water

MDPI

Article

Occurrence, Distribution, and Sources of Aliphatic and Cyclic Hydrocarbons in Sediments from Two Different Lagoons along the Red Sea Coast of Saudi Arabia

Mubarak T. Al-Otaibi [1,2], Ahmed I. Rushdi [3], Najeeb Rasul [4,5], Abdulqader Bazeyad [2], Khalid F. Al-Mutlaq [2], Saud S. Aloud [1] and Hattan A. Alharbi [2,*]

[1] Department of Soil Science, College of Food and Agriculture Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia; mmubarakk@ksu.edu.sa (M.T.A.-O.); alouds@ksu.edu.sa (S.S.A.)
[2] Department of Plant Protection, College of Food and Agriculture Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia; abazeyad@ksu.edu.sa (A.B.); almutlaqk@gmail.com (K.F.A.-M.)
[3] ETAL, 2951 SE Midvale Drive, Corvallis, OR 97333, USA; aimrushdi@gmail.com
[4] Saudi Geological Survey, Jeddah 21514, Saudi Arabia; najeeb_rasul@hotmail.com
[5] Geological and Geophysical Research Systems, Mississauga, ON L4T 0A1, Canada
* Correspondence: halharbii@ksu.edu.sa

Abstract: Surface sediment samples from Al-Qahma lagoon in the southern part and Al-Wajh lagoon in the northern part of the Red Sea coast of Saudi Arabia were collected by a Van Veen grab sampler to determine the characteristics, distribution, and sources of aliphatic and cyclic hydrocarbons. The total extractable organic matter (TEOM) was extracted with a dichloromethane/methanol mixture after drying and sieving the sediments and identified by gas chromatography–mass spectrometry. The TEOM comprised n-alkanes (302.6 ± 446.7 ng·g^{-1} and 64 ± 50 ng·g^{-1}), hopanes (29.8 ± 132.3 ng·g^{-1} and 1.0 ± 2.5 ng·g^{-1}), steranes (0.0 and traces), n-alkanoic acids (745.8 ± 799.6 ng·g^{-1} and 120.7 ± 92.0 ng·g^{-1}), n-alkanols (457.4 ± 1085.6 ng·g^{-1} and 49.7 ± 32.3 ng·g^{-1}), polycyclic aromatic hydrocarbons (PAHs) (54.5 ± 96.8 ng·g^{-1} and 7.8 ± 8.5 ng·g^{-1}), and phthalates (185.3 ± 169.9 ng·g^{-1} and 67.4 ± 70.4 ng·g^{-1}) in the Al-Qahma and Al-Wajh lagoon sediments, respectively. The percentages of the various sources relative to total aliphatic and cyclic hydrocarbon concentrations were 6.9 ± 6% for terrestrial plants, 53.7 ± 19% for algae, 10 ± 2% for microbial, 16 ± 12% for petroleum, and 13.4 ± 7 for plasticizer inputs in Al-Qahma lagoon. In Al-Wajh lagoon, they were 9.7 ± 4% for terrestrial plants, 30.8 ± 14% for algae, 25.2 ± 5% for bacteria, 11.2 ± 3% for petroleum, and 23.1 ± 11% for plasticizers.

Keywords: Al-Qahma lagoon; Al-Wajh lagoon; Red Sea; aliphatic hydrocarbons; PAHs; surface sediments; GC-MS

check for updates

Citation: Al-Otaibi, M.T.; Rushdi, A.I.; Rasul, N.; Bazeyad, A.; Al-Mutlaq, K.F.; Aloud, S.S.; Alharbi, H.A. Occurrence, Distribution, and Sources of Aliphatic and Cyclic Hydrocarbons in Sediments from Two Different Lagoons along the Red Sea Coast of Saudi Arabia. *Water* **2024**, *16*, 187. https://doi.org/10.3390/w16010187

Academic Editors: Hyeon-Seo Cho and Huiho Jeong

Received: 3 December 2023
Revised: 24 December 2023
Accepted: 28 December 2023
Published: 4 January 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The Red Sea plays a significant role in the economies of its bordering nations, with its contributions spanning fishing, tourism, leisure activities, and shipping routes. The coastal habitats of the Red Sea are among the most unique and diverse ecosystems in the world [1]. They are primarily shaped by its geographical and environmental conditions such as geological formation, high salinity, and warm and clear water [2–4]. Situated along the Red Sea, the coast of Saudi Arabia is recognized for its diverse coastal habitats, such as mangroves [5–7], coral reefs [8,9], seagrass meadows [10–13], and rocky beaches [14], which support a wide array of marine life. These diverse coastal habitats, including coastal lagoon ecosystems along the Red Sea coast of Saudi Arabia, emphasize the region's ecological importance and its role in conserving marine biodiversity.

Coastal lagoons are ecologically significant ecosystems that play a vital role in supporting biodiversity and environmental health. They serve as crucial nurseries for various fish species, contributing to the sustainability of fisheries [15–17]; they also offer vital breeding and feeding grounds for migratory birds [18–20]. They play a major role in nutrient cycling

and carbon sequestration [21,22] and act as natural buffers against coastal erosion and storm surges, providing essential protection to nearby communities [23–25].

Marine organic matter (OM) generally serves as a key indicator in the analysis of biogeochemical processes in coastal sediments. It encompasses various compound classes, including carbohydrates, lipids, proteins, and other organic compounds [26–28]. Within the water column, sediment, and sediment–water interface, this mixture of molecules undergoes degradation and alteration processes [29]. Among these compounds are aliphatic and cyclic hydrocarbons, exhibiting distinct and significant characteristics attributed to different sources due to their resistance to degradation and early diagenetic alteration. These compounds serve as useful tracers for identifying the sources of hydrocarbons because they originate from both anthropogenic activities (such as petroleum) and natural sources (including terrestrial higher plant waxes, aquatic phytoplankton, and bacteria) as well as the biochemical degradation products of in situ natural organic matter [30,31].

Petroleum hydrocarbons are the primary anthropogenic inputs in coastal zones [32–34]. These inputs primarily originate from onshore oilfield operations, liquid discharges from refineries, spills and accidents, petrochemical plants and shipping activities, natural oil seeps, and sewage discharges [35,36]. Notably, oil tankers and oil terminals significantly contribute to petroleum residues in the Red Sea [37–40]. The coastal ecosystems along the Red Sea shores are severely contaminated with oil-related products [41,42]. Moreover, oil pollution in the coastal environment of Saudi Arabia's Red Sea might occur by sewage discharge from offshore platforms, ship traffic, tour boats, ferries, private yachts, leisure activities, and littering [43–45]. Additionally, petroleum-related products can be introduced into the coastal environment through the deposition of transported atmospheric particulate matter, resuspension of soil by winds, and seasonal runoff of streams and floods [46,47].

In Saudi Arabia, the coastal development of the Red Sea is part of the Saudi Giga-Project (The Red Sea Project, Vision 2030); however, such activities might disrupt the ecosystems and introduce the pollution to marine life [48]. Previous studies have shown that coastal sediments from Obhur lagoon north of Jeddah city in the Red Sea are contaminated with diverse groups of hydrocarbons from petroleum products and plasticizers from littering [49]. However, there is no information about the characteristics, sources, and levels of sedimentary organic matter in other lagoons along the Red Sea coast of Saudi Arabia. For example, the Al-Wajh Bank is part of a major coastal development as a tourist destination in the north of the Red Sea [48]. Thus, it is essential to establish baseline data of the abundance, distribution, levels, and origin of natural and anthropogenic organic matter in the coastal sediments of different habitats in the region.

The objectives of this research are to determine the compositions, levels, distribution, and sources of aliphatic and cyclic hydrocarbons in surface sediment total extractable organic matter (TEOM) from Al-Qahma lagoon in the southern part and Al-Wajh lagoon in the northern part of the Red Sea coast of Saudi Arabia. This relies on the analysis of essential parameters and molecular markers.

2. Study Areas

The study areas were the Al-Qahma and Al-Wajh lagoons on the Red Sea coast of Saudi Arabia (Figure 1). Al-Qahma lagoon, located in the southwestern region, is a captivating coastal feature characterized by its unique and diverse ecosystem. The lagoon is a vital habitat for various bird species and aquatic life. It is known for its picturesque landscapes, with extensive seagrass beds and mangroves that provide crucial breeding and forging grounds for a multitude of bird species, including flamingos and herons [50]. The lagoon serves as a refuge for marine life, supporting an array of fish species and diverse wildlife, making it a site of great environmental and recreational value to the Kingdom of Saudi Arabia. The water depths range from 4 m to 40 m (average = 19 m).

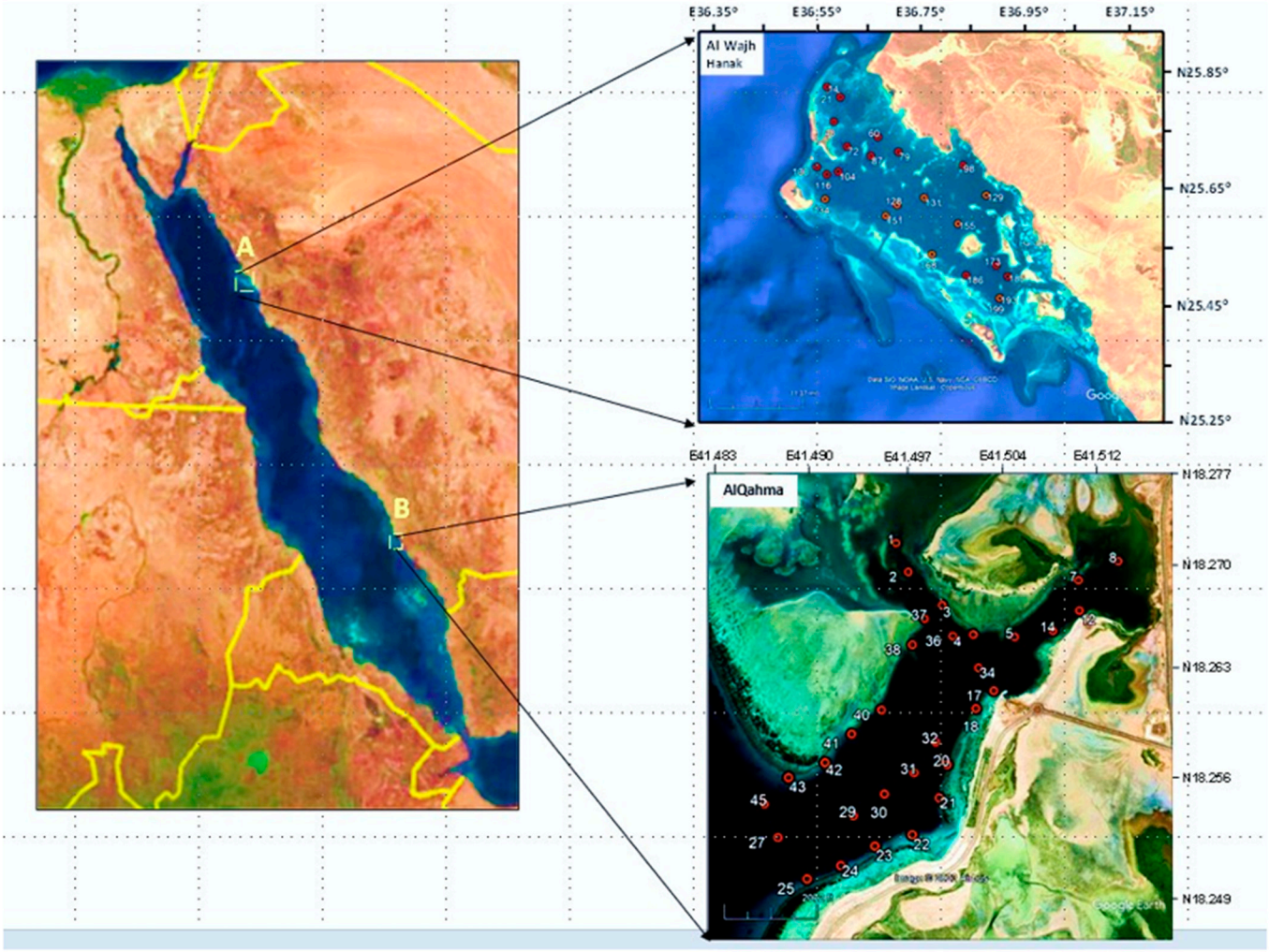

Figure 1. Maps of sampling locations and sites of the Al-Qahma lagoon in the southern and Al-Wajh lagoon in the northern parts of the Red Sea coast of Saudi Arabia.

Al-Wajh lagoon, situated in the northern part of the Red Sea coast of Saudi Arabia, is a remarkable coastal feature with significant ecological importance. This lagoon is renowned for its scenic attraction, characterized by aquamarine waters and a surrounding landscape of mangroves, seagrass beds, and sand shores. These diverse coastal habitats provide crucial breeding and feeding grounds for various marine species, making it a thriving ecosystem for resident and migratory bird species. The water depths vary from 5 m to 36 m (average = 22 m).

3. Materials and Methods

3.1. Sample Collection

In February 2022, we obtained 31 surface sediment samples from Al-Qahma lagoon in the south and in August 2022, we gathered 24 samples from Al-Wajh lagoon in the north (Figure 1). These samples were collected using Van Veen grab samplers (size = 0.1 m^2- 15 L). The locations and water depths of the selected sites ranged from 1 to 23 m for Al-Qahma and 5 to 35 m for Al-Wajh. After collection, the samples were promptly placed in ice boxes (~−4 °C) and then transferred to a laboratory freezer (−18 °C) within a timeframe of 4–5 h. To prepare the sediment samples for analysis, approximately 50 g of each sample was defrosted and dried at room temperature, using a clean spatula. Then, the samples underwent a grinding and sieving process to obtain fine particles measuring less than 125 µm in size to facilitate the total extraction of the organic matter.

3.1.1. Extraction of Sediment Samples

The extraction procedure followed the method outlined by Rushdi et al. [51,52]. Each dried and ground sample, weighing approximately 15 g, underwent three rounds of extraction through ultrasonic agitation, each lasting 15 min. The extraction utilized 20 mL of dichloromethane (DCM) and 10 mL of methanol (MeOH). This process occurred in a 150 mL precleaned beaker. To separate sediment particles from the extract, a filtration unit with a Whatman GF/A filter (particle retention = 1.6 µm) made of annealed glass fiber was employed. The filtrate was initially concentrated on a rotary evaporator, reduced to a volume of around 50 µL using dry nitrogen gas. The extract volume was then precisely adjusted to 100 µL by adding a mixture of DCM:MeOH (21, *v*:*v*).

3.1.2. Instrumental Analysis

For the analysis of the total extract, gas chromatography–mass spectrometry (GC-MS) was employed, utilizing a Hewlett-Packard 6890 GC coupled to a 5975-mass selective detector from Agilent (Palo Alto, CA, USA) 6890N. A capillary column made of Agilent DB-5MS fused silica, measuring 30 m in length, 0.25 mm in internal diameter, and with a film thickness of 0.25 µm, was used. Helium served as the carrier gas during the analysis. The GC oven temperature was set to 65 °C initially and held for 2 min. It was then ramped up to 310 °C at a rate of 6 °C per minute, followed by an isothermal final hold for 20 min. The MS operated in electron impact mode with an ion source energy of 70 eV. The acquisition of mass spectrometric data was facilitated using the ChemStation data system. Prior to GC-MS analysis, a 50 uL aliquot of each total extract underwent derivatization using a silylating agent, specifically N,O-bis (trimethylsilyl)trifluoroacetamide (BSFTA) from Pierce Chemical Co (Dallas, TX, USA). This process aimed to substitute the hydrogen in hydroxyl groups with trimethylsilyl (TMS) groups, enhancing the GC resolution of polar compounds. All samples were injected in a splitless manner, with the injector temperature maintained at 270 °C.

3.1.3. Identification and Quantification

The identification of hydrocarbon compounds relied on comparing their retention times with those of external standards and utilizing GC-MS data. The identification of n-alkanes, fatty acid methyl esters (FAME), n-alkanoic acids, n-alkanols, hopanes, steranes, polycyclic aromatic hydrocarbons (PAHs), and plasticizers (mainly phthalates) is based primarily on their key ion pattern and mass spectra (i.e., *m*/*z* 85, 87, 117, 103, 191, 217/218, 128/178/202/228/252/276/300, and 149, respectively). Quantification was performed by examining the total ion current (TIC) GC profiles through the external standard method, utilizing authentic compounds representative of each homologous series [47,53,54].

We determined the limit of detection (LOD) and limit of quantification (LoQ) for the samples using the same approach. Employing the least-square method, we fitted concentrations of various standards against their relative responses, yielding significant correlations with correlation coefficients (R^2 = 0.9–0.98). Data analysis was conducted using SPSS 16.0 (IBM-Statistical Package for Social Science, Version 16.0). Average response factors for each compound were calculated, and quantification relies on the peak areas derived from the total ion current (TIC) trace. Integration parameters, initially set at a threshold of 10, were chosen from the ChemStation integrator. Relative ion counts were converted to compound mass using the area counts of external standards determined under identical instrumental operating conditions. The concentration of each compound was calculated using the following formula: $[C_{(s)}$ (ng/g) = C_{st} (ng/µL). $V_{inj,st}$ (µL). A_s (counts). V_{TEXT} (µL)]/[A_{st} (count). $V_{inj,s}$ (µL). Wt_{sed} (g)], where C, A, V, and Wt represent concentration, count, volume, and weight, respectively. The subscripts s, st, inj, and sed denote the sample, standard, injected, and sediment, respectively.

3.1.4. Quality Control

All reagents and solvents employed for extraction were tested to identify possible contaminations. To evaluate potential background contamination arising from laboratory procedures, an examination of procedural blanks was conducted. Additionally, after every set of three samples, blank extractions were carried out to verify the precision and dependability of the analysis. For testing recoveries, n-tetracosane-d50 was introduced into sediment samples, and the measured concentrations were subsequently adjusted. The analysis and quantification of procedural blanks for both sediments and solvents were undertaken to ensure the absence of noteworthy background interferences. Blank extractions were systematically performed in sets of three samples throughout the entirety of the chemical analysis.

4. Results and Discussion

The composition analysis of sediments collected from the Al-Qahma and Al-Wajh lagoons, as summarized in Table 1, revealed the presence of various components. These included n-alkanes, hopanes, methyl n-alkanoates, n-alkanoic acids, n-alkanols, polycyclic aromatic hydrocarbons (PAHs), and phthalates as illustrated in Figure 2. These compounds originate from both natural and human-related sources and can offer valuable insight into their origins. The existence and characteristic features of these homologous series in the ecosystem can be utilized to determine their primary origin in the environment [46,47,52,53,55,56].

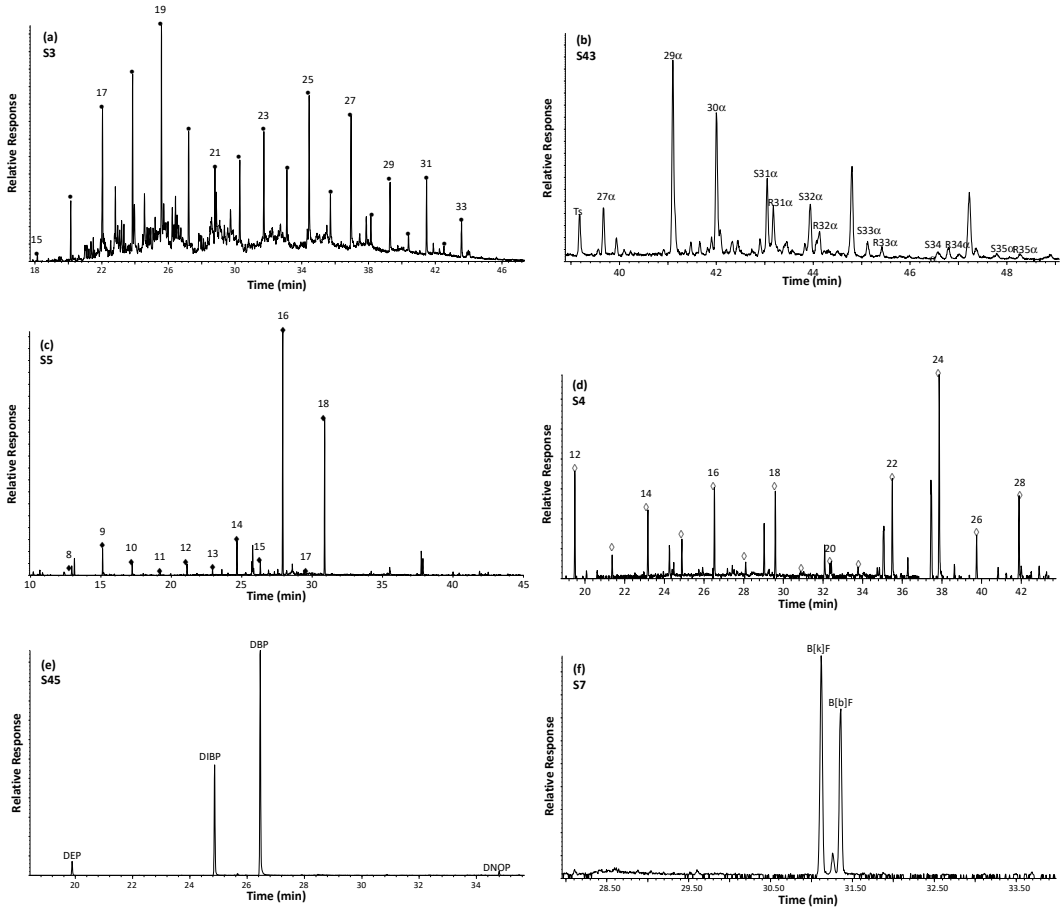

Figure 2. Examples of typical GC-MS key ion plots for (**a**) n-alkanes (m/z 85), (**b**) hopanes (m/z 191), (**c**) n-alkanoic acids (m/z 117 as TMS), (**d**) n-alkanols (m/z 103 as TMS), (**e**) phthalates (m/z 149), and (**f**) PAHs (m/z 202, 228, 252, and 276) in sediment samples from Al-Qahma and Al-Wajh lagoons, Red Sea coast of Saudi Arabia.

Table 1. Concentrations of various aliphatic and cyclic hydrocarbons and their geochemical indices in the sediments from the Al-Qahma and Al-Wajh lagoons, Red Sea coast of Saudi Arabia.

	Al-Qahma	Al-Wajh
n-Alkanes		
Range	15–33	14–33
Cmax	17, 19, 20, 24, 25, 27	16, 18, 20
Concentration range (ng/g)	0–1048	11–278
Average concentration ± SD (ng/g)	235 ± 232	64 ± 50
CPI (o/e)	1.2 ± 0.6	0.4 ± 0.1
TAR	0.75 ± 0.58	0.11 ± 0.05
LMW/HMW	2.0 ± 0.9	13.0 ± 2.2
Wax n-Alkanes (ng/g)	25.3 ± 36.5	1.0 ± 0.9
Algal n-Alkanes (ng/g)	58.6 ± 109.9	12.6 ± 13.5
Bacterial n-Alkanes (ng/g)	51.3 ± 55.6	28.4 ± 17.7
Petroleum n-Alkanes (ng/g)	167.4 ± 264.0	22.0 ± 19.0
Hopanes		
Range	27–35	27–34
Cmax	29, 30	29, 30
Concentration range (ng/g)	0–736.3	0–9.5
Average concentration ± SD (ng/g)	29.8 ± 132.3	1.0 ± 2.5
C31 S/(R+S)	0.67 ± 0.10	0.60 ± 0.07
C32 S/(R+S)	0.71 ± 0.14	0.62 ± 0.07
Steranes	**ND**	**T**
n-Alkanoic Acids		
Range	9–20	5–21
Cmax	16	16, 17, 18
Concentration range (ng/g)	43.3–2973.2	4.1–304.0
Average concentration ± SD (ng/g)	745.8 ± 799.6	120.7 ± 92.0
CPI (e/o)	15.3 ± 13.5	0.9 ± 1.0
n-Alkanols		
Range	12–28	11–26
Cmax	16, 18, 22, 24	16, 18, 22
Concentration range (ng/g)	27.2–5607.5	10.2–162.1
Average concentration ± SD (ng/g)	457.4 ± 1085.6	49.7 ± 32.3
CPI (e/o)	6.2 ± 4.8	4.7 ± 1.0
PAH		
Concentration range (ng/g)	0–545.4	0–38.0
Average concentration ± SD (ng/g)	54.5 ± 96.8	7.8 ± 8.5
Ant/(Ant + Phe)	0.75 ± 0.38	0.50 ± 0.15
Plasticizers		
Concentration range (ng/g)	34.9–822.7	18.9–312.4
Average concentration ± SD (ng/g)	185.3 ± 169.9	67.4 ± 70.4

4.1. n-Alkanes

The total extractable organic matter (TEOM) of the sediment samples from the Al-Qahma and Al-Wajh lagoons contained n-alkanes ranging from C_{15} to C_{33} and C_{14} to C_{33}, respectively (Table 1), with the highest concentrations (C_{max}) found at mainly 17, 19, 20, 24, 25, and 27 in Al-Qahma and 16, 18, and 20 in Al-Wajh. The n-alkane total concentration ranged from 0 ng/g to 1048 ng/g (average = 235 ± 232 ng/g) in sediments from Al-Qahma and from 11 ng/g to 278 ng/g (average = 64 ± 50 ng/g) in Al-Wajh (Tables 1 and S1 (Supplementary Materials S1)). Their special concentration distributions are shown in Figure 3a,b, where the Al-Qahma lagoon in the south had a higher concentration range than Al-Wajh in the north, as shown in Figure 3a, indicating that the topography, sediment transport hydrography, and biota of the lagoon, as well as human activities around them, impact the distribution of these alkanes. The concentrations observed in this study were comparable to those documented in the Gulf of Suez, Egypt (ranging from 34 to 553 ng/g according to [57]); Jiaozhou Bay, China (0.5 to 8.2 µg/g as reported by [58]); Yellow River estuary in China (ranging from 0.356 to 0.572 mg/kg according to [58]); Patos Lagoon

(ranging from 0.28 to 36.4 µg/g based on [59]); and Obhur Lagoon (with concentrations of 89.3 to 140.6 ng/g, as reported by [51]). However, these levels were lower in comparison to the findings in other regions, such as the Caspian coast in Iran (ranging from 249 to 3900 µg/g as per [60]); the Eastern Mediterranean Coast (ranging from 1.6 to 14.7 µg/g, based on [61]); and the Northern Arabian Gulf (ranging from 5654 to 29,941 ng/g, according to [53]).

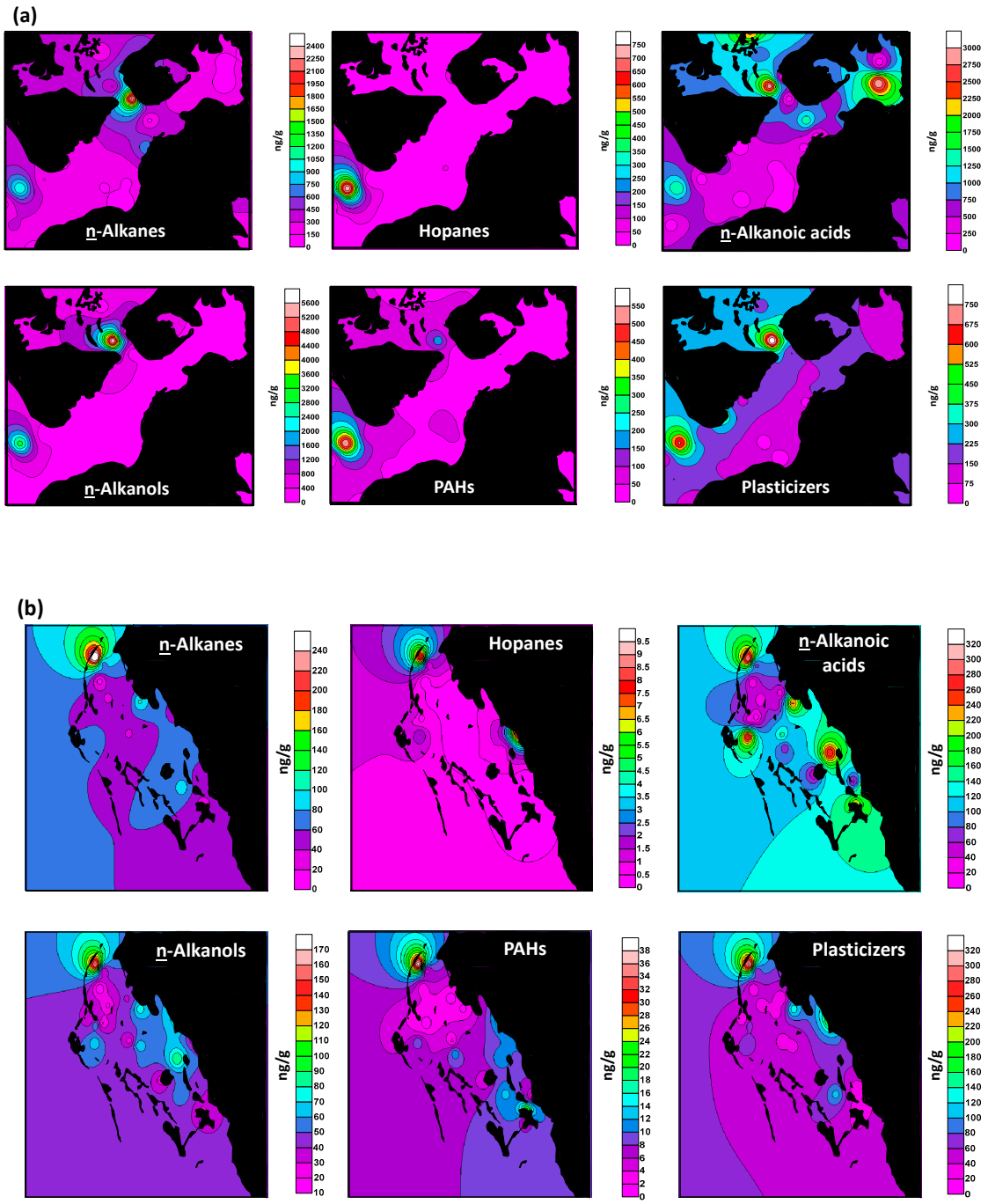

Figure 3. Spatial concentration distributions of various lipid tracers in the sediments of the (**a**) Al-Qahma and (**b**) Al-Wajh lagoons along the Red Sea coast of Saudi Arbia.

The presence of n-alkanes primarily results from both biogenic and anthropogenic inputs, and one can pinpoint their origins by examining the distribution patterns within their homologous series. The occurrence and identification of n-alkanes within ecosystems are valuable indicators for assessing the origins, transport, and preservation of organic

matter in the environment. Key factors tied to n-alkane characteristics and sources are the carbon number maximum (C_{max}) of the predominant n-alkane within the homologous series and the carbon preference index (CPI) as established by [62]. The $CPI_{o/e}$ developed by [63] can be determined using the following equation:

$$CPI_{(\frac{o}{e})} = \frac{\sum nC_{odd}}{\sum nC_{even}}$$

The analyzed samples exhibited the highest concentrations in distinct n-alkanes, as indicated in Tables 1 and S1. These findings suggest a range of origins, encompassing contributions from diverse natural sources like higher terrestrial plants and aquatic flora, along with human-made inputs predominantly from petroleum products [64–66]. The high concentrations observed across various n-alkanes (Tables 1 and S1) underscore the influence of both natural elements and anthropogenic factors, particularly the impact of petroleum products [65,66].

Higher molecular weight n-alkanes were also detected in the sediments from the Arabian Gulf [46,47], implying that plant waxes of tropical vegetation have a high C_{max} [64]. Commonly, the n-alkane $CPI_{(o/e)}$ has been utilized to gauge the repercussions and sway of biogenic and anthropogenic contributions [46,62,67]. In the sediment of the two lagoons, the $CPI_{(o/e)}$ values for the entire n-alkane ranges were estimated to be 1.2 ± 0.6 for the Al-Qahma lagoon and 0.4 ± 0.1 for the Al-Wajh lagoon (Table 1). These values indicated that n-alkanes in the sediments of the lagoons were originally derived from different sources, including petroleum-related products, phytoplankton, bacteria, and small amounts from higher plant waxes.

To determine the varying contributions of different sources, n-alkane concentrations derived from plant wax were computed using the procedure outlined by [68]. The sediment samples in the Al-Qahma lagoon exhibited plant wax concentrations of 52.3 ± 36.5 ng/g, while those in the Al-Wajh lagoon contained 1.0 ± 0.9 ng/g (Table 1). The ratios of TAR_{alk} (terrestrial-to-marine n-alkanes [69]):

$$TAR_{alk} = \frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}}$$

were estimated and obtained and found in the range of 0.75 ± 0.58 for the Al-Qahma lagoon and 0.11 ± 0.05 for the Al-Wajh lagoon (Table 1). These low values indicated that terrestrial plant sources were not significant contributors to these sediments, whereas Al-Wajh showed less contribution from terrestrial sources. The low-to-high molecular weight (LMW/HMW) ratios, which were 2.2 ± 0.9 for Al-Qahma and 13.0 ± 2.2 for Al-Wajh, confirm that algal and bacterial inputs of n-alkanes were substantial. The same method employed to compute n-alkane concentrations from plant wax was also used to determine the concentrations of n-alkanes originating from algae and aquatic bacteria. The concentrations of algal n-alkanes were 58.6 ± 109.9 ng/g in sediments from Al-Qahma and 12.6 ± 13.5 ng/g in the Al-Wajh lagoon. The bacterial n-alkane concentrations were 51.3 ± 55.3 ng/g and 28.4 ± 17.7 ng/g in the sediments from the Al-Qahma and Al-Wajh lagoons, respectively (Table 1, Figure 4a). The contributions of petroleum n-alkanes were subsequently determined by abstracting the calculated plant wax, algal, and bacterial n-alkanes from the total n-alkane concentrations. Their concentrations were 167.4 ± 264.0 ng/g in sediments from Al-Qahma and 22.0 ± 19.0 ng/g in the Al-Wahj lagoon (Table 1, Figure 4a). The absence of the isoprenoid pristane and phytane in the lagoon sediments is probably due to biodegradation and high oxidation processes.

The percentages of the various sources relative to total n-alkane concentrations were computed and estimated to be 7.8 ± 6.8% for terrestrial plants, 16.8 ± 7.0% for algae, 20.7 ± 7.4% for microbial, and 52.9 ± 13.1% for petroleum inputs in the Al-Qahma lagoon. In the Al-Wajh lagoon, they were 1.4 ± 0.4% for terrestrial plants, 18.7 ± 4.1% for algae, 45.8 ± 5.9% for bacteria, and 34.0 ± 4.7% for petroleum (Figure 5a).

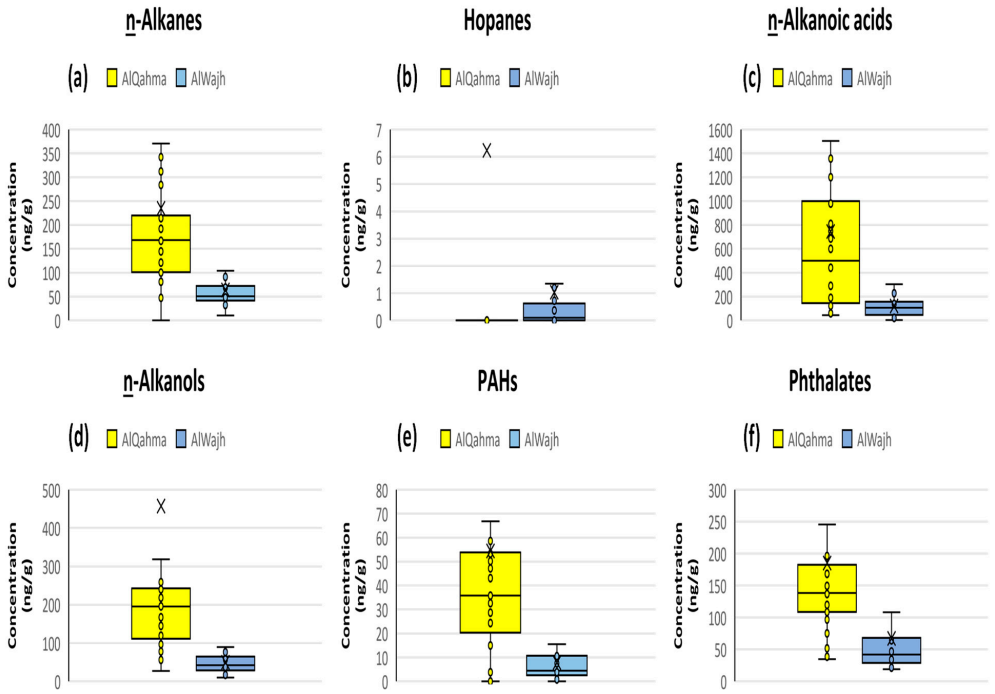

Figure 4. Box plots of the concentrations of (**a**) n-alkanes, (**b**) hopanes, (**c**) n-alkanoic acids, (**d**) n-alkanols, (**e**) PAHs, and (**f**) phthalates in sediments from the Al-Qahma and Al-Wajh lagoons, Saudi Arabia.

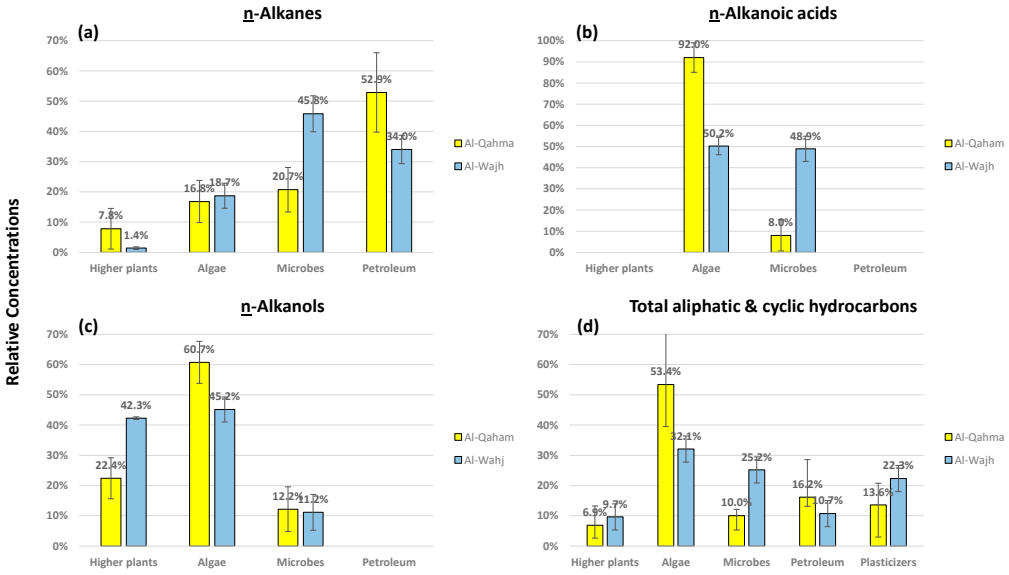

Figure 5. Plots showing the relative concentrations (%) of the terrestrial (higher plants), aquatic (algae), bacterial (microbes), and petroleum inputs of (**a**) n-alkanes (**b**) n-alkanoic acids, (**c**) n-alkanols and (**d**) total aliphatic and cyclic hydrocarbons in the sediments from the Al-Qahma and Al-Wajh lagoons, Red Sea coast of Saudi Arabia. (Algae include algal, diatomic, and planktonic inputs.)

4.2. Hopanes and Steranes

Hopane biomarkers were only detected in Al-Qahma lagoon sediments and hopanes with traces of steranes were measured in Al-Wajh lagoon samples. Hopanes ranged from C_{27} to C_{35} in Al-Qahma and from C_{27} to C_{34} in the Al-Wajh lagoon, where the C_{max} values were 29 and 30 for both lagoons (Table 1, Figure 2c). Hopane concentrations varied from 0.0 ng/g to 736.3 ng/g (average = 29.8 ± 132.3 ng/g) in sediments from Al-Qahma and from 0.0 ng/g to 9.5 ng/g in Al-Wajh (Table 1, Figures 3a,b and 4b). These concentrations

fell within the range of the levels observed in the sediments of the estuary of Paranagaue Bary-Southeast Atlantic (41.2–198 ng/g [70]). They exceeded the concentrations found in coastal sediments of Qatar (0.0–32.9 ng/g [71]), yet they were lower than the values determined in the coastal canal of Thailand (1510–17,114 ng/g [72]), the Iranian coast of Arabian/Persian Gulf (189–3713 ng/g, 42–3864 ng/g [73]), and the estuary in Malaysia (023–2.45 mg/kg [74]).

The presence of hopane biomarkers in the environment points to the possibility that the organic matter originated from fossil fuel residues [73]. Hopanes are commonly employed as tracers to identify the contributions of fossil fuel in the environment primarily because they exhibit resistance to alteration and degradation processes [56]. Consequently, we utilized hopane biomarkers to discern the presence of petroleum-related products in the environment. The maximum identified hopanes were at the C_{30} and/or C_{29} homologues of the thermodynamically sTable 17α(H),21β(H) configuration and minor 17β(H),21α(H)-hopanes (Table S1). These configurations of isomers usually take place in mature sedimentary rocks and crude oils due to the diagenetic interconversion of the 17β(H),21β(H)-hopane precursors of bacterial origins [75]. The hopane distribution extended from C_{27} to C_{35} for the α,β-series with usually mature C-22 R/S (sinister/rectus enantiomers at carbon 22) pairs of the prevalent homologs > C_{30} [75]. Elevated concentration distributions of the 22S hopane relative to the equivalent 22R isomer are normally related to petroleum and vehicle engine exhaust [55]. The 22S/(S+R) ratios for the extended hopanes of C_{31} and C_{32} were 0.67 ± 0.10 and 0.71 ± 0.14 for sediments from the Al-Qahma lagoon, whereas in Al-Wajh they were 0.60 ± 0.0.7 and 0.62 ± 0.07. These ratios were analogous to the estimates reported for mature crude oil and petroleum hydrocarbons [76,77]. Accordingly, these ratios confirmed that the sources of the hopanes in both lagoon sediments were petroleum-related inputs.

4.3. n-Alkanoic Acids

n-Alkanoic acids in the sediments from Al-Qahma lagoon ranged from C_9 to C_{20} with a C_{max} at 16, and concentrations varied from 43.3 to 2973.2 ng/g (average = 745.8 ± 799.6 ng/g). They were from C_5 to C_{21} in the sediments from Al-Wajh and had concentrations from 4.1 to 304.0 ng/g (average = 120.7 ± 92.0 ng/g) (Table 1, Figures 3a,b and 4c).

The main sources of n-alkanoic acids in the environment include terrestrial plants, plankton, diatoms, algae, and microbial mats. The n-alkanoic acids from terrestrial plants are evident by homologues of even carbon-numbered at >C_{20}, while those from plankton, algae, and diatoms are prominent also by even carbon-numbered homologues < C_{20} [78,79]. Microbial n-alkanoic acids are represented by odd carbon-numbered and branched homologues < C_{20} [80]. At this point, we interpreted the detected fatty acids > C_{20} as inputs from terrestrial sources and those < C_{20} from aquatic algal and planktonic sources. The inputs from terrestrial plants were 0.00 ng/ng in the two zones. The n-alkanoic acids from algal, planktonic, and diatom sources were 677.5 ± 726.6 ng/g in the Al-Qahma lagoon and 57.7 ± 63.0 ng/g in Al-Wajh (Table S1). The microbial sources of n-alkanoic acids were 68.3 ± 76.0 ng/g and 36.1 ± 28.6 ng/g in the Al-Qahma and Al-Wajh lagoons, respectively (Table S1), demonstrating that the main sources of n-alkanoic acids in the sediments of the lagoons were from aquatic biota.

The percentages from algae, diatoms, and planktons were 92.0 ± 3.2% in the Al-Qahma lagoon and 50.2 ± 28.0% in the Al-Wajh lagoon, whereas the fractions of microbial contributions were 8.0 ± 3.2% in the former and 48.9 ± 12.1% in the latter (Figure 5). Apparently, aquatic phytoplankton and diatoms were the major sources of fatty acids in the sediments of the Al-Qahma lagoon and microbial inputs were major in the Al-Wajh lagoon.

4.4. n-Alkanols

The n-alkanols were significant in the lagoon sediments ranging from C_{12} to C_{28} in Al-Qahma and C_{11} to C_{26} in Al-Wajh, with maxima at C_{16}, C_{18}, C_{22}, and C_{24} in both lagoons (Table 1). The total concentrations of the n-alkanols varyied from 27.2 ng/g to 5607.5 ng/g

(average = 457.4 ± 1085.6 ng/g) in Al-Qahma and from 10.18 ng/g to 162.1 ng/g (average = 49.7 ± 32.3 ng/g) in the Al-Wajh lagoon (Table 1, Figures 3a,b and 4d).

The presence of n-alkanols in the environment with C_{max} at 28, 30, or 32 and a strong even carbon-numbered preponderance suggests semitropical to tropical vascular plant wax inputs in environments [54,81]. The pronounced concentration levels of n-alkanols with a C_{max} at 28 or 30 indicate that the initial source of these compounds is terrestrial wax plants. The presence of the even carbon-numbered short-chain ($<C_{20}$) n-alkanols suggests algal sources and those with odd carbon numbers indicate microbial sources [82]. The concentrations of higher plant n-alkanols were 129.1 ± 362.6 ng/g (range = 0.0–1935.3 ng/g) in Al-Qahma and 23.3 ± 10.6 ng/g (range = 3.0–46.3 ng/g) in Al-Wajh. The algal n-alkanols were 247.8 ± 532.6 ng/g (range = 9.3–2744.2 ng/g) and 28.7 ± 22.1 ng/g (range = 7.1–118.4 ng/g) in sediments from the Al-Qahma and Al-Wajh lagoons, respectively. The microbial n-alkanol concentrations were 66.4 ± 165.7 ng/g (range = 0.0–796.3 ng/g) in Al-Qahma and 7.3 ± 5.6 ng/g (range = 1.9–29.0 ng/g) in Al-Wajh (Table S1, Figures 3a,b and 4d). Therefore, the fractions of terrestrial n-alkanols were 22.4 ± 11.9% in Al-Qahma and 42.3 ± 23.5% in the Al-Wajh lagoon (Table S1). The relative amounts from algae, diatoms, and planktons were 60.7 ± 10.8% and 45.2 ± 8.8% in Al-Qahma and Al-Wajh, respectively. The microbial portions were 12.1 ± 5.3% in Al-Qahma and 11.2 ± 2.6% in Al-Wajh (Figure 5c). The ratios of terrestrial/aquatic n-alkanols in the lagoon sediments were 0.40 ± 0.28 in Al-Qahma and 0.97 ± 0.44 in Al-Wajh, suggesting that n-alkanols from aquatic (algae, diatoms, plankton, and microbes) sources were prevalent in both lagoons.

4.5. Polycyclic Aromatic Hydrocarbons (PAHs)

The total PAH concentrations in the lagoon sediment samples ranged from 0 to 545.4 ng/g (average = 45.5 ± 96.8 ng/g) in Al-Qahma and 0 to 38.0 ng/g in Al-Wajh (Table 1, Figures 3a,b and 4e). The main PAHs detected in these sediments were benzo[*k*]fluoranthene, and benzo[*b*]fluoranthene with minor amounts of phenanthrene (Phe) and anthracene (Ant) (Table S1, Figure 3f). The levels were in the concentration ranges determined in other places of the Gulf [83,84]. The lack of low molecular weight aromatic and alkyl aromatic hydrocarbons, such as alkylnaphthalenes and pheanthrene/ alkylphenanthrenes, is probably attributed to their elimination owing to high water solubility [85]. The elevated temperatures during summer in the region lead to substantial depletion of PAHs, particularly those with low molecular weights [86]. Additionally, the characteristics of sediment and the direction of water currents impact the concentration of PAHs in the gulf, with high levels being observed in semi-enclosed areas like bays and harbors [83,86].

The Ant/(Ant + Phe) ratio has been applied to distinguish between petrogenic and coal/fuel sources, where a low value (<0.1) of petrogenic inputs and a high value (>0.1) suggests coal and fuel sources [87]. Here the ratio values were >0.1 (0.75 ± 0.38 for Al-Qahma and 0.50 ± 0.15 for Al-Wajh), confirming that these PAHs were from coal and fuel combustion.

4.6. Plasticizers

Diethyl-, diisobutyl-, dibutyl-, and dioctyl-phthalates were the main plasticizers detected in the sediment samples of the two lagoons (Figure 2e). The total concentrations of these phthalates ranged from 34.9 ng/g to 822.7 ng/g (average = 185.3 ± 169.9 ng/g) in Al-Qahma and 18.9 to 312.4 ng/g (average = 67.4 ± 70.4 ng/g) in Al-Wajh (Table 1 and Figures 3a,b and 4f). Dibutyl phthalate (DBP) was the main plasticizer detected in these two lagoon sediments. The total concentrations of the phthalates in the sediments of the lagoons were much lower than the quantities measured in Campeche, Mexico (18,292–21,702 ng/g [88]); the Asalouyeh harbor coast of Iran (mean = 5180 ng/g [89]); the Arabian/Persian Gulf of the Saudi Arabia coast (31–2799 ng/g [46]); comparable to the values in Santos Bay, Brazil (0.0–182 ng/g [90]); and moderately higher than the concentrations in the coast of Qatar (7.8 ± 0.7 ng/g [71]).

Plastic waste and litter in marine environments have been identified as a serious environmental concern [91–95]. About 269,000 tons of plastic fragments have been projected floating on oceanic surface waters [96], which represent 60–95% of marine debris [97,98]. Plasticizers, mainly phthalates, make up the mass chemical composition of plastics and are very stable compounds in the environment [99]. They are harmful and detrimental substances to marine organisms [100,101].

4.7. Natural versus Anthropogenic Sources

Obviously, the contributions of natural biogenic versus anthropogenic sources of aliphatic and cyclic lipids vary between the two lagoons. The estimated relative concentrations in the percentage of the terrestrial plant inputs are 6.9 ± 6.4% in Al-Qahma and 9.7 ± 4.2% in the Al-Wajh lagoon, and the inputs of algae are 53.4 ± 18.5% in the former and 32.1 ± 13.8% in the latter. The microbial inputs are 10.0 ± 2.1% and 25.2 ± 4.7% in the Al-Qahma and Al-Wahj lagoons, respectively (Figure 5d). Therefore, the inputs of biogenic sources (including partial n-alkanes, n-alkanoic acids, and n-alkanols) are 70.6 ± 15.0% in Al-Qahma and 65.7 ± 12.2% in the Al-Wajh lagoon in the north (Figure 6). The estimated anthropogenic inputs of these lipids from petroleum-related sources (based on n-alkanes, hopanes, steranes, and PAHs) are 16.0 ± 12.3% in the Al-Qahma lagoon and 11.1 ± 3.2% in the Al-Wajh lagoon. These values are much lower than the proportions found in Obhur lagoon (43–62%) [51]. The plasticizer (mainly phthalates) inputs from littering are 13.4 ± 7.0% and 23.1 ± 10.8% in Al-Qahma and Al-Wajh, respectively. The results confirmed that natural inputs are the main sources of these aliphatic and cyclic compounds in these lagoons. Petroleum-related inputs were relatively higher in the Al-Qahma lagoon in the south, whereas the plasticizers were higher in the Al-Wajh lagoon in the north.

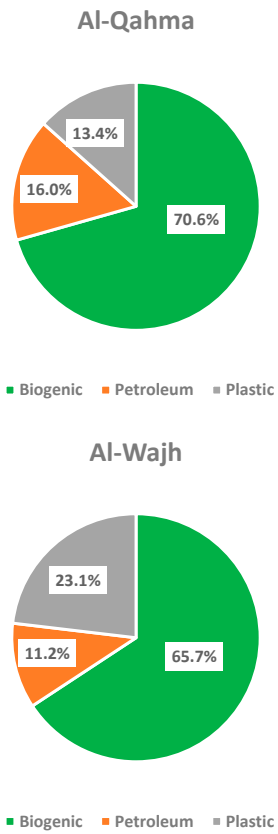

Figure 6. Plots showing the percentages of the natural, petroleum-related, and plastic sources in the sediments from the Al-Qahma and Al-Wajh lagoons, Red Sea coast of Saudi Arabia.

5. Conclusions

GC-MS techniques were employed to characterize the total solvent-extractable organic matter (TEOM) present in sediments obtained from both the Al-Qahma lagoon in the south and the Al-Wajh lagoon in the north of the Red Sea coast of Saudi Arabia. Analysis showed both biogenic and anthropogenic sources of the TEOM. The biogenic inputs of aliphatic and cyclic hydrocarbons in the two lagoons were considerably major (71% in Al-Qahma and 66% in Al-Wajh) relative to anthropogenic sources. The presence of n-alkanes with CPI ~1, hopanes and PAHs from petroleum production, and plasticizers (mainly phthalates) from litter and waste were moderate in these sediments. The anthropogenic sources of these lipids in the Al-Qahma lagoon sediments made up 16% and 11% in Al-Wajh was from petroleum-related products, whereas the plasticizer sources made up 13% in the Al-Qahma lagoon and 23% in the Al-Wajh lagoon.

The areas are bliss for nature enthusiasts, birdwatchers, and those interested in coastal biodiversity, offering a tranquil setting to appreciate the beauty of Saudi Arabia's coastal environment while recognizing its vital role in preserving marine life and avian populations. Future urbanization and development around these regions will introduce pollutants and have serious effects on the environmental conditions and health of these pristine ecosystems. Thus, the preservation and careful management of coastal lagoons are not only scientifically justified but essential for maintaining ecological balance, sustainable resource utilization, and resilience in the face of environmental challenges. Linking the preservation and careful management of coastal lagoons to the UN SDG Life Below Water involves recognizing their role in maintaining ecological balance, supporting sustainable resource utilization, and enhancing resilience in the face of environmental challenges. By doing so, we contribute to the global efforts aimed at achieving a sustainable and thriving future for marine ecosystems and communities.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w16010187/s1. Table S1. Concentrations (ng/g), chemical parameters and proportions of various chemical groups in surface sediments from Al-Qahma and Al-Wajh lagoons, Red Sea coast of Saudi Arabia.

Author Contributions: M.T.A.-O.: Methodology, investigation, data curation, writing—original draft, visualization. H.A.A.: Conceptualization, methodology, investigation, data curation, writing—original draft, visualization, project administration, funding acquisition. A.I.R.: Methodology, investigation, formal data analysis, writing—review and editing. N.R.: Methodology, investigation, data curation, writing—review and editing. A.B.: Methodology, investigation, writing—review and editing. K.F.A.-M.: Investigation, writing—review and editing. S.S.A.: Investigation, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the National Plan for Science, Technology, and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award Number NPST 13-ENV2233-02-R.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We thank the Saudi Geological Survey (SGS) for providing the samples.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Price, A.R. Characteristics and assessment of critical and other marine habitats in the ROPME sea area and the Red Sea. In Proceedings of the ROPME Workshops on Coastal Area Development; UNEP Regional Seas Report and Studies. Regional Organization for the Protection of the Marine Environment: Granada, Kuwait, 1998; pp. 57–71.
2. DeCarlo, T.M.; Carvalho, S.; Gajdzik, L.; Hardenstine, R.S.; Tanabe, L.K.; Villalobos, R.; Berumen, M.L. Patterns, drivers, and ecological implications of upwelling in coral reef habitats of the southern Red Sea. *J. Geophys. Res. Ocean.* **2021**, *126*, e2020JC016493. [CrossRef]
3. Bosworth, W. Geological evolution of the Red Sea: Historical background, review, and synthesis. In *The Red Sea: The Formation, Morphology, Oceanography and Environment of a Young Ocean Basin*; Springer: Berlin/Heidelberg, Germany, 2015; pp. 45–78.

4. Rasul, N.M.; Stewart, I.C.; Vine, P.; Nawab, Z.A. *Introduction to Oceanographic and Biological Aspects of the Red Sea*; Springer: Berlin/Heidelberg, Germany, 2019.
5. Almahasheer, H.; Serrano, O.; Duarte, C.M.; Arias-Ortiz, A.; Masque, P.; Irigoien, X. Low carbon sink capacity of Red Sea mangroves. *Sci. Rep.* **2017**, *7*, 9700. [CrossRef] [PubMed]
6. Almahasheer, H.; Aljowair, A.; Duarte, C.M.; Irigoien, X. Decadal stability of Red Sea mangroves. *Estuar. Coast. Shelf Sci.* **2016**, *169*, 164–172. [CrossRef]
7. Almahasheer, H.; Duarte, C.M.; Irigoien, X. Phenology and Growth dynamics of Avicennia marina in the Central Red Sea. *Sci. Rep.* **2016**, *6*, 37785. [CrossRef] [PubMed]
8. Bruckner, A.W.; Dempsey, A.C. The status, threats, and resilience of reef-building corals of the Saudi Arabian Red Sea. In *The Red Sea: The Formation, Morphology, Oceanography and Environment of a Young Ocean Basin*; Springer: Berlin/Heidelberg, Germany, 2015; pp. 471–486.
9. Riegl, B.M.; Bruckner, A.W.; Rowlands, G.P.; Purkis, S.J.; Renaud, P. Red Sea coral reef trajectories over 2 decades suggest increasing community homogenization and decline in coral size. *PLoS ONE* **2012**, *7*, 38396. [CrossRef]
10. Hamylton, S. Hyperspectral remote sensing of the geomorphic features and habitats of the Al Wajh Bank reef system, Saudi Arabia, Red Sea. In *Seafloor Geomorphology as Benthic Habitat*; Elsevier: Amsterdam, The Netherlands, 2012; pp. 357–363.
11. Atta, C.J.; Coker, D.J.; Sinclair-Taylor, T.H.; DiBattista, J.D.; Kattan, A.; Monroe, A.A.; Berumen, M.L. Conspicuous and cryptic reef fishes from a unique and economically important region in the northern Red Sea. *PLoS ONE* **2019**, *14*, 0223365. [CrossRef]
12. Thadi, S. Preferential Hydrodynamic, Geomorphological, and Vegetation Ecology Conditions for Turtle Nesting; Al Wajh Bank, Saudi Arabia. Master's Thesis, Delft University of Technology, Delft, The Netherlands, 2021.
13. Zhan, P.; Krokos, G.; Gittings, J.A.; Raitsos, D.E.; Guo, D.; Papagiannopoulos, N.; Hoteit, I. Physical forcing of phytoplankton dynamics in the Al-Wajh lagoon (Red Sea). *Limnol. Oceanogr. Lett.* **2022**, *7*, 373–384. [CrossRef]
14. Friedman, G.M. Geology and geochemistry of reefs, carbonate sediments, and waters, Gulf of Aqaba (Elat), Red Sea. *J. Sediment. Res.* **1968**, *38*, 895–919.
15. Tournois, J.; Darnaude, A.M.; Ferraton, F.; Aliaume, C.; Mercier, L.; McKenzie, D.J. Lagoon nurseries make a major contribution to adult populations of a highly prized coastal fish. *Limnol. Oceanogr.* **2017**, *62*, 1219–1233. [CrossRef]
16. Tamborski, J.; Beek, P.; Rodellas, V.; Monnin, C.; Bergsma, E.; Stieglitz, T.; Beck, A. Temporal variability of lagoon–sea water exchange and seawater circulation through a Mediterranean barrier beach. *Limnol. Oceanogr.* **2019**, *64*, 2059–2080. [CrossRef]
17. Mignucci, A.; Forget, F.; Villeneuve, R.; Derridj, O.; McKindsey, C.W.; McKenzie, D.J.; Bourjea, J. Residency, home range and inter-annual fidelity of three coastal fish species in a Mediterranean coastal lagoon. *Estuar. Coast. Shelf Sci.* **2023**, *292*, 108450. [CrossRef]
18. Green, A.J.; Jenkins, K.M.; Bell, D.; Morris, P.J.; Kingsford, R.T. The potential role of waterbirds in dispersing invertebrates and plants in arid Australia. *Freshw. Biol.* **2008**, *53*, 380–392. [CrossRef]
19. Tavares, D.C.; Guadagnin, D.L.; Moura, J.F.; Siciliano, S.; Merico, A. Environmental and anthropogenic factors structuring waterbird habitats of tropical coastal lagoons: Implications for management. *Biol. Conserv.* **2015**, *186*, 12–21. [CrossRef]
20. Samaraweera, M.; Chandrajith, R.; Jayasena, N. Birds of different feeding habits as biomonitors for trace elements in a wetland of the Central Asian Flyway, Sri Lanka. *Chemosphere* **2022**, *306*, 135602. [CrossRef] [PubMed]
21. Viaroli, P.; Bartoli, M.; Giordani, G.; Naldi, M.; Orfanidis, S.; Zaldivar, J.M. Community shifts, alternative stable states, biogeochemical controls and feedbacks in eutrophic coastal lagoons: A brief overview. *Aquat. Conserv. Mar. Freshw. Ecosyst.* **2008**, *18*, 105–117. [CrossRef]
22. Danovaro, R.; Pusceddu, A. Biodiversity and ecosystem functioning in coastal lagoons: Does microbial diversity play any role? *Estuar. Coast. Shelf Sci.* **2007**, *75*, 4–12. [CrossRef]
23. Duvat, V. Coastal protection structures in Tarawa atoll, Republic of Kiribati. *Sustain. Sci.* **2013**, *8*, 363–379. [CrossRef]
24. Tognin, D.; D'Alpaos, A.; Marani, M.; Carniello, L. Marsh resilience to sea-level rise reduced by storm-surge barriers in the Venice Lagoon. *Nat. Geosci.* **2021**, *14*, 906–911. [CrossRef]
25. Inácio, M.; Barboza, F.R.; Villoslada, M. The protection of coastal lagoons as a nature-based solution to mitigate coastal floods. *Curr. Opin. Environ. Sci. Health* **2023**, *34*, 100491. [CrossRef]
26. Rushdi, A. Lipid Tracers in Coastal Sediments of the Northwestern Arabian/Persian Gulf: Characteristics, Sources, Distribution, and Possible Ecological Impacts. In *The Arabian Seas: Biodiversity, Environmental Challenges and Conservation Measures*; Jawad, L.A., Ed.; Springer: Cham, Switzerland, 2021.
27. Cecinato, A.; Bacaloni, A.; Romagnoli, P.; Perilli, M.; Balducci, C. Molecular signatures of organic particulates as tracers of emission sources. *Environ. Sci. Pollut. Res.* **2022**, *29*, 65904–65923. [CrossRef]
28. Derrien, M.; Yang, L.; Hur, J. Lipid biomarkers and spectroscopic indices for identifying organic matter sources in aquatic environments: A review. *Water Res.* **2017**, *112*, 58–71. [CrossRef] [PubMed]
29. Burd, A.B.; Frey, S.; Cabre, A.; Ito, T.; Levine, N.M.; Lønborg, C.; Long, M.; Mauritz, M.; Thomas, R.Q.; Stephens, B.M. Terrestrial and marine perspectives on modeling organic matter degradation pathways. *Glob. Chang. Biol.* **2016**, *22*, 121–136. [CrossRef] [PubMed]
30. Stern, G.A.; Macdonald, C.R.; Carvalho, P.C.; Wolfe, T.; Ferraz, F. Baseline levels and characterization of hydrocarbons in surface marine sediments along the transportation corridor in Hudson Bay: A multivariate analysis of n-alkanes, PAHs and biomarkers. *Sci. Total Environ.* **2023**, *855*, 158718. [CrossRef] [PubMed]

31. Luo, G.; Yang, H.; Algeo, T.J.; Hallmann, C.; Xie, S. Lipid biomarkers for the reconstruction of deep-time environmental conditions. *Earth-Sci. Rev.* **2019**, *189*, 99–124. [CrossRef]
32. Liu, L.Y.; Wang, J.Z.; Wong, C.S.; Qiu, J.W.; Zeng, E.Y. Application of multiple geochemical markers to investigate organic pollution in a dynamic coastal zone. *Environ. Toxicol. Chem.* **2013**, *32*, 312–319. [CrossRef] [PubMed]
33. Fernandes, G.M.; Martins, D.A.; Dos Santos, R.P.; de Santiago, I.S.; Nascimento, L.S.; Oliveira, A.H.; Yamamoto, F.Y.; Cavalcante, R.M. Levels, source appointment, and ecological risk of petroleum hydrocarbons in tropical coastal ecosystems (northeast Brazil): Baseline for future monitoring programmes of an oil spill area. *Environ. Pollut.* **2022**, *296*, 118709. [CrossRef] [PubMed]
34. Turner, N.R.; Renegar, D.A. Petroleum hydrocarbon toxicity to corals: A review. *Mar. Pollut. Bull.* **2017**, *119*, 1–16. [CrossRef]
35. Jahan, S.; Strezov, V. Effect of shipping on the distribution of trace elements and petroleum hydrocarbons in the coastal basins of Australia: A review. *Mar. Freshw. Res.* **2019**, *71*, 794–809. [CrossRef]
36. Guo, W.; Wang, X.; Liu, S.; Kong, X.; Wang, P.; Xu, T. Long-term petroleum hydrocarbons pollution after a coastal oil spill. *J. Mar. Sci. Eng.* **2022**, *10*, 1380. [CrossRef]
37. El Nemr, A.; El-Sikaily, A.; Khaled, A.; Said, T.O.; Abd-Alla, A.M. Determination of hydrocarbons in mussels from the Egyptian Red Sea coast. *Environ. Monit. Assess.* **2004**, *96*, 251–261. [CrossRef]
38. AL-LIHAIBI, S. Petroleum hydrocarbons in sediments from Jeddah coast of Saudi Red Sea following the 1996 fuel oil spill. *Science* **2000**, *11*, 27–41. [CrossRef]
39. Shimy, T.M. Marine pollution as indicated by oil accumulated on clams collected from the western coasts of the Red Sea, Egypt. *Energy Sources* **1997**, *19*, 153–161. [CrossRef]
40. Huynh, B.Q.; Kwong, L.H.; Kiang, M.V.; Chin, E.T.; Mohareb, A.M.; Jumaan, A.O.; Basu, S.; Geldsetzer, P.; Karaki, F.M.; Rehkopf, D.H. Public health impacts of an imminent Red Sea oil spill. *Nat. Sustain.* **2021**, *4*, 1084–1091. [CrossRef] [PubMed]
41. Shetaia, Y.M.; Mohamed, T.M.; Farahat, L.A.; ElMekawy, A. Potential biodegradation of crude petroleum oil by newly isolated halotolerant microbial strains from polluted Red Sea area. *Mar. Pollut. Bull.* **2016**, *111*, 435–442. [CrossRef]
42. Alhudhodi, A.H.; Alduwais, A.K.; Aldhafeeri, Z.M.; Al-Shamsi, M.A.S.; Alharbi, B.H. Contamination assessment of mangrove ecosystems in the red sea coast by polycyclic aromatic hydrocarbons. *Int. J. Environ. Res. Public Health* **2022**, *19*, 5474. [CrossRef]
43. Tolosa, I.; Mesa, M.; Alonso-Hernandez, C. Steroid markers to assess sewage and other sources of organic contaminants in surface sediments of Cienfuegos Bay, Cuba. *Mar. Pollut. Bull.* **2014**, *86*, 84–90. [CrossRef]
44. Davenport, J.; Davenport, J.L. The impact of tourism and personal leisure transport on coastal environments: A review. *Estuar. Coast. Shelf Sci.* **2006**, *67*, 280–292. [CrossRef]
45. de Oliveira, A.H.B.; Fernandes, G.M.; Dos Santos, F.R.; de Almeida, N.M.; Nogueira, T.R.; de Quadros Melo, D.; Martins, L.L.; Cavalcante, R.M.; do Nascimento, R.F.; Reddy, C.M. Insights about levels and source appointment of petroleum hydrocarbons in Brazilian semi-arid coastal: Baseline status assessment for ocean decade targets. *Environ. Sci. Pollut. Res.* **2023**, *30*, 58002–58018. [CrossRef]
46. Rushdi, A.I.; El-Mubarak, A.H.; Simoneit, B.R.; Goni, M.A.; Qurban, M.A.; Bazeyad, A.Y.; Al-Mutlaq, K.F. Natural and anthropogenic sources of extractable organic matter in sediments from the coastal zone of the Arabian Gulf in Saudi Arabia. *Arab. J. Geosci.* **2022**, *15*, 1446. [CrossRef]
47. Rushdi, A.I.; Al-Mutlaq, K.F.; Simoneit, B.R.T.; Al-Azri, A.; DouAbul, A.A.Z.; Al-Zarban, S.; Al-Yamani, F. Characteristics of lipid tracers to the Arabian Gulf by run-off from rivers and atmospheric dust transport. *Arab. J. Geosci.* **2010**, *3*, 113–131. [CrossRef]
48. Chalastani, V.I.; Manetos, P.; Al-Suwailem, A.M.; Hale, J.A.; Vijayan, A.P.; Pagano, J.; Williamson, I.; Henshaw, S.D.; Albaseet, R.; Butt, F. Reconciling tourism development and conservation outcomes through marine spatial planning for a Saudi Giga-Project in the Red Sea (The Red Sea Project, Vision 2030). *Front. Mar. Sci.* **2020**, *7*, 168. [CrossRef]
49. Rushdi, A.I.; Rasul, N.M.; Bazeyad, A.; Dumenden, R. Distribution and sources of hydrocarbon compounds in sediments from Obhur Lagoon: Red Sea coast of Saudi Arabia. In *Oceanographic and Biological Aspects of the Red Sea*; Springer: Cham, Switzerland, 2019; pp. 133–146.
50. Rushdi, A.I.; El-Mubarak, A.H.; Simoneit, B.R.T.; Goni, M.A.; Qurban, M.A.; Bazeyad, A.Y.; Al-Otaibi, M.T.; Muhammed, Z.N. Levels, spatial distributions, and provision of petroleum hydrocarbons and phthalates in sediments from Obhur lagoon, Red Sea coast of Saudi Arabia. *Environ. Geochem.* **2023**. [CrossRef]
51. Rushdi, A.I.; Simoneit, B.R.T.; DouAbul, A.A.Z.; Al-Mutlaq, K.F.; El-Mubarak, A.H.; Qurban, M.; Goni, M.A. Occurrence, distribution and sources of polar lipid tracers in sediments from the Shatt al-Arab River, Iraq—Polar compounds. *Sci. Total Environ.* **2014**, *471*, 180–192. [CrossRef] [PubMed]
52. Rushdi, A.I.; DouAbul, A.A.; Simoneit, B.R.; El-Mubarak, A.H.; Al-Mutlaq, K.F.; Qurban, M.A.; Goni, M.A. Nonpolar lipid tracers in sediments from the Shatt al-Arab River of Iraq and the northwestern Arabian Gulf. *Arab. J. Geosci.* **2014**, *7*, 5495–5508. [CrossRef]
53. Saleh, A.M.S. Toward an Extraordinary Ecotourism Destination on the Shoreline of Aseer Region, Kingdom of Saudi Arabia. Doctoral Dissertation, Illinois Institute of Technology, Chicago, IL, USA, 2022.
54. Rushdi, A.I.; DouAboul, A.A.; Mohammed, S.S.; Simoneit, B.R.T. Distribution and sources of extractable organic matter in the Mesopotamian wetland marsh sediments of Iraq: I—Aliphatic lipids. *Environ. Geol.* **2006**, *50*, 857–866. [CrossRef]
55. Simoneit, B.R.T. Application of molecular marker analysis to vehicular exhaust for source reconciliation. *Int. J. Environ. Anal. Chem.* **1985**, *22*, 203–233. [CrossRef]

56. Bouloubassi, I.; Fillaux, J.; Saliot, A. Hydrocarbons in surface sediments from the Changjiang (Yangtze River) Estuary, East China Sea. *Mar. Pollut. Bull.* **2001**, *42*, 1335–1346. [CrossRef]
57. El Nemr, A.; El-Sadaawy, M.M.; Khaled, A.; El-Sikaily, A. Distribution patterns and risks posed of polycyclic aromatic hydrocarbons contaminated in the surface sediment of the Red Sea coast (Egypt). *Desalin. Water Treat.* **2014**, *52*, 7964–7982. [CrossRef]
58. Wang, X.C.; Sun, S.; Ma, H.Q.; Liu, Y. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Mar. Pollut. Bull.* **2006**, *52*, 129–138. [CrossRef]
59. Neves, P.A.; Costa, P.G.; Portz, L.C.; Garcia, M.R.; Fillmann, G. Levels and sources of hydrocarbons in the Patos Lagoon estuary and Cassino Beach mud bank (South Atlantic, Brazil): Evidence of transference between environments. *Environ. Monit. Assess.* **2023**, *195*, 484. [CrossRef]
60. Shirneshan, G.; Bakhtiari, A.R.; Memariani, M. Distribution and origins of n-alkanes, hopanes, and steranes in rivers and marine sediments from Southwest Caspian coast, Iran: Implications for identifying petroleum hydrocarbon inputs. *Environ. Sci. Pollut. Res.* **2016**, *23*, 17484–17495. [CrossRef]
61. Tsapakis, M.; Dakanali, E.; Stephanou, E.G.; Karakassis, I. PAHs and n-alkanes in Mediterranean coastal marine sediments: Aquaculture as a significant point source. *J. Environ. Monit.* **2010**, *12*, 958–963. [CrossRef] [PubMed]
62. Bray, E.E.; Evans, E.D. Distribution of n-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* **1961**, *22*, 2–15. [CrossRef]
63. Mazurek, M.A.; Simoneit, B.R.T. Characterization of biogenic and petroleum derived organic matter in aerosols over remote, rural and urban areas. In *Identification and Analysis of Organic Pollutants in Air*; Kieth, L.H., Ed.; American Chemical Soc Symp. Ann Arbor Science/Butterworth Publishers: Woburn, MA, USA, 1984; pp. 353–370.
64. Simoneit, B.R.T. The organic chemistry of marine sediments. In *Chemical Oceanography*, 2nd ed.; Riley, J.P., Chester, R., Eds.; Academic Press: New York, NY, USA, 1978; pp. 233–311.
65. Zhang, Z.; Zhao, M.; Eglinton, G.; Lu, H.; Huang, C.-Y. Leaf wax lipids as paleovegetational and paleoenvironmental proxies for the Chinese Loess Plateau over the last 170 kyr. *Quat. Sci. Rev.* **2006**, *25*, 575–594. [CrossRef]
66. Ficken, K.J.; Li, B.; Swain, D.E.; Eglinton, G. An n-alkanes proxy for the sedimentary input of submerged/floating fresh water aquatic macrophytes. *Org. Geochem.* **2000**, *31*, 745–749. [CrossRef]
67. Diefendorf, A.F.; KH, F.; Wing, S.L. A comparison of terpenoid and leaf fossil vegetation proxies in Paleocene and Eocene Bighorn Basin sediments. *Org. Geochem.* **2014**, *71*, 30–42. [CrossRef]
68. Simoneit, B.R.T. Organic matter of troposphere—V: Application of molecular analysis to biogenic emissions into troposphere for source reconciliations. *J. Atmos. Chem.* **1989**, *8*, 251–275. [CrossRef]
69. Bourbonniere, R.A.; Meyers, P.A. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnol. Oceanogr.* **1996**, *41*, 352–359. [CrossRef]
70. Garcia, M.R.; Cattani, A.P.; Cunha Lana, P.; Figueira, R.C.L.; Martins, C.C. Petroleum biomarkers as tracers of low-level chronic oil contamination of coastal environments: A systematic approach in a subtropical mangrove. *Environ. Pollut.* **2019**, *249*, 1060–1070. [CrossRef]
71. Rushdi, A.I.; Al-Shaikh, I.; El-Mubarak, A.H.; Alnaimi, H.A.; Al-Shamary, N.; Hassan, H.M.; Assali, M.A. Characteristics and sources of anthropogenic and biogenic hydrocarbons in sediments from the coast of Qatar. *Mar. Pollut. Bull.* **2017**, *124*, 56–66. [CrossRef]
72. Boonyatumanond, R.; Wattayakorn, G.; Togo, A.; Takada, H. Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Mar. Pollut. Bull.* **2006**, *52*, 942–956. [CrossRef] [PubMed]
73. Jafarabadi, A.R.; Dashtbozorg, M.; Bakhtiari, A.R.; Maisano, M.; Cappello, T. Geochemical imprints of occurrence, vertical distribution and sources of aliphatic hydrocarbons, aliphatic ketones, hopanes and steranes in sediment cores from ten Iranian Coral Islands, Persian Gulf. *Mar. Pollut. Bull.* **2019**, *144*, 287–298. [CrossRef] [PubMed]
74. Keshavarzifard, M.; Zakaria, M.P.; Sharifinia, M.; Grathwohl, P.; Keshavarzifard, S.; Sharifi, R.; Mehr, M.R. Determination of hydrocarbon sources in major rivers and estuaries of peninsular Malaysia using aliphatic hydrocarbons and hopanes as biomarkers. *Environ. Forensics* **2022**, *23*, 255–268. [CrossRef]
75. Peters, K.E.; Moldowan, J.M. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*; Prentice-Hall: Englewood Cliffs, NJ, USA, 1993.
76. Rushdi, A.I.; Simoneit, B.R.T. Hydrothermal alteration of organic matter in sediments of the northeastern Pacific Ocean: Part 1. Middle Valley, Juan de Fuca Ridge. *Appl. Geochem.* **2002**, *17*, 1401–1428. [CrossRef]
77. Rushdi, A.I.; Simoneit, B.R.T. Hydrothermal alteration of organic matter in sediments of the Northeastern Pacific Ocean: Part 2. *Escanaba Trough, Gorda Ridge Appl. Geochem.* **2002**, *17*, 1467–1494. [CrossRef]
78. Budge, S.M.; Parish, C.C. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. *Org. Geochem.* **1998**, *29*, 1547–1559. [CrossRef]
79. Khotimchenko, S.V.; Vaskovsky, V.E.; Titlyanova, T.V. Fatty acids of marine algae from the Pacific coast of North California. *Bot. Mar.* **2002**, *45*, 17–22. [CrossRef]
80. Oyo-Ita, O.E.; Oyo-Ita, I.O. Fatty acid and alcohol distributions and sources in surface sediments of Imo River, southeast Niger Delta, Nigeria. *Environ. Nat. Resour. Res.* **2012**, *2*, 101–113. [CrossRef]

81. Treignier, C.; Derenne, S.; Saliot, A. Terrestrial and marine n-alcohol inputs and degradation processes relating to a sudden turbidity current in the Zaire canyon. *Org. Geochem.* **2006**, *37*, 1170–1184. [CrossRef]
82. Mudge, S.M.; Belanger, S.E.; DeLeo, P.C. *Fatty Alcohols: Anthropogenic and Natural Occurrence in the Environment*; Royal Society of Chemistry: London, UK, 2018.
83. Gevao, B.; Boyle, E.A.; Carrasco, G.G.; Ghadban, A.N.; Zafar, J.; Bahloul, M. Spatial and temporal distributions of polycyclic aromatic hydrocarbons in the Northern Arabian Gulf sediments. *Mar. Pollut. Bull.* **2016**, *112*, 218–224. [CrossRef]
84. Soliman, Y.S.; Al Ansari, E.M.S.; Wade, T.L. Concentration, composition and sources of PAHs in the coastal sediments of the exclusive economic zone (EEZ) of Qatar, Arabian Gulf. *Mar. Pollut. Bull.* **2014**, *85*, 542–548. [CrossRef] [PubMed]
85. Kawka, O.E.; Simoneit, B.R. Polycyclic aromatic hydrocarbons in hydrothermal petroleums from the Guaymas Basin spreading center. *Appl. Geochem.* **1990**, *5*, 17–27. [CrossRef]
86. Soliman, Y.S.; Alansari, E.M.; Sericano, J.L.; Wade, T.L. Spatio-temporal distribution and sources identifications of polycyclic aromatic hydrocarbons and their alkyl homolog in surface sediments in the central Arabian Gulf. *Sci. Total Environ.* **2019**, *658*, 787–797. [CrossRef] [PubMed]
87. Yunker, M.B.; Macdonald, R.W.; Vingarzan, R.; Mitchell, R.H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **2002**, *33*, 489–515. [CrossRef]
88. Ramirez, M.M.B.; Caamal, R.D.; Osten, J.R. Occurrence and seasonal distribution of microplastics and phthalates in sediments from the urban channel of the Ria and coast of Campeche, Mexico. *Sci. Total Environ.* **2019**, *672*, 97–105. [CrossRef] [PubMed]
89. Arfaeinia, H.; Fazlzadeh, M.; Taghizadeh, F.; Saeedi, R.; Spitz, J.; Dobaradaran, S. Phthalate acid esters (PAEs) accumulation in coastal sediments from regions with different land use configuration along the Persian Gulf. *Ecotoxicol. Environ. Saf.* **2019**, *169*, 496–506. [CrossRef] [PubMed]
90. Cesar, A.; Lia, L.R.B.; Pereira, C.D.S.; Santos, A.R.; Cortez, F.S.; Choueri, R.B.; Rachid, B.R.F. Environmental assessment of dredged sediment in the major Latin American seaport (Santos, São Paulo—Brazil): An integrated approach. *Sci. Total Environ.* **2014**, *497*, 679–687. [CrossRef]
91. Sivadas, S.K.; Mishra, P.; Kaviarasan, T.; Sambandam, M.; Dhineka, K.; Murthy, M.R.; Hoehn, D. Litter and plastic monitoring in the Indian marine environment: A review of current research, policies, waste management, and a roadmap for multidisciplinary action. *Mar. Pollut. Bull.* **2022**, *176*, 113424. [CrossRef]
92. Isobe, A.; Iwasaki, S. The fate of missing ocean plastics: Are they just a marine environmental problem? *Sci. Total Environ.* **2022**, *825*, 153935. [CrossRef]
93. Jang, M.; Shim, W.J.; Han, G.M.; Cho, Y.; Hong, S.H. Plastic debris as a mobile source of additive chemicals in marine environments: In-situ evidence. *Sci. Total Environ.* **2023**, *856*, 158893. [CrossRef]
94. Fan, S.; Yan, Z.; Qiao, L.; Gui, F.; Li, T.; Yang, Q.; Ren, C. Biological effects on the migration and transformation of microplastics in the marine environment. *Mar. Environ. Res.* **2023**, *185*, 105875. [CrossRef] [PubMed]
95. Peng, L.; Fu, D.; Qi, H.; Lan, C.Q.; Yu, H.; Ge, C. Micro-and nano-plastics in marine environment: Source, distribution and threats—A review. *Sci. Total Environ.* **2020**, *698*, 134254. [CrossRef] [PubMed]
96. Xanthos, D.; Walker, T.R. International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): A review. *Mar. Pollut. Bull.* **2017**, *118*, 17–26. [CrossRef] [PubMed]
97. Walker, T.R.; Reid, K.; Arnould, J.P.Y.; Croxall, J.P. Marine debris surveys at Bird Island, South Georgia 1990–1995. *Mar. Pollut. Bull.* **1997**, *34*, 61–65. [CrossRef]
98. Surhoff, T.J.; Scholz-Bottcher, B.M. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics—A lab experiment. *Mar. Pollut. Bull.* **2016**, *102*, 84–94. [CrossRef]
99. Dong, C.D.; Huang, C.P.; Nguyen, T.B.; Hsiung, C.F.; Wu, C.H.; Lin, Y.L.; Hung, C.M. The degradation of phthalate esters in marine sediments by persulfate over iron–cerium oxide catalyst. *Sci. Total Environ.* **2019**, *696*, 133973. [CrossRef]
100. Tranganida, A.; Hall, A.J.; Armstrong, H.C.; Moss, S.E.; Bennett, K.A. Consequences of in vitro benzyl butyl phthalate exposure for blubber gene expression and insulin-induced Akt activation in juvenile grey seals. *Environ. Pollut.* **2023**, *316*, 120688. [CrossRef]
101. Squillante, J.; Scivicco, M.; Ariano, A.; Nolasco, A.; Esposito, F.; Cacciola, N.A.; Cirillo, T. Occurrence of phthalate esters and preliminary data on microplastics in fish from the Tyrrhenian sea (Italy) and impact on human health. *Environ. Pollut.* **2023**, *316*, 120664. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.