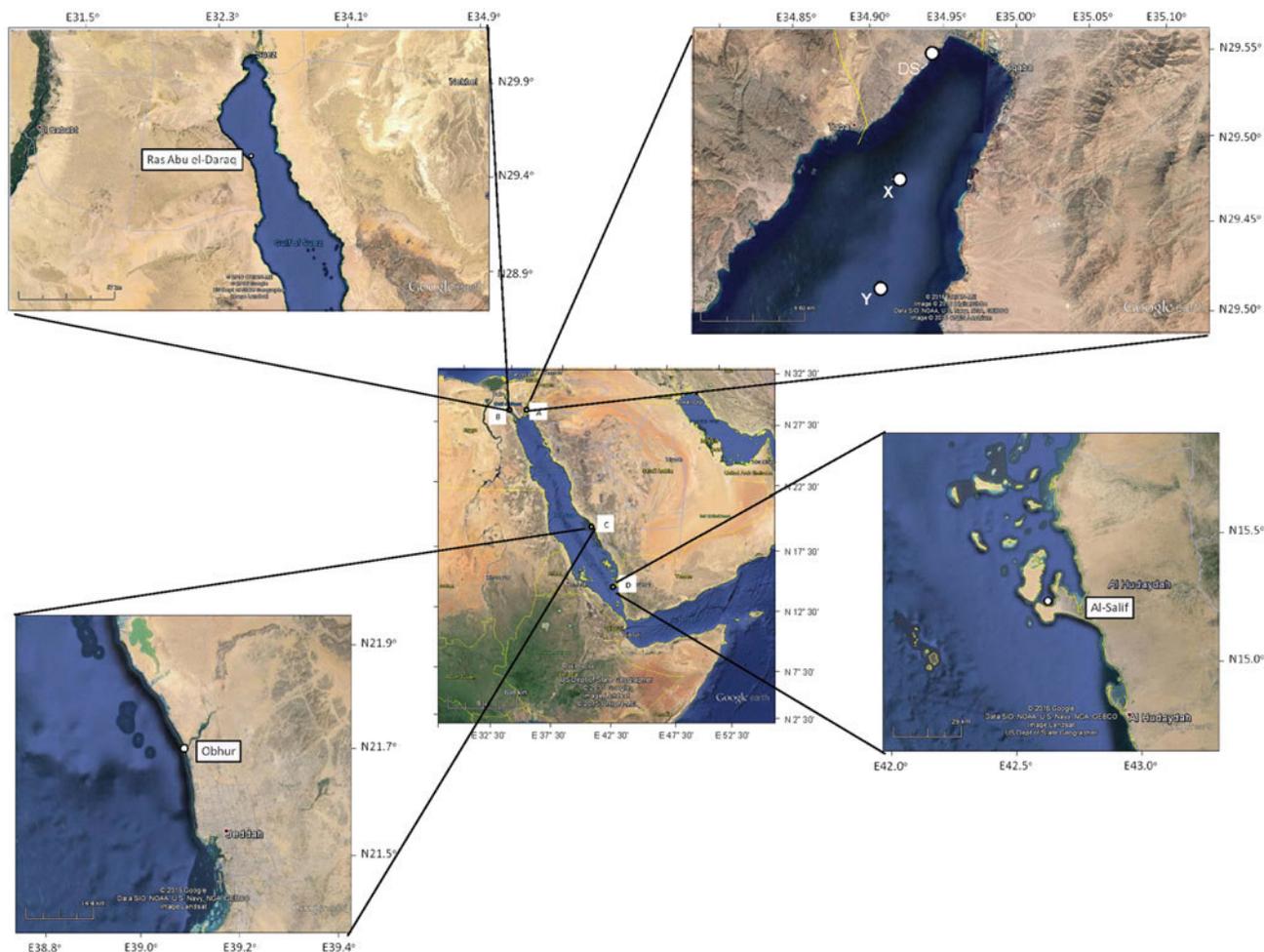


Fig. 4.1 Map showing the areas and sampling locations for the atmospheric dust, surface seawater particulate matter, and sediment samples from the Gulf of Aqaba, Gulf of Suez and coastal zones of Saudi Arabia and Yemen

Yemen were collected by Peterson grab samplers from the uppermost 15–30 cm of the sea bed sediment. The samples were removed from the middle of the grab, wrapped in pre-cleaned aluminum foil and stored frozen at $-20\text{ }^{\circ}\text{C}$. Before solvent extraction, the samples were air dried and sieved to pass $250\text{ }\mu\text{m}$ mesh. Grain size was not determined, and rocks and sand were removed by sieving. The sediment samples were mostly fine sand and silt in appearance after sieving.

Extraction

The dust and SSPM filters were extracted three times by placing each filter in a pre-cleaned beaker and adding a mixture of dichloromethane/methanol (DCM/MeOH, 2:1, v/v) under ultrasonic agitation. The final volume of the

filtrate was adjusted to $50\text{ }\mu\text{L}$ for the dust and $100\text{ }\mu\text{L}$ for the SSPM samples. For sediments, about 5 g of each sieved sample was extracted three times using ultrasonic agitation for a 15 min period each with 30 mL of DCM and 10 mL of MeOH. The extraction was carried out in a 150 mL pre-cleaned beaker. The extract was then passed through a filtration unit containing an annealed glass fiber filter for the removal of suspended particles. The filtrate was first concentrated on a rotary evaporator and then reduced using a stream of dry nitrogen gas to a volume of approximately $200\text{ }\mu\text{L}$. The volume was then adjusted to $500\text{ }\mu\text{L}$ exactly by addition of DCM/MeOH (3:1, v/v). A $50\text{ }\mu\text{L}$ aliquot of each total extract of sediments and a $20\text{ }\mu\text{L}$ aliquot of each extract of dust and SSPM was derivatized with silylating reagent [N, O-bis(trimethylsilyl)trifluoroacetamide, Pierce Chemical Co.] before analysis by gas chromatography-mass spectrometry (GC-MS). This derivatizing agent replaces the H in

hydroxyl groups with a trimethylsilyl [(CH₃)₃Si, i.e., TMS] group for better GC resolution of polar compounds (Stalling et al. 1968).

Quality Control

All solvents used in the sample extraction were tested for any possible contaminant. Procedural blanks were analyzed to provide a qualitative and quantitative assessment of background contamination introduced by analytical preparation. Blank extracts were performed through the entire project with each batch of three samples. The levels of background contamination were insignificant in all procedural blanks. The recoveries of external standards (tetracosane for n-alkanes; hexadecanoic acid for n-alkanoic acids, alkyl alkanolates and n-alkanols; sitosterol for triterpenoids; glucose for monosaccharides; and sucrose for disaccharides) ranged from 72 to 105%.

Instrumental Analysis

The analysis of the extracts was carried out by GC-MS, using a Hewlett-Packard 6890 GC coupled to a 5973 Mass Selective Detector with a DB-5 (Agilent) fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film

thickness), and helium as carrier gas. The GC was temperature programmed from 65 °C (2 min initial time) to 300 °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. Data were acquired and processed with a Hewlett-Packard ChemStation. Compounds were identified by GC retention index and comparison of mass spectra with those of authentic standards, literature and library data, and identified mixtures. Unknown compounds were characterized by interpretation of the fragmentation pattern of their mass spectra. The concentration (mass) of the total extract (in micrograms) was obtained from the GC-MS total ion current (TIC) profiles using the external standard method. Average response factors were calculated for the various compounds. Each compound's quantification was based on the compound peak area derived from the ion fragmentogram and correlated with the TIC. The compound relative concentration was calculated according to the method described by Rushdi et al. (2010).

Results

The main features of the GC-MS data for dust, SSPM and sediment extracts are shown in Fig. 4.2. The major compounds of the extracts (Table 4.1) comprise lipids and biomarkers from both autochthonous marine and

Fig. 4.2 Examples of GC-MS total ion current (TIC) traces of total extracts (silylated) of **a** dust sample from the Gulf of Aqaba, **b** surface seawater particulate matter (SSPM) from the Gulf of Aqaba, **c1** and **c2** sediment samples from the Gulf of Suez, **d** sediment sample from the coast of Saudi Arabia, and **e** sediment sample from the coast of Yemen

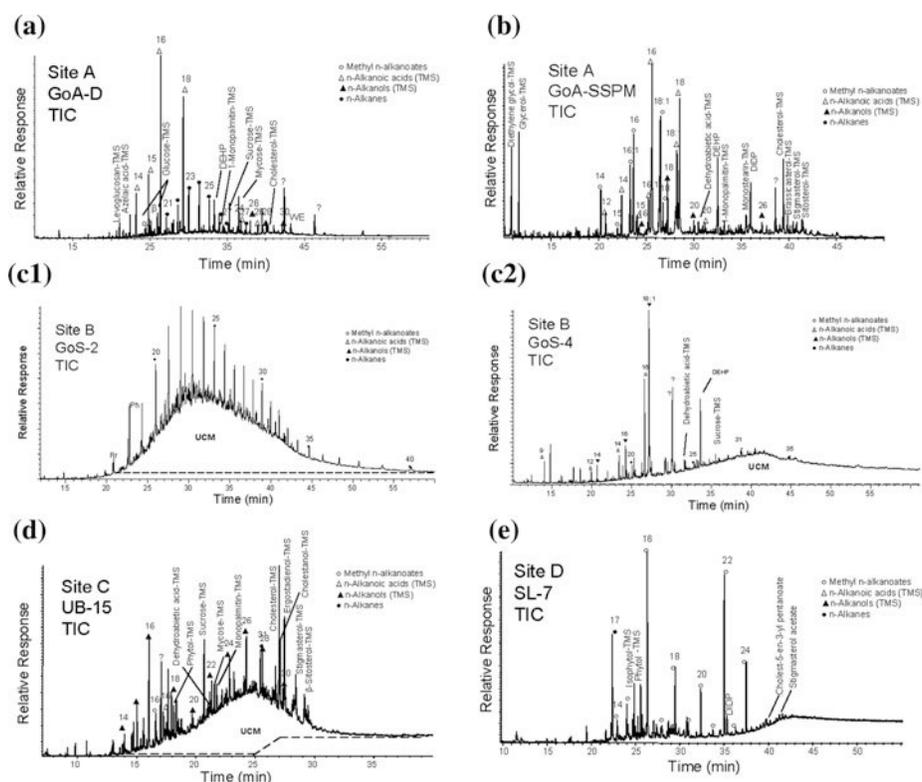


Table 4.1 The concentration in ng/g (relative concentrations in % of total extract weight) of the various compound groups and biogeochemical parameters of the dust, SSPM and sediment samples collected from the Gulf of Aqaba, Gulf of Suez and coastal zones of Saudi Arabia and Yemen

	Dust	SSPM	Sediments			
	Gulf of Aqaba		Gulf of Suez		Saudi Arabia	Yemen
			I	II		
Latitude (N)	29° 32' 24.88"	X = 29° 27' 31.99" Y = 29° 32' 32.01"	29° 23' 12.30"	29° 23' 14.58"	21°42' 23.73"	15°15' 35.11"
Longitude (E)	34° 56' 40.60"	X = 34° 55' 20.10" Y = 34° 55' 00.49"	32° 34' 10.16"	32° 34' 44.07"	39° 05' 09.82"	42° 39' 08.85"
	n = 5	n = 6	n = 3	n = 3	n = 3	n = 4
Compound						
<i>n</i> -Alkanes						
Range	19–33	22–40	16–37	T	16–35	16–35
C _{max}	25	31	24,26		29	17
Total concentration	1415 ± 668 (5.9 ± 2.8)	28 ± 22 (1.8 ± 1.5)	35.2 ± 8.6 (22.1 ± 5.4)		33 ± 23 (15.9 ± 11.2)	2003 ± 2725 (57.9 ± 78.8)
CPI _(o/e) ^a	1.33 ± 0.11	1.75 ± 0.26	0.60 ± 0.1		1.91 ± 0.14	2.96 ± 2.57
Wax <i>n</i> -alkanes						
Total concentration	197 ± 115 (0.82 ± 0.48)	8.5 ± 7.3 (0.57 ± 0.49)	T		16 ± 10 (3.1 ± 1.3)	443 ± 739 (22.1 ± 36.9)
% alkanes	13.5 ± 1.7	27.9 ± 5.7			49 ± 3	38.2 ± 46.8
<i>n</i> -Alkanoic acids						
Range	9–30	8–14	8–28	8–28	ND	ND
C _{max}	18	16	18	16		
Total concentration	21331 ± 462 (88.7 ± 1.82)	684 + 366 (45.6 + 24.4)	8.2 ± 3.2 (13.7 ± 6.0)	51.2 ± 24.3 (59.2 ± 28.4)		
CPI _(e/o) ^b	3.69 (0.03)	5.00 (4.02)	7.11 (3.23)	8.60 (9.56)		
Methyl <i>n</i> -alkanoates						
Range	14–18	12–32	12–18	12–18	14–26	14–26
C _{max}	16	16	18	16	16	16
Total concentration	115 ± 26 (0.42 ± 0.11)	220 ± 152 (14.7 ± 10.1)	0.1 ± 0.2 (0.29 ± 0.51)	0.8 ± 0.2 (0.97 ± 0.23)	9.1 ± 12.3 (4.5 ± 6.0)	1454 ± 1685 (42.1 ± 48.8)
CPI _(e/o) ^b	16.7 (8.4)	9.9 (3.2)	9.03 (5.15)	10.51 (6.11)	13.35 (8.25)	9.53 (6.39)
<i>n</i> -Alkanols						
Range	16–32	14–30	ND	ND	14–32	ND
C _{max}	26	18			16,30	
Total concentration	782 ± 113 (3.3 ± 0.5)	113 ± 56 (7.5 ± 3.8)			67 ± 43 (13 ± 9.1)	
CPI _(e/o) ^b	17.1(2.1)	12.5 (4.9)			6.44 (1.44)	
Steroids						
Range	27	27–30	27–29	27–29	27–30	ND
C _{max}	27	27	27	27	27	
Total concentration	34 ± 21 (0.1 ± .09)	203 ± 116 (13.6 ± 7.7)	0.2 ± 0.4 (0.6 ± 1.0)	1.6 ± 0.6 (2.0 ± 0.7)	30.7 ± 5.8 (15.0 ± 2.8)	

(continued)

Table 4.1 (continued)

	Dust	SSPM	Sediments			
	Gulf of Aqaba		Gulf of Suez		Saudi Arabia	Yemen
			I	II		
Carbohydrates						
Total concentration			1.0 ± 1.1 (1.3 ± 1.4)	2.2 ± 2.4 (2.7 ± 3.0)	8.7 ± 14.3 (4.2 ± 7.0)	
Hopanes						
Range	ND	ND	27–35	27–35	27–35	ND
C _{max}			30	30	30	
Total concentration			3.9 ± 1.6 (11.2 ± 4.7)	1.4 ± 2.5 (1.8 ± 3.1)	14.9 ± 6.4 (7.2 ± 3.1)	
Steranes						
Range	ND	ND	27–29	ND	27–30	ND
C _{max}			27		29	
Relative concentration (%)			7.4 ± 2.1 (21.1 ± 6.0)		12.9 ± 6.1 (4.1 ± 2.4)	
Plasticizers						
Total concentration	384 ± 16 (1.6 ± 0.1)	166 ± 22 (16.8 ± 2.2)	1.1 ± 0.1 (3.2 ± 0.4)	4.6 ± 1.9 (6.0 ± 2.5)	9.7 ± 5.4 (4.7 ± 2.6)	
UCM						
Total concentration	ND	ND	62 ± 1.4 (26.7 ± 2.9)	31.4 ± 5.1 (27.5 ± 10.0)	81 ± 23 (31.1 ± 12.0)	

^aCPI = (total nC (odd))/(total nC (even)),

^bCPI = (total nC (even))/(total nC (odd)). T = trace; ND = not detected

allochthonous terrigenous sources and contain considerable amounts of anthropogenic organic compounds. The composition includes *n*-alkanes, *n*-alkanoic acids, methyl *n*-alkanoates, *n*-alkanols, steroids, carbohydrates, hopane and sterane biomarkers, plasticizers and an unresolved complex mixture (UCM) of branched and cyclic compounds (Fig. 4.3). The presence of these different compounds can be used to identify source origins (Simoneit 1984, 1985; Rushdi et al. 2016a, b). The dominant compound classes in the dust total extracts were *n*-alkanoic acids (88.7 ± 1.8%), *n*-alkanes (5.9 ± 2.8%), *n*-alkanols (3.3 ± 0.5%), plasticizers (1.6 ± 0.1%), methyl *n*-alkanoates (0.4 ± 0.1%), and steroids (0.1 ± 0.1%). The carbon preference indices (CPI) were 1.33 ± 0.11, 3.69 ± 0.03, and 16.7 ± 8.4 for *n*-alkanes, *n*-alkanoic acids, and methyl *n*-alkanoates, respectively (Table 4.1).

The total extract compositions of the SSPM consist of mixtures of *n*-alkanoic acids (45.6 ± 24.4%), plasticizers (16.8 ± 2.2%), methyl *n*-alkanoates (14.7 ± 10.1%), steroids (13.6 ± 7.7%), *n*-alkanols (7.5 ± 3.8%), and *n*-alkanes (1.8 ± 1.5) from different input sources (Table 4.1). The CPI values for *n*-alkanes, *n*-alkanoic acids, methyl *n*-alkanoates, and *n*-alkanols were 1.75 ± 0.26, 5.00 ± 4.02, 9.9 ± 3.2, and 12.5 ± 4.9, respectively.

The major components of the Gulf of Suez sediment total extracts are UCM (28.5 ± 10.1 to 40.7 ± 4.38%), *n*-alkanoic acids (13.7 ± 6.0 to 59.2 ± 28.4%), *n*-alkanes (traces to 22.1 ± 5.4%), hopanes (1.68 ± 2.89 to 7.0 ± 2.9%), steranes (0 to 13.2 ± 3.7%), plasticizers (1.98 ± 0.23 to 5.50 ± 2.28%), steroids (0.36 ± 0.52 to 1.83 ± 0.66%), and carbohydrates (0.81 ± 0.88 to 2.48 ± 2.75%) (Table 4.1), with CPI values of 0.60 ± 0.10 for *n*-alkanes, 7.11 ± 3.23 to 8.60 ± 9.56 for *n*-alkanoic acids, and 9.03 ± 5.15 to 10.51 ± 6.11 for methyl *n*-alkanoates. The dominant components of the sediment total extracts from the coastal zone of Saudi Arabia are UCM (43.1 ± 12.0%), *n*-alkanols (13.0 ± 8.4%), *n*-alkanes (6.4 ± 4.5%), steroids (6.0 ± 1.1%), hopanes (5.7 ± 2.4%), steranes (5.2 ± 2.2%), plasticizers (1.88 ± 1.04%), and methyl *n*-alkanoates (1.80 ± 2.40%) (Table 4.1). The CPI values of *n*-alkanes, methyl *n*-alkanoates and *n*-alkanols are 1.91 ± 0.14, 13.35 ± 8.25 and 6.44 ± 1.44, respectively. The major components of the sediments from the coastal zone of Yemen include *n*-alkanes (57.9 ± 78.8%), and methyl *n*-alkanoates (42.1 ± 48.8%), with CPI values of 2.96 ± 2.57 for *n*-alkanes and 9.53 ± 6.39 for methyl *n*-alkanoates.

Discussion

The organic compounds in the total extracts of the dust, SSPM, and surface sediments consist of varied compounds, which can be used to identify their potential sources. These compounds are mainly *n*-alkanes (from both natural and anthropogenic sources), *n*-alkanoic acids, *n*-alkanols, methyl *n*-alkanoates, steroids (mainly from natural origins), hopanes, steranes and UCM (from petroleum inputs), and plasticizers (anthropogenic sources).

Natural Biogenic Sources

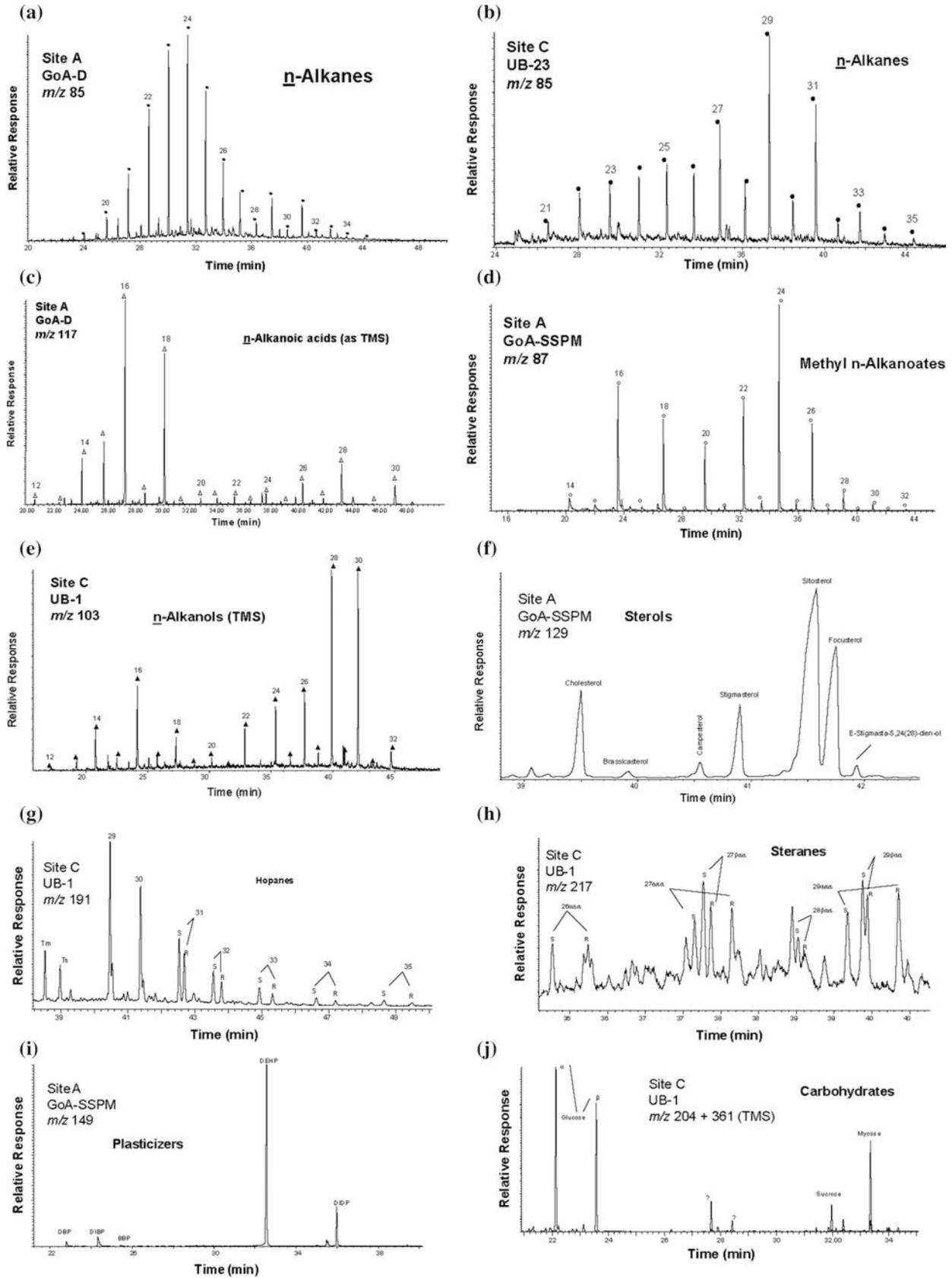
The *n*-alkanes are derived from biogenic, fossil, and anthropogenic sources and can be differentiated based on their distribution pattern in the samples. These compounds can be found in all ecosystems and are especially suitable for assessing the origin, source, and fate of organic matter in the environment (Bush and McInerney 2016; Tarasov et al. 2013; Isaji et al. 2015; Street et al. 2013; Zech et al. 2015). The carbon number maximum (C_{max}) and the CPI of *n*-alkanes are key parameters to characterize their sources (Simoneit 1977, 1978; Oros and Simoneit 2001a, b; Mirante et al. 2013; Urban et al. 2016). Generally, plant wax *n*-alkanes have a C_{max} in the range of 25 to 31 with a maximum at 27, 29 or 31, which varies depending on the plant species as well as the season and locality (e.g., Eglinton and Hamilton 1967; Simoneit 1977, 1989; Simoneit and Mazurek 1982; Mazurek et al. 1991; Rogge et al. 1993; Stephanou and Stratigakis 1993; Abas and Simoneit 1998; Oros and Simoneit 2001a, b; Rushdi et al. 2016a, b). The C_{max} of the most abundant *n*-alkane can be used as an indicator of relative source input (Simoneit 2002).

The *n*-alkanes in atmospheric dust samples range from C_{19} to C_{33} , with a C_{max} at 25 and CPI values of 1.33 (Table 4.1), indicating a mixture of vehicle emissions (CPI = 0.77–0.88) and terrestrial vascular plant wax (CPI > 3.0) (Schauer et al. 2002; Oros and Simoneit 2001a, b). The contribution of wax *n*-alkanes (from plants) was calculated following the method developed by Simoneit et al. (1991) and found to be 1% of the total *n*-alkanes. The major *n*-alkanes in the SSPM samples range from C_{22} to C_{40} , with a C_{max} at 31 and CPI values of 1.75 (Table 4.1), indicating a significant contribution from natural plant waxes. The input of vascular plant waxes in the SSPM is estimated to be 28%. The dominant *n*-alkanes in the sediment samples from the Gulf of Suez range from C_{16} to C_{37} , with C_{max} at 24 and 26 and a CPI of 0.60, indicating that the prevailing source is petroleum input (Table 4.1). For the sediment samples from the coast of Saudi Arabia, the *n*-alkanes range from C_{16} to C_{35} , with C_{max} at 29 and a CPI of 1.91 (Table 4.1), confirming that input from plant wax is a

major source (estimated as 49% of the total *n*-alkanes, Table 4.1). The *n*-alkanes of the sediment samples from the coast of Yemen also range from C_{16} to C_{35} , with C_{max} at 17 indicating a marine planktonic input (Cranwell et al. 1987) and a CPI of 2.96, supporting a biogenic contribution from both marine and higher plant sources. The samples with a C_{max} at 29 are characteristic of biogenic sources from terrestrial higher plants (Table 4.1) as shown in the samples of SSPM and Saudi Arabian sediments. The lower CPI and C_{max} for *n*-alkanes in the sample from the Gulf of Suez (Figs. 4.2c1 and Table 4.1) indicate the predominance of petroleum sources. The *n*-alkanes in the samples with higher CPI and C_{max} at 29 and/or 31, as shown in the SSPM and sediments from the Saudi Arabian coast, have a significant contribution from higher plant waxes with minor microbial inputs.

The distributions of the *n*-alkanoic acids, methyl *n*-alkanoates, and *n*-alkanols in the different sample extracts (Fig. 4.3c, d, e) are all consistent with biogenic sources. The *n*-alkanoic acids are present in all samples except in the coastal sediments of Saudi Arabia and Yemen (Table 4.1). They have a strong even carbon number predominance $>C_8$, which confirms that they are of a biotic origin (Kolattukudy et al. 1976; Simoneit 1978; Cranwell 1974; Wiesenberg and Schwark 2006). Their distributions from C_8 to C_{18} indicate a microbial origin, and those from C_{20} to C_{30} reflect an origin from higher plant wax (Cranwell 1973; Simoneit 1978). Palmitic and stearic acids (C_{16} , C_{18}) are the dominant saturated homologues and are interpreted to be derived from mainly microbial, and to a lesser degree from terrestrial higher plant sources. The *n*-alkanoic acids in the atmospheric dust samples range from C_9 to C_{30} , with a C_{max} at 18 and a $CPI_{(e/o)}$ of 3.69 indicating both microbial and terrestrial plant sources. The *n*-alkanoic acids in the SSPM samples range from C_8 to C_{14} , with a C_{max} at 16 and a $CPI_{(e/o)}$ of 5.0, indicating that these fatty acids are predominantly from marine microbial sources. The sediment samples from the Gulf of Suez, have *n*-alkanoic acids from C_8 to C_{28} , with a C_{max} at 16 or 18 and $CPI_{(e/o)}$ ranging from 7.11 to 8.6, confirming admixed marine microbial and terrestrial plant sources. The *n*-alkanoic acids are not detected in the sediment samples from the coastal zone of Saudi Arabia and Yemen.

Methyl *n*-alkanoates, reported as the alkanolic acids, are present in all samples. In the atmospheric dust samples, they range from C_{14} to C_{18} , with C_{max} at 16 and a $CPI_{(e/o)}$ of 16.7. In the SSPM samples they have a wider range (C_{12} to C_{32} , Fig. 4.3d), with C_{max} at 16 and 18 and a $CPI_{(e/o)}$ of 9.9 (Table 4.1). The Gulf of Suez sediment samples have methyl *n*-alkanoates only from C_{12} to C_{18} , with C_{max} at 16 and $CPI_{(e/o)}$ of 9.03 and 10.51. The sediment samples from the coastal zones of Saudi Arabia and Yemen contain methyl *n*-



◀ **Fig. 4.3** Examples of typical GC-MS key ion plots for various compound series found in various dust, SSPM and sediments from different parts of the Red Sea: **a** dust sample, m/z 85 *n*-alkanes, **b** sediment sample from the coast of Saudi Arabia, m/z 85 *n*-alkanes, **c** dust sample, m/z 117 *n*-alkanoic acids as TMS esters, **d** SSPM, m/z 87 methyl *n*-alkanoates, **e** sediment samples from the coast of Saudi Arabia, m/z 103 *n*-alkanols as TMS ethers, **f** SSPM, m/z 129 steroids as

TMS ethers, **g** sediment sample from the coast of Saudi Arabia, m/z 191 hopane biomarkers, **h** sediment sample from the coast of Saudi Arabia, m/z 217/218 sterane biomarker, **i** SSPM sample, m/z 149 plasticizers (DBP = di-*n*-butyl phthalate, DIBP = diisobutyl phthalate, BBP = butyl benzyl phthalate, DEHP = di(ethylhexyl) phthalate, DIDP = di-isodecyl phthalate), and **j** sediment sample from the coast of Saudi Arabia, m/z 204/361 carbohydrates

alkanoates from C_{14} to C_{26} , also with C_{max} at 16 and $CPI_{(e/o)}$ of 13.4 and 9.6, respectively. The even carbon dominances confirm the natural biogenic sources of these compounds from microbial activity ($<C_{18}$) and terrestrial higher plants ($>C_{18}$).

The *n*-alkanols are found in the atmospheric dust, SSPM and sediment samples from the coast of Saudi Arabia. They range from C_{16} to C_{32} in the dust sample, from C_{14} to C_{30} in the SSPM samples and from C_{14} to C_{32} in sediment samples from the coast of Saudi Arabia (Fig. 4.3e), with C_{max} at 26 for the samples, 18 for the SSPM, and 16 and 30 for the sediments. The CPI values range from 6.4 ± 1.4 for the Saudi coastal sediments, to 17.1 ± 2.1 for dust samples. It is 12.5 ± 4.9 for SSPM.

Steroids are derived primarily from terrestrial plant and animal sources and they occur in all ecosystems. Therefore, the sources and fate of the steroids can be used to distinguish organic matter types in the environment (Philp 1985; Bataillon et al. 2016; Ortiz et al. 2016). They also occur in fossil fuels as steroid hydrocarbons, that is, steranes (Philp 1985; Hostettler et al. 1999). The natural steroids generally range from C_{26} to C_{30} and comprise a variety of molecules usually as 3-hydroxysteroids (Moreau et al. 2002). Cholesterol is a major compound in animal lipids and in some algal plankton. Steroids are known as phytosterol in higher plants and range from C_{28} to C_{30} with one or two carbon-carbon double bonds, typically one in the sterol nucleus and a second in an alkyl side chain. Only cholesterol is detected in the atmospheric dust samples (Fig. 4.2a), indicating that urban processes including food preparation (Omar et al. 2007; Rogge et al. 1991) are major sources of organic matter to atmospheric dust in the area. The steroids in the SSPM samples range from C_{27} to C_{30} , where cholesterol is the major compound with variable amounts of brassicasterol, campesterol, stigmasterol, sitosterol, and fucosterol (Fig. 4.3f), indicating that these steroids are of both marine and terrestrial origins. The Gulf of Suez sediment samples have steroids ranging from C_{27} to C_{29} , while those from the coastal zone of Saudi Arabia range to C_{30} , again confirming the contribution of both marine and terrestrial inputs. Steroids were not detected in sediment samples from the coast of Yemen. The concentrations of steroids are high in the SSPM and sediment samples from the coast of Saudi Arabia. The general steroid distribution shows cholesterol, stigmasterol, sitosterol and fucosterol are dominant, with brassicasterol

and dinosterol as minor components. Cholesterol (in part), dinosterol, and brassicasterol are interpreted to be from algal plankton in the aquatic environment (Didyk et al. 1978; Robinson et al. 1984; Volkman et al. 1998; Giner and Boyer 1998; Giner and Li 2001; Bode et al. 2003). The dominance of sitosterol in the samples is interpreted to originate from terrigenous sources (Barbier et al. 1981; Simoneit et al. 1983; Moreau et al. 2002).

Carbohydrates, which are detected only in sediment samples from the Gulf of Suez and the coast of Saudi Arabia, are attributed primarily to microbial and fungal biomass (Lehninger 1970), extracellular carbohydrates, and degradation of detrital cellulose from various natural sources (Rushdi et al. 2005, 2006a; Medeiros and Simoneit 2007). The carbohydrates are mainly α - and β -glucose, sucrose, and mycose (also known as trehalose, Fig. 4.3j). Various agricultural soils have been analyzed for carbohydrate contents, where glucose, sucrose, and mycose are typical for microbial and fungal biomass (Simoneit et al. 2004; Rogge et al. 2006; Medeiros and Simoneit 2007). The presence of a mixture of various lipid compound classes and carbohydrates in the total extracts indicates that the natural biogenic sources are mainly from the surrounding vegetation, microbial biomass, and detrital organic matter.

Additional minor tracers from particle fallout of biomass burning smoke and from wash-in of eroded soil particles are recognizable in the dust aerosols and in some sediments. These are levoglucosan from burning of cellulose (Fig. 4.2a) and dehydroabietic acid from vaporization of resin from burning of conifer wood (Simoneit 2002). The presence of saccharides in the dust aerosols, consisting of α - and β -glucose, sucrose and mycose (Fig. 4.2a), indicates that advected soil particles are part of the dust transport (Simoneit et al. 2004). Dehydroabietic acid can also be deposited in sediments by soil erosion/flood events, which also contribute the saccharides of soil (Fig. 4.2c2 and d).

Anthropogenic Sources

The presence of *n*-alkanes with $CPI \leq 1.0$ and UCM (Fig. 4.2 c1) in the SSPM samples supports an origin from un-degraded crude oil. The elevated concentrations of *n*-alkanes in the sediment samples from the Gulf of Suez with a CPI of 0.6 specify a major contribution from oil related

sources. The occurrence of *n*-alkanes in the dust samples with C_{max} at 25 and a CPI of 1.3 suggest a contribution from fossil fuel sources.

Hopane and sterane hydrocarbons are biomarkers for petroleum and its products (Philp 1985; Simoneit 1985; Peters and Moldowan 1993) and can be used to identify organic matter derived from fossil fuel. They are only found in sediment samples from the Gulf of Suez and the coastal zone of Saudi Arabia (Table 4.1). The hopane biomarkers range from C_{27} to C_{35} , with C_{max} at 30 (e.g., Figure 4.3g) and relative concentrations from 1.8% to 11.2% of the total extracts, respectively. The steranes are also only detectable in these sediment samples, with relative concentrations of 21.1% and 13.1% of the total extracts, respectively (Fig. 4.3h).

Plasticizers, including di-*n*-butyl phthalate (DBP), diisobutyl phthalate (DIBP), butyl benzyl phthalate (BBP) and di(ethylhexyl) phthalate (DEHP), which can be released to the environment due to bio- and photo-degradation of plastic wastes, are present in the dust, SSPM, and sediment samples

from the coast of the Gulf of Suez and Saudi Arabia (Fig. 4.3i). Their relative concentrations are 1.6% in the dust, 16.8% in the SSPM from the Gulf of Aqaba, 3.2 to 6.0% in the sediment from the Gulf of Suez, and 4.7% in the sediments from the coast of Saudi Arabia.

The total organic matter extracts obtained from sediment samples usually contain an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons. These UCM hydrocarbons are derived mainly from fossil fuel utilization and/or oil spills, as well as to a minor extent from diagenesis of microbial detritus. They appear on the GC traces as a signal above the baseline with the resolved compounds superimposed (Fig. 4.2c1, c2, d; Simoneit 1984, 1985). Diesel vehicle exhaust shows a bimodal UCM, which is derived both from the fuel (lower C_{max}) and the lubricating oil (higher C_{max}), while exhaust from gasoline engines exhibits a narrow UCM (Simoneit 1984, 1985; Bi et al. 2002). Biogenic hydrocarbons derived from higher plants exhibit no UCM, and those from decomposition of algal detritus show a narrow UCM at $C_{max} = 20$ (Simoneit 1978;

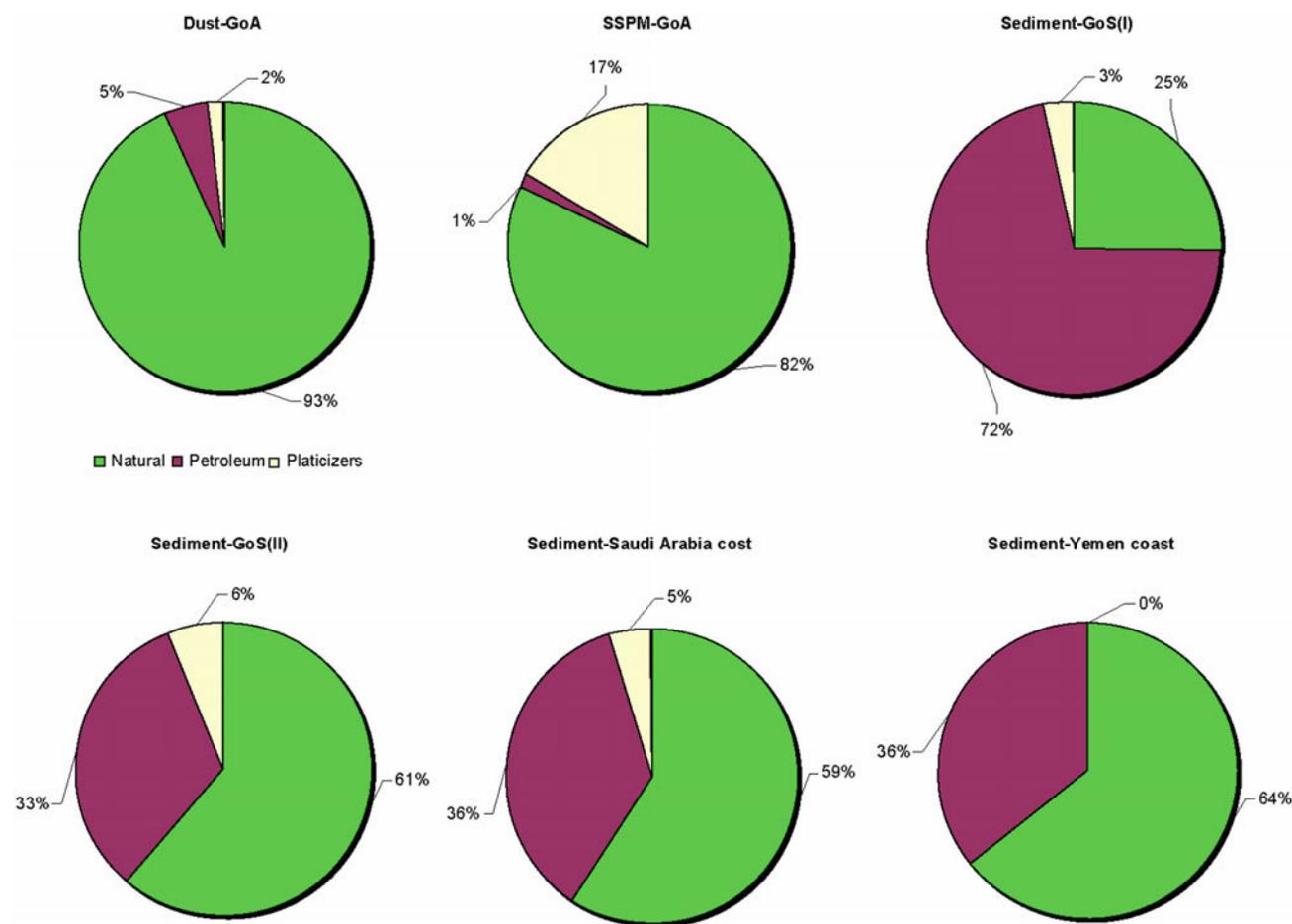


Fig. 4.4 Pie plots of the contribution of natural (green), petroleum residues (brown), and plasticizers (yellow) in extractable organic matter from atmospheric dust from the Gulf of Suez, surface seawater

particulate matter from the Gulf of Aqaba, and sediments from the coastal zones of the Gulf of Suez, Saudi Arabia, and Yemen

Simoneit and Mazurek 1982). Sediment samples contaminated by biodegraded petroleum residues have higher UCMs (Peters and Moldowan 1993). The occurrence of the UCM together with hopane and sterane biomarkers generally confirms the contamination by residues from petroleum and petroleum products (Simoneit 1984, 1985).

Natural Versus Anthropogenic Sources

The contributions of natural biogenic versus anthropogenic (petroleum and plasticizers) sources varied as shown in Fig. 4.4. The natural sources in aerosol dust are high ($93 \pm 3.8\%$ of total extract by weight) relative to anthropogenic sources (petroleum = $5 \pm 2\%$ and plasticizers = $1.6 \pm 0.1\%$). Also, natural inputs are the dominant sources ($82 \pm 46\%$) in surface seawater particulate matter followed by plasticizers ($17 \pm 2\%$) and petroleum residues ($1.2 \pm 1.0\%$). The natural sources are also dominant in the sediments, except for one area of the Gulf of Suez, and range from $61 \pm 35\%$ to $64 \pm 86\%$. The petroleum and oil-related sources are significant in all sediments, ranging from $33 \pm 14\%$ to $36 \pm 21\%$ with less input from plasticizers ranging from 0% to $6 \pm 2\%$. The exception is the sediment in the vicinity of oil production activities, where the petroleum sources are higher ($72 \pm 27\%$; e.g., site I in the Gulf of Suez), followed by natural inputs ($25 \pm 12\%$) and plasticizers ($3.1 \pm 0.4\%$). This indicates that natural biogenic sources are major sources of organic matter ($>60\%$) in the Red Sea, where anthropogenic (mainly petroleum) inputs are apparently only significant in sediments ($>30\%$). It also indicates that short- or long-range transport of fine dust particles, and coastal human activities including oil production and transportation could be major sources of organic detritus and pollutants to the marine environment.

Conclusions

The analyses of dust, surface seawater particulate matter and sediments from various locations of the Red Sea show that natural biogenic and anthropogenic sources are both contributors to their organic matter contents, but the relative contributions vary spatially. The organic compounds include *n*-alkanes, methyl *n*-alkanoates, *n*-alkanols, *n*-alkanoic acids, sterols, carbohydrates, hopane and sterane biomarkers, and UCM. The natural sources of organic compounds are mainly from terrestrial vegetation, marine primary production and microbial inputs. They are higher in atmospheric dust and surface seawater particulate matter compared to the sediments. Anthropogenic organic compounds are more important in sediments ($>30\%$) and depend on the location and the types of human coastal activities.

The results of this study indicate that both natural and anthropogenic components contribute to organic inputs in the Red Sea. Thus, to carefully construct any predictive model for short- or long-range transport of such components in dust aerosols, coastal natural and/or anthropogenic inputs, and to understand their impacts on the coastal environments and the biogeochemical cycles of carbon in the marine environment, reliable information and analytical data are needed. Such information and data should include the sources, characteristics, and composition of both organic and inorganic components delivered by these processes. In addition, chemical composition (i.e., organic and inorganic) and physical properties of the coastal shelf sediments of the Red Sea and of the fine aerosol dust are lacking. Thus, national and international scientific collaborations and efforts must be initiated to study the impacts of these processes and sources on the biogeochemistry of the Red Sea.

Acknowledgements The authors thank Dr. Najeeb M.A. Rasul for the invitation to participate in this book project.

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