

Distribution and Sources of Aliphatic Hydrocarbons in Surface Sediments of Al-Arbaeen Lagoon, Jeddah, Saudi Arabia

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Abstract

Al-Arbaeen lagoon, in the central part of Jeddah city, well-known for tourists and fisheries, receive high inputs of organic matter mostly anthropogenic. Samples of surficial bottom sediments were collected from eighteen stations along the Al-Arbaeen lagoon and have been analyzed and characterized in terms of their contents of biogenic and anthropogenic hydrocarbon biomarkers. The analysis of aliphatic hydrocarbons in surficial sediments, based on GC/MS and biomarkers (triterpane and sterane) fingerprinting, showed that these hydrocarbons were mainly derived from petroleum sources. The coastal sediments analyses of all sites of the study area indicate that levels of petroleum hydrocarbons (60.13-2510.35 µg/g dry wt total hydrocarbons) are generally far higher than those from sediments adjacent to effluent discharge sites of a sewage treatment plant in Chesapeake Bay, USA. The continuous deposition of hydrocarbons in Al-Arbaeen lagoon might be connected with different pollutant sources (petrogenic and/or biogenic) via the effluent discharge point and/or the highly urbanized areas located very close to the lagoon.

Keywords: Sediments, Hydrocarbons, Aliphatic Hydrocarbons, Pollution, Al-Arbaeen Lagoon, Jeddah, Saudi Arabia.

Introduction

Throughout the world, the discharge of untreated sewage to coastal and estuarine waters has been a common practice, usually containing large volumes of solids from human wastes, street runoff, eroded soils, and industrial wastes [1]. As a rule, untreated sewage carries a wide variety of pollutants to the coastal zone, and it is accepted that it is one of the major sources of pollutants. Regulations on ocean disposal of wastes by coastal nations and international agencies have reduced the volume of wastes by the application of sewage treatment plants (STPs). Historically, these systems have been focused on the reduction of conventional pollutants, such as total suspended solids (TSS) or sludge, biological oxygen demand (BOD), fecal coliform bacteria, pH, oil and grease. However, many potentially toxic substances are not removed from sewage effluent, including heavy metals, synthetic organic chemicals, and chlorine [2].

Jeddah is one of the biggest cities on the coast of the Red Sea, and it is the economic capital of Saudi Arabia. It lies at the central part of the eastern coast of the Red Sea and extends about 100 km. The population of the city is more than three million [3]. Since the seventies the city has seen a vast human and economic expansion. Industrialization is being grown rapidly and is mainly largest represented by refineries, petrochemicals and food processing. As a trade center, the city is connected to the other parts of the world through a highly developed maritime transport network and its Islamic Port is one of the greatest ports on the Red Sea.

Sewage dumping into the coastal water is one of the major causes of marine environmental pollution. Jeddah has a vast network to collect urban wastes. The collected sewage is treated in several Sewage Treatment Stations (STS), however, due to the rapid expansion of the city and its increasing of population the treatment capacity of the STS is largely insufficient and great part of the raw sewage is being dumped in the coastal area. Numerous hazardous heavy metals were detected in the sediments and waters in areas receiving sewage effluents near Jeddah. El Sayed and Niaz [4] detected high concentrations of Cu and Zn in the sediments of the southern coast of Jeddah where sewage is massively discharged. Basaham [5] showed the enrichment of the sediments with Zn, Pb, Ni, Co, Cr and Cu and attributed it to sewage dumping in the Al-Arbaeen lagoon. Recently, the investigations showed that the sediments of Al-Shabab lagoon contained high concentrations of heavy

metals (e.g. Cd, Pb, Cu, Zn) and hydrocarbons, which were attributed to sewage discharge in the lagoon [6,7].

The lacking of STPs treatment capacity is allowing the untreated or partially treated sewage discharging in the Southern Corniche area [4,8-10], Al-Arbaeen Lagoon [5,11] and in Al-Shabab Lagoon [6,7].

Estuaries and lagoons areas serve as final receptors of natural and anthropogenic organic matter derived from land and carried by river and atmosphere [12,13]. Hydrocarbons are important component of land derived organic inputs towards coastal areas. Studies on hydrocarbons in the aquatic environment can be based on the analysis of the water column, organisms and sediments. However, sedimentary hydrocarbons have received special attention as these compounds are readily adsorbed onto particulate matter, and bottom sediments ultimately act as reservoir of hydrophobic contaminants [14,15]. A large fraction of these compounds derives from terrestrial and marine biological sources like vascular plants, animals, bacteria, macro- and microalgae [16]. Certain hydrocarbons are produced from bacterial and chemical degradation of naturally occurring lipids. Moreover, petroleum related sources also contribute to significant and major hydrocarbon inputs. As the major constituents of petroleum [17,18], hydrocarbons may enter the marine environment through riverine discharges, shipping activities, sewage disposal, offshore oil production and transport, oil spills as well as from pyrolysis/combustion of fossil fuel such as vehicles power plants, industrial processes and refuse burning [19-22]. Hydrocarbons are commonly found in the environment as complex mixtures deriving from multiple sources. Therefore, the confident discrimination between biogenic and anthropogenic origin, as well as the further recognition of inputs from petrogenic, pyrogenic and domestic waste sources, require the

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Received January 22, 2016; Accepted March 08, 2016; Published March 22, 2016

Citation: Turki AJ (2016) Distribution and Sources of Aliphatic Hydrocarbons in Surface Sediments of Al-Arbaeen Lagoon, Jeddah, Saudi Arabia. J Fisheries Livest Prod 4: 173. doi: 10.4172/2332-2608.1000173

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use of geochemical or molecular markers. Geochemical or molecular markers are compounds that maintain the “signature” of their origins and structural modifications which occurred during transport. Thus, the use of these compounds is also needed as various hydrocarbon classes show differences in their residence time, stability, transport mechanisms and fate, depending on their physical-chemical properties and sources [13,23,24].

To the author’s knowledge, the majority of the studies to date in Al-Arbaeen lagoon focused on water quality and inorganic components, which is the first study on hydrocarbons in this important part of Jeddah [5,11,25,26]. Thus, this study was conducted with concerning the analysis of sediments from various sites in the Al-Arbaeen lagoon, paying special attention to the source and distribution of aliphatic hydrocarbons.

Material and Methods

The study area

A complete description of the study area is given by Basaham [5] and El Rayis and Moammar [25]. Briefly, Al-Arbaeen lagoon is composed of a semi-enclosed lagoon, Al-Arbaeen lagoon (Figure 1). Al-Arbaeen lagoon is located in the central part of Jeddah, Saudi Arabia. It is a shallow (average depth about 4 m), tropical, anoxic, semi-enclosed basin, surrounded by residential areas and is connected to the Red Sea through a mouth at its northwestern end [5]. The lagoon is formed from two parts, a land ward proper lagoon and a seaward connected channel. These two parts form V-shape and there is a blind

end open drain at its south tip. At the blind end there is an outfall for wastewater effluent discharges from nearby sewage treatment plant at site C (STPc). Its discharge rate is 68.000 m³/d. Another drain is also there but open to the northern board side of the Al-Arbaeen proper lagoon, it receives wastewater from a bypass of a sewage pumping station (SPS). The discharge from this source occurs only during the storm events.

It worth to mention that both the connected channels of the lagoon were recently formed after the extension of the land area of Jeddah City more westwards on the account of the sea, in 1985 [25].

Recently, a construction has been accomplished for the extension of the Islamic Port which has created a new barrier for water circulation. An external lagoon is being created; its water is composed of a mixture of seawater and wastewater discharged into Al-Shabab and Al-Arbaeen lagoons. The water appears turbid and unpleasant odor. Most of the islets that represented a transient land for some migratory and resident birds have disappeared under the new platforms.

According to El Rayis and Moammar [25], the permanent water exchange with the open water is taking place in the top two-meter surface layer, which is the depth of the sills. The subsurface water is accidentally exchanged during rough weather. This situation leads to the accumulation of organic matter and the creation of anoxic conditions in the bottom layer [25]. The installation of anoxic conditions was certainly accelerated by the daily dumping of about forty thousand cubic meters of treated and raw sewage into the lagoon for several years. Since 1996, dumping has been officially being stopped and the sewage effluent has been directed and evacuated to the south of the city. However, a recent study demonstrated that sewage discharge is continuing and condition of the lagoon is continuously deteriorating [26].

Sampling and sample preparation

The sediments samples were collected from the locations (Figure 1) using a grab sampler. Surficial samples were picked from the middle of the grab with a Teflon spoon and transferred to glass containers. All glassware had been previously cleaned with detergents, distilled water, acetone and dichloromethane. All reagents, were HPLC grade. The samples were frozen on board, placed inside an ice chest, transported to the laboratory and kept frozen until processed. For grain size analysis, samples were air dried, homogenized and then kept at -20°C. The portions taken for the analysis of carbonate, total organic carbon contents and hydrocarbons were ground with a pestle and mortar.

Analytical procedures

Carbonate content was determined by treating the dry powdered samples with 5% hydrochloric acid (HCl 37%, BDH). The weight of acid soluble material (CaCO₃) was expressed as a percentage of the total weight of the sample. Organic carbon was determined in the sediments by wet dichromate-sulphuric acid oxidation method modified from the method described by Le Core [27]. Sediment grain size fractions were classified as fine (mud; < 0.063 mm), sand (0.063 – 2 mm) and gravel (> 2 mm), they were carried out using the standard dry sieving technique [28].

Extraction and fractionation of hydrocarbons

A known weight of dried sediments was extracted in a soxhlet apparatus using dichloromethane (DCM) and methanol (93:7 v/v) for 48 h. Before extraction commenced, an internal standard (1-icosene) was added to the sediment for the quantitation of saturated hydrocarbons. The resulting extract, of each sediment sample, was concentrated

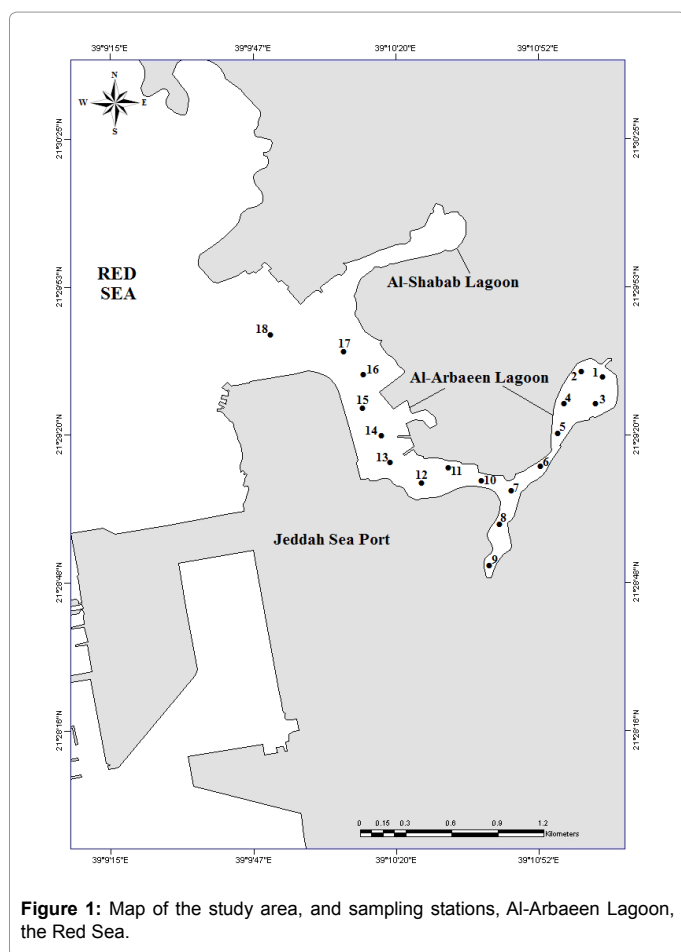


Figure 1: Map of the study area, and sampling stations, Al-Arbaeen Lagoon, the Red Sea.

down to a few milliliters (ca. 2 ml of solvent remaining) using rotary evaporator. This reduced extract was quantitatively transferred with DCM washings to a volumetric flask (25 ml). Extractable organic matter (EOM) was determined by evaporating a small measure volume of the final extract (ca. 5 ml). Clean up and isolation of hydrocarbon fractions was carried out by column chromatography method described by Aceves et al. [29]. A column filled with 8 g of each 5% water deactivated alumina (70-230 mesh, Merck) (bottom) and silica (70-230 mesh, Merck) (top) was used. The following fractions were collected: 1) 20 ml of *n*-hexane (alkane and alkenes), 2) 20 ml of 10% methylene chloride in *n*-hexane (monocyclic aromatic hydrocarbons), and 3) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons). The F_1 was concentrated again on a rotary evaporator, transferred to a vial, and then the volume was adjusted to 1 ml exactly using a stream of filtered nitrogen gas. An aliquot of 1 μ l of each extract was subjected to GC-MS analysis.

Instrumental analysis

The total concentration of petroleum hydrocarbons was measured in extracts using a ultraviolet fluorescence technique (UVF, Shimadzu RF-5000 model spectrofluorometer). Excitation was fixed at 310 nm and the emission intensity was quantified at 360 nm. Light Arabian crude oil was used as the standard for results expression.

The aliphatic fractions were subsequently analyzed by Gas chromatography-mass spectrometry (GC/MS), using a Shimadzu QP2010 (with software of LabSolutions series) with split/splitless injection. The end of the GC column was introduced into the electron impact (EI) source of a Shimadzu QP2010 quadruple mass selective detector. The acquisition was controlled by a Shimadzu QP2010 Computer in full Scan Mode for identification purpose and in total ionization chromatography (TIC) for greater sensitivity. The gas chromatograph was fitted with an Rtx⁻¹ fused silica capillary column (30 m x 0.25 mm i.e.; 0.25 μ m film thickness, Crossbond[®] 100% dimethyl polysiloxane) and the injection solvent was dichloromethane. The temperature in the GC oven was programmed from 50-300°C at 4°C/min and the final temperature held for 20 minutes; the injection port temperature was 250°C. Helium was employed as the carrier gas (flow rate 1.22 ml/min; pressure 69.8 Kpa). MS operation conditions were: EI ionization, ion source 250°C, electron energy 70 eV, interface temperature 250°C with a scan range of *m/z* 40 to 550 and a scan time of 1 scan/s. Compounds were identified by comparing relative retention times and mass fragmentogram response with standards and literature data.

Quality control/quality assurance

All data were subject to quality and control procedures. Procedural blanks were carried between each batch of four samples, and no contamination was found. Calibration standards were run at the beginning of each working day before each sample batch to establish the calibration curves for aliphatic mixture. All samples were spiked with internal standard. Instrument detection limit (IDL) were calculated according to USEPA [30], through seven-point calibration curve and extrapolated for determining the y axis intercepts which was found to be 0.016 μ g/g. The method detection limit (MDL) was determined as the concentration of individual aliphatic standard in a sample giving a peak with a signal-to-noise (S/N) and ranged from 0.01-0.05 μ g/g. The recoveries ranged between 86% and 123% with relative standard deviation (RSD%) < 20%.

Results and Discussion

Geochemical studies

a) **Grain size distribution:** Results of grain size analysis of

sediments and their textural classification are presented in Table 1. The surface sediments are composed predominantly of gravelly sand and sandy mud. The size distributions are relatively varied with variation of locations at all sites of Al-Arbaeen lagoon (Table 1 and Figure 2). Mud content was higher followed by sand and gravel. It was clearly found that the mud content were variable in the lagoon (Figure 2).

Grain size plays an important role in controlling organic pollutants concentrations in sediments. The variability in texture composition of sediments profile along the study zone seems to be attributed to the kind of sediment transport processes, reworking and marine wave mechanism originated by wind actions reduce the size of sediments toward the sea. The distribution of the various type of sediments on the variations of their textural and granulometrical characteristics are controlled to great extent by the hydrodynamic factors of currents and waves, nature of coastal sediments input and the ecological conditions of the shelf [31,32].

Sample No.	Gravel (%)	Sand (%)	Mud (%)	CaCO ₃ (%)	Organic Carbon (%)
1	4	37	59	1	4.6
2	1	48	51	17	5.3
3	18	28	54	6	5.2
4	32	15	53	6	4.3
5	30	29	41	10	5.1
6	16	4	80	5	6.0
7	39	12	49	6	5.5
8	7	32	61	8	6.0
9	12	35	53	8	6.2
10	15	28	57	6	3.2
11	17	13	70	8	4.8
12	21	44	35	20	3.6
13	2	19	79	56	3.3
14	25	37	38	42	5.8
15	26	70	4	22	2.8
16	21	8	71	32	2.3
17	3	6	91	22	2.1
18	29	58	25	60	2.5

Table 1: Major sediment characteristics.

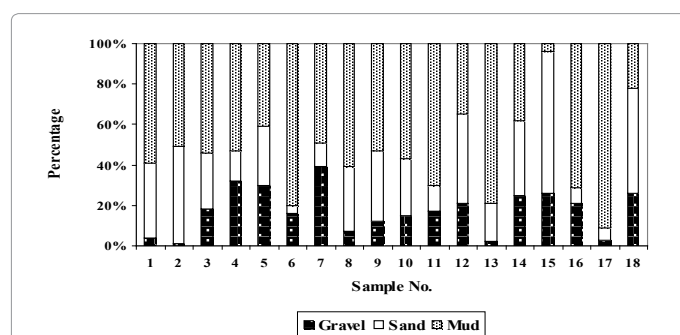


Figure 2: Grain size distributions in sediments at Al-Arbaeen lagoon, Jeddah.

b) **Total organic carbon (TOC) and carbonate contents:** In Table 1, the results of the TOC and carbonate carbon analyses of the surface sediments from Al-Arbaeen lagoon are shown. The 1st highest TOC value was 6.2% at site 9 and the 2nd highest value was 6% at both sites of 6 and 8 (Table 1). Low values of TOC were found at sites near the entrance of the lagoon. The carbonate content was found to be varied from sites to site. The higher content of carbonate carbon was found at the entrance site of the lagoon (sites 13-18) compared to other sites (Table 1).

		Gravel	Sand	Mud	TOC	CaCO ₃	TPHs	EOM
Gravel	Pearson Correlation	1						
Sand	Pearson Correlation	0.06	1					
Mud	Pearson Correlation	-0.166	-0.85**	1				
TOC	Pearson Correlation	0.1	-0.1	0.04	1			
CaCO ₃	Pearson Correlation	0.01	0.27	-0.16	-0.50*	1		
TPHs	Pearson Correlation	-0.02	-0.06	0.03	0.56*	-0.21	1	
EOM	Pearson Correlation	0.01	-0.15	0.07	0.67**	-0.19	0.71**	1

**Correlation is significant at the 0.01 level (2-tailed).

*Correlation is significant at the 0.05 level (2-tailed).

Table 2: Pearson correlation coefficients for the %gravel, %sand, %mud, %TOC and %CaCO₃ in sediments from Al-Arbaeen Lagoon, Significance (2-tailed) in parentheses.

Sample No.	THCs Concentration (ug/g)	EOM (mg/g)
1	60.13	1.86
2	320.25	32.10
3	419.69	36.23
4	392.52	29.61
5	739.93	37.23
6	802.12	39.87
7	1226.95	32.09
8	1801.82	40.98
9	2510.35	51.53
10	690.62	30.29
11	513.55	25.69
12	422.60	32.15
13	712.79	39.60
14	920.16	37.83
15	615.86	19.71
16	466.67	16.53
17	380.79	12.19
18	197.21	8.35

Table 3: Total hydrocarbons (THCs; ug/g) and Extractable Organic Matter (EOM; mg/g) in surface sediment samples from Al-Arbaeen lagoon.

The organic carbon content, in sediments of Al-Arbaeen lagoon, is higher as expected and ranges between 2.1 (station 17) and 6.2 % (station 9). These values are higher than those measured in the uncontaminated Red Sea sediments, which ranged between 0.3-0.5% [33,34], and the sediments of the Southern Corniche [4] and Al-Shabab lagoon [6] which ranged between 3-4%. However, Al-Arbaeen lagoon receives much greater quantities of wastewater and its water is less frequently flushed to the sea due to its confined morphology. Organic content decreases in sites near the entrance of the lagoon where the influence of sewage discharge decreases with distance.

In undisturbed coastal environments, carbonate, mud and organic carbon are usually intercorrelated; organic carbon is generally positively correlated with the mud fraction and negatively correlated with carbonate while carbonate co-varies with the coarse fraction. In the study area, sewage dumping and land filling have created particular conditions that have ruptured the natural equilibrium and disturbed the traditional relationships. Neither of these natural associations was clearly identified in Al-Arbaeen sediments; only organic carbon correlates negatively and significantly with carbonate (Table 2).

Hydrocarbons: Hydrocarbons found in recent aquatic sediments reflect natural and anthropogenic inputs from the water column by transport and sedimentation as well as the diagenetic processes taking place within the sediment [35]. In this study the EOM and TPH in sediments collected from various parts of Al-Arbaeen lagoon are presented in Table 3.

a) Extractable organic matter: It is noteworthy that the highest concentration of extractable organic matter (EOM) was observed at stations 9 and 8 which are close to the southern board side of the Al-Arbaeen proper lagoon. Thus, the average concentration of EOM in sediments from Al-Arbaeen lagoon is 29.10 mg/g dry weight. The recorded values of EMO of the present study are much higher in the Red Sea sediments than that of the Arabian Gulf [36,37] and the Red Sea [38]. The present results are more similar with the finding of Turki et al. [6] who studied at Al-Shabab lagoon.

b) Total petroleum hydrocarbons: The total petroleum hydrocarbons, as the sum of total aliphatic and total aromatic hydrocarbons, were measured by UV fluorescence. In terms of total petroleum hydrocarbons (TPH), as Light Arabian crude oil, concentrations in the surface sediment samples from Al-Arbaeen lagoon are shown in Table 3. The concentrations of total petroleum hydrocarbons varied greatly. The highest concentrations of TPHs were 2510.35, 1801.82, 1226.95 and 920.16 µg/g at the stations of 9, 8, 16 and 14, respectively, whereas the lowest concentration was 60.13 µg/g at site 1.

In "unpolluted" intertidal and estuarine sediments concentration generally range from sub-ug/g to approximately 10 µg/g [15,39], although may be two or three times higher where significant inputs of *n*-alkanes derived from plant waxes. Organic-rich marine sediments may contain up to 2900 µg/g which have been reported in surface sediments from New York Bight [40]. A more detailed analysis of the hydrocarbon constituents is generally required to assess the magnitude of anthropogenic contamination when concentrations of hydrocarbons are < 50 µg/g [41].

Concentrations of total hydrocarbons in the sediment samples from Al-Arbaeen lagoon are quite different. The highest concentration was found in samples collected from the southern board side of the Al-Arbaeen proper lagoon (Table 3). This could be a result of continuous deposition of hydrocarbons derived from different pollutant sources (petrogenic and/or biogenic) via the effluent discharge point and/or the highly urbanized areas located very close to the lagoon. The lowest concentration was found near the effluent discharge point (station 1), at the northern board side of the Al-Arbaeen proper lagoon, even though this area is subject to wastewater discharge. This partly explained by a lower EOM content when compared to other more contaminated stations. These values can be compared, for instance, with the hydrocarbon levels in several British and Spanish estuaries: 10-100 µg/g [42] and 1-250 µg/g [43] respectively, or those from sediments adjacent to effluent discharge sites of a sewage treatment plant in Chesapeake Bay, USA (2-150 µg/g) [44]. The levels of sedimentary hydrocarbons in Al-Arbaeen lagoon are far higher than those of these samples, which also correspond to petroleum polluted area. However, due to substantial differences in sampling and analytical methods, as well as differences in sediment types (such as grain size, %CaCO₃ and total organic matter), comparison with previously reported data provide indicative trends only.

Although gravimetry does not differentiate between biogenic and anthropogenic sources of hydrocarbons, its values usually reflect the degree of pollution within a certain area [45]. In the present study, the surface sediments displayed considerable variation between individual stations. The variability in hydrocarbon content per station is the largest in the southern board side of the Al-Arbaeen proper lagoon, suggesting that waste water discharge and urbanized area are located very close to these sites and those are the probable source of at least some of these hydrocarbons. However, the spatial variation in levels probably relates

to sedimentation characteristics, and hence somewhat lower organic carbon (%TOC) content [46]. This is partly explained by a lower EOM content when compared to other more contaminated stations. The grain size is also a very important factor which contributes to the accumulation of hydrocarbons in sediments, because the finer particles have a higher adsorptive capacity for organic substances owing to their greater effective surface area than coarse sediment fractions [47].

Al-Ghadban et al. [48] stated that total organic carbon content can be considered as an indicator of hydrocarbon pollution only when the total petroleum hydrocarbon is very high. An impressive positive relationship could be deduced between petroleum hydrocarbon concentrations in sediments and their corresponding values of organic carbon in sediments ($r=0.56$) (Table 2). The total petroleum hydrocarbons showed strong correlation with the concentrations of EOM ($r=0.71$, at the 0.01 level) in Table 2. Therefore, it is suggested that the observed distribution of petroleum hydrocarbons associated with sediments is governed by the EOM, and probably controlled by the localized sources of inputs.

c) Aliphatic hydrocarbons: The aliphatics (or *n*-paraffins) have been used as biological markers quite successfully for several decades, as a result of their abundance and ease of detection by gas chromatography

(GC) alone or gas chromatography mass spectrometry (GCMS) [18]. In the chromatogram, the relative abundance for the individual compounds up to about *n*-C₃₅ appears as regularly spaced peaks, with pristane (*i*-C₁₉) eluting immediately after *n*-C₁₇ and phytane (*i*-C₂₀) after the *n*-C₁₈ compound [49]. The aliphatic hydrocarbons of sediments exhibit different distributions depending on their origin.

Examples of chromatograms of aliphatic hydrocarbons isolated from the surface sediments from Al-Arbaeen lagoon are shown in Figure 3. These chromatograms clearly show that the dominant identified components in the aliphatic hydrocarbons are *n*-alkanes.

Peak identification was performed by comparison with retention times of authentic standards and by GC/MS (including selective ion monitoring; *m/z* 71 for *n*-alkanes; *m/z* 217 for steranes; *m/z* 191 for terpanes).

Boehm et al. [50] defined chemical fingerprinting as the application of analytical chemistry to identify the sources of complex environmental pollutants, including petroleum. Chemical fingerprinting provides information about sources of pollution, biodegradation, correlation among pollution components, and consequently it can be applied for environmental quality control purposes [51]. The aliphatic hydrocarbon fraction of the surface sediments showed a variable

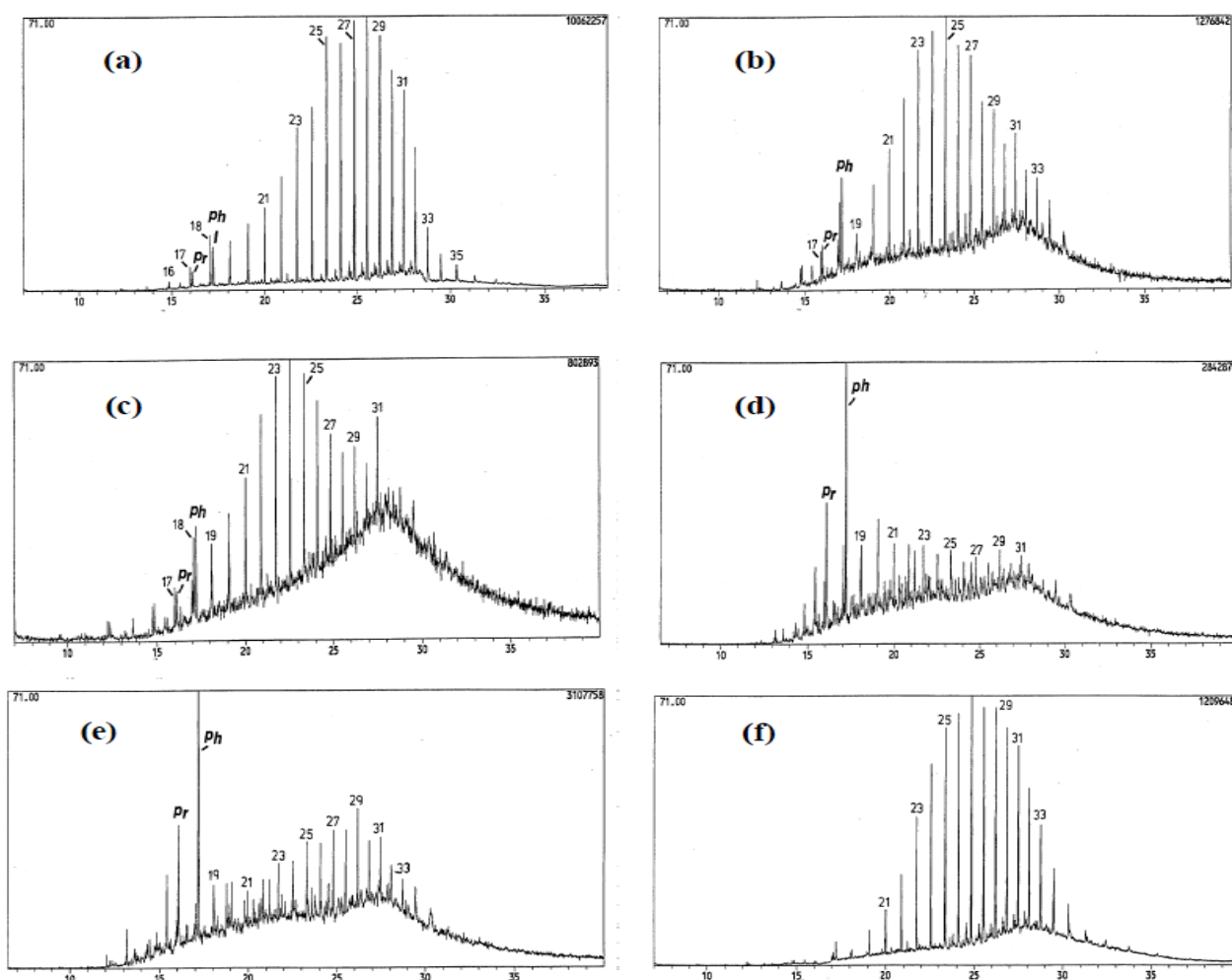


Figure 3: Mass chromatograms (*m/z* 71) showing *n*-alkanes distribution in sediments from Al-Arbaeen lagoon: (a) site 1; (b) site 5; (c) site 7; (d) site 9; (e) site 14 and (f) site 18. Pr: pristane; Ph: phytane. Numbers *n* (16–33) indicates carbon numbers of *n*-alkanes.

distribution of resolved components, which in some cases overlaid an unresolved complex mixture (UCM). The UCM is generally considered to be a mixture of many structurally complex isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by capillary GC columns [39,52,53]. The high abundance of UCM in the sample is a positive indication of chronic oil-pollution [38]. However, some UCM distributions, mainly in the lower molecular weight range can also be attributed to bacterial degradation of natural organic matter such as algal detritus [54,55].

Many features of the hydrocarbon distributions shown by gas chromatograms are similar throughout the study region although some striking inconsistencies were found. The representative fraction 1 (saturate) distributions are shown in 3. The dominant identified components in the aliphatic hydrocarbons are *n*-alkanes which are present as homologous series from about *n*-C₁₆ to about *n*-C₃₃. In addition a series of isoprenoid hydrocarbons were present. Similar distributions of aliphatic hydrocarbons were found in sediments from Tess Bay and the Tess Estuary [56].

On the other hand, the aliphatic hydrocarbon fingerprint found in all sediments suggests inputs from various sources: (i) biogenic for low molecular weight (from *n*-C₁₄ to *n*-C₁₉) *n*-alkanes and (ii) degraded organic matter and a widespread petroleum contamination evidence by the presence of a large unresolved complex mixture (UCM) [13,15,57,58].

d) Normal alkanes (*n*-alkanes) and unresolved complex mixture (UCM): *N*-Alkanes generally constitute the major fraction of aliphatic hydrocarbons, which may be used to detect its presence in the environment [56,59] and their distribution patterns are characterized by carbon-number range and predominances depending on the nature of the source material and its microbial or geochemical alteration. The gas chromatograms (*m/z* 71 profile) of saturated hydrocarbons (Figure 3) for Al-Arbaeen lagoon has a unimodal distribution, which is maximized in the higher molecular weight range and declines towards lower molecular weight *n*-alkanes.

The chromatogram of the saturated alkane fractions displayed an unusual bimodal distribution centered on *n*-C₁₅-*n*-C₂₀ and *n*-C₂₁-*n*-C₃₃, all chromatograms showed varying degrees of a resolved complex mixture (UCM) of compounds, which were not quantified in the present study. A unimodal envelope predominated with an elution range between *n*-C₁₅ and *n*-C₂₀ and maximum between the elution region of *n*-C₁₇ and *n*-C₁₈. The odd carbon-number compounds in the range of *n*-C₂₁-*n*-C₃₃ predominated, and *n*-C₂₁, *n*-C₂₅, *n*-C₂₇ and *n*-C₂₉ were the major alkanes in most samples (3). A proportion of longer-chain *n*-alkanes, *n*-C₂₃-*n*-C₃₅, increases with a decrease in human activity. High concentrations of short-chain *n*-alkanes are due to the dominance of *n*-C₁₈ which is not characteristic for biogenic sources [60]. Marine phytoplanktonic hydrocarbons characterized by low odd carbon numbered *n*-alkanes (*n*-C₁₇) were mainly identified in the investigated study as well as the long-chain homologues (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) derived from terrestrial higher plant waxes. This distribution pattern is indicative of a prominent terrigenous input derived from higher plant waxes [15,61-63].

GC/MS Chromatograms of the *n*-alkane fraction showed the presence of the well-known UCM (Figure 3). UCM is one of the more convincing indications of the petrogenic pollution of these organisms by weathered or biodegraded petroleum and/or its derivatives in sediment [64,65]. On the other hand, the anthropogenic contribution is evident from the presence of the UCM in all sample. UCM was the major component of the aliphatic hydrocarbon fraction appearing in the GC trace as a unimodal hump in the range *n*-C₁₆-*n*-C₃₃, one UCM

at station 7 (3c). Also, the presence of the high UCM signal in this station among the other stations indicated that the sample was exposed to the chronic pollution.

e) Isoprenoid Hydrocarbon: The isoprenoid hydrocarbons pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are present in most petroleum, usually as major constituents of a much wider distribution of isoprenoid alkanes, and thus are often considered as good indicators of petroleum contamination [15,63]. However, a high concentration of pristane alone can be derived from zooplankton, while phytane is practically absent in uncontaminated recent sediments [15, 66]. Biogenic sources of the compounds are important, for example they can derive from the phytol side chain of chlorophyll, either under reducing conditions (phytane) or oxidising conditions (pristane) and can also originate from lipids of zooplankton and bacteria and are not primary constituents of most terrestrial biota [67].

Both pristane and phytane were found at all stations (Figure 3). The content of phytane was much higher than that of pristane, which suggests that the collected sediments were contaminated by petroleum products.

Generally, the results show the presence of both natural (e.g., terrestrial and marine plants) and anthropogenic (e.g., petroleum and synthetics) organic compounds and their alteration products in environmental samples. There also remained some compounds that could not be identified and assigned to either a natural or anthropogenic origin. Most of these unknown compounds were likely alteration products (i.e., chemical, physical, and biological), or secondary metabolites (i.e., bacteria, plant, animal, and fungi) that were difficult to identify based on their mass spectral signatures alone.

f) Triterpanes and steranes: Another useful indicator of the origin of the hydrocarbons is alicyclic hydrocarbons, especially terpane and sterane biomarkers [68]. Such sterane and hopane signatures also confirm the presence of mature petroleum in sediments. This criterion has been documented for characterizing the origin and the degree of maturation of crude oils [69] and for determining correlation indexes of crude oils [57,70,71]. A series of C₂₇-C₃₅ pentacyclic triterpanes (hopanes) were identified in nine sediment samples on the basis primarily of their mass spectra and GC retention time. 4 show *m/z* 191 mass fragmentogram of sediment sample from Al-Arbaeen lagoon. This ion occurs in the spectra of hopanes, hopenes and some other triterpenoid hydrocarbons, and is commonly used to fingerprint oil contamination in sediments. Among the triterpanes, pentacyclic triterpanes (or hopanes) have also been used for tracing hydrocarbons of petrogenic origin [72].

Hopanes (4) comprise a series of 17 α (H), 21 β (H) compounds, maximizing at the C₂₉ and C₂₉₋₃₅ (peak 1-19). Such isomeric configurations are thermodynamically stable and occur in crude oils and mature rock [73]. They are derived from the diagenetic inter-conversion of the 17 β (H), 21 β (H) homologues of bacterial origin. Extended hopanes (C \geq 31) were also present as pairs of the C₂₂ diastereoisomers (22R, 22S) in a ratio of ca. 60:40 (8:9; 12:13), which also typifies petrogenic material. Similar hopane distributions have been reported from sediments and surface particles of the Yangtze river in East China Sea [74,75], and also from sediments of the Huanghe river in Northern China [76] as well as from aerosols in urban area from China [77]. Petroleum-related hopanes are persistent to environmental alteration and, therefore, can be used to detect oil pollution in recent sediments even after fairly extensive degradation has occurred, and/

are positively correlated with the EOM. It is suggested, therefore, that the observed distribution of petroleum hydrocarbons associated with sediments is governed by the EOM.

Concentrations of TPHs in the sediment samples from Al-Arbaeen lagoon are quite different, with the highest concentrations occurring in samples collected from the southern board side of the Al-Arbaeen proper lagoon. This could be a result of continuous deposition of hydrocarbons derived from different pollutant sources (petrogenic and/or biogenic) *via* the effluent discharge point and/or the highly urbanized areas located very close to the lagoon. Concentrations of TPHs were also very high and comparable to polluted sediments.

The distribution of aliphatic hydrocarbons in all sediments suggests inputs from various sources (biogenic and/or petrogenic). Based on the examination of the geochemical markers both hopane and sterane profiles, which have been proposed as being useful fingerprints of oils, provide convincing evidence that petroleum derived from hydrocarbons are widespread in the sediments of the study area.

Acknowledgment

The author would like to thank the Deanship of Scientific Research, of King Abdulaziz University, for financial support. Thanks are also due to Prof. G. Niaz who kindly revised the manuscript.

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